IMPROVEMENTS IN THE PERFORMANCE ANALYSES OF INTERNAL COMBUSTION ENGINE CYCLES.

by

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CONTENTS.

INTRODUCTION & SUMMARY

The purpose of this thesis is to collate the analytical and experimental work carried out by the writer in the field of Applied Thermodynamics concerning the performance analyses of internal combustion engine cycles, actual and theoretical. In view of the diversity of the subject matter the material is presented in eleven separate, though not unrelated, sections, so that each section is to a certain extent complete in itself. The work divides itself into three main parts, the determination and tabulation of properties of gases, the construction of energy charts and the application of a Second Law Analysis to theoretical and actual cycles.

The publication of "Tables of Properties of Gases"(1)* by Dr. E. W. Geyer and the writer was the result of a combined effort to produce tabulated values of properties of gases, having in mind the requirements of calculations connected with dissociation at high temperatures and pressures in engine cylinders. All the calculations appearing in this thesis are based on the properties appearing in the above publication. It is intended to avoid repetition of the principles set down in the book but to furnish some additional background information. Accordingly the writer

*Numbers refer to bibliography on page 130 has prepared a section on specific heats which is in the main historical and is designed to lead up to a short section on tabulated values of thermal properties. The latter section includes discussion of "Gas Tables" (2) of which a review by the writer was published in Engineering (3). In "Tables of Properties of Gases" the establishment of the equilibrium constant was by means of the van't Hoff equilibrium box. A more elegant method is obtained using Gibbs' function and a treatment taken from Roberts (4) and, modified, is presented here.

The natural development from tabulated properties is to the construction of energy charts, especially for dissociated gas mixtures. Apart from the work of Hershey, Eberhardt and Hottel (5) this was not a field where there was much previous work. The writer has had to be content with providing the basic theory and a simple illustration of the use of such a chart (6). The computation of charts similar to those of the above workers would constitute too heavy a task for a single worker. However, the theory as reproduced here is an improved version of the published work and the writer believes that this contribution to the theory is to a certain extent original. The particular point is emphasised in both sections 5 and 7.

A new approach to the assessment of plant performance is made possible by means of the Second Law Analysis, a method of analysis suggested first by Keenan(7) and one which does not seem to have been developed. It was with a view to renewing interest in this method of analysis that the writer published two articles(8,9), where the analysis was shown for a number of different plants. The object of a Second Law Analysis is to give a numerical value to the thermodynamic loss or "irreversibility" in any process. This is done by means of the concept of available energy or availability, to use the term Keenan coined. Although this type of analysis enables one to put a figure on a thermodynamic loss it does not point the way to removing the loss, and for a quick and general assessment of performance the conventional energy account is naturally to be preferred. In certain cases where a comparison between one plant arrangement and another is being made, particularly in the more complicated arrangements, the Second Law Analysis is of value. The method has the advantage of a thermodynamic basis, an advantage which shows itself very clearly in the application to combustion chamber performance. It may be that with the complexities of future plant a more refined method of analysis such as this will come into general use. In this thesis the application of the analysis is to internal combustion engine performance. Except for an application given by Keenan(10), and this is to an ideal cycle, the writer knows of no other work where the analysis is given for an internal combustion engine, either in a theoretical or actual case. The concluding sections of this thesis are devoted to the application of the Second Law Analysis to ideal and actual cycles.

The performance of a petrol engine operating on an idealised cycle is given for a number of mixture strengths and compression ratios. The theoretical results are compared with the actual results of tests carried out by the writer, the purpose being to show that the theoretical values have some connection with actual performance although the gap between actual and theoretical performance is somewhat large due to the type of experimental unit used. Although an ideal cycle does not form a good basis for a Second Law Analysis the problem posed offers the opportunity of showing the application when there is dissociation, how to deal with rich mixtures and how to calculate and correct entropy values to a common basis. The skill gained in dealing with ideal cycles is of great use when dealing with actual cycles. The results are presented in such a manner and in such detail that they can be readily checked.

Three tests were carried out on a Gas Engine and four tests on an Oil Engine, the results being used to yield a Second Law Analysis as well as the conventional energy accounts. In the case of the Gas Engine the analysis appear to be very satisfactory but in the case of the Oil Engine such good agreement is not obtained. In order to analyse each process occurring in the engine cylinder it is necessary to estimate that point in the cycle when combustion is complete. This may be done by plotting the indicator diagrams to a logarithmic base for pressure and volume, and the point on the expansion line where the slope changes may be taken as a guide in this estimate. In the case of the Gas Engine this issue does not arise since the attaining of the maximum pressure would appear to correspond with the completion of combustion, but in the Oil Engine such is not the case. Examination of the results as a whole shows, as would be expected, that the largest loss occurs during the combustion process. The loss due to the release of the cylinder gases is much the same for all the tests and, indeed, not much different from the corresponding results obtained in Table 9.23 for the theoretical cycles. The loss during compression is greatest for the Oil Engine due to the higher compression ratio and consequently larger heat flow. The figures for expansion are not comparable.

In conclusion one may say that a Second Law Analysis enables one to make a quantitative study of thermodynamic losses not only in internal combustion engines but also in all other types of plant. The concept of available and unavailable energy has an instructional value particularly with respect to the function entropy which is seen to be a more useful parameter of state than many would care to believe. In certain cases the analysis provides a proper thermodynamic basis for assessing performance by eliminating empirical factors. The application of the method of analysis to problems involving both friction and heat transfer at the same time would constitute a challenge to be met in the future.

List of Symbols.

All pressures are absolute.

Symbol	Designation	Units
P	Pressure	atmosphere: lb/ft^2
p	Pressure	lb/in^2
V	Volume	ft^3
v	Volume	ft^3/lb.
T	Temperature	°F. abs.
E	Internal Energy	B.T.U./lb.mol.; B.T.U./lb.
H	Enthalpy	B.T.U./lb.mol.; B.T.U./lb.
S	Entropy	B.T.U./lb.mol.°F.
s	Entropy	B.T.U./lb.°F.
R	Universal Gas Constant.	ft.lb/lb.mol.°F.
R	Gas Constant	ft.lb/lb.°F.
J	Mechanical Equivalent	ft.lb/B.T.U.
$\frac{R}{J}$		1.9869 B.T.U./lb.mol.°F.
Q	Heat quantity	B.T.U./lb.mol.; B.T.U./lb.
W	Mechanical work	ft.lb.; B.T.U.
$H_{p(v)}$	Lower heat of reaction at constant pressure (volume)	B.T.U./lb.mol.; B.T.U./lb.
K_p	Equilibrium constant	Pressures in atmospheres
G (or F)	Gibbs' function (F is used in Tables of Properties of Gases)	B.T.U./lb.mol.°F.
m	Number of mols.	
A.M.W.	Apparent molecular weight.	lb.

Symbol.	Designation	Units
a.e.	Available energy	B.T.U./lb.
u.e.	Unavailable energy	B.T.U./lb.
T_o	Datum temperature	^oF. abs.
p_o	Datum pressure	lb/in^2.
b	Availability function	B.T.U./lb.
u	Velocity	ft/sec.
C	Specific heat	B.T.U./lb.mol.F^o.
c	Specific heat	B.T.U./lb.F^o.
γ	Isentropic index, ratio of specific heats	
x	Mols. of CO per mol. of mixture	
y	Mols. of H_2 per mol. of mixture	

SPECIFIC HEATS.

By the very nature of the problem of the analysis of the performance of internal combustion engines experimenters have concerned themselves with thermal properties, viz., the specific heats. Examination of a few published works over the last fifty years shows that a comprehensive survey may be made by dividing this period into three, a period prior to 1920, a period from 1920 to 1935 and a period subsequent to 1935. The years 1920 and 1935 may be taken as the approximate dates marking the transition from one period to the next. In the period prior to 1920 the determination of specific heats was made mainly by calorimetric means and the results of experiments showed great variation. Nevertheless, such experimenters as Hopkinson(11) and Clerk(12) were not deterred from examining the performance of internal combustion engines. The end of the early period was marked by the introduction of alternative methods of measuring specific heats, notably the theoretical estimates of the physicist. This led to a thorough examination of all specific heat data resulting in the rejection of values now known to be outdated. In 1924 Partington and Shilling(13) publishad a comprehensive survey of the literature on specific heats. Pye(14) and Goodenough(15) who both contributed much to the analysis of the internal combustion engine also surveyed the literature on specific heats. During the period from 1924 to 1935 engineers became increasingly aware of the variation of specific heat with temperature and the practice of expressing the specific heat of a gas as a linear or quadratic function of temperature became widespread. The year 1935 pointed the way to a new period, a period when the theoretical determinations of the physicist were to match the best calorimetric measurements. Further, it was shown that the linear and quadratic relations in terms of temperature were not a proper means of expressing the new specific heats. In 1940 the third and current period was established by Heck(16) who published tabulated values of thermodynamic functions, such as internal energy, enthalpy and entropy and the clumsy expressions for specific heats disappeared. It is true to say that at the present time tables of properties of gases are now used for all serious work where a reasonable degree of accuracy is warranted. Charts and graphs based on the latest values of the specific heats are being used.

The period prior to 1920

The best survey of this period is given by Pye(14) and it will suffice to examine his contribution along with that of Goodenough(15) without examining in detail the references which they give.

The methods of measurement were of three types:

(a) Constant pressure experiments, the gas being heated externally, usually at atmospheric pressure.

(b) Experiments of a special nature devised by Clerk(17) in which a given mass of gas was alternately compressed and expanded.

(c) Constant volume experiments or explosion experiments.

Both Pye and Goodenough agree that the chief experimenters under type (a) were Reynault(i)*, Wiedmann(ii), Holborn and Austen(iii), Holborn and Henning(iv), and Swann(v) and under type (c) were Mallard and Le Chatelier(vi), Langen(vii), Pier(viii) and Bjerrum(ix). The conclusions which Pye and Goodenough drew from the results were much the same. They both attached great weight to the low temperature measurements of Swann and also to the work of Bjerrum and Pier. The problem which faced Goodenough and how he weighted his own values is best shown by means of his own diagram (Fig.18), Fig (1.1).

The various straight lines represent the equations proposed by Langen, Pier, Holborn and Henning and Lewis and Randall (x). Further Goodenough compared his values for three gases with those which Pye suggested as being the best

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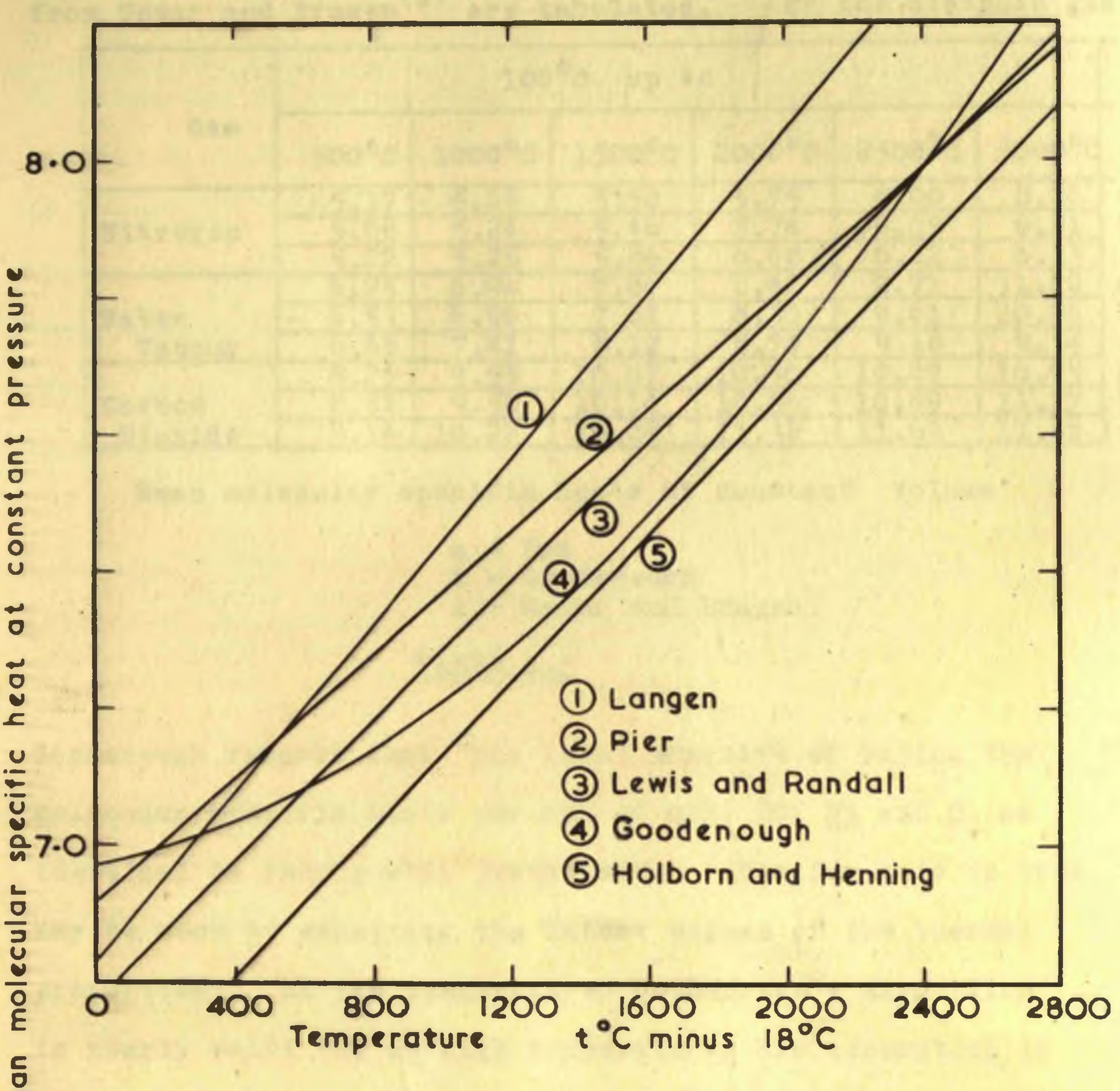
* A list of these references is given at the end of the section, page 14.



SPECIFIC HEATS OF DIATOMIC GASES, O_2, N_2, & CO

FIG.1.1

mean values. The following table 1.1 shows the comparison and, in addition, the corresponding mean values taken from Geyer and Bruges(1) are tabulated. Of the diatomic gases Goodenough remarks that "the usual practice of taking the molecular specific heats per mol of air, CO, N_2 and O_2 as identical is fairly well justified". How far this is true may be seen by examining the latest values of the thermal properties. At low temperatures Goodenough's assumption is nearly valid but at high temperatures his assumption is not acceptible. In order to reconcile the measurements of Swann and Bjerrum Goodenough found that it was necessary to use a second degree equation to express the specific heat in terms of the temperature. This may be seen by examining Fig. 1.1.

Gas	100°C. up to						
	500°C	1000°C	1500°C	2000°C	2500°C	3000°C	
Nitrogen	5.17	5.28	5.50	5.75	6.00	6.30	a
	5.08	5.24	5.46	5.74	6.09	6.51	b
	5.22	5.28	5.86	6.08	6.22	6.33	c
Water Vapour	6.25	6.94	7.64	8.42	9.71	11.20	a
	6.53	6.96	7.61	8.50	9.61	10.96	b
	6.68	7.41	8.12	8.70	9.18	9.54	c
Carbon Dioxide	8.25	9.55	10.07	10.50	10.87	10.95	a
	8.52	9.50	10.14	10.56	10.89	11.17	b
	9.14	10.22	10.88	11.32	11.63	11.88	c

Mean molecular specific heats at constant volume

a - Pye
b - Goodenough
c - Geyer and Bruges.

TABLE 1.1

The value of Pye's survey lies not so much in the criticism of the experimental results as in his analysis of the technical difficulty of carrying out the experiments. He makes the following observations which were true in 1920 and which would be true at the present time were experiments of types (a), (b) and (c) to be carried out. The fact that theory has advanced does not invalidate his survey. A temperature limit of 1400°C. is imposed on constant pressure experiments, a temperature far below the maximum attainable in an internal combustion engine. The experiments of Clerk are subject to a wide range of experimental error since the accuracy of the values obtained depends on the correct allocation of the heat loss to the cylinder walls between the compression and expansion strokes. It seems very difficult to obtain reliable results by experiments of this kind. The reliability of the results of the explosion experiments "depends entirely", writes Pye, "on an accurate allowance being made for any loss of energy by conduction or radiation up to the point of maximum pressure". It is assumed that the gases are in equilibrium when the maximum pressure is reached and that the effect of dissociation can be neglected. Pye concludes his contribution by comparing the observed and calculated volumetric specific heats for the triatomic molecule CO_2. There is close agreement and it must have seemed probable to experimenters that values calculated on the basis of the new quantum theory would surpass in accuracy values obtained by calorimetric means. A number of years were to elapse before a complete set of theoretical values was collated and accepted.

References:

(i) Reynault, Memoires de l'Academie, Jan. 26, 1862
(ii) Wiedemann, Annales der Physik, Vol. 157
(iii) Holborn and Austen, Wiss. Abhandl. der Reichsanstalt, 1905, iv.
(iv) Holborn and Henning, Ann. der Physik (4), Vol. 23, 1907.
(v) Swann, Proceedings of the Royal Society, 1909, A 82.
(vi) Mallard and Le Chatelier, Ann. des Mines, 1883, 4, p.379.
(vii) Langen, Zeit. des Ver. Deutschen Ing., 1903, xivii.
(viii) Pier, Zeit. für Elektrochem, Vol. 15, 1909, p.536 and Vol. 16, 1910, p.897.
(ix) Bjerrum, Zeit. für Elektrochem, Vol. 18, 1212, p.101.
(x) Lewis and Randall, Journal of the American Chemical Society, Vol. 34, 1912.

The period from 1920 to 1935.

This period must be regarded as one of transition. It was a period during which the theoretical determinations of the physicists developed to such an extent that the values of specific heats accepted in 1920 could be shown to be palpably wrong in 1935. Yet the publication, in 1924, of "The specific heats of gases" by Partington and Shilling(13) provided an authoritative work which was to serve as a reference book for many. No fewer than 352 references were given and few would doubt that the values presented were the best then obtainable. In order that the difference between the older values and the new values calculated on the basis of the quantum theory may be appreciated figures 1, 2 and 3 from "Tables of Properties of Gases" are reproduced here (Fig. 1.2). It is quite clear that the previous practice of treating all diatomic gases as identical is wrong and also that the"quantum values" for CO_2 and H_2O are greatly different from the earlier values. Although a useful summary of the "quantum values" was given by Lewis and von Elbe(18) in 1935 engineers were slow to accept the new specific heats. This was probably due to a number of reasons. The transition period was relatively short and there would be a natural reticence in accepting new values. In any case the use of a functional relationship between the specific heat and the temperature over wide ranges of temperature was now difficult to support and the possibility of having to accept tabulated values of the thermal properties had to be faced.

The period subsequent to 1935

In 1940 the publication of a paper entitled "The New Specific Heats" by Heck(16) did much to establish the latest

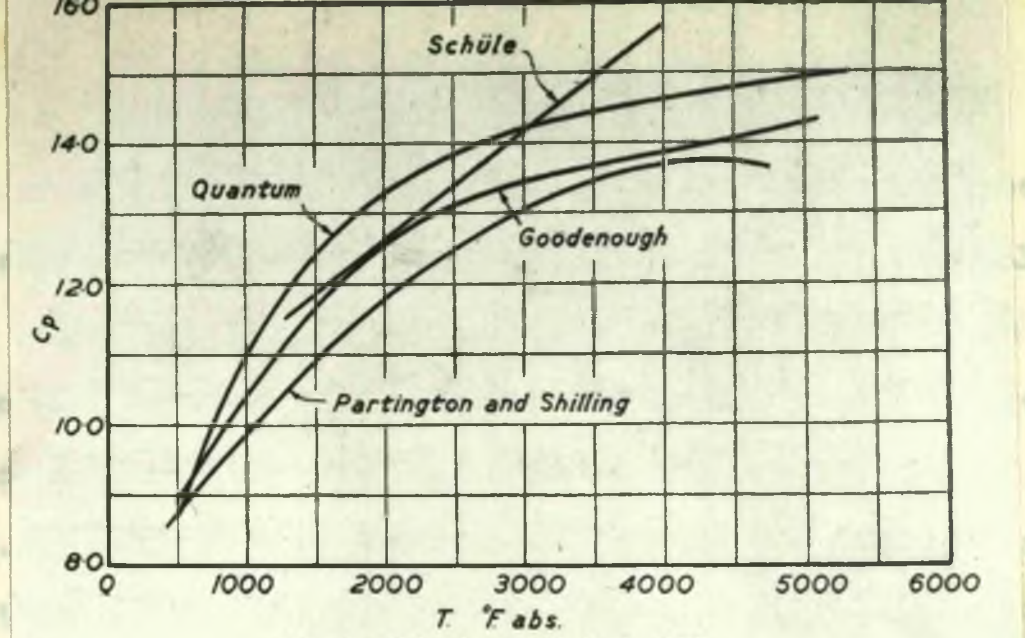


FIG. 1. Molecular specific heats of CO_2.

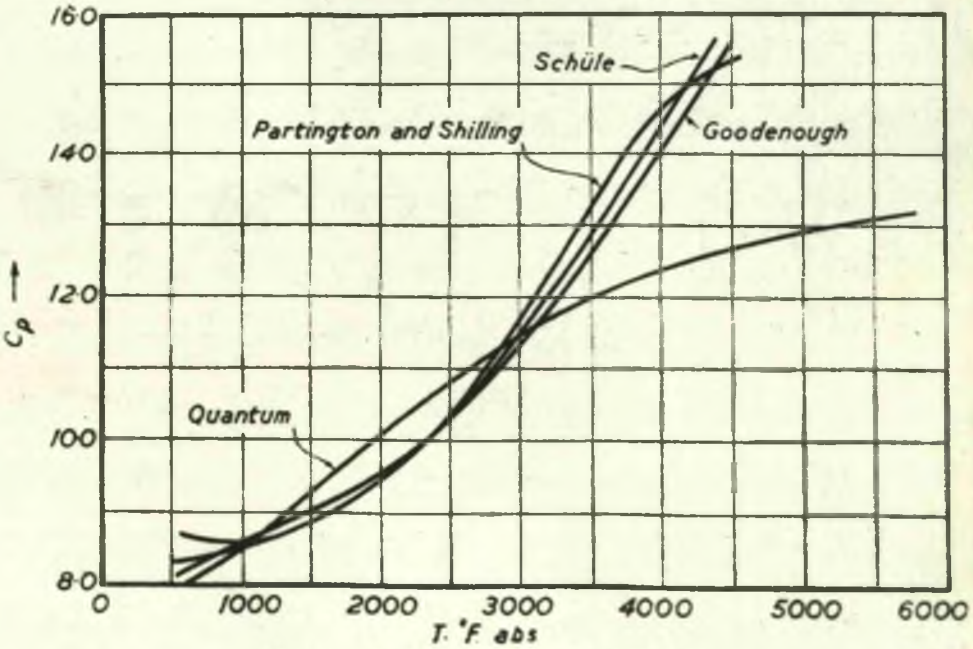


FIG. 2. Molecular specific heats of H_2O.

FIG.1.2

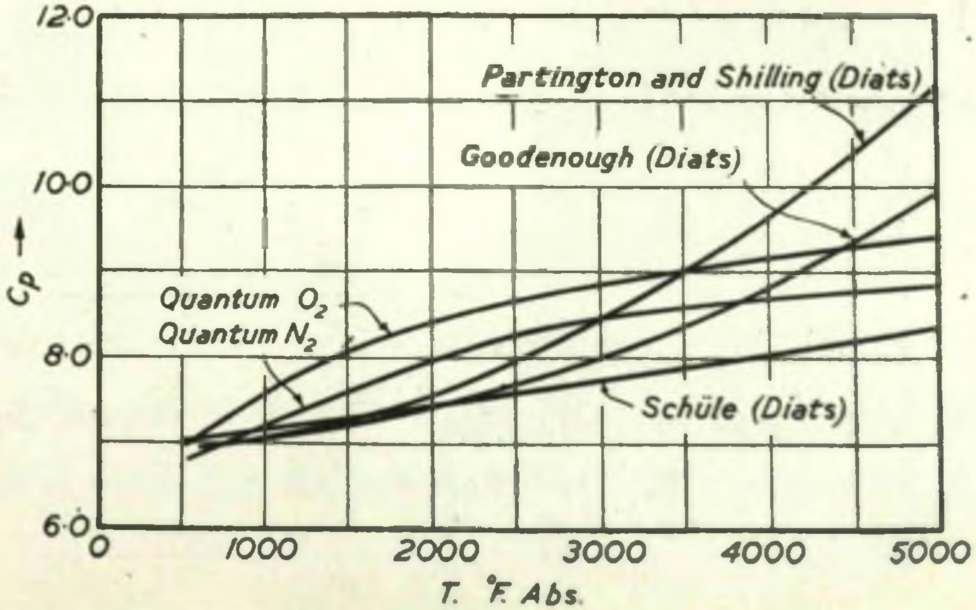


FIG. 3. Molecular specific heats of diatomics.

values of the thermal properties although these had been accepted for some years by physical chemists. The value of Heck's paper lies not so much in the paper itself as in the addenda and discussion. It was the first time the properties had been listed in units familiar to the engineer (B.T.U./lb.mol. - °F.) and the first time an author asserted "that the thermal properties of gases should be brought to expression by numerical tables, analogous to the table for superheated steam." Heck listed only the values of c_p, heat content (enthalpy) and internal energy for N_2, O_2, CO, H_2, CO_2 and H_2O at 100 degree intervals from 600 to 5400°R. Heck chose 540°R as his temperature datum but the omission of values for entropy is to be noted.

In the discussion of the paper a number of important points were made. Briefly these were as follows: (a) the values of the properties listed were for a gas at zero pressure; (b) it was observed that the effect of pressure could be neglected in all cases where the pressure was low ($<$ 150 lb/in^2. for air); (c) the presentation of the properties in the form of tabulated values was approved; and (d) it was agreed that there would not be significant change in the values then obtained. Apart from the useful criticism which Heck received, Johnston and Gordon, who are listed among the authorities, contributed to the discussion. Thus Heck's work was fully endorsed and the way to future work was opened.

The application of the new properties to the construction of energy charts was shown by Dr. Geyer(19). The writer shared in this work where the properties were listed and at a later date Dr. Geyer and the writer, as co-author, published "Thermal Properties of Gases"(1), having in mind the presentation of properties specially useful for combustion problems where the effects of dissociation would need to be considered. Another worker in this field is Justi(20) of whom mention should be made. The values listed by Justi are essantially the same as those listed by others. In sections 2 and 5 the writer discusses in detail energy charts and his own work on tables of properties of gases. It is appropriate to record at the end of this section, that the writer was fortunate enough to review "Gas Tables"(3) for "Engineering" and a copy of the review is given in Appendix II. In view of the importance of tabulated values the writer ventured to express his own opinion in so far as this appeared to coincide with that of the authors of "Gas Tables".

TABULATED VALUES OF THERMAL PROPERTIES

The values which have been listed by Heck(16), Justi(20), Keenan and Kaye(2), and Geyer and Bruges(1) are based in the main on determinations by a group of physical chemists. The application of the methods of Statistical Thermodynamics and Quantum Mechanics enables the thermal properties to be calculated using observations on the spectrum emitted by each gas to fix the various energy levels which the molecule of the gas may assume. However, the values so obtained are for the gas in the ideal gaseous state at zero pressure. It so happens that the effect of pressure may be neglected in many practical cases and the engineer is able to adopt the latest "quantum values" provided he does not overlook this factor. Keenan and Kaye in "Gas Tables" are careful to emphasise this point and all their tables are prefaced with the heading "at low pressures".

In view of the importance of tabulated values of thermal properties it is proposed to re-examine some aspects of the work which were discussed in "Tables of Properties of Gases" and to introduce some new matter. It is proper to record that the latest values of the thermal properties are those to be found in "Gas Tables". However, the differences between the values listed in the two sets of tables are small enough to be discounted as can be seen from the accompanying table (2.1). That there is a difference between the properties listed by Keenan and Kaye and those listed by Dr. Geyer and the writer is due to the fact that the corrections made by Rossini(21) were not accessible to the latter when their tables were prepared. Rossini found that new spectroscopic data had not invalidated the earlier computations and that only corrections due to alterations in the fundamental constants need be considered.

TABLE 2.1

Comparison between internal energy values (B.T.U./lb.mol.)

Temperature		5000°F.abs.		1000°F.abs.		Difference	
Gas	O_2	32157.0 32188	31.0	5101.6 5104	2.4	27055.4 27084	28.6
	N_2	30150.5 30193	42.5	4992.0 4998	6.0	25158.5 25195	36.5
	CO_2	54070.6 54197	126.4	6696.2 6722	25.8	47374.4 47475	100.6
	H_2O	43398.0 43656	258.0	6093.0 6130	37.0	37305.0 37526	221.0
	CO	30473.4 30514	40.6	5006.3 5010	3.7	25467.1 25504	36.9
	H_2	28294.0 28319	25.0	4878.6 4882	3.4	23415.4 23437	21.6

For each gas the upper number represents the value given by Keenan and Kaye and the lower that given by Geyer and Bruges.

He listed these corrections as arising from the following: "(a) Change in the value of the gas constant R from 1.9869 to 1.98718 cal/deg. mol, the ratio being 1.00014; (b) change in the value of the constant of the Sackur - Tetrode equation from entropy of translation from - 2.300 to - 2.3141 cal/deg. mol; (c) change in the value of $\frac{hc}{k}$ from 1.43242 to 1.43847 cm. deg., the ratio being 1.004224; (d) changes in the atomic weights of hydrogen and carbon from 1.0078 to 1.0080 and from 12.00 to 12.010, respectively; (e) correction for rotational stretching of CO_2 and H_2O." In the above context h, c and k are the symbols for Planck's constant, the velocity of light and Boltzmann's constant respectively. The manner in which Rossini handled the corrections need not be detailed here but it will suffice to state that tables of the values of the properties of the common gases were provided in a manner similar to that in which the original workers published their results.

In the original works the thermal properties were listed over wide ranges of temperature and in some cases the gaps in the temperature scale were large. This meant that where Heck had not provided values Dr. Geyer and the writer had to adopt methods similar to those used by Heck. For example, it was convenient to express the specific heat, enthalpy, etc. as a function of the temperature in the form

$A + BT + CT^2$, where A, B and C are constants. The constants could be determined from the properties listed at three temperatures and the values of the property at intermediate temperatures could be calculated. It was recognised that such a method of filling in the gaps would require checking since there would be regions where one quadratic function would give way to another. The values of the property were listed in tabular fashion (table 2.2) and the differences, to the third difference, taken to allow the values to be "smoothed". Since the thermal properties may be expressed

TABLE 2.2

Check on values of E for O_2 by difference

T^oF.abs.	E	δ_1	δ_2	δ_3
1000	5104			
		565		
1100	5669		13	
		578		2
1200	6247		11	
		589		0
1300	6836		11	
		600		2
1400	7436		9	
		609		0
1500	8045		9	
		618		2
1600	8663		7	
		625		0
1700	9288		7	
		632		0
1800	9920		7	
		639		1
1900	10559		6	
		645		
2000	11204			

as a quadratic in T to a very close approximation over small ranges of temperature the third difference, δ_3, approximates to zero. For a quadratic series the third difference is zero as may be seen from table 2.3. In view of the relation between the enthalpy, entropy and free energy it was sufficient to determine only two functions in order to obtain the other. Generally the values of enthalpy and entropy were established from which the free energy and internal energy were found.

TABLE 2.3

Differences for a quadratic series n^2

n	n^2	δ_1	δ_2	δ_3
1	1			
		3		
2	4		2	
		5		0
3	9		2	
		7		0
4	16		2	
		9		0
5	25		2	
		11		0
6	36		2	
		13		0
7	49		2	
		15		0
8	64		2	
		17		0
9	81		2	
		19		
10	100			

DETERMINATION OF THE EQUILIBRIUM CONSTANT

If the general principle of the conservation of energy is applied to a physical or chemical system we may write for an infinitesimal change in the system.

$$dQ + dW = dE \qquad \ldots\ldots\ldots\ldots\ldots\ldots 3.1$$

where dQ = heat entering the system from the surroundings,

dW = work given to the system by external forces,

and dE = increase in the internal energy of the system.

Further, applying the principle of the increase in entropy, a corollary of the Second Law of Thermodynamics,

$$dS \geq \frac{dQ}{T}, \qquad \ldots\ldots\ldots\ldots 3.2$$

where the symbols S and T represent the entropy and temperature of the system.

Equation 3.2 becomes $dS - \frac{dQ}{T} \geq 0 \qquad \ldots\ldots\ldots 3.3$

or on substitution from equation 3.1,

$$dS - \frac{dE - dW}{T} \geq 0 \qquad \ldots\ldots\ldots\ldots\ldots 3.4$$

$$\text{or} \quad dE - TdS \leq dW \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.5$$

This last equation may be extended to cover the case when the temperature and external pressure remain constant and a new function may be introduced to give a very simple condition for equilibrium.

When the temperature and external pressure are constant $dW = - PdV$, since the work given to the system will be reflected only by a change in the volume of the system, dV, equation 3.5 becomes

$$dE + PdV - TdS \leq 0 \quad \text{.............3.6}$$

$$\text{or} \quad d\,(E + PV - TS) \leq 0 \quad \text{.............3.7}$$

because dp = 0 and dT = 0.

The quantity (E + PV - TS) is known as the thermodynamic potential or Gibbs' Function, commonly denoted by the symbol, G. The condition of equilibrium becomes

$$dG \leq 0 \quad \text{..............3.8}$$

If a system is allowed to proceed to a state of equilibrium under isothermal conditions at constant pressure the entropy tends to a maximum and the thermodynamic potential, G, tends to a minimum. The condition for equilibrium implied in equation 3.8 may be applied to determine the equilibrium constant for a mixture of gases which may react chemically with one another.

For a mixture of gases the entropy is given by

$$S = \Sigma m_1 s_1 + \Sigma\left\{m_1 \frac{R}{J} \log \frac{\Sigma m}{m_1}\right\} - \Sigma m \frac{R}{J} \log_e P$$

$$= \Sigma m_1 s_1 + \Sigma\left\{m_1 \frac{R}{J} \log \frac{\Sigma m}{m_1}\right\} \quad , \text{ if } P = 1 \text{ atmos.,}$$

$$= \Sigma m_1 s_1 - \Sigma\left\{m_1 \frac{R}{J} \log p_1\right\} \quad \text{.............3.9}$$

where p_1 = partial pressure of the first gas

since $p_1 = \dfrac{m_1}{\Sigma m}$,

and the enthalpy by

$$H = \Sigma m_1 h_1 \quad \ldots\ldots\ldots\ldots\ldots\ldots 3.10$$

Hence $G = H - TS$,

$$\text{or} \quad G = \Sigma m_1 h_1 - T\left\{\Sigma m_1 s_1 - \Sigma\left(m_1 \frac{R}{J} \log p_1\right)\right\}$$

$$= \Sigma m_1 h_1 - T\,\Sigma m_1 s_1 + T\,\Sigma\left(m_1 \frac{R}{J} \log p_1\right)$$

$$= \Sigma m_1 \left\{g_1 + \frac{RT}{J} \log p_1\right\} \quad \ldots\ldots\ldots 3.11$$

where $g_1 = h_1 - TS_1$, the thermodynamic potential of the first gas at one atmosphere pressure.

If the gases are in equilibrium we have for any virtual change, for which $\delta T = 0$ and $\delta P = 0$, $\delta G = 0$ by equation 3.8. Thus the variation in G as given by equation 3.11 must be zero. Differentiating we have

$$\delta G = \Sigma\left(g_1 + \frac{RT}{J} \log p_1\right)\delta m_1 + \Sigma m_1\,\delta\left(g_1 + \frac{RT}{J} \log p_1\right) \ldots 3.12$$

as the condition for equilibrium. The second sum vanishes as $\delta g_1 = \delta g_2 = \ldots 0$, as g_1, g_2, etc., are functions of temperature and pressure and these do not change.

$$\text{Further} \quad \Sigma m_1\,\delta \log p_1 \qquad \left(\frac{RT}{J} = \text{constant}\right)$$

$$= \frac{m_1}{p_1}\delta p_1 + \frac{m_2}{p_2}\delta p_2 + \quad \ldots\ldots\ldots,$$

$$= \Sigma m\,\delta p_1 + \Sigma m\,\delta p_2 + \quad \ldots\ldots\ldots,$$

$$= \Sigma m\,(\delta p_1 + \delta p_2 + \ldots\ldots\ldots),$$

$$= 0,$$

since $p_1 + p_2 + \ldots\ldots\ldots\ldots = P = 1$ atmos.

$$\text{i.e.} \quad \delta p_1 + \delta p_2 + \quad \ldots\ldots \quad = 0$$

The condition for equilibrium becomes

$$\Sigma \left\{ g_1 + \frac{RT}{J} \log p_1 \right\} \delta m_1 = 0 \quad \ldots\ldots\ldots 3.13$$

For a mixture of reacting gases the equation representing the chemical reaction may be written as

$$m_1A_1 + m_2A_2 + m_3A_3 + \ldots\ldots\ldots\ldots = 0 \quad \ldots .3.14$$

where m_1, m_2, ... are the number of mols of the gases A_1, A_2, ... taking part in the reaction.

Now $\frac{\delta m_1}{m_1} = \frac{\delta m_2}{m_2} = \frac{\delta m_3}{m_3} = \ldots\ldots\ldots\ldots$ This may be shown by considering a reaction, e.g.,

$$- CO - \frac{1}{2} O_2 + CO_2 = 0,$$

which represents the formation of CO_2 from CO and O_2. If one molecule of CO_2 is dissociated one molecule of CO and one half molecule of O_2 appear.

Equation 3.13 becomes

$$\Sigma m_1 \left\{ g_1 + \frac{RT}{J} \log p_1 \right\} = 0$$

or $m_1 \log p_1 + m_2 \log p_2 + \ldots\ldots\ldots\ldots\ldots$

$$= - \frac{m_1g_1 + m_2g_2 + \ldots\ldots}{\frac{RT}{J}} \quad \ldots\ldots\ldots 3.15$$

The expression on the right hand side of this equation is constant when pressure and temperature are constant so the condition of equilibrium becomes

$$\Sigma m_1 \log p_1 = \log Kp \quad \ldots\ldots\ldots\ldots\ldots 3.16$$

where Kp is the equilibrium constant and has a unique value for any reaction at a given temperature and pressure.

Rewriting equation 3.16 we get

$$p_1^{m_1} \cdot p_2^{m_2} \cdot p_3^{m_3} \cdot \ldots\ldots = Kp$$

For the reaction cited above, $- CO - \frac{1}{2} O_2 + CO_2 = 0$,

$$Kp = \frac{p_{CO_2}}{p_{CO} \cdot p_{O_2}^{\frac{1}{2}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.17$$

The effect of temperature change on the equilibrium constant.

Now $\log Kp = - \frac{\sum m_1 g_1}{RT}$ by equation 3.15 and differentiating with respect to T, pressure constant,

$$\left(\frac{\partial \log Kp}{\partial T}\right)_P = \frac{1}{RT^2}\left\{m_1g_1 + m_2g_2 + \ldots\ldots\right\}$$

$$- \frac{1}{RT}\left\{m_1 \frac{\partial g_1}{\partial T} + m_2 \frac{\partial g_2}{\partial T} + \ldots\ldots\right\}$$

$$= \frac{1}{RT^2}\left\{m_1g_1 + m_2g_2 + \ldots\ldots\ldots\ldots - m_1 TS_1 - m_2 TS_2 - \ldots\ldots\ldots\right\}$$

since $\left(\frac{\partial g}{\partial T}\right)_P = - S$, in general

i.e. $\left(\frac{\partial \log Kp}{\partial T}\right)_P = \frac{1}{RT^2}\left\{m_1h_1 + m_2h_2 + \ldots\ldots\ldots\right\}$

or $\left(\frac{\partial \log Kp}{\partial T}\right)_P = \frac{Hp}{RT^2} \quad \ldots\ldots\ldots\ldots\ldots 3.18,$

since the term in brackets represents the change in enthalpy for the reaction or the heat of reaction at constant pressure.

For the reaction $- CO - \frac{1}{2} O_2 + CO_2 = 0$, representing the formation of CO_2 from CO and O_2, H_p is -ve, or $\left(\frac{\partial \log Kp}{\partial T}\right)_P$ = -ve

In other words as the temperature is increased K_p tends to become smaller. By equation 3.17 the reaction is reversed and equilibrium is displaced towards the formation of CO and O_2.

<u>The effect of change of pressure on the equilibrium constant.</u>

Again $\log K_p = -\frac{\Sigma m_1 g_1}{RT}$ by equation 3.15

$$\left(\frac{\partial \log K_p}{\partial P}\right)_T = -\frac{1}{RT} \Sigma m_1 \left(\frac{\partial g_1}{\partial p}\right)_T$$

$$= -\frac{1}{RT} \Sigma m_1 v_1$$

since $\left(\frac{\partial g}{\partial p}\right)_T = v$, in general

$$\text{i.e. } \left(\frac{\partial \log K_p}{\partial P}\right)_T = -\frac{\Delta V}{RT} \quad \ldots\ldots\ldots\ldots 3.19$$

where ΔV is the change in volume for the reaction. For the reaction considered in the previous section ΔV is - ve and $\left(\frac{\partial \log K_p}{\partial P}\right)_T = +$ ve. In other words as the pressure is increased K_p tends to become greater. By equation 3.17 the reaction proceeds in the direction assumed and dissociation is suppressed.

The Availability Function

The study and application of the Second Law of Thermodynamics is facilitated by means of the concept of available and unavailable energy. The function entropy is related to this concept since in any process the increase in entropy is measured by the increase in the unavailable energy divided by the lowest available or sink temperature. In any system the available energy is that maximum portion of the total energy which may be converted to useful work and the remainder is the unavailable energy or that portion of the whole which cannot be converted to useful work by any means whatsoever. In some ideal engine cycles, for example the Carnot cycle, the heat reservoirs are assumed to have indefinitely large capacity but in practice the source is finite and only the sink reservoir or the atmosphere may be assumed to have infinite proportions. Although the purpose of this section is the examination of the latter case it is worth examining the Carnot cycle.

Consider the Carnot cycle as represented in Fig. 4.1. Suppose an engine operating between temperature limits T_1 and T_o, the sink temperature or temperature of the surroundings, receives Q_1 units of heat at T_1 and delivers mechanical work to the surroundings. The maximum amount of

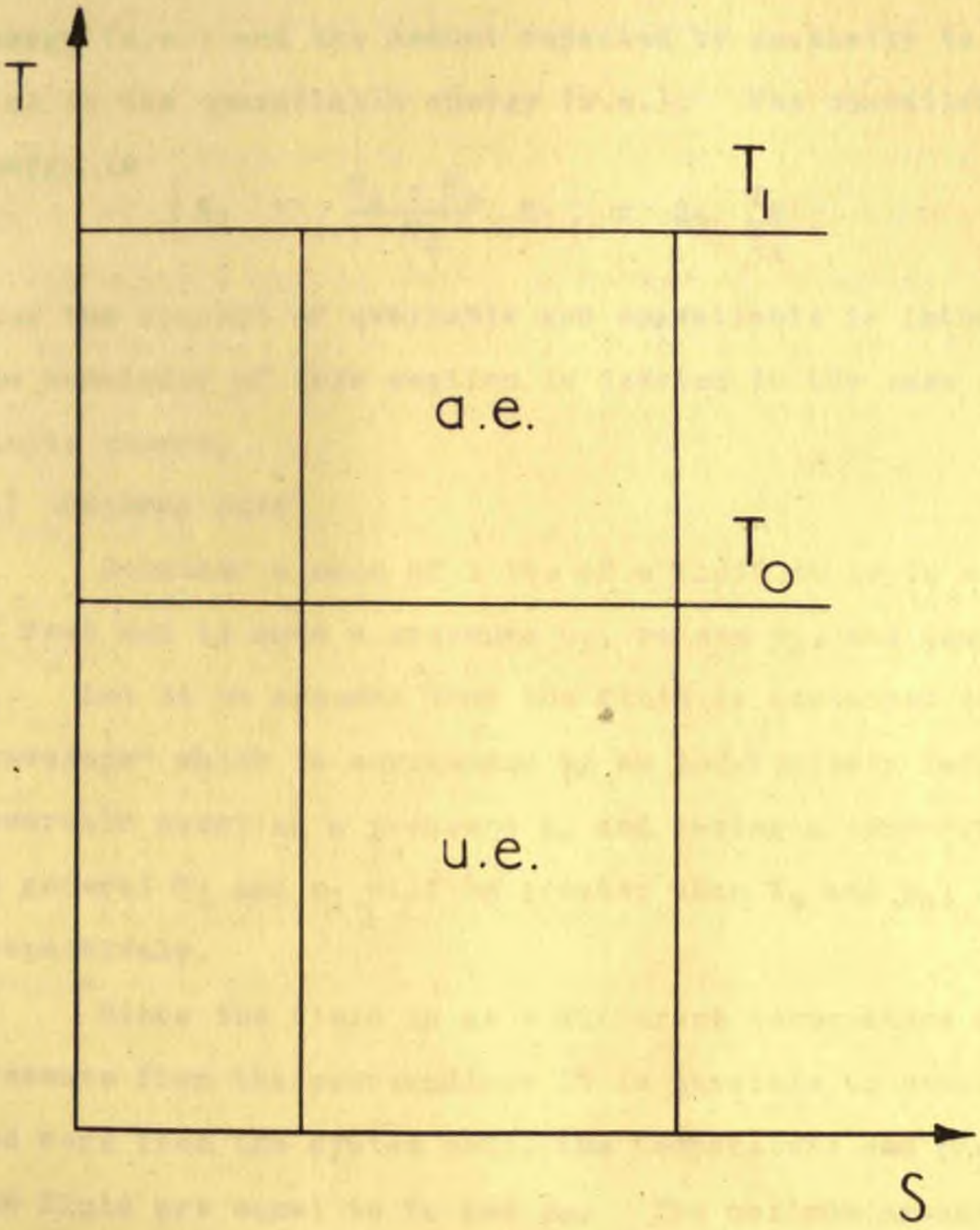


FIG.4.1

work which may be delivered is $\frac{T_1 - T_o}{T_1} Q_1$, a fact which may be established by a corollary of the Second Law. That is to say, due to the reception of Q_1 units of heat by the engine from the reservoir only $\frac{T_1 - T_o}{T_1} Q_1$ units of work are available. Hence this amount is said to be the available energy (a.e.) and the amount rejected by necessity to the sink is the unavailable energy (u.e.). The unavailable energy is

$$\left\{ Q_1 - \frac{T_1 - T_o}{T_1} Q_1 \right\} = Q_1 \frac{T_o}{T_1} .$$

Thus the concept of available and unavailable is introduced. The remainder of this section is devoted to the case of the finite source.

(a) General case

Consider a mass of 1 lb. of a fluid to be in a state of rest and to have a pressure p_1, volume v_1, and temperature T_1. Let it be assumed that the fluid is contained in an "envelope" which is surrounded by an indefinitely large reservoir exerting a pressure p_o and having a temperature T_o. In general T_1 and p_1 will be greater than T_o and p_o respectively.

Since the fluid is at a different temperature and pressure from the surroundings it is possible to obtain heat and work from the system until the temperature and pressure of the fluid are equal to T_o and p_o. The maximum amount of work which may be delivered by the fluid to the surroundings is that quantity given by a reversible engine which brings the fluid from state (1) to that state in equilibrium with the surroundings.

The maximum work is estimated by assuming that the heat given out by the fluid is delivered in an indefinitely large number of steps to a series of Carnot engines working between the temperature of the fluid at any instant as source and the temperature of the surroundings. The work delivered by the engines may be stored in a "spring reservoir" [*] or work store. Assuming that the fluid has reached a condition where the pressure, volume and temperature have the values p, v and T respectively, the abstraction of dQ units of heat from the fluid will give $-\left(\frac{T - T_0}{T}\right) dQ$ units of work from the Carnot engine operating at this temperature level. It is to be noted that dQ is negative when heat is given up by the fluid and $(T - T_0)$ is positive - the opposite is true when heat is absorbed by the fluid. In addition to the work obtained due to the exchange of energy between the fluid and the surroundings work may be obtained if $p > p_o$. Thus the maximum work obtainable in the small step is

$$-\left(\frac{T - T_0}{T}\right) dQ + (p - p_0)\, dv \quad \ldots\ldots\ldots\ldots 4.1$$

---

[*] Lewis and Randall, "Thermodynamics", John Wiley & Co. Inc.

Rewriting equation 4.1 gives

$$-\left\{1-\frac{T_o}{T}\right\}dQ + pdV - p_o\,dV \quad \ldots\ldots\ldots\ldots\ldots 4.2$$

Now for a reversible change $ds = \frac{dQ}{T}$ and equation 4.2 becomes

$$-\,dQ + T_o\,ds + pdV - p_o\,dV \quad \ldots\ldots\ldots\ldots\ldots\ldots 4.3$$

Also $dQ = dE + pdV$ by the 1st Law and so we may write

$$-\,dE = -\,dQ + pdV \text{ and equation 4.3 becomes}$$

$$-\,dE - p_o\,dV + T_o\,ds \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.4$$

Integration from state (1) to state (0) gives

$$-\int_1^o dE - \int_1^o p_o\,dV + \int_1^o T_o\,ds$$

$$\text{i.e.} - (E_o - E_1) - p_o(v_o - v_1) + T_o(s_o - s_1)$$

$$\text{or} \quad (E_1 - T_o s_1 + p_o v_1) - (E_o - T_o s_o + p_o v_o) \ldots\ldots\ldots 4.5$$

The difference in availability between any two states x and y of the system, with reference to the surroundings at T_o and p_o is given by

$$(E_y - T_o s_y + p_o v_y) - (E_x - T_o s_x + p_o v_x) \ldots\ldots\ldots\ldots 4.6$$

using equation 4.5. The function $(E - T_o s + p_o v)$ is a function of the state and it would be possible to construct a chart using the function as one of the parameters.

(b) Change at constant volume.

The availability at the point (1) with reference to T_o is given by equation 4.5. Thus

$$\text{a.e.} = (E_1 - T_o s_1) - (E_o - T_o s_o) \ldots\ldots\ldots\ldots 4.7$$

$$= (E_1 - E_o) - T_o\,(s_1 - s_o), \text{ since } v_1 = v_o.$$

On inspection it is seen that b_1 represents the triangular area shown shaded in Fig. 4.2.

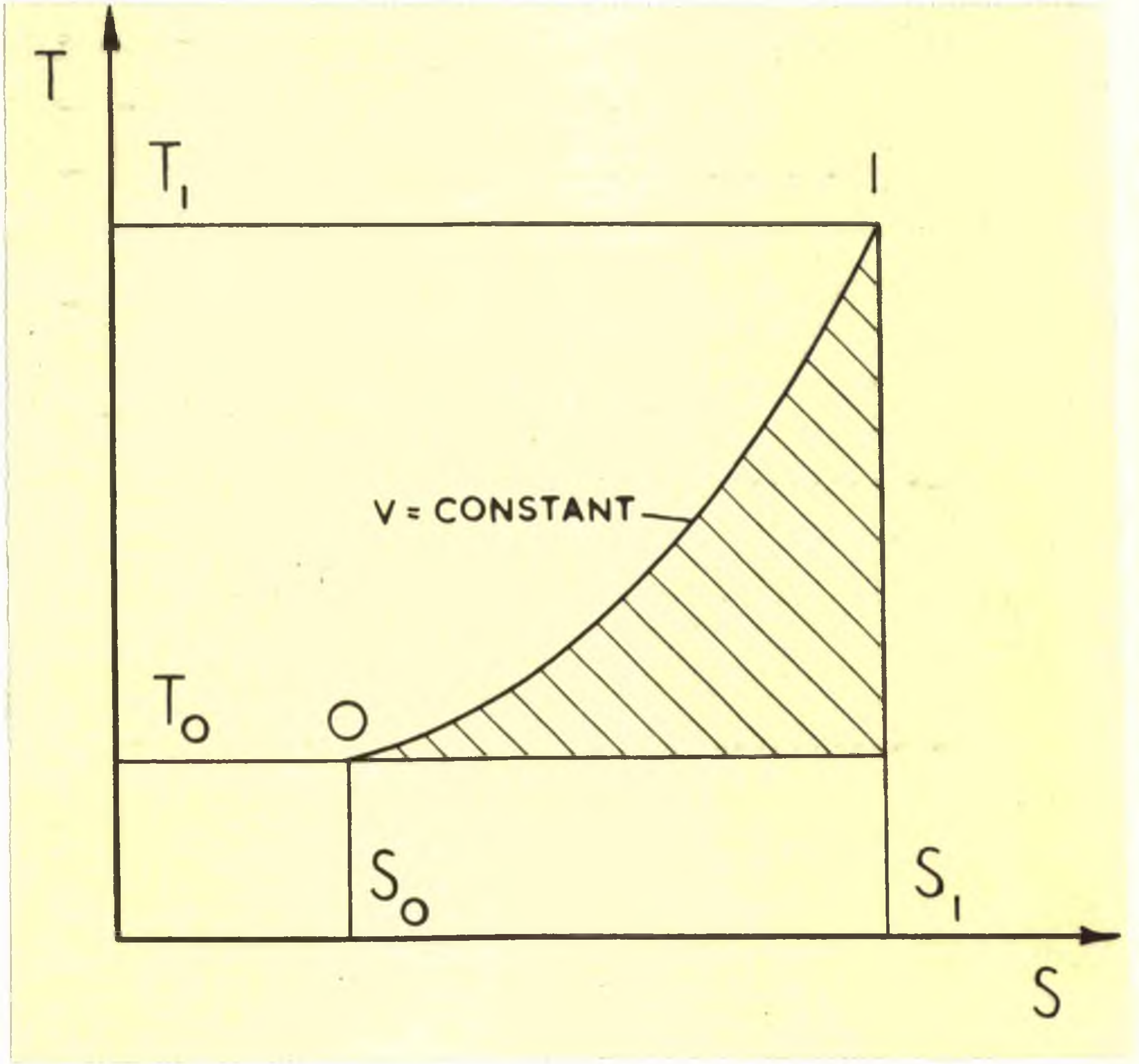


FIG.4.2

(c) Change at constant pressure ($p = p_o$)

Here a.e. $= (E_1 - T_os_1 + p_1v_1) - (E_o - T_os_o + p_ov_o)$

$= (H_1 - T_os_1) - (H_o - T_os_o)$ 4.8

$= (H_1 - H_o) - T_o(s_1 - s_o)$, since $p_1 = p_o$.

As in the constant case b_1 represents the shaded area in Fig. 4.3.

(d) Steady flow.

Consider the case of the steady flow of a fluid from conditions (p_1 v_1 T_1) to conditions (p_2 v_2 T_2) as shown in Fig. 4.4. In this instance let it be assumed that the kinetic energy of the fluid is small relative to the total energy at sections (1) and (2) and that any potential energy which the fluid may possess by virtue of its height above some datum may be neglected. The availability of each unit mass as it comes to section (1), with respect to the surroundings at p_o and T_o, is increased by the amount of the displacement work or energy of flow (pressure work), p_1v_1, less the work which must be expended on the surroundings. This may be made more evident by removing the unit following section (1) and replacing it with a cylinder and a piston, such that the pressure p_o acts on the back of the piston. The work which is available for "storage" as each unit mass comes to section (1) is $(p_1 - p_o)\ v_1$. The unit mass may be removed then and allowed to yield its available energy amounting to $\Big[E - T_os + p_ov\Big]_o^1$, as given by equation (4.5)

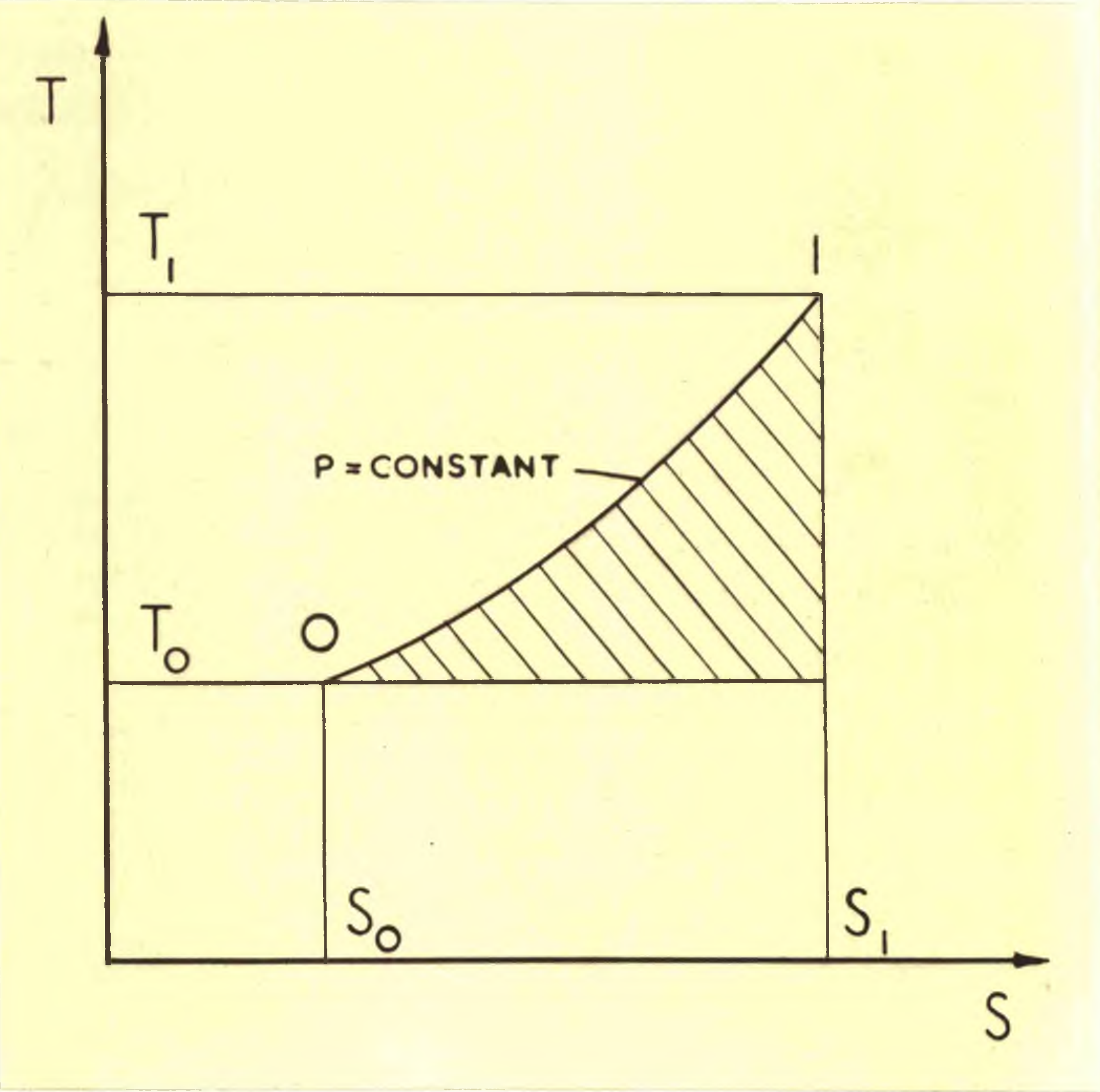


FIG.4.3

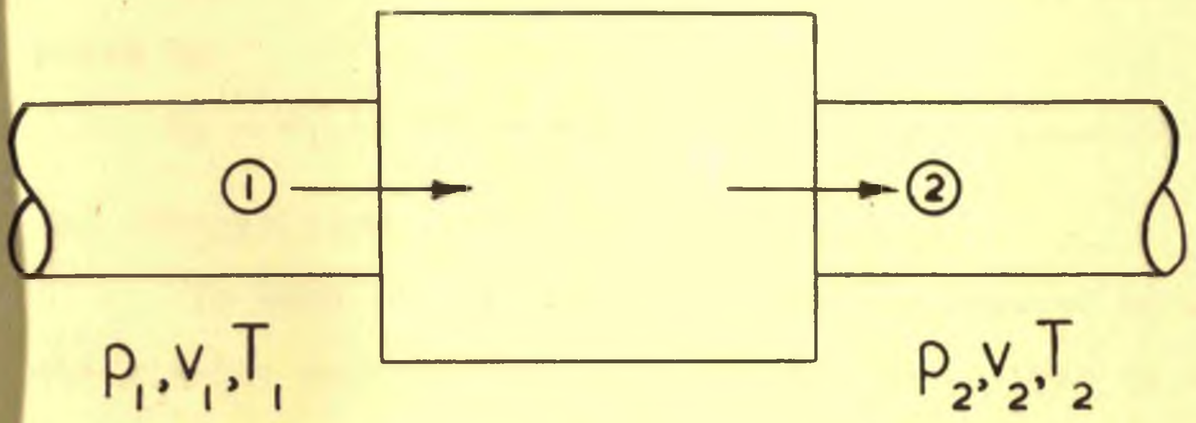


FIG.4.4

The availability at section (1) is given by

$$\Big[E - T_o s + p_o v\Big]_o^1 + (p_1 - p_o)\, v_1 \,,$$

$$= \Big[E - T_o s + p_o v + (p - p_o)\, v\Big]_o^1$$

$$= \Big[E - T_o s + pv\Big]_o^1 , \quad - \quad \text{but} \quad H = E + pv$$

$$= \Big[H - T_o s\Big]_o^1 \qquad \ldots\ldots\ldots\ldots\ldots\ldots 4.9$$

Keenan uses the symbol b to denote the quantity $(H - T_o s)$. The change in availability between sections (1) and (2) is given by

$$b_2 - b_1 = (H_2 - T_o s_o) - (H_1 - T_o s_1) \qquad \ldots\ldots\ldots\ldots 4.10$$

(e) Steady flow - velocity included.

In case (d) if the velocities are denoted by u_1 and u_2 the kinetic energy of flow is wholly convertible to mechanical work. Before doing work, $p_1 v_1$, in the cylinder mentioned above, the fluid may be allowed to pass in a reversible manner through a turbine disc, designed so that the fluid emerges with indefinitely small velocity. The work done on the disc at section (1) will be $\frac{u_1^2}{2g}$ and this may be given to the work store. Thus the change in availability between sections (1) and (2) will be

$$\left(b_2 + \frac{u_2^2}{2g}\right) - \left(b_1 + \frac{u_1^2}{2g}\right) \qquad \ldots\ldots\ldots\ldots\ldots 4.11$$

extending equation 4.10 to include the kinetic energy terms.

(f) Potential energy.

In most cases the potential energy of a fluid, with respect to some datum, need not be considered; but for dense fluids, such as water, the potential energy should be considered.

Evaluation of Irreversibility

Expressing the 1st Law in the form

$$dQ = dE + p_o\,dv + dW \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.12$$

where dQ = the heat added to the system,

dE = the increase in the internal energy of the system,

p_o = the pressure of the surroundings,

dv = the increase in the volume of the system,

and dW = the useful work delivered to the surroundings

one may rewrite the equation and subtract $T_o ds$ from each side to get

$$(dE + p_o dv - T_o ds) = (dQ - T_o ds - dW) \quad \ldots\ldots\ldots 4.13.$$

Substitution of the inequality of Clausius, $ds \geq \frac{dQ}{T}$, into equation 4.13 yields

$$(dE + p_o dv - T_o ds) \leq \left[\frac{T - T_o}{T}\,dQ - dW\right] \quad \ldots\ldots\ldots 4.14$$

Equation 4.14 shows that the increase in availability (left hand side) may be equal to or less than $\left[\frac{T - T_o}{T}\,dQ - dW\right]$.

Thus the irreversibility in any process is given by

$$\left[\frac{T - T_o}{T}\,dQ - dW\right] - \left[dE + p_o dv - T_o ds\right] \text{ or by}$$

$$\left[\int \frac{T - T_o}{T}\,dQ - W\right] - \Delta\left[E + p_o v - T_o s\right] \quad \ldots\ldots\ldots\ldots 4.15$$

An alternative form for the irreversibility may be obtained by examination of equation 4.14. Equation 4.14 was established by the introduction of the inequality $ds \geq \frac{dQ}{T}$ or $T_0 ds - T_0 \frac{dQ}{T}$. Thus the irreversibility is given by $T_0 ds - T_0 \frac{dQ}{T} = d\,(T_0 s) - T_0 \frac{dQ}{T}$, which on integration becomes

$$\Delta (T_0 s) - T_0 \int \frac{dQ}{T} \quad \ldots\ldots\ldots\ldots 4.16$$

Equation 4.16 may be applied conveniently to a fluid which undergoes a closed thermodynamic cycle since the entropy of the fluid is the same at the beginning and end of the cycle. For this case $\Delta (T_0 s) = 0$ and the irreversibility is given by $- T_0 \int \frac{dQ}{T}$.

In a flow process the irreversibility is given by

$$\left[\int \frac{T - T_0}{T} \, dQ - W \right] - \Delta \left[H - T_0 s \right] \quad \ldots\ldots\ldots\ldots 4.17$$

The manner in which equations 4.15 and 4.17 may be applied must be examined in greater detail. The representation of a state change on a p - v diagram by a line implies reversibility for the change. In other words, if the area is taken to be the work quantity then there can be no internal friction and the path of change could in theory, at least, be retraversed. In low speed reciprocating units the indicator diagram is accepted as representing the true p - v changes even though there may be heat losses from the fluid to the cylinder walls. The path on the p - v diagram represents a reversible change for the fluid although not a reversible change for the whole system, where the word system is taken to include not only the fluid in the cylinder but also all the heat reservoirs taking part in the process. In units where the production of work is achieved by virtue of a flow process, in turbines, nozzles, etc., the apparent paths traced on p - v diagrams do not represent work and such changes are irreversible. Fortunately most flow processes are assumed to be adiabatic and the irreversibility is easily found by equation 4.17 since $dQ = 0$. If in any process there is both flow of heat and internal friction an analysis is impossible unless the value of $\int \frac{dQ}{T}$ can be found. In a reciprocating unit it is necessary to assume that the frictional effects are negligible over the main parts of the cycle.

Application of equation 4.15 in compression:-

Let a gas be compressed from state (1) to state (2), the nett work of compression being W, T_o and p_o, temperature and pressure of surroundings.

$$(a.e.)_{\text{state (2)}} = E_2 + \frac{p_o\, v_2}{54} - T_o s_2$$

$$(a.e)_{\text{state (1)}} = E_1 + \frac{p_o\, v_1}{5.4} - T_o s_1$$

$$\text{Increase in a.e.} = (E_2 - E_1) + \frac{p_o(v_2 - v_1)}{5.4} - T_o(s_2 - s_1) \quad \ldots 4.18$$

useful work expended on the fluid,

$$W = (E_2 - E_1) - Q + \frac{p_o(v_2 - v_1)}{5.4} \quad \ldots\ldots\ldots 4.19$$

and
$$\int_1^2 \frac{T - T_o}{T}\, dQ = \left\{ Q - T_o\,(s_2 - s_1) \right\} \quad \ldots\ldots\ldots\ldots\ldots 4.20$$

Applying equation 4.15 and substituting from 4.18, 4.19 and 4.20

above, the irreversibility

$$= \left\{Q - T_o(s_2 - s_1)\right\} + \left\{(E_2 - E_1) - Q + \frac{p_o(v_2 - v_1)}{5.4}\right\}$$

$$- \left\{(E_2 - E_1) + \frac{p_o(v_2 - v_1)}{5.4} - T_o(s_2 - s_1)\right\}$$

$$= 0$$

The amount by which equation 4.19 exceeds equation 4.18 represents the loss of a.e., given by equation 4.20, due to the transfer of heat from the fluid to the surroundings. The loss of a.e. due to the heat transfer is the irreversibility so far as returning the system to its original state is concerned. Equation 4.20 represents the minimum amount of work required to return the system to its original state.

A similar analysis holds for expansion. Application of equation 4.15 to combustion process:-

It has to be assumed that the combustion process is a physically reversible process, if not chemically so. During the combustion period work may be done on or by the system and heat may be lost to the surroundings. A number of cases fall to be considered, for example (a) when there is no loss of heat or work done, (b), when there is loss of heat but no work done and (c) when there is both loss of heat and exchange of work.

Application of equation 4.15 in above cases:-

(a) Decrease in a.e. $= \left(E_2 - \frac{p_o v_2}{5.4} - T_o s_2\right) - \left(E_1 - \frac{p_o v_1}{5.4} - T_o s_1\right)$

$= (E_2 - E_1) - T_o(s_2 - s_1)$, since $v_2 = v_1$,

$= - T_o (s_2 - s_1)$, since $E_2 = E_1$.

Also $\int \frac{T - T_o}{T} \, dQ = 0$ and $W = 0$.

Hence irreversibility $= T_o (s_2 - s_1)$

(b) Decrease in a.e. $= (E_2 - E_1) - T_o (s_2 - s_1)$

$= - Q - T_o (s_2 - s_1)$

where $Q = E_1 - E_2$

The heat lost to the surroundings may be put to zero if the energy released within the fluid is modified accordingly.

Hence $\int \frac{T - T_o}{T} \, dQ = 0$ and $W = 0$ and the irreversibility

$= Q + T_o (s_2 - s_1)$.

The accompanying diagram, Fig. 4.5, shows the analysis.

The irreversibility is the energy which is unrecoverable and this amounts to $Q + T_o(s_2 - s_1)$. Let C be the point which would have been reached from A if there had been no loss of heat. Let B be the point actually reached where the loss of heat is equal to Q, area BCDE. The effective amount of energy released is now represented by the area ABEF but of this amount the area HGEF $= T_o(s_2 - s_1)$ is rendered unavailable. Hence the total irreversibility is $Q + T_o (s_2 - s_1)$ as given above.

(c) If W = nett work done by the fluid then part of the decrease of availability, $Q + T_o(s_2 - s_1)$, Q, s_2 and s_1 being

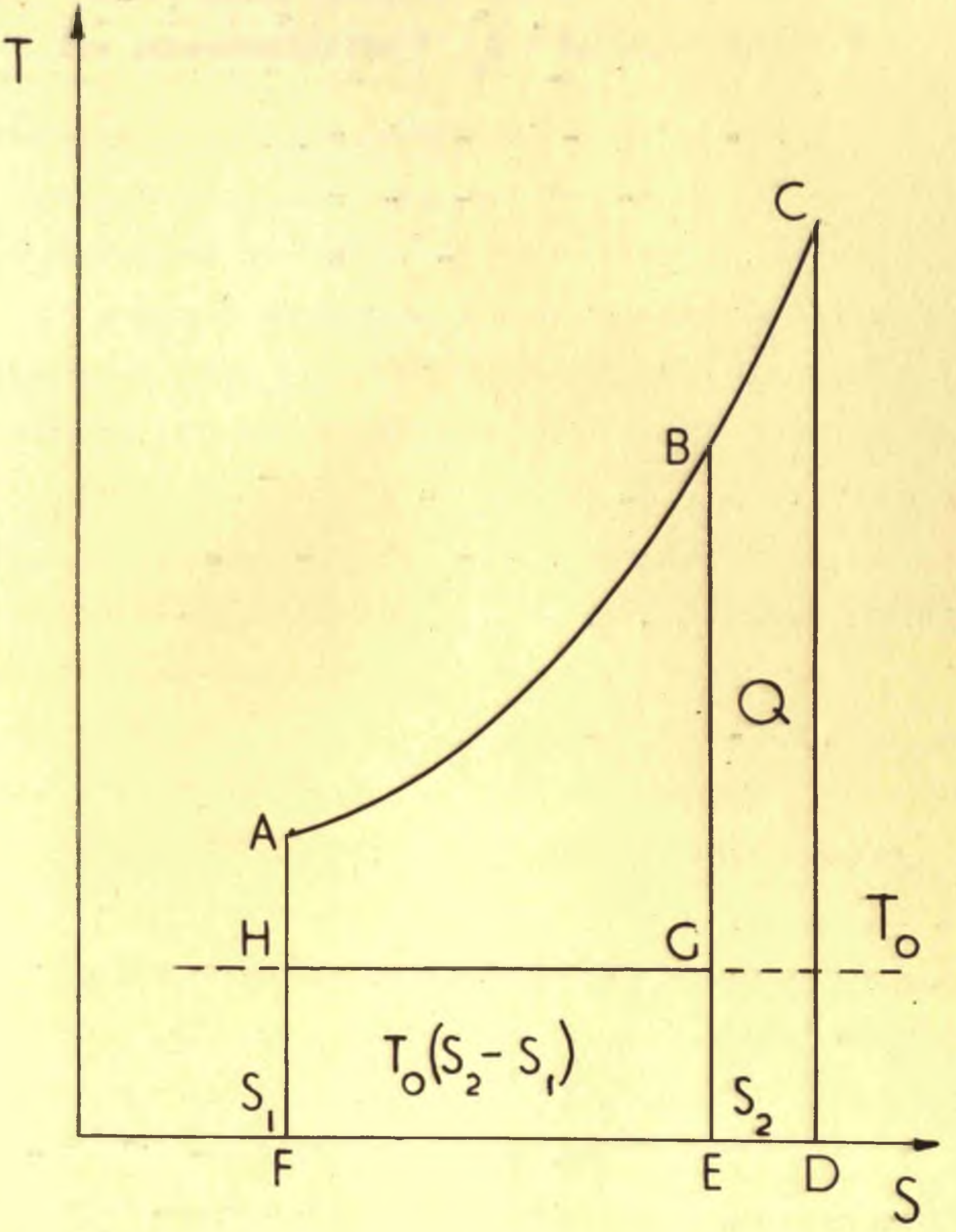


FIG. 4.5

the values appropriate to this case, is accounted for by W. Hence using equation 4.15

$$\text{the irreversibility} = \left\{Q + T_0\ (s_2 - s_1)\right\} - W$$

Dissociated Gas Mixtures - Single Gas

At sufficiently high temperatures ($>2,500^{\circ}$F. abs.) a gas, such as CO_2, ceases to exist as a single gas but dissociates into two component gases CO and O_2 according to the reversible chemical equation $CO + \frac{1}{2} O_2 \rightleftarrows CO_2$. It is not to be thought that dissociation cannot occur at low temperatures but the effect is so small as not to be of account. Consider one mol. of CO_2 at some temperature T and pressure P let the degree of dissociation be x, so that the dissociated mixture, under conditions of thermal equilibrium, will consist of x mol of CO, 0.5x mol. of O_2 and (1 - x) mol. of CO_2. The value of x will lie between 0 and 1, corresponding to the undissociated and completely dissociated states, and the value of x can be only that value which satisfies the condition of equilibrium at the temperature and pressure of the mixture. The condition of equilibrium for this reaction is given by $K_p = \dfrac{p_{CO_2}}{p_{CO}\, p_{O_2}^{\frac{1}{2}}}$, as in equation 3.17,

where p_{CO_2}, p_{CO} and p_{O_2} are the partial pressures of the respective gases, CO_2, CO and O_2. In terms of the total pressure, P, and the total number of mols, (1 + 0.5x),

$$K_p = \frac{1 - x}{x\,(0.5x)^{\frac{1}{2}}} \left(\frac{1 + 0.5x}{P}\right)^{\frac{1}{2}} \quad \ldots\ldots\ldots 5.1$$

since $p_{CO_2} = \frac{1 - x}{1 + 0.5x} P$, $p_{CO} = \frac{x}{1 + 0.5x} P$ and $p_{O_2} = \frac{0.5x}{1 + 0.5x} P$.

For any given values of pressure and temperature equation 5.1 determines the value of x but in order to calculate thermal quantities another equation has to be established.

The 1st Law of Thermodynamics, as applied to a gas, may be expressed symbolically as

$$dQ = dE + \frac{PdV}{J} , \qquad \ldots\ldots\ldots\ldots\ldots 5.2$$

for an elementary change,

where dQ = the heat supplied to the system,

dE = the increase in the internal energy of the system,

and $\frac{PdV}{J}$ = the work done by the system.

In order to apply this equation to a gas in the dissociated state it suffices to define the internal energy of the system as

$$E = x E_{CO} + 0.5x E_{O_2} + (1 - x) E_{CO_2} \qquad \ldots\ldots\ldots 5.3$$

where x is the degree of dissociation at some temperature T and pressure P.

For a change at constant pressure

$$dQ = dH,$$

where H is the enthalpy of the system and is given by

$$H = x H_{CO} + 0.5x H_{O_2} + (1 - x) H_{CO_2} .$$

Hence $dQ = x\, d\, H_{CO} + 0.5x\, d\, H_{O_2} + (1 - x)\, d\, H_{CO_2}$

$$+ (H_{CO} + 0.5 H_{O_2} - H_{CO_2})\, dx \ \ldots\ldots 5.4$$

The difference $\overline{H_{CO} + 0.5 H_{O_2}} - \overline{H}_{CO_2}$ in equation 5.4 implies the difference ΔE_0 and hence equation 5.4 may be written as

$$Q_p = \Big[xH_{CO} + 0.5x\,H_{O_2} + (1 - x)\,H_{CO_2} \Big]_{T_1}^{T_2} + \int_{x_1,T_1}^{x_2,T_2} H_p dx$$

$$= H_2 - H_1 + \int_{x_1 = 0}^{x = x_2} H_p dx \qquad \ldots\ldots\ldots\ldots 5.5$$

where H_2 = the enthalpy of the dissociated mixture at T_2

and H_1 = the enthalpy of the CO_2 initially

$$= \Big[H_{CO_2} \Big]_{T_1}$$

The quantity Q_p as given by equation 5.5 represents the area below the constant pressure heating curve in Fig. 5.1. The curve is plotted in the following way: At any temperature, T, the value of x is found from equation 5.1. Hence the composition at any pressure and temperature is known. The total entropy at any temperature T and pressure P where the degree of dissociation is x is given by

$$S = (1 - x)\,S_{CO_2} + xS_{CO} + 0.5xS_{O_2}$$
$$+ \frac{R}{J}\left\{(1 - x)\log \frac{1 + 0.5x}{1 - x} + x\log\frac{1 + 0.5x}{x} + 0.5x\log\frac{1 + 0.5x}{0.5x}\right\}$$
$$- (1 + 0.5x)\,\frac{R}{J}\log P \qquad \ldots\ldots\ldots\ldots 5.6$$

(See Appemdix I)

A very close approximation to the value of Q_p may be obtained by assuming the heat of reaction constant and equal to ΔE_0 over the range T_1 to T_2. Thus

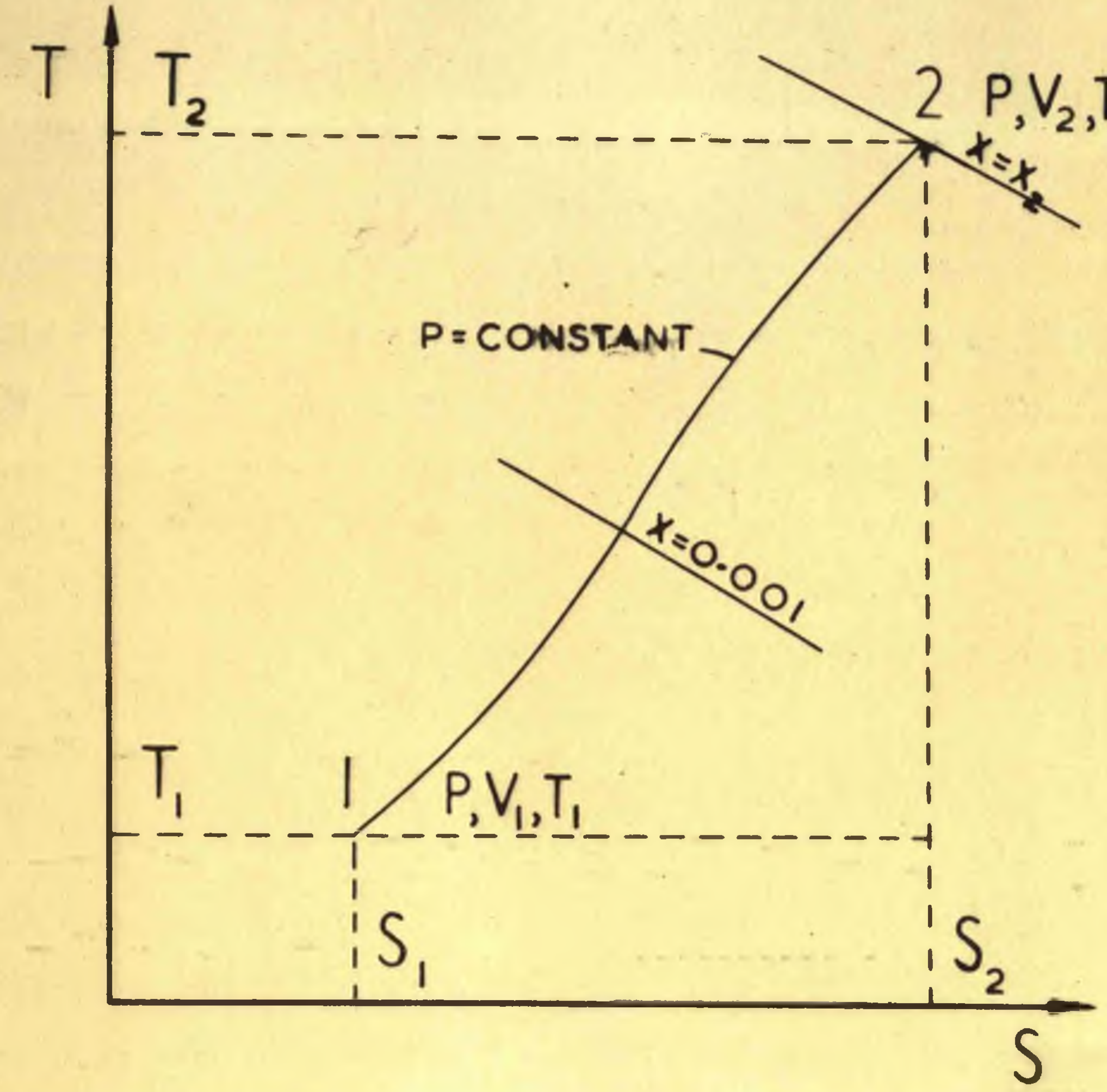


FIG. 5.1

$$Q_p = \Big[H_{CO_2}\Big]_{T_2} - \Big[H_{CO_2}\Big]_{T_1} + x_2\Big[H_{CO} + 0.5xH_{O_2} - H_{CO_2}\Big]_{T_2}$$

$$+ \int_1^2 (\Delta E_o + H_{CO} + 0.5\, H_{O_2} - H_{CO_2})\, dx$$

since $H_p = \Delta E_o + H_{CO} + 0.5\, H_{O2} - H_{CO_2}$. That is

$$Q_p = \Big[H_{CO_2}\Big]_{T_2} - \Big[H_{CO_2}\Big]_{T_1} + x_2\Big[\Delta E_o + H_{CO} + 0.5\, H_{O_2} - H_{CO_2}\Big]_{T_2}$$

$$+ \int_1^2 (H_{CO} + 0.5\, H_{O_2} - H_{CO_2})\, dx$$

$$= \Big[H_{CO_2}\Big]_{T_2} - \Big[H_{CO_2}\Big]_{T_1} + x_2\, H_{p_2} + \int_1^2 (H_{CO} + 0.5\, H_{O_2} - H_{CO_2})\, dx, \qquad ....5.7$$

since ΔE_o is constant and $x_1 = 0$.

If H_p is assumed constant and equal to ΔE_o, $H_{CO} + 0.5\, H_{O_2} = H_{CO_2}$ and the integral in equation 5.7 vanishes leaving

$$Q_p = \Big[H_{CO_2}\Big]_{T_2} - \Big[H_{CO_2}\Big]_{T_1} + x_2\, H_{p_2} \qquad ....5.8$$

The difference between the true value of Q_p, as given by equation 5.5, and the approximate value given by equation 5.8 is $\int_1^2 (H_{CO} + 0.5\, H_{O_2} - H_{CO_2})\, dx$. In this instance the difference $\overline{H_{CO} + 0.5\, O_2} - \bar{H}_{CO_2}$ does not imply the difference ΔE_o since this quantity was abstracted in the line before equation 5.7. In the following section for the constant volume case the inclusion or exclusion of $\triangle E_0$ will be understood from the context.

For a change at constant volume let one mol. of CO_2 be heated at constant volume V, from initial conditions (P_1, V, T_1) to final conditions (P_2, V, T_2), the degree of dissociation being taken initially as zero and finally as x_2. In a constant volume process equation 5.1 becomes

$$K_p = \left(\frac{(1 - x)}{x\ (0.5x)^{\frac{1}{2}}}\right)\left(\frac{T_1}{P_1 T}\right)^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots 5.9$$

where the degree of dissociation is x at any temperature T. At the initial point $P_1V = \frac{R}{J} T_1$ and $PV = m \frac{R}{J} T$ at any point (P, V, T,) where m is the total number of mols. of the dissociated mixture. It follows that $\left(\frac{1 + 0.5x}{P}\right) = \left(\frac{T_1}{P_1 T}\right)$ and equation 5.9 is established from equation 5.1. For given initial conditions the composition of the dissociated mixture is found using equation 5.9 and the total entropy using equation 5.6. A curve of constant volume may be plotted.

The area below the constant volume heating curve in Fig. 5.2 is given by integration of the equation $dQ = dE$ where $E = x\,E_{CO} + 0.5x\,E_{O_2} + (1 - x)\,E_{CO_2}$.

$$\text{Now } dE = x\,dE_{CO} + 0.5x\,dE_{O_2} + (1 - x)\,dE_{CO_2} + (E_{CO} + 0.5\,E_{O_2} - E_{CO_2})\,dx$$

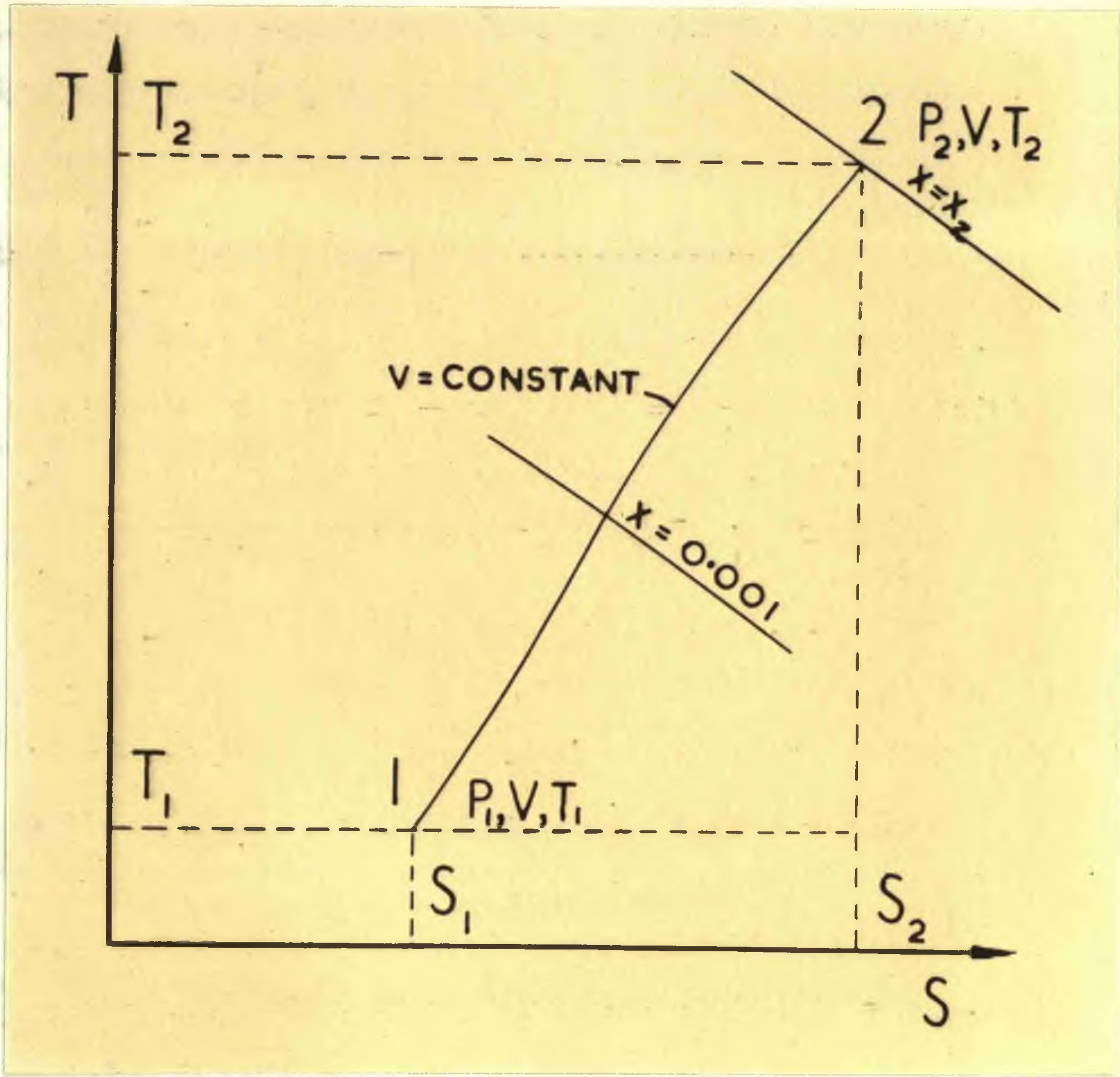


FIG. 5.2

$$\text{i.e. } Q_v = \Big[x\,E_{CO} + 0.5x\,E_{O_2} + (1 - x)\,E_{CO_2}\Big]_{T_1}^{T_2} + \int_{x_1T_1}^{x_2T_2} H_v\,dx$$

$$= E_2 - E_1 + \int_{x_1=0}^{x=x_2} H_v\,dx \quad \text{..........5.10} \;/$$

where Q_v = the heat supplied at constant volume,

E_2 = the internal energy of the dissociated mixture,

$= \Big[(1 - x)\,E_{CO_2} + x\,E_{CO} + 0.5x\,E_{O_2}\Big]_{T_2}$, and

E_1 = the internal energy of the CO_2 initially,

$= \Big[E_{CO_2}\Big]_{T_1}$.

Equation 5.10 becomes

$$Q_v = \Big[(1 - x)\,E_{CO_2} + x\,E_{CO} + 0.5x\,E_{O_2}\Big]_{T_2} - \Big[E_{CO_2}\Big]_{T_1}$$

$$+ \int_1^2 (E_{CO} + \tfrac{1}{2}E_{O_2} + \Delta E_0 - E_{CO_2})\,dx$$

since $H_v = E_{CO} + \frac{1}{2}E_{O_2} + \Delta E_0 - E_{CO_2}$.

$$Q_v = \Big[E_{CO_2}\Big]_{T_2} - \Big[E_{CO_2}\Big]_{T_1} + x_2\Big[\Delta E_0 + E_{CO} + \tfrac{1}{2}E_{O_2} - E_{CO_2}\Big]_{T_2}$$

$$+ \int_1^2 (E_{CO} + 0.5\,E_{O_2} - E_{CO_2})\,dx \quad \text{............5.11}$$

since ΔE_0 is constant and $x_1 = 0$.

/ In "Engineering" (6) the writer used H_p and this is in error. It is to be noted that Schüle(22) used W_p, the 'Warmetonung', and as the writer was following Schüle's work closely when the article for "Engineering" was prepared the error was repeated.

If H_v is assumed constant and equal to ΔE_0 $E_{CO} + 0.5\,E_{O_2} = E_{CO_2}$ and the integral in equation 5.11 vanishes leaving

$$Q_v = \Big[E_{CO_2}\Big]_{T_2} - \Big[E_{CO_2}\Big]_{T_1} + x_2\,H_{v_2} \quad \text{............5.12}$$

The difference between the true value of Q_v as given by equation 5.11 and the approximate value as given by equation 5.12 is $\int_1^2 (E_{CO} + \frac{1}{2}\,E_{O_2} - E_{CO_2})\,dx$.

The validity of equations 5.5 and 5.10 may be tested by evaluating $\int TdS$ along a constant pressure or constant volume curve. As a check this will be done for a constant pressure change.

At any point where the degree of dissociation is x and the pressure is P the total entropy is given by equation 5.6

$$\text{i.e.}\quad S = x\,S_{CO} + 0.5x\,S_{O_2} + (1 - x)\,S_{CO_2}$$
$$+ \frac{R}{J}\Big\{x \log \frac{1 + 0.5x}{x} + 0.5x \log \frac{1 + 0.5x}{x}$$
$$+ (1 - x) \log \frac{1 + 0.5x}{x}$$
$$- \frac{R}{J}(1 + 0.5x) \log P.$$

Rearranging the logarithmic quantities

$$S = x\,S_{CO} + 0.5x\,S_{O_2} + (1 - x)\,S_{CO_2}$$
$$+ \frac{R}{J}\,(1 + 0.5x)\log(1 + 0.5x) - x \log x - 0.5x \log 0.5x$$
$$- (1 - x)\log(1 - x) - (1 + 0.5x) \log P \quad \text{......5.13}$$

Differentiating equation 5.13

$$dS = xdS_{CO} + 0.5xdS_{O_2} + (1 - x)\, dS_{CO_2} + (S_{CO} + 0.5S_{O_2} - S_{CO_2})dx$$
$$+ \frac{R}{J}\Big[(1 + 0.5x)\frac{1}{(1 + 0.5x)}\, 0.5 + 0.5 \log\,(1 + 0.5x)$$
$$- \Big\{x\,\frac{1}{x} + \log x + 0.5x\,\frac{1}{0.5x}\, 0.5 + 0.5 \log 0.5x$$
$$+ (1 - x)\,\frac{1}{(1 - x)}(-1) + (-1)\log(1 - x) + 0.5\log P\Big\}\Big]\, dx,$$

which reduces to

$$dS = xdS_{CO} + 0.5xdS_{O_2} + (1 - x)\, dS_{CO_2} + (S_{CO} + 0.5S_{O_2} - S_{CO_2})\, dx$$
$$+ \frac{R}{J} \log \left\{ \frac{1 - x}{x\,(0.5x)^{\frac{1}{2}}} \cdot \frac{(1 + 0.5x)^{\frac{1}{2}}}{(\,P\,)^{\frac{1}{2}}} \right\} dx$$

Hence

$$dS = x\, dS_{CO} + 0.5xdS_{O_2} + (1 - x)\, dS_{CO_2}$$
$$+ (S_{CO} + 0.5S_{O_2} - S_{CO_2})\, dx$$
$$+ \frac{R}{J} \log K_p \,.\, dx$$

Equation 3.18 gives for this reaction

$$\frac{R}{J}\left(\frac{\partial \log K_p}{\partial T}\right)_P = - \frac{H_p}{T^2}$$

i.e. $\frac{R}{J} \log K_p = \frac{H_p}{T} + c$ 5.14

or $\frac{RT}{J} \log K_p = H_p + c\, T$ 5.15

where c is a constant.

The left hand side of equation 5.15 represents the change in the standard free energies or maximum work and H_p is the change in the enthalpies or heat of reaction at constant pressure. Hence $c = -(S_{CO} + 0.5\, S_{O_2} - S_{CO_2})$. Substituting the value of $\frac{R}{J}\log K_p$ as given by equation 5.14 in the above expression for dS,

$$dS = x\, dS_{CO} + 0.5x\, dS_{O_2} + (1 - x)\, dS_{CO_2} + \frac{H_p}{T}\, dx$$

$$\text{i.e. } TdS = xTdS_{CO} + 0.5x\, TdS_{O_2} + (1 - x)\, TdS_{CO_2} + H_p\, dx$$

$$\text{or } \quad dQ = TdS$$

$$= x\, dH_{CO} + 0.5x\, dH_{O_2} + (1 - x)\, dH_{CO_2} + H_p\, dx$$

$$= dH,$$

where dH is as given by equation 5.4.

Making use of the equations obtained above it is possible to construct a temperature - entropy chart for CO_2. The chart shown in Fig. 5.3 is for one pound of CO_2 and it will be seen that five constant pressure curves, shown by full lines, and five constant volume curves, shown by broken lines, run from the bottom left-hand corner to the top right-hand corner of the grid. A series of pressures ranging from 0.01 to 100 atmospheres and a series of values of x ranging from 0.001 to 0.7 were chosen. For any value of P substitution of each value of x in turn in equation 5.1 gives the value of the right-hand side, and, by referring to a table of equilibrium constants, the value of T can be found which satisfies the values of x and P assumed. Thus a relationship between x and T is obtained for each value of P. Table 5.1 gives the values of x and T for P = one atmosphere and the entropy, s, is listed also.

FIG. 5.3

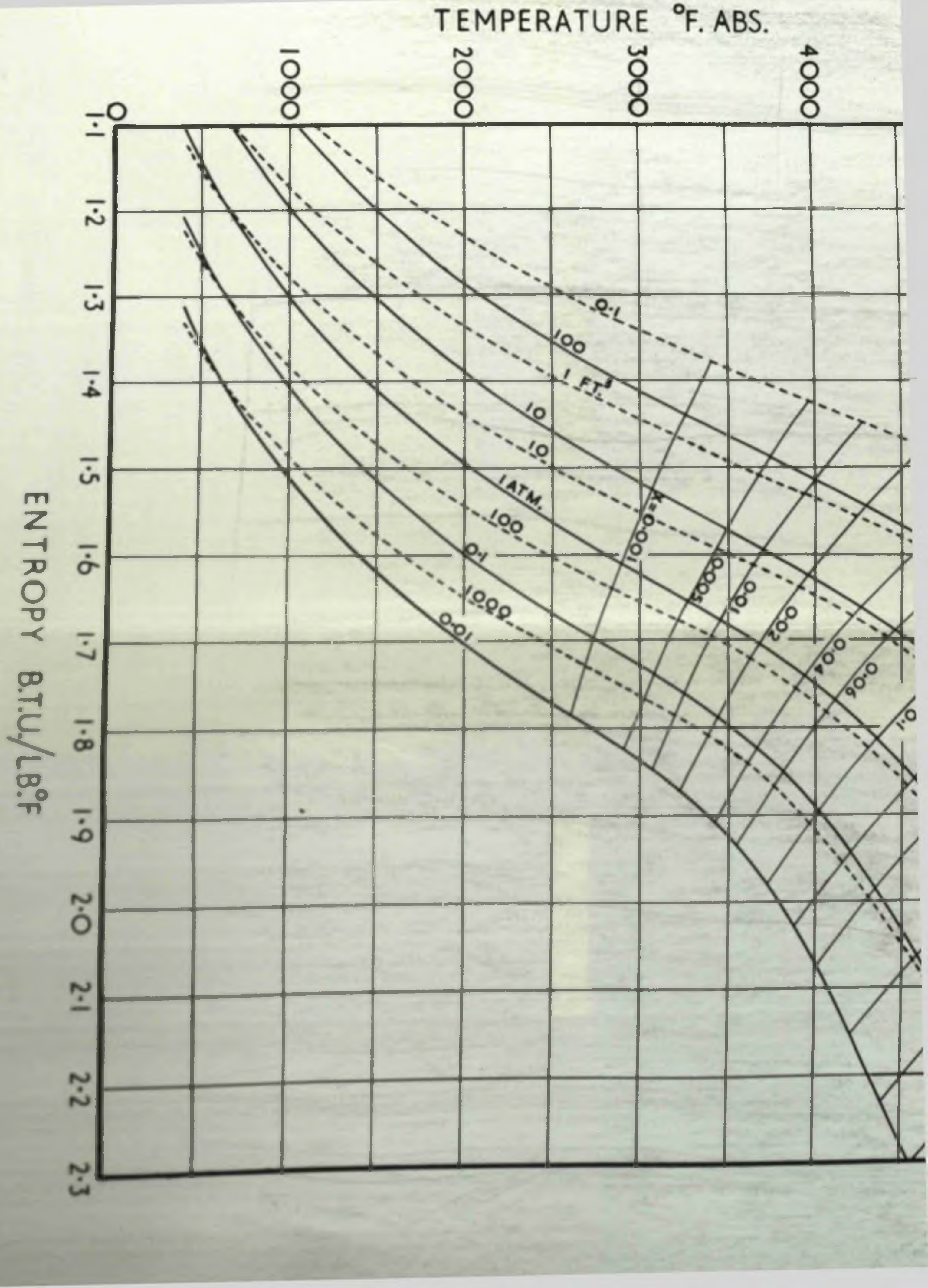

TEMPERATURE °F. ABS.
0
1000
2000
3000
4000
ENTROPY B.T.U./LB.°F
1·1
1·2
1·3
1·4
1·5
1·6
1·7
1·8
1·9
2·0
2·1
2·2
2·3
0·1
100
1 FT.³
10
10
1 ATM.
100
0·1
1000
0·01
X=0·001
0·005
0·01
0·02
0·04
0·06
0·1

TABLE 5.1

P = 1 atmos.		
x	T°F.abs.	S Btu/lb. °F.
0.001	2892	1.611
0.005	3269	1.654
0.01	3465	1.677
0.02	3688	1.705
0.04	3944	1.741
0.06	4112	1.769
0.10	4352	1.813
0.15	4570	1.859
0.2	4747	1.900
0.3	5036	1.975
0.4	5290	2.043
0.5	5535	2.106
0.6	5798	2.168
0.7	6099	2.229

At 4570°F. abs. the value of x is 0.15 and the equilibrium mixture consists of 0.15 mol. of CO, 0.85 mol. of CO_2 and 0.075 mol. of O_2. The details of the calculation using equation 5.6 are shown in table 5.2.

TABLE 5.2

Gas	m mols.	S $\frac{\text{Btu}}{\text{lb.mol.}^\circ\text{F.}}$	m S	$\frac{\Sigma m}{m}$	$m\frac{R}{J}\log\frac{\Sigma m}{m}$
CO	0.150	64.002	9.600	7.1667	0.587
CO_2	0.850	77.458	65.839	1.2647	0.397
O_2	0.075	66.421	4.982	14.3330	0.397
Σm = 1.075		ΣmS =	80.421	$\Sigma\left\{m\frac{R}{J}\log\frac{\Sigma m}{m}\right\}$ =	1.381

The total entropy at the temperature of 4570°F. abs. and at one atmosphere pressure is 80.421 + 1.381

= 81.802 B.T.U./lb.mol.°F.

= 1.859 B.T.U./lb.°F.

The construction of lines of constant volume involves the choice of some datum temperature. In this case the datum was chosen as 400°F. abs. Table 5.3 gives the initial conditions of pressure and temperature for the five volumes chosen.

TABLE 5.3

T °F. abs.	v $ft^3/lb.$	P atmospheres.
400	0.1	66.383
400	1.0	6.6383
400	10.0	0.66383
400	100.0	0.066383
400	1000.0	0.0066383

Substitution of corresponding values of T_1 and P_1 as given by table 5.3 in equation 5.9 yields an equation in x and T which may be rewritten as $\log K_p - \frac{1}{2} \log T = \log f(x)$. The right hand side of this equation may be evaluated for a series of values of x and the corresponding value of T found from a graph of $\log K_p - \frac{1}{2} \log T$ to a base of T.

TABLE 5.4.

v = 0.1 ft^3		
x	T °F. abs.	s BTU/lb. °F.
0.001	3407	1.377
0.005	3970	1.424
0.01	4276	1.448
0.02	4640	1.478
0.04	5080	1.515
0.06	5384	1.542
0.10	5837	1.583
0.15	6288	1.626

For the volume, $v = 0.1\ ft^3/lb.$, table 5.4 shows the values of T and s for the values x already used for the construction of the constant pressure lines. The entropy values in table 5.4 were determined using equation 5.6 the total pressure at any point was given by $P = \frac{(1 + 0.5x)\ P_1 T}{T_1}$ where $P_1 = 66.383$ atm. and $T_1 = 400$ °F. abs. from table 5.3.

The construction of those parts of the curves lying in the undissociated region ($x < 0.001$) requires no description.

Examination of the chart for one pound of CO_2 as shown in Fig. 5.3 illustrates the conclusions drawn in section 3, in particular, equations 3.18 and 3.19. It is clear that the degree of dissociation increases with temperature and that increase of pressure at constant temperature tends to suppress dissociation. There is a considerable divergence of the curves at temperatures above 3500°F. abs. and it is evident that the horizontal intercept between like curves increases with increasing temperature whereas in the undissociated region the horizontal intercept between like curves remains constant.

The temperature - entropy chart as representing the properties of a substance, while having a fundamental significance, shows energy quantities as areas. This feature is a handicap and the use of the enthalpy - entropy (Mollier) chart is widely acknowledged for most engineering problems. For the analysis of internal combustion engine cycles a chart representing the enthalpy or the internal energy of the fluid to a base of entropy is best suited. Equations 5.5 and 5.10 give expressions for thermal quantities corresponding to the enthalpy and internal energy for an undissociated gas. In the dissociated region the areas beneath the curves do represent changes in enthalpy and internal energy in the accepted sense but these quantities have been denoted by the symbols Q_p and Q_v in order to emphasise the presence of the chemical effect and to avoid confusion at this stage.

Table 5.5 shows, in tabular form, the calculations necessary with the pressure taken as one atmosphere to evaluate Q_p. The integral $\int H_p dx$ is obtained graphically. Table 5.6 gives the value of Q_v when v is taken as 0.1 ft^3 If it is decided to plot Q_v to a base of entropy, as shown in Fig. 5.4, the curves of constant volume are easily plotted using the values of entropy determined previously but the temperature lines and lines of constant Q_p value have to be interpolated making use of Fig. 5.3 as far as possible. Lines of constant x are shown although this is not essential. The ordinate may be taken as Q_p or Q_v depending on the purpose for which the chart is constructed. It is convenient to represent on the ordinate axis that function which is used more frequently than the other.

FIG.5.4

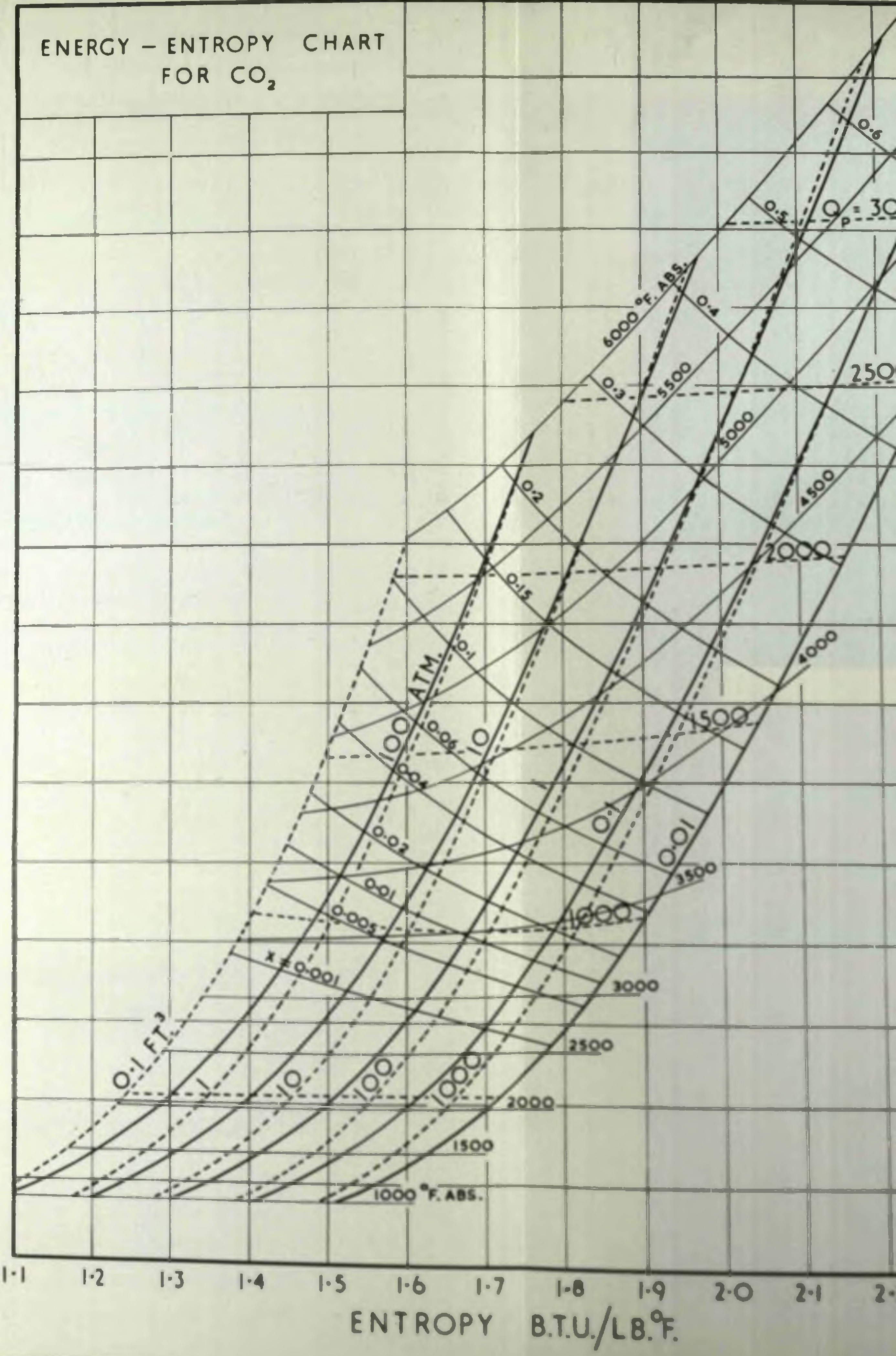

ENERGY – ENTROPY CHART FOR CO_2
Q_p = 30
250
2000
1500
1000
6000 °F. ABS.
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000 °F. ABS.
0·6
0·5
0·4
0·3
0·2
0·15
0·1
0·06
0·04
0·02
0·01
0·005
X = 0·001
100 ATM.
10
1
0·1
0·01
0·1 FT.³
1
10
100
1000
1·1
1·2
1·3
1·4
1·5
1·6
1·7
1·8
1·9
2·0
2·1
2·
ENTROPY B.T.U./LB.°F.

TABLE 5.5

x	T	$x\,H_{CO}$	$\frac{1}{2}\,x\,H_{O_2}$	$(1-x)H_{CO_2}$	H_p	$\int_0^x H_p\,dx$	Q_p $\frac{\text{B.T.U.}}{\text{lb.mol.}}$	Q_p $\frac{\text{B.T.U.}}{\text{lb.}}$
0.001	2,892	22	11	33,296	120,354	121	33,450	760.2
0.005	3,269	127	66	38,507	119,876	601	39,301	893.2
0.01	3,465	270	140	41,109	119,657	1,200	42,719	970.9
0.02	3,688	578	300	43,860	119,327	2,395	47,133	1,071
0.04	3,944	1,246	646	46,555	118,970	4,778	53,225	1,210
0.06	4,112	1,957	1,016	47,902	118,760	7,155	58,030	1,319
0.1	4,352	3,473	1,804	49,049	118,435	11,899	66,225	1,505
0.15	4,570	5,497	2,857	49,065	118,137	17,813	75,232	1,710
0.2	4,747	7,642	3,975	48,282	117,894	23,714	83,613	1,900
0.3	5,036	12,230	6,369	45,270	117,495	35,484	99,353	2,258
0.4	5,290	17,209	8,973	41,087	117,141	47,216	114,485	2,602
0.5	5,535	22,601	11,799	36,078	116,802	58,913	129,391	2,941
0.6	5,798	28,526	14,915	30,446	116,445	70,575	144,462	3,283
0.7	6,099	35,162	18,419	24,199	116,040	82,199	159,979	3,626

TABLE 5.6

x	T	$x\,E_{CO}$	$\frac{1}{2}\,x\,E_{O_2}$	$(1-x)E_{CO_2}$	H_v	$\int_0 H_v\,dx$	Q_v $\frac{\text{B.T.U.}}{\text{lb.mol.}}$	Q_v $\frac{\text{B.T.U.}}{\text{lb.}}$
0.001	2841	16	9	26973	117595	119	27117	615
0.005	3216	92	48	31393	116750	588	32121	730
0.01	3412	198	104	33640	116301	1171	35113	798
0.02	3632	424	223	35991	115794	2331	38969	886
0.04	3891	918	482	38388	115192	4641	44429	1010
0.06	4062	1447	760	39625	114792	6941	48773	1108
0.1	4306	2577	1355	40738	114220	11521	56191	1277
0.15	4534	4098	2156	40955	113683	17219	64428	1464
0.2	4718	5716	3010	40438	113010	22886	72050	1638
0.3	5028	9212	4860	38193	112511	34162	86427	1964
0.4	5304	13044	6892	34889	111852	45380	100205	2277
0.5	5574	17237	9123	30834	111216	56533	113727	2585
0.6	5866	21897	11615	26194	110530	67620	127326	2894

Dissociated Gas Mixtures - General Case.

The calculation of the composition of a dissociated gas mixture is as complicated as the number of equilibria chosen. Lewis and von Elbe(23) list the following equilibria when working with inflammable mixtures:

$$CO_2 \rightleftarrows CO + \tfrac{1}{2} O_2 \qquad \ldots\ldots\ldots\ldots 6.1$$

$$H_2O \rightleftarrows H_2 + \tfrac{1}{2} O_2 \qquad \ldots\ldots\ldots\ldots 6.2$$

$$H_2O \rightleftarrows OH + \tfrac{1}{2} H_2 \qquad \ldots\ldots\ldots\ldots 6.3$$

$$\tfrac{1}{2} N_2 + \tfrac{1}{2} O_2 \rightleftarrows NO \qquad \ldots\ldots\ldots\ldots 6.4$$

$$H_2 \rightleftarrows H + H \qquad \ldots\ldots\ldots\ldots 6.5$$

$$O_2 \rightleftarrows O + O \qquad \ldots\ldots\ldots\ldots 6.6$$

They do not consider mixtures rich enough to require the inclusion of equilibria involving radicals like C_2, CH etc. Although not the products of dissociation, peroxides of nitrogen and aldehydes have been detected in engine cylinders and in the exhaust of petrol engines. Pye(24) discussed these gases with reference to detonation as a chemical problem and mentions especially the name of Egerton(25) and those associated with him. It would appear that the number of equilibria to be considered in calculating the properties of the working fluid in internal combustion engines may be limited to the six listed above.

Hershey, Eberhardt and Hottel(5) in their work used the method of trial and error in solving the six equations for a given temperature and pressure. No doubt the work would be very laborious as the writer has experience of the calculations involved with only four unknowns. However, a method using punched cards and high speed computing machines to determine the gas composition at any pressure and temperature has been compiled in the Explosives and Physical Sciences Division of the Bureau of Mines at Pittsburgh(26). Other methods of programming the calculations have been put forward, see especially Brinkley(27), Kandiner and Brinkley(28), Damköhler and Edse(29), Sacksel, Mantis and Bell(30), Winternitz(31), Fehling and Leser(32) and Zeise(33). Although some of the methods advanced are attractive the writer felt that working alone he could not match the resources at the disposal of Lewis and von Elbe, their associates and others.

Construction of Energy Charts for Internal Combustion Engine Performance.

By extending the principles developed in section 5 for a single gas to a mixture of gases it is possible to construct charts for a mixture of gases and to include the effects of dissociation. The application of the new specific heats to the construction of energy charts for undissociated gas mixtures has been shown by Dr. Geyer(19) and the writer(6) has shown how charts for a dissociated mixture may be constructed. The type of chart developed in section 5 and shown in Fig. 5.4 for a single gas may be applied to the determination of the ideal cycle in an internal combustion engine. Before doing this, however, it is necessary to consider the limitations of such a chart and those additional factors which will affect its use.

(a) One chart serves for one air - fuel ratio only, as it is practically impossible to indicate the effect of different air - fuel ratios on a single chart.

(b) If it is considered that dissociation should be taken into account distinction must be made between the pre-and post - combustion mixtures, in which case a separate chart for the pre - combustion mixture must be drawn.

(c) The pre - combustion mixture is affected by the gases left in the cylinder after exhaust has taken place. The combustion and amount of the residual gases must be determined if the chart for the pre - combustion mixture is to take account of them.

(d) The mass of the residual gases is affected by variation in compression ratio, and so, strictly speaking, any one chart will be correct for one compression ratio only.

(e) It is assumed that the gases obey the gas laws and that at all points the mixture is in thermodynamic equilibrium.

If these five conditions are adhered to rigidly any chart will have very little use as it will be possible to represent only one cycle on it. This difficulty may be overcome without appreciable error by assuming a mean value for the mass of the residual gases, with the result that the only limitation placed upon the use of the chart is the fuel - air ratio.

The properties of one pound of the working fluid of an engine running on the chemically correct mixture of carbon monoxide and air are shown in Figs. 6.1, 6.2 and 6.3. It has been assumed that a fresh charge fills the cylinder for each cycle, the residual gases being completely purged. Only the dissociation of CO_2 has been taken into account with the object of allowing a comparison to be made between Fig. 5.3 and Fig. 6.2. It is to be noted that the number of mols. of CO per mol. of CO_2 (at any given pressure) is slightly more in the second case than in the first but that the distortion of the curves is less.

The chart for the pre - combustion mixture is shown in Fig. $\overset{6.2}{6.1}$ where enthalpy and internal energy are plotted to a base of entropy with the horizontal lines representing temperature. The properties of the post - combustion mixture in the dissociated region are shown in Fig. 6.2. ? The equations upon which the constant pressure and constant volume curves are based are respectively

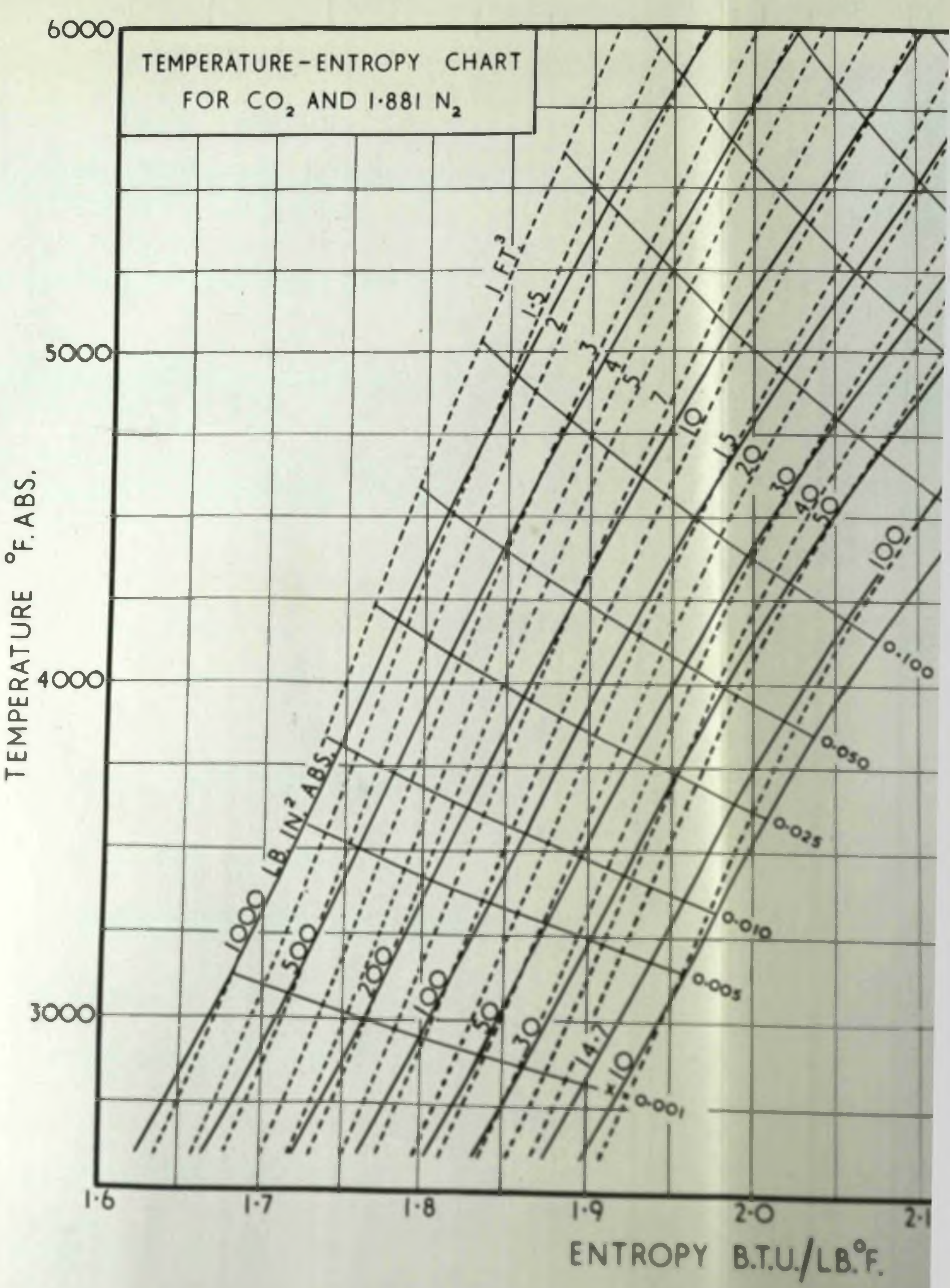
$$K_{p_{CO_2}} = \frac{1-x}{x}\left(\frac{5.762-x}{x}\right)^{\frac{1}{2}}\cdot\frac{1}{P^{\frac{1}{2}}} \quad ....6.1$$

and
$$K_{p_{CO_2}} = 33.947\left(\frac{1-x}{x}\right)\left(\frac{2}{x}\right)^{\frac{1}{2}}\left(P_1T\right)^{-\frac{1}{2}} \quad ....6.2$$

assuming $T_1 = 400^{\circ}$F. abs.

The method of setting up and solving these two equations for a series of values of x has been described in section 5 for

FIG.6.1



TEMPERATURE – ENTROPY CHART FOR CO_2 AND 1·881 N_2

FIG. 6.2

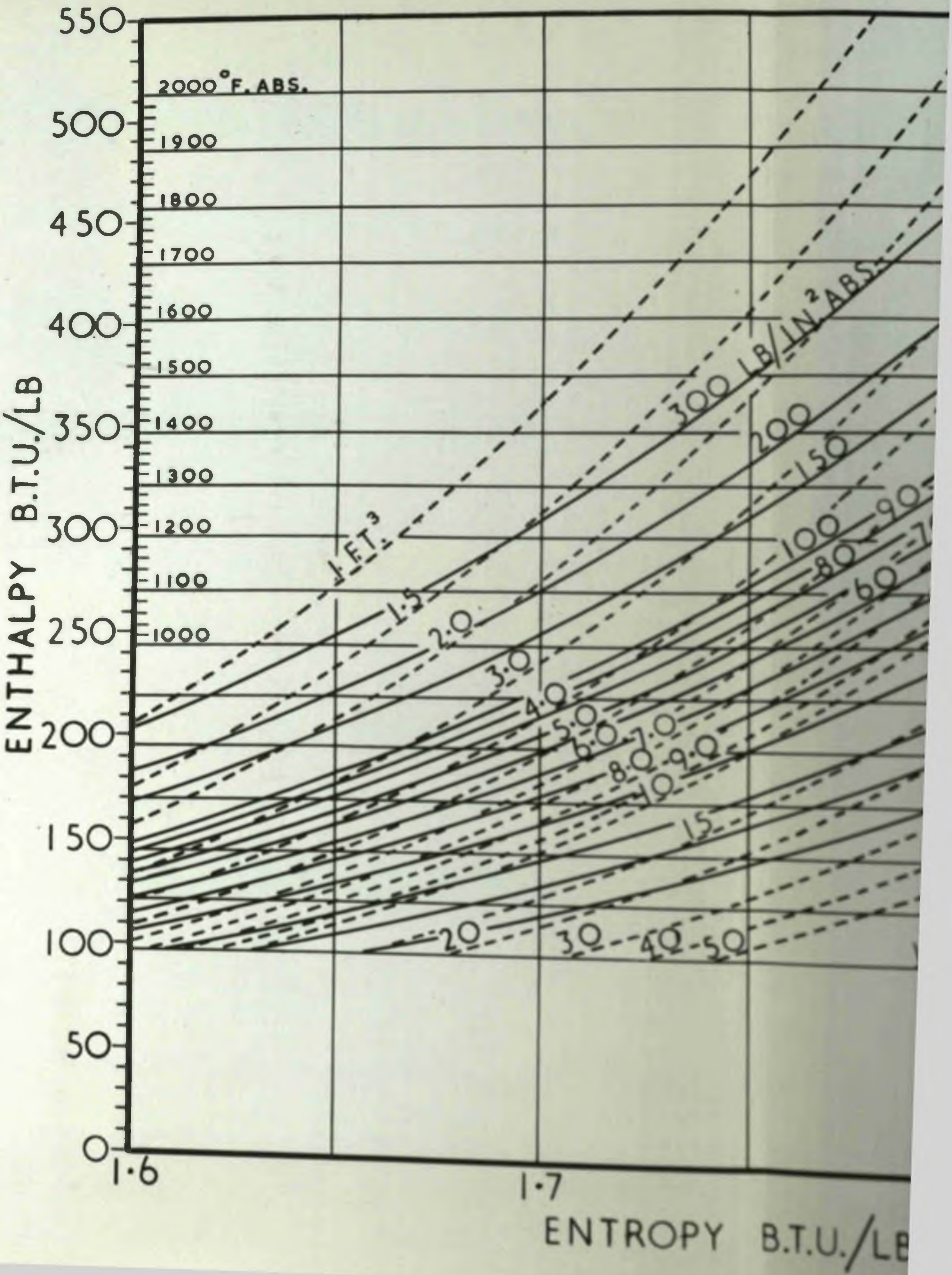
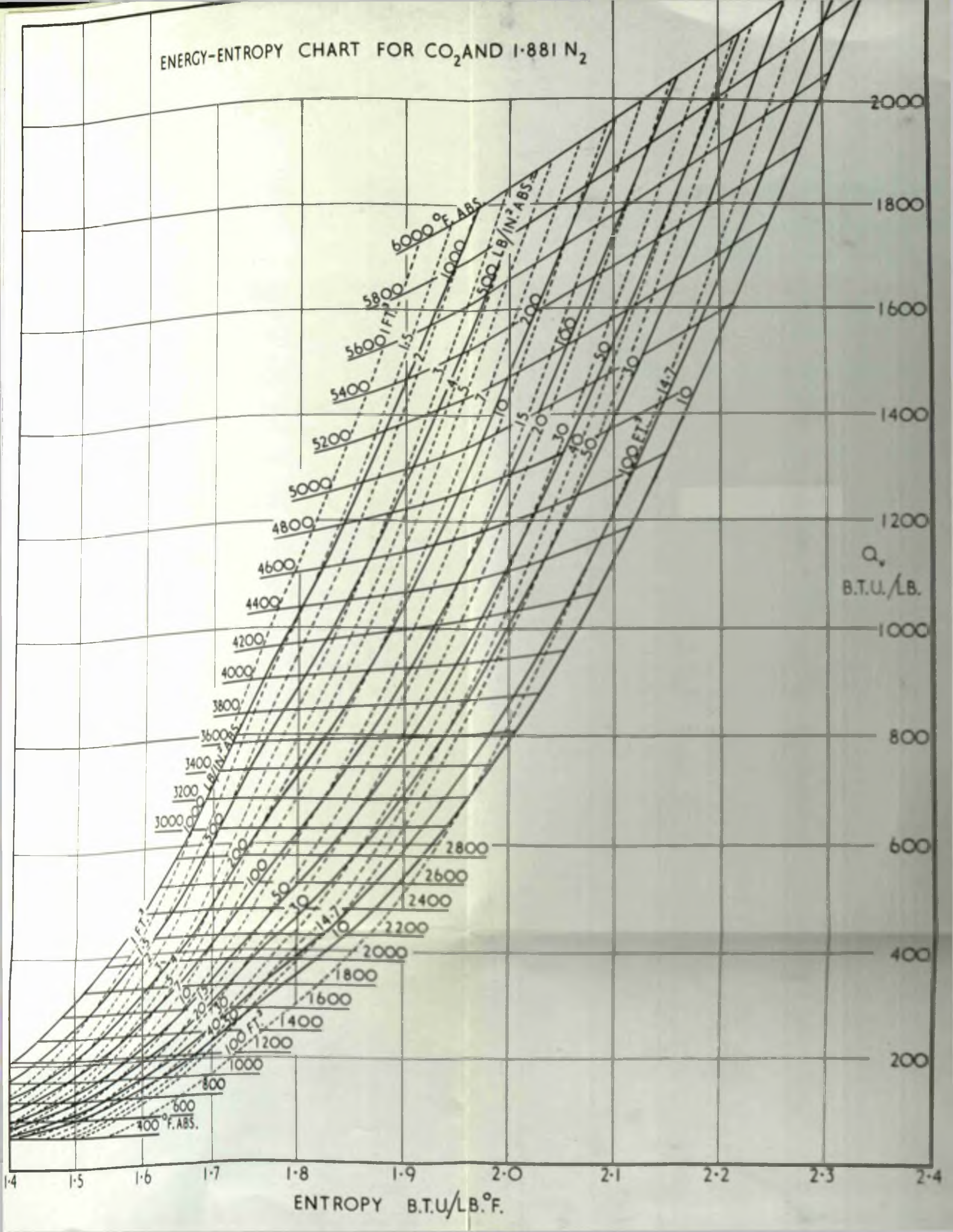

ENTHALPY B.T.U./LB
550
500
450
400
350
300
250
200
150
100
50
0
2000°F. ABS.
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
1 FT.3
1·5
2·0
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10
15
20
30
40
50
300 LB/IN.2 ABS.
200
150
100
90
80
70
60
1·6
1·7
ENTROPY B.T.U./LB

FIG. 6.3



ENERGY-ENTROPY CHART FOR CO_2 AND $1{\cdot}881\ N_2$

a single gas. The evaluation of Q_p and Q_v was based on the form of equations 5.8 and 5.12. In view of the number of functions which can be represented on an energy chart, (vide Fig. 5.4) the functions Q_p and x have been omitted from Fig. 6.3 to avoid confusion - the value of x is not generally needed at all and Q_p is not required in the problem given here as an example.

The ideal attainable efficiency of an internal combustion engine operating on the constant volume or Otto cycle maybe determined using the charts. Assume the temperature and pressure at the beginning of compression are 550°F. abs. and 14.7 lb/in^2 abs. respectively and that the volume compression ratio is 6. The initial state point is located on the compression chart, Fig. 6.1 where the pressure line corresponding to 14.7 lb/in^2 cuts the temperature line 550°F. abs. The volume at this point is 14 ft^3 and the internal energy is 95 B.T.U./lb. The volume at the end of compression is 14/6 or 2.33 ft^3 and since the compression is isentropic the temperature and internal energy can be read off as 1100°F. abs. and 194 B.T.U./lb. The work (absolute) of compression is thus 99 B.T.U./lb. Heating at constant volume commences from some point on Fig. 6.3 where the volume line, 2.33 ft^3, cuts the temperature line 1100°F. abs. and the heat added per pound is read from table 6.1. Generally it is taken that the fuel is completely burned at the lower

TABLE 6.1

°F. abs.	B.T.U./lb.
800	1253
900	1253
1000	1252
1100	1251
1200	1249
1300	1248
1400	1246

temperature and that all the heat liberated is available for heating up the products from this temperature. Table 6.1 shows the heat liberated at constant volume per pound of charge for different temperatures, obtained by dividing the heat of reaction per pound mol. of CO by the total mass associated with one mol., in this case 96.67 lb. The heat available in this case is 1251 B.T.U./lb., which, added to the value of Q_v at 1100°F. abs., gives the final value of Q_v as 1421 B.T.U./lb. and a maximum temperature of 5270°F. abs. From this point isentropic expansion takes place until the volume is 14. The temperature at the end of expansion is 3990°F. abs. with Q_v equal to 920 B.T.U./lb. The expansion work (absolute) is thus 501 B.T.U./lb. giving the net work per cycle as (501 - 99) = 402 B.T.U./lb. and an ideal attainable efficiency of $\frac{402}{1251}$, or 32%.

Discussion of energy charts to determine internal combustion performance would not be complete without special reference to the work of Hershey, Eberhardt and Hottel(5).

They produced a set of charts for the pre - and post - combustion mixtures for octane - air mixtures for three mixture strengths, 85, 100 and 110% air. The charts were energy - entropy charts of the type which the writer has described in this section and the only information not obtainable from the charts was the composition. The difficulty associated with the variation in the mass of the residual gases, see (d) above, was overcome by using a mean value. Undoubtedly these workers were the first to produce charts which could be used for a variety of purposes, "the calculation of the performance of various ideal engine cycles, including unthrottled, throttled, supercharged, variable - cut - off, compression - ignition and gas turbines". Although the value of the work cannot be denied the writer found that much of the fundamental knowledge essential to the understanding of the construction of the charts was missing. It was with a view to removing some of the mystery attached to the theory underlying dissociated gas mixtures that the writer made his contribution.

Calculation of the Maximum Attainable Temperature of a Combustible Mixture under Adiabatic Conditions.

The determination of the maximum temperature attainable in the cylinder of an internal combustion engine forms an important part of the analysis of an ideal engine cycle. In the modern reciprocating unit the case of combustion at constant pressure does not occur and only combustion at constant volume need be considered. The maximum temperature is estimated with reference to a thermal equation alone if dissociation is neglected, or with reference to a thermal equation and those equations which determine the equilibrium of the gases in the final state corresponding to the maximum temperature if dissociation is taken into consideration.

(a) Dissociation neglected:

The thermal equation expresses the principle that the energy of the reactants (i.e the pre-combustion mixture at the initial temperature) is equal to the energy of the products (i.e. the post-combustion mixture) at the maximum temperature. This is true for any combustible mixture reacting under constant volume conditions since no work or heat is exchanged with the surroundings. To illustrate this principle in symbols consider the case of the reaction at constant volume of CO with O_2 to form CO_2. The thermal equation may be written as $$\left[E_{CO} + \tfrac{1}{2} E_{O_2}\right]_{T_1} + \Delta E_0 = \left[E_{CO_2}\right]_{T_2} \quad \text{.........7.1}$$

where T_1 and T_2 are the initial and final temperatures. Equation 7.1 might be interpreted as follows: the reactants are cooled to the absolute zero of temperature and the energy given up $\left[E_{CO} + \tfrac{1}{2} E_{O_2}\right]_{T_1}$ is stored; the reaction is allowed to take place and the heat of reaction, ΔE_0, liberated at the absolute zero of temperature, is added to the energy already stored; the total energy stored is used to heat up the CO_2 so that the final energy of the CO_2, $\left[E_{CO_2}\right]_{T_2}$ is equal to $\left[E_{CO} + \tfrac{1}{2} E_{O_2}\right]_{T_1} + \Delta E_0$; the whole process is carried out at constant volume.

Equation 7.1 may be rewritten as

$$H_{v_{T_1}} + \left[E_{CO_2}\right]_{T_1} = \left[E_{CO_2}\right]_{T_2} \quad \text{........7.2}$$

since $\left[E_{CO} + \tfrac{1}{2} E_{O_2} - E_{CO_2}\right]_{T_1} + \Delta E_0 = H_{v_{T_1}}$.

Equation 7.2 becomes

$$H_{v_{T_1}} = \left[E_{CO_2}\right]_{T_1}^{T_2} \quad \text{.............7.3}$$

Equation 7.3 expresses the equality of the heat of reaction at constant volume at temperature, T_1, with the increase in the energy of the CO_2 from T_1 to T_2. A third way of writing equation 7.1 is possible using the expression

$$\left[E_{CO} + \frac{1}{2}E_{O_2} - E_{CO_2}\right]_{T_2} + \Delta E_0 = H_{v_{T_2}}$$

or
$$\left[E_{CO_2}\right]_{T_2} - \Delta E_0 = \left[E_{CO} + \frac{1}{2}E_{O_2}\right]_{T_2} - H_{v_{T_2}}$$

Equations 7.1 becomes

$$\left[E_{CO} + \frac{1}{2}E_{O_2}\right]_{T_1} = \left[E_{CO} + \frac{1}{2}E_{O_2}\right]_{T_2} - H_{v_{T_2}}$$

i.e.
$$H_{v_{T_2}} = \left[E_{CO} + \frac{1}{2}E_{O_2}\right]_{T_1}^{T_2} \quad \text{. ....7.4}$$

Thus there are three ways, as given by equations 7.1, 7.3 and 7.4 of expressing the conservation of energy in an adiabatic combustion process.

In the general case - assuming excess air - the products of combustion will consist of CO_2, H_2O, O_2 and N_2 and if the effects of dissociation are neglected the thermal equation may be written as

$$H_{v_{T_1}} = \left[E_{CO_2} + E_{H_2O} + E_{O_2} + E_{N_2}\right]_{T_1}^{T_2} \quad \text{........7.5}$$

where T_1 and T_2 are the initial and final temperatures and $H_{v_{T_1}}$ is the heat available at T_1 to raise the temperature of the products. (Compare equations 7.5 and 7.3).

(b) Dissociation considered:

All workers assume that chemical equilibrium exists between the reacting gases when the maximum temperature is reached. If a simple reaction is considered, as in (a) above, then the condition of equilibrium for a constant volume change is given by

$$K_p = \frac{1 - x}{x\,(0.5x)^{\frac{1}{2}}} \left(\frac{T_1}{P_1 T_2} \right)^{\frac{1}{2}} \qquad \ldots\ldots\ldots\ldots 5.9$$

where T_1, P_1 represent the initial temperature, pressure, and T_2 represents the final temperature. The thermal balance is obtained by equation 5.12 which may be written as

$$H_{v_1} = \Big[E_{CO_2} \Big]_{T_1}^{T_2} + x\,H_{v_2} \qquad \ldots\ldots\ldots\ldots\ldots 7.6$$

where H_{v_1} is the heat available at T_1 to raise the temperature of the products to the maximum temperature T_2.

When Dr. Geyer and the writer first studied dissociation they used the thermal equation given by Goodenough(15). This was in effect that given above by equation 7.6, and this equation or combinations of it was used by Dr. Geyer and the writer in Tables of Properties of Gases. However, in studying the subject further the writer discovered that the principle laid down by Goodenough implied a path for the heating of the product or products from T_1 to T_2. For the simple case under review equation 7.6 suggests that the CO_2 is heated from T_1 to T_2 and allowed to dissociate at T_2. In an actual fact no process could occur in this manner since the CO_2 would begin to dissociate before the temperature T_2 is reached. In other words equation 7.6 does not represent the area under a constant volume heating curve on the T-S diagram. A full account of the theory involved over this point is given in section 5. The fact that Schüle(22) showed the heat added (H_{v_1}) as the area beneath the curve prompted the writer to contribute an article (6) on the subject. Further the writer wished to remove any possibility of criticism of the methods used in Tables of Properties of Gases. The extent to which the approximate equations may be applied depends on the amount of dissociation. Where the amount of dissociation is appreciable it would be wrong to use the approximate forms but for internal combustion engine work the approximate forms suffice.

Among the present authorities on combustion the writer would cite Lewis and von Elbe(23). In setting up a thermal equation they consider the reaction to occur as follows:-

(a) Complete combustion at the initial temperature;

(b) Dissociation of dissociable products at the <u>initial</u> temperature;

(c) Heating of dissociated products to the final temperature.

Three methods of setting down the thermal equation may be classified as I, Goodenough's method, II, a variation of I, and III, the method of Lewis and von Elbe. That the methods are the same may be seen in the following:-

Example - $CO + \frac{1}{2} O_2 \rightarrow CO_2$

Thermal equation - $Q = \left[E_{CO_2}\right]_{T_1}^{T_2} + x\, H_{v_2}$

Method I

$$H_{v_1} = \left[E_{CO_2}\right]_{T_2} - \left[E_{CO_2}\right]_{T_1} + x\, H_{v_2}$$

This assumes that all the heat is liberated at T_1 and that the CO_2 is heated to T_2 before dissociation occurs.

Method II

If it is assumed that the reactants are heated to T_2 before allowing reaction and dissociation then

$$(1 - x)\, H_{v_2} = \left[E_{CO} + \frac{1}{2} E_{O_2}\right]_{T_2} - \left[E_{CO} + \frac{1}{2} E_{O_2}\right]_{T_1}$$

This is the same as I as is shown below

$$H_{v_2} = \left[E_{CO} + \frac{1}{2} E_{O_2} - E_{CO_2} + \Delta E_0\right]_{T_2}$$

$$H_{v_1} = \left[E_{CO} + \frac{1}{2} E_{O_2} - E_{CO_2} + \Delta E_0\right]_{T_1}$$

Now

$$(1 - x)\left[E_{CO} + \frac{1}{2} E_{O_2} - E_{CO_2} + \Delta E_0\right]_{T_2} = \left[E_{CO} + \frac{1}{2} E_{O_2}\right]_{T_2} - \left[E_{CO} + \frac{1}{2} E_{O_2}\right]_{T_1}$$

i.e. $\left[E_{CO} + \frac{1}{2} E_{O_2} - E_{CO_2} + E_0\right]_{T_2} - x H_{v_2} = \left[E_{CO} + \frac{1}{2} E_{O_2}\right]_{T_2} - \left[E_{CO} + \frac{1}{2} E_{O_2}\right]_{T_1}$

i.e. $\left[E_{CO} + \frac{1}{2} E_{O_2}\right]_{T_1} + \Delta E_0 = \left[E_{CO_2}\right]_{T_2} + x\, H_{v_2}$

or $H_{v_1} + \left[E_{CO_2}\right]_{T_1} = \left[E_{CO_2}\right]_{T_1} + x\, H_{v_2}$

i.e. $H_{v_1} = \left[E_{CO_2}\right]_{T_2} - \left[E_{CO_2}\right]_{T_1} + x H_{v_2}$ - as I

Method III

If the method of Lewis and von Elbe is considered one has

$$\begin{aligned}
H_{v_1} &= \left[x E_{CO} + 0.5x E_{O_2} + (1 - x) E_{CO_2}\right]_{T_1}^{T_2} + x H_{v_1} \\
&= \left[x E_{CO} + 0.5x E_{O_2} + (1 - x) E_{CO_2}\right]_{T_2} \\
&\qquad - \left[x E_{CO} + 0.5x E_{O_2} + (1 - x) E_{CO_2}\right]_{T_1} \\
&\qquad\qquad + \left[x E_{CO} + 0.5x E_{O_2} - x E_{CO_2} + x \Delta E_0\right]_{T_1} \\
&= \left[x E_{CO} + 0.5x E_{O_2} - x E_{CO_2}\right]_{T_2} + \left[E_{CO_2}\right]_{T_2} \\
&\qquad - \left[x E_{CO} + 0.5x E_{O_2} - x E_{CO_2}\right]_{T_1} - \left[E_{CO_2}\right]_{T_1} \\
&\qquad + \left[x E_{CO} + 0.5x E_{O_2} - x E_{CO_2} + x \Delta E_0\right]_{T_1} \\
&= \left[E_{CO_2}\right]_{T_2} - \left[E_{CO_2}\right]_{T_1} + \left[x E_{CO} + 0.5E_{O_2} - x E_{CO_2} + x \Delta E_0\right]_{T_2} \\
&= \left[E_{CO_2}\right]_{T_2} - \left[E_{CO_2}\right]_{T_1} + x H_{v_2} \qquad \text{- as I}
\end{aligned}$$

As before, in the general case - assuming excess air - the products of combustion will consist of CO_2, H_2O, O_2 and N_2. If the equilibria $CO_2 \rightleftarrows CO + \frac{1}{2} O_2$, $H_2O \rightleftarrows H_2 + \frac{1}{2} O_2$, $OH + \frac{1}{2} H_2 \rightleftarrows H_2O$ and $\frac{1}{2} N_2 + \frac{1}{2} O_2 \rightleftarrows NO$ are considered then the thermal equation is given by

$$H_{v_1} = \left[E_{CO_2} + E_{H_2O} + E_{O_2} + E_{N_2} \right]_{T_1}^{T_2} + \left[x\, H_{v_{CO}} + y\, H_{v_{H_2}} + u\, H_{v_{OH}} + z\, H_{v_{NO}} \right]_{T_2} \quad \ldots .7.7$$

and the equilibrium equations by

$$K_{p_{CO_2}} = \frac{p_{CO_2}}{p_{CO} \cdot p_{O_2}^{\frac{1}{2}}} \quad \ldots\ldots\ldots 7.8$$

$$K_{p_{w.g.}} = \frac{p_{CO} \cdot p_{H_2O}}{p_{H_2} \cdot p_{CO_2}} \quad \ldots\ldots\ldots\ldots 7.9$$

$$K_{p_{OH}} = \frac{p_{H_2O}}{p_{OH} \cdot p_{H_2}^{\frac{1}{2}}} \quad \ldots\ldots\ldots 7.10 \text{ and}$$

$$K_{p_{NO}} = \frac{p_{N_2}}{p_{NO}^{\cancel{\frac{1}{2}}} \cdot p_{O_2}^{\frac{1}{2}}} \quad \ldots\ldots\ldots\ldots 7.11$$

where x, y, u and z represent the number of mols. of CO_2, H_2, OH and NO formed due to the equilibria considered. The method of solving equations 7.7, 8, 9, 10 and 11 is detailed in Tables of Properties of Gases (page 51, for example). In the work of this thesis the writer has not considered as many variables. A fuller discussion of the number of equilibria which might be considered is given in section 6. The method of solving the equations is by trial and error. However, with three unknowns the work is reduced, i.e. if the effect of the formation of NO and OH is neglected and only the dissociation of the triatomic molecules CO_2 and H_2O is considered.

Examples.

The following examples are given to illustrate the results of a number of calculations which the writer made when he first worked on dissociation problems. No details of the calculations are given as the method has been adequately illustrated in section 9 and in Tables of Properties of Gases. The purpose of giving the examples is to show (a) the effect of considering the formation of OH and NO and (b), in example (C) the agreement with the value Pye$^{(24)}$ gives.

Maximum attainable temperatures - volume constant.

(A) $H_2 + 0.5O_2 + 1.881\ N_2 \rightarrow H_2O + 1.881\ N_2$

(i) Considering the equilibrium $H_2O \rightleftarrows H_2 + \frac{1}{2}O_2$

(ii) Considering the equilibrium $H_2O \rightleftarrows \frac{1}{2}H_2 + OH$

(iii) Considering both (i) and (ii)

Result:

Initial pressure and temperature, 1 atmos. and 600°F. abs.

(i) 5160°F. abs. 8.19% H_2O dissociated to H_2

(ii) 5128°F. abs. 7.72% " " " OH

(iii) 5055°F. abs. (4.4% H_2O dissociated to OH
(5.52% " " " H_2

(B) $CO + 0.5\ O_2 + 1.881\ N_2 \rightarrow CO_2 + 1.881\ N_2$

(i) Considering the equilibrium $CO_2 \rightleftarrows CO + \frac{1}{2}O_2$

(ii) Considering (i) and the formation of NO according to the equilibrium $\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightleftarrows NO$.

Result:

Initial pressure and temperature, 1 atmos. and 600°F. abs.

(i) 4908°F. abs. 19.16% CO_2 dissociated to CO

(ii) 4867°F. abs. (19% CO_2 dissociated to CO
(1% N_2 " " NO

(C) The combustion of benzene with the "correct" air in an internal combustion engine to which the following data supply:[†]

Temperature of charge at end of suction - 100°C.

Pressure of charge at end of suction, 1 atm. (671.4°F. abs.)

Volume compression ratio - 5

Temperature and pressure at the end of isentropic compression, 1160°F. abs. and 8.639 atm.

Considering the equilibria $CO_2 \rightleftarrows CO - \frac{1}{2} O_2$ and $H_2O \quad H_2 - \frac{1}{2} O_2$ and taking the heat supplied at constant volume to be the same as that which Pye used the following result was obtained (Pye's values in brackets.)

T_{max} = 5350°F. abs. (5360°F. abs.)

25% (25%) CO_2 dissociated to CO

4.2% (4.6%) H_2O " " H_2

(D) Example (C) including the formation of NO

T_{max} = 5285°F. abs.

25.3% CO_2 dissociated to CO

4.32% H_2O " " H_2

1.64% N_2 " " NO

[†] Pye, I.C. Engine, p 67.

(E) Example (D) including the formation of OH

$$T_{max} = 5248^{\circ}F.\ abs.$$

Ideal Petrol Engine Cycle.

The analyses of the twenty eight ideal cycles, of which the results are given in the following section, were based on an "open" Otto cycle. The "closed" or conventional Otto cycle, yielding the value of $1 - \left(\frac{1}{r_c}\right)^{\gamma - 1}$ for the thermal efficiency when γ is taken as constant, is applicable when the working substance does not leave the working chamber, and when no distinction is made between the pre- and post-combustion mixture. Since this cycle is so far removed from actual operating conditions an "open" cycle was adopted as a basis for computing the ideal performance.

"Open" Otto Cycle:-

(i) Suction at constant atmospheric pressure - the effect of clearance gases being neglected (see (v)).

(ii) Isentropic compression.

(iii) Combustion at constant volume under adiabatic conditions.

(iv) Isentropic expansion until the initial volume is reached, at which point release occurs.

(v) Release - adiabatic expansion through the exhaust valve until the gases have expanded to atmospheric pressure. It is convenient to assume that all the gases in the cylinder leave and that there are no gases left in the clearance volume at the end of the exhaust stroke during which the pressure is assumed to be atmospheric.

(vi) The exhaust gases are cooled at constant pressure until the base temperature is reached.

In view of the calculative effort imposed by considering the clearance gases it was decided to neglect them and to assume that the limit of performance would be reached when a fresh charge filled the total cylinder volume for each cycle. If the clearance gases are included in any analysis it will be necessary to recalculate the cycle having estimated the temperature at the end of suction. Examination of other work, notably that of Goodenough and Felbeck(34), showed that a value of 600°F. abs. might be taken as a mean for the compression ratios considered. Using the charts previously constructed for an ideal engine running on CO the writer was able to show to a close approximation how the temperature at the end of suction might be expected to vary with variation in compression ratio. The results of these calculations are shown in Fig. 8.1 together with four values given by Goodenough and Felbeck for octane.

$T_6 = T_1 = (600^\circ\text{F. abs.})$

$p_6 = p_5 = p_1 = p_a =$ atmos. pressure

$V_4 = V_1$

$V_2 = V_3 =$ clearance volume

$$E_1 = \left[E_{\text{reactants}}\right]_{T_1} + \Delta E_o$$

$$E_2 = \left[E_{\text{reactants}}\right]_{T_2} + \Delta E_0$$

$\Delta E_0 =$ heat of reaction at absolute zero of temperature

$$E_3 = \left[E_{\text{products}}\right]_{T_3}$$

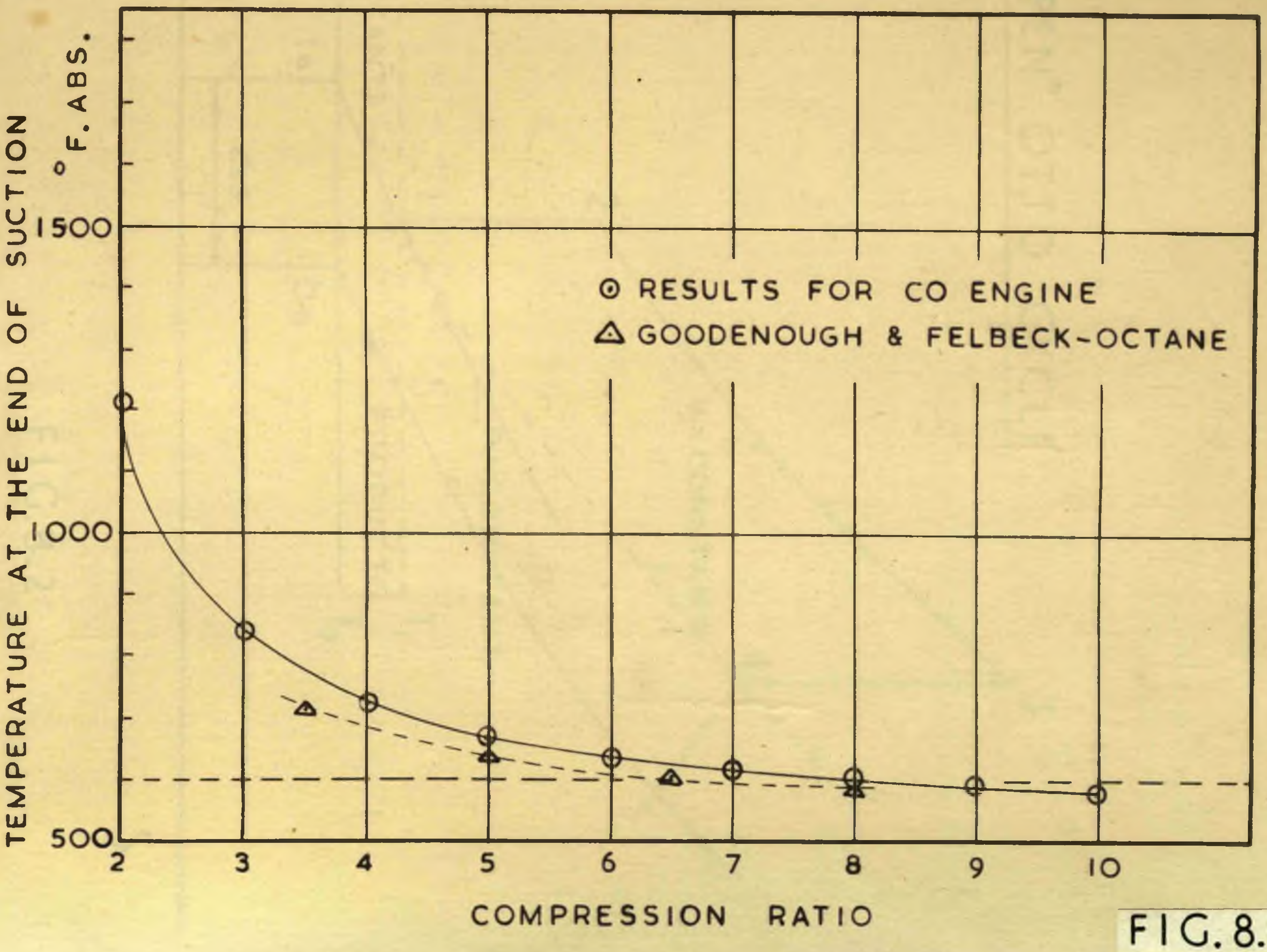
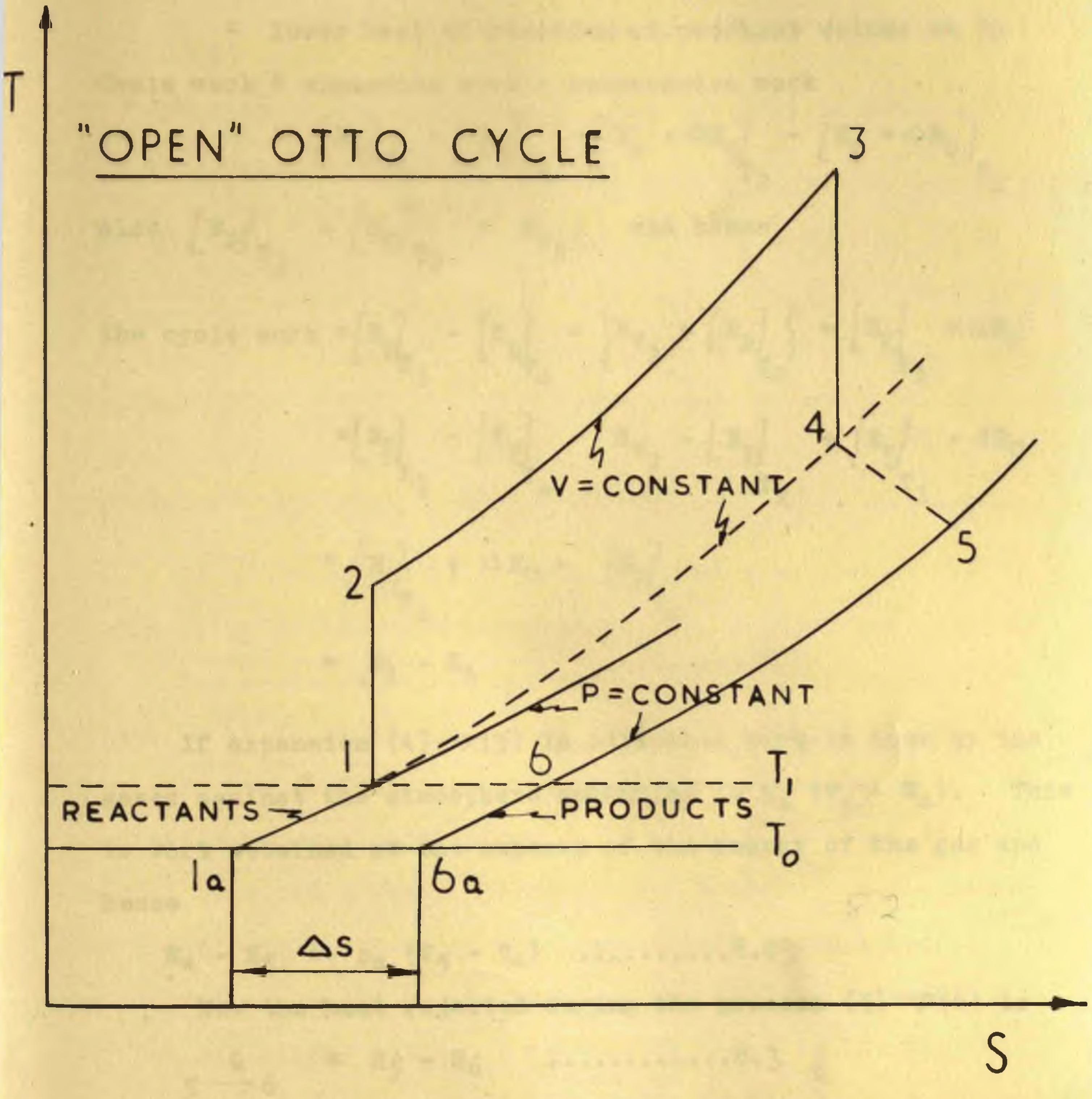

TEMPERATURE AT THE END OF SUCTION °F. ABS.
1500
1000
500
2
3
4
5
6
7
8
9
10
COMPRESSION RATIO
⊙ RESULTS FOR CO ENGINE
△ GOODENOUGH & FELBECK-OCTANE

FIG. 8.1



"OPEN" OTTO CYCLE
T
S
3
4
5
2
1
6
1a
6a
V = CONSTANT
P = CONSTANT
REACTANTS
PRODUCTS
T_1
T_0
Δs

FIG.8.2

$$E_4 = \left[E_{\text{products}}\right]_{T_4}$$

$$H_{v_2} = \left[E_{\text{reactants}} - E_{\text{products}}\right]_{T_2} + \Delta E_0 \quad \text{or} \quad \left[E_r - E_p\right]_{T_2} + \Delta E_0$$

= lower heat of reaction at constant volume at T_2

Cycle work = expansion work - compression work

$$= \left[E_p\right]_{T_3} - \left[E_p\right]_{T_4} - \left[E_r + \Delta E_0\right]_{T_2} - \left[E_r + \Delta E_0\right]_{T_1}$$

Also $\left[E_p\right]_{T_3} - \left[E_p\right]_{T_2} = H_{v_2}$ and hence

$$\text{the cycle work} = \left[E_p\right]_{T_3} - \left[E_p\right]_{T_4} - \left\{H_{v_2} + \left[E_p\right]_{T_2}\right\} + \left[E_r\right]_{T_1} + \Delta E_0$$

$$= \left[E_p\right]_{T_3} - \left[E_p\right]_{T_4} - H_{v_2} - \left[E_p\right]_{T_2} + \left[E_r\right]_{T_1} + \Delta E_0$$

$$= \left[E_r\right]_{T_1} + \Delta E_0 - \left[E_p\right]_{T_4}$$

$$= E_1 - E_4 \qquad ....8.1$$

If expansion (4) → (5) is adiabatic, work is done by the gases against the atmosphere amounting to $p_a\ (V_5 - V_4)$. This is work obtained at the expense of the energy of the gas and hence

$$E_4 - E_5 = p_a\ (V_5 - V_4) \qquad .1........8.2$$

Now the heat rejected during the process (5) → (6) is

$$\underset{5 \rightarrow 6}{Q} = H_5 - H_6 \qquad ....8.3$$

Regrouping equation (2) gives

$$E_4 + p_aV_4 = E_5 + p_aV_5 = H_5 \ldots\ldots\ldots 8.4$$

and substituting in 8.3 gives the heat rejected

$$Q_{5 \rightarrow 6} = E_4 + p_aV_4 - H_6 \ldots\ldots\ldots 8.5$$

The addition of the work done 8.1 and the heat rejected gives the heat supplied which is

$$(E_1 - E_4) + (E_4 + p_aV_4 - H_6)$$

$$= E_1 + p_aV_4 - H_6 \qquad\qquad V_4 = V_1$$

$$\qquad\qquad p_aV_4 = p_aV_1$$

$$= H_1 - H_6 \qquad\qquad E - p_aV_1 = H_1$$

Further $H_1 = \left[H_r\right]_{T_1} + \Delta E_0$ and $H_6 = \left[H_p\right]_{T_1}$

and $H_{p_{T_1}} = H_1 - H_6 =$ heat supplied.

It is conventional to take the heat supplied as that value of H_p at the base temperature, T_0, and not the value at T_1. The above relations are not invalidated by doing this since H_p at T_1 bears a definite relation to H_p at T_0 and in any case one is free to choose any common denominator in estimating thermal efficiency. In this connection it is useful to quote Hershey, Eberhardt and Hottel(5) who stated in a footnote. "There is little unanimity among automotive engineers as to the proper value to use for the denominator of the efficiency ratio. A reasonable value is the maximum possible work from a reversible engine operating in surroundings at constant pressure and temperature and discharging its products of combustion at partial pressures equal to those existing in the products of perfect combustion of fuel with theoretical air at room temperature and pressure. That value is given by the thermodynamic quantity ΔF, the "free energy" change at the pressure and temperature of the surroundings, from liquid octane to products of combustion, water as liquid.

A more commonly used quantity, however, is the net heat of combustion at constant pressure ΔH, with fuel and product water both as vapour. The justifications for its use are that (a) it is perhaps a more familiar quantity to engineers, (b) it differs but little from ΔF numerically in the case of motor fuels and (c) no error is introduced in using any arbitrary value for the denominator provided the same value is used in other related calculations."

The above quotation illustrates the facts of the case so clearly that there is little to add. However, when it is desired to make a Second Law Analysis the distinction which Hershey, Eberhardt and Hottel draw between ΔF and ΔH has to be observed. This is because the entropies of the reactants and products are never the same at the base temperature. In fact the entropy of the products with octane is always greater than the entropy of the reactants with reference to a common datum. If H_p represents the heat available at T_0 - heat which could be measured in a calorimeter - then $T_0 \Delta s$ represents the "bound energy" or that amount which cannot be converted to work by even a reversible engine working at constant temperature and pressure. If the value of H_p is to be used as the denominator in a Second Law Analysis the $T_0 \Delta S$ term has to be made to vanish. This can be done only by making $s_{1a} = s_{6a}$ - in other words the entropies of the products are corrected to the common reference state at 1a by subtracting Δs, or, by correcting the entropies of the reactants to the common reference state at 6a by adding Δs. The writer preferred the first method and has called the term $T_0 \Delta s$ the "chemical effect". In the analysis the "chemical effect" is shown as a separate item since the only irreversibility affected is that due to the combustion process.

The only workers who gave any indication of how the entropies were calculated were Hershey, Eberhardt and Hottel(5). Even here the reader is confronted by the following statement: "For further quantitative consideration of the entropy concept, essential to an understanding of the technique of calculating the diagrams but not to their intelligent use, the reader is referred to any standard text book on thermodynamics". The writer would challenge this statement but it is difficult to prove them wrong because of the obscurity surrounding this point. Keenan(10) using the H.E. and H charts found $\Delta S = 0.055$ whereas the writer obtained 0.064 for an exactly similar problem. The reason for this difference the writer believes may lie in the fact that the above workers appear to have calculated the entropy of a mixture of gases by assuming that each gas occupied its own partial volume at the total pressure whereas the writer took each gas to occupy the total volume exerting its own partial pressure, a state more likely to fit any actual case since the gases of the reactants and the products are mixed both entering and leaving the engine.

Ideal Petrol Engine Cycle. (Results).

The equation

$$(1 + \alpha)\ C_8H_{18} + 12.5O_2 + 47.024N_2$$

$$\longrightarrow a\ CO + b\ CO_2 + c\ H_2O + d\ O_2 + 47.024N_2$$

represents the general case of the combustion of octane vapour with air, the symbol $\underline{\alpha}$ being the measure of the mixture strength. For given values of $\underline{\alpha}$ the unknown number of mols. a, b, c and d may be found. Mixtures weak in fuel correspond to negative values of $\underline{\alpha}$ and rich mixtures to positive values of $\underline{\alpha}$

The main results of the calculations are given in the following tables:-

<u>Table 9.1</u> The compositions by volume or mols. of the pre- and post-combustion mixtures together with the apparent molecular weights (A.M.W.) and gas constants (R, ft.lb/lb.°F.).

<u>Table 9.2</u> The volumes (ft³/lb.) and the entropies (B.T.U./lb.°F) of the reactants at 520 and 600°F. abs., the pressure being 14.7 lb/in².

<u>Table 9.3</u> The pressures (lb/in².), volumes (ft³/lb.), temperatures (°F. abs.) and entropies (B.T.U./lb.°F.) at the end of compression. Values are for reactants.

<u>Table 9.4,5,6,7</u> The pressures (lb/in².), volumes(ft³/lb.) temperatures (°F. abs.), entropies (B.T.U./lb.°F.) at the end of constant volume burning, at the end of expansion, after release, and at the initial temperature respectively.

Table 9.8 The values of x and y for the dissociated mixture at the end of combustion.

Table 9.9 The internal energy values of the post-combustion mixture at the temperature at the end of compression.

Table 9.10 The energy available to heat one mol of products from the temperature at the end of compression to the maximum temperature.

Table 9.11 Relation between "mixture strength" and "percentage air", etc.

Table 9.12 Expansion, compression and cycle works, B.T.U./lb.

Table 9.13 Thermal efficiencies.

Table 9.14 Mean effective pressures, lb/in^2.

Table 9.15 Specific consumptions, lb/h.p.hour.

Tables 9.16,17,18,19,20,21 and 22. Energy values (E) and available energy (a.e.) values together with values of $\frac{p_o v}{5.404}$ and $T_o s$. All values are B.T.U./lb., with $p_o = 14.7\ lb/in^2$ and $T_o = 520°F$. abs.

Table 9.23 Irreversibilities, B.T.U./lb.

The determination of the properties listed in the first seven tables offers no special difficulty apart from the calculation of the maximum attainable temperature and the properties associated with this state. The effect of dissociation at the end of expansion has been neglected, the effect being small, being worst for the "correct" air/fuel ratio and resulting in the temperature at the end of expansion being overestimated by 50 and 100 degrees. Thus, although the entropy

(Continued on page 97)

TABLE 9.1

Pre-combustion mixtures.

Gas / α	-0.3	-0.2	-0.1	0	0.1	0.2	0.3
C_8H_{18}	0.0116	0.0133	0.0149	0.0165	0.0181	0.0198	0.0214
O_2	0.2076	0.2072	0.2069	0.2065	0.2062	0.2058	0.2055
N_2	0.7808	0.7795	0.7782	0.7770	0.7757	0.7744	0.7731
A.M.W	29.827	29.972	30.110	30.245	30.381	30.526	30.663
R	51.799	51.559	51.322	51.093	50.865	50.623	50.397

Post-combustion mixtures.

Gas / α	-0.3	-0.2	-0.1	0	0.1	0.2	0.3
CO_2	0.0894	0.1014	0.1133	0.1250	0.0959	0.0682	0.0420
H_2O	0.1005	0.1141	0.1274	0.1406	0.1506	0.1602	0.1693
O_2	0.0598	0.0396	0.0197	- CO →	0.0380	0.0742	0.1085
N_2	0.7503	0.7449	0.7396	0.7344	0.7155	0.6974	0.6802
A.M.W	28.665	28.640	28.617	28.594	28.029	27.490	26.979
R	53.910	53.957	54.000	54.044	55.133	56.214	57.279

TABLE 9.2

	α	-0.3	-0.2	-0.1	0	0.1	0.2	0.3
520°F. abs.	v_{1a}	12.724	12.665	12.607	12.551	12.495	12.436	12.380
	s_{1a}	1.613	1.609	1.605	1.602	1.598	1.595	1.591
600°F. abs.	v_1	14.682	14.614	14.547	14.482	14.418	14.349	14.285
	s_1	1.649	1.645	1.642	1.639	1.635	1.632	1.629

$p = 14.7$ lb/in^2.

TABLE 9.3

r_c	α	-0.3	-0.2	-0.1	0	0.1	0.2	0.3
6	p_2	162.88	161.26	159.94	158.61	156.85	155.97	154.94
	v_2	2.447	2.436	2.425	2.414	2.403	2.392	2.381
	T_2	1108	1097	1088	1079	1067	1061	1054
	s_2	1.649	1.645	1.642	1.639	1.635	1.632	1.629
7	p_2	199.63	197.57	195.68	193.80	191.57	190.19	188.99
	v_2	2.097	2.088	2.078	2.069	2.060	2.050	2.041
	T_2	1164	1152	1141	1130	1117	1109	1102
	s_2	1.649	1.645	1.642	1.639	1.635	1.632	1.629
8	p_2	237.94	235.20	232.85	230.50	227.75	226.18	224.42
	v_2	1.835	1.827	1.818	1.810	1.802	1.794	1.786
	T_2	1214	1200	1188	1176	1162	1154	1145
	s_2	1.649	1.645	1.642	1.639	1.635	1.632	1.629
9	p_2	277.61	274.30	271.44	268.57	264.82	263.06	260.85
	v_2	1.631	1.624	1.616	1.609	1.602	1.594	1.587
	T_2	1259	1244	1231	1218	1201	1193	1183
	s_2	1.649	1.645	1.642	1.639	1.635	1.632	1.629

TABLE 9.4

r_c	α	-0.3	-0.2	-0.1	0	0.1	0.2	0.3
6	p_3	667.57	715.95	753.74	778.38	777.47	771.90	743.67
	v_3	2.447	2.436	2.425	2.414	2.403	2.392	2.381
	T_3	4535	4852	5085	5215	5255	5251	5059
	s_3	2.037	2.067	2.093	2.117	2.141	2.171	2.182
7	p_3	786.10	842.38	886.29	915.02	913.85	906.73	873.97
	v_3	2.097	2.088	2.078	2.069	2.060	2.050	2.041
	T_3	4577	4893	5125	5255	5295	5287	5096
	s_3	2.029	2.058	2.085	2.108	2.132	2.161	2.173
8	p_3	906.26	969.98	1020.0	1052.7	1051.3	1043.1	1005.5
	v_3	1.835	1.827	1.818	1.810	1.802	1.794	1.786
	T_3	4617	4930	5161	5290	5330	5322	5130
	s_3	2.022	2.051	2.077	2.101	2.123	2.154	2.165
9	p_3	1028.2	1099.0	1154.9	1191.9	1190.2	1180.1	1137.8
	v_3	1.631	1.624	1.616	1.609	1.602	1.594	1.587
	T_3	4657	4965	5194	5320	5365	5352	5160
	s_3	2.016	2.045	2.069	2.094	2.117	2.146	2.158

TABLE 9.5

r_c	α	-0.3	-0.2	-0.1	0	0.1	0.2	0.3
6	p_4	69.97	76.80	83.59	90.26	85.21	81.36	77.62
	v_4	14.682	14.614	14.547	14.482	14.418	14.349	14.285
	T_4	2856	3138	3412	3684	3478	3321	3168
	s_4	2.037	2.067	2.093	2.117	2.141	2.171	2.182
7	p_4	67.72	74.45	80.97	87.44	82.49	78.69	75.04
	v_4	14.682	14.614	14.547	14.482	14.418	14.349	14.285
	T_4	2764	3040	3305	3569	3367	3212	3063
	s_4	2.029	2.058	2.085	2.108	2.132	2.161	2.173
8	p_4	65.88	72.28	78.74	85.06	80.02	76.49	72.86
	v_4	14.682	14.614	14.547	14.482	14.418	14.349	14.285
	T_4	2689	2957	3214	3472	3266	3122	2974
	s_4	2.022	2.051	2.077	2.101	2.123	2.154	2.165
9	p_4	64.26	70.61	76.42	83.06	78.23	74.46	70.98
	v_4	14.682	14.614	14.547	14.482	14.418	14.349	14.285
	T_4	2623	2886	3119	3390	3193	3039	2897
	s_4	2.016	2.045	2.069	2.094	2.117	2.146	2.158

TABLE 9.6

r_c	α	-0.3	-0.2	-0.1	0	0.1	0.2	0.3
6	v_5	60.206	66.248	72.143	78.048	75.011	72.870	70.706
	T_5	2364	2599	2828	3057	2880	2744	2613
	s_5	2.085	2.120	2.151	2.179	2.201	2.229	2.239
7	v_5	58.321	64.209	69.923	75.648	72.667	70.506	68.406
	T_5	2290	2519	2741	2963	2790	2655	2528
	s_5	2.075	2.110	2.141	2.169	2.190	2.218	2.228
8	v_5	56.768	62.501	68.010	73.631	70.505	68.568	66.430
	T_5	2229	2452	2666	2884	2707	2582	2355
	s_5	2.067	2.101	2.132	2.160	2.180	2.209	2.219
9	v_5	55.418	61.023	66.046	71.921	68.968	66.789	64.753
	T_5	2176	2394	2589	2817	2648	2515	2393
	s_5	2.060	2.094	2.122	2.152	2.173	2.200	2.210

$p = 14.7 \text{ lb/in}^2$

TABLE 9.7

	α	-0.3	-0.2	-0.1	0	0.1	0.2	0.3
520°F. abs.	v_{6a}	13.243	13.255	13.265	13.276	13.544	13.809	14.071
	s_{6a}	1.665	1.667	1.667	1.666	1.704	1.745	1.868

$p = 14.7$ lb/in^2.

TABLE 9.8

r_c	α	-0.3	-0.2	-0.1	0	0.1	0.2	0.3
6	x	0.002436	0.006452	0.014200	0.025913	0.042156	0.05381	0.06429
	y	0.000357	0.001132	0.002515	0.004789	0.008734	0.02039	0.04421
7	x	0.002476	0.006576	0.014230	0.025856	0.042028	0.05392	0.06410
	y	0.000431	0.001121	0.002506	0.004741	0.008647	0.02028	0.04440
8	x	0.002409	0.006555	0.014270	0.025906	0.042088	0.05401	0.06429
	y	0.000420	0.001109	0.002495	0.004728	0.008607	0.02019	0.04421
9	x	0.002152	0.006551	0.014300	0.026056	0.042069	0.05408	0.06446
	y	0.000371	0.001100	0.002492	0.004738	0.008204	0.02012	0.04404

The values of x for α = 0.1, 0.2 and 0.3 are the total number of mols. of CO per mol. of undissociated products.

TABLE 9.9

r_c \ α	-0.3	-0.2	-0.1	0	0.1	0.2	0.3
6	5894	5868	5855	5840	5725	5648	5569
7	6221	6196	6170	6145	6013	5923	5840
8	6514	6477	6452	6423	6284	6184	6085
9	6782	6743	6711	6679	6514	6413	6302

B.T.U./lb. mol. of products.

TABLE 9.10

r_c \ α	-0.3	-0.2	-0.1	0	0.1	0.2	0.3
6	24599	28041	31243	34414	32242	30360	28411
7	24609	28052	31255	34426	32255	30376	28428
8	24619	28062	31266	34439	32271	30395	28447
9	24628	28072	31277	34450	32283	30409	28466

TABLE 9.11

Mixture strength α	%	Air %	Air %excess	Air/fuel by weight	Fuel/air by weight
rich	30	76.9	-23.1	11.630	0.08598
	20	83.3	-16.7	12.598	0.07938
	10	90.9	- 9.1	13.748	0.07274
"correct"	0	100.0	0	15.124	0.06612
	10	111.1	+11.1	16.803	0.05951
	20	125.0	+25.0	18.905	0.05290
weak	30	142.9	+42.9	21.612	0.04627

TABLE 9.12

r_c	α	-0.3	-0.2	-0.1	0	0.1	0.2	0.3
6	Expansion	453.27	493.48	524.58	552.26	552.00	546.80	534.71
	Compression	99.62	98.56	97.84	97.02	95.49	95.29	94.74
	Cycle Work	353.65	394.92	426.74	455.24	456.51	451.51	439.97
7	Expansion	488.31	530.83	564.77	594.98	593.37	587.16	573.82
	Compression	111.42	110.35	109.24	108.09	106.43	105.89	105.42
	Cycle Work	376.89	420.48	455.53	486.89	486.94	481.27	468.40
8	Expansion	517.72	562.56	599.32	631.71	630.94	621.73	607.62
	Compression	121.99	120.58	119.46	118.22	116.46	116.05	115.28
	Cycle Work	395.73	441.98	479.86	513.49	514.48	505.68	492.34
9	Expansion	543.87	590.46	633.86	663.52	659.45	652.94	636.97
	Compression	131.68	130.18	128.91	127.57	125.17	124.89	123.98
	Cycle Work	412.19	460.28	504.95	535.95	534.28	528.05	512.99

All values B.T.U./lb.

TABLE 9.13 Thermal efficiencies.

r_c \ α	-0.3	-0.2	-0.1	0	0.1	0.2	0.3
6	0.414	0.405	0.392	0.380	0.349	0.317	0.287
7	0.441	0.431	0.419	0.406	0.372	0.338	0.305
8	0.463	0.453	0.441	0.428	0.393	0.355	0.321
9	0.482	0.472	0.464	0.447	0.408	0.370	0.334
Values based on lower heat release					0.399	0.411	0.421
					0.425	0.438	0.448
					0.449	0.461	0.471
					0.468	0.481	0.491

TABLE 9.14.

Mean effective pressures, lb/in^2.

r_c α	-0.3	-0.2	-0.1	0	0.1	0.2	0.3
6	156.20	175.22	190.19	203.82	205.33	204.01	199.71
7	161.88	181.38	197.44	211.95	212.88	211.45	206.70
8	166.49	186.76	203.77	219.01	219.99	217.61	212.81
9	170.71	191.45	211.07	225.01	225.28	223.78	218.35

TABLE 9.15

Specific consumptions lb/h.p.hr.

r_c α	-0.3	-0.2	-0.1	0	0.1	0.2	0.3
6	0.319	0.326	0.336	0.348	0.379	0.417	0.460
7	0.299	0.306	0.315	0.325	0.355	0.391	0.432
8	0.285	0.291	0.299	0.308	0.336	0.372	0.411
9	0.274	0.280	0.284	0.295	0.323	0.356	0.394

TABLE 9.16

$\alpha = -0.3$

r_c	T	E	$\frac{p_o v}{5.404}$	$T_o s$	a.e.
6	520	949.45	34.61	838.76	145.30
	600	964.05	39.96	857.48	146.53
	1108	1063.67	6.66	857.48	212.85
	4535	1063.67	6.66	1059.24	11.09
	2856	610.40	39.96	1059.24	-408.88
	2364	488.12	163.77	1084.20	-432.31
	520	92.87	36.02	865.80	-736.91
7	520	949.45	34.61	838.76	145.30
	600	964.05	39.96	857.48	146.53
	1164	1075.47	5.70	857.48	223.69
	4577	1075.47	5.70	1055.08	26.09
	2764	587.16	39.96	1055.08	-428.02
	2290	470.01	158.65	1079.00	-450.34
	520	92.87	36.02	865.80	-736.91
8	520	949.45	34.61	838.76	145.30
	600	964.05	39.96	857.48	146.53
	1214	1086.04	4.99	857.48	233.55
	4617	1086.04	4.99	1051.44	39.59
	2689	568.32	39.92	1051.44	-443.20
	2229	455.40	154.42	1074.84	-465.02
	520	92.87	36.02	865.80	-736.91
9	520	949.45	34.61	838.76	145.30
	600	964.05	39.96	857.48	146.53
	1259	1095.73	4.44	857.48	242.69
	4657	1095.73	4.44	1048.32	51.85
	2623	551.86	39.96	1048.32	-456.50
	2176	442.63	150.75	1071.20	-477.82
	520	92.87	36.02	865.80	-736.91

TABLE 9.17

$\alpha = -0.2$

r_c	T	E	$\frac{p_o v}{5.404}$	$T_o s$	a.e.
6	520	1070.72	34.45	836.68	268.49
	600	1085.42	39.94	855.40	269.96
	1097	1183.98	6.66	855.40	335.24
	4852	1183.98	6.66	1074.84	115.80
	3138	690.50	39.94	1074.84	-344.40
	2599	551.82	180.21	1102.40	-370.37
	520	93.37	36.06	866.84	-737.41
	520	1070.72	34.45	836.68	268.49
	600	1085.42	39.94	855.40	269.96
	1152	1195.77	5.71	855.40	346.08
	4893	1195.77	5.71	1070.16	131.32
	3040	664.94	39.94	1070.16	-365.28
	2519	531.81	174.66	1097.20	-390.73
	520	93.37	36.06	866.84	-737.41
8	520	1070.72	34.45	836.68	268.49
	600	1085.42	39.94	855.40	269.96
	1200	1206.00	4.99	855.40	355.59
	4930	1206.00	4.99	1066.52	144.47
	2957	643.44	39.94	1066.52	-383.14
	2452	514.94	170.02	1092.52	-407.56
	520	93.37	36.06	866.84	-737.41
9	520	1070.72	34.45	836.68	268.49
	600	1085.42	39.94	855.40	269.96
	1244	1215.60	4.44	855.40	364.64
	4965	1215.60	4.44	1063.40	156.64
	2886	625.14	39.94	1063.40	-398.32
	2394	500.66	166.00	1088.88	-422.22
	520	93.37	36.06	866.84	-737.41

TABLE 9.18

$\alpha = -0.1$

r_c	T	E	$\frac{p_o v}{5.404}$	$T_o s$	a.e
6	520	1183.7	34.29	834.60	383.41
	600	1198.52	39.57	853.84	384.25
	1088	1296.36	6.60	853.84	449.12
	5085	1296.36	6.60	1088.36	214.60
	3412	771.78	39.57	1088.36	-277.01
	2828	617.08	196.24	1118.52	-305.20
	520	93.83	36.08	866.84	-736.93
7	520	1183.7	34.29	834.60	383.41
	600	1198.52	39.57	853.84	384.25
	1141	1307.76	5.65	853.84	459.57
	5125	1307.76	5.65	1084.20	299.21
	3305	742.99	39.57	1084.20	-301.64
	2741	594.33	190.21	1113.32	-328.78
	520	93.83	36.08	866.84	-736.93
8	520	1183.7	34.29	834.60	383.41
	600	1198.52	39.57	853.84	384.25
	1188	1317.98	4.95	853.84	469.09
	5161	1317.98	4.95	1080.04	242.89
	3214	718.66	39.57	1080.04	-321.81
	2666	575.22	185.00	1108.64	-348.42
	520	93.83	36.08	866.84	-736.93
9	520	1183.7	34.29	834.60	383.41
	600	1198.52	39.57	853.84	384.25
	1231	1327.33	4.40	853.84	477.89
	5194	1327.33	4.40	1075.88	255.85
	3119	693.47	39.57	1075.88	-342.84
	2589	555.37	179.66	1103.44	-368.41
	520	93.83	36.08	866.84	-736.93

TABLE 9.19

$\alpha = 0$

r_c	T	E	$\frac{p_0 v}{5.404}$	$T_0 s$	a.e
6	520	1295.80	34.14	833.04	496.90
	600	1310.70	39.39	852.28	497.81
	1079	1407.72	6.57	852.28	562.01
	5215	1407.72	6.57	1100.84	313.45
	3684	855.46	39.39	1100.84	-205.99
	3057	684.72	212.31	1133.08	-236.05
	520	94.25	36.11	866.32	-735.96
7	520	1295.80	34.14	833.04	496.90
	600	1310.70	39.39	852.28	497.81
	1130	1418.79	5.63	852.28	572.14
	5255	1418.79	5.63	1096.16	328.26
	3569	823.81	39.39	1096.16	-232.96
	2963	659.61	205.78	1127.88	-262.49
	520	94.25	36.11	866.32	-735.96
8	520	1295.80	34.14	833.04	496.90
	600	1310.70	39.39	852.28	497.81
	1176	1428.91	4.92	852.28	581.55
	5290	1428.91	4.92	1092.52	341.31
	3472	797.20	39.39	1092.52	-255.93
	2884	638.49	200.29	1123.20	-284.42
	520	94.25	36.11	866.32	-735.96
9	520	1295.80	34.14	833.04	496.90
	600	1310.70	39.39	852.28	497.81
	1218	1438.26	4.38	852.28	590.36
	5320	1438.26	4.38	1088.88	353.76
	3390	774.74	39.39	1088.88	-274.75
	2817	620.69	195.64	1119.04	-302.71
	520	94.25	36.11	866.32	-735.96

TABLE 9.20

$\alpha = 0.1$

r_c	T	E	$\frac{p_o v}{5.404}$	$T_o s$	a.e.
6	520	1406.87	33.99	830.96	609.90
	600	1421.87	39.22	850.20	610.89
	1067	1517.36	6.54	850.20	673.70
	5255	1517.36	6.54	1113.32	410.58
	3478	965.36	39.22	1113.32	-108.74
	2880	803.75	204.05	1144.52	-136.72
	520	258.95	36.84	886.08	-590.29
7	520	1406.87	33.99	830.96	609.90
	600	1421.87	39.22	850.20	610.89
	1117	1528.30	5.60	850.20	683.70
	5295	1528.30	5.60	1108.64	425.26
	3367	934.93	39.22	1108.64	-134.49
	2790	779.70	197.67	1138.80	-161.43
	520	258.95	36.84	886.08	-590.29
8	520	1406.87	33.99	830.96	609.90
	600	1421.87	39.22	850.20	610.89
	1162	1538.33	4.90	850.20	693.03
	5330	1538.33	4.90	1103.96	439.27
	3266	907.39	39.22	1103.96	-157.35
	2707	758.01	191.79	1133.60	-183.80
	520	258.95	36.84	886.08	-590.29
9	520	1406.87	33.99	830.96	609.90
	600	1421.87	39.22	850.20	610.89
	1201	1547.04	4.36	850.20	701.20
	5365	1547.04	4.36	1100.84	450.56
	3193	887.59	39.22	1100.84	-174.03
	2648	742.42	187.61	1129.96	-199.93
	520	258.95	36.84	886.08	-590.29

TABLE 9.21

$\alpha = 0.2$

r_c	T	E	$\frac{p_oV}{5.404}$	T_os	a.e.
6	520	1523.75	33.83	829.40	728.18
	600	1538.85	39.03	848.64	729.24
	1061	1634.14	6.51	848.64	792.01
	5251	1634.14	6.51	1128.92	511.73
	3321	1087.34	39.03	1128.92	- 2.55
	2744	932.38	198.22	1159.08	- 28.48
	520	422.16	37.56	907.40	-447.68
7	520	1523.75	33.83	829.40	728.18
	600	1538.85	39.03	848.64	729.24
	1109	1644.75	5.58	848.64	801.69
	5287	1644.75	5.58	1123.72	526.61
	3212	1057.59	39.03	1123.72	- 27.10
	2655	909.06	191.79	1153.36	- 52.51
	520	422.16	37.56	907.40	-447.68
8	520	1523.75	33.83	829.40	728.19
	600	1538.85	39.03	848.64	729.24
	1154	1654.91	4.88	848.64	811.15
	5322	1654.91	4.88	1120.08	539.71
	3122	1033.18	39.03	1120.08	- 47.87
	2582	889.93	186.52	1148.68	- 72.23
	520	422.16	37.56	907.40	-447.68
9	520	1523.75	33.83	829.40	728.19
	600	1538.85	39.03	848.64	729.24
	1193	1663.75	4.34	848.64	819.45
	5352	1663.75	4.34	1115.92	552.17
	3039	1010.81	39.03	1115.92	- 66.08
	2515	872.39	181.68	1144.00	- 89.93
	520	422.16	37.56	907.40	-447.68

TABLE 9.22

$\alpha = 0.3$

r_c	T	E	$\frac{p_0 v}{5.404}$	$T_0 s$	a.e.
6	520	1632.73	33.68	827.32	839.09
	600	1647.93	38.86	847.08	839.71
	1054	1742.67	6.48	847.08	902.07
	5059	1742.67	6.48	1134.64	614.51
	3168	1207.96	38.86	1134.64	112.18
	2613	1059.70	192.34	1164.28	87.76
	520	582.85	38.28	971.36	-350.23
7	520	1632.73	33.68	827.32	839.09
	600	1647.93	38.86	847.08	839.71
	1102	1753.35	5.55	847.08	911.82
	5096	1753.35	5.55	1129.96	628.94
	3063	1179.53	38.86	1129.96	88.43
	2528	1037.53	186.08	1158.56	65.05
	520	582.85	38.28	971.36	-350.23
8	520	1632.73	33.68	827.32	839.09
	600	1647.93	38.86	847.08	839.71
	1145	1763.21	4.86	847.08	920.99
	5130	1763.21	4.86	1125.80	642.27
	2974	1155.59	38.86	1125.80	68.65
	2455	1018.96	180.70	1153.88	45.78
	520	582.85	38.28	971.36	-350.23
9	520	1632.73	33.68	827.32	839.09
	600	1647.93	38.86	847.08	839.71
	1183	1771.91	4.32	847.08	929.15
	5160	1771.91	4.32	1122.16	654.07
	2897	1134.94	38.86	1122.16	51.64
	2393	1002.88	176.14	1149.20	29.82
	520	582.85	38.28	971.36	-350.23

TABLE 9.23

Irreversibilities

r_c	α	-0.3	-0.2	-0.1	0	0.1	0.2	0.3
6	Suction	-1.23	-1.47	-0.84	-0.91	-0.99	-1.06	-0.62
	Compression	0	0	0	0	0	0	0
	Combustion	201.76 174.72	219.44 189.28	234.52 202.30	248.56 215.28	263.12 208.00	280.28 202.28	287.56 143.52
	Expansion	0	0	0	0	0	0	0
	Release	23.43	25.97	28.19	30.06	27.98	25.93	24.42
	Exhaust	304.60	367.04	431.73	499.91	453.57	419.20	437.99
	Chemical Effect	-27.04	-30.16	-32.24	-33.28	-55.12	-78.00	-144.04
	Σ (losses)	501.52	580.22	661.36	744.34	688.56	646.35	605.31
	H_p	855.18	975.77	1088.14	1199.61	1145.08	1097.86	1045.32
	H_p - (work)	501.53	580.85	661.40	744.37	688.57	646.35	605.35
7	Suction	-1.23	-1.47	-0.84	-0.91	-0.99	-1.06	-0.62
	Compression	0	0	0	0	0	0	0
	Combustion	197.60 170.56	214.76 184.60	230.36 198.12	243.88 210.60	258.44 203.32	275.08 197.08	282.88 138.84
	Expansion	0	0	0	0	0	0	0
	Release	22.32	25.45	27.14	29.53	26.94	25.41	23.38
	Exhaust	286.57	346.68	408.15	473.47	428.86	395.17	415.28
	Chemical Effect	-27.04	-30.16	-32.24	-33.28	-55.12	-78.00	-144.04
	Σ (losses)	478.22	555.26	632.57	712.69	658.13	616.60	576.88
	H_p	855.18	975.77	1088.14	1199.61	1145.08	1097.86	1045.32
	H_p - (work)	478.29	555.29	632.61	712.72	658.14	616.59	576.92
8	Suction	-1.23	-1.47	-0.84	-0.91	-0.99	-1.06	-0.62
	Compression	0	0	0	0	0	0	0
	Combustion	193.96 166.92	211.12 180.96	226.20 193.96	240.24 206.96	253.76 198.64	271.44 193.00	278.72 134.68
	Expansion	0	0	0	0	0	0	0
	Release	21.82	24.42	26.61	28.49	26.45	24.36	22.87
	Exhaust	271.89	329.85	388.51	451.54	406.49	375.45	396.01
	Chemical Effect	-27.04	-30.16	-32.24	-33.28	-55.12	-78.00	-144.04
	(losses)	459.40	533.76	608.24	686.08	630.59	592.19	552.94
	H_p	855.18	975.77	1088.14	1199.61	1145.08	1097.86	1045.32
	H_p - (work)	459.45	533.79	608.28	686.12	630.60	592.18	552.98
	Suction	-1.23	-1.47	-0.84	-0.91	-0.99	-1.06	-0.62

and volume values are correct, the values of the pressure and energy are slightly in error at the end of expansion.

Sample calculations.

(a) Entropy of pre-combustion mixture at beginning of compression, $\alpha = 0.3$; $T = 600^{\circ}$F. abs. For theory see Appendix I.

Gas	m	S_T	m S_T	$\frac{\Sigma m}{m}$	m $4.575 \log_{10} \frac{\Sigma m}{m}$
C_8H_{18}	0.0116	115.981	1.345	86.207	0.103
O_2	0.2076	49.816	10.342	4.8170	0.648
N_2	0.7808	46.574	36.365	1.2807	0.384
	Σm = 1.0000	$\Sigma(mS_T)$ = 48.052			1.135

$$S = 48.052 + 1.135$$

$$= 49.187 \text{ B.T.U./lb.mol.}^{\circ}\text{F.} \quad \text{or since A.M.W.} = 29.827$$

$$s_1 = 1.649 \text{ B.T.U./lb.}^{\circ}\text{F.}$$

N.B. $\frac{R}{J} \log_e x = 1.9869 \times 2.30258 \log_{10} x = 4.575 \log_{10} x$

(b) Volume of pre-combustion mixture, $\alpha = -0.3$; $T = 600^{\circ}$F. abs.

$$v_1 = \frac{R\,T_1}{144\,p_1} = \frac{51.799 \times 600}{144 \times 14.7} = 14.682 \text{ ft}^3/\text{lb.}$$

(c) Pressure.

The pressures are related to the volumes and temperatures by the equation $\frac{pv}{T}$ = constant, e.g. $\frac{p_1v_1}{T_1} = \frac{p_2v_2}{T_2}$, allowance being made for change in number of mols where that occurs.

(d) Calculation of the maximum temperature.

There are three cases to consider: (i) weak mixtures, (ii) rich mixtures where dissociation of CO_2 occurs and (iii) rich mixtures where dissociation of CO_2 is suppressed.

(i) $\alpha = -0.2 \quad r_c = 7$

For this case $T_2 = 1152^\circ$F. abs. and the composition of the products is as given in table 9.1

The value of p_2 is given in table 9.3 as 197.57 lb/in^2 or 13.44 atm.

Composition at T_2:

CO_2	0.1014
H_2O	0.1141
O_2	0.0396
N_2	0.7449
$\Sigma m =$	1.0000 (m_2)

Composition at T_3:

CO_2	0.1014 - x
H_2O	0.1141 - y
CO	x
H_2	y
O_2	0.0396 + 0.5x + 0.5y
N_2	0.7449
$\Sigma m =$	1 + 0.5x + 0.5y (m_3)

Now $p_2 v_2 = m_2 \frac{R}{J} T_2$

and $p_3 v_3 = m_3 \frac{R}{J} T_3$

but $v_2 = v_3$

$$\text{i.e.} \quad \frac{p_2}{p_3} = \frac{m_2 T_2}{m_3 T_3}$$

$$\frac{m_3}{p_3} = \frac{m_2 T_2}{p_2 T_3} = \frac{1152}{13.44 T_3} = \frac{85.714}{T_3}$$

$$K_{p_{CO_2}} = \frac{(0.1014 - x)}{x(0.0396 + 0.5x + 0.5y)^{\frac{1}{2}}} \cdot \left(\frac{85.714}{T_s}\right)^{\frac{1}{2}} \quad \ldots\ldots I$$

$$K_{p_{w.g.}} = \frac{(0.1141 - y)\,x}{y\,(0.1014 - x)} \qquad \text{.........II}$$

The thermal equation is set up on the basis of equation 7.7

The value of $E_2 = 6196$ is given in table 9.9 and the heat available for raising the temperature of one mol of products is given by 28062, being the entry in table 9.10. The latter value is found by multiplying the heat of combustion at constant volume of C_8H_{18} at T_2 by the number of mols. of octane in one mol of reactants and correcting for the difference between the apparent molecular weights of the reactants and products.

$$\text{e.g.} \quad \frac{0.0133 \times 2207279 \times 28.640}{29.972} = 28052$$

The thermal equation becomes

$$28052 = E_3 - 6196 + \left\{ x\, H_{v_{CO}} + y\, H_{v_{H_2}} \right\}_{T_3} \qquad \text{......III}$$

A value of T_3 has to be chosen such that equations I, II and III are satisfied. That value is found to be 4893°F. abs.

$E_3 = 33390$ and equation III becomes

$$28052 = 33390 - 6196 + 112799x + 103632\,y$$

$$\text{i.e.} \quad 103632y = 858 - 112799x$$

$$y = 0.008279 - 1.088457x$$

If this value of y is substituted in equation II a value for x is found. If T_3 is correctly chosen equation I will be satisfied.

Equation II becomes

$$6.992 = \frac{(0.1141 - 0.008279 + 1.088457x)\,x}{(0.008279 - 1.088457x)(0.1014 - x)}$$

$$\text{i.e.} \quad 6.52203x^2 - 0.935415x + 0.0058698 = 0$$

$$x = \frac{0.935415 \pm \sqrt{(0.87500 - 0.15313)}}{13.04406} = 0.006576$$

(taking the negative sign) and $y = 0.001121$

The right hand side of I becomes 9.1558 of which $\log_{10}$ is 0.9617 as against the tabulated value of $\log_{10} K_{p_{CO_2}}$ of 0.9617

(ii) $\alpha = 0.1$, $r_c = 6$, $T_2 = 1067$°F. abs.

$p_2 = 156.85$ lb/in². or 10.670 atm.

Composition at T_2:	
CO	0.0380
CO_2	0.0959
H_2O	0.1506
N_2	0.7155
Σm =	1.0000 (m_2)

Composition at T_3:	
CO	$0.0380 + x$
CO_2	$0.0959 - x$
H_2O	$0.1506 - y$
H_2	y
O_2	$0.5x + 0.5y$
N_2	0.7155
Σm =	$1 + 0.5x + 0.5y$ (m_3)

$$\text{Now} \quad \frac{m_3}{p_3} = \frac{m_2\,T_2}{p_2\,T_3} = \frac{1067}{10.67 \times T_3} = \frac{100}{T_3}$$

$$K_{p_{CO_2}} = \frac{(0.0959 - x)}{(0.0380 + x)\,(0.5x + 0.5y)^{\frac{1}{2}}} = \left(\frac{100}{T_3}\right)^{\frac{1}{2}} \quad .....I$$

$$K_{p_{w.y.}} = \frac{(0.1506 - y)\,(0.0380 + x)}{y\,(0.0959 - x)} \quad ....II$$

Owing to the presence of CO - due to incomplete combustion - the temperature at which both equations I and II become effective is found by putting $x = 0$. If this is done it is possible to show that both equations become effective between

5000 and 5100°F. abs. It is important to know when this occurs as the thermal equation may be affected. In this case the thermal equation is

$$32242 = E_3 - 5725 + \left\{ x\, H_{v_{CO}} + y\, H_{v_{H_2}} \right\}_{T_3} \quad \ldots\ldots\text{III}$$

Proceeding as in (i) above it is found that the equations are satisfied when $T_3 = 5255$°F. abs. yielding $x = 0.004156$ and $y = 0.008734$.

(iii) $\alpha = 0.2$, $r_c = 6$, $T_2 = 1061$°F. abs.

Composition at T_2:		Composition at T_3:	
CO	0.0742	CO	0.0742 - y
CO_2	0.0682	CO_2	0.0682 + y
H_2O	0.1602	H_2O	0.1602 - y
N_2	0.6974	H_2	y
		N_2	0.6974

In this case the amount of CO present is so great that the dissociation of CO_2 to CO and O_2 cannot proceed and the composition of the equilibrium mixture is determined by the water gas reaction alone.

$$\text{Hence } K_{p_{w.y.}} = \frac{(0.1602 - y)\,(0.0742 - y)}{y \times (0.0682 + y)} \quad \ldots\ldots\text{II}$$

where y = number of mols of H_2 formed.

The formation of y mols of H_2 results in the formation of 0.5y mols of O_2 which will combine with y mols of CO to form y mols of CO_2. The corresponding thermal equation is

$$30360 = E_3 - 5648 + \left\{ y\, H_{v_{H_2}} - y\, H_{v_{CO}} \right\}_{T_3} \quad \ldots\ldots\text{III}$$

A value of T_3 has to be chosen so that equations II and III are satisfied - in this case $T_3 = 5251^{o}$F. abs. However since $H_{v_{H_2}} \doteqdot H_{v_{CO}}$ and y is small the contribution which the term in the brackets in equation III makes is small and T_3 may be found to a very good approximation by neglecting the term in the brackets.

Values of x and y are given in table 9.8.

(e) Heat available for heating one mol. of products. (rich mixtures).

The heat available is found as in (d)(i) above the values being modified due to the presence of CO.

e.g. $\alpha = -0.3$, $r_c = 9$, $T_2 = 1183^{o}$F. abs.

$$\text{Heat available (uncorrected)} = \frac{0.0214\ H_v\ (C_8H_{18}) \times 26.979}{30.663}$$

$$= 41.571 \text{ B.T.U./lb.mol. of products}$$

where $H_v\ (C_8H_{18}) = 2207785$ B.T.U./lb.mol.

Correction for CO present $= 0.1085 \times H_{v_{CO}}$

$= 13105$ B.T.U./lb.mol products

where $H_v(CO) = 120787$ B.T.U./lb.mol.

Heat available (corrected) $= 41571 - 13105$

$= 28466$ B.T.U./lb.mol. products.

This value may be found in table 9.10.

(e) Energy values.

(i) $\alpha = 0$: $T_2 = 1079^{o}$E. abs.; $r_c = 6$

To make a check on E_3 - $T_3 = 5215^{o}$F. abs.

$$E_3 = E_{reactants} @ T_2 + \Delta E_o$$

$E_{reactants}$ = 6154.4 B.T.U./lb.mol.

ΔE_0 = 0.0165 x 2207422 = 36422 B.T.U./lb.mol.

E_3 = 42576.4 B.T.U./lb. mol. reactants

Also, as a check

E_3 = $E_{products}$ @ T_2 + heat added

as given in tables 9.9 and 9.10 respectively

i.e. E_3 = 5840 + 34414

= 40254 B.T.U./lb.mol. products

$= \frac{30.245}{28.594} \times 40254$

= 42578.2 B.T.U./lb.mol. reactants

(ii) $\alpha = 0.3$, T_{6a} = 520°F. abs.

E_{6a} (uncorrected) = 2687 B.T.U./lb.mol.

= 99.60 B.T.U./lb.

This value does not include the energy in the CO which is for this mixture $\frac{0.1085 \times 120163}{26.979}$ = 483.25 B.T.U./lb.

E_{6a} (corrected) = 99.60 + 483.25

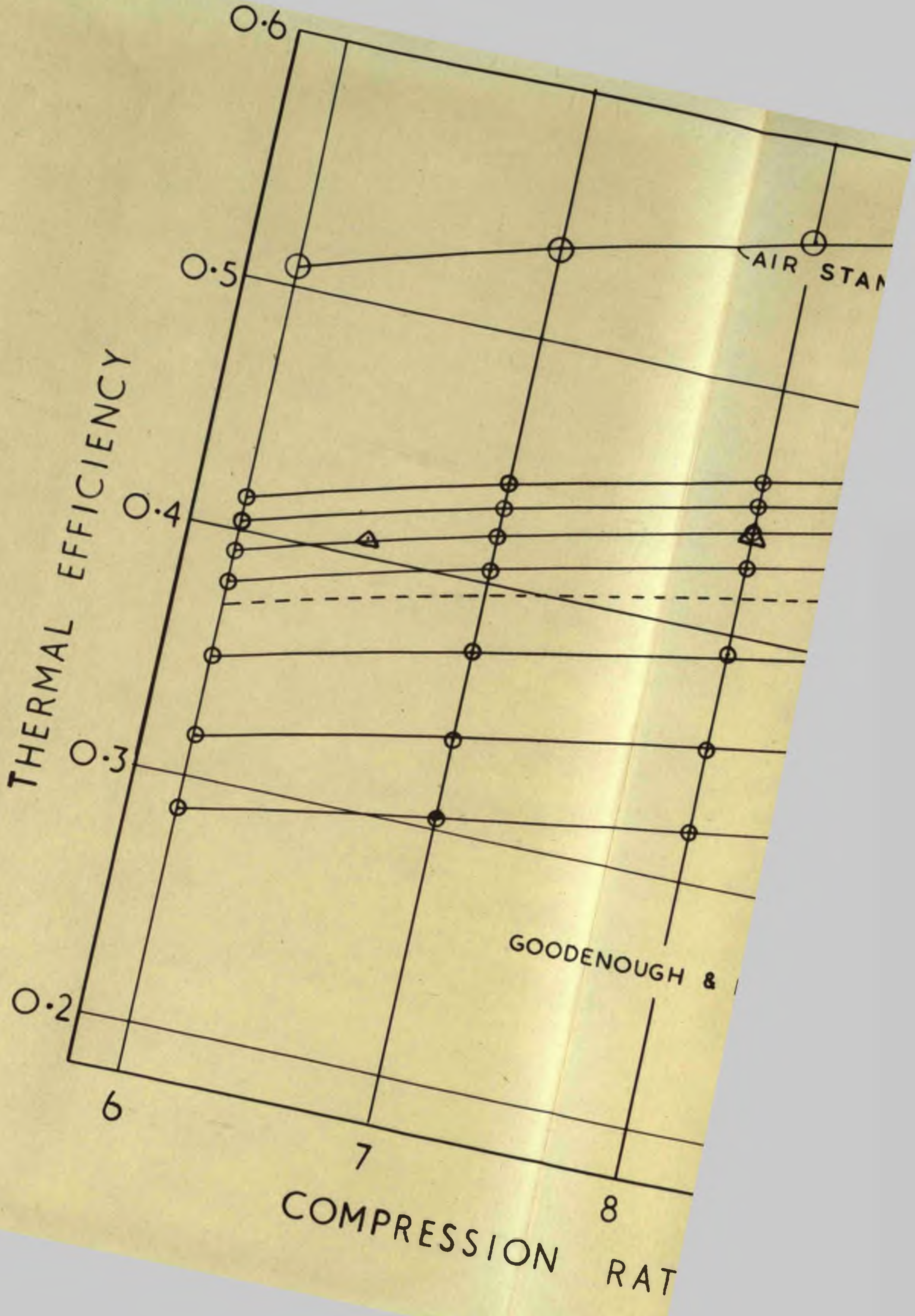
= 582.85 B.T.U./lb.

Comments on Results.

General.

If the thermal efficiency is taken as a criterion comparison of the writer's values (Fig 9.1) with those of other workers shows that there is good agreement, notably in the case of Goodenough and Felbeck$^{(34)}$. Values given by Pye$^{(24)}$ for benzene ($\alpha = 0$) are shown together with results for octane ($\alpha = 0$) furnished by David and Leah$^{(35)}$. In the latter case

FIG. 9.1


0·6
0·5
0·4
0·3
0·2
THERMAL EFFICIENCY
AIR STAN
GOODENOUGH &
6
7
8
COMPRESSION RAT

the value appears to be about 1% lower than what the writer found. In view of the fact that David and Leah never showed how their results were obtained, see correspondence(36), the writer is inclined to judge his work by the standard of Goodenough and Felbeck and by Pye's work - e.g. calculation of maximum temperature, see page 72 . There seems little doubt that the calculated results are acceptible.

A comparison between the calculated values of the mean effective pressures and those actually obtained by the writer in an E6 Ricardo variable compression engine is made in Fig. 9.2. The upper group of curves represent the theoretical performance and the lower group the indicated values. In this instance the indicated values were obtained from brake values, corrected for friction losses by motoring the engine. Similarity between the calculated and actual results is seen quite clearly and on this basis the theoretical values are supported.

So far as the representation of the results for a 1st Law Analysis is concerned the thermal efficiency, table 9.13 suffices. In an ideal cycle, where no heat is assumed to be lost through the cylinder wall, of the heat supplied a certain fraction the thermal efficiency, appears as work and the rest as heat in the exhaust. Accordingly no graphical representation is given.

<u>2nd Law Analysis</u> Table 9.23

The irreversibility was calculated on the basis of

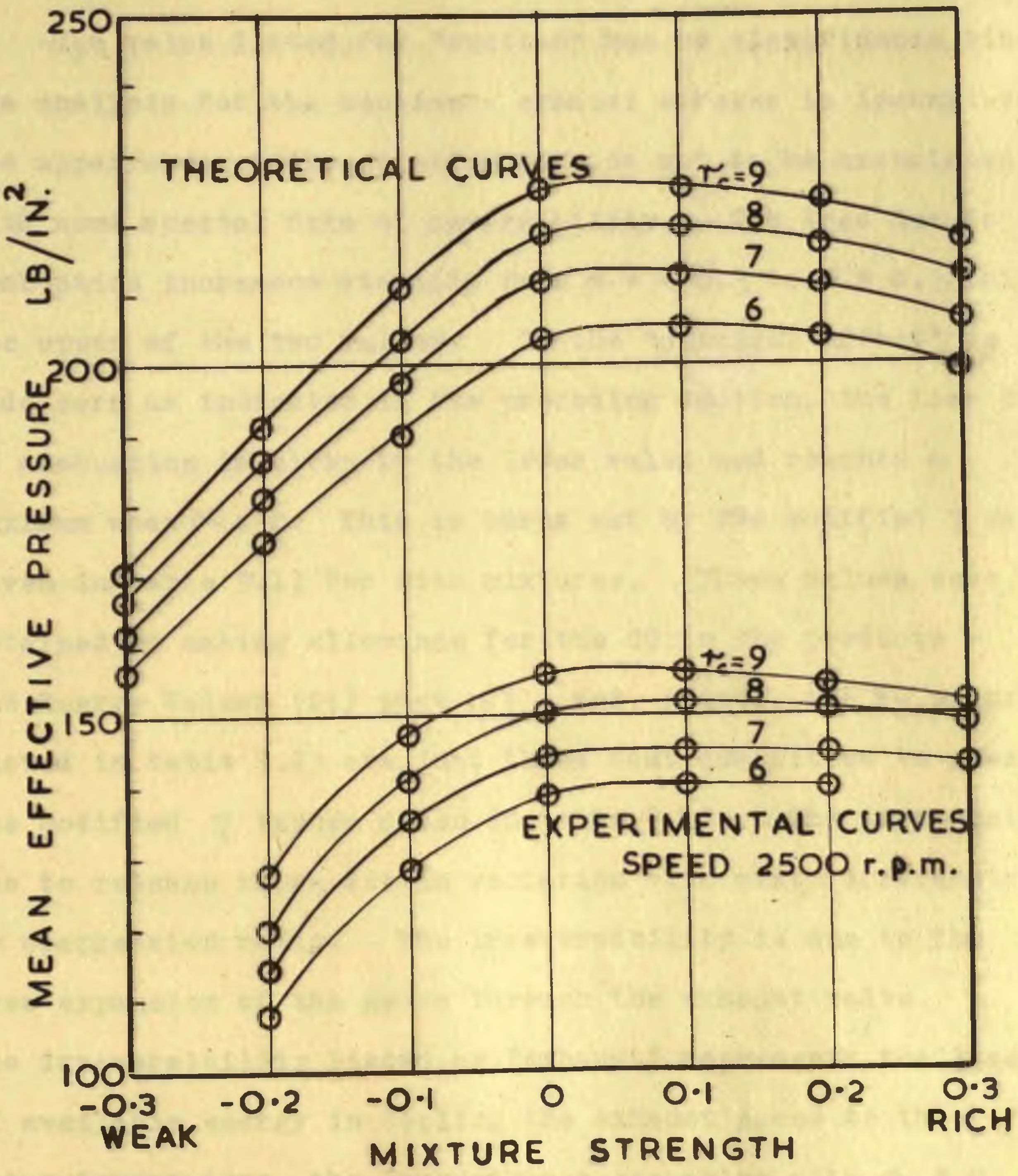

250
200
150
100
MEAN EFFECTIVE PRESSURE LB/IN.^{2}
THEORETICAL CURVES
$r_c=9$
8
7
6
$r_c=9$
8
7
6
EXPERIMENTAL CURVES
SPEED 2500 r.p.m.
-0·3
WEAK
-0·2
-0·1
0
0·1
0·2
0·3
RICH
MIXTURE STRENGTH

FIG.9.2

equation 4.15, the term in dQ being zero for each part of the cycle. Since compression and expansion are taken to be isentropic no thermodynamic loss occurs during these parts of the cycle.

The value listed for "suction" has no significance since the analysis for the suction - exhaust strokes is incomplete. The appearance of the negative sign is not to be associated with some special form of reversibility. The loss due to combustion increases steadily from $\alpha = -0.3$ to $\alpha = 0.3$ taking the upper of the two values. If the "chemical effect" is made zero as indicated in the preceding section, the loss due to combustion is given by the lower value and reaches a maximum when $\alpha = 0$. This is borne out by the modified η values given in table 9.13 for rich mixtures. These values were obtained by making allowance for the CO in the products - see Energy Values (ii) page 103 , and, indeed, the H_p values listed in table 9.23 are just these heat quantities to give the modified η values given in table 9.13. The irreversibility due to release shows little variation with mixture strength or compression ratio. The irreversibility is due to the free expansion of the gases through the exhaust valve. The irreversibility listed as "exhaust" represents the loss of available energy in cooling the exhaust gases to the datum temperature, the largest loss occurring with $\alpha = 0$

corresponding to the maximum exhaust temperature. The "chemical effect" increases steadily from $\alpha = -0.3$ to $\alpha = 0.3$ due to the increasing amount of fuel present but with rich mixtures there is a marked rate of increase due to incomplete combustion.

If the total irreversibility, Σ (losses), is compared with, H_p - (cycle work), the agreement between the entries in table 9.23 is very good.

GAS ENGINE EXPERIMENTS - RESULTS.

The following results were obtained from three tests, designated as A, B and C, on a single cylinder, four-stroke cycle Crossley gas engine, fitted with "hit-and-miss" governing. The stroke and clearance volumes were 0.334 and 0.092 ft^3 respectively.

TABLE 10.1

	A	B	C
Gas Consumption, ft^3/min. measured at S.T.P.	4.016	3.664	3.425
Air Consumption, lb/min.	1.747	1.791	1.867
Speed, r.p.m.	211.0	211.2	217.8
Explosions per minute	105.3	105.7	109.0
Missed cycles per minute	0	0	0
Indicated horsepower	11.40	10.85	9.38
Brake horsepower	9.91	9.32	8.28
Mechanical efficiency	0.87	0.86	0.88
Heat in jacket cooling water, B.T.U./min.	673.0	539.7	459.9
Laboratory temperature, °F.	73	73	73
Heat in exhaust gases, B.T.U./min. with respect to laboratory temperature	439.0	409.2	359.0
Atmospheric pressure, lb/in^2.	14.66	14.66	14.66
Pressure at end of exhaust stroke, † lb/in^2.	14.66	14.66	14.66
Pressure at end of suction stroke lb/in^2. †	13.96	13.96	13.96

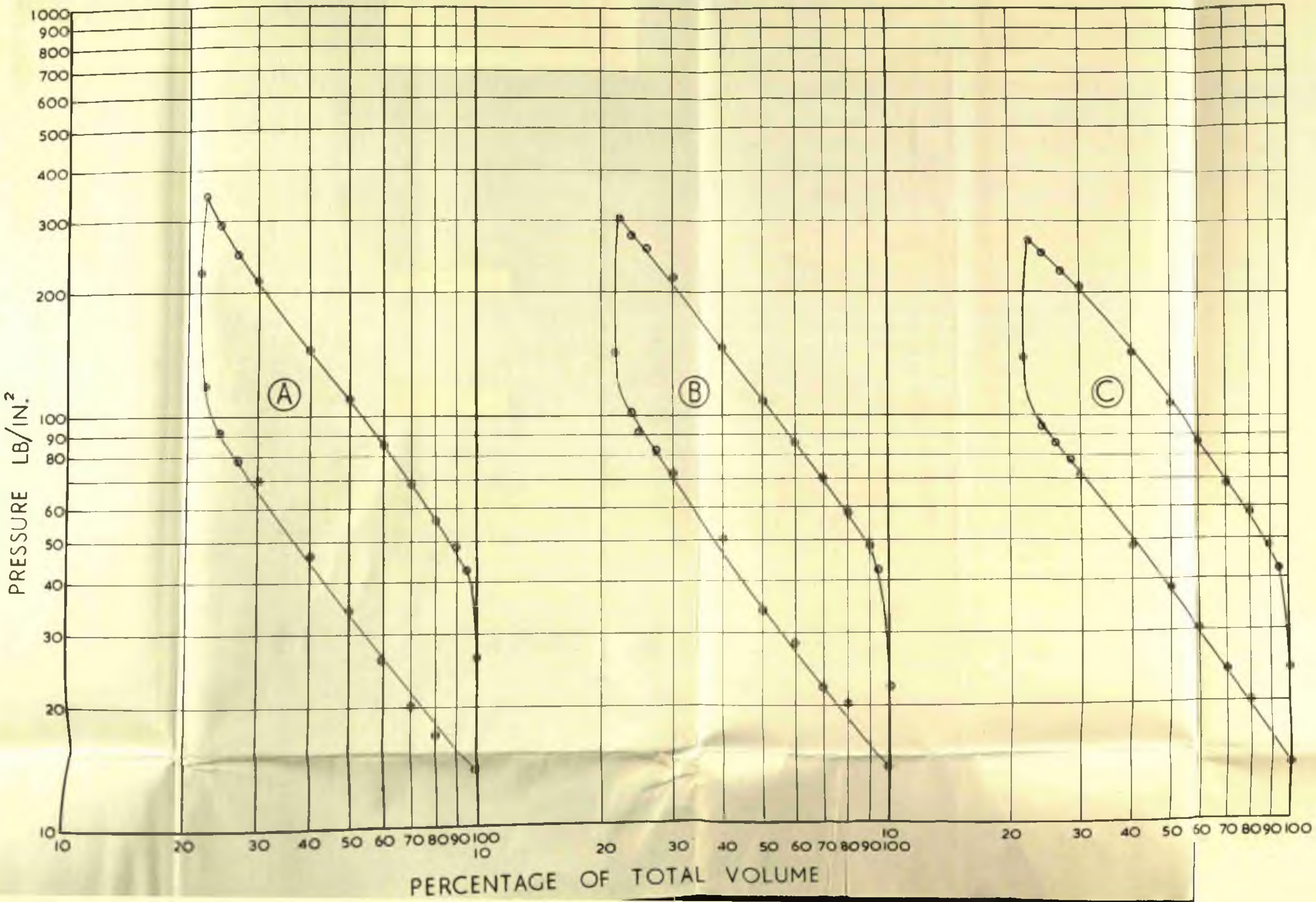
† obtained using light spring.

The above results enable the conventional energy account for each test to be drawn up. These are detailed below, table 10.2, and represented graphically in Fig. 10.1 A, B and C.

FIG.10.1

FIG.10.2

PRESSURE-VOLUME DIAGRAMS FOR GAS ENGINE



ENERGY ACCOUNTS FOR GAS ENGINE

Ⓐ	CYCLE WORK	JACKET HEAT	EXHAUST HEAT	RAD
	27·3%	38·1%	24·8%	9·8

Ⓑ	CYCLE WORK	JACKET HEAT	EXHAUST HEAT	RAD
	28·5%	33·4%	25·4%	12·7

Ⓒ	CYCLE WORK	JACKET HEAT	EXHAUST HEAT	RAD.
	26·4%	30·6%	23·8%	19·2%

TABLE 10.2

	A		B		C	
	BTU/min	%	BTU/min	%	BTU/min	%
Heat supplied	1767	100	1612	100	1507	100
Cycle work	483	27.3	460	28.5	398	26.4
Jacket heat	673	38.1	539.7	33.4	460	30.6
Exhaust heat	439	24.8	409.2	25.4	359	23.8
Balance, radiation etc.	172	9.8	203.1	12.7	290	19.2

L.C.V. = 440 B.T.U./ft.^{3}

In view of the need to obtain the smoothest possible running conditions the engine was loaded so as to obviate missed cycles. For each air-fuel ratio there was a brake load just sufficient to keep the speed below that at which the governor mechanism would operate. In order to get a representative indicator card for each test a large number of cards were taken and that card which showed the average performance was selected. A Maihak indicator was used, the drive to the indicator being provided by an eccentric on the crankshaft designed to give a true reproduction of the piston movement. The indicator diagrams are shown in Fig. 10.2 (see table 10.3) having been replotted as log (pressure) against log (percentage of total volume). The pressures at the end of the exhaust and suction strokes were obtained using a light spring.

In addition to the indicator diagrams the following observations were made. The gas consumption was obtained from a dry meter which had been calibrated previously. The air consumption was measured by applying the air box theory of Watson and Schofield(36) which was reexamined by King(37). The engine was loaded by the conventional type of rope brake and the rate of flow of jacket water, furnished by a constant head tank, was measured in tanks fitted with calibrated floats. The engine was fitted with an exhaust calorimeter of special design. The calorimeter consists of a bank of ten tubes through which the exhaust gases pass, the cooling medium being water. The design of the calorimeter is such that with a good flow of water, entering at 50°F. it is possible to cool the gases to the laboratory temperature. If this is done the exhaust gases are cooled below the dew-point (around 130°F.) and the heat given up and carried away by the water includes the greater part of the heat of condensation given up by the water vapour in the exhaust gases. In view of the fact that the analysis being carried out is based on a lower calorific value for the fuel gas, the flow of water through the exhaust calorimeter was adjusted so as to give a temperature well above the dew-point for the exhaust gases leaving. The heat in the exhaust gases as reckoned from the laboratory temperature of 73°F. was calculated on the assumption that the water vapour remained as a gas and it is this value which is listed in table 10.1.

TABLE 10.3

Analysis of Indicator Cards.

A			B			C		
%V	Comp^n.	Exp^n.	%V	Comp^n.	Exp^n.	%V	Comp^n.	Exp^n.
21.6	224	224	21.6	142	142	21.6	138	138
22.3	118	344 ⌿	23.7	102	302 ⌿	24.0	94 *	268 ⌿
24.2	92 *	290	24.8	91 *	274	26.0	86	250
26.8	78	246	27.1	82	354	28.2	78	226
30	70	214	30	72	216	30	70	206
40	46	146	40	50	146	40	48	142
50	34	110	50	34	108	50	38	106
60	26	84	60	28	86	60	30	86
70	20	68	70	22	70	70	24	68
80	17	56	80	20	58	80	20	58
90	-	48 ø	90	-	48 ø	90		48 ø
95	-	42	95	-	42	95		42
100	13.96	26	100	13.96	22	100	13.96	24

Pressures in lb/in^2.

* This point is taken as end of compression or beginning of combustion period.

⌿ Maximum pressure corresponding to end of combustion

ø Release.

Calculation of the temperature at the end of suction.

Composition of fuel gas by volume:

CO_2	0.033
C_nH_m assumed C_2H_4	0.020
O_2	0.009
CO	0.152
CH_4	0.180
H_2	0.498
N_2	0.108

A.M.W. = 13.456

R = 114.91

	A	B	C
Air/gas ratio:	5.418	6.086	6.788

Compositions of products of combustion by volume:

	A	B	C
CO_2	0.0665	0.0599	0.0543
H_2O	0.1474	0.1328	0.1203
O_2	0.0650	0.0793	0.0915
N_2	0.7211	0.7280	0.7339
A.M.W.	27.850	27.948	28.031
R	55.52	55.32	55.16

Exhaust temperature, as reckoned from exhaust calorimeter, taken to be equal to the temperature of the residual gases at the beginning of suction:

A	B	C	
1547	1479	1453	°F. abs.

	A	B	C	
Mass of residual gases	0.002261	0.002374	0.002423	lb/cycle.
Mass of air	0.016590	0.016940	0.017140	
Mass of fuel gas	0.001428	0.001298	0.001178	
Mass of charge	0.020279	0.020612	0.020741	
R for charge	58.11	57.64	57.25	

Temperature of charge at end of suction = $\frac{144\ p\ V}{wR}$, and as applied to conditions at this point gives $\frac{144 \times 13.96 \times 0.426}{wR}$

	A	B	C	
Temperature at end of suction	727	721	721	°F. abs.

Composition of the charge:

The volume of the residual gases, reduced to S.T.P., is

	A	B	C	
	0.0292	0.0305	0.0311	ft^3/cycle
or	0.7664	0.8790	0.9873	ft^3/ft^3 of fuel gas

The composition of the pre-combustion charge is made up by combining the composition of the residual gases, air, and fuel gas per ft^3 of fuel gas, as detailed below.

TABLE 10.4 (see page 113)

Using the value of the temperature, obtained for the charge at the end of suction, the temperatures and pressures at the other main points of the cycle may be found from measurements on the indicator cards. Allowance must be made for the change in the number of mols. during the combustion process. These results are given in the following table (10.5)

TABLE 10.5

Point	Property	A	B	C
At end of compression.	pressure, lb/in^2.	92	91	94
	temperature, °F. abs.	1159	1165	1165
At end of combustion	pressure, lb/in^2.	344	302	268
	temperature, °F. abs.	3818	3547	3200
At release	pressure, lb/in^2.	48	48	48
	temperature, °F. abs.	2150	2141	2149

By measurement from the indicator diagrams the following work quantities were found.

TABLE 10.4

		C_2H_4	CO	CH_4	H_2	CO_2	H_2O	O_2	N_2
A	Residuals	-	-	-	-	0.0510	0.1130	0.0498	0.5527
	Air	-	-	-	-	-	-	1.1320	4.2860
	Fuel gas	0.020	0.152	0.180	0.498	0.033	-	0.0090	0.1080
	Total	0.020	0.152	0.180	0.498	0.0840	0.1130	1.1908	4.9467
	Mols	0.0028	0.0212	0.0251	0.0693	0.0117	0.0157	0.1657	0.6885
B	Residuals	-	-	-	-	0.0527	0.1167	0.0697	0.6399
	Air	-	-	-	-	-	-	1.2720	4.8140
	Fuel gas	0.020	0.152	0.180	0.498	0.033	-	0.0090	0.1080
	Total	0.020	0.152	0.180	0.498	0.0857	0.1167	1.3507	5.5619
	Mols	0.0025	0.0191	0.0226	0.0625	0.0108	0.0147	0.1696	0.6982
C	Residuals	-	-	-	-	0.0536	0.1188	0.0903	0.7246
	Air	-	-	-	-	-	-	1.4190	5.3690
	Fuel gas	0.020	0.152	0.180	0.498	0.033	-	0.0090	0.1080
	Total	0.020	0.152	0.180	0.498	0.0866	0.1188	1.5183	6.2016
	Mols	0.0023	0.0173	0.0205	0.0567	0.0099	0.0135	0.1730	0.7068

	A	B	C
A.M.W. for above compositions:	26.59	26.81	27.00

TABLE 10.6

		A	B	C
Compression work	Gross	+94.2	+93.0	+99.7
	Nett	+51.0	+50.8	+56.4
Work exchanged during combustion	Gross	+ 5.4	- 4.4	-10.8
	Nett	+ 4.3	- 4.4	-10.8
Expansion work to point of release	Gross	-310.3	-285.7	-250.0
	Nett	-272.6	-288.6	-213.3
Work done during release.	Nett	-14.0	- 9.0	-8.7

All values given are B.T.U./lb. charge.

Positive sign denotes work given to the charge.

Negative sign " " done by the charge.

Estimation of ΔE_o:-

The measured lower calorific value of the fuel gas was 440 B.T.U./ft^3, measured at S.T.P. or $440 \times \frac{492}{533} = 406$ B.T.U./ft^3, measured at 533°F. abs. and 14.7 lb/in^2.

Density of fuel gas at 533°F. abs. and 14.7 lb/in^2

$$= \frac{144 \times 14.7}{114.9 \times 533} = 0.03456 \text{ lb/ft}^3$$

Hence lower heat of reaction at constant pressure at 533°F. abs.

$$H_p = 11748 \text{ B.T.U./lb.}$$

Using values, listed later, for energies the following values are found:

Enthalpy of air at 533°F. abs. = 128.7 B.T.U./lb.

" " gas " " " = 280.8 B.T.U./lb.

" " products " " " = 136.7 B.T.U./lb.

In the case of test A the ratio air/gas is 11.62 by weight and in this case the following expressions hold.

Enthalpy of reactants = 280.8 + 11.62 x 128.7
= 1776.3 B.T.U./lb. fuel gas

Enthalpy of products = 12.62 x 136.7
= 1725.1 B.T.U./lb. fuel gas

The difference between the enthalpies above, 51.2 is the amount by which H_p exceeds ΔE_o. Hence

ΔE_o = 11748 - 51.2 = 11697 B.T.U./lb. fuel gas.

Distribution of heat loss from charge to cylinder walls:

Using the values of energy, listed later, and the work quantities listed in table 10.6 it possible to estimate the heat loss for each part of the cycle. The heat loss is denoted by the symbol Q and is listed for the three tests in the following table.

TABLE 10.7

Q	A	B	C
Heat loss during suction.	0	0	0
Heat loss during compression.	5.7	4.2	11.6
Heat loss during combustion.	167.7	153.8	172.6
Heat loss during expansion	127.1	74.8	13.2
Heat loss during release	14.6	11.3	6.8
Heat loss during exhaust stroke	0	0	0

From the estimated values of pressure and temperature at the main points of the cycle it is possible to evaluate values of energy, entropy and specific volume which in turn enable the function $(E + \frac{p_o v}{5.404} - T_o s)$ to be evaluated. The following table gives the values of E, v and s on the basis of one pound of charge - except where otherwise indicated.

TABLE 10.8

		T°F. abs.	E $\frac{BTU}{lb.}$	v $\frac{ft^3}{lb}$	s $\frac{BTU}{lb.°F.}$
Fuel gas, per lb. fuel gas		533	202.1	28.87	3.105
Air, per lb. air		533	92.0	13.50	1.644
At the end of suction	A	727	961.3	21.02	1.870
	B	721	872.0	20.67	1.854
	C	721	798.6	20.53	1.841
At the end of compression	A	1159	1048.7	5.08	1.858
	B	1165	960.8	5.12	1.846
	C	1165	886.7	4.93	1.831
At the end of combustion	A	3818	886.4	4.28	2.079
	B	3547	802.6	4.51	2.053
	C	3200	703.3	4.57	2.018
At the end of expansion	A	2150	449.0	17.3	2.029
	B	2141	442.1	17.1	2.019
	C	2149	440.1	17.1	2.012
At the end of release	A	1715	345.1	45.0	2.044
	B	1727	342.1	45.1	2.030
	C	1729	342.1	45.1	2.030
Exhaust gases	A	533	98.7	13.98	1.721
	B	533	98.0	13.93	1.715
	C	533	97;3	13.89	1.711

Sample calculations with respect to table 10.8.:-

In case A, to find E, v and s at 727°F. abs. and 13.96 lb/in^2.: Setting out the calculation in a tabular fashion the following results are obtained:

TABLE 10.9

Gas	mols.	mE	mS	$\frac{\Sigma m}{m}$	m 4.575log$_{10}\frac{\Sigma m}{m}$
C_2H_4	0.0028	17	0.160	357.14	0.033
CO	0.0212	77	1.048	47.169	0.162
CH_4	0.0251	115	1.184	39.841	0.184
H_2	0.0693	244	2.310	14.430	0.368
CO_2	0.0117	52	0.631	85.470	0.103
H_2O	0.0157	69	0.747	63.694	0.130
O_2	0.1657	602	8.480	6.0350	0.592
N_2	0.6885	2488	32.979	1.4524	0.511
	1.0000	3664BTU/lb mol.	47.539		2.083
		137.8BTU/lb.			

$-4.575\log_{10}\frac{13.96}{14.7} = +0.102$

$$S = 47.539 + 2.083 + 0.102$$

$$= 49.724 \text{ B.T.U./lb.mol.}^{\circ}\text{F.}$$

$$\text{i.e.} \quad s = 1.870 \text{ B.T.U./lb.}^{\circ}\text{F.}$$

$$v = \frac{RT}{144\ p} = \frac{58.11 \times 727}{144 \times 13.96}$$

$$= 21.02 \text{ ft}^3\text{/lb.}$$

Total E value = 137.8 + $w\Delta E_o$, for the amount of fuel gas present $w_g \Delta E_o$ for A = 823.5 and

$$E = 137.8 + 823.5$$

$$= 961.3 \text{ B.T.U./lb.}$$

Since the analysis is given per pound of charge it is convenient to have the corresponding masses of fuel gas, air, and residuals, denoted below by the symbols, w_g, w_a and w_r respectively. The values of ΔE_o for each test are appended.

TABLE 10.10

	A	B	C	
w_g	0.07040	0.06297	0.05680	lb/lb. charge
w_a	0.81808	0.82185	0.82638	
w_r	0.11152	0.11518	0.11682	
Total	1.00000	1.00000	1.00000	
$w_g \Delta E_o$	823.5	736.6	664.4	BTU/lb. charge

TABLE 10.11 B.T.U./lb. charge.

	T°F. abs.	E	$\frac{p_0 v}{5.404}$	$T_0 s$	a.e	δ(a.e.)
(A) Gas - air	533	912.6	35.4	815.0	133.0	
At end of suction	727	961.3	57.0	963.7	54.6	-78.4
At end of compression	1159	1048.7	13.8	957.3	105.2	+ 50.6
At end of combustion	3818	886.4	11.6	1108.1	-210.1	-315.3
At end of expansion	2150	449.0	46.9	1081.5	-585.6	-375.5
At end of release	1715	345.1	122.1	1089.5	-622.3	- 36.7
Cooling of exhaust	1715 533	306.6 87.7	108.5 33.7	968.0 815.0	-552.9 -693.6	-140.7
(B) Gas - Air	533	824.9	35.0	808.6	51.3	
At end of suction	721	872.0	56.1	959.4	-31.3	- 82.6
At end of compression	1165	960.8	13.9	955.1	+19.6	+ 50.7
At end of combustion	3547	802.6	12.2	1094.2	-279.4	-299.0
At end of expansion	2141	442.1	46.4	1076.1	-587.6	-308.2
At end of release	1727	342.2	122.3	1085.7	-621.2	- 33.6
Cooling of exhaust	1727 533	302.8 86.7	108.2 33.4	960.6 808.6	-549.6 -688.5	-138.9
(C) Gas - air	533	751.9	34.6	805.4	- 18.9	
At end of suction	721	798.6	55.7	956.2	-101.9	- 83.0
At end of compression	1165	886.7	13.4	950.9	- 50.8	+ 51.1
At end of combustion	3200	703.3	12.4	1075.6	-359.9	-309.1
At end of expansion	2149	440.1	46.4	1072.4	-585.9	-226.0
At end of release	1729	342.1	122.3	1082.0	-617.6	- 31.7
Cooling of exhaust	1729 533	302.1 85.9	108.0 33.3	955.6 805.4	-545.5 -686.2	-140.7

$p_0 = 14.66$ lb/in^2. $T_0 = 533$°F. abs.

TABLE 10.12 B.T.U./lb. charge.

Irreversibilities.

	A	B	C
Suction	9.0	11.1	10.9
Compression	0.4	0.1	5.3
Combustion	319.6	294.6	298.3
Expansion	102.9	59.6	12.7
Release	22.7	24.6	23.0
Exhaust	140.7	138.9	140.7
Σ (losses)	595.3	528.9	490.9
H_p - (cycle work)	595.3	528.6	490.9

The details of the calculations leading up to the evaluation of the available energy (a.e.) and the values of the irreversibility are shown in tables 10.11 and 10.12. Some further explanation is necessary and this is given with respect to test B, as follows:

Except for the first two entries the values listed in table 10.8 are for one pound of charge. Accordingly, these are the values which can be substituted to give the entries in table 10.11, allowance being made for the pressure of residuals, both during suction and during the cooling of the exhaust. During the test a loss of 12.7%, see table 10.2, occurred due to radiation, heat unaccounted for, errors etc. but it will be difficult to account for this heat in a Second Law Analysis. To get over the difficulty this heat may be included in the exhaust and a temperature of 1727°F. abs. is found to be the apparent temperature at the end of release, although the measured temperature of the exhaust was 1479°F. abs. The difference between these two temperatures accounts for best part of the error of 12.7%. In any case there was a short length of pipe between the engine exhaust passage and the calorimeter and although well lagged there is an unmeasured heat loss here.

<u>Gas + air</u>

The value of E

$= 0.06297 \times 202.1 + 0.82185 \times 92. + 736.6$

$= 824.9$ B.T.U./lb.

using the values given in tables 10.8 and 10.10.

The value of s, in the same way,

= 0.06297 x 3.105 + 0.82185 x 1.644

= 1.547 B.T.U./lb.°F.

Cooling of exhaust and release.

If it is assumed that so far as release is concerned the whole of the charge takes part it will be correct to assume that only 0.88482 lb. of products are cooled to the temperature of 533°F. abs. Thus the last two entries in table 10.11, see brackets, are for 0.88482 lb. of products.

Correction of entropy values.

Entropy of gas + air = 1.547

Entropy of 0.88482 lb. products = 0.88482 x 1.715

= 1.517

Correction for gas and air = - (1.547 - 1.517)

= - 0.030

The correction for the pre-combustion mixture is found by comparing the entropy of the charge at 533°F. abs. and 14.66 lb/in.² with the corresponding entropy of the products.

Correction for pre-combustion mixture = -(1.769 - 1.715)

= - 0.054

The entropy of the charge at 533°F. abs. and 14.66 lb/in.² is 1.783 for A, 1.769 for B and 1.758 for C.

Irreversibilities.

Loss during suction = decrease in available energy allowance being made for the energy available in the residual gases. The energy available in the residual gases is 0.11518 x -621.2 = -71.5. Hence the loss during suction = 82.6 - 71.5 = 11.1, neglecting any work or heat quantities which may be exchanged during suction. The loss during compression, combustion and expansion is calculated on the basis of equation 4.15 and the variations of this equation discussed in section 4. The loss during release is difficult to estimate since this is in the main a loss due to free expansion accompanied by heat flow. If the loss of available energy through heat flow is neglected - it will be a small quantity - equation 4.15 is applicable. The loss involved in cooling the exhaust to the base temperature is for 0.88482 lb. of products and is obtained directly from table 10.11.

The summation of the losses amounts to 528.9 B.T.U./lb. charge as shown in table 10.12. This figure must be the same as the total energy available less the work done. The total energy available is (688.5 + 51.3) = 739.8 B.T.U./lb. being the decrease in a.e. as the fluid passes through the plant. Since the entropies have been corrected it is seen that H_p = (824.9 + 35.0) - (86.7 + 33.4)

= 859.9 - 120.1 = 739.8 B.T.U./lb.

For case B, H_p - (cycle work) = 739.8 - 211.2

= 528.6 B.T.U./lb.

The cycle work is found by summing the items listed in table 10.6.

Oil Engine Experiments - Results.

The following results, table 11.1, were obtained from four tests, nominally designated as Full, 3/4, 1/2 and 1/4 load respectively, on a single cylinder four-stroke cycle Ruston-Hornsby Oil Engine. The stroke and clearance volumes were 0.3579 ft^3 and 0.0291 ft^3 respectively giving a compression ratio of 13.3. Fuel injection was timed to commence at top dead centre.

TABLE 11.1

Load	Full	3/4	1/2	1/4
Oil consumption, lb/min.	0.1304	0.1038	0.0922	0.0830
Air consumption, lb/min.	3.588	3.642	3.726	3.804
Air/fuel ratio	27.52	35.09	40.41	45.83
Speed, r.p.m.	311.3	314.4	315.7	318.8
Indicated horsepower	18.31	15.88	12.55	10.82
Brake horsepower	15.97	12.58	9.40	5.92
Mechanical efficiency-	0.872	0.793	0.749	0.547
Heat in jacket cooling water, B.T.U./min.	877.5	718.8	579.5	532.2
Laboratory temperature, $^{\circ}F$.	65	65	65	65
Atmospheric pressure, lb/in^2.	14.7	14.7	14.7	14.7
*Pressure at end of exhaust stroke, lb/in^2.	15.7	15.7	15.7	15.7
*Pressure at end of suction stroke, lb/in^2.	13.9	13.9	13.9	13.9
Temperature of exhaust gases, $^{\circ}F$. abs.	1270	1155	1065	970

* obtained using light spring.

The type of exhaust calorimeter fitted to the engine permitted too large a heat loss to the surroundings between the exhaust passage and the calorimeter. The "mean exhaust temperature" was obtained using a Chromel - Alumel thermocouple in the exhaust pipe close to the engine. The value of this observation is recorded in table 11.1. In the conventional energy accounts, detailed below in table 11.2 and illustrated diagrammatically in Fig. 11.1, the heat in the exhaust gases has been found by difference, neglecting any loss due to radiation. In any case it is convenient to include this unmeasured loss with the heat in the exhaust gases for the purpose of a Second Law Analysis, as was done in the case of the Gas Engine analysis.

TABLE 11.2

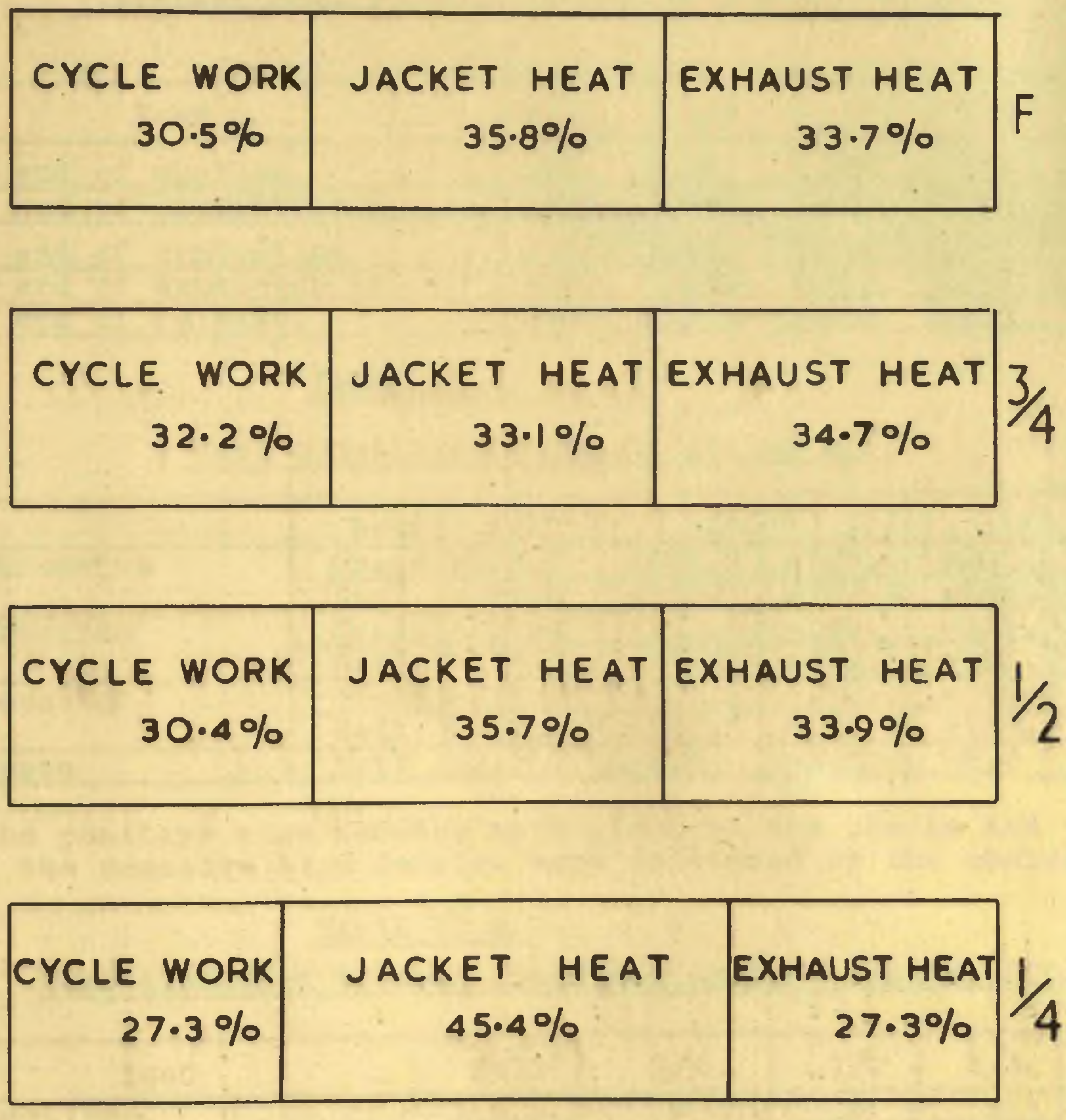
Load	Full		3/4		1/2		1/4	
	BTU/min	%	BTU/min	%	BTU/min	%	BTU/min	%
Heat supplied	2577	100	2052	100	1822	100	1640	100
Cycle work	776	30.5	673	32.3	532	30.4	459	27.3
Jacket heat	923	35.8	678	33.1	648	35.6	760	46.4
Exhaust heat	878	33.7	701	34.6	642	34.0	421	36.3

H.C.V. of fuel = 19,764 B.T.U./lb.

TABLE 11.3

Analysis of Indicator Cards.

	Load	Full		3/4		1/2		1/4	
Point	%V	Comp^n.	Exp^n.	Comp^n.	Exp^n.	Comp^n.	Exp^n.	Comp^n.	Exp^n
1	100	13.90	36	13.90	27	13.90	21	13.90	24
r	93.9	-	45	-	42	-	39	-	33
2	84.8	-	60	-	51	-	42	-	36
3	72.1	24	69	24	60	24	54	21	48
4	59.7	30	90	33	78	33	69	27	57
5	46.6	45	123	45	102	45	93	45	78
6	33.9	72	171	69	144	69	141	69	117
7	26.4	102	228	99	204	99	189	99	159
8	20.9	138	270	138	246	135	237	135	204
9	16.6	-	315	189	321	183	297	183	273
10	13.7	228	384	234	363	234	336	231	318
11	12.1	-	420	273	393	273	366	261	345
12	9.78	360	480	354	450	360	438	342	432
13	8.15	447	576	441	522	432	486	435	468
14	7.70	470	-	477	-	474	-	471	-



ENERGY ACCOUNTS FOR OIL ENGINE

FIG.11.1

End of combustion period - point 8: F, 3/4, 1/2 loads

- point 9: 1/4 load.

Release begins at the point r - all loads.

TABLE 11.4.

Temperatures at main points of cycle, °F. abs.

Load	Full	3/4	1/2	1/4
At end of suction	602	597	584	575
At end of compression	1530	1540	1497	1465
At end of combustion	2366$^{(8)}$	2151$^{(8)}$	2036$^{(8)}$	1840$^{(9)}$
At end of expansion (f)	1772	1650	1505	1258
At end of release.	1436	1289	1180	1005

TABLE 11.5

Work quantities, B.T.U./lb. of air.

	Load	Full	3/4	1/2	1/4
Compression	Gross	+206.7	+202.7	+198.9	+202.6
	Nett	+164.4	+160.7	+157.6	+161.8
Combustion	Gross	-161.4	-157.5	-139.7	-115.7
	Nett	-155.3	-151.5	-133.8	-111.8
Expansion	Gross	-258.8	-220.7	-202.2	-198.8
	Nett	-225.4	-187.5	-169.5	-164.8
Release	Nett	-2.8	-2.8	-2.8	-2.8

The positive sign denotes work given to the charge and the negative sign denotes work delivered by the charge.

TABLE 11.6

Heat exchanged between fluid and cylinder walls, BTU/lb. air

Load	Full	3/4	1/2	1/4
Suction	0	0	0	0
Compression	-28.2	-20.6	-29.9	-30.8
Combustion	-329.6	-242.4	-208.7	-217.0
Expansion	+112.0	+101.4	+79.2	+69.3
Release	-11.4	-25.0	-22.0	-17.1
Exhaust stroke	0	0	0	0

The positive sign denotes heat absorbed by the charge and the negative sign denotes heat given up by the charge.

TABLE 11.7

Volumetric Composition of products of combustion.

Load	Full	3/4	1/2	1/4
CO_2	0.0735	0.0580	0.0506	0.0447
H_2O	0.0659	0.0520	0.0453	0.0401
O_2	0.0958	0.1196	0.1311	0.1402
N_2	0.7648	0.7704	0.7730	0.7750
Total	1.0000	1.0000	1.0000	1.0000
A.M.W.	28.90	28.88	28.88	28.88
R	53.47	53.51	53.51	53.51

TABLE 11.8

Cylinder and exhaust gases per lb. of air.

Load	Full	3/4	1/2	1/4
Compression gases	1.0420	1.0460	1.0490	1.0530
Combustion and Expansion gases	1.0784	1.0744	1.0736	1.0750
Exhaust gases	1.0360	1.0280	1.0250	1.0220

The main results of the calculations are given in tables 11.2 to 11.10, the calculations being carried out in a manner similar to that employed in the case of the Gas Engine. The results given in the energy account, table 11.2 do not show any unusual characteristics. The analysis of the indicator diagrams, Fig. 11.2 shows an unusual exchange of heat during expansion. From the logarithmic plot of the p-v diagrams it seems that the combustion period might be taken to be complete at point 8 for full, 3/4 and 1/2 loads and at point 9 for 1/4 load. If this is assumed it is found that of the apparent heat loss during combustion a considerable fraction

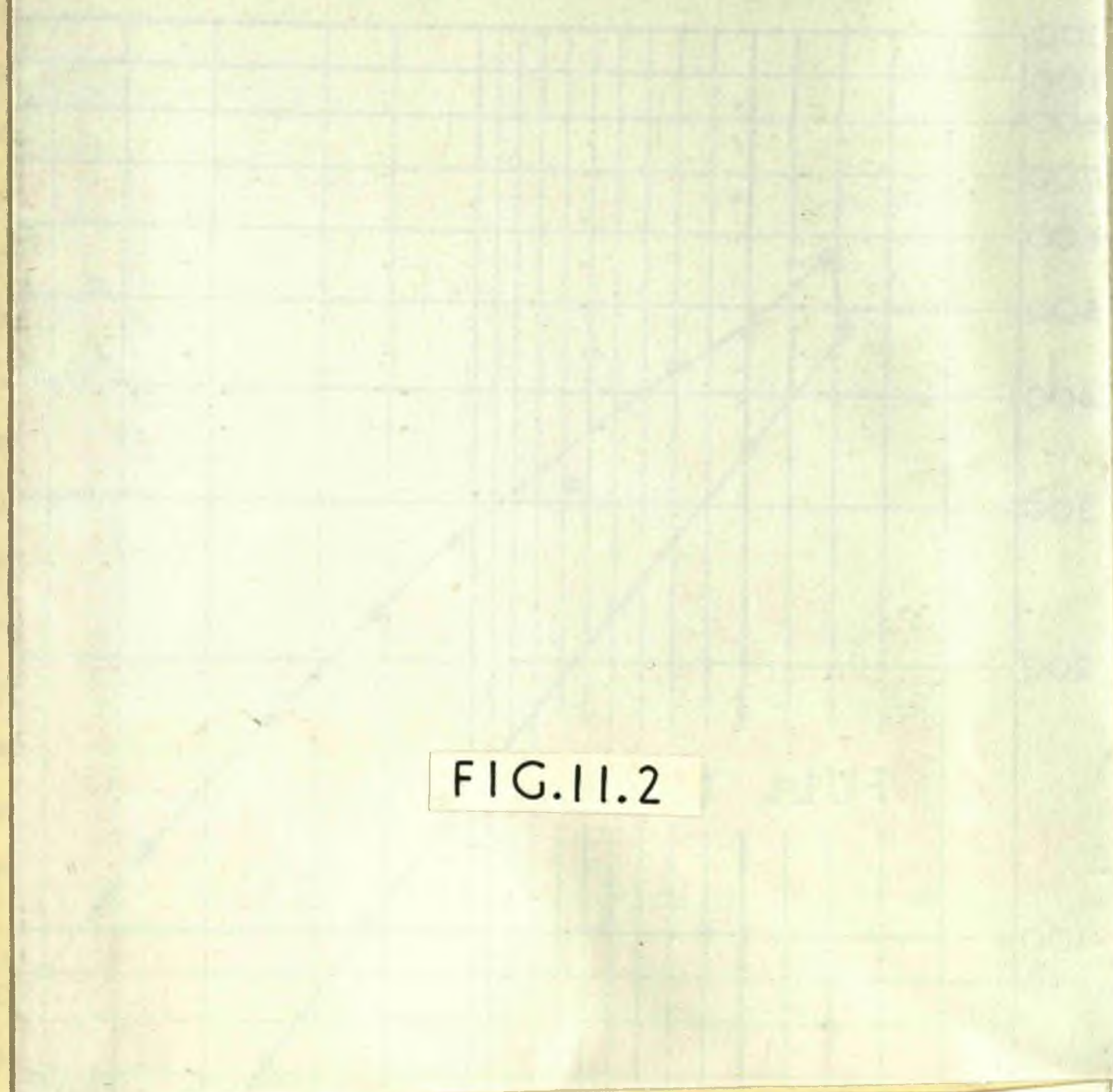
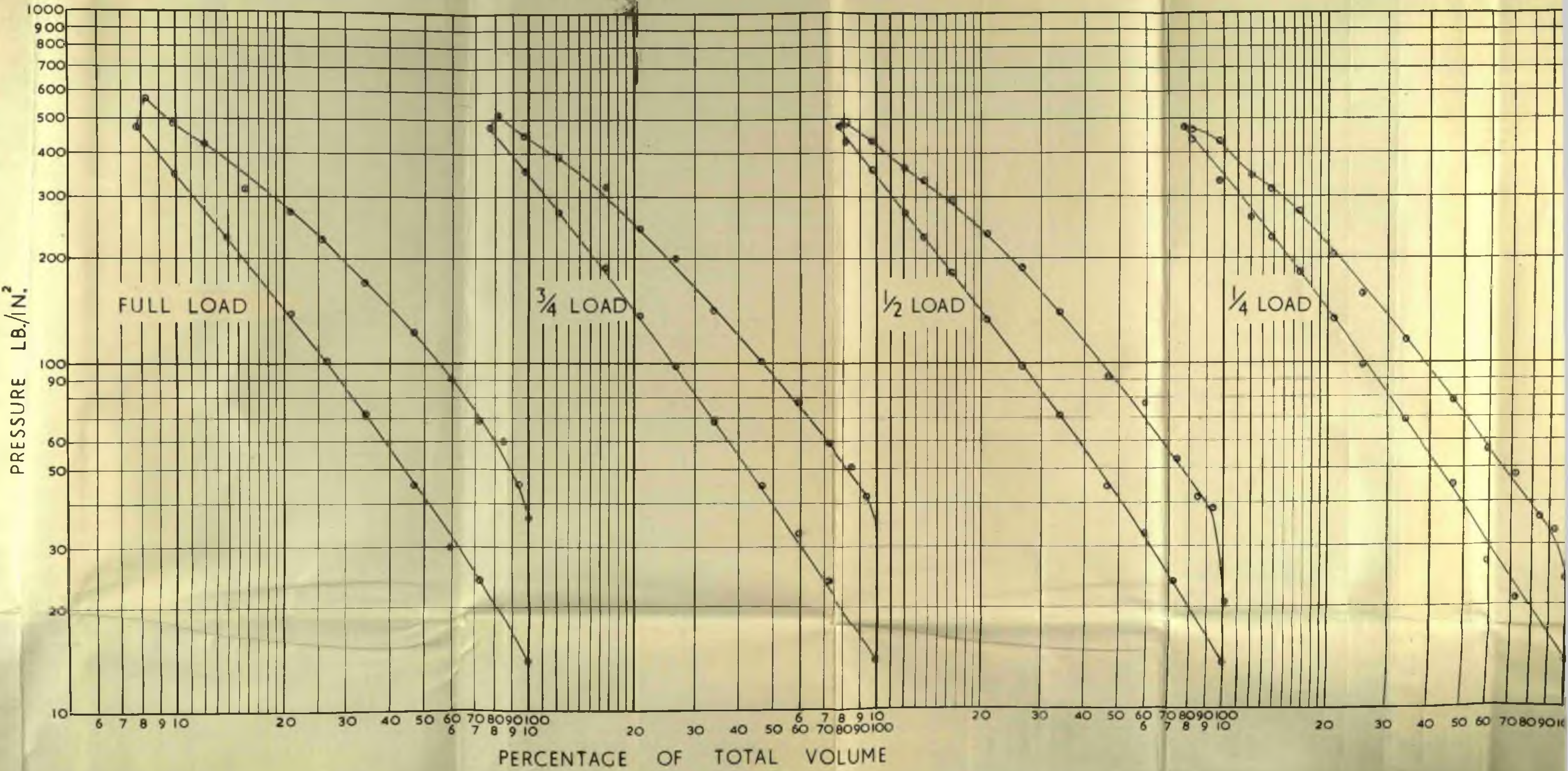


FIG.11.2

PRESSURE-VOLUME DIAGRAMS FOR OIL ENGINE



of the heat is returned during the main part of the expansion stroke. It is as though some of the heat lost during combustion is returned from areas in the cylinder uncooled by jacket water during the later part of the expansion stroke. It matters little, so far as the Second Law Analysis is concerned, whether this is true or not. If what is suggested is true the return of heat is equivalent to a proportionate return of available energy and the main part of the expansion stroke appears with a negative "irreversibility" since the work obtained is greater than the decrease in available energy measured. If the explanation given above, is not accepted then it must be assumed that point 8 (9), where the slope of the expansion line changes, is not the point where combustion is complete and that this point should be further down the expansion line. In fact, it might be as well to omit this point from the analysis and continue to the point of release.

The composition of the fuel was taken to be C, 0.87; H, 0.13, with a H.C.V. of 19,764 B.T.U./lb. which was used in the energy account. For a Second Law Analysis it was convenient to assume ΔE_0 = 19764 B.T.U./lb. although this leads to a slightly lower H_p value as given by table 11.9. For example, full load test H_p = 713.1 B.T.U./lb. air as against 718.2 B.T.U./lb. air if H.C.V. of fuel is 19764. The analysis was carried out on the basis of one pound of air, care being taken to correct the entropies to an air basis as though one pound of air represented the air and fuel.

TABLE 11.9 B.T.U./lb. of air.

Full	T	E	$\frac{p_o v}{5.404}$	$T_o s$	a.e.	(a.e.)
Air	525	808.5	36.2	861.5	-16.8	
		(844.7)				
End of suction	602	826.1	45.7	917.7	-45.9	-29.1
End of compression	1530	1004.6	3.4	913.5	94.5	+140.4
End of combustion	2366	513.6	9.5	1017.9	-494.8	-589.3
End of expansion	1772	366.8	42.9	1039.0	-629.3	-134.5
End of release	1436	289.0	106.4	1048.4	-653.0	- 23.7
Cooling of exhaust	1436	277.6	102.2	1003.3	-623.5	
		(131.6)				-106.4
	525	95.5	36.1	861.5	-729.9	
		(713.1)				
3/4 Air	525	653.5	36.2	861.5	-171.8	
		(689.7)				
End of suction	597	670.7	45.5	915.6	-199.4	- 27.6
End of compression	1540	852.8	3.4	917.7	- 61.5	+137.9
End of combustion	2151	452.9	9.5	1003.7	-541.3	-479.8
End of expansion	1650	333.6	42.7	1028.9	-652.6	-111.3
End of release	1289	253.2	95.2	1031.0	-682.6	- 30.0
Cooling of exhaust	1289	242.3	91.1	985.4	-652.0	
		(130.5)				- 79.0
	525	94.4	36.1	861.5	-731.0	
		(559.2)				
1/2 Air	525	579.4	36.2	861.5	-245.9	
		(615.6)				
End of suction	584	594.5	44.6	919.8	-280.7	- 34.8
End of compression	1497	770.5	3.4	916.7	-142.8	+137.9
End of combustion	2036	422.1	9.3	997.0	-565.6	-422.8
End of expansion	1505	299.1	41.9	1019.0	-678.0	-112.4
End of release	1180	229.2	87.2	1020.1	-703.7	- 25.7
Cooling of exhaust	1180	218.6	81.1	972.8	-673.1	
		(130.0)				-58.4
	525	93.9	36.1	861.5		
		(485.6)				
1/4 Air	525	521.5	36.2	861.5	-303.5	
		(557.7)				
End of suction	575	535.4	44.1	915.1	-335.6	- 31.8
End of compression	1465	707.2	3.3	916.7	-206.2	+129.4
End of combustion	1840	374.5	7.3	978.0	-596.2	-390.0
End of expansion	1258	244.9	41.4	1001.6	-715.3	-119.1
End of release	1005	192.0	74.3	999.0	-732.7	- 17.4
Cooling of exhaust	1005	182.5	70.6	948.6	-695.5	
		(129.6)				- 36.4
	525	93.5	36.1	861.5	-731.9	
		(428.1)				

$p_o = 14.7$ lb/in^2 ; $T_o = 525^\circ$F. abs.

TABLE 11.10

Irreversibilities. B.T.U./lb. of air.

Load	Full	3/4	1/2	1/4
Suction	4.2 (34.2)	0.1 (30.1)	4.6 (34.6)	-3.0 (27.0)
Compression	24.0	22.8	19.7	32.4
Combustion	434.0	328.3	289.0	278.2
Expansion	-90.9	-76.2	-57.1	-45.7
Release	23.7	27.2	22.9	14.6
Exhaust	106.4	79.0	58.4	36.4
(losses)	501.4(531.4	381.2(411.2)	337.5(367.5)	313.1(343.1)
H_p	713.1	559.2	485.6	428.1
Cycle work	219.1(189.1	181.1(151.1)	148.5(118.5)	117.6(87.6)
H_p-(cycle work)	494.0(524.0	378.1(408.2)	337.1(367.1)	310.5(340.5)

It is necessary to imagine that the fuel is present with the air before combustion, indeed in the air intake, although in fact it is not in the cylinder until the end of injection. If the fuel is not included it would appear that a greater mass left the engine than entered it. The evaluation of the irreversibilities, table 11.10, offers no difficulty apart from the appearance of a negative result for the suction loss on 1/4 load. The writer believes that this may be due to the fact that the pumping loss has been neglected. In the case of the Gas Engine the pumping loss was small and in the analysis the work equivalent of the loss was neglected. In the Oil Engine test the pumping loss was large due to what appeared to be too small an inlet valve and too long an exhaust system. The pumping loss was practically the same on all loads and amounted to 30 B.T.U./lb. air. It might be considered that this work represents the loss of available energy during exhaust and suction, available energy which has to be taken from the cycle work to give a reduced gross work. If it is considered reasonable to include this loss along with the suction loss the total becomes more comparable with the equivalent loss in the gas engine, where the analysis is for a pound of charge. In any case the pumping loss in the gas engine is small and a larger loss in the oil engine is to be expected. The figures in brackets, table 11.10 show the losses if the figure of 30 is included.

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APPENDIX I

The Entropy of a Gaseous Mixture.

The entropy of one mol of a gas at any temperature T, one atmosphere pressure, is given by

$$S_T = \int_0^T \frac{C_p dT}{T} .$$

Thus the entropy of m mols of a single gas at temperature T, one atmosphere pressure is mS_T.

The entropy of a mixture of gases at any temperature T and each at one atmosphere: Consider a container, divided into a number of partitions, each of which contains a different gas at temperature T and at one atmosphere pressure. The total entropy will be

$$S = m_1 S_1 + m_2 S_2 + \ldots\ldots\ldots = \Sigma(m S_T).$$

If the partitions are removed, the gases will diffuse into one another until each gas may be considered as occupying the total volume of the container and exerting a pressure equal to its partial pressure in the final mixture. This diffusion or mixing is an irreversible process so it may be inferred that the entropy of the mixture will be greater than the sum of the entropies of the gases taken individually $[\Sigma(m S_T)]$. The mixing may be "rendered" reversible by imagining the gases to expand through permeable pistons (Planck, Theory of Heat) and it is possible to compute the increase in entropy for each gas in turn by considering it to have expanded from one atmosphere down to its own partial pressure as though the other gases were not present. If m_1 mols expand from one atmosphere pressure to p_1, the partial pressure of gas (1), the work in isothermal expansion is

$$m_1 \frac{RT}{J} \log_e \frac{1}{p_1} \; ; \quad \text{but } p_1 \times \Sigma m = 1 \times m_1 ; \quad \text{i.e. } p_1 = \frac{m_1}{\Sigma m}$$

The increase in entropy accompanying this change is $m_1 \frac{R}{J} \log_e \frac{\Sigma m}{m_1}$ and similarly for the other gases. The total entropy of a gaseous mixture at temperature T, one atmosphere pressure, is $\Sigma(m\, S_T) + \Sigma\left(m \frac{R}{J} \log_e \frac{\Sigma m}{m}\right)$.

The entropy of a mixture at one atmosphere is given above and the change of entropy due to isothermal compression of the whole mixture from 1 to P atmospheres is $\Sigma\, m \frac{R}{J} \log_e P$. Thus the total entropy of a gas mixture at any temperature T and pressure P is given by

$$S = \Sigma(m\, S_T) + \Sigma\left(m \frac{R}{J} \log_e \frac{\Sigma m}{m}\right) - \Sigma m \frac{R}{J} \log_e P.$$

The value of S, given above, is in molal units since the values of S_T listed in "Tables of Properties of Gases" are for the pound molecule or mol. The value of the entropy in pound units is found by dividing the value of S by the apparent molecular weight (A.M.W.) of the mixture.

The internal energy of a gas mixture.

If m_1, m_2, ... denote the number of mols. of each gas comprising a mixture the internal energy of the mixture is given by

$$E_m = \frac{m_1 E_1 + m_2 E_2 + \ldots\ldots}{m_1 + m_2 +}$$

$$= \frac{\Sigma m E}{\Sigma m} \quad \text{B.T.U./lb. mol.}$$

The values of E for individual gases are listed in "Tables of Properties of Gases". Since the E values are given in mol units values per pound are found by dividing by the apparent molecular weight (A.M.W.) of the mixture.

Enthalpy values may be found in a similar way.