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# CHEMICAL EQUILIBRIUM

# and its

# CONCEPTUAL DIFFICULTIES

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# ABSTRACT

This report presents the procedures, results and conclusions of an investigation of the conceptual difficultes experienced by pupils studying the topic of chemical equilibrium during the Higher Grade and Sixth Year Studies courses of the Scottish Certificate of Education.

At Higher Grade, a twenty three item objective test was developed and administered to 255 pupils in thirteen schools. The test showed that many pupils suffered from one or more of a variety of misconceptions, some of which appeared to be due to inaccurate teaching, and some of which appeared to be a result of tacit assumptions made by pupils. It is suggested that some physical analogies may be the agents responsible for some of these tacitly assumed misconceptions. Consequently, suggested remedial action requires that, firstly, a more accurately realistic approach to the teaching of chemical equilibrium be adopted with less use of 'middle category' analogies, that is to say, analogies that are neither very far from nor very near to the equilibrium which they purport to explain, and secondly, that the teacher should be aware of the tacit assumptions which pupils may make and actively forestall these by appropriate use of negative instances.

At Sixth Year Studies, a structural, cognitive and informational programme covering Section 2 of the syllabus, using a concrete-empirical approach written in accord with educational theory on the teaching of new subject matter, was developed and used in a matched pairs design involving forty nine pairs of pupils in ten schools. Control pupils were taught Section 2 in the manner normally used in the school. Experimental pupils used the programme, with or without teacher assistance; the programme was so written that it could function as a self-teach programme. A twenty eight item objective

test was administered to both control and experimental pupils. A t-test of the results of the objective test showed that the overall performance of the experimental pupils in the test was significantly better than the overall performance of the control pupils, but that the improved performance of experimental pupils was largely due to those who had obtained a Band A in Higher Grade chemistry.

A detailed analysis of the responses to each question showed that pupils suffered from a variety of misconceptions, and that these misconceptions, by their nature, might be due to inaccurate teaching though the possibility of incorrect tacit assumptions by pupils could not be excluded.

While the research carried out a Higher Grade was fairly conclusive, that carried out at the Sixth Year Studies level was less so in that it left questions unanswered and suggested further research.

# INTRODUCTION

On the basis of a knowledge of chemical equilibrium, explanations and predictions of the behaviour of physical, chemical and biological systems can be offered. The concept of chemical equilibrium is fundamental to almost every aspect of science. It arises in discussions of solubility, diffusion, chromatography and partition; it explains the phenomena of vapour pressure and osmosis, hydrolysis and ionisation; it provides an underlying theory with which to explain oxidation and reduction, precipitation and dissociation; it dictates the conditions under which ammonia can be synthesised and water decomposed, the conditions under which iron may be extracted from its ore and the conditions under which iron corrodes and reverts to its ore, the conditions under which a living tree will grow and a dead one decay.

An understanding of the concept of chemical equilibrium provides a clear view of the difference between and the significance of the relationship which exists between matter and energy, of the implications on the one hand of the conservation of energy and on the other hand of the inevitable conversion with time of useful energy to non-useful energy, with its economic implications for the future.

Thus it is important that pupils acquire a clear understanding of the concept of chemical equilibrium at whatever level they encounter it, and that better methods of presentation, if available, should be applied, and should be applied whenever the time is considered appropriate for their application, neither too early nor too late. It is important that misconceptual knowledge should be constantly safeguarded against, either by avoiding the use of agents and techniques which unwittingly give rise to it or, accepting that it must inevitably arise in some teaching situations, by teaching against it. Misconceptions arising from inappropriate and injudicious teaching are longlasting and eradicated only with difficulty, if at all.

This thesis records the author's success or lack of it in uncovering some of those specific and general instances of misconceptual knowledge acquired by pupils in the secondary teaching situation, and details the reasons for and reasoning behind the development and application of a novel method of teaching chemical equilibrium for the Certificate of Sixth Year Studies.

Chapter 1 begins with a brief summary of the historial development of the concept of chemical equilibrium from the 13th Century to the present day, and continues with a description of the interpretation of the concept in the present secondary teaching situation.

# PART I

# SURVEY OF THE CONCEPT OF CHEMICAL EQUILIBRIUM

## CHAPTER 1

# BACKGROUND TO THE CONCEPT OF CHEMICAL EQUILIBRIUM

### 1.1 Brief historical Summary of the Development of the Concept of Chemical Equilibrium.

A basic aspect of the concept of chemical equilibrium is the knowledge that substances tend to react, tend to demonstrate a force or 'affinity' to change which varies from substance to substance. The doctrine of chemical affinity is believed to have its origins in the Geber Texts. Geber is thought to have lived during the 13th century. The Geber texts were intended to teach the 'mastery of the enoblement of metals' and as such were a significant contribution somewhat apart from the more alchemistic approach of that time. Thus Geber examined the affinity of sulphur and mercury for other metals in a manner characterised by attention to practical detail and the recording of results, a manner more characteristic of the methods of later chemists than of the nebulous quality relationships, symbolic allusion and illusions of the true alchemists. He established a primitive activities list of metals based on the increasing ease of combustibility of the metals with sulphur:

$$\text{gold} < \text{tin} < \text{silver} < \text{lead} < \text{copper} < \text{iron}$$

He found that the combustion of the metals in air followed the same order.

The introduction of the term 'affinity' is usually credited to Albertus Magnus sometime during the 13th Century. This was followed by the development of activity series of metals by Paracelsus (1493-1541) and Stahl (1660-1774) where the latter extended the concept to include displacement of one metal by another. Geoffrey (1672-1731) and Bergman (1735-1784) drew up displacement tables of substances. Bergman recognised that the placement of a substance, though normally determined by its affinity, might be affected by temperature. Ercker, as early as 1574, held the opinion that some metals could displace other metals. These early references to affinity gave no effective consideration to the part played by varying quantity of substance; the effect of variation of quantity of substance on a reaction is not considered to be of importance. Boyle in 1764 in talking about the properties of air commented that quantity could in some circumstances compensate for lack of strength.

In 1810, Berthollet (1748-1822), writing in Researches into the Laws of Chemical Affinity, applied both affinity and quantity considerations to forward and reverse reactions and defined reversibility in a way which is virtually identical with the modern conception of chemical equilibrium: "It follows .... that the action of a substance which tends to decompose a combination, diminishes ....... whilst, on the contrary, the action of that which has been eliminated, increases in proportion to the augmentation of its quantity, until equilibrium of the contending forces ends the operation, and limits the effect." Berthollet applied the term equilibrium to describe a balanced situation resulting from the operation of equal and opposite forces, but the conception at this stage was a static one, analogous to the more familiar equilibrium encountered in mechanics. Berthollet's major contribution lay in his stress of the importance of quantity.

That a chemical equilibrium results from the simultaneous operation of two opposed reactions of equal rate was pointed out by Williamson (1824-1904) in 1850.

Guldberg and Waage in 1864 published the Law of Mass Action, equating at equilibrium the chemical forces or affinities of the opposed reactions, and deriving eventually an expression of the equilibrium constant. Their most important contribution was experimental proof that in an incomplete reaction a definite equilibrium is reached and can be approached from either direction. Guldberg and Waage were the first to appreciate qualitatively the implications of a balanced reaction but were slow to formulate a mathematical expression for the equilibrium constant (1879), which they did only after Horstmann had done so for gases (1873) and van't Hoff for esterification (1877).

Although there was a clearer idea of dynamic chemical equilibrium, the phenomenon of chemical affinity, the driving force of reaction, was still a mystery. Berthollet had regarded the force as similar to gravitational force. Berthelot (1827-1907) and Thomsen (1826-1908) considered the heat evolved by a reaction to be a measure of the driving force, but reactions also occurred which were endothermic.

Carnot (1796-1832) had enunciated the second law of thermodynamics in 1824. Clausius (1822-1888) and Gibbs (1839-1903) developed the second law about 1867 and during the 1870's respectively. Van't Hoff (1852-1911) in 1884, in his Studies in Chemical Dynamics, and having due regard to the second law, asserted that the maximum work available from the operation of a chemical process was a measure of the chemical affinity. The elusive driving force of chemical reaction was recognised at last. And, on a minor note, van't Hoff introduced the reversed arrow convention still used today.

The maximum work of van't Hoff was replaced by 'free energy', a term coined by Helmholtz (1821-1894), and given the symbol G in honour of Gibbs. By the late 19th Century, therefore, a system in dynamic chemical equilibrium was recognised as a system of minimum free energy in which forward and reverse reactions proceed at equal rate. This is the modern interpretation.

## 1.2 The Concept of Chemical Equilibrium in the Secondary Teaching Situation.

### 1.2(1) Background to the Syllabus

In 1962, the Scottish Education Department adopted an 'Alternative' syllabus in chemistry (1). In 1969, in the light of experience gained with the Alternative syllabus during the preceding six years, the Subject Panel of the Scottish Certificate of Education Examination Board suggested to the Board that certain alterations be made to the Alternative syllabuses and explanatory notes. These alterations and the rationale for them and the revised syllabuses and explanatory notes were published (2) in booklet form in 1969. At the same time, since the Alternative syllabuses had been adopted by all schools presenting for the Scottish Certificate of Education, and since the examinations in the Traditional syllabuses were phased out in 1971, the designation Alternative was no longer required and ceased to be used.

The syllabuses and explanatory notes were reprinted (3) in 1975 with some minor alterations and additions.

### 1.2(2) Interpretation of Syllabus and Explanatory Notes (1975) with regard to Chemical Equilibrium at Ordinary Grade.

There are three distinct opportunities during the Ordinary Grade course when the concept of dynamic chemical equilibrium might be introduced. These are:

(i) I.5 The Ionisation of Water (A I.1).

The explanatory notes suggest a discussion of reversibility of the reaction $H_2O \longrightarrow H^+(aq) + OH^-(aq)$ and equilibrium.

(ii) K.4 Conversion of Sulphur Dioxode into Sulphur Trioxide (A I.2).

The explanatory notes suggest a discussion of the possibility of the direct combination of sulphur dioxide and oxygen, and of the need for a catalyst.

There is no mention of reversibility and/or equilibrium, but there is ample opportunity at this point in the syllabus for the teacher to introduce the concept of chemical equilibrium if this is thought desirable, and some teachers may interpret the explanatory notes in this way.

(iii) M.3 Manufacture of Ammonia by the Haber Process (A I.3). The explanatory notes suggest that simple kinetic reasons be offered to explain the effects of temperature and pressure, and catalyst on a mixture of nitrogen and hydrogen.

The notes make no reference to reversibility and/or equilibrium, but again there is opportunity for the teacher to introduce the concept of dynamic chemical equilibrium if this is considered desirable, and again some teachers may interpret the explanatory notes in this way.

In contrast to the revised Syllabuses and Notes (3), the original Circular 512 (1) made clear reference to reversibility and equilibrium in each of these cases (10.9, 11.4 and 12.2 respectively in the original sections) and since none of these references to equilibrium was expressly deleted in the 1969 revision (2) it was felt that the Board should be approached and asked if they might clarify the position with regard to the teaching of chemical equilibrium at the Ordinary Grade. A letter to this effect was sent to the Senior Examination Officer of the Board on 18th November 1974.

A reply was received (private communication) from the Senior Examination Officer of the Board, from which the position with regard to the teaching of chemical equilibrium at Ordinary Grade is as follows. Teachers are free to interpret the syllabus and explanatory notes in the light of their own circumstances, having regard to the standard implied by question papers. His own personal view is that the syllabus involves only an awareness of the concept of equilibrium in relation to the ionisation of water, combination of sulphur dioxide and oxygen, and combination of nitrogen and hydrogen, and that a kinetic approach should be used to assist understanding of the effects of temperature, pressure and catalyst. The explanation of such effects should certainly not involve any formal mathematical treatment nor the application of the Le Chatelier Theorem. Further, he continues, the item banks avoid the concept of equilibrium as such with regard to the formation of sulphur trioxide and ammonia.

An examination of Ordinary Grade examination papers over the last six years shows that, apart from the use of and reference to the reversed arrow convention, the topic of chemical equilibrium hardly arises. This suggests that Examiners, Setters, Moderators and Item-writers have appeared to regard the proper study of chemical equilibrium as a matter for post Ordinary grade study.

In a further communication the Senior Examination Officer adds that the Principal Examiner suggests that the reversed arrow convention might be interpreted with emphasis on reversibility rather than the attainment of equilibrium.

In view of these comments it was decided not to pursue an investigation of the topic of chemical equilibrium at Ordinary grade.

### 1.2(3) Interpretation of Syllabus and Explanatory Notes (1975) with regard to Chemical Equilibrium at Higher Grade

The Higher grade syllabus consists of four broad areas of work:

| | |
|---|---|
| Section P | Atoms, Molecules and the Mole. |
| Section Q | Bonding and the Periodic Table. |
| Section R | Chemical Reactions. |
| Section S | Carbon Compounds. |

The concept of chemical equilibrium is introduced in the latter part of Section R (A I.4-7). The first five subsections, R.1 to R.5, deal with the effects of concentration, temperature, light and catalysts on reaction rate, and introduce the concepts of reaction mechanism, activation energy and collision theory. R.6 suggests that equilibrium be interpreted as resulting from two opposing reactions occurring at equal rates. The same equilibrium position is attained irrespective of the starting point of the reaction. R.7 introduces the Le Chatelier Principle as a means of predicting the effect on an equilibrium system of alterations in concentration of reactants, pressure in gaseous systems, and temperature. The effect of catalysts on the equilibrium system should be discussed. R.8 applies the new conceptual knowledge about equilibrium to the Contact Process and the Haber Process which are now interpreted in terms of dynamic equilibrium in contrast to their simpler interpretations in terms of reversibility at Ordinary grade. The ionisation of water, and the effect on this equilibrium of the dissolution of a variety of salts is investigated. The Le Chatelier Principle is used predictively.

The treatment of Section R suggested by the explanatory notes, and assumed from an examination of past question papers, is such that the pupil acquires a qualitative understanding of the concept of dynamic chemical equilibrium.

The approach, therefore, to chemical equilibrium adopted in Section R of the Higher grade course is essentially one which centres on the qualitative concept of equal and opposite rates of reaction at equilibrium resulting in an equilibrium system of unchanging composition in a closed vessel. This approach will be referred to as the Rates Approach throughout the rest of this report.

It is the first purpose of this investigation to establish whether or not misconceptual knowledge arises during the teaching of Section R in relation to the concept of dynamic chemical equilibrium, and, if so, to describe it and account for it, and to suggest finally a proper course of remedial action.

### 1.2(4) Certificate of Sixth Year Studies and Chemical Equilibrium.

The Certificate of Sixth Year Studies syllabus in chemistry consists of nine areas of work (4):

Section 1. Revision of Molar Concept.
Section 2. Energies in Macroscopic Systems.
Section 3. Practical Techniques in Chemistry.
Section 4. Spectra and Structure.
Section 5. Energy in Relation to Bonding.
Section 6. The Chemistry of the Carbon Group.

Section 7. Solution Chemistry.
Section 8. Electronic Structure and the Periodic Table.
Section 9. The Transition Elements.

The concept of chemical equilibrium is taught in Section 2 (A I.8). The first three subsections, 2.1,2.2 and 2.3, consider enthalpy change, Hess's Law and bond energies. The next three subsections, 2.4,2.5 and 2.6, deal with the concept of free energy, in particular its relationship to the e.m.f. of a chemical cell. The syllabus notes state that the mathematical relationship between $\Delta G$ and $\Delta G^o$ is not required. Subsections 2.7 and 2.8 deal with the concept of entropy, which is linked qualitatively with disorder and quantitatively with enthalpy and free energy in the form of the Gibbs-Helmholtz equation, $\Delta G = \Delta H - T\Delta S$. Subsection 2.9 deals with equilibrium and the equilibrium constant. The latter is explained in terms of concentration. Subsection 2.10 considers the controlling influence of enthalphy change and entropy change on a variety of physical and chemical equilibria: chromatography, ion exchange, diffusion, osmosis, dialysis, distribution, concentration cell, vapour pressure.

The treatment of Section 2, based on an examination of past question papers, is such that the pupil acquires both a qualitative and simple quantitative appreciation of the concept of equilibrium, but no great depth of treatment is required. The concept is developed through enthalpy, free energy and entropy such that the state of equilibrium eventually attained in a particular circumstance takes the form of a mixture of constant composition and minimum free energy. The dynamic aspect emphasised at the Higher grade is implicit in this new interpretation, that is to say, forward and reverse reactions proceed at equal rates, and the same constant composition equilibrium system is established irrespective of the starting point, and can only be established in a closed vessel.

In developing the concept of chemical equilibrium at the Certificate of Sixth Year Studies level the teacher has to teach and the pupil learn a variety of new conceptual material: reversibility, irreversibility, available/optional work, free energy, qrev, entropy, systems and surroundings, equilibrium constant, and others. This approach is, therefore, essentially a thermodynamic approach and so will be referred to in the rest of this report as the Thermodynamic Approach.

It is the second purpose of this investigation to establish the nature of the conceptual difficulties experienced by pupils in studying Section 2 of the Certificate of Sixth Year Studies syllabus (4), to develop, if required, an alternative method of teaching this part of the syllabus, and in this event to establish by the application of a suitable test procedure whether or not the alternative method is successful in avoiding, correcting and minimising misconceptual knowledge about chemical equilibrium.

Consequently, Chapter 2 of this report is an account of the author's assessment of teaching and learning difficulties associated with chemical equilibrium at Higher grade and Certificate of Sixth Year Studies. This assessment is based on a review of the literature and a personal enquiry among teachers, science advisers and others associated with administration of the certificate examinations.

| | Explanatory Notes | Suggested Practical Work |
|---|---|---|
| I.3. Reduction of oxides. | Some of this work is revision. The object is to relate these reactions to the activity series. | D. Action of heat on $Ag_2O$.<br>P. Reduction of various oxides by gas.<br>P. Reduction of oxides by carbon. |
| I.4. Do all metals form ions equally readily in solution? | *Idea* of electrode potential. [It is not intended that electrode potential should be dealt with fully; there is no need to define standard electrode potentials, but merely to show that there is a difference with different metals.] | P. There are several simple ways of comparing "electrode" potentials, e.g., the wet filter paper method. |
| I.5. The ionisation of water. | Low conductivity of water indicates small degree of ionisation. Covalent bonding might be indicated. Discuss neutrality of water; what ions are present.<br>What happens when $H^+(aq)$ ions removed, e.g. replaced by $Na^+(aq)$ in order to discuss reversibility of<br>$H_2O \rightarrow H^+(aq) + OH^-(aq)$<br>and equilibrium. | D. Show that "pure" water conducts slightly. |
| I.6. Oxidation and reduction as transfer of electrons. Electrolytic oxidation and reduction. | Oxidation and reduction are defined in terms of loss and gain of electrons. Show oxidation and reduction in electrolytic and voltaic cells. Discussion of extraction of aluminium simply in terms of $Al^{3+} + 3e \rightarrow Al$. | P. Characteristic tests for $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$.<br>P. Test for iodine.<br>P. Pupils set up cells in which $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$ and $I + e \rightarrow I^-$ and test that redox has occurred. |

| K.3. *contd.* | *Explanatory Notes* | *Suggested Practical Work* |
|---|---|---|
| | Use of sulphites:—<br>(a) bleaching,<br>(b) disinfectants, preservation,<br>(c) a convenient source of sulphur dioxide in the laboratory. | P. Bleaching action of $SO_3^{2-}(aq)$<br>P. Action of dilute HCl or $H_2SO_4$ on $SO_3^{2-}$. |
| K.4. Conversion of sulphur dioxide into sulphur trioxide. | Discussion of possibility of direct combination of sulphur dioxide and oxygen. The need for a catalyst.<br>Effect of a catalyst. | D. Preparation of sulphur trioxide. |
| K.5. Conversion of sulphur trioxide into sulphuric acid. | Outline of manufacture of sulphuric acid by Contact Process. | D. Pass $SO_3$ from K.4 into water and concentrated $H_2SO_4$. |
| K.6. Properties of concentrated and dilute sulphuric acid. | Reactions of the concentrated acid should be dealt with on the basis of (a) its relative involatility, (b) its dehydrating action, (c) its acceptance of electrons.<br>**The class should be warned of the danger of working with the concentrated acid.**<br>Reactions of the dilute acid should be compared with those of the concentrated acid, and the differences explained. | P. The following *test-tube* experiments should be tried. Action of concentrated $H_2SO_4$ on:—<br>(a) a chloride;<br>(b) a nitrate: The $HNO_3$ can be distilled off and its presence can be detected by adding copper → brown fumes;<br>(c) $CuSO_4$ crystals;<br>(d) cane sugar (or syrup);<br>(e) copper;<br>(f) zinc;<br>(g) carbon. |

| | *Explanatory Notes* | *Suggested Practical Work* |
|---|---|---|
| M.2. Ammonia. | Purely in order to acquaint the pupils with the nature of ammonia the action of sodium hydroxide on ammonium salts should be studied. | P. Test-tube experiments on action of NaOH on ammonium salts. Note smell and effect on indicator paper. |
| | The solubility of the gas in water with formation of excess $OH^-$ (aq) should be demonstrated and explained. | P. Solubility of $NH_3$. |
| | Decomposition of the gas by passing sparks through it. | D. Spark mixture of nitrogen and hydrogen over "medicinal paraffin." |
| | The fact that the gas cannot be made by heating nitrogen and hydrogen together without a catalyst and that ammonia is decomposed on heating forms an introduction to the Haber process. | D. Spark ammonia gas over "medicinal paraffin." |
| M.3. Manufacture of ammonia by Haber synthesis. | Simple kinetic picture to explain the effects of temperature, pressure, catalyst on a mixture of nitrogen and hydrogen. | |
| M.4. Oxidation of ammonia. | | D. Burn $NH_3$. |
| | | D. Pass $NH_3$ over hot CuO. Collect nitrogen and water. |

| **R. Chemical Reactions** | *Explanatory Notes* | *Suggested Practical Work* |
|---|---|---|
| R.1. Factors affecting speed of reaction. | A preliminary survey of factors such as particle size, concentration, temperature, light, catalysts and inhibitors, will be essentially a bringing together of ideas established at previous points in the course. | |
| | This can be followed by more detailed consideration of the more important factors.<br>The fact that reactions vary greatly in speed, from the practically instantaneous to the very slow, should be brought out. | P. Effect of temperature on, *for example*, the oxidation of HI, decomposition of $NH_4NO_2$ solution, action of $KMnO_4$ on oxalic acid. |
| | | P. Effect of concentration can be shown by action of acids on metals. |
| | | P. Effect of particle size can be shown by action of dilute HCl on marble chips and chalk. |
| | | P. Pyrophoric lead and iron. |
| | | P. Effect of light on silver halides. |
| | | D. Action of water on mixture of aluminium and iodine to show effect of catalyst. |

| | *Explanatory Notes* | *Suggested Practical Work* |
|---|---|---|
| R.2. Reaction mechanism and effect of concentration. | The fact that concentrations of reacting species are changing as a reaction proceeds is a complicating factor. Reaction rates should not be measured and it is sufficient for the present purpose to keep all the initial concentrations constant except the one under study and to observe the time required for the reaction to proceed to a given point. The simplest system to use for this purpose is a " clock " reaction. | P. A clock reaction may be studied, e.g. $S_2O_3^{2-}+H^+$;<br>or $S_2O_8^{2-}+2I^-$;<br>or $H_2O_2+I^-$; |
| | Several of these are available and they can be used also to examine the effect of temperature and catalysts. There is no need for pupils to know the actual reactions involved. | These reactions can be used to show the effect of concentration, temperature and catalysts on reaction speed. |
| | The results obtained are then considered in terms of a collision theory. | |
| | The concept of a reaction mechanism involving a rate-determining step should be developed here and the point established that an overall chemical equation cannot be used to predict the effect of concentration changes upon reaction rate. | |
| R.3. Effect of temperature.<br>Activation energy. | The effect of temperature can be interpreted from the viewpoint of a simple kinetic theory and the need for a given minimum collision energy before reaction occurs. A simple discussion of the distribution of energies is appropriate here. | |
| | The formation of an activated complex during reaction should be discussed and its relation with activation energy established. | |

|  | *Explanatory Notes* | *Suggested Practical Work* |
|---|---|---|
| R.3. *contd.* | The supply of activation energy in both exothermic and endothermic reactions should be dealt with.<br>A simple discussion of collision geometry should be included. |  |
| **R.4. The effect of catalysts.** | Catalysis can be regarded at this stage as the provision of an alternative reaction pathway involving different intermediate complexes with different activation energies.<br>Homogeneous and heterogeneous catalysis. |  |
| **R.5. The effect of light.** | Light energy as a source of activation energy. Mention of photosyntheses (no details of mechanism required). |  |
|  | Reactions of chlorine with hydrogen and methane involve the concept of a chain reaction. | D. Explosion of hydrogen and chlorine. (Care.) |
| **R.6. The idea of equilibrium.** | Simple ideas of equilibrium have already been met with, e.g. in acid-alkali reactions, and the phenomenon can now be interpreted as resulting from two opposing reactions occurring at equal rates.<br>The same equilibrium position will be attained irrespective of the starting point of a reaction. | P. System $KI(aq)+I_2/CHCl_3$<br>and $KI(aq)/CHCl_3+I_2$ |

|  | *Explanatory Notes* | *Suggested Practical Work* |
|---|---|---|
| R.7. Factors influencing the position of equilibrium. | Le Chatelier's principle is a useful predictive tool at this stage and can be used in the discussion of the experimental results observed on the position of equilibrium resulting from changes in concentration of reactants (pressure in gaseous systems) and temperature. It must be remembered that the principle applies only to systems in equilibrium.<br>The importance of the fact that catalysts have no effect on equilibrium position should be discussed. | P. Experiments on effects of concentration, temperature and pressure on equilibrium, e.g. $ICl + Cl_2 \rightleftharpoons ICl_3$;<br>$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$<br>$Fe^{3+}(aq) + NCS^-(aq) \rightleftharpoons FeNCS^{2+}(aq)$<br>A selection only should be used. |
| R.8. Equilibrium in practice. | The concepts arising from the present study of equilibrium should now be applied to situations such as the Contact Process, the Haber Process, the pH of salt solutions such as sodium ethanoate, ammonium chloride, bismuth chloride, etc. |  |
| S. **Carbon Compounds** | Some of the work of this section may already have been covered in sections L, N and O. It is intended that the treatment should be based on a practical acquaintance with organic substances and their reactions. Small-scale techniques should be used for organic reactions. |  |
| S.1. The alkanes. | Homologous series and isomerism.<br>Introduction to nomenclature of organic compounds.<br>Properties associated with saturation. | P. Properties associated with saturated hydrocarbons, e.g. $C_5H_{12}$, $C_6H_{14}$. |
|  | Brief mention of alkyl halides as a route to the alcohols: R-H→R-Br→R-OH<br>[No mechanism required.] | P. Reactions of alkyl halides with aqueous $AgNO_3$ before and after hydrolysis with aqueous alkali. |

| | Chemical Theory | Suggested Practical Work |
|---|---|---|
| 2. | Energies in Macroscopic Systems | |
| 2.1 | Enthalpy. AH.<br>Relation to heats of reaction (including combustion). | Heats of combustions of a series of alcohols. |
| 2.2 | Hess's Law | $NaOH(s)/H_2O$ or $Zn/Cu^{2+}$<br>$NaOH(s)/HCl$ $Cu//Ag^+$<br>$NaOH(aq)/HCl$ $Zn/Ag^+$ |
| 2.3 | Bond Energies | |
| 2.4 | Free Energy AG. Reaction carried out infinitely slowly to give maximum available work | |
| 2.5 | Definition of E. Revision of redox series. Write half-cell reactions as reduction reactions e.g. $Na^+ + e \rightarrow Na$ | Measurement of e.m.f. of a chemical cell.<br>$Zn/Ag^+$ or $Cu/Ag^+$ |
| 2.6 | AG = -nFE (not derived but show relation of electrical units to work).<br>Potential for a spontaneous reaction positive. Free energy change for a spontaneous reaction negative.<br>(Mathematical relation between $AG^o$ and AG not required). | Metals and non-metals in acids to examine for spontaneity of reaction.<br>Check against E from Tables |
| 2.7 | Comparison between AG and AH. Difference is entropy term.<br>Entropy S as a measure of disorder.<br>Change in entropy AS.<br>AG = AH - TAS. | $Zn/Ag^+$ or $Cu/Ag^+$ reaction<br>Comparison of AG and AH values. |
| 2.8 | Simple calculation using these quantities. Link up between entropy and physical condition - e.g. liberation of gas, AS term positive favours reaction | Spontaneous endothermic reaction, $NH_4CNS/Ba(OH)_2.8H_2O$ or $CoCl_2$ hydrate/$SOCl_2$<br>Thermal decomposition of $NaHCO_3$. |
| 2.9 | State of equilibrium.<br>Equilibrium constant. Define in terms of concentration.<br>K is not additive but log K is. | Calculation of equilibrium constant. $PbSO_4/NaI(aq)$ or colorimetrically measure $K_a$ for indicators and weak acids during solution chemistry topic. |
| 2.10 | Controlling factors in equilibria. | |
| | (a) predominantly enthalpy | (a) Chromatography<br>Ion Exchange Resins |
| | (b) predominantly entropy | (b) Diffusion<br>Osmosis<br>Dialysis<br>Distribution<br>Concentration Cell |
| | (c) both | (c) Vapour pressure |
| | | (qualitative only) |

# CHAPTER 2

# ASSESSMENT OF CONCEPTUAL DIFFICULTIES ENCOUNTERED IN TEACHING AND LEARNING THE CONCEPT OF CHEMICAL EQUILIBRIUM

## 2.1 Conceptual Difficulties associated with the Teaching of Chemical equilibrium reported in the Literature.

Driscoll (5) administered a 39 item multiple choice test to 450 first year science students at the University of Melbourne and at the Secondary Teachers College, Melbourne. The study attempted to identify some of the misconceptions and invalid approaches to problems prevalent in this area. Few of the questions required straight recall; most belonged to the higher Bloom categories. Some 100 students were additionally asked to account in free response fashion for their choice of response to a small number of selected questions. This was to ascertain if the correct response had been chosen for the correct reason. The free response accounts showed that on some occasions the students arrived at the correct answer for the wrong reason, and that more often several misconceptions were consecutively used in arriving at the wrong answer.

The misconceptions which were found to be present in a significant proportion of students are:

1. Confusion between amount and concentration.
2. Application of equilibrium relations to other than equilibrium considerations, particularly confusion of rate and extent.
3. Uncertainty concerning the constancy or otherwise of the equilibrium constant.
4. Uncertainty concerning the quantitative and/or qualitative significance of the equilibrium law.
5. Failure to appreciate the significance of constant concentration terms.

Misconceptions which were looked for and found to be absent are:

6. Uncertainty about the essential similarity of gaseous and solution equilibria.
7. Neglect of significance of, or confusion caused by, simultaneous equilibria.

Misconception 1 relates to the difficulty experienced by students in applying Le Chatelier type reasoning to a disturbed equilibrium system in order to deduce how a particular species will alter, and to consider this alteration in terms of increased or decreased amount or increased or decreased concentration, if any. (Note that Driscoll uses the term 'amount' in the sense of 'mass'.) A variety of equilibrium problem situations were presented to the student. These required the application of Le Chatelier type reasoning for their solution.

Although the problem situations presented to the students by Driscoll were generally of a higher level than would be encountered by pupils at the Higher grade or at the Certificate of Sixth Year Studies level, the observations made by Driscoll are relevant to the present investigation because the conceptual difficulties experienced by the students in Driscoll's investigation are also experienced by Scottish pupils, if only in embryonic form.

i) Le Chatelier predictions are often wrong unless the student knows the correct answer in advance, whereupon "one can juggle the reasoning to fit the required answer".

ii) There are occasions when the Principle can be used, and occasions when it cannot be used, and students have great difficulty in distinguishing between the two. And those who have previously been misled by the Principle "become excessively tentative and cautious in using it". The Principle has its limitations which are very difficult to specify.

iii) The use of the Le Chatelier Principle encourages anthropomorphic reasoning, that is to say, inanimate systems acquire the attributes of animate ones in that they 'try to resist' imposed changes.

Misconception 2 Driscoll found that students confused rate of reaction with extent of reaction; they found it difficult to distinguish between 'how fast' and 'how far'. For example, given that the equilibrium percentage of a species was greater at lower temperature, students would assert that the rate at which the species was formed at the lower temperature was greater. He also found that the basic dynamism of chemical equilibrium was not well understood. Thus students would assert that if the composition of a mixture did not change with time, the mixture must be in a state of equilibrium. They failed to appreciate that no apparent change might be observable for kinetic reasons. Driscoll makes the point that students are often not aware of lack of knowledge in a particular subject matter and "are altogether too happy to plunge into confident (but wrong) predictions". Driscoll considers that it is impossible to consider the question of changes in equilibrium without simultaneously considering rates of reaction, i.e. kinetics. He suggests that a partial remedy for the confusion that currently exists between rate and extent of reaction is to acknowledge that there is a tendency towards confusion and to deliberately teach, if only in self-defence, the basic principles of reaction kinetics. "... many students will develop firmly held, common-sense, apparently self-evident but nonetheless incorrect ideas about reaction rates and will confuse ... equilibrium and kinetics."

Misconceptions 3, 4 and 5 are outwith the scope of this investigation and so will not be discussed.
Driscoll expresses some doubts about the reliability of his results. Firstly, the reliability may be suspect due to chance errors arising from the arduous nature of the test and the conditions under which it was administered, in a very hot crowded lecture room. Secondly, the sample consisted entirely of students who had qualified to matriculate in chemistry and so was lacking in weaker students.

Driscoll (6) discusses at some length the variety of statements of the Le Chatelier Principle and applies these in turn to selected equilibrium systems. He comments that authors of text books find some difficulty in framing a general statement of the Principle which gives unambiguous and correct predictions in all cases. He suggests that a statement of the Principle which was framed to cover all eventualities would be too difficult for matriculated students. By way of compromise, he advocates the teaching of one or more restricted statements, each applicable to a certain specific situation (A II.1A).

De Heer (7) discusses the Principle of Le Chatelier and Braun which may be expressed as follows:
If a chemical system in equilibrium is subjected to a perturbation (stress), the equilibrium will be shifted (a reaction will occur) such as to partially undo this perturbation (oppose the stress). He discusses the effect of increased temperature on an equilibrium system and then discusses the effect of increased volume on an equilibrium system. In the former case the system adjusts so as to aid the heat transfer from the surroundings to the system, while in the latter the system changes in such direction that it opposes the volume change. Thus, in the former case the Principle is invalid, in the latter case it is valid.

He continues with a discussion of the $N_2 + 3H_2 \rightleftharpoons 2NH_3$ system in which the addition of more nitrogen at constant pressure may shift the equilibrium system one way or the other depending on the mole percent of nitrogen already there.

The problem then is one of devising a clear and unambiguous statement of the Principle. A correct formulation is offered (A II.1B) but this is acknowledged to be too difficult for general use. An alternative course is suggested: the Principle should be replaced with a small number of rules each of which has a limited range of applicability.

Standen (8) takes exception to de Heer's analysis of the Principle (7), and contends that the Principle is entirely valid if properly understood. Standen emphasises the importance of 'environmental stress', and applies the Principle from this standpoint. Thus an increase in environmental temperature imposes a stress on an equilibrium system and this system will adjust in such direction (the heat absorbing one) to undo this stress. An increase in environmental pressure will impose a stress on an equilibrium system, which will adjust so as to undo this stress.

With regard to the $N_2 + 3H_2 \rightleftharpoons 2NH_3$ equilibrium, Standen maintains that the Principle is inapplicable because the addition of more nitrogen cannot be considered as an environmental stress. Standen considers that, in the context of the Principle, only two environmental stresses are valid: change in temperature and change in pressure. But if the Principle is applied, notwithstanding, then a concentration change (added nitrogen) has to be considered together with a pressure change (if the addition is made at constant volume) or with a volume change (if the addition is made at constant pressure). At constant pressure the concentration increase of nitrogen and the volume increase of the system may have opposite effects, and since the Principle is qualitative it does not allow of any firm conclusion.

Standen believes that, provided the Principle is restricted to qualitative applications, it may be applied very widely, in physical, psychological, economic and sociological fields as well as chemical ones ..... "a principle that is true, worthwhile, and widely (though not universally) applicable."

De Heer (9) asserts that Standen's arguments (8) are mostly misleading or irrelevant, and in part plainly incorrect.

Haig (10) argues, briefly, along the same lines as de Heer, while Lewis (11), Wood (12), Seale (13) and Angus (14) adopt a defensive stance in agreement with Standen.

Johnstone (15) investigated and evaluated the new syllabuses in Alternative chemistry introduced into Scottish Secondary Schools during the 1960s. One aspect of the evaluation was a subjective assessment by 1045 (80% of total asked) first year (1969-1970) university students of the secondary course in chemistry which they had just completed. Of these, 45% rated chemical equilibrium as it arises in Section R of the Higher grade course 'difficult to grasp'. Johnstone suggests that this may be due to the faulty assimilation of new ideas into an existing mental framework based on a static concept of equilibrium - such as that encountered in physics. Thus the addition of material to the right side of a balanced beam causes it to dip towards the right whereas the addition of material to the right of a reaction sequence causes the reaction to go to the left. He suggests that the essential contrast between the static and dynamic concepts might be highlighted by the use of a suitable dynamic model. He also suggests that the Higher grade pupils might find difficulty in coping with the competing variables of pressure, temperature and concentration, and acknowledges the high degree of formal thinking required in applying the Le Chatelier Principle.

In a separate evaluation of subjective opinion of Certificate of Sixth Year Studies candidates (766 in 1970, 850 in 1971) thermodynamics emerged as a subject fairly well accepted by pupils: 27% rated it easy, 55% moderate, 15% difficult and 3% nil response. This opinion was substantiated by good performance in thermodynamics questions in the certificate examinations. In the latter there was better than superficial knowledge since pupils coped well with the more thought provoking aspects of the questions; and the thermodynamics questions were generally popular.

In contrast, however, a survey of 189 teachers of Certificate of Sixth Year Studies rated the thermodynamics part of the syllabus, Section 2, the most difficult part of the syllabus to teach. Johnstone suggests that the reason for this pupil-teacher contrast of opinion might be the lack of immediate familiarity by the teacher for the subject matter resulting in a fresher, more sympathetic presentation of the subject to the pupil.

Johnstone, Morrison and Sharp (16) discuss student reactions to course topics at Ordinary and Higher grade and at Certificate of Sixth Year Studies level. In order to assess the reliability of students' subjective opinions, the results of six independently set objective tests of the same topic areas were analysed (A II.1C). Some agreement between the subjective opinions and the performance in the tests for a particular topic area is evident, that is to say, topics which pupils found easy have generally higher facility values, and topics found difficult have generally lower facility values.

The Principal Examiner's report (17) for the 1974 certificate examinations makes the following specific comment on the performance of candidates on Question 8 of the Higher grade examination (A II.1D). "In teaching the topic of equilibrium a common example is the mixture of sodium enthanoate and ethanoic acid in solution. This question asked about the inverse case - a weak base and its salt. Few candidates were able to begin to answer it."

Hildebrand (18) expresses the opinion that there is no topic which causes students more difficulty than chemical equilibrium, that the subject is inherently a difficult one, and that it sometimes bothers teachers and writers of text books as well. Some blame for the difficulty experienced in appreciating the concept of dynamic equilibrium may be due to the lack of awareness of the statistical basis of chemical equilibrium; a student has to think imaginatively in terms of the simultaneous behaviours of different numbers and kinds of particles. It might be easier if simple probability theory had a place in early mathematics teaching. And the newness of terms employed places the student on unfamiliar ground which makes a problem situation that much more difficult. Hildebrand suggests the analogy of a school dance as a partial solution since it illustrates the essential statistical and dynamic aspects of chemical equilibrium.

The illustration is, of course, only qualitative, but this is a necessary preliminary to a quantitative view. His reason for this latter assertion is, however, not Piagetian. Rather it is practical, because qualitative answers are more often required than quantitative ones, and because the mechanical application of formulae to get right answers only without understanding, is bad teaching.

Hackerman (19) criticises the use of phraseology which implies that changes in the composition of an equilibrium system have a directional quality. He gives some examples: "... equilibrium point is displaced in the direction of ...", "... disturbs the equilibrium to the left ...", "... the reaction to the left becomes more nearly complete ...". The result of this directional implication is that students imagine the substances on the different sides of the reversed arrow to be separate entities, such that it seems perfectly reasonable to apply heat or pressure to one side only of an equilibrium system, or that a concentration on one side can be varied in isolation from the substances on the other side, having no effect on them. It also results in the mistaken impression that collisions occur between reactant particles and between product particles but not between reactant and product particles.

Hackerman stresses the importance of thinking in terms of the composition of the equilibrium mixture where the equilibrium mixture is viewed as a single entity. Stressing the importance of composition highlights the difference, also, between extent of reaction and rate of reaction, that is to say, between completeness and yield. The latter concept of yield requires the same information as the former concept of completeness, but in addition requires knowledge of the time taken to reach equilibrium.

Hackerman also suggests that the use of print of different intensity in conjunction with the reversed arrow convention in which the arrows are of equal length might be a better method of indicating a difference in the relative concentrations of reactant and product than the use of the reversed arrow convention in which the arrows are of unequal length.

Adams (20) discusses the derivation of the equilibrium constant from the Law of Mass Action and suggests some permutational analogies to help overcome some of the difficulties experienced by students in understanding the form of the constant. He comments that while analogies may be useful in explaining some steps in the derivation of the constant, a more rigorous mathematical approach is more convincing.

Kent (21) asserts that considerable confusion results from the lack of emphasis of the dimensionless nature of the equilibrium constant. Some students, for example, are confused by the elimination of units, when these are used, when taking the logarithm of the constant for thermodynamic calculations. "Automatic removal does not rectify their presence initially." The presence of units in any expression which is to be converted to exponential form is incorrect.

Wright (22) discusses the case against teaching thermodynamics in schools. He expresses the view that thermodynamics is conceptually too difficult for pupils in schools, and that it is a subject which most teachers are inadequately trained to teach. He points out that thermodynamics often appears to be 'not chemistry' because of the underlying physical and mathematical mode of presentation; and this perhaps accounts for its unpopularity with students. Since thermodynamics does not invoke particular molecular models, it is a subject peculiarly unsuited to elementary teaching. It is a topic which enjoys the reputation of being a difficult one at university. The inability of teachers in schools to cope with the subject is partly due to this inherent difficulty, but also due to the "perfectly scandalous inaccuracy of the 'thermodynamics' taught in no small number of universities".

Wright pinpoints two particularly prevalent and dangerous misconceptions: (i) that entropy is a name given to a quantitative measure of disorder at the molecular level, and (ii) that it is permissible to speak of the entropy of the universe and its increase. He asserts that both of these beliefs are disastrously wrong. The concept of entropy must be viewed only in a macroscopic sense, while the entropy of the universe is an entirely improper concept. He acknowledges that entropy is a stumbling block to many students but deprecates the tendency to simplify a concept to that level where it is no longer correct. He recommends that the beginner, though he or she may find it difficult at first, should be given a derivation which is rigorous and logical. He asserts that some of the 'simplified' derivations are not difficult to follow, but impossible.

Ogborn (23) takes the view, though with caution, that some thermodynamics presented at school is better than none, and sees the problem rather as one of presentation. He maintains that a later formal presentation of the subject at University makes it appear to be remote and lacking in meaning. Consequently he suggests offering the pupils a simple statistical discussion first as a "ladder up which to climb", to be followed by a transition to macroscopic thermodynamics at a later stage.

Ogborn sees difficulty in the presentation of the concept of entropy, and has some constructive suggestions to make on a possible approach based on "counting microstates". He feels that the linking of entropy with disorder should be avoided.

He also sees the incompetence of most teachers in the subject, "an incompetence which worries the teacher even more than the expert", as a major difficulty. The proper teaching of thermodynamics in a limited way in schools requires first of all that steps be taken to help the teacher with books, courses and detailed guidance.

McGlashan (24) comments on the usual presentation of thermodynamics, that it is incredibly badly presented, for the most part by people who do not understand it. (How often are undergraduates asked to calculate the results of impossible experiments on imaginary substances?) One reason is the repeated attempt to introduce the subject historically where in fact the history of thermodynamics is more difficult than thermodynamics itself. He condemns the use of the Carnot Cycle explicitly. Further, he insists that emphasis should be placed on using thermodynamics in real chemical situations.

He describes thermodynamics as a subject which deals with mass, length, time, current and temperature, as a collection of useful relations between quantities, every one of which is independently variable.

He maintains that much of the difficulty students have with thermodynamics stems from a lack of clear appreciation of the system and the independent variables controlling it; the mathematics itself causes little trouble since the mathematics needed in thermodynamics is elementary and easy. And difficulties arise as often from the student's failure to understand the first law as from his failure to understand the second law.

McGlashan condemns the linking of entropy with disorder, randomness or mixed-upness, except in three special cases: the mixing of ideal gases, the mixing of isotopes, and crystals at near absolute zero. Otherwise the concept of increased mixed-upness is invalid in "one's beakers of liquids at ordinary temperatures". Thus a supersaturated solution of sodium thiosulphate effectively isolated in a Dewar flask will spontaneously crystallise when seeded, and in so doing will exhibit a decrease in mixed-upness, and an increase in entropy.

Even worse, when the second law is applied to the astronomical universe it apparently implies ultimate and total mixed-upness as the inevitable fate of the universe. McGlashan maintains that there is no evidence that thermodynamics is applicable to the astronomical universe, even assuming the latter were bounded and isolated (whatever that might mean). That the fate of the universe is ultimate chaos is more an act of faith than an act of reasoned thermodynamics.

Spice (25) considers that there is a strong case for including a simple treatment of some of the leading thermodynamic ideas in a Sixth Form course. He lays down three conditions which an introductory course should fulfil:

1. It should start on ground already familiar to the pupil.
2. It should be rigorous up to a point, and no part of it should subsequently require to be unlearned.
3. It should have obvious practical value.

Spice stresses the importance of explaining very carefully the meanings of certain thermodynamic ideas like 'reversible process', 'system and surroundings' and 'state function'. He emphasises the distinction between the treatment of single atoms and molecules and the treatment of large assemblies of these; quantities like entropy, free energy and temperature only have meaning at the macroscopic level.

Case (26) developed an experimental mathematically-based thermodynamic approach to chemical equilibrium. The course was of a highly formal nature. It consisted of six distinct teaching units:

1. The Gas Laws and a review of essential mathematics.
2. The First Law of Thermodynamics.
3. The Second Law of Thermodynamics.
4. The Equilibrium Constant for gas reactions.
5. The thermodynamic Equilibrium Constant for aqueous reactions.
6. Applications of the thermodynamic Equilibrium Constant.

These took the form of six daily lessons. Achievement was assessed by testing at the end of each unit and by administering an overall test at the end of the course.

The programme was taught to 89 pupils of a comprehensive rural-suburban high school. The mean Terman-McNemar Intelligence Quotient of these 89 pupils was 121, with a standard deviation of 12.

At the end of the course only one student in five was considered to have acquired an acceptable grasp of the topic of chemical equilibrium. The criterion for acceptance was: an overall score of at least 70% on the six individual unit tests, the final test and 12 selected key items. Case selected the latter items as being those he considered absolutely essential to an understanding of chemical equilibrium.

A middle group of students, three in five, were judged to have acquired a level of understanding varying from good to poor, while at the lower end one student in five was considered not to have grasped the significance of the mathematically based course at all.

Case comments that the topic of entropy was "most difficult for almost everyone", so much so that this part of the programme would require reappraisal.

## 2.2 Assessment of Conceptual Difficulties and Other Aspects of the teaching of Chemical Equilibrium by Teachers.

### 2.2(1) The Letter of Enquiry

It was thought advisable to ask practising teachers and others in key educational positions for help in establishing the nature of conceptual difficulties encountered in teaching chemical equilibrium at all levels. A letter (A II.2) was therefore sent to 38 principal teachers of chemistry in schools throughout Scotland, two science advisers and three persons associated with the setting, marking and administration of the certificate examinations in chemistry.

It was thought better to ask the recipients some general questions about aspects of the teaching of equilibrium rather than leave them to guess at what was being looked for. Thus they were asked for their interpretation of the syllabuses and explanatory notes during

Form III and IV, (Ordinary grade), and to comment on difficulties experienced at any stage in the secondary course, and to outline their approach to the topic. In the latter instance they were asked if they made use of models and analogies.

Some specific questions were then asked: was the concept of dynamism accepted in Form III and IV; was the equilibrium constant taught in Form V (Higher grade); were the concepts associated with the free energy (thermodynamic) approach to equilibrium understood.

Some respondents gave very full replies, most supplied information in answer to some of the questions, and - after a second request for information had been sent off - fourteen made no reply at all. Thus 29 replies were received. These are discussed below.

### 2.2(2) Teachers' Interpretations of Syllabuses and Explanatory Notes (3) with respect to Reversibility and Dynamism.

The concept of reversibility is extensively taught during the Ordinary grade course and about one third of the respondents restricted the treatment of the ionisation of water (I.5), the Contact Process (K.4) and the Haber Process (M.3) to one of reversibility. About two thirds introduce the dynamic concept of equal and oppositely occurring reactions, although the treatment varies in depth from a casual mention to a very full treatment, invoking, if not by name, the spirit of the Le Chatelier Principle. In this latter case, the school concerned was one which had a record of high academic achievement. Opinions as to whether or not the dynamic concept is understood by Ordinary grade pupils are fairly evenly divided.

Commenting on the explanatory notes in general, one person expressed the opinion that they were 'virtually non-existent'. One other person found difficulty in interpreting the meaning of 'simple kinetic picture' (A I.3). Two persons commented adversely on I.5 to the effect that, it was impossible to make sense of it, and that it was like 'diving in at the deep end'. Another expressed dissatisfaction at the kind of practical work offered at Higher grade during Section R (A I.4-7): the iodine equilibrium between water and chloroform is not obviously dynamic, the colour changes associated with the change of pressure on the nitrogen dioxide/tetroxide equilibrium are not convincing and the iodine monochloride/ trichloride system employs unfamiliar substances.

### 2.2(3) Difficulties encountered in teaching the Concept of Chemical Equilibrium; Subjective Assessment by Teachers.

Other than the interpretative difficulties just discussed above, the Ordinary course posed little of a conceptually difficult nature. There was, however, much comment about the difficulties experienced by pupils in coping or trying to cope with the concept of equilibrium at the Higher grade. By contrast, Section 2 of the Certificate of Sixth Year Studies course caused little trouble.

At Higher grade, difficulties associated with one or other of the Le Chatelier type problem situations were particularly prevalent. Salt hydrolysis and the pH values of salt solutions were found to be very difficult to teach effectively. Some pupils thought there were no hydroxyl ions in an acid solution. Similarly, pupils found it difficult to consider and deduce the resultant effect on an equilibrium system of alterations in pressure, temperature and concentration. There was difficulty in deciding whether to think in terms of the pressure variable or the volume variable when one or other of these was altered. Catalysis posed a variety of problems. Some pupils seemed to think that a catalyst only affected the forward reaction, others that it had no effect on an equilibrium system, others that it could be used to drive the equilibrium in the desired direction, still others that it produced more product. Some thought heat and light were catalysts. Some confused "rates of reaction and yield".

Some pupils found it difficult to accept that the same equilibrium position could be reached from either direction, while others could not distinguish between equilibrium and non-equilibrium situations, and became confused about the part played by activation energy and the part played by the overall enthalpy change.

The Haber Process and the Contact Process were thought of as if they were closed equilibrium systems when in fact they were not allowed to attain the equilibrium state at all.

The teaching of Section 2 of the Certificate of Sixth Year Studies course (A I.8) was less affected by conceptual difficulty. Of twenty nine replies, eleven chose to make no comment in response to this part of the enquiry, mainly because they had not had experience teaching this part of the syllabus and so did not feel qualified to pass comment.

Of the eighteen who passed comment, twelve considered there were no real conceptual difficulties and that the pupils reacted quite well to the alternative approach to chemical equilibrium. The concepts involved did not seem to cause any trouble. One person commented that entropy was well received "provided it was given a physical reality as degree of disorder".

The remaining six expressed some doubts about the ability of pupils to understand this new conceptual material and some suggested that, even though the pupils might be able to manipulate equations and get right answers, it was doubtful if they had any clear idea of what free energy was. And two of these six persons suggested that perhaps teachers in general were not actually aware in some cases of their own limitations in this area.

Of these six persons, two pointed to specific examples of conceptual difficulty. One pointed out that the syllabus was wrong in the first case since it was not the free energy change that was related to the equilibrium constant but the standard free energy change. The other thought that pupils could not conceive of the idea of a free energy well, and that free energy in general was an obscure quantity.

### 2.2(4) The Use of the Equilibrium Constant

Only one principal teacher of chemistry actively used the quilibrium constant during the Higher grade course and found it useful in a qualitative way. Two other principal teachers had tried to use it but had abandoned it because their pupils found it confusing.

### 2.2(5) Models and Analogies employed by Teachers

A variety of analogies are used by teachers to demonstrate and simulate the establishment of equilibrium. These are listed below.

1. Water being transferred between two containers by different beakers.
2. Mice jumping back and forth between two containers.
3. Twin connected goldfish bowls.
4. Fan operated enthalpy box with adjustable reactant and product levels.
5. A simple see-saw.
6. A mechanical balance.
7. A pupil walking up a down-escalator.
8. Water flowing into and out of sink at same rate.
9. Pupils simultaneously coming and going in one room.
10. Swimming against the current.
11. School dance.
12. Molecular pupils.

Analogy No. 1 was a particularly popular means of demonstrating the dynamic aspect of chemical equilibrium.

### 2.2(6) Some Models and Analogies suggested in the Literature.

Dainton and Fisher (27) describe a 'wind machine' which essentially consists of two compartments separated by a vertical movable barrier. The bottoms of the compartments are constructed of wire mesh to allow of the passage of a current of air, and are adjustable relative to each other to allow simulation of endothermic and exothermic reactions. Temperature, pressure and Le Chatelier type effects can be demonstrated. The machine can also be used to demonstrate entropic effects by employing coloured balls and varying the area of one or other of the compartments.

The machine is offered as partial remedy for the neglect which the kinetic aspect of equilibrium often suffers at the expense of the Le Chatelier type approach.

Alden and Smuckler (28) describe a model which is very similar to that described by Dainton and Fisher.

Weigang (29) describes a model for demonstrating the dynamic aspect of chemical equilibrium. The model is essentially a mechanised version of the transfer of water between two containers. Small concealed pumps are used to transfer water through tubes of different bore; and the efficiency of the pumps is determined by the head of water against which the transfer is made.

MacDonald (30) describes an analogy which depicts how the individual concentrations of a four component equilibrium system alter when the concentration of one of the components is increased.

Alyea and Dutton (31) have compiled a wide selection of models and analogies.

Hotchkiss (32) developed an Air Table Model for illustrating chemical equilibrium in a simulation by means of variously coloured air-bearing perspex pucks. Simultaneous bond dissociation and formation can be illustrated, leading to a clear understanding of the dynamic aspect of chemical equilibrium. The film loop of the model in action has the additional advantage that it can be stopped as required and a count of the various 'species' in the equilibrium mixture recorded.

## 2.3 Studies of the teaching of Concepts in general, and of the Concept of Chemical Equilibrium in particular reported in the Literature.

Shayer (33) discusses the implications of Piaget's work for the development of science courses. Statistical knowledge of the conceptual progress of school populations should be used to determine the content and structural presentation of courses. Shayer points out that though the three stages, intuitive, concrete and formal, may appear to supersede each other, they do rather augment each other. Thus a pupil who has reached the formal stage will not often carry out his reasoning at this level. He will often revert to the concrete and intuitive level, and even where symbolic formal thought is employed it will always be based on previously acquired intuitive and concrete knowledge. The implication of this is that, even with pupils who have demonstrated their ability to reason formally, new conceptual material must be introduced initially in an intuitive and concrete way. And practical work tends to fulfil this role.

Bass and Montague (34) comment that the developmental sequences which Piaget has identified form an excellent basis for instruction which is consistent with psychological processes. Bass and Montague applied such a Piaget based sequence of instruction to two problems: equilibrium in a mechanical balance and equilibrium of a cart on an inclined plane. The subjects were ninth grade students.

The sequence of instruction on the balance proved successful, but not so for the inclined plane. There was no obvious reason for the latter but it is suggested that the problem was perhaps too complex.

Some implications for further study were noted. If a student is to acquire new knowledge, there should be a 'match' between the instructional method and the student's mental stage. Programmed instruction may fail in this respect, in which event the active intervention by a well qualified teacher may be preferable. Further, it is suggested that Piaget's developmental sequences lack the fine structure to be truly helpful to the curriculum developers. And, finally, it is suggested that a Gagné type task analysis be applied in conjunction with Piaget's developmental sequences in the construction of learning hierarchies.

Lovell (35) repeated ten of Inhelder and Piaget's fifteen experiments and confirmed the main stages in the development of logical thinking proposed by them. Lovell comments that instruction as such does not seem to affect achievement as much as might be expected. Instruction by direct teaching is only of real lasting value when the thinking skills are almost or actually available in the subject, otherwise the knowledge is either forgotten or rote learned and regurgitated when required. He also expresses the opinion that the cultural milieu, climate of opinion or general experiences to which the person is subjected are important in developing thinking skills; the classroom atmosphere, the way in which the teacher poses and discusses problems have their effect.

Frederick (36) comments that the study of concept learning is a "hodge-podge" of bits and pieces. Much is said that has not been properly verified, and many variables are but little understood. Much of the knowledge is inferential rather than factual. Nevertheless, it is generally accepted that hypothetico-deductive thinking, the ability to consider and discard hypotheses, develops during the teens. But even so, students and ourselves alike often stoop to concrete thought processes in the acquisition of new concepts. And their acquisition is affected by a variety of other factors: strategies and cognitive style, mediation, personal traits, motivation, pre-training, practice, feedback and re-inforcement.

Ausubel (37) writes that the principal factor which affects and influences the learning and retention of new meaningful subject matter is the individual's cognitive structure, that is to say, the individual's organisation, stability and clarity of knowledge in a particular subject matter with respect to 'knowing'. If an individual's cognitive structure in a particular subject matter is clear, unambiguous, stable and well organised, it will facilitate the acquisition of new related subject matter, and vice versa. Hence, it is by strengthening relevant aspects of the pre-existing cognitive structure that the acquisition of new meaningful material can be facilitated. Deliberate attempts to do this are at the heart of the educational process.

Most new ideational material encountered by pupils in the school setting is relatable to pre-existing aspects of knowledge, to a background of meaningful ideas and information. The curriculum is planned in such a way that it allows of the introduction of new ideas in untraumatic fashion.

Most new concepts, if they are to be meaningful, must be anchored to established subsuming concepts in the cognitive structure and progressively assimilated until their individuality is lost in the body of the new overall cognitive structure.

Once it has been decided what are the concepts to be taught in a particular subject area, attention can be focussed on what order to introduce them and to what anchoring ideas to relate them. If the principle similarities and differences between a new concept and the pre-existing relevant conceptual material can be clearly, precisely and effectively pointed out to the pupil, it seems reasonable to suppose that the new concept will be accepted with fewer ambiguities, fewer conflicting meanings, fewer misconceptions suggested by the learner's prior knowledge of related concepts. And that the newly acquired knowledge in conjunction with analogous prior knowledge will form in time during the retention period an essentially misconception free whole.

Mealings (38) investigated the problem solving ability of about 120 children of mental age 11+ to 18+ by having them individually talk out their solutions to problems which arose as they were taken individually through a series of experiments in science. He related the quality of the children's thinking (concrete - when a particular logical form is still not independent of its concrete form - to formal - when abstract thought is possible) to their mental age. He then considered the relevance of the results to science teaching in general.

It was found that the ability to solve problems at the formal level was clearly correlated with mental age rather than chronological age, that there was no sex difference in problem solving ability. Mental age appeared to be the only critical factor though interest had a modifying influence on achievement.

Formal operations developed gradually from a mental age of 13 onwards where the actual mental age at which a problem could be solved depended on its difficulty. Difficulty, however, was not to be equated with complexity but rather with the quality of reasoning required. For example, only one child out of 27 with mental ages below 16 was able to successfully devise a method of determining if a white powder was a single substance or a mixture of two substances where the experimental technique was quite a simple one, one of dissolving, filtering and evaporating.

Since logical growth is gradual, it follows, therefore, that the transition from qualitative concrete practice to quantitative formal thought should be gradual. Too abrupt a transition will lead to a loss of interest.

Buell and Bradley (39) selected the equilibrium between undissolved salt and its saturated solution as the vehicle for a study of the use of propositional thinking by a group of 56 first year and 14 second year Ohio secondary school children. Comprehension of variables, constants, dynamism and solubility curves was assessed at various Piagetian levels initially by a pretest and after two weeks of laboratory work and discussion, by a posttest. It was concluded that contact with practical solubility and informal discussion did not improve logical thinking about variables, and other aspects of the solubility equilibrium. It would seem, therefore, that logical operations and critical thinking can only be taught purposefully; they are not 'caught'. Indeed, the two weeks training seemed to be confusing since there was a drop in the percentage showing logical operations.

Averch et al. (40) examined a wide variety of educational researches carried out in the United States. They excluded from consideration all researches which could not stand up to a close critical scrutiny of their procedures; the vast majority of researches fell into this category. From their examination of the remainder it was concluded, in general terms, that there was apparently no single variant of the existing educational system that was related positively to student cognitive outcome. Non-cognitive outcomes appeared to be impossible to assess. There were in some cases transient and temporary improvements in cognitive achievement but these soon disappeared. The critical factor would appear to be the basic academic ability of the pupil.

Averch et al. discuss programmed instruction and point out that over the last decade or so there has been much interest in this mode of instruction, though this has now waned somewhat since there is no evidence to support the view that programmed instruction is superior to conventional classroom teaching. Work on the presentation of material suggests that it is not so much the medium of instruction that is important as its sequencing and organisation, though some methods of presentation are better for some tasks and for some students. However it is difficult to match students, task characteristics and mode of presentation. Thus the characteristic features of the programmed instructional method, careful sequencing of instructional tasks involving continuous participation on the part of the learner with immediate feedback, have not been shown to be superior to good conventional teaching.

Carrol (41) suggests, since it is not possible to tailor-make courses to suit individual students, a compromise combination of the inductive and deductive methods is probably desirable. He also recommends the use of negative instances for sharpening concepts but would discourage the use of non-instances.

Sakmyser (42) compared the effectiveness of teaching chemical equilibrium by inductive and deductive programmed instruction. They started by listing the concepts, facts and ideas to be taught, and used these to formulate the behavioural objectives. The latter were then arranged in two orders, one inductive and one deductive, vetted by other educationalists, revised and finalised. A group of 150 students were divided randomly, half assigned to one programme and half to the other. An analysis of variance showed that neither programme was significantly better in teaching chemical equilibrium. Further analysis showed that the different programmes were superior for individuals with different personality traits (outgoing, anxious, critical, precise, creative) and skills (in algebra and reading).

Gagné and Brown (43) investigated the effectiveness of three different kinds of programmed instruction (Rule & Example, Discovery, Guided Discovery) in achieving understanding of a variety of number concepts. The Guided Discovery programme led to a superior performance in problem solving situations. It is inferred that this is because this programme required systematic reinstatement of learned concepts where the Rule & Example programme did not and the Discovery programme left them to chance.

Johnson & Stratton (44) evaluated the effectiveness of teaching a group of word concepts by four separate and different methods, by a fifth method which was a mixture of the other four, and by a control method. The subjects were 200 students in general psychology, divided randomly into six groups.

The performance of each of the five experimental groups was superior to that of the control group; the performance of those on the mixed programme was superior to the performances of those on the four separate programmes; the performances of those on the four separate programmes were not different. The superiority of the mixed programme supports the common practice of teachers and writers of text books. Kempa and Dubé (45) showed that cognitive learning styles varied to a marked extent with ability in chemistry: the more academic high achiever type of pupil was more inclined towards pure science, and showed a greater tendency to acquire new knowledge, while the less academic pupil showed the reverse characteristics.

Malpas (46) describes dynamic chemical equilibrium as one of many examples of an auto-regulatory (feedback) system in that it is sensitive and adaptable to conditions imposed upon it. In order to understand the concept of chemical equilibrium, sixth form pupils have to master a complex set of formal (abstract) relationships. He suggests that pupils perhaps need more time to explore not only various aspects of particular equilibrium systems but to contrast the pre-equilibrium state with the equilibrium state.

He pleads strongly in favour of using, initially, the less conceptually difficult kind of equilibrium system, such as the system obtained by the dissociation of calcium carbonate where only one species has to be considered. He sees the more familiar ester hydrolysis, by contrast, as a much more conceptually difficult system to work with because it consists of four components which must all be considered simultaneously.

He makes use of a graphical presentation to explore the manner in which concentrations alter over time at different temperature.

## 2.4 A Summing-up

The assessment of conceptual difficulties encountered in teaching and learning the concept of chemical equilibrium recorded in this Chapter point to some specific and some general areas of the syllabus where conceptual difficulties are experienced by pupils. These are listed in Tables 2.1 and 2.2.

Table 2.1 Suggested Conceptual Difficulties at Higher Grade
Rates Approach

1. Left and right sidednes.
2. Inherent 'equal and opposite' quality of equilibrium.
3. Interpretation of the reversed arrow convention.
4. Equilibrium/non-equilibrium situations and activation energy.
5. Effect of variables; Le Chatelier; hydrolysis of salts.
6. Catalysis in general.
7. Rate and extent. (This aspect is probably covered by 4 and 6 above.) Meaning of yield.
8. Closed and open systems.

These difficulties will be examined in detail and expanded upon in Part II of this report.

Table 2.2 Suggested Conceptual Difficulties at S.Y.S.
Thermodynamics Approach

Meaning of reversible process.
Free energy.
Free energy well at equilibrium.
Use of $\Delta G$ in the expression for equilibrium constant instead of $\Delta G^o$.
Entropy notoriously difficult; its mystique.
Entropy a measure of disorder at molecular level.
Increasing entropy of the universe an invalid concept.
Systems and surroundings.

These conceptual difficulties will be examined in detail and expanded upon in Part III of this report.

# A II.1

A "If a system in equilibrium is subjected to an alteration in conditions (change in volume, addition or removal of heat, change in mass of reactant), the system will tend to adjust itself so as to reduce the resulting changes in its related specific property (pressure, temperature, and concentration respectively)."

B The change in an intensive variable caused by changing the corresponding extensive variable is <u>smaller</u> if chemical equilibrium is maintained than if no reaction could take place in the system ......... IIa

The change in an extensive variable caused by changing the corresponding intensive variable is <u>larger</u> if chemical equilibrium is maintained than if no reaction could take place in the system ......... IIb

C Comparison of results of O-Grade students in objective tests with the degree of difficulty they thought they had experienced in the same topics:

| Topic | Number of Items | Students' Reaction | Percentage of Students giving Correct Response | |
|---|---|---|---|---|
| G1 | 4 | Easy | 69, 85, 63, 89 | Av. 77 |
| H2 | 3 | Inconclusive | 46, 55, 57 | Av. 53 |
| H3 | 6 | Difficult | 10, 40, 38, 30, 27, 27 | Av. 29 |
| I1 | 4 | Easy | 45, 75, 56, 59 | Av. 59 |
| I3 | 4 | Difficult | 35, 49, 46, 30 | Av. 40 |
| L3 | 4 | Difficult | 45, 54, 24, 50 | Av. 43 |
| N1 | 2 | Inconclusive | 51, 53 | Av. 52 |
| N2 | 3 | Difficult | 30, 31, 32 | Av. 31 |
| N6 | 3 | Inconclusive | 78, 43, 45 | Av. 55 |

(Topic Difficulties in Chemistry, Table 2.)

D Ques. 8. 0.1 M ammonium hydroxide has a pH of 11.1. On addition of some solid ammonium chloride the pH changes to 9. Explain why this occurs. (3)

A II.2

Chemistry Department,
The University,
GLASGOW G12 8QQ

18th December, 1974

I am looking into the topic of chemical equilibrium as it arises during Ordinary Grade, Higher Grade and the Certificate of Sixth Year Studies, with a view to finding out which areas are difficult for pupils, and hope ultimately to formulate some ideas and suggestions on how these difficulties may be avoided or overcome.

By way of preliminary fact-finding I should like to ask you how you interpret the relevant explanatory notes in the Scottish Certificate of Education Examination Board revised Circular No. 512, in particular at the Form III and Form IV level. And in general I am interested in your opinion of the level of difficulty and in your approach to teaching the topic at the various grades. Do you, for example, in your approach, make use of models and analogies?

The sort of information I am after is something along the following lines:-

Forms III and IV - Do you think the pupils understand the idea of chemical dynamic equilibrium? Have you any preferred method of getting the idea over to them?

Form V - Are there any areas where, in your opinion, the pupils find undue difficulty? Do you use the equilibrium constant?

Form VI - Do you feel the pupils can cope with the concepts built into the free energy approach to equilibrium?

I shall be most grateful for any comments you care to make, no matter how brief they may be.

Yours sincerely,

John J. MacDonald

# PART II

# CONCEPTUAL DIFFICULTIES
# AT
# HIGHER GRADE

# CHAPTER 3

# DESIGN AND SCOPE OF THE INVESTIGATION AT HIGHER GRADE

## 3.1 Introductory Comments

It was considered that the survey of chemical equilibrium reported in Part I was such as to warrant a more detailed investigation of the conceptual difficulties experienced by pupils at Higher Grade (Table 2.1). It was therefore decided to construct an objective test, the Rates Approach Test, to assess the breadth and depth of this misconceptual knowledge. Before proceeding with this task, however, it was thought necessary to carry out a preliminary assessment of this misconceptual knowledge and, at the same time, assess the validity of the questions which would ultimately be incorporated in the Rates Approach Test.

This preliminary assessment and validation was achieved by means of (a) a Free Response Questionnaire and (b) an Interview Session Questionnaire.

## 3.2 The Free Response Questionnaire*

The Free Response Questionnaire consisted of sixty two questions of varied type. The questionnaire was divided into three approximately equivalent sets of questions so that, in effect, triplicate sub-questionnaires of 21, 21 and 20 questions respectively were available since the questions within each set tested the same supposed conceptual difficulties in slightly different ways.

The significant feature of the Questionnaire was that it was given as an open-ended test, to interpret at will. Pupils were encouraged to be quite free and frank in their written responses. By this means it was hoped to assess, not only the nature of conceptual difficulties, but also if the test were in fact validly measuring what the author

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*The Free Response Questionnaire is not included in pocket since it is very similar in content and structure to the Interview Session Questionnaire, which is included as Pocket Item 1.

was attempting to measure, or were pupils, instead, giving the wrong 'impression' of the state of their knowledge for an unrelated or irrelevant reason.

On the day of the test, forty two pupils were available in the author's school, a large comprehensive secondary. These pupils were divided into three equal ability groups on the basis of Ordinary Grade performance and performance in class tests. Each group of pupils was given a different set of questions so that a triplicate assay of the conceptual difficulties and validation of the questions was achieved.

In order to ensure that the final list of conceptual difficulties around which the Rates Approach Test would be built was as comprehensive and exhaustive as possible, the Questionnaire not only asked about the difficulties listed in Table 2.1 but also asked about related topics: the conservation of atoms, the conservation of mass, collision theory, and about matter and energy since these latter concepts are basic to the research to be carried out at the Certificate of Sixth Year Studies level. And the pupils were also asked to arrange some selected concepts which arise during the teaching of chemical equilibrium at Higher grade in what they thought to be a logical order of presentation in order to establish if there were a preferred logical mode of presentation.

The results of the Free Response Questionnaire suggested a few questions be modified, a few abandoned and a few introduced, but these changes were minimal. The revised version of the Free Response Questionnaire was called the Interview Session Questionnaire and was administered by interview to pupils of another large comprehensive secondary school.

## 3.3 The Interview Session Questionnaire

The revised Free Response Questionnaire was called the Interview Session Questionnaire (Pocket Item 1).

This questionnaire consisted of three approximately equivalent sets of questions;Set 1, Set 2 and Set 3. There were twenty one questions of varied type in each of the three Sets.

Three interviewers were involved, the author and two others with acknowledged experience of teaching. Each interviewer talked out the problems posed by his or her Set with about five pupils, one at a time over the course of an hour, covering most of the questions in the Set. The pupils were selected for interview by the Principal Teacher who was asked to select what she considered to be a representative spread of ability in the year group. Each pupil, therefore, was taken through about four questions; and subjective assessment was made by the interviewer of the conceptual difficulties experienced by the pupil, on the one hand, and of the validity of the questions in actually detecting these difficulties, on the other hand. After the morning's session it was agreed by all three interviewers, two of whom in a sense were independent witnesses, that difficulties did exist for the pupils and that the questions were acceptably valid in detecting these difficulties.

The topics tested and the allocation of questions to these topics are recorded in Table 3.1.

Table 3.1 Interview Session Questionnaire: Topics and Questions

| Topic | Question Numbers |
|---|---|
| 1. Left and right sidedness | 1.8, 1.9, 2.7, 2.8a, 2.9, 2.10, 3.8, 3.9, 3.11, 3.17, 3.18a |
| 2. Inherent equal and opposite quality of chemical equilibrium | 1.5, 1.21, 2.4, 2.8b, 2.18, 3.10, 3.14b and 3.14c. |
| 3. Interpretation of reversed arrow convention | 1.6, 2.5, 2.6, 3.4, 3.7 |
| 4. Distinguishing equilibrium and non-equilibrium situation | 1.7, 2.12. |
| 5. Effect of variables on an equilibrium system, including Le Chatelier and the hydrolysis of salts | 1.10, 1.16, 2.11, 1.13, 3.12a, 3.12b, 3.13, 3.18b. |
| 6. Catalysis | 1.14, 1.15, 2.14, 3.15. |
| 7. Closed and open systems, yield. | 2.21, 3.21. |
| 8. Conservation of atoms | 1.3, 1.4, 2.1 |
| 9. Conservation of mass | 1.2 |
| 10. Balancing chemical equations | 2.2, 3.3. |
| 11. Mass versus concentration | 2.3, 3.5. |
| 12. Matter versus energy | 1.1. |
| 13. Forms of energy | 1.20, 3.1, 3.19, 3.20. |
| 14. Conservation of energy | 3.2. |
| 15. Kinetic particle theory | 1.11, 1.12, 1.13. |
| 16. Collision theory of chemical reaction. | 1.17, 1.19, 2.16, 2.19. |
| 17. Concept sequence in rates approach to equilibrium | 1.18, 2.15, 2.17, 2.20, 3.6, 3.16. |

Topics 1 to 7 are the conceptual difficulties reported in Table 2.1. Topics 8 to 17 have been included for the reasons given on page 50. The written and verbal responses offered by pupils showed that topics 1 to 6 and topics 12 to 15 required further testing and these, therefore, were included in the Rates Approach Test. Topic 17 also required some further attention but this was given outwith the Rates Approach Test (for which see 3.5).

## 3.4 The Rates Approach Test

### 3.4(1) Design of the Rates Approach Test

On the strength of the information gathered in the survey of chemical equilibrium of Part I and of the preliminary assessment of these and other difficulties described in 3.2 and 3.3, a Rates Approach Test (Pocket Item 2) was made up.

The test consisted of twenty three objective questions. Each question consisted of a stem which stated the problem, followed by four response options, A, B, C and D, of which one only was correct. An additional response option E was offered in each question which the pupil was requested to choose should he not know which response was correct. It was hoped that this would minimise guessing.

The nature of the research being undertaken placed the level of the investigation at the Piagetian III stage of development. The questions are constructed in the higher Bloom categories, the majority group of questions being evaluative (Table 3.2). Considering the complexity of the questions it was considered that twenty three questions were enough to expect Form V to tackle.

The conceptual difficulties tested and the allocation of questions to these difficulties are shown in Table 3.2.

Pupils were additionally asked to explain their choice of response for five questions, questions 3, 6, 11, 14 and 21. These questions were marked ** . This request was made in order to establish whether or not the correct response was made for the correct reason. Questions 3 and 14 were included since they both deal with the pupil's ability to distinguish between equilibrium and non-equilibrium situations, which is perhaps one of the most fundamental aspects of the concept of chemical equilibrium. Questions 6, 11, and 21 were included since they deal with aspects of the concepts of matter and energy which are fundamental to the research to be carried out at the Sixth Year Studies level.

Table 3.2 Rates approach Test: Topics, Question Numbers and Abilities.

| Topics | Question No. and Bloom Ability |
|---|---|
| 1. Left and right sidedness | 4(Co), 9(Co), 17(Ev). |
| 2. Inherent equal and opposite quality of chemical equilibrium | 5(Co), 8(Co), |
| 3. Interpretation of reversed arrow convention | 18(Co) |
| 4. Distinguishing equilibrium and non-equilibrium situations | 3(Ev), 14(Ap). |
| 5. Effect of variables on anequilibrium system, including Le Chatelier and the hydrolysis of salts. | 1(Ev), 10(Ev), 13(Ev), 15(Ev), 16(Ev). |
| 6. Catalysis | 2(Kn), 7(Ev), 12(Ap), 19(Ap), 20(Ev). |
| 7. Matter and energy | 6(Co), 11(Ev), 21(Co), 22(Kn), 23(Ev). |

The number of questions allocated to each of the topics to be investigated was determined by the kind and variety of individual misconceptions considered possible within any one of these topics. The ability which any one question was considered to test in its particular topic area is indicated in brackets, and is:

a) Kn for 'knowledge', requiring simple recall,
b) Co for 'comprehension', requiring understanding in addition to simple recall,
c) Ap for 'application', requiring application of knowledge which has been recalled and understood,
d) Ev for 'evaluation', which requires the ability to evaluate recalled and understood information in an applied situation.

The Rates Approach Test was weighted rather heavily on the evaluative side - eleven questions were considered to test evaluation in one way or another while only two were considered to test simple recall - as a consequence of the type of investigation being carried out.

### 3.4(2) Scope of the Rates Approach Test.

The Rates Approach Test was ready towards the end of May, 1975, which left five weeks or so till the end of the school session. Consequently, arrangements for the administration of the test were made informally by telephone and personal visit in order to save time, and nineteen schools agreed to help. Because of the personal element involved in making the sample selection - the author relied on cooperation of teachers in his former county (Dunbarton) and his existing county (Lanark) - the sample is weighted in favour of borough schools from these counties.

The national distribution of schools is shown in Table 3.3.

Table 3.3 Type and number of Scottish Secondary Schools

| Type | Number |
|---|---|
| Comprehensive City School | 111 |
| Borough, County & Rural Comprehensive Schools | 267 |
| Grant Aided Schools | 30 |
| Independent Schools | 33 |

Of the nineteen schools which agreed to help, thirteen made returns, and these schools are shown in Table 3.4.

Table 3.4 Schools and Returns in Rates Approach Test

| Type | School Code | No. of Returns |
|---|---|---|
| City | 07 | 15 |
| Borough & County | 02 | 15 |
| | 03 | 39 |
| | 04 | 20 |
| | 10 | 15 |
| | 11 | 11 |
| | 12 | 19 |
| | 14 | 20 |
| | 15 | 13 |
| | 16 | 21 |
| | 17 | 21 |
| | 19 | 9 |
| Grant-aided | 00 | 37 |
| | | Total = 255 |

One independent school was approached but was not able to help because the Scottish syllabus was not taught in chemistry.

### 3.4(3) Sample Characteristics

Pupils were asked to record whether they had obtained a Band A, B or C (A III.1) in the Ordinary Grade examination in chemistry in the previous session. They were also asked to record whether they had studied physics to Higher Grade, to Ordinary Grade only, or not at all. These data are shown in Table 3.5.

Table 3.5 Pupil Characteristics - Nine Subgroups

| Sub-group | Band in Chemistry at O Grade | Course in Physics | Number of Pupils |
|---|---|---|---|
| 1 | A | Higher | 155 |
| 2 | | Ordinary | 13 |
| 3 | | None | 14 |
| 4 | B | Higher | 33 |
| 5 | | Ordinary | 12 |
| 6 | | None | 7 |
| 7 | C | Higher | 11 |
| 8 | | Ordinary | 8 |
| 9 | | None | 2 |

The information on the quality of pass in chemistry was required in order to allow the Rates Approach Test to be statistically validated against a prior related test. The information on the course taken in physics was required to assess the effect, if any, of such a course on the performance of pupils in the Rates Approach Test.

Some of the nine subgroups of Table 3.5 are too small for statistical treatment. The nine subgroups are therefore condensed to four subgroups as shown in Table 3.6.

Table 3.6 Pupil Characteristics - Four Subgroups

| Subgroup | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Band in Chemistry at Ordinary grade | A | A | B/C | B/C |
| Course taken in Physics | Higher | Ordinary or none | Higher | Ordinary or none |
| Number of Pupils | 155 | 27 | 44 | 29 |

These subgroupings were chosen because (a) they gave reasonable numbers per subgroup for statistical purposes, and (b) they represented an acceptable division of ability in chemistry since Band A corresponds to five ranges of marks while Bands B and C together correspond to four ranges (A III.1).

### 3.4(4) Statistical Treatment of the Rates Approach Test

(i) Reliability A test is reliable if, when administered on two separate occasions to the same pupils, these pupils achieve the same scores, that is to say, scores which are not significantly different from each other between occasions. However, when the data gathering technique consists of an objective test which is administered on one occasion only, the Kuder-Richardson procedure (A III.2(A)) for assessing reliability can be used. This procedure will therefore be used to assess the reliability of the Rates Approach Test.

(ii) Validity A test is valid if it measures that which it sets out to measure.

A subjective assessment of the validity of the Rates Approach Test is described in 3.2 and 3.3.

Since the Rates Approach Test attempts to measure conceptual ability in chemistry, there should be a correlation between the results obtained by pupils in the Test and the results obtained by the same pupils in a prior test in chemistry, namely the Ordinary Grade examination. Admittedly, this latter examination is not as conceptually difficult as the Rates Approach Test, but it does measure ability in chemistry, albeit at a more elementary level.

Thus the validity of the Rates Approach Test will be assessed statistically by computing a biserial correlation coefficient (A III.2(B)) between the scores achieved by pupils in the Rates Approach Test and the quality of pass obtained by the same pupils in the Ordinary grade examination in chemistry of the previous session. The quality of pass is discussed in 3.4(3).

(iii) Effect of physics The effect of the course taken in physics (if any) on the results of the Rates Approach Test will be assessed by performing an Analysis of Variance on data for the four subgroups shown in Table 3.6. Given that the Anova of these multiple group data shows an F ratio which is significant at the significance level chosen (5%), the specific source or sources of this significance can be located by application of the Scheffé Method (S-Method) of Multiple Contrasts (A III.3). This statistical procedure is applicable to multigroup contrasts when the numbers in each group are different. It is also recommended for use where contrasts between pairs of means in addition to contrasts between individual means are to be made.

(iv) Normality of Rates Approach Test Scores Since the application of the Kuder-Richardson formula, the determination of the Biserial Correlation Coefficient, the Analysis of Variance and the Scheffé Method are parametric procedures, they require that the distribution of scores of pupils on the Rates Approach Test be not significantly different from the normal distribution. Consequently, the observed scores on the Rates Approach Test will be reduced to expected scores for a normal distribution and a $\chi^2$ test of significance between the two carried out.

## 3.5 Concept Sequence at Higher Grade

Some attempt had been made by means of the Free Response Questionnaire and the Interview Session Questionnaire to assess the logical order of presentation of the individual concepts encountered by pupils during the Higher Grade course on chemical equilibrium. It was decided to exclude this aspect of the overall investigation from the Rates Approach Test and, instead, to assess it separately. The principal teacher of chemistry of a local comprehensive secondary school agreed to issue two jumbled lists of the concepts on two separate occasions to two different groups of pupils who had just returned to school after the certificate examinations. Each group of pupils contained a spread of ability.

The jumbled lists of concepts were:

List 1

Energy of Activation
Equilibrium
Collision Theory
Equal and Opposite Rates
Activated Complex

List 2

Rate Determining Step
Reaction Mechanism
Energy of Activation
Activated Complex

List 1 was presented to a group of nine pupils. List 2 was presented to another group of fourteen pupils. In each case the pupils were asked to consider which order they thought would be most logically acceptable as an order of presentation.

A 'best' overall logical Concept Sequence was arrived at by a simple inspection of the orders suggested (pp. 78 and 79).

## A III.1

Ordinary Grade Examination in Chemistry,
Scottish Certificate of Education Examination Board

Results will be recorded on candidates' certificates in terms of five bands, A to E, as follows:

| Scaled % Mark | Range | Band |
|---|---|---|
| 100 - 90 | 1 | A |
| 89 - 85 | 2 | |
| 84 - 80 | 3 | |
| 79 - 75 | 4 | |
| 74 - 70 | 5 | |
| 69 - 65 | 6 | B |
| 64 - 60 | 7 | |
| 59 - 55 | 8 | C |
| 54 - 50 | 9 | |
| 49 - 45 | 10 | D |
| 44 - 40 | 11 | |
| 39 - 35 | 12 | E |
| 34 - 30 | 13 | |
| Below 30 | 14 | No award |

A/

Computation of the Kuder-Richardson coefficient $r_{KR}$ uses the formula:-

$$r_{KR} = \frac{N}{N-1}\left[1 - \frac{\leq pq}{S2}\right]$$

where N = number of items in test (23),
S = standard deviation of all scores in the test (3.80),
p = proportion passing each item,
q = proportion failing each item.

p is the facility value; q = 1 - p.

B/

Biserial Correlation Coefficient

This may be used when actual marks are available for one measure (scores on the Rates Approach Test) and a dichotomous classification for the other (A or B/C pass in the certificate examination) where a continuous distribution underlies the latter.

$$r_{bis} = \frac{m_A - m_{B/C}}{S} \cdot \frac{pq}{h}$$

where $m_A$ = mean score on the Rates Approach Test of those who gained a Band A. Ordinary chemistry,
$m_{B/C}$ = mean score on the Rates Approach Test of those who gained a Band B or C. in Ordinary chemistry.
S = standard deviation of scores of whole group of pupils,
p = proportion gaining a Band A.
q = proportion gaining Bands B and C.
h = height of the normal curve at the deviate dividing the area in the proportion p and q, and is obtained from Tables.

## Scheffé Method of Multiple Contrasts

The application of this method is discussed in Statistical Methods in Education and Psychology, Glass and Stanley, pp. 388-397. An outline of the procedure is illustrated below.

| | Contrast required | Estimate of contrast $\hat{\psi}$ | Estimate of S.D. of contrast $\hat{\sigma}$ | Ratio $\hat{\psi}/\hat{\sigma}$ |
|---|---|---|---|---|
| 1. | $\mu_1 - \mu_2$ | $\overline{X}_1 - \overline{X}_2$ | $\sqrt{MS_w\left(\frac{1}{n_1} + \frac{1}{n_2}\right)}$ | $x_1$ |
| 2. | $\mu_1 - \mu_3$ | $\overline{X}_1 - \overline{X}_3$ | $\sqrt{MS_w\left(\frac{1}{n_1} + \frac{1}{n_3}\right)}$ | $x_2$ |
| 3. | $\mu_1 - \mu_4$ | $\overline{X}_1 - \overline{X}_4$ | $\sqrt{MS_w\left(\frac{1}{n_1} + \frac{1}{n_4}\right)}$ | $x_3$ |
| 4. | $\mu_2 - \mu_3$ | $\overline{X}_2 - \overline{X}_3$ | $\sqrt{MS_w\left(\frac{1}{n_2} + \frac{1}{n_3}\right)}$ | $x_4$ |
| 5. | $\mu_2 - \mu_4$ | $\overline{X}_2 - \overline{X}_4$ | $\sqrt{MS_w\left(\frac{1}{n_2} + \frac{1}{n_4}\right)}$ | $x_5$ |
| 6. | $\mu_3 - \mu_4$ | $\overline{X}_3 - \overline{X}_4$ | $\sqrt{MS_w\left(\frac{1}{n_3} + \frac{1}{n_4}\right)}$ | $x_6$ |
| 7. | $\frac{\mu_1+\mu_2}{2} - \frac{\mu_3+\mu_4}{2}$ | $\frac{\overline{X}_1 + \overline{X}_2}{2} - \frac{\overline{X}_3 + \overline{X}_4}{2}$ | $\sqrt{MS_w\left(\frac{1}{4n_1} + \frac{1}{4n_2} + \frac{1}{4n_3} + \frac{1}{4n_4}\right)}$ | $x_7$ |
| 8. | $\frac{\mu_1+\mu_2}{2} - \frac{\mu_3+\mu_4}{2}$ | $\frac{\overline{X}_1 + \overline{X}_3}{2} - \frac{\overline{X}_2 + \overline{X}_4}{2}$ | $\sqrt{MS_w\left(\frac{1}{4n_1} + \frac{1}{4n_2} + \frac{1}{4n_3} + \frac{1}{4n_4}\right)}$ | $x_8$ |

If the absolute value of the ratio $\hat{\psi}/\hat{\sigma}$ exceeds the value of $\sqrt{(J - 1)\ {}_{.95}F_{J-1,N-J}}$, the contrast is significant at the 5% level.

# CHAPTER 4

# RESULTS

## 4.1 The Free Response and Interview Session Questionnaires

The written and verbal responses to these questionnaires were assessed subjectively. This assessment of the presence or absence of conceptual difficulty in the variety of topics examined is reported in Table 4.1

Table 4.1 Assessment of Conceptual Difficulties by means of the Free Response and Interview Session Questionnaires.

| Topic | Subjective assessment |
|---|---|
| 1. Left and right sidedness | Considerable confusion. Pupils seem to think that systems are compartmentalised. |
| 2. Inherent equal and opposite quality of equilibrium systems | Pupils are generally aware of dynamic quality but often argue that one or other reaction is greater at equilibrium. |
| 3. Interpretation of reversed arrow convention | When the arrows are of unequal length, the longer one implies greater rate at equilibrium. |
| 4. Distinguishing equilibrium and non-equilibrium situations | Pupils appear to be generally quite unable to distinguish between these situations. |
| 5. Effect of variables on an equilibrium system, including Le Chatelier and the hydrolysis of salts | Eight questions were allocated, and responses varied from moderate to very poor. The pupils appear to find this 'variables' aspect difficult. |
| 6. Catalysis | A superficial knowledge exists liberally laced with misconceptions. Pupils tend to select anything containing the word 'increase'. |

Table 4.1 (contd.)

| Topic | Subjective Assessment |
|---|---|
| 7. Closed and open systems; yield | Good response |
| 8. Conservation of atoms | Good response |
| 9. Conservation of mass | Good response |
| 10. Balancing chemical equations | Good response |
| 11. Mass versus concentration | Good response |
| 12. Matter versus energy | Some confusion |
| 13. Forms of energy | Much confusion |
| 14. Conservation of energy | Pupils are quite unaware of this basic concept |
| 15. Kinetic Particle Theory | Some confusion |
| 16. Collision Theory | Good response |
| 17. Concept Sequence in rates approach to equilibrium | Questions were over ambitious and too difficult. It was decided to make this a separate issue. |

The preliminary assessment employing the Free Response and Interview Session Questionnaires provided an assessment of conceptual difficulties in general agreement with that obtained from the Survey described and reported in Part I. Additionally, it provided evidence of conceptual difficulty in the area of matter and energy, particularly the latter.

The Rates Approach Test examined the particularly sensitive areas 1 to 6 and 12 to 15 in a manner (by objective testing) which allowed the reliability and validity of the test to be assessed statistically.

## 4.2 The Rates Approach Test

### 4.2(1) Facility Values and Discriminatory Powers

The facility values and discriminatory powers obtained with the sample of 255 pupils are given in Table 4.2

Table 4.2 Rates Approach Test; Facility Values and Discriminatory Powers

| Topic | Ques. No. & ability | Key | F.V. | $T_1 - T_3$ |
|---|---|---|---|---|
| 1. Left and right sidedness | 4 Co | B | 0.55 | 0.49 |
| | 9 Co | C | 0.21 | 0.27 |
| | 17 Ev | D | 0.22 | 0.21 |
| 2. Inherent equal and opposite quality of chemical equilibrium | 5 Co | C | 0.26 | 0.33 |
| | 8 Co | A | 0.42 | 0.52 |
| 3. Interpretation of reversed arrow convention | 18 Co | C | 0.15 | 0.22 |
| 4. Distinguishing equilibrium and non-equilibrium situations | 3 Ev | B | 0.28 | 0.16 |
| | 14 Ap | D | 0.13 | 0.24 |
| 5. Effect of variables on an equilibrium system, including Le Chatelier and the hydrolysis of salts | 1 Ev | D | 0.09 | -0.02 |
| | 10 Ev | C | 0.31 | 0.38 |
| | 13 Ev | C | 0.40 | 0.59 |
| | 15 Ev | C | 0.46 | 0.58 |
| | 16 Ev | A | 0.52 | 0.52 |
| 6. Catalysis | 2 Kn | B | 0.63 | 0.48 |
| | 7 Ev | D | 0.45 | 0.53 |
| | 12 Ap | D | 0.67 | 0.52 |
| | 19 Ap | A | 0.32 | 0.21 |
| | 20 Ev | A | 0.76 | 0.39 |
| 7. Matter and energy | 6 Co | C | 0.62 | 0.55 |
| | 11 Ev | B | 0.15 | 0.22 |
| | 21 Co | B | 0.68 | 0.39 |
| | 22 Kn | C | 0.56 | 0.31 |
| | 23 Ev | A | 0.32 | 0.33 |

$T_1 - T_3$ is the difference between the facility values of the top third and the bottom third (A IV.1) on the test as a whole, and is therefore a measure of the discriminatory power of the question. The facility value of at least one question in each topic area is very low. The implications of this will be discussed in Chapter 5.

### 4.2(2) Frequency (%) of responses

The percentage frequencies (to the nearest whole number) of selection of correct and incorrect responses is given in Table 4.3.

Table 4.3 Frequency (%) of responses

| Question No. | A | B | C | D | E |
|---|---|---|---|---|---|
| 4 | 17 | 55* | 2 | 8 | 18 |
| 9 | 20 | 28 | 21* | 19 | 12 |
| 17 | 31 | 14 | 17 | 22* | 16 |
| 5 | 32 | 4 | 26* | 27 | 11 |
| 8 | 42* | 30 | 16 | 6 | 6 |
| 18 | 30 | 11 | 15* | 14 | 30 |
| 3 | 10 | 28* | 28 | 2 | 32 |
| 14 | 36 | 19 | 4 | 13* | 28 |
| 1 | 32 | 6 | 47 | 9* | 6 |
| 10 | 42 | 8 | 31* | 5 | 14 |
| 13 | 17 | 20 | 40* | 5 | 18 |
| 15 | 18 | 13 | 46* | 4 | 19 |
| 16 | 52* | 23 | 16 | 3 | 6 |
| 2 | 9 | 63* | 18 | 6 | 4 |
| 7 | 30 | 11 | 6 | 45* | 8 |
| 12 | 6 | 2 | 25 | 67* | 0 |
| 19 | 32* | 13 | 17 | 33 | 5 |
| 20 | 76* | 4 | 4 | 12 | 4 |
| 6 | 4 | 2 | 62* | 4 | 28 |
| 11 | 38 | 15* | 22 | 1 | 24 |
| 21 | 4 | 68* | 3 | 6 | 19 |
| 22 | 35 | 2 | 56* | 3 | 4 |
| 23 | 32* | 13 | 38 | 3 | 14 |

Correct responses are marked with an asterisk

### 4.2(3) Observed and Expected Frequencies of Scores on the Rates Approach Test for the Whole Group

The observed frequencies of pupils' scores in the Rates Approach Test are given in Table 4.4.

Since it is proposed to establish the reliability and validity of the Rates Approach Test by techniques which assume underlying normality of the distribution of scores on the Rates Approach Test, the frequencies which would be expected of a group of 255 pupils whose mean score is 9.17 and standard deviation is 3.80 have been calculated (A IV.2) and are shown in Table 4.4.

The computation of $\chi^2$ (A IV.2) between observed and expected frequencies gives the value 23.05 for 15 df, and so the observed frequencies do not differ significantly from normality since $\chi^2_{.95} = 25.0$.

Observed and expected frequencies of scores are shown graphically in Figure 4.1.

Table 4.4 Observed and expected Frequencies of Scores on Rates Approach Test - Whole Group

| Score | Observed Frequency | Expected Frequency |
|---|---|---|
| 0 | - | 1.5 |
| 1 | - | 2.6 |
| 2 | 2 | 4.5 |
| 3 | 9 | 7.2 |
| 4 | 17 | 10.6 |
| 5 | 21 | 14.8 |
| 6 | 23 | 18.9 |
| 7 | 18 | 22.7 |
| 8 | 29 | 25.4 |
| 9 | 24 | 26.7 |
| 10 | 23 | 26.0 |
| 11 | 25 | 23.8 |
| 12 | 10 | 20.2 |
| 13 | 15 | 16.1 |
| 14 | 16 | 12.0 |
| 15 | 8 | 8.3 |
| 16 | 6 | 5.4 |
| 17 | 4 | 3.2 |
| 18 | 3 | 1.8 |
| 19 | 1 | 0.9 |
| 20 | - | 0.5 |
| 21 | 1 | 0.1 |
| 22 | - | - |
| 23 | - | - |
|  | 255 | 253.2 |

.Figure 4.1 Observed and Expected Frequencies of Scores in Rates Approach Test

### 4.2(4) Reliability of the Rates Approach Test

The Kuder-Richardson formula (A III.2(a)) was used to compute the coefficient of reliability of the Rates Approach Test. Computation of $r_{KR}$ (A IV.3) gave a value of 0.71.

### 4.2(5) Validity of the Rates Approach Test

The validity of the Rates Approach Test was determined statistically by computing the biserial correlation coefficient (A III.2(B)) between Test scores of those pupils who obtained Band A in Ordinary Grade chemistry and those who obtained Bands B and C. The biserial correlation coefficient is 0.54 (A IV.4).

Data on which the computation of the biserial correlation coefficient was based are given in Table 4.5.

Table 4.5 Frequencies of Scores, Numbers and Means of Subgroups A and B/C

| Score | Frequencies<br>Subgroup A | <br>Subgroup B/C |
|---|---|---|
| 0 | - | - |
| 1 | - | - |
| 2 | 1 | 1 |
| 3 | 5 | 4 |
| 4 | 5 | 12 |
| 5 | 8 | 13 |
| 6 | 15 | 8 |
| 7 | 10 | 8 |
| 8 | 21 | 8 |
| 9 | 18 | 6 |
| 10 | 17 | 6 |
| 11 | 20 | 5 |
| 12 | 9 | 1 |
| 13 | 15 | - |
| 14 | 15 | 1 |
| 15 | 8 | - |
| 16 | 6 | - |
| 17 | 4 | - |
| 18 | 3 | - |
| 19 | 1 | - |
| 20 | - | - |
| 21 | 1 | - |
| 22 | - | - |
| 23 | - | - |
| Number | 182 | 73 |
| Mean | 10.22 | 6.71 |

### 4.2(6) Effect of Physics

In order to assess the effect on performance in the Rates Approach Test of the course taken in physics (if any), the four subgroups of Table 3.6 (page 58) were subjected to analysis of variance and several contrasts then made using the Scheffé Method (A III.3).

The statistics of the four subgroups (A IV.5) are summarised in Table 4.6.

Table 4.6 Statistics of Pupil Subgroups

| Subgroup | 1 | 2 | 3 | 4 | Whole Group |
|---|---|---|---|---|---|
| Band in Ordinary Grade Chemistry | A | A | B or C | B or C | |
| Was Higher Physics studied? | Yes | No | Yes | No | |
| Number of pupils | 155 | 27 | 44 | 29 | 255 |
| Mean Score | 10.42 | 9.07 | 7.25 | 5.89 | 9.17 |
| Standard Deviation | 3.72 | 3.54 | 2.66 | 2.35 | 3.80 |

The results of the analysis of variance are shown in Table 4.7

Table 4.7 Analysis of Variance

| Source | Sum of Squares | df | Mean Square | F |
|---|---|---|---|---|
| Between | 686 | 3 | 228.7 | 19.2 |
| Within | 2976 | 251 | 11.9 | |
| Total | 3662 | 254 | | |

$$_{.95}F_{3,251} = 2.64$$

Hence, one or more significant differences exist within the four subgroups.

Contrasts were made between means of subgroups and between pairs of means as shown in Table 4.8 using the Scheffé Method (A III.3).

Table 4.8 Source of Significance within Four Subgroups (5% level)

| Contrast | Estimate of Contrast ($\bar{X}_i - \bar{X}_j$) | S.D. of Contrast $\hat{\sigma}$ | Ratio $\hat{\psi}/\hat{\sigma}$ | Significance |
|---|---|---|---|---|
| 1. $\mu_1 - \mu_2$ | 1.35 | 0.7006 | 1.93 | No |
| 2. $\mu_1 - \mu_3$ | 3.17 | 0.5739 | 5.52 | Yes |
| 3. $\mu_1 - \mu_4$ | 4.54 | 0.6979 | 6.49 | Yes |
| 4. $\mu_2 - \mu_3$ | 1.82 | 0.8214 | 2.22 | No |
| 5. $\mu_2 - \mu_4$ | 3.18 | 0.8987 | 3.54 | Yes |
| 6. $\mu_3 - \mu_4$ | 1.36 | 0.8037 | 1.69 | No |
| 7. $\frac{\mu_1+\mu_2}{2} - \frac{\mu_3+\mu_4}{2}$ | 3.17 | 0.5474 | 5.80 | Yes |
| 8. $\frac{\mu_1+\mu_3}{2} - \frac{\mu_2+\mu_4}{2}$ | 1.35 | 0.5474 | 2.47 | No |

Contrasts are significant at the 5% level if the absolute value of the ratio in Table 4.8 is greater than the value of:

$$\sqrt{(J - 1)\ {}_{.95}F_{J-1,N-J}} = \sqrt{(4 - 1)\ {}_{.95}F_{3,251}}$$

$$= \sqrt{3(2.64)}$$

$$= 2.81$$

Thus contrasts 2, 3, 5 and 7 are significant at the 5% level. Subgroups 1 and 3 are significantly different, and so also are subgroups 1 and 4. Subgroups 2 and 4 are also significantly different. The most important feature of these results relate to contrasts 7 and 8.

Contrast 7. There is a significant difference in performance between pupils with Band A and pupils with Bands B/C in chemistry irrespective of whether they have or have not studied Higher physics. Contrast 8. There is no significant difference between pupils who have studied Higher physics and pupils who have not studied Higher physics.

### 4.2(7) Pupils' Written Accounts of Reasons for selecting Responses to Questions 3, 6, 11, 14 and 21.

Pupils' written accounts of their reasoning in selecting responses to the five questions 3, 6, 11, 14 and 21 were variable. About 5% of the pupils offered nothing at all while about 50% were quite diligent and offered something on each question. The remaining 45% or so supplied intermediate accounts.

⁑⁑ 3. Which of the following is a reliable way of deciding if a mixture is in a state of chemical equilibrium?

A When the mixture is heated its composition changes.
B When a catalyst known to be effective in the reaction is added, the composition of the mixture remains the same.
C The composition of the mixture does not change with time.
D When the mixture is compressed its composition remains the same.
E I do not know which of these options is correct.

Question 3. This question attempted to test the pupil's ability to distinguish between an equilibrium situation and a non-equilibrium situation. A subjective assessment of the written accounts of reasoning employed in selecting a response showed that one pupil in ten appreciated the significance of introducing a catalyst to the mixture (correct response B). The facility value, however, was somewhat higher at 0.28. As many pupils, 28%, chose response C and asserted in their written comments that, since the composition did not change with time, the mixture must be at equilibrium

⁑⁑ 6. Which of the following lists contains an 'odd man out'?

A Oxygen, petrol, mist, sawdust.
B Sand, steam, fluorine, paraffin.
C Ethanol, flour, heat, nitrogen.
D Chlorine, methanol, silica, vapour.
E I do not know.

Question 6. This question was an 'odd man out' question on matter and energy terms. Some pupils expressed difficulty in knowing how to interpret the question; they did not quite understand what was required of them. Accordingly, about one pupil in four chose response E. These pupils gave no indication in their written responses that they recognised response C as the only one containing a form of energy. About two pupils in three, however, did spot the energy term in response C, and appeared in their written comments to be quite pleased with themselves for having done so.

** 11. When water at 100 °C absorbs heat and changes to steam at 100 °C,

A the potential energy of the molecules remains the same but their kinetic energy increases.

B the kinetic energy of the molecules remains the same but their potential energy increases.

C both the potential energy and kinetic energy of the molecules increase.

D neither the potential energy nor the kinetic energy of the molecules increases.

E I do not know how the potential energy and/or the kinetic energy of the molecules is affected.

Question 11. This question asked about potential and kinetic energy, and in general caused chaos. The biologists (of the 255 subjects, 27 had taken biology to Ordinary grade and 45 to Higher grade) tended to take the view that 'this was physics' and they were, therefore, excused from knowing anything about it.

The most popular choice was response A, i.e., molecules of steam at 100 °C are generally thought to have higher kinetic energies (on average) than molecules of water at 100 °C

** 14. Nitrogen monoxide mostly decomposes when heated:

$$2NO \longrightarrow N_2 + O_2$$

On this evidence decide which of the following statements is correct.

A The forward reaction absorbs heat.

B Nitrogen monoxide would decompose at room temperature except that it lacks activation energy at this low temperature.

C If allowed to cool, the nitrogen and oxygen would tend to recombine to reform nitrogen monoxide.

D It is not possible to say whether the forward reaction is exothermic or endothermic.

E I do not know which of these statements is correct.

Question 14. This question again tested the pupils' ability to distinguish between equilibrium and non-equilibrium situations. The most popular choice was response A, and this was well documented by the pupils in the fashion that 'since the reaction went to the right when heated then it must be endothermic.'. The question had a facility value of 0.13, but only about on e third of this 13% who chose the correct response seemed to have a clear idea that the heat supplied was activation energy.

** 21. Which one of the following lists differs in a significant way from the other three?

A Copper, heat, neon.

B Helium, tin, water.

C Argon, zinc, light.

D Gold, sound, krypton.

E I can see no significant difference between these lists.

Question 21. This question was similar in type to question 6, and received much the same kind of written comment.

## 4.3 Concept Sequence in the Rates Approach to Equilibrium

Some pupils, nine and fourteen respectively, were asked to arrange concepts arising in the Rates Approach to equilibrium in logical order.

Table 4.9 shows how nine pupils arranged concepts which arise during the Rates Approach to equilibrium.

Table 4.9

| Concept | No. of pupils placing concept | | | | |
|---|---|---|---|---|---|
| | 1st | 2nd | 3rd | 4th | 5th |
| Equilibrium | 0 | 0 | 1 | 2 | 6 |
| Equal and opposite rates | 1 | 0 | 1 | 5 | 2 |
| Activated complex | 1 | 3 | 4 | 0 | 1 |
| Energy of activation | 1 | 5 | 2 | 1 | 0 |
| Collision theory | 6 | 1 | 1 | 1 | 0 |

No statistical treatment of these figures has been attempted. The figures are merely considered at face value.

Table 4.10 shows the way in which fourteen other pupils arranged concepts arising in the Rates Approach.

Table 4.10

| Concept | No. of pupils placing concept | | | |
|---|---|---|---|---|
| | 1st | 2nd | 3rd | 4th |
| Rate determining step | 0 | 2 | 3 | 9 |
| Activated complex | 0 | 5 | 7 | 2 |
| Energy of activation | 1 | 7 | 3 | 3 |
| Reaction mechanism | 13 | 0 | 1 | 0 |

These figures are again simply taken at face value.

Figure 4.2 shows the Concept Sequence obtained from this information.

Fig. 4.2 Concept Sequence in Rates Approach

# A IV.1

Facility Values of Upper ($T_1$), Middle ($T_2$) and Lower ($T_3$) Thirds, and Discriminatory Powers.

| Question No. | Facility Values |  |  | Discriminatory Powers |  |  |
|---|---|---|---|---|---|---|
|  | $T_1$ | $T_2$ | $T_3$ | $T_1 - T_2$ | $T_2 - T_3$ | $T_1 - T_3$ |
| 1 | 0.07 | 0.11 | 0.09 | -0.04 | 0.01 | -0.02 |
| 2 | 0.88 | 0.60 | 0.40 | 0.28 | 0.20 | 0.48 |
| 3 | 0.39 | 0.24 | 0.22 | 0.15 | 0.01 | 0.16 |
| 4 | 0.81 | 0.52 | 0.32 | 0.29 | 0.20 | 0.49 |
| 5 | 0.47 | 0.18 | 0.14 | 0.29 | 0.04 | 0.33 |
| 6 | 0.91 | 0.61 | 0.35 | 0.29 | 0.26 | 0.55 |
| 7 | 0.71 | 0.46 | 0.18 | 0.25 | 0.28 | 0.53 |
| 8 | 0.69 | 0.38 | 0.18 | 0.32 | 0.20 | 0.52 |
| 9 | 0.35 | 0.20 | 0.08 | 0.15 | 0.12 | 0.27 |
| 10 | 0.51 | 0.29 | 0.13 | 0.21 | 0.16 | 0.38 |
| 11 | 0.26 | 0.14 | 0.04 | 0.12 | 0.11 | 0.22 |
| 12 | 0.88 | 0.78 | 0.36 | 0.11 | 0.41 | 0.52 |
| 13 | 0.72 | 0.35 | 0.13 | 0.36 | 0.22 | 0.59 |
| 14 | 0.27 | 0.08 | 0.04 | 0.19 | 0.05 | 0.24 |
| 15 | 0.76 | 0.44 | 0.19 | 0.33 | 0.25 | 0.58 |
| 16 | 0.79 | 0.51 | 0.27 | 0.28 | 0.24 | 0.52 |
| 17 | 0.34 | 0.20 | 0.13 | 0.14 | 0.07 | 0.21 |
| 18 | 0.28 | 0.11 | 0.06 | 0.18 | 0.05 | 0.22 |
| 19 | 0.41 | 0.35 | 0.20 | 0.06 | 0.15 | 0.21 |
| 20 | 0.95 | 0.76 | 0.56 | 0.19 | 0.20 | 0.39 |
| 21 | 0.86 | 0.71 | 0.47 | 0.15 | 0.24 | 0.39 |
| 22 | 0.69 | 0.61 | 0.39 | 0.08 | 0.22 | 0.31 |
| 23 | 0.49 | 0.29 | 0.16 | 0.20 | 0.13 | 0.33 |

Computation of Expected Frequencies . Computation of $\chi^2$.

| Score | Observed Frequency (O) | Class boundary (X) | $\frac{(X - \bar{X})}{SD}$ (Z) | Area to Z | Area within class boundary | Expected Frequency (E) | $\lvert O - E\rvert$ | $(O - E)^2$ | $\frac{(O - E)^2}{E}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | -0.5 | -2.5450 | -0.4945 | | | | | |
| 0 | - | | | | 0.0059 | 1.5 | 1.5 | 2.25 | 1.50 |
| | | 0.5 | -2.2815 | -0.4886 | | | | | |
| 1 | - | | | | 0.0104 | 2.6 | 2.6 | 6.76 | 2.60 |
| | | 1.5 | -2.0184 | -0.4782 | | | | | |
| 2 | 2 | | | | 0.0178 | 4.5 | 2.5 | 6.25 | 1.39 |
| | | 2.5 | -1.7552 | -0.4604 | | | | | |
| 3 | 9 | | | | 0.0283 | 7.2 | 1.8 | 3.24 | 0.45 |
| | | 3.5 | -1.4920 | -0.4321 | | | | | |
| 4 | 17 | | | | 0.0414 | 10.6 | 6.4 | 40.96 | 3.86 |
| | | 4.5 | -1.2289 | -0.3907 | | | | | |
| 5 | 21 | | | | 0.0579 | 14.8 | 6.2 | 38.44 | 2.60 |
| | | 5.5 | -0.9656 | -0.3328 | | | | | |
| 6 | 23 | | | | 0.0740 | 18.9 | 4.1 | 16.81 | 0.89 |
| | | 6.5 | -0.7026 | -0.2588 | | | | | |
| 7 | 18 | | | | 0.0892 | 22.7 | 4.7 | 22.09 | 0.97 |
| | | 7.5 | -0.4394 | -0.1696 | | | | | |
| 8 | 29 | | | | 0.0997 | 25.4 | 3.6 | 12.96 | 0.51 |
| | | 8.5 | -0.1763 | -0.0699 | | | | | |
| 9 | 24 | | | | 0.1046 | 26.7 | 2.7 | 7.29 | 0.27 |
| | | 9.5 | +0.0868 | +0.0347 | | | | | |
| 10 | 23 | | | | 0.1021 | 26.0 | 3.0 | 9.00 | 0.35 |
| | | 10.5 | +0.3500 | +0.1368 | | | | | |
| 11 | 25 | | | | 0.0934 | 23.8 | 1.2 | 1.44 | 0.06 |
| | | 11.5 | +0.6130 | +0.2302 | | | | | |
| 12 | 10 | | | | 0.0791 | 20.2 | 10.2 | 104.04 | 5.15 |
| | | 12.5 | +0.8763 | +0.3093 | | | | | |
| 13 | 15 | | | | 0.0633 | 16.1 | 1.1 | 1.21 | 0.08 |
| | | 13.5 | +1.1394 | +0.3726 | | | | | |
| 14 | 16 | | | | 0.0470 | 12.0 | 4.0 | 16.00 | 1.33 |
| | | 14.5 | +1.4026 | +0.4196 | | | | | |
| 15 | 8 | | | | 0.0325 | 8.3 | 0.3 | 0.09 | 0.01 |
| | | 15.5 | +1.6658 | +0.4521 | | | | | |
| 16 | 6 | | | | 0.0210 | 5.4 | 0.6 | 0.36 | 0.07 |
| | | 16.5 | +1.9289 | +0.4731 | | | | | |
| 17 | 4 | | | | 0.0127 | 3.2 | | | |
| | | 17.5 | +2.1921 | +0.4858 | | | | | |
| 18 | 3 | | | | 0.0072 | 1.8 | | | |
| | | 18.5 | +2.4552 | +0.4930 | | | | | |
| 19 | 1 | | | | 0.0037 | 0.9 | | | |
| | | 19.5 | +2.7184 | +0.4967 | | | | | |
| 20 | - }9 | | | | 0.0019 | 0.5 }6.5 | 2.5 | 6.25 | 0.96 |
| | | 20.5 | +2.9816 | +0.4986 | | | | | |
| 21 | 1 | | | | 0.0002 | 0.1 | | | |
| | | 21.5 | +3.2447 | +0.4988 | | | | | |
| 22 | - | | | | 0.0001 | - | | | |
| | | 22.5 | +3.5079 | +0.4989 | | | | | |
| 23 | - | | | | 0.0001 | - | | | |
| | | 23.5 | +3.7710 | +0.4990 | | | | | |
| | 255 | | | | | 253.2 | | | 23.05 = $\chi^2$ |

$\bar{X}$ = 9.17; S.D. = 3.80

df = k - 1 - m where k = 18, m = 2
Hence, df = 15.

## A IV.3

$$r_{KR} = \frac{N}{N - 1}\left[1 - \frac{\Sigma pq}{S^2}\right]$$

$N = 23$

$S^2 = 3.80^2 = 14.44$

| Item | p | q | pq |
|---|---|---|---|
| 1 | 0.09 | 0.91 | 0.0819 |
| 2 | 0.63 | 0.37 | 0.2331 |
| 3 | 0.28 | 0.72 | 0.2016 |
| 4 | 0.55 | 0.45 | 0.2475 |
| 5 | 0.26 | 0.74 | 0.1924 |
| 6 | 0.62 | 0.38 | 0.2356 |
| 7 | 0.45 | 0.55 | 0.2475 |
| 8 | 0.42 | 0.58 | 0.2436 |
| 9 | 0.21 | 0.79 | 0.1659 |
| 10 | 0.31 | 0.69 | 0.2139 |
| 11 | 0.15 | 0.85 | 0.1275 |
| 12 | 0.67 | 0.33 | 0.2211 |
| 13 | 0.40 | 0.60 | 0.2400 |
| 14 | 0.13 | 0.87 | 0.1131 |
| 15 | 0.46 | 0.54 | 0.2484 |
| 16 | 0.52 | 0.48 | 0.2496 |
| 17 | 0.22 | 0.78 | 0.1716 |
| 18 | 0.15 | 0.85 | 0.1275 |
| 19 | 0.32 | 0.68 | 0.2175 |
| 20 | 0.76 | 0.24 | 0.1824 |
| 21 | 0.68 | 0.32 | 0.2176 |
| 22 | 0.56 | 0.44 | 0.2464 |
| 23 | 0.32 | 0.68 | 0.2176 |
|  |  |  | 4.6433 |

$$r_{KR} = \frac{23}{22}\left[1 - \frac{4.6433}{14.44}\right]$$

$$= 1.05 \left[1 - 0.32\right]$$

$$= \underline{0.71}$$

A IV.4

Computation of biserial correlation coefficient:

$$r_{bis} = \frac{m_A - m_{B/C}}{S} \quad \frac{pq}{h}$$

$m_A$ = 10.22
$m_{B/C}$ = 6.71
S = 3.80
p = 182/255 = 0.71
q = 73/255 = 0.29
h = 0.343 (from tables)

Hence $r_{bis}$ = 0.54

## A IV.5

| | Subgroups | | | |
|---|---|---|---|---|
| Score | 1 | 2 | 3 | 4 |
| 0 | - | - | - | - |
| 1 | - | - | - | - |
| 2 | - | 1 | 1 | - |
| 3 | 5 | - | - | 4 |
| 4 | 5 | - | 6 | 6 |
| 5 | 5 | 3 | 8 | 5 |
| 6 | 14 | 1 | 3 | 5 |
| 7 | 7 | 3 | 7 | 1 |
| 8 | 16 | 5 | 5 | 3 |
| 9 | 13 | 5 | 3 | 3 |
| 10 | 15 | 2 | 6 | - |
| 11 | 18 | 2 | 3 | 2 |
| 12 | 9 | - | 1 | - |
| 13 | 13 | 2 | - | - |
| 14 | 14 | 1 | 1 | - |
| 15 | 7 | 1 | - | - |
| 16 | 6 | - | - | - |
| 17 | 4 | - | - | - |
| 18 | 3 | - | - | - |
| 19 | - | 1 | - | - |
| 20 | - | - | - | - |
| 21 | 1 | - | - | - |
| 22 | - | - | - | - |
| 23 | - | - | - | - |
| n | 155 | 27 | 44 | 29 |
| $\Sigma X$ | 1603 | 245 | 319 | 171 |
| $(\Sigma X)^2$ | 2569 609 | 60 025 | 101 761 | 29 241 |
| $\Sigma X^2$ | 18 769 | 2549 | 2617 | 1163 |

# CHAPTER 5

# DISCUSSION

The results of the Rates Approach Test are discussed. The questions are considered one at a time in categories 1 to 7 of Table 4.2 (page 66) under these topic headings. Questions 13 and 15 of Topic 5 are considered together since they are very similar. Each question is reproduced, preceded by the facility value and the discriminatory factor. The percentages of pupils selecting each response are also shown. Correct responses are marked * . Pupils were asked to give a written account of their reasoning in selecting responses in five questions marked ** .

## 5.1 Left and Rightsidedness

Question 4 F.V. = 0.55 D.F. = 0.49

When equilibrium is established in the system

$$P + Q \rightleftharpoons R + S$$

the percentage of each of the four constituents is constant, i.e. the mixture has a constant composition.

Among which species are collisions occuring?

| | | |
|---|---|---|
| 17% | A | Ps are colliding with Qs while Rs are colliding with Ss only. |
| 55% | B* | Ps, Qs, Rs and Ss are all colliding with each other. |
| 2% | C | Ps are colliding with Ss while Qs are colliding with Rs only. |
| 8% | D | Collisions between Ps and Qs and between Rs and Ss are no longer occurring. |
| 18% | E | I do not know which of these options is the correct one. |

The question was quite well done. Nevertheless, 45% of pupils were unable to select the correct response, which reflects a lack of appreciation of 'what is going on' inside the equilibrium system. More particularly, response A has shades of left and rightsidedness about it, and was chosen by 17% of the pupils.

Question 9 F.V. = 0.21 D.F. = 0.27

In the familiar Haber system at equilibrium

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

the application of increased pressure to the right hand side only will drive the equilibrium to the left.

How would you comment on this statement?

| | | |
|---|---|---|
| 20% | A | It is correct. |
| 28% | B | It is incorrect; the equilibrium would in fact be driven to the right. |
| 21% | C* | It is quite unreasonable, and impracticable. |
| 19% | D | It is correct as long as the nitrogen and hydrogen are continuously removed. |
| 12% | E | I do not know which option to choose. |

The results of this question give some cause for concern. About four out of five pupils completing the Higher grade course appear to visualise equilibrium systems as consisting of two independent and separate compartments rather than the one whole; or, at best, are not sure. This leads them to make false deductions about problem situations.

What is the origin of this misconcept of 'left and right sidedness'. One can only surmise that some of the variety of introductory material used to convey the concept of chemical equilibrium unwittingly results in pupils adopting a compartmental view of the equilibrium system. It is a basic tenet of Ausubel's psychology of learning (37) that new subject matter presented to a pupil is initially anchored by the pupil to some part of his existing cognitive structure which the new idea resembles, or seems to resemble. In so doing, the pupil may modify the new concept to make it fit the existing cognitive structure giving rise to a misconception. There are, it would seem, several occasions when this might occur during the teaching of chemical equilibrium.

a) Pupils arrive at a study of chemical equilibrium with an already established and firmly held concept of static, two sided equilibrium derived from physical and mechanical experiences. Unless care is taken to deliberately point out the differences between the chemical concept and the more intuitive physical concept, pupils may tacitly - and justifiably - interpret what the teacher says of chemical equilibrium in terms of what they already know about physical equilibrium, and a static two sided picture arises.

b) The use of the chemical equation with its centrally placed reversed arrow symbol possibly also contributes to the two sided view. Again, pupils are liable to make the tacit accumption of two sidedness. Unfortunately, they will not announce that they have just done so and so the teacher is quite unaware that this has occurred; pupils presumably tend to assume that which they think the teacher means to say.

c) Various physical analogies are employed in conveying the concept of chemical equilibrium (2.2(5)). Some of these, and in particular the two most popular ones (No. 1 and No. 4) actually consist of two sides. It is hardly surprising, therefore, that pupils should make tacit assumptions of left and right sidedness. Indeed, one begins to consider it surprising that some do not.

d) Some of the actual equilibrium systems themselves have two 'sides'. The partitioning of iodine between two solvents, the equilibrium between iodine monochloride and iodine trichloride, where the latter is apparently well removed in the upper portion of the tube from the former in the lower portion of the tube, possibly consolidate this compartmental view of an equilibrium system.

e) Enthalpy changes are often depicted diagramatically where the diagram shows a left side and right side at different levels with a hump between them.

As a consequence, the pupil tacitly adopts a false picture of an equilibrium system about which the teacher is quite unaware, a picture which may lead him to make false deductions about problem situations, which lead him to imagine, for example, that the pressure of the right hand side of an equilibrium system can be increased without increasing the pressure on the left hand side. And this reasoning probably extends to other variables (not tested in this study) such as temperature and concentration.

What then is the answer? Mostly it is to be aware of the kinds of assumptions which pupils are likely to make in a given teaching situation and actively dispel these as they arise. This might seem to require in the teacher a sixth sense in reading the minds of pupils, but it is not perhaps too difficult given an awareness of the part of the teacher of the kinds of assumptions which his pupils are liable to make.

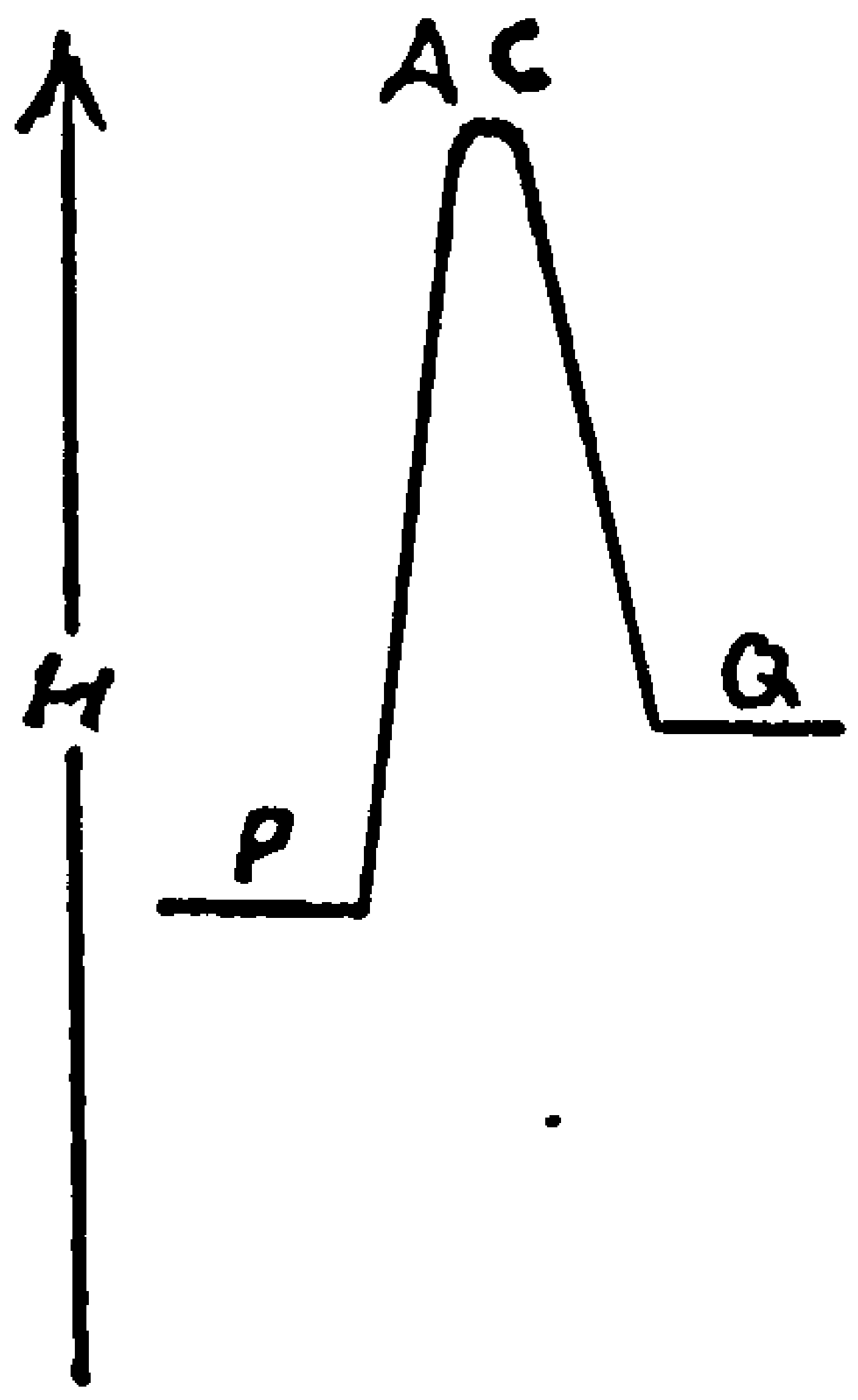
Alternatively, the teacher might restructure his approach so that misconceptions do not arise in the first place. This is particularly the case with the use of analogies. Analogies which are liable to misinterpretation should perhaps be avoided. Thus, analogies 1 to 6 (2.2(5)) perhaps create more problems than they solve. These analogies are reasonably close to that which they purport to explain, and so are eminently capable of being confused in the pupils' minds with the real chemical equilibrium. This would imply that safer analogies are either those which are so far removed conceptually from the real equilibrium situation that there is no chance of confusion, or are those which are so close that there is no chance of conflict. There are, unfortunately, relatively few of these 'safer' analogies.

Question 17 F.V. = 0.22 D.F. = 0.21

The accompanying enthalpy diagram refers to the equilibrium;

$P \rightleftharpoons Q$

In the equilibrium mixture of P and Q.



| | | |
|---|---|---|
| 31% | A | the proportion of P will be greater than that of Q. |
| 14% | B | the proportion of P will be less than that of Q. |
| 17% | C | the forward rate of reaction will be less than the backward rate. |
| 22% | D* | it is not possible to say whether P or Q will have the higher proportion. |
| 16% | E | I do not know which of these options to choose. |

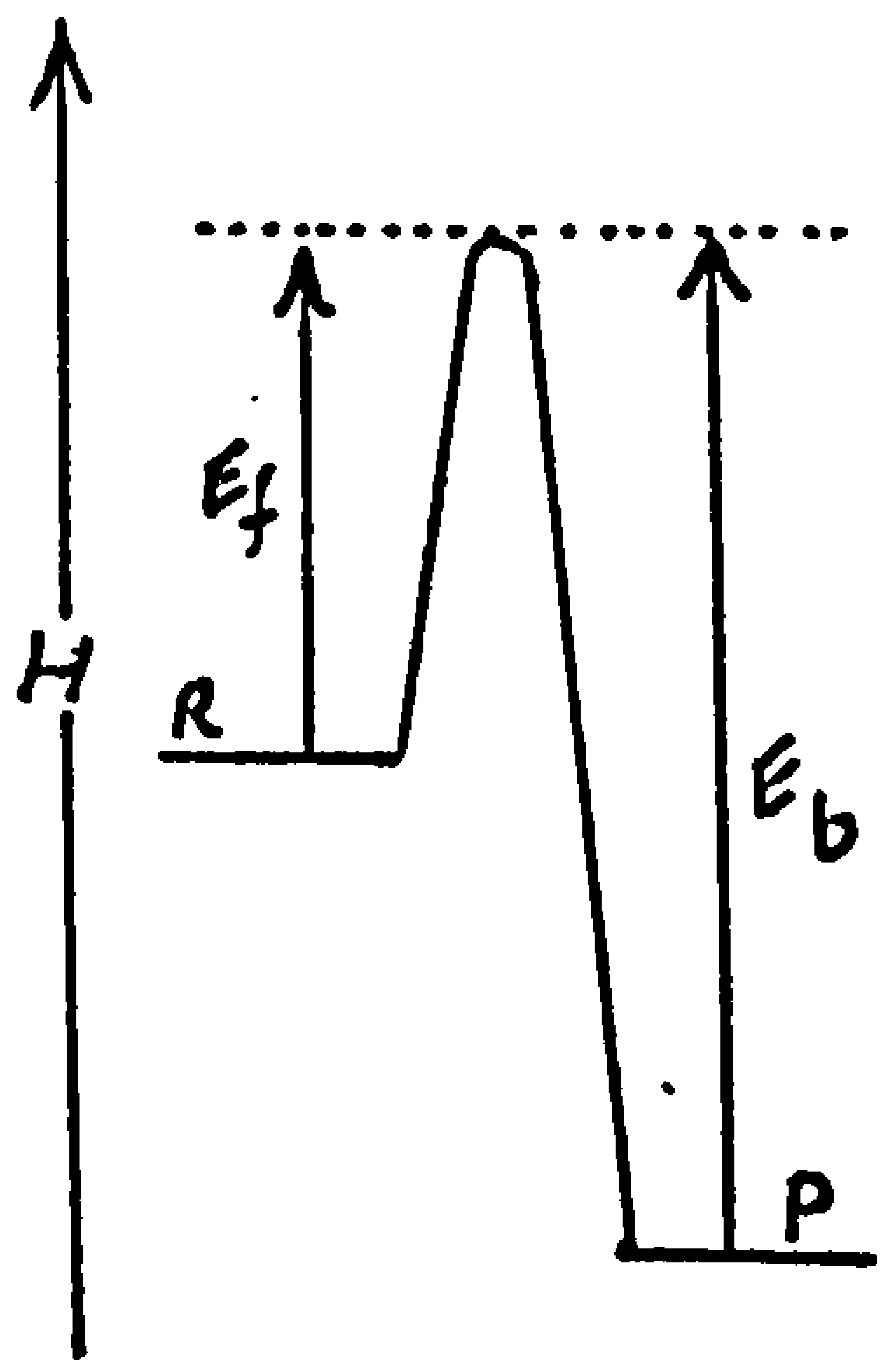
This question attempts to assess 'left and right sidedness' from the viewpoint of macroscopic enthalpy change (where question 4 assessed it from the viewpoint of molecular collisions). However, the results of the question are difficult to interpret reliably. Those who chose response D may still see the system compartmentally; while those who chose response A probably see the system compartmentally. It is not possible to draw firmer conclusions than these. It is difficult to offer a reason to explain why 14% chose response B. Selection of response C shows confusion between rates of reaction and magnitude of the energy of activation, probably derived from a knowledge of the effect of a catalyst on energy of activation and reaction rate.

It was suggested in the discussion of question 9 that the familiar chemical equation and some of the commonly used physical analogies may unwittingly contribute to left and right sidedness; it is possible that the familiar enthalpy diagram also makes such a contribution.

## 5.2 Inherent Equal and Opposite Quality of Equilibrium Systems

Question 5 F.V. = 0.26 D.F. = 0.33

In the context of an enthalpy diagram, activation energy is viewed as a "hurdle" to be overcome if reactants are to change into products, and vice versa.



In a particular system <u>at equilibrium</u>, the forward activation energy, $E_f$, is less than the backward activation energy, $E_b$.

Select the correct statement:

32% A The forward rate of reaction will be greater than the backward rate of reaction.

4% B The backward rate of reaction could be zero.

26% C* Both forward and reverse rates of reaction are equal.

27% D The equilibrium mixture will have a higher percentage of product than reactant.

11% E I do not know which is the correct statement.

Pupils with any awareness of the equal and opposite quality of an equilibrium system would, it was supposed, have little hesitation in selecting response C. But 74% of pupils did not, which leads one to conclude that the equal and opposite dynamic nature of an equilibrium system is accepted so superficially (if at all) that moderately plausible distractors can succeed in diverting the majority of pupils.

The plausibility of response A probably stems from the emphasis placed on the increase in rate of reaction which results from a reduction in activation energy upon the introduction of a catalyst.

The reason why 27% of the pupils selected response D is a little obscure. One might speculate that the simple physical relationship between an upper and a lower level leads pupils to assume that there must of necessity be more material at the lower level. Pupils who opted for response D are possibly 'left and rightsided' thinkers and see the equilibrium system as an upper left compartment and a lower right compartment.

Question 8 F.V. = 0.42 D.F. = 0.52

Here is an equilibrium system which you probably first encountered in Form III:

$$H_2O(aq) \rightleftharpoons H^+(aq) + OH^-(aq)$$

Only about one molecule of water in every 500 000 000 or so is ionised at any one instant in time.

Which of the following statements is correct?

| | | |
|---|---|---|
| 42% | A* | Both forward and reverse rates are equal. |
| 30% | B | The reverse rate is greater than the forward rate. |
| 16% | C | Most water molecules never suffer ionisation. |
| 6% | D | The forward rate is greater than the reverse rate. |
| 6% | E | I do not know which option is correct. |

An unexpectedly large percentage of pupils opted for response B, although, in view of the findings for question 5, it is not too surprising that this proportion of pupils should be prepared to abandon the equal and opposite condition for what, to them, is a more plausible response.

For these pupils, the equal and opposite rates requirement apparently conflicted with the large excess of reactant over product. The latter 'unbalanced' situation could apparently only be explained away by the contention that the reverse reaction be greater than the forward reaction. It would be interesting to ask these pupils, "What would be the composition of a mixture in which the forward and reverse rates of reaction are equal?"! Would it beg the answer, "50% reactant, 50% product."?

There would seem, according to these results, to be a tendency to think like this. If this is so, the remedy involves specific teaching to counteract it.

Whichever way one looks at this question, 58% of pupils were ill-prepared to accept that the forward and reverse rates of reaction were equal at equilibrium, irrespective of anything else.

## 5.3 Interpretation of the Reversed Arrow Convention

Question 18 F.V. = 0.15 D.F. = 0.22

Contrast the following equilibria:

1. $C_2H_5NH_2(aq) + H_2O(aq) \rightleftharpoons C_2H_5NH_3^+(aq) + OH^-(aq)$
2. $NH_3(aq) + H_2O(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

and decide which of the following statements is correct.

30% A In each of them, the reverse rate of reaction is greater than the forward rate of reaction.

11% B The forward rate of reaction in 1 is greater than the forward rate of reaction in 2.

15% C* In each, the forward and reverse rates are equal, and system 1 contains a higher percentage of product than system 2.

14% D The percentage of reactant in each system is the same.

30% E I do not know which of these statements is correct.

This question attempted to assess the pupils' interpretations of the reversed arrow symbol in that particular instance where the forward and reversed arrows are of unequal length.

It has already been shown that the pupils' acceptance of an equal and opposite rates situation at equilibrium is superficial (5.2), and so it is hardly surprising that only 15% have chosen the correct response in the above situation. Response A is very popular; the longer arrow is interpreted as implying greater rate of reaction at equilibrium, which is impossible. Even response B demonstrates this same tendency to equate arrow length with rate of reaction.

### 5.4 Distinguishing Equilibrium and Non-equilibrium Situations

Question 3. F.V. = 0.28 D.F. = 0.16

** Which of the following is a reliable way of deciding if a mixture is in a state of chemical equilibrium?

10% A When the mixture is heated its composition changes.

28% B* When a catalyst known to be effective in the reaction is added, the composition of the mixture remains the same.

28% C The composition of the mixture does not change with time.

2% D When the mixture is compressed its composition remains the same.

32% E I do not know which of these options is correct.

It was anticipated in designing this question that most pupils might select response C since it was judged that the constant composition criterion at attainment of equilibrium is easier to conceive of than the co-occurrence of equal and opposite reactions. It was considered that responses A and D would probably play no real part in the pupils' thought processes, although, as it happened, response A attracted a higher than expected percentage of pupils. Having said all this, it is a puzzling feature of this question that, given responses B and C as serious contenders for selection, as many as 32% of pupils should have chosen response E. Does this reflect an unexpected sophistication on the part of the pupils in that they are perhaps conditioned to select response C but are perhaps inclined to select, but have no prior familiarity with, response B, and so they resolve the conflict by selecting response E?

Thus one might hazard a guess that something between 28% and 60% of pupils have no clear conception that no change in composition with time is no guarantee that a chemical equilibrium is established.

The results of the assessment of the written responses to this question (4.2(7)) suggest that perhaps only about 10% of pupils have a clear conception of the meaning of response B, and consequently some of the 28% who chose response B might very well have been guessing. If this is the case, then the figure of 60% quoted above is a very conservative estimate.

Question 14. F.V. = 0.13 D.F. = 0.24

** Nitrogen monoxide mostly decomposes when heated:

$$2NO \longrightarrow N_2 + O_2$$

On this evidence decide which of the following statements is correct.

36% A The forward reaction absorbs heat.

19% B Nitrogen monoxide would decompose at room temperature except that it lacks activation energy at this low temperature.

4% C If allowed to cool, the nitrogen and oxygen would tend to recombine to reform nitrogen monoxide.

13%* D* It is not possible to say whether the forward reaction is exothermic or endothermic.

28% E I do not know which of these statements is correct.

The stem stressed the importance of interpreting the responses to this question on the evidence that heating leads to decomposition but that this decomposition is not complete. This is rather important, for otherwise some pupils might select an answer in keeping with prior knowledge of the behaviour of nitrogen monoxide. Despite the risk of clouding the issue with prior inadmissible knowledge, it was considered better to work with a real reaction than one employing abstract code letters since these have a confounding effect.

The results of question 4 lead one to suppose that perhaps as few as 10% pupils can make a reasoned attempt at distinguishing an equilibrium situation from a non-equilibrium situation. Question 14 confirms this general finding; only 13% chose the correct response and assessment of the written responses (4.2(7)) indicates that perhaps only about one third of these did so for good reason.

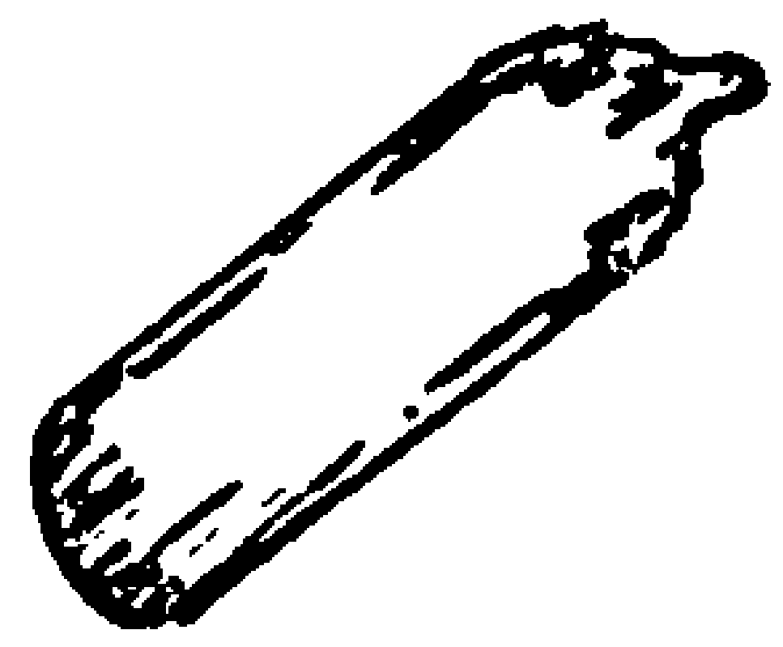
Response A was popular. It was a simple answer to an apparently simple question. Since the reaction moved to the right when heated it must obviously be absorbing heat, in accordance with, probably, Le Chatelier's Principle. That the system being heated might not be an equilibrium system did not occur to these pupils.

Response B is a correct statement but an incorrect response on the basis of the evidence available. Pupils who selected this response made the incorrect assumption that the nitrogen dioxide was not in a state of equilibrium prior to heating - an opposite inference to response A.

Response C is a consequence of response A. Both responses make the assumption that one is dealing with an equilibrium system. Response C is perhaps not a good option since selection of response A should automatically exclude response C. This would perhaps explain why only 4% of pupils chose it.

### 5.5 Effect of Variables on an Equilibrium System

Question 1. F.V. = 0.09 D.F. = -0.02



A sealed ampoule contains a mixture of dinitrogen tetroxide and nitrogen dioxide at equilibrium:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad AH\ +ve$$

When the temperature of the bulb is increased, the pressure of the gas will unavoidably be increased at the same time. Considering these two effects separately, which of the following options correctly describes their effects on the equilibrium system?

| | | Because of the temperature rise, equilibrium will ... | Because of the pressure rise, equilibrium will ... |
|---|---|---|---|
| 32% | A | shift to the left | shift to the left |
| 6% | B | shift to the left | be unaffected |
| 47% | C | shift to the right | shift to the left |
| 9% | D* | shift to the right | be unaffected |
| 6% | E | I do not know which option is a correct description. | |

This question caused a high degree of confusion, particularly with respect to the pressure variable part.

If the temperature variable only had been placed under test, a facility value of 0.56 (= 0.47 + 0.09) would have been obtained for what was essentially a two response question. This indicates, at best, a moderate ability in dealing with the temperature variable, at worst, little or no ability, for such a facility value is little different from what might be expected on a two option question on the basis of pure guesswork alone.

If the pressure variable only had been placed under test, a facility value of 0.15 would have been obtained on what was essentially a two response question. This is very poor. Admittedly, the situation presented to pupils was an unusual one in that there is a change in pressure without a change in volume. (The change in volume of the glass ampoule is negligible in this context.) This may therefore be judged to be an unfair question to ask of pupils following the Higher grade syllabus in view of the very limited coverage accorded the Le Chatelier Theorem in that syllabus. If this is so, then aspects of the application of the Le Chatelier Theorem will have to be unlearned in the event of a pupil proceeding to a University course which includes chemistry.

Question 10. F.V. = 0.31 D.F. = 0.38

An equilibrium exists between undissolved and dissolved salt, which determines the maximum solubility of the salt at a given temperature.

Manganese sulphate dissolves with liberation of heat:

$$MnSO_4(s) + aq \rightleftharpoons MnSO_4(aq) \qquad AH\ -ve$$

At a higher temperature will its maximum solubility be

42% A more?

8% B the same?

31% C* less?

5% D unpredictable?

14% E I do not know.

This question was a straightforward test of the pupils' ability to use Le Chatelier type reasoning with respect to the temperature variable. About two out of three pupils seemed to be unable to do so. Perhaps some pupils chose response A in the mistaken belief that salts are more soluble at higher temperature.

Questions 13 and 15 are essentially the same and will be considered together.

Question 13. F.V. = 0.40 D.F. = 0.59

Ammonia dissolves and reacts with water; the following equilibrium is set up:

$$NH_3(aq) + H_2O(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

When ammonium ion is added (in the form of ammonium chloride, which dissolves with negligible volume change), what will happen to the mass of hydroxyl ion in solution?

| | | |
|---|---|---|
| 17% | A | It will increase. |
| 20% | B | It will remain the same. |
| 40% | C* | It will decrease. |
| 5% | D | It is not possible to say without more information. |
| 18% | E | I do not know what will happen to the mass of hydroxyl ion in solution. |

Question 15. F.V. = 0.46 D.F. = 0.58

Ethanoic acid dissolves and reacts with water; an equilibrium is set up according to:

$$CH_3COOH(aq) + H_2O(aq) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

When ethanoate ion is added (in the form of sodium ethanoate, which dissolves with negligible volume change), what will happen to the concentration of hydroxonium ion?

| | | |
|---|---|---|
| 18% | A | It will increase. |
| 13% | B | It will remain the same. |
| 46% | C* | It will decrease. |
| 4% | D | It is not possible to say without more information. |
| 19% | E | I do not know. |

These questions confirm the impression so far gained that Le Chatelier type reasoning is difficult for the majority of pupils. It is interesting that questions 13 and 15 had the highest discriminatory factors for the entire test. This is indicative of the difficulty experienced by pupils, particularly the less able ones, in applying the Le Chatelier Principle. The facility values for the top thirds (A. IV.1) for each question were 0.72 and 0.76, and for the bottom thirds, 0.13 and 0.19 respectively.

Question 16. F.V. = 0.52 D.F. = 0.52

A reaction vessel of fixed volume contains an equilibrium mixture of hydrogen iodide, hydrogen and iodine:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

If some hydrogen gas be added to the reaction vessel, what will happen to the mass of iodine gas in the vessel?

52% A* It will decrease.
23% B It will remain the same.
16% C It will increase.
3% D It is not possible to say without more information.
6% E I do not know.

The same general comments apply to question 16 as apply to questions 13 and 15.

In general, therefore, the five questions dealing with Le Chatelier type problems showed up little of a misconceptual nature, except for question 1, which showed that pupils have a false idea of the effect of the pressure variable. But this question was an unfair one to ask of Higher grade pupils who, in answering it, were merely following instructions; they were taught to reason this way. The five questions did show that the brighter pupils were those who more often succeeded in applying Le Chatelier type reasoning to a successful conclusion.

## 5.6 Catalysis

Question 2. F.V. = 0.63 D.F. = 0.48

If a catalyst can increase the rate of the forward reaction in an equilibrium system, how will it affect the rate of the backward reaction?

9% A It will have no effect.

63% B* It will increase the backward rate.

18% C It will decrease the backward rate.

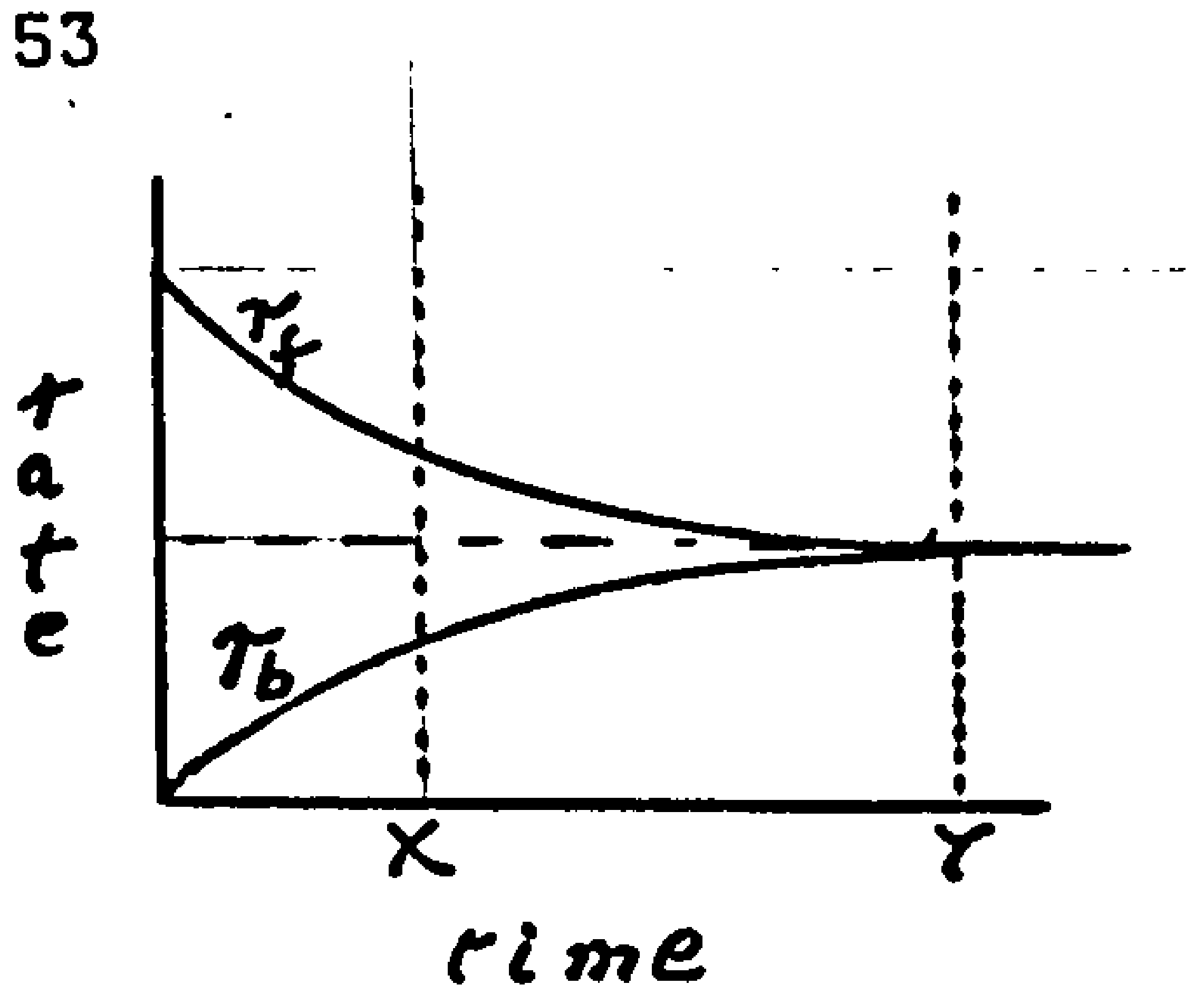
6% D It depends on the equilibrium system.

4% E I do not know.

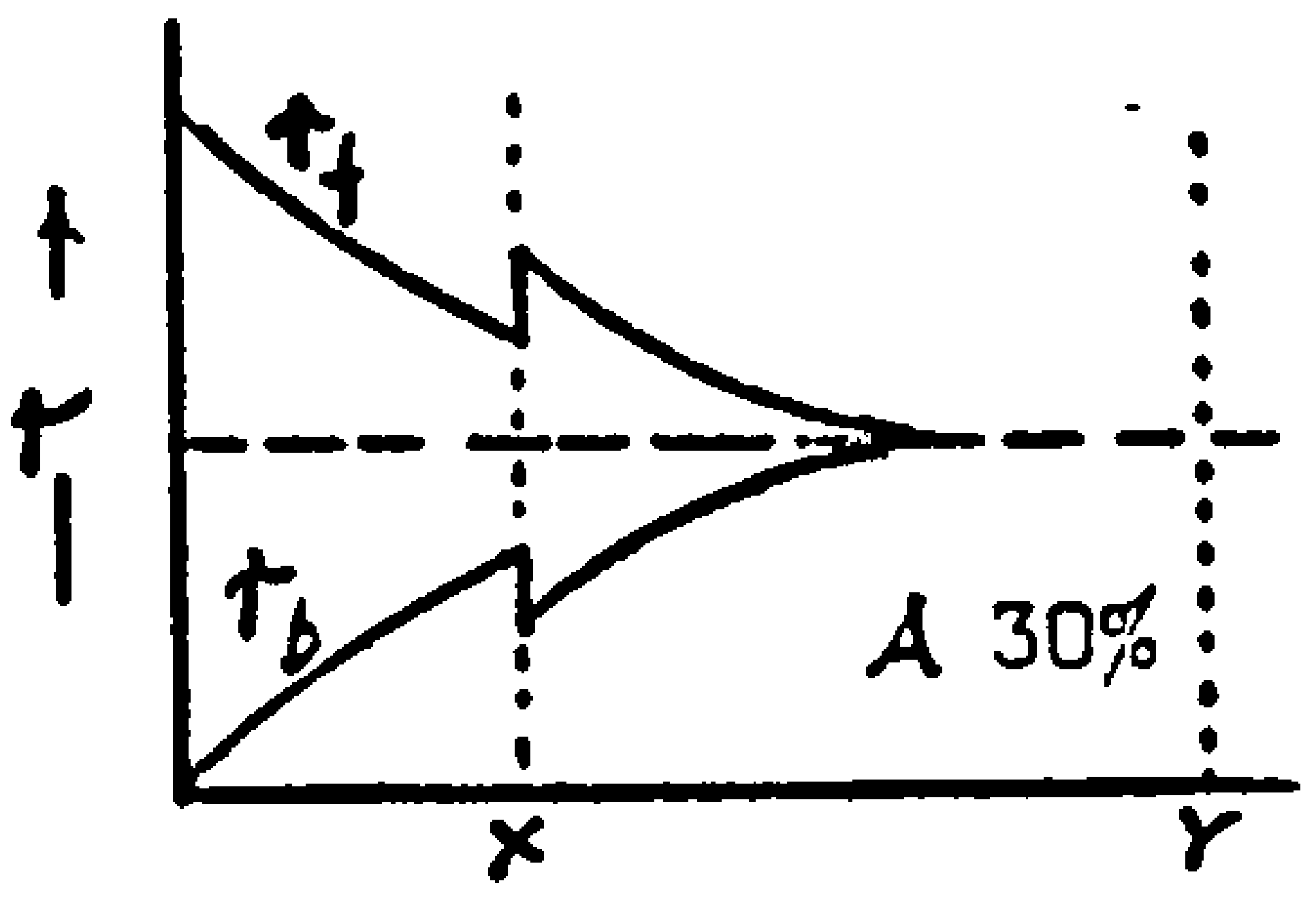
The significant feature of the responses to this question are the 27% of pupils who considered that a catalyst either has no effect on or decreases the rate of the backward reaction. This was a fairly substantial proportion of one in four, more or less. When one remembers that the inherent dynamic nature of an equilibrium system is not well assimilated by most pupils (5.2 and 5.3), it is likely that a proper understanding of the concept of catalysis will only be acquired by the minority of pupils who have grasped the dynamic concept. But a question as simple and direct as the one above could be interpreted by pupils in terms of the Ordinary grade concept of reversibility, in the absence of the dynamic concept, which might explain why 63% were able to choose the correct answer when a substantial proportion of this 63% will be quite uncertain about the dynamic concept.

Question 7 F.V. = 0.45 D.F. = 0.53

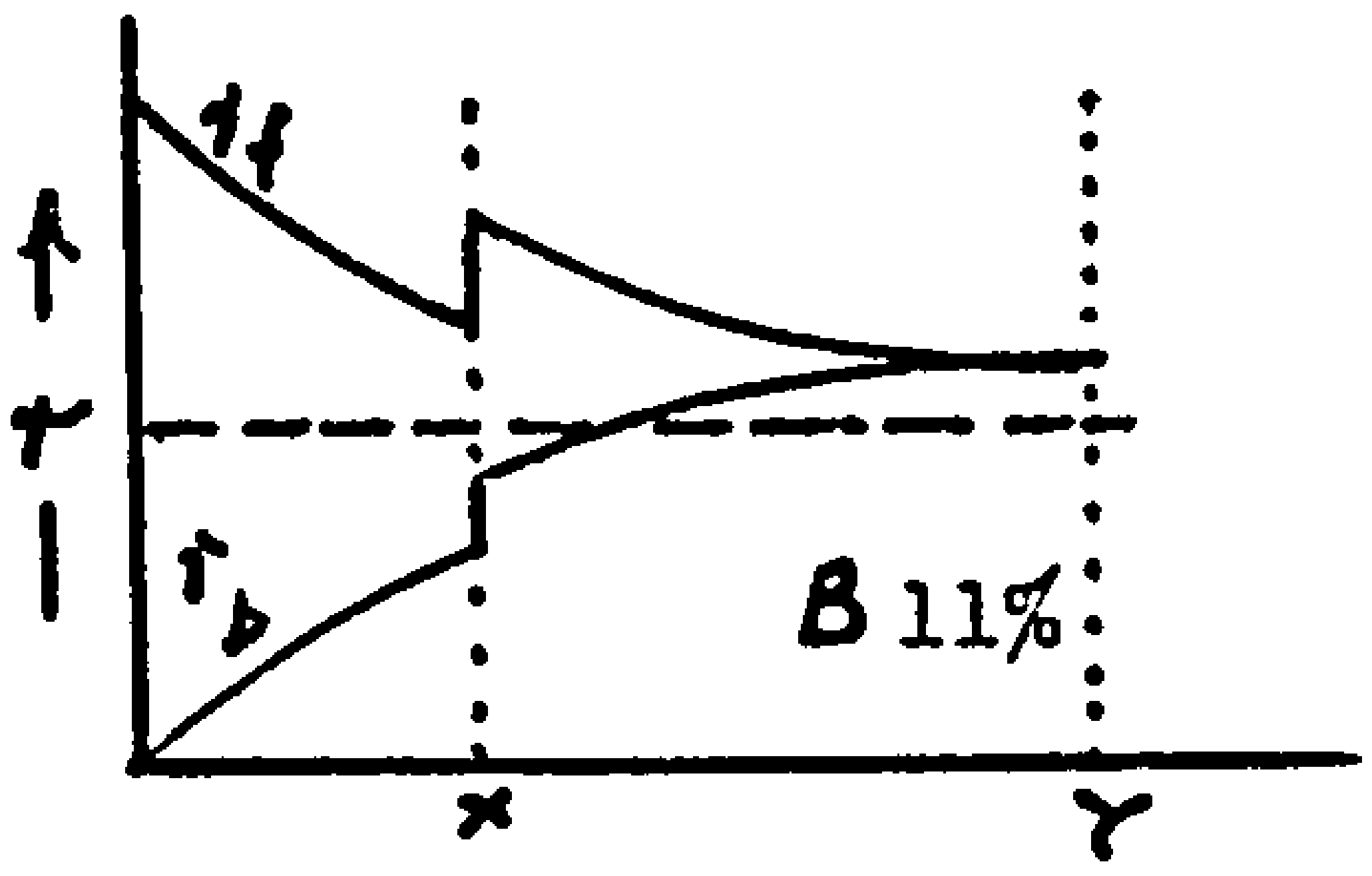
As a non-equilibrium system approaches equilibrium the forward and backward rates of reaction become equal, thus:-



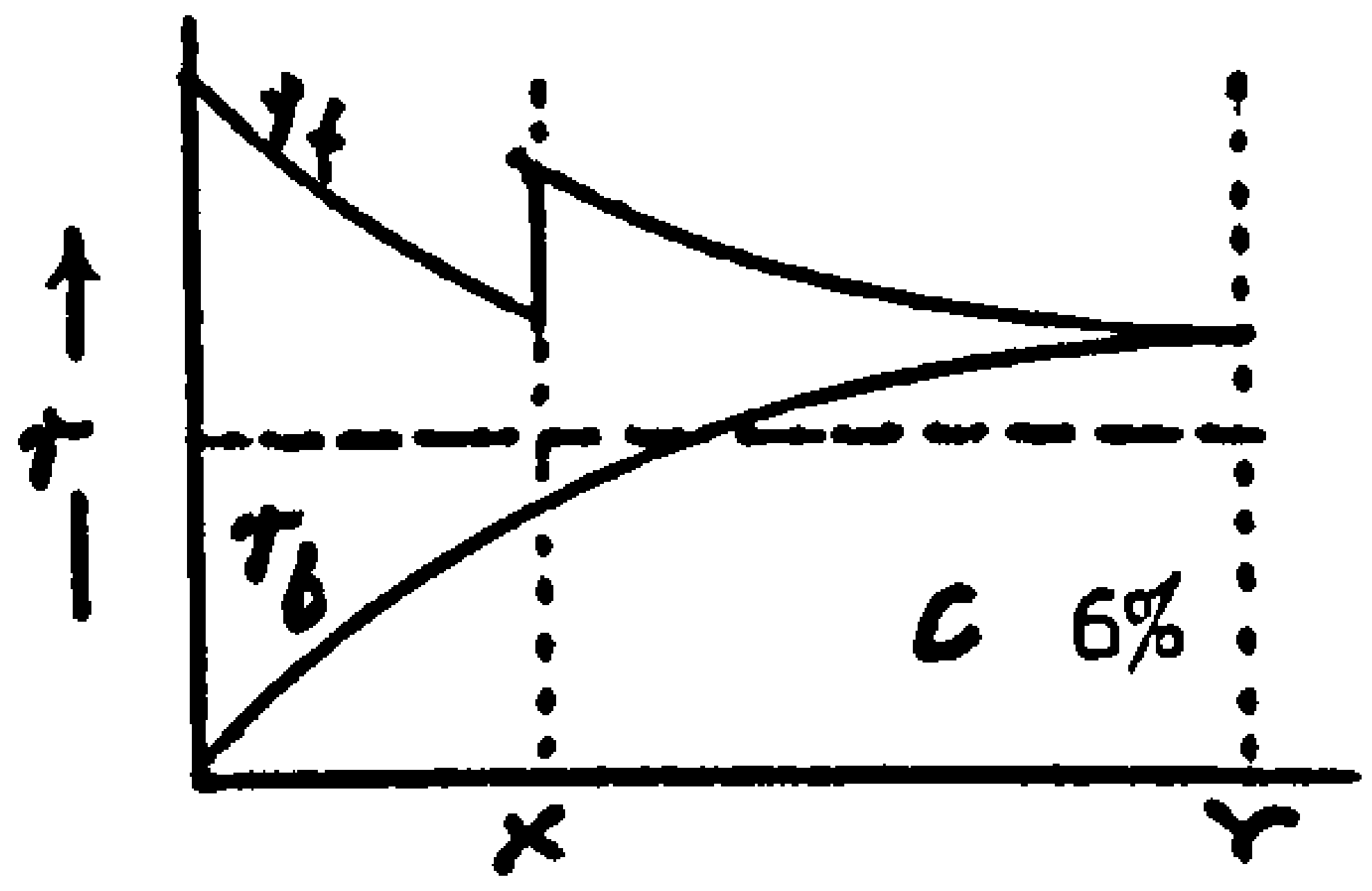
If a catalyst were added at time X,
what effect would it have on the forward and/or
backward rate of reaction?



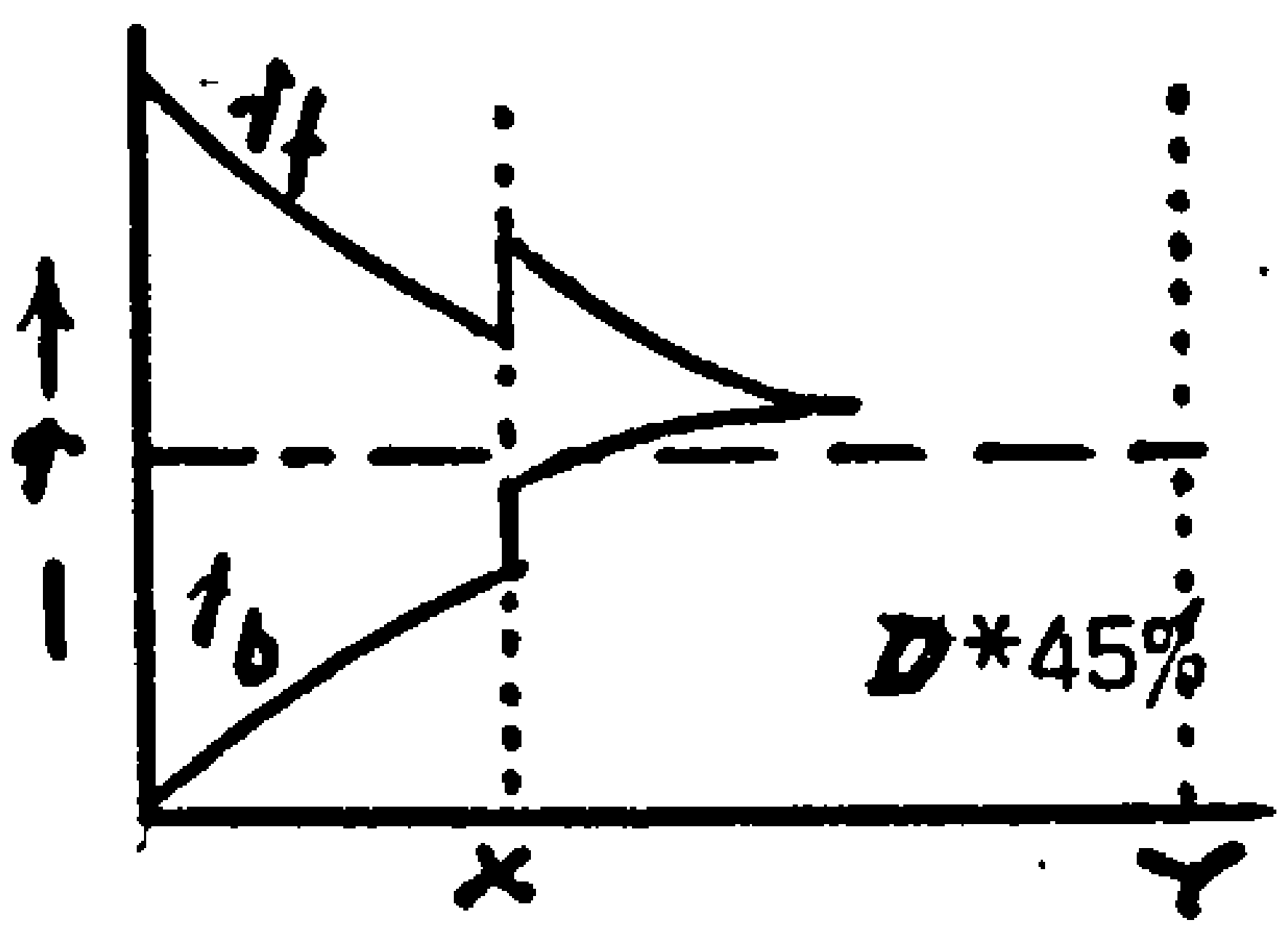
$r_f$ increased;
$r_b$ decreased;
equilm. sooner.



$r_f$ increased;
$r_b$ increased;
equilim. in same
time.



$r_f$ increased;
$r_b$ unaffected;
equilm. in same
time.



$r_f$ increased;
$r_b$ increased;
equilm. sooner.

8% I do not know.

N.B. $r_f$ = forward rate; $r_b$ = backward rate.

The significant feature of the responses to this question are the 36% of pupils who consider that a catalyst either has no effect on or decreases the rate of the backward reaction. This is in keeping with the findings of question 2. However, this question was rather more difficult since it not only tested the effect of a catalyst on the backward rate of reaction but asked about the time taken to reach equilibrium, and a graphical presentation was used in conjunction with the written response to make the meanings of each response quite clear. However, 75% of pupils chose responses including the option 'equilibrium sooner', and this is encouraging.

Question 12. F.V. = 0.67 D.F. = 0.52

Which of the following is a correct description of a catalyst?

| | | |
|---|---|---|
| 6% | A | It supplies energy to the reactants so enabling them to react more quickly. |
| 2% | B | It is a substance which has no effect on the reactions occurring in a system at equilibrium. |
| 25% | C | It ensures that reactants are more quickly and more completely converted into products. |
| 67% | D* | It offers a less "energy requiring" alternative reaction mechanism. |
| 0% | E | I do not know which of these is a correct description of a catalyst. |

Although response C seemed a good one at the time the question was made up, it could perhaps be misinterpreted by pupils. Have the 25% of pupils who chose response C interpreted 'more completely' as meaning a higher percentage of product in the equilibrium mixture (as they should)? Or have they been pre-occupied by 'more quickly' and overlooked the true significance of 'more completely'? If the former is the case, then there is a misconception here that should not be too difficult to correct.

Question 19 F.V. = 0.32 D.F. = 0.21

Which of the following correctly describes the action of a catalyst?

| | | |
|---|---|---|
| 32% | A* | It acts as a "market square", facilitating exchange of energy between reactant molecules and between product molecules. |
| 13% | B | It causes more product to be formed at equilibrium, which equilibrium is also caused to be established sooner. |
| 17% | C | It is a substance which can be used to drive an equilibrium in the desired direction. |
| 33% | D | It is a substance which has no effect on the system at equilibrium. |
| 5% | E | I do not know which of these options is a correct description of a catalyst. |

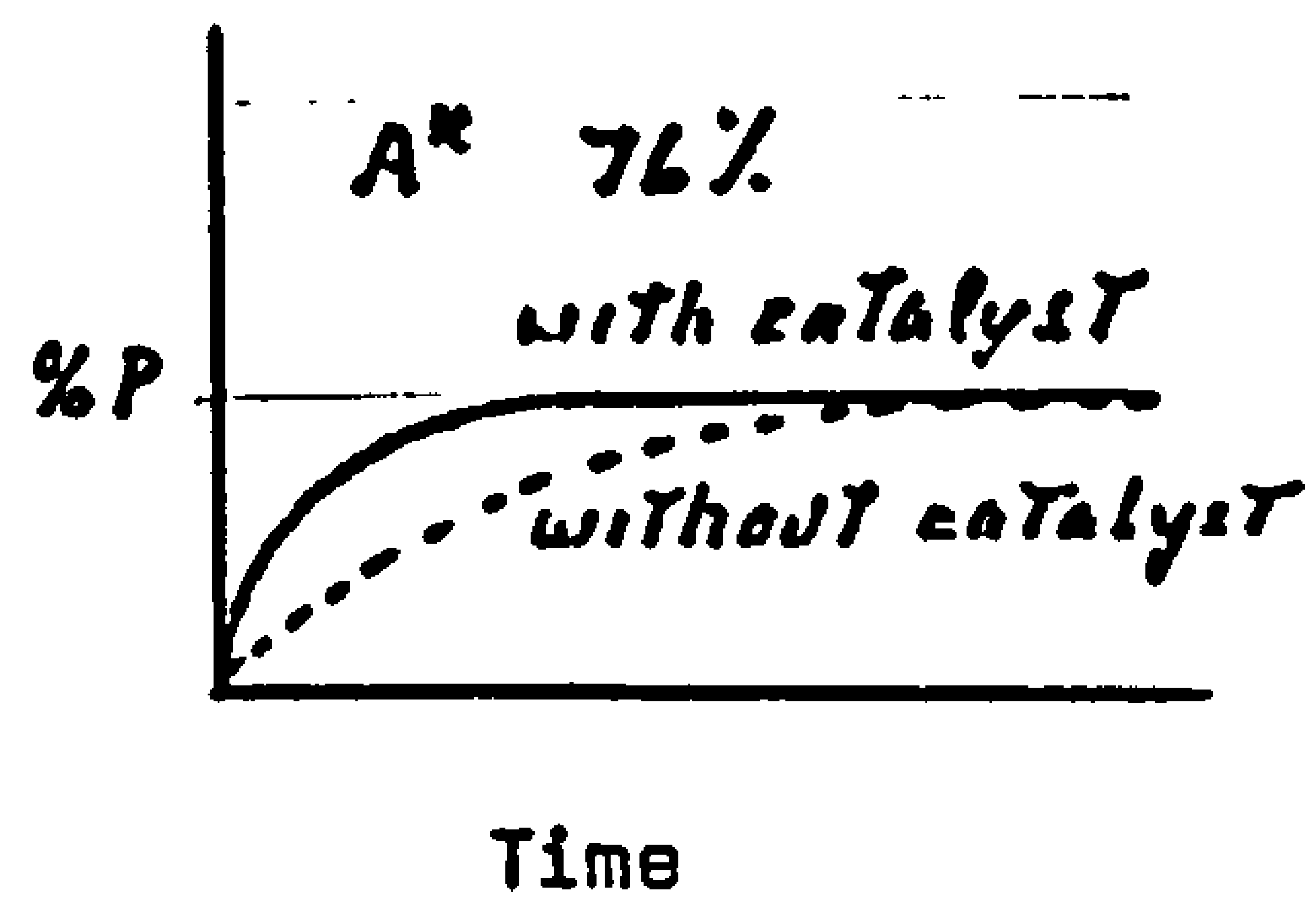
In the discussion of question 12 there was some doubt on the implications of the 25% of pupils who chose response C. In view of the 13% of pupils who chose response B of question 19, it can be concluded that there is some tendency among pupils to think that a catalyst gives a higher percentage of product in the equilibrium mixture. It is most likely, therefore, that some part of the teaching of catalysis leads pupils to make this erroneous assumption, but it is not easy to identify the source of the misconception. Perhaps it stems from confusion with increased 'yield'.

The significance of the 17% of pupils who chose response C is something of a mystery. This particular response was suggested by E. Drever of the Department of Education, University of Stirling (private communication) since he had noticed that it was a mistake which occurred quite frequently in Higher chemistry scripts. He suggested that it might perhaps be being taught in some schools.

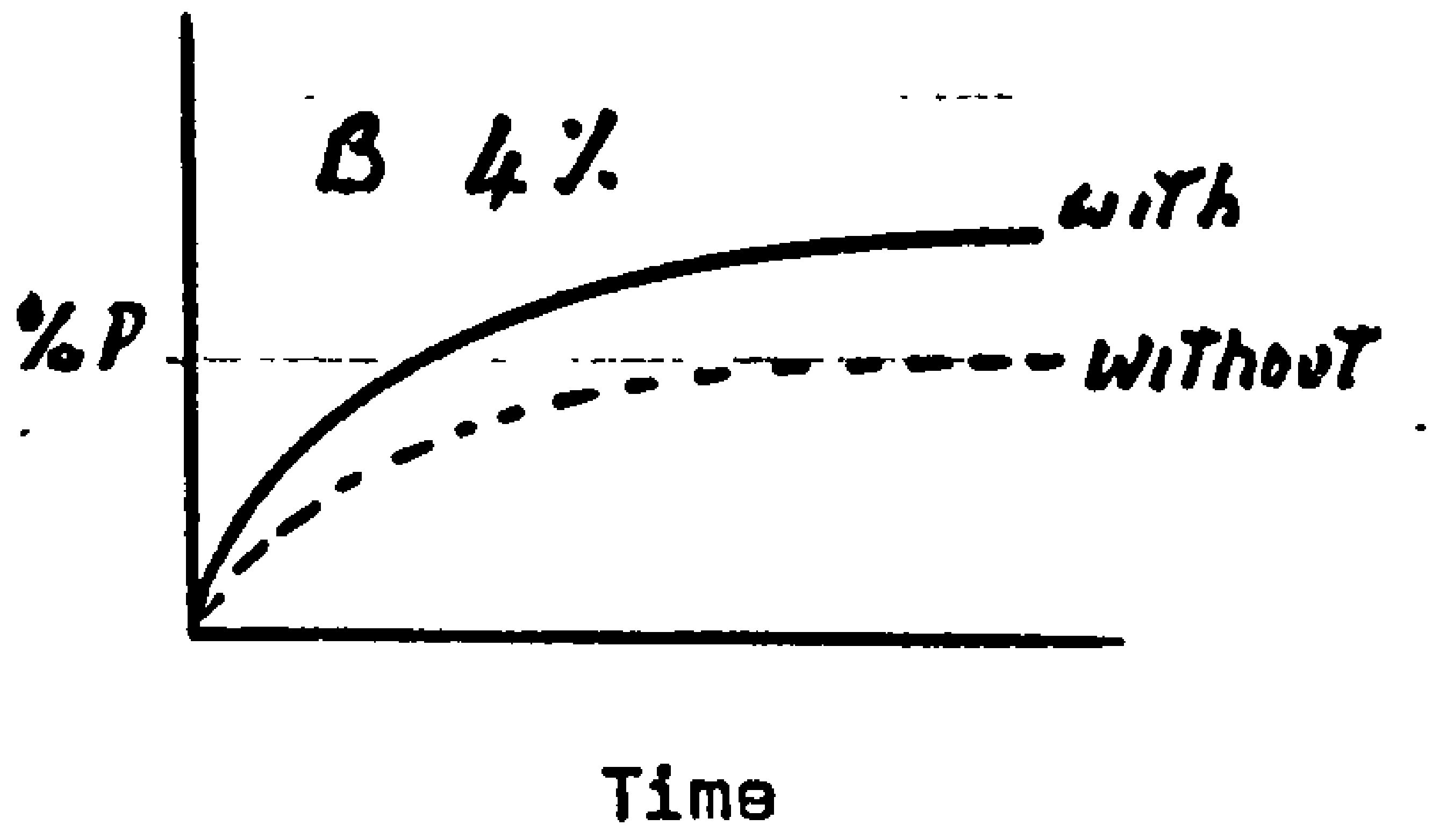
Response D attracted 33% of the pupils, and should be considered in conjunction with response B of question 12. It is quite clear, then, that pupils are interpreting response D of question 19 in terms of no effect on composition, which is correct.

Question 20. F.V. = 0.76 D.F. = 0.39

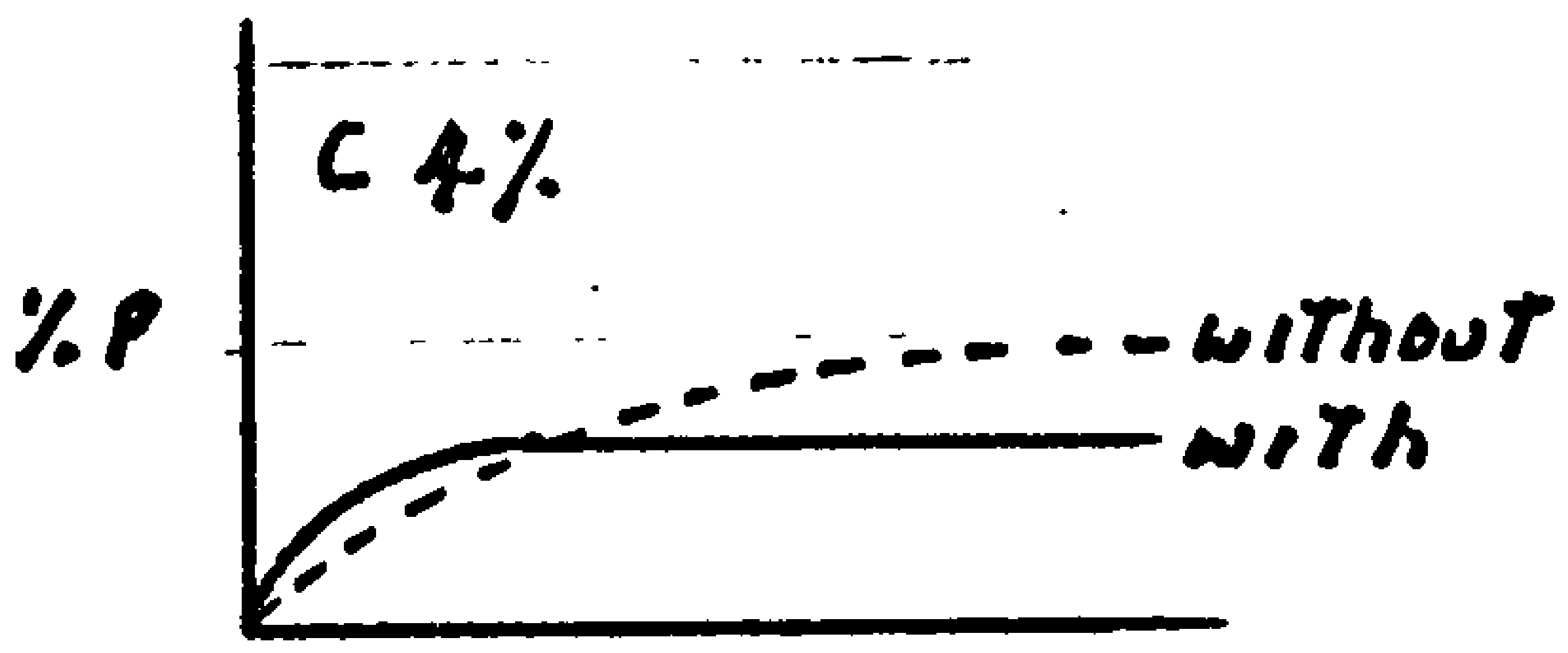
Which of the following graphs represents the effect of a catalyst on the formation of product in a mixture approaching equilibrium?



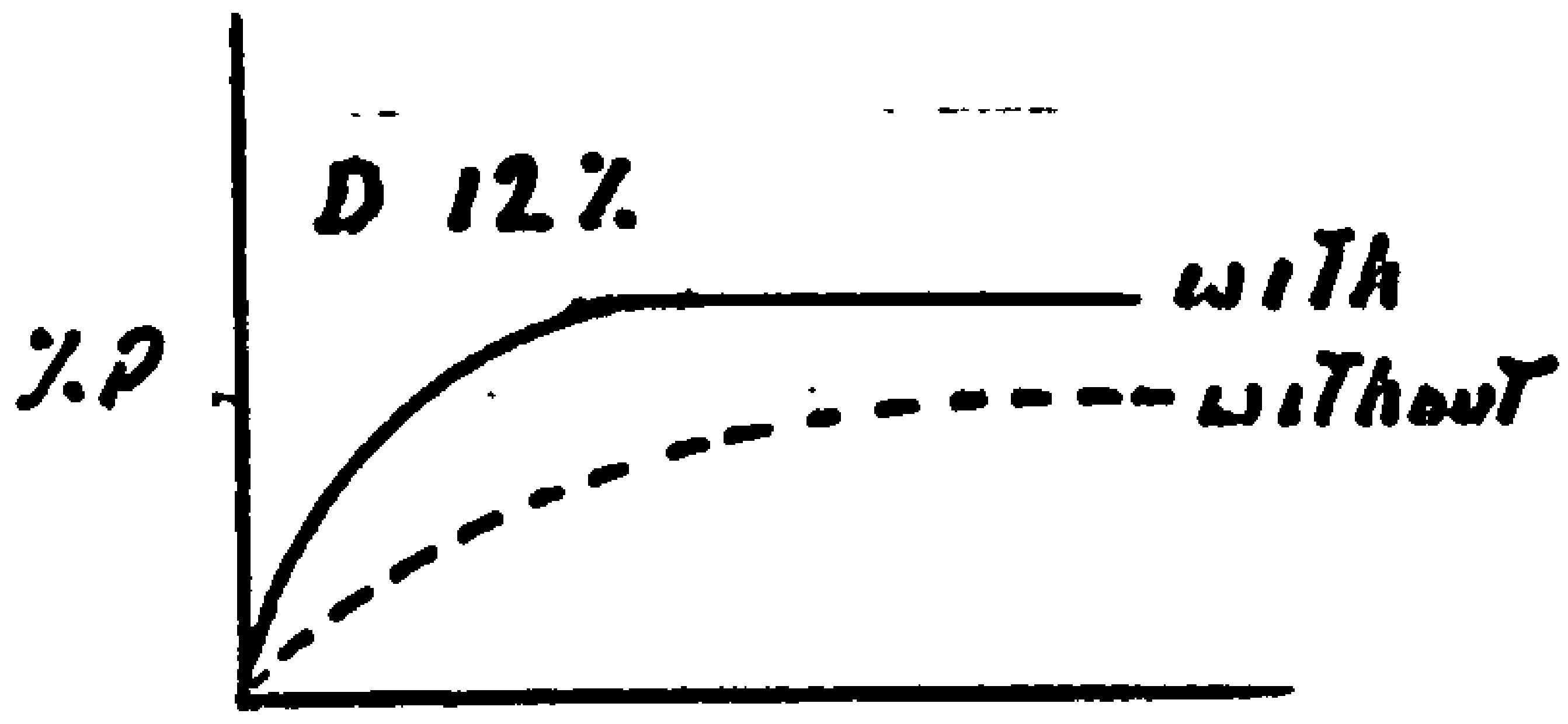
Same equilibrium % product, but obtained sooner.



Greater equilibrium % product after same time.



Smaller equilibrium %
product, but obtained
sooner.



Greater equilibrium %
product, and obtained
sooner.

4%    E    I do not know

There is again some indication that pupils, 12% in this case, think that a catalyst gives rise to more product at equilibrium, which is in agreement with the conclusions of questions 19 and 12.

## 5.7 Matter and energy

### 5.7(1) Distinguishing Matter and Energy

Question 6.    F.V. = 0.62    D.F. = 0.55

** Which of the following lists contains an 'odd man out'?

| | | |
|---|---|---|
| 4% | A | Oxygen, petrol, mist, sawdust. |
| 2% | B | Sand, steam, fluorine, paraffin. |
| 62% | C* | Ethanol, flour, heat, nitrogen. |
| 4% | D | Chlorine, methanol, silica, vapour. |
| 28% | E | I do not know. |

Those pupils who chose response E and offered written comment to account for their choice of E did not appear to recognise the presence of a form of energy in response C while those who chose response C commented that they did so for the very good reason that it was the only response containing a form of energy. Thus 62% of pupils are quite able to distinguish matter from energy while 38% may not be able to do so. The small percentages who chose the incorrect responses A, B and D and offered written comment to account for their choice based their choice on some or other incorrect premise, such as the pupil who said he chose response D because chlorine was an element while all the other substances were compounds. Oddly enough, and rather a surprising feature of the results of this question, no pupil chose an incorrect response for a valid reason.

The discriminatory power of the question was very good. The facility values of the top, middle and bottom thirds were 0.91, 0.61 and 0.35 respectively.

Question 21. F.V. = 0.68 D.F. = 0.39

**** Which one of the following lists differs in a significant way from the other three?

| | | |
|---|---|---|
| 4% | A | Copper, heat, neon. |
| 68% | B* | Helium, tin, water. |
| 3% | C | Argon, zinc, light. |
| 6% | D | Gold, sound, krypton. |
| 19% | E | I can see no significant difference between these lists. |

The same general comments apply to question 21 as apply to question 6. One pupil chose response A because it was the only option which "did not contain a substance which travelled in waves". The significance of this statement is obscure. Another pupil wrote about question 21, "All but one contains some form of wave motion, like sound (transverse waves), and heat, and light (both electro-magnetic waves). 'B' contains no waves and so is the odd man out (assuming that the water is fairly still)."

The facility values for the top, middle and bottom thirds are 0.86, 0.71 and 0.47 respectively.

## 5.7(2) Potential Energy and Kinetic Energy

Question 11. F.V. = 0.15 D.F. = 0.22

** When water at 100 °C absorbs heat and changes to steam at 100 °C,

| | | |
|---|---|---|
| 38% | A | the potential energy of the molecules remains the same but their kinetic energy increases. |
| 15% | B* | the kinetic energy of the molecules remains the same but their potential energy increases. |
| 22% | C | both the potential energy and kinetic energy of the molecules increase. |
| 1% | D | neither the potential energy nor the kinetic energy of the molecules increases. |
| 24% | E | I do not know how the potential energy and/or the kinetic energy of the molecules is affected. |

The written comments for this question were erratic and illogical, and showed most pupils to have no clear conception of the nature of the energy absorbed at the boiling point. The 15% who chose the correct response offered simple and correct reasoning: since there was no change in temperature, the kinetic energy of the molecules remains the same, and so there would have to be an increase in potential energy. The most popular incorrect reason offered to explain a choice of A or C was something to the effect that molecules of a gas (steam) must move faster than molecules of a liquid (water).

## 5.7(3) Kinetic Particle Theory

Question 22. F.V. = 0.56 D.F. = 0.31

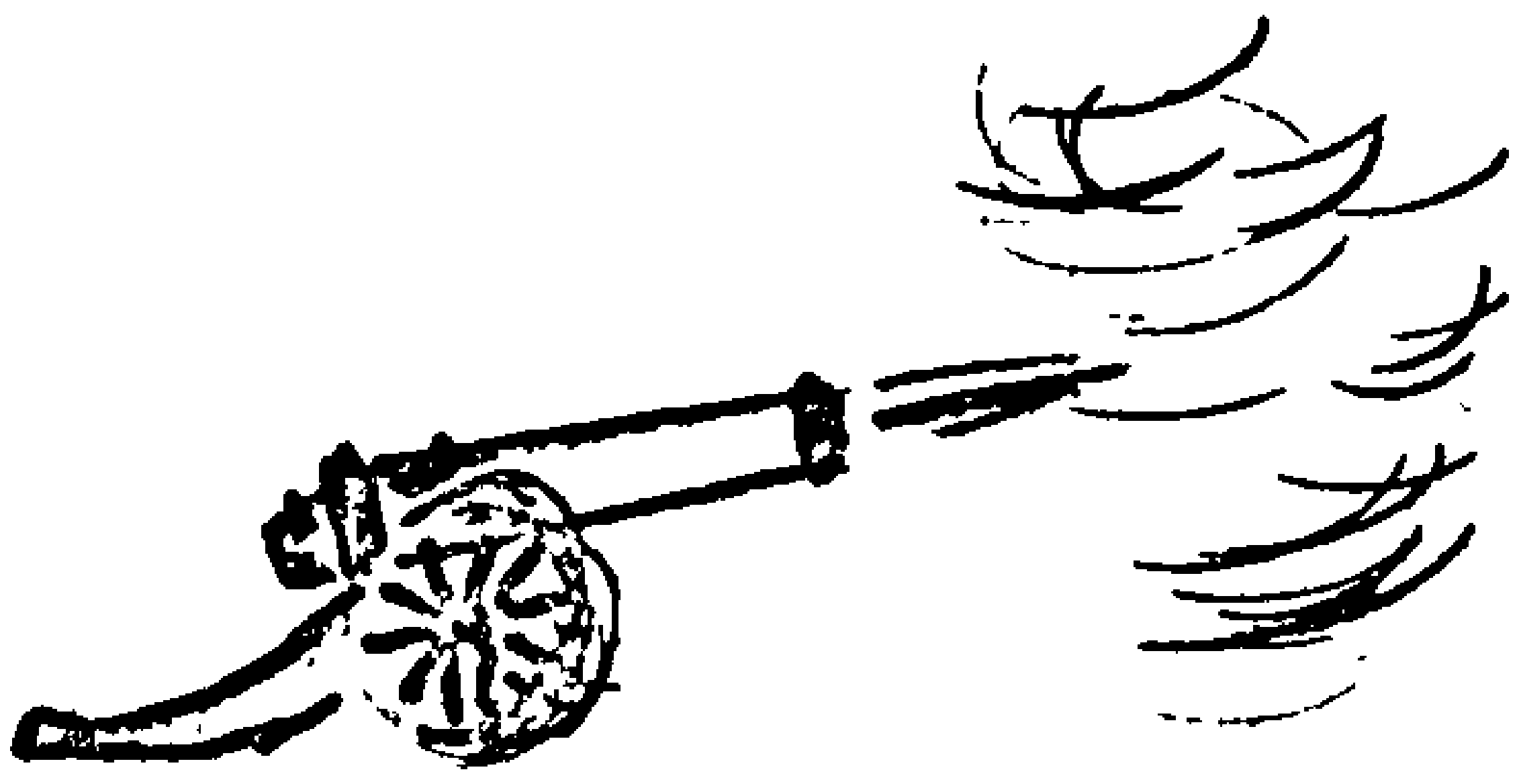
What is the effect on an individual molecule of raising the temperature of the gas?

| | | |
|---|---|---|
| 35% | A | The molecule travels faster. |
| 2% | B | The molecule becomes hotter. |
| 56% | C* | The molecule's average speed is greater. |
| 3% | D | It is not possible to say. |
| 4% | E | I do not know. |

It was anticipated that this question might have a high facility value in the region of 0.9. It is surprising, therefore, that the facility value was much lower. Response C is such an obvious choice one would imagine, that it is puzzling why 35% of pupils chose response A. It would seem that these pupils, even in Form V, have no clear conception of the range of speeds exhibited by molecules, and of their interchange, in a gas.

### 5.7(4) Conservation of Energy

Question 23. F.V. = 0.32 D.F. = 0.33



When a cannon is fired blank, x joules of heat are produced in and around the cannon.

When an identical charge of powder is used to fire off a cannon-ball, y joules of heat are produced in and around the cannon.

Which of the following statements is correc?

32%* A x is greater than y.
13% B x is equal to y.
38% C x is less than y.
3% D It depends on the quality of the gunpowder.
14% E I do not know.

The Conservation of Energy is one of those very fundamental concepts about which every pupil should have at least a working knowledge.

The concept arises in the Higher grade chemistry syllabus in Section Q.1 as a justification for Hess's Law; it arises in the physics syllabus in Sections K.3 and N.2; it arises in the biology syllabus in Section III. And yet, to judge from the results of this question, 68% of pupils have no clear conception of the implications of the concept in an applied situation, as above.

The conclusions to be drawn from the discussion of the results of the Rates Approach Test are presented in Chapter 6.

# CHAPTER 6

# CONCLUSIONS

## 6.1 Conceptual Difficulties experienced by pupils

1. A majority of pupils appear to suffer from the misconception that equilibrium systems are compartmentalised, that is to say, that they have left sides and right sides which are independent of each other and which can therefore be acted upon independently.

2. A majority of pupils appear to have conceptual difficulty in grasping the idea that forward and reverse rates of reaction occur equally at equilibrium.

3. A majority of pupils appear to suffer from the misconception that where the reversed arrow symbol employs arrows of unequal length, the longer arrow implies greater rate of reaction than does the shorter arrow.

4. A majority of pupils have conceptual difficulty in distinguishing between equilibrium and non-equilibrium situations.

5. A majority of pupils find Le Chatelier type manipulations of variables conceptually difficult, the difficulties being very marked for the poorer pupils. The majority of pupils suffer from the misconception that increased pressure alters the composition of a mixture in that direction which results in a reduction in pressure.

6. Pupils suffer in varying degrees from a variety of misconceptions relating to the action and effect of catalysts on reaction rates and equilibrium systems: catalysts have no effect on reverse rate; catalysts decrease the reverse rate; catalysts cause the formation of a higher percentage of product in the equilibrium mixture; catalysts can be used to drive the equilibrium in the desired direction.

7. Poorer pupils have conceptual difficulty in distinguishing between matter and energy. A majority of pupils have difficulty in distinguishing between potential and kinetic energy at the molecular level; and many pupils do not appreciate the variation in molecular speeds. A majority of pupils have not yet conceived of the Conservation of Energy.

## 6.2 Why do these Conceptual Difficulties exist?

Given an ideal teaching situation, it is possible that a significant proportion of pupils will still experience conceptual difficulty with aspects of the concept of chemical equilibrium because of the inherent abstract nature of the topic. With less than the ideal situation, that is to say, any real situation, conceptual difficulties arise which might otherwise have been avoided.

There might be occasions when these latter arise through faulty teaching, but these are probably minimal. The misconception about the effect of increased pressure on an equilibrium system fits into this category, but it must also be remembered that this is the accepted way of teaching this aspect of the course.

It is more probable that the presence of a misconception is more often the result of a tacit assumption adopted by the pupil with respect to what he, the pupil, thinks the teacher implies rather than what the teacher actually means, a tacit assumption about which the teacher is quite unaware. This would account for misconceptions like left and rightsidedness, the reversed arrow symbol, and catalysis in general.

The abstract nature of the concept would account for the basic difficulty experienced by many pupils, particularly the poorer ones - in the absence of any distinct misconception as such, in understanding the dynamic concept, in distinguishing between equilibrium and non-equilibrium situations, in mentally manipulating Le Chatelier type problems, and in dealing with energy considerations in general.

## 6.3 How can these Conceptual Difficulties be avoided?

Instances of inaccurate teaching may be corrected by direct action. With regard to the pressure variable misconception resulting from misapplication of the Le Chatelier Principle, one solution might be a more thorough treatment of the Principle with greater emphasis on its qualitative limitations. The author, however, does not think this would be advisable at Higher Grade. Another solution might be abandonment (partly or wholly) of the Principle and its substitution by the equilibrium constant expression for the Equilibrium Law, treated in an essentially qualitative fashion. This is merely a suggestion; whether it is a good suggestion or a bad one is difficult to assess without a proper investigation. There is some evidence that the static equilibrium system so emphasised in physics teaching may be confused with the dynamic equilibrium system emphasised in chemistry teaching and may have a confounding effect on pupils' reasonings employing the Principle. The use of the equilibrium constant might circumvent this difficulty.

The remedial action suggested by the author (Pocket Item 3) employs the Le Chatelier Principle with a degree of caution.

Teachers should be aware of the tacit assumptions which pupils are liable to adopt in a given teaching situation and either use methodology which avoids or minimises such misinterpretation, or, if this is not possible, actively teach against these assumed misconceptions by appropriate use of positive and, particularly, negative instances.

Over and above these recommendations, it must be realised that the topic of chemical equilibrium contains such abstract formal material that, even with a concrete presentation, much of it is only assimilable by pupils who have attained the stage of formal operations, and, consequently, there are pupils to whom the concept, either partly or wholly, will prove to be a stumbling block.

## 6.4 Remedial Action

Prior to his involvement in this study, the author had developed nineteen worksheets covering Section R of the Higher grade course. In view of the findings of this study, these worksheets were modified and expanded where conceptual difficulties had been found, giving twenty four revised worksheets. These were supplied to each of the thirteen schools who had made returns of the Rates Approach Test. The modified and expanded areas in the worksheets are marked by a margin line, and these only are given as Pocket Item 3.

No request was made that the worksheets be used; they were merely offered as a possible solution to the conceptual difficulties experienced by pupils. Nor, for lack of time, was any attempt made to follow up the effects of the remedial action.

# PART III

# CONCEPTUAL DIFFICULTIES
AT
CERTIFICATE OF SIXTH YEAR STUDIES

# CHAPTER 7

# DESIGN AND SCOPE OF THE INVESTIGATION AT THE CERTIFICATE OF SIXTH YEAR STUDIES LEVEL

## 7.1 The Need for the Research

The search of the literature extended from late October, 1974 to early May, 1975 (A. VII.1), and the results of the written enquiry were not fully available until April, 1975. By the time some positive indication of the conceptual difficulties experienced by pupils studying the thermodynamics part of the Certificate of Sixth Year Studies course, Section 2 - Energies in Macroscopic Systems, was available, it was too late to design, construct and administer a test comparable in strength to the Rates Approach Test. Even if time had been available, it is doubtful if many Sixth Year Studies pupils would have been available after the certificate examinations. And furthermore, the list of conceptual difficulties relating to Section 2 of the Sixth Year Studies course was rather limited and (in the author's opinion) not a true reflection of the difficulties experienced by pupils and, perhaps, some teachers in covering this part of the syllabus. A principal teacher of chemistry, in reply to the letter of enquiry (A II.2), wrote, "I frankly do not feel that pupils have any clear idea of the concept of free energy, and I admit that I, too, have some difficulty in visualising it. I find that the pupils have no difficulty with the ideas of equilibrium and free energy so far as applying them to particular situations is concerned, but I do not think there is any basic concept of free energy and equilibrium."

The thermodynamic approach to chemical equilibrium presents pupils with a variety of new abstract material which may pose conceptual difficulties to a lesser or greater extent. The task at the Certificate of Sixth Year Studies level, therefore, was one of developing a method by which these concepts could be presented to pupils in a form which they could relate to existing cognitive structure and so assimilate it.

Consequently, it was decided to construct a programme, the Thermodynamics Approach Programme (Pocket Item 4), specifically developed for this purpose, and to assess the effectiveness of the Programme by appropriate statistical methods.

## 7.2 Summary of Educational Theory underlying the Development of the Thermodynamics Approach Programme

(i) Concept Teaching. It has been shown (26) that a formal, rigorous, mathematical presentation of chemical equilibrium, which must lean heavily on thermodynamic theory, is too difficult for all but the very brightest of pupils.

Others (33, 34, 36) have suggested that it might be advisable to resort to concrete thought in new problem situations. This view is also held by Ausubel (Educational Psychology; A Cognitive View, page 220) who asserts that generally mature students tend to function at a relatively concrete and intuitive level when confronted with new subject matter in which they are as yet unsophisticated. For this reason, a concrete-empirical approach to chemical equilibrium was constructed around the concept of a falling, spinning weight. This approach was embodied in the Thermodynamics Approach Programme.

Conceptual problems, of course, are not all equally difficult, and the concrete presentation of abstract concepts will not always succeed. Such presentation, however, provides the pupil with the opportunity of meeting the concepts in relatable and intelligible form, which may lead to assimilation.

There is, next, the need to move from concrete to formal thought leading to assimilation of the new material in abstract form.

Finally, abstraction requires that the conceptual knowledge be generalised, that is to say, that the conceptual knowledge become applicable to analogous situations as well as the particular ones which instanced its acquisition and internalisation. Thus questions involving analogous problem situations are built into the self-tests at the end of each unit of the Programme.

(ii) Method of Presentation. Much research has been carried out on different methods of presentation (40, 41, 42, 43, 44, 45, 46). In general, it would appear that pupil performance and achievement is independent of the technique of instruction employed and dependent instead, at least in so far as cognitive achievement is concerned, simply on basic academic ability. There is no evidence to support the view that programmed instruction is superior to class conventional teaching (40). Nor does it matter whether or not the technique employed is deductive or inductive, though different pupils are suited to different techniques (42, 43). Since it is not possible to tailor-make courses to suit individual pupils, a combination of the inductive and deductive techniques is probably desirable (41, 44). There is general support for the view that cognitive material must be properly sequenced (34, 37). And, further, it helps if the learner knows in advance what to look for and has the correct anchoring ideas clearly pointed out to him (37). Limited use of negative instances is recommended (41).

In general, the Programme is a compromise between the Gagne approach, which employs a smooth, graded upward climb of carefully constructed objectives as shown in Figure 7.1, and the Bruner approach, which employs shock producing disequilibria to provoke re-appraisal and restructuring. That the acquisition of conceptual knowledge is assisted by 'conceptual conflict' is also a fundamental tenet of Piaget's theory of intellectual development. The self-tests at the end of each unit of the Programme are included for this purpose, and are designed in such a way as to create such conflict, leading to restructuring of conceptual knowledge to eliminate contradictions - a process described by Piaget as equilibration.

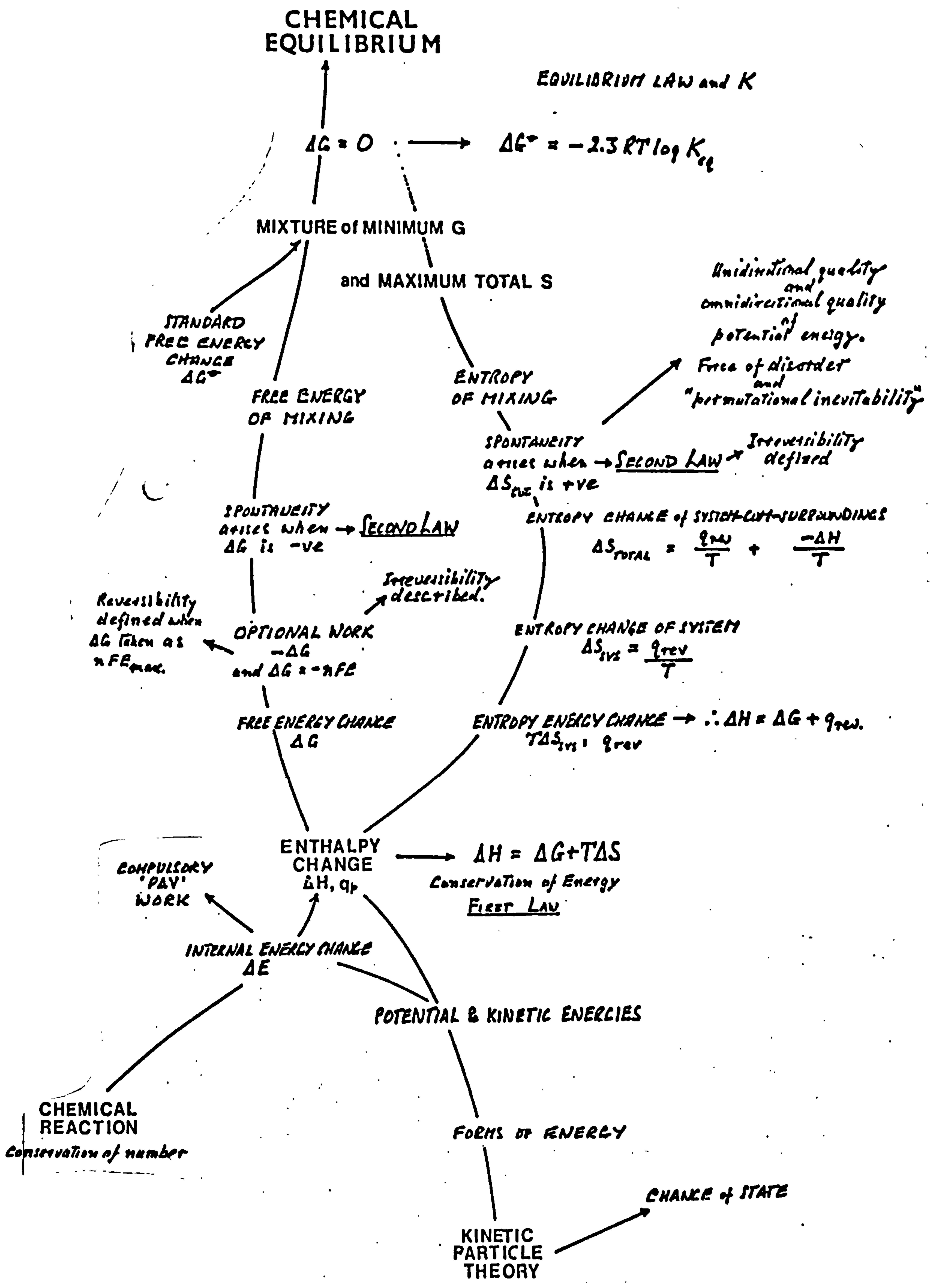


Figure 7.1 Concept Sequence in Thermodynamics Approach to Equilibrium.

## 7.3 Thermodynamics Approach Programme

### 7.3(1) Development and Construction of the Thermodynamics Approach Programme.

A Programme was written which embodied the findings of the search of the literature (Chapter 2) summarised in 7.2. The salient points of the Programme are displayed in Figure 7.1, and are explained in the following paragraphs.

The logical starting point for the development of thermodynamic theory is the concept of enthalpy change. Pupils are already familiar with this concept, though their knowledge of it is rather limited since the concept is not treated in any great depth at Higher grade. Further, as shown in Part II, most pupils suffer from misconceptions in the general area of energy and so it is necessary to clear up these misconceptions first (Unit 1).

The meaning of enthalpy change is explained in concrete terms (Unit 2), the opportunity being taken to dispose of PΔV work as far as the rest of the Programme is concerned, and, at the same time, to stress the relevance and importance of the Conservation of Energy. The achievement of these aims requires the introduction of the concept of a system and its surroundings.

Some applications of the Conservation of Energy in the form of Hess's Law are dealt with in order to calculate a variety of bond energies (Unit 3). These allow pupils some time to consolidate the concept of enthalpy change before going on to the concepts of free energy and reversibility.

It is essential to stress the difference between the chemical and the thermodynamic meanings of reversibility and irreversibility (Unit 4). Reversibility can be defined initially in the context of the 'falling weight' physical analogy which has been used for this purpose. The Programme defines the reversible situation as one resulting from maximum demand on optional work, such that the reversibility of the process and its (infinite) slowness are consequences rather than prior conditions. Free energy not taken as work is otherwise obtained as heat. The definition of irreversibility requires a fairly sophisticated knowledge of the concept of entropy value, and so cannot be given until much later in the Programme. It is adequate for the time being to describe the irreversible operation of a change as any operation other than reversible. When the process is operated fully irreversibly (no demand at all being made on it to do work) the heat change with the surroundings is the enthalpy change. At this point in the Programme the symbol $q_{rev}$ is cautiously introduced as the heat change during the reversible operation, and spontaneity is defined in terms of free energy change, an acceptable definition of the Second Law.

The enthalpy change is now shown to be the <u>result</u> of the interplay between the free energy change, liberated as heat, and the entropy energy change which can only be exchanged with the surroundings as heat, but may be liberated or absorbed as the case may be. The additive and consequential nature of enthalpy change is stressed throughout the entire Programme. The use of the term 'entropy energy' is defended in the sense that it is a potential energy change which is not available for conversion to work done, but the term cannot be explained at this point. The substitution of TAS for $q_{rev}$ in the expression $AH = AG + q_{rev}$ is defended on the grounds that it is correct symbolism, but the precise meaning of TAS cannot be explained at this point either. It is more than sufficient that pupils appreciate conceptually in concrete terms that enthalpy change results from the liberation of potential energy as heat which might otherwise have been 'put to work', moderated by the liberation or absorption of potential energy which by its difference from the former (yet to be explained) could not be so used. And the use of a falling weight whose spin decreases or increases as it descends is defended on the grounds that nothing better is available with which to treat a very difficult abstraction ($q_{rev}$) concretely. Care is taken, however, to repeatedly warn pupils that the falling spinning weight is an analogic device and not a real weight. (Unit 5).

The variety of new conceptual material acquired concretely in the first five units of the Programme is now transferred to real chemical systems (Unit 6). The irreversible operation of a reaction and its reversible operation in the form of an electrolytic cell are explained. Some initial comments on the need for standard conditions are made, and the origin of the Standard Reversible Electrode Potentials, $E^o$, is explained.

Entropy value and entropy energy are now discussed in some detail (Unit 7). At this point in the Programme, the use of the formulation TAS for the symbol $q_{rev}$ is justified. This requires some sophistication in the concept of entropy value. The Programme defines entropy value in terms of accessible microstates, the notion of 'disorder' being used to complement this definition. The justification for the inclusion of disorder is that it is a very popular device which is used apparently, in the author's opinion, to explain the meaning of entropy. The Programme defines entropy value as a measure of 'disorder' where the latter is defined as the number of accessible microstates. Entropy, therefore, emerges as a value analogous in some respects to pH value, a concept with which pupils are familiar and which therefore is used as the anchoring idea for entropy. Some care, however, is needed in doing so since pH is an intensive property while entropy is extensive.

A discussion of entropy value in terms of thermal and configurational microstates is offered with explanatory examples (conduction in the former and diffusion in the latter) and an explanation given that TAS is an energy term (7.7). Some further consolidation of the concepts of system and surroundings is undertaken, leading to a definition of the Second Law in terms of change in total entropy value. Irreversibility is now defined in the thermodynamic sense. Finally, the equation between $q_{rev}$ and $T\Delta S_{sys}$ is explained in detail (7.12), and, assuming AH to be zero, the free energy of mixing and entropy of mixing explained by $\Delta G = -T\Delta S$.

Before going on to the study of free energy and equilibrium (Unit 9), some explanation of the fundamental difference between free energy change (AG) and entropy energy change ($q_{rev}$) is offered (Unit 8). These are distinguished on the basis of a unidirectional quality and an omnidirectional quality. The former, the characteristic of free energy change, could be used to do work because the move from initial to final state exhibits a "resultant" effect; the latter, a characteristic of entropy energy change could not be so used because the energy was just as scattered in the final state as in the initial state, and consequently exhibited no "resultant" effect during the change from initial to final state dictated by the free energy change.

The underlying drive of a reaction results from the tendency of its parts to move to and exist in any one of a set of microstates which are collectively permutationally more probable. For large numbers of parts (of energy and/or matter) this practically rules out the occurrence of the improbable, such as the spontaneous separation of gases or the passage of heat from a cold to a hot body because the probability of occurrence is so small as to be of no consequence.

The remainder of the unit (Unit 8) deals with specific examples of equilibria; AH is treated as a consequence, not a condition.

The concept of standard free energy change is introduced (Unit 9) and developed to convey the concept of a mixture of minimum free energy at equilibrium, a mixture in which AG is zero. Since the standard change is a new idea, it is introduced concretely, but almost immediately transferred to abstract formal operations with real systems.

Formal presentation of free energy and its determining effect on equilibrium is continued (Unit 10). The equilibrium constant and its relationship with the standard free energy change is developed.

Examples of equilibria and their dependence on free energy are given (Unit 11).

## 7.3(2) Unit Titles and Purposes

Each of the eleven units of the Programme is preceded by a statement of general purpose of the unit.

Here are the titles and purposes of the units.

### Unit 1. Ground clearing operation

1. To clear up false ideas about matter and energy which you may have acquired.
2. To revise your ideas about the Kinetic Particle Theory of Matter.
3. To discuss the various forms of energy.
4. To consider the form of energy and work terms.

### Unit 2. Enthalpy change

1. To show the connection between internal energy change, enthalpy change and compulsory work.
2. To introduce the ideas of system and surroundings.
3. To stress the potential nature of enthalpy change.
4. To consider that energy is conserved in physical and chemical change.

### Unit 3. Bond energies

1. To calculate some bond energies with the aid of Hess's Law.

### Unit 4. Reversibility and free energy, by physical analogy

1. To discuss early ideas about reversible and irreversible reactions.
2. To introduce the concepts of thermodynamic reversibility and irreversibility.
3. To define free energy in terms of optional work capability, and establish the link between free energy and reaction spontaneity.

### Unit 5. Enthalpy, free energy and entropy energy, by physical analogy.

1. To show how the enthalpy change is the result of a free energy change and an entropy energy change.

2. To discuss the enthalpy change and the reversible heat change for a spontaneous change in which the entropy energy change is negative.
3. To discuss the enthalpy change and the reversible heat change for a spontaneous change in which the entropy energy change is positive.

### Unit 6. Energy changes in chemical reactions

1. To contrast the irreversible and reversible operation of a chemical reaction.
2. To show how the enthalpy change for a chemical reaction is related to the free energy change and the entropy energy change.
3. To show that optional work in an electrical circuit is nFE.

### Unit 7. Entropy and entropy energy

1. To define entropy value as indicative of disorder.
2. To discuss the implications of change in total entropy value.
3. To define system, surroundings and universe.
4. To show that change in entropy energy is equal to TAS.
5. To explain the term 'free energy of mixing'.

### Unit 8. Spontaneous processes

1. To offer a fundamental explanation for the occurrence of reactions.
2. To offer a fundamental explanation of the difference between free energy and entropy energy.
3. To explain a variety of processes in terms of free energy change and entropy change.

### Unit 9. Equilibrium and free energy

1. To introduce $AG^{o}$.
2. To consider the various free energy changes during a chemical reaction.

Unit 10. Free energy and the equilibrium constant

1. To develop the concept of the equilibrium constant.
2. To state the relationship between the standard free energy change and the equilibrium constant.
3. To show how the sign and magnitude of the standard free energy change affects the composition of a mixture coming to equilibrium.

Unit 11. Equilibria and free energy

1. To show how some equilibria can be explained in terms of free energy change.

Each unit was considered to be the equivalent of a half-hour lesson. This was in keeping with the normal allocation of time to this part (Section 2) of the Sixth Year Studies syllabus, that is to say, about twenty hours of which about six hours are spent in theory and the remainder in practical work.

### 7.3(3) Specific Unit Cognitive Objectives

Each unit of the Programme is followed by a list of the specific cognitive objectives of the unit.

Unit 1.

You should
1. know the difference between matter and energy.
2. know the three states of matter.
3. understand what happens to particles during so-called physical and chemical change.
4. know the various forms of energy.
5. know the difference between potential and kinetic energy.
6. understand the Kinetic Particle Theory.
7. know that an energy term equals a force term multiplied by a quantity term.
8. know what this programme means by 'compulsory PAV work'.
9. know that electrical work is nFE.

Unit 2.

You should 1. be aware that in a change there is a 'system' part and a 'surroundings' part.
2. understand AH to be the constant pressure heat change.
3. realise the need for the same before and after temperature in enthalpy change.
4. know that enthalpy change is a potential energy term.
5. understand the First Law of Thermodynamics.
6. be aware of some heats of reaction.
7. know Hess's Law.
8. be able to apply Hess's Law.

Unit 3.

You should 1. know how to calculate some bond energies.
2. have some general ideas of the 'strength' of bonds.
3. understand what is meant by 'endothermic compound'.

Unit 4.

You should 1. know what is meant at O Grade and H Grade by reversible reaction and irreversible reaction.
2. know that free energy is potential energy which is available for doing work.
3. know that a change is operated reversibly when it is made to do the maximum work.
4. realise that free energy not used to do work appears instead as heat.
5. know that a change is operated irreversibly when something less than the maximum demand is made on it to do work.
6. know that the heat change under complete irreversible operation is AH.
7. know that the heat change under reversible operation is $q_{rev}$.
8. know that a reversible change 'occurs' through a continuing equilibrium state.

### Unit 4 (contd.)

9. know that a reversible change is a balanced change and that the slightest push in the opposite direction reverses it, which is why it is called reversible.
10. know that a reversible change occurs infinitely slowly.
11. know reversibility is an ideal limit.
12. reversible processes are unobservable.
13. know that only irreversible processes are observable.
14. know the meaning of spontaneity.

### Unit 5.

You should

1. know that the enthalphy change is the summed effect of a free energy term and an entropy energy term.
2. know that in the relationship AH = AG + TAS, TAS = $q_{rev}$.
3. If AG and TAS are exchanged as heat, AH is obtained; while if AG is used to do work, the only heat change can be TAS.

### Unit 6.

You should

1. know how a chemical reaction may be performed irreversibly.
2. know how a chemical reaction may be performed reversibly.
3. know that in electrical terms, optional work is nFE where AG = -nFE.
4. be aware of the need for standard conditions.
5. have some knowledge of the interplay between AG and TAS in deciding the value of AH in a chemical reaction; and understand the meaning of $q_{rev}$.

### Unit 7.

You should

1. be aware of the distinction between entropy value and entropy energy.
2. have a clearer idea of system, surroundings and universe.
3. appreciate that the statement 'increase in entropy' is vague unless 'of what' is known.

Unit 7 (contd.)

4. appreciate that a spontaneous reaction, for kinetic reasons, may take a very long time to occur.
5. understand that mixing is accompanied by a decrease in free energy and an increase in entropy value.
6. understand that an entropy value
   a) is a measure of disorder.
   b) is zero at absolute zero.
   c) always increases with increase in temperature.
   d) always increases during melting.
   e) always increases during boiling, and evaporation.
   f) always increases when larger molecules change into smaller molecules.
   g) always increases as a result of mixing.
   h) is lowest for hard solids, higher for soft solids, higher still for liquids, and highest of all for gases.
   i) for 2 mole amounts is double the entropy value for 1 mole amount, other things being equal.
   j) in total always increases in a spontaneous change.

Unit 8.

You should

1. know that the controlling factor in a reaction is that the free energy change be negative.
2. know why diffusion occurs.
3. be able to explain why a minority of spontaneous reactions are endothermic
4. understand the occurrence of a variety of phenomena.

Unit 9.

You should

1. know that most of the enthalpy changes, free energy changes, entropy changes and entropy energy changes you have worked with are standard ones.
2. understand what is implied by the standard change.
3. realise the importance of the free energy of mixing in determining the composition of the equilibrium mixture.

Unit 9 (contd.)

4. understand the significance of $AG = 0$.
5. be aware of some of the characteristics of the equilibrium system.

Unit 10.

You should

1. know the relationship $AG^{o} = -2.3RT \log K_{eq}$.
2. know how the sign of $AG^{o}$ influences the composition of the equilibrium mixture.
3. have some idea of the equilibrium constant.

Unit 11.

You should

1. be able to interpret selected practical work in terms of free energy change.

### 7.3(4) Design of the Research: Applying the Thermodynamics Approach Programme

It was considered that a matched pairs design would be the best procedure to use in view of the smaller number of pupils who study for the Certificate of Sixth Year Studies. Such a design requires that individual pupils in the control group are matched with individual pupils in the experimental group on the basis of some prior criterion performance related to the problem in hand. This helps to ensure that the two groups, the control group and the experimental group, have effectively the same dependent variable scores before administration of the experimental treatment, the Thermodynamics Approach Programme, so that differences produced by the treatment can be the more reliably assessed and attributed to the treatment. The basic pattern of the matched pairs design is illustrated in Figure 7.2.

With this in mind, twenty five schools with the highest number of presentations in Sixth Year Studies in the previous year were approached and asked if they would participate in the research. Nineteen schools agreed to help provisionally. Each of these schools at the beginning of Session 1975-1976 was sent ten copies of the Thermodynamics Approach Programme. Each school was briefed on the selection of matched pairs. It was suggested that matching should be done largely on the basis of performance in Higher grade chemistry of the previous session though it was also suggested that it might be advisable to consider other factors, such as class tests or personality, in deciding a final pairing. It was suggested that boys and girls should be equally divided between groups. Otherwise, matching was done by the teacher in charge.

### 7.3(5) Limitations and difficulties in Design

One School (Code 37) already used the falling (but not spinning) weight analogy in the usual approach, but otherwise stated that the emphases were quite different from those of the Programme. It was considered that this was a minor infringement of the conditions adopted for control and experimental groups and so the returns from this school were not excluded.

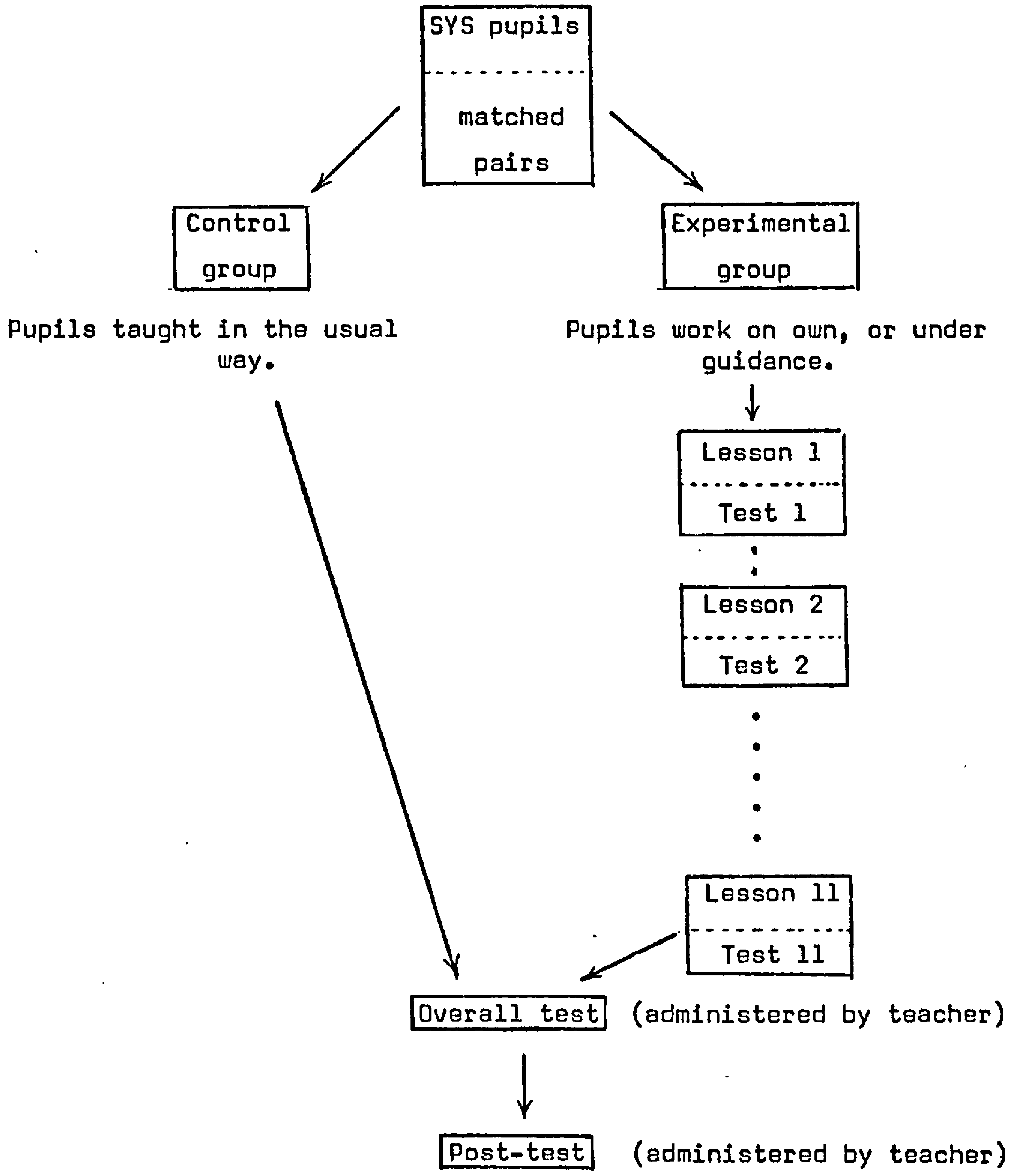


Figure 7.2 Matched Pairs Design

One school (Code 23) agreed to help in so far as the Programme was used to augment normal class teaching for one group, the experimental group, while the other group, the control group, received only class teaching. It was considered that the results from this school should not be excluded since in effect experimental pupils were being exposed to the concrete-empirical approach while the control were not.

### 7.3(6) Statement of Null Hypothesis

The null hypothesis ($H_0$) is:

The use of a concrete-empirical method of teaching the thermodynamic approach to chemical equilibrium in place of the conventional method does not produce a significant difference in concept formation with respect to this topic.

## 7.4 Assessment of the Thermodynamics Approach Programme

### 7.4(1) Assessment of Pupil Work-books

Schools were asked to supply work-books used by pupils in doing the self-tests at the end of each unit of the Programme.

### 7.4(2) Verbal and Written Assessment by Pupils and Teachers

Both pupils and teachers were asked to make any verbal or written comment on any aspect of the Programme.

### 7.4(3) Assessment by Objective Testing

It was proposed to assess the effectiveness of the Programme by applying an objective test to both control and experimental pupils at the end of the thermodynamics section, and to assess retention by the administration of the same test two months later. However, it was not possible to administer the latter post-test due to lack of time.

A test, the Thermodynamics Approach Test (Pocket Item 5), was made up.

## 7.5 Thermodynamics Approach Test

### 7.5(1) Construction of the Thermodynamics Approach Test

On the strength of the information gathered in the survey of chemical equilibrium of Part I, and bearing in mind the fairly limited coverage of thermodynamics required by Section 2 of the syllabus notes (A I.8), it was decided to make up a Thermodynamics Approach Test (Pocket Item 5) to assess understanding of some crucial concepts in this part of the course. An objective test consisting of twenty eight questions was made up. Each question consisted of a stem which stated the problem, followed by four response options, A, B, C or D, of which one only was correct. An additional response E was offered for pupils who did not know which response was correct. Pupils were asked to select E rather than guess. The concepts tested and the questions allocated to them are shown in Table 7.1.

Table 7.1 Thermodynamics Approach Test; Topics, Question Numbers and Abilities.

| Topic | Question Number & Ability |
|---|---|
| 1. Matter and Energy | 1(Co), 23(Co). |
| 2. Potential Energy and Kinetic Energy | 2(Ev), 17(Co). |
| 3. Spontaneity and Change in Free Energy. | 25(Ev), 8(Kn), 26(Co), 12(Ev), 18(Ev), 11(Ev), 22(Kn). |
| 4. Spontaneity and Speed | 21(Co), 6(Co). |
| 5. Work versus Heat | 3(Ev), 10(Ev), 24(Ev), 4(Ev). |
| 6. Reversibility and Irreversibility | 5(Ev), 9(Co), 7(Co). |
| 7. Entropy | 16(Co), 13(Ap), 27(Co). |
| 8. The Equilibrium State | |
| (i) Free Energy of Mixing | 14(Ap). |
| (ii) Free Energy Well | 20(Kn), 28(Ev). |
| (iii) Composition at $K_{eq} = 1$ | 15(Ap). |
| (iv) Common Sense | 19(Ap). |
| Implications in a Cell | |

Kn = knowledge: question requires straight recall

Co = Comprehension: question requires comprehension of recalled material.

Ap = Application: question requires application of material which has been recalled and understood.

Ev = Evaluation: question requires evaluation of a situation in which recalled and understood material is applied.

### 7.5(2) Scope of the Thermodynamics Approach Test

Of the nineteen schools which agreed to belp in the thermodynamics research, eleven made returns of pupil responses to the Thermodynamics Approach Test and ten of these provided one or more matched pairs together with varying numbers of unmatched pupils. These data are collected in Table 7.2. School codes used during the research are given in place of names in order to preserve anonymity.

Table 7.2 Returns; Thermodynamics Approach Test

| School Code | Total No. of Pupils | | Matched Pairs |
|---|---|---|---|
| | Control | Experimental | |
| 22 | 8 | 8 | 8 |
| 23 | 12 | 8 | 6 |
| 26 | 6 | 9 | 6 |
| 27 | 3 | 3 | 1 |
| 28 | 12 | 6 | 6 |
| 32 | 12 | 9 | 8 |
| 33 | 3 | 4 | 3 |
| 34 | 1 | 2 | - |
| 35 | 4 | 5 | 4 |
| 37 | 4 | 4 | 4 |
| 39 | 4 | 3 | 3 |
| | 69 | 61 | 49 |

Teachers had difficulty in matching some pupils, usually because their performances in the Higher grade examination in chemistry were different. However, forty nine pairs of teacher-matched pupils were obtained for statistical treatment.

Data on performance of each member of the matched pairs in the Higher grade chemistry and physics examinations of the previous session is collected in Table 7.3. Pupils were asked to supply information on the Band they obtained in chemistry and physics. At the time of asking, it was thought that physics might have some significant effect on performance in the objective test, but it was shown in Part II (page 74) that this was not so in relation to the Rates Approach Test, and it is assumed that this is also the case with respect to the Thermodynamics Approach Test. Consequently, no treatment of the prior performance in physics is offered.

Unmatched pupils (twenty in the control groups and twelve in the experimental groups) are not included in the remainder of the report.

Table 7.3 **Prior Performance of Matched Pair Pupils in Higher Grade Chemistry and Physics**

| School Code | Band in Higher Chem. | | Band in Higher Phys. | |
|---|---|---|---|---|
| | Control | Experimental | Control | Experimental |
| 22 | A | A | A | A |
| | A | A | A | A |
| | A | A | A | B |
| | A | A | B | A |
| | A | A | B | A |
| | B | A | B | C |
| | B | B | B | C |
| | B | B | C | B |
| 23 | A | A | A | B |
| | A | A | A | B |
| | A | A | B | A |
| | A | A | B | A |
| | B | B | A | B |
| | C | C | C | B |
| 26 | A | A | A | A |
| | A | A | A | A |
| | A | A | A | A |
| | A | A | A | A |
| | A | A | A | A |
| | B | B | A | A |
| 27 | B | B | B | B |
| 28 | A | A | A | A |
| | A | A | A | A |
| | A | A | A | A |
| | B | B | A | A |
| | B | B | B | A |
| | C | C | C | C |

Table 7.3 (Prior Performance of Matched Pair Pupils in Higher Grade Chemistry and Physics) contd.

| School Code | Band in Higher Chem. | | Band in Higher Phys. | |
|---|---|---|---|---|
| | Control | Experimental | Control | Experimental |
| 32 | A | A | A | A |
| | A | A | A | A |
| | B | B | B | C |
| | B | B | B | - |
| | B | A | C | B |
| | B | B | C | B |
| | C | B | - | C |
| | C | C | C | C |
| 33 | A | A | A | C |
| | A | A | B | A |
| | A | A | C | B |
| 35 | A | A | A | A |
| | B | B | B | B |
| | B | B | C | B |
| | C | C | C | B |
| 37 | A | A | A | A |
| | A | A | A | A |
| | A | A | A | A |
| | A | A | A | A |
| 39 | A | A | A | A |
| | A | B | B | D |
| | B | A | B | B |

Prior performance in chemistry in the certificate examinations of the previous session was the main matching variable used by teachers. Of the forty nine matched pairs, forty four have corresponding Bands in Higher chemistry.

The data on prior performance in chemistry of Table 7.3 are condensed in Table 7.4

Table 7.4 Summary of Prior Performance of Pupils in Higher Grade Chemistry; Matched Pairs.

| | Number of Pupils | |
|---|---|---|
| Band | Control | Experimental |
| A | 29 | 31 |
| B or C | 20 | 18 |

### 7.5 (3) Limitations of Thermodynamics Approach Test

The Thermodynamics Approach Programme and the Thermodynamics Approach Test were written by the author. Questions and problem situations arising in the latter may, therefore, bear some resemblance to those used in the self-tests at the end of each unit of the former. The author was aware of this danger and attempted to make the Thermodynamics Approach Test as impartial as possible but was not entirely successful in this respect. Some assessment of the possible effects of this bias on the results of the Thermodynamics Approach Test is offered in 9.2.

It was not possible, for lack of time, to validate the Thermodynamics Approach Test in the manner of the Rates Approach Test (by free response and interview techniques). Consequently, statistical validation only is offered.

### 7.5(4) Statistical Treatment of Thermodynamics Approach Test

(i) Reliability The Kuder-Richardson procedure (A III.2 (A)) will be used to assess the reliability of the Thermodynamics Approach Test in relation to (a) control pupils and (b) experimental pupils.

(ii) Validity, The validity of the Thermodynamics Approach Test with respect to (a) control pupils and (b) experimental pupils will be assessed statistically by computing the biserial correlation coefficient (A III.2 (B)) between the scores achieved by pupils in the Test and the prior performance of these pupils in Higher grade chemistry (Table 7.3).

(iii) Acceptance or Rejection of the Null Hypothesis. Matched scores for control and experimental pupils will be subjected to a 't' test. For forty nine matched pairs the 't' statistic is significant at the 1% level for a two-tailed test if it exceeds the value 2.68. Hence, if 't' is less than or equal to 2.68 the null hypothesis of no difference will be accepted; if 't' is greater than 2.68 the null hypothesis will be rejected.

At 1% level of significance is selected to diminish the chance of rejection of the null hypothesis in view of the comments in 7.5(3).

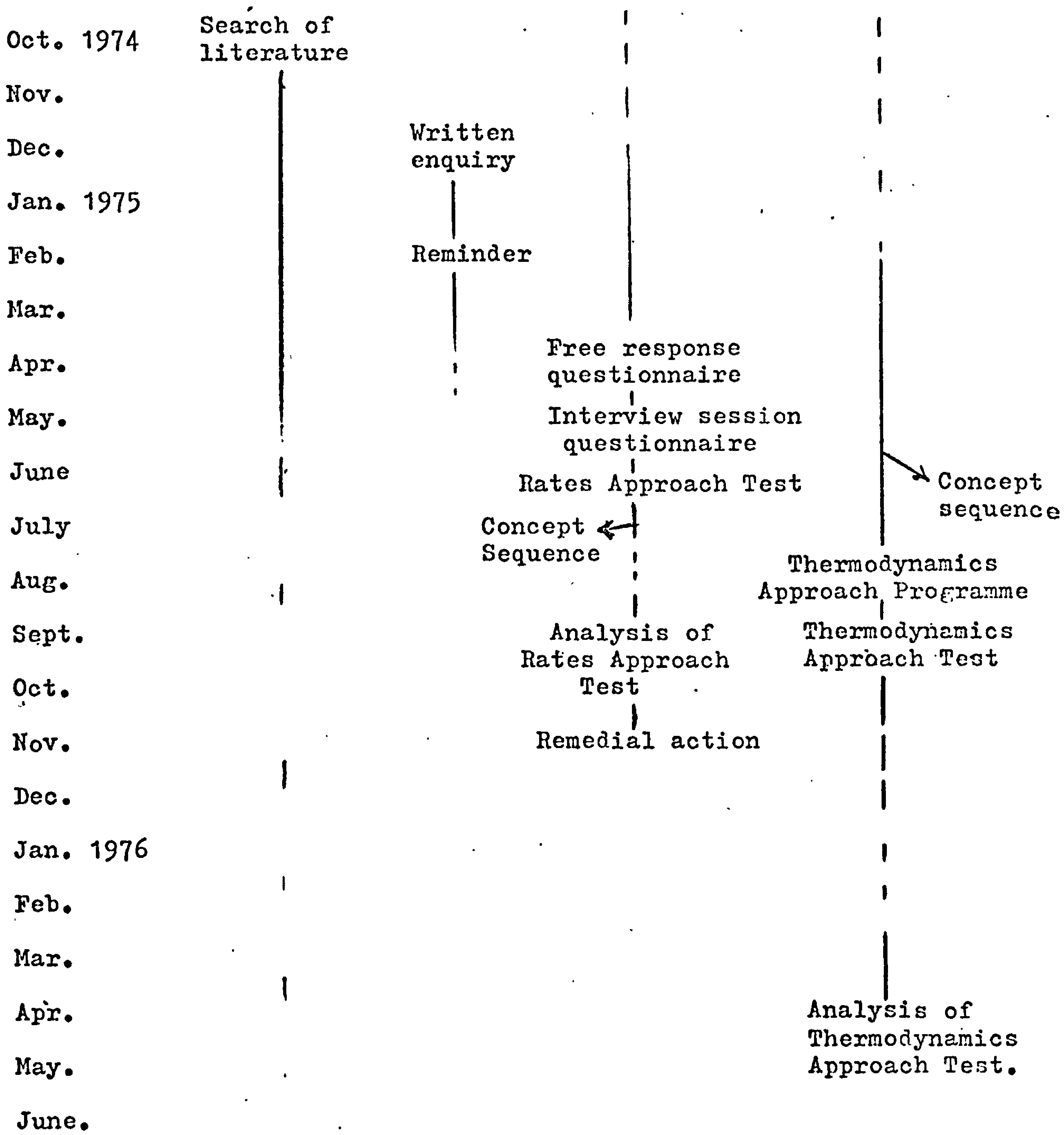
A two-tailed test will be used because it is not known in advance whether the Programme will produce better or poorer performance.

(iv) Normality of Scores Since the Kuder-Richardson procedure, the computation of biserial correlation coefficients and the computation of the 't' statistic require underlying normality of scores, the observed scores will be reduced to expected scores and a $\chi^2$ test of significance between observed and expected scores if normal made in the case of (a) control pupils and (b) experimental pupils.

(v) Source of Significance In the event that the null hypothesis is rejected, the source of the significance will be investigated (Wilcoxon Matched-Pairs Signed Ranks Test, 8.2(2)).

## A VII.1

Chronological Development of the Study



# CHAPTER 8

# RESULTS

## 8.1 Results of Thermodynamics Approach Test

### 8.1(1) Facility Values and Discriminatory Factors

The facility values and discriminatory factors obtained with the sample of forty nine matched pairs are given in Table 8.1.

Table 8.1 Thermodynamics Approach Test: Facility Values and Discriminatory Factors.

| Topic | Ques. No. & Ability | Key | F.V. Control Group | F.V. Exper. Group | $T_1 - T_3$ Control Group | $T_1 - T_3$ Exper. Group |
|---|---|---|---|---|---|---|
| 1. Matter and Energy | 1(Co) | B | 0.86 | 0.96 | 0.29 | 0.06 |
| | 23(co) | C | 0.73 | 0.84 | 0.35 | 0.11 |
| 2. Potential Energy versus Kinetic | 2(Ev) | B | 0.29 | 0.65 | 0.07 | 0.47 |
| Energy | 17(Co) | B | 0.18 | 0.55 | 0.19 | 0.28 |
| 3. Spontaneity and | 25(Ev) | C | 0.92 | 0.96 | 0.18 | 0.06 |
| Free Energy Change | 8(Kn) | A | 0.90 | 0.84 | 0.29 | 0.35 |
| | 26(Co) | B | 0.86 | 0.71 | 0.35 | 0.40 |
| | 12(Ev) | B | 0.78 | 0.65 | 0.35 | 0.34 |
| | 18(Ev) | A | 0.80 | 0.67 | 0.29 | 0.40 |
| | 11(Ev) | D | 0.18 | 0.29 | -0.05 | 0.57 |
| | 22(Kn) | D | 0.59 | 0.63 | 0.35 | 0.35 |
| 4. Spontaneity and | 21(Co) | D | 0.71 | 0.49 | 0.58 | 0.58 |
| Speed | 6(Co) | D | 0.33 | 0.61 | 0.38 | 0.46 |

Table 8.1 continue

| Topic | Ques. No. & Ability | Key | F.V. Control Group | F.V. Exper. Group | $T_1 - T_3$ Control Group | $T_1 - T_3$ Exper. Group |
|---|---|---|---|---|---|---|
| 5. Work versus Heat | 3(Ev) | C | 0.12 | 0.31 | 0.07 | 0.57 |
| | 10(Ev) | C | 0.22 | 0.35 | 0.32 | 0.69 |
| | 24(Ev) | C | 0.41 | 0.55 | 0.09 | 0.28 |
| | 4(Ev) | A | 0.45 | 0.80 | 0.82 | 0.41 |
| 6. Reversibility & Irreversibility | 5(Ev) | C | 0.29 | 0.49 | 0.08 | 0.33 |
| | 9(Co) | C | 0.22 | 0.45 | 0.08 | 0.94 |
| | 7(Co) | B | 0.27 | 0.61 | 0.38 | 0.58 |
| 7. Entropy | 16(Co) | C | 0.92 | 0.86 | 0.24 | 0.35 |
| | 13(Ap) | C | 0.45 | 0.47 | 0.88 | 0.27 |
| | 27(Co) | A | 0.67 | 0.78 | 0.16 | 0.17 |
| 8. Equilibrium State | | | | | | |
| (i) Free Energy of Mixing | 14(Ap) | D | 0.02 | 0.06 | -0.06 | 0.19 |
| (ii) Free Energy Well | 20(Kn) | D | 0.51 | 0.47 | 0.39 | 0.82 |
| | 28(Ev) | A | 0.43 | 0.41 | 0.51 | 0.51 |
| (iii) Composition when $K_{eq} = 1$ | 15(Ap) | D | 0.16 | 0.29 | 0.19 | 0.14 |
| (iv) Common Sense Implications in a Cell | 19(Ap) | D | 0.49 | 0.65 | 0.45 | 0.47 |

For each item, $T_1 - T_3$ is the difference between the facility value of the top third of pupils, based on the performance of all pupils in the whole test, and the facility value of the bottom third of pupils.

Facility values for $T_1$, $T_2$ and $T_3$ are given in Appendix VIII.1. Discriminatory factors $T_1$-$T_2$, $T_2$-$T_3$ and $T_1$-$T_3$ are given in Appendix VIII.2.

## 8.1(2) Frequency (%) of Responses in Thermodynamics Approach Test

The frequency percentage with which pupils selected responses to the Thermodynamics Approach Test are recorded in Table 8.2.

Table 8.2 Frequency (%) of Responses

| | Frequency (%) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Question | Control | | | | | | Experimental | | | | | |
| | A | B | C | D | E | NA | A | B | C | D | E | NA |
| 1 | 2 | 86* | 0 | 4 | 8 | - | 0 | 96* | 0 | 0 | 4 | - |
| 2 | 51 | 29* | 18 | 0 | 2 | - | 23 | 65* | 8 | 4 | 0 | - |
| 3 | 70 | 6 | 12* | 6 | 6 | - | 49 | 4 | 31* | 6 | 10 | - |
| 4 | 45* | 18 | 31 | 0 | 6 | - | 80* | 12 | 6 | 0 | 2 | - |
| 5 | 35 | 24 | 29* | 6 | 6 | - | 23 | 14 | 49* | 0 | 12 | 2 |
| 6 | 18 | 25 | 18 | 33* | 6 | - | 17 | 10 | 0 | 61* | 12 | - |
| 7 | 12 | 27* | 8 | 14 | 37 | 2 | 4 | 61* | 6 | 17 | 12 | - |
| 8 | 90* | 0 | 2 | 4 | 4 | - | 84* | 4 | 6 | 2 | 4 | - |
| 9 | 33 | 6 | 22* | 8 | 31 | - | 31 | 6 | 45 | 4 | 14 | - |
| 10 | 56 | 2 | 22* | 14 | 6 | - | 39 | 0 | 35* | 18 | 8 | - |
| 11 | 48 | 8 | 22 | 18* | 4 | - | 39 | 10 | 16 | 29* | 6 | - |
| 12 | 8 | 78* | 2 | 10 | 2 | - | 8 | 65* | 0 | 17 | 10 | - |
| 13 | 33 | 8 | 45* | 10 | 4 | - | 25 | 0 | 47* | 12 | 14 | 2 |
| 14 | 16 | 4 | 68 | 2* | 10 | - | 19 | 8 | 51 | 6* | 16 | - |
| 15 | 78 | 4 | 0 | 16* | 2 | - | 55 | 4 | 4 | 29* | 8 | - |
| 16 | 4 | 2 | 92* | 0 | 2 | - | 4 | 0 | 86* | 2 | 8 | - |
| 17 | 38 | 18* | 20 | 8 | 16 | - | 19 | 55* | 6 | 6 | 14 | - |
| 18 | 80* | 14 | 4 | 0 | 2 | - | 67* | 11 | 6 | 8 | 8 | - |
| 19 | 18 | 21 | 6 | 49* | 6 | - | 10 | 8 | 13 | 65* | 4 | - |
| 20 | 4 | 6 | 18 | 51* | 21 | - | 6 | 6 | 14 | 47* | 25 | 2 |
| 21 | 19 | 4 | 4 | 71* | 2 | - | 27 | 6 | 8 | 49* | 10 | - |
| 22 | 10 | 6 | 4 | 59* | 21 | - | 17 | 4 | 4 | 63* | 12 | - |
| 23 | 4 | 4 | 73* | 13 | 6 | - | 2 | 2 | 84* | 8 | 2 | 2 |
| 24 | 33 | 22 | 41* | 0 | 4 | - | 21 | 18 | 55* | 0 | 6 | - |
| 25 | 2 | 0 | 92* | 4 | 2 | - | 0 | 0 | 96* | 2 | 2 | - |
| 26 | 2 | 86* | 0 | 10 | 2 | - | 4 | 71* | 8 | 9 | 6 | 2 |
| 27 | 67* | 17 | 0 | 14 | 2 | - | 78* | 2 | 0 | 18 | 2 | - |
| 28 | 43* | 10 | 2 | 20 | 25 | - | 41* | 14 | 2 | 23 | 20 | - |

Correct responses are marked * . NA - no answer

### 8.(3) Means and Standard Deviations

Table 8.3 Means and Standard Deviations of Pupil Scores on Thermodynamics Approach Test

| | Control | Experimental |
|---|---|---|
| N | 49 | 49 |
| $\bar{X}$ | 13.76 | 16.39 |
| S.D. | 3.89 | 5.04 |

### 8.1(4) Observed and Expected Frequencies of Scores of Control and Experimental Pupils

Since it is proposed to establish the reliability and validity of the Thermodynamics Approach Test by techniques which assume underlying normality of distribution of scores, and to apply a t-test of differences between control and experimental groups which makes the same assumption, the expected frequencies of scores have been computed for control pupils (A VIII.3) and for experimental pupils (A VIII.4) and a $\chi^2$ test of significance between observed and expected scores in each group carried out. Observed and expected frequencies are shown in Table 8.4, and data on the $\chi^2$ tests are given below. Significance levels are set at 5%.

(i) Control Pupils. The computation of $\chi^2$ (A VIII.3) between observed and expected frequencies of scores gives the value 14.57 for 7 df, and so the observed frequencies differ significantly from normality since $\chi^2_{.95} = 14.1$. However, since the failure to achieve normality is only marginal, and the sample size somewhat on the small side, it is proposed, despite this adverse result, to proceed with the parametric procedures outlined in 7.5(4).

Observed and expected frequencies of scores for the control group are shown graphically in Figure 8.1.

(ii) Experimental Pupils. The computation of $X^2$ (A VIII.4) between observed and expected frequencies of scores gives the value 10.61 for 5 df, and so the observed frequencies do not differ significantly from normality since $X^2_{.95} = 11.1$.

Observed and expected frequencies of scores for the experimental group are shown graphically in Figure 8.1.

### 8.1(5) Reliability

Kuder-Richardson coefficients of reliability were computed for control pupils (A VIII.5) and experimental pupils (A VIII.6).

$r_{KR}$ (control) = 0.70

$r_{KR}$ (experimental) = 0.81

### 8.1(6) Validity

Within each group (control and experimental), biserial correlation coefficients were separately computed between pupils' scores on the Thermodynamics Approach Test and their prior performance in Higher Grade chemistry in terms of Band A or Bands B/C. The detailed computations of the biserial coefficients for control pupils and for experimental pupils are given in Appendices VIII.7 and VIII.8 respectively, and the results of such computations are shown in summary in Table 8.5.

Table 8.5 Biserial Correlation Coefficients

| | Control | | Experimental | |
|---|---|---|---|---|
| Band in Higher Grade Chemistry | A | B/C | A | B/C |
| N | 29 | 20 | 31 | 18 |
| $\overline{X}$ | 15.31 | 11.50 | 18.74 | 12.33 |
| $r_{biserial}$ | 0.62 | | 0.78 | |

Table 8.4 Observed and Expected Frequencies of Pupil Scores on Thermodynamics Approach Test

| | Frequency in Control Group | | Frequency in Experimental Group | |
|---|---|---|---|---|
| Score | Observed | Expected | Observed | Expected |
| 0 | - | - | - | - |
| 1 | - | - | - | - |
| 2 | 1 | - | - | 0.1 |
| 3 | - | 0.1 | - | 0.1 |
| 4 | - | 0.2 | - | 0.2 |
| 5 | - | 0.4 | - | 0.3 |
| 6 | - | 0.7 | - | 0.5 |
| 7 | - | 1.1 | - | 0.7 |
| 8 | - | 1.7 | 1 | 1.0 |
| 9 | 3 | 2.3 | 2 | 1.3 |
| 10 | 7 | 3.2 | 4 | 1.7 |
| 11 | 6 | 3.9 | 2 | 2.2 |
| 12 | 3 | 4.5 | 2 | 2.7 |
| 13 | 4 | 4.9 | 4 | 3.1 |
| 14 | 2 | 5.0 | 7 | 3.5 |
| 15 | 6 | 4.8 | 2 | 3.7 |
| 16 | 8 | 4.1 | 4 | 3.9 |
| 17 | 2 | 3.6 | 2 | 3.9 |
| 18 | 2 | 2.8 | 3 | 3.7 |
| 19 | 2 | 2.1 | 4 | 3.4 |
| 20 | - | 1.4 | 2 | 3.0 |
| 21 | 1 | 0.9 | 1 | 2.6 |
| 22 | - | 0.6 | - | 2.1 |
| 23 | 2 | 0.3 | 3 | 1.7 |
| 24 | - | 0.2 | 1 | 1.2 |
| 25 | - | 0.1 | 2 | 0.9 |
| 26 | - | - | 2 | 0.6 |
| 27 | - | - | 1 | 0.4 |
| 28 | - | - | - | 0.3 |
| | 49 | 48.9 | 49 | 48.8 |

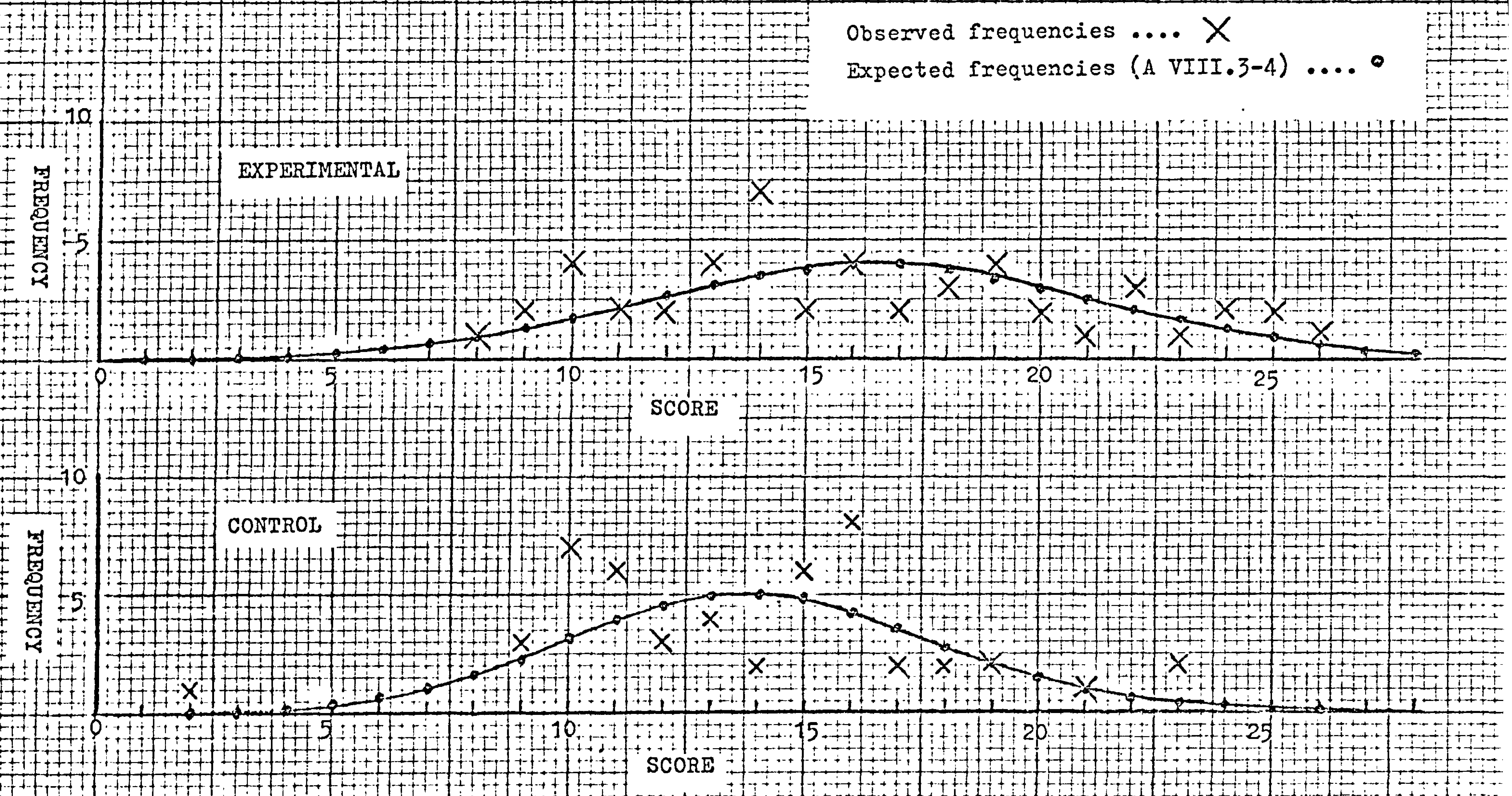


Figure 8.1 Observed and Expected Scores in Thermodynamics Approach Test

## 8.2 Statistical Analysis

### 8.2(1) Matched Pairs Design

A t-test was applied to the matched pairs scores shown in Table 8.6.

Table 8.6 Matched pairs scores

| School | Control scores | Experimental scores | D |
|---|---|---|---|
| 22 | 19 | 12 | -7 |
| | 14 | 18 | 4 |
| | 15 | 18 | 3 |
| | 13 | 15 | 2 |
| | 11 | 16 | 5 |
| | 11 | 16 | 5 |
| | 10 | 8 | 8 |
| | 15 | 9 | -6 |
| 23 | 16 | 14 | -2 |
| | 15 | 13 | -2 |
| | 14 | 18 | 4 |
| | 10 | 19 | 9 |
| | 13 | 12 | -1 |
| | 10 | 14 | 4 |
| 26 | 18 | 27 | 9 |
| | 18 | 20 | 2 |
| | 15 | 23 | 8 |
| | 16 | 19 | 3 |
| | 15 | 13 | -2 |
| | 9 | 16 | 7 |
| 27 | 13 | 14 | 1 |

28/

For a matched pairs design

$$t = \frac{\left|\bar{X}_c - \bar{X}_e\right|}{\sqrt{\dfrac{\Sigma D^2 - (\Sigma D)^2/n}{n(n-1)}}}$$

$\bar{X}_c = 13.76$

$\bar{X}_e = 16.39$

$n = 49$

$\Sigma D = 139$

$(\Sigma D)^2 = 19321$

$\Sigma D^2 = 1643$

$df = 48$

$t = 3.61$, hence $P < .001$ for a two-tailed test.

The probability that the observed differences in the scores of the Control Group and the Experimental Group are due to chance is so small that the better performance of the Experimental Group may reasonably be ascribed to the Thermodynamics Approach Programme.

Consequently,/

Table 8.6 Matched pairs scores - (contd.)

| School | Control scores | Experimental scores | D |
|---|---|---|---|
| 28 | 12 | 13 | 1 |
| | 10 | 25 | 15 |
| | 12 | 13 | 1 |
| | 21 | 10 | -11 |
| | 13 | 11 | -2 |
| | 9 | 10 | 1 |
| 32 | 12 | 23 | 11 |
| | 16 | 20 | 4 |
| | 2 | 9 | 7 |
| | 10 | 19 | 9 |
| | 16 | 14 | -2 |
| | 11 | 14 | 3 |
| | 10 | 11 | 1 |
| | 9 | 10 | 1 |
| 33 | 16 | 23 | 7 |
| | 11 | 26 | 15 |
| | 17 | 17 | 0 |
| 35 | 16 | 25 | 9 |
| | 16 | 16 | 0 |
| | 10 | 14 | 4 |
| | 11 | 10 | -1 |
| 37 | 16 | 14 | -2 |
| | 19 | 21 | 2 |
| | 23 | 26 | 3 |
| | 23 | 24 | 1 |
| 39 | 15 | 19 | 4 |
| | 17 | 15 | -2 |
| | 11 | 17 | 6 |

Consequently, the null hypothesis of no difference is rejected.

## 8.2(2) Source of Significance

Overall scores in the Thermodynamics Approach Test by the experimental group were found to the significantly better at the 0.1% level than the overall scores of the control group.

The data of Table 8.7 show that improved performance in the Test was largely confined to pupils who had gained Band A in the Higher Grade examination in chemistry of the previous session. Pupils who had gained Bands B or C showed only marginal improvement.

Table 8.7 Means and Standard Deviations of A and B/C Subgroups

| Band in Higher Grade Chemistry | Control | | Experimental | |
|---|---|---|---|---|
| | A | B/C | A | B/C |
| N | 29 | 20 | 31 | 18 |
| $\overline{X}$ | 15.31 | 11.50 | 18.74 | 12.33 |
| S.D. | 3.24 | 2.33 | 4.49 | 2.96 |

It was considered that the marginal improvement demonstrated by B/C experimental pupils over B/C control pupils might indeed not be significant, and that some statistical assessment of the difference in performance was desirable.

Under the circumstances, a non-parametric test was chosen which neither required symmetry nor normality of the distribution of B/C control and B/C experimental scores, namely, the Wilcoxon Matched-Pairs Signed-Ranks Test. The application of this test is illustrated in Table 8.8 and information on its application is given in Appendix VIII.10.

The test was applied to seventeen matched B/C pairs only. The selection of these seventeen pairs (A VIII.9) resulted in equal numbers where these were not initially available, there had been twenty B/C control compared with eighteen B/C experimental, and resulted in the elimination of one pair where the teacher concerned had matched an A control with a B experimental (School 39, A VIII.10).

An arbitrary 5% level of significance was adopted together with a null hypothesis of no difference in performance of B/C control and B/C experimental pupils.

Table 8.8. Wilcoxon Matched-Pairs Signed Ranks Test of B/C Scores

| | Scores | | | (1) | (2) | (3) | |
|---|---|---|---|---|---|---|---|
| Pair | Control B/C Pupils | Experimental B/C Pupils | d | Rank of d | Signed Rank | Negative and Positive Sums | |
| a | 10 | 8 | -2 | 7.5 | -7.5 | -7.5 | |
| b | 15 | 9 | -6 | 12 | -12 | -12 | |
| c | 13 | 12 | -1 | 3.5 | -3.5 | -3.5 | |
| d | 10 | 14 | 4 | 10.5 | 10.5 | | 10.5 |
| e | 9 | 16 | 7 | 13.5 | 13.5 | | 13.5 |
| f | 13 | 14 | 1 | 3.5 | 3.5 | | 3.5 |
| g | 21 | 10 | -11 | 16 | -16 | -16 | |
| h | 13 | 11 | -2 | 7.5 | -7.5 | -7.5 | |
| i | 9 | 10 | 1 | 3.5 | 3.5 | | 3.5 |
| j | 2 | 9 | 7 | 13.5 | 13.5 | | 13.5 |
| k | 10 | 19 | 9 | 15 | 15 | | 15 |
| l | 11 | 14 | 3 | 9 | 9 | | 9 |
| m | 10 | 11 | 1 | 3.5 | 3.5 | | 3.5 |
| n | 9 | 10 | 1 | 3.5 | 3.5 | | 3.5 |
| o | 16 | 16 | 0 | exclude | | | |
| p | 10 | 14 | 4 | 10.5 | 10.5 | | 10.5 |
| q | 11 | 10 | -1 | 3.5 | -3.5 | -3.5 | |
| $\bar{X}$ | 11.29 | 12.18 | | | | -50 | 75.5 |

$T = 50$; $N = 16$ (= number of matched pairs - number of pairs whose d's equal zero).

From tables, $T = 20$ for $\alpha = .01$, and $T = 30$ for $\alpha = .05$, for a two-tailed test. Therefore, the null hypothesis, $H_o$, is accepted and there is no significant difference in the performance in the Thermodynamics Approach Test between control and experimental pupils who gained B or C passes in Higher Grade chemistry. The highly significant improvement in performance known to have occurred with the whole experimental group is to be credited to those pupils who obtained an A pass in Higher Grade chemistry.

## 8.3 Assessment of Pupil Self-Test Work-books

Schools were asked to forward work-books in which pupils had carried out the self-test at the end of each unit to the author for assessment. The work-books were then to be returned within a week or so. Two schools forwarded work-books, seven (school 22) and four (school 33) respectively.

In all cases the self-tests had been conscientiously carried out and there was little evidence of misconceptual knowledge except in one case where the pupil had failed to realise that in the expression

$$AG = AG^o + RT \ln \text{'Ratio'}$$

the 'Ratio' is equal to the equilibrium constant only when AG is zero. However, this idea is outwith the syllabus of the Certificate of Sixth Year Studies; it was introduced into the Thermodynamics Approach Programme only in an effort to make sense of the relationship $AG^o = -RT \ln K_{eq}$.

## 8.4 Subjective Assessment of the Thermodynamics Approach Programme by Teachers and Pupils

Subjective assessment was recorded in letters to the author: eight teachers commented on their own and their pupils' opinions of the Programme. These comments are summarised below.

In general, the Programme was considered to be too long, too wordy and too detailed; its sheer bulk presented a daunting prospect. Some felt that this part of the syllabus did not require such emphasis. In particular, Unit 7 (Entropy and Entropy Energy) was criticised.

One teacher felt the Programme was over-ambitious in its self-teach format, and that it might be more acceptable if conveyed by direct conventional teaching. This teacher felt that the less able pupils became lost halfway through the Programme.

There was some feeling that the attempt to simplify the abstract content of thermodynamics by the use of physical analogies had not worked since the analogies themselves were quite sophisticated and often 'went over the heads' of the pupils. Some pupils, however, considered the Programme to be of some value.

Several teachers complained that the questions in the Thermodynamics Approach Test were at times so similar to those in the self-tests at the end of each unit that the experimental pupils could not help but do better.

The tendency in the Programme to postpone the discussion of topics 'until later' irritated some.

One teacher was pleased with the coverage given to the underlying theory of the practical work in Units 8 and 11 (a verbal comment).

## A VIII.1

## Facility Values

| Question | Control | | | Experimental | | |
|---|---|---|---|---|---|---|
| | $T_1$ | $T_2$ | $T_3$ | $T_1$ | $T_2$ | $T_3$ |
| 1 | 1.00 | 0.88 | 0.71 | 1.00 | 0.94 | 0.94 |
| 2 | 0.25 | 0.44 | 0.18 | 0.94 | 0.56 | 0.47 |
| 3 | 0.19 | 0.06 | 0.12 | 0.63 | 0.25 | 0.06 |
| 4 | 0.88 | 0.44 | 0.06 | 1.00 | 0.81 | 0.59 |
| 5 | 0.38 | 0.19 | 0.29 | 0.69 | 0.44 | 0.35 |
| 6 | 0.50 | 0.38 | 0.12 | 0.88 | 0.56 | 0.41 |
| 7 | 0.44 | 0.31 | 0.06 | 0.94 | 0.56 | 0.35 |
| 8 | 1.00 | 1.00 | 0.71 | 1.00 | 0.88 | 0.65 |
| 9 | 0.38 | 0.00 | 0.29 | 0.94 | 0.44 | 0.00 |
| 10 | 0.44 | 0.13 | 0.12 | 0.75 | 0.25 | 0.06 |
| 11 | 0.19 | 0.13 | 0.24 | 0.63 | 0.19 | 0.06 |
| 12 | 0.94 | 0.81 | 0.59 | 0.81 | 0.69 | 0.47 |
| 13 | 0.88 | 0.50 | 0.00 | 0.63 | 0.44 | 0.35 |
| 14 | 0.00 | 0.00 | 0.06 | 0.19 | 0.00 | 0.00 |
| 15 | 0.25 | 0.19 | 0.06 | 0.31 | 0.38 | 0.18 |
| 16 | 1.00 | 1.00 | 0.76 | 1.00 | 0.94 | 0.65 |
| 17 | 0.31 | 0.13 | 0.12 | 0.69 | 0.56 | 0.41 |
| 18 | 0,94 | 0.81 | 0.65 | 0.88 | 0.69 | 0.47 |
| 19 | 0.69 | 0.56 | 0.24 | 0.94 | 0.56 | 0.47 |
| 20 | 0.69 | 0.56 | 0.29 | 0.88 | 0.50 | 0.06 |
| 21 | 0.94 | 0.88 | 0.35 | 0.81 | 0.44 | 0.24 |
| 22 | 0.88 | 0.38 | 0.53 | 0.88 | 0.50 | 0.53 |
| 23 | 0.88 | 0.81 | 0.53 | 0.88 | 0.88 | 0.76 |
| 24 | 0.50 | 0.31 | 0.41 | 0.69 | 0.56 | 0.41 |
| 25 | 1.00 | 0.94 | 0.82 | 1.00 | 0.94 | 0.94 |
| 26 | 1.00 | 0.94 | 0.65 | 0.88 | 0.81 | 0.47 |
| 27 | 0.69 | 0.81 | 0.53 | 0.88 | 0.75 | 0.71 |
| 28 | 0.75 | 0.31 | 0.24 | 0.75 | 0.25 | 0.24 |

## A VIII. 2

| Question | Control | | | Experimental | | |
|---|---|---|---|---|---|---|
| | $T_1$-$T_2$ | $T_2$-$T_3$ | $T_1$-$T_3$ | $T_1$-$T_2$ | $T_2$-$T_3$ | $T_1$-$T_3$ |
| 1 | 0.13 | 0.17 | 0.29 | 0.06 | -0.00 | 0.06 |
| 2 | -0.19 | 0.26 | 0.07 | 0.38 | 0.09 | 0.47 |
| 3 | 0.13 | -0.06 | 0.07 | 0.38 | 0.19 | 0.57 |
| 4 | 0.44 | 0.38 | 0.82 | 0.19 | 0.22 | 0.41 |
| 5 | 0.19 | -0.11 | 0.08 | 0.25 | 0.08 | 0.33 |
| 6 | 0.13 | 0.26 | 0.38 | 0.31 | 0.15 | 0.46 |
| 7 | 0.13 | 0.25 | 0.38 | 0.38 | 0.21 | 0.58 |
| 8 | 0.00 | 0.29 | 0.29 | 0.13 | 0.23 | 0.35 |
| 9 | 0.38 | -0.29 | 0.08 | 0.50 | 0.44 | 0.94 |
| 10 | 0.31 | 0.01 | 0.32 | 0.50 | 0.19 | 0.69 |
| 11 | 0.06 | -0.11 | -0.05 | 0.44 | 0.13 | 0.57 |
| 12 | 0.13 | 0.22 | 0.35 | 0.13 | 0.22 | 0.34 |
| 13 | 0.38 | 0.50 | 0.88 | 0.19 | 0.08 | 0.27 |
| 14 | 0.00 | -0.06 | -0.06 | 0.19 | 0.00 | 0.19 |
| 15 | 0.06 | 0.13 | 0.19 | -0.06 | 0.20 | 0.14 |
| 16 | 0.00 | 0.24 | 0.24 | 0.06 | 0.29 | 0.35 |
| 17 | 0.19 | 0.01 | 0.19 | 0.13 | 0.15 | 0.28 |
| 18 | 0.13 | 0.17 | 0.29 | 0.19 | 0.22 | 0.40 |
| 19 | 0.13 | 0.33 | 0.45 | 0.38 | 0.09 | 0.47 |
| 20 | 0.13 | 0.27 | 0.39 | 0.38 | 0.44 | 0.82 |
| 21 | 0.06 | 0.52 | 0.58 | 0.38 | 0.20 | 0.58 |
| 22 | 0.50 | -0.15 | 0.35 | 0.38 | -0.03 | 0.35 |
| 23 | 0.06 | 0.28 | 0.35 | 0.00 | 0.11 | 0.11 |
| 24 | 0.19 | -0.10 | 0.09 | 0.13 | 0.15 | 0.28 |
| 25 | 0.06 | 0.11 | 0.18 | 0.06 | -0.00 | 0.06 |
| 26 | 0.06 | 0.29 | 0.35 | 0.06 | 0.34 | 0.40 |
| 27 | -0.13 | 0.28 | 0.16 | 0.13 | 0.04 | 0.17 |
| 28 | 0.44 | 0.08 | 0.51 | 0.50 | 0.01 | 0.51 |

Computation of Expected Frequencies in Control Group

Computation of $\chi^2$.

| Score | Observed frequency (O) | | Class boundary (X) | $\frac{(X - \bar{X})}{SD}$ (Z) | Area to Z | Area within class boundary | Expected frequency (E) | | $\frac{(O - E)^2}{E}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | -0.5 | -3.6686 | | | | | |
| 0 | - | | 0.5 | -3.4114 | | | | | |
| 1 | - | | 1.5 | -3.1541 | 0.4990 | | | | |
| 2 | 1 | | 2.5 | -2.8968 | 0.4981 | 0.0009 | 0.04 | | |
| 3 | - | | 3.5 | -2.6396 | 0.4959 | 0.0022 | 0.11 | | |
| 4 | - | | 4.5 | -2.3823 | 0.4913 | 0.0046 | 0.22 | | |
| 5 | - | 1 | 5.5 | -2.1250 | 0.4834 | 0.0079 | 0.39 | 4.28 | 2.51 |
| 6 | - | | 6.5 | -1.8678 | 0.4693 | 0.0141 | 0.69 | | |
| 7 | - | | 7.5 | -1.6105 | 0.4463 | 0.0230 | 1.13 | | |
| 8 | - | | 8.5 | -1.3532 | 0.4115 | 0.0348 | 1.70 | | |
| 9 | 3 | 10 | 9.5 | -1.0960 | 0.3643 | 0.0472 | 2.31 | 5.49 | 3.70 |
| 10 | 7 | | 10.5 | -0.8387 | 0.2995 | 0.0648 | 3.18 | | |
| 11 | 6 | | 11.5 | -0.5814 | 0.2190 | 0.0805 | 3.94 | | 1.08 |
| 12 | 3 | | 12.5 | -0.3242 | 0.1273 | 0.0918 | 4.50 | | 0.50 |
| 13 | 4 | | 13.5 | -0.0669 | 0.0265 | 0.1007 | 4.93 | | 0.18 |
| 14 | 2 | | 14.5 | 0.1904 | 0.0753 | 0.1018 | 4.99 | | 1.79 |
| 15 | 6 | | 15.5 | 0.4476 | 0.1736 | 0.0983 | 4.82 | | 0.29 |
| 16 | 8 | | 16.5 | 0.7049 | 0.2580 | 0.0844 | 4.14 | | 3.60 |
| 17 | 2 | 4 | 17.5 | 0.9622 | 0.3315 | 0.0735 | 3.60 | 6.38 | 0.89 |
| 18 | 2 | | 18.5 | 1.2194 | 0.3883 | 0.0568 | 2.78 | | |
| 19 | 2 | | 19.5 | 1.4767 | 0.4306 | 0.0423 | 2.07 | | |
| 20 | - | | 20.5 | 1.7340 | 0.4582 | 0.0276 | 1.35 | | |
| 21 | 1 | | 21.5 | 1.9913 | 0.4767 | 0.0185 | 0.91 | | |
| 22 | - | | 22.5 | 2.2685 | 0.4884 | 0.0117 | 0.57 | 5.41 | 0.03 |
| 23 | 2 | 3 | 23.5 | 2.5058 | 0.4940 | 0.0056 | 0.27 | | |
| 24 | - | | 24.5 | 2.7631 | 0.4971 | 0.0031 | 0.15 | | |
| 25 | - | | 25.5 | 3.0203 | 0.4987 | 0.0016 | 0.08 | | |
| 26 | - | | 26.5 | 3.2776 | 0.4990 | 0.0003 | 0.01 | | |
| 27 | - | | 27.5 | 3.5349 | | | | | |
| 28 | - | | 28.5 | 3.7921 | | | | | |
| | 49 | | | | | | 48.88 | | 14.57 = $\chi^2$ |

$\bar{X}$ = 13.76; SD = 3.89.

Frequencies in adjacent cells have been combined.

df = k - 1 - m where k = 10 and m = 2; hence df = 7.

A VIII.4

Computation of Expected Frquencies in Experimental Group

Computation of $\chi^2$.

| Score | Observed frequency (O) | | Class boundary (X) | $\frac{(X - \bar{X})}{SD}$ (Z) | Area to Z | Area within class boundary | Expected frequency | | $\frac{(O - E)^2}{E}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | -0.5 | -3.3512 | | | | | |
| 0 | - | 3 | 0.5 | -3.1528 | | | | | |
| 1 | - | | 1.5 | -2.9544 | 0.4984 | | | | |
| 2 | - | | 2.5 | -2.7560 | 0.4970 | 0.0014 | 0.07 | 4.13 | 0.31 |
| 3 | - | | 3.5 | -2.5575 | 0.4947 | 0.0023 | 0.11 | | |
| 4 | - | | 4.5 | -2.3591 | 0.4909 | 0.0038 | 0.19 | | |
| 5 | - | | 5.5 | -2.1607 | 0.4846 | 0.0063 | 0.31 | | |
| 6 | - | | 6.5 | -1.9623 | 0.4752 | 0.0094 | 0.46 | | |
| 7 | - | | 7.5 | -1.7639 | 0.4611 | 0.0141 | 0.69 | | |
| 8 | 1 | | 8.5 | -1.5655 | 0.4412 | 0.0199 | 0.98 | | |
| 9 | 2 | | 9.5 | -1.3671 | 0.4142 | 0.0270 | 1.32 | | |
| 10 | 4 | 8 | 10.5 | -1.1687 | 0.3788 | 0.0354 | 1.73 | 6.57 | 0.31 |
| 11 | 2 | | 11.5 | -0.9702 | 0.3349 | 0.0439 | 2.15 | | |
| 12 | 2 | | 12.5 | -0.7718 | 0.2800 | 0.0549 | 2.69 | | |
| 13 | 4 | 11 | 13.5 | -0.5734 | 0.2168 | 0.0632 | 3.10 | 6.56 | 3.00 |
| 14 | 7 | | 14.5 | -0.3750 | 0.1461 | 0.0707 | 3.46 | | |
| 15 | 2 | 6 | 15.5 | -0.1766 | 0.0700 | 0.0761 | 3.73 | 7.59 | 0.33 |
| 16 | 4 | | 16.5 | 0.0218 | 0.0087 | 0.0787 | 3.86 | | |
| 17 | 2 | 5 | 17.5 | 0.2202 | 0.0872 | 0.0785 | 3.85 | 7.51 | 0.84 |
| 18 | 3 | | 18.5 | 0.4187 | 0.1619 | 0.0747 | 3.66 | | |
| 19 | 4 | 6 | 19.5 | 0.6171 | 0.2314 | 0.0695 | 3.41 | 6.41 | 0.03 |
| 20 | 2 | | 20.5 | 0.8155 | 0.2926 | 0.0612 | 3.00 | | |
| 21 | 1 | 1 | 21.5 | 1.0139 | 0.3447 | 0.0521 | 2.55 | 4.63 | 2.85 |
| 22 | - | | 22.5 | 1.2123 | 0.3872 | 0.0425 | 2.08 | | |
| 23 | 3 | 9 | 23.5 | 1.4107 | 0.4208 | 0.0336 | 1.65 | 5.12 | 2.94 |
| 24 | 1 | | 24.5 | 1.6091 | 0.4462 | 0.0254 | 1.24 | | |
| 25 | 2 | | 25.5 | 1.8075 | 0.4647 | 0.0185 | 0.91 | | |
| 26 | 2 | | 26.5 | 2.0059 | 0.4776 | 0.0129 | 0.63 | | |
| 27 | 1 | | 27.5 | 2.2044 | 0.4862 | 0.0086 | 0.42 | | |
| 28 | - | | 28.5 | 2.4028 | 0.4918 | 0.0056 | 0.27 | | |
| | 49 | | | | | | 48.52 | | 10.61 = $\chi^2$ |

$\bar{X} = 16.39$; SD = 5.04.

Frequencies in adjacent cells have been combined.

df = k - 1 - m where k = 8 and m = 2; hence df = 5.

## A VIII.5

Computation of Kuder-Richardson Coefficient of Reliability for Control Pupils.

| Question | p | q | pq |
|---|---|---|---|
| 1 | 0.86 | 0.14 | 0.1204 |
| 2 | 0.29 | 0.71 | 0.2059 |
| 3 | 0.12 | 0.88 | 0.1056 |
| 4 | 0.45 | 0.55 | 0.2475 |
| 5 | 0.29 | 0.71 | 0.2059 |
| 6 | 0.33 | 0.67 | 0.2211 |
| 7 | 0.27 | 0.73 | 0.1971 |
| 8 | 0.90 | 0.10 | 0.0900 |
| 9 | 0.22 | 0.78 | 0.1716 |
| 10 | 0.22 | 0.78 | 0.1716 |
| 11 | 0.18 | 0.82 | 0.1476 |
| 12 | 0.78 | 0.22 | 0.1716 |
| 13 | 0.45 | 0.55 | 0.2475 |
| 14 | 0.02 | 0.98 | 0.0196 |
| 15 | 0.16 | 0.84 | 0.1344 |
| 16 | 0.92 | 0.08 | 0.0736 |
| 17 | 0.18 | 0.82 | 0.1476 |
| 18 | 0.80 | 0.20 | 0.1600 |
| 19 | 0.49 | 0.51 | 0.2499 |
| 20 | 0.51 | 0.49 | 0.2499 |
| 21 | 0.71 | 0.29 | 0.2059 |
| 22 | 0.59 | 0.41 | 0.2419 |
| 23 | 0.73 | 0.27 | 0.1971 |
| 24 | 0.41 | 0.59 | 0.2419 |
| 25 | 0.92 | 0.08 | 0.0736 |
| 26 | 0.86 | 0.14 | 0.1204 |
| 27 | 0.67 | 0.33 | 0.2211 |
| 28 | 0.43 | 0.57 | 0.2451 |

$4.8854 = \Sigma pq$

$$r_{KR} = \frac{N}{N-1} \cdot \frac{S^2 - \Sigma pq}{S^2}$$

$N$ = number of items in test = 28

$S$ = standard deviation of scores in test = 3.89

$p$ = proportion of pupils who pass each item (= F.V.)

$q$ = proportion of pupils who fail each item

Hence, $r_{KR} = 0.70$

## A VIII.6

### Computation of Kuder-Richardson Coefficient of Reliability for Experimental Pupils

| Question | p | q | pq |
|---|---|---|---|
| 1 | 0.96 | 0.04 | 0.0384 |
| 2 | 0.65 | 0.35 | 0.2275 |
| 3 | 0.31 | 0.69 | 0.2139 |
| 4 | 0.80 | 0.20 | 0.1600 |
| 5 | 0.49 | 0.51 | 0.2499 |
| 6 | 0.61 | 0.39 | 0.2379 |
| 7 | 0.61 | 0.39 | 0.2379 |
| 8 | 0.84 | 0.16 | 0.1344 |
| 9 | 0.45 | 0.55 | 0.2475 |
| 10 | 0.35 | 0.65 | 0.2275 |
| 11 | 0.29 | 0.71 | 0.2059 |
| 12 | 0.65 | 0.35 | 0.2275 |
| 13 | 0.47 | 0.53 | 0.2491 |
| 14 | 0.06 | 0.94 | 0.0564 |
| 15 | 0.29 | 0.71 | 0.2059 |
| 16 | 0.86 | 0.14 | 0.1204 |
| 17 | 0.55 | 0.45 | 0.2475 |
| 18 | 0.67 | 0.33 | 0.2211 |
| 19 | 0.65 | 0.35 | 0.2275 |
| 20 | 0.47 | 0.53 | 0.2491 |
| 21 | 0.49 | 0.51 | 0.2499 |
| 22 | 0.63 | 0.37 | 0.2331 |
| 23 | 0.84 | 0.16 | 0.1344 |
| 24 | 0.55 | 0.45 | 0.2475 |
| 25 | 0.96 | 0.04 | 0.0384 |
| 26 | 0.71 | 0.29 | 0.2059 |
| 27 | 0.78 | 0.22 | 0.1716 |
| 28 | 0.41 | 0.59 | 0.2419 |
|  |  |  | 5.5080 = $\Sigma pq$ |

$$r_{KR} = \frac{N}{N-1} \cdot \frac{S^2 - \Sigma pq}{S^2}$$

N = number of items in test = 28

S = standard deviation of scores in test = 5.04

p = proportion of pupils who pass each item (= F.V.)

q = proportion of pupils who fail each item

Hence, $r_{KR} = 0.81$

# A VIII.7

## Computation of Biserial Correlation Coefficient for Control Pupils

| School | Band in H-Chem. | Score |
|---|---|---|
| 22 | A | 19 |
| | A | 14 |
| | A | 15 |
| | A | 13 |
| | A | 11 |
| | B | 11 |
| | B | 10 |
| | B | 15 |
| 23 | A | 16 |
| | A | 15 |
| | A | 14 |
| | A | 10 |
| | B | 13 |
| | C | 10 |
| 26 | A | 18 |
| | A | 18 |
| | A | 15 |
| | A | 16 |
| | A | 15 |
| | B | 9 |
| 27 | B | 13 |
| 28 | A | 12 |
| | A | 10 |
| | A | 12 |
| | B | 21 |
| | B | 13 |
| | C | 9 |
| 32 | A | 12 |
| | A | 16 |
| | B | 2 |
| | B | 10 |
| | B | 16 |
| | B | 11 |
| | C | 10 |
| | C | 9 |
| 33 | A | 16 |
| | A | 11 |
| | A | 17 |
| 35 | A | 16 |
| | B | 16 |
| | B | 10 |
| | C | 11 |
| 37 | A | 16 |
| | A | 19 |
| | A | 23 |
| | A | 23 |
| 39 | A | 15 |
| | A | 17 |
| | B | 11 |

$$r_{bis} = \frac{\overline{X}_A - \overline{X}_{B/C}}{S} \; \frac{pq}{h}$$

$\overline{X}_A = 15.31$

$\overline{X}_{B/C} = 11.50$

$S$ = standard deviation of all control scores = 3.89

$p$ = proportion with Band A = 0.592

$q$ = proportion with Bands B or C = 0.408

$h$ = height of normal curve at point which divides area in ratio 0.592:0.408 = 0.3836 (from tables)

Hence, $r_{bis} = 0.62$

## A VIII.8

### Computation of Biserial Correlation Coefficient for Experimental Pupils

| School | Band in H-Chem. | Score |
|---|---|---|
| 22 | A | 12 |
| | A | 18 |
| | A | 18 |
| | A | 15 |
| | A | 16 |
| | A | 16 |
| | B | 8 |
| | B | 9 |
| 23 | A | 14 |
| | A | 13 |
| | A | 18 |
| | A | 19 |
| | B | 12 |
| | C | 14 |
| 26 | A | 27 |
| | A | 20 |
| | A | 23 |
| | A | 19 |
| | A | 13 |
| | B | 16 |
| 27 | B | 14 |
| 28 | A | 13 |
| | A | 25 |
| | A | 13 |
| | B | 10 |
| | B | 11 |
| | C | 10 |
| 32 | A | 23 |
| | A | 20 |
| | B | 9 |
| | B | 19 |
| | A | 14 |
| | B | 14 |
| | B | 11 |
| | C | 10 |
| 33 | A | 23 |
| | A | 26 |
| | A | 17 |
| 35 | A | 25 |
| | B | 16 |
| | B | 14 |
| | C | 10 |
| 37 | A | 14 |
| | A | 21 |
| | A | 26 |
| | A | 24 |
| 39 | A | 19 |
| | B | 15 |
| | A | 17 |

$$r_{bis} = \frac{\bar{X}_A - \bar{X}_{B/C}}{S} \; \frac{pq}{h}$$

$\bar{X}_A = 18.74$

$\bar{X}_{B/C} = 12.33$

$S$ = standard deviation of all experimental scores
= 5.04

$p$ = proportion with Band A
= 0.633

$q$ = proportion with Bands B or C
= 0.367

$h$ = height of normal curve at point which divides area in ratio 0.633:0.367
= 0.3765 (from tables)

Hence, $r_{bis} = 0.78$

## A VIII.9

### Scores of Matched B/C Pairs

| School | Control | | Experimental | | Pair |
|---|---|---|---|---|---|
| | Band in H-Chem. | Score | Band in H-Chem. | Score | |
| 22 | A | 19 | A | 12 | |
| | A | 14 | A | 18 | |
| | A | 15 | A | 18 | |
| | A | 13 | A | 15 | |
| | A | 11 | A | 16 | |
| | B | 11 | A | 16 | |
| | B | 10* | B | 8* | a |
| | B | 15* | B | 9* | b |
| 23 | A | 16 | A | 14 | |
| | A | 15 | A | 13 | |
| | A | 14 | A | 18 | |
| | A | 10 | A | 19 | |
| | B | 13* | B | 12* | c |
| | C | 10* | C | 14* | d |
| 26 | A | 18 | A | 27 | |
| | A | 18 | A | 20 | |
| | A | 15 | A | 23 | |
| | A | 16 | A | 19 | |
| | A | 15 | A | 13 | |
| | B | 9* | B | 16* | e |
| 27 | B | 13* | B | 14* | f |
| 28 | A | 12 | A | 13 | |
| | A | 10 | A | 25 | |
| | A | 12 | A | 13 | |
| | B | 21* | B | 10* | g |
| | B | 13* | B | 11* | h |
| | C | 9* | C | 10* | i |
| 32 | A | 12 | A | 23 | |
| | A | 16 | A | 20 | |
| | B | 2* | B | 9* | j |
| | B | 10* | B | 19* | k |
| | B | 16 | A | 14 | |
| | B | 11* | B | 14* | l |
| | C | 10* | B | 11* | m |
| | C | 9* | C | 10* | n |
| 33 | A | 16 | A | 23 | |
| | A | 11 | A | 26 | |
| | A | 17 | A | 17 | |
| 35 | A | 16 | A | 25 | |
| | B | 16* | B | 16* | o |
| | B | 10* | B | 14* | p |
| | C | 11* | C | 10* | q |
| 37 | A | 16 | A | 14 | |
| | A | 19 | A | 21 | |
| | A | 23 | A | 26 | |
| | A | 23 | A | 24 | |
| 39 | A | 15 | A | 19 | |
| | A | 17 | B | 15 | |
| | B | 11 | A | 17 | |

Pairs marked * were used in the Wilcoxon Matched-Pairs Signed Ranks Test.

## A VIII.10

## The Wilcoxon Matched-Pairs Signed-Ranks Test.

This test is discussed in 'Non-Parametric Statistics for Behavioural Sciences', by Sidney Siegel, 1956, pages 75-83.

Let d = the difference in scores for any matched pair. Each pair therefore has one difference score. Difference scores may be negative, positive or zero.

Column (1). Difference scores are ranked in order without respect to sign. Difference scores of zero are excluded from the analysis. Where ties occur in ranking order, equal ranks are assigned. For example, in Table 8.8 six d's have equal unsigned values of 1. Each is therefore assigned the rank $3.5 = \frac{1 + 2 + 3 + 4 + 5 + 6}{6}$. There are then two equal unsigned values of 2 which are each assigned the rank $7.5 = \frac{7 + 8}{2}$, and so on.

Column (2). The ranks of d are given the same sign as the d value from which they are derived.

Column (3). Negative ranks and positive ranks are separately totalled. The smaller of the two totals without respect to sign is the T value.

Tables of Critical Values of T for the Wilcoxon Matched-Pairs Signed-Ranks Test are available. (Non-Parametric Statistics, Siegel, page 254.)

# CHAPTER 9

# DISCUSSION

## 9.1 Rejection of the Null Hypothesis

The t-test between control and experimental pupils' scores in the Thermodynamics Approach Test showed the experimental pupils to have performed significantly better than the control, leading to rejection of the null hypothesis (8.2(1) ), and that the improvement was largely confined to those pupils who had obtained Band A awards in Higher Grade chemistry.

In general, therefore, it would appear that a concrete-empirical approach to chemical equilibrium allowed the more academic pupils an opportunity to grasp the conceptual implications of the thermodynamic approach which they might otherwise not have grasped, and, to judge by their performance in the Test, to transfer the concretely acquired concepts to relevant formalised problem situations.

The application of the Wilcoxon Test indicated that the marginal improvement demonstrated by pupils who had obtained Bands B or C at Higher Grade was not significant and could therefore have occurred by chance. This poorer performance may be ascribed to one or more failures:

(i) These pupils were unable to apply themselves to a self-teach programme.
(ii) These pupils were unable, assuming due application, to understand the basic concrete-empirical approach.
(iii) These pupils were able to understand the concrete-empirical approach but were unable to transfer the concretely acquired knowledge to abstract situations.

There cannot, of course, be any sharp division between these categories.

If (i) is an explanation, then an answer might be active conventional teaching of the concrete-empirical approach. A test of this hypothesis would require that this be done in comparison with a single, formally taught presentation of the same subject matter in a suitable research design.

It is not possible to assess the importance of (ii) since questions directly related to the concrete-empirical analogies used in the Programme, though used in the Unit self-tests, were excluded from the Thermodynamics Approach Test since it would have been unfair on control pupils not to have done so.

It is probable that (iii) contributed to the poorer performance of the less academic pupils on the assumption that some of these pupils have not reached formal operations on some of the required abstractions, depending on the difficulty of the latter.

## 9.2 Subjective Assessment of the Thermodynamics Approach Programme by Teachers and Pupils

The author acknowledges that the Programme was highly detailed and consequently bulky. This was a result of the self-teach format of the programme; meanings had to be conveyed in detail, sometimes repetitively. In the event of teacher presentation of the same material, the bulk could be reduced considerably since much could be said and allowed to go unrecorded. And such a presentation would probably be more acceptable to the whole range of pupil ability.

It was noted that some teachers felt the analogies often'went over the heads' of the pupils. It is the author's opinion that where this occurred there would also be trouble with real chemical systems, and that this trouble might be more severe. Perhaps active teaching of the implications of the analogies would lessen the difficulties experienced by these pupils.

Some teachers complained that questions in the Thermodynamics Approach Test were similar to questions in the self-tests of the Programme and that, consequently, the experimental pupils could not help but do better. The author has searched the Programme self-tests and the Thermodynamics Approach Test and extracted those questions which are similar. These are shown in Table 9.1.

Table 9.1 Related Questions in Programme Self-Tests and the Thermodynamics Approach Test.

| Thermodynamics Approach Test Ques. | Thermodynamics Approach Programme Self-Tests Ques. | Page | Resemblance | Facility Values Control | Facility Values Exper. |
|---|---|---|---|---|---|
| 2 | 4 | 1.9 | Identical | 0.29 | 0.65 |
| 14 | 8.b | 10.9 | Similar | 0.02 | 0.06 |
| 16 | 5 | 7.19 | Similar | 0.92 | 0.86 |
| 19 | 2 | 8.16 | Very similar | 0.49 | 0.65 |
| 20 | 2 | 9.10 | Similar | 0.51 | 0.47 |
| 25 | 1.b | 5.7 | Very similar | 0.92 | 0.96 |

Apart from questions 2 and 19 of the Test, the differences in facility values are marginal and of opposed sign. It is unlikely that the removal of questions 2 and 19 from the statistical analysis recorded in 8.2 would have significant effect.

However, there is bound to be some bias effect if only because the Programme and the Test were constructed by one individual, but it does not seem to be possible to assess the extent of this bias. It would perhaps have been advisable to have had the Test constructed by an independent 'third party'.

There was some criticism of the tendency in the Programme, at times, to postpone the discussion of a particular topic 'until later'. This, in fact, was a difficulty experienced by the author in developing the Programme, that is to say, it was necessary, on occasions, to take one idea on trust in order to explain another; for example, the concept of irreversibility was used to explain enthalpy change but was not itself explained until page 7.8 of the Programme.

## 9.3 Thermodynamic Concepts

The pupil responses to the Thermodynamics Approach Test are considered question by question in the categories 1 to 8 of Table 8.1. Each question is reproduced, preceded by the facility values and discriminatory factors of control and experimental groups in that order. The percentage of pupils selecting each response are also shown. Correct responses are marked * .

### 9.3(1) Matter and Energy

Question 1 F.V. = 0.86/0.96 D.F. = 0.29/0.06 (C/E)

Which one of the following lists differs in a significant way from the other three?

| C | E | | |
|---|---|---|---|
| 2% | - | A | Copper, heat, neon. |
| 86% | 96% | B* | Helium, tin, water. |
| - | - | C | Argon, zinc, light. |
| 4% | - | D | Gold, sound, krypton. |
| 8% | 4% | E | I can see no significant difference between these lists. |

Question 23 F.V. = 0.73/0.84 D.F. = 0.35/0.11 (C/E)

Which of the following lists contains an 'odd man out'?

| C | E | | |
|---|---|---|---|
| 4% | 2% | A | Oxygen, petrol, mist, sawdust |
| 4% | 2% | B | Sand, steam, fluorine, paraffin |
| 73% | 84% | C* | Ethanol, flour, heat, nitrogen |
| 13% | 8% | D | Chlorine, methanol, silica, vapour. |
| 6% | 2% | E | I do not know |
| - | 2% | NA | |

These two questions were used in the Rates Approach Test and are discussed in 5.7(1). In that test, question 1 above obtained a facility value of 0.68, and so there has been a marked improvement over the year. In that test, question 23 above obtained a facility value of 0.62, and so there has been a similar improvement over the year.

With respect to the Thermodynamics Approach Test, experimental pupils have shown a somewhat better improvement than control pupils on both questions. This is probably a result of the coverage afforded matter and energy in Unit 1.

The very low discriminatory factors for experimental pupils are due to the very high facility values obtained by the bottom thirds ($T_3$) in each question (A VIII.1).

### 9.3(2) Potential Energy versus Kinetic Energy

Question 2 F.V. = 0.29/0.65 D.F. = 0.07/0.47 (C/E)

When water at 100 °C absorbs heat and changes to steam at 100 °C,

| C | E | | |
|---|---|---|---|
| 51% | 23% | A | the potential energy of the molecules remains the same but their kinetic energy increases. |
| 29% | 65% | B* | the kinetic energy of the molecules remains the same but their potential energy increases. |
| 18% | 8% | C | both the potential energy and the kinetic energy of the molecules increase. |
| - | 4% | D | neither the potential energy nor the kinetic energy of the molecules increases. |
| 2% | - | E | I do not know how the potential energy and/or the kinetic energy of the molecules is affected. |

This question was used in the self-test to Unit 1 (Q.4, page 1.9) and so experimental pupils had encountered it before.

Experimental pupils showed improved performance compared with control pupils, though a higher facility value than 0.65 was hoped for. Control pupils are still generally under the impression that kinetic energy increases at the boiling point.

This question was also used in the Rates Approach Test and discussed in 5.7(2). On that occasion it obtained a facility value of 0.15.

Question 17 F.V. = 0.18/0.55 D.F. = 0.19/0.28 (C/E)

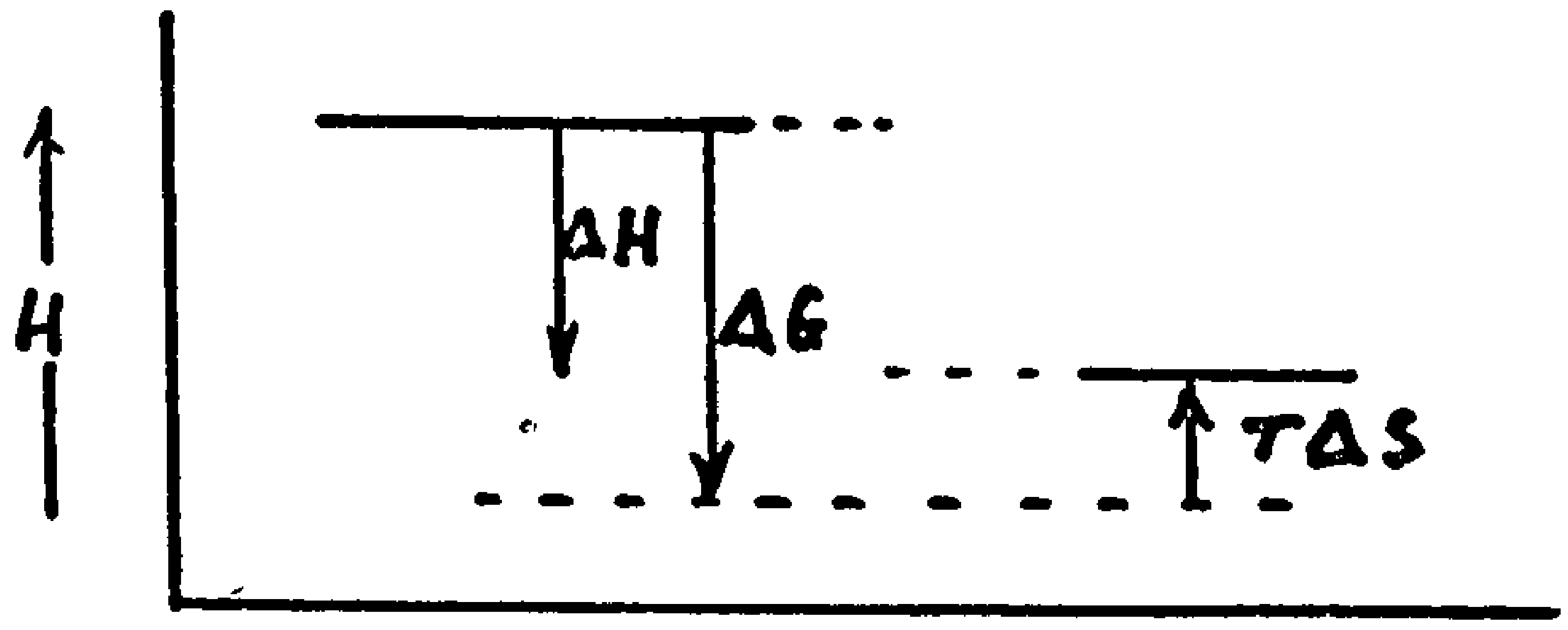
Change in free energy is AG; change in entropy energy is TAS. Which of the following options is <u>incorrect?</u>

| C | E | | |
|---|---|---|---|
| 38% | 19% | A | At constant temperature, both these changes are potential energy changes. |
| 18% | 55% | B* | At constant temperature, the former is a potential energy change while the latter is a kinetic energy change. |
| 20% | 6% | C | The former may or may not be used to do work, while the latter may not be used to do work. |
| 8% | 6% | D | Free energy has an 'organised' quality, while entropy energy has a 'disorganised' quality. |
| 16% | 14% | E | I do not know which of these options is <u>incorrect</u>. |

Responses A and B were the focus of attention here. Control pupils are not at all sure of the potential nature of entropy energy. In contrast, 55% of experimental pupils recognised B as the incorrect response.

### 9.3(3) <u>Spontaneity and Free Energy Change</u>

Question 25 F.V. = 0.92/0.96 D.F. = 0.18/
0.06



This enthalpy diagram refers to one of the following equations. Which one?

Question 25 contd.

| C | E | | |
|---|---|---|---|
| 2% | - | A | $HgO \rightarrow Hg + \frac{1}{2}O_2$ AH +ve, AG -ve, TAS +ve. |
| - | - | B | $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$ AH +ve, AG +ve, TAS -ve, |
| 92% | 96% | C* | $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$ AH -ve, AG -ve, TAS +ve, |
| 4% | 2% | D | $N_2 + 3H_2 \rightarrow 2NH_3$ AH -ve, AG -ve, TAS -ve, |
| 2% | 2% | E | I do not know which one of these equations is depicted by the diagram. |

This question was a test of the sign convention.
(The vertical axis should have read 'PE' instead of 'H'.)

Question 8 F.V. = 0.90/0.84 D.F. = 0.29/0.35 (C/E)

Spontaneity requires that

| C | E | | |
|---|---|---|---|
| 90% | 84% | A* | the free energy change must be negative. |
| - | 4% | B | the enthalpy change must be negative. |
| 2% | 6% | C | the entropy energy change of the reacting system must be positive (T being constant). |
| 4% | 2% | D | $q_{rev}$ must be negative. |
| 4% | 4% | E | I do not know which of these options is correct. |

Question 26 F.V. = 0.86/0.71 D.F. = 0.25/0.40 (C/E)

For a spontaneous reaction in a closed system

| C | E | | |
|---|---|---|---|
| 2% | 4% | A | AG may be positive |
| 86% | 71% | B* | AG is always negative. |
| - | 8% | C | TAS is always negative. |
| 10% | 9% | D | TAS is never negative. |
| 2% | 6% | E | I do not know which of these options is correct. |
| | 2% | | NA |

There was general acceptance that spontaneity requires a negative free energy change although the Programme appears to have had a slightly adverse effect, particularly in question 26. This latter question also indicates that there is perhaps some tendency to think that TAS is never negative.

Question 12  F.V. = 0.78/0.65  D.F. = 0.35/0.34  (C/E)

The enthalpy change associated with a particular process is positive. The increase in entropy value associated with the same process is positive. Which one of the following statements is correct? The reaction will

| C | E | | |
|---|---|---|---|
| 8% | 8% | A | tend to be spontaneous at lower temperatures. |
| 78% | 65% | B* | tend to be spontaneous at higher temperatures. |
| 2% | - | C | be spontaneous at any temperature. |
| 10% | 17% | D | never occur spontaneously, no matter what the temperature. |
| 2% | 10% | E | I do not know which of these options is correct. |

This question assumes knowledge of the link between free energy change and spontaneity, an assumption which is justified to judge from the results of the two previous questions, 8 and 26. A majority of pupils, 78% of control and 65% of experimental, appeared to be able to apply the Gibbs-Helmholtz equation to decide the sign of AG and hence make a decision about spontaneity (or perhaps relied on memory of the supposed known behaviour of endothermic reactions). There is some tendency to think that endothermic reactions do not occur spontaneously.

Question 18  F.V. = 0.80/0.67  D.F. = 0.29/0.49  (C/E)

Which of the following statements about endothermic reactions is correct?

Question 18 contd.

| C | E | | |
|---|---|---|---|
| 80% | 67% | A* | Endothermic reactions are spontaneous if accompanied by a large enough increase in entropy energy. |
| 14% | 11% | B | Endothermic reactions are never spontaneous at less than room temperature. |
| 4% | 6% | C | Spontaneous endothermic reactions become non-spontaneous at higher temperatures. |
| - | 8% | D | Endothermic reactions become exothermic at lower temperatures. |
| 2% | 8% | E | I do not know which of these options is correct. |

The same general comments apply to the results of this question as apply to the results of question 12 above, and again experimental pupils performed less well than control pupils.

Question 11 F.V. = 0.18/0.29 D.F. = -0.05/0.57 (C/E)

A stretched elastic band (at room temperature) is released. It contracts spontaneously to its original shape. Given that the entropy of the rubber <u>increases</u> as it contracts, would you consequently expect the temperature of the rubber

| C | E | | |
|---|---|---|---|
| 48% | 39% | A | to increase? |
| 8% | 10% | B | to remain the same? |
| 22% | 16% | C | to decrease? |
| 18% | 29% | D* | Or is it not possible to say without more information? |
| 4% | 6% | E | I do not know which of these options is correct. |

As conceived, this question was a rather more difficult test of free energy change and spontaneity. That the rubber band contracts spontaneously means that AG must be negative; and AS is stated to be positive, and so also must be TAS. There is, therefore, no way of knowing which is the greater, AG or TAS, and so it is not possible to say whether AH is positive or negative and hence comment on temperature change.

Question 22 F.V. = 0.59/0.63 D.F. = 0.35/0.35 (C/E)

| C | E | | A plant grows in sunlight because |
|---|---|---|---|
| 10% | 17% | A | the free energy change of the growing plant is positive. |
| 6% | 4% | B | the entropy change in the sun is negative. |
| 4% | 4% | C | all reactions are reversible to some extent. |
| 59% | 63% | D* | work is done on the plant by sunlight. |
| 21% | 12% | E | I do not know which of these options is correct. |

The facility values for control and experimental pupils indicate that pupils are largely aware that work has to be done to bring about the growth of a plant.

## 9.3(4) Spontaneity and Speed

Question 21 F.V. = 0.71/0.49 D.F. = 0.58/0.58 (C/E)

If the free energy change accompanying a reaction is

| C | E | | AG = -200 kJ mol$^{-1}$, the reaction |
|---|---|---|---|
| 19% | 27% | A | will occur rapidly. |
| 4% | 6% | B | will be accompanied by a negative enthalpy change. |
| 4% | 8% | C | cannot be carried out reversibly. |
| 71% | 49% | D* | will be spontaneous, but may take a very long time to occur. |
| 2% | 10% | E | I do not know which of these options is correct. |

The results of this question are disappointing. The point is repeatedly made in the Programme that the speed of a reaction is in no way determined by the magnitude of the free energy change. Control pupils are very much more aware of this point. One wonders, in retrospect, just how thoroughly the Programme was read?

Question 6 F.V. = 0.33/0.61 D.F. = 0.38/0.46 (C/E)

A mixture of cold hydrogen and oxygen contained in a closed vessel reacts exceedingly slowly. Under such circumstances, the reaction

| C | E | | |
|---|---|---|---|
| 18% | 17% | A | will yield the maximum available/optional work. |
| 25% | 10% | B | is being operated reversibly. |
| 18% | - | C | is not spontaneous. |
| 33% | 61% | D* | is held back by a kinetic snag |
| 6% | 12% | E | I do not know which of these options is correct. |

The results of this question are rather more encouraging. Experimental pupils are much more aware of the effect of a kinetic snag on the rate at which a reaction occurs. Nor did any of the experimental pupils select response C so that there is less tendency for experimental pupils to equate slowness and non-spontaneity.

Considering both questions together, there is some tendency for pupils, more particularly experimental pupils, to relate the magnitude of the free energy change to the speed at which a reaction will occur; and at the same time, pupils accept, more particularly experimental ones, that a reaction may be slowed down by a kinetic snag. There is a contradiction here which would perhaps be best resolved by talking out the questions with pupils. Had there been more time available for the construction of the Thermodynamics Approach Test, such validation would have been carried out in advance of issuing the test to schools.

### 9.3(5) Work versus Heat

One of the most fundamental concepts which the Thermodynamics Approach Test set out to test was the conservation of energy. Thus if work were obtained from a reaction, the heat change accompanying the reaction was altered correspondingly.

Question 3 F.V. = 0.12/0.31 D.F. = 0.07/0.57 (C/E)

A spontaneous reaction has the following characteristics:

$$AH = -20\ kJ\ mol^{-1}$$
$$AG = -60\ kJ\ mol^{-1}$$
$$TAS = +40\ kJ\ mol^{-1}$$

| C | E | | The reaction |
|---|---|---|---|
| 70% | 49% | A | will always be exothermic no matter how it is performed. |
| 6% | 4% | B | will be exothermic if 30 kJ of work are done by it. |
| 12% | 31% | C* | will be endothermic if 30 kJ of work are done by it. |
| 6% | 6% | D | will be endothermic when performed irreversibly. |
| 6% | 10% | E | I do not know which of these options is correct. |

A majority of control pupils appear to be unaware that this reaction will become endothermic if it is called upon to do anything in excess of 20 kJ of work; only 12% of control pupils selected the correct response. The performance of experimental pupils is better than that of control pupils, but still leaves much room for improvement.

Question 10 F.V. = 0.22/0.35 D.F. = 0.32/0.69 (C/E)

The data:

$$AH = -100\ kJ\ mol^{-1}$$
$$AG = -60\ kJ\ mol^{-1}$$
$$TAS = -40\ kJ\ mol^{-1}$$

| C | E | | refer to a reaction during the occurrence of which |
|---|---|---|---|
| 56% | 39% | A | 100 kJ of heat are expelled while at the same time 60 kJ of work are done. |
| 2% | - | B | When no work is done, AG becomes zero. |
| 22% | 35% | C* | 40 kJ of heat are expelled if 60 kJ of work are done on something in the surroundings. |
| 14% | 18% | D | a maximum of 100 kJ of work can be done if the reaction is carried out reversibly. |
| 6% | 8% | E | I do not know which of these options is correct. |

The response pattern to this question is very similar to that for the above question 3. Precisely the same comments apply.

Question 24 F.V. = 0.41/0.55 D.F. = 0.09/0.28 (C/E)

The enthalpy change for a reaction is AH = -60 kJ mol$^{-1}$. When the reaction is carried out in a cell such that the maximum work is done, AG being equal to -70 kJ mol$^{-1}$, how much heat is exchanged with the surroundings?

| C | E | |
|---|---|---|
| 33% | 21% | A 60 kJ are evolved to the surroundings. |
| 22% | 18% | B 10 kJ are evolved to the surroundings. |
| 41% | 55% | C* 10 kJ are absorbed from the surroundings. |
| - | - | D 70 kJ are absorbed from the surroundings. |
| 4% | 6% | E I do not know which response is correct. |

The response pattern to this question conveys the same impression so far gained from the two preceding questions, that is to say, there is a lack of awareness, more especially among control pupils, of the effect on the heat change of work being done. However, facility values for this question are higher than for the two preceding questions, probably a result of the more familiar terrain, that is to say, the problem being set in a cell situation.

Question 4 F.V. = 0.45/0.80 D.F. = 0.82/0.41 (C/E)

When a cannon is fired blank, x joules of heat are produced in and around the cannon. When an identical charge of powder is used to fire off a cannon-ball, y joules of heat are produced in and around the cannon.

| C | E | Which of the following statements is correct? |
|---|---|---|
| 45% | 80% | A* x is greater than y. |
| 18% | 12% | B x is equal to y. |
| 31% | 6% | C x is less than y. |
| - | - | D It depends on the quality of the gunpowder. |
| 6% | 2% | E I do not know. |

This question is an applied test of the concept of the conservation of energy. It was used in the Rates Approach Test, where it obtained a facility value of 0.32.

The content of the question was taught in the Programme (page 5.5, Pocket Item 4) and so experimental pupils would be expected to know the answer. The question therefore is not an entirely fair one. However, it does convey the same general impression as do the other three questions (3, 10 and 24), that it to say, that control pupils are less aware that work is done at the expense of heat evolved.

### 9.3(6) Reversibility and Irreversibility

A major difficulty in designing questions to test a specific concept is that of avoiding overlap with some other conceptual area. Thus, though question 5 below was specifically invented to test the concept of reversibility, it could equally well be considered in 9.3(5) above.

Question 5 F.V. = 0.29/0.49 D.F. = 0.08/0.33 (C/E)

For a reaction, AH = -100 kJ mol$^{-1}$ and AG = -60 kJ mol$^{-1}$. How much heat would the surroundings gain during the reversible operation of the reaction?

| C | E | | |
|---|---|---|---|
| 35% | 23% | A | 100 kJ |
| 24% | 14% | B | 60 kJ |
| 29% | 49% | C* | 40 kJ |
| 6% | - | D | 160 kJ |
| 6% | 12% | E | I do not know. |

Experimental pupils are much more aware of the meaning of 'reversible operation' than control pupils. This is in agreement with the general findings of 9.3(5) where comprehension of 'work instead of heat' is probably dictated by comprehension of reversible operation since this represents the limiting demand which can be made on the system to do work.

Question 6 F.V. = 0.27/0.61 D.F. = 0.38/0.58 (C/E)

A mixture of cold hydrogen and oxygen contained in a closed vessel reacts exceedingly slowly. Under such circumstances, the reaction

| C | E | | |
|---|---|---|---|
| 18% | 17% | A | will yield the maximum available/optional work. |
| 25% | 10% | B | is being operated reversibly |
| 18% | - | C | is not spontaneous. |
| 33% | 61% | D* | is held back by a kinetic snag. |
| 6% | 12% | E | I do not know which of these options is correct. |

This question has been considered under 9.3(4). It is reconsidered here for the information which the selection of <u>incorrect</u> responses may convey about reversibility.

It would appear that 43% of control pupils are confusing 'slowness' with reversibility while 27% of experimental pupils are so doing.

Question 9 F.V. = 0.22/0.45 D.F. = 0.08/0.94 (C/E)

When all the free energy of a reaction is used to do work, the heat change with the surroundings is

| C | E | | |
|---|---|---|---|
| 33% | 31% | A | AH. |
| 6% | 6% | B | greater than AH. |
| 22% | 45% | C* | $q_{rev}$. |
| 8% | 4% | D | less than $q_{rev}$. |
| 31% | 14% | E | I do not know. |

Experimental pupils are more aware than control pupils that the heat change under the above conditions is $q_{rev}$. This, however, may merely be the result of familiarity with terminology. There is some suggestion (verbal comment by a teacher) that $q_{rev}$ was not usually used for the reversible heat change in the Sixth Year Studies course though it was extensively used in the Programme.

Question 7 F.V. = 0.27/0.61 D.F. = 0.38/0.58 (C/E)

Which of the following is a characteristic of a reaction which is operated such that none of the available/optional work is taken as work?

| C | E | | |
|---|---|---|---|
| 12% | 4% | A | It is an ideal limit at which a minimum heat is evolved. |
| 27% | 61% | B* | Its occurrence results in a maximum heat evolved. |
| 8% | 6% | C | It cannot be observed. |
| 14% | 17% | D | Its occurrence is opposed by an equal force. |
| 37% | 12% | E | I do not know which of these options is correct. |

The results of this question are most encouraging in that 61% of experimental pupils were able to select the correct response. Consistent with the observations so far made, control pupils are not as informed of the difference between reversible and irreversible operation of a reaction, and the accompanying heat change, as are experimental pupils.

### 9.3(7) Entropy

Question 16 F.V. = 0.92/0.86 D.F. = 0.24/0.35 (C/E)

Which of the following processes would be accompanied by a decrease in entropy of the substance involved?

| C | E | | |
|---|---|---|---|
| 4% | 4% | A | Decomposition. |
| 2% | - | B | Boiling |
| 92% | 86% | C* | Polymerisation |
| - | 2% | D | Combustion. |
| 2% | 8% | E | I do not know. |

This question was simple recall or comprehension and was well done by both control and experimental pupils with little to choose between them.

Question 13 F.V. = 0.45/0.47 D.F. = 0.88/0.27 (C/E)

| C | E | | Ice will melt spontaneously at 1 °C because |
|---|---|---|---|
| 33% | 25% | A | the entropy of water is greater than the entropy of ice. |
| 8% | - | B | the entropy of the surroundings decreases as the ice melts. |
| 45% | 47% | C* | the change in total entropy of melting ice and surroundings is positive. |
| 10% | 12% | D | the change in total entropy of melting ice and surroundings is negative. |
| 4% | 14% | E | I do not know which of these options is correct. |

The facility values for both groups are approximately equal but the discriminatory powers are very different. The question was highly discriminating for control pupils in that none of the bottom third ($T_3$) got the question right (A VIII.1). The control group, therefore, appear to have been able to deduce the significance of total change in entropy value while the experimental group were perhaps generally more aware of this to start with and might, therefore, be expected to have performed better.

The percentages of pupils attracted by response A indicate a lack of appreciation of the distinction between system and surroundings.

Question 27 F.V. = 0.67/0.78 D.F. = 0.16/0.17 (C/E)

| C | E | | Which of the following statements is a nonsense statement? |
|---|---|---|---|
| 67% | 78% | A* | When water boils to steam, entropy is created. |
| 17% | 2% | B | A reaction which is exothermic increases the entropy of the surroundings. |
| - | - | C | Entropy is a measure of disorder. |
| 14% | 18% | D | Every occurring reaction is accompanied by an increase in total disorder. |
| 2% | 2% | E | I do not know which of these statements is a nonsense statement. |

Facility values, for these questions are quite high but, in the absence of prior validation, it is difficult to know just exactly why a majority of pupils consider the statement 'entropy is created' to be nonsense.

There is a popular tendency at all levels to talk and write about entropy as if it were a mystical form of matter and/or energy which might be created or destroyed or otherwise moved from place to place, and it may be that the Programme has succeeded in persuading pupils to think of the concept as a value. This might account for some proportion of the 78% of experimental pupils who selected response A. But it may not account for the 67% of control pupils who selected this response. It is possible that these latter, or some proportion of them, might ordinarily have considered 'creation of entropy' a quite acceptable statement. For this particular question, however, these pupils may have selected response A indirectly by ruling out B, C and D, though, under such circumstances, response E was available to them.

No pupils selected response C. One may suppose that pupils regard entropy, therefore, as a measure of disorder, though it would be informative to discuss with them how they interpret disorder. It is the author's opinion, that disorder is popularly interpreted as chaos, that tumbled building bricks have a higher entropy value than the original neat pile; or that a broken bottle has a higher entropy value than the original whole! These possibilities suggest questions, in retrospect, which might have been asked in the Thermodynamics Approach Test.

Another feature of the concept of entropy value which may give rise to conceptual conflict in the minds of pupils and students alike is its 'pseudo' extensive quality. In its method of usage it is extensive, and this would appear to make it reasonable and logical to relate it to other extensive properties like mass and energy. And this appears to be the common practice. However, unlike mass and energy, entropy (value) is not conserved during physical and chemical change, and since conservation is a prerequisite to rational thought involving extensive properties, it would seem - wrongly of course - that entropy is not capable of rational explanation.

N.B. The term 'pseudo' is used above in the sense that entropy values are only additive when the separate parts are accessible to each other. For example, the entropy value of two moles of a gas is only double the entropy value of one mole of the same gas when the two moles are considered as a single entity, otherwise the entropy value of two separate moles is less. This restriction does not operate with 'true' extensive properties.

Question 11 F.V. = 0.18/0.29 D.F. = -0.05/0.57 (C/E)

A stretched elastic band (at room temperature) is released. It contracts spontaneously to its original shape. Given that the entropy of the rubber <u>increases</u> as it contracts, would you consequently expect the temperature of the rubber

| C | E | | |
|---|---|---|---|
| 48% | 39% | A | to increase? |
| 8% | 10% | B | to remain the same? |
| 22% | 16% | C | to decrease? |
| 18% | 29% | D* | Or is it not possible to say without more information? |
| 4% | 6% | E | I do not know which of these options is correct. |

There would appear to be some tendency to equate increase in temperature (incorrect response A) with increase in entropy, perhaps through some misconceptual notion of disorder. However, the author would prefer to talk through this question with pupils before coming to any firm conclusion about why such relatively high percentages of pupils selected response A.

This question has been considered under 9.3(3). It is reconsidered here for the insight which selection of the <u>incorrect</u> response A may give into misconceptual knowledge of entropy.

9.3(8) The Equilibrium State

## (i) Free Energy of Mixing

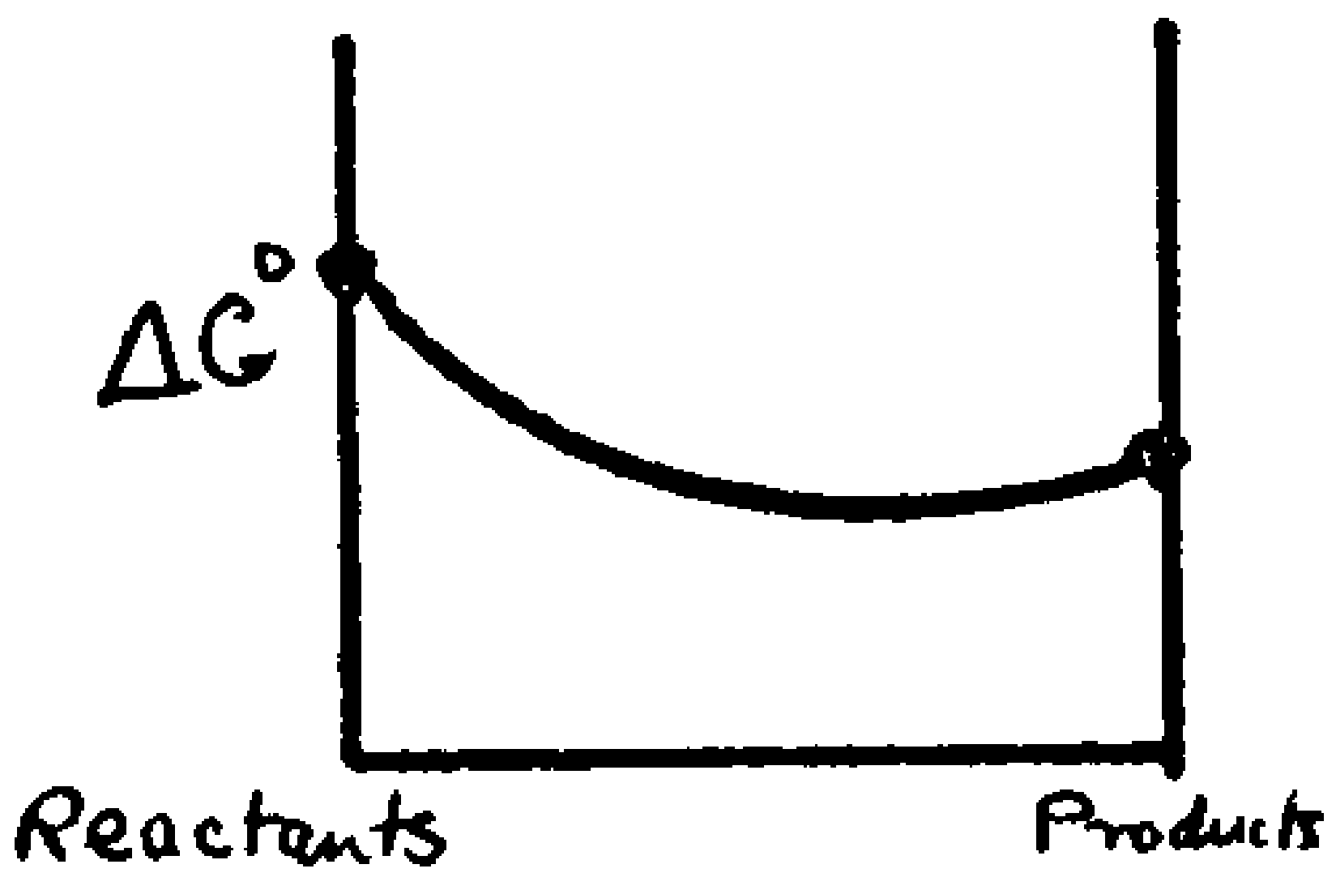
Question 14 F.V. = 0.02/0.06 D.F. = -0.06/0.19 (C/E)

Here is an equilibrium system:

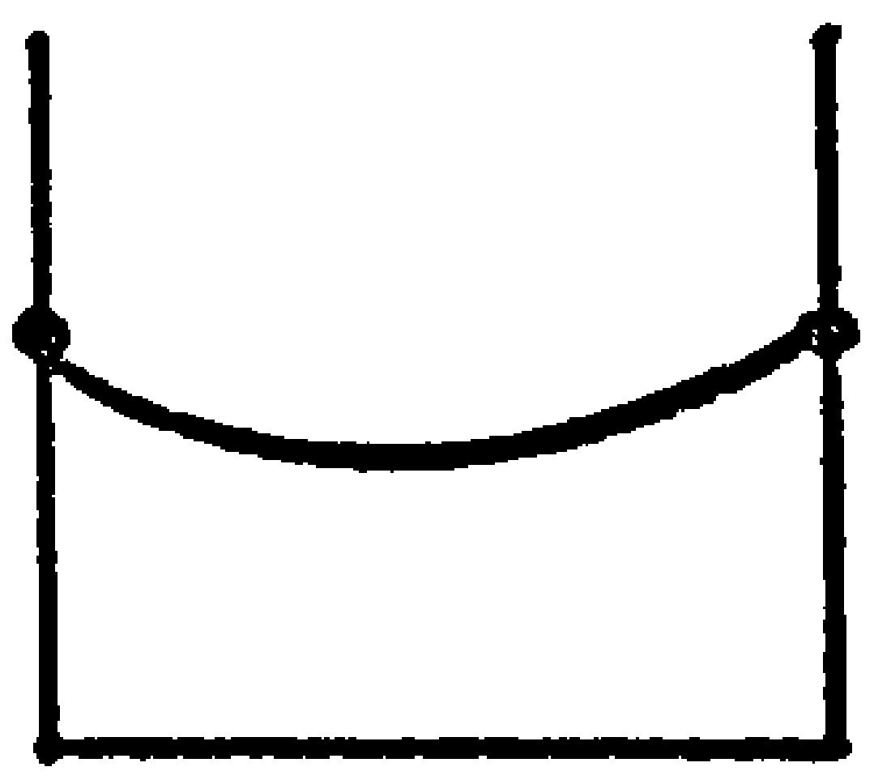
$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$$

At room temperature, $AG^o$ is positive. Which of the following free energy profiles corresponds to this equilibrium system?

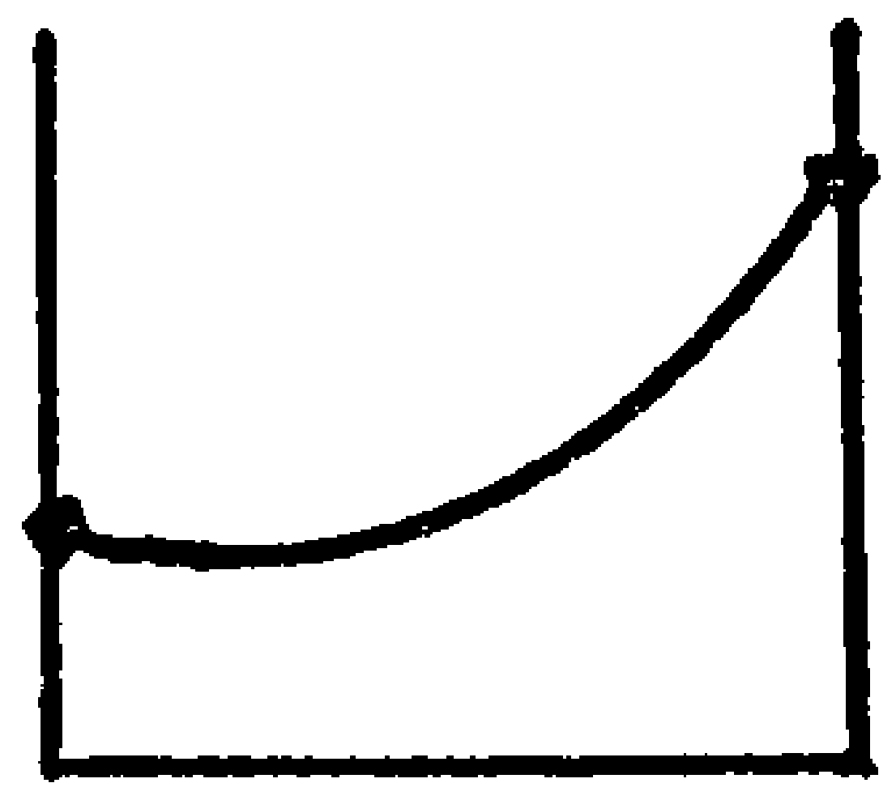
A 16% 19%



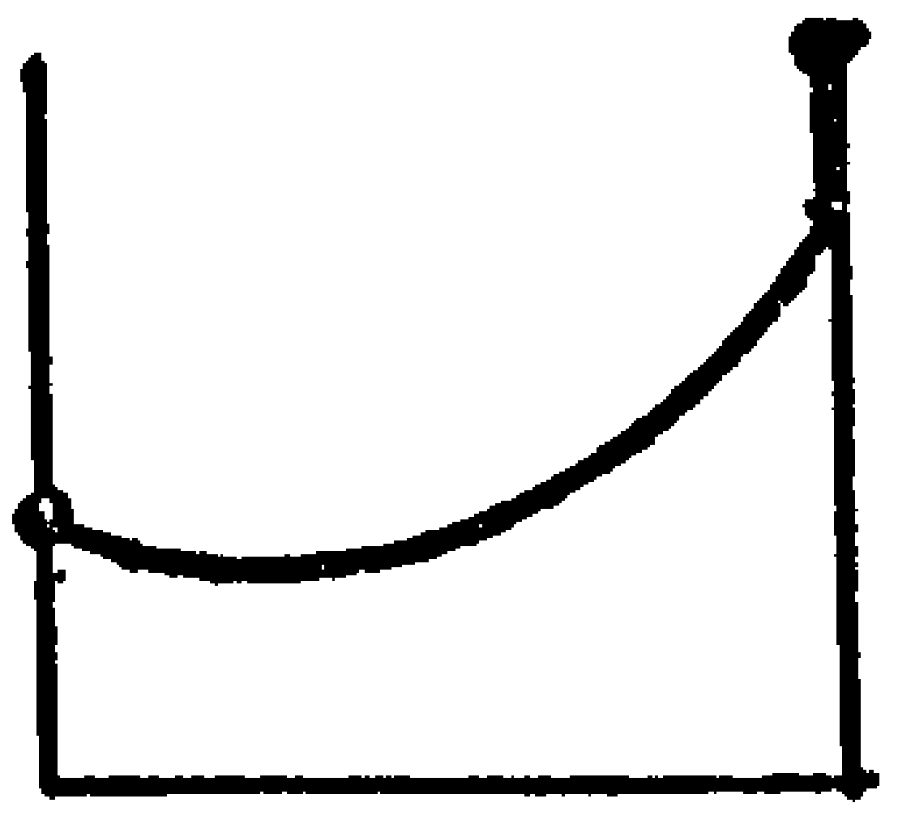
B 4% 8%



C 68% 51%



D* 2% 6%



10% 16% E I do not know which of these profiles is the correct one.

The facility values are extremely low for a question which, for experimental pupils at any rate, required a fairly straightforward interpretation of the free energy of mixing. Indeed, it would appear that experimental pupils did not perhaps progress this far (Unit 9) in the Programme, otherwise a higher facility value would have been obtained.

Irrespective of this, some direct teaching of the importance of the free energy of mixing would seem to be called for.

## (ii) The Free Energy Well

Question 20 F.V. = 0.51/0.47 D.F. = 0.39/0.82 (C/E)

In a system at equilibrium, departure from equilibrium will be accompanied by

Question 20 (contd.)

| C | E | | |
|---|---|---|---|
| 4% | 6% | A | a negative enthalpy change. |
| 6% | 6% | B | a positive enthalpy change. |
| 18% | 14% | C | a negative free energy change. |
| 51% | 47% | D* | a positive free energy change. |
| 21% | 25% | E | I do not know which of these options is correct |
| | 2% | NA | |

The facility values are much the same but the discriminatory powers are very different. It would appear that control pupils are possibly functioning in terms of straight recall in that all have been exposed to the idea of a free energy well at equilibrium, and so the facility values for $T_1$, 0.69, for $T_2$, 0.56, and for $T_3$, 0.29, show a gradual decrease across the spectrum of pupil ability. By contrast, the facility values for $T_1$, $T_2$ and $T_3$ for experimental pupils are 0.88, 0.50 and 0.06 respectively and would seem to indicate that the less academic pupils either did not reach this part of the Programme (Unit 9) or, if they did reach it, were not able to understand it. These views are substantiated by the relatively large percentages of pupils, 21% and 25% in control and experimental groups respectively, who opted for response E.

Question 28 F.V. = 0.43/0.41 D.F. = 0.51/0.51 (C/E)

If the ionisation:

$$2H_2O(l) \longrightarrow H_3O^+(aq) + OH^-(aq)$$

were to go to completion, it would be accompanied by an increase in free energy (and a simultaneous decrease in total entropy).

The ionisation, in fact, proceeds to a slight extent to give an equilibrium mixture:

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

The reason for this is that

Question 28 (contd.)

| C | E | | |
|---|---|---|---|
| 43% | 41% | A* | there is a decrease in free energy until the equilibrium composition is attained. |
| 10% | 14% | B | all reactions proceed to some extent. |
| 2% | 2% | C | a slight increase in free energy is allowable. |
| 20% | 23% | D | molecules continually collide, and so some ions are bound to form |
| 25% | 20% | E | I do not know which of these options is correct. |

This question was designed as a rather more difficult test of the concept of a free energy well. It was a difficult question to design for control and experimental pupils simultaneously since it used the concept of Standard Free Energy change which could not be mentioned as such since this is not included in the Sixth Year Studies syllabus. Hence it was considered that experimental pupils might have an advantage over control pupils since the standard concept is introduced in Unit 9. In fact, facility values and discriminatory factors are, for all practical purposes, the same. A majority of pupils, therefore, control and experimental alike, have not understood the concept of a free energy well..

### (iii) Composition when $K_{eq} = 1$

Question 15 F.V. = 0.16/0.29 D.F. = 0.19/0.14 (C/E)

When the equilibrium constant for a system is 1, the composition of the equilibrium mixture consists of

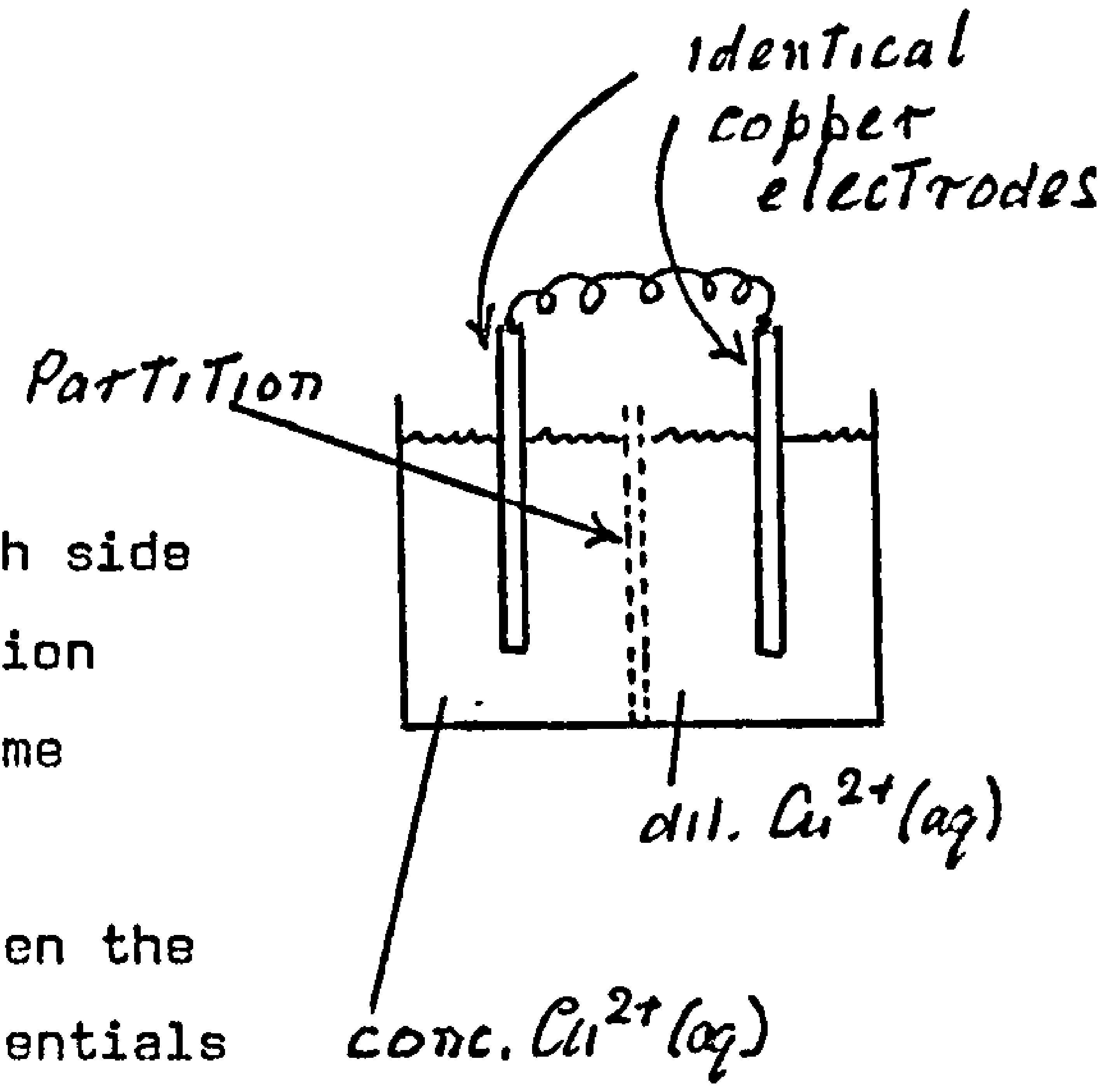
| C | E | | |
|---|---|---|---|
| 78% | 55% | A | 50% reactant plus 50% product. |
| 4% | 4% | B | slightly more product than reactant. |
| - | 4% | C | slightly less product than reactant. |
| 16% | 29% | D* | It is not possible to say without more information of the particular equilibrium system. |
| 2% | 8% | E | I do not know which of these options is correct. |

There is a distinct misconceptual knowledge about the composition of an equilibrium mixture described by an equilibrium constant equal to 1. This point was covered quite fully in Unit 10, and so it would appear that many experimental pupils either did not reach this part of the Programme or, having reached it, did not understand it.

### (iv) Common Sense Implications of a Cell at Equilibrium

Question 19 F.V. = 0.49/0.65 D.F. = 0.45/0.47 (C/E)

A concentration cell is shown opposite. Which of the following options is incorrect?



A concentration cell eventually stops working when

| C | E | | |
|---|---|---|---|
| 18% | 10% | A | the solutions on each side of the porous partition have acquired the same concentration. |
| 21% | 8% | D | the difference between the actual electrode potentials of each half cell is zero. |
| 6% | 13% | C | the difference between the free energies of the contents of each half cell (mole for mole) is zero. |
| 49% | 65% | D* | when the concentration of solute in one half cell has fallen to zero. |
| 6% | 4% | E | I do not know which of these options is incorrect |

As originally conceived this question was a test of the general 'state of affairs at equilibrium', and a cell situation was chosen since it was felt that this was probably the most familiar setting.

The performance of experimental pupils is better than that of control pupils except in respect of response C. To judge by the percentage of pupils, control pupils particularly, selecting responses A and B, there is some lack of appreciation in common-sense terms of what has happened to a cell when it stops working.

# CHAPTER 10

# CONCLUSIONS

## 10.1 The Thermodynamics Approach Programme, a Concrete-Empirical Approach to Chemical Equilibrium

(i) The t-test of the scores of the matched pairs showed experimental pupils to have performed better than control pupils at the 0.1% level of significance.

(ii) The better performance of experimental pupils was largely, if not entirely, due to the better performance of the pupils who had previously gained a Band A in the Higher Grade chemistry examination.

(iii) The performance of experimental pupils who had previously gained either a Band B or a Band C was not significantly better than that of control pupils at the 5% level of significance.

(iv) There was some evidence that some (perhaps a majority) of experimental pupils had not progressed as far as the later units of the Programme.

## 10.2 Conceptual Difficulties experienced by All Pupils

1. A majority of control pupils have no clear conception of kinetic energy at the micro level (molecules at the boiling point of the liquid increase in average kinetic energy) or of kinetic energy at the macro level ($T\Delta S$ is a kinetic energy term at constant temperature).

A minority of experimental pupils suffer from the same misconceptions.

2. There is a tendency for some pupils in general (1 in 6) to think that endothermic reactions do not occur spontaneously.

3. Control pupils (1 in 3) and experimental pupils (1 in 2) do not know that the rate of a reaction is independent of the magnitude of the free energy change.

4. Control pupils (2 in 3) and experimental pupils (1 in 3) do not know that a spontaneous reaction may be held back by a kinetic snag.

5. Control pupils (2 in 3) and experimental pupils (1 in 2) do not know that the heat change accompanying a reaction is correspondingly altered when work is done by the reaction.

6. (a) Control pupils (2 in 3) and experimental pupils (1 in 2) have no clear conception of the meaning of 'reversible operation'.

(b) Control pupils (1 in 2) and experimental pupils (1 in 4) equate slowness with reversible operation.

(c) Control pupils (3 in 4) and experimental pupils (1 in 3) do not know that maximum heat is evolved when no work is done by the reaction.

7. Control pupils (1 in 3) and experimental pupils (1 in 4) have no clear conception of the distinction between system and surroundings.

8. (a) Entropy is interpreted as a measure of disorder. This may or may not be acceptable depending on how disorder is interpreted.

(b) Control pupils (1 in 2) and experimental pupils (1 in 3) appear to equate increase in temperature with increase in entropy, the former being a consequence of the latter, perhaps through some misconceptual notion of disorder.

9. (a) Pupils in general have no conception of the free energy of mixing.

(b) Control and experimental pupils (1 in 2 of each) have no conception of free energy well.

(c) Control pupils (4 in 5) and experimental pupils (1 in 2) think that the composition of an equilibrium system 50:50 of reactant:product when $K_{eq} = 1$.

N.B. The proportions quoted throughout the above account are very approximate and are only intended as a rough guide.

## 10.3 Why do these Conceptual Difficulties Exist

There is little doubt that the thermodynamic approach to chemical equilibrium, whichever way it is offered, is subject to a variety of conceptual hurdles which pupils find difficult, in varying degrees, to overcome.

As with the Higher Grade course, there is probably a problem of misinterpretation, that is to say, a tendency for the pupil to assume what he thinks the teacher implies. But this is probably less marked at the Sixth Year Studies level than at Higher Grade. By contrast at this latter level, inaccurate and uninformed teaching may at times make a major contribution to the conceptual difficulties experienced by pupils.

## 10.4 How can these Conceptual Difficulties be Avoided?

The concrete-empirical approach has met with a measure of success. This success might have been more marked, particularly for less academic pupils, had a direct teaching format instead of a self-teach one been used.

In the event of direct teaching, of whatever approach, some action probably requires to be taken to ensure that teaching staff are as familiar with basic thermodynamic concepts as will allow them to transfer knowledge in unambiguous and misconception-free form.

# PART IV

# A FINAL ASSESSMENT

# CHAPTER 11

# CONCLUDING REMARKS

## 11.1 An Overview

An investigation of the conceptual difficulties experienced by pupils studying chemical equilibrium at the Higher Grade of the Scottish Certificate of Education in chemistry has been carried out and reported in detail in Part II.

The use of a concrete-empirical method of presenting the thermodynamic approach to chemical equilibrium at the Certificate of Sixth Year Studies level was compared in a matched pairs design with the normal method(s) of presentation. The results of the study are reported fully in Part III together with the conceptual difficulties experienced by pupils uncovered during the course of study.

A concept sequence chart (Fig. 4.2, page 79) was offered in Part II. A concept sequence chart (Fig. 7.1, page 115) was offered in Part III. These separate charts are fused in one overall concept sequence chart in the accompanying Fig. 11.1.

## 11.2 Suggestions for Future Research

Some aspects of the Higher Grade syllabus could perhaps warrant closer scrutiny. Thus the use of the Le Chatelier Theorem, or otherwise, might be worth a closer critical examination. The use of physical analogies constitutes a minor research topic in its own right. Some of these analogies appear to be responsible for some of the prevalent misconceptions about chemical equilibrium at Higher Grade, notwithstanding the fact that the concrete-empirical approach adopted at Sixth Year Studies level is based on a physical analogy.

At Sixth Year Studies, there is a case for pursuing a further study of the effectiveness of the concrete-empirical approach by direct teaching in comparison with direct teaching of a conventional less concrete approach. This would require the development of a revised final test, constructed perhaps by a third party to preserve impartiality, and revised in the light of the pupils' responses to the existing Thermodynamics Approach Test. The author sees such a study in the present climate of opinion as highly desirable.

"The teaching of thermodynamics in schools is a topic which still evokes strongly held points of view. Although the debate has continued for over a decade, no end appears to be at hand. ..... such an important subject deserves a new assessment." Education in Chemistry, 1974, 11, p. 10.

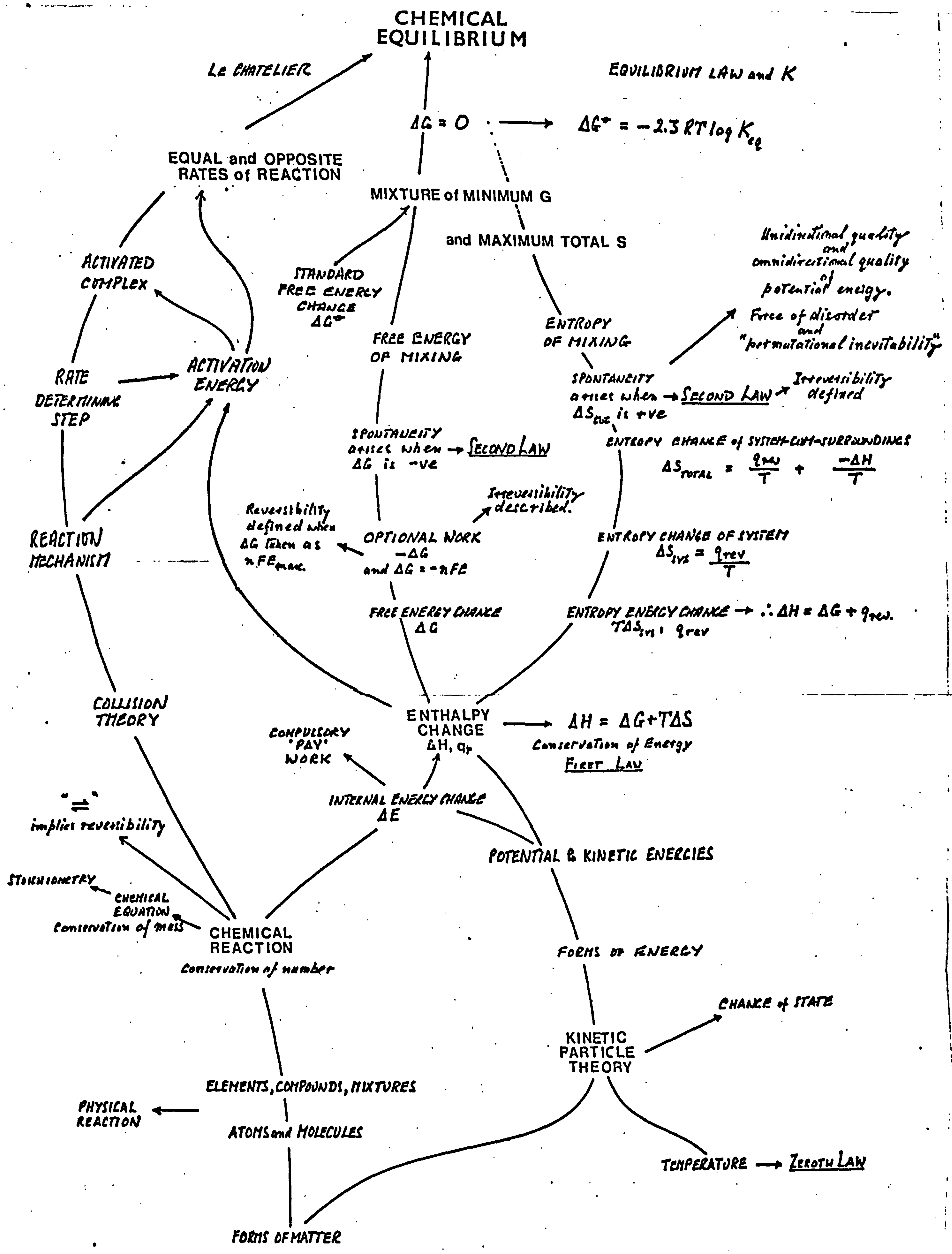


Fig 11.1 Concept Sequence Chart

Sept. 1975

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# CHEMICAL EQUILIBRIUM

# and its

# CONCEPTUAL DIFFICULTIES

by John J. MacDonald

A thesis submitted in part fulfilment of the requirements for the degree of Master of Science of the University of Glasgow.

# Volume 2

# POCKET ITEMS

Item 1. Interview Session Questionnaire.

Item 2. Rates Approach Test.

Item 3. Remedial Action at Higher Grade.

Item 4. Thermodynamics Approach Programme.

Item 5. Thermodynamics Approach Test.

## POCKET ITEM 1

## INTERVIEW SESSION QUESTIONNAIRE

Interview Session Questionnaire SET 1.

1.1 Glass, heat, flour, light, mist, sound.

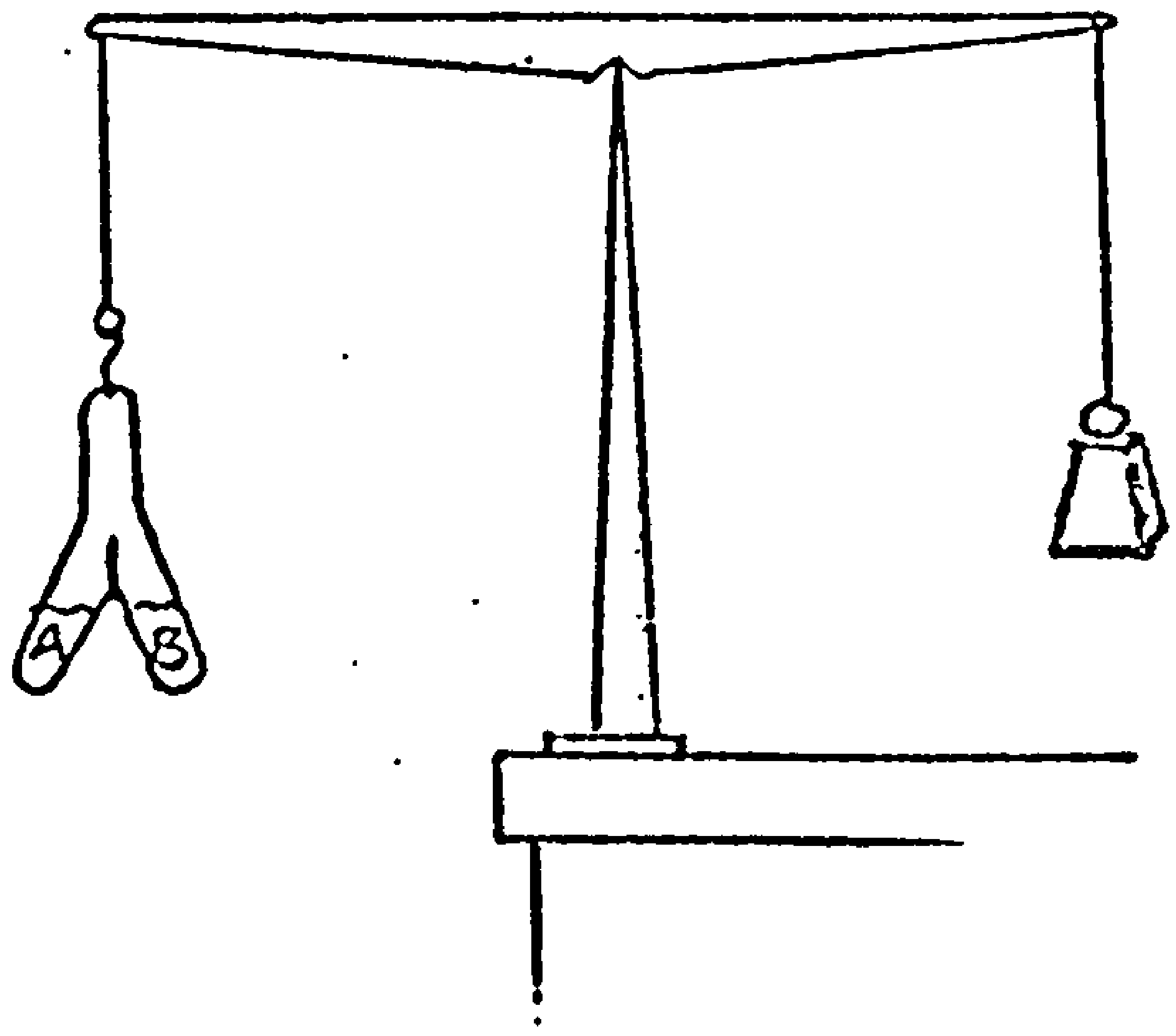
Examine the above list.
On the answer sheet provided write the names of those you consider to be forms of matter.

1.2 The left-hand limb of the sealed tube contains reagent A while the right-hand limb contains reagent B.

The whole assembly is at rest.

Reagent A is tipped into reagent B and the system allowed to come to rest.

How will the final state of the balance compare with the initial?



Will it be

A just the same.?

B down on the l.h.s., up on the r.h.s.?

C up on the l.h.s. , down on the r.h.s.?

1.3 When 50 $cm^3$ alcohol are mixed with 50 $cm^3$ water the final volume is only 97 $cm^3$, approximately. This is explained by arguing that the smaller particles of one substance fit into the spaces between the larger particles of the other substance.

When 50 $cm^3$ carbon disulphide and 50 $cm^3$ benzene are mixed the final volume is about 103 $cm^3$.

Can you explain this apparent contradiction?

1.4 In chemistry we are concerned with the making and breaking of bonds.

what explanation can you offer to explain why the chemical decomposition of ammonia gas (by electric spark) doubles the volume?

1.5 If a reversible reaction proceeds from left to right at low temperature, and from right to left at high temperature, what will happen at an intermediate temperature?

1.6 Discuss the following convention.

a) Reactants $\rightleftharpoons$ Products

b) Reactants $\rightleftharpoons$ PRODUCTS

1.7 Which of the following would be a reliable basis for deciding whether or not a particular mixture of substances was in a state of chemical equilibrium.

a) The composition of the mixture did not change with time.

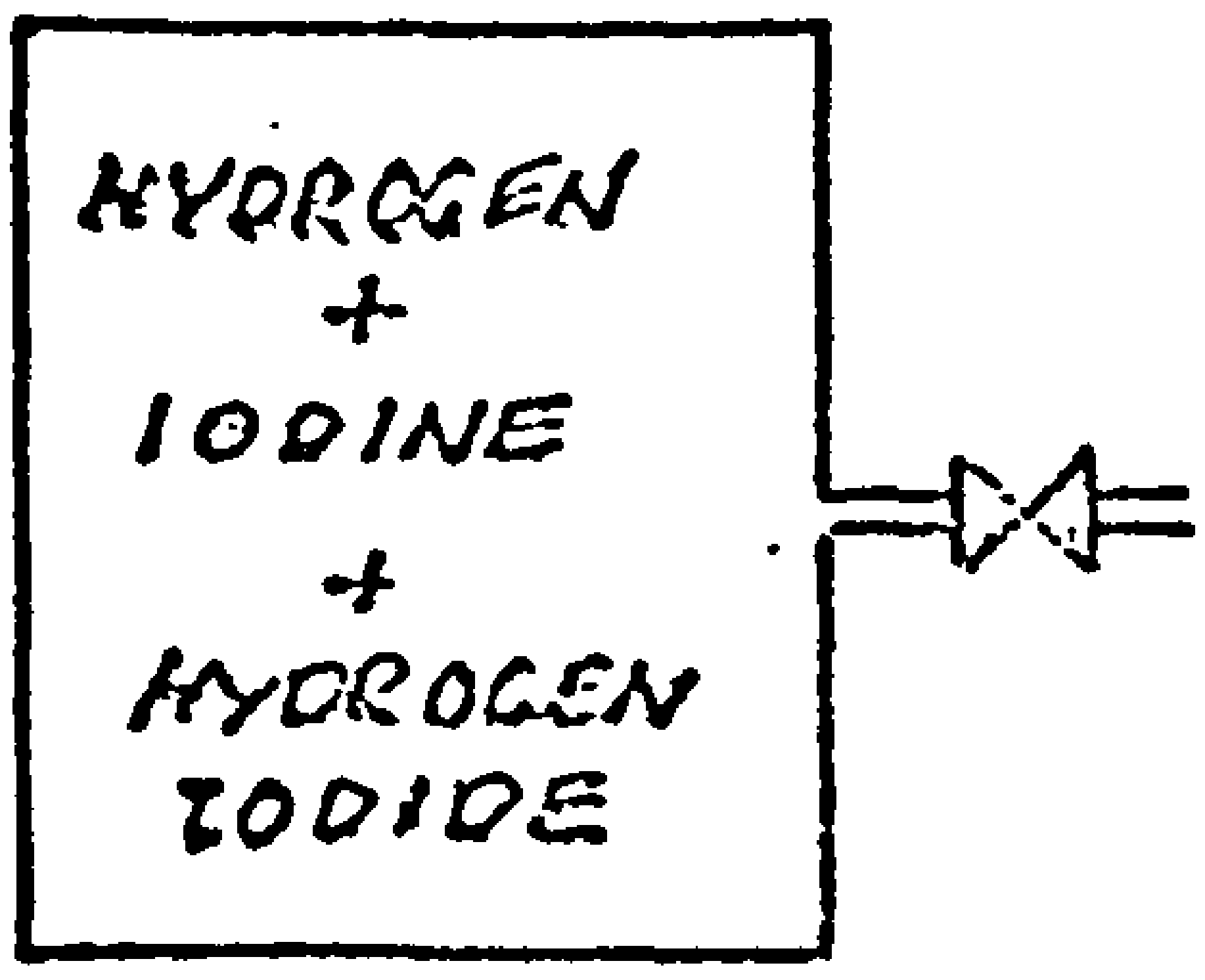
b) When the mixture was heated and then cooled, it departed from and returned to its original composition.

c) When a catalyst known to be effective in the reaction was added, the composition remained the same.

1.8 What does the statement that 'the equilibrium shifted to the right' convey to you?

1.9 What physical picture do you have of the 'left-hand side' and 'the right-hand side' of an equilibrium system?

1.10



This question refers to the following equilibrium

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

The metal reaction vessel shown opposite contains an equilibrium mixture of known composition

If a quantity of hydrogen iodide is withdrawn, and sufficient time allowed for equilibrium to be established, how will its composition compare with the original composition?

1.11 If a reaction is proceeding in the gaseous state, what will happen to the rate of the reaction if the pressure is increased by compressing the gas (temperature being constant).

1.12 Here is an equilibrium system:

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

What happens to the forward rate if the pressure is increased by compression?

1.13 The average speed of a molecule of hydrogen gas at room temperature is about 7000 km per hour. (The bullet from a high velocity rifle travels at only 3500 km per hour!) Nevertheless the hydrogen molecule travels a distance of only about 1 cm during a second, suffering 10 000 000 000 collisions on the way.

What is the effect on this molecule of raising the temperature of the gas?

A It travels faster.

B It becomes hotter.

C Its average velocity is greater.

1.14 For a particular equilibrium system, if a catalyst can increase the rate of the forward reaction, how will it affect the rate of the backward reaction?

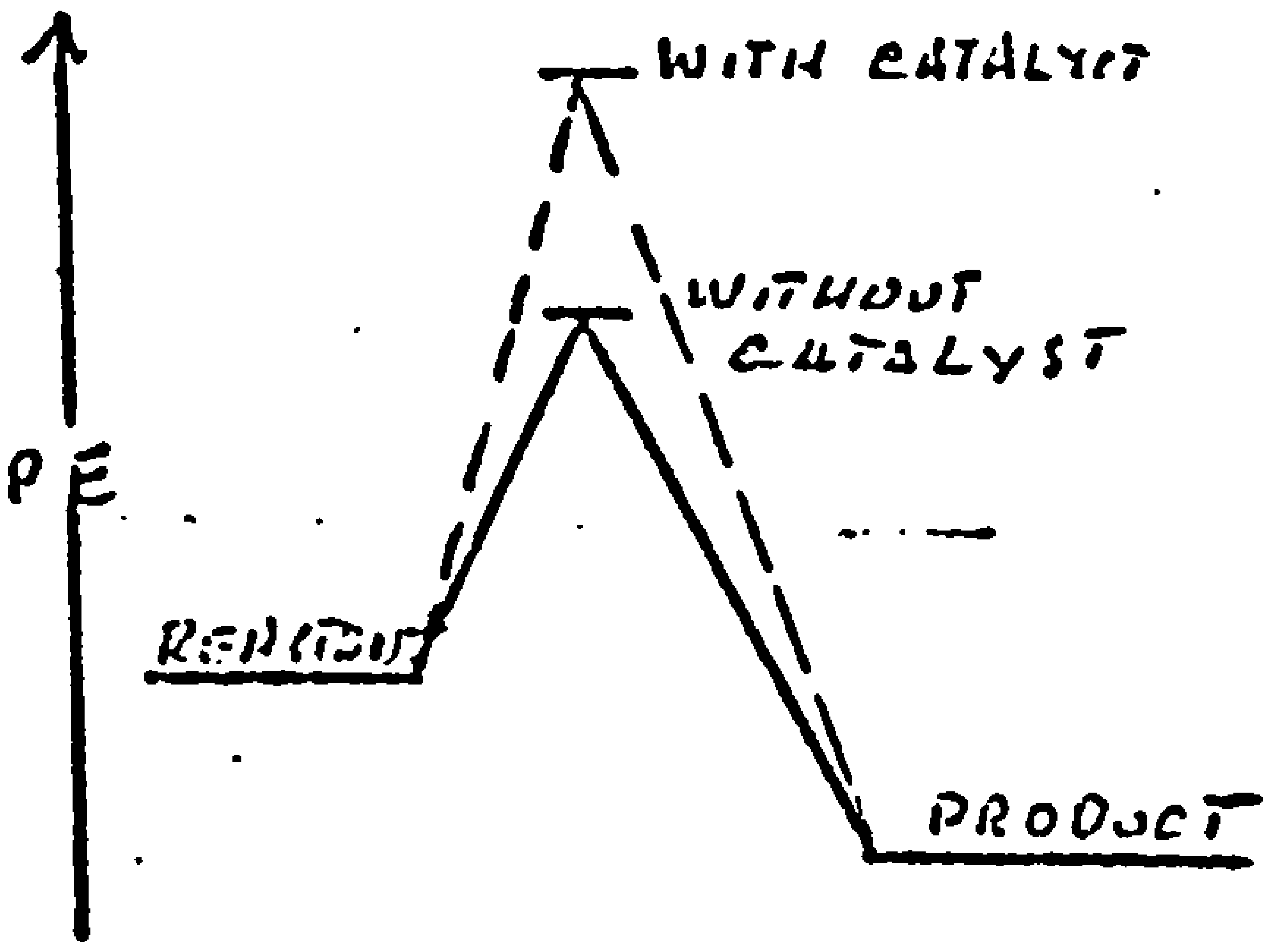
A No effect.

B Increase it.

C Decrease it.

D Stop it.

1.15 Instances of so-called negative catalysis are known, that is to say, instances where the reaction is slowed down by the substance added.



Does this mean, as indicated in the enthalpy diagram opposite, that the activated complex involving the catalyst has higher potential energy than the activated complex not involving the catalyst.

1.16 Here is an equilibrium system:

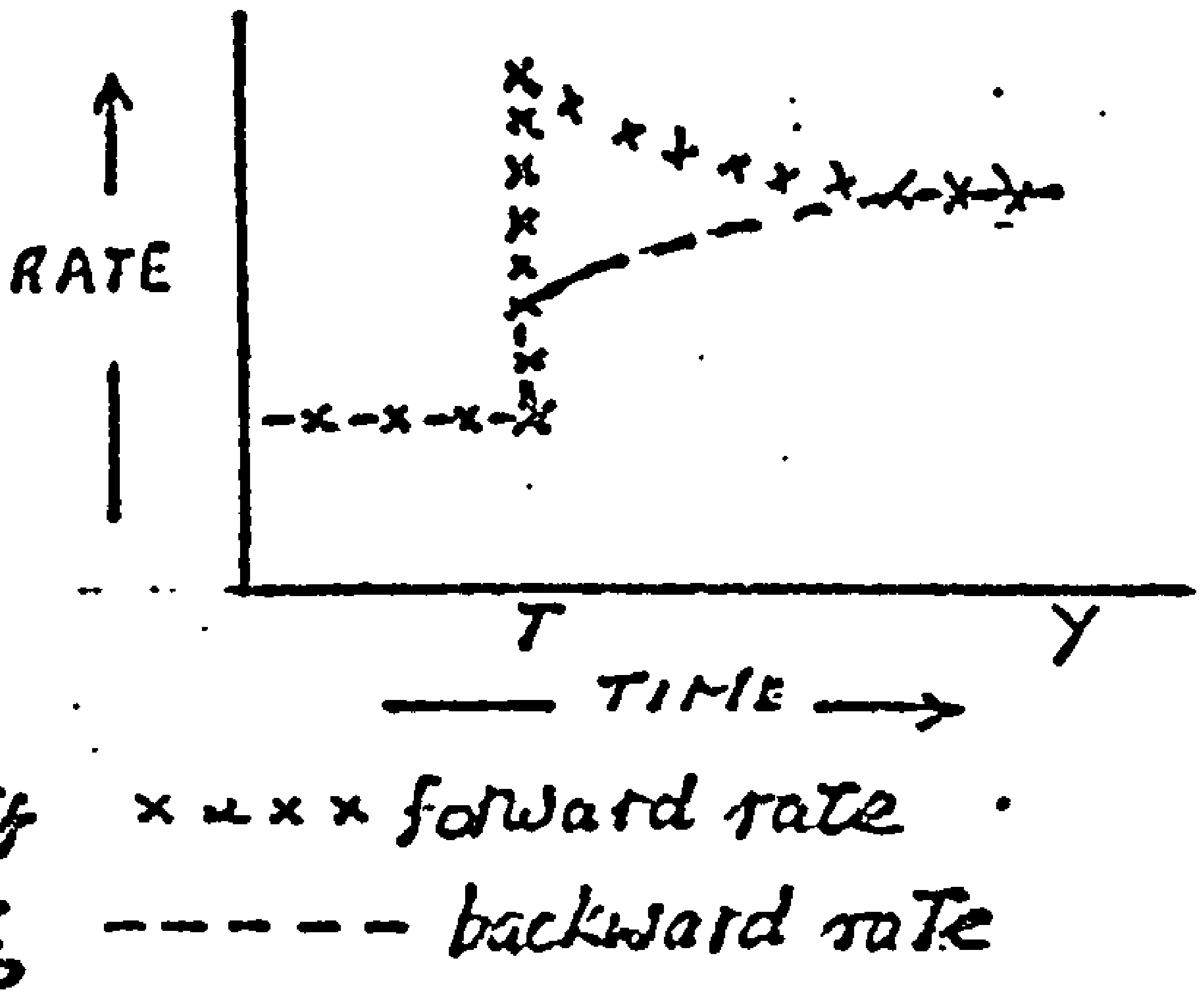
$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g) \qquad \Delta H \ -ve$$

At equilibrium the forward rate exactly equals the backward rate.

If one of the controlling variables is altered a new equilibrium composition is eventually established.

Study the rate curves shown alongside. (These will be explained if required.)

Suggest which variable has been altered at time T.



1.17 When two molecules react with each other, three of the following are necessary conditions. Which three?

- A They must collide with the correct orientation.
- B They must be out of reach of spectator molecules.
- C They must possess at least a certain minimum kinetic energy.
- D They must be higher up than other molecules.
- E They must collide.

Having made your selection, arrange your three choices in what you think is the best <u>logical</u> order.

1.18 The rate determining step is acknowledged as the slowest of the several individual steps between reactant and product.

a) Which one of the following should logically <u>precede</u> a discussion of rate determining step?

b) Which one of the following should logically <u>follow</u> a discussion of rate determining step?

Reaction mechanism
Catalysts
Activation Energy
Chemical equations
Enthalpy change

Physical change
Equilibrium
Reversibility
Collision theory
Activated complex

1.19 Two molecules approach each other on collision course with the correct orientation for reaction. In which of the following cases do they react?

A Each molecule has the minimum activation energy.

B One molecule has the minimum activation energy, the other has less than the minimum.

C One molecule has more than the minimum activation energy, the other has the minimum.

D One molecule has more than the minimum activation energy, the other has less.

1.20 When a molecule possesses 'activation energy' the energy is usually in the form of

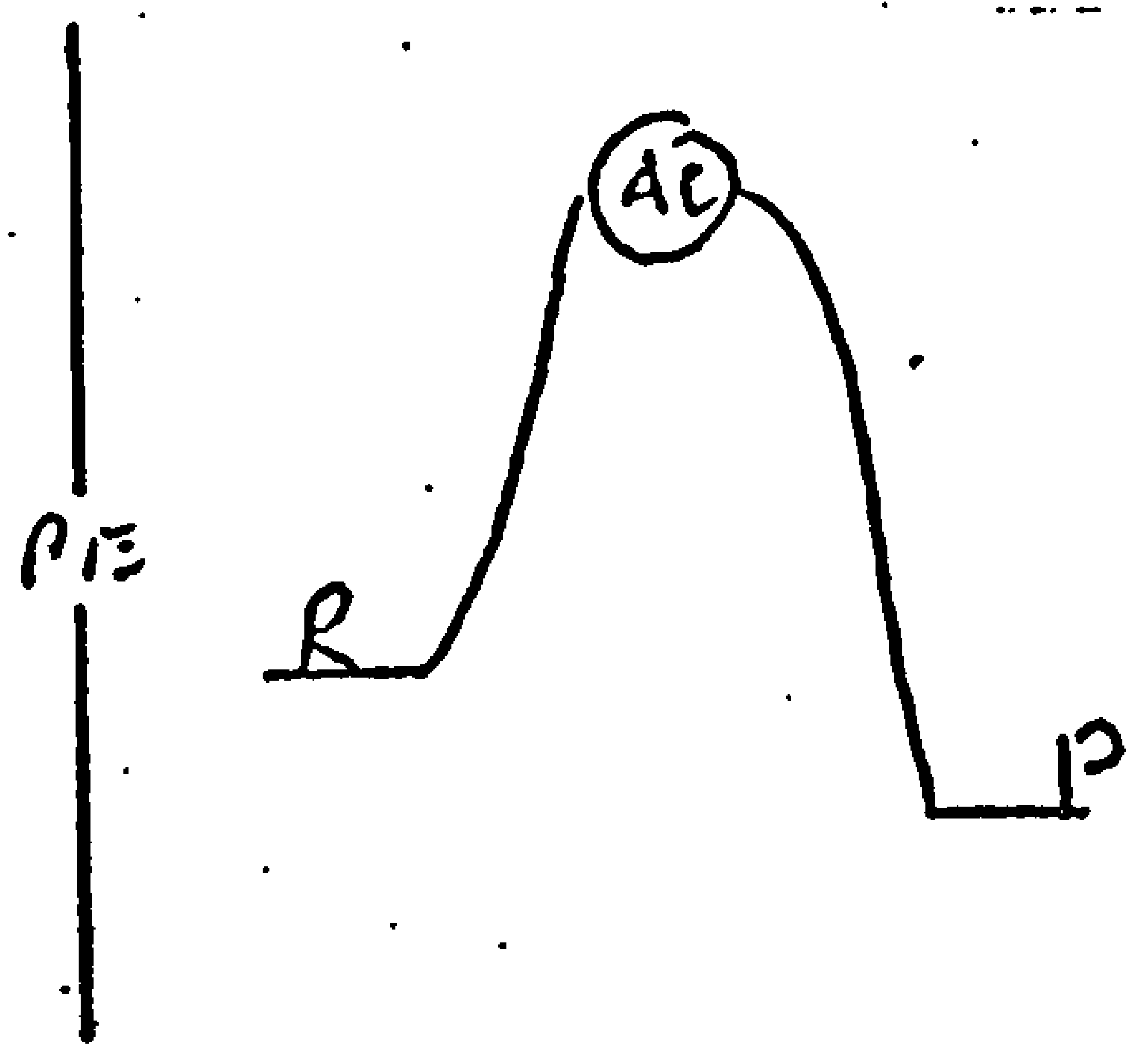
A Kinetic energy

B Potential energy

C electrical energy

D Heat energy

1.21



A system to which the opposite enthalpy diagram applies has come to equilibrium.

This means that

A the activated complex is no longer being formed.

B the activated complex is still being formed and breaks down int R and P.

C the activated complex is still being formed and breaks down into P in preference to R.

Interview Session Questionnaire SET 2

2.1 1 g neon gas consists of n atoms, and occupies 1 litre.

How many atoms of neon are there in ½ g neon?

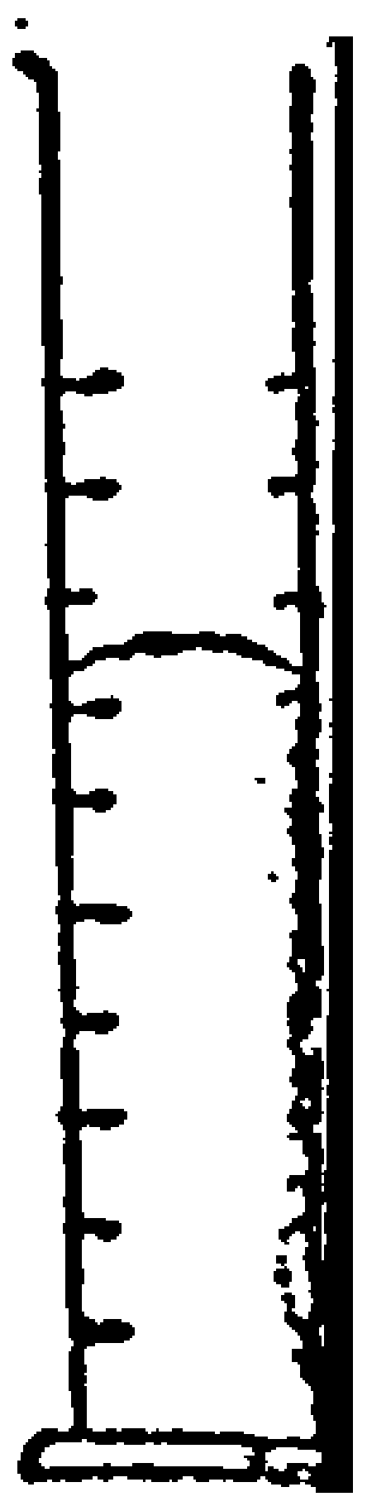
If this litre of neon gas be compressed to ½ litre, how many atoms of neon does the ½ litre consist of?

2.2 Balance:

$$H_2S + O_2 \longrightarrow H_2O + SO_2$$

2.3 A 100 cm³ measuring cylinder contains only 75 cm³ mercury.

What is the concentration of mercury?



A This is not a reasonable question.

B 75%

C It depends on the total volume of the measurihg cylinder.

D It is always 100%.

2.4 Can you define the word 'equilibrium'?

2.5 Discuss the following convention.

a) Reactants $\rightleftharpoons$ Products

b) Reactants $\xrightleftharpoons{\quad}$ Products

2.6 Discuss the following convention.

a) Reactants $\rightleftharpoons$ Products

b) Reactants $\rightleftarrows$ Products

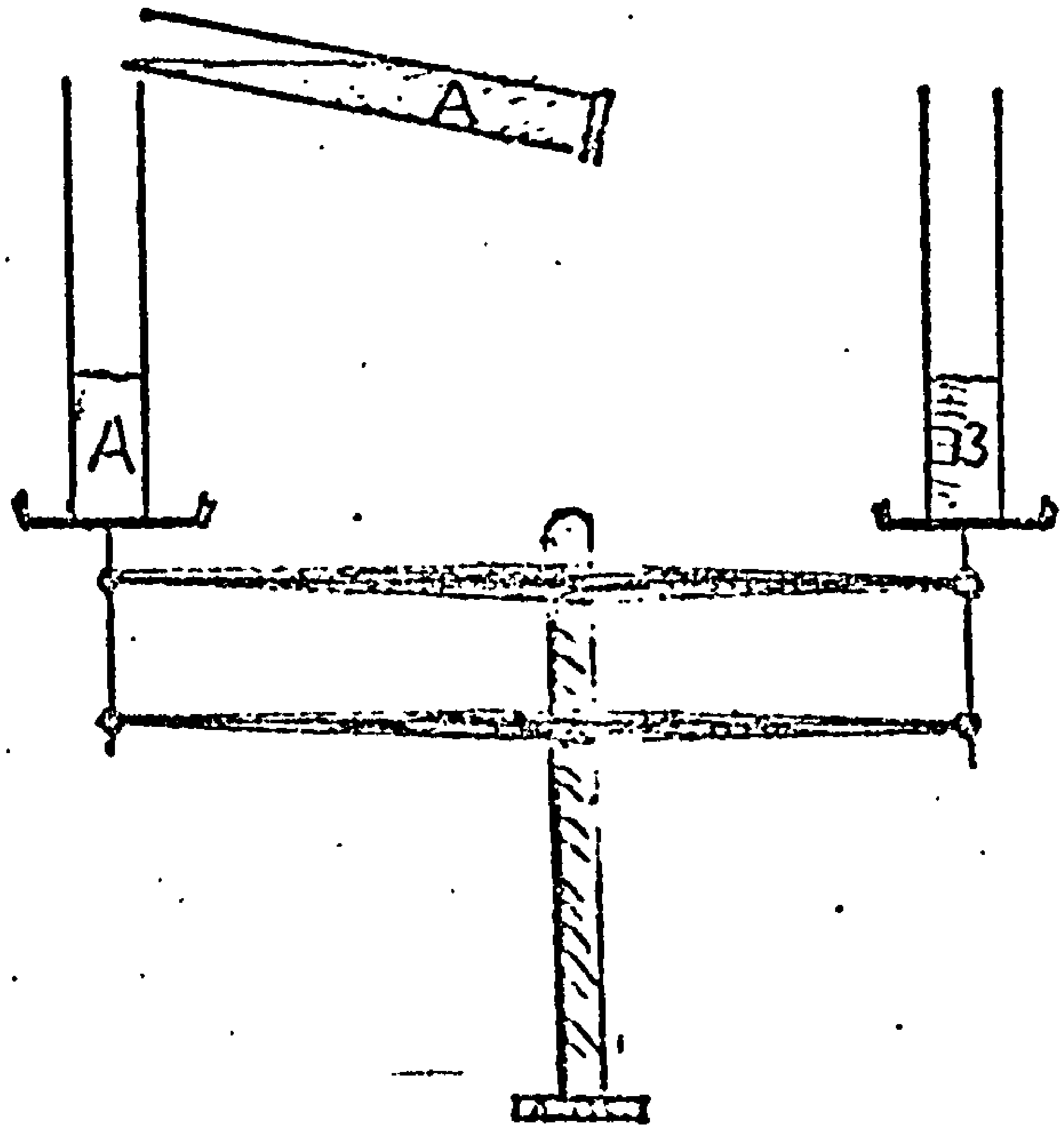
2.7 Here is a much studied equilibrium:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

At equilibrium, at a specific temperature, the number of reactant molecules equals the number of product molecules.

If the total number of molecules before equilibrium is established is 20, how many molecules of each kind would there be at equilibrium?

2.8



A measuring cylinder on the left pan of a balance contains some liquid A; a measuring cylinder on the right pan of the balance contains some liquid B.

More A is added.

a) Do you see any link between this set-up and chemical equilibrium.

b) Is there any point of contrast, that is to say, some aspect of this experiment which is very different from chemical equilibrium?

2.9

Here is an equilibrium system:

$$N_2(g) \quad + \quad C_2H_2(g) \quad \rightleftharpoons \quad 2HCN \quad ; \quad \Delta H \ +ve$$

As long as the left-hand side only of the equilibrium system is heated, no additional hydrogen cyanide will be formed.

Comment on this statement.

A Seems reasonable under the circumstances.

B Is a quite unreasonable statement.

C It would all depend on the relative activation energies.

2.10 Consider the following equilibrium:

$$A \quad + \quad B \quad \rightleftharpoons \quad C \quad + \quad D$$

If the equilibrium moves to the right, will the new equilibrium contain

A More B and less A

B More D and less C

C More B and more D and less A and less C

D More C and More D and less A and less B

2.11 Here is an equilibrium system:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \quad ; \Delta H \ -ve$$

What is the result of adding more $CO(g)$?

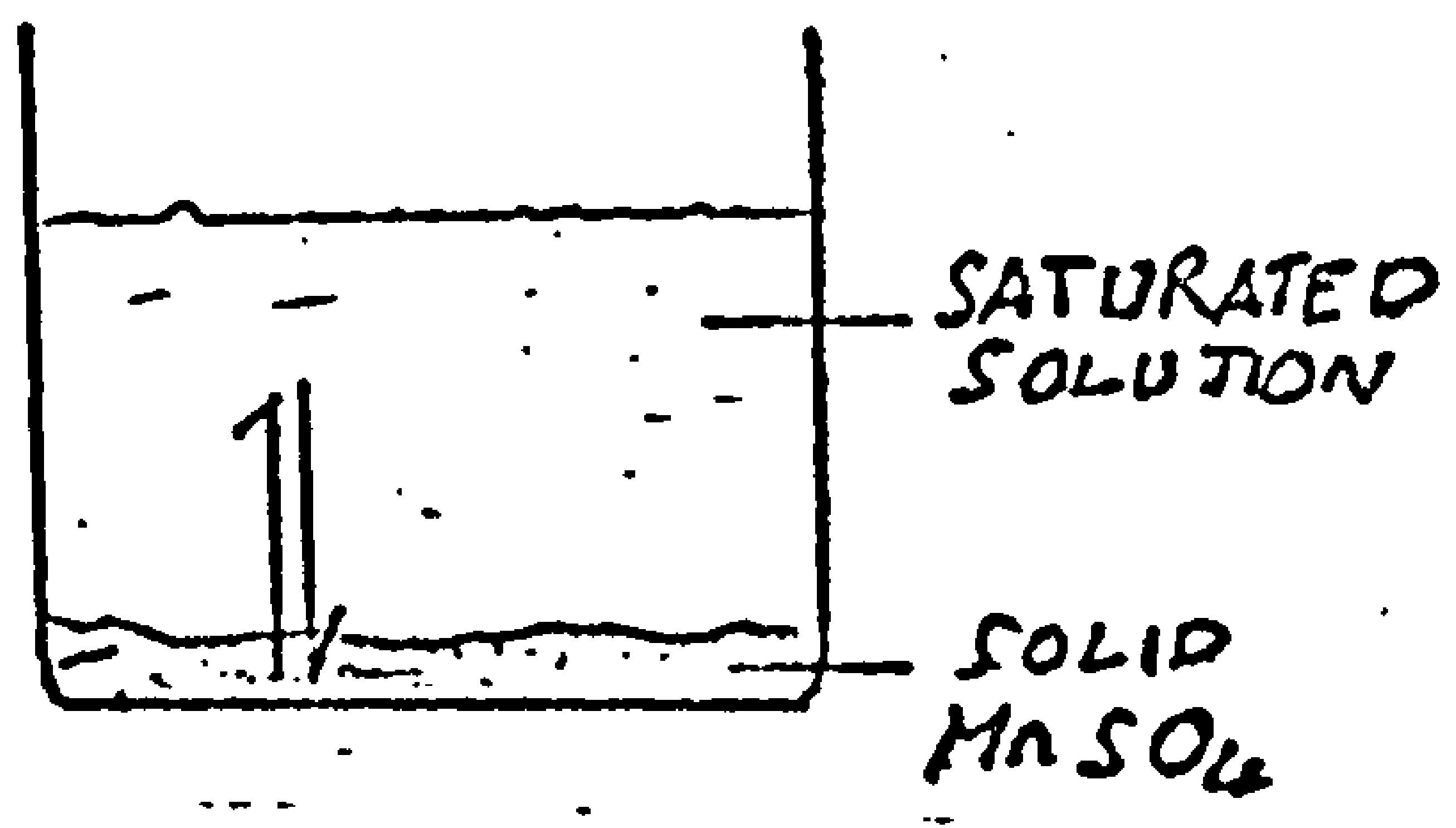
2.12 A well known equilibrium system is represented by:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \quad ; \Delta H \ +ve$$

Would you agree that nitrogen oxide is more stable at high temperature than at low temperature?

How do you reconcile this assertion with the fact that nitrogen oxide mostly decomposes when strongly heated?

2.13



A dynamic equilibrium exists between undissolved salt and dissolved salt.

$$MnSO_4(s) + aq \rightleftharpoons MnSO_4(aq); \Delta H \ +ve$$

What happens when the temperature is raised?

2.14 Which of the following do you consider to be a characteristic of a catalyst?

A It acts as a sort of 'market square' for reaction between reactant and product molecule.

B It acts as a sort of 'spiders web', trapping reactant and product molecules temporarily so that they have a chance to react with each other.

C It ensures that molecules do not have to bump into each other quite so forcibly if done in the presence of the catalyst.

D It provides an alternative reaction mechanism.

2.15 If you were asked to write an essay on reaction rates and were given the following topics as paragraph headings, in which order would you logically discuss them?

-Activated complex - equal and opposite rates - activation energy - collision theory.

2.16 If two molecules are to react with each other,

A they must approach from a relatively great distance.

B one of them must be stationary, or nearly so.

C they must collide with each other.

2.17 The idea of 'reaction mechanism' arises during a discussion of rates of reaction.

a) Which one of the following ideas would logically precede it?

b) Which one of the following ideas would logically follow it?

Reversibility

Physical change

Activation energy

Collision theory

Enthalpy change

Activated Complex

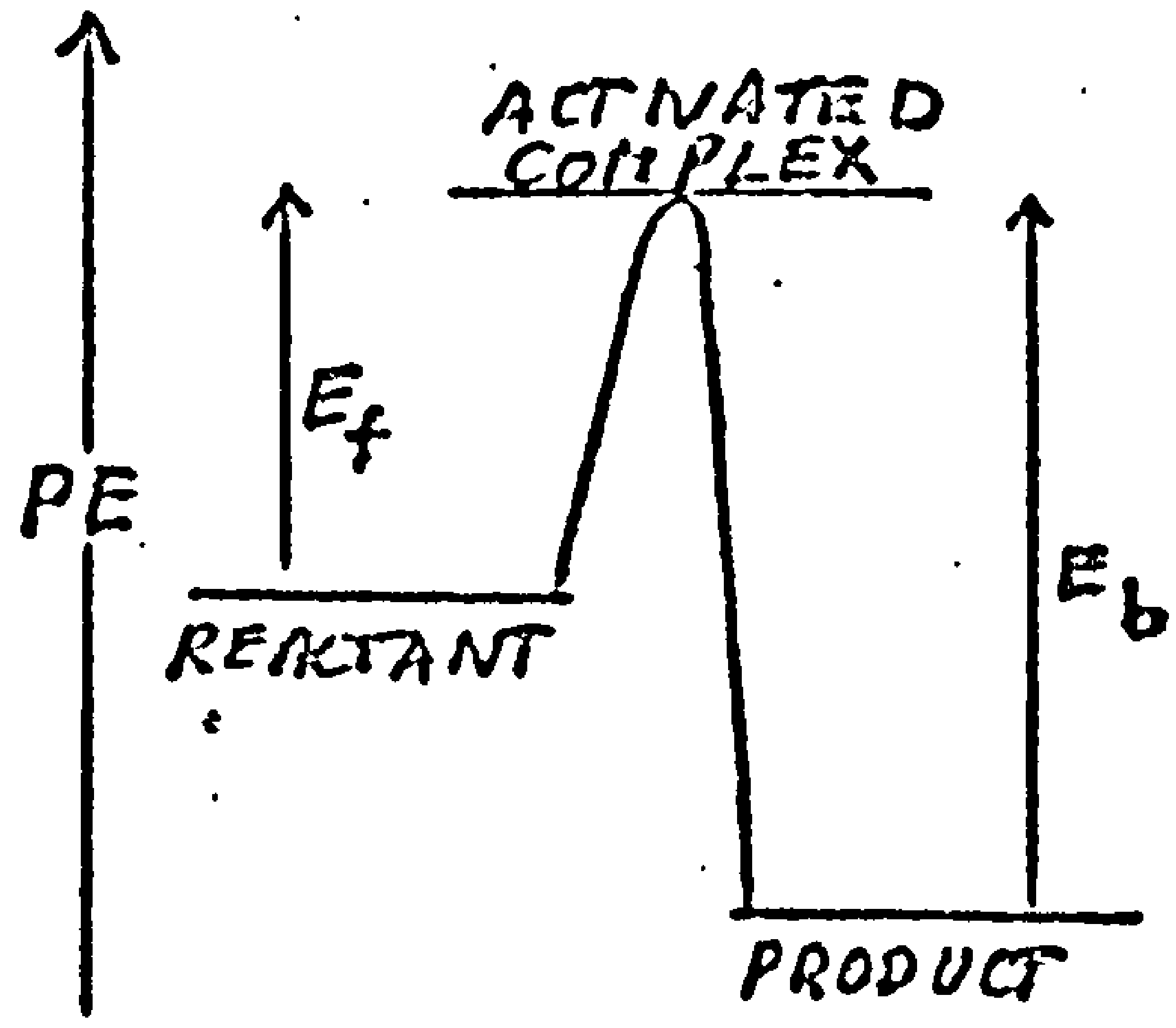
Rate determining step

Catalysts

Equilibrium

Chemical equation

2.18 Activation energy is defined as the minimum energy which must be availble if reaction is to occur.



In a particular system <u>at equilibrium</u>, $E_f$ is less than $E_b$.

Select the correct statement(s) from the following options.

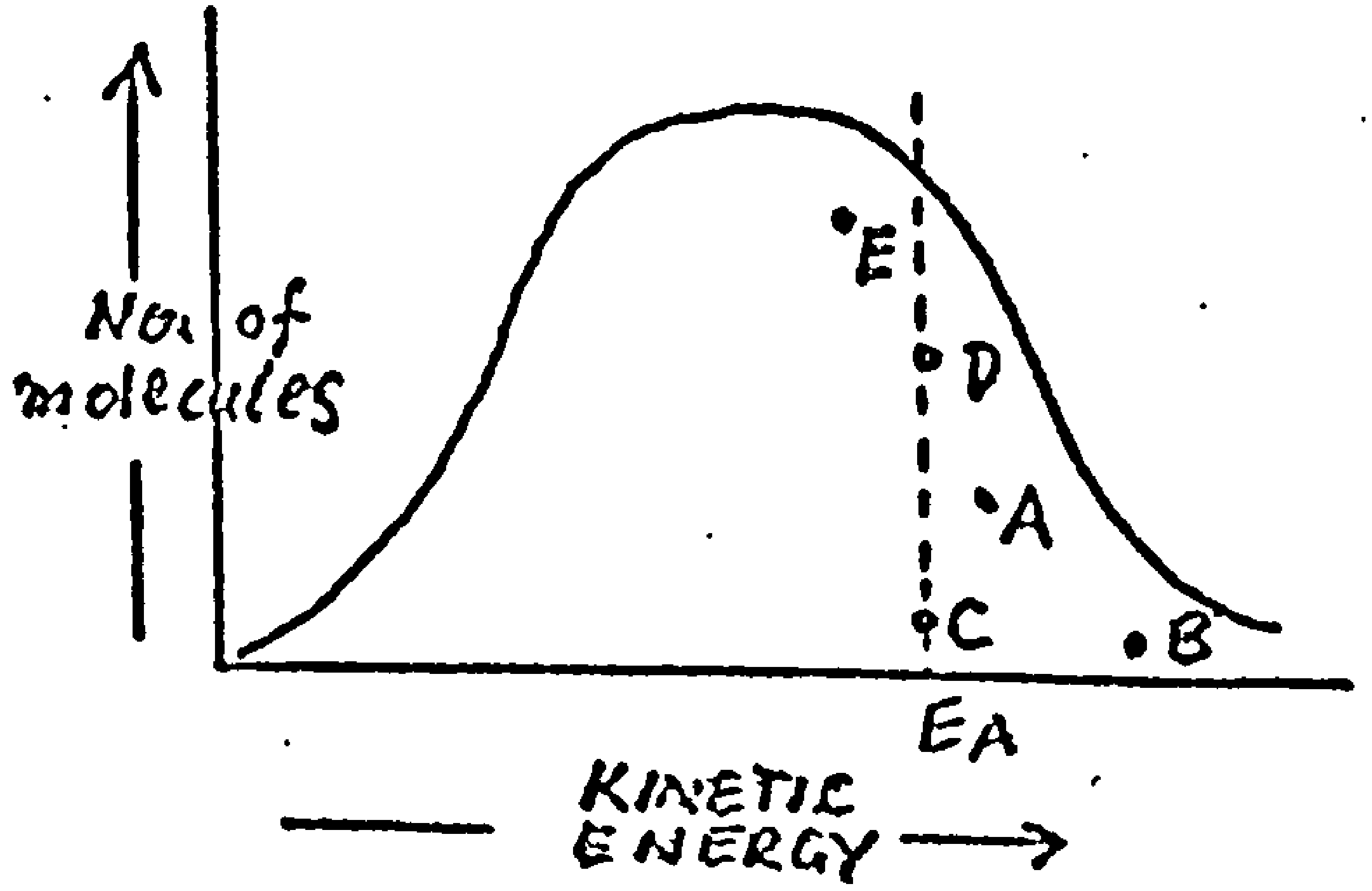
A The forward rate will be greater than the backward rate.

B The backward rate could be zero.

C Both forward and reverse rates are equal.

D The equilibrium mixture will have a higher percentage of product.

2.19



Pick out two molecules which, if they possessed the kinetic energy shown, would fit into the following categories

A Would definitely react on collision

B Would just react on collision.

C Would not react on collision

D Might or might not react on collisi

2.20 Arrange some or all of the following items in a logical sequence:

equal and opposite rates, collision theory, activated complex, activation energy, equilibrium.

2.21 The word 'yield' often arises in discussing the industrial operation of reversible reactions, frequently in the context 'a catalyst improves the yield'.

In what way does a catalyst improve the yield?

A It accelerates forward and reverse reactions in such a way that more product is formed at equilibrium.

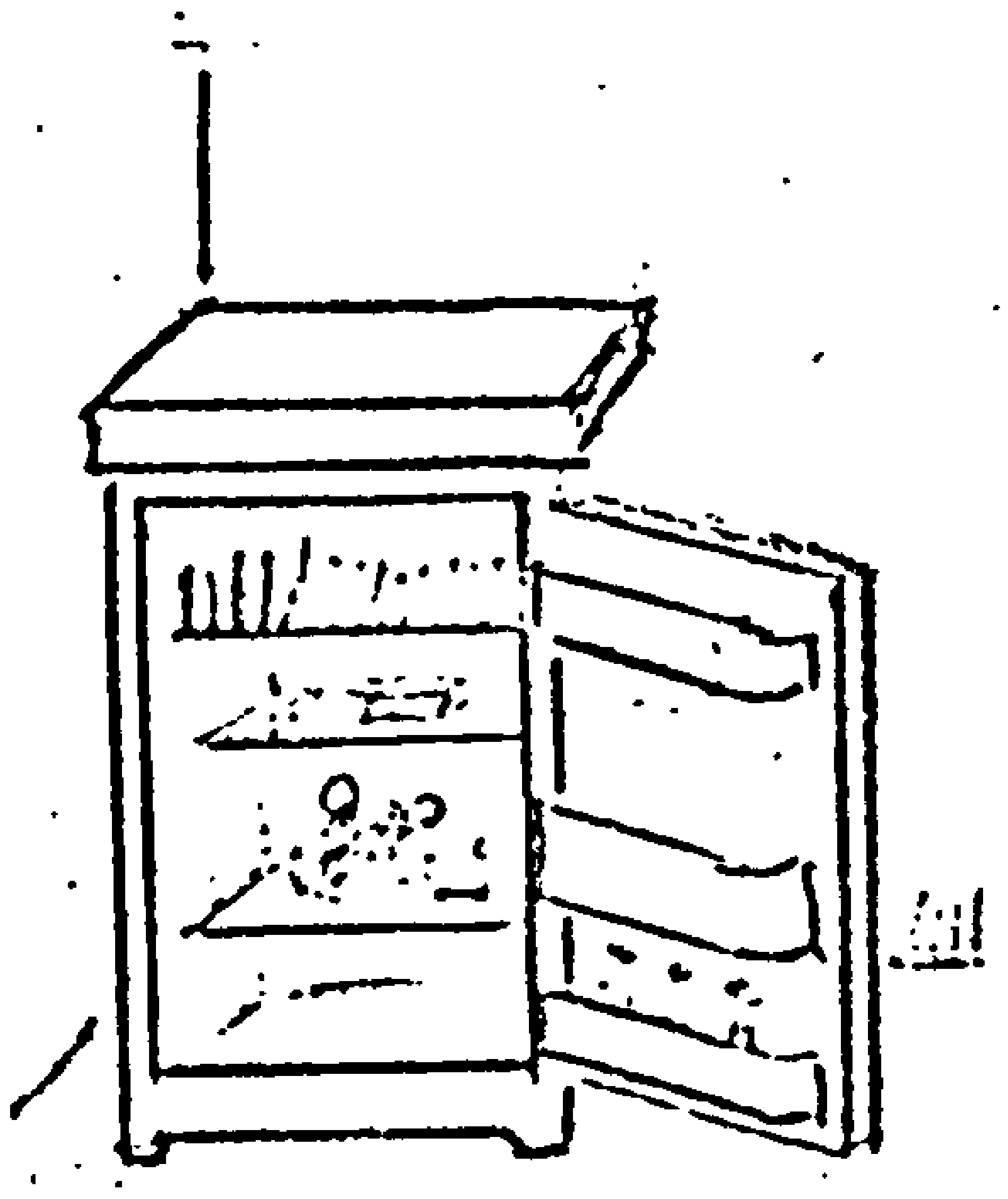
B What you get, you get in a shorter time, not necessarily at equilibrium.

Interview Session Questionnaire SET 3

3.1 A distinguishing characteristic of energy is 'agitation'.

Comment.

3.2 Assuming your kitchen at home to be perfectly insulated so that heat can neither enter it or leave it, would leaving the fridge door open cause the temperature in the kitchen to drop?



3.3 Can you balance:

$$H_2O_2 \longrightarrow H_2O + O_2 \quad ?$$

3.4 Discuss the following convention.

a) Reactants $\rightleftharpoons$ Products

b) Reactants $\rightleftharpoons$ Products

3.5 When the water in a steam boiler is heated some water changes to steam.

How will this affect

a) the amount of steam in the boiler?

b) the concentration of steam in the boiler?

c) the amount of water in the boiler?

d) the concentration of water in the boiler?

(You may consider some of these questions unreasonable, in which case please say so.)

3.6 Arrange the following topics in any kind of logical order or pattern you think appropriate.

Enthalpy change - chemical reaction - activation energy - rates of reaction - collision theory.

3.7 Here is an equilibrium which you probably first encountered in Form III.

$$H_2O(aq) \rightleftharpoons H^+(aq) + OH^-(aq)$$

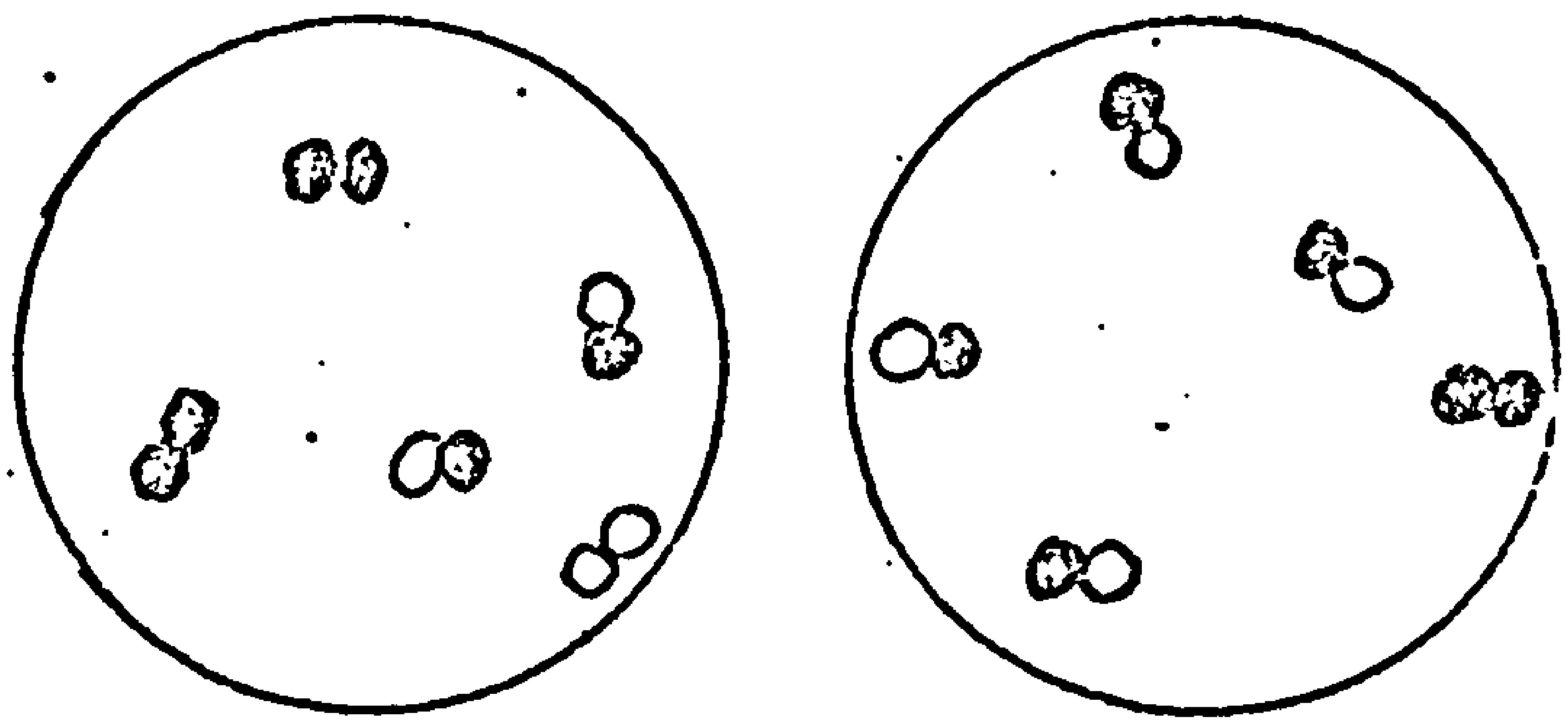
Only one molecule in every 500 000 000 or so is ionised at any one instant in time. What does this convey about the relative magnitudes of the forward and backward rates of reaction?

A The forward rate is greater than the backward rate.

B The forward rate is less "efficient" than the backward rate.

C Both rates are the same.

3.8 Here are two imaginary pictures. The first represents a portion of an equilibrium system; the second represents the same portion in space an instant later.



a) How many molecules are there in each picture?

b) Comment on their behaviour.

c) Was the original description 'portion of an equilibrium system' justified?

3.9 In the familiar Haber system

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

the application of greater pressure to the "right hand side" only will drive the equilibrium to the left.

Comment on this assertion.

3.10 When ethanoic acid and ethanol react with each other the reaction "stops at roughly the half-way stage".

What does this suggest to you?

3.11 Consider the equilibrium system shown:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Will the composition at equilibrium be 40% $SO_2$, 20% $O_2$ and 40% $SO_3$?

3.12

$N_2O_4$ / $NO_2$

A sealed ampoule contains an equilibrium mixture of dinitrogen tetroxide and nitrogen dioxide:

$$N_2O_4(g) \rightleftharpoons 2NO_2 \quad \Delta H \ +ve$$

If the temperature of the bulb is increased the pressure is also increased.

a) On the basis of the temperature change only, predict what will happen to the composition of the equilibrium mixture.

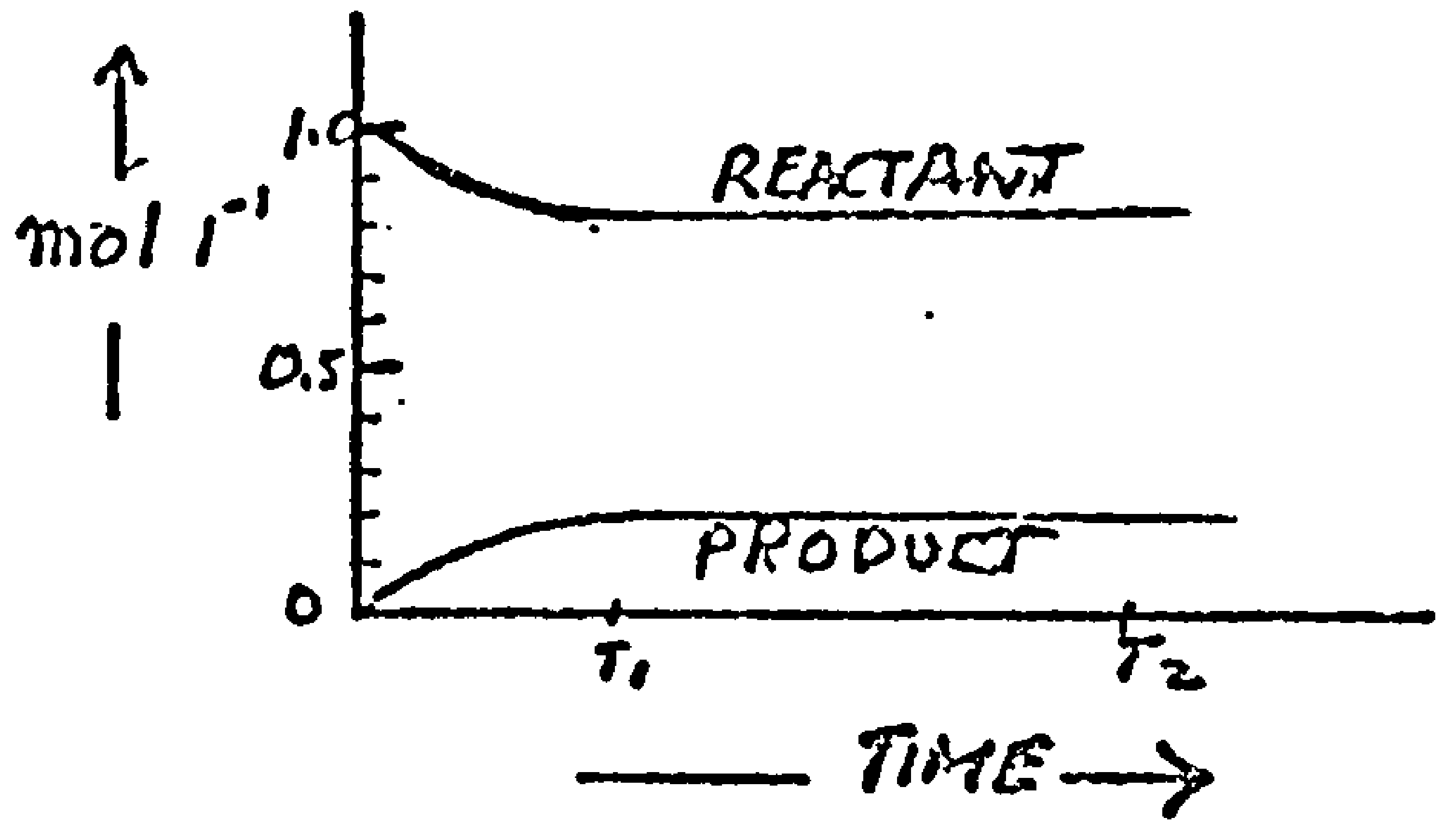
b) On the basis of the pressure change only predict what will happen to the composition of the equilibrium mixture.

3.13 Here is an equilibrium system:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

What happens to the $H^+$ concentration if a quantity of sodium ethanoate solution is added?

3.14 Reactant ⇌ Product



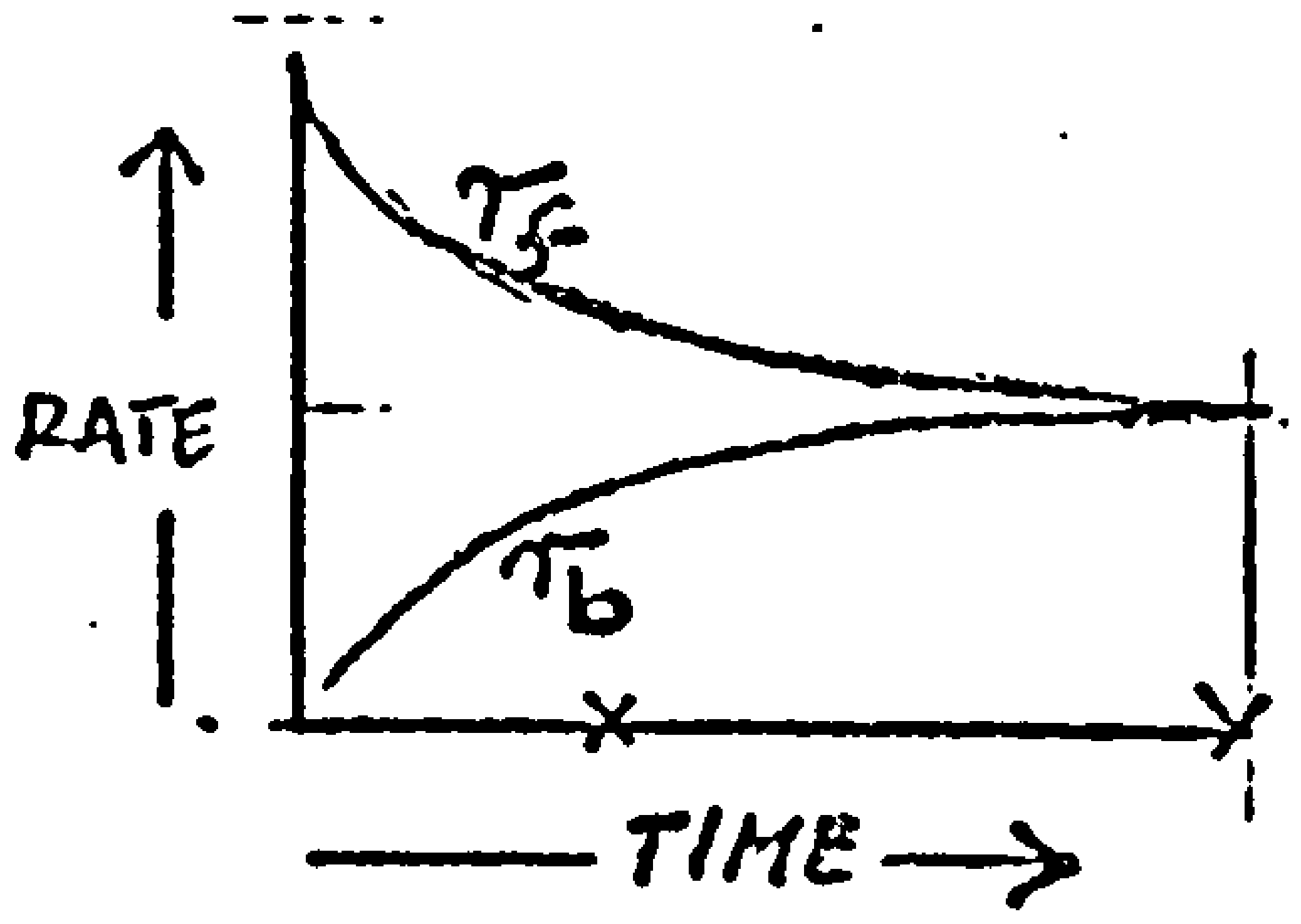
The initial concentration of a reactant is 1 mol l$^{-1}$

a) What is the concentration of reactant and of product at time $T_1$?

b) What has happened at time $T_1$?

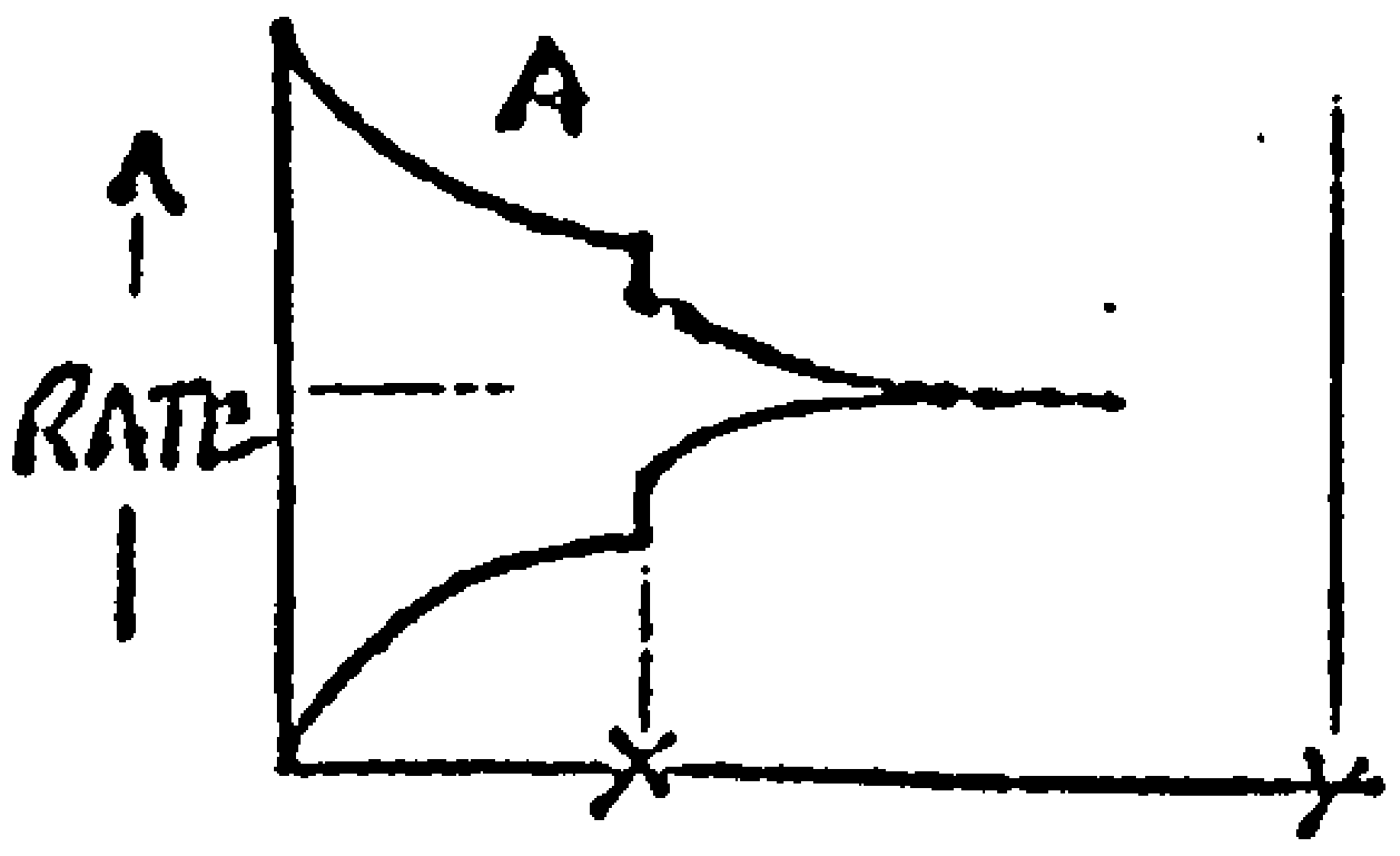
c) What is happening between $T_1$ and $T_2$?

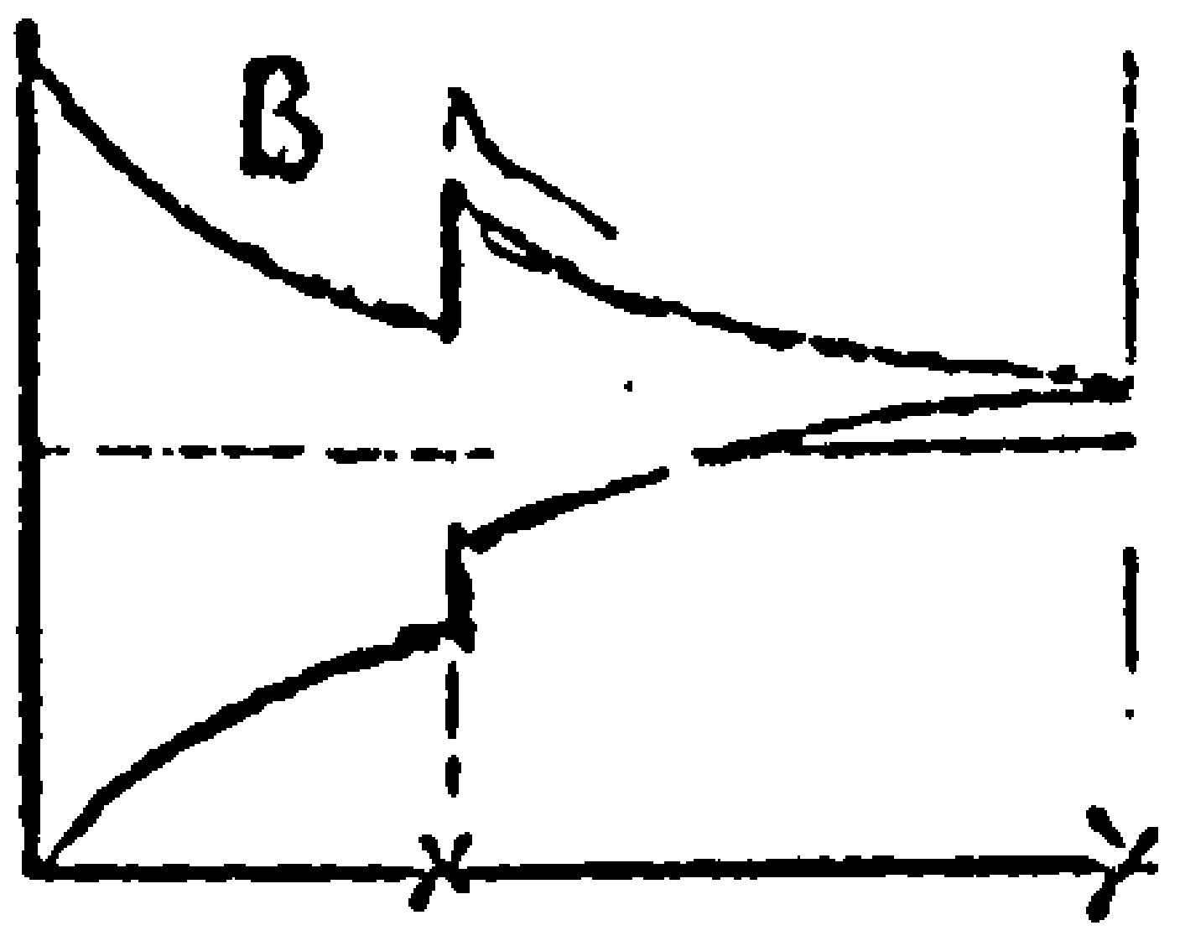
3.15 As a non-equilibrium system approaches equilibrium the forward and back ward rates of reaction become equal.

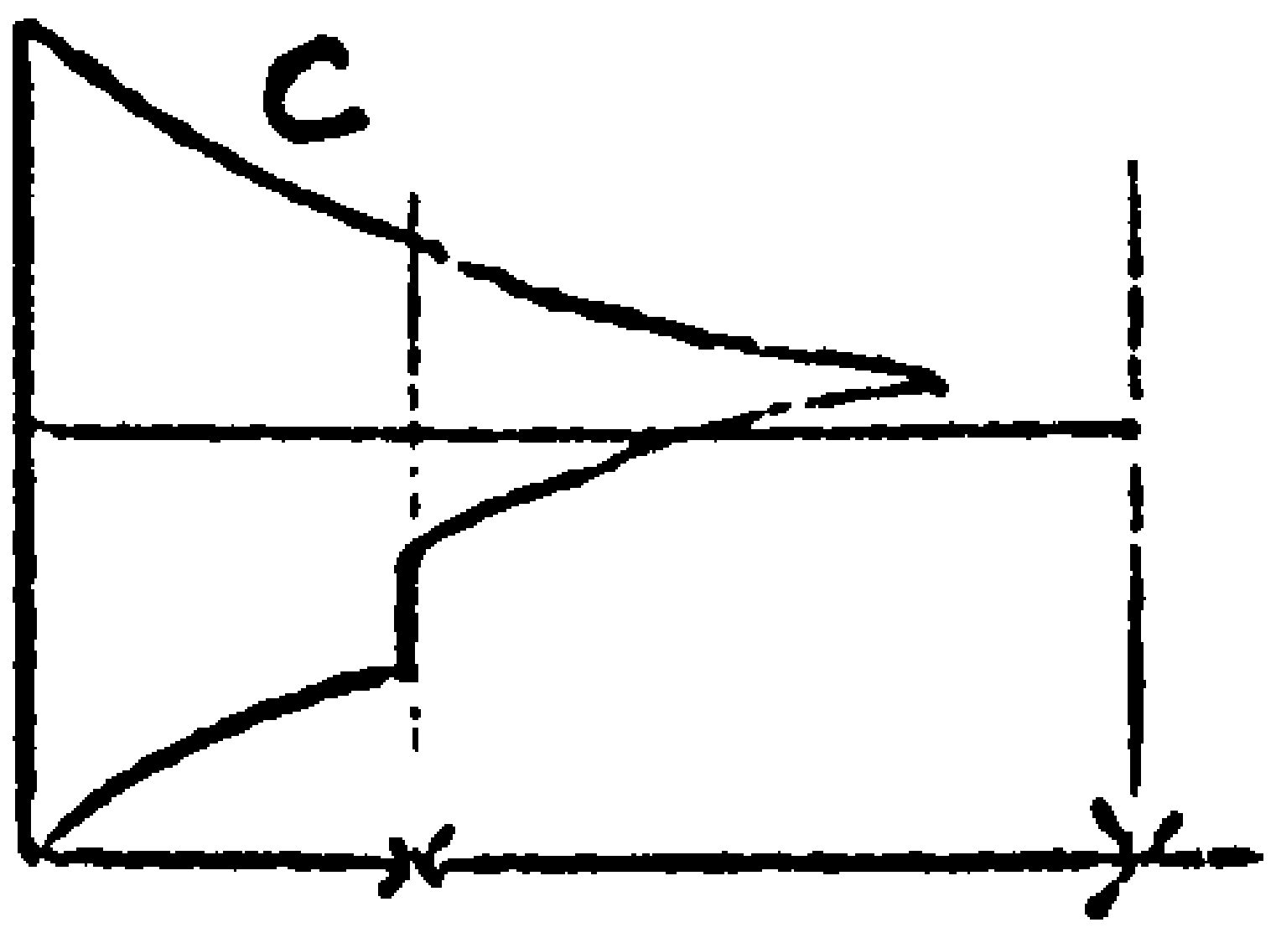


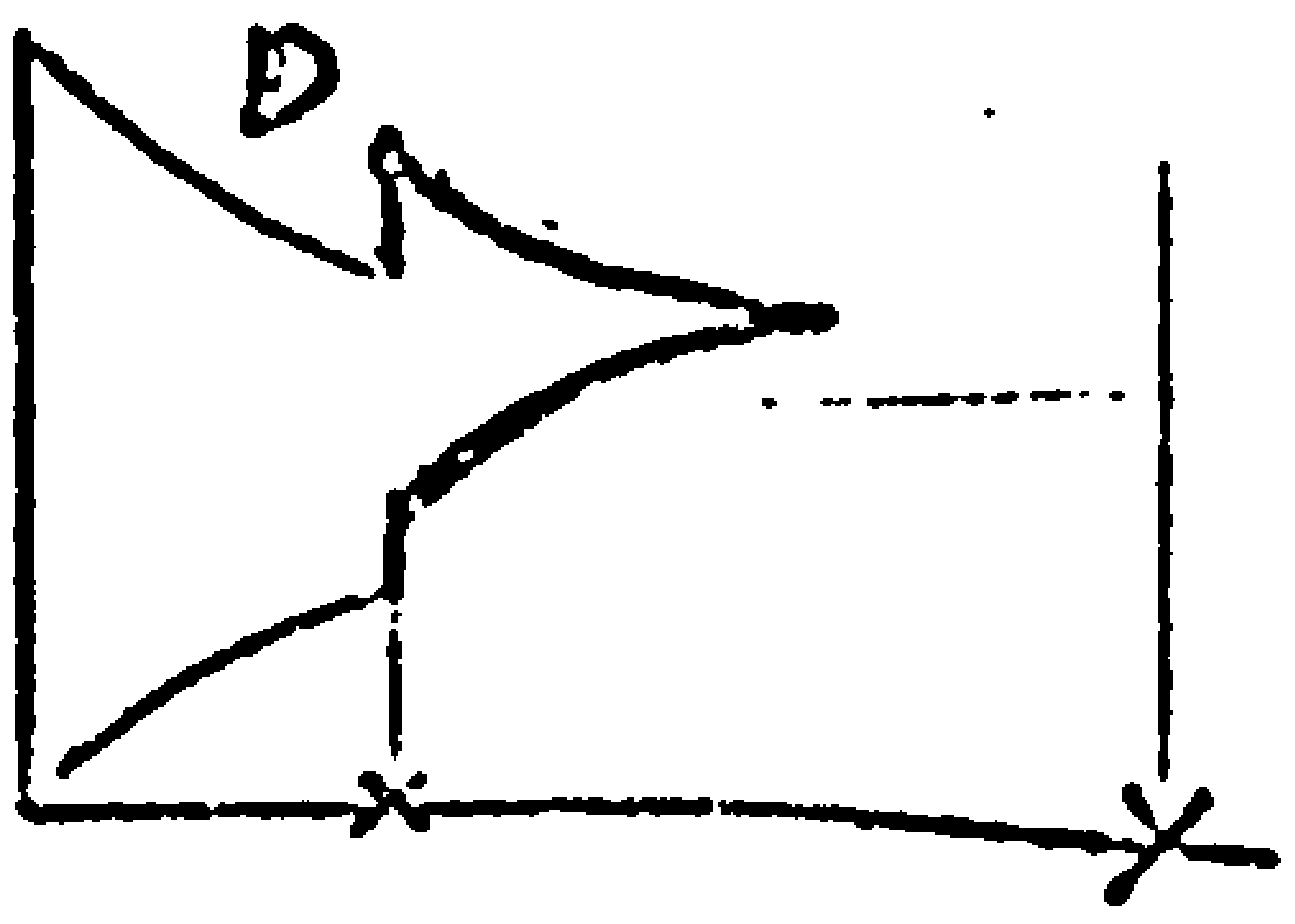
If a catalyst were added at time $T_x$ what would happen to $r_f$ and $r_b$?

The following graphs are possible solutions. (The meaning of each graph will be explained if required.)









3.16 Arrange the following topics in a logical sequence.

Activated complex - rate determining step - activation energy.

3.17 When equilibrium is established in the system:

$$A + B \rightleftharpoons C + D$$

the percetage of A, the percentage of B, the percentage of C and the percentage of D are all constant, and of course add up to 100%.

Among which species are collisions occurring?

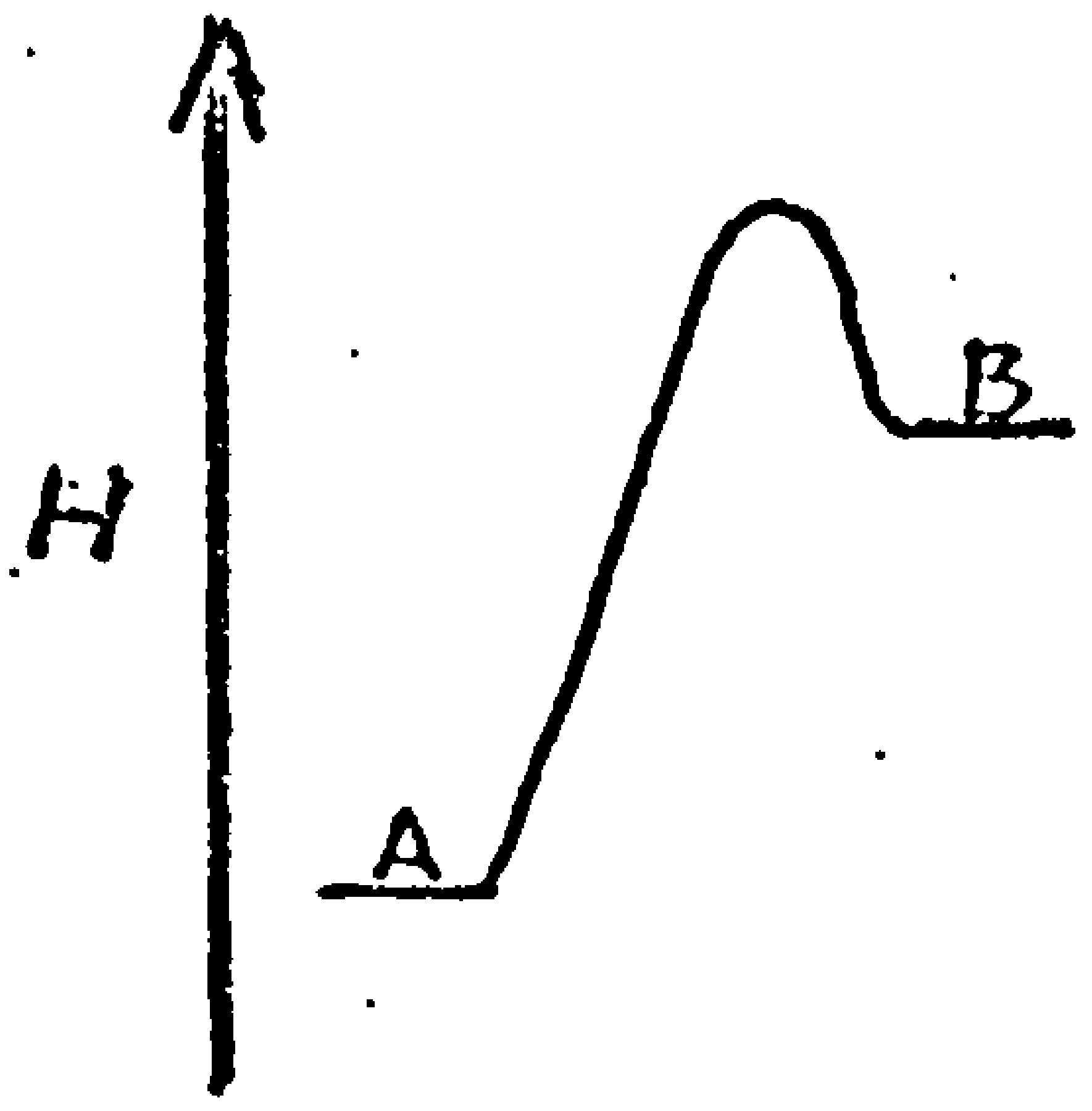
A As are colliding with Bs only.

B As are colliding with Bs while Cs are colliding with Ds, ONLY.

C As, Bs, Cs and Ds are all colliding with each other.

D As are colliding with Ds while Bs are colliding Cs, ONLY.

3.18



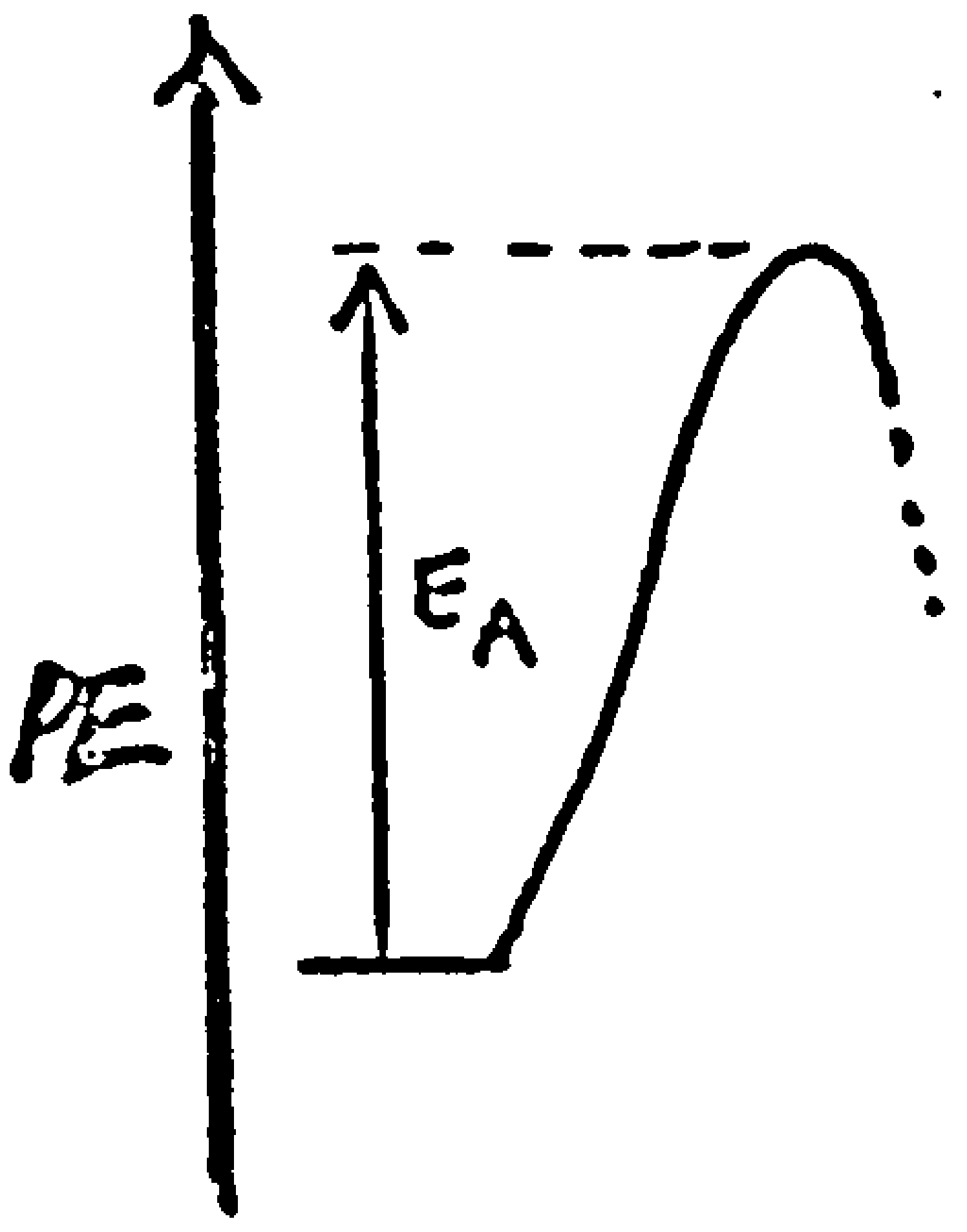
The enthalpy diagram shown opposite refers to the equilibrium

$$A \rightleftharpoons B$$

a) At equilibrium, which species will there be most of - A or B?

b) If the temperature is increased both forward and backward rates are increased. Which is increased most?

3.19



$E_A$ is the activation energy of a particular reaction.

If the temperature is increased, will the activation energy at the higher temperature be

A just the same,

B less,

C more,

D impossible to specify?

3.20 How can heat be given out without decrease of temperature?

When water at 100 °C absorbs heat and changes to steam at 100 °C

A the potential energy of the molecules remains the same but their kinetic energy is different.

B the potential energy of the molecules increases but their kinetic energy remains the same.

C Both the potential energy and the kinetic energy of the molecules increase.

3.21 The word 'yield' often arises in discussing the industrial operation of reversible reactions, frequently in the context 'a catalyst improves the yield'.

What does yield mean to you?

Is it

A the percentage of product in the mixture at equilibrium?

B the mass of product which can be extracted from the reaction chamber before or at equilibrium?

C what you get in a given time?

# POCKET ITEM 2

# RATES APPROACH TEST

UNIVERSITY of GLASGOW

Research in Chemical Education

## CHEMICAL EQUILIBRIUM

Dear pupil,

You are asked to consider the following questions which deal directly or indirectly with the topic of chemical equilibrium.

The questions are of familiar construction, one of the four options A to D being correct in each question. An additional option E has, however, been added to each question.

These questions have been designed, not so much to test your ability in this area of chemistry, more to find out which aspects of chemical equilibrium cause you trouble. It is therefore very important that you select option E if you do not know which option is the correct one. Please do not guess.

Some questions are marked thus **. I should like, in these instances, to know the reasoning which led you to make your choice. Will you, therefore, please write a brief note to this effect on page eight.

| | |
|---|---|
| Your name: | |
| Were you awarded an A, B or C pass in O-grade chemistry? | |
| What certificate course have you followed in biology? | |
| What certificate course have you followed in physics? | |

Before beginning the paper, please note:

a) The enthalpy change quoted after a chemical equation refers to the 'left to right' direction. Thus, ΔH -ve means that the forward reaction evolves heat while the backward reaction absorbs heat.

b) An 'equilibrium system' is contained by a closed vessel. Addition or removal of material is considered to be made through a valve as required, but heat can pass in either direction through the walls of the vessel.

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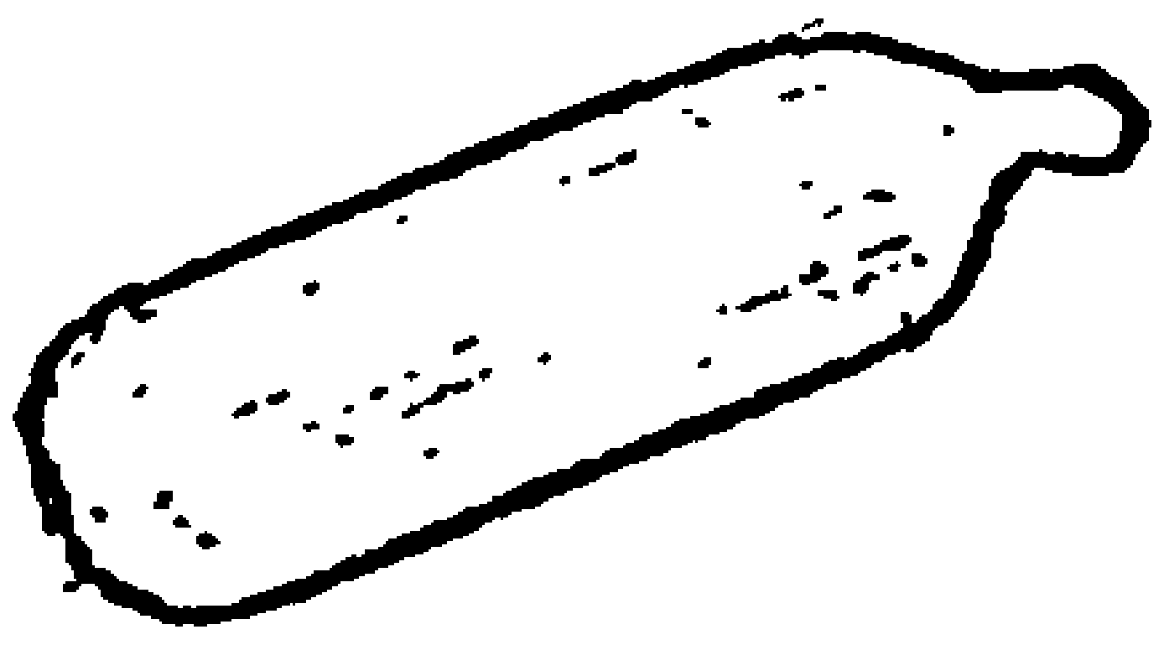


1. A sealed ampoule contains a mixture of dinitrogen tetroxide and nitrogen dioxide at equilibrium:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H \text{ +ve}$$

When the temperature of the bulb is increased, the pressure of the gas will unavoidably be increased at the same time. Considering these two effects <u>separately</u>, which of the following options correctly describes their effects on the equilibrium system?

| | Because of the temperature rise, equilibrium will ... | Because of the pressure rise, equilibrium will ... |
|---|---|---|
| A | shift to the left. | shift to the left. |
| B | shift to the left. | be unaffected. |
| C | shift to the right | shift to the left. |
| D | shift to the right | be unaffected. |
| E | I do not know which option is correct. | |

---

2. If a catalyst can increase the rate of the forward reaction in an equilibrium system, how will it affect the rate of the backward reaction

A It will have no effect.
B It will increase the backward rate.
C It will decrease the backward rate.
D It depends on the equilibrium system.
E I do not know.

---

** ** 3. Which of the following is a <u>reliable</u> way of deciding if a mixture is in a state of chemical equilibrium?

A When the mixture is heated its composition changes.
B When a catalyst known to be effective in the reaction is added, the composition of the mixture remains the same.
C The composition of the mixture does not change with time.
D When the mixture is compressed its composition remains the same.
E I do not know which of these options is correct.

---

4. When equilibrium is established in the system

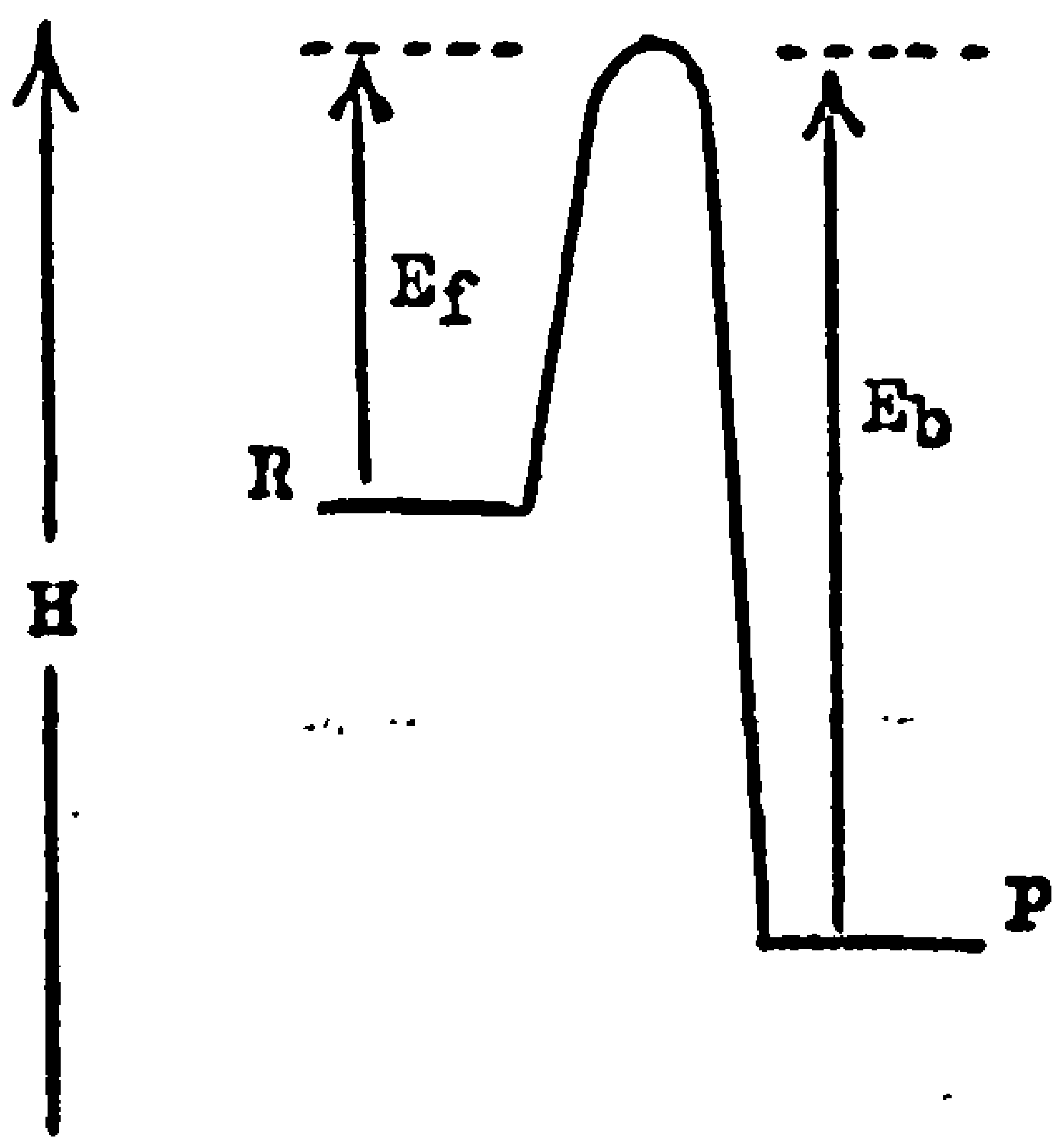
$$P + Q \rightleftharpoons R + S$$

the percentage of each of the four constituents is constant, i.e. the mixture has a constant composition.

Among which species are collisions occurring?

A Ps are colliding with Qs while Rs are colliding with Ss only.
B Ps, Qs, Rs and Ss are all colliding with each other.
C Ps are colliding with Ss while Qs are colliding with Rs only.
D Collisions between Ps and Qs and between Rs and Ss are no longer occurring.
E I do not know which of these options is the correct one.

5. In the context of an enthalpy diagram, activation energy is viewed as a "hurdle" to be overcome if reactants are to change into products, and vice versa.



In a particular system at equilibrium, the forward activation energy, $E_f$, is less than the backward activation energy, $E_b$.

Select the correct statement:

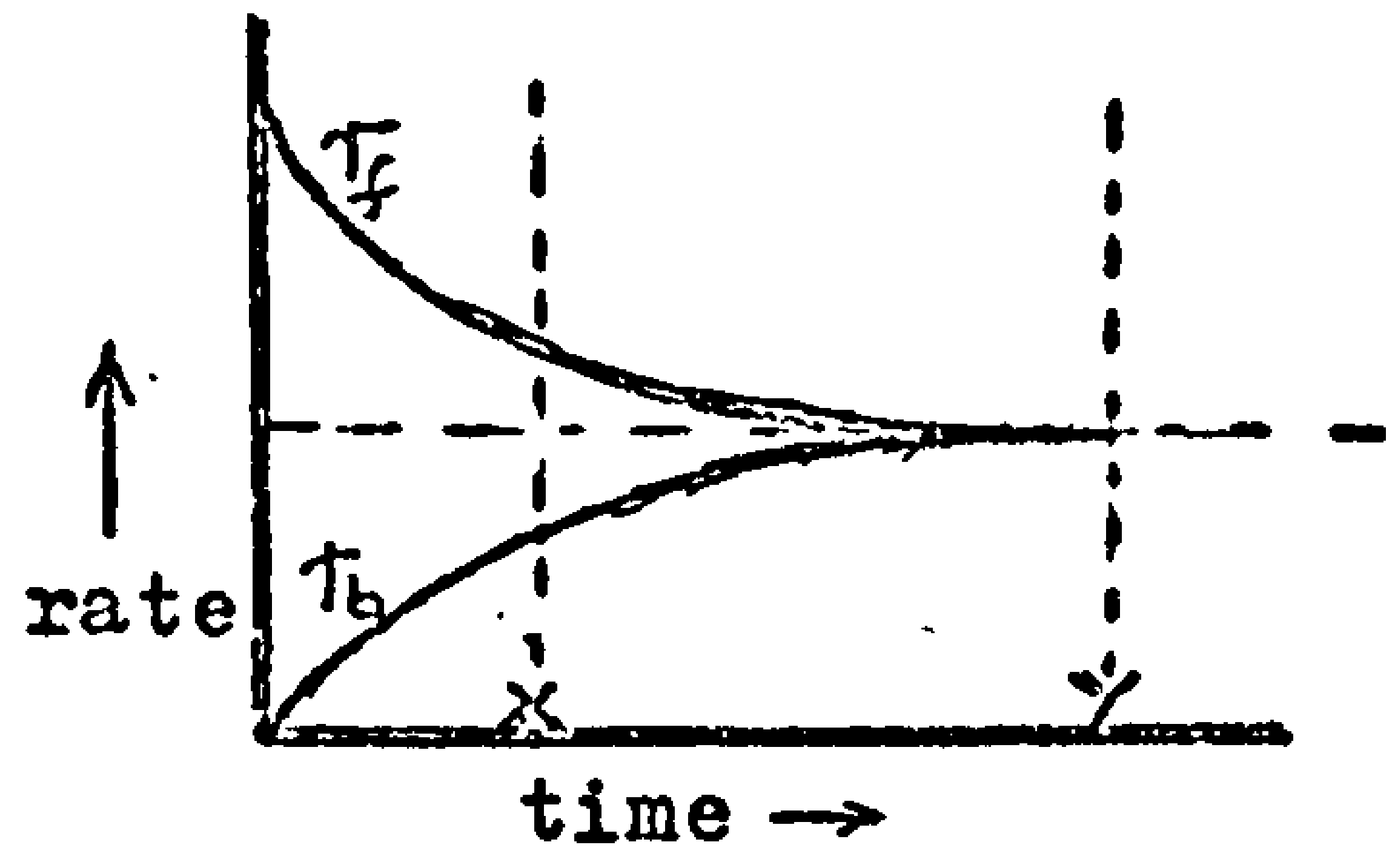
A The forward rate of reaction will be greater than the backward rate of reaction.
B The backward rate of reation could be zero.
C Both forward and reverse rates of reaction are equal.
D The equilibrium mixture will have a higher percentage of product than reactant.
E I do not know which is the correct statement.

---

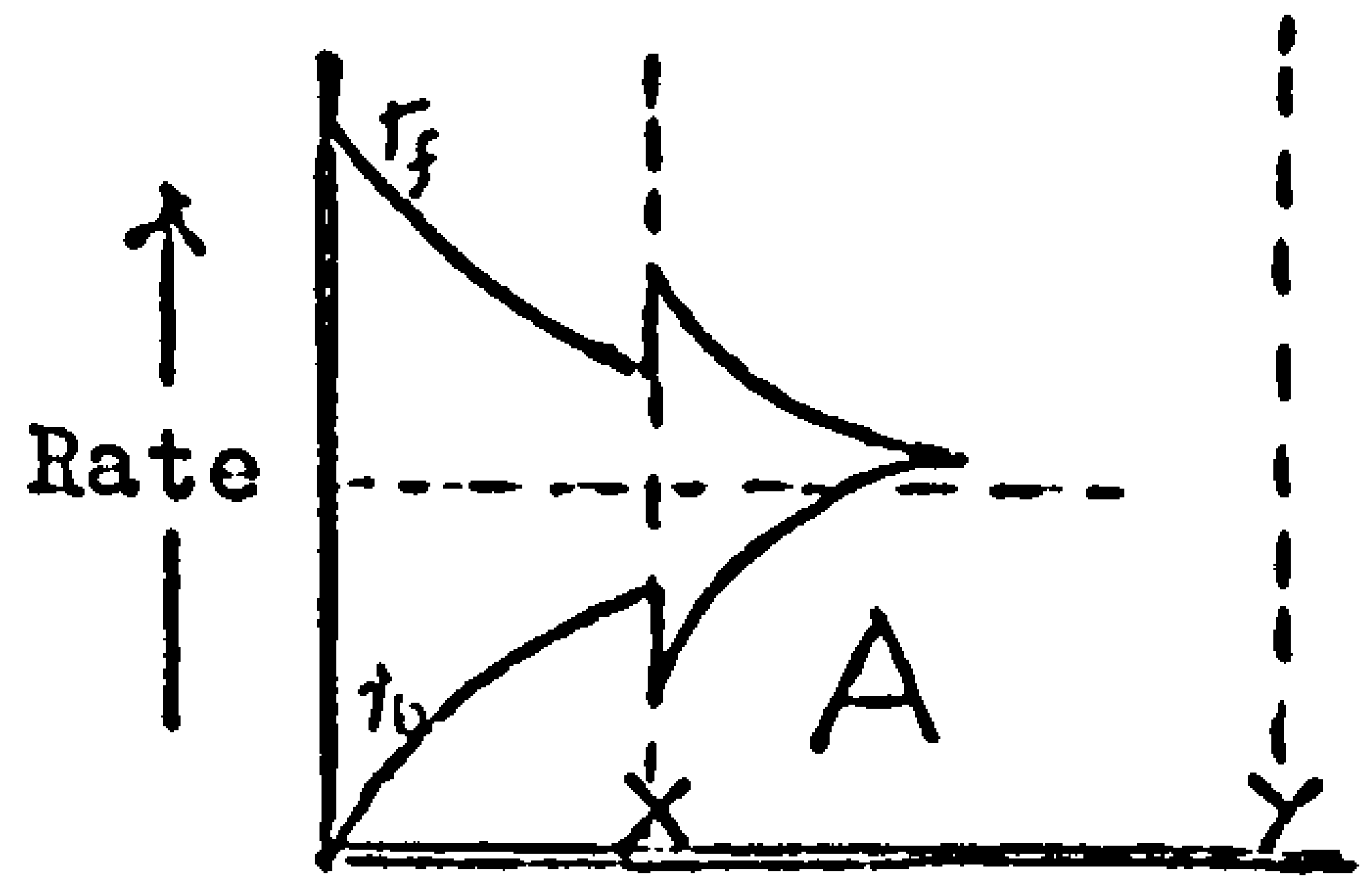
* 6. Which of the following lists contains an 'odd man out'?

Oxygen, petrol, mist, sawdust.
Sand, steam, fluorine, paraffin.
Ethanol, flour, heat, nitrogen.
Chlorine, methanol, silica, vapour.
I do not know.

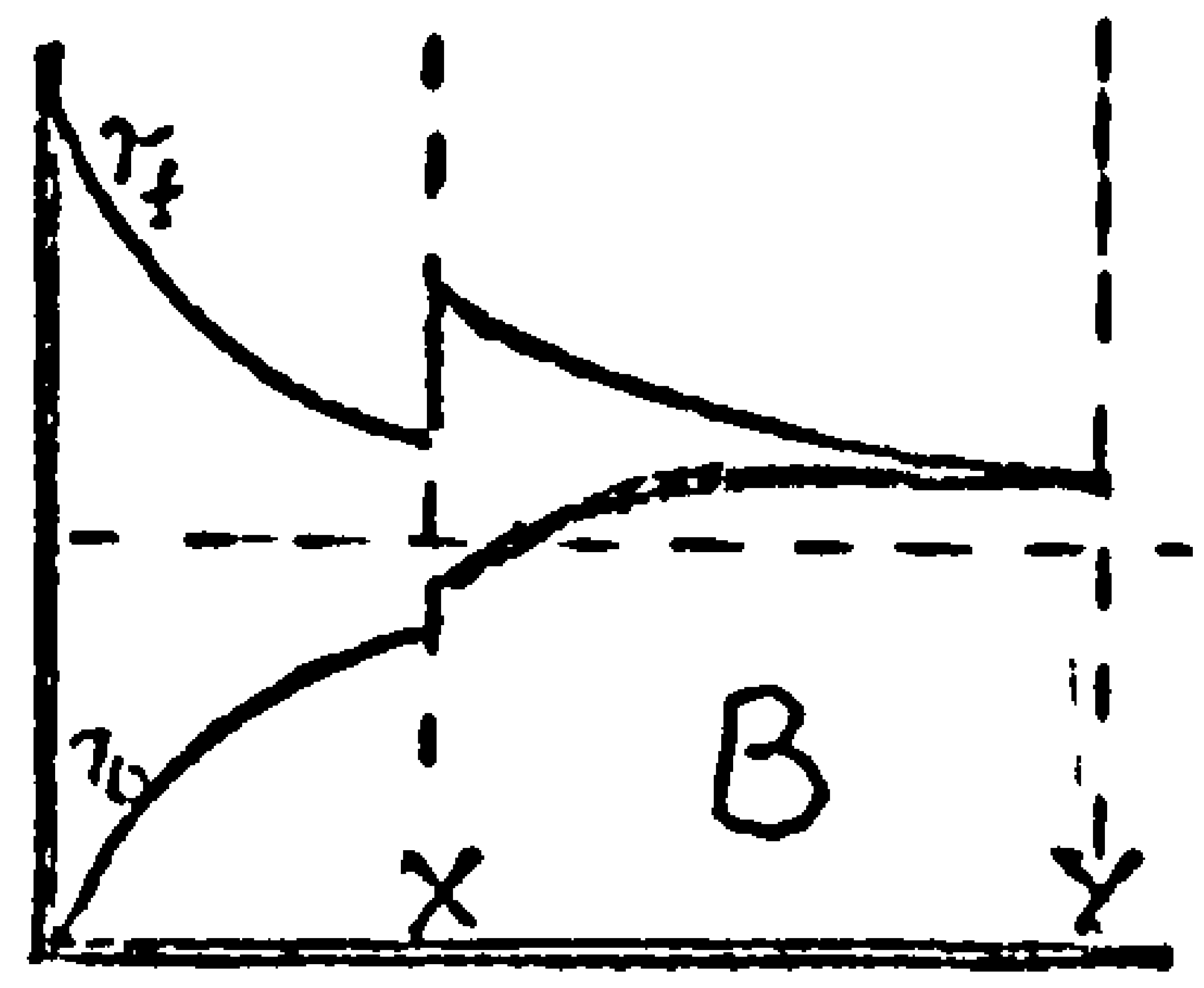
7. As a non-equilibrium system approaches equilibrium the forward and backward rates of reaction become equal, thus:



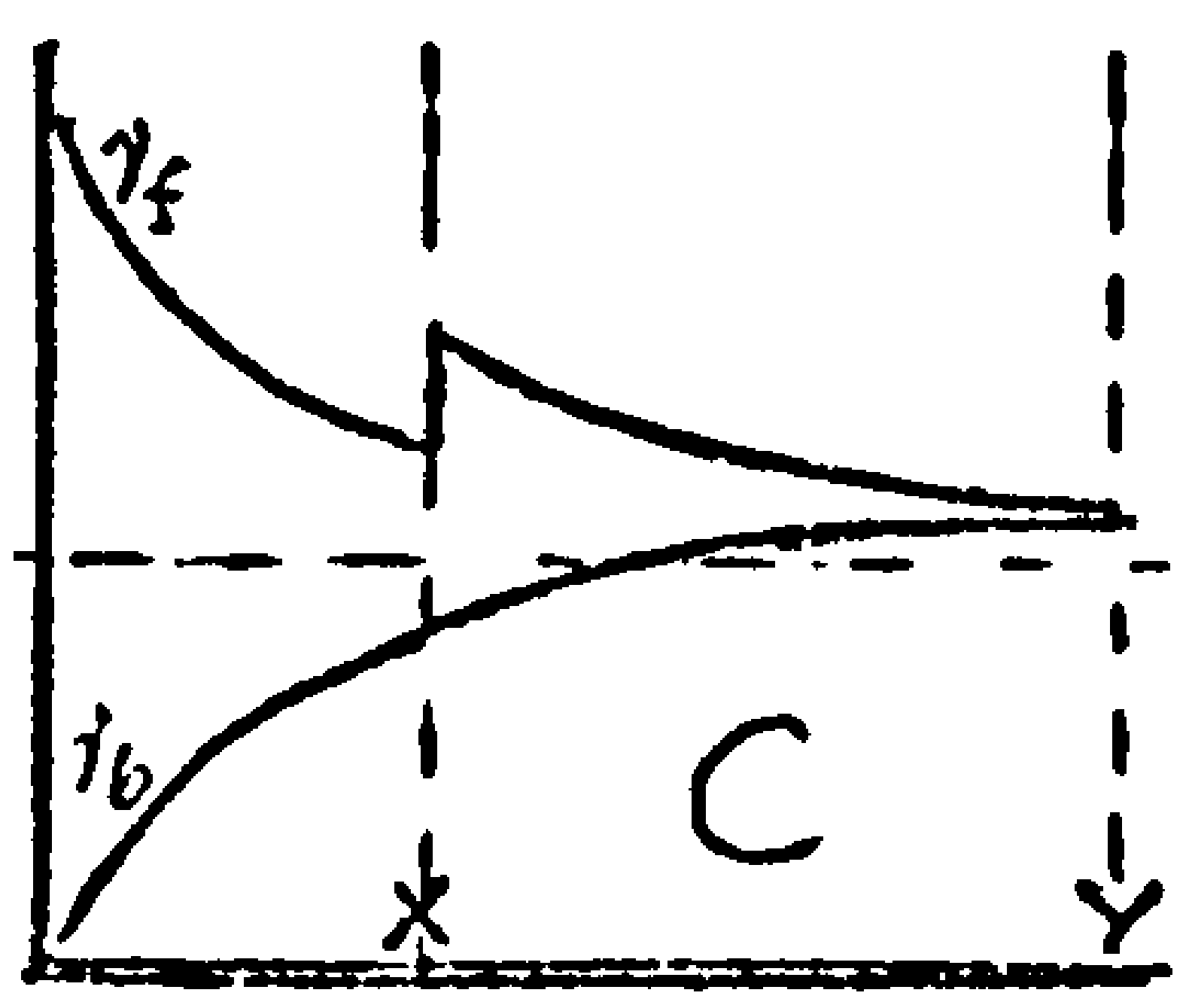
If a catalyst were added at time X, what effect would it have on the forward and/or backward rate of reaction?



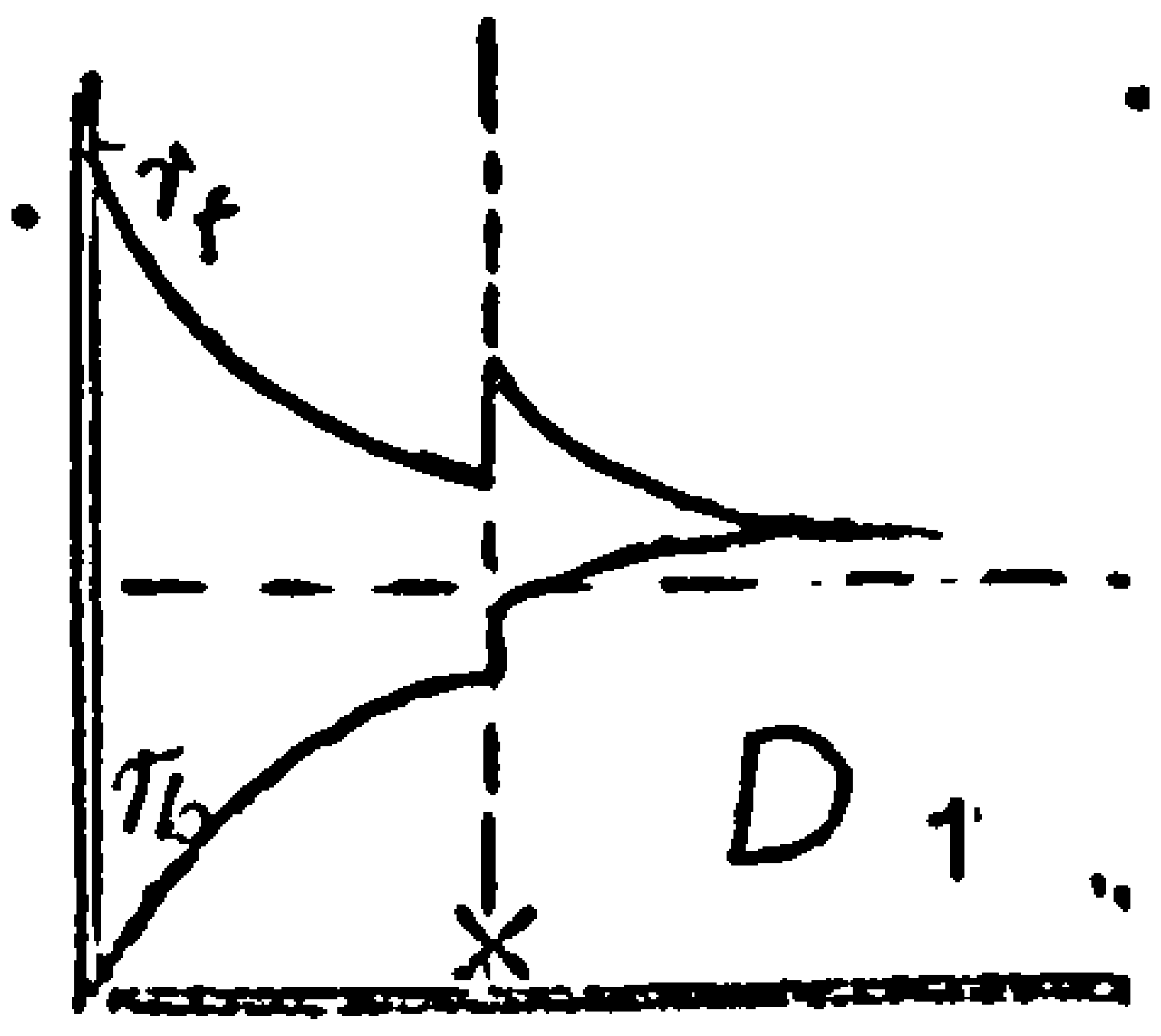
$r_f$ increased;
$r_b$ decreased;
equilm. sooner.



$r_f$ increased;
$r_b$ increased;
equilm. in same time.



$r_f$ unaffected;
$r_b$ increased;
equilm. in same time.



$r_f$ increased;
$r_b$ increased;
equilm. sooner.

E I do not know.

($r_f$ = forward rate; $r_b$ = backward rat

7

8. Here is an equilibrium system which you probably first encountered in Form III:

$$H_2O(aq) \rightleftharpoons H^+(aq) + OH^-(aq)$$

Only about one molecule of water in every 500 000 000 or so is ionised at any one instant in time.

Which of the following statements is correct?

A Both forward and reverse rates are equal.
B The reverse rate is greater than the forward rate.
C Most water molecules never suffer ionisation.
D The forward rate is greater than the reverse rate.
E I do not know which option is correct.

---

9. In the familiar Haber system at equilibrium

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

the application of increased pressure to the right hand side <u>only</u> will drive the equilibrium to the left.

How would you comment on this statement?

A It is correct.
B It is incorrect; the equilibrium would in fact be driven to the right.
C It is quite unreasonable, and impracticable.
D It is correct as long as the nitrogen and hydrogen are continuousl removed.
E I do not know which option to choose.

---

10. An equilibrium exists between undissolved and dissolved salt, which determines the maximum solubility of the salt at a given temperature.

Manganese sulphate dissolves with liberation of heat:

$$MnSO_4(s) + aq \rightleftharpoons MnSO_4(aq) \qquad \Delta H \text{ -ve}$$

At a higher temperature will its maximum solubility be

A more?
B the same?
C less?
D unpredictable?
E I do not know.

---

** 11. When water at 100 °C absorbs heat and changes to steam at 100 °C,

A the potential energy of the molecules remains the same but their kinetic energy increases.
B the kinetic energy of the molecules remains the same but their potential energy increases.
C both the potential energy and kinetic energy of the molecules increase.
D neither the potential energy nor the kinetic energy of the molecules increases.
E I do not know how the potential energy and/or the kinetic energy of the molecules is affected.

12. Which of the following is a correct description of a catalyst?

A It supplies energy to the reactants so enabling them to react more quickly.
B It is a substance which has no effect on the reactions occurring in a system at equilibrium
C It ensures that reactants are more quickly and more completely converted into products.
D It offers a less "energy requiring" alternative reaction mechanism.
E I do not know which of these is a correct description of a catalyst.

---

13. Ammonia dissolves and reacts with water; the following equilibrium is set up:

$$NH_3(aq) + H_2O(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

When ammonium ion is added (in the form of ammonium chloride, which dissolves with negligible volume change), what will happen to the mass of hydroxyl ion in solution?

A It will increase.
B It will remain the same.
C It will decrease.
D It is not possible to say without more information.
E I do not know what will happen to the mass of hydroxyl ion in solution.

---

14. Nitrogen monoxide mostly decomposes when heated:

$$2NO \longrightarrow N_2 + O_2$$

<u>On this evidence</u> decide which of the following statements is correct.

A The forward reaction absorbs heat.
B Nitrogen monoxide would decompose at room temperature except that it lacks activation energy at this low temperature.
C If allowed to cool, the nitrogen and oxygen would tend to recombine to reform nitrogen monoxide.
D It is not possible to say whether the forward reaction is exothermic or endothermic.
E I do not know which of these statements is correct.

---

15. Ethanoic acid dissolves and reacts with water; an equilibrium is set up according to:

$$CH_3COOH(aq) + H_2O(aq) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

When ethanoate ion is added (in the form of sodium ethanoate, which dissolves with negligible volume change), what will happen to the concentration of hydroxonium ion.

A It will increase.
B It will remain the same.
C It will decrease.
D It is not possible to say without more information.
E I do not know.

16. A reaction vessel of fixed volume contains an equilibrium mixture of hydrogen iodide, hydrogen and iodine:

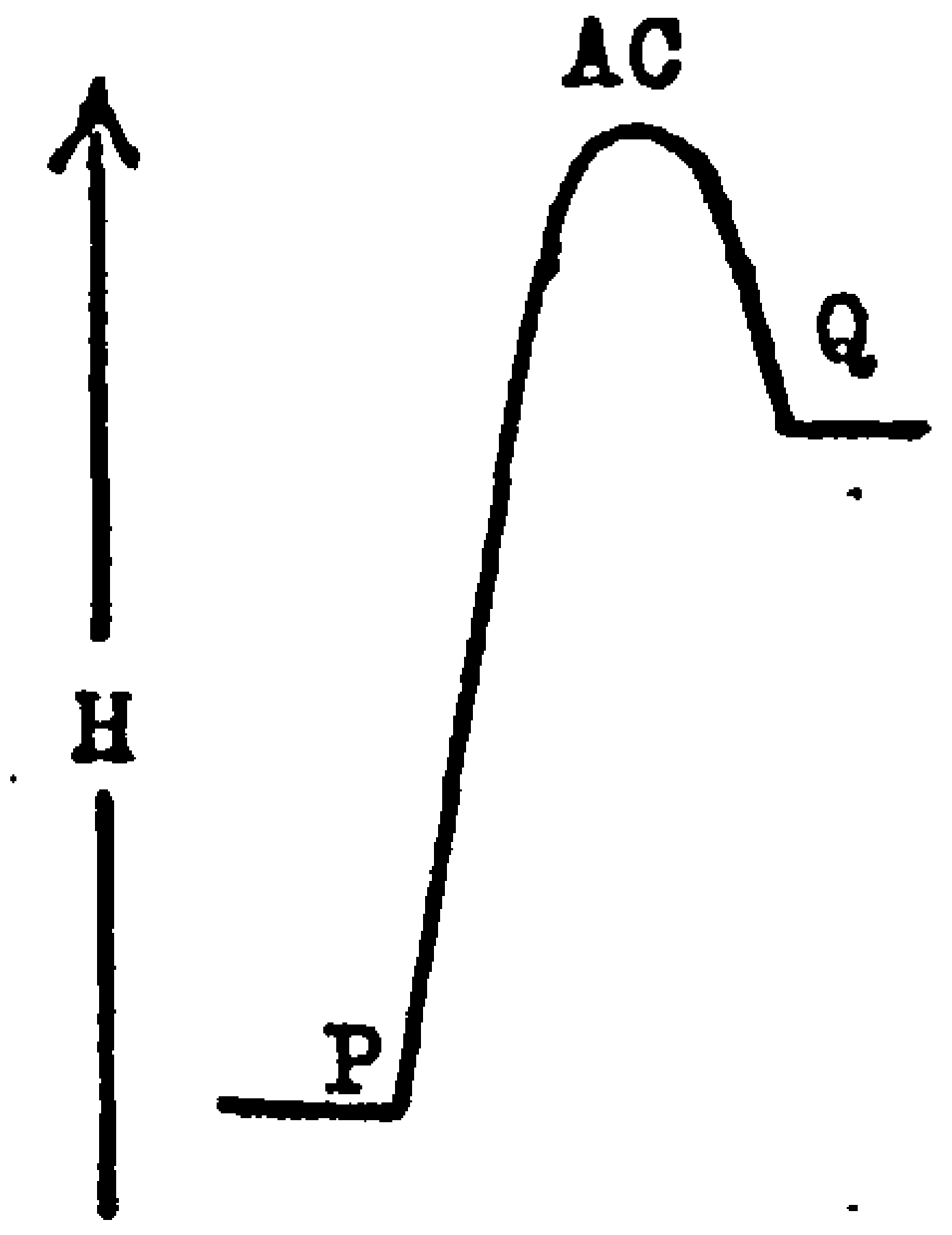
$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

If some hydrogen gas be added to the reaction vessel, what will happen to the mass of iodine gas in the vessel?

It will decrease.
It will remain the same.
It will increase.
It is not possible to say without more information.
I do not know.

---

17. The accompanying enthalpy diagram refers to the equilibrium:



$$P \rightleftharpoons Q$$

In the equilibrium mixture of P and Q,

A the proportion of P will be greater than that of Q.
B the proportion of P will be less than that of Q.
C the forward rate of reaction will be less than the backward rate.
D it is not possible to say whether P or Q will have the higher proportion.
E I do not know which of these options to choose.

---

18. Contrast the following equilibria:

1. $C_2H_5NH_2(aq) + H_2O(aq) \rightleftharpoons C_2H_5NH_3^+(aq) + OH^-(aq)$
2. $NH_3(aq) + H_2O(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

and decide which of the following statements is correct.

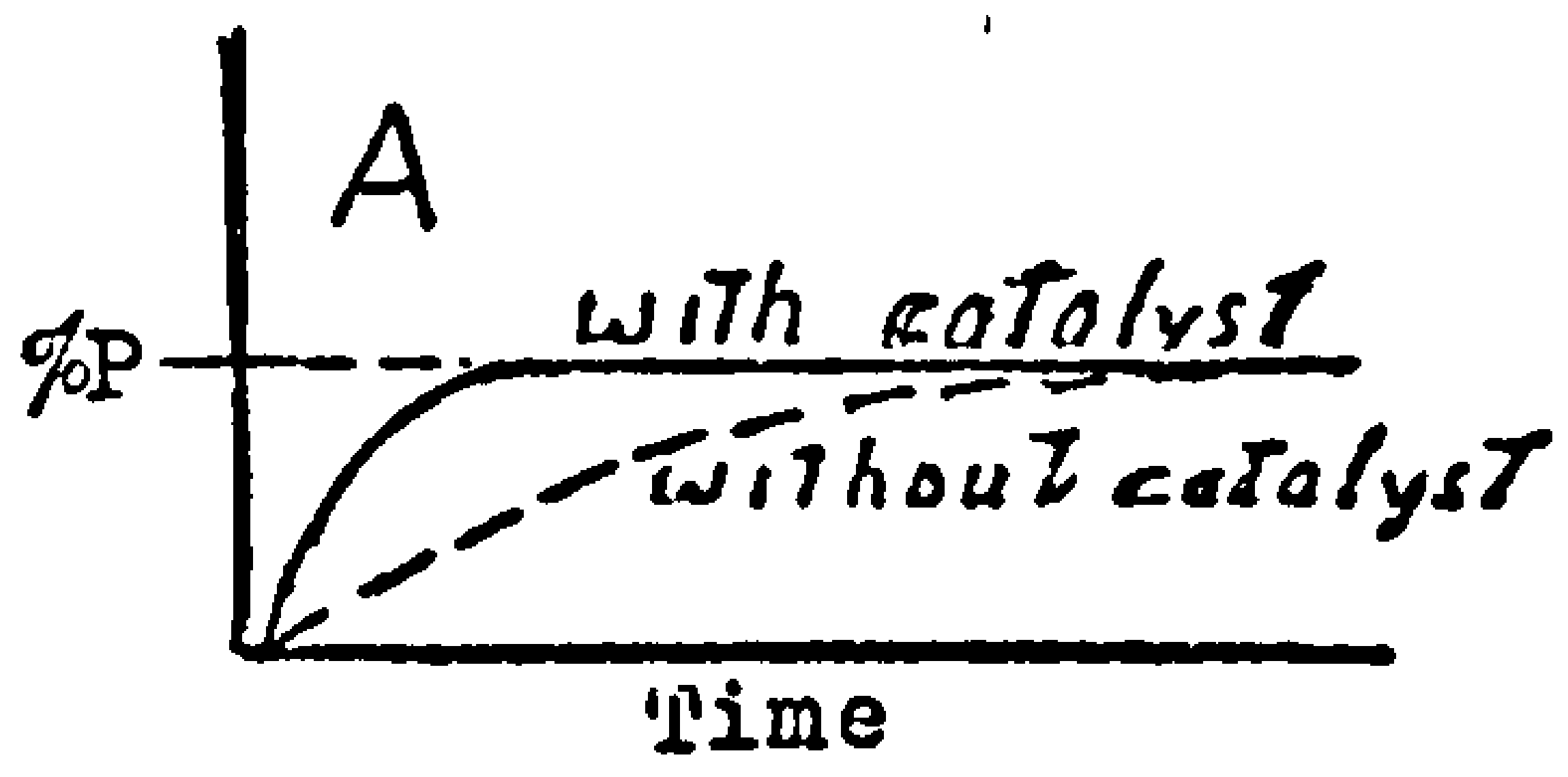
A In each of them, the reverse rate of reaction is greater than the forward rate of reaction.
B The forward rate of reaction in 1 is greater than the forward rate of reaction in 2.
C In each, the forward and reverse rates are equal, and system 1 contains a higher percentage of product than system 2.
D The percentage of reactant in each system is the same.
E I do not know which of these statements is correct.

---

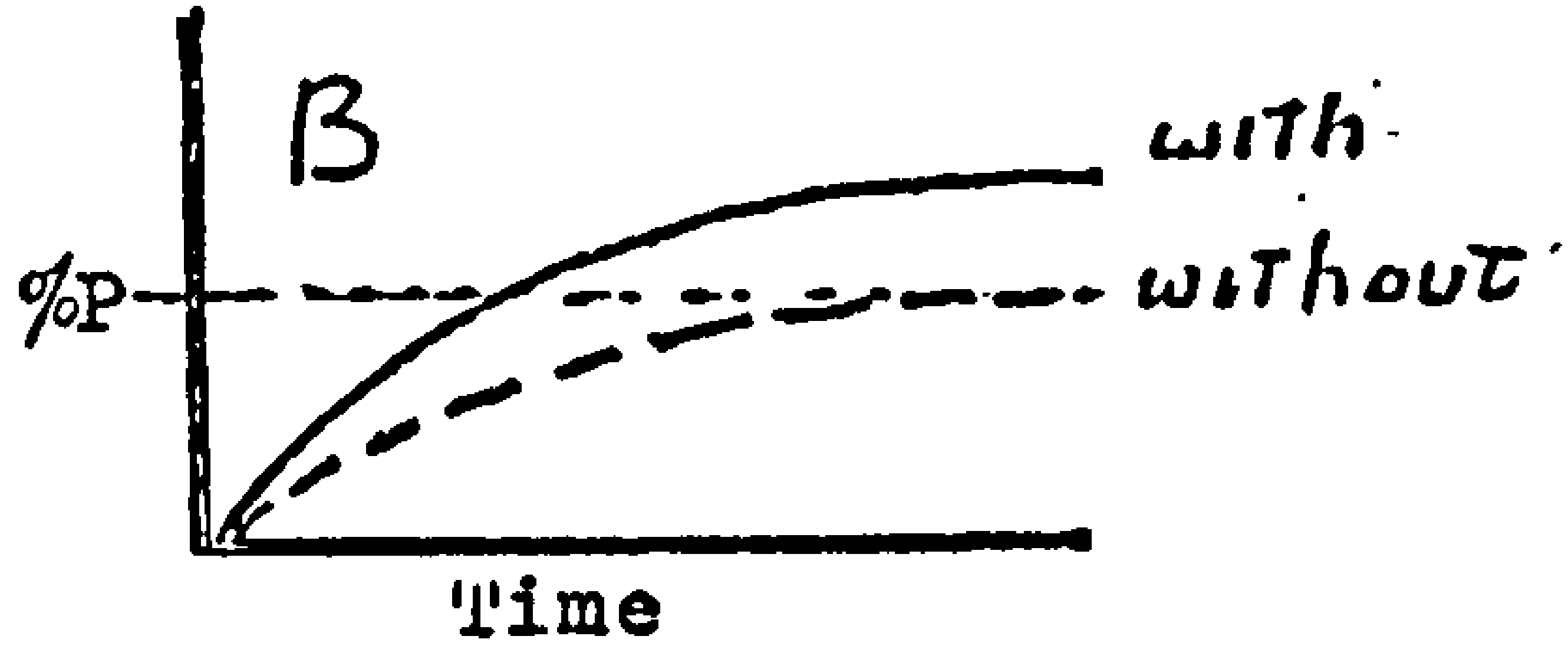
19. Which of the following correctly describes the action of a catalyst?

A It acts as a "market square", facilitating exchange of energy between reactant molecules and between product molecules.
B It causes more product to be formed at equilibrium, which equilibrium is also caused to be established sooner.
C It is a substance which can be used to drive an equilibrium in the desired direction.
D It is a substance which has no effect on the system at equilibrium
E I do not know which of these options is a correct description of a catalyst.

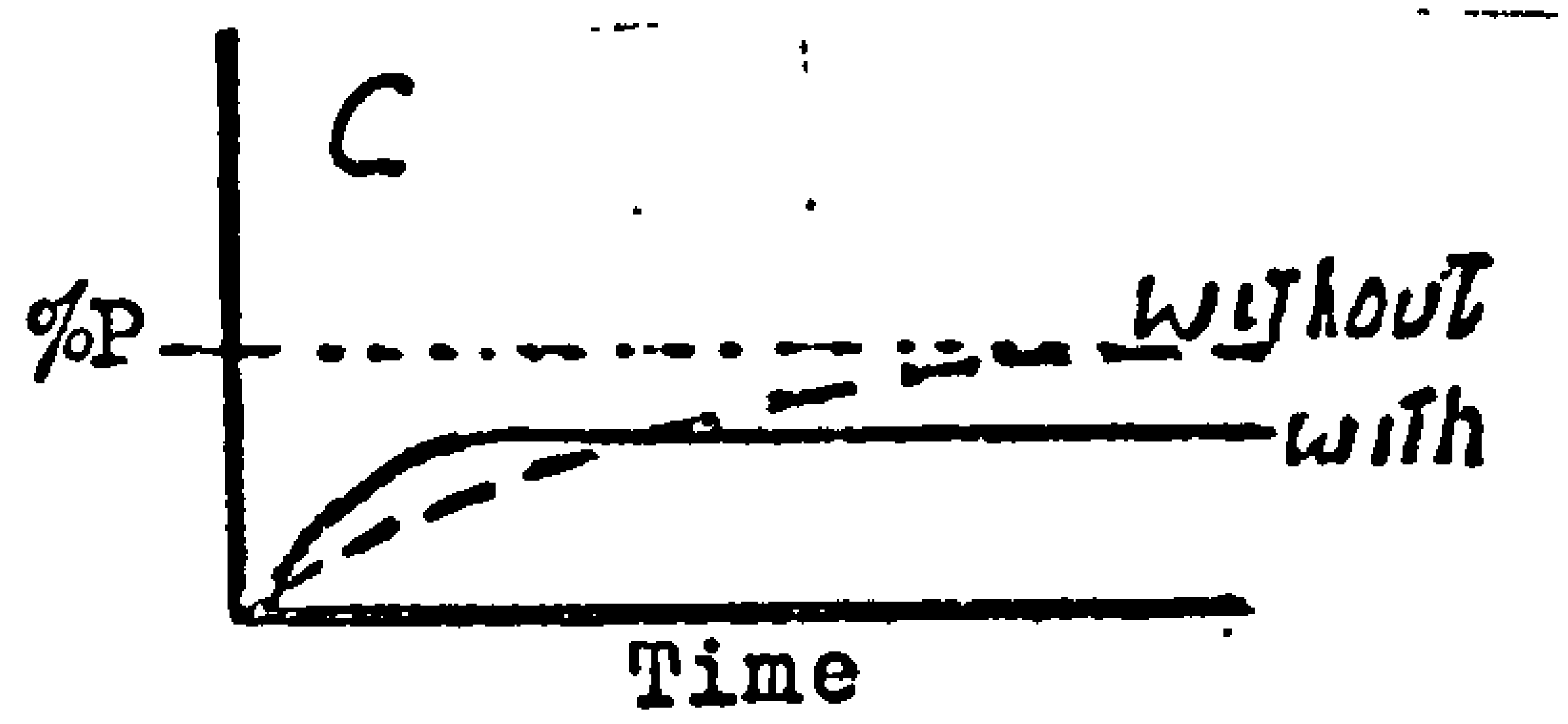
20. Which of the following graphs represents the effect of a catalyst on the formation of product in a mixture approaching equilibrium?



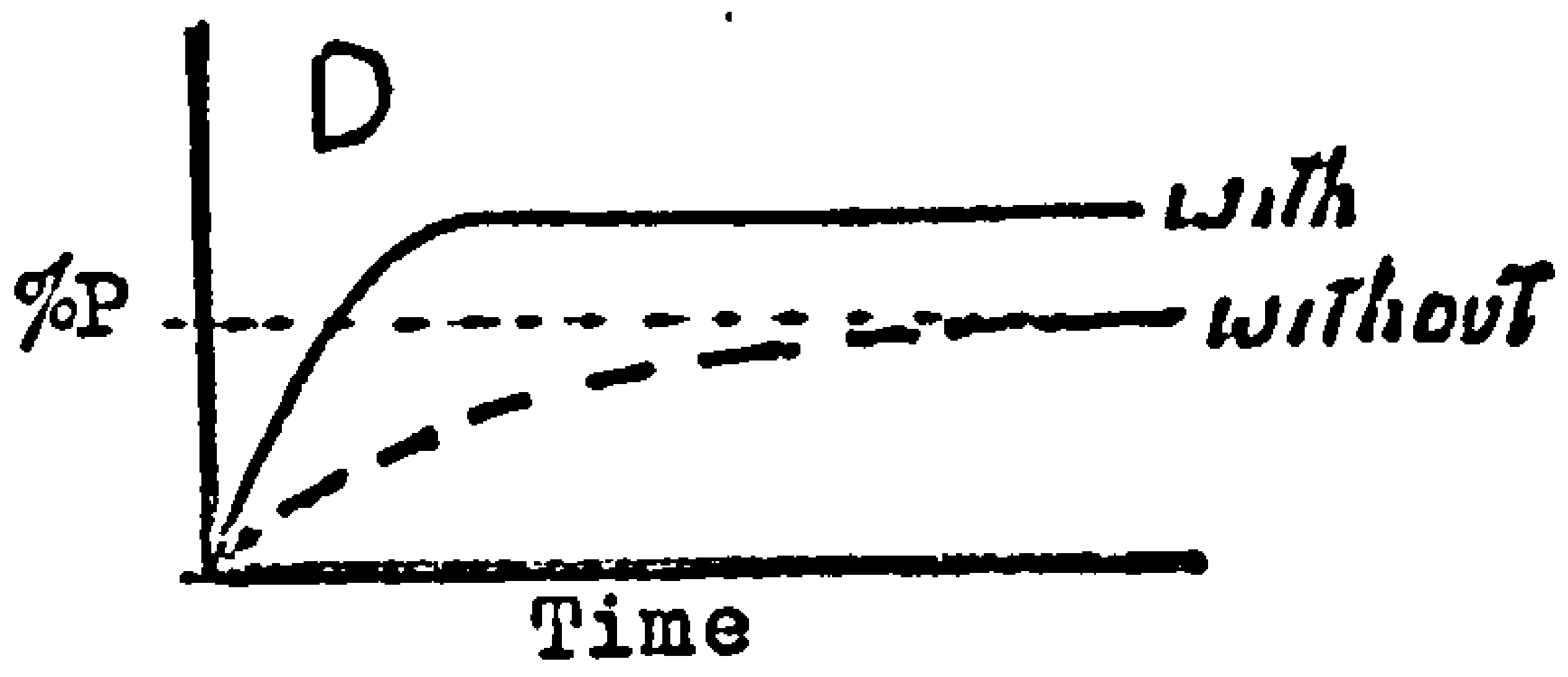
Same equilibrium % product, but obtained sooner.



Greater equilibrium % product after same time.



Smaller equilibrium % product, but obtained sooner.



Greater equilibrium % product, and obtained sooner.

E I do not know.

---

21. Which one of the following lists differs in a significant way from the other three?

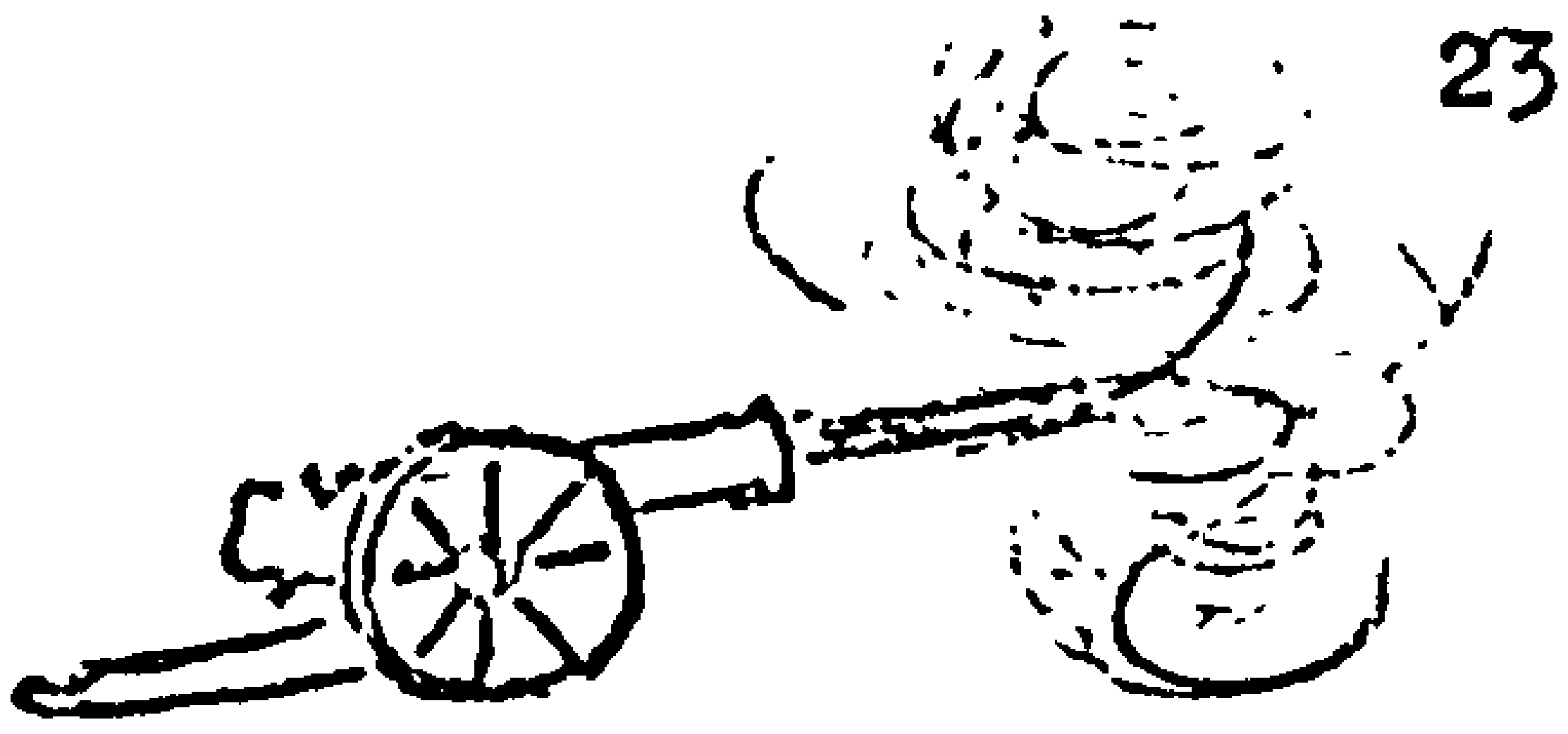
A Copper, heat, neon.
B Helium, tin, water.
C Argon, zinc, light.
D Gold, sound, krypton.
E I can see no significant difference between these lists.

---

22. What is the effect on an <u>individual</u> molecule of raising the temperature of the gas?

A The molecule travels faster.
B The molecule becomes hotter.
C The molecule's average speed is greater.
D It is not possible to say.
E I do not know.

---



23. When a cannon is fired blank, x joules of heat are produced in and around the canon.

When an identical charge of powder is used to fire off a canon-ball, y joules of heat are produced in and around the canon.

Which of the following statements is correct?

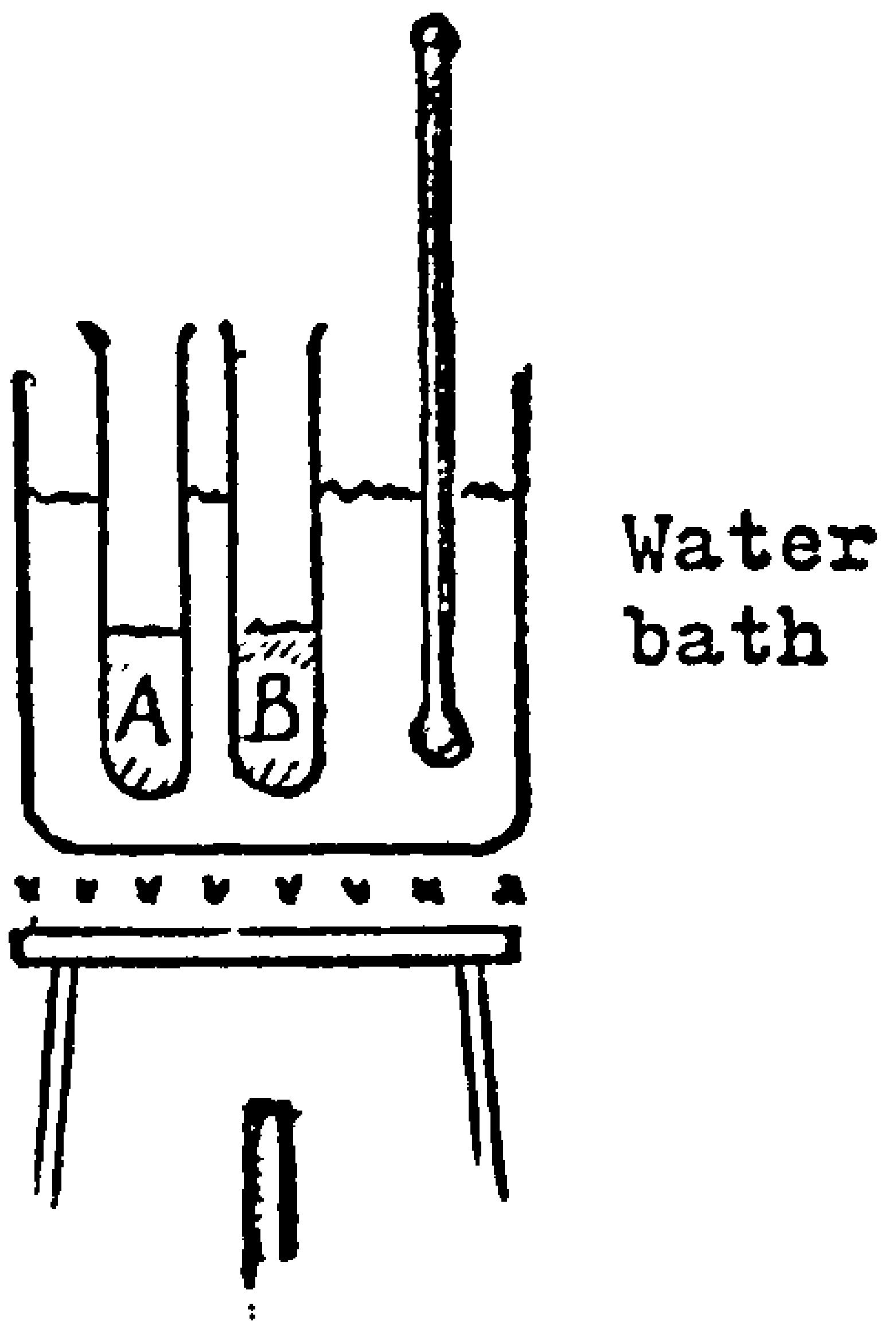
A x is greater than y.
B x is equal to y.
C x is less than y.
D It depends on the quality of the gunpowder.
E I do not know.

# POCKET ITEM 3

## REMEDIAL ACTION AT HIGHER GRADE

## The temperature variable in more detail; and activation energy.

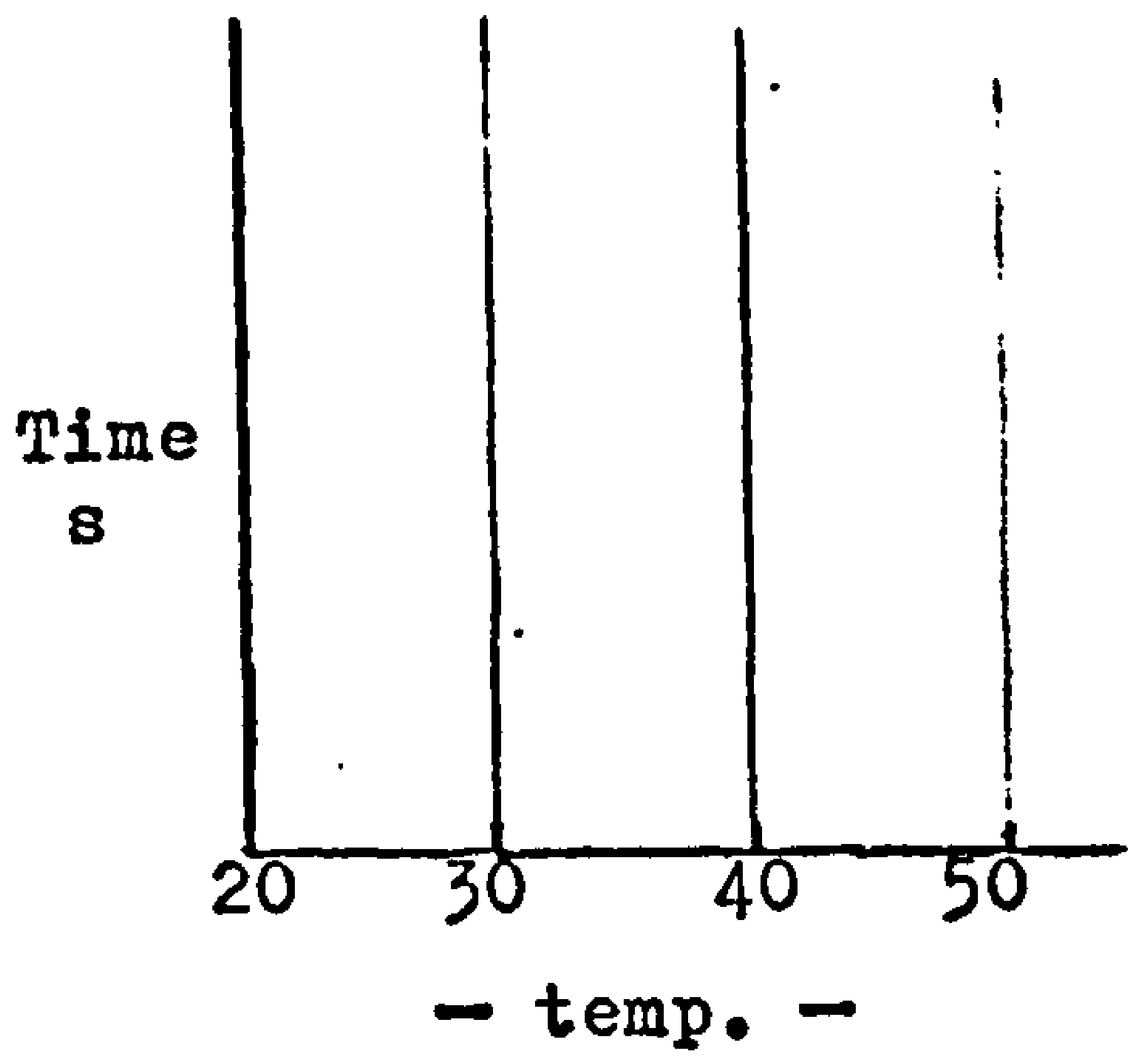
An iodine clock reaction will be used to study the effect of temperature variation on reaction rate.

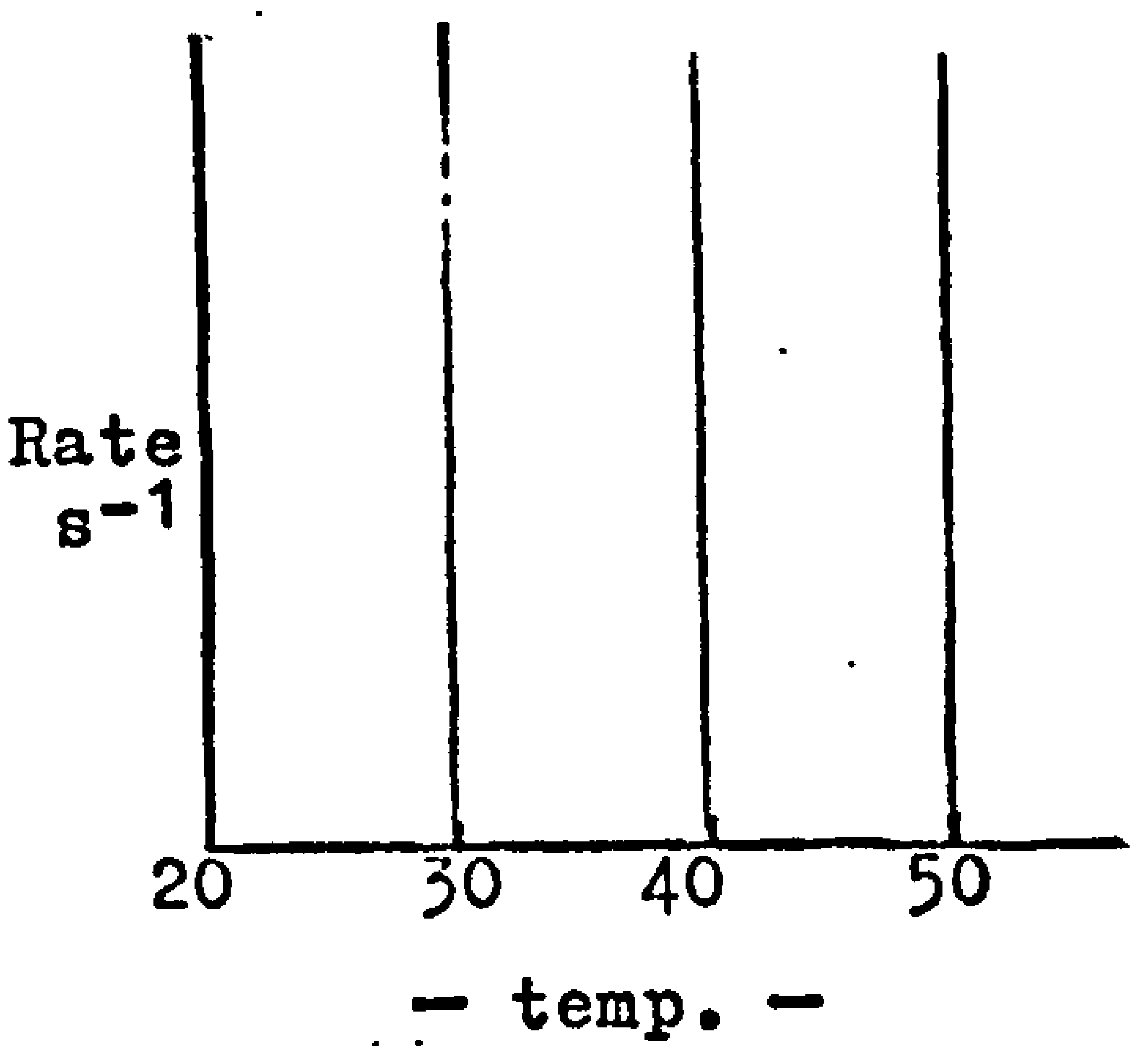


Use 5 $cm^3$ solution A and 5 $cm^3$ solution B. Bring both to the required temperature in a water bath, and then mix.

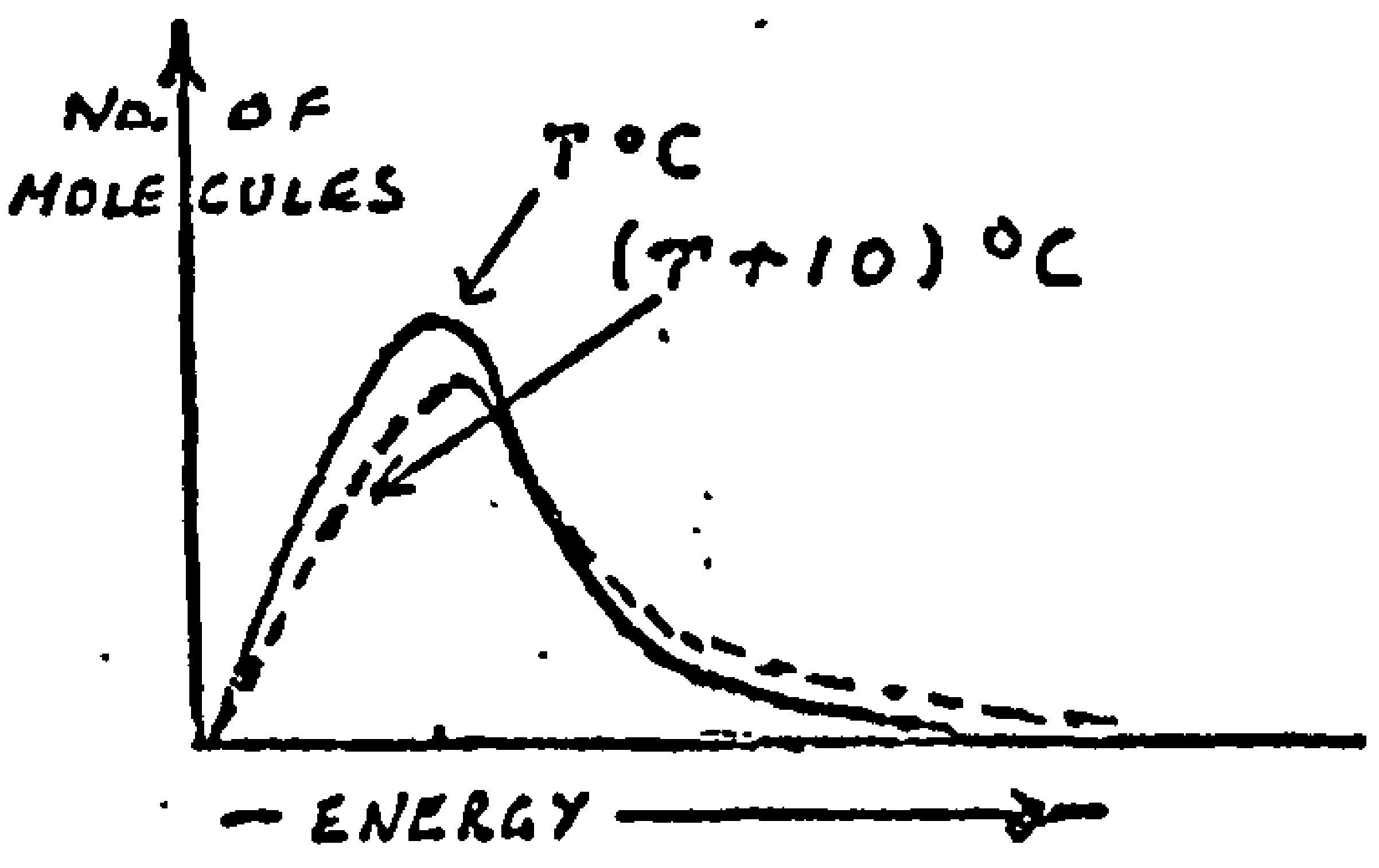
| Temp. °C | Time s | Rate $s^{-1}$ |
|---|---|---|
| 20 | | |
| 30 | | |
| 40 | | |
| 50 | | |

Complete the following graphs:





## Energy distribution among molecules.



Molecules of liquids and gases are in continouous motion, colliding frequently. At any instant, a few molecules may have zero velocity, a few may have velocities far in excess of the average, but the majority of molecules will have velocities, and hence kinetic energies, grouped about the average. An instant later, because of molecular collisions, the same general situation will exist - but for different molecules.

Temperature is determined by the average kinetic energy of all the molecules. Increasing the temperature increases the average kinetic energy of the molecules, and so increases the <u>average</u> speed of the molecules.

It is found that raising the temperature of a reaction by say 10 °C may very well double, treble, quadruple the rate of the reaction, depending on the reaction. <u>This implies that reaction not only requires collision but requires energetic collision</u>.

Activated complex  Only the most energetic molecules may react on collision because only the most energetic molecules may have enough energy to form the intermediate activated complex:

Reactant molecules on collision course with correct orientation. (Badly oriented molecules may only react if they are more energetic.)

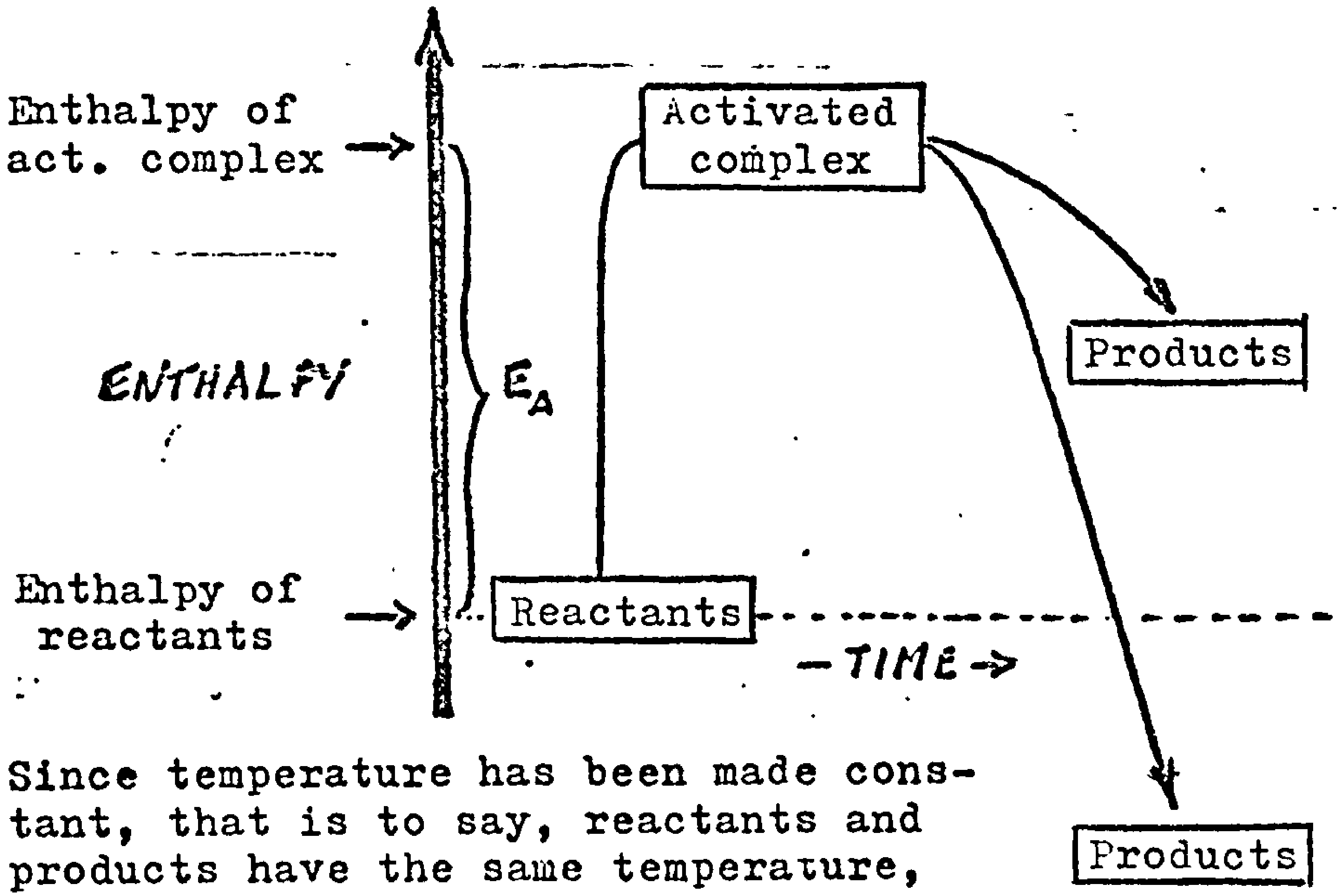
Short-lived activated complex. Kinetic energy of reactants has been transformed into potential energy. The intermediate will only form if sufficient k.e. is available.

Product molecules.

A reaction between two particles therefore requires that
1) they must collide,
2) they must do so with enough energy,
3) they should preferably have a suitable orientation of collision.

Activation Energy

Temperature is constant throughout.



If reaction is endo energetic, the enthalpy of products may lie at this level. $\Delta H$ is +ve.

If reaction is exo-energetic, the enthalpy of products may lie at this level. $\Delta H$ is -ve.

Since temperature has been made constant, that is to say, reactants and products have the same temperature, then kinetic energy is constant throughout. Therefore, these enthalpy changes are due only to changes in potential energy. The above 'enthalpy diagram' is therefore a 'potential energy diagram'.
Now, the energy of activation, symbol $E_A$, is the difference between th potential energy of the activated complex and the potential enegy of the reactants, usually quoted per mole of the latter. In order that reactant molecules form the 'particles' of the activated complex, they must collide with sufficient kinetic energy, which is therefore the source of the activated complex's additional potential energy.
Activation energy gives some indication of the likelihood of a reactio occurring - the lower it is, the lesser the k.e. (as heat) which need supplied to start the reaction, if it is not already occurring.
Activation energy is independent of temperature.

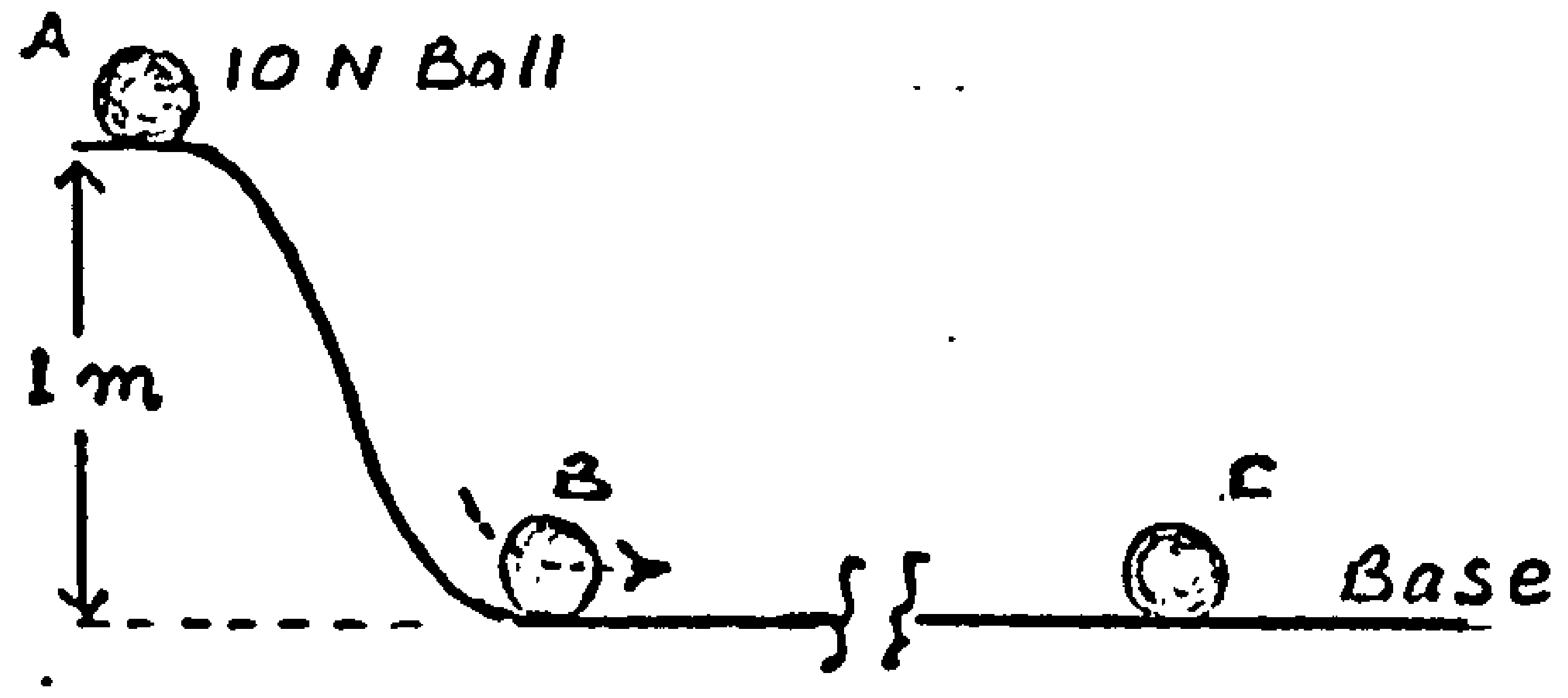
## Energy and its conservation

Basically, all forms of energy (light, heat, etc.,) can be explained in terms of potential and/or kinetic energy. There are, therefore, two kinds of energy: potential energy and kinetic energy.

Potential energy relates to 'position'. A stretched spring possesses more potential energy than it does when relaxed.

Kinetic energy relates to 'motion'. An object moving at 10 m $s^{-1}$ possesses more kinetic energy than it does when moving at 5 m $s^{-1}$.

In all changes, energy is conserved.



At A, the stationary ball possesses 10 J of potential energy relative to the base.

At B, the same ball will possess no potential energy relative to the base, but will possess 10 J kinetic energy, assuming no energy has been lost as heat.

At C, the stationary ball has no potential energy relative to the base and no kinetic energy relative to the base. 10 J of energy have been dissipated in the ball and its surroundings as heat.

All chemical changes are accompanied by the evolution or absorption of heat. Consider the case where heat is evolved; the reverse argument applies for absorption. Where heat is evolved, the enthalpy change is negative and the products contain less energy than the reactants at constant temperature; the heat evolved may be regarded as having been removed. Since temperature is constant, there is no change in kinetic energy for this particular 'system', be it in the form of reactants or products. Thus the enthalpy change is a potential energy change.

The enthalpy change accompanying the combustion of a charge of gunpowder is negative; heat is evolved. But what if an identical charge of powder is used to fire a bullet, how is the enthalpy change affected. Is more heat evolved, or less, or just the same? The answer is less. It is less by the amount of kinetic energy 'taken away by the bullet'. Of course, this kinetic energy is dissipated as heat when the bullet strikes ground and comes to rest, and so the total heat evolved is eventually just the same, but in this example the heat is released in two places!

It is proven fact that a machine gun firing blank shot becomes hotter than when firing live ammunition, surprising as this may seem.

Although it is usual in chemistry to operate the 'constant temperature condition', which fixes the enthalpy change as a potential energy change, it is not essential to always do so. Thus, the cooling of 1 mole of benzene from 80 °C to 10 °C is accompanied by the evolution of about 10 J heat. The enthalpy change, AH, is equal to -10 J, and is due mostly, this time, to a decrease in kinetic energy because of the decrease in temperature; there is a minor contribution due to a decrease in potential energy.

For changes at constant temperature, then, the enthalpy change is a potential energy change.

The conversion of 1 mole of ice at 0 °C to 1 mole of water at 0 °C requires that it absorb the molar latent heat of fusion. This latent heat is a potential energy term: there is an increase in potential energy on melting; there is no increase in kinetic energy. The average kinetic energy of an H20 molecule in ice at 0 °C is the same as the average kinetic energy of a molecule of $H_2O$ in water at 0 °C.

Similarly, the average kinetic energy of a molecule of H20 in water at 100 °C is the same as the average kinetic energy of a molecule of H20 in steam at 100 °C.

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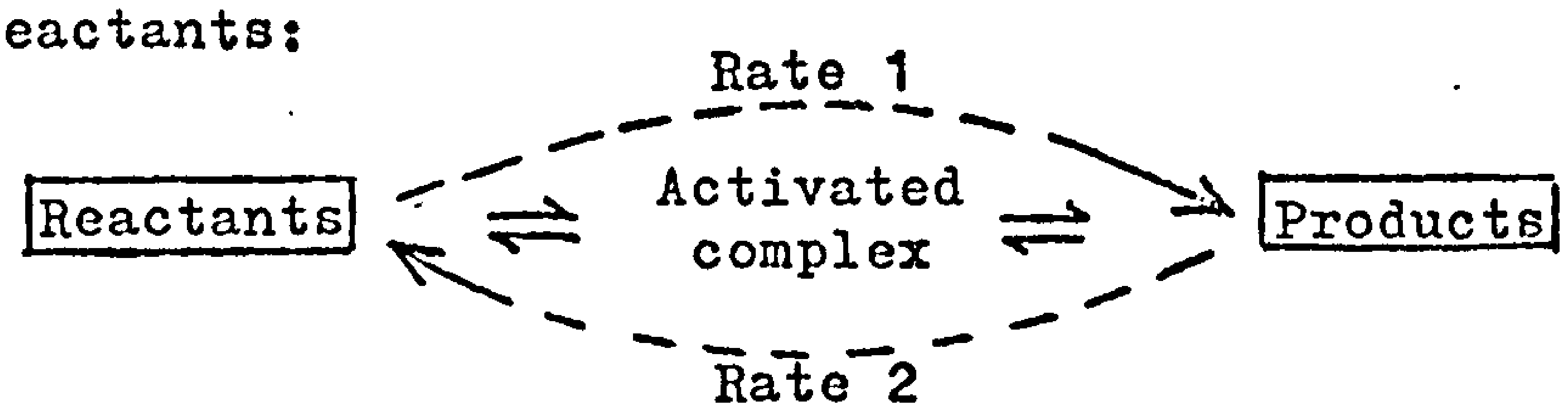
## The idea of equilibrium

Many chemical reactions are significantly reversible, that is to say, the products of the reaction are capable of reacting to reform the original reactants:

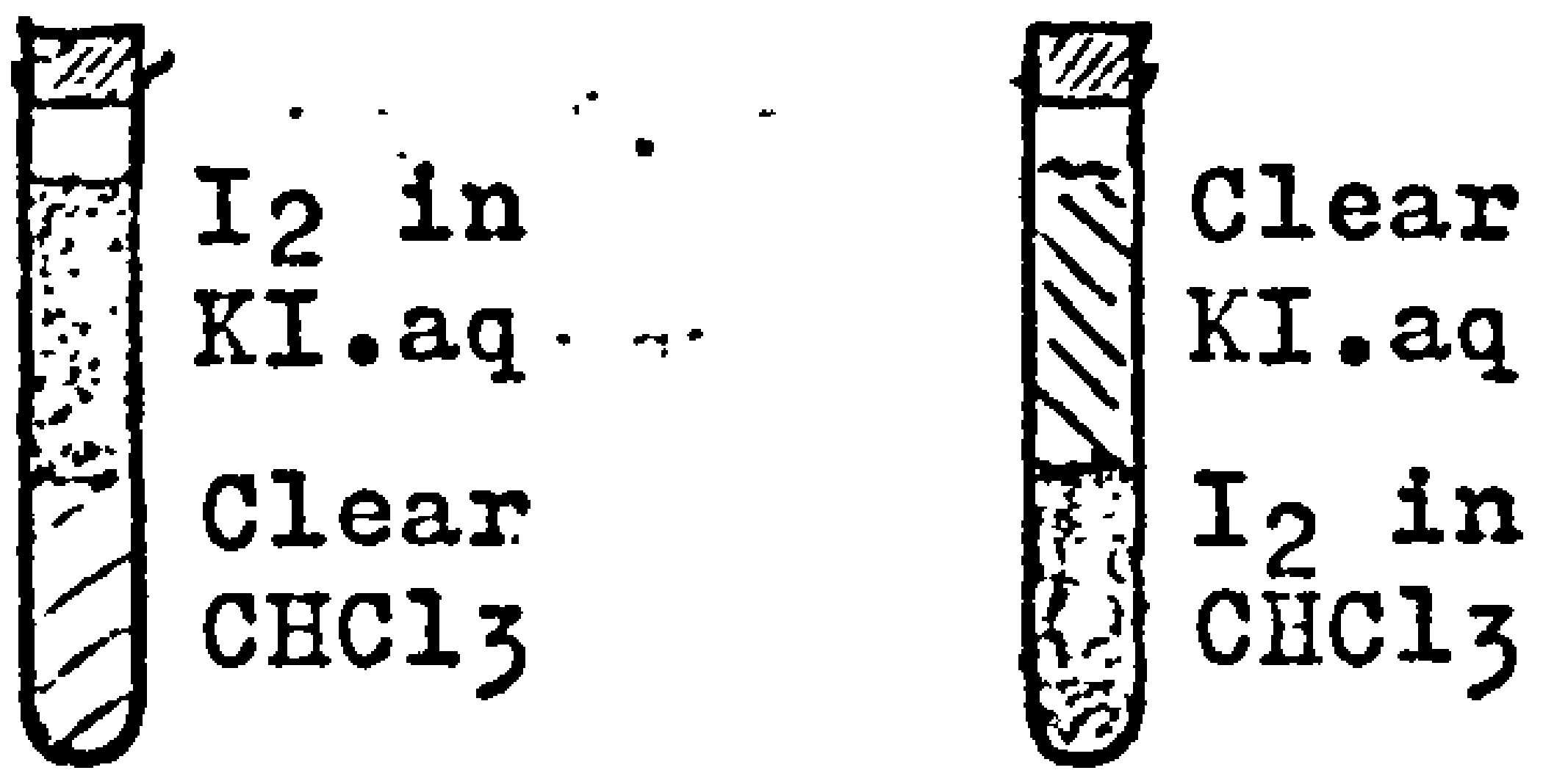


If, under a given set of conditions and after the elapse of due time, the rate of the forward reaction has become equal to the rate of the reverse reaction,

i.e. Rate 1 = Rate 2

then the mixture of reactants and products has a fixed composition and is called an equilibrium mixture; dynamic equilibrium has been established.

For a given set of conditions, is the same equilibrium established from either direction? Carry out the following experiment:



Place 5 $cm^3$ of each liquid in the tubes as shown.

Stopper tightly.

Invert each several times to distribute the solute iodine between the two competing solvents.

Is the same equilibrium distribution of iodine obtained in each case?

## Le Chatelier's Principle

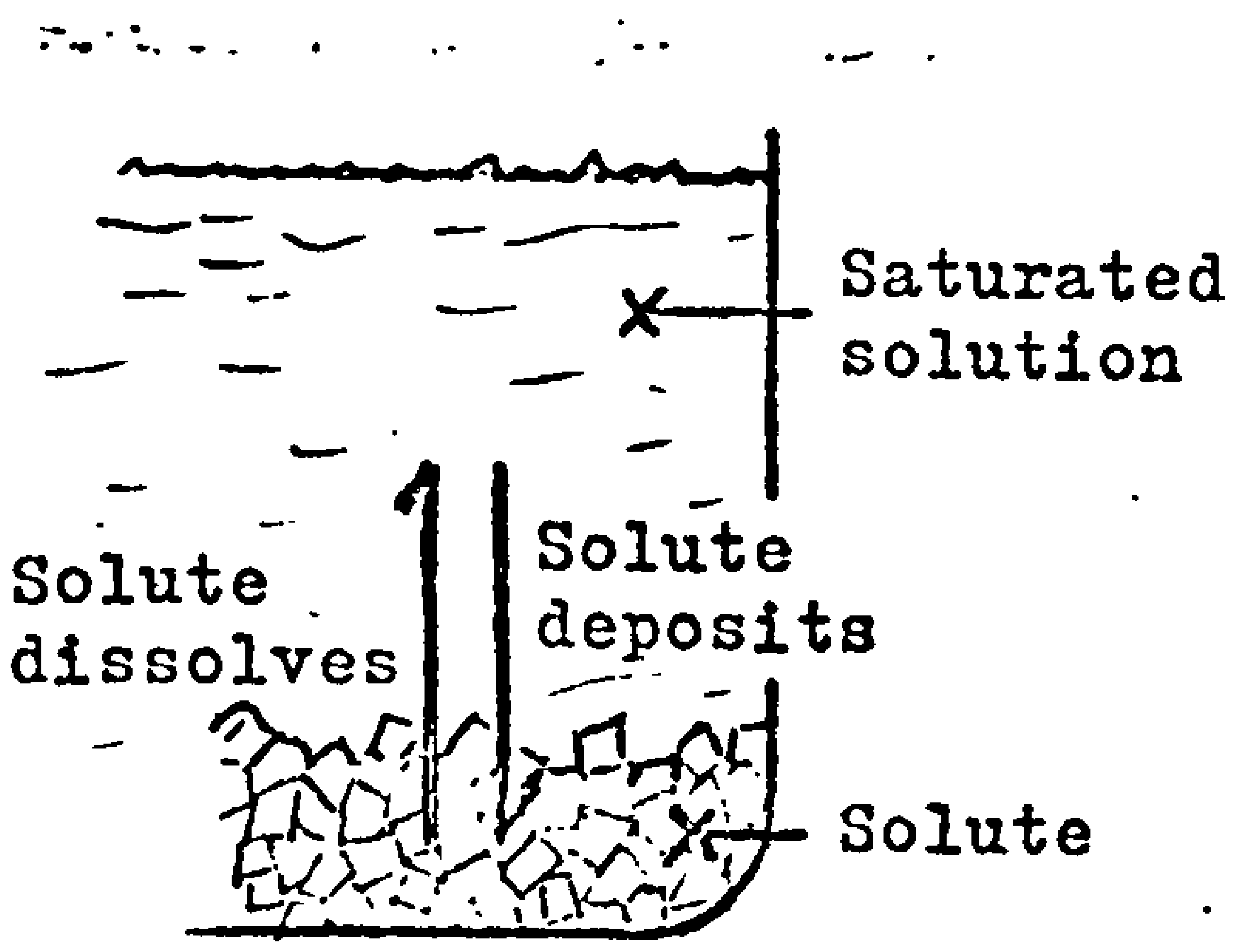
The composition of an equilibrium is sensitive to changes in the conditions - such as temperature - under which the equilibrium exists; the addition of or removal of one or more of the substances present in the equilibrium mixture will upset the equilibrium leading to the formation, in due course, of a new equilibrium.

Before going further check that you are quite clear on the meanings of amount, concentration and composition.

Observation of the actual results of such changes led Le Chatelier to put forward the following theorem: when the circumstances under which an equilibrium exists are changed, the composition of the mixture alters in that way which tends to annul the change. Thus, if a system at equilibrium is heated, it will adjust in that direction which absorbs heat since this will tend to annul the increased temperature; if the concentration of one of the substances in an equilibrium is decreased, the system will adjust so as to tend to restore the compound to its original concentratio

The theorem is notoriously difficult to apply. I suggest it be applied here only to temperature and concentration changes. With alterations to other variables adopt the 'line of least resistance'; e.g. if pressure be increased, that reaction will occur which leads to a decrease in volume. This approach will usually give the right answer (though it helps to know in advance what the right answer is! )

# The temperature variable and equilibrium



A saturated solution is in dynamic equilibrium with undissolved solute: just as quickly as solute deposits from solution, fresh solute dissolves from the stock of undissolved solute lying at the bottom of the container. The composition of the saturated solution is constant under a given set of conditions.

Some solution processes are endothermic; heat is absorbed as the solute dissolves.

Some solution processes are exothermic; heat is evolved as the solute dissolves.

Add a few grammes of KCl to 10 $cm^3$ or so of water. Is the $AH_{soln}$ positive or negative?

Add a few grammes of $MnSO_4$ to 10 $cm^3$ or so of water. Is $AH_{soln}$ positive or negative?

Apply Le Chatelier's Theorem to "heating a saturated solution" and predict, by drawing an approximate solubility curve for each, how you think the solubility of of each of these salts should change with change in temperature.

Sol^y

Refer to a suitable data book and find out if your predictions are correct.

Temp.

The effect of heating a saturated solution of manganese II sulphate will be demonstrated. What do you observe happens to the solubility of this salt with increasing temperature?

Note that the Le Chatelier Theorem can only be applied to an equilibrium situation. This is very important. Thus it is not entirely justifiable to make a prediction on the strength of information obtained from a non-equilibrium situation, as was done above. The above salts, however, were carefully chosen to give the right answers despite this built in error. With other salts, however, you will run into trouble. For example, calcium chloride dissolves exothermically, and - contrary you might think to Le Chatelier - is more soluble the higher the temperature! The answer to this apparent contradiction is: if you could add calcium chloride to water in the extensively hydrated form in which it exists in the equilibrium mixture then it would dissolve endothermically. The same argument applies to caustic soda, which dissolves with much evolution of heat and is more solube the higher the temperature.

When tap water is heated, but not boiled, bubbles of air are expelled. Is the dissolving of air in water an endo or an exo process?

N.B. While the solubility of all gases decreases with rise in temperature, the solubility of the vast majority of solids increases with rise in temperature.

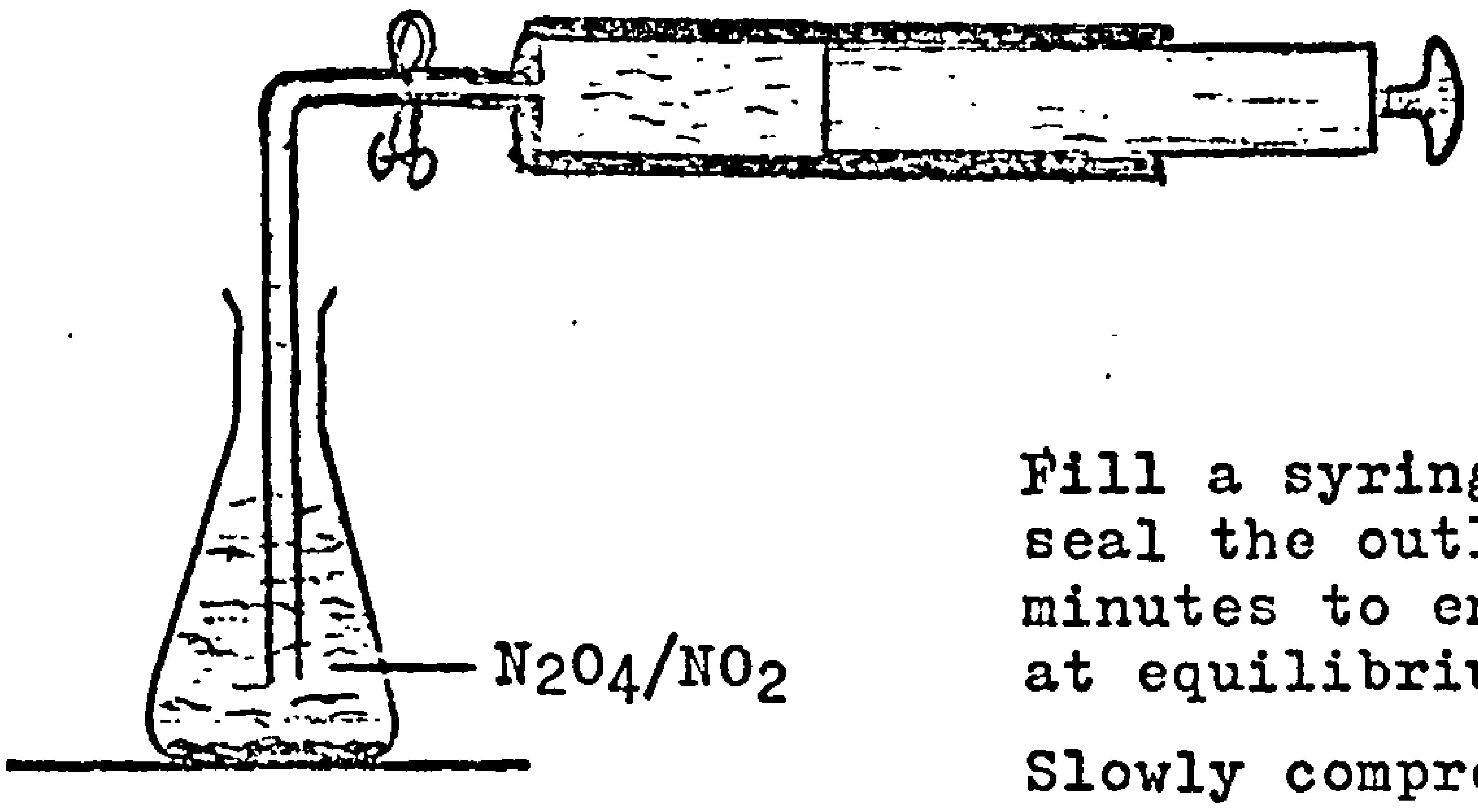
## The pressure variable and equilibrium

Increased pressure implies decreased volume. Accepting this to be sc and applying our rule of 'line of least resistance', then the system will alter chemically in favour of those substances which occupy less volume.

$$N_2O_4 \rightleftharpoons 2NO_2$$

| | |
|---|---|
| yellow<br>dinitrogen<br>tetroxide | dark brown<br>nitrogen<br>dioxide |

At room temperature, the equilibrium composition is 85% $N_2O_4$, 15% $NO_2$.



Fill a syringe with the gas mixture, seal the outlet and leave for a few minutes to ensure that the mixture is at equilibrium.

Slowly compress the gas mixture to say half its original volume and maintain there for a few minutes to ensure that the new equilibrium is established at room temperature.

Using the change in colour as a guide (if you cannot picture the origin colour you will have to run a control alongside this experiment) say which of the two species, $N_2O_4$ or $NO_2$, is favoured by higher pressure.

What effect will pressure change have on the following equilibrium:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

Note: the above oxides of nitrogen are poisonous; a fume cupboard must be used when filling the syringe.

The truth of the matter is that pressure change of itself has no effect on an equilibrium mixture, except in so far as it causes a change in concentration, which does have an effect. Thus the addition of say neon gas to an equilibrium mixture at constant volume will not alter the composition since, although there is an increase in pressure there is no change in the concentration of the equilibrium's reacting species. Similarly, when an equilibrium mixture is heated at constant volume, the increase in temperature will have an effect, but the increase in pressure which goes along with it will not.

The application of Le Chatelier's Theorem is fraught with all manner of difficulties. In general, at the Higher Grade, keep the approach simple:-

a) for temperature increase: both $r_f$ and $r_b$ are increased, but the heat absorbing one is favoured.

b) for concentration increase: adjustment occurs which tends to decrease the increased concentration.

c) for pressure increase: both $r_f$ and $r_b$ are increased, but the one which leads to a decrease in volume is favoured.

d) for volume decrease: both $r_f$ and $r_b$ are increased, but the one which leads to a decrease in volume is favoured.

Left and right sidedness There is a fairly widespread misconception that equilibrium mixtures, or systems as they are more often called, have a left hand side and a right hand side. Certainly the equation representing an equilibrium system has a left hand side and a right hand side, but equilibrium systems as such do not. Consider the Haber system:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Although it is possible to increase the concentration "on the right hand side", it is not possible to increase the temperature, nor is it possible to increase the pressure, on the right hand side. This equilibrium system consists of a homogeneous mixture of all three reacting species all in the one container. Thus, though concentration of individual species can be altered, changes in temperature and pressure will affect all species. Note however that some equilibrium systems consist, apparently, of two parts - see R.12, R.13, R.14 - but these equilibrium systems must each be regarded as one whole system. Avoid left and right sidedness.

A wide variety of physical analogies are used to demonstrate the basics of chemical equilibria. These serve their purpose well, but are unfortunately attended by an over-emphasis of left and right sidedness.

## Testing to see if equilibrium has been established

If a catalyst which is known to be effective is added to the reaction mixture, and no change in composition occurs, then the mixture in a state of chemical equilibrium.

It is not valid to use 'no change in composition with time' as a test since the the mixture may be far from equilibrium and reacting so slowly as to not detectably change in composition with time.

Thus, a cold mixture of hydrogen and oxygen is perfectly stable for very long periods, and so would show no change in composition with time; but the mixture is not at equilibrium. The insertion of

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(l)$$

an effective catalyst will cause a rapid move to the equilibrium sta

## Hydrolysis reactions summarised

Hydrolysis of a weak acid (ionisation):

$$CH_3COOH(aq) + H_2O(aq) \overset{\rightharpoonup}{\longleftarrow} CH_3COO^-(aq) + H_3O^+(aq)$$

Hydrolysis of a weak base (ionisation):

$$NH_3(aq) + H_2O(aq) \overset{\rightharpoonup}{\longleftarrow} NH_4^+(aq) + OH^-(aq)$$

Hydrolysis of the salt of a weak acid and strong base:

$$CH_3COO^-(aq) + H_2O(aq) \overset{\rightharpoonup}{\longleftarrow} CH_3COOH(aq) + OH^-(aq)$$

Hydrolysis of the salt of a strong acid and weak base:

$$NH_4^+(aq) + H_2O(aq) \overset{\rightharpoonup}{\longleftarrow} NH_3(aq) + H_3O^+(aq)$$

Hydrolysis of an ester:

$$CH_3COOC_2H_5(l) + H_2O(l) \rightleftharpoons CH_3COOH(l) + C_2H_5OH(l)$$

- note that the radical group $C_2H_5$ is sometimes represented by the symbol Et; thus, EtOH is ethanol, and MeOH is methanol, and so on.

The reversed arrow convention $\rightleftharpoons$ at O Grade implies reversibility. At H Grade it implies 'equal and opposite' rates of reaction.

The reversed arrow convention $\overset{\rightharpoonup}{\longleftarrow}$ implies 'equal and opposite' rates of reaction, and also implies that the equilibrium mixture contains more reactant than product. (I do not know, however, of any official ruling on this latter interpretation of the convention.) It does <u>not</u>, as far as I am aware, imply that the reverse reaction is greater than the forward reaction, for if the system is in equilibrium the forward and reverse rates of reaction <u>must</u> be equal.

Applying Le Chatelier

1. $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$; ΔH -ve
   Increase temperature.

2. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; ΔH -ve
   Compress to a smaller volume.

3. $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$; ΔH -ve
   Remove some $Cl_2(g)$ at c.v..

4. $NH_4^+(aq) + H_2O(aq) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$
   Add more $NH_4Cl(s)$

5. $CH_3COO^-(aq) + H_2O(aq) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$
   Add more $CH_3COONa(s)$.

6. $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$
   Add some ethanol.

7. $N_2(g) + C_2H_2(g) \rightleftharpoons 2HCN(g)$; ΔH +ve
   Increase temperature at c.v.

8. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
   Compress the system.

9. $H_2(g) + I_2(s) \rightleftharpoons 2HI(g)$
   Compress the system.

9. What happens to the pH value of aqueous ethanoic acid when the fully ionisable solid salt sodium ethanoate is added?

10. What happens to the pH value of aqueous ammonia when the fully ionisable salt ammonium chloride is added?

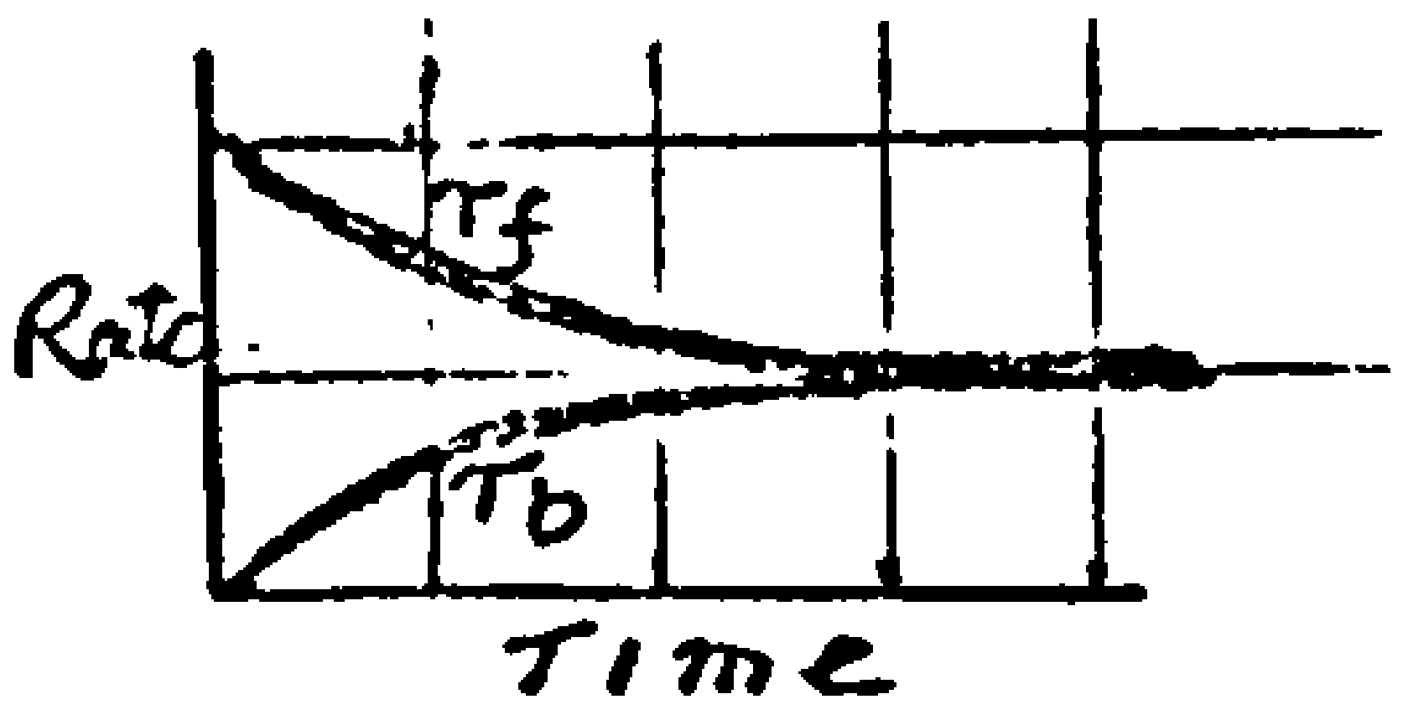
Try question 4(b)(iii), 1970. (This question illustrates the difficulty of distinguishing between an equilibrium situation and a non-equilibrium situation.)

## Equilibria and catalysts.

Systems at equilibrium are disturbed by changes in temperature and concentration, and by pressure/volume changes (where these cause changes in concentration).

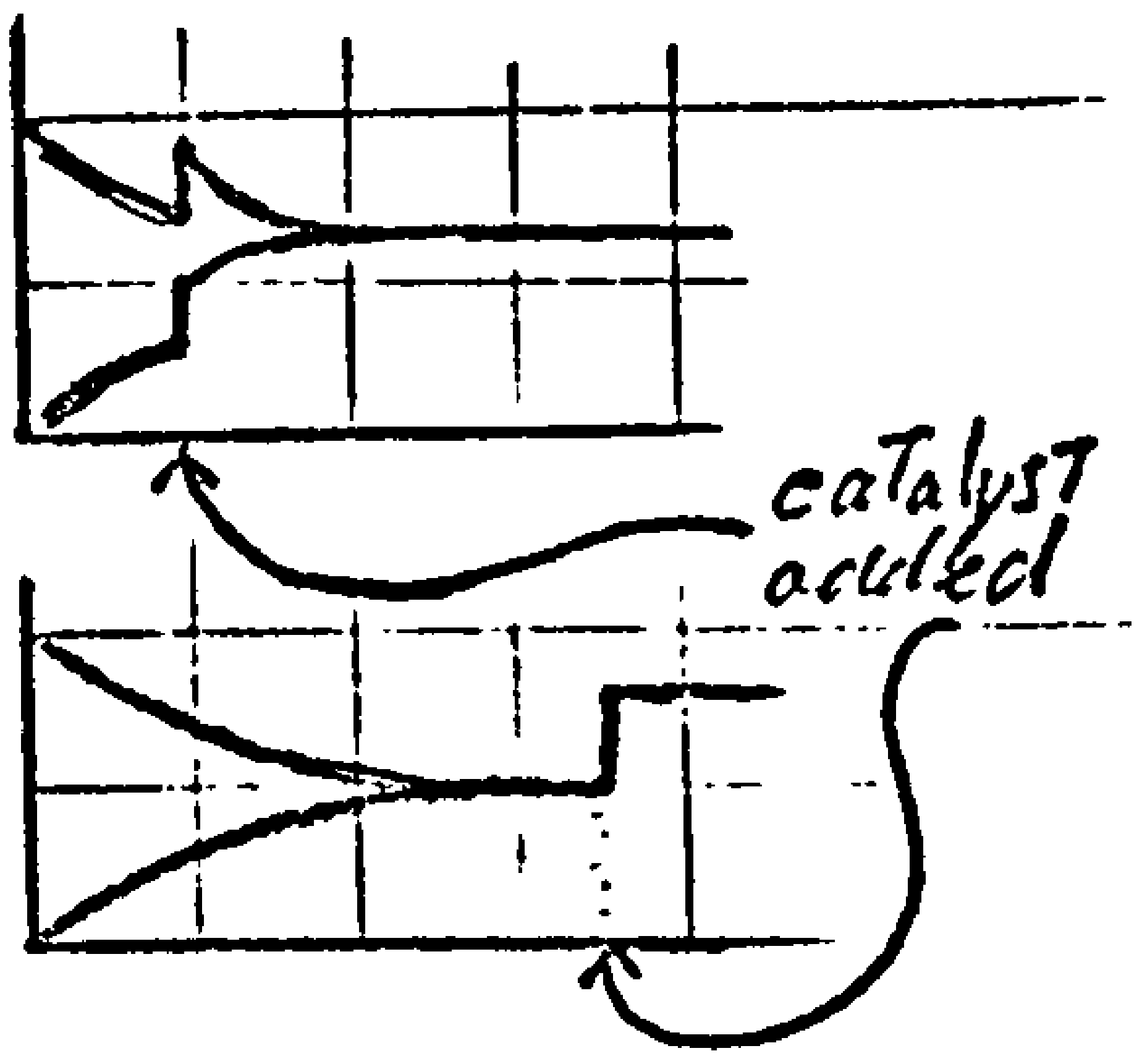
Systems at equilibrium are not disturbed by the introduction of a catalyst; the composition of the equilibrium mixture does not change. The equilibrium system is, however, affected by the catalyst: the rates of the forward and reverse reactions are increased equally.

As a non-equilibrium system approaches equilibrium, the forward and backward rates of reaction become equal:-

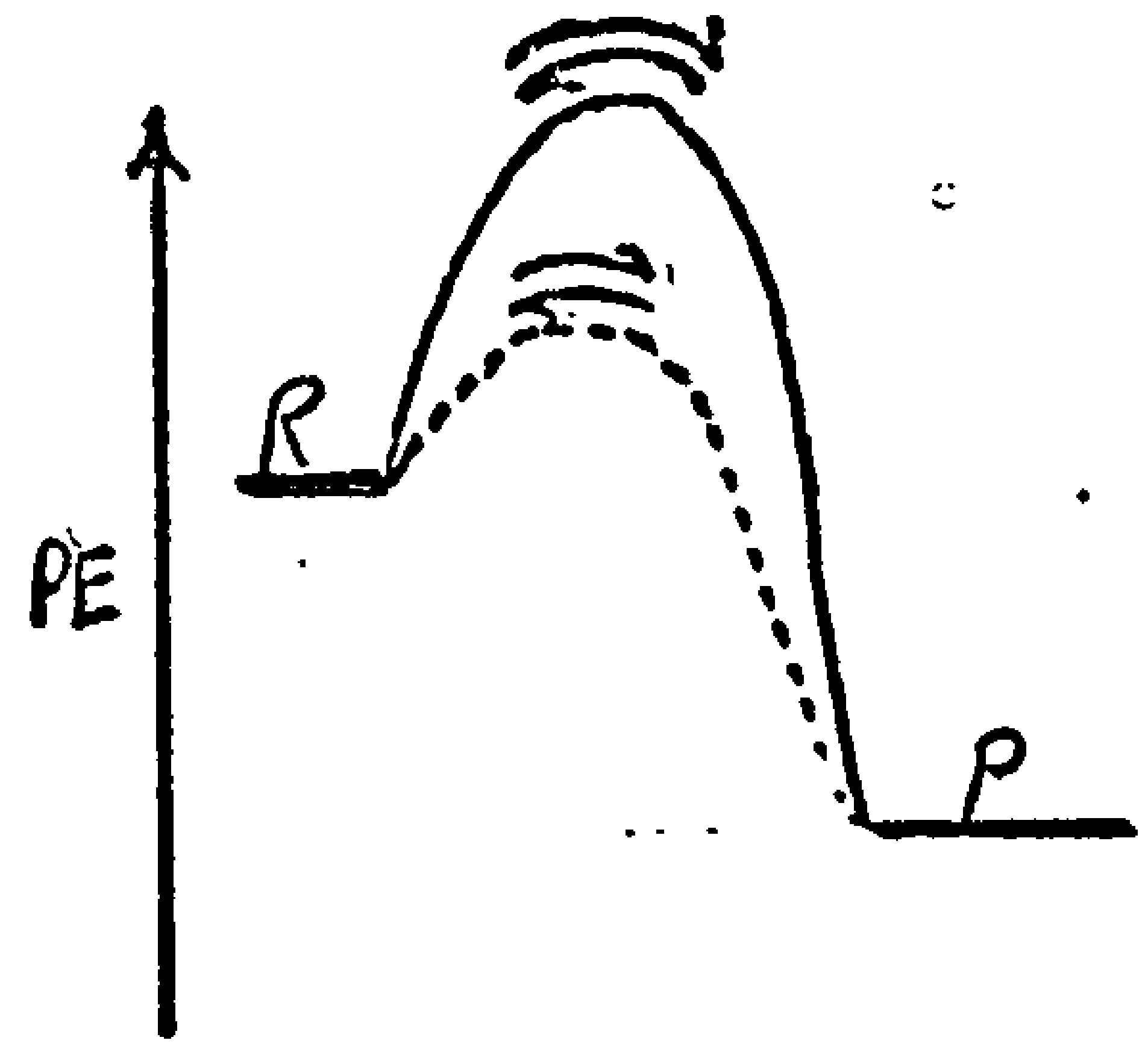


When a catalyst is added before equilibrium is reached, both rates of reaction, $r_f$ and $r_b$ are increased so that equilibrium, the same equilibrium, is established sooner:-

When a catalyst is added at equilibrium, $r_f$ and $r_b$ - which are equal and opposite - are increased equally; there is no change in composition;-



A catalyst allows the formation of an activated (transition) complex of lower potential energy. At equilibrium, the rates of reaction through the complex are equal; the rates of reaction through the catalyst-complex are also equal, but greater than through the normal complex.



The enthalpy diagram opposite refers to a system for which AH (forward) is -ve. At low temperature, product will predominate; at high temperatures, reactant will predoninate. There is a tendency to think that, since P is 'lower', there must always be more P in the equilibrium mixture. This is not so.

A catalyst does not supply energy to the reactants.
A catalyst does have an effect on reactions occurring in an equilibrium system.
A catalyst allows the formation of the same equilibrium mixture sooner.
A catalyst acts as a 'market square', facilitating exchange of energy between reactant molecules and between product molecules.
A catalyst cannot be used to drive an equilibrium in a desired direction; it merely accelerates the rates of reactions, and gives whatever will be given sooner.

# POCKET ITEM 4

# THERMODYNAMICS APPROACH PROGRAMME

# ENERGIES IN MACROSCOPIC SYSTEMS

## THERMODYNAMICS APPROACH PROGRAMME

Bóltzmann (1844-1906) once said, "How awkward is the human mind in divining the nature of things when forsaken by the analogy of what we see and touch directly."

This learning programme is an attempt to explain the underlying meanings of the First and Second Laws of Thermodynamics and their relationship with the concept of chemical equilibrium by the use of just such a physical analogy: a falling spinning weight.

There are dangers inherent in the use of such a device, but the quality of understanding of the variety of concepts here involved is at times so desperately poor that the use of any 'concrete-experimental' approach, whatever its category, is probably to be welcomed.

Consequently, I make no apologies for the invention of a concrete-experimental approach which breaks the Second Law in order to explain it.

This programme is due in very great measure to the assistance afforded me by Dr. G. Webb and Dr. A. H. Johnstone of the University of Glasgow, to whom much of the credit is due.

John J. MacDonald.
August 1975

## Study Unit 1

# GROUND CLEARING OPERATION

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## PURPOSE

1. To clear up false ideas about matter and energy which you may have acquired.
2. To revise your ideas about the Kinetic Particle Theory of Matter.
3. To discuss the various forms of energy.
4. To consider the form of energy and work terms.

---

## PRESENTATION

Introduction. You may find the content of this first Study Unit to be over-simple. This being so, you should progress through it very rapidly and pass on to Study Unit 2.

On the other hand, the content may be such as to give you food for thought; you may have to revise your ideas, or otherwise alter or extend them in some way or other.

The three states of matter. When we look about us we see material things in a multitude of shapes, sizes and colourations. We can readily detect those objects which have shape of their own, such as copper coins, wooden desks. These are called solid objects.

Other materials assume the shape of their container, and have a distinct upper boundary or surface, such as water, milk, petrol. These are called liquids. A third category, much less obvious, has no distinct shape in so far as there is no clear-cut boundary between one example and another; we cannot visually distinguish where hydrogen released from a balloon ends and air begins. These are called gases.

There are, of course, more subtle points of distinction: glass, which completely lacks a crystalline structure, is in reality a liquid of such high viscosity that in effect it is describable as a solid! But whatever our 'yardstick', all materials can be allocated to one or other of the three states of matter: solid, liquid or gas.

Liquids and gases, having no rigid shape of their own, have in common the ability to flow, and are therefore called fluids.

MATTER

Anything which
occupies space.

| Solid | Liquid | Gas |
|---|---|---|
| Shape of its own; sharp visible boundary | Shape of container: sharp visible boundary. | Shape of container; no visible boundary. |

## Physical and chemical change.

A pure substance is composed of a particular kind of particle. If we have enough of these particles we have a visible sample of the substance.

Suppose we now change this sample: by grinding it, by heating it, by exposing it to sunlight, and so on. If the original particles have persisted, then the sample is still of the original substance. Any changes - the substance may be a powder where it was a single crystal, or it may be a liquid where it was a solid - are described as physical changes. Thus the conversion of water into steam is a physical change because the particles of water are also the particles of steam. A physical change produces no new substance.

By this definition, crystallisation, melting, dissolving, diffusion, mixing are all physical changes; so also is the incandescence (glow) produced by passing an electric current through the tungsten filament of an electric lamp.

If on the other hand, new particles are formed, then the original substance can no longer be present as such. Perhaps its particles have shaken apart into simpler particles, or perhaps they have collided and joined up to make more complex particles, and so on. Whatever the reason, since new particles have been created out of old, then new substances are present. Such a change is described as a chemical change. A chemical change produces a new substance.

By this definition, the combustion of petrol in a car engine, the decomposition of water into hydrogen and oxygen by an electric current, the decay of a dead tree, the growth of a plant, the rusting of iron are all examples of chemical change.

But although a distinction between physical and chemical change is a preliminary aid to understanding the behaviour of matter, it must be remembered that such a distinction is a gross simplification.

It is by no means always easy to say, "This is a physical change, that is a chemical change.". The melting of ice, for example, breaks hydrogen bonds, the boiling of a metal breaks metallic bonding, the cleavage of a diamond crystal breaks covalent bonds.

By our simple definition - that no new substance be formed - these changes must be physical. And yet, in the sense that distinct chemical bonds between particles are broken, these changes could be described as chemical changes. The best way out of this dilemma is to think, not so much in terms of physical and chemical change, but merely in terms of change. What is important is that we have some idea of what is actually happening whatever we call it.

Energy and the states of matter. Energy, unlike matter, is non-concrete, or abstract. A jar cannot be filled with energy in the same way that it can be filled with water. Heat cannot be weighed, nor can light nor sound. Energy is, however, always associated with matter: hot water has more heat energy in it than the same amount of cold water; or the energy may be in transit, as is the case with light, from one object to another.

Potential energy. Differences in potential energy arise from positional differences. Thus a boy at the top of a ladder occupies a position of higher energy than he would at the bottom of the ladder. When at the top of the ladder he is said to be the possessor of greater positional or potential energy than when at the bottom of the ladder. The force of gravity is, of course, entirely responsible for this existence of 'height' potential energy; in the absence of a gravitational force there would be no 'height' potential energy, the boy would be weightless and in a state of static equilibrium, neither rising nor falling with the elapse of time.

There are other kinds of potential energies, not connected with height, and not therefore dependent on gravity. For example, a spring in a compressed condition possesses potential energy due to this condition.

The essential feature of potential energy, therefore, is one of position.

Kinetic energy. An object in motion possesses more energy than the same object at rest, other things being equal. Thus a car travelling at speed possesses more 'moving' energy than does the same car travelling slowly. This kind of energy is called kinetic energy.

The essential feature of kinetic energy, therefore, is one of movement.

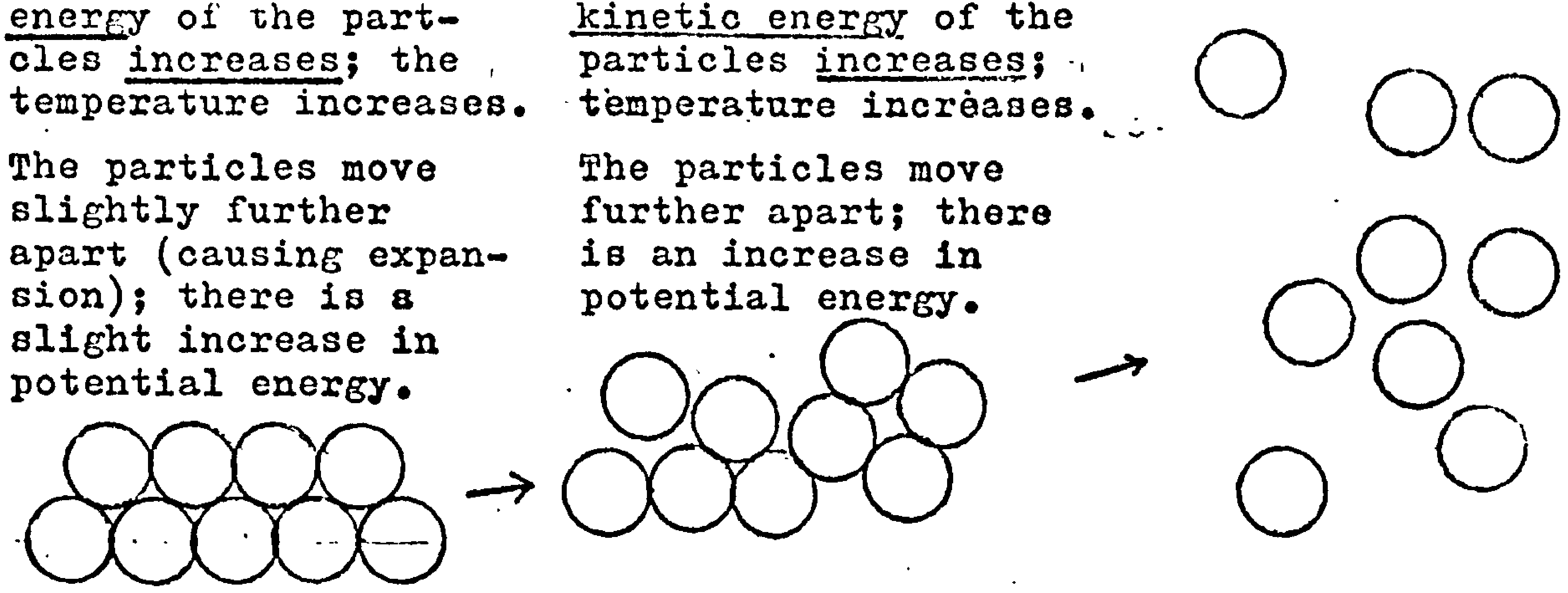
Heat, light and sound can be explained in terms of potential energy and kinetic energy. Thus there are only two distinct fundamental forms of energy: potential energy and kinetic energy.

The kinetic particle theory of matter. Matter is composed of particles, be they molecules, ions, atoms or mixtures of these; and these particles possess kinetic energy, that is, they are moving. The movement may be fairly restricted; it may be of a vibrational kind as is the case with particles of solids. Or it may be less restricted; it may be rotational and translational (from place to place) as well as vibrational as is the case with particles of liquids and gases.

In addition, particles possess potential energy to a greater or lesser extent according to how they are 'placed about each other' in the non-moving sense: are they on average close together or far apart, are there lots of smaller particles or fewer larger particles, are the individual atoms and ions and molecules or whatever tightly bonded within and between or loosely bonded?

A rearrangement of the way the particles are placed about each other, as occurs during a physical change or during a chemical change may result in a new arrangement of lower potential energy, and energy is released; or it may result in a new arrangement of higher potential energy, and energy is absorbed.

Consider the heating of a solid from some temperature below its melting point to some temperature in excess of its boiling point:



① Heat is supplied to the solid; its particles vibrate more. The average kinetic energy of the particles increases; the temperature increases.

The particles move slightly further apart (causing expansion); there is a slight increase in potential energy.

② Temperature is constant while the solid melts; there is no change in average kinetic energy of particles.

Latent heat of fusion is potential energy.

③ As the liquid is heated from its melting point to its boiling point, the average kinetic energy of the particles increases; temperature increases.

The particles move further apart; there is an increase in potential energy.

④ Similarly, latent heat of evaporation is potential energy.

⑤ The same general comments apply to the heating of the gas..

Fig. 1.1

Ice and water can have the same temperature. Molecules of ice in ice at 0 °C and molecules of water in water at 0 °C have the same average kinetic energies. This is why ice and water can have the same temperature. It is a popular misconception that molecules of water of necessity must 'move faster' than molecules of ice. This is, of course, true at temperatures above 0 °C. But at 0 °C the vibrational kinetic energies of molecules of ice is on average the same as the kinetic energies of molecules of water at 0 °C, which kinetic energies are vibrational, rotational and translational.

The latent heat of fusion is used to overcome the forces of attraction between the ice molecules so that they become differently positioned; latent heat is potential, not kinetic. Its absorption therefore produces no rise in temperature, it brings about a change of state.

Water and steam can have the same temperature. The average speed of a water molecule in water at 100 °C is the same as the average speed of steam molecule in steam at 100 °C, Molecules of steam are however much further apart than molecules of water.

The latent heat of evaporation in no way affects the kinetic energies of the molecules; it is consumed entirely in increasing their potential energies.

## Distribution of kinetic energy among the molecules of liquids and gases.

Molecules are in a state of rapid motion, colliding frequently; a molecule of hydrogen gas suffers approximately 10 000 000 000 collisions per second at room temperature.

At any instant, some molecules have zero speed, some have speeds far in excess of the average, but the majority of molecules have speeds - and hence kinetic energies - grouped about the average. An instant later, because of molecular collision, the same general situation exists - but for different molecules.

This distribution of kinetic energy among the total number of molecules is illustrated by the full line in the following graph.

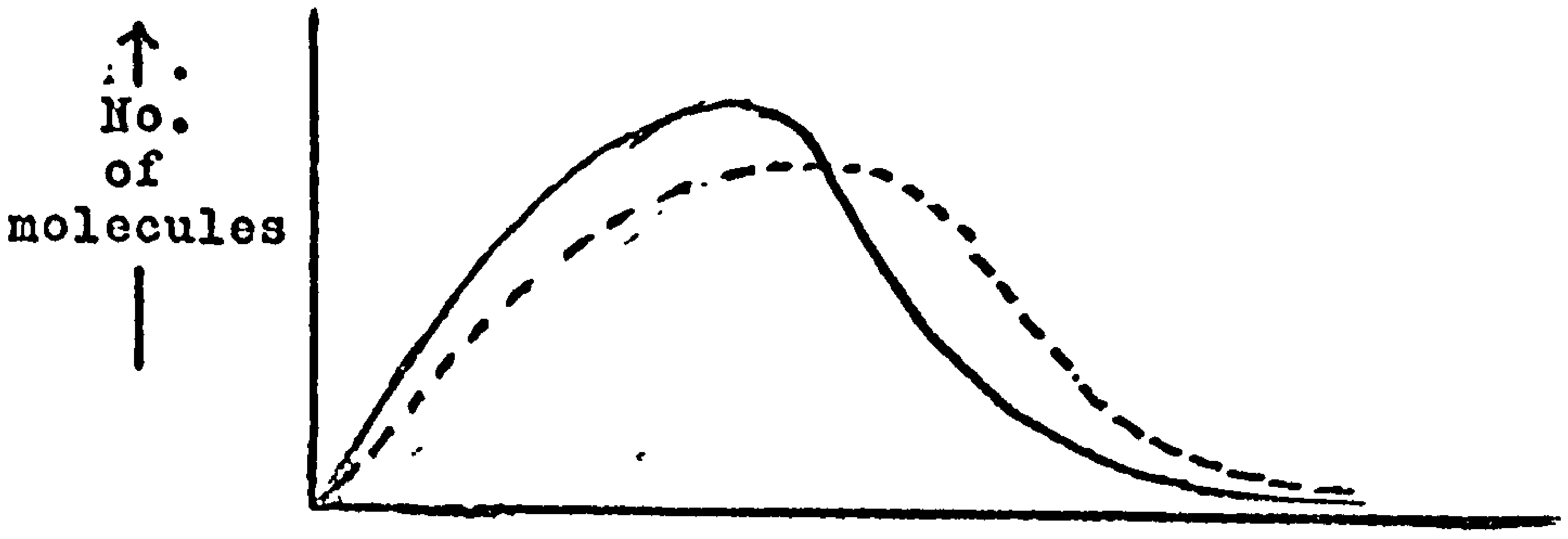


Fig. 1.2

Temperature is determined by the average kinetic energy; increasing the temperature increases the average kinetic energy. The dotted line in the above graph illustrates the distribution of kinetic energy among the same molecules at a higher temperature.

A look at some fundamental units.

The unit of mass is the kilogramme.

Mass is proportional to 'accelerability'.

The unit of length is the metre. This gives us the square metre and the cubic metre as derived units of area and volume.

Volume is proportional to space occupied.

The unit of amount is the mole.

Amount is proportional to numbers of particles. 1 mole amount of a substance consists of $6 \times 10^{23}$ particles of the substance.

The unit of force or weight is the newton. It is that force which would cause a kilogramme mass to accelerate 1 metre faster each second.

The unit of energy is the joule. It is the energy, assuming no wastage, required to raise a 1 newton weight through a distance of 1 metre. At the same time, the work done in raising the weight is 1 joule. Energy and work have the same units.

The energy required to raise a 3 newton weight through 3 metres, and the work done in doing so, is 9 joules. Thus:

$$\boxed{\begin{array}{c}\text{Energy term}\\\text{(in joules)}\end{array} = \begin{array}{c}\text{Force term}\\\text{(in newtons)}\end{array} \times \begin{array}{c}\text{Quantity term}\\\text{(in metres)}\end{array}}$$

and this is, in general, true of an energy term - that is to say, an energy term is equal to the product of a force term and quantity term.

Note that a joule (J) is equal to a newton.metre (Nm).

There are two other instances of "work done" with which you should be quite familiar.

i) Work done during expansion. Now it happens sometimes that as the result of a physical change or a chemical change, expansion unavoidably occurs against the surrounding atmosphere. This assumes that the reaction, be it the boiling of water or the evolution of carbon dioxide gas from a mixture of acid and carbonate, is taking place in an open vessel. And the atmosphere exerts an opposing pressure against which this expansion must occur - like the weight exerting a downward opposing force against which the upward movement must occur.

The energy term corresponding to the work done during expansion is:

$$\begin{array}{ccccc}\text{Energy term} & = & \text{Pressure} & \times & \text{Volume change}\\ \text{(J)} & & (\text{N.m}^{-2}) & & (\text{m}^3)\\ & = & P & \times & AV\end{array}$$

This energy term, therefore, is PAV, and may be described as compulsory work in the sense that it must be done if the reaction is carried out at constant pressure. If the reaction were carried out at constant volume, i.e. in a closed container, AV would be zero; there would be no compulsory work.

Note that the energy term is composed of a force term (the pressure) multiplied by a quantity term (the volume change).

Note also that the argument is equally valid for contraction, in which case compulsory work is done, not by the reaction on the surroundings, but by the surroundings on the reaction.

ii) Electrical work. By a similar argument the work done in forcing a quantity of electricity past a point in a circuit is equal to the product of the force term (in this case, the potential difference) and the quantity term (in this case, electrical charge);

$$\underset{(J)}{\text{Energy term}} = \underset{(\text{volts, V})}{\text{Potential difference}} \times \underset{(\text{coulombs, C})}{\text{Electrical charge}}$$

$$= E \times nF$$

Thus, just as 1 joule may be defined as 1 newton.metre, it may also be defined as 1 volt.coulomb.

In short, the energy term associated with the work done in pushing electrons past a point in a circuit is nFE, where

$n$ = number of faradays of electrons

$F$ = the faraday = $9.65 \times 10^4$ coulombs of electrons

$E$ = potential difference

Note 1. A coulomb of electricity is the amount of electricity passing a point in a circuit each second when 1 ampere is flowing in the circuit.

$$\underset{(C)}{1 \text{ coulomb}} = \underset{(A)}{1 \text{ ampere}} \times \underset{(s)}{1 \text{ second}}$$

$$= \underset{(As)}{1 \text{ ampere.second}}$$

Thus a current of 3 amperes flowing in a circuit for 20 seconds corresponds to 60 coulombs of electricity.

Note 2. The faraday is one mole amount of electrons, that is to say, it is an amount of electricity consisting of $6.0 \times 10^{23}$ electrons.

Energy terms and their associated force and quantity terms

| Type of work | Symbol | Force term | Quantity term |
|---|---|---|---|
| Lifting a weight | force x distance | weight | height |
| Change in volume | PΔV | pressure | volume |
| Electrical work | nFE | potential difference | charge |

Table 1.1

Study Unit 1 What you should know.

You should

1. know the difference between matter and energy.
2. know the three states of matter.
3. understand what happens to particles during so-called physical and chemical change.
4. know the various forms of energy.
5. know the difference between potential and kinetic energy.
6. understand the Kinetic Particle Theory.
7. know that an energy term equals a force term multiplied by a quantity term.
8. know what this programme means by 'compulsory $P\Delta V$ work'.
9. know that electrical work is $nFE$.

---

Question 1. A Daniell cell is operated such that 0.01 A is drawn from it for 10 minutes at 1.05 V. How much work can be done?

| | |
|---|---|
| 1 6.3 J | 2 6.3 kJ |
| 3 0.105 J | |

Question 2. What amount of energy is associated with the loss of 3 faradays of electrons at a constant potential difference of 2 V?

| | |
|---|---|
| 1 6 J | 2 $5.79 \times 10^5$ J |
| 3 579 kJ | 4 57.9 J |

Question 3. What is the effect on an individual molecule of raising the temperature of the gas?

| | |
|---|---|
| 1 The speed of the molecule increases. | 2 The molecule becomes hotter. |
| 3 The average speed of the molecule increases. | 4 The effective volume of the molecule increases. |

Question 4. When water at 100 °C absorbs heat and changes to steam at 100 °C how are the potential energies and the kinetic energies of the molecules affected?

| | |
|---|---|
| 1 The average potential energy of the molecules remains the same but their average kinetic energy increases. | 2 The average potential energy of th molecules increases but their average kinetic energy remains the sam |
| 3 Both the average potential energy and the average kinetic energy of the molecules increase. | 4 Neither the potential energy nor the kinetic energy of the molecule is affected. |

Question 5. What principle is embodied in Hess's Law?

| | |
|---|---|
| 1 The conservation of mass | 2 The conservation of energy. |
| 3 Enthalpy change is a constant-pressure change. | 4 The principle of heat summation. |

Question 1.

| | |
|---|---|
| Response 1: 6.3 J | This is the correct answer.<br>Work = nFE<br>= quantity x potential difference<br>(C) (V)<br>= 0.01 x 10 x 60 x 1.05<br>(A) (s) (V)<br>= 6.3 coulomb.volts<br>= 6.3 J |
| Response 2: 6.3 kJ | This error indicates some confusion with the units involved. Look over the correct solution in Response 1. 6.3 J is otherwise written 6.3 x $10^{-3}$ kJ. |
| Response 3: 0.105 J | This incorrect answer indicates that time was not converted from minutes to seconds. A coulomb is the amount of electricity delivered by 1 ampere flowing for 1 second. 1 ampere flowing for 1 minute is equal to 60 coulombs. |

---

Question 2

| | |
|---|---|
| Response 1: 6 J | This answer is incorrect. You have not converted the quantity of electricity expressed in faradays into coulombs.<br>Energy = nFE<br>= 3 x 2<br>F V<br>= 6 faraday.volts<br>But 1 faraday.volt equals 9.65 x 104 J<br>Energy = 6 x 9.65 x 104 J<br>= 5.79 x $10^5$ J |
| Response 2: 5.79 x $10^5$ J | This is the correct response.<br>Energy = nFE<br>= 3 x 9.65 x 104 x 2<br>C V<br>= 5.79 x $10^5$ J |
| Response 3: 579 kJ | This response is also correct. |
| Response 4: 57.9 J | You have omitted the factor 104. |

---

Question 3

| | |
|---|---|
| Response 1 | This is an incorrect response. The 'speed' of a molecule is a very variable quantity, It is important to specify that the <u>average</u> speed of the molecule increases. |
| Response 2 | This is an incorrect response. Temperature is the degree of hotness of a body. The degree of hotness is determined by the average kinetic energy of all the molecules at that spot where the temperature is being measured. The molecules collectively convey, by virtue of their kinetic energies, a temperature reading. |

Question 3 continued

| | |
|---|---|
| Response 2 | At the very extreme, therefore, a single molecule, it might be argued, should convey a temperature reading in accord with its kinetic energy, but this is quite impracticable. The molecule, however, does not in any way 'have a temperature'.<br>Temperature is a property of large numbers of molecule |
| Response 3 | This is the correct response. |
| Response 4 | This also is a correct response. The average kinetic energy of the molecules at the higher temperature is greater. But the average distance apart is also up a little .... which represents a slight increase in potential energy .... and so the molecule in effect carves out a slightly larger volume of space in which to move aound. The molecule itself has not increased in actual size. |

---

## Question 4

| | |
|---|---|
| Response 1 | This is an incorrect response. It is a popular misconception that, for a given substance, molecules in the gaseous state 'travel faster' than they do in the liquid state. This is generally true, except at the boiling point, freezing point and transition point between two polymorphic froms of the one substance.<br>At the boiling point, the average speed of water molecules is the same as the average speed of steam molecules; that is to say, their average kinetic energies are the same and so therefore are their temperatures. |
| Response 2 | This is the correct response. |
| Response 3 | This response is incorrect, though plausible. In fact, if the temperature remains constant - as it does at the boiling point - there is no change in the average kinetic energy of the molecules. |
| Response 4 | This is quite wrong. |

---

## Question 5

| | |
|---|---|
| Response 1 | This is an incorrect response. Hess's Law assumes that mass is conserved in physical and chemical reactio It then goes on to concern itself with the conservation of energy. |
| Response 2 | This is the correct response. |
| Response 3 | Hess's Law certainly deals with the enthalpy changes which occur in progressing from a reactant to a product via different routes, but it is not concerned with defining the nature of the enthalpy change. |
| Response 4 | This is a correct response: the summed enthalpy changes are the same irrespective of the route taken. |

Study Unit 2

# ENTHALPY CHANGE

---

## PURPOSE

1. To show the connection between internal energy change, enthalpy change and compulsory work.
2. To introduce the ideas of system and surroundings.
3. To stress the potential nature of enthalpy change.
4. To consider that energy is conserved in physical and chemical change.

---

## PRESENTATION

Introduction. In much of what follows, in this Study Unit and in subsequent Study Units, I shall resort to the use of a falling and perhaps spinning weight in an attempt to explain the underlying meaning of the concepts encountered.

Internal energy. The total internal energy of an amount of matter is its total stock of energy. This total energy content would be part potential, part kinetic.

The total absolute energy content of an amount of matter is an inestimable quantity. But differences in energy content can be determined experimentally by measuring the energy, usually as heat, evolved or absorbed over the period of a change.

Now, there is no reason why, for argument's sake and in the name of simplicity, the same basic reasoning cannot be applied to a falling weight as can be applied to a physical or chemical change.

Suppose we call the thing we are interested in, in this case the weight about to fall, the system (and make a habit of shading it so that its limits are abvious); suppose we call all other things around the system, which presumably extend to infinity, the surroundin and leave these unshaded.

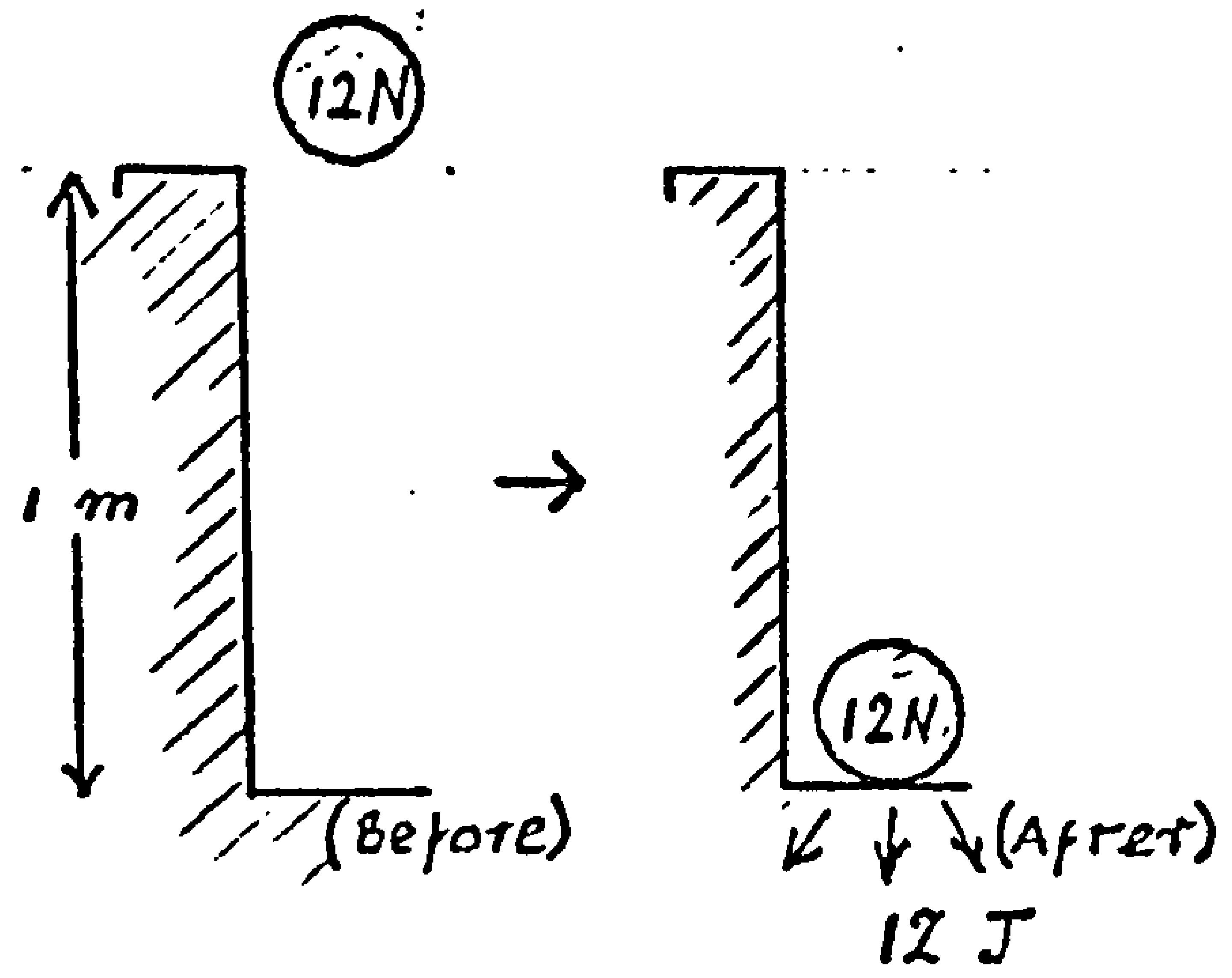


Fig. 2.1

Now refer to Fig. 2.1

A 12 N weight located 1 m above a base surface possesses 12 J more potential energy than it would if located instead on that surface, irrespective of its absolute potential energy content.

If the weight be allowed to drop, this 12 J of potential energy converts to 12 J of kinetic energy at that instant just before impact with the base plate.

At the instant of impact, the 12 J of kinetic energy converts to 12 J of heat.

If we assume all the heat produced on impact to be lost to the vastness of the surroundings, then the change in internal energy of the weight (called the system) is:

$$\Delta E = -12 \text{ J}$$

Loss of energy by the system is given a negative sign.

This analogy represents a chemical reaction in an enclosed constant volume vessel, such that the conversion of reactant to product results in the loss of energy to the surroundings. Heat is lost through the boundary of the system to the surroundings. No work is done. This lack of performance of work is a characteristic of the constant volume change.

If however the same chemical reaction were carried out at constant pressure, as is frequently done in open apparatus, and if the products happened to have a greater volume, say, than the reactants, then some energy - which would otherwise have been evolved as heat during the constant volume change - is used instead to push back the surroundi atmosphere; and so the heat evolved - in this particular example - would be less by this much.

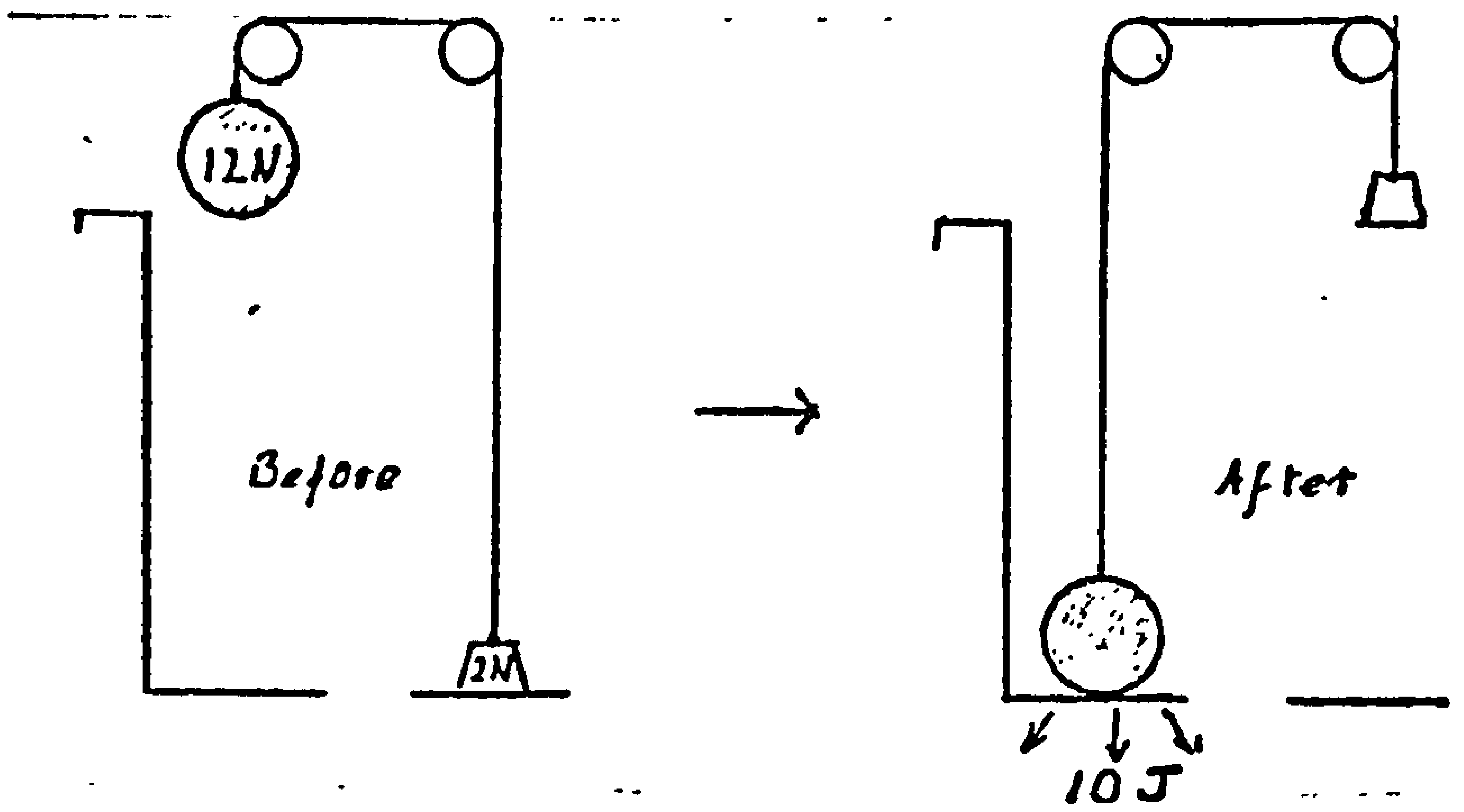


Fig. 2.2

Suppose that 2 J of work are done on the surroundings by the descending 12 N weight. Then only 10 J of heat, instead of 12 J of heat, will be released to the surroundings:

| Change in internal energy | = | Heat exchange between system and surroundings | + | Work done by system |
|---|---|---|---|---|
| $\Delta E$ | | $q_p$ | | $w$ |
| $-12$ J | | $-10$ J | | $-2$ J |

Energy lost by the system is given a negative sign.

The quantity $q_p$, the heat exchange between system and surroundings at constant pressure, is called the enthalpy change, and is normally symbolised as $\Delta H$, i.e.,

$$\Delta E = \Delta H + w$$

I have chosen to define w as 'compulsory work' in the sense that, if the reaction is carried out at constant pressure and is one which entails a change in volume, then work will be done one way or the other. The only way to avoid compulsory work being done is to carry out the reaction at constant volume in an enclosed vessel,

whereupon $\quad w = \text{zero}$

and $\quad \Delta E = q_v$

Compulsory work is sometimes referred to as "P$\Delta$V" work.

Here is a chemical example

$$C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g)$$

When 1 mole of carbon and ½ mole of oxygen react (at some particular temperature and pressure) to form 1 mole of carbon monoxide, and the reaction occurs at constant volume, the heat change is

$$q_v = \Delta E = -113 \text{ kJ}$$

When the reaction is performed at constant pressure, the heat change is

$$q_p = \Delta H = -111 \text{ kJ}$$

Note that the enthalpy change is down a bit on the pure internal energy change because 2 kJ of energy are allocated to doing the compulsory work of expansion and so cannot be expelled as heat.

Note also that there is no great difference between the two values. One could quote the enthalpy change value for a constant volume reaction; the error in doing so would be fairly minor. Indeed, enthalpy changes are often in fact just so quoted.

Refering again to the falling weight depicted in Fig. 2.2 , it will be seen that, for all practical purposes, the weight can in future be regarded as a 10 N weight, and that the physical analogy represents a constant pressure process during which some work is done against the surroundings (2 joules worth), but work in which we are no longer interested; compulsory PAV work is no longer of any consequence to the development of this structured programme.

The analogy, when used later in this programme, will be depicted as shown opposite. This implies that it represents a constant pressure process, that some 'compulsory PAV' work is being done, which is of no interest for our purpose, that the weight in effect is a 10 N weight, and that the heat change with the surroundings has the right to be labeled 'AH'.

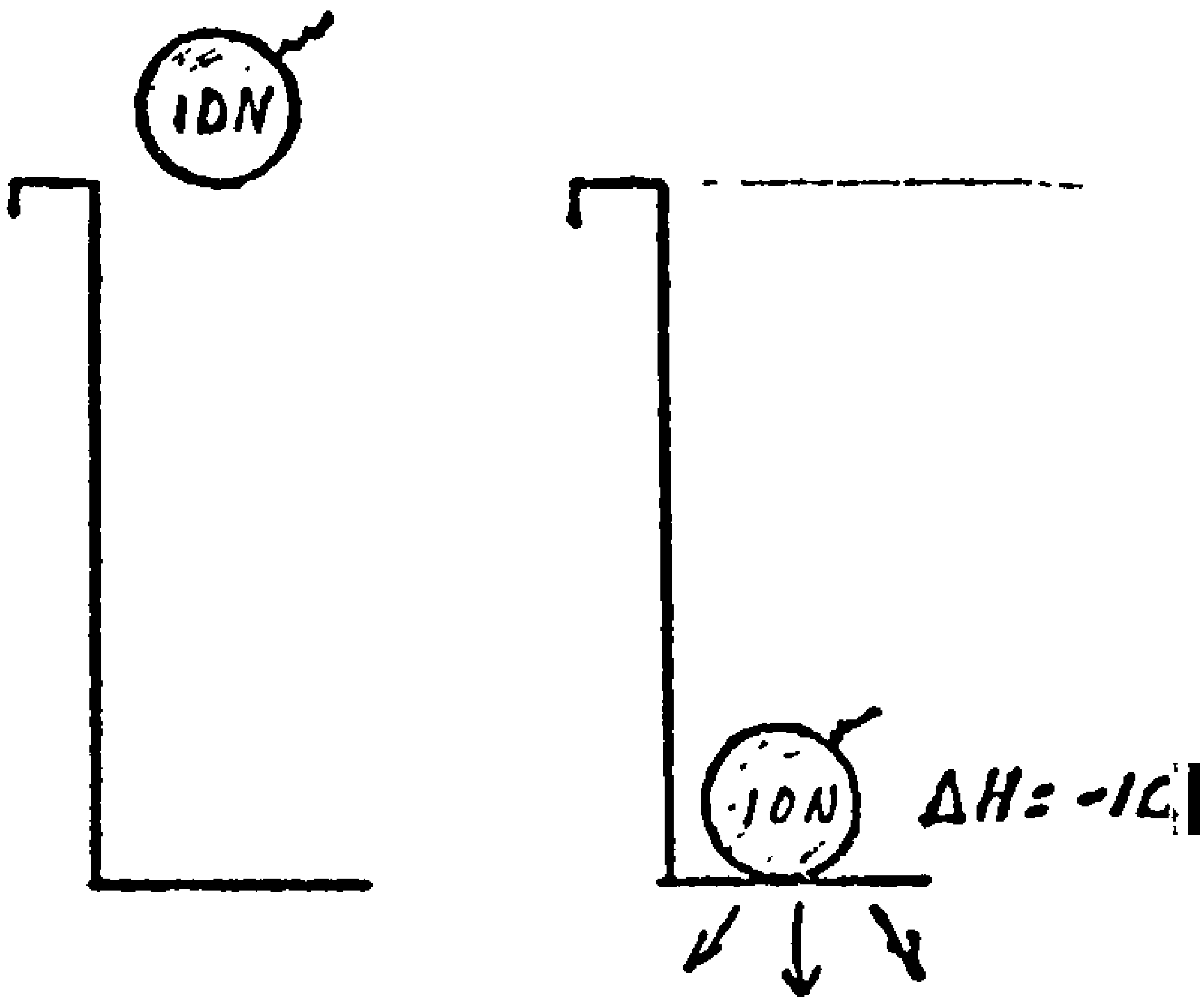


Fig. 2.3

You should now understand enthalpy change to be the heat exchanged between a system and its surroundings under constant pressure conditions. Standard pressure is 1 atmosphere (virtually 760 mmHg).

The constant temperature requirement. In discussing enthalpy change it is essential to compare the enthalpy of the products at a temperature with the enthalpy of the reactants at the same temperature, whatever it is. If this were not so there would be an infinite variety of enthalpy changes, depending on the starting temperature and the finishing temperature.

The usual reference or standard temperature is 25 °C, 298 °K, although it should be noted that the enthalpy change, AH, for a reaction does not vary significantly at different temperature levels. Thus AH for a particular reaction carried out at 100 °C before and after is virtually identical with AH for the same reaction carried out at 25 °C before and after.

An important aspect of the constant temperature requirement is that it fixes the kinetic energy of the products equal to the kinetic energy of the reactants. Consequently, the enthalpy change is a potential energy change. This is very important.

Finally, the foregoing discussion makes the assumption that in any physical or chemical change energy is conserved. During physical and chemical changes energy can neither be created nor destroyed. This, essentially, is a statement of the First Law of Thermodynamics. You will already be familiar with it in the form of Hess's Law.

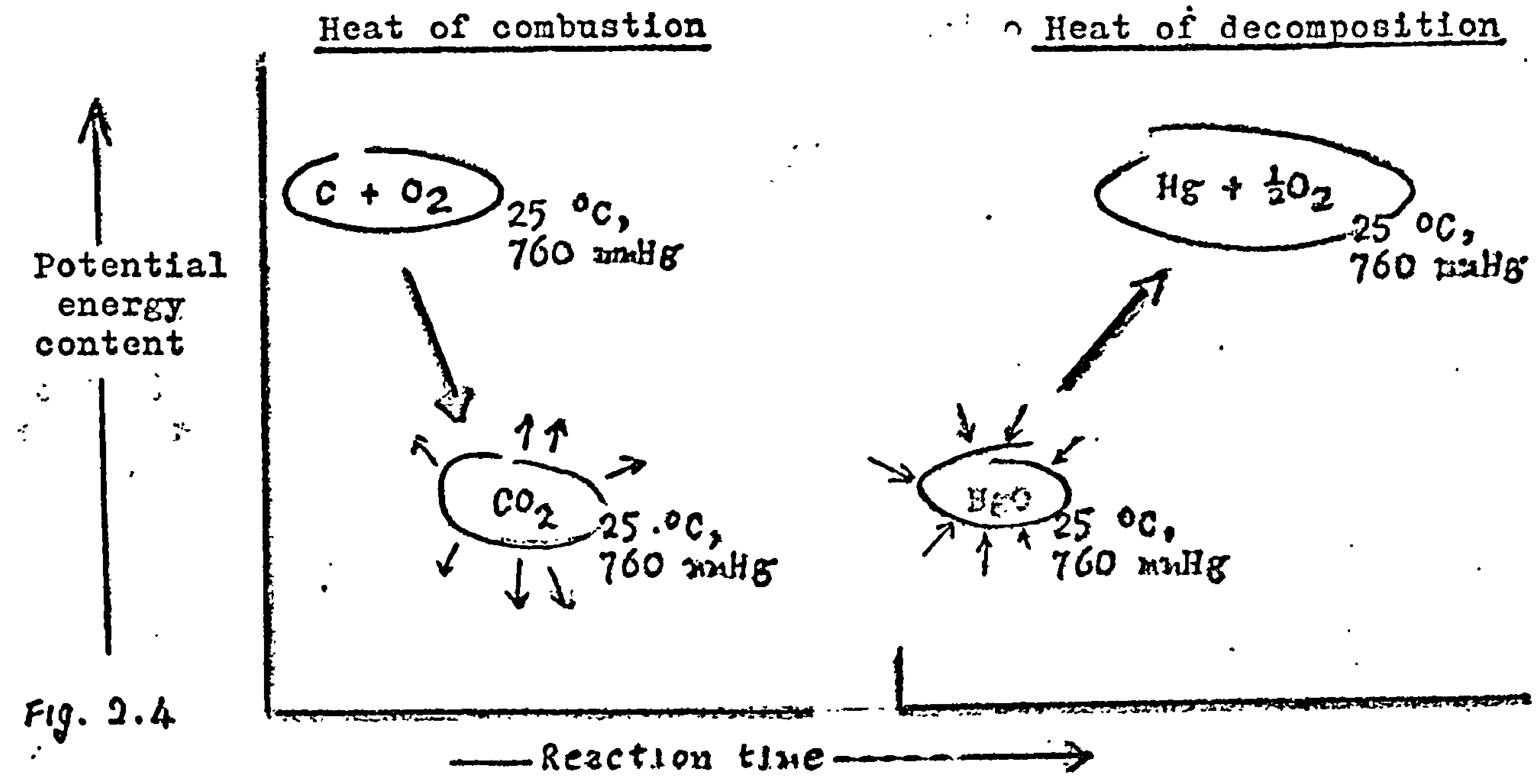


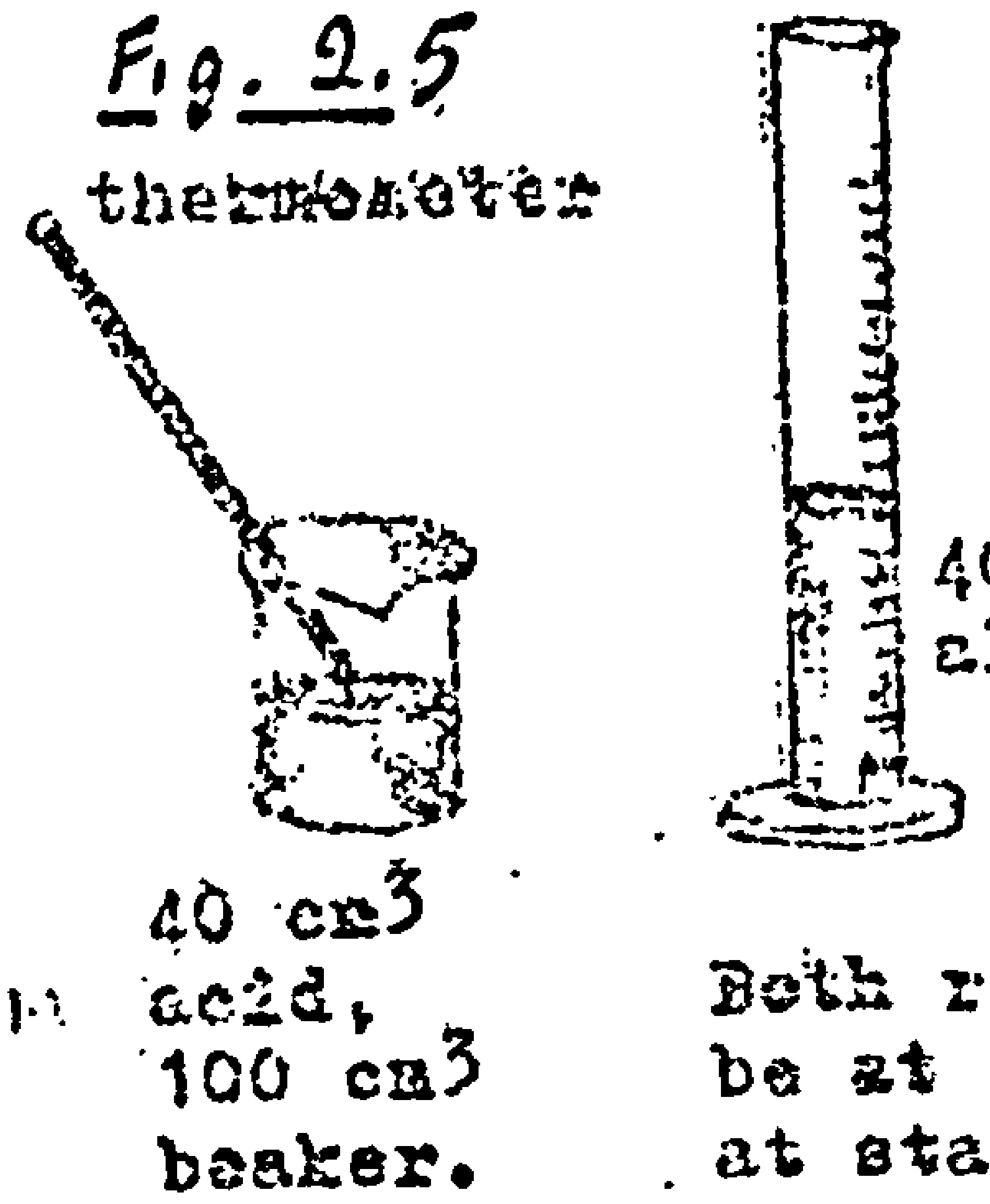
Fig. 2.4

| | | |
|---|---|---|
| Energy, usually as heat, is | lost to surroundings | absorbed from surroundings |
| Enthalpy change, ΔH | −ve | +ve |
| Type of reaction | exoenergetic, mostly exothermic. | endoenergetic, usually endothermic. |

The change in potential energy content at constant pressure is called the enthalpy change.

## Heat of neutralisation

Fig. 2.5



Both reagents must be at room temperature at start of experiment.

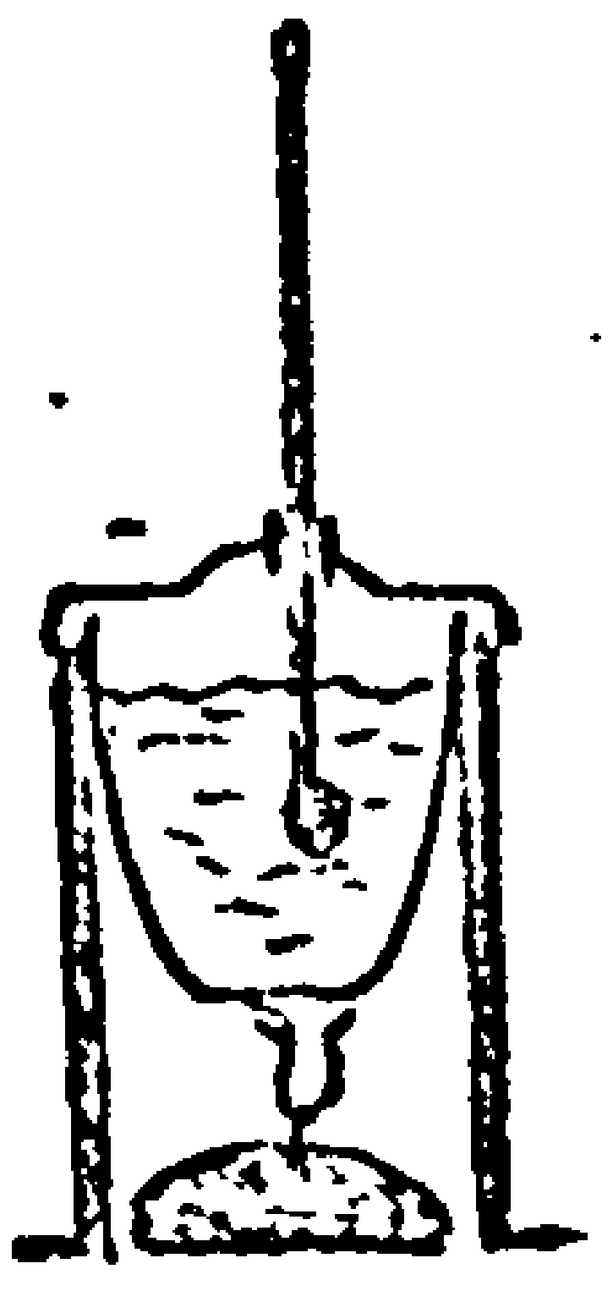
Mix and stir. Note maximum rise in temperature.

Calculate the enthalpy change per mole of water formed: $\underbrace{c}_{4.2\ kJ\ kg^{-1}} \times \underbrace{m}_{kg} \times \underbrace{\Delta\theta}_{^\circ C}$

(Disregard the beaker in your calculation)

| ACID | ALKALI | IONIC REACTION | $\Delta H$; kJ $mole^{-1}$ |
|---|---|---|---|
| M.HCl | M.NaOH | $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ | 56.4 |

## Heat of combustion



The energy (as heat) released by the combustion of a mole amount of reactant (an alcohol) is to be calculated.

A burner containing the alcohol is used to heat water in a copper calorimeter.

Determine the weight of the burner before and after combustion, taking care that no alcohol is lost by evaporation. The decrease in weight of the burner is equal to the weight of alcohol burned.

Know also the weight of the copper calorimeter, the weight of water contained by it, and the temperatures before and after heating.

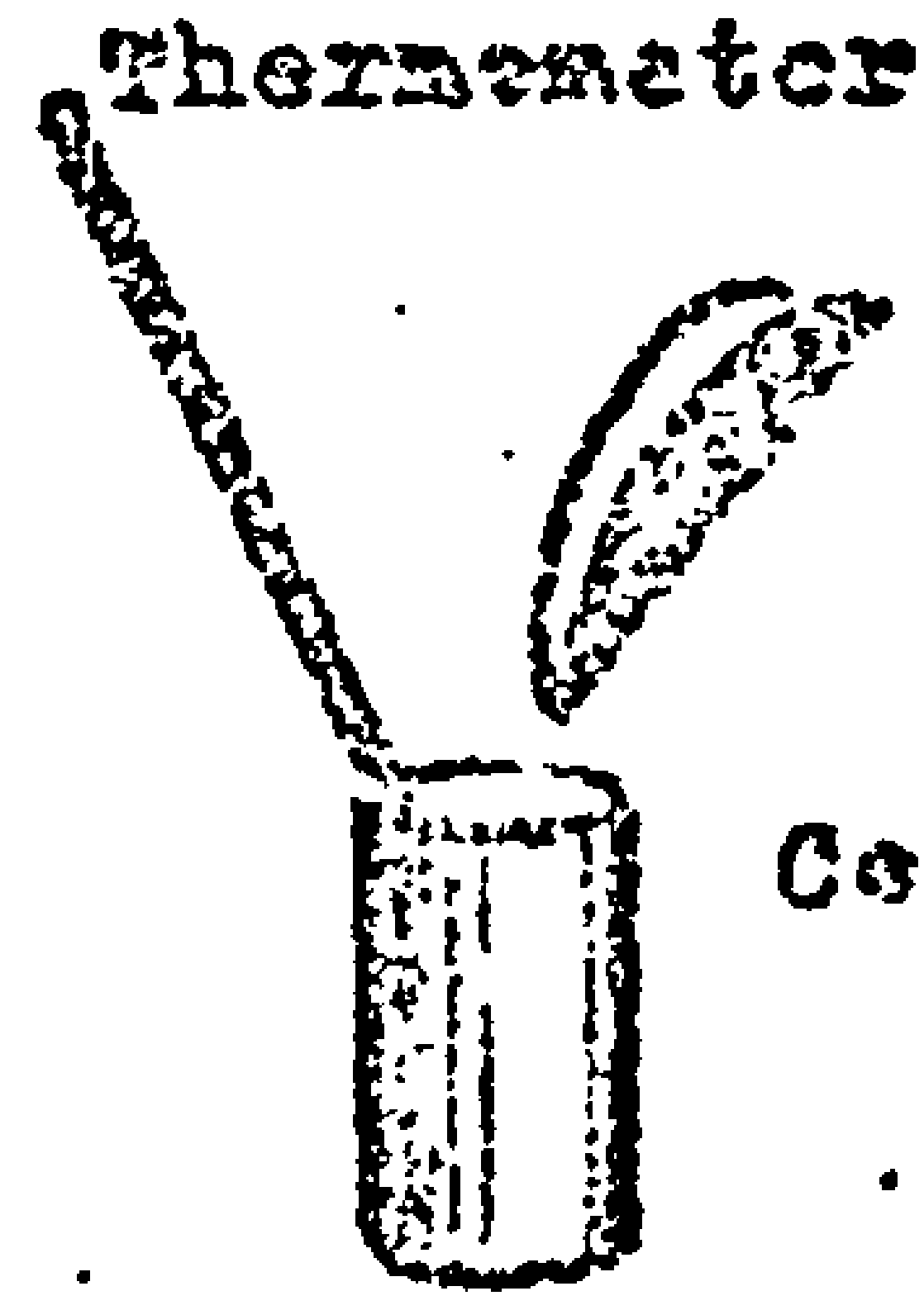
| ALCOHOL | $\Delta H$ of combustion; kJ $mole^{-1}$ |
|---|---|
| Methanol $CH_3OH$ | 715 |
| Ethanol $CH_3CH_2OH$ | 1370 |
| Propanol $CH_3CH_2CH_2OH$ | 2010 |
| Butanol $CH_3CH_2CH_2CH_2OH$ | 2670 |

Table 2.1

## Heat of solution

To be calculated: the energy (as heat) change accompanying the dissolution of one mole of solute in water.

The quantity of water used is such that further dilution produces no detectable temperature change



Solute under test. The filter paper containing about 2 g is weighed before and after adding the solute. The difference in weight is the weight of solute added.

Copper calorimeter containing known weight of water, say 100

Note the change in temperature.

Fig. 2.6

Calculate ΔH of solution per mole of solute.

| SOLUTE | ΔH of solution; kJ mole$^{-1}$ |
|---|---|
| Two or three solutes should be tackled as directed by your supervisor. | Some solutes dissolve exothermically, others dissolve endothermically. |

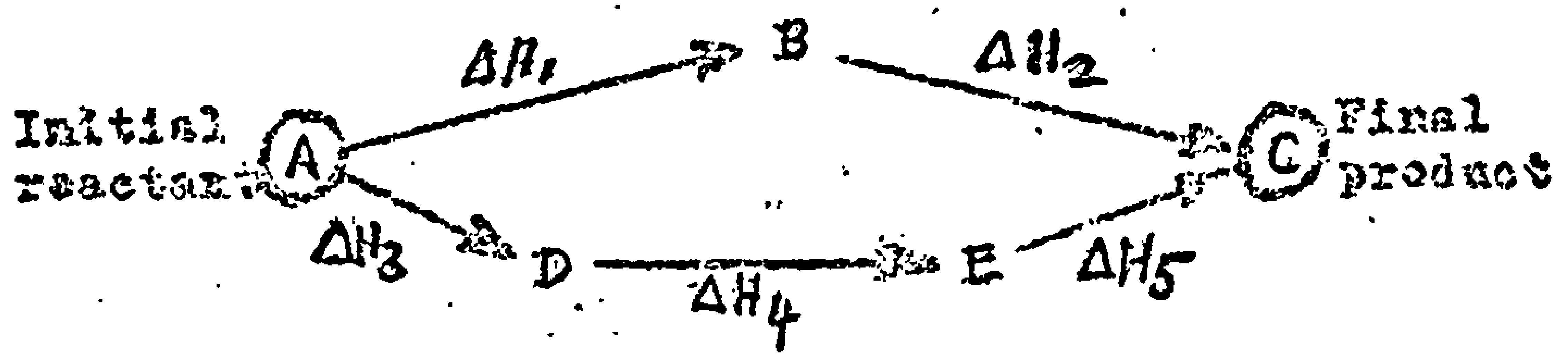
*E.g. $NaOH(s) + 5H_2O \longrightarrow$ conc. NaOH soln. $\Delta H = -37.6$ kJ

and further dilution with more water $\longrightarrow NaOH(aq)$ $\underline{\Delta H = -6.7 \text{ kJ}}$

Addition of still more water produces no further heat change, and so the heat of solution is $\Delta H = -44.3$ kJ mol$^{-1}$. $\underline{\Delta H = -44.3 \text{ kJ}}$

## Hess's Law

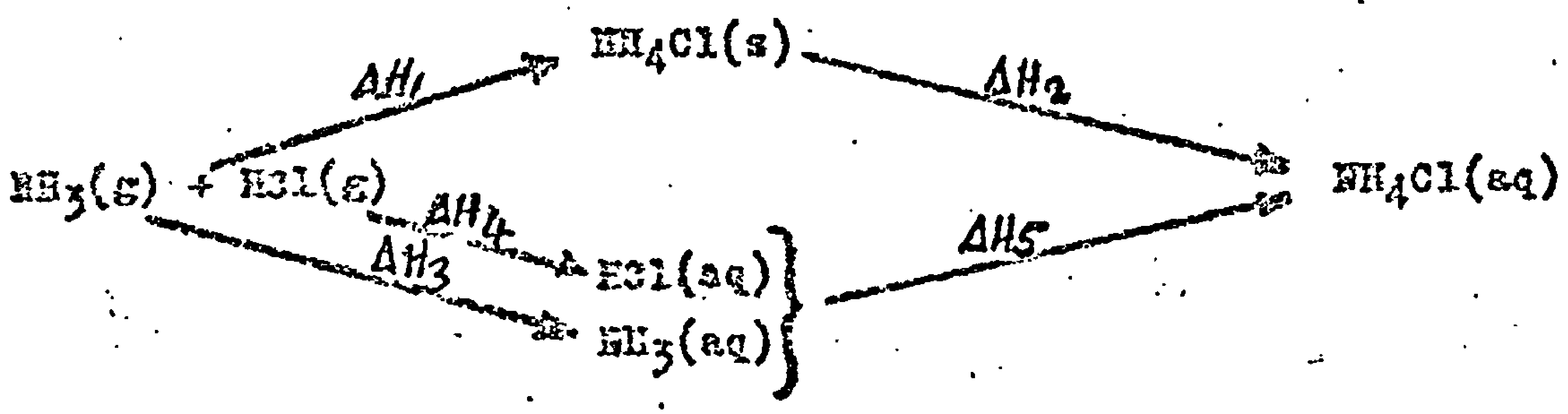
The overall enthalpy change is independent of the route taken.



$$\Delta H_1 + \Delta H_2 = \Delta H_3 + \Delta H_4 + \Delta H_5$$

= a consequence of the conservation of energy.

Results obtained for a real situation are as follows:



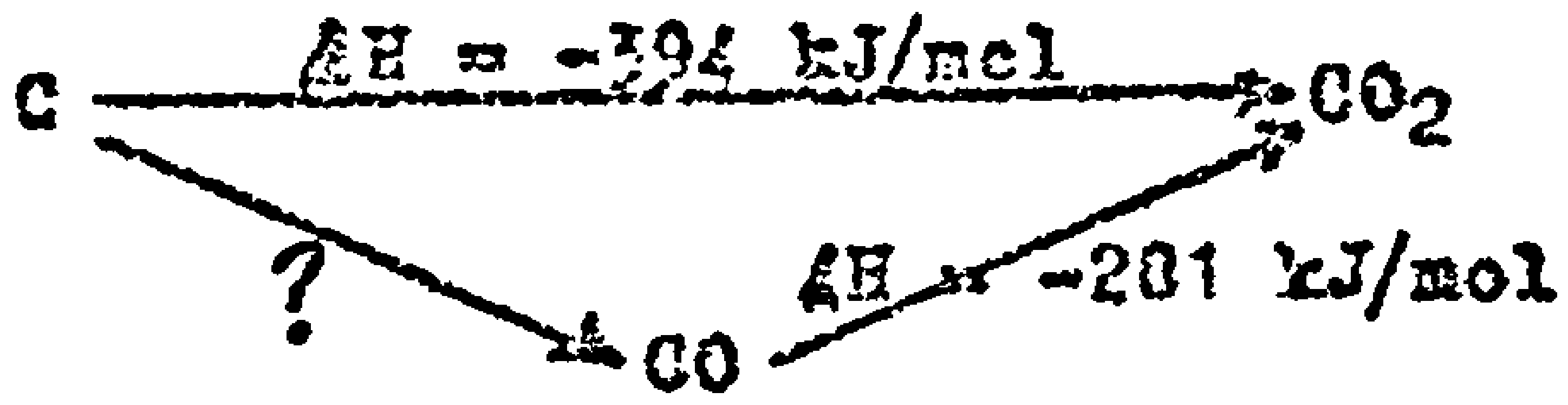
$\Delta H_1 = -176.8$ kJ mole$^{-1}$
$\Delta H_2 = +16.4$ kJ mole$^{-1}$
$-160.4$ kJ mole$^{-1}$

$\Delta H_3 = -35.3$ kJ mole$^{-1}$
$\Delta H_4 = -72.7$ kJ mole$^{-1}$
$\Delta H_5 = -51.7$ kJ mole$^{-1}$
$-159.7$ kJ mole$^{-1}$

## Application of Hess's Law

Hess's Law allows us to deduce enthalpy changes for reactions which cannot be carried out experimentally, for example, the enthalpy of formation of carbon monoxide.

The combustion of a mole of carbon to carbon monoxide only is not possible, hence:



$$\text{Unknown } \Delta H + -281 = -394$$

$$\text{Unknown } \Delta H = -113 \text{ kJ mol}^{-1} \text{ CO}$$

Alternatively, the equations may be manipulated as follows:

| | | | |
|---|---|---|---|
| Given | $C + O_2 = CO_2$ | $\Delta H = -394 \text{ kJ mol}^{-1}$ | (1) |
| and | $CO + \frac{1}{2}O_2 = CO_2$ | $\Delta H = -281 \text{ kJ mol}^{-1}$, | (2) |
| then | $C + O_2 = CO_2$ | $\Delta H = -394 \text{ kJ mol}^{-1}$ | (3) |
| and | $CO_2 = CO + \frac{1}{2}O_2$ | $\Delta H = +281 \text{ kJ mol}^{-1}$ | (4) |
| | $C + \frac{1}{2}O_2 = CO$ | $\Delta H = -113 \text{ kJ mol}^{-1}$ | (5) |

This method is more generally applicable and should be used in preference to the diagrammatic method shown on the preceding page.

Technique. Equations 1 and 2 are known; they represent reactions which can be carried out in the laboratory.

The enthalpy change for reaction 5 is required, but this reaction cannot be carried out.

If 3 and 4 are added together, the required enthalpy change is obtained. Equation 3 is the same as equation 1 while equation 4 is equation 2 reversed.

## Calculation of AH

Elements are arbitrarily given zero enthalpies of formation, symbolised $AHf = 0$; it is impossible to deduce their actual enthalpies of formation.

The arbitrary enthalpy, H, of an element may therefore be taken as zero.

Compounds, therefore, being formed by the combination of elements, will have arbitrary enthalpies which are greater than zero if heat is absorbed when they form, or which are less than zero if heat is evolved when they form. Such enthalpies of formation are depicted in Figure 2.7 for $C_2H_4$, which has a positive enthalpy of formation, and for CO2 and 2H2O, which have negative enthalpies of formation.

Numerical values are quoted for a 'before and after' pressure of 1 atmosphere, and customarily for a temperature of 298 K (25 °C).

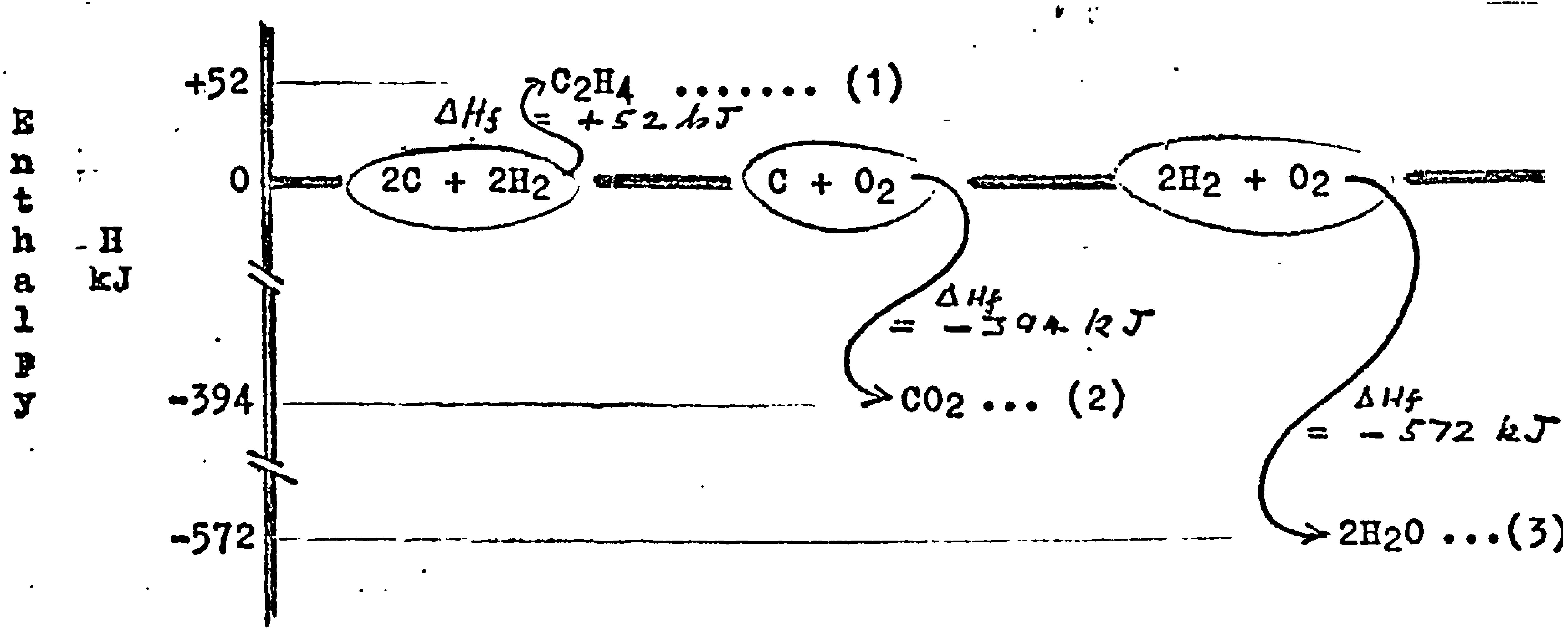


Fig. 2.7

Figure 2.7 shows that the arbitrary enthalpy of formation of ethene, $C_2H_4$, is such that 52 kJ of heat are absorbed when 1 mole of ethene is formed from 2 moles of carbon and 2 moles of hydrogen at a constant pressure of 1 atmosphere, and at constant temperature. This is symbolised: $AHf = +52$ kJ mol-1.

If you refer to a data book you will find this value, though it may vary slightly from book to book. (The data book will also use the symbol $AH_f^o$ instead of $AH_f$. The reason for this will be explained later.)

Thus $2C + 2H_2 \longrightarrow C_2H_4$; $AH_f = +52$ kJ mol$^{-1}$ .... 1

Similarly $C + O_2 \longrightarrow CO_2$; $AH_f = -394$ kJ mol$^{-1}$ ... 2

and $2H_2 + O_2 \longrightarrow 2H_2O$; $AH = -572$ kJ .... 3

Now use the data given on page 2.10 to calculate the enthalpy change for the combustion of a mole of ethene.

ΔH for $C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$ is required.

1st method

| | | |
|---|---|---|
| Reverse (1) | $C_2H_4 \longrightarrow 2C + 2H_2$ | $\Delta H = -52$ kJ |
| Double (2) | $2C + 2O_2 \longrightarrow 2CO_2$ | $\Delta H = -788$ kJ |
| (3) as it is | $2H_2 + O_2 \longrightarrow 2H_2O$ | $\Delta H = -572$ kJ |
| Add: | $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$ | $\Delta H = -1412$ kJ |

It is always advisable to write down clearly - before starting - the exact form of the required equation. The available equations are then 'juggled' such that when added, the required equation is obtained.

2nd method

Substitute the arbitrary enthalpy values.

| $C_2H_4$ | + | $3O_2$ | $\longrightarrow$ | $2CO_2$ | + | $2H_2O$ |
|---|---|---|---|---|---|---|
| H = +52 kJ | | H = zero | | H = 2 x -394 kJ | | H = -572 kJ |

and $\Delta H = \Sigma H$ of products $- \Sigma H$ of reactants

$$= (2 \times -394 + -572) - (+52 + \text{zero}) \text{ kJ}$$

$$= \underline{-1412 \text{ kJ}}$$

Note: $\boxed{\text{Enthalpy change}} = \boxed{\text{Summed enthalpies of products}} - \boxed{\text{Summed enthalpies of reactants}}$

## Study Unit 2 What you should know.

You should

1. be aware that in a change there is a 'system' part and a 'surroundings' part.
2. understand AH to be the constant pressure heat change.
3. realise the need for the same before and after temperature in enthalpy change.
4. know that enthalpy change is a potential energy term.
5. understand the First Law of Thermodynamics.
6. be aware of some heats of reaction.
7. know Hess's Law.
8. be able to apply Hess's Law.

---

Question 1 The change in potential energy content at constant pressure is:

| | |
|---|---|
| 1 the enthalpy change. | 2 the heat change qp |
| 3 $\Delta H$ | 4 the enthalpy |

Question 2 When a change occurs at constant temperature and much heat is evolved, does this mean that:

1 the products are poorer in potential energy than the reactants?

2 the products are poorer in kinetic energy than the reactants?

3 the law of conservation of energy has been broken?

4 the enthalpy change for the reaction is negative?

Question 3 Which of the following is (are) not contrary to the law of conservation of energy?

| | |
|---|---|
| 1 Water at the foot of the Niagara Falls is 1/10th degree C warmer than it was at the top. | 2 When ice cools, heat is evolved. |
| 3 A swinging pendulum at its lowest point has slightly less kinetic energy than it had potential energy at its highest point. | 4 A ball set in motion round the inside of a glass bowl eventually loses all its kinetic energy. |

Question 4 Refer to the table of mean bond dissociation energies on page 38 of your Three Figure Tables to calculate the enthalpy change accompanying the reaction

$$C_2H_4 + Cl_2 \rightarrow CH_2ClCH_2Cl$$

| | |
|---|---|
| 1 +155 kJ | 2 -184 kJ |
| 3 -435 kJ | 4 Some other answer |

**Question 1**

| | |
|---|---|
| Response 1 | This response is correct. |
| Response 2 | This response is correct. |
| Response 3 | This response is Correct. |
| Response 4 | This response is incorrect. The absolute ehthalpy is an unknown quantity. |

**Question 2**

| | |
|---|---|
| Response 1 | This is a correct response. |
| Response 2 | This is incorrect. If the temperature is constant there is no change in kinetic emergy total. |
| Response 3 | The law of conservation of energy has not been broken. The heat evolved is equal to the decrease in potential energy suffered by the reactnats changing into products. |
| Response 4 | This is correct. Heat lost by the system is given a negative sign. |

**Question 3**

| | |
|---|---|
| Response 1 | This response is not contrary to the law of conservation of energy. The potential energy of water at the top of the Falls is converted to kinetic energy which on impact is converted to heat. |
| Response 2 | This is a correct response. Cooling always results in the loss of energy by the object cooling.. |
| Response 3 | If the pendulum were swinging in a vacuum so that there was no friction with the air, and if the pivot point at which the pendulum was supported were frictionless, then kinetic energy and potential energy would interchange indefinitely. In a real situation, the kinetic energy continuously converts to heat energy and so the pendulum eventually runs out of both potential energy and kinetic energy. This is not contrary to the law of conservation of energy. |
| Response 4 | This is not contrary to the law of conservation of energy. The same general reasons apply here as in Response 3. |

**Question 4**

| | |
|---|---|
| Response 1: 155 kJ | This is incorrect. In deducing the answer, you have included the formation of only one C-Cl bond instead of two. |
| Response 2: -184 kJ | This is correct. |
| Response 3: -435 kJ | This is incorrect. You have forgotten to include the breaking of the C=C double bond. |
| Response 4 | A variety of other errors are also possible.<br>Here is the correct solution. |

Question 4 continued

Response 4

Here is the correct solution

$$H_2C{=}CH_2 + Cl{-}Cl \longrightarrow Cl{-}CH_2{-}CH_2{-}Cl$$

Bonds to be broken: one C = C bond; AH = +598 kJ
one Cl-Cl bond; AH = +243 kJ
AH +841 kJ

Bonds to be made: one C-C bond; AH = -347 kJ
two C-Cl bonds; AH = -678 kJ
AH -1025 kJ

AH for the whole reaction is the sum of the bond breaking and bond making processes:

$AH_{total}$ = +841 + -1025 Kj
= <u>-184 kJ</u>

# Study Unit 3

## BOND ENERGIES

---

PURPOSE

1. To calculate some bond energies with the aid of Hess's Law.

---

PRESENTATION

Introduction. You will have been introduced to Hess's Law during Form V, at which point you will have applied the law to calculate some bond energies, such as C-H, C-C and perhaps O-H. And again, during the study of carbon compounds, you will in particular have deduced the energies of the C-C bond, the C=C bond and the C≡C bond.

This unit does little more than revise this work. You may therefore find it an easy unit to work through, in which case you should progress fairly rapidly to Unit 4.

The bond energies will be deduced by a schematic presentation of Hess's Law. However, since the 'equation solving' technique is generally more applicable to problem solving, I have used this method as well.

A great deal can be said about bond energies, but later sections of the C.S.Y.S. syllabus are concerned with this topic. This unit sets out to show that the C=C bond is stronger than the C-C bond, though not twice as strong; and that the C≡C bond is stronger still, though not three times as strong.

Calculation of bond energies The energy released by the formation of a mole of carbon-hydrogen bonds will be calculated first since this information is required in order to calculate the energy released by the formation of carbon-carbon bonds.

The energy released by the formation of carbon-hydrogen bonds may be calculated by considering the formation of methane, $CH_4$, which contains only this kind of bond.

What in fact is required is the enthalpy change for the reaction

$$C(\text{gaseous, monatomic}) + 4H(\text{gaseous, monatomic}) \longrightarrow CH_4(\text{gaseous})$$

since this enthalpy change represents the energy released when a mole of isolated carbon atoms come together with four moles of isolated hydrogen atoms to form one mole of isolated methane molecules, and in so doing form four moles of C-H bonds.

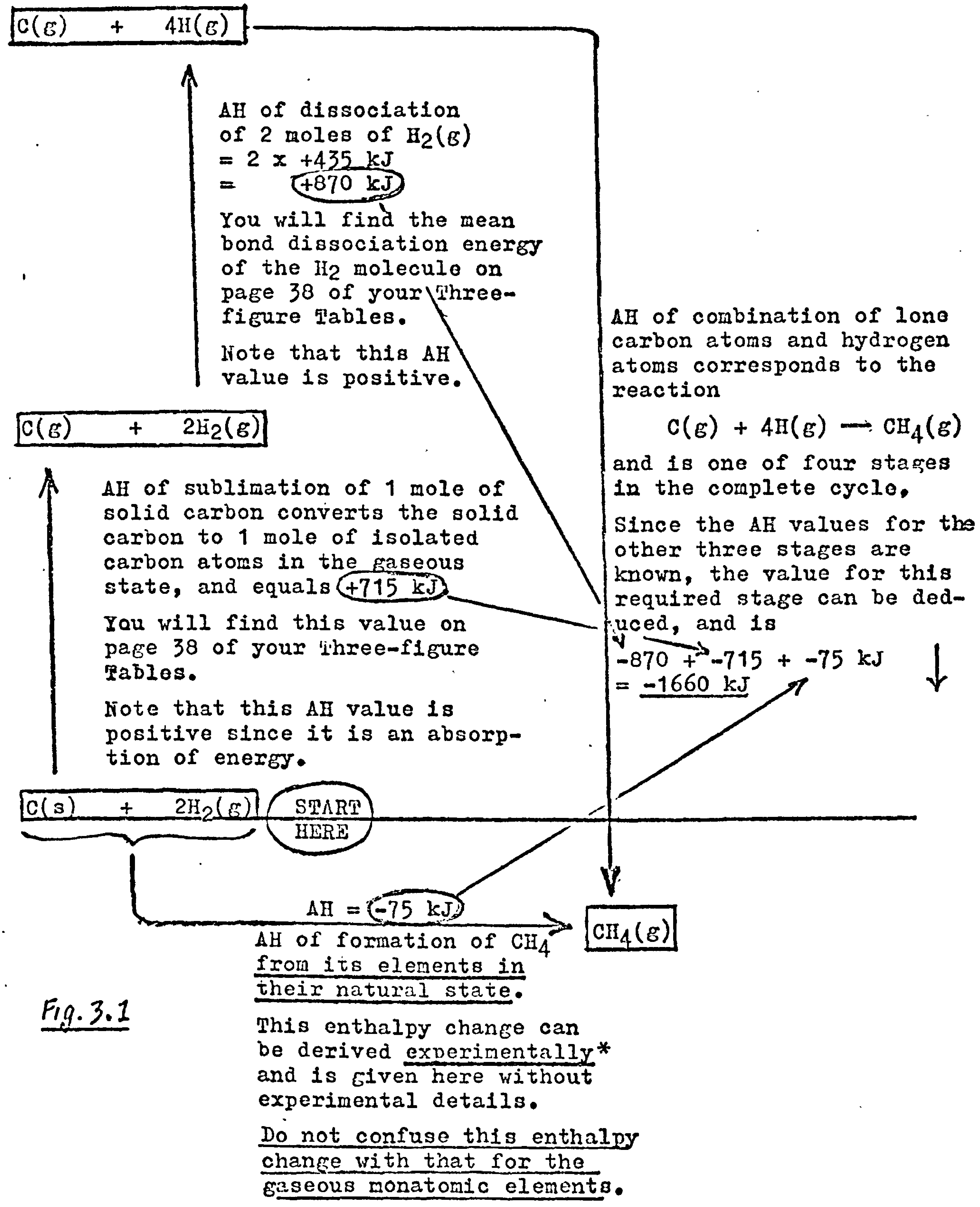
What is required, then, is the enthalpy change, $\Delta H$, for the reaction

$$C(g) \quad + \quad 4H(g) \longrightarrow CH_4(g)$$

This enthalpy change divided by 4 will give the average enthalpy of formation of one mole of C-H bonds, that is, the average C-H bond energy in kJ $mol^{-1}$.

The required enthalpy change is obtained by applying Hess's Law.

Schematic method -



ΔH of dissociation of 2 moles of $H_2(g)$
$= 2 \times +435$ kJ
$= +870$ kJ

You will find the mean bond dissociation energy of the $H_2$ molecule on page 38 of your Three-figure Tables.

Note that this ΔH value is positive.

ΔH of sublimation of 1 mole of solid carbon converts the solid carbon to 1 mole of isolated carbon atoms in the gaseous state, and equals +715 kJ

You will find this value on page 38 of your Three-figure Tables.

Note that this ΔH value is positive since it is an absorption of energy.

ΔH of combination of lone carbon atoms and hydrogen atoms corresponds to the reaction

$$C(g) + 4H(g) \longrightarrow CH_4(g)$$

and is one of four stages in the complete cycle.

Since the ΔH values for the other three stages are known, the value for this required stage can be deduced, and is

$-870 + -715 + -75$ kJ
$=$ $-1660$ kJ

ΔH = −75 kJ

ΔH of formation of $CH_4$ from its elements in their natural state.

This enthalpy change can be derived experimentally* and is given here without experimental details.

Do not confuse this enthalpy change with that for the gaseous monatomic elements.

Fig. 3.1

Thus, the energy liberated by the formation of 4 moles of C-H bonds is 1660 kJ.

Therefore, the energy of formation of the C-H bond $= \frac{-1660}{4}$ kJ mol$^{-1}$
$= -415$ kJ mol$^{-1}$

*From heats of combustion.

You may prefer to simplify the scheme shown in Figure 3.1 by ignoring the sign convention until the end of the calculation.

NOT TO SCALE

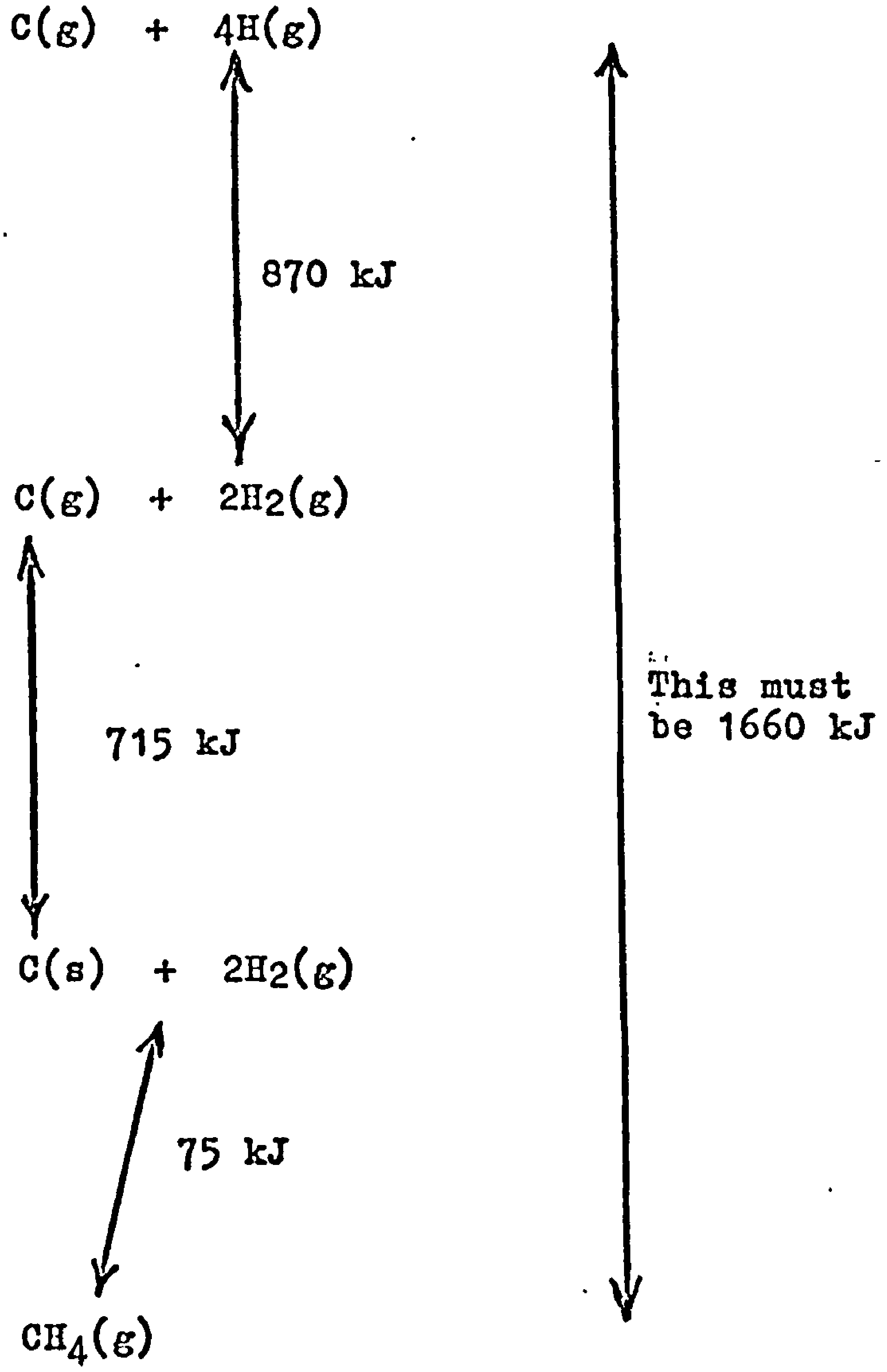


Fig. 3.2

Having established that the relevant enthalpy change is numerically equal to 1660 kJ, now decide its sign.

The reaction $C(g) + 4H(g) \longrightarrow CH_4(g)$ will be exothermic, and therefore ΔH will be negative and will equal -1660 kJ.

Dividing by 4 gives the enthalpy of formation of one mole of C-H bonds since 1660 kJ are evolved by the formation of 4 moles of C-H bonds.

The average C-H bond energy is therefore 415 kJ $mol^{-1}$ in the sense that this is the energy released by the formation of a mole of these bonds or is the energy required to break a mole of these bonds.

Equation solving method. This method, by my experience, usually requires considerable tutorial effort; it is not suited to programmed instruction. Perhaps you will be able to cope with it.

| | | |
|---|---|---|
| Required: | $C(g) + 4H(g) \rightarrow CH_4(g)$ | AH = ? |
| Given: (1) | $C(s) \rightarrow C(g)$ | AH = +715 kJ |
| (2) | $H_2(g) \rightarrow 2H(g)$ | AH = +435 kJ |
| (3) | $C(s) + 2H_2(g) \rightarrow CH_4(g)$ | AH = -75 kJ |
| Reverse (1) | $C(g) \rightarrow C(s)$ | AH = -715 kJ |
| Reverse and double (2) | $4H(g) \rightarrow 2H_2(g)$ | AH = -870 kJ |
| Use (3) as it is | $C(s) + 2H_2(g) \rightarrow CH_4(g)$ | AH = -75 kJ |
| Add | $C(g) + 4H(g) \rightarrow CH_4(g)$ | AH = -1660 kJ |

From which, as before, the energy of formation of the C-H bond is -415 kJ $mol^{-1}$.

Note that, conversely, the bond dissociation energy is +415 kJ $mol^{-1}$. You might like to check that this value is in very close agreement with the value quoted on page 38 of your Three-figure Tables.

## Calculating the carbon to carbon bond energies in $C_2H_6$, $C_2H_4$ and $C_2H_2$.

It would be better, at this point in the discussion, to have a preliminary look at the method by which such calculations are made. The method can then be applied to the three hydrocarbons simultaneously in order to contrast them.

Initially, then, consider only ethane, $C_2H_6$.

In order to calculate the energy released by the formation of a mole of C-C bonds, we must first deduce somehow the heat evolved by the reaction

$$2C(g) + 6H(g) \longrightarrow C_2H_6(g) \qquad \text{AH} = ?$$

because

ΔH the total heat evolved = that due to the formation of 6 moles of C-H bonds + that due to the formation of 1 mole of C-C bonds

and if we know the first and the second terms we can deduce the third one.

Now, the first term, as you will see shortly, can be deduced most simply by a schematic presentation of Hess's Law. It turns out to have the value AH = -2820 kJ, meaning that 2820 kJ of heat are evolved by two moles of carbon atoms and six moles of hydrogen atoms coming together, as it were, from infinity to form the bonds in one mole of ethane molecules.

There is a slight complication with the second term. According to our previous calculation of the C-H bond strength, this second term should have the value AH = 6 x -415 kJ = -2490 kJ. But the strength of the C-H bond varies slightly according to the nature of its neighbours, that is to say, what molecule it finds itself in. If you check with page 38 of your Three-figure Tables you will see that the bond dissociation energies are particularly quoted as mean values. Consequently, and without further explanation, I shall take the value of the C-H bond for the second term above as 412 kJ instead of 415 kJ. The full value of the second term will therefore be AH = 6 x -412 kJ = -2472 kJ.

Thus, the heat evolved by the formation of one mole of C-C bonds in ethane molecules is 2820 - 2472 kJ = 348 kJ.

Hence, AH of formation of the C-C bond = $-348$ kJ mol$^{-1}$

We are now in a position to contrast the strengths of the carbon to carbon bonds in ethane, ethene and ethine.

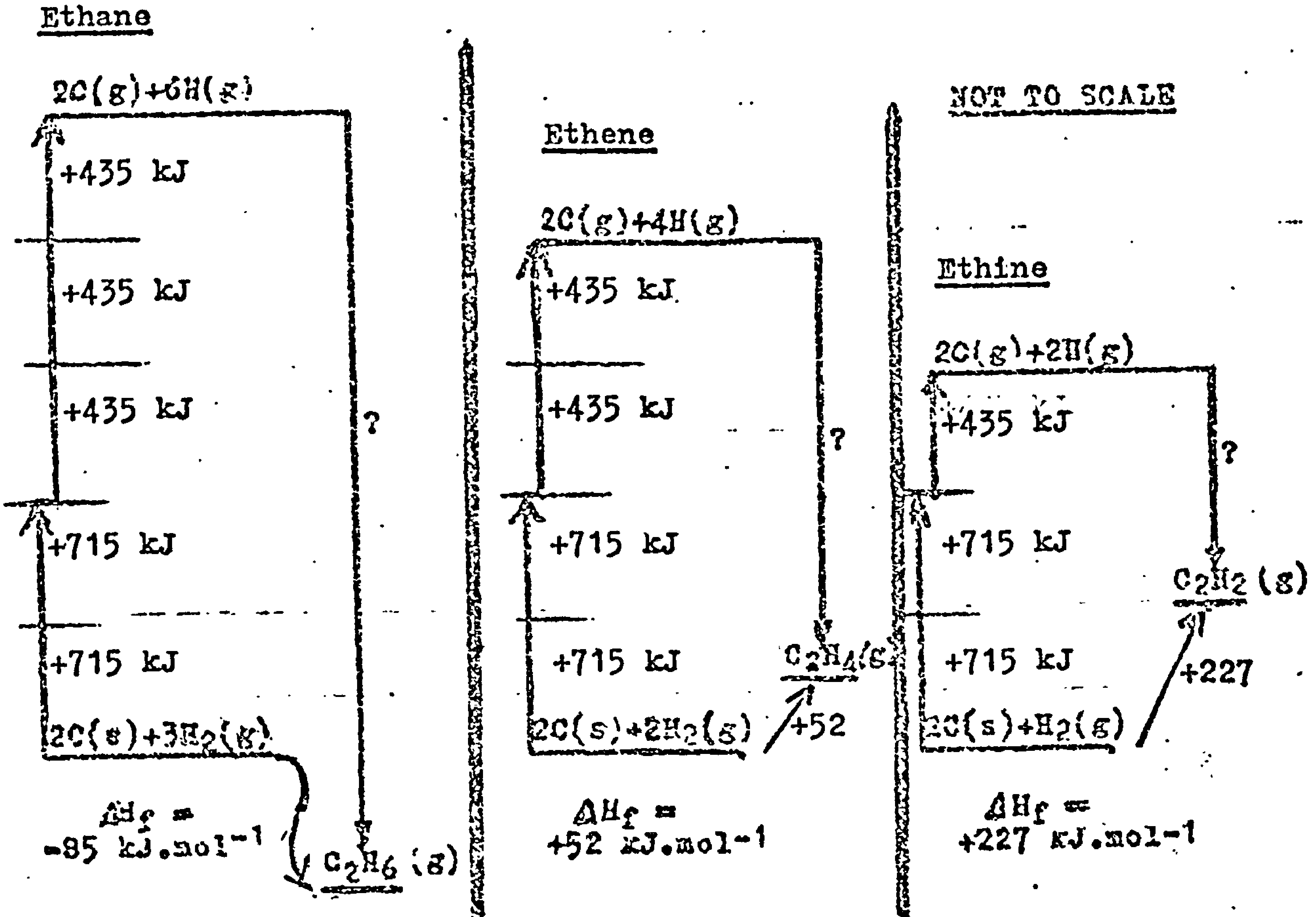
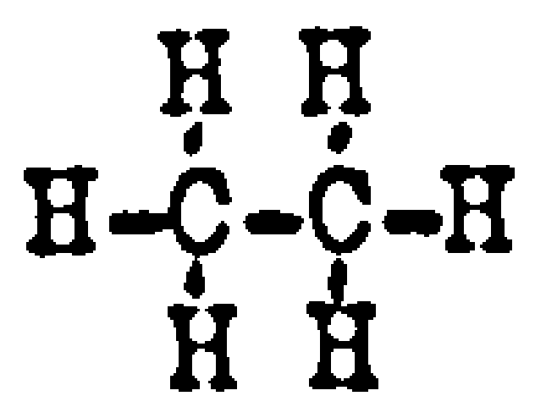


Fig. 3.3

For ethane: $2C(g) + 6H(g) \rightarrow C_2H_6(g)$


$H_3C{-}CH_3$

AH = 3 x -435 = -1305 kJ
+ 2 x -715 = -1430 kJ
+ 1 x -85 = -85 kJ
-2820 kJ

Formation of 6 moles C-H bonds and 1 mole C-C bonds evolves 2820 kJ
But, formation of 6 moles C-H bonds only evolves 6 x 412 = 2472 kJ

Therefore, formation of 1 mole of C-C bonds only evolves 2820 - 2472 kJ
= 348 kJ

and AH formation C-C bond = $-348$ kJ mol$^{-1}$

<u>For ethene:</u> $2C(g) + 4H(g) \rightarrow C_2H_4(g)$ AH = 2 x -435 = -870 kJ
+ 2 x -715 = -1430 kJ
+ 1 x +52 = +52 kJ
-2248 kJ

H H
C=C
H H

Formation of 4 moles of C-H and 1 mole C=C bonds evolves 2248 kJ
But formation of 4 moles of <u>C-H bonds only</u> evolves 4 x 412 = 1648 kJ

Therefore, formation of 1 mole of C=C bonds evolves 2248 - 1648 kJ
= 600 kJ

and AH formation of C=C bond = <u>-600 kJ mol$^{-1}$</u>

<u>For ethine:</u> $2C(g) + 2H(g) \rightarrow C_2H_2(g)$ AH = 1 x -435 = -435 kJ
+ 2 x -715 = -1430 kJ
+ 1 x +227 = +227 kJ
-1638 kJ

H-C≡C-H

Formation of 2 moles of C-H and 1 mole of C≡C bonds evolves 1638 kJ
But formation of 2 moles of C-H bonds only evolves 2 x 412 = 824 kJ

Therefore, formation of 1 mole of C≡C bonds evolves 1638 - 824 kJ
= 814 kJ

and AH formation of C≡C bond = <u>-814 kJ mol$^{-1}$</u>

Table 3.1 Summary of carbon-carbon bonding

| Bond | C-C | C=C | C≡C |
|---|---|---|---|
| Bond energy (kJ mol$^{-1}$) | 348 | 600 | 814 |
| Strength of C to C linkage | → | increases | → |
| Energy released per single bond when on its own, when part of a double bond, and when part of a triple bond. | 348 | 300 | 271 |
| Stability of C to C linkage | → | decreases | → |

The carbon-carbon double bond is much stronger that the carbon-carbon single bond, but it is not twice as strong. Less energy is released by the formation of a single bond when it is part of a double bond than when it is on its own. This can be ascribed to the strain associated with bonds which are bent out of their preferred tetrahedral arrangement. This means that there is still some potential energy locked up in the double bond which might otherwise have been released if two separate single bonds had formed instead of the double bond.

The carbon-carbon triple bond is even more strained, and so the energy released by a single bond when it is part of a triple bond is markedly less than when it is a single bond on its own.

(Note that this argument does not necessarily apply to other elements than carbon; for example, the nitrogen-nitrogen triple bond is much more than three times stronger than the nitrogen-nitrogen single bond.)

The lack of stability of the acetylenic triple bond is reflected in the positive heat of formation of ethine, that is to say, in the absorption of heat when ethine is formed from its elements in their normal state at 25 °C and 1 atmosphere:

$$2C(s) \quad + \quad H_2(g) \quad \longrightarrow \quad C_2H_2 ; \qquad \Delta H = +227.1 \text{ kJ mol}^{-1}$$

Ethine is, therefore, described as an endothermic compound. You may at this point be puzzled by the apparently contradictory facts:

a) bond formation is always exothermic - if no energy is released, no bond is formed, and
b) the heat of formation of ethine (which involves bond formation) is endothermic.

But remember that the heat of formation is an overall process which requires bond breaking in solid carbon and gaseous molecular hydrogen (energy absorbing) before the lone carbon atoms and lone hydrogen atoms bond together to form ethine (energy evolving).

The endothermic character of ethine's heat of formation is often advanced as an explanation for ethine's lack of stability. This is correct in as far as it goes, but still leaves unanswered the question: why is less energy released when lone carbon atons and lone hydrogen atoms bond to form ethine than might otherwise be released? The answer has to do with the strain which arises when three covalent bonds are twisted out of their more usual tetrahedral orientation and forcibly aligned parallel to each other between the same two carbon atoms.

Ethene, also, is an endothermic compound, but much less so; its heat of formation is +52.1 kJ mol$^{-1}$. Ethane, by contrast, is exothermic; its heat of formation is -85.3 kJ mol$^{-1}$.

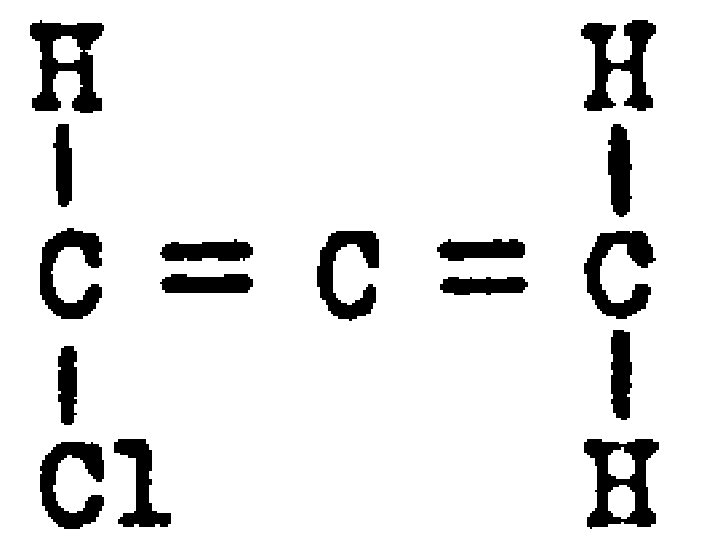
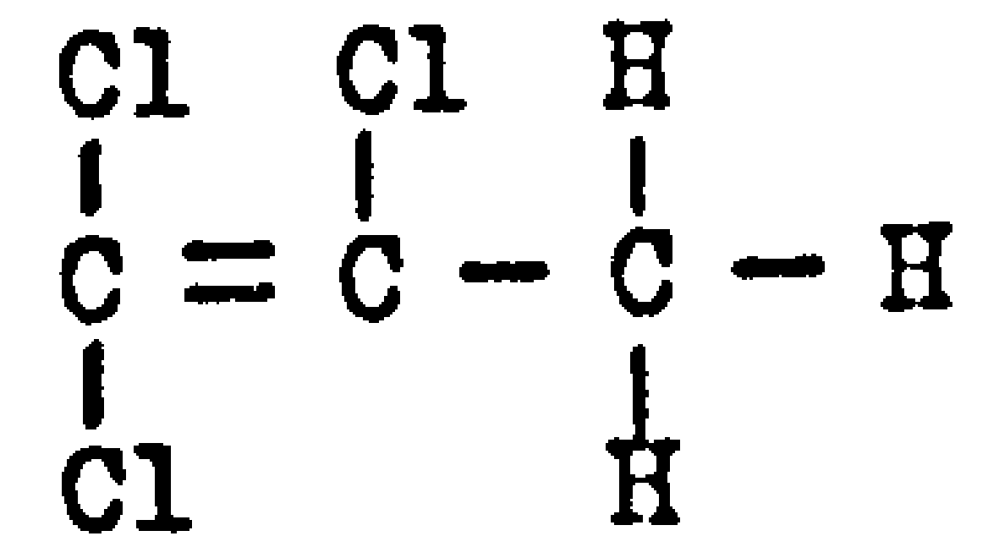
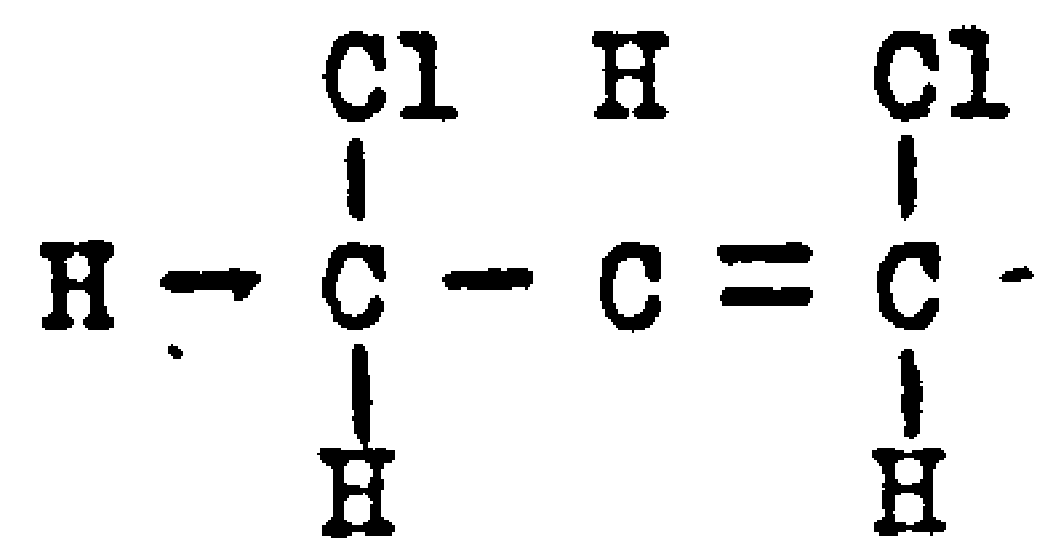
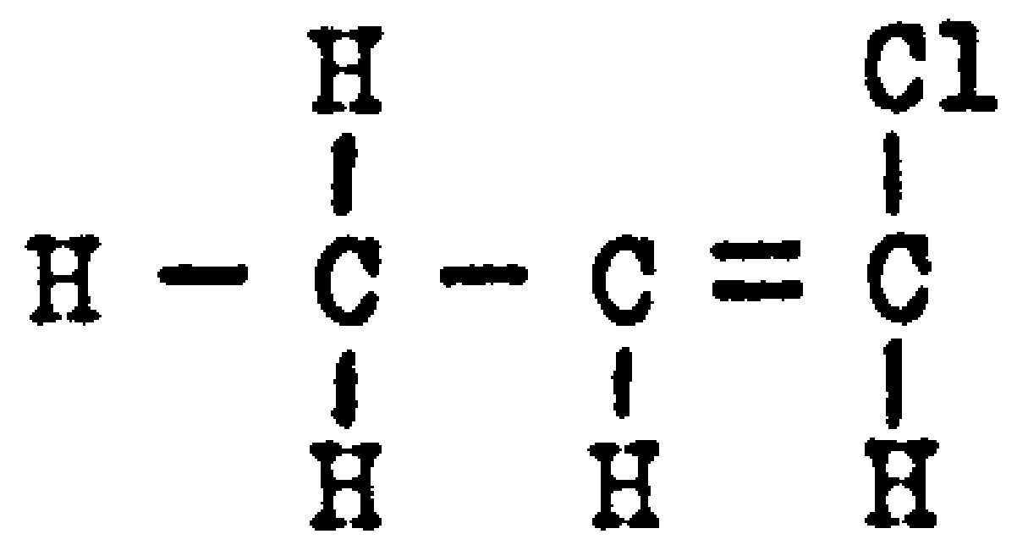
Study Unit 3 What you should know.

You should
1. know how to calculate some bond energies.
2. have some general ideas of the 'strength' of bonds.
3. understand what is meant by 'endothermic compound'.

Question 1 The energies of formation of some bonds are:

| Bond | AH kJ mol$^{-1}$ |
|---|---|
| C − H | −412 |
| C − C | −347 |
| C = C | −598 |
| C − Cl | −339 |

The heat of formation of a chlorinated hydocarbon from its gaseous monatomic elements is AH = −3344 kJ mol$^{-1}$. Which of the offered formulae correspondsto this heat of formation?

| | |
|---|---|
| 1  $\mathrm{CHCl{=}C{=}CH_2}$ | 2  $\mathrm{CCl_2{=}CCl{-}CH_3}$ |
| 3  $\mathrm{CH_2Cl{-}CH{=}CHCl}$ | 4  $\mathrm{CH_3{-}CH{=}CHCl}$ |

Question 2 Calculate the heat of formation of gaseous hydrogen chloride per mole from the following data:

| Bond | AH(formation) kJ mol$^{-1}$ |
|---|---|
| H − H | −435 |
| Cl − Cl | −243 |
| H − Cl | −431 |

| | |
|---|---|
| 1 +245 kJ | 2 −184 kJ |
| 3 +92 kJ | 4 −92 kJ |

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

## Question 1

**Responses 1,2 and 3** These responses are incorrect.

**Response 4** This response is correct.

| Bond | Number | AH(kJ) |
|---|---|---|
| C – H | 5 | 5 x -412 = -2060 |
| C – C | 1 | 1 x -347 = -347 |
| C = C | 1 | 1 x -598 = -598 |
| C – Cl | 1 | 1 x -339 = -339 |
| | | -3344 |

## Question 2

**Response 1** This response is incorrect. You have not taken two H – Cl bond energies into account. The exothermic part of the overall bonding process is equal to 2 x -431 kJ.

**Response 2** This response is incorrect. You have calculated the heat of formation of two moles of hydrogen chloride. The correct answer is ½ x -184 kJ.

**Response 3** This response is numerically correct bu the sign of the heat change is wrong. Heat evolved is given a negative sign: AH is -ve.

**Response 4** This response is correct.

The formation of 2 moles HCl requires:

1 H – H bond to be broken AH = +435 kJ
1 Cl – Cl bond to be broken AH = +243 kJ
2 H – Cl bonds to be made AH = -862 kJ

Total of bond breaking and making processes AH = -184 kJ

and for 1 mole HCl AH = -92 kJ

## Study Unit 4

# REVERSIBILITY & FREE ENERGY by physical analogy.

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## PURPOSE

1. To discuss early ideas about reversible and irreversible reactions.
2. To introduce the concepts of thermodynamic reversibility and irreversibility.
3. To define free energy in terms of optional work capability, and establish the link between free energy and reaction spontaneity

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## PRESENTATION

Introduction. The concepts of thermodynamic reversibility and irreversibility, and their relationship to free energy, have in the past proven to be stumbling blocks to students. I am hopeful that the use of a concret-experimental prop will make them less so.

Reversible and irreversible reactions. A reversible reaction is one which can move in either the forward or reverse direction, according to the prevailing conditions. Thus:

$$Hg + \tfrac{1}{2}O_2 \underset{\text{at high temperature}}{\overset{\text{at low temperature}}{\rightleftarrows}} HgO$$

At some intermediate temperature both reactions may be proceeding at the same time and at the same rate, in which latter case an equilibrium mixture of constant composition exists and is signified:

$$Hg + \tfrac{1}{2}O_2 \rightleftharpoons HgO$$

This example is very crude and lacks essential detail which would allow you to picture the exact equilibrium situation. But such detail does not concern you here. The important point is that your idea of reversibility is linked descriptively to a reaction which can go in either direction.

In a similar descriptive sense, an irreversible reaction is taken to be one which cannot be reversed. The burning of a match might be quoted as an irreversible reaction. But then some teachers will contend that all reactions are reversible, that no matter how far the reaction may proceed to the right there is always always the possibility, under suitable conditions, of at least some reactant remaining, no matter how little; that an irreversible reaction is therefore just an extreme example of a reversible reaction. The important point is that your your idea of irreversibility is linked descriptively to a reaction which effectively goes only in the one direction, be this right or wrong.

When the terms 'reversibility' and 'irreversibility' are used in the thermodynamic sense, they have a somewhat different meaning, only loosely connected with the above descriptive meanings. When used in the thermodynamic sense, the terms refer very specifically to the way in which the reactions are operated. You will see that, in the thermodynamic sense, any reaction which occurs is of necessity irreversible. The only situation which is reversible is the equilibrium situation, in which there is no net reaction.

**Thermodynamic reversibility and irreversibility.** Before proceeding further, revise pages 2.1 to 2.3, and in particular make sure you understand the meaning of the physical analogy depicted in Fig. 2.3.

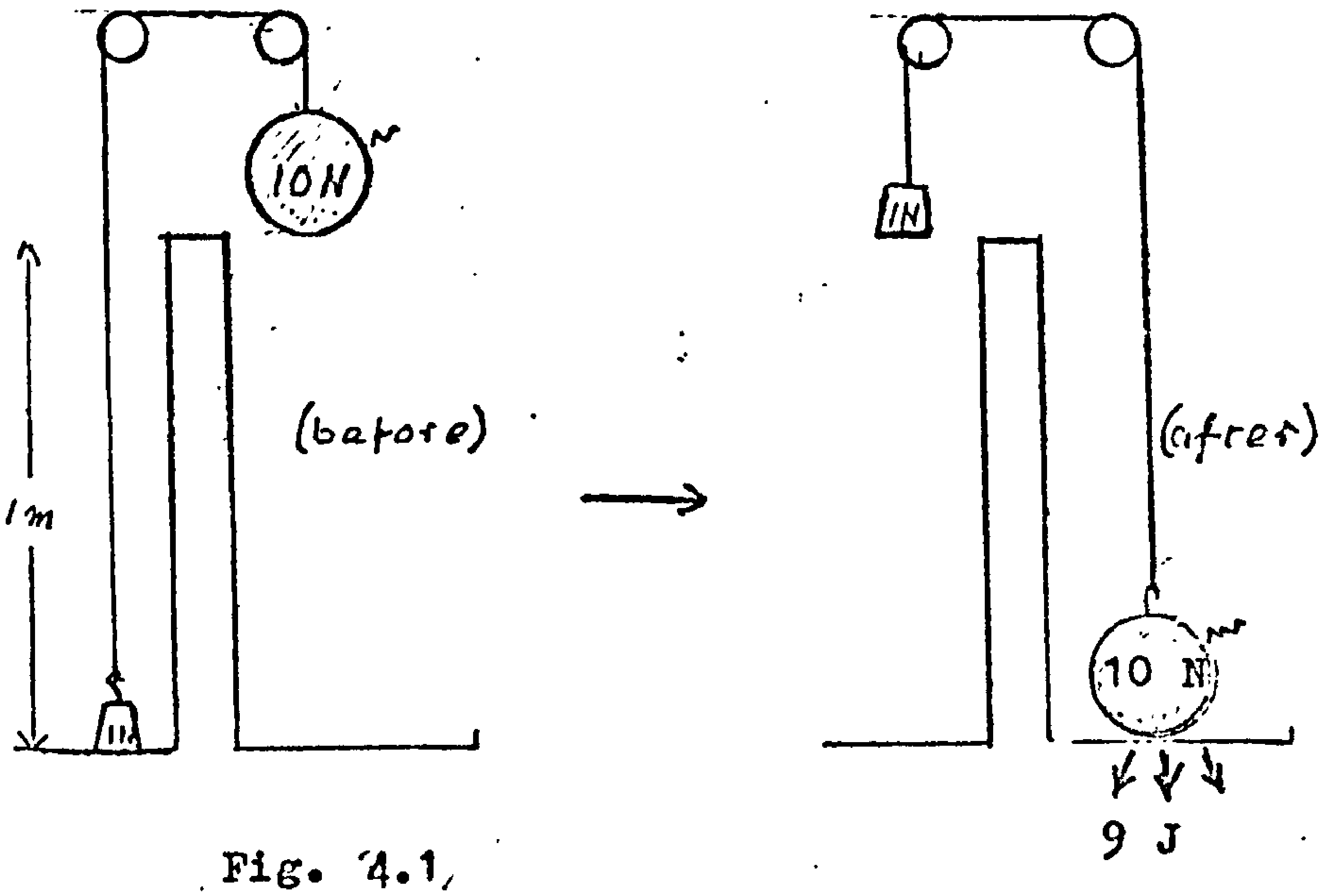

Fig. 4.1

This time, however, the weight is linked to a 1 N load by a pulley system.

We have opted to get some work out of the weight for, as it descends, it will have to do 1 joule of work 'on the surroundings', where it will be stored until such time as it is released in its own right.

At the same time, since energy is conserved, only 9 joules of heat instead of 10 will be released to the surroundings by the impact of the falling weight.

As the optional work load is increased correspondingly less heat is evolved to the surroundings by the impact of the weight. The maximum optional work available, assuming the pulleys to be frictionless, is something just infinitesimally less than 10 joules, by which point no heat at all is released to the surroundings by the impact of the weight!

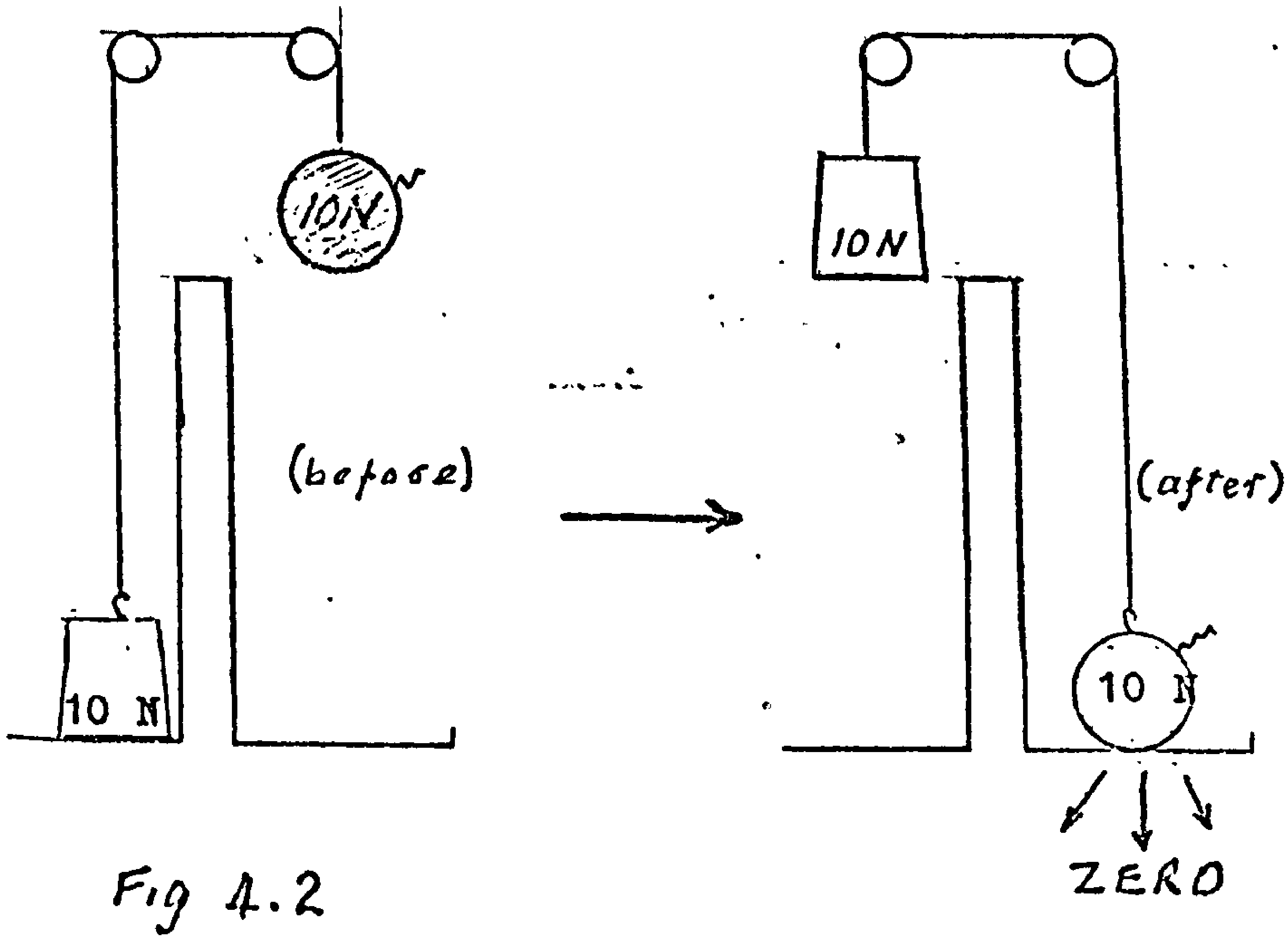

Fig 4.2

Potential energy which is available for doing work, if we opt to use it so, is otherwise called free energy.

In this simple physical analogy, all the potential energy is of the free energy kind, that is to say, all of the 'enthalpy' change is available, at least in theory for doing optional work.

This is by no means always the case, particularly for chemical changes, but we shall come to this other aspect of the whole enthalpy change shortly.

In this example, the change in free energy of the 'system' is -10 J, and this change is symbolised AG.

Free energy is given the symbol G in honour of Josiah Willard Gibbs (1839 - 1903), founder of modern chemical thermodynamics.

When a change is carried out in such a way that a maximum demand is made on the free energy, maximum optional work being done, then the change is said to be carried out reversibly. A reversible change is illustrated in Fig. 4.2 . It is imperative to realise that work is obtained at the expense of the heat change; it is one or the other - you cannot have it both ways. The change can of course be performed between the two extremes, as illustrated by Fig 4.1.

When a change is carried out without claim being made on the free energy, no optional work being done, the change is said to be carried out irreversibly. An irreversible change is illustrated in Fig. 2.3 (...and also Figs. 2.2 and 2.1.)

The heat change under irreversible operation of the change is equal to 10 J evolved. In chemical terminology AH = -10 J. (Fig. 2.3)

An alternative symbol for AH is $q_{irrev}$, though this is not much used. Thus:

$$AH = q_{irrev} = -10\ J$$

The heat change under reversible operation of the change (assuming such operation to be possible) is, in this example, zero. (Fig. 4.2)

The symbol for the heat exchange between system and surroundings during the reversible operation of a change is $q_{rev}$, and is extensively used.

You must not confuse the enthalpy change with the reversible heat change.

In this physical analogy

Heat change under irreversible operation = Enthalpy change = AH = $q_{irrev}$ = -10 J (Fig. 2.

Heat change under reversible operation = $q_{rev}$ = zero (Fig. 4.2)

Summarising.

The weight in the raised position possesses 10 J of potential energy relative to the base. Since this potential energy is of such a kind that it can be used to do optional work, it is called free energy.

When the weight descends, the change in free energy of the system, symbolised AG, is -10 J.

If the weight descends 'irreversibly', no optional work being done by it on the surroundings, the heat evolved to the surroundings is derived from the decrease in free energy of the system, and is AH = -10 J

If the weight descends 'reversibly', maximum optional work being done by it on the surroundings, then 10 J of optional work are done in lieu of the enthalpy change, and no heat is evolved.

In short: AH = AG

| AH | | AG |
|---|---|---|
| You get this if the change is operated irreversibly | OR | you get this as optional work if the change is operated reversibly |

- but you cannot get both completely at the same time; you can only get the one at the expense of the other.

During the reversible change the sytem is in a continuing state of equilibrium with the surroundings (as the weight descends, the load rises). As long as the load is infinitesimally less than the weight, something just infinitesimally short of the maximum work will be obtained, and will be obtained infinitesimally slowly. At any instant during the progress of this change, the slightest push in the opposite direction will reverse the change - hence the concept of 'reversibility' peculiar to thermodynamics. (An attempt will be made later to justify the use of the description 'irreversible' for the non-reversible operation of a change.)

Further, one of the conditions often required of reversible changes is that they be carried out slowly. This is not strictly correct. Rather, the proper performance of a reversible change requires that the downfalling weight be more or less equally opposed by the load to be raised, and consequently the reaction will occur slowly whether we like it or not. Slowness, therfore, is more of a consequence than a condition.

It is important to realise that the reversible operation of a change is an ideal limit, quite unrealisable in practice. It is that imaginary limit at which maximum work is available, i.e. that limit at which the attempt is made to convert the entire free energy into optional work. Such a process is quite unobservable since it will occur infinitely slowly.

The natural, irreversible process is observable since it occurs in a finite time. The description irreversible is applied to the change even when some work is obtained, or when none is obtained. The term reversible is applied only when the attempt is made to take the maximum work.

Thus, in the thermodynamic sense, any reaction which occurs must be irreversible. The only situation which is reversible is the equilibrium situation, in which there is no net reaction.

**Spontaneity.** The descent of a weight is characterised by a negative change in the 'free energy' of the weight. Whether the weight does optional work during its descent, or does not and ultimately yields its free energy as heat, does not matter. The important point is that the descent of the weight, which is the natural way for a weight to behave, is characterised by a negative free energy change.

For a reaction in a system to be spontaneous, its occurrence must be accompanied by a negative free energy change of the system.

This is, in effect, a statement of the Second Law of Thermodynamics.

The advantage of this definition of spontaneity over other definitions is that it allows decisions about reaction spontaneity to be made from consideration of the system only, without reference to the simultaneous changes going on in the surroundings. A more thorough explanation of this latter point will ge offered later in the programme.

Thus, where the First Law is essentially a statement of conservation of energy, the Second Law takes the conservation of energy for granted and goes on to concern itself with the direction of change, that is to say, it says which direction will be the spontaneous direction, ..... but it says nothing about the speed at which the reaction will occur.

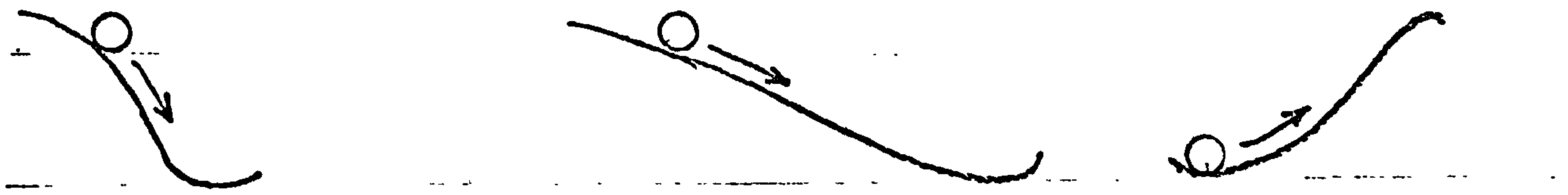

Fig. 4.3

This 'reaction' is spontaneous because the overall change is accompanied by a decrease in 'free energy'.

This reaction is equally spontaneous, but it will take a little longer!

This reaction is not spontaneous.

In the thermodynamic sense, spontaneity implies nothing about speed of reaction. If the free energy change is negative, the reaction will occur; it may take a few seconds, like the action of acid on carbonate, or a few million years, or aeons.

The rate of reaction between cold hydrogen and oxygen is exceedingly low, but given enough time the reaction should run virtually to completion. The low rate of reaction is a consequence of a kinetic snag, namely a lack of adquate activation energy. That the reaction does eventually run to virtual completion is due to its negative free energy change, the reaction being allowed to proceed by the presence at any one instant of a very small proportion of molecules with high enough activation energy.

Study Unit 4 What you should know.

You should

1. know what is meant at O Grade and H Grade by reversible reaction and irreversible reaction.
2. know that free energy is potential energy which is available for doing work.
3. know that a change is operated reversibly when it is made to do the maximum work.
4. realise that free energy not used to do work appears instead as heat
5. know that a change is operated irreversibly when something less than the maximum demand is made on it to do work.
6. know that the heat change under complete irreversible operation is ΔH.
7. know that the heat change under reversible operation is $q_{rev}$.
8. know that a reversible change 'occurs' through a continuing equilibrium state.
9. know that a reversible change is a balanced change and that the slightest push in the opposite direction reverses it, which is why it is called reversible.
10. know that a reversible change occurs ihfinitely slowly.
11. know reversibility is an ideal limit.
12. reversible processes are unobservalble.
13. know that only irreversible processes are observable.
14. know the meaning of spontaneity.

---

Question 1 When a spontaneous reaction is carried out irreversibly

| | |
|---|---|
| 1 no optional work may be done in which case AG will be zero. | 2 the heat change with the surroundings is AH |
| 3 the heat change is qrev. | |

Question 2 Is it possible to

| | |
|---|---|
| 1 operate a reversible reaction reversibly? | 2 operate a reversible reaction irreversibly? |
| 3 operate an irreversible reaction reversibly? | 4 operate an irreversible reaction irreversibly? |

Question 3 A match-head reacts spontaneously but very slowly with air. Is the reaction occurring reversibly?

---

Question 4 Which of the following, if any, is (are) characteristic of the irreversible operation of a spontnaeous reaction?

| | |
|---|---|
| 1 It occurs very slowly | 2 It is an attempt to get the maximum work from a change. |
| 3 The opposing load must be less than the driving force. | 4 It is observable.. |

Question 5 If the free energy change accompanying the occurrence of a process is -10 kJ, the process

| | |
|---|---|
| 1 will not be spontaneous. | 2 will occur very rapidly. |
| 3 will be able to do a maximum 10 kJ of optional work if operated reversibly. | |

Question 1

| | |
|---|---|
| Response 1 | This response is incorrect on two counts. Firstly, some optional work may be done during the irreversible operation, or none at all. Secondly, the free energy change for a spontaneous reaction is negative no matter how it is carried out. |
| Response 2 | This response is correct. |
| Response 3 | This response is incorrect. When the attempt is made to carry out the reaction reversibly, AG is consumed (or occupied) entirely in doing optional work, and is not therefore expelled as heat. Any heat expelled during the reversible operation must come from some other source than the free energy decrease, for which see next Study Unit. |

Question 2

| | |
|---|---|
| Response 1 | Yes. If the attempt is made to carry out a reaction so that maximum optional work is done by it, the reaction - whatever it be - is said to be being 'operated reversibly'. |
| Response 2 | Yes. If the reaction - whatever it be - is allowed to occur naturally, no demand being made on it to do optional work, then the reaction is being operated irreversibly.<br>How a chemical reaction can be operated reversibly will be discussed in Study Unit 6. |
| Response 3 | Yes. As for Response 1. |
| Response 4 | Yes. As for Response 2. |

Question 3

| | |
|---|---|
| Response 1 | No. Since the match-head reacts spontaneously with the air, the free energy change must be negative, that is, AG is -ve. But no attempt is being made to convert this free energy to 'work done on something' in the surroundings; it is merely being released as heat. The reaction is proceeding irreversibly. The slowness is a result of a kinetic snag: a lack of adequate activation energy. |

Question 4

| | |
|---|---|
| Response 1 | This is not characteristic. A reaction operated irreversibly may occur rapidly or slowly. All that can be said is that, because the free energy change is negative, the reaction <u>can</u> occur. |
| Response 2 | No. This attempt to get the maximum work is a characteristic of the reversible operation of a change. |
| Response 3 | Yes. If the opposing load is as great as the driving force, then a reversible situation exists. For the irreversible change the opposing load must be less than the driving force, or absent altogether. |
| Response 4 | Yes, since it occurs in a finite time. |

Question 5

| | |
|---|---|
| Response 1 | This is incorrect. If the free energy change is negative, whatever its value, the change is spontaneous. |
| Response 2 | This is incorrect. It is impossible to say from free energy considerations alone how fast a reaction will be. For example, the free energy change accompanying the combination of hydrogen and oxygen is very negative, but hydrogen and oxygen can co-exist without apparent reaction for a very long time. The reason for the inactivity is kinetic: lack of adequate activation energy. |
| Response 3 | This is correct. But remember that in practical terms the reversible operation takes infinitely long to achieve. |

Study Unit 5

## ENTHALPY, FREE ENERGY & ENTROPY ENERGY by physical analogy

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PURPOSE

1. To show how the enthalpy change is the result of a free energy change and an entropy energy change.
2. To discuss the enthalpy change and the reversible heat change for a spontaneous change in which the entropy energy change is negative.
3. To discuss the enthalpy change and the reversible heat change for a spntaneous change in which the entropy energy change is positive.

---

Source of enthalpy change. Up to this point in the programme, the 'enthalpy' change associated with a 'reaction' has been ascribed only to a decrease in the 'free energy' of the system.

That the total enthalpy change accompanying a chemical reaction is never entirely due to change in potential energy of the free energy kind has already been alluded to (page 4.2).The enthalpy change is due in part to a form of stored energy which cannot be converted into optional work, which from of potential energy - to distinguish it from free energy - I shall call entropy energy. An attempt will be made later to show in what way these two kinds of potential energy, i.e. free energy and entropy energy, differ from each other.

For the moment, however, let us concern ourselves with the interplay between these two kinds of stored energy and how, when acting together, they decide the value of the overall enthalpy change.

Unfortunately, there is no equivalent of chemical entropy energy in the world of mechanical objects. Thus, although it was easy to find a physical analogy to explain the concept of free energy, it is not quite so easy to find one to explain the concept of entropy energy. But, bearing in mind that the distinctive feature of entropy energy is its 'unavailability' - it is not available for doing optional work - then a comparison of some sort can be drawn with a weight which is ready to fall and is also spinning, for the latter, in an analogy of the type invented for this programme, will not affect the value of the maximum optional work. That the weight is in a 'state of spin' as it descends will not affect the weight's load lifting capability, within the artificial limitations of this physical analogy.

But it will affect the value of the 'enthalpy' change.

Cautionary note. Remember that we are using the actual potential energy of a raised weight to simulate the free energy of a real chemical system. The weight's actual potential energy is our "mechanical equivalent of chemical free energy". Now we are about to use what is in reality rotational kinetic energy of a spinning weight as the "mechanical equivalent of chemical entropy energy".

This sounds more difficult than it really is, and if you can grasp underlying principle, then you will be in a position to transfer your understanding to a real chemical situation. This particular unit is quite crucial.

There is, unfortunately, danger in using a physical analogy like this; the danger is that you will become confused between the unreal (the physical analogy) and the real (actual weight, physical reactions and chemical reactions).

I shall refer to the "mechanical equivalent of chemical entropy energy" simply as "spin". A decrease in spin, therefore, simulates a chemical reaction which is accompanied by a decrease in potential energy of the entropy energy kind; an increase in spin simulates a chemical reaction which is accompanied by an increase in potential energy of the entropy energy kind.

Changes in entropy energy in real chemical reactions are symbolised $T\Delta S$; the reason for this will emerge later. Since we are already using the correct chemical symbolism for enthalpy and free energy change, $\Delta H$ and $\Delta G$, in discussing the operation of the physical analogy, then we will use the symbol $T\Delta S$ as well.

### Full chemical reactions by physical analogy.

We shall now have a look at some simulated reactions whose enthalpy change is a result of a free energy change and an entropy energy change.

We shall restrict the discussion to spontaneous changes, which immediately fixes the free energy change as negative.

Whether the entropy energy change is negative or positive depends on the particular reaction, and is quite independent of the free energy change.

The combination of hydrogen and oxygen to form water entails a decrease in entropy energy; the product water has less potential energy of the entropy energy kind than do the hydrogen and oxygen from which the water was formed. The combustion of a match, on the other hand, entails an increase in entropy energy.

Why this happens to be the case will be explained later.

You will have noticed that there are occasions when a particular topic has to be postponed for later explanation, This is something I would ask you to bear with in the hope that it will 'come out right in the end'. One of the great difficulties in explaining these basic concepts is that it is not possible to explain A until B has been explained, while it is not possible to explain B until A has been explained! The solution to this dilemna is to take one on trust while the other is explained. I am afraid that this happens some few times in this programme.

We shall continue now with a look at the irreversible and reversible operation of a spontannous reaction for which the entropy energy change is negative, and then a spontaneous reaction for which the entropy energy change is positive.

Consider a spontaneous reaction during the course of which there is a negative entropy energy change; since the reaction is spontaneous, the free energy change is also negative.

Apply the physical analogy. Let the free energy change be AG = -10 J as before, and let the entropy energy change be TAS = -3 J. Imagine, therefore, a 10 N weight one metre above a base to be spinning with 3 J of 'spin'.

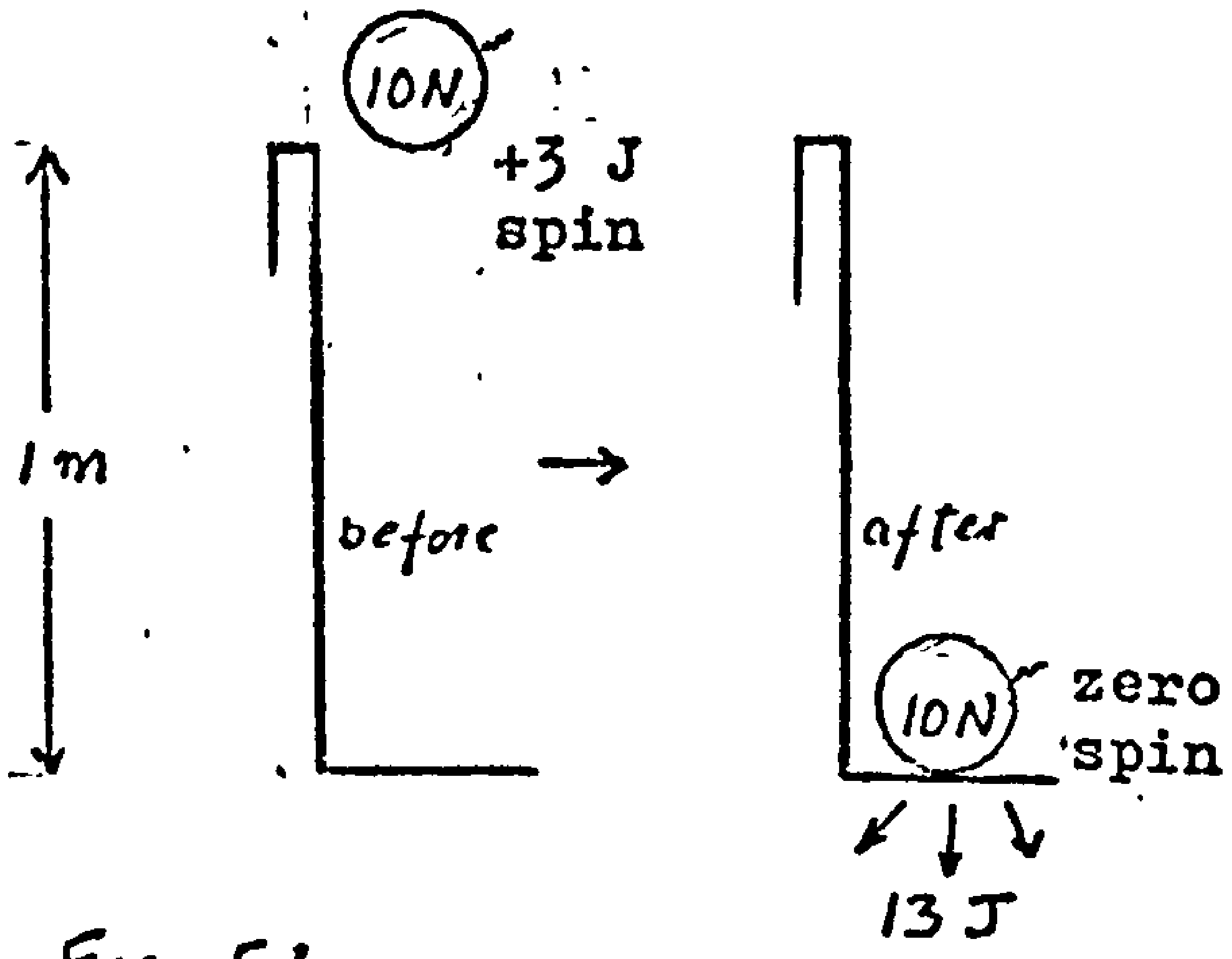


Fig. 5.1

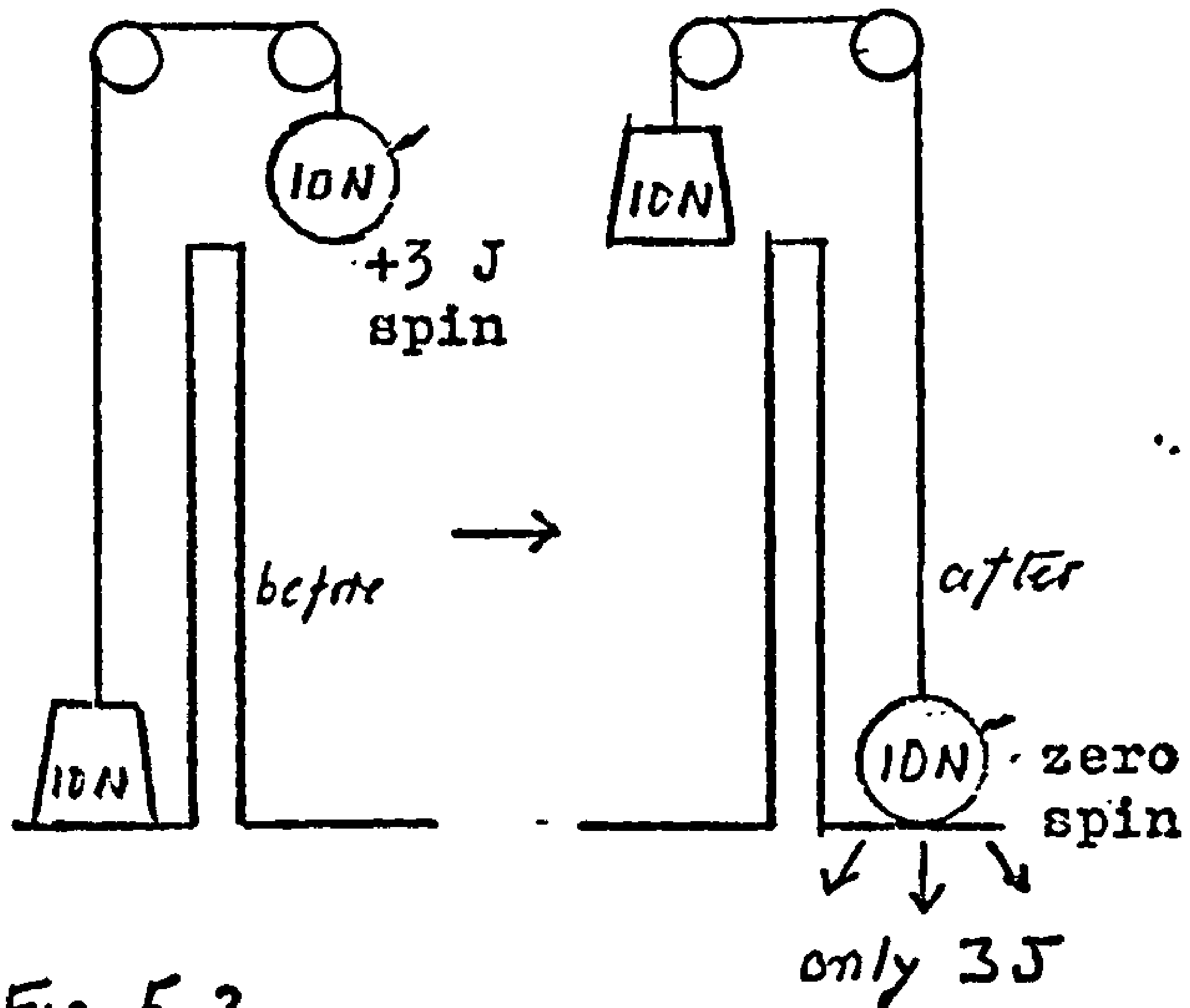


Fig. 5.2

Irreversible operation

The entire potential energy of the system is expelled to the surroundings as heat:

AH = -13 J

and this is derived from a decrease in the free energy of the system:

AG = -10 J

and from a decrease in the entropy energy of the system:

TAS = -3 J

| Thus: | AH | = | AG | + | TAS |
|---|---|---|---|---|---|
| | -13 J | | -10 J | | -3 J |

Reversible operation

The decrease in free energy of the descending weight is consumed in doing an equivalent amount of optional work on the surroundings. The 3 joules of 'entropy energy' cannot be used to do optional work and is expelled from the system as heat.

TAS = $q_{rev}$ = -3 J

Thus the heat change with the surroundings under irreversible operation of the change, which is AH, is very different from the heat change with the surroundings under reversible operation of the change, which is $q_{rev}$. The former is -13 J; the latter is -3 J.

In general, $\boxed{AH} = \boxed{AG + TAS} = \boxed{AG + q_{rev}}$.

Now consider a spontaneous reaction during the course of which there happens to be a positive entropy energy change; since the reaction is spontaneous, it entails a negative free energy change.

Apply the physical analogy. Let the free energy change be AG = -10 J as before, and let the entropy energy change be TAS = +3 J. Imagine, therefore, a 10 N weight one metre above a base, and imagine that as it descends it acquires 3 J of 'spin'.

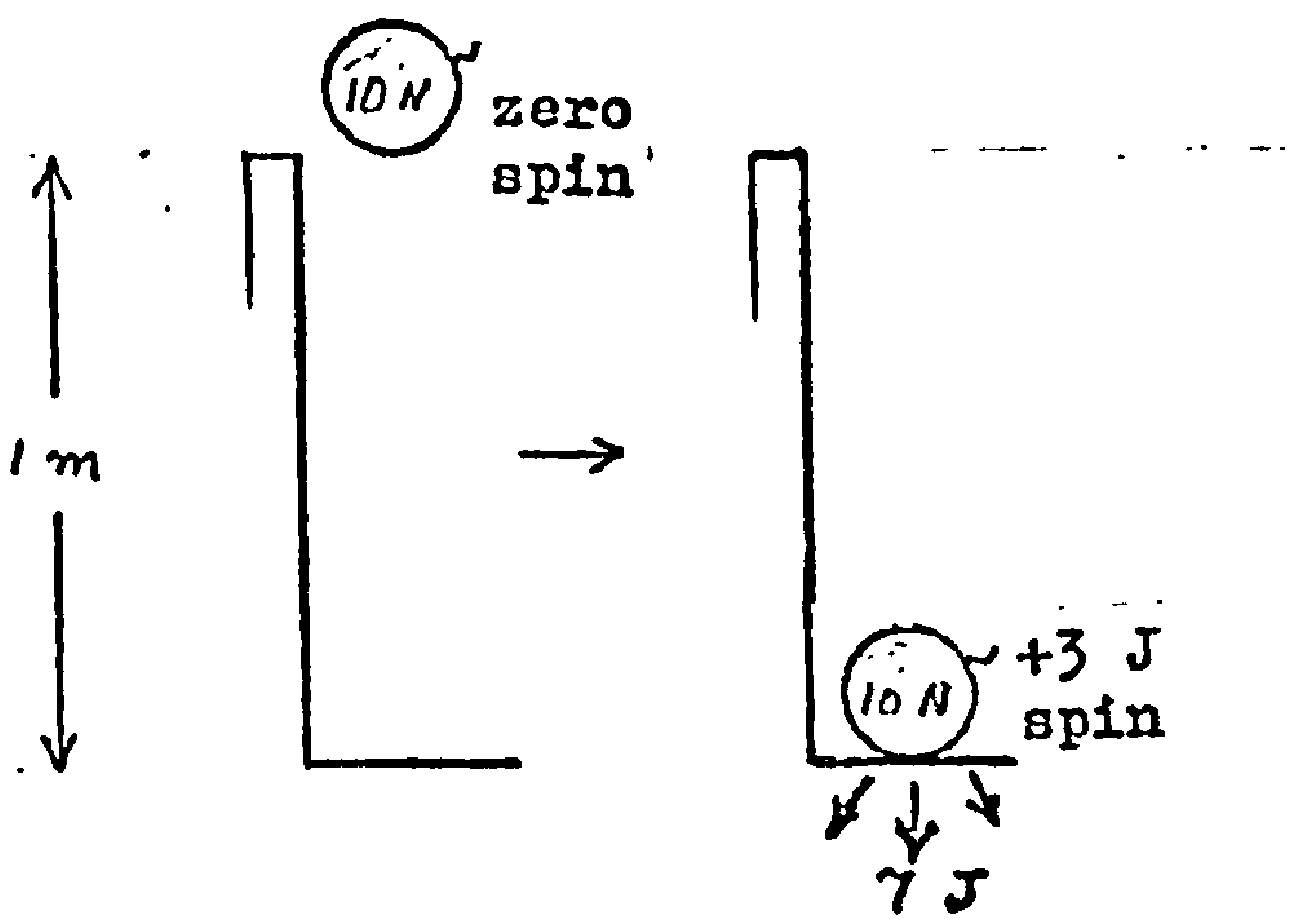


Fig. 5.3
Irreversible operation

No optional work is demanded of the free energy of the system.

The enthalpy change will be

AH = -7 J

Why? The decrease in free energy of the system is equal to 10 joules. But 3 joules of this are consumed in accounting for the increase in entropy energy.

Thus: AH = AG + TAS
-7 J  -10 J  +3 J

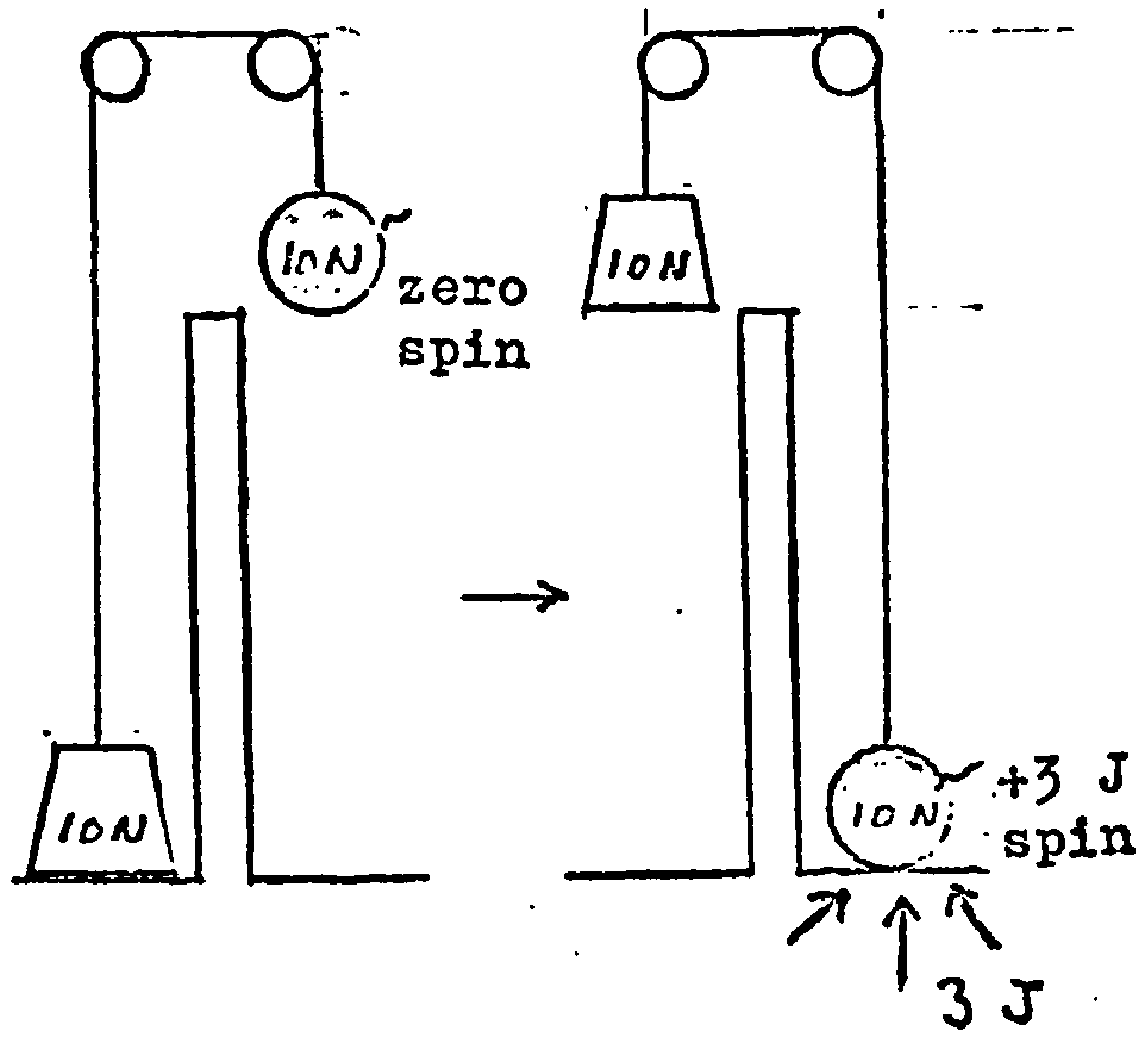


Fig. 5.4
Reversible operation

The decrease in 'free energy' of the descending weight is consumed in doing an equivalent amount of optional work on the surroundings. And if the reaction occurs with an increase in entropy energy, this energy has to be accounted for. Since it cannot be derived from the free energy - which is fully allocated to doing work - it is (in a real chemical reaction) simply absorbed form the surroundings. Thus AG is realised as work done and the heat change with the surroundings is restricted to TAS = $q_{rev}$ = +3 J.

In this particular analogy of a chemical reaction, the enthalpy change, which of course specifies irreversible conditions, is negative; the reaction is naturally exothermic. But under limiting ideal reversible conditions the heat change, $q_{rev}$, is positive; the reaction, if only in theory, has become endothermic.

Reflect for a few moments on the explosion of a charge of powder. The combustion of gunpowder is highly exothermic; AH is negative. The combustion is associated with a very large decrease in free energy as reactants convert to products; AG is negative. The combustion entails a large increase in entropy energy; TAS is positive; take this on trust for the moment.

$$\begin{array}{ccccc} \Delta H & = & \Delta G & + & T\Delta S \\ -ve & & -ve & & +ve \end{array}$$

If a charge of powder be set off in the open, no demand being made on the reaction to do optional work, the heat evolved is due to the very large supply of free energy, less some used up in increasing the entropy energy of the products compared with the reactants.

If, on the other hand, the same charge of powder be used to fire off a cannon-ball, some of the free energy is used and stored in the cannon-ball as it 'flies through the air'. Thus the enthalpy change is down a bit; the reaction is beginning to acquire some reversible character. In fact we are no longer justified in using the term enthalpy change since the reaction is not entirely irreversible.

It is established fact that weaponry firing live ammunition becomes less hot than it does when firing blank.

Indeed, if the shot could be fired reversibly, which of course is a complete practical impossibility, the shot firing would be endothermic!

Table 5.1 Spontaneous changes in a system

<table>
<tr><td colspan="3">Spontaneous changes in a system can be made to do work on the surroundings:</td></tr>
<tr><td></td><td>Reversible operation: the work attempted is a maximum.</td><td>Irreversible operation: the work done by the system is less than the maximum.</td></tr>
<tr><td>Net work</td><td>$-\Delta G$</td><td>Zero to something just less than $-\Delta G$</td></tr>
<tr><td></td><td colspan="2">(E.g. if $\Delta G$ were -10 J, then the maximum work which could be done on the surroundings would be 10 J. But if the change were executed at 'less than perfectly reversible', then an amount of work less than 10 J would be done. In the event of no optional work being done at all, then the accompanying heat exchange between system and surroundings is the enthalpy change.)</td></tr>
<tr><td>Heat exchange</td><td>$T\Delta S$, $q_{rev}$</td><td>$T\Delta S$ to $\Delta H$</td></tr>
</table>

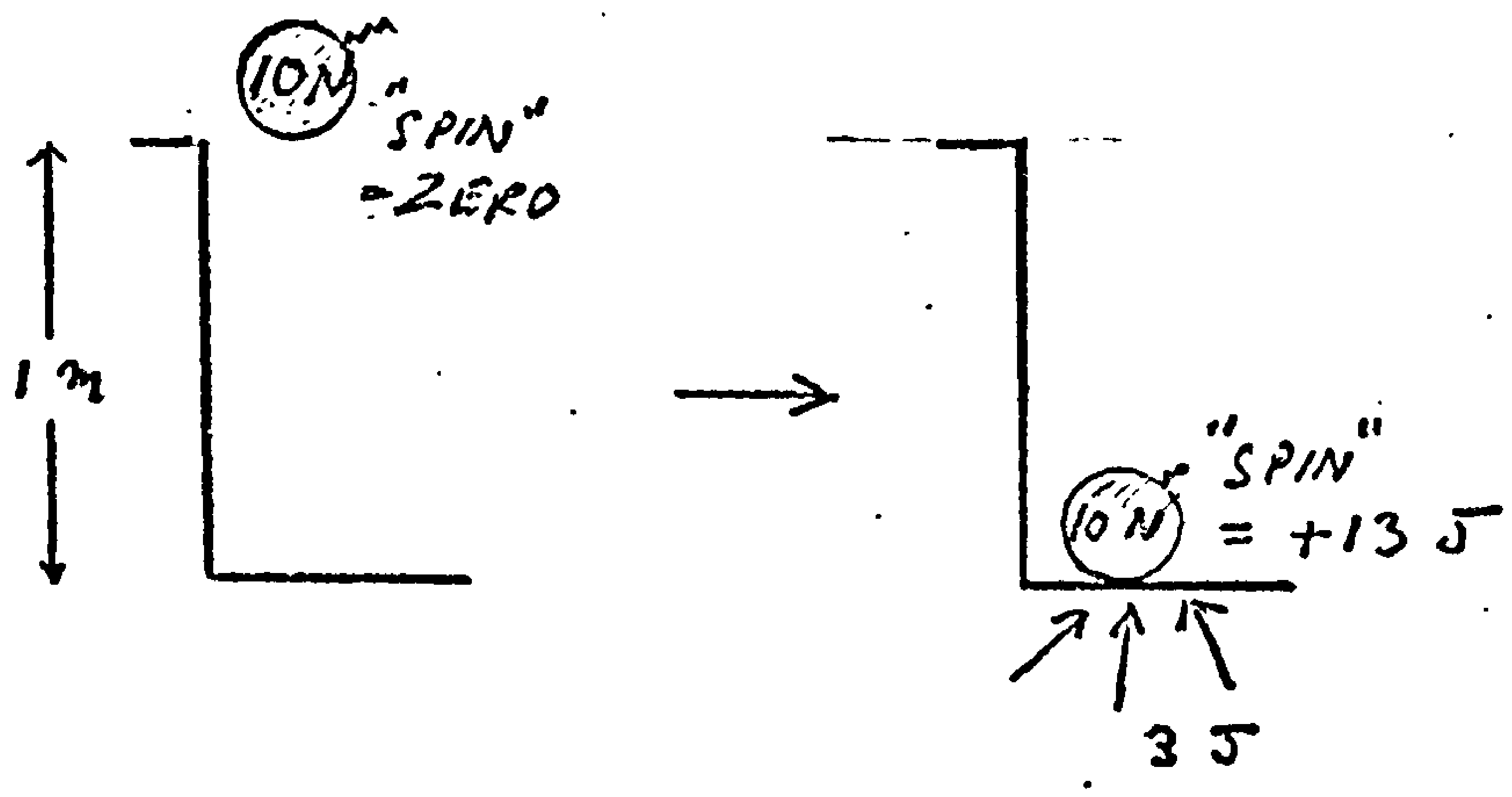
Study Unit 5 What you should know.

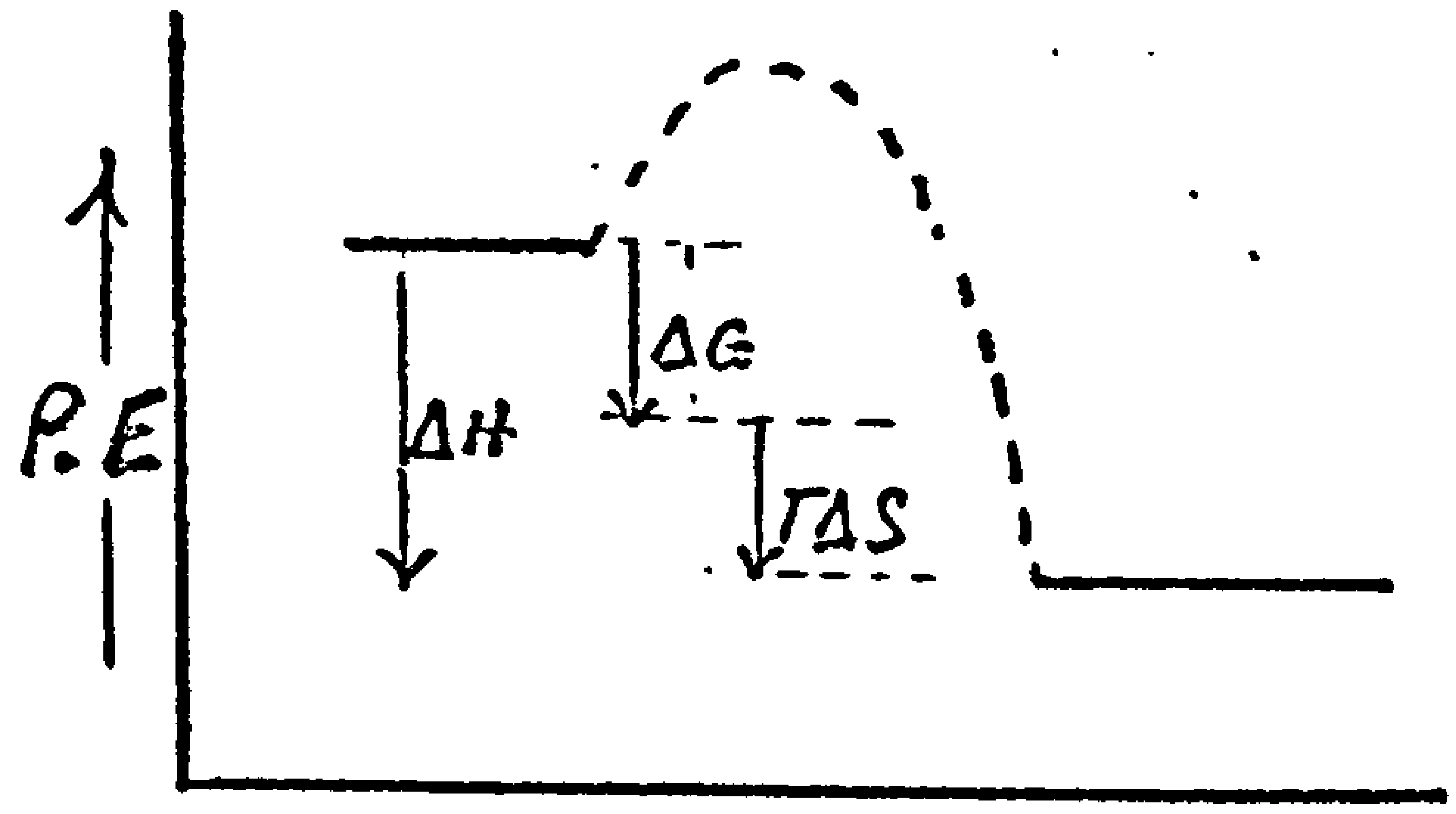
You should

1. know that the enthalpy change is the summed effect of a free energy term and an entropy energy term.
2. know that in the relationship $\Delta H = \Delta G + T\Delta S$, $T\Delta S = q_{rev}$.
3. If $\Delta G$ and $T\Delta S$ are exchanged as heat, $\Delta H$ is obtained; while if $\Delta G$ is used to do work, the only heat change can be $T\Delta S$.

Question 1a The physical analogy shown below depicts one of the following chemical reactions. Which one?

| | | |
|---|---|---|
| 1 | $HgO \rightarrow Hg + \frac{1}{2}O_2$ | AH +ve, AG -ve, TAS +ve. |
| 2 | $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$ | AH +ve, AG +ve, TAS -ve |
| 3 | $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$ | AH -ve, AG -ve, TAS +ve |
| 4 | $N_2 + 3H_2 \rightarrow 2NH_3$ | AH -ve, AG -ve, TAS -ve. |





Question 1b The enthalpy diagram shown above refers to one of the reactions given in Question 1a. Which one?

Question 2 When a spontaneous reaction is carried out irreversibly, the enthalpy change might be zero. Comment.

Question 3 If the free energy change accompanying a reaction is AG = -100 kJ, the process will be endothermic if operated reversibly. Comment.

| | |
|---|---|
| Question 1a | |
| Response 1 | This is correct.<br>The analogy depicts a reaction for which AG is negative. This eliminates 2.<br>The analogy depicts a reaction for which TAS is positive. This eliminates 4.<br>The analogy depicts a reaction in which the increase in entropy energy is greater than the decrease in free energy so that heat is absorbed from the surroundings to make up the difference, i.e. AH is positive.<br>The analogy in fact depicts a spontaneous endothermic reaction. The decomposition of mercury oxide is such a spontaneous endothermic reaction at high temperature. |
| Responses 2,3 and 4 | See above. |
| Question 1b | The enthalpy diagram depicts a reaction for which AH, AG and TAS are all negative, and so corresponds to reaction 4. |
| Question 2 | Yes. If the process is spontaneous, AG must be negative. If TAS is as positive as AG is negative, the AH will be zero. |
| Question 3 | It might be. If the process is operated reversibly, AG is consumed completely in doing optional work on something somewhere in the surroundings; none of it is expelled as heat.<br>If the reaction is accompanied by a decrease in entropy energy, TAS -ve. then the reversible process will be exothermic; $q_{rev}$ will be negative.<br>On the other hand, if the reaction is accompanied by and increase in entropy energy, TAS +ve, then the reversible operation will be endothermic; $q_{rev}$ will be positive. |

## Study Unit 6

## ENERGY CHANGES in chemical reactions

---

PURPOSE

1. To contrast the irreversible and reversible operation of a chemical reaction.

2. To show how the enthalpy change for a chemical reaction is related to the free energy change and the entropy energy change.

3. To show that optional work in an electrical circuit is nFE.

---

Irreversible performance of a reaction. Reactants are allowed to convert to products in such apparatus that the heat evolved can be accurately measured. Practical details are given on pages 3 and 4 of Memorandum Number 16, Practical Work in Sixth Year Studies Chemistry.

The enthalpy change for the reaction:

$$Cu(s) + 2Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$$

turns out to be AH = -147.2 kJ for the equation as written.

This enthalpy change is derived from a free energy change, AG, and from an entropy energy change, TAS.

Now AH is negative. And since the reaction occurs spontaneously, AG must also be negative (page 4.5). Applying the equation

$$AH = AG + TAS$$

we accept that TAS might be positive or negative.

We cannot readily measure the entropy energy change, TAS, for the reaction. Remember that TAS is $q_{rev}$, which is the heat change under reversible operation of the reaction, and the reversible operation of the reaction takes an infinitly long time. The measurement of heat change over an infinity of time, during the idealistic reversible operation of the reaction, is not a practicable proposition.

But we can measure the force with which the reaction will attempt to occur under reversible conditions, and in so doing measure AG.

Just as the downward acting weight on one side of our imaginary pulley can be made to 'act reversibly' by opposing its action by an equal and opposite load, then the above reaction can likewise be made to act reversibly by arranging it to occur in such a way that its occurrence can be equally opposed.

Just as the maximum load which a downward acting weight can lift is an estimate of the 'free energy' change associated with the downward progress of the weight, then the maximum force required to oppose the above chemical reaction such that it just stops the reaction occuring can be used to calculate the value of the maximum optional work that the reaction is capable of performing, and will attempt to perform under - and only under - reversible conditions.

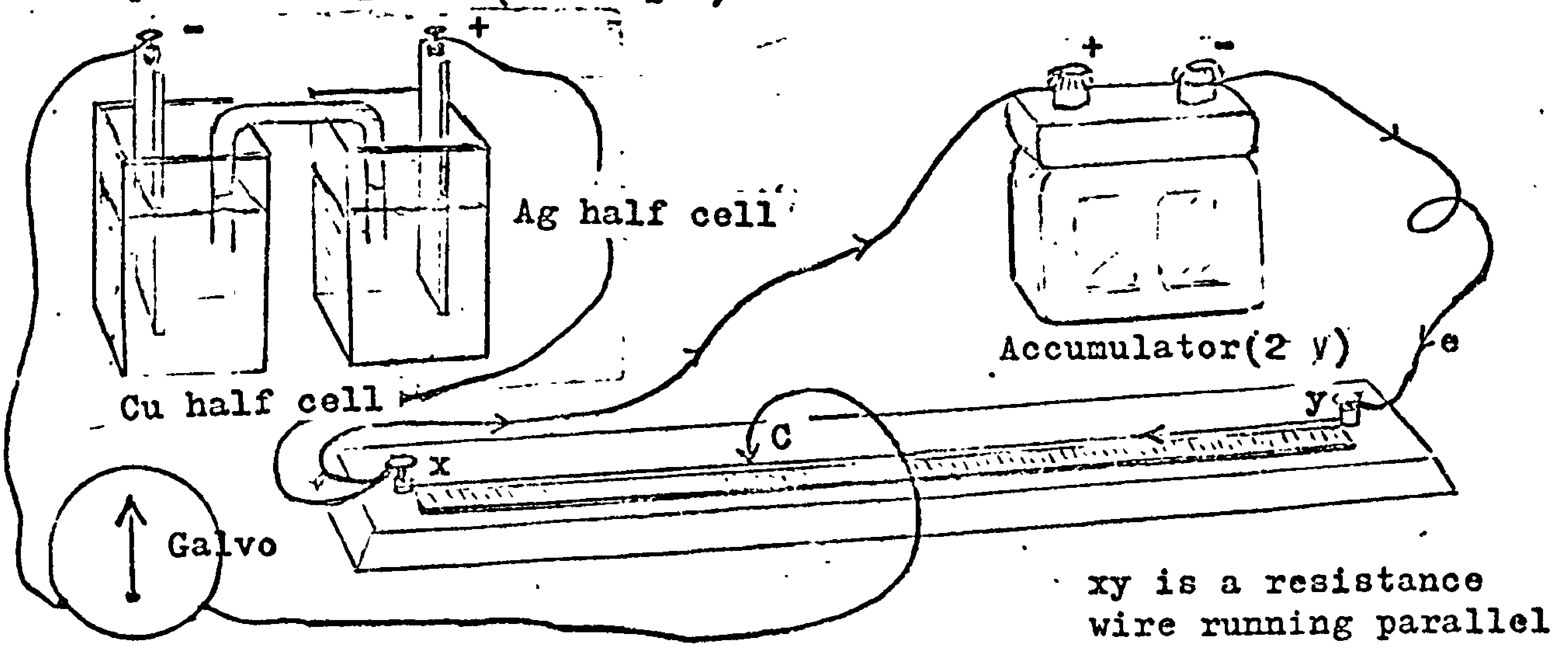
The same reaction comes to a standstill under reversible conditions. I shall explain it as occurring infinitely slowly.

Reversible performance of same reaction. The reaction

$$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

requires the transfer of two moles of electrons. This transfer is the counterpart of the downfalling weight.

The reaction may be engineered to occur such that this transfer takes place via an external wire, that is to say, the reaction may be carried out in an electrochemical cell. The transfer can then be opposed by 'an infinitesimally less than equal' force .... by applying an e.m.f. in the opposite direction. A 'reversible' situation is thus created.



xy is a resistance wire running parallel with a meter stick.

Fig. 4

Current from the accumulator passes continuously along the resistance wire from y to x. Whether current in the circuit containing the experimental cell moves in a clockwise or anticlockwise direction, or not at all, depends on the location of the contact C.

If contact C is located at end x, current will flow without external hindrance in the experimental cell circuit - namely from the negative terminal to the experimental cell through C to x to the positive terminal of the experimental cell.

As the contact C is progressively moved towards end y, the experimental cell will be subject to an increasing and opposing push by the accumulator: at some point between x and y the e.m.f. of the experimental cell will be equally opposed by the electrical pressure exerted by the accumulator.

A balanced or reversible situation now exists in the experimental cell circuit.

The e.m.f. exerted by the experimental cell under these conditions is the maximum it can exert. It is the force with which it is attempting to push two moles of electrons round the test circuit while in reality nothing is happening, as when the downward acting weight is equally apposed by a load (Figure 4.2).

As already discussed the work done in electrical terms is nFE, where nF is the amount of electricity in faradays and E is the e.m.f..

Thus, the maximum optional work which the experimental cell can do, in theory at least, is that which it can do under reversible conditions, and is equal to nFE joules where E is the reversible e.m.f. of the cell.

At the same time, the maximum optional work has already been shown to be derivable from the decrease in free energy of the reacting system, and is AG.

Therefore, $\boxed{AG \quad = \quad -nFE}$

AG: the change in free energy, a negative number of joules if the reaction is spontaneous

-nFE: - the optional work done under reversible conditions, the same positive number of joules since E is positive if the reaction is spontaneous

It turns out that the reversible e.m.f. for the reaction

$$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag$$

has the value 0.46 V. The details of how this value is deduced from the experimental set-up pictured on the prvious page need not arise here. Since two moles of electrons are involved in the transfer, n has the value 2. And F is equal to 96 500 coulombs.

Therefore $\quad AG = -nFE = -2 \times 96\,500 \times 0.46\ J$

$\quad = -88.2$ kJ for the reaction as written.

Therefore $\quad TAS = AH - AG = -147.2 - -88.2\ kJ$

$\quad = -59.0\ kJ$

Summarising. If the reaction implied by the equation

$$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

be carried out in the natural irreversible way, the enthalpy change is such that 147.2 kJ of heat are evolved, and this is derived from a decrease of free energy of 88.2 kJ and a decrease of entropy energy of 59.0 kJ as the reactants convert to products.

If the reaction could be carried out reversibly, 88.2 kJ of optional work could be done on something somewhere in the surroundings and only 59.0 kJ of heat, $q_{rev}$, would be evolved to the surroundings.

An initial comment on standard states. The energy changes associated with reactions must obviously depend on the amounts of substances involved, and on the conditions under which the reactions are carried out. I have avoided confusing the main theme of the development of this programme by trying to consider too much at one time. Consequently, much has been left unsaid; the argument is difficult enough as it is. The topic of standard state has been carefully avoided, but is of such major importance that some time will be devoted to it towards the end of this programme.

Suffice it to say that the measurements of cell e.m.f.s are not only done under reversible conditions, but with very particular regard to particular concentrations, pressures and states of purity (temperature is less important), and the values obtained under such standard reversible conditions are called standard e.m.f. values.

Any one standard e.m.f. of a cell is the result of two standard electrode potentials for each of the two half cells making up the cell. You should remember from form V work that if one of these two half cells is a hydrogen half cell, whose electrode potential is conventionally taken as zero, then the whole e.m.f. of the cell operating reversibly in standard form is taken as the standard electrode potential of the other half cell, whatever it is.

Standard electrode potentials are signified $E^o$. These are the values listed in your Three Figure Tables.

Similarly, standard enthalpy changes, standard free energy changes and standard entropy energy changes can be symbolised $AH^o$, $AG^o$ and $TAS^o$ respectively. These may or may not be used from here on. They are to be interpreted, for the time being, as more specific instances of $AH$, $AG$ and $TAS$.

Here are two more examples of cell reactions to read through.

i) The Clark Cell:

$$Zn(s) + Hg_2SO_4(paste) \rightarrow Zn^{2+}(aq) + 2Hg(l) + SO_4^{2-}(aq$$

| Standard Enthalpy Change | = | Standard Optional Work | + | Standard Entropy Energy Change |
|---|---|---|---|---|
| $AH^o$ | | $AG^o$ | | $TAS^o$ |
| -343 kJ | | -276 kJ | | -67 kJ |

343 kJ of heat are evolved under standard irreversible conditions, which is derived from that type of potential energy, amounting to 276 kJ, which could be used to do work, and that type of potential energy, amounting to 67 kJ, which is not available to do work.

The irreversible reaction is highly exothermic; $AH^o = -343$ kJ.

Alternatively, 276 kJ of work could be done by the reactants changeing into products under reversible conditions, in which case 67 kJ of heat would be released to the surroundings.

The reversible reaction is exothermic, but less so; $q^o_{rev} = -67$ kJ.

ii) A cell based on the reaction between cadmium metal and mercury iodide paste:

$$Cd(s) + HgI_2(paste) \rightarrow Cd^{2+}(aq) + Hg(l) + 2I^-(aq)$$

$$\begin{array}{ccccc} AH^o & = & AG^o & + & TAS^o \\ -57\text{ kJ} & & -83\text{ kJ} & & +26\text{ kJ} \end{array}$$

57 kJ of heat are evolved under standard irreversible conditions, which is derived from the free energy type of potential energy, amounting to 83 kJ, diminished by the entropy energy increase, amounting to 26 kJ, of the products compared with the reactants.

The irreversible reaction is exothermic; $AH^o = -57$ kJ.

Alternatively, 83 kJ of optional work could be done under standard reversible conditions, whereupon 26 kJ of heat would be absorbed by the cell from the surroundings to account for the entropy energy increase which must occur if the reaction occurs.

The reversible reaction is therefore endothermic; $q^o_{rev} = +26$ kJ.

## Study Unit 6 What you should know.

You should

1. know how a chemical reaction may be performed irreversibly.
2. know how a chamical reaction may be performed reversilbly.
3. know that in electrical terms, optional work is nFE where AG = -nFE.
4. be aware of the need for standard conditions.
5. have some knowledge of the interplay between AG and TAS in deciding the value of AH in a chemical reaction; and understand the meaning of qrev.

---

Question 1 AH for a reaction is -220 kJ mol$^{-1}$; AS is -115 J K$^{-1}$ mol$^{-1}$. Calculate the free energy change, AG, for the reaction at 400 °C.

Note. The enthalpy change is quoted in kilojoules per mole of product (or reactant, as the case may be, while the change in entropy value, AS, is quoted in joules per kelvin per mole. More will be said later about the concept of entropy value. In the meantime, however, you must be careful to convert to a common unit: either convert kilojoules to joules, or joules to kilojoules. Since AG is usually quoted in kilojoules, the latter way is probably better.

Note. Temperature in calculations is kelvin temperature, which is equal to celsius temperature plus 273; thus 400 °C = 673 K.

---

Question 2 Given AH = AG + TAS, say what happens to AG for a reaction attended by a decrease in entropy value when the temperature at which the reaction is conducted is raised.

| | |
|---|---|
| 1 AG is unaffected. | 2 AG becomes less negative. |
| 3 AG becomes more positive | 4 AG may become zero. |

---

Question 3 The enthalpy change associated with a particular process is AH = +41.1 kJ mol$^{-1}$; AS, the increase in entropy value associated with the same process, is +0.11 kJ mol$^{-1}$. Which one of the following statements is correct?

| | |
|---|---|
| 1 The reaction will never occur spontaneously, no matter what the temperature. | 2 The reaction will occur spontaneously at any temperature. |
| 3 The reaction will only occur spontaneously at high temperature. | 4 The reaction will only occur spontaneously at low temperature. |

**Question 1**

$$\begin{aligned} AG &= AH - TAS \\ &= \underset{\text{kJ}}{-220} - \underset{\text{K}}{(400 + 273)} \times \underset{\text{kJ K}^{-1}}{\frac{-115}{1000}} \qquad \text{mol}^{-1} \\ &= \underline{-143\ \text{kJ mol}^{-1}} \end{aligned}$$

**Question 2**

Both AH and AS for a particular reaction can can be taken as constants over a not too large temperature range. Thus the enthalpy change and the change in entropy value for a given reaction are much the same when the reaction is carried out at 500 K and at, say, 600 K.

The equation AH = AG + TAS contains, therefore, two variables: AG and T. If one is altered, the other is altered.

**Response 1**

This response is incorrect. When the temperature at which a reaction is carried out is altered, the free energy change accompanying the reaction is altered. AG is temperature dependent.

**Responses 2, 3, 4.**

Each of these responses can be correct, depending on the sign of the change in entropy value.

Referring to the equation AH = AG + TAS; if AS is negative and T is increased, AG may become less negative, zero, more positive.

Thus a reaction which is spontaneous at room temperature may not be spontaneous at higher temperature. An example of such a reaction is

$$N_2 + 3H_2 = 2NH_3$$

which occurs spontaneously (but very slowly) at room temperature but not at a higher temperature.

Note that if the change in entropy value accompanying a reaction were positive, and T were increased, TAS would become more positive, and - if AH is to remain the same - AG would become less positive, zero, negative.

Thus a reaction which is not spontaneous at room temperature may become spontaneous at higher temperature. An example of such a reaction is $CaCO_3 = CaO + CO_2$

**Question 3**

**Responses 1, 2, 4.**

These responses are incorrect.

**Response 3**

Since AG = AH - TAS, then TAS has to exceed 41.1 kJ mol$^{-1}$ if AG is to be negative. This will only occur at and above a particular temperature.

This particular temperature above which AG is negative is 41.1/0.11 K = 373 K = 100 °C.

## Study Unit 7

# ENTROPY & ENTROPY ENERGY

---

PURPOSE

1. To define entropy value as indicative of disorder,
2. To discuss the implications of change in total entropy value.
3. To define 'system', 'surroundings' and 'universe'.
4. To show that change in entropy energy is equal to TAS
5. To expain 'free energy of mixing'.

---

Introduction. Once you have grasped the ideas of reversibility and irreversibility (the latter has still to be explained ), you should not have too much trouble in understanding qrev as the possible heat change between system and surroundings during the reversible operation of the change, and as the heat change which in conjunction with AG is responsible for the value of the enthalpy change during the irreversible operation of the change.

This particular Study Unit is perhaps a difficult one. I would suggest that you read the whole unit through fairly quickly without dwelling on difficult parts because subsequent parts may provide some of the answers. I would then suggest that you re-read the unit more slowly several times before attempting the Self-test.

Entropy defined

The change in entropy energy content of a system has been labeled here TAS without attempt at justification; it was felt that some preliminary attempt should be made to show how entropy energy operated in conjunction with free energy to give the enthalpy change accompanying a reaction, and there was little choice by but to use the correct notation.

Entropy and entropy energy are linked with the idea of disorder, and the statement made that an increase in entropy, implying disorder, is a favourable condition of reaction; the distinction between entropy and entropy energy is often glossed over. But to describe an increase in entropy as a 'favourable' condition of reaction is less than useful since it gives no clear indication of whether the reaction will or will not occur. There are in fact many reactions which occur with a decrease in entropy. But more of this later.

That increase in disorder is a natural tendency is generally acceptable in a vague sort of way. With little effort, one can think of many instances of increasing disorder. Some are listed below. But at the same time, one can also think of instances of decreasing disorder. Some of these are listed below.

Events which are accompanied by an increase in disorder:

1. Gases mix and do not unmix.
2. Wood burns and does not unburn.
3. Real weights fall down and convert their potential energy to disorganised heat energy.
4. Iron rusts
5. Ice melts in your hand.
6. Hydrogen and iodine combine
7. People in your class today will be scattered far and wide 20 years from now.
8. Trees decay and do not undecay.
9. A glass shatters when it is dropped.
10. An explosion.

Events which are accompanied by a decrease in disorder:

1. Plants grow.
2. Animals grow.
3. Steam condenses at room temperature.
4. Hens produce eggs.
5. Crystallisation.
6. Iron forms in the blast furnace.
7. Reactions in the sun.
8. Water freezes on a cold day.

Each one of these events, be it attended by an increase in disorder or a decrease in disorder, does actually occur. On the surface, therefore, it would seem unjustified to rely on an increase in disorder as a condition of a reaction occurring. And yet each one of the above events is accompanied by an increase in total disorder.

Just exactly what is meant by this last sentence should emerge as you progress through this unit; the unit is largely devoted to this one aspect of reaction. The unit will simultaneously try to show how changes in disorder are linked with changes in energy.

Thus the idea of 'increase in disorder' requires much amplification. But it must be stated emphatically that entropy is not disorder, any more than pH is hydrogen ion concentration; entropy is, however, related to disorder in much the same way that pH is related to hydrogen ion concentration. Thus, just as the pH value of a solution is indicative of the hydrogen ion concentration of the solution, the entropy value of a substance is indicative of the state of disorder of the substance. The entropy value of a substance is indicative of the number of arrangements of particles of the substance with bundles of energy in the substance. The greater the number of arrangements available, the greater is the disorder. (Note that there are times when it is better to think of energy as discrete like matter, that a given amount of energy in a particular circumstance consists of so many bundles or packets of energy. The proper word for these bundles or packets is quanta.)

Thus if a change occurs such that the final state is more disordered than the initial state, then the final state has the greater entropy value.

You can create disorder, but you cannot create entropy!

It is a popular misconception of entropy that it is a 'thing', some mystical form of matter and/or energy. It is not. It is a value indicative of the degree of disorder of the amount of substance.

## Disorder defined

The state of disorder of a piece of matter is equivalent to the number of possible arrangements of energy and matter within the piece of material.

Each individual arrangement of scattered energy over scattered particle is called a microstate. The life of any one particular microstate is exceedingly short since particles are in continuous motion. Any one microstate is as probable as any other.

The addition of energy creates more permutations of the scattered energy, and so creates more disorder. Such disorder is described as thermal disorder, and the entropy value indicative of the degree of thermal disorder is called the thermal entropy value. An increase in temperature increases the thermal entropy value of a substance (among other things).

That part of the disorder attributable to the possible arrangements of material particles is described as mixing or configurational disorder, and the entropy value indicative of the degree of this kind of disorder is called the mixing or configurational entropy value. Diffusion leads to a mixture of higher configurational entropy value.

Thus, for a particular piece of material:

$$\begin{matrix}\text{Entropy} & & \text{Thermal} & & \text{Configurational}\\ \text{value} & = & \text{entropy} & + & \text{entropy}\\ (S) & & \text{value} & & \text{value}\end{matrix}$$

The entropy value is indicative of the total number of microstates available within the piece of material

The total number of available fluctuating microstates is equivalent to the disorder of the piece of matter, in terms of varying energy scattering among varying particle locations.

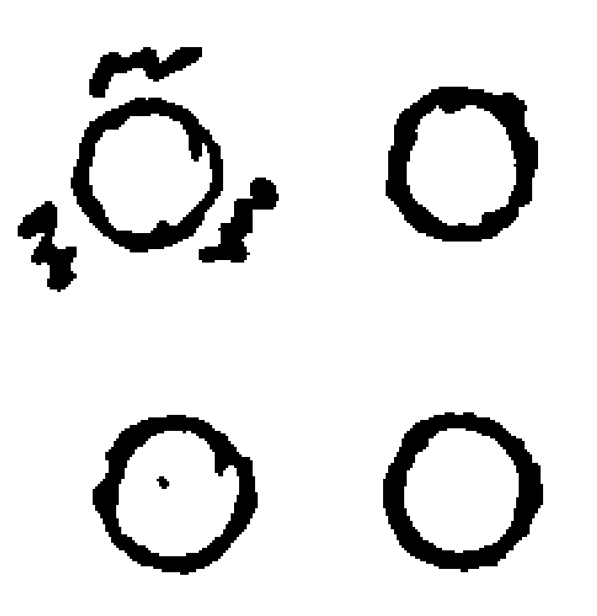
A substance in the liquid state has a greater entropy value than it has in the solid state, and it has a greater entropy value still when it is in the gaseous state.

## More about thermal disorder

Thermal disorder is equal to the number of arrangements by which energy quanta can be scattered among the particles of the material.

Each individual scattering is called a thermal microstate. The assumption is made that individual microstates have equal probability; that is to say, any one thermal arrangement is as likely to occur as any other.

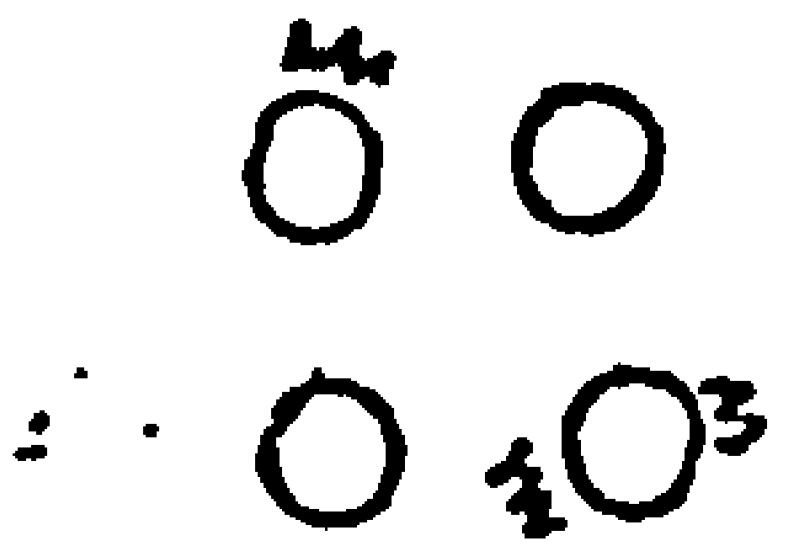
Consider the microstates resulting from the scattering of three quanta of energy among four otherwise identical particles (remembering that in a real situation very much larger numbers are involved).



A first way of scattering the three quanta:

1 particle has all 3 quanta; 3 particles have none.

Number of microstates = 4, since the three quanta can be given to any one of the four particles.



A second way of scattering the three quanta:

1 particle has 2 quanta; 1 particle has 1 quantum; and 2 particles have none.

Number of microstates = 12. Two quanta can be given to any one of four particles and one qunatum can then be given to any one of three remaining particles, so that the number of arrangements is 4 x 3. There are, therefore, twelve different ways in which three quanta can be allocated to four particles when two are given to one particle and one is given to another particle.

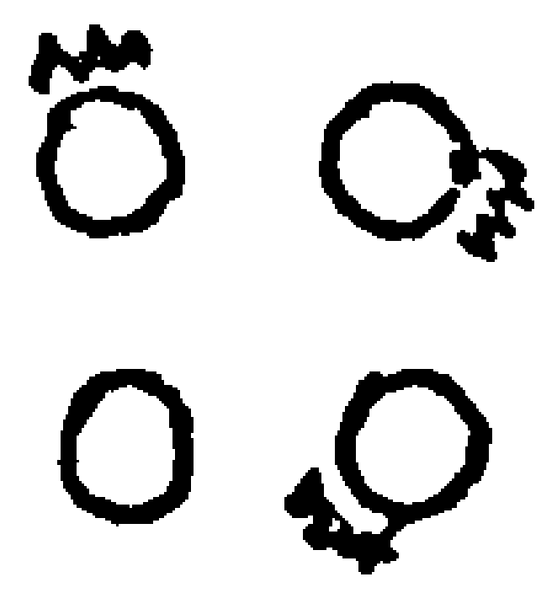


Fig 7.1

A third way of scattering the three quanta:

3 particles each have 1 quantum; 1 particle has none.

Number of microstates = 4, since there are four ways of "not giving a particle a quantum".

Overall number of microstates = 20

Any one of these 20 thermal microstates is as likely as any other; but, on a snap observation, the chance of finding the energy distribute 2 and 1 is greater because there are 12 ways in which the energy can be arranged like this.

You will find that, in general, there is one kind of arrangement which is very probable, just as the 2 and 1 arrangement illustrated above is more probable than the other two available arrangements considered together. In fact, with large numbers of quanta scattered among large numbers of particles, you will find - if you go into the mathematics of it - that the very probable arrangement is about the only one that counts; that all the other less probable arrangements combined are quite insignificant in comparison with that one kind of very probable arrangement.

This is why change occurs. If an assembly of energy and matter happens not to be in its most probable condition, and the opportunity is given for it to move to the very probable condition, then it will do so, and a reaction will be observed to occur.

Consider the conduction of heat. By our experience, heat conducts from a hot body to a cold body. We would be very surprised if heat were to spontaneously pass from a cold body to a hot body so that the cold body became colder and the hot body hotter. Why, then, does heat spontaneously pass from a hot body to a cold body? Because such a transfer entails a move to a more probable arrangement of quanta. If the two bodies are in contact, it is inevitable - from a permutational point of view - that heat will conduct from the hot body to the cold body. This is because those arrangements by which energy becomes scattered throughout the final 'uniform temperature condition' (when conduction stops) are infinitely more probable than those arrangements which exist before conduction starts.

There is a measurable probability (albeit an exceedingly small one) of the energy arrangements of the hot and cold body staying as they are so that no conduction occurs. There is an even smaller probability of the energy arrangements drifting to less probable ones so that heat is observed to flow from the cold body to the hot body! This could occur .... tomorrow, in a few million years, but in practical terms, never.

You may, at this point, wonder why the loss of a given amount of heat by the hot body and the gain of the same amount of heat by the cold body should make any difference at all, since what one loses, the other gains. This is true in terms of amount of heat, but not disorder. The loss of an amount of heat by a hot body decreases its thermal disorder; the gain of the same amount of heat by the cold body increases its thermal disorder. But the increase in disorder of the cold body is greater than the decrease in disorder of the hot body, for the transfer of a given amount of heat. Why is this? Because an amount of heat breaks up into more quanta at the lower temperature*. If an amount of heat can migrate from a hot region to a cold region, it will break up into more bundles of energy, there will be greater opportunities of scattering and randomisation creating a more probable state of affairs .... and so heat conducts from a hot body to a cold body. We gain more microstates than we lose. At thermal equilibrium the thermal energy is randomised in the most probable way.

Since conduction leads to an increase in total disorder, it is accompanied by an increase in total entropy value.

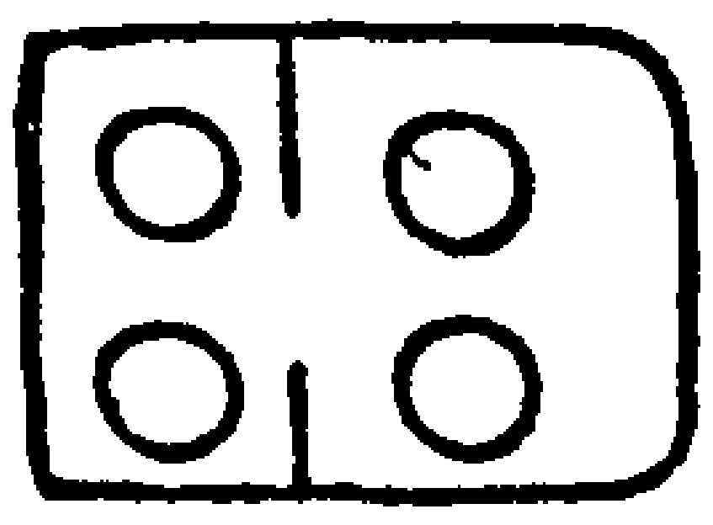
You will see that all spontaneous processes are accompanied by an increase in total entropy value. We have also come to accept at various points in the programme that spontaneous change is accompanied by a decrease in free energy. The link between these two statements, either one of which is a statement of the Second Law, will be enlarged upon throughout the programme.

*It would seem at times that to every answer there is a question. If you want an answer to this statement, I suggest you consult The Second Law, H. A. Bent, pages 151 and 152.

## More about configurational (= locational) disorder

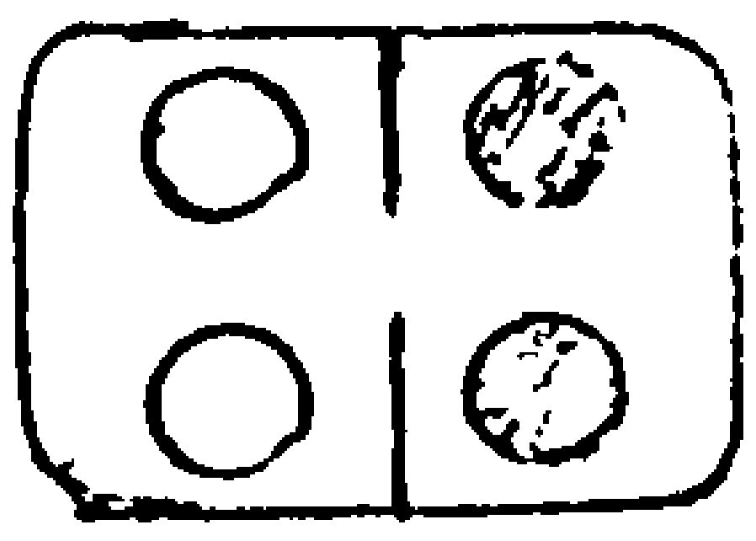
Configurational disorder is equal to the number of arrangements by which the particles of a substance may be located physically within a given volume of space.

Consider four identical particles, two on each side of a partition:



Number of possible arrangements = 1

Now consider four particles, two of one kind and two of another kind separated by a partition:



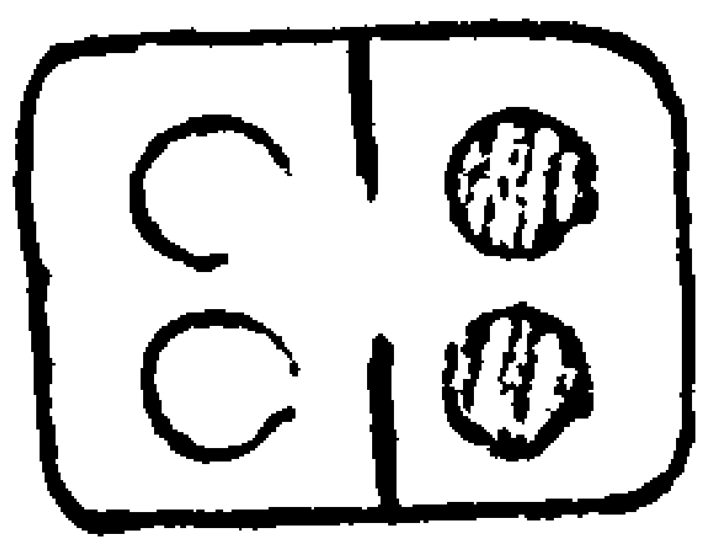
Separate state

No. of microstates = 1

Mixed state

No. of microstates =

Fig 7.2



Separate state

No. of microstates = 1

Total no. of microstates =

The probability of finding the particles, on a snap observation, in the mixed condition is greater than the probability of finding them in an unmixed condition.

For eight particles, four 'white' to the left of the partition and four 'black' to the right of the partition initially, the various numbers of microstates and probabilities are as follows.

| Particles to left of partition | Particles to right of partition | No. of microstates | Probability of 'mix'. |
|---|---|---|---|
| 4 W | 4 B | 1 | 1/70 |
| 3 W + 1 B | 1 W + 3 B | 16 | 16/70 |
| 2 W + 2 B | 2 W + 2 B | 36 | 36/70 |
| 1 W + 3 B | 3 W + 1 B | 16 | 16/70 |
| 4 B | 4 W | 1 | 1/70 |

The probability of finding the particles not only in a mixed condition but in the 'well mixed' condition corresponding to two of each kind on either side of the partition is greater than the other summed probabilities, 36/70 as against 34/70.

For large numbers of particles, the probability of finding the component particles in one or other of the well mixed microstates as against finding them in any of the other mixed microstates or in one of the two unmixed microstates is a certainty for all practical purposes.

Consider diffusion. The probability that two different gases will move to 'the well mixed' condition is one for all practical purposes. This is why diffusion occurs. It does not occur 'because particles can move'; particles could move and still not mix, but the probability of this happening is zero for all practical purposes. The probability that the gases should unmix, or that the ink in a fountain pen should spontaneously separate into dye and water, is zero for all practical purposes.

The number of arrangements of the mixed state is greatest, and so the disorder is greatest. There is therefore an increase in locational disorder on diffusion, and therefore an increase in the configurational entropy value indicative of this disorder. The entropy value of the mixture is greater than the summed entropy values of the separate gases.

That diffusion occurs spontaneously is well known. Again, a spontaneous process is characterised by an increase in total entropy. That it occurs spontaneously means, also, that its occurrence entails a decrease in free energy. Once again, therefore, the link between increase in total entropy value and decrease in free energy shows itself in spontaneous change. It is not possible to say too much about this link until the meanings of 'system' and 'surroundings' are made clear.

## Combining thermal and configurational disorder

Conduction was used to illustrate thermal disorder; diffusion was used to illustrate configurational disorder.

In most changes, chemical ones in particular, both kinds of disorder are involved, and the change in entropy value during a reaction is partly due to a change in thermal disorder and partly due to a change in configurational disorder (heat may be absorbed, large molecules may break up into more smaller molecules).

For the remainder of this programme there will be no emphasis on the different kinds of disorder and their associated entropy values. A change in entropy value will therefore be due to one or the other, or both, but this will no longer concern us.

## What is the connection between entropy and energy?

It takes energy to create disorder. The disorder created by the input of a particular amount of energy depends on the temperature of the object receiving the energy: the lower the temperature of the object, the more disorder is created by the input of the given amount of energy (page 7.5). The mathematics of it are such that the input of an amount of energy at 600 K creates increased disorder which is measured by a corresponding increase in entropy value, while the input of the same amount of energy at half the temperature, 300 K, causes double the increase in entropy value. In terms of change in entropy value, symbolised AS, and temperature, energy may be expressed as

$$\text{Energy} = T \times AS$$

The mathematical derivation of entropy value is such that it has the units kJ mol-1 K$^{-1}$, that is to say, kilojoules per mole per degree kelvin, and this is quite in order for it means that the product TAS is an energy term in kJ mol$^{-1}$ since the units of temperature cancel.

## The system and its surroundings.

In the discussions of energy changes accompanying chemical reactions, the chemical reaction has been considered as a system. The existence of surroundings was acknowledged and then carefully avoided, except in so far as the operation of the reaction in the system required that heat be evolved into the surroundings, or that heat be removed from the surroundings, or that optional work be done on something somewhere in the surroundings. The reason for this ignoring of the surroundings is that decisions about reaction spontaneity in the system need only consider the free energy change in the system, which of course must be negative if the reaction is to occur.

But the surroundings have a very real existence, and when the topic of change in entropy value is to be discussed, the surroundings must be considered with the system if the discussion is to make any sense. It turns out that when a reaction occurs in a system, for which therefore the free energy change must be negative, that the change in total entropy value of the system and surroundings considered together is always positive.

There are therefore two ways of saying the same thing about the spontaneity of a reaction:

i) A reaction in a system is spontaneous if the free energy change associated with its occurrence is negative.

ii) A reaction in a system is spontaneous if the change in total entropy value of system-cum-surroundings is positive.

The correctness of this latter statement has been alluded to (pages 7.5 and 7.7) and is easily shown to be true by physical analogy (see additional note at end of this unit). Both statements are statements of the Second Law of Thermodynamics.

The system-cum-surroundings is often described as a "universe", not necessarily the astronomical universe. The chemist's "universe" might very well consist of the flask on the bench within which the reaction is going on (the system) together with the space enclosed by the walls, ceiling and floor of the lecture room (the surroundings).

This alternative statement of the Second Law is often rephrased to read, "The entropy of the universe is always increasing".

This follows logically by reasoning that if any net reaction is to occur, the free energy change accompanying its occurrence must be negative while at the same time the total entropy value of the reacting part plus the surrounding part must increase .... and since only such reactions can occur, then the total entropy value is increasing.

Here lies the true meaning of thermodynamic irreversibility: if a reaction occurs it is attended by an increase in total disorder; if the reaction is caused to be reversed by being coupled to another 'driving' reaction, it may very well be reversed - but its reversal will be attended by a further increase in total disorder for both reactions working together .... so that it is quite impossible to to re-establish exactly the original 'state of affairs'. In this sense any change which occurs, by virtue of its occurring, is irreversible.

The only situation which is reversible in the thermodynamic sense is the equilibrium situation which arises when the free energy drive is equally opposed by a load in an attempt to make the change do a maximum optional work.

It turns out that when the free energy change associated with a projected reaction is zero, implying therefore an equilibrium situation, that the change in total entropy value associated with the same projected change is also zero.

And, if the free energy change associated with a projected reaction reaction is positive, implying therefore that the reaction cannot occur, then the change in total entropy value turns out to be negative.

The Second Law is an experimental generalisation; what it maintains about the direction of change has been observed experimentally to be so. No error attributable to the law has yet been established. The law does not attempt to explain the observed direction of change; it merely describes.

A brief explanation of the direction of change has been offered (page 7.4 and following), and mention will be made of it later in this programme.

**Changes for which AG is positive.** Another point which would perhaps be better mentioned here in very general terms is the occurrence of reactions for which the free energy change is positive. This is akin to a ball spontaneously rising from floor to table, which is by our experience impossible. But a ball can rise from floor to table, if lifted.

In this latter instance, the lifter is the system, and the ball is the object in the surroundings on which optional work is being done. The free energy change in the lifter's body as he lifts the ball is negative; the potential energy change of the ball as it rises is positive. The negative free energy change in the lifter's body is greater than the positive potential energy change of the ball. If it were not, the lifter would 'not be strong enough to lift the ball'.

If the ball be replaced by a chemical reaction whose occurrence is accompanied by a positive free energy change inlieu of the ball's positive potential energy change, then a comparable situation exists.

This is the case with photosynthesis, whose occurrence is accompanied by an increase in free energy; photosynthesis is no more spontaneous that the unassisted rising of a ball from floor to table.

Just as an individual can reach out and lift a ball, the sun can reach out and grow a plant. The sun is the system; the plant is is the object in the surroundings. In a sense, the sun is the downfalling weight, the plant is the load to be raised. The free energy change in the sun is negative; the energy is radiated in part as light; light has a unidirectional quality, and can do work; work is done on the plant, and it grows.

The free energy the plant derives from the light can be no greater than the free energy that 'went into making it in the sun'.

Thus a spontaneous reaction in a system, for which the free energy change must be negative, can be responsible for the occurrence of a non-spontaneous reaction, for which the free energy change is positive, somewhere in the surroundings. The limitation is that the decrease in free energy of the system must be marginally if not substantially greater than the increase in free energy of the non-spontaneous reaction.

This sounds like another statement of the Second Law. Why? Because it is specifying the conditions under which a reaction will occur in a specified direction.

---

In terms of change in entropy value, an alternative argument may be advanced as follows.

Lifter lifts ball. Lifter is the system; ball is part of the surroundings. Chemical reactions in lifter's body result in the combustion of glucose.

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O \qquad AH\ -ve$$

The reaction in the system is attended by an increase in entropy in the system: 7 molecules are converted to 12 molecules, which represents a fair increase in disorder.

The reaction is very exothermic. This is a result of a negative free energy change and a negative entropy energy change:

$$AH = AG + TAS = -ve$$

Remember that some of the AG has been used to lift the ball, but not much of it, Surplus AG is simply converted to heat which, with the TAS, is lost to the surroundings. Thus the surroundings gain heat, and so the entropy value of the surroundings increases.

The lifting of a ball, therefore, results in an increase in entropy value of both lifter and surroundings. Total entropy value, therefore, is increased.

---

Sun grows plant. The sun is the system. Reactions in the sun are spontaneous, and so they must be accompanied by a decrease in free energy. The nuclear reactions in the sun result in the conversion of hydrogen into helium; it will probably take four atoms of the former to make every one atom of the latter. The reactions are therefore attended by a decrease in entropy value of the system.

Considerable binding energy is consequently released and radiated to the surroundings where its ultimate fate is to become randomised as heat energy by absorption by interstallar material in the universe at large. Thus the astronomical universe at large increases in entropy value. The astrononical universe is playing the role of the surroundings, and so there is an increase in the entropy value of the surroundings

This latter increase is greater than the decrease in entropy value of the system, and so there is the inevitable increase in total entropy value associated with the occurrence of a spontaneous change.

That some objects in the surroundings, namely plant and animal life, should show a local decrease in entropy value does not significantly affect the entropy change in the surroundings, which is positive.

The local decrease in entropy value associated with the growing plant, due to

$$6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2,$$

is relatively insignificant.

The system and surroundings collectively are called a 'universe'.

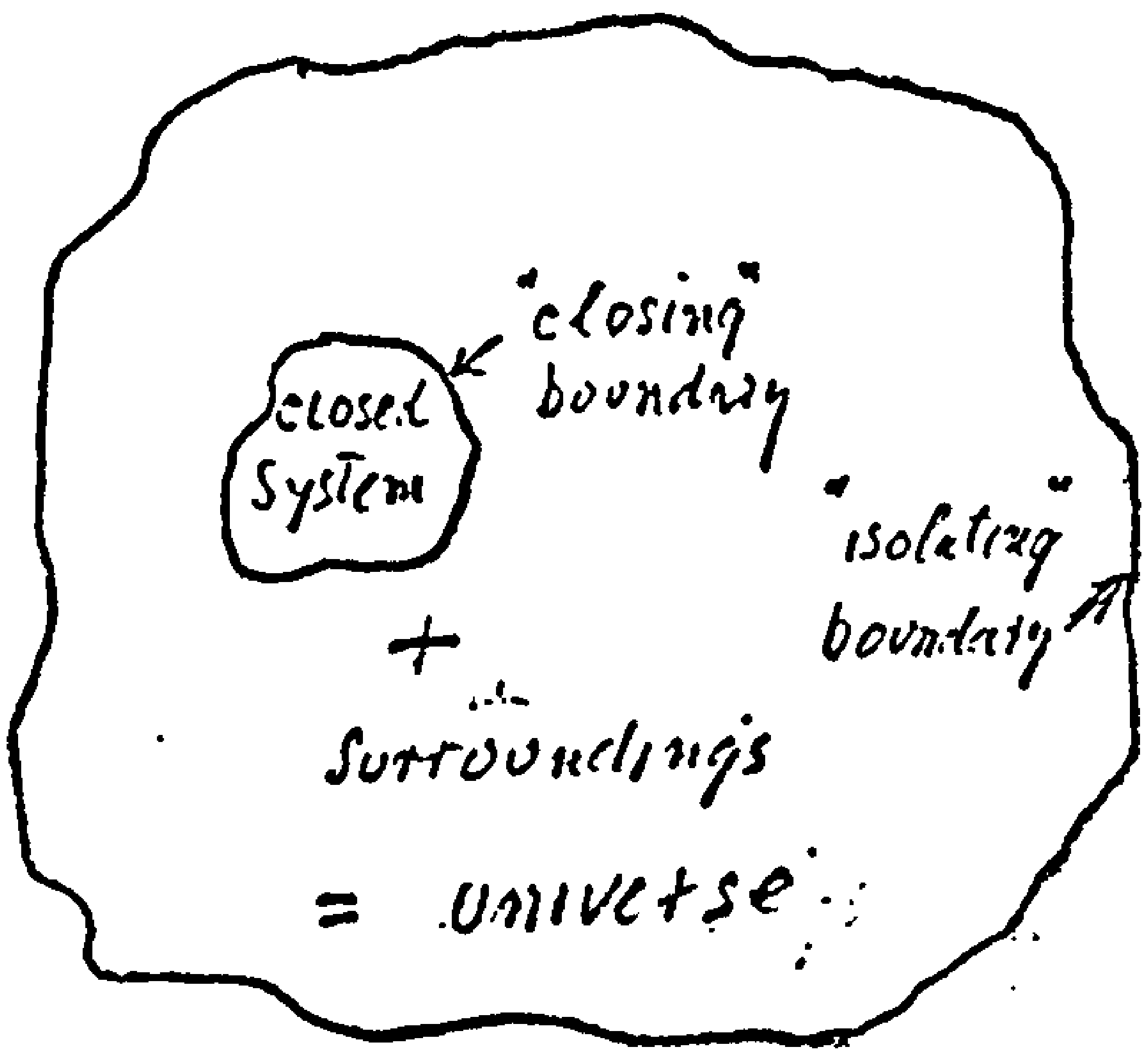


Fig. 7.3

A universe in this context is an isolated assemblage of matter and energy; neither matter nor energy can enter or leave the universe, hence the description 'isolated'.

Changes occur within the universe in accord with the above rules; that is to say, changes will occur in the system portion of the universe if the free energy change in that portion is negative; or saying the same thing in a different way, changes will occur in system portion if the <u>whole</u> entropy change is positive.

In discussions of this kind, a <u>closed</u> system is implied. A closed system is one retained by a boundary which prevents matter passing in our out, but which allows energy to pass in or out. The boundary may be imagined to be flexible so that reactions occurring within the system do so at constant pressure.

As a change within the system proceeds, and is of necessity accompanied by a decrease in free energy of the system,

a) the entropy value of the system may increase while the entropy value of the surroundings may decrease - but the former more than the latter, so that the overall change in entropy value is positive.
b) the entropy value of the system may decrease while the entropy value of the surroundings increases - the latter more than the former.
c) the entropy value of the system and the entropy value of the surroundings both increase.

Any one of these three possibilities results in an increase in total entropy value. Note in particular possibility (b), where the entropy value of the system actually decreases but the reaction still occurs because the entropy value of the surroundings increases more so - a result of the reaction being markedly exothermic, AH -ve, since heat passed into the surroundings will increase its disorder and so increase its entropy value.

The significance of this latter comment is that chemical reactions will occur despite their own local decrease in entropy value if they are exothermic enough.

The simplest way therefore to decide if a reaction will go is to deduce the value for AG from the relationship AH = AG + TAS.

If AG turns out to be positive, the reaction will not go; if AG turns out to be zero, an equilibrium situation exists; if AG turns out to be negative, the reaction can go, but may not for kinetic reasons.

A change in a system, be it fusion or combustion or whatever, is inevitably accompanied by a change in entropy value, symbolised AS.

Depending on the change, AS may be large or small, negative or positive; it may be due to altered energy scattering (such as is the case when heat is absorbed by a block of iron, essentially), or it may be due to altered particle scattering (such as is the case with gaseous diffusion), or one or other combination of these (as is generally the case with chemical reactions).

The dual nature of an entropy change - that it can consist of a thermal energy part and/or a configurational particle part - will not be much used in the remainder of this programme. In general, changes in entropy value will be quoted without reference to the nature of the change in entropy value.

It has been mentioned here, however, for two reasons. Firstly, it allows the presentation of a 'thermal' argument to justify the use of the symbolism TAS for entropy energy. Secondly, it allows the presentation of a 'configurational' argument to explain the concept of free energy of mixing, which latter is essential for a proper understanding of chemical equilibrium.

Entropy energy is TAS. When heat is given to some matter at 300 K, the entropy value of the matter is increased. (Assume that not much heat is involved and the piece of matter is fairly large, so that the change in temperature is minimal, sufficiently so for it to be taken as 300 K, throughout the addition of heat.)

When the same amount of heat is given to the same amount of matter, but at a temperature of 600 K, the increase in entropy value is half what it was at 300 K.

Thus, for the transfer of an amount of heat, doubling the temperature halves the associated change in entropy value of the material involved.

Therefore, the entropy energy of a system can be justifiably represented by TAS. (Refer to page 7.6.)

In terms of disorder, the additional microstates created at 300 K - over and above those already present - are more significant than the additional microstates created at 600 K - over and above those already there at the higher temperature. Energy absorbed by a low temperature body breaks up into more quanta than does the same energy absorbed by a high temperature body.

The lower the temperature, then, at which the entropy energy is absorbed, the greater is the entropy increase. In the extreme case, namely at the absolute zero, the increase in entropy would be infinite. This implies that at the absolute zero there is no disorder, only perfect order consisting of one single microstate for which the entropy value is zero; any increase in entropy at all would therefore represent an infinite increase.

When disorder vanishes, entropy becomes zero. Entropy does not vanish!

Problem 7.1
What is the increase in entropy value associated with the absorption of 400 J of heat at 300 K?

$$TAS = 400\ J$$

$$AS = \frac{400}{300}\ J\ K^{-1}$$

$$= 1\tfrac{1}{3}\ J\ K^{-1}$$

Note that entropy values have units 'joules per degree kelvin'

---

**AS = q/T** The Gibbs-Helmholtz equation

$$AH = AG + TAS$$

could be expressed alternatively as

$$AH = AG + q_{rev}$$

where $q_{rev}$ was that portion of the total enthalpy change which (whatever the reason) was not available to do optional work. Irrespective of how the reaction was performed, the reaction was attended by an energy change $q_{rev} = TAS$: if the reaction were carried out irreversibly, $q_{rev}$ and AG together were responsible for the enthalpy change; if the attempt were made to carry out the reaction reversibly, then - since AG was consumed doing optional work - the entire heat change between system and surroundings was due to $q_{rev}$.

Thus, the change in entropy value of the system, irrespective of how the reaction is performed, as reactants convert to products, is:

$$AS = \frac{q_{rev}}{T}$$

---

But remember that the surroundings are affected by the enthalpy change during the irreversible operation of the reaction. If AH of the system is negative, the surroundings gain this heat; if AH of the system is positive, the surroundings lose this heat. Thus -AH is to the surroundings what $q_{rev}$ is to the system.

Therefore,

$$AS_{surr} = \frac{-AH}{T}$$

If you are uncertain why $q_{rev}$ is equal to TAS of the system, go back and study Figures 5.1 to 5.4.

In general, therefore, change in entropy value, AS, is equal to q/T.

In particular

| | | | | |
|---|---|---|---|---|
| Change in entropy value of system | = $\frac{q_{rev}}{T}$ ; | Change in entropy value of surroundings | = | $\frac{-AH}{T}$ |
| no matter how the change is effected. | | only when the change is effected irreversibly | | |

Problems 7.2, 7.3, 7.4 and 7.5 refer to the same reaction.

Problem 7.2. What is the change in entropy value of the substances in a reacting system which suffers a decrease in entropy energy equal to 30 kJ at 300 K?

$TAS_{sys}$ = $-30$ kJ (per mole of reactant or product)

Therefore $AS_{sys}$ = $-30/300$ kJ $K^{-1}$ $mol^{-1}$

= $-0.1$ kJ $K^{-1}$ $mol^{-1}$

= $-100$ J $K^{-1}$ $mol^{-1}$ since entropy values are usually expressed J $K^{-1}$ $mol^{-1}$

---

Problem 7.3. What is the change in entropy value of the surroundings at 300 K when the enthalpy change for the reaction is $\Delta H = -90$ kJ $mol^{-1}$?

Heat gained by surroundings = $+90$ kJ $mol^{-1}$ (= $-AH$)

Therefore $AS_{surr}$ = $+90/300$ kJ $K^{-1}$ $mol^{-1}$ (= $-AH/T$)

= $+0.3$ kJ $K^{-1}$ $mol^{-1}$

= $+300$ J $K^{-1}$ $mol^{-1}$

---

Problem 7.4 What is the free energy change in this reaction?

$AG$ = $AH$ - $TAS_{sys}$

= $-90$ - $-30$ kJ $mol^{-1}$

= $-60$ kJ $mol^{-1}$

---

Problem 7.5 What is the reversible heat change for this reaction?

The reversible heat change is that which woould occur between the system and surroundings if the reaction could be operated reversibly, and is equal to $TAS_{sys}$, symbolised $q_{rev}$.

$q_{rev}$ = $TAS_{sys}$ = $-30$ kJ $mol^{-1}$

---

Note that the decrease in free energy (60 kJ) and the decrease in entropy energy (30 kJ) account for the enthalpy change, which equals 90 kJ of heat evolved. If all the free energy were <u>redirected</u> to do optional work, say by lifting a load in the surroundings somewhere, the decrease in free energy of the system would - if it could occur - be equally opposed by an "increase in free energy somewhere in the surroundings", and only 30 kJ of heat would be evolved to the surroundings .... if it could occur. In effect such a situation would be the reversible equilibrium situation you should now be familiar with, and the 30 kJ of heat would be the reversible heat change, $q_{rev}$.

Free energy of mixing. Imagine two gases, say oxygen and nitrogen, to be retained within the one vessel and separated by a partition.

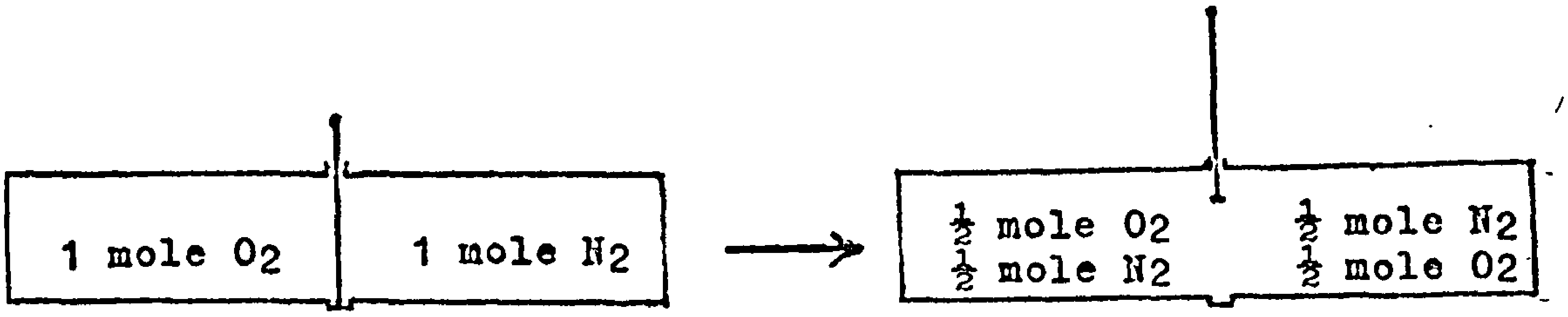


Fig. 7.4

As soon as the partition is removed, spontaneous diffusional mixing occurs, producing ultimately a uniform mixture of the two gases.

The free energy change accompanying the diffusion must be negative since the diffusion occurs spontaneously. The gases, in a sense, 'fall into each other'.

The enthalpy change associated with the mixing is zero. There is no heat exchange with the surroundings. The surroundings need not therefore enter the discussion. We need only concern ourselves with the system.

If there has been a decrease in free energy, where has it gone? It has not left the vessel. The answer is that it has converted to an equivalent amount of entropy energy. The product mixture is poorer in free energy and richer by an equal amount in entropy energy than the separate gases.

Since $\Delta H = 0$ $\qquad \Delta G = -T\Delta S$

The free energy decrease accompanying the mixing of mole amounts each of oxygen and nitrogen is about 3.4 kJ at 25 °C.

So $\qquad \Delta G = -3.4$ kJ

Therefore $\qquad T\Delta S = +3.4$ kJ

In the case of diffusion, the increase in entropy value resulting from the mixing may be taken as entirely due to an increase in the configurational entropy value.

When the entropy value reaches a maximum, the free energy reaches a minimum, and the diffusion is complete; a uniform mixture exists throughout the vessel. The free energy of the mixture of A and B is less than the free energy of A and B when separate.

The free energy of mixing minimum is a property of the system and only of the system. It is all important in determining where a mixture in physical or chemical reaction will settle at constant composition, i.e. equilibrium. This is dealt with in the last few units of this programme.

A closer look at entropy values. As already pointed out, the entropy value of an amount of matter is increased by raising the temperature. This is a consequence of an increase in thermal disorder, for the most part.

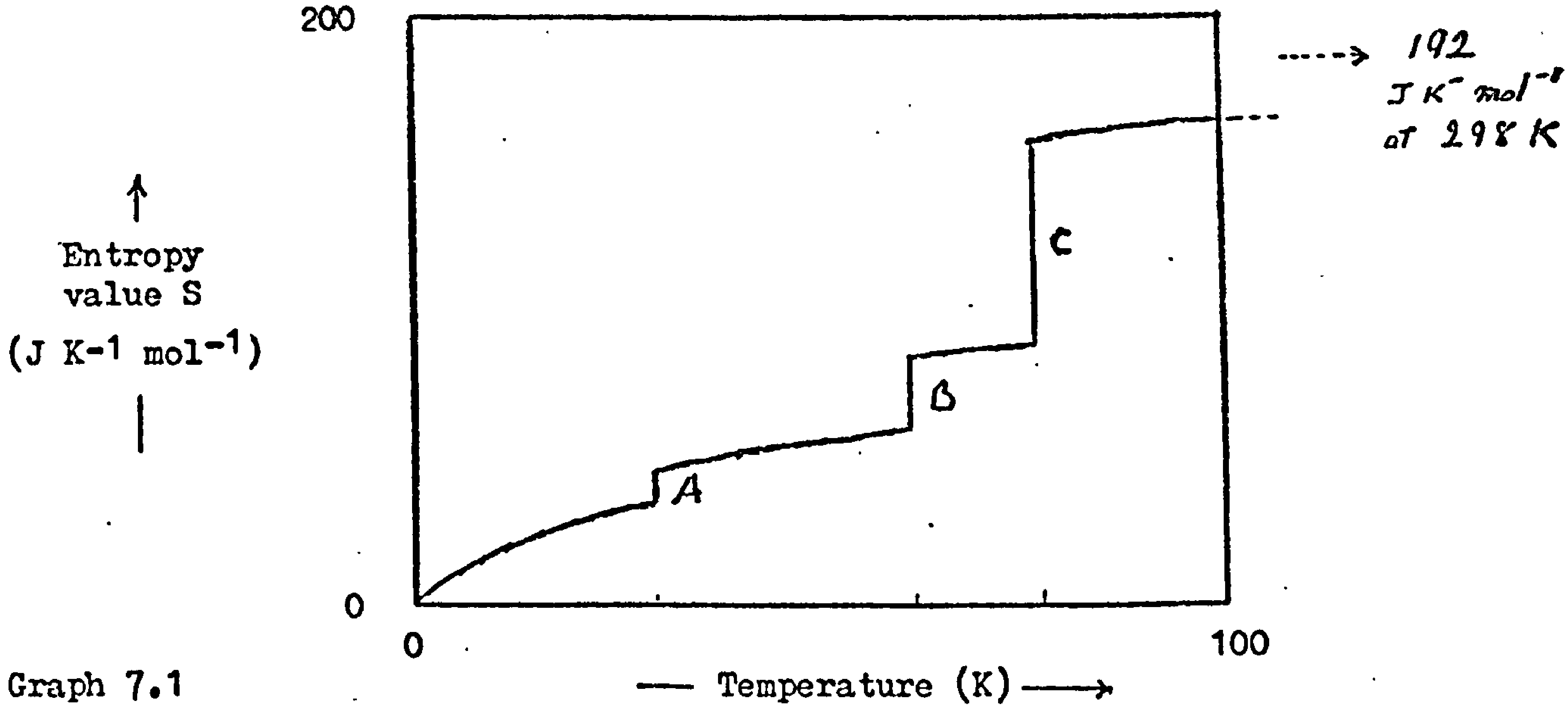
Change of state from solid to liquid will also bring about an increase in the entropy value of an amount of matter, this time without change of temperature. Such increase in entropy value is a consequence of an increase in configurational disorder.

The latter explanation also applies to transitions of one polymorph to another. Thus the transition

$$\text{Rhombic sulphur} \xrightarrow[+\ heat]{96\ ^\circ C} \text{Monoclinic sulphur}$$

gives a polymorph of higher entropy value.

Graph 7.1 shows how the entropy value of nitrogen alters as its temperature is increased from 0 K to 100 K. It includes one transition and two changes of state.



Graph 7.1

The otherwise smooth curve is interupted by three sharp increases in entropy value, at A, B and C.

That at A is due to the transition of one crystalline form of nitrogen to an other. As this occurs, heat is absorbed without change of temperature. This heat is the latent heat of transition.

That at B is due to solid nitrogen melting to liquid nitrogen. The latent heat of fusion is absorbed as this occurs.

That at C is due to liquid nitrogen boiling to nitrogen gas. The latent heat of vaporisation is absorbed.

The increase in disorder on boiling is more marked than on melting. This is indicated by the much greater increase in entropy value at the boiling point as compared with the melting point.

Of the three changes, the transition involves the least increase in disorder.

If you refer to a data book (e.g. Chemistry Data Book, Stark & Wallace, S.I. Edition, 1970, page 41.) you will see that the entropy value for nitrogen is quoted as 192 J $K^{-1}$ $mol^{-1}$. This is the entropy value at 298 K. Consequently, it ought not to be used at another temperature, for the entropy value at another temperature is not quite the same. However, the entropy value does not vary much with change in temperature, so long as the nitrogen is gaseous.

Problem 7.6

What then is the change in entropy value accompanying the complete conversion of 1 mole nitrogen and 3 moles hydrogen into 2 moles ammonia at 500 K?

| | $N_2$ + | $3H_2$ $\longrightarrow$ | $2NH_3$ | |
|---|---|---|---|---|
| | S = 192 | S = 3 x 131 | S = 2 x 193 | J $K^{-1}$ |
| | We should use a slightly larger value if we are going to do the calculation at 500 K instead of 298 K. | Same comment. S at 500 K is a bit more than 131 J $K^{-1}$ $mol^{-1}$. | Same comment. | |
| S values | 192 | 393 | 386 | J $K^{-1}$ |

Therefore, AS = 386 - (192 + 393) J $K^{-1}$

= -199 J $K^{-1}$

AS = -199 J $K^{-1}$ is the entropy change at 298 K. At 500 K, AS would be slightly different, but the error can be ignored.

Thus the entropy value of 2 moles of ammonia is less than the entropy value of 1 mole of nitrogen plus the entropy value of 3 moles of hydrogen.

Note that at the start of this reaction, the reactants consisted of 1 molar volume of nitrogen and 3 molar volumes of hydrogen not yet mixed.

This is a very important point and will be explained shortly.

Here are some entropy values.

| Substance | Entropy value J $K^{-1}$ $mol^{-1}$ |
|---|---|
| Diamond | 2.4 |
| Graphite | 5.7 |
| Gold | 47.7 |
| Sodium | 51.0 |
| Bromine | 152.0 |
| Nitrogen | 192.0 |
| Carbon dioxide | 214,0 |

Table 7.2

Study Unit 7 Waht you should know.

You should
1. be aware of the distintion beteen entropy value and entropy energy.
2. have a clearer idea of system, surroundings and universe.
3. appreciate that the statement 'increase in entropy' is vague unless 'of what' is known.
4. appreciate that a spontaneous reaction, for kinetic reasons, may take a very long time to occur.
5. understand that mixing is accompanied by a decrease in free energy and an increase in entropy value.
6. understand that an entropy value
   a) is a measure of disorder.
   b) is zero at absolute zero.
   c) always increases with increase in temperature.
   d) always increases during melting.
   e) always increases during boiling, and evaporation.
   f) always increases when larger molecules change into smaller molecules.
   g) always increases as a result of mixing.
   h) is lowest for hard solids, higher for soft solids, higher still for liquids, and highest of all for gases.
   i) for 2 mole amounts is double the entropy value for 1 mole amount, other things being equal.
   j) in total always increases in a spontaneous change

And all the king's horses and all the king's men,
Couldn't put Humpty together again.

---

Question 1 A supercooled saturated solution is stable until seeded with a crystal of the solute, whereupon rapid spontaneous crystallisation occurs. But a crystalline solid has a lower entropy value than the dissolved solute. Does this mean that the spontaneous crystallisation of a supercooled saturated solution is accompanied by

| | |
|---|---|
| 1 a decrease in entropy value? | 2 an increase in total entropy value? |
| 3 a decrease in free energy? | 4 an increase in the entropy value of the residual solution? |

Question 2 Silver chlorite decomposes spontaneously at room temperature. The enthalpy change, $\Delta H$, for the reaction is zero. Does this mean that

| | |
|---|---|
| 1 the decrease in free energy is equal to the increase in entropy energy? | 2 the increase in free energy is equal to the decrease in entropy energy? |
| 3 the decomposition is attended by an increase in total entropy value? | 4 the reaction would become faster if the temperature were raised? |

Question 3 What value would you expect $\Delta S$ for the reaction $H_2(g) + \frac{1}{2}O_2(g) \text{ — } H_2O(1)$ to have?

| | |
|---|---|
| 1 A negative value because gases are converting to a liquid. | 2 A negative value because $\Delta H$ is negative. |
| 3 A positive value because $H_2O$ molecules are more 'mixed' than $H_2$ and $O_2$ separately. | 4 A negative value because there is a decrease in the number of molecules. |

Question 4 The enthalpy of fusion of sodium chloride is 30 kJ $mol^{-1}$ approximately. The melting point of sodium chloride is 809 °C. Calculate the change in entropy value accompanying melting.

---

Question 5 Which of the processes listed opposite would be accompanied by a decrease in entropy value?

| |
|---|
| 1 hydrogenation |
| 2 polymerisation |
| 3 decomposition |

---

Question 6 The change in entropy value accompanying the reaction

$$2H_2O(l) \longrightarrow H_3O^+(aq) + OH^-(aq)$$

is $-80.5$ J $K^{-1}$ $mol^{-1}$. How do you explain the decrease in entropy value?

---

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### Question 1

Response 1

This response begs the question "decrease in entropy value of what?" As with all the other changes you have encountered, it is very important when discussing entropy to have a clear idea of system as against surroundings.

As the response stands, it is impossible to comment on it.

Response 2

This response is correct. If the process occurs spontaneously, it must be accompanied by an increase in the total entropy value.

Response 3

This response is correct. If the process occurs spontaneously, it must be accompanied by a decrease in free energy, and of the system is understood.

Response 4

This response is correct.

The supercooled saturated solution can be regarded as an isolated system; the surroundings need not enter the argument. The decrease in entropy value which occurs as the solute crystallises is more than offset by the increase in entropy value of the residual solution due to

a) increased randomness of the water molecules no longer attached to the solute particles, especially in the case of ionic solutes, and
b) increased randomness of all species present because of a rise in temperature caused by the free energy decrease exceeding the entropy energy increase ... AH is negative; such crystallisations are usually exothermic.

---

### Question 2

Response 1

Yes.

Response 2

No.

Response 3

If the changes in the system and surroundings were examined, it would be found that this in fact was the case.

Response 4

This response is in no way dependent on the enthalpy, free energy or entropy energy change. The reaction would, for kinetic reasons, certainly become faster if the temperature were raised.

---

### Question 3

Response 1

This response is correct.

Response 2

AS is not determined by AH. The reverse is partly true, that is, AH is due in part to TAS, the rest of AH being due to AG.

Response 3

This response is over-ridden by the conversion gaseous reactants to liquid product, even if the product is a bit more mixed up.

| | |
|---|---|
| Response 3, continued | Other things being equal, a more 'mixed' product would account for an increase in entropy. For example, the reaction<br>$N_2(g) + O_2(g) — 2NO(g)$<br>is accompanied by an increase in entropy value. |
| Response 4 | This response is correct, other things being equal. |
| Question 4 | At the melting point, solid and liquid salt can co-exist at equilibrium, at which point AG is zero.<br>Thus AH = TAS<br>Therefore AS = AH/T.<br>$= {}^{-}30/1082$ kJ $K^{-1}$ $mol^{-1}$<br>$= 0.028$ kJ $K^{-1}$ $mol^{-1}$<br>$= 28$ J $K^{-1}$ $mol^{-1}$ |
| Question 5 | |
| Response 1 | Hydrogenation would be accompanied by a decrease in entropy value. The hydrogen would be lost as a free entity; and the hydrogenation of liquid oils often produces solid fats. |
| Response 2 | Polymerisation would produce a decrease in entropy value. |
| Response 3 | Decomposition would result, probably, in an increase in entropy value. |
| Question 6 | The decrease in entropy value is a result of the incressed ordering imposed on the surrounding water molecules by the electric fields of the ions. |

## Additional note: the Second Law, by physical analogy.

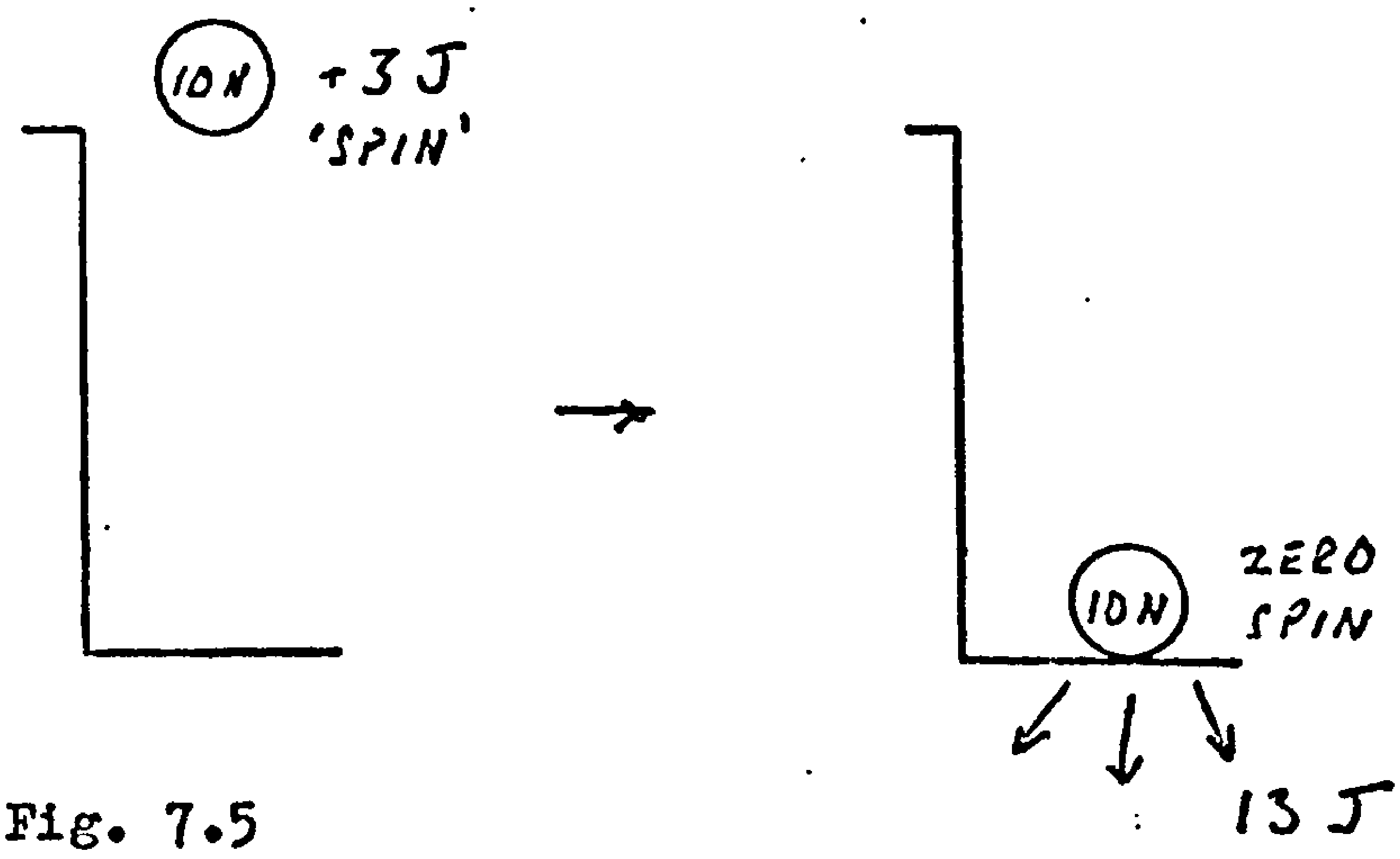

Fig. 7.5

The analogy represents a spontaneous change (AG -ve) in which the entropy energy change is negative.

Change in entropy energy of system '$TAS_{sys}$' = -3 J

Change in entropy energy of surroundings '$TAS_{surr}$' = +13 J
(The energy released into the vastness of the surroundings is derived from the enthalpy change, AH = -13 J, and is therefore 13 J. This energy is scattered in the surroundings as entropy energy.)

Change in total entropy energy of
system-cum-surroundings '$TAS_{tot}$' = -3 + +13 J
= +10 J

The change in total entropy energy is positive, and since temperature T is constant, the change in total entropy value, AStot, is positive.

If you care to try any negative numerical value for AG (the change must be negative if it is to be spontaneous) and any value, negative or positive, for $TAS_{sys}$, you will always find that the above argument leads to the conclusion that

when a spontaneous reaction occurs, for which the free energy change of the system must be negative, it is always accompanied by a positive change in total entropy value of system and surroundings.

This is the Second Law of Thermodynamics.

If you extend the argument to a 'weightless' weight, which is an analogy for an equilibrium situation, you will find that the free energy change is zero, and that it is associated with no change in total entropy value.

If you extend the argument to a weight rising upwards, an event which does not occur spontaneously, an event for which the free energy change would be positive, you will find that it is accompanied by a negative change in total entropy value.

These latter illustrations are outwith the programme.

## SPONTANEOUS PROCESSES

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### PURPOSE

1. To offer a fundamental explanation for the occurrence of reactions.

2. To offer a fundamental explanation of the difference between free energy and entropy energy.

3. To explain a variety of processes in terms of free energy change and entropy change.

---

Introduction. The views expressed in the earlier parts of this unit are my own personal interpretations of the reason for reaction spontaneity which interpretations I have chosen to expain in terms of the 'force of disorder'.

Similarly, the explanation of the difference between free energy - that it has a resultant unidirectional quality - and entropy energy - that it does not - are personal views.

They may help you to come to terms with some of the very basics of what is, in detail, a complex subject.

The unit then continues with an analysis of a variety of spontaneous processes: diffusion, osmosis, dialysis, distribution, the concentration cell, ion exchange and chromatography. The same fundamental reason is offered to explain each of these. The coverage however is theoretical, little practical experimental detail being given. I feel the latter is best left to your supervisor since the particular experiment adopted in to each case will vary from school to school.

### Why does a reaction take the direction it does?

What is the underlying reason why a net reaction moves in that direction rather than this direction? An answer might be, "Because when it moves in that direction it is accompanied by a decrease in free energy.".

This has become our means of judging reaction spontaneity.

But why is it that a decrease in the free energy store of a system is a condition of reaction in the system?

One may ask the same question about a real weight. Why is it that a decrease in the potential energy of a weight is a condition of its falling?

A more fundamental reason is that the weight falls merely because it is pulled on by the force of gravity. The weight only possesses what potential energy it possesses by permission of the force of gravity. If the force of gravity were less, the potential energy of the weight would be less. If the force of gravity were zero, the weight would have no potential energy. It would be weightless ... suspended motionless ... in a state of static equilibrium; or it could be argued that it was falling at a rate equal to that at which it was rising .... a kind of dynamic equilibrium.

The important point, however, is that the weight possesses 'free energy' as a consequence of the pull on it by the force of gravity.

In a similar way, a chemical system possesses free energy as a consequence of the pull exerted on its parts by the force of disorder. By force of disorder I mean the inevitable drive exhibited by energy quanta and particles alike to move to arrangements which are collectively more probable than those arrangements initially occupied by the quanta and particles. Assuming that there is no kinetic snag, it is a permutational inevitability that this will occur.

Given the opportunity to move to a final system-cum-surroundings with greater possibilities of energy and particle scattering than the initial system-cum-surroundings, then it is a mathematical certainty (as near as makes no difference) that such a change will occur. This is why a spontaneous reaction is always accompanied by an increase in total disorder, which shows itself in a measurable way as an increase in total entropy value.
Note that this argument includes both system and surroundings.

During this transit to the final more randomised state, some of the system's stock of potential energy can be latched onto to do optional work 'as it passes'; this part of the total stock of potential energy is the free energy part. Some of the total stock cannot be so used; this part I have called entropy energy - it is as randomised in the initial state as it will be in the final state, and lacking any resultant directional motion is quite useless for doing work.

Should the proposed final system-cum-surroundings be no more randomised than the initial, then there is no reason why any change should occur. The change in total entropy value for the proposed change would be zero; or saying the same thing in a different way, the force of disorder would be zero and so also, therefore, would be the free energy change of the system. With no force of disorder to draw on the system's energy there could be no free energy change.

The difference between free energy and entropy energy. The essential feature of free energy, and the feature which allows of its use for optional work, is that it has a resultant 'unidirectional' quality.

Thus, the real weight will fall in one specific direction, namely downwards, and the downfalling can be put to work.

The transfer of electrons from zinc atoms to aqueous copper ions can be induced to occur via an external wire, and their unidirectional motion can be put to work.

Sound waves travel in straight lines. Sound waves have a unidirectional quality (from source outwards) and so can be converted to work. Otherwise this work capability is dissipated in the surroundings as heat, i.e. as 'omnidirectional' molecular motion.

Light, similarly, has a unidirectional quality; it may also be converted to work. Otherwise it is randomised by absorption at a surface and converted to heat. Photosynthesis makes use of the unidirectional quality of light: work is done on the growing plant which causes it to grow.
A beam of light can rotate a small paddle wheel.

In diffusion, molecules of two different gases separated by a partition will each, on removal of the partition, exhibit a resultant motion in opposite directions, each of which motions can be put to work .... diminishing with time until a uniform mixture arises. The 'uniform mixture' will consist of any one of an infinite (virtually) number of the well mixed permutations. There are so many well mixed configurations that the chances of a less than well mixed configuration arising as the end-product of diffusion are zero for all practical purposes. The probability of the gases remaining in the unmixed state is infinitely less than this!

This resultant motion is the source of the free energy change during diffusion, which free energy is swopped, as it were, for an equivalent amount of entropy energy once the diffusion is complete. The fundamental driving force is of course the drive to disorder; it is the inevitable arisal of this disorder which is responsible for AG in the first place.

There is therefore a natural tendency for free energy, in the absence of a demand on it to do optional work, to degrade to the poorer quality 'omnidirectional' energy. Thus the free energy of diffusion becomes the entropy energy of the mixed condition; there is no change in temperature, and no exchange of heat between the gases and the surroundings. Thus light becomes heat on absorption, which represents an increase in entropy energy.

But even heat energy itself, omnidirectional as it is, can be converted to work, at least in part.

This possibility arises when a hot object is connected to a cold object. In such a circumstance there will be a resultant unidirectional flow of heat from the hot object to the cold object. This, of course, is within our experience of what always happens. Without going into details, the free energy change accompanying conduction of heat turns out to be negative. (Imagine the two objects to be the system; the surroundings need not enter the picture.)

The greater the difference in the temperatures of the hot and the cold object, the more of the heat transfer is capable of doing optional work.

Indeed, if the temperature of the cold object could be kept at absolute zero (which is impossible) all the heat transfer could be put to work.

The limitation on the use of heat as a source of work is the difference in the temperatures of the hot part and the cold part.

If the temperatures are the same no work can be obtained; and no heat would transfer anyhow.

Maximum efficiency in an engine is obtained by making the hot part as hot as possible and the cold part as cold as possible. This gives the largest free energy change possible. The problem then is one of getting as much of the free energy change as work and as little of it as heat as can be managed.

The force of disorder exerted by an alternative system-cum- surroundings acts on the free energy of a system, for which free energy it is responsible, in a manner similar to that by which the force of gravity exerted by a planet acts on the potential energy of a weight, for the creation of which potential energy it is responsible.

## Controlling factor in reaction.

In any net reaction which occurs, the free energy change must be negative.

This is the simplest means by which to make a decision on reaction spontaneity

Remember that its great advantage is that it requires only the system to be considered; this is usually very much simpler than having to consider system-cum-surroundings in terms of change in total entropy.

The value for AG will usually be derived from a knowledge of AH and TAS.

Diffusion. Diffusion is spontaneous intermingling of particles at the atomic level.

It is most easily observed to occur between gases since in this case it is most rapid. The free energy change accompanying diffusion is negative; the free energy of the mixture is less than that of the original separate gases. This aspect of diffusion has been much emphasised in this programme because it will be used shortly to show how it determines where a mixture of reactants and products in chemical reaction settle at constant composition.

Diffusion also occurs between liquids if it can, that is, if the liquids are miscible. The free energy change is, of course, negative, but the diffusion is much slower.

In the event that the liquids are immiscible, the free energy of their mixing is positive .... which is why they do not mix!

That diffusion in liquids is slower is a kinetic consideration and has nothing to do with the thermodynamics of the process. Thus the free energy change accompanying diffusion in solids, whether it be negative or positive, is of secondary consideration to the kinetics of the process, that is, the lack of mobility of the component particles of the solids. There can be, though, some surface diffusional effects.

For the purposes of this programme it can be taken that the free energy of the unmixed gases is converted completely into the entropy energy of the mixed product, AG = -TAS. (This is ideal behaviour; in reality, and for reasons which need not concern us, these two quantities, AG and -TAS, would not necessarily be equal, and so some heat might be evolved into the surroundings or might be absorbed from the surroundings, giving a small negative value or a small positive value for AH as the case may be.)

Since, therefore, AG = -TAS, free potential energy is converted completely to entropy potential energy and there is no change in temperature. The increase in entropy energy at constant temperature is TAS and so, since T does not change, AS is responsible for the increase. This is one way of arguing that there is an increase in entropy on mixing.

Whether you offer the increase in entropy or the decrease in free energy as a reason for the occurrence of diffusion depends very much on how you choose to reason about the process.

By my way of thinking, the former is the more fundamental since it is closer to the real reason for change, that is to say, the inevitable transition to more totally disordered state when this is accessible.

A variety of examples will now follow in which either the decrease in free energy of the system or the increase in total entropy value of the system and surroundings, or both, will be advanced as explanations for the occurrence of the change. The value of the enthalpy change will be mentioned only in so far as it is a consequence of the interplay between the free energy change (which is always of the system) and the entropy energy change of the system.

Thus, in general, $AH_{system} = AG_{system} + TAS_{system}$

In discussing the specific cases of change in entropy value which arise in problem dealing, you have to be very clear in your mind as to whether you mean entropy change in the sytem, or the surroundings, or both: in the last instance you have the right to talk about change in total entropy value. But also, if the surroundings are not involved (AH zero, meaning heat is neither evolved to or absorbed from the surroundings), then any entropy change in the sytem can be the only entropy change, and so - although only the system is considered - can be referred to as the total entropy change.

Spontaneous endothermic reactions in general. Endothermic reactions do not usually occur at room temperature, while the same endothermic reactions occur at higher temperature.

This means that the free energy change accompanying an endothermic at room temperature is likely to be positive, while the free energy change accompanying the same endothermic reaction at higher temperature is negative.

For an endothermic reaction, AH is positive. If the reaction is not spontaneous at room temperature, then AG at room temperature is positive.

| | AG | + | TAS | = | AH |
|---|---|---|---|---|---|
| Low temp. | The free energy change is positive | | and the entropy energy change is negligible since T is small. | | AH consequently is observed to be positive, and the reaction is describe as endothermic. |
| High temp. | The free energy change will become negative when the temperature is raised ...... | | if TAS is positive, because TAS will become markedly positive, T being large, ..... | | while AH remains more or less constan |

Only if the entropy change accompanying the reaction is positive, will raising the temperature convert a non-spontaneous reaction to a spontaneous one.

But some endothermic reactions, even at room temperature, are attended by a large enough increase in entropy at room temperature for them to occur spontaneously without heating. This is especially the case with reactions producing gases from solids.

**Spontaneous endothermic reaction.** The reaction between hydrated cobalt chloride and thionyl chloride occurs spontaneously at room temperature, and is accompanied by the absorption of much heat, that is to say, the reaction mixture (the system) is observed to grow colder and would have to absorb heat from the surrounding air (the surroundings) if the tempera- were to remain constant. Thus AH is positive.

$$CoCl_2.6H_2O(s) \ + \ 6SOCl_2(l) \ \rightarrow \ CoCl_2(s) \ + \ 12HCl(g) \ + \ 6SO_2(g)$$

That the reaction occurs means that the free energy change accompanying its occurrence is negative: AG is -ve.

The summed entropy values for the products, two of which are gases, are greater than the summed entropy values for the reactants. The change in entropy value of the system is positive. This is usually to be expected when gaseous products are produced from non-gaseous reactants.

One final point: since the reaction is spontaneous., the change in the total entropy value of the systen-cum-surroundings must be positive. This turns out to be so. Heat absorbed from the surroundings lowers the entropy value of the surroundings; but the simultaneous increase in entropy value of the system is greater than the decrease in entropy value of the surroundings.

Thus, spontaneous reactions are endothermic when their occurrence is accompanied by a relatively large increase in entropy energy.

At low temperature, this arises when the increase in entropy, AS, is large.

At high temperature, this arises because T and/or AS is large.

Otherwise, spontaneous reactions are exothermic, especially at low temperature, because AH approximates to AG, which must be negative in a spontaneous reaction.

Osmosis. Osmosis is a spontaneous diffusional process which occurs between a solution and the pure solvent. The solution and the pure solvent are separated by a semipermeable membrane* Solvent diffuses through the membrane into the solution, so diluting it, and increasing its volume. The solution develops a 'back-pressure' which eventually stops the inflow of solvent. This is called the solution's osmotic pressure.

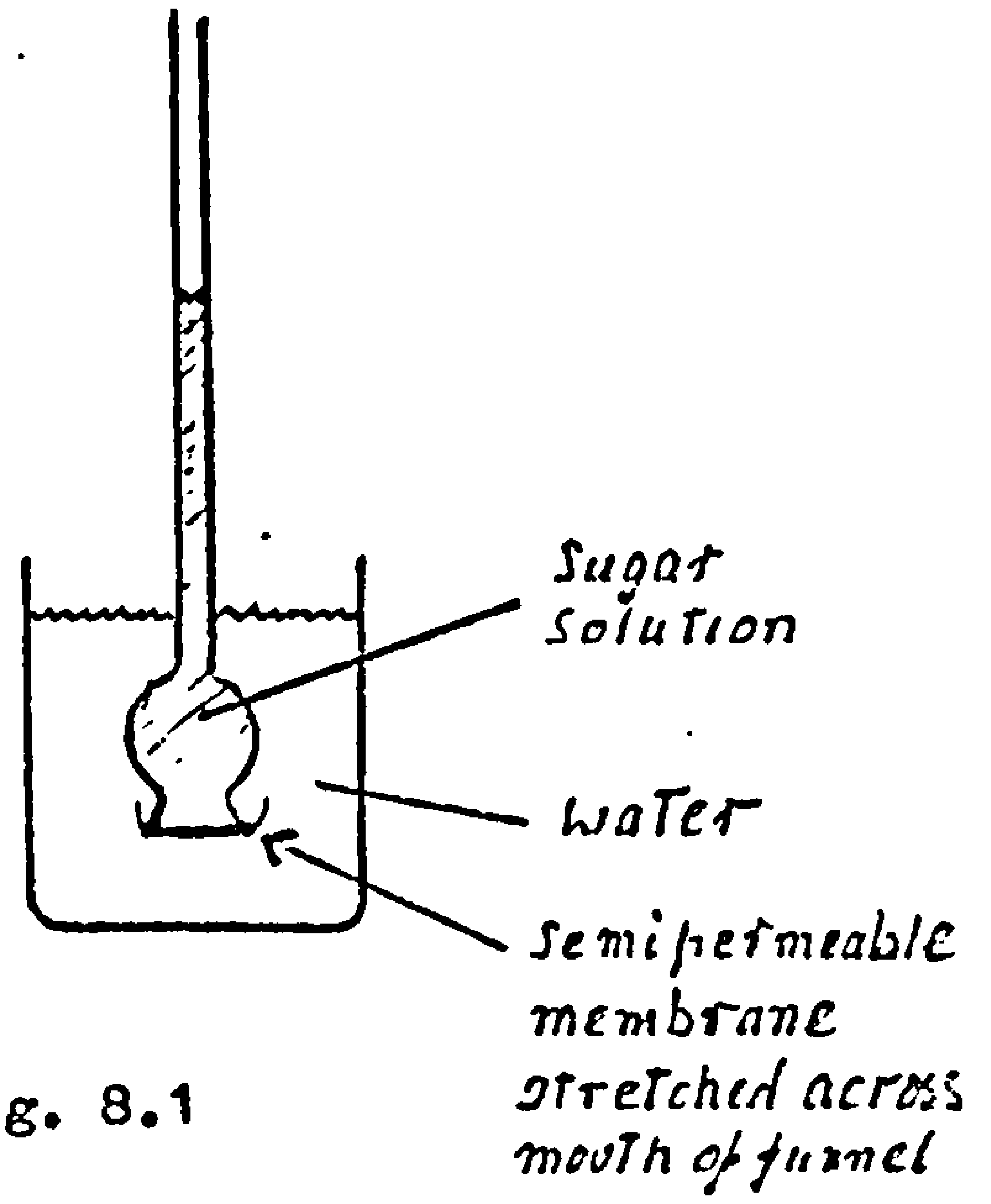

Fig. 8.1

Why does it occur?

We have established that the free energy of a substance is decreased on mixing: A in the mixture of A and B has a lower free energy than pure A.

Thus, the free energy of 1 mole (say) of pure water outside the membrane decreases when this 1 mole of water diffuses to the mixed condition inside the membrane.

Pure water diffuses into the mixed condition because such diffusion is accompanied by a decrease in free energy.

Alternatively, 1 mole of water inside the membrane is more spread out - it is 'diluted with solute' - and so has a higher entropy value than would the same mole of water outside the membrane.

Pure water diffuses into the mixed condition because such diffusion is accompanied by an increase in entropy value.

By the same argument, solute molecules should diffuse outwards. Eventually uniform solutions of the same concentration should arise on each side of the membrane. This would represent an equilibrium situation of minimum free energy and maximum entropy value.

The semipermeable membrane tends to block the outward diffusion of solute molecules. Further, the heavier solute molecules move relatively slowly.

Osmosis consists of a 'double acting' diffusional process, each of which has an attendant free energy decrease accompanying it, but only one of which is permitted to occur.

If osmosis is to work, the solute must be something of relatively high molecular mass, such as sucrose, $C_{12}H_{22}O_{11}$; this solute has a molecular mass of 342 u.

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*A semipermeable membrane is one which will permit solvent molecules to pass through it but not solute molecules.

Dialysis . Dialysis is a method of separating substances in true solution from substances in colloidal dispersion. Like osmosis it depends on spontaneous diffusion. (See additional note on colloids, page 8. )

One phase consists of the colloid dispersed in the true solution - say starch dispersed in sodium chloride solution; the other phase consists of the pure solvent.- say water. These are separated by a membrane which is impenetrable to starch molecules, but which will allow sodium ions, chlorine ions and water molecules to pass.

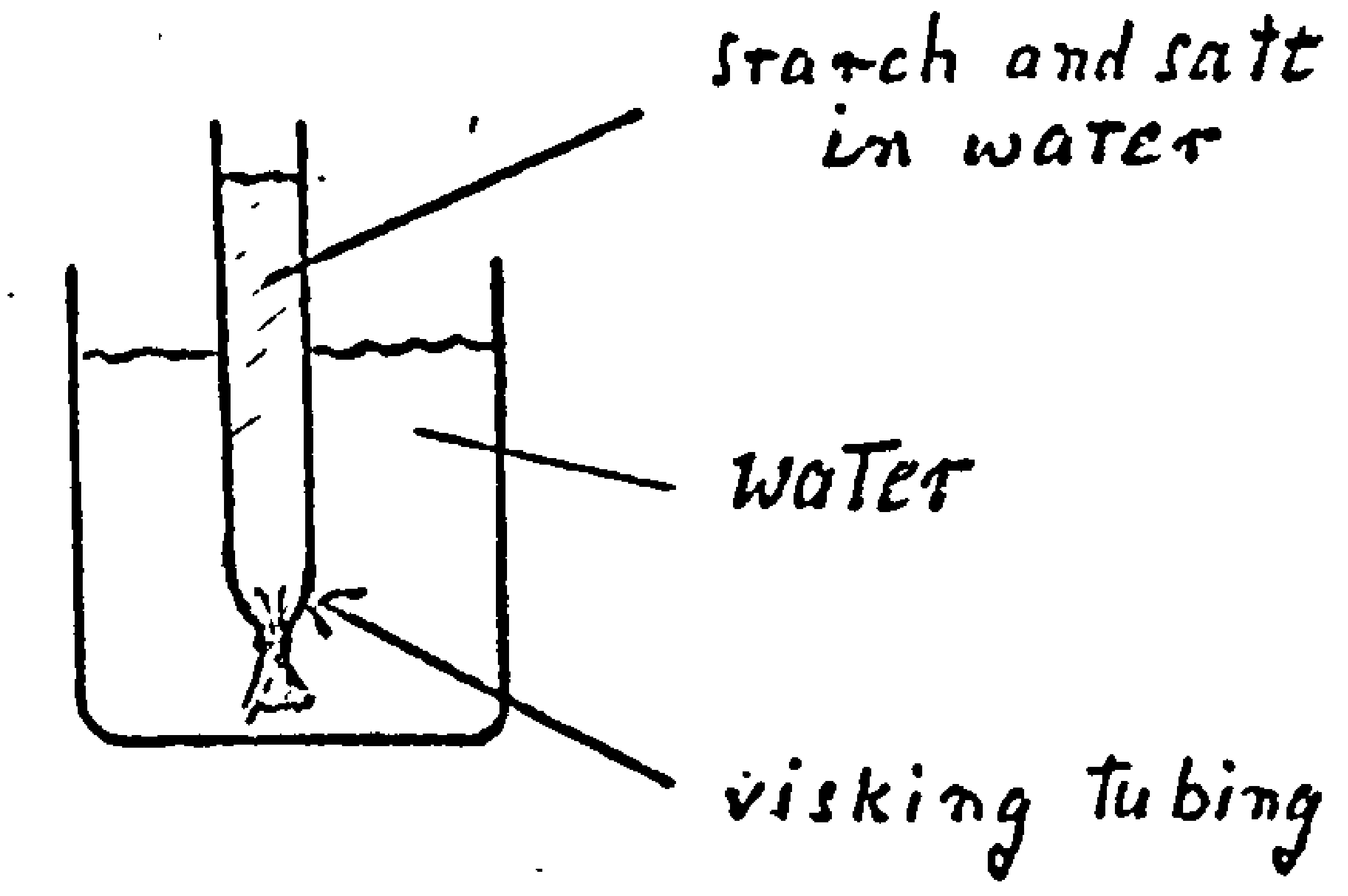


Fig. 8.2

What happens with time?

Water molecules diffuse into the dialyser for the reasons already given under the heading of osmosis.

But ions also diffuse out of the dialyser.

This is in keeping with their becoming more mixed and therefore of lower free energy or, if you prefer, more spread out and therefore of higher entropy value.

In practice, the dialyser is placed in gently flowing water; an equilibrium situation is avoided. The dialysis is complete when no salt remains in the dialyser.

Thus a complete washing of the colloid can be achieved given time. Such is the case with the washing of blood in a 'kidney machine'.

Distribution of a solute between two solvents. When a substance is added to two immiscible liquids, in each of which it can dissolve, and shaken with these, the added substance will dissolve such that the ratio

$$\frac{\text{Concentration of solute in first solvent}}{\text{Concentration of solute in second solvent}}$$

is constant at a particular temperature. (There are some other qualifications which need not concern us.)

Note that it is a ratio of concentrations. If therefore the volume of one solvent were increased in a particular experiment, that solvent would certainly dissolve more of the solute but only in so far as the ratio of of the final concentrations was still the same, provided the temperature was unchanged.

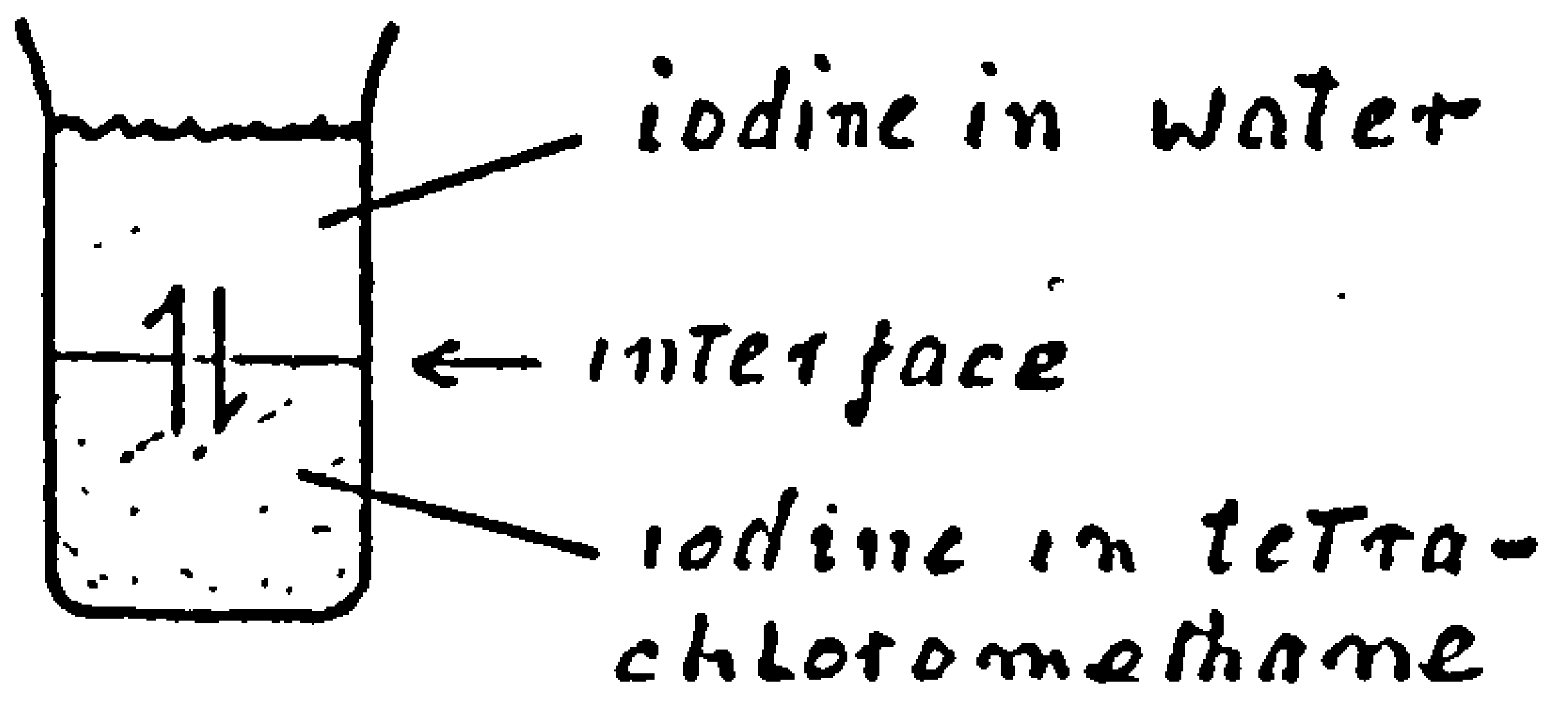


Fig. 8.3

It turns out that the distribution of iodine in water and tetrachloromethane is such that

$$\frac{\text{Concentration of } I_2 \text{ in } CCl_4}{\text{Concentration of } I_2 \text{ in } H_2O} \doteqdot \frac{86}{1}$$

If more water were used, more of the iodine would dissolve in the water but only until the concentration ratio of 86/1 was restored.

The precise value of this ratio is determined by that equilibrium mixture which, for the substances involved, has a minimum free energy and a maximum entropy value.

Concentration cell. A concentration cell is a cell whose driving force derives from the spontaneous diffusion of a substance from a region of high concentration to one of low concentration.

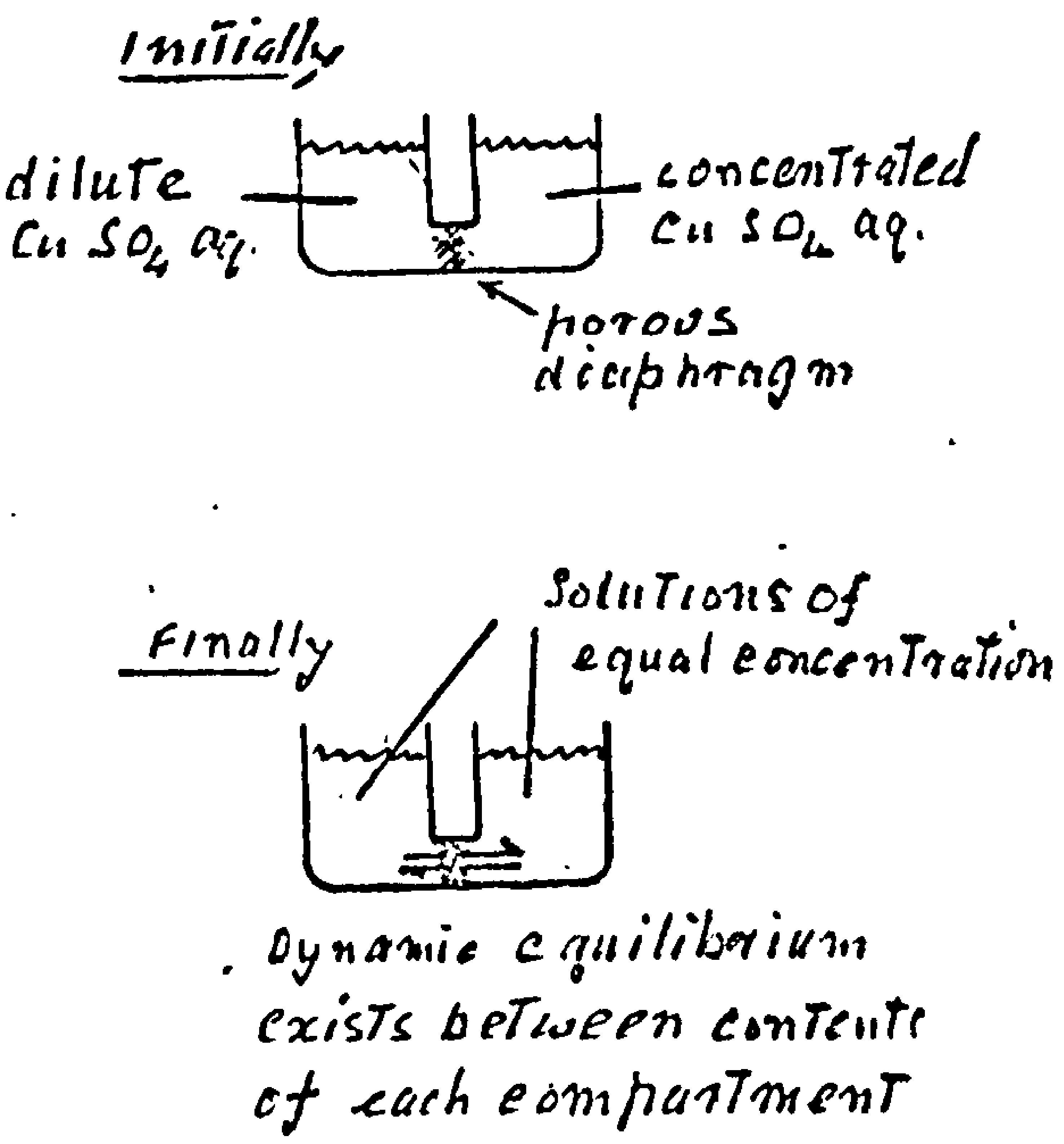


Fig. 8.4

Suppose we have two solutions of copper sulphate, one more concentrated than the other, separated by a porous diaphragm.

Diffusion of solute will occur in each direction through the diaphragm; diffusion of solvent will occur in each direction through the diaphragm.

But two predominant net processes will occur, each of which entails a decrease in free energy and an increase in entropy value

i) Water will diffuse from the dilute copper sulphate solution (in which the water is 'more concentrated') into the concentrate copper sulphate solution, so diluting it.

The free energy and entropy argument supporting this net flow has already been given: a mole of water making such a move loses free energy (it becomes more mixed) and increases its entropy value (it becomes more spread out).

ii) Copper ions and sulphate ions will diffuse from the concentrated solution to the dilute solution, so increasing its concentration. In so doing, one mole of solute becomes more mixed and so suffers a decrease in free energy, and becomes more spread out and so acquires a higher entropy value.

Remember that throughout all these diffusional change, free energy converts to entropy energy.

The end result of these two net processes is the production of an equilibrium situation of minimum free energy and maximum entropy value, which is achieved when the solutions on each side of the diaphragm are the same, i.e. have the same concentration.

Note that two-way diffusion will still be occurring but that there is no change in composition with time.

A concentration cell can be manipulated to produce electrical current.

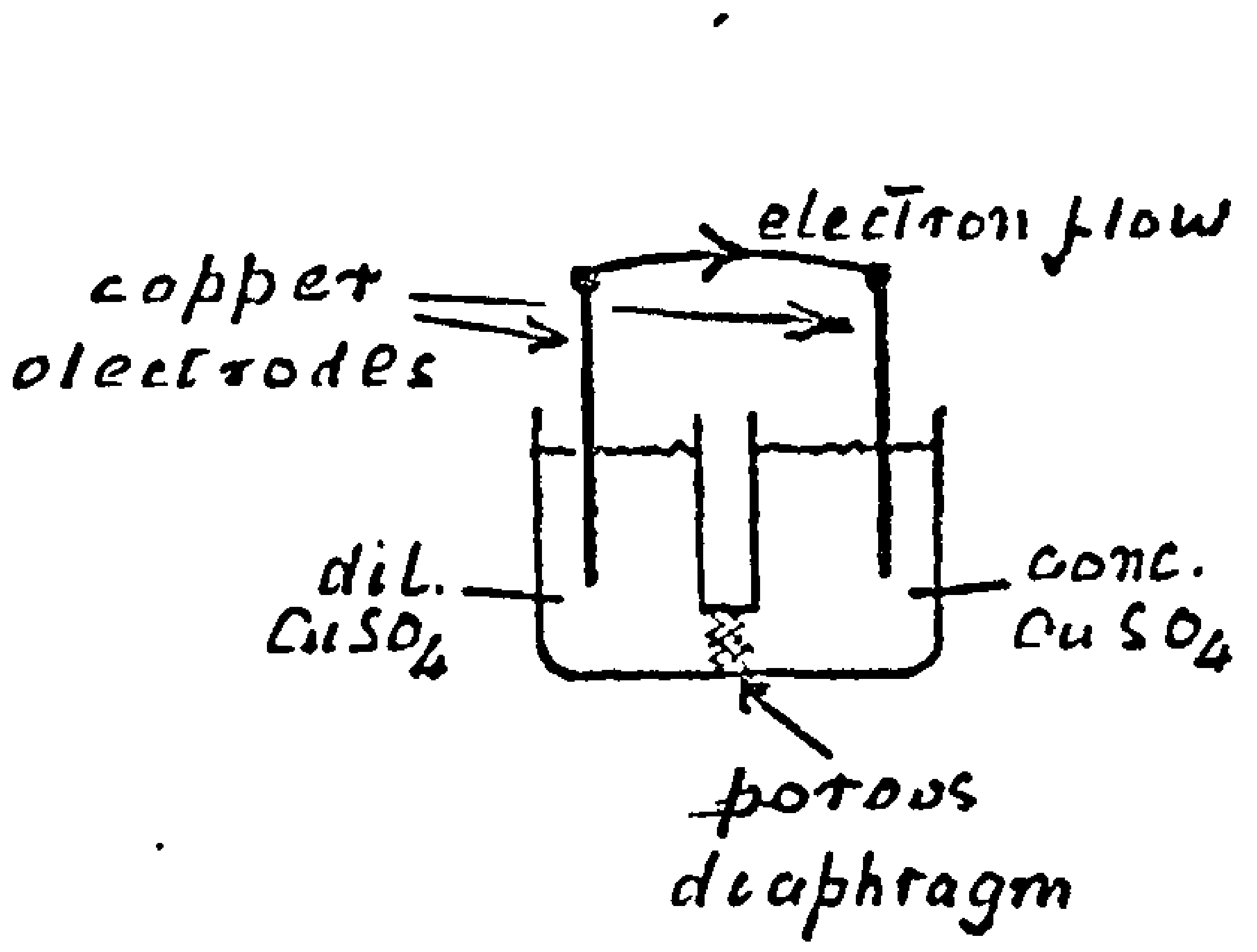


Fig. 8.5

The argument is the same as before.

That which occurs is consistent with a decrease in free energy and an increase in entropy value.

Thus the electrode reactions to occur are those which permit the ultimate formation of uniform solution concentratio throughout the entire cell since these electrode reactions of necessity must be accompanied by a decrease in free energy and an increase in entropy value.

In a cell, therefore, consisting of copper sulphate solutions of differing concentrations and copper electrodes:

Electrode reaction on 'dilute side' is $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e$

Copper is lost from the surface of the electrode as copper ion in solution, increasing the concentration of copper ion in solution.

Electrons pass over onto the electrode on the 'concentrated side'.

Electrode reaction on the 'concentrated side' is $Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$

Copper ion is removed from solution and deposited as copper on the electrode, decreasing the concentration of copper ion in solution.

Current will flow until the concentration of copper ion in each half cell is the same.

No mention of sulphate ion has been made in this discussion. It is not technically possible to construct a circuit which will deal with sulphate ion in the way that the above circuit has coped with copper ion. Such a circuit would require a 'sulphate' electrode. The sulphate ion, therefore, are left to diffuse through the porous plug in their own time in the familiar way.

Ion exchange. Ion exchange is a process which operates at the interface between a solution and some types of solid whereby ions in solution and ions attached to the solid exchange places.

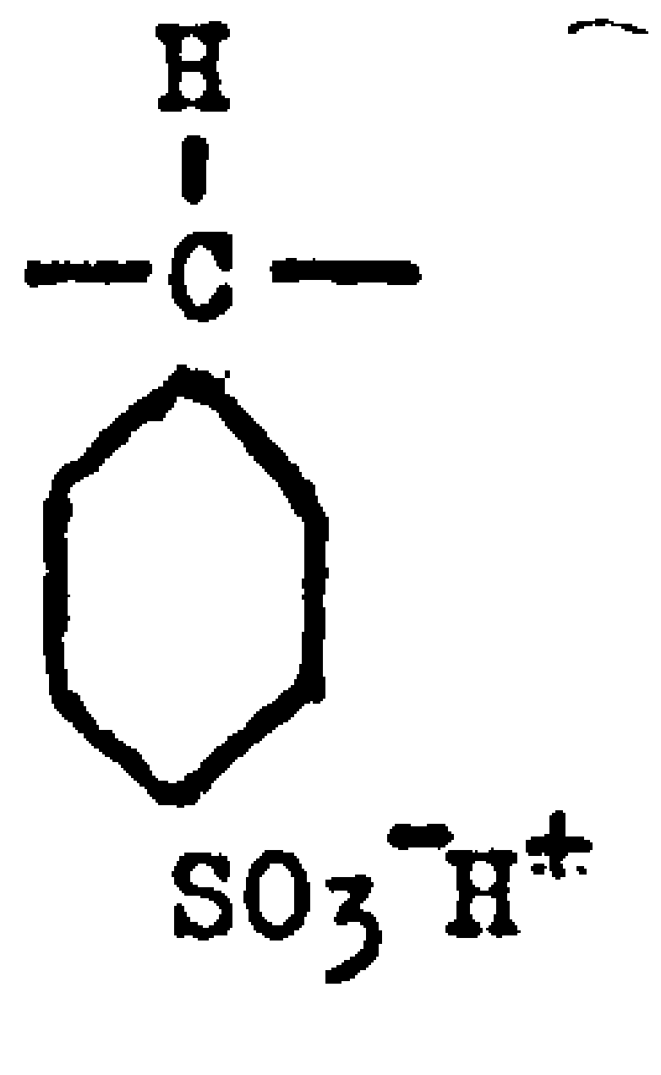
The typical ion exchange material is porous with a three-dimensional structure. The apparent volume of the material gives little indication of the actual extent of internal surface area; the material is honeycombed with tunnels and cavities through which aqueous solutions can percolate.

The traditional ion exchange material belongs to a group of inorganic substances called the zeolites, which are complex metal alumino-silicates. The permutites used to soften water are sodium zeolites. These latter exchange - under the correct operating conditions - one $Ca^{2+}$ (from water to permutite) for two $Na^+$ (from permutite to water); the removal of $Ca^{2+}$ from the water renders the water soft.

The sodium permutite is eventually converted to calcium permutite and is no longer useful for softening water. Sodium permutite is regenerated by passing concentrated brine through the permutite.

A variety of inorganic and organic materials are now used. Some are natural, some synthetic. Some are cationic exchangers, some anionic. The former exchange cations, such as does sodium permutite. The latter exchange anions.

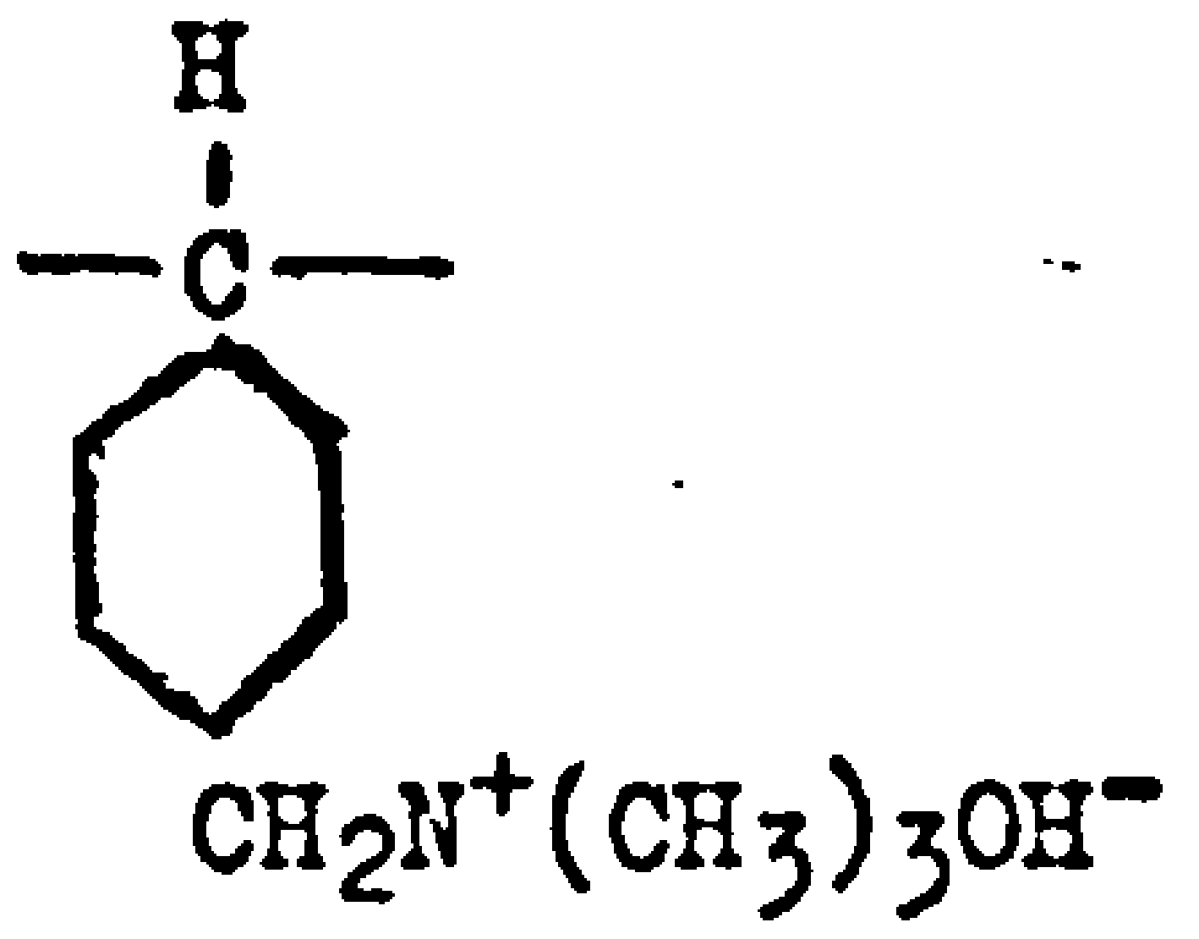
Cation exchange



One synthetic cationic exchange resin is based on polystyrene polymer.

Hydrogen cations can be lost to solution by the resin in exchange for an equivalent number of other cations.

Anion exchange



A synthetic anionic exchange resin is also based on polystyrene polymer.

Hydroxyl anions can be lost to solution by the resin in exchange for an equivalent number of other anions.

When sodium chloride solution is put through two such resins in series,
a) sodium ions are replaced by hydrogen ions in the cationic exchanger,
b) chlorine ions are replaced by hydroxyl ions in the anionic exchanger.

Since hydrogen ions and hydroxyl ions react to from water, the issuing liquid is pure water; it is called 'de-ionised water', and is commonly used instead of distilled water.

Why does ion exchange occur?

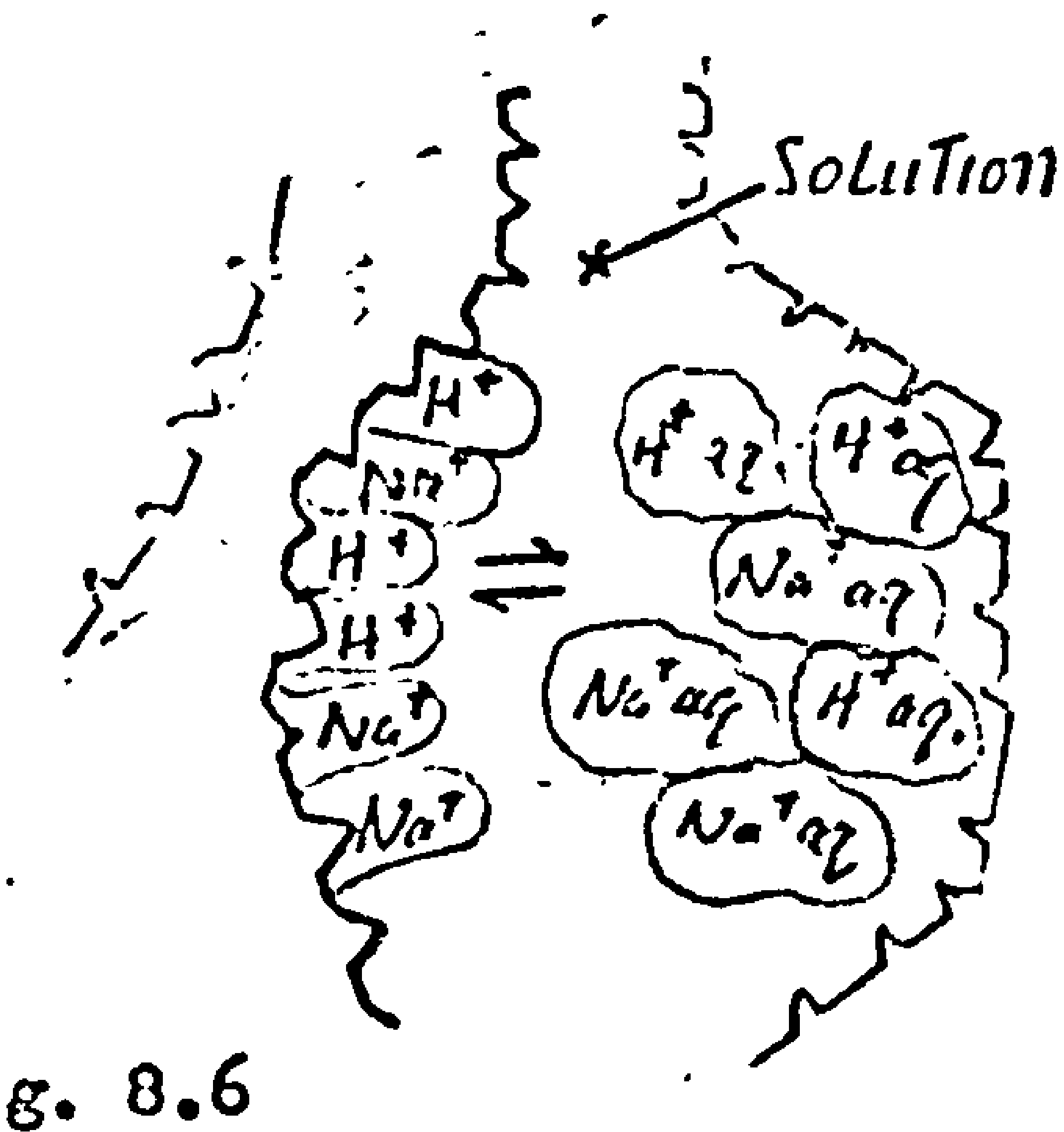


Fig. 8.6

The process is diffusional.

Consider the case of the exchange of hydrogen ion from the resin for sodium ion in solution.

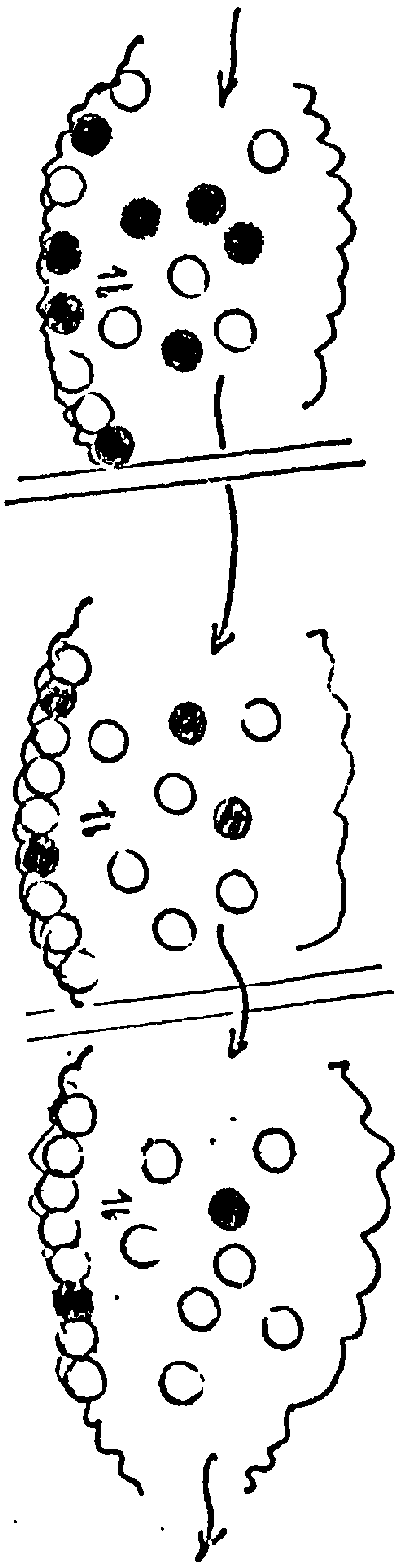
Imagine a cavity or channel within which exchange is occurring. Consider this in two parts.

i) One part consists of hydrogen ions <u>only</u> attached to the resin but at the same time protruding into the aqueous phase.

ii) The other part consists of sodium ions <u>only</u> in the aqueous phase.

Mixing will produce, ultimately, an equilibrium 'mix' of minimum free energy and maximum entropy value.

Thus the efficient functioning of an ion exchange column requires that it be used <u>slowly</u> to allow the two parts to come as close to equilibrium as possible. This allows maximum exchange to occur.



Further, as the solution progresses down the column its equilibrium concentration of sodium ion will diminish, and if the column is <u>long</u> enough the liquid emerging should contain practically no sodium ion.

Fig 8.7

Chromatography. The same general comments apply to chromatography as apply to the distribution of a solute between two immiscible solvents. The difference is that in chromatography two or more solutes are involved (these are to be separated) and one of the two solvents moves (the mobiles phase) while the other solvent does not (the stationary phase).

Chronatography is a process whereby a mixture of solutes is separated as a result of the different way each solute partitions itself between a mobile phase and a stationary phase.

Consider the case of the separation of two solutes by means of a liquid stationary phase and a liquid mobile phase.

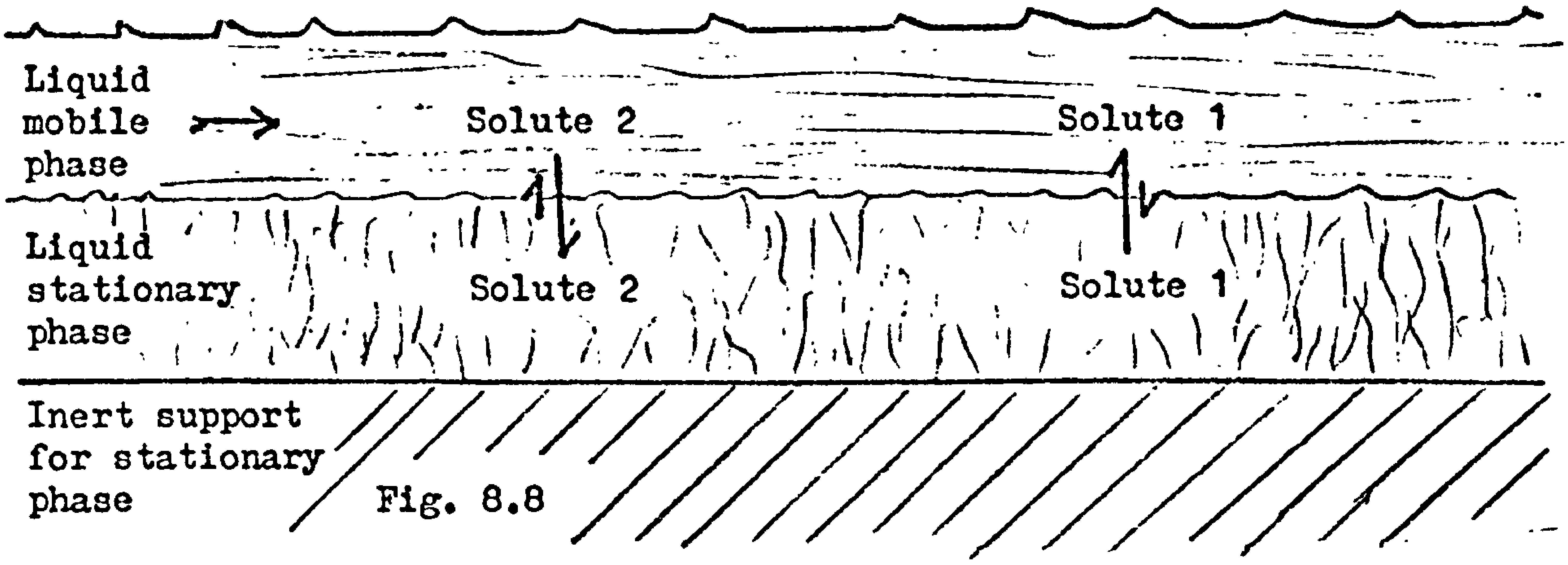


Fig. 8.8

The stationary phase and mobile phase may both be liquids; the stationary phase consists of a liquid solvent immobilised by adsorption on an otherwise inert solid base.

The stationary phase may be a liquid and the mobile phase a gas.

The stationary phase may be a solid and the mobile phase a liquid or a gas.

Each solute will partition itself between the two solvents such that the final equilibrium mix has minimum free energy and maximum entropy value for that particular solute.

Suppose solute 1 is concentrated almost entirely in the mobile phase. It will travel through the chromatographic column at something just less than the speed of the mobile phase.

Suppose solute 2 is concentrated almost entirely in the stationary phase. Its rate of progress through the column will be exceedingly slow.

Thus, two solutes which enter the column at the same time - in the form of a small injected sample - leave at different times, and so a separation is effected.

The movement of a solute through the column under a particular set of conditions is characterised by the retardation factor, Rf, which is defined as

$$Rf = \frac{\text{distance travelled by solute}}{\text{distance travelled by solvent}} \quad \text{in same time.}$$

In the extreme example quoted above, Rf for solute 1 is almost unity, while Rf for solute 2 is almost zero. In practice, the difference between the retardation factors is much less.

Since the functioning of the column requires the establishment of an equilibrium between the two phase solutions of each particular solute, then the column must be operated slowly. If it is operated too quickly, both solutes will simply emerge together.

On the other hand, if the process is operated too slowly, there is risk of sideways diffusion of each solute, and the emerging bands of solute become broad and overlapped.

There is, therefore, an optimum rate of flow.

Summary of mixing phenomena. In each of the mixing phenomena just discussed - diffusion, osmosis, dialysis, distribution, concentration cell, ion exchange, and chromatography - the decrease in free energy and (simultaneous) increase in entropy have been offered to explain the process. The argument in each case, with some variation, has been something like the following.

The free energy of the mix is less than the sum of the free energies of the separate parts; the decrease in free energy on mixing is accounted for by an equivalent increase in entropy energy of the mix compared with the initial separate parts; the entropy value of the mix is greater than the sum of the entropy values of the separate parts before mixing.

Decrease in free energy in the system has come to be our means of deciding that a change is spontaneous. Increase in total entropy value is equally valid, and since each of the mixing phenomena occurs without involving the surroundings, then the increase in the system's entropy value is, in this case, also the only and total increase in entropy value. Consequently, increase in entropy value of the diffusing system was offered as an alternative justification for change.

This argument makes the assumption that the decrease in free energy is accounted for by an equal increase in entropy energy:

$AH = 0 \qquad\qquad AG = -TAS_{sys}$

This is not strictly accurate. The increase in entropy energy may be less than the decrease in free energy, in which case some heat is evolved. AH therefore acquires a small negative value. Or the increase in entropy energy may be more than the decrease in free energy, in which case some heat is absorbed. AH therefore acquires a small positive value.

I should now point out that I have not offered, at any time, here or elsewhere, the enthalpy change as a 'controlling factor' in change. I have invariably relegated it to the role of a 'consequence' rather than a 'cause'.

The controlling factor, kinetics allowing, is observed to be

a decrease in the free energy
of the system,

or alternatively, an increase in the total entropy value
of the system-cum-surroundings.

and the underlying reason for these is the force of disorder.

Study Unit 8 What you should know.

You should
1. know that the controlling factor in a reaction is that the free energy change be negative.
2. know why diffusion occurs.
3. be able to explain why a minority of spontaneous reactions are endothermic
4. understnad the occurrence of a variety of phenomena.

Question 1 When anydrous calcium chloride is left exposed to air, moisture is absorbed from the air and a solution of calcium chloride is formed (deliquescence). Comment:

| | |
|---|---|
| 1 The mixture of calcium chloride and water has a lower free energy than the calcium chloride and water vapour separately. | 2 The mixture of calcium chloride and water has a higher entropy value than the calcium chloride and water vapour separately. |
| 3 Heat is evolved during the deliquescence of calcium chloride since the decrease in free energy is only partly consumed by the increase in entropy energy. This latter is held back a bit due to the ordering influence of the ions. | |

Question 2 A concentration cell eventually stops working because

| | |
|---|---|
| 1 the solutions on each side of the porous partition have acquired the same concentration. | 2 the difference between the actual electrode potentials of each half cell is zero; that is, each half cell is exerting the same pull on electrons. |
| 3 the e.m.f. of the cell is zero | 4 the free energy change accompany- further diffusion is no longer negative; that is, further diffusion cannot occur since AG would be zero (or worse still, positive.) |

Question 1

| | |
|---|---|
| Response 1 | This response is correct, a mole for mole basis is implied. |
| Response 2 | This response is correct. The calcium chloride and enclosed air may be regarded as an isolated system. The two components of this isolated system move to a state of equilibrium of maximum entropy value (and minimum free energy) when the anhydrous calcium chloride has become a solution in equilibrium with the residual moisture vapour in the enclosed air sample.<br>Note that if the enclosed air sample were initially perfectly dry, and a solution of calcium chloride were placed in it, the calcium chloride solution would lose moisture to the air .... until the same final equilibrium state was attained. |
| Response 3 | This response is correct. That heat is evolved by the hydration and solvation of calcium chloride is taken as evidence that the decrease in free energy - which must be negative - is not fully accounted for by the increase in entropy energy. |

Question 2

| | |
|---|---|
| Response 1 | This response is correct. |
| Response 2 | When a cell is constructed from electrodes of the same material and from identical ionic solutes, the only difference being one of relative concentration, then the resultant e.m.f. of the cell is due to the latter. Once the concentrations have become equal, the electron 'pull' exerted by each elctrode of the cell will be equal, and so there will be no net flow of current. The e.m.f. of the cell will be zero. |
| Response 3 | This response is correct. See Response 2. |
| Response 4 | This response is correct. The free energy drive exists, as it were, to produce a final mixture of lowest free energy. Prior to the arrival at this state of minimum free energy, the change in free energy is negative. Once the minimum free energy state is reached, further free energy change would be zero .... and then positive. |

Additional note on colloids

The following table categorises some of the distinctive features of true solutions, true suspensions, and the 'in-between' colloids. Colloids may be referred to as 'sols', in the sense that they are not quite solutions, or as colloidal dispersions.

Table 8.1 Comparison of solutions, colloids and suspensions.

| | Solutions | Colloids | Suspensions |
|---|---|---|---|
| Particles | Individual atoms, molecules or ions. | Groups of atoms, molecules or ions, or large molecules. | Large groups of atoms, molecules or ions. |
| Size range | Less than 1 nm approximately. | Between 1 nm and 1 μm approximately. | Greater than 1 μm approximately. |
| Homogeneous or heterogeneous | Homogeneous | Heterogeneous | Heterogeneous |
| | | These may look homogeneous but closer inspection will show up two distinct phases; the liquid phase and the 'suspended' phase. | |

Study Unit 9

## EQUILIBRIUM & FREE ENERGY

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PURPOSE

1. To introduce $AG^{o}$.
2. To consider the various free energy changes during a chemical reaction.

---

PRESENTATION

Introduction. This unit sets out to show how changes in actual free energy during the course of a chemical reaction are the result of the standard free energy change and the free energy of mixing acting together.

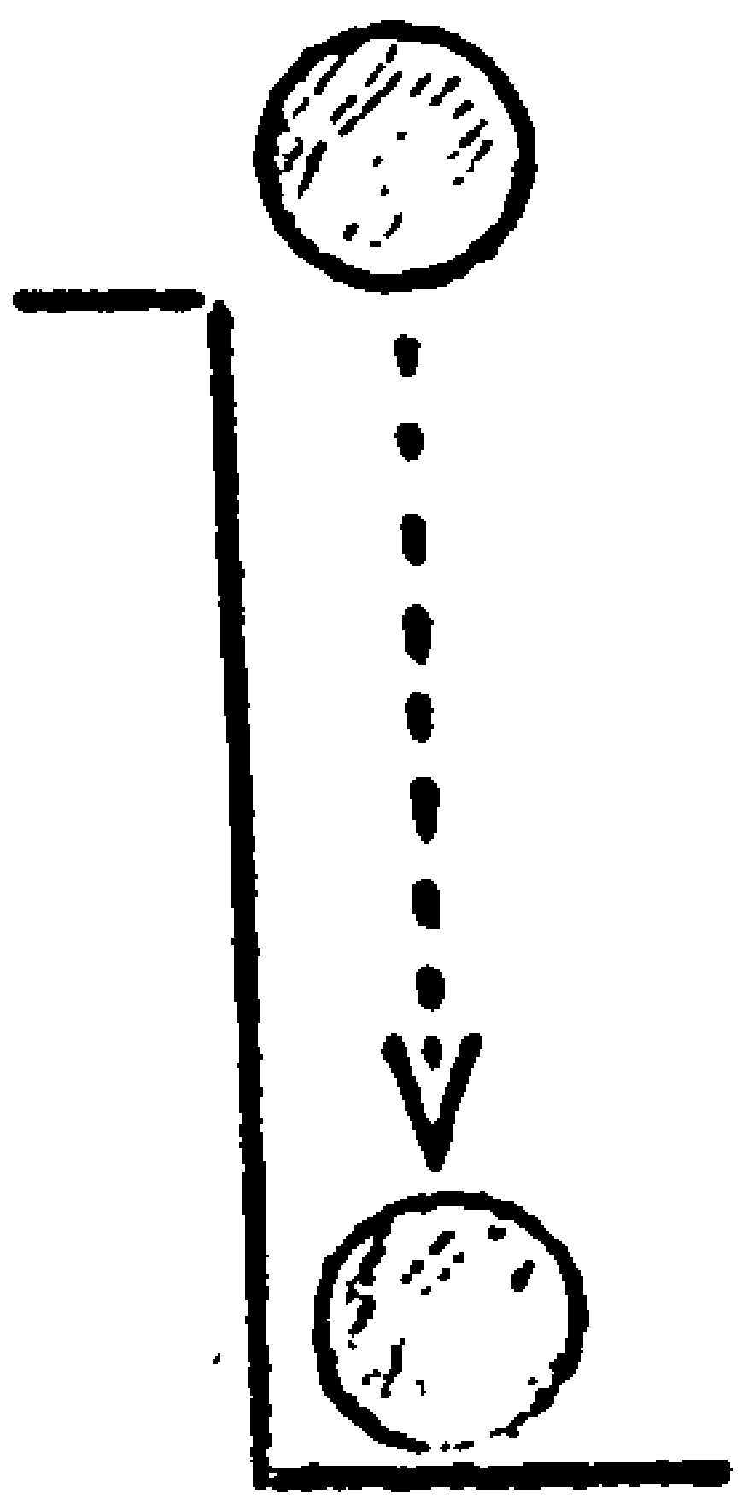
### Equilibrium

In terms of reaction spontaneity, previous units may be summarised as follows.

| REACTION | $AG_{sys}$ | $AS_{sys}$ and $AS_{surr}$ | $AS_{tot}$ |
|---|---|---|---|
| Spontaneous | -ve | Any values provided the sum is +ve. | +ve |
| Equilibrium | Zero | Equal and opposite | Zero |
| Non-spontaneous | +ve | Any values provided the sum is -ve. | -ve |

A closer look at $AG^{o}$ and the other AGs Revert now to the original analogy drawn with a falling weight.

This may represent pure reactant under standard conditions (0% product)



The weight in this position has more 'free energy' than .....

This may represent pure product under standard conditions (100% product)

it has in this position.

The difference between these two extremes in terms of a chemical reaction (albeit an artificial one!) is $AG^{o}$.

Fig. 9.1

The analogy to be drawn with a chemical change is:

$$\text{Pure reactants of higher free energy} \xrightarrow[\text{to}]{\text{changes}} \text{pure products of lower free energy}$$

.... to which $AG^{o}$ applies only if <u>1 mole</u> of <u>pure</u> product is formed from <u>pure</u> reactant at <u>1 atmosphere</u>. The standard free energy change does not insist on a particular temperature; standard free energy changes are quoted at any temperature. The values quoted in data books are quoted at 298 K (usually).

The requirement of purity eliminates complications due to mixing, which latter causes a decrease in free energy in its own right irrespective of anything else.

Here is an example. The standard free energy of formation of $NO_2$ has been determined and is $AG^{o} = 51.8$ kJ $mol^{-1}$. This is the standard free energy change for the reaction

$$\tfrac{1}{2}N_2 \quad + \quad O_2 \longrightarrow NO_2$$

Check that this value is correct by reference to a suitable data book.

If the elementary substances like nitrogen and oxygen are allocated zero standard free energies of formation, as is done with enthalpies, because the absolute values are not determinable, then the standard free energies of formation are:

| | $\tfrac{1}{2}N_2$ | + | $O_2 \longrightarrow$ | $NO_2$ |
|---|---|---|---|---|
| | $AG^{o}=$ zero | | $AG^{o}=$ zero | $AG^{o}= +51.8$ kJ |

The technique for dealing with free energy changes is the same as that you have used to deal with enthalpy changes. It is possible to deduce the standard free energy change for a reaction which cannot be carried out, by suitable addition, doubling, halving, and so on, of equations and their associated standard free energy changes for reactions which can be carried out. This technique will be known to you. It is no more difficult with free energies than it is with enthalpies, but it does require a lot of practice. Note in passing that the enthalpy changes you have worked with in Form V have generally been standard enthalpy changes though this point may not have been mentioned.

Problem 9.1

What is the standard free energy change for the reaction

| | | | | |
|---|---|---|---|---|
| | $2NO_2$ | $\longrightarrow$ | $N_2O_4$ ? | (completely) |
| $AG^{o}_{f}$ from tables | $2 \times 51.8$ | | 98.3 | kJ |

Therefore $AG^{o} = 98.3 - 103.6$ J
$= -5.3$ kJ $mol^{-1}$ $N_2O_4$

The standard free energy change for the reverse reaction

$$N_2O_4 \longrightarrow 2NO_2 \quad \text{(completely)}$$

is $AG^{o} = +5.2$ kJ per 2 mole $NO_2$, and is therefore $AG^{o} = +2.65$ kJ $mol^{-1}$.

The second reaction occurs spontaneously "despite its positive $AG^{o}$". How is the spontaneous occurrence of the second reaction reconciled with the positive standard free energy change.

The answer has to do with the free energy of mixing which is superimposed on the standard free energy change.

In order to extend the argument to include this effect, the physical analogy may be drawn obliquely instead of vertically.

For a reaction for which $AG^{o}$ is negative:

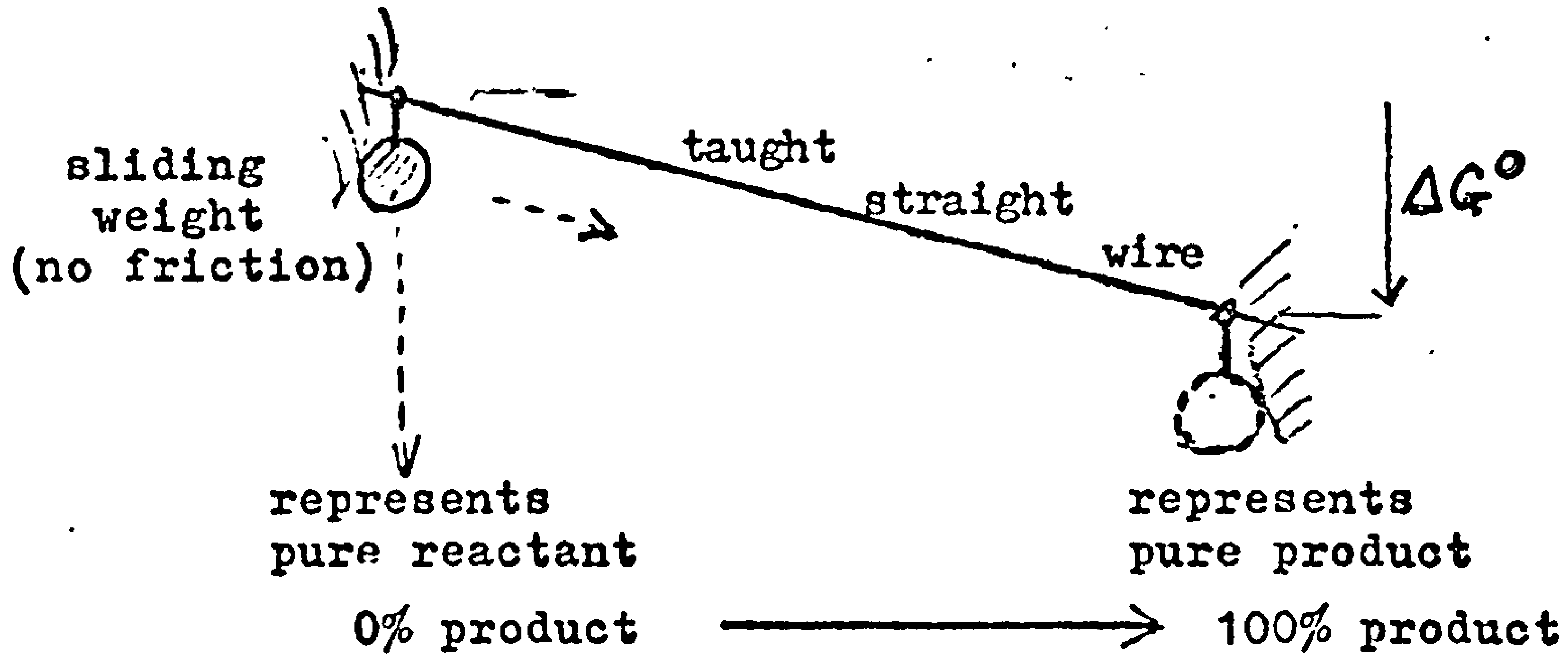


Fig. 9.2

Imagine the weight to be in process of sliding down the wire. Its progress down the wire represents a decrease in the amount of reactant and an increase in the amount of product, from the one extreme to the other.

From the 'standard' point of view, the free energy of an amount of isolated reactant is consistently greater than the free energy of the amount of isolated product it can change into. If the standard free energy change were the only free energy change, then the reaction would go to completion.

This is a strict, non-practicable argument, for it excludes additional effects due to mixing of reactant and product which must operate during the real occurrence of the reaction. The standard change assumes the product to be produced in isolation from a reactant held in isolation.

The relationship between the standard enthalpy change, the standard free energy change and the standard entropy energy change is given by the standard form of the Gibbs-Helmholtz equation:

$$AH^{o} = AG^{o} + TAS^{o}$$

For conditions other than standard, for example, for the formation of a fraction of a mole of product, then the non-standard form of the equation is used

$$AH = AG + TAS$$

## Free energy of mixing superimposed on the standard free energy change

The free energy of mixing is always negative, and is likely to be most marked at about the half way stage in a chemical reaction. At either extreme - pure separate reactant or reactants before and pure separate product or products after - the free energy of mixing will be absent.

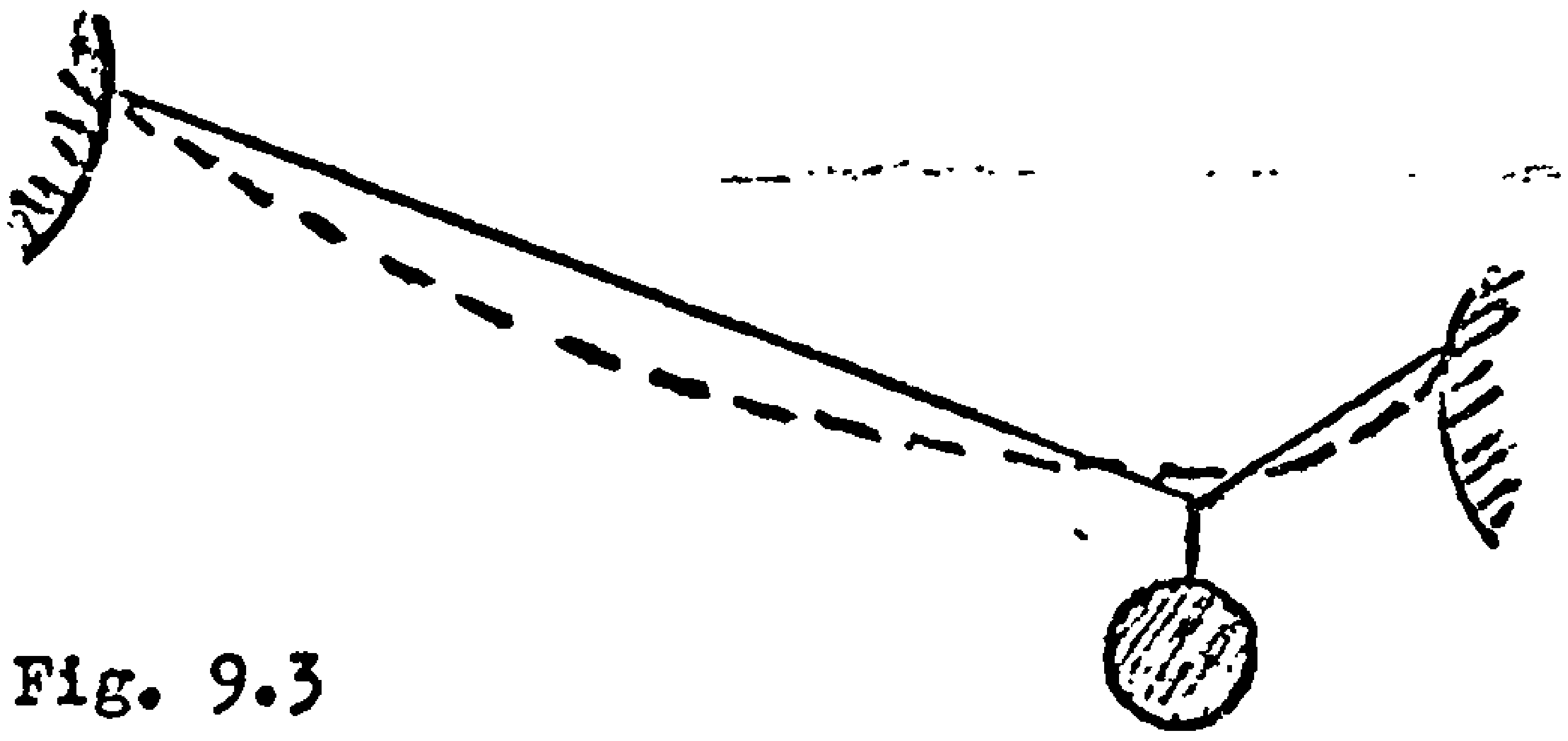


Fig. 9.3

Thus the actual free energy profile for a reaction for which $AG^o$ is negative is of the same general form as that obtained by allowing a movable weight to find its rest position under the influence of gravity on an inclined elastic band.

The actual free energy profile is obtained by combining the standard free energy change and the mixing free energy change.

The synthesis of ammonia. The effect of the free energy of mixing on the synthesis of ammonia will now be looked at in particular.

The reaction: $\frac{1}{2}N_2 + 1\frac{1}{2}H_2 = NH_3$

Standard thermodynamic data:

$AH^o = -46$ kJ mol$^{-1}$

$AG^o = -16.5$ kJ mol$^{-1}$

$TAS^o = -29.5$ kJ mol$^{-1}$ all at 298 K

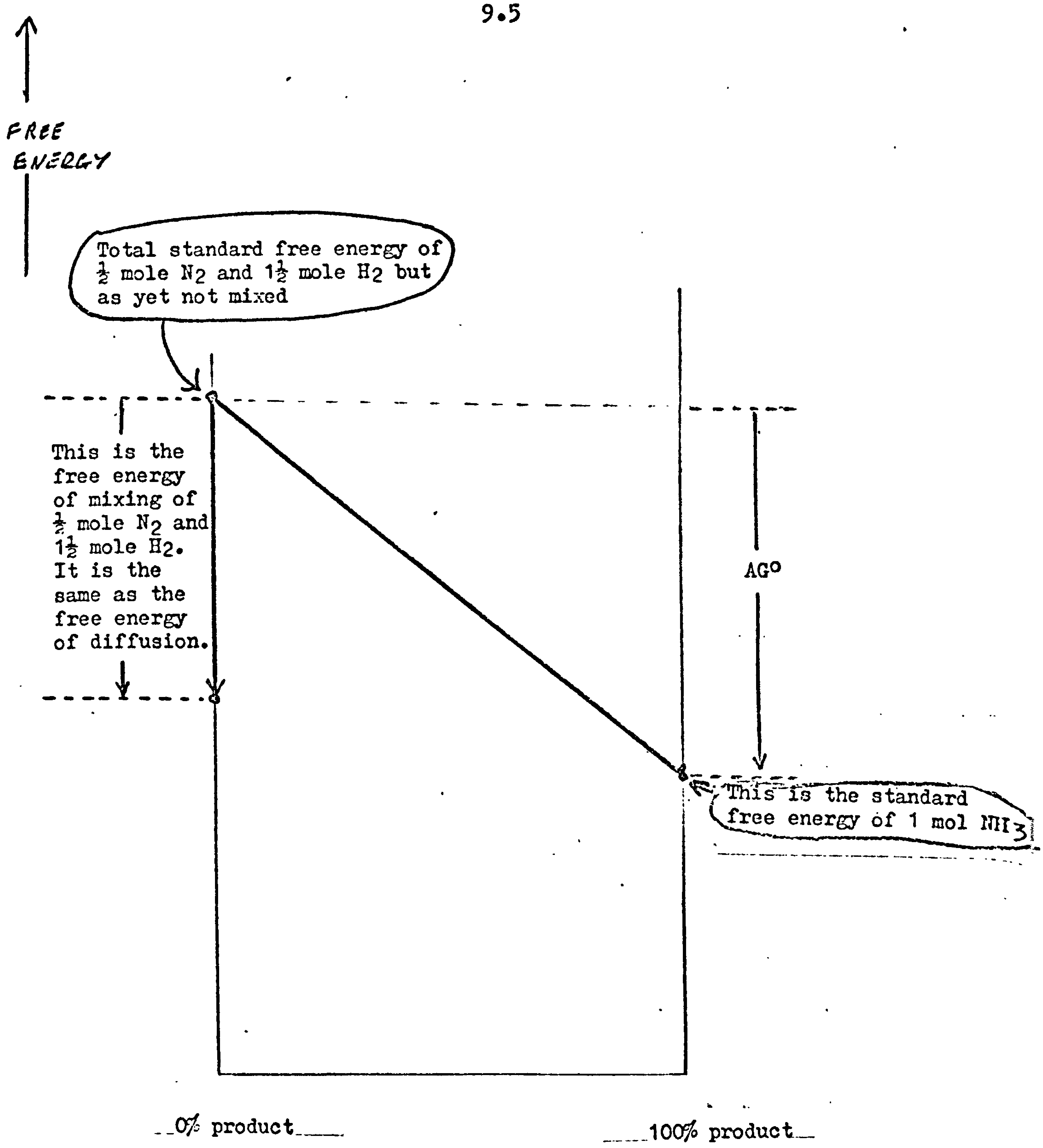
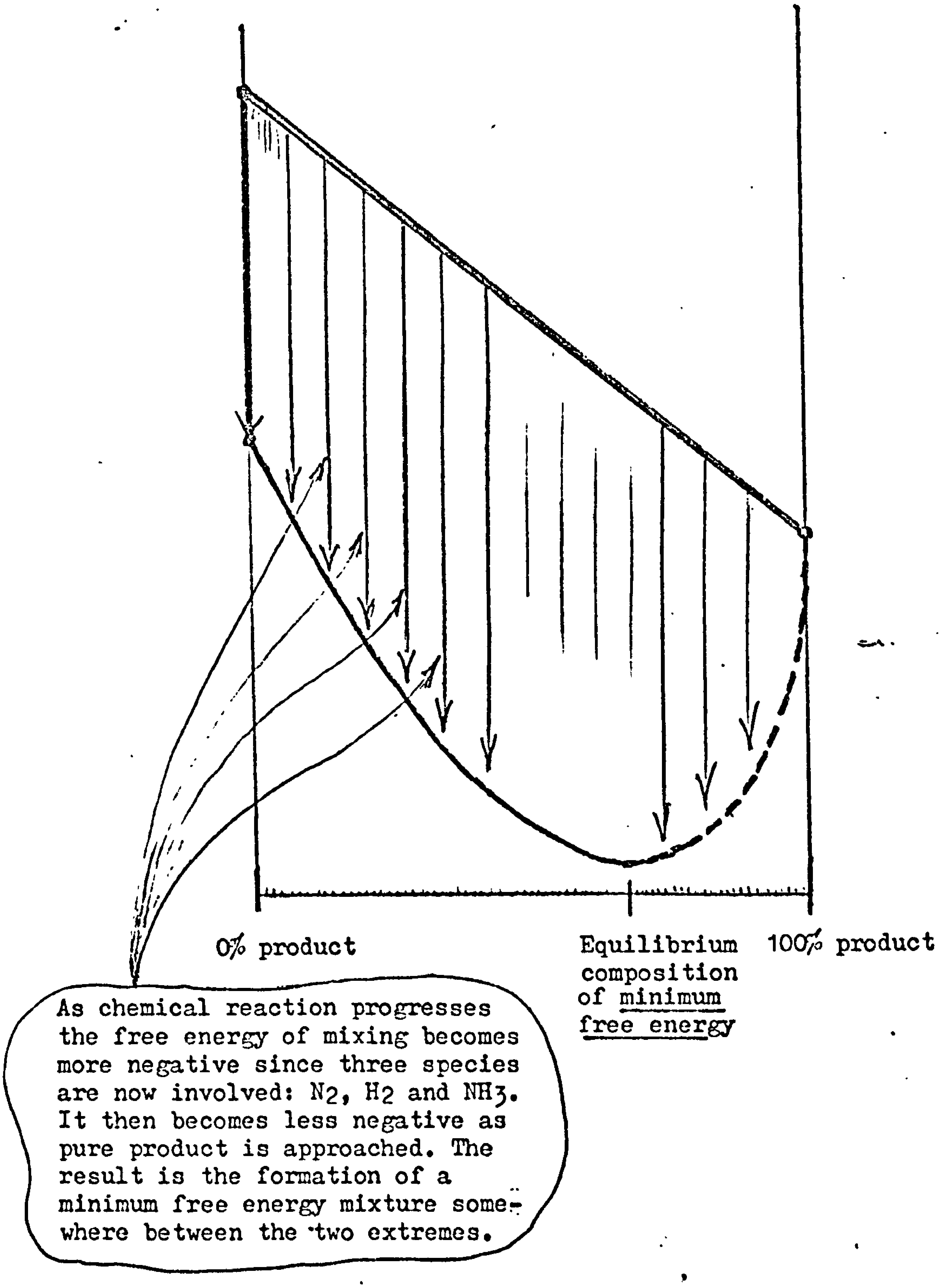

FREE ENERGY
Total standard free energy of ½ mole $N_2$ and 1½ mole $H_2$ but as yet not mixed
This is the free energy of mixing of ½ mole $N_2$ and 1½ mole $H_2$. It is the same as the free energy of diffusion.
ΔG°
This is the standard free energy of 1 mol $NH_3$
0% product
100% product

Fig. 9.4



As chemical reaction progresses the free energy of mixing becomes more negative since three species are now involved: $N_2$, $H_2$ and $NH_3$. It then becomes less negative as pure product is approached. The result is the formation of a minimum free energy mixture somewhere between the two extremes.

Fig. 9.5

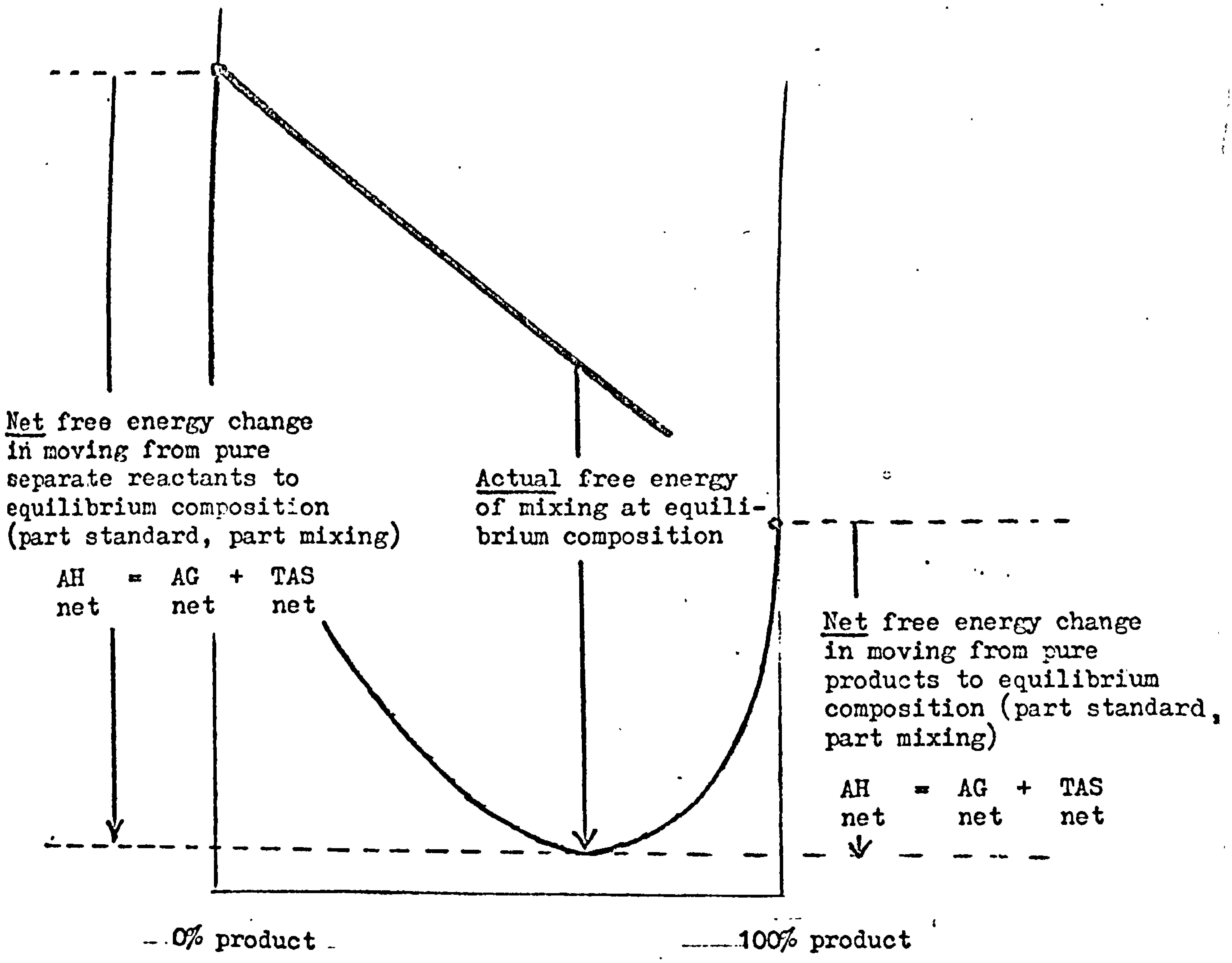

Net free energy change in moving from pure separate reactants to equilibrium composition (part standard, part mixing)
AH = AG + TAS
net net net
Actual free energy of mixing at equilibrium composition
Net free energy change in moving from pure products to equilibrium composition (part standard, part mixing)
AH = AG + TAS
net net net
0% product
100% product

Fig. 9.6

The free energy of the reaction mixture has a minimum value at a particular composition. At this composition

| | | |
|---|---|---|
| the free energy<br>per mole of reactant<br>in the mixture<br>of reactant and product | = | the free energy<br>of an equivalent amount of product<br>in the same mixture<br>of reactant and product |

The difference between the free energies of equivalent amounts of reactant and product in the mixture at this composition is zero; AG = 0. There is, therefore, no net change in composition with time.

Thus, a mixture in a state of equilibrium possesses minimum free energy.

At any composition to the left of the equilibrium composition, the conversion of reactant to equivalent amount of product entails a negative free energy change, and so it occurs (kinetics allowing). When eventually such conversion is attended by no change in free energy, AG = 0, then no further net change occurs ..... the mixture has reached a state of minimum free energy ..... equilibrium exists ...and the composition of the mixture is the equilibrium composition.

This argument is equally valid for compositions to the right of the equilibrium composition. These will adjust so as to arrive at the same equilibrium composition (kinetics allowing).

Thus AG at any composition other than the equilibrium composition is negative; at the equilibrium composition it is zero.

However, molecules are in continous motion. Random collisions - if energetic enough and correctly orientated - will lead to reaction. But any tendency for the reaction mixture to drift, in either direction, from the equilibrium composition will be counteracted by the free energy drive back to the equilibrium composition. Suppose, for example, that by chance collision a slightly higher percentage of ammonia than the equilibrium composition calls for is created. This being so, the free energy of the ammonia in the mixture will be slightly greater than that of the nitrogen/hydrogen in the mixture. Consequently the composition will return to that required by the minimum free energy.

Thus, the essential features of an equilibrium system are

1. continous reaction in which the forward and backward reactions are equal and opposite, a dynamic picture,
2. fixed unchanging composition apart from minor local fluctuations, a static picture.

Note that an equilibrium system can only exist in a closed vessel. Note, also, because of the dynamic nature of equilibrium, that the same equilibrium can be established either from reactants or from products.

'The equilibrium conposition cannot escape from the free energy trap.'

Study Unit 9 What you should know.

You should
1. know that most of the enthalpy changes, free energy changes, entropy changes and entropy energy changes you have worked with a standard ones.
2. understand what is implied by the standard change.
3. realise the importance of the free energy of mixing in determining the composition of the equilibrium mixture.
4. understand the significance of $\Delta G = 0$.
5 be aware of some of the characteristics of the equilbrium sytem.

---

Question 1 In order to answer this question you will require to refer to a chemistry data book. The particular answers selected here have been taken from Chemistry Data Book, Stark & Wallace, S.I. Edition 1970. But note, if using this data book, that the column headings $AG^{o}$ and $AH^{o}$ on page 38 should be changed over. Note also that values vary a bit from book to book.

a) Find the standard enthalpy change, $AH^{o}$, for the formation of 1 mole water at 25 °C (298 K) from its gaseous elements, that is, the standard enthalpy change for the reaction:

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l)$$

b) Determine from the given data the standard entropy change for the same reaction occurring at 25 °C.

c) Calculate the standard free energy change, $AG^{o}$, for the same reaction occurring at 25 °C.

d) Calculate the standard free energy change, $AG^{o}$, for the same reaction occurring at 90 °C.

Question 2 When a system is at equilibrium, departure from equilibrium will be accompanied by

| | |
|---|---|
| 1 a positive free energy change | 2 a negative enthalpy change |
| 3 a positive change in the entropy value of the system. | 4 a negative change in the total entropy value of system-cum-surroundings. |

Question 3 Deduce the standard free energy change for the reaction

$$Zn(s) + Pb^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Pb(s)$$

from data on page 40 of your Three Figure Tables.

---

Question 1

a) $AH^{o} = -286 \text{ kJ mol}^{-1}$

b)

| | | | | | |
|---|---|---|---|---|---|
| Equation: | $H_2(g)$ | + $\frac{1}{2}O_2(g)$ | $\rightarrow$ | $H_2O(l)$ | |
| $S^{o}$: | 131 | 102.5 | | 69.9 | $\text{J K}^{-1}\text{ mol}^{-1}$ |

Therefore $AS^{o} = 69.9 - 102.5 - 131 \text{ J K}^{-1}\text{ mol}^{-1}$

$= -163.6 \text{ J K}^{-1}\text{ mol}^{-1}$

c) at 25 °C

$$AG^{o} = AH^{o} - TAS^{o}$$
$$= -286 - 298 \times -163.6/1000 \text{ kJ mol}^{-1}$$
$$= -286 + 49 \text{ kJ mol}^{-1}$$
$$= -237 \text{ kJ mol}^{-1}$$

Check that this figure is the figure offered in data books for the stnadard free energy change at 25 °C.

d) at 90 °C

$$AG^{o} = AH^{o} - TAS^{o}$$
$$= -286 - 363 \times -163.6/1000 \text{ kJ mol}^{-1}$$
$$= -286 + 59 \text{ kJ mol}^{-1}$$
$$= -227 \text{ kJ mol}^{-1}$$

Question 2

| | |
|---|---|
| Response 1 | This response is correct. |
| Response 2 | The enthalpy change could be negative or positive, depending on the sign of TAS and its magnitude. |
| Response 3 | This response is incorrect. The change in entropy value will be positive or negative; it depends on the reaction. |
| Response 4 | This response is correct. A change for which AG is positive (= non-spontaneous) would be equivalent to a change for which the $AS_{total}$ is negative (= non-spontaneous). |

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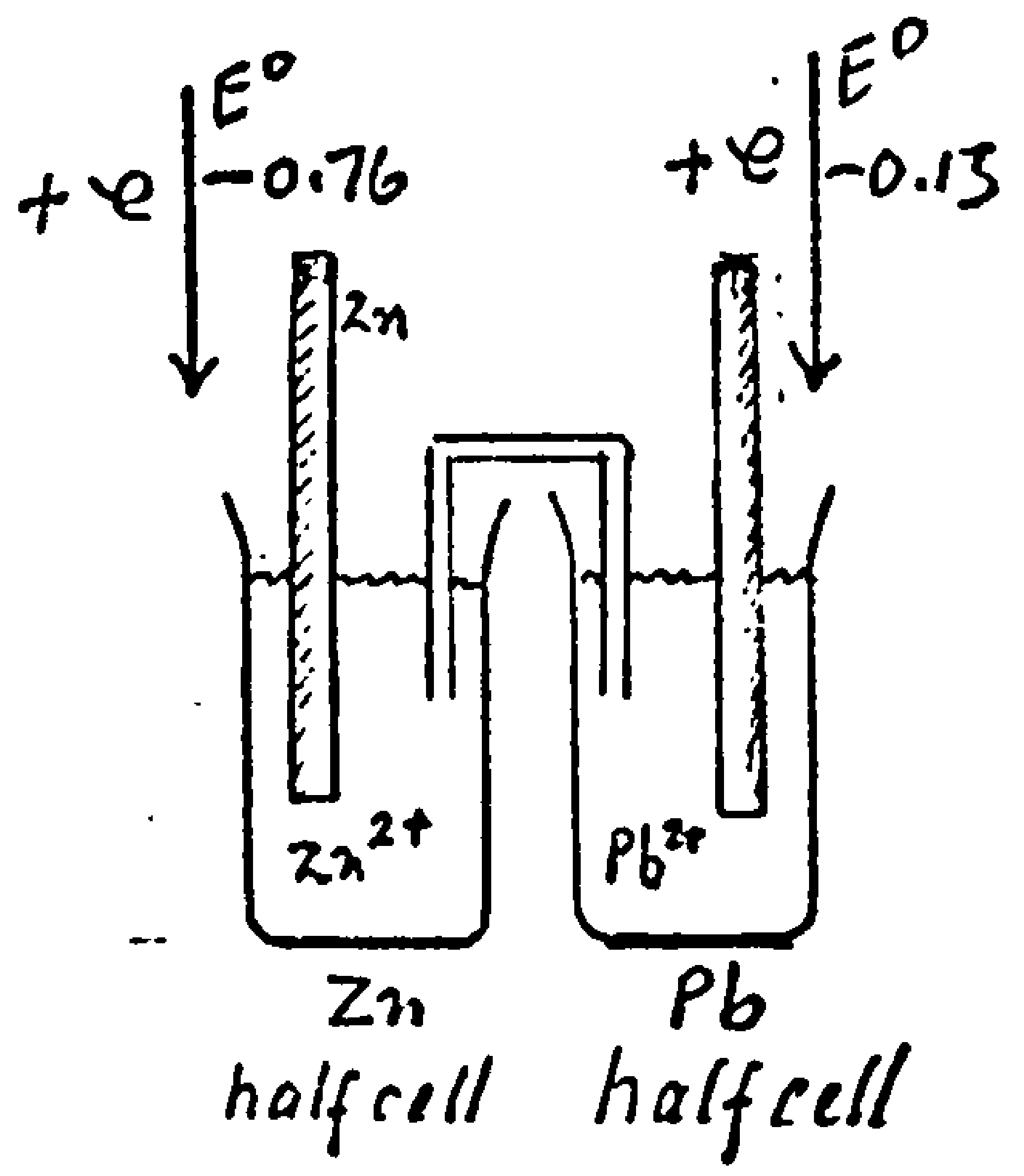
Question 3



$$\begin{array}{llr}
Zn(s) & \longrightarrow Zn^{2+}(aq) + 2e & +0.76\ V \\
2e + Pb^{2+}(aq) & \longrightarrow Pb(s) & -0.13\ V \\
\hline
\underline{Zn(s) + Pb^{2+}(aq)} & \underline{— Zn^{2+}(aq) + Pb(s)} & \underline{+0.63\ V}
\end{array}$$

Thus the difference between the electrodes of the two standard half cells, '$\Delta E^o$', is the maximum reversible e.m.f. of the standard cell, and is equal to +0.63 V.

The standard free energy change, therefore, is $\Delta G^o = -nFE^o$ ($E^o$ now being taken as the whole cell e.m.f.) $= -2 \times 9.65 \times 10^4 \times 0.63$ J mol$^{-1}$

$$= -1.216 \times 105 \text{ J mol-1}$$

$$= \underline{-1.216 \times 10^2 \text{ kJ mol-1}}$$

Note that $E^o$ as a symbol may represent either the standard potential of a <u>single</u> electrode, or the standard e.m.f. of a <u>cell</u>. In the latter case, to be consistent, the symbol '$\Delta E^o$' should be used since the e.m.f. of a cell is the difference between two electrodes. Thus $\Delta G^o = -nF\underline{\Delta E}$ but this is rarely seen. Similarly, $\Delta G = -nF\underline{\Delta E}$ for non standard conditions. Thus, when the difference between the potetials of two half cells is zero, i.e. '$\underline{\Delta E}$' = zero, then $\Delta G = 0$ and an equilibrium situation exists.

# Study Unit 10

## FREE ENERGY and the EQUILIBRIUM CONSTANT

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### PURPOSE

1. To develop the concept of the equilibrium constant.
2. To state the relationship between the standard free energy change and the equilibrium constant.
3. To show how the sign and magnitude of the standard free energy change affects the composition of a mixture coming to equilibrium.

---

### PRESENTATION

Introduction. This unit will introduce the concept of the equilibrium constant; but the treatment is very brief. My main purpose, initially, is to show that this constant ratio, whatever it really is, is related to the standard free energy change for the reaction whose equilibrium system it describes. Some equilibrium constants are then quoted in the last pages or so of this Unit.

Little or no mention will be made of the effect of change of variables on an equilibrium composition. The application of the Le Chatelier Principle was dealt with during Form V, and can be of use here; but the Priciple is notoriously difficult of application, and frequently only gives the right answer to those who already know what the right answer is!

### More about $AG^o$

When $AG^o$ is negative, the standard line slopes downwards from left to right; the right hand end is lower than the left hand end. This will tend to act with the free energy of mixing to give a minimum to the right rather than to the left. The equilibrium mixture will tend to contain a higher proportion of product and a lower proportion of reactant. (See Figure 10.3.)

When $AG^o$ is zero, the standard line is horizontal. This will act with the free energy of mixing to give a minimum at or somewhere about the middle mark. Exactly where depends on the particular equilibrium system; $AG^o$ being zero does not mean that the composition of the equilibrium mixture will nesessarily be product:reactant equal to 50:50; but if not, it will not be too far away. You will understand the reason for this when you examine the free energy profile for the synthesis of ammonia at that temperature where $AG^o$ is zero.

When $AG^o$ is positive, the standard line slopes upwards from left to right, and the equilibrium composition tends to be richer in reactant than product. This case is dealt with shortly.

## The relationship between $AG^{o}$ and $K_{eq}$.

It can be shown that the value of AG for any composition of reaction mixture is related to $AG^{o}$, the standard free energy change for the reaction, by the expression

$$AG = AG^{o} + 2.3RT \log \frac{\text{Product concentrations}}{\text{Reactant concentrations}}$$

R is a constant called the molar gas constant; $R = 0.0083\ \text{kJ mol}^{-1}\ \text{K}^{-1}$

T is the temperature in kelvins (K).

The ratio $\frac{\text{Product concentrations}}{\text{Reactant concentrations}}$ expresses the relative concentration products and reactants as the reaction proceeds from one extreme (reactants only) to the other extreme (products only). At some intermediate composition the ratio describes the relative concentration of products and reactants in the equilibrium mixture. This occurs at that composition which corresponds to the minimum point on the free energy profile. At this composition the ratio is the equilibrium ratio or constant (for the exact form of which see later).

That composition which corresponds with the minimum in free energy of the reaction mixture is the equilibrium composition, at which

$AG = 0$,

and the ratio $\frac{\text{Product concentrations}}{\text{Reactant concentrations}}$ is equal to the equilibrium constant, symbolised $K_{eq}$.

Thus at equilibrium

$$\boxed{\begin{aligned} AG^{o} &= -2.3RT \log K_{eq} \\ &= -0.02T \log K_{eq} \end{aligned}}$$

where $AG^{o}$ is expressed in kJ.

## Calculation of equilibrium constants

If the standard free energy change for a reaction is known (it could perhaps have been determined experimentallyfrom the relationship $AG^{o} = -nFEo$), the equilibrium constant for the reaction can be calculated from the relationship $AG^{o} = -\text{const.} \log K_{eq}$.

Conversely, if the equilibrium constant can be determined experimentally, the standard free energy change for the reaction can be calculated.

### Problem 10.1

Calculate the equilibrium constant for the synthesis of ammonia at 298 K.

From tables $AG^{o} = -16.5\ \text{kJ mol}^{-1}$

Therefore: $-16.5 = -0.02 \times 298 \times \log K_{eq}$

from which $K_{eq} = 5.9 \times 10^{2}$

Without examining the exact form of the equilibrium constant, the value $5.9 \times 10^{2}$, conveys the information that an equilibrium mixture of nitrogen, hydrogen and ammonia at room temperature contains 'more product than reactant'.

The ratio of products:reactants is somewhere in the region of 590:1.

The equilibrium would be described as lying over to the right.

On this basis, the conversion of nitrogen and hydrogen to ammonia at room temperature is certainly, thermodynamically feasible. Unfortunately, it is not kinetically feasible, because the rate of reaction is exceedingly low.

Moving to a higher temperature will tend to overcome the kinetic snag, which is essentially one of insufficient activation energy at the lower temperature, but how will it affect the standard free energy change and consequently the equilibrium constant for the reaction?

Problem 10.2

Calculate $AG^o$ for the synthesis of ammonia at 800 K, and hence deduce the equilibrium constant at 800 K

Use $AG^o = AH^o - TAS^o$ to compute the value of $AG^o$. Then use $AG^o = -0.02T \log K_{eq}$ to compute the value of $K_{eq}$.

$AG^o$ The values for $AH^o$ and $TAS^o$ are required in order to compute $AG^o$.

From tables, $AH^o = -46.2$ kJ mol$^{-1}$ at 298 K. This value is used at 800 K since enthalpy change is not markedly affected by the temperature at which the reaction occurs.

$AS^o$ is calculated from tables as follows:

$$\begin{array}{ccccccc} \frac{1}{2}N_2 & + & 1\frac{1}{2}H_2 & \longrightarrow & NH_3 & & \\ S^o = 96 & & S^o = 196.5 & & S^o = 193 & & J\ K^{-1} \end{array}$$

$$AS^o = 193 - (96 + 196.5)\ J\ K^{-1}\ mol^{-1}$$

$$= -99.5\ J\ K^{-1}\ mol^{-1}$$

This is the change in standard entropy value for the reaction. Although it has been calculated from data quoted at 298 K, it does not vary much with temperature and so can be taken as the change in standard entropy value at 800 K.

It now has to be multiplied by T (=800) and divided by 1000 to convert it to the standard entropy energy change expressed in kilojoules instead of joules.

At 800 K $$TAS^o = \frac{800 \times -99.5}{1000}\ kJ\ mol^{-1}$$

$$= -79.6\ kJ\ mol^{-1}$$

Hence from $$AG^o = AH^o - TAS^o$$

substituting $$AG^o = -46.2 - -79.6\ kJ\ mol^{-1}$$

$$= +33.4\ kJ\ mol^{-1}$$

Note that at the higher temperature of 800 K, the standard free energy change is positive; it had been negative at the lower temperature.

$K_{eq}$ Applying $AG^o = -0.02T \log K_{eq}$, and substituting +33.4 for $AG^o$ and 800 for T, the equilibrium constant turns out to have the value

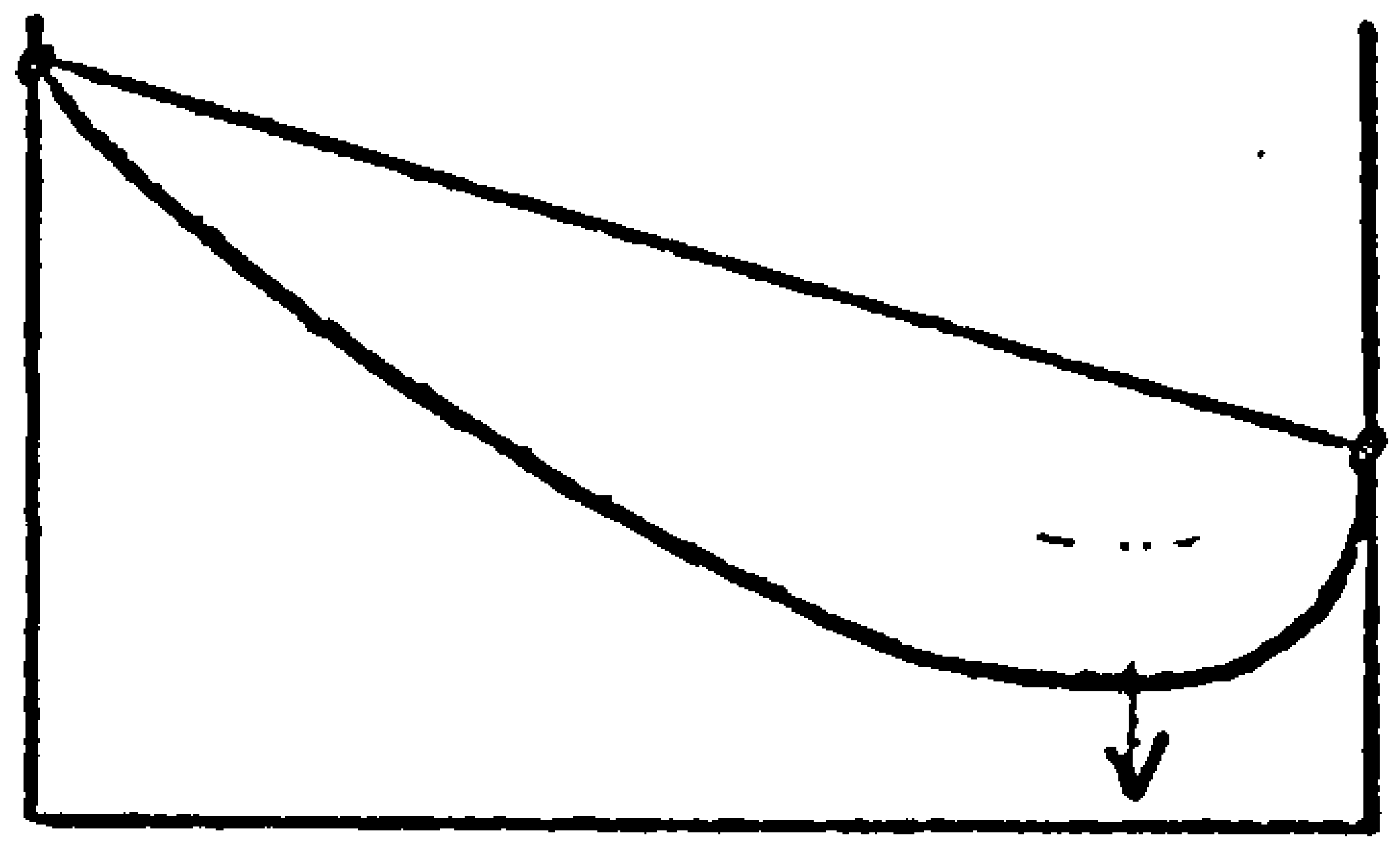
$$K_{eq} = 8.2 \times 10^{-3}$$

The equilibrium mixture contains little product.

The ratio of products:reactants is somewhere in the region of 0.0082:1.

The general shape of the free energy profile. The results obtained for the Haber equilibrium system are summarised below. These apply in general terms to other equilibrium systems.

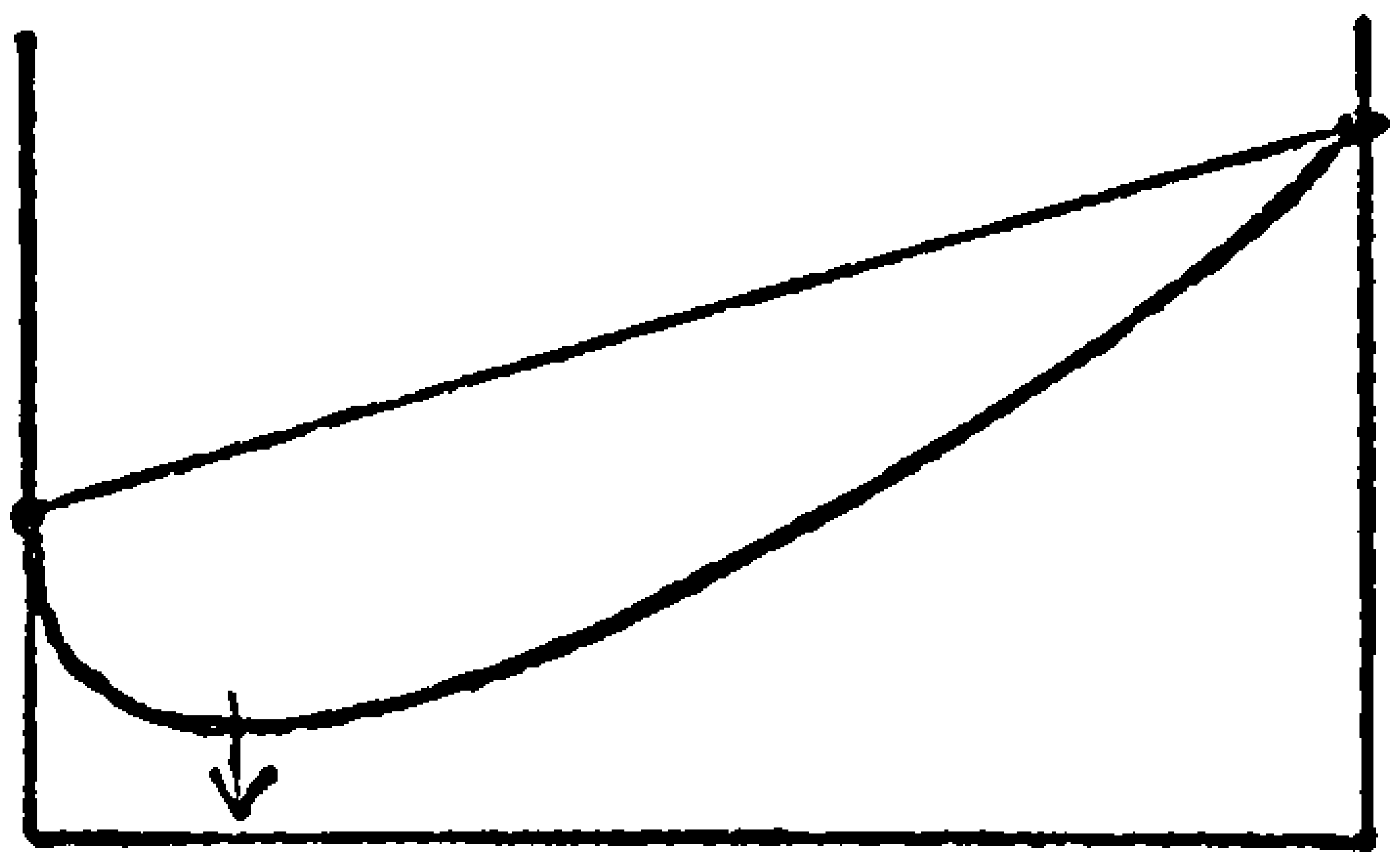
If $AG^o$ is negative, the free energy profile has this shape:



$K_{eq}$ is greater than unity. The equilibrium mixture is richer in products tnan reactants.

Fig. 10.1

If $AG^o$ is positive, the free energy profile has this shape:



$K_{eq}$ is less than unity. The equilibrium mixture is richer in reactants than products.

Fig. 10.2

If $AG^o$ is zero, the standard line is horizontal and the sag induced on it produces a minimum somewhere in the middle region of composition:

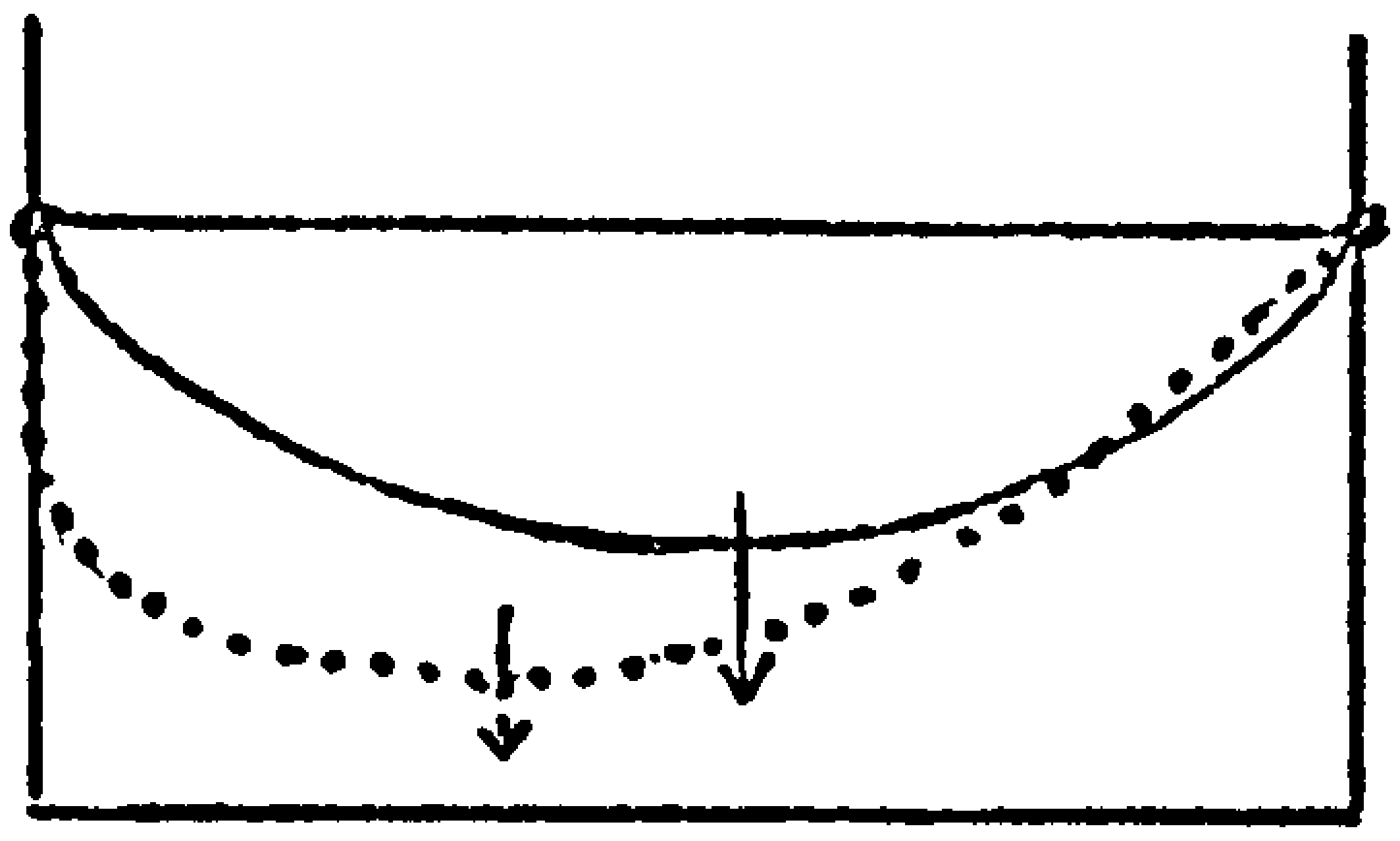


Fig. 10.3

The dotted line represents the particular case of N synthesis at a temperat where $\Delta G^o$ is zero

$$\text{If } AG^o = -2.3RT \log K_{eq}, \text{ and } AG^o = 0,$$
$$\text{then} \quad \log K_{eq} = 0$$
$$\text{and} \quad K_{eq} = 1$$

The equilibrium mixture contains approximately equal amounts of product and reactant, depending on the particular equilibrium system involved.

| $AG^o$ kJ $mol^{-1}$ | $K_{eq}$ no units | |
|---|---|---|
| -46.0 | $10^8$ | - the reaction occurs to virtual competion. |
| -11.3 | $10^2$ | |
| Zero | 1 | |
| +11.3 | $10^{-2}$ | |
| +46.0 | $10^{-8}$ | - the reaction virtually does not occur. |

Note that every 5.9 kJ $mol^{-1}$ difference in $AG^o$ changes the value of the equilibrium constant by a single power of ten, e.g. 105 may go to $10^6$.

Table 10.1

## The Equilibrium Law

It can be shown experimentally that the concentrations of the reactant and product species in an equilibrium system are related to each other mathematically as follows.

For example, in the general case where $2A \rightleftharpoons 3C + D$

then
$$K_{eq} = \frac{[C]^3[D]}{[A]^2}$$

If the equilibrium system had been written as $3C + D \rightleftharpoons 2A$ it would still be the same system, but the equilibrium constant would be the reciprocal
$$K_{eq} = \frac{[A]^2}{[C]^3[D]}$$

When an equilibrium constant is given, some clear indication must also be given of which way the reaction is to be written.

Here are three examples of equilibrium constants. These relate to reactions you have come across in Form V and earlier.

a) The making of an ester, ethyl ethanoate.

$$CH_3COOH(l) + C_2H_5CH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

$$K_{eq} = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$ found by

experiment to be $= 4$ (approx.) at room temperature.

b) The ionisation of ethanoic acid by water.

$$CH_3COOH(aq) + H_2O(aq) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

$$K_{eq} = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]}$$

But $[H_2O]$ in dilute aqueous solutions is little affected by changes in concentrations among the other dissolved species, and so $[H_2O]$ is a species which for all practical purposes does not vary. It is called a 'constant concentration term'. The value of the equilibrium constant is not therefore dependent on it, and so

$$K_{eq} = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

$$= 1.8 \times 10^{-5} \text{ at room temperature.}$$

c) The solution of the sparingly soluble salt silver chloride, AgCl.

$$AgCl(s) + aq \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$K_{eq} = \frac{[Ag^+][Cl^-]}{[AgCl][aq]}$$

But $K_{eq}$ is not affected by the amount of solid silver chloride, as long as there is some, so the term $[AgCl]$ is in effect a constant.

And the term $[aq]$ is a constant concentration term, as explained above.

The equilibrium constant is therefore only dependent on $[Ag^+]$ and $[Cl^-]$.

This example is not required by the C.S.Y.S syllabus

$$K_{eq} = [Ag^+][Cl^-]$$

$$= 1.7 \times 10^{-10} \text{ at room temperature.}$$

Study Unit 10 What you should know.

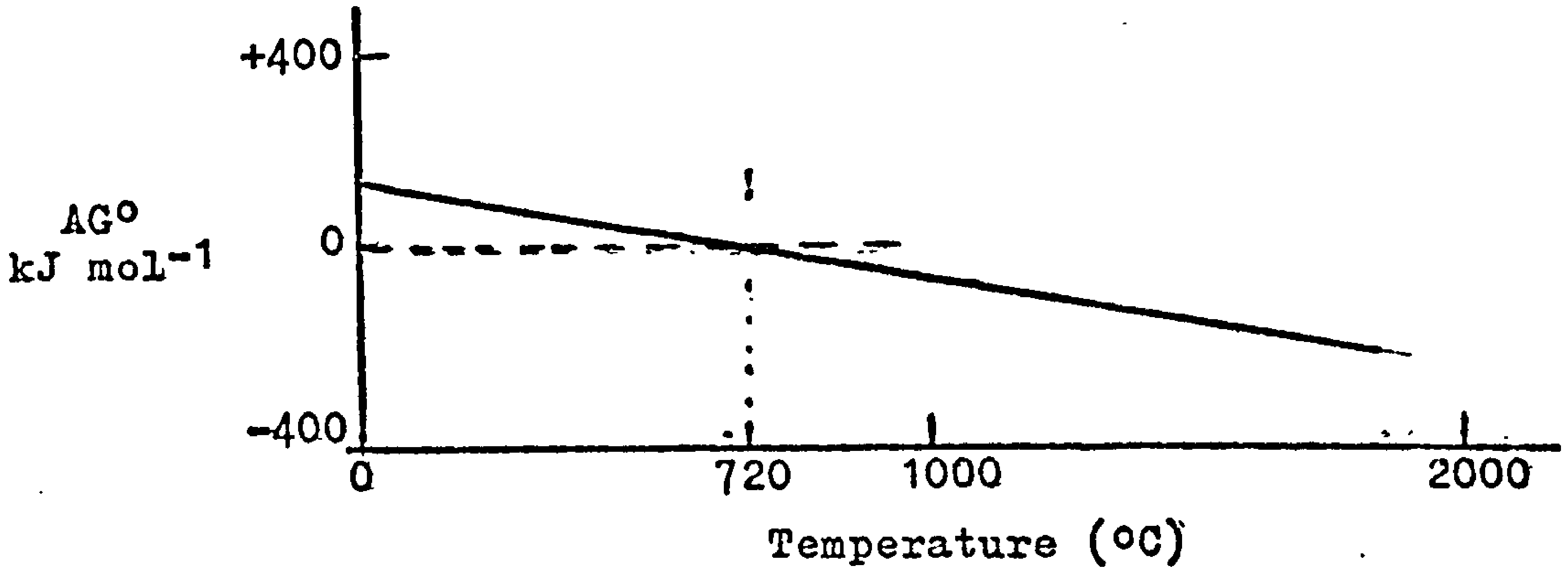
You should

1. know the relationship $AG^{o} = -2.3RT \log K_{eq}$
2. know how the sign of $AG^{o}$ influences the composition of the equilibrium mixture.
3. have some idea of the equilibrium constant.

---

Question 1 The accompanying graph shows how the standard free energy change, $\Delta G^o$, for the reaction

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g) \qquad \Delta H^o \ +ve$$



varies with temperature. Which of the following statements, if any, is correct?

| | |
|---|---|
| 1 Below 720 °C, $\Delta G^o$ is positive, and so CO spontaneously decomposes into C and $CO_2$. | 2 At 720 °C, the equilibrium constant, $K_{eq}$, is zero. |
| 3 $\Delta G$ for the reaction as written above is always negative. | 4 The proportion of CO in the equilibrium mixture increases as the temperature is increased |

Question 2 If $\Delta G^o$ for a reaction, left to right, is positive, will the reaction be spontaneous from left to right?

| | |
|---|---|
| 1 No | 2 Yes; but the reaction will occur very slowly. |
| 3 Yes; but how far the reaction will proceed before settling at an equilibrium composition is not possible to say. | |

---

Question 3 When A and B react to form C

$$A + B \rightleftharpoons C$$

the equilibrium mixture of A, B and C at a particular temperature contains only about 1% C. This means that

| | |
|---|---|
| 1 $AG^{o}$ is positive. | 2 AG at equilibrium is zero. |
| 3 $AG_{net}$ (from pure reactants to the equilibrium mixture is negative. | 4 AGnet (from pure product to the equilibrium mixture is positive. |

Question 4 If AH for a reaction is negative,

| | |
|---|---|
| 1 AG could be positive or negative. | 2 AS for the reaction is likely to be negative. |

Question 5 Consider the following data on ionisation:

| Acid | $AH^{o}$ (kJ $mol^{-1}$) | $AG^{o}$ (kJ $mol^{-1}$) |
|---|---|---|
| Ethanoic Acid | Nil | +10 |
| Trichlorethanoic Acid | Nil | +5 |

a) Which is the strongeracid of the two?
b) Why is it the stronger acid?

---

Question 6 A and B react to form C and D. 1 mole A and 2 moles B are mixed and allowed to react. Eventually an equilibrium mixture

$$A + B \rightleftharpoons C + D$$

of A, B, C and D is formed, which contains $\frac{3}{4}$ mole each of C and D. What is the equilibrium constant for this system?

---

Question 7 A saturated solution of silver chloride is described by the equilibrium constant Keq = $[Ag^{+}][Cl^{-}] = 1.7 \times 10^{-10}$. What is the solubility of silver chloride? (The value of the equilibrium constant is based on units 'moles per litre'.)

---

---

Question 8 Here is an equilibrium system:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

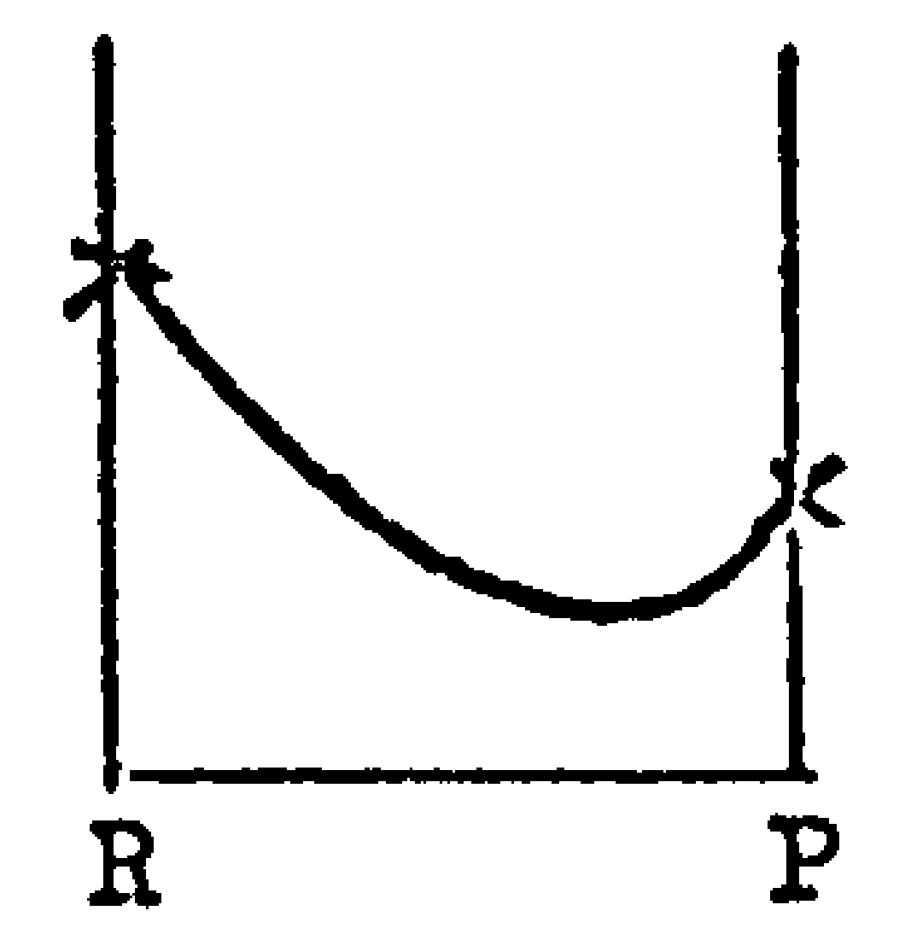
At 25 °C, AG° = +5.4 kJ mol$^{-1}$ ($N_2O_4$);
at 75 °C, AG° = −2.1 kJ mol$^{-1}$ ($N_2O_4$).

a) How does the equilibrium mixture vary with temperature?

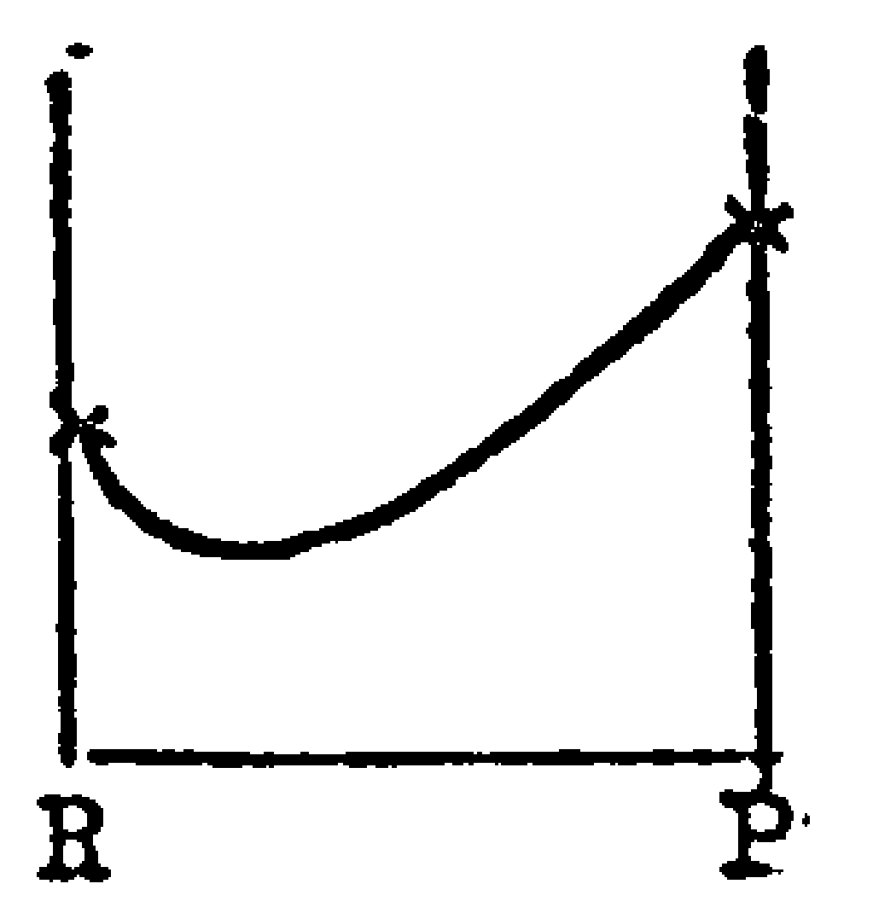
| | |
|---|---|
| 1 There is little or no decomposition at 25 °C. | 2 The equilibrium mixture at 50 °C will probably contain about half and half product and reactant. |
| 3 The dissociation becomes less complete as the temperature is raised. | |

b) Which of the following free energy profiles corresponds to this equilibrium system at 25 °C?

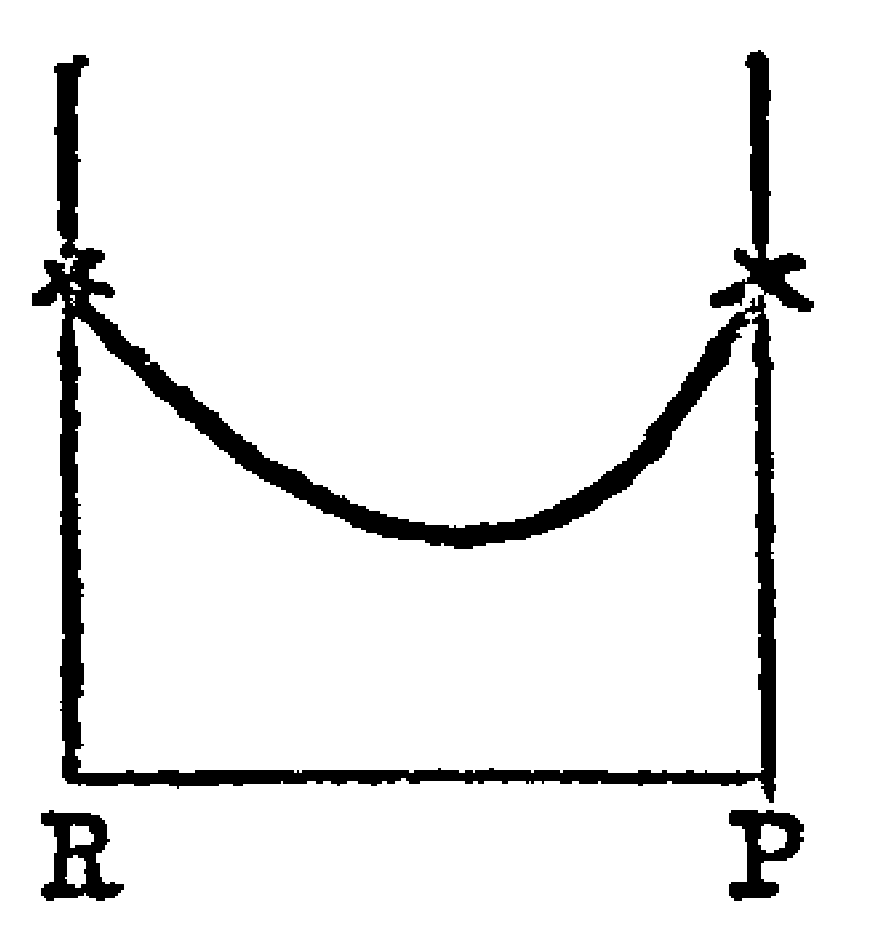
1



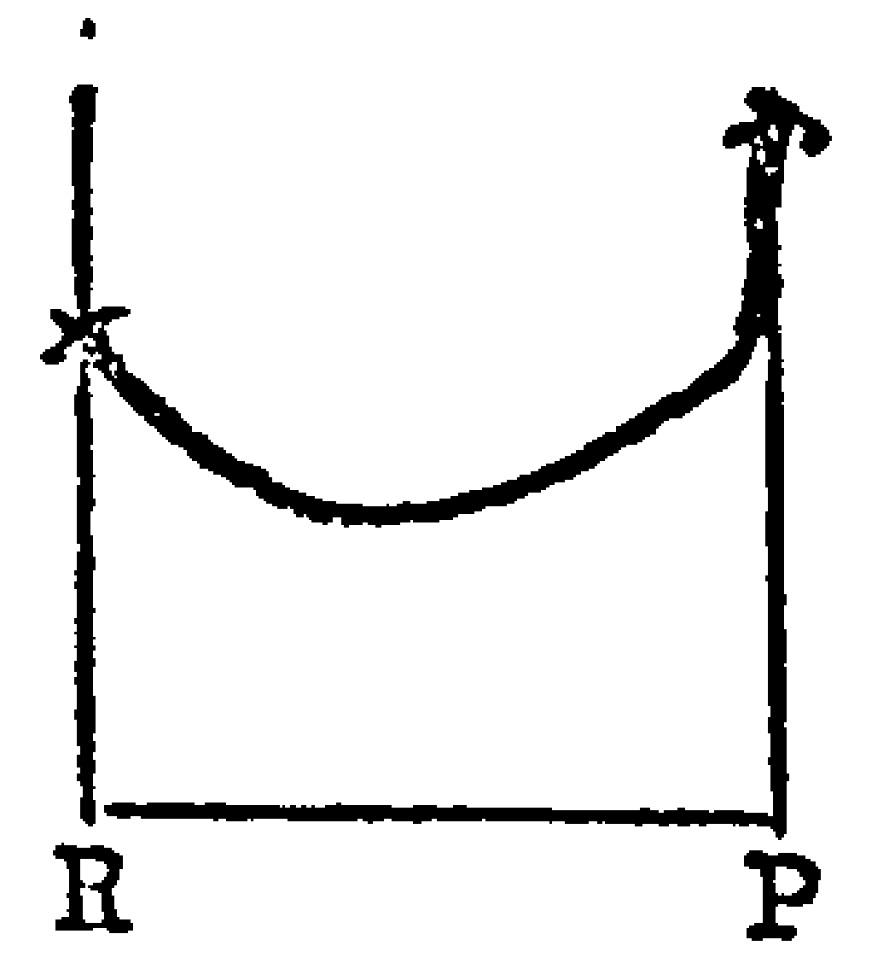
2



3



4



### Question 1

| | |
|---|---|
| Response 1 | When $AG^o$ is positive, the equilibrium mixture contains more reactant than product. Thus CO pure CO will decocompose, given enough time, until the equilibrium mixture contains that percentage of CO dictated by the value of $AG^o$. |
| Response 2 | This response is incorrect. At 720 °C the value of $AG^o$ is zero, and so $K_{eq}$ is equal to 1. |
| Response 3 | This response is incorrect. Starting with reactants only, the actual value of AG is negative until the equilibrium composition is reached, at which point it becomes zero, and if the reaction were to proceed further would become positive. |
| Response 4 | This response is correct. $AG^o$ becomes more negative with increasing temperature, and so the equilibrium position 'shifts to the right'. |

### Question 2

| | |
|---|---|
| Response 1 | This response is incorrect. The spontaneity of a reaction is determined by the actual free energy change, which in theory is always negative from either the pure reactant or pure product starting point. Thus if $AG^o$ is positive the reaction will proceed to an equilibrium mix, one containing more reactant though than product. If $AG^o$ is very positive, the reaction - for all practical purposes - may be said not to proceed. |
| Response 2 | $AG^o$ gives no information about the speed of a reaction. |
| Response 3 | This response is correct. |

### Question 3

| | |
|---|---|
| Response 1 | This response is correct. |
| Response 2 | This response applies in general to any equilibrium situation. |
| Response 3 | This response is correct. |
| Response 4 | This response is incorrect. The net free energy change from pure product to the equilibrium mixture will also be negative. |

### Question 4

~~This response is correct~~

| | |
|---|---|
| Response 1 | This response is correct. |
| Response 2 | This response is incorrect. AS might easily be positive if AG were negative enough to ensure that AH was negative. |

**Question 5**

a) The stronger acid is trichlorethanoic acid because AG° for the ionisation of this acid is less positive (equivalent to its being more negative) than is AG° for the ionisation of ethanoic acid. Thus, of the two ionisations:

$$CH_3COOH(aq) + H_2O(aq) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

$$CCl_3COOH(aq) + H_2O(aq) \rightleftharpoons CCl_3COO^-)aq) + H_3O^+(aq)$$

the second one gives an equilibrium mixture containing the more hydroxonium ion (other things being equal). But both acids are weak acids since the AG° values for each are positive .... but trichlorethanoic acid is less weak.

b) Given that AH° in each ionisation is zero, then the increase in free energy in each ionisation can be equated to a decrease in entropy energy in each case, which is therefore more marked for ethanoic acid and less marked for trichlorethanoic acid. Thus trichlorethanoic acid is a <u>stronger</u> acid because AG° is <u>less positive</u>, because AS° is less negative .... because the trichlorethanoate ion is relatively larger than the ethanoate ion and so does not exert the same orienting effect on water molecules. (For a given charge, the larger the ion the lower is its 'surface charge density'.

**Question 6**

| | A | + | B | ⟶ | C | + | D | |
|---|---|---|---|---|---|---|---|---|
| Initially: | 1 | | 2 | | 0 | | 0 | mol l$^{-1}$ |
| Finally: | $1 - \frac{3}{4}$ | | $2 - \frac{3}{4}$ | | $\frac{3}{4}$ | | $\frac{3}{4}$ | mol l$^{-1}$ |
| = | $\frac{1}{4}$ | | $1\frac{1}{4}$ | | $\frac{3}{4}$ | | $\frac{3}{4}$ | mol l$^{-1}$ |

$$K_{eq} = \frac{[C][D]}{[A][B]}$$

$$= \frac{\frac{3}{4} \times \frac{3}{4}}{\frac{1}{4} \times 1\frac{1}{4}}$$

$$= 1.8$$

**Question 7**

If $[Ag^+(aq)][Cl^-(aq)] = 1.7 \times 10^{-10} = K_{eq}$;

then $[Ag^+(aq)] = [Cl^-(aq)] = 1.3 \times 10^{-5}$ mol l$^{-1}$.

Hence the solubility of silver chloride = <u>1.3 x 10$^{-5}$ mol l$^{-1}$</u>

(Remember that 1 mole AB will give 1 mole of A$^+$ and 1 mole of B$^-$ when it dissolves.)

Question 8

| | | |
|---|---|---|
| a) | Response 1 | This response is incorrect. If you refer to Table 10.1 you will see that a standard free energy change $AG^{o} = +5.4$ kJ $mol^{-1}$ corresponds to an equilibrium constant of about $10^{-1}$. About 10% dissociation has there-occurred. |
| | Response 2 | This response is very approximately correct. |
| | Response 3 | This response is incorrect. The dissociation in fact becomes more complete as the temperature is increased. |
| b) | Response 1 | This is not the correct response. This profile corresponds to a temperature at which $AG^{o}$ is negative. |
| | Response 2 | This is the correct response. |
| | Response 3 | This response corresponds to that temperature at which $AG^{o}$ is about zero. |
| | Response 4 | This profile refers to some other equilibrium system in which <u>two</u> different products are formed. This can be deduced from the vertical portion at the product end. |

## Study Unit 11

## EQUILBRIA & FREE ENERGY

---

PURPOSE

1. To show how some equilibria can be explained in terms of free energy change.

---

PRESENTATION

Introduction This unit will discuss, briefly, the topics of vapour pressure, solubility, thermal decomposition and transition temperature in terms of change in free energy. The topics chosen are those which form the basis of some of the practical work you will carry out. Specific details of experimental procedure have been omitted since the exact form of the experimental work will vary from school to school.

1. Water and its vapour pressure.

At 25 °C, $AG^o$ for $H_2O(l) \rightleftharpoons H_2O(g)$ is positive.

This means that the equilibrium established at 25 °C between the liquid and the gas is 'tilted' in favour of the liquid.

It turns out that the free energy of 1 mole of pure water at 25 °C is equal to the free energy of 1 mole of pure water vapour at 25 °C when it exerts a pressure of only 23.7 mmHg, which is much less than its standard state pressure.

At 100 °C, $AG^o$ for $H_2O(l) \rightleftharpoons H_2O(g)$ is zero.

This means that the equilibrium established at 100 °C between the liquid and the gas is 'split equally' between the two.

Thus the free energy of 1 mole of pure water at 100 °C is equal to the free energy of 1 mole of pure water vapour at 100 °C when it exerts a standard one atmosphere pressure, 760 mmHg.

These two cases are illustrated diagrammatically below.

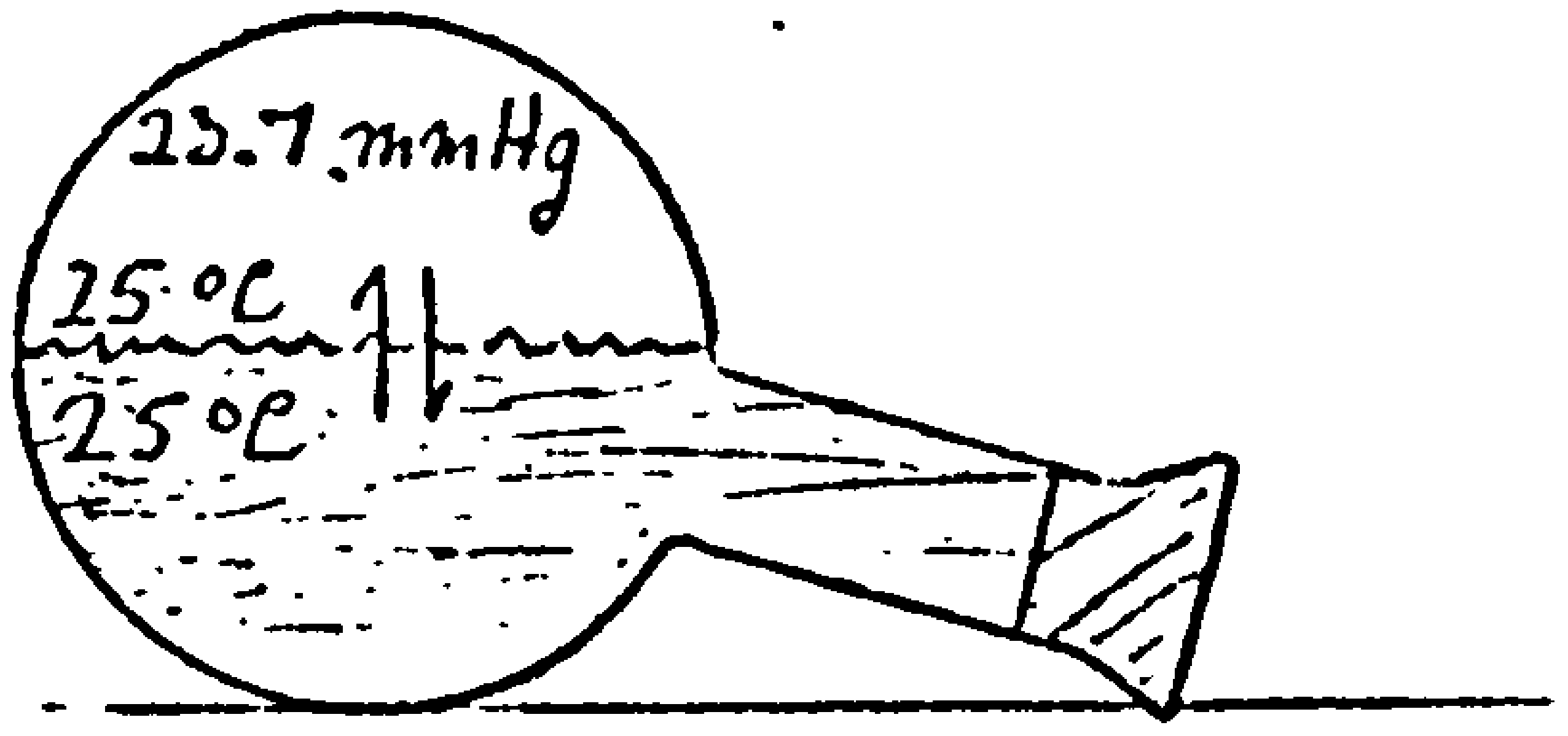


Fig. 11.1

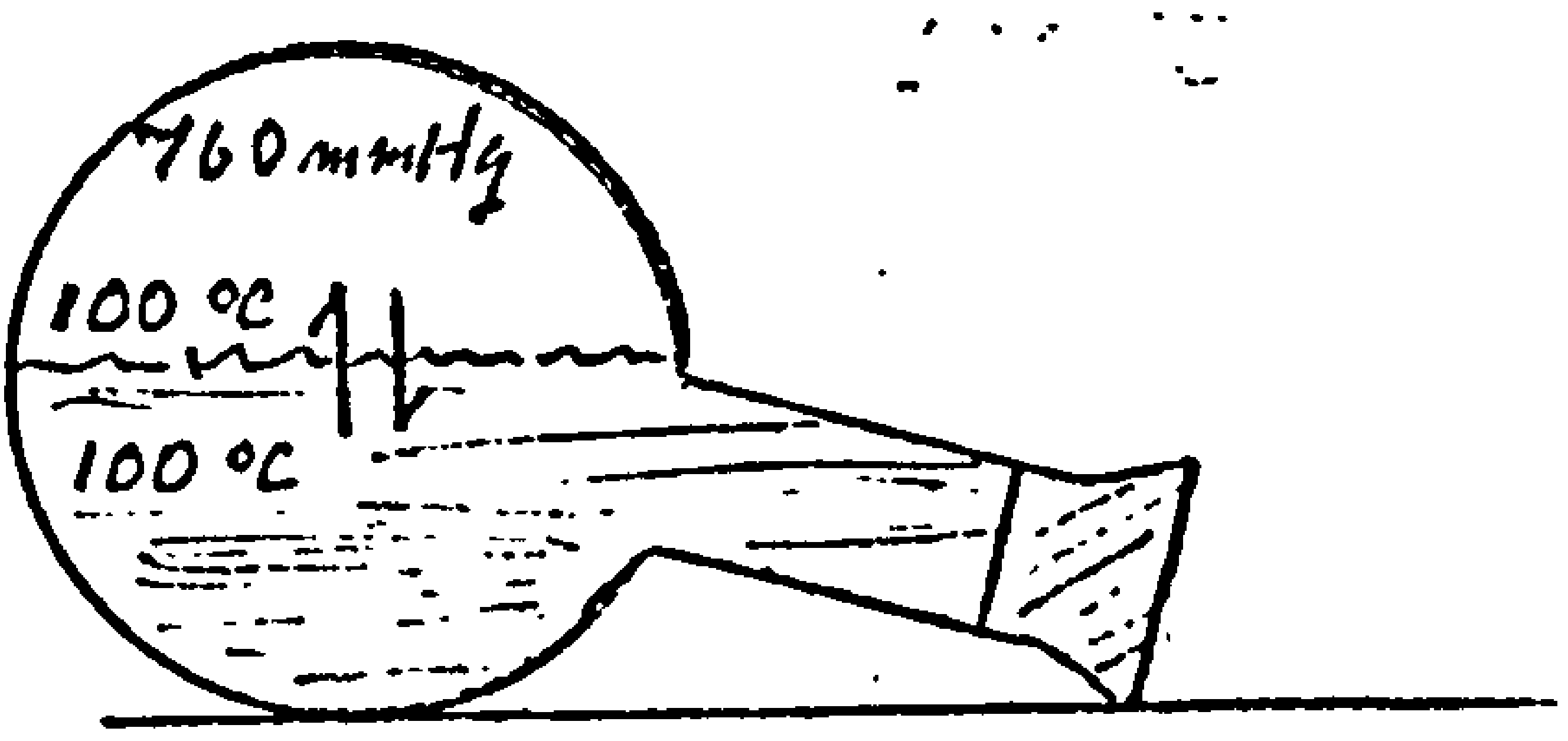


Fig. 11.2

Since at equilibrium AG = 0, then at equilibrium

$$AH_{actual} = TAS_{actual}$$

Thus the temperature at which a particular equilibrium will exist can be deduced from the relationship

$$T_{eq} = \frac{AH_{actual}}{AS_{actual}}$$

The equilibrium vapour pressure of water increases with temperature.

Problem 11.1

Calculate the temperature at which water sets up an equilibrium water vapour pressure of 1 atmosphere, i.e. the temperature at which water in an open vessel will boil with continued input of heat.

$$T_{eq} = \frac{\text{Actual } \Delta H}{\text{Actual } \Delta S}$$

ΔH is the enthalpy if vapourisation, otherwise called the latent heat of evaporation. It is equal to 41.1 kJ $mol^{-1}$.

ΔS is the entropy of vaporisation. It is the change in entropy value associated with the change

$$\underset{\text{one atmosphere}}{\underset{\text{1 mole at}}{H_2O(l)}} \longrightarrow \underset{\text{one atmosphere}}{\underset{\text{1 mole at}}{H_2O(g)}}$$

and is equal to 0.11 kJ $K^{-1}$ $mol^{-1}$.

Hence

$$\begin{aligned} T_b &= \frac{41.1}{0.11} \text{ K} \\ &= 373 \text{ K} \\ &= \underline{100\ ^{o}C} \end{aligned}$$

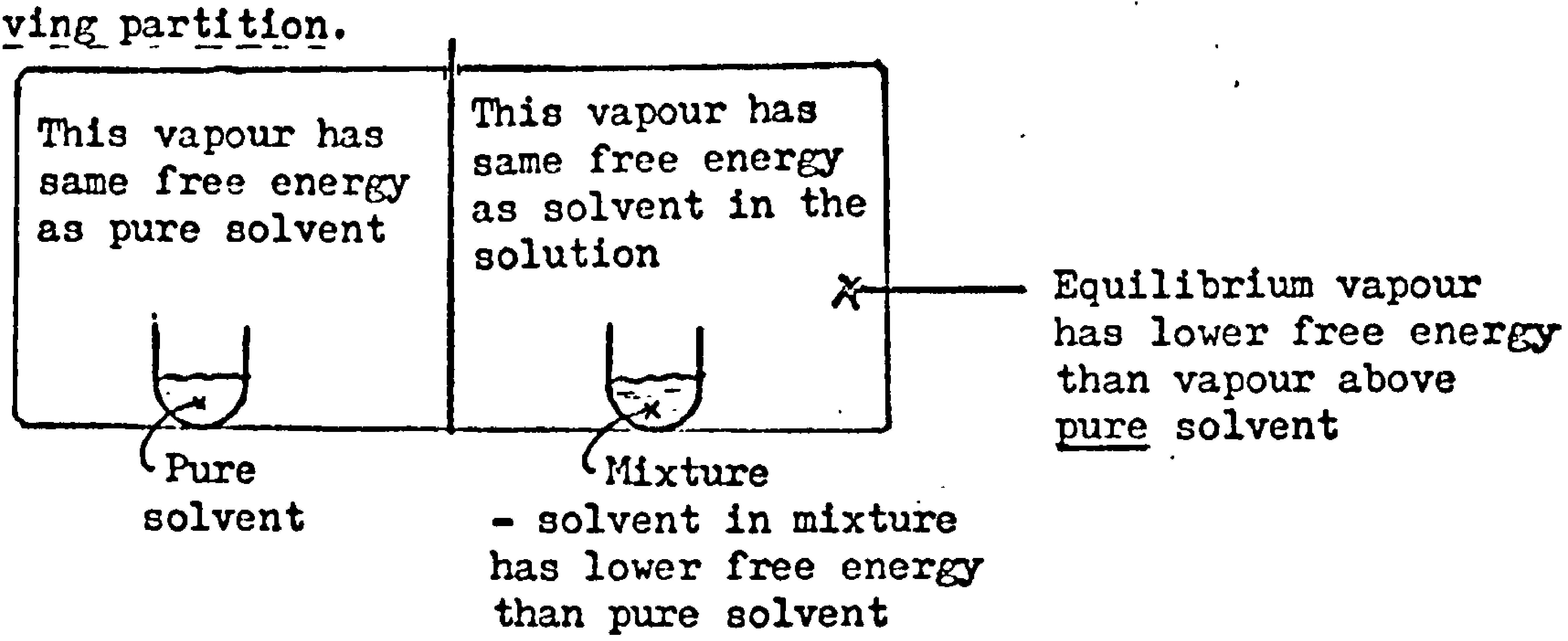
It would be equally possible to deduce the the temperature at which water would set up an equilibrium vapour pressure of say 50 mmHg, or whatever, in a closed vessel, or saying the same thing in a different way, to find the temperature at which water would boil in an open vessel in an environment whose pressure was only 50 mmHg. It requires a knowledge of the enthalpy of vaporisation at that pressure, and similar knowledge of the entropy change.

## The effect of a soluble impurity on the vapour pressure.

A soluble impurity lowers the free energy of a solvent. The mixture has a lower free energy than the sum of the free energies of the separate solute and solvent. This argument was developed in order to explain diffusion (page 7.15) in particular, and has been much used throughout the programme; that is to say, mixing occurs because the move from separate species to mixture is accompanied by a decrease in free energy. Thus the solute in the mixture has a lower free energy than the solute before mixing; the solvent in the mixture has a lower free energy than the solvent before mixing. (And the loss in free energy is compensated for by an increase in entropy energy, i.e. the mixture has a higher entropy value than the sum of the entropy values of the solute and solvent before mixing.)

Apply this knowledge to the situation depicted in Figure 11.3.

Before removing partition.



After removing partition.

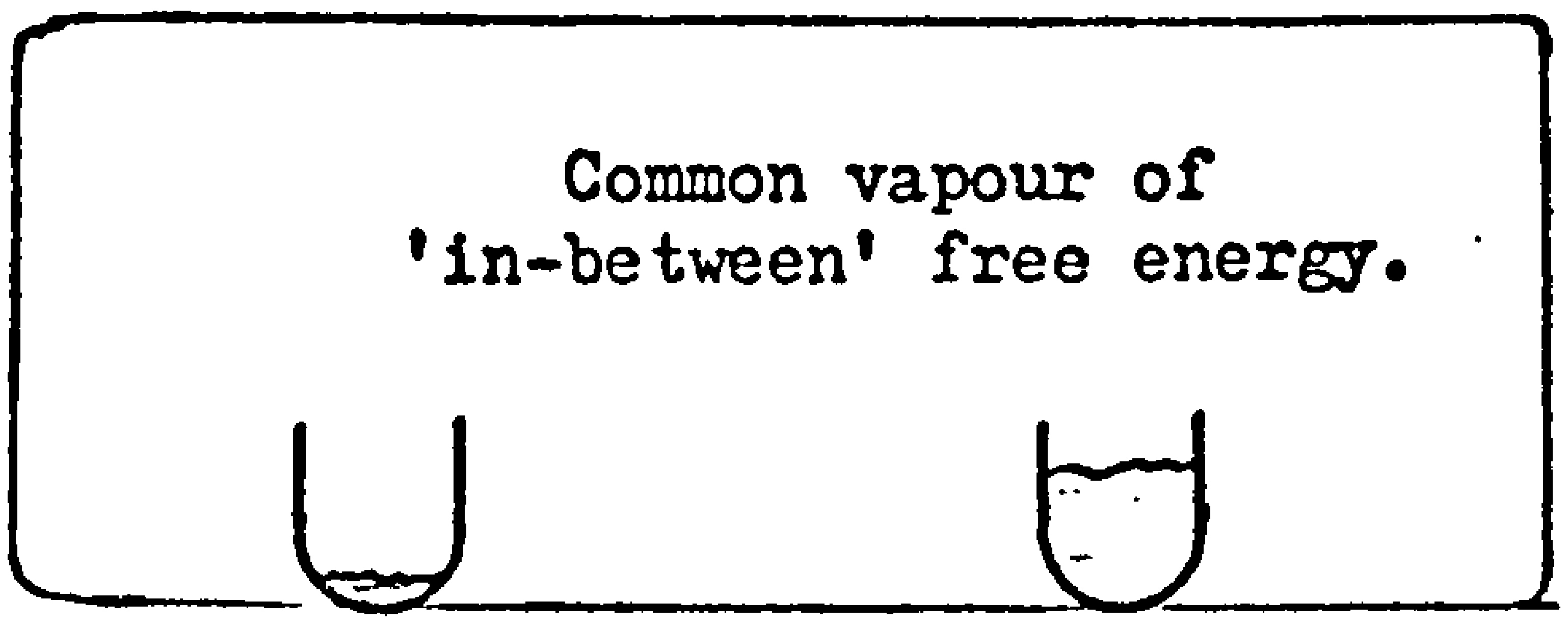


Fig. 11.3

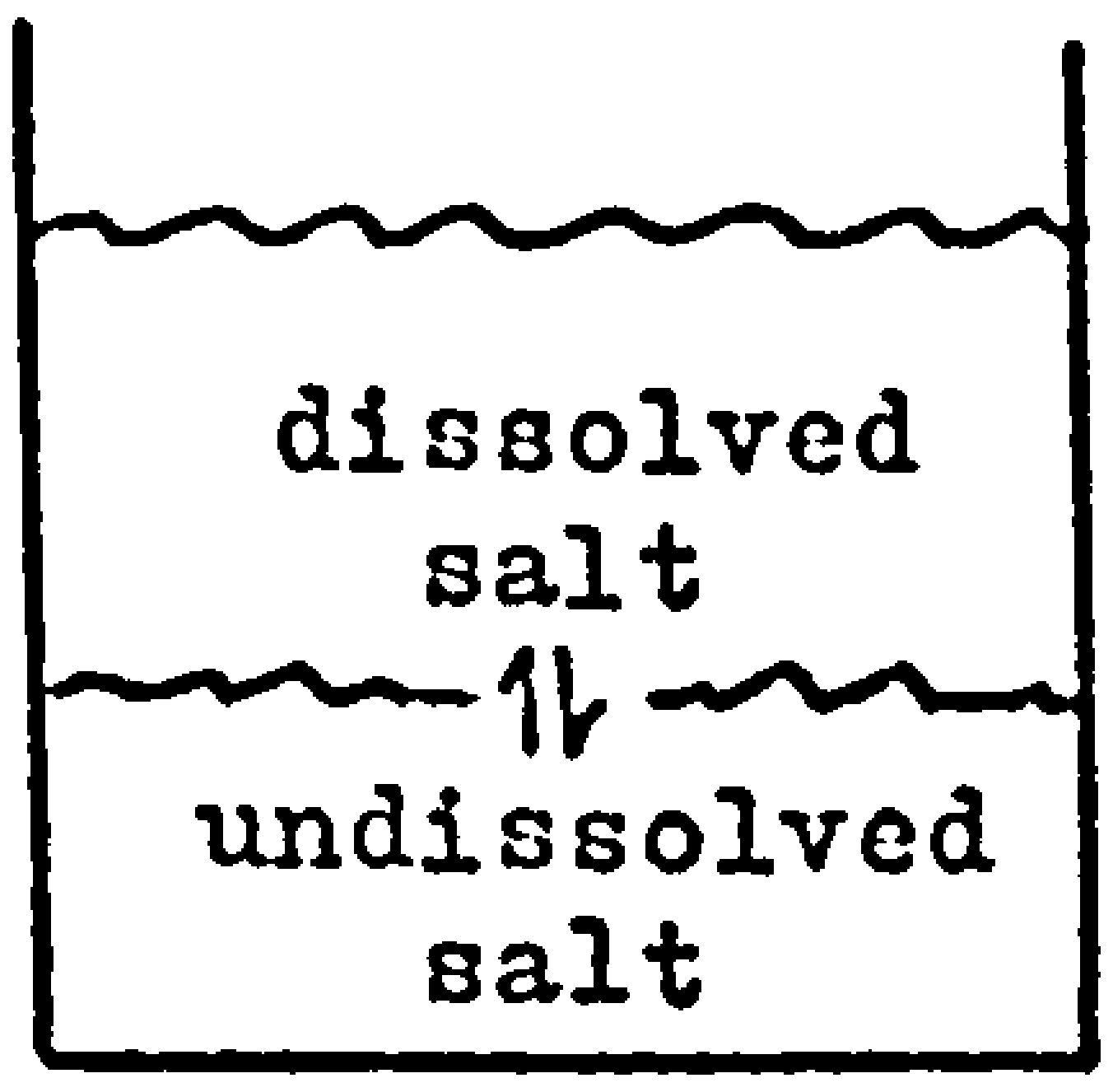
In effect, the equilibrium vapour pressure over the solution is less than the equilibrium vapour pressure over the pure solvent. Thus, the presence of a soluble impurity lowers the vapour pressure.

By a similar argument, a soluble impurity raises the boiling point: the liquid has to be heated that bit more to acquire an equilibrium vapour pressure of 760 mmHg, which it would otherwise achieve at a lower temperature in the absence of the solute.

2. Solubility of salts.

All salts dissolve to some extent. Some are highly soluble, while others are scarcely soluble.

In general, an equilibrium is set up between residual undissolved salt and dissolved salt in the saturated solution.



$$\text{Salt(s)} \rightleftharpoons \text{Salt(aq)}$$

If AG$^{o}$ for the dissolution of the salt is very positive, the equilibrium lies well over to the left (G$^{o}$ line slopes up from left to right), and the salt is practically insoluble.

If AG$^{o}$ for the dissolution of the salt is very negative, the equilibrium lies well over to the right, and the salt is highly soluble.

In all cases, an equilibrium will exist between undissolved and dissolve salt in the saturated solution such that the free energy of the contents of the beaker is a minimum.

Consider the dissolution of lead chloride.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

For this reaction, $\Delta G^o$ is very positive. (at 298 K)

The equilibrium constant, therefore, turns out to be very small: $1.6 \times 10^{-5}$. This means that the equilibrium lies very much to the left, and very little lead chloride dissolves in water (at 298 K).

The actual form of the equilibrium constant in this case is worth a closer look:

$$K_{eq} = \frac{[Pb^{2+}] \times [Cl^-]^2}{[PbCl_2]}$$

where $[Pb^{2+}]$ is the concentration of lead ion in the saturated solution and is quoted say in moles per litre.

where $[Cl^-]^2$ is the square of the total concentration of chlorine ion in the saturated solution.

The concentration term in the denominator poses something of a problem. since lead chloride is undissolved solid. It is not possible to have a 'concentration of undissolve solute'. So long as it is there it will furnish ions for solution, but it does not matter how much is there, whether it be a gramme or a kilogramme, so long as there is <u>some</u> there. This is a difficult point to appreciate

Suffice it to say that it does not actually figure in the equilibrium constant, which is written as

$$K_{eq} = [Pb^{2+}]\,[Cl^-]^2 = 1.6 \times 10^{-5}$$

This is a difficult point to appreciate. Look at it this way. The product $[Pb^{2+}]\,[Cl^-]^2$ has a particular numerical value at a particular temperature. This numerical value is in no way affected by the <u>amount</u> of solid lead chloride lying on the bottom of the container, so long as there is some there. There must be some there to ensure that the concentrations of lead ion and chlorine ion are the maximum they can be.

Since the numerical value of the constant is not affected, therefore, by the actual amount of solid lead chloride, then the latter cannot figure in it.

The constant is equal to $[Pb^{2+}][Cl^-]^2$ and will only change its value if this product were different, as it would be at a different temperature.

Thus $[PbCl_2]$ can be ignored. It is often just simply described as a "constant concentration term", but this is not - in one sense - quite right; it is perhaps best regarded as "not a concentration term at all".

The concept of the equilibrium constant is quite an extensive one and it is not my purpose here to say much about it. Some other examples of equilibrium constants are given at the end of this Study Unit.

3. Thermal decomposition of sodium hydrogen carbonate.

At what temperature does sodium hydrogencarbonate decompose?

At room temperature, AG° is very positive: +14.5 kJ mol$^{-1}$ approximately. This means that equilibrium in the system

$$NaHCO_3 \rightleftharpoons \tfrac{1}{2}Na_2CO_3 + \tfrac{1}{2}H_2O + \tfrac{1}{2}CO_2$$

lies well over to the left. Extremely little decomposition occurs at 25 °C.

As the temperature is increased, AG° becomes less positive, the equilibrium pressure of $H_2O$ and $CO_2$ increases as product concentrations increase and reactant is consumed.

Active decomposition occurs under normal atmospheric pressure when the equilibrium preesure of $H_2O$ and $CO_2$ reaches a value equal to atmospheric pressure, which occurs about 105 °C.

At this point, the actual free energy of the reactant equals the summed free energies of the products, for equivalent amounts.

At the decomposition temperature, an equilibrium exists in which AG = 0. Thus AHactual = TASactual, and if these values for AH and AS are known, the decomposition temperature can be calculated.

AH° and AS° can be obtained or deduced from tables. They are not the actual values at the decomposition temperature, but they are close enough to give an answer within 5 degrees or so of the experimentally determined value.

The effect of heating and the ultimate decomposition of $NaHCO_3$ is thermodynamically very similar to the effect of heating and the ultimate boiling of water.

Just as the boiling point of water is to someextent dependent on atmospheric pressure, then so also is the decomposition of sodium hydrogencarbonate dependent to some extent on atmospheric pressure.

4. The thermal decomposition of the decahydrate, $Na_2SO_4.10H_2O$, can be considered in the same way as the boiling of water or the decomposition of sodium hydrogencarbonate.

That is to say, at what temperature does the free energy of the solid hydrate equal the free energy of water vapour at one atmosphere. At this temperature the water vapour would actively be lost to the surroundings from an open vessel ... a kind of boiling.

The temperature at which loss of water of crystallisation will therefore occur is that temperature at which AG for the equilibrium sytem (if the vessel were closed) would be zero. It would be therefore that temperature at which the actual enthalpy change and the actual entropy change would be such that

$$T = \frac{AH}{AS}$$ T is the transition temperature

The standard values obtained or deducible from tables are close enough to give a fairly accurate idea of the temperature at which the transition from decahydrate to anhydrous salt will occur at atmospheric pressure.

| Reaction | $Na_2SO_4.10H_2O$ | $\rightleftharpoons$ | $Na_2SO_4$ | + | $10H_2O$ |
|---|---|---|---|---|---|
| From tables<br>$H^o$ | -4319 | | -1385 | | 10 x -285.5 kJ m |

from which $AH^o$ = -1385 + -2855 - -4319 kJ mol$^{-1}$

= +79.0 kJ mol$^{-1}$

| | | | | | |
|---|---|---|---|---|---|
| From tables<br>$S^o$ | 593.6 | | 149.3 | | 10 x 69.8 J K$^{-1}$ m |

from which $AS^o$ = 149.3 + 698 - 593.6 J K-1 mol-1

= 253.7 J K$^{-1}$ mol$^{-1}$

= 0.254 kJ K$^{-1}$ mol$^{-1}$

Therefore $T = \frac{AH}{AS}$ in general at equilibrium

$= \frac{79.0}{0.254}$ K

= 311 K

= 38 °C which is very close to the value you should obtain experimentally.

Study Unit 11 What you should know.

You should 1. be able to interpret selected practical work in terms of free energy change.

---

Question 1 Ice and water can co-exist at equilibrium as long as heat is neither gained nor lost. If ice and water contained in a closed jar be placed in a warm room, which part of the entire assemblage would you regard as the 'system'?

| | |
|---|---|
| 1 The ice | 2 The ice and the water |
| 3 The ice, water and jar. | 4 The entire contents of the warm room. |

Question 2 An ionic salt, AB, dissolves in water to give a saturated solution. Which of the following is the equilibrium constant for the equilibrium between undissolved salt and dissolved salt?

| | | | |
|---|---|---|---|
| 1 $\frac{[A^{+}(aq)][B^{-}(aq)]}{[AB(s)]}$ | 2 $\frac{[AB(aq)]}{[AB(s)]}$ | 3 $\frac{[A^{+}(aq)][B^{-}(aq)]}{[AB(}$ | 4 $[A^{+}(aq)][B^{-}(aq)]$ |

Question 3 What is the pressure inside an evacuated ampoule half full of water placed in an oil bath at 100 °C?

| | |
|---|---|
| 1 Zero | 2 Less than 1 atmosphere |
| 3 Equal to 1 atmosphere | 4 More than 1 atmosphere |

| | |
|---|---|
| Question 1 | The ice and water could be regarded as the system, the jar as the enclosing boundary, and the room as the surroundings. |
| Question 2 | |
| Response 1 | This response is correct, but AB(s) is not taken into consideration. |
| Response 2 | This response is incorrect. |
| Response 3 | This response is incorrect; the denominator term is wrong. |
| Response 4 | This response is correct. |
| Question 3 | Response 3 is correct. The equilibrium saturated water vapour pressure at 100 °C is 760 mmHg. |

The first time you go through the subject, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don't understand it, but by this time you are so used to the subject it doesn't bother you any more.

On thermodynamics by Sommerfeld

# POCKET ITEM 5

# THERMODYNAMICS APPROACH TEST

UNIVERSITY of GLASGOW

Research in Chemical Education

# ENERGIES IN MACROSCOPIC SYSTEMS

Dear pupil,

You are asked to consider the following questions which deal with energies in macroscopic systems and their relationship with chemical equilibrium.

The questions are of familiar construction, one of the four options A to D being a correct response to be selected by you.

The questions have been designed to find out which aspects of this part of the Certificate of Sixth Year Studies syllabus cause you trouble. For this reason an additional option E has been offered in each question in the event that you do not know which option is correct. It is very important that you select option E if you do not know which option is the correct one. Please do not guess. For the purposes of this research an E is infinitely more informative than a guess, so please do not hesitate to select E to even a majority of the questions if you feel justified in doing so. The results of this test will not count for or against you in any way.

John MacDonald

1. Which one of the following lists differs in a significant way from the other three?

A Copper, heat, neon.
B Helium, tin, water.
C Argon, zinc, light.
D Gold, sound, krypton.
E I can see no significant difference between these lists.

---

2. When water at 100 °C absorbs heat and changes to steam at 100 °C,

A the potential energy of the molecules remains the same but their kinetic energy increases.
B the kinetic energy of the molecules remains the same but their potential energy increases.
C both the potential energy and the kinetic energy of the molecules increase.
D neither the potential energy nor the kinetic energy of the molecules increases.
E I do not know how the potential energy and/or the kinetic energy of the molecules is affected.

---

3. A spontaneous reaction has the following characteristics:

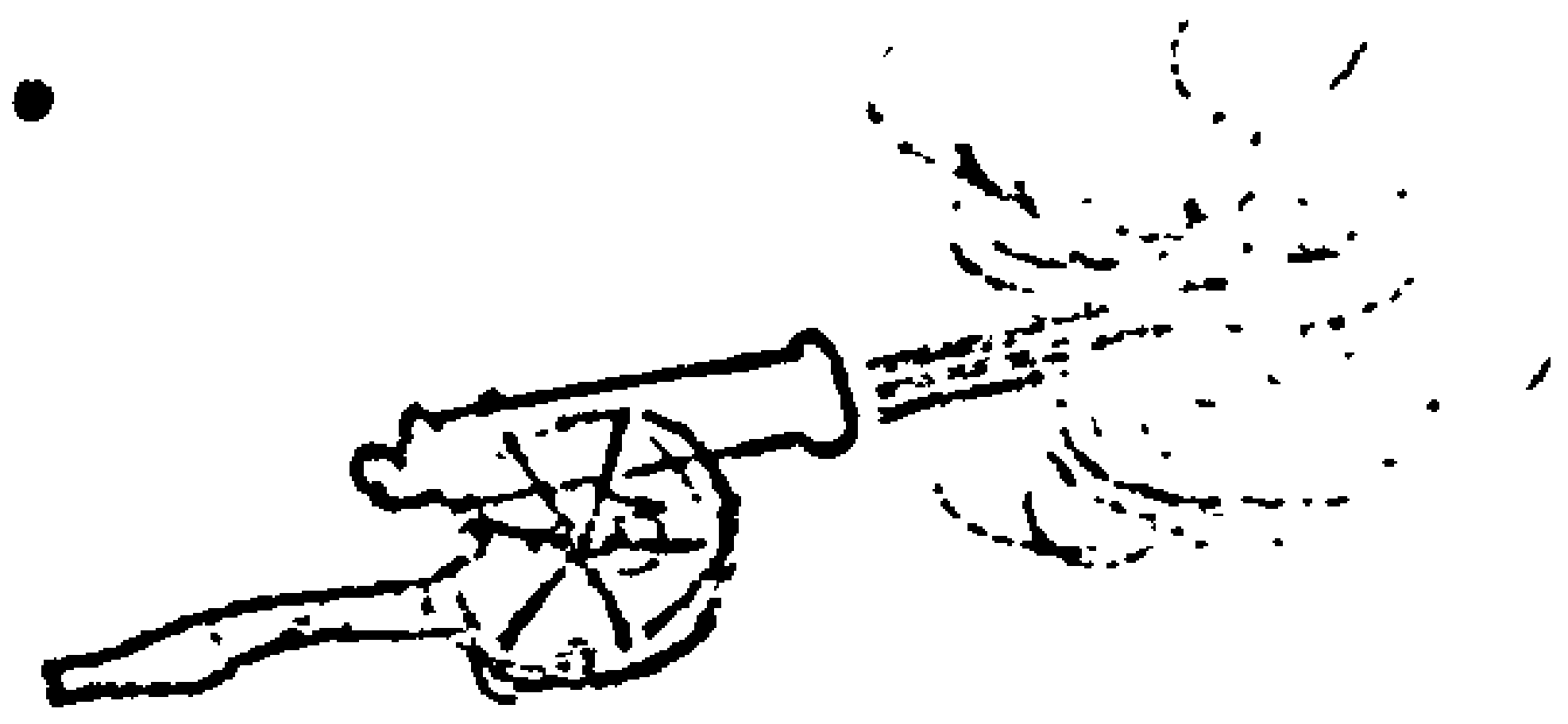
AH = -20 kJ $mol^{-1}$
AG = -60 kJ $mol^{-1}$
TAS = +40 kJ $mol^{-1}$

The reaction

A will always be exothermic no matter how it is performed.
B will be exothermic if 30 kJ of work are done by it.
C will be endothermic if 30 kJ of work are done by it.
D will be endothermic when performed irreversibly.
E I do not know which of these options is correct.

---

4.



When a cannon is fired blank, x joules of heat are produced in and around the cannon.

When an identical charge of powder is used to fire off a cannon-ball, y joules of heat are produced in and around the cannon.

Which of the following statements is correct?

A x is greater than y.
B x is equal to y.
C x is less than y.
D It depends on the quality of the gunpowder.
E I do not know.

---

5. For a reaction, AH = -100 kJ $mol^{-1}$ and AG = -60 kJ $mol^{-1}$. How much heat would the surroundings gain during the reversible operation of the reaction?

A 100 kJ
B 60 kJ
C 40 kJ
D 160 kJ
E I do not know.

6. A mixture of cold hydrogen and oxygen contained in a closed vessel reacts exceedingly slowly. Under such circumstances, the reaction

A will yield the maximum available/optional work.
B is being operated reversibly.
C is not spontaneous.
D is held back by a kinetic snag.
E I do not know which of these options is correct.

7. Which of the following is a characteristic of a reaction which is operated such that none of the available/optional work is taken as work?

A It is an ideal limit at which a minimum heat is evolved.
B Its occurrence results in a maximum heat evolved.
C It cannot be observed.
D Its occurrence is opposed by an equal force.
E I do not know which of these options is correct.

8. Spontaneity requires that

A the free energy change must be negative.
B the enthalpy change must be negative.
C the entropy energy change of the reacting system must be positive (T being constant).
D $q_{rev}$ must be negative.
E I do not know which of these options is correct.

9. When all the free energy of a reaction is used to do work, the heat change with the surroundings is

A AH.
B greater than AH.
C $q_{rev}$.
D less than $q_{rev}$.
E I do not know.

10. The data:

$$\begin{aligned} AH &= -100\ \text{kJ mol}^{-1} \\ AG &= -60\ \text{kJ mol}^{-1} \\ TAS &= -40\ \text{kJ mol}^{-1} \end{aligned}$$

refer to a reaction during the occurrence of which

A 100 kJ of heat are expelled while at the same time 60 kJ of work are done.
B When no work is done, AG becomes zero.
C 40 kJ of heat are expelled if 60 kJ of work are done on something in the surroundings.
D a maximum of 100 kJ of work can be done if the reaction is carried out reversibly.
E I do not know which of these options is correct.

11. A stretched elastic band (at room temperature) is released. It contracts spontaneously to its original shape. Given that the entropy of the rubber <u>increases</u> as it contracts, would you consequently expect the temperature of the rubber

A to increase?
B to remain the same?
C to decrease?
D Or is it not possible to say without more information?
E I do not know which of these options is correct.

---

12. The enthalpy change associated with a particular process is positive. The increase in entropy value associated with the same process is positive. Which one of the following statements is correct? The reaction will

A tend to be spontaneous at lower temperatures.
B tend to be spontaneous at higher temperatures.
C be spontaneous at any temperature.
D never occur spontaneously, no matter what the temperature.
E I do not know which of these options is correct.

---

13. Ice will melt spontaneously at 1 °C because

A the entropy of water is greater than the entropy of ice.
B the entropy of the surroundings decreases as the ice melts.
C the change in total entropy of melting ice and surroundings is positive.
D the change in total entropy of melting ice and surroundings is negative.
E I do not know which of these options is correct.

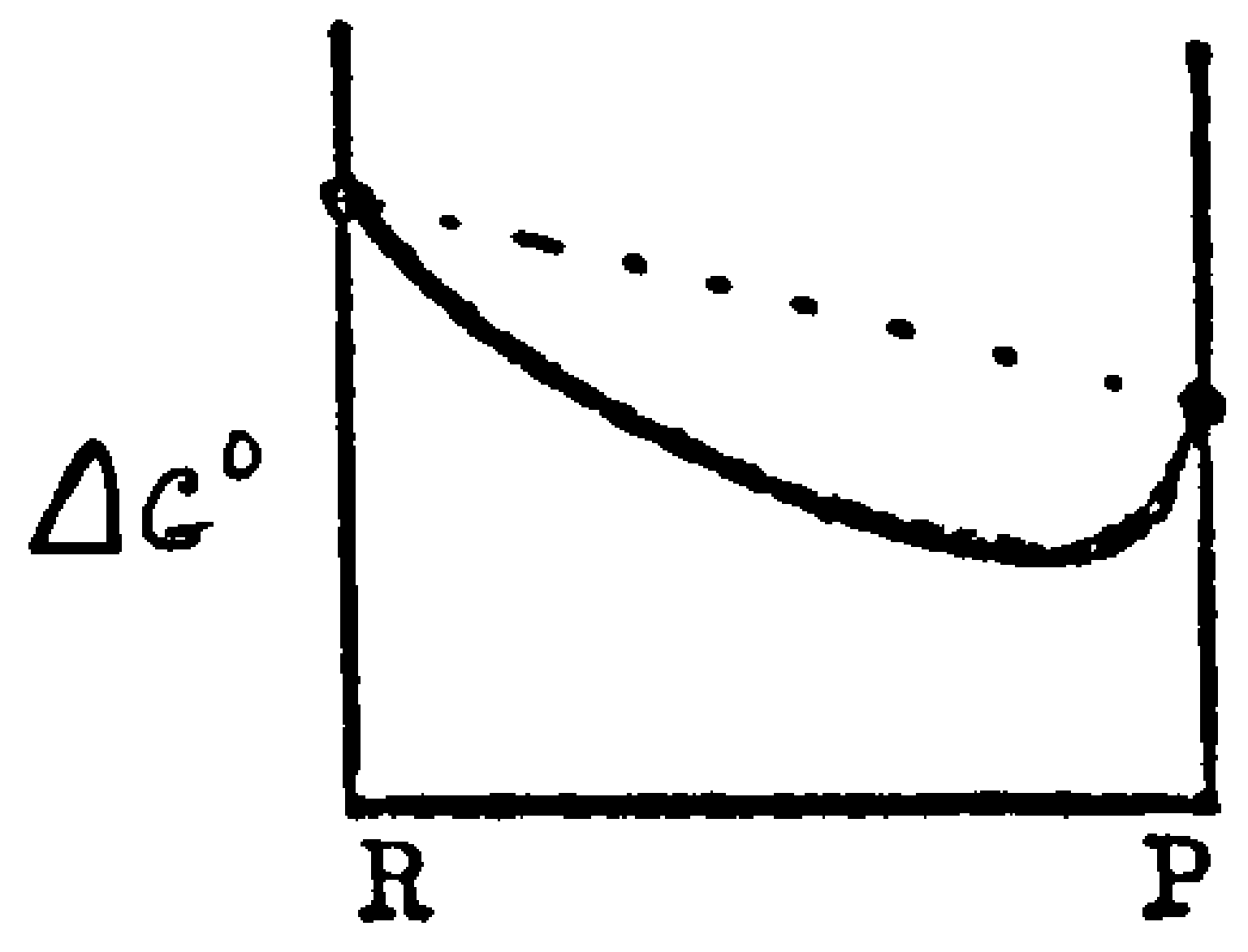
---

14. Here is an equilibrium system:

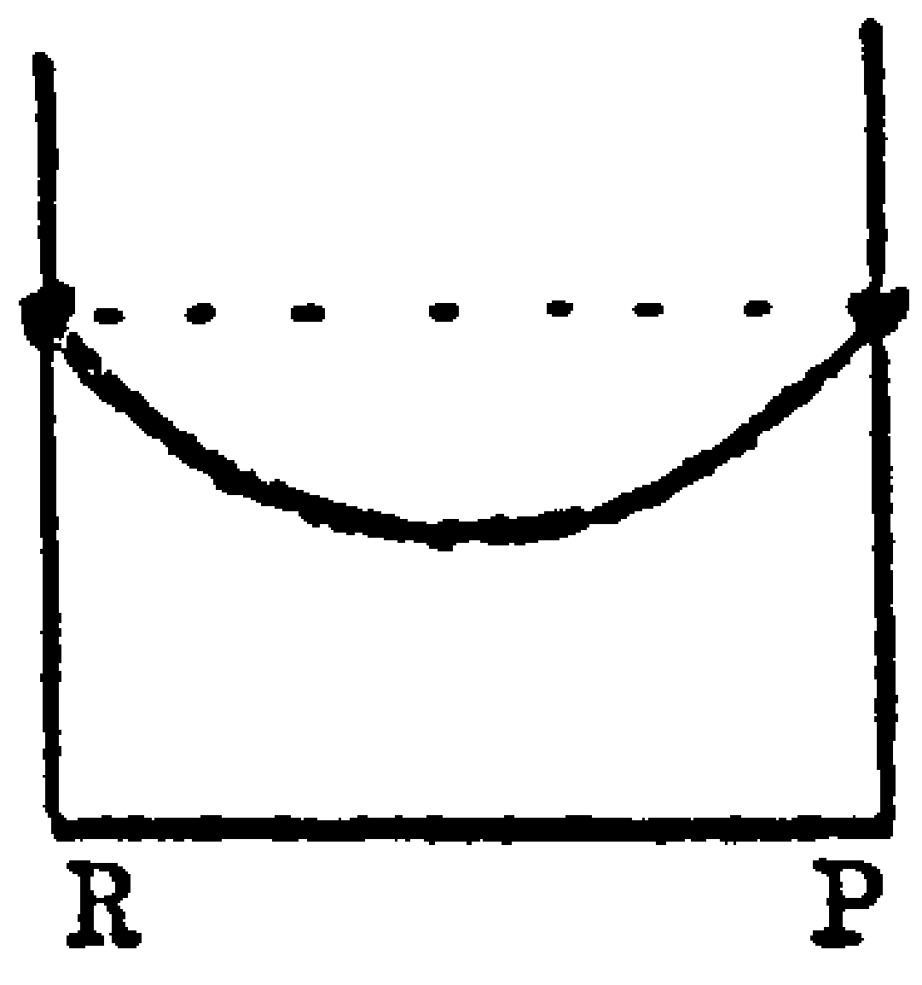
$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$$

At room temperature, ΔG° is positive. Which of the following free energy profiles corresponds to this equilibrium system?

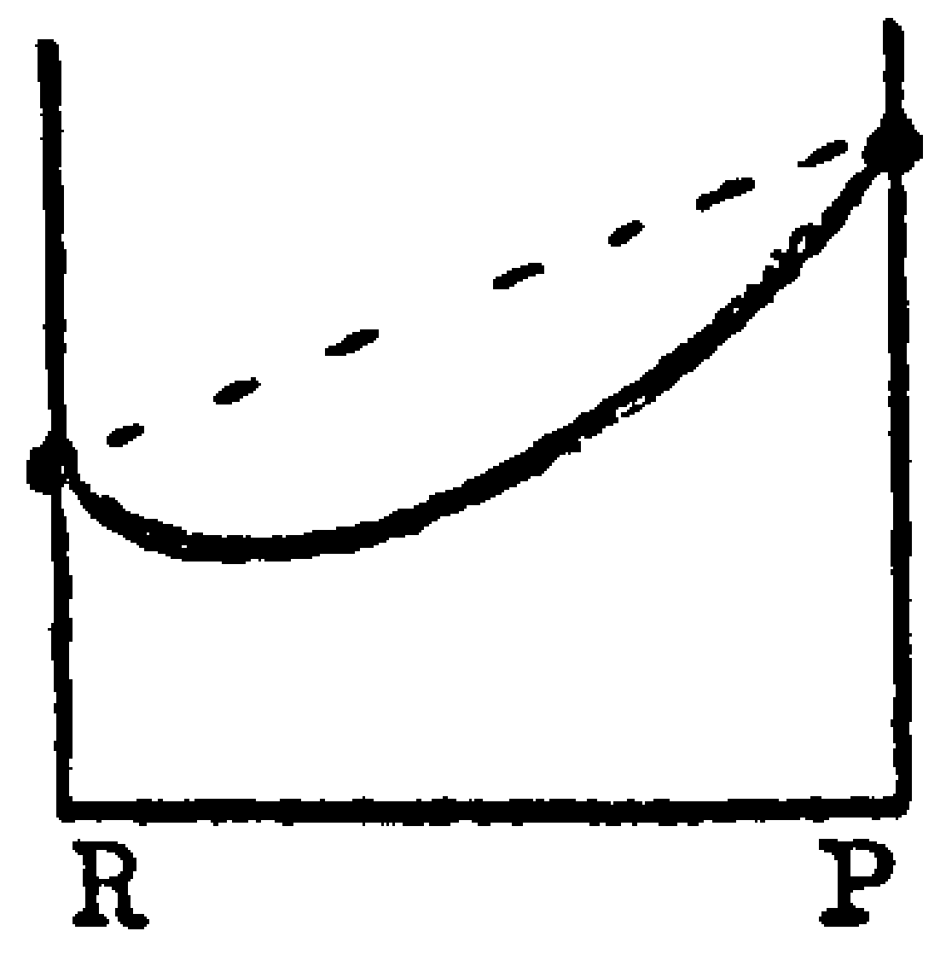
A



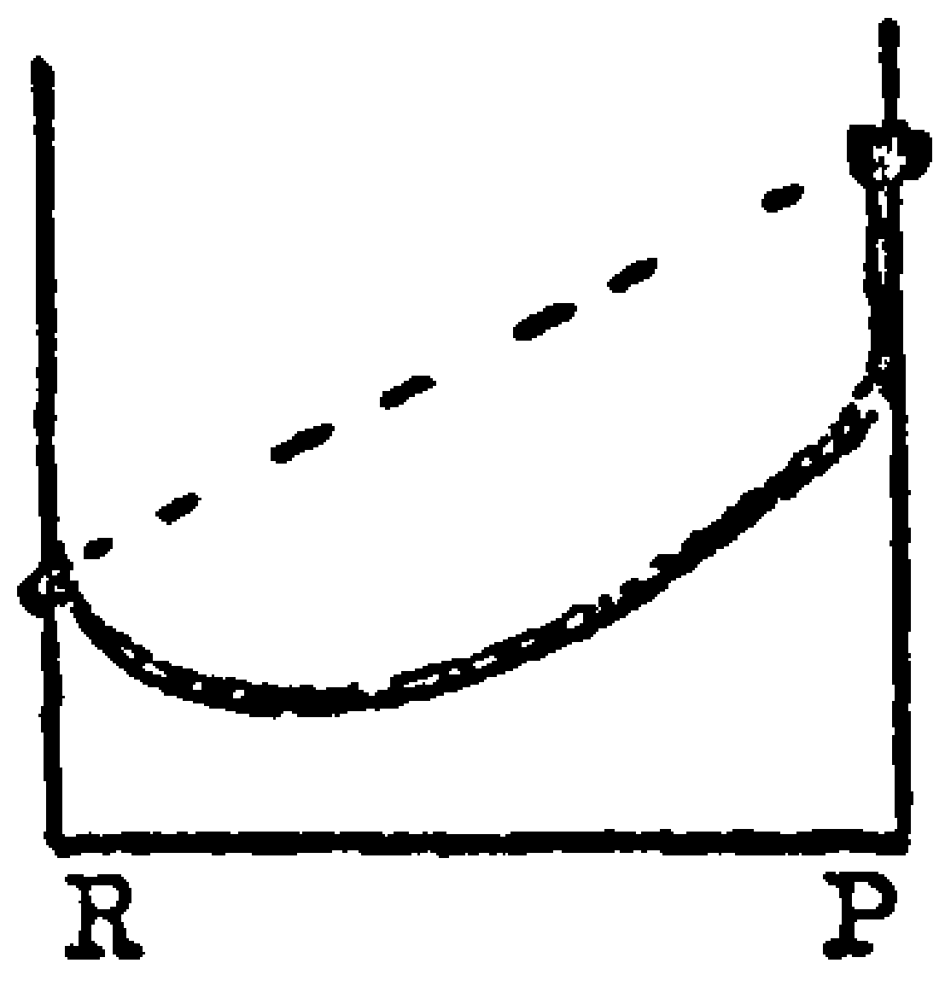
B



C



D



E I do not know which of these profiles is the correct one.

---

15. When the equilibrium constant for a system is 1, the composition of the equilibrium mixture consists of

A 50% reactant plus 50% product.
B slightly more product than reactant.
C slightly less product than reactant.
D It is not possible to say without more information of the particular equilibrium system.
E I do not know which of these options is correct.

16. Which of the following processes would be accompanied by a decrease in entropy of the substances involved?

A Decomposition.
B Boiling.
C Polymerisation.
D Combustion.
E I do not know.

---

17. Change in free energy is AG; change in entropy energy is TAS. Which of the following options is <u>incorrect</u>?

A At constant temperature, both these changes are potential energy changes.
B At constant temperature, the former is a potential energy change while the latter is a kinetic energy change.
C The former may or may not be used to do work, while the latter may not be used to do work.
D Free energy has an 'organised' quality, while entropy energy has a 'disorganised' quality.
E I do not know which of these options is <u>incorrect</u>.

---

18. Which of the following statements about endothermic reactions is correct?

A Endothermic reactions are spontaneous if accompanied by a large enough increase in entropy energy.
B Endothermic reactions are never spontaneous at less than room temperature.
C Spontaneous endothermic reactions become non-spontaneous at higher temperatures.
D Endothermic reactions become exothermic at lower temperatures.
E I do not know which of these options is correct.

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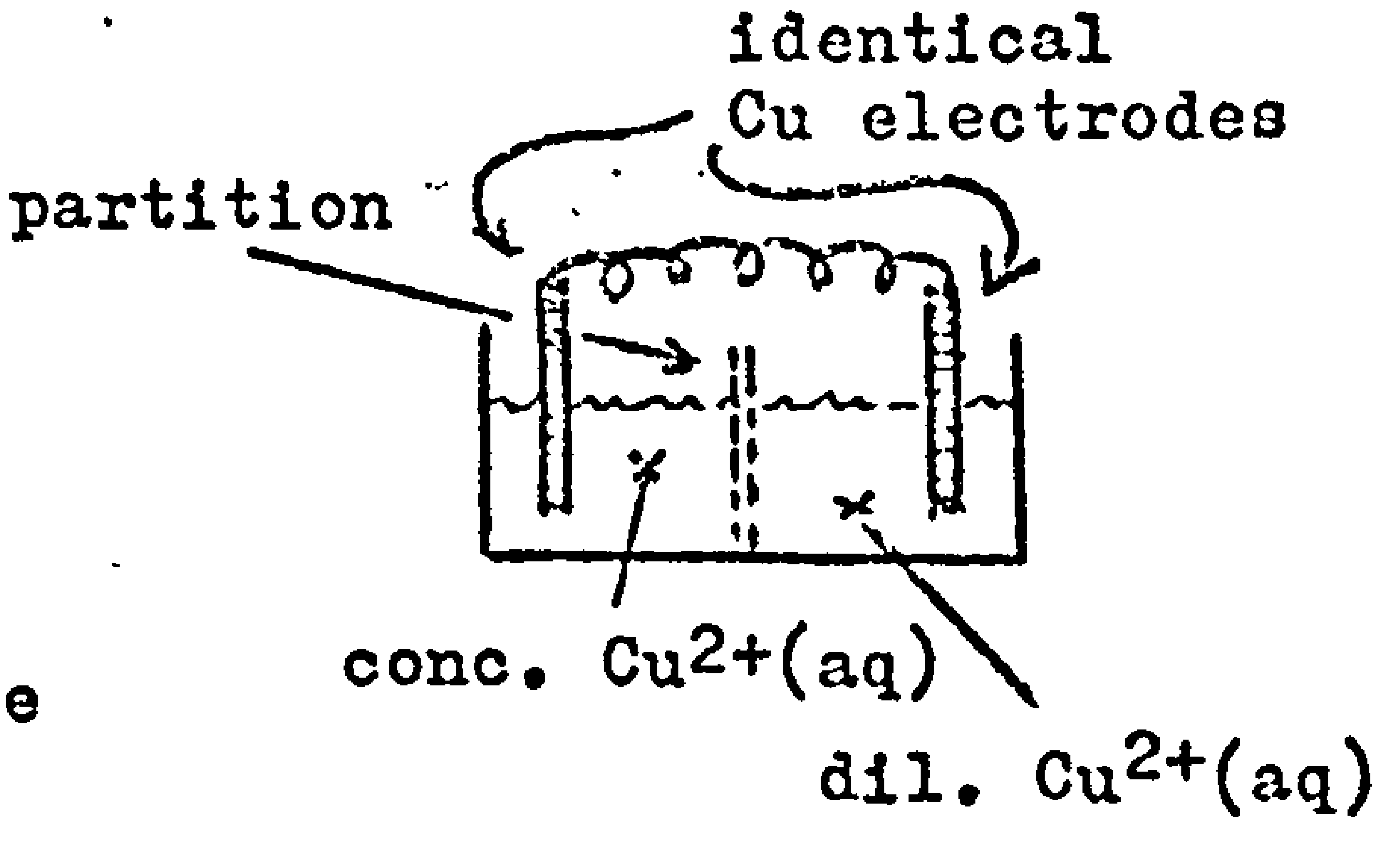
19. A concentration cell is shown opposite.



Which of the following options is <u>incorrect</u>?

A concentration cell eventually stops working when

A the solutions on each side of the porous partition have acquired the same concentration.
B the difference between the actual electrode potentials of each half cell is zero.
C the difference between the free energies of the contents of each half cell (mole for mole) is zero.
D when the concentration of solute in one half cell has fallen to zero.
E I do not know which of these options is <u>incorrect</u>.

20. In a system at equilibrium, departure from equilibrium will be accompanied by

A a negative enthalpy change.
B a positive enthalpy change.
C a negative free energy change.
D a positive free energy change.
E I do not know which of these options is correct.

21. If the free energy change accompanying a reaction is AG = -200 kJ mol$^{-1}$, the reaction

A will occur rapidly.
B will be accompanied by a negative enthalpy change.
C cannot be carried out reversibly.
D will be spontaneous, but may take a very long time to occur.
E I do not know which of these options is correct.

22. A plant grows in sunlight because

A the free energy change of the growing plant is positive.
B the entropy change in the sun is negative.
C all reactions are reversible to some extent.
D work is done on the plant by sunlight.
E I do not know which of these options is correct.

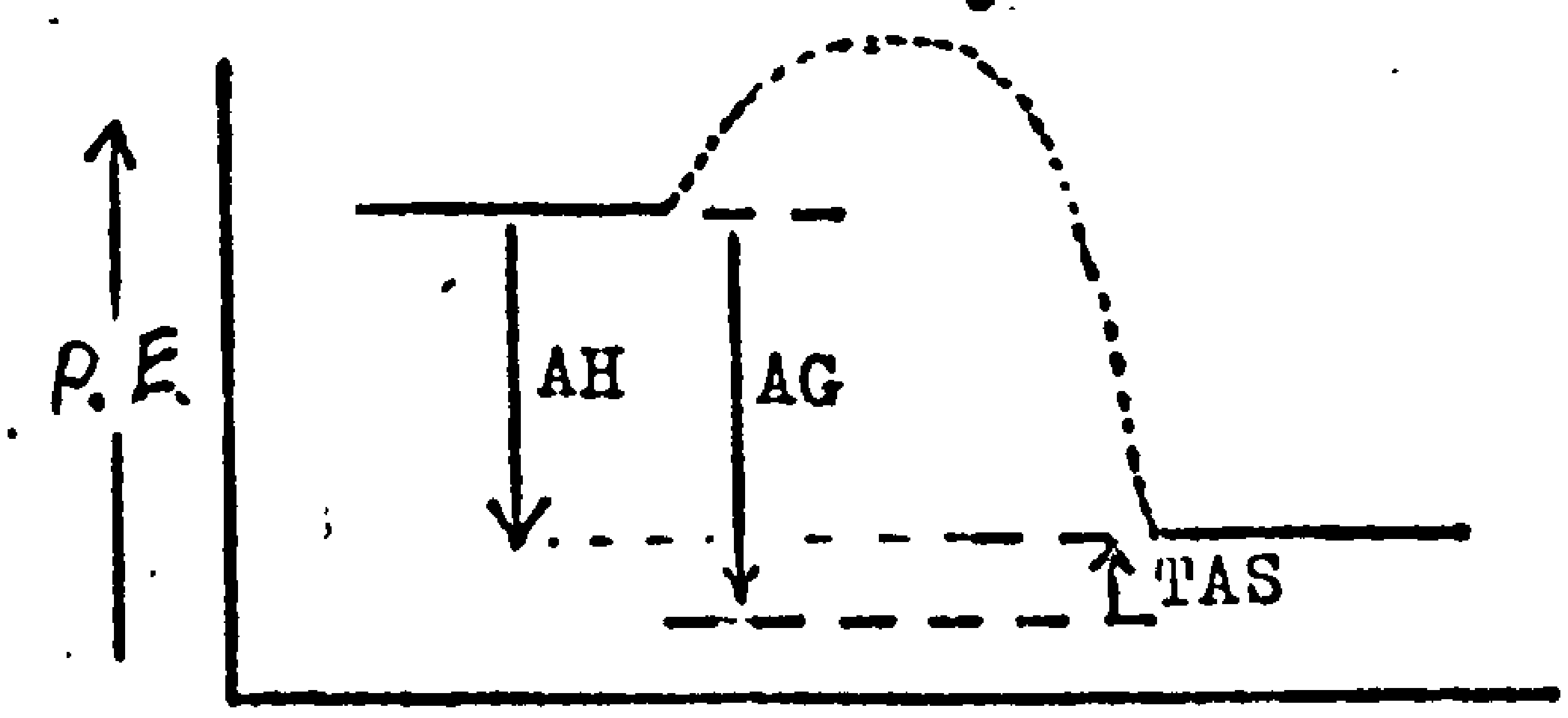
23. Which of the following lists contains an 'odd man out'?

A Oxygen, petrol, mist, sawdust.
B Sand, steam, fluorine, paraffin.
C Ethanol, flour, heat, nitrogen.
D Chlorine, methanol, silica, vapour.
E I do not know.

24. The enthalpy change for a reaction is AH = -60 kJ mol$^{-1}$. When the reaction is carried out in a cell such that maximum work is done, AG being equal to -70 kJ mol$^{-1}$, how much heat is exchanged with the surroundings?

A 60 kJ are evolved to the surroundings.
B 10 kJ are evolved to the surroundings.
C 10 kJ are absorbed from the surroundings.
D 70 kJ are absorbed from the surroundings.

25.



This enthalpy diagram refers to one of the following equations. Which one?

A $HgO \rightarrow Hg + \frac{1}{2}O_2$ AH +ve, AG -ve, TAS +ve.
B $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$ AH +ve, AG +ve, TAS -ve.
C $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$ AH -ve, AG -ve, TAS +ve.
D $N_2 + 3H_2 \rightarrow 2NH_3$ AH -ve, AG -ve, TAS -ve.
E I do not know which one of these equations is depicted by the diagram.

---

26. For a spontaneous reaction in a closed system

A AG may be positive.
B AG is always negative.
C TAS is always negative.
D TAS is never negative.
E I do not know which of these options is correct.

---

27. Which of the following statements is a nonsense statement?

A When water boils to steam, entropy is created.
B A reaction which is exothermic increases the entropy of the surroundings.
C Entropy is a measure of disorder.
D Every occurring reaction is accompanied by an increase in total disorder.
E I do not know which of these statements is a nonsense statement.

---

28. If the ionisation:

$$2H_2O(l) \longrightarrow H_3O^+(aq) + OH^-(aq)$$

were to go to completion, it would be accompanied by an increase in free energy (and a simultaneous decrease in total entropy).

The ionisation, in fact, proceeds to a slight extent to give an equilibrium mixture:

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

The reason for this is that

A there is a decrease in free energy until the equilibrium composition is attained.
B all reactions proceed to some extent.
C a slight increase in free energy is allowable.
D molecules continually collide, and so some ions are bound to form.
E I do not know which of these options is correct.