THESIS

Submitted to the University of Glasgow
for the Degree of Doctor of Science.

"Heavy Water and the Structure of Crystalline Hydrates".

With an additional paper on

"The Photosynthesis of Carbohydrates in vitro with Visible Light".

By

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PREFACE.

The chief part (Part 1.) of this thesis is divided into three sections. In the first section a short historical survey of theories of the structures of salt hydrates is given, and the reasons for undertaking the present work are outlined. The results of this work are summarized and considered from various points of view in Section 11. Full experimental details and measurements are given in the experimental section.

The additional paper (Part 11.) is in two parts : an historical and theoretical section, and the description of the experimental work with detailed results.

Parts of the work described in this thesis have been published in Nature, in the Transactions of the Faraday Society, and in the Journal of the Chemical Society.

I desire to express my gratitude to Professor G.G.Henderson, F.R.S., for affording me opportunities of carrying out the work described in Part 1, and for his interest and encouragement. My thanks are also due to the Chemical Society for a grant which defrayed part of the cost of the work, and to Imperial Chemical Industries, Ltd., for a gift of heavy water. I am also grateful to the Carnegie Trustees for the award of a Teaching Fellowship during the tenure of which the greater part of this work was performed.

The work described in the additional paper was carried out in the Sir William Ramsay Laboratories of Inorganic and Physical Chemistry, University College, London, during the tenure of a Ramsay Memorial Fellowship. I am grateful to the Trustees for the award of this Fellowship, and to Professor F.G.Donnan, F.R.S., for his interest and for his valuable advice and suggestions.

Glasgow.
April, 1937.

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PART 1.

HEAVY WATER and the STRUCTURE
of CRYSTALLINE HYDRATES.

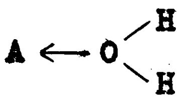
1. HISTORICAL and THEORETICAL

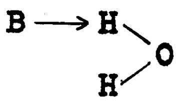
The first attempt to devise structures for crystalline salt hydrates was made by Werner (1) who suggested that they might be considered as co-ordination compounds. As is well known, Werner had accounted for the formation of the ammines and other complex compounds by the postulation of a subsidiary or co-ordination valency for the metallic radicle, and that it was by the satisfaction of such co-ordination valencies that these complexes were formed. It was by this means also, according to Werner, that salt hydrates were formed, these being co-ordination compounds in which the water molecules were, in general, attached to the metallic radicle. Thus, for example, nickel sulphate hexahydrate was considered as $Ni(H_2O)_6,SO_4$, and beryllium sulphate tetrahydrate as $Be(H_2O)_4,SO_4$. Werner was able, in certain cases, to identify the number of water molecules in the hydrated salt with the co-ordination number of the metal, but in many other examples this was not possible, the number of water molecules being larger than the co-ordination number. This led Werner to make a hypothetical allocation of the water molecules between the cation and the anion: thus copper sulphate pentahydrate was assumed to have the structure $Cu(H_2O)_4,SO_4(H_2O)$; in strontium chloride hexahydrate the water was assumed to belong to the cation, and in lithium sulphate monohydrate the water molecule was associated with the anion.

In certain salts, however, the number of water molecules was found to be in excess of the co-ordination number of the metallic radicle even after allowance had been made for the hydration of the acid radicle. To explain this, Werner suggested two hypotheses, first, that double water molecules $(H_2O)_2$ such as are known to exist in water itself might take the place of single water molecules, or secondly, that some of the water molecules in the hydrate might have no part in the molecular structure, being held only by the crystalline forces.

Werner's views have been satisfactorily interpreted by Sidgwick (2) by the use of the modern electronic theory of valency. On this theory the co-ordination valency of Werner becomes a co-ordinate link, i.e., a covalent link in which both shared electrons are contributed by one atom or group.

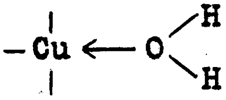
According to Sidgwick, water molecules can be co--ordinated to other atoms in two ways, either by the oxygen of the water acting as donor, or the hydrogen acting as acceptor:

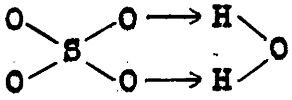




Since an atom is likely to act as a donor when negatively charged, and as an acceptor when positively charged, it is probable that, in hydration, cations will act as acceptors and form the link with the oxygen of the water, while anions will form the co-ordinate link with the hydrogen of the water.

Such a linkage through the hydrogen is known as a "hydrogen bond" (3).





Thus the hydration of cations and of anions can be accounted for on an electronic basis. It would appear, from statistical evidence that hydration of cations is more common than the hydration of anions, as would be expected on this electronic explanation. The difficulty of explaining the cases of excessively hydrated salts still persists unless the possibility of double water molecules is assumed.

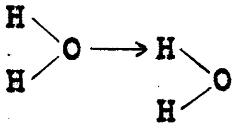
In contrast to this structural view of crystalline hydrates, a physical theory of hydration has been formulated by Fajans (4), Born (5), Kossel (6), and Garrick (7). This theory is electrostatic, and according to it the stability of salt hydrates is due to the electrical dipole nature of the water molecule - an assumption first made by Debye (8). The polar water molecules are held simply by electrostatic attraction and no bonds, as such, are formed. The theory takes into account such molecular properties as size, charge, and dipole moment, and it is claimed that from these the effective co-ordination number can be calculated, the results being in good agreement with general experimental evidence.

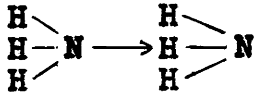
No such quantitative conclusions can be reached on the structural theory.

In the last few years the structures of a number of hydrates have been examined by X-ray methods and the results of these investigations have led to a clearer idea of the part played by the water of crystallisation. In general, the hypothesis of Werner has been justified by the X-ray work; thus in beryllium sulphate tetrahydrate, it has been shown (9) that each beryllium atom is surrounded by a tetrahedron of four water molecules, the whole forming a composite positive ion, such as was postulated by Werner in writing the formula for this hydrate as $Be(H_2O)_4,SO_4$. Again, each copper atom in copper sulphate pentahydrate, according to Beevers and Lipson (10), is surrounded by an octahedron of four water molecules and two oxygen atoms (from the sulphate ion), while the fifth water molecule is not co-ordinated to the copper, but seems to play some part in holding the structure together.

The discovery of heavy hydrogen (deuterium) and the consequent availability of heavy water (deuterium oxide) have suggested the possibility of obtaining new experimental evidence of value in studying the hydration of salts.

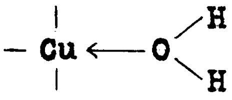
The view has been expressed by Lewis and Schutz (11) that "hydrogen bonds" (p. 3) containing deuterium are more stable than those containing ordinary light hydrogen. This view receives considerable support from a comparison of the vapour pressures of deuterium compounds with those of the corresponding hydrogen compounds. Thus, the vapour pressures of deuterium oxide, D_2O, and deutero-ammonia, ND_3, are considerably lower than those of ordinary water and ammonia: these compounds are generally believed to be largely associated in the liquid state, due to the formation of such hydrogen bonds.

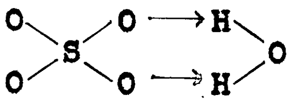




On the other hand, the vapour pressures of deutochloric acid, DCl, and hydrochloric acid, where there are supposed to be few, if any, hydrogen bonds, show little difference.

It has been pointed out that Sidgwick's views on the hydration of cations and anions (p. 2) necessitate the formation of "hydrogen bonds" in one case only; the water associated with anions is bound by a co-ordinate link with the hydrogen of the water. No "hydrogen bonds" are formed in cationic hydration. In the following illustration which was used earlier the hydrogen bonds are shown in red.





Shortly after the discovery of heavy water there were many unsuccessful attempts to obtain an enrichment of the heavy hydrogen isotope in ordinary water by the crystallisation of various salts, the crystal water and the water from the mother liquor being examined for the deuterium content. In general, there was little or no theoretical justification considered, the experiments seemed only to represent attempts to procure a simple method of preparing more concentrated solutions of heavy water.

Day, Hughes, Ingold and Wilson (12), however, made a reasoned attempt to demonstrate isotopic discrimination during the crystallisation of certain hydrates. These workers, on consideration of the relative strengths of the hydrogen and deuterium bonds, concluded that if Sidgwick's views on the hydration of cations and anions (as illustrated above) were correct, and that if hydrogen bonds were formed only in the case of anion-hydration, then a certain isotopic discrimination should occur. They considered that on crystallisation from a mixture of light and heavy water, a salt whose water of crystallisation was considered to be attached to the cation should discriminate in favour of the light water, since in this case the hydrogen of the water has no direct effect, the factor causing the discrimination being the relatively greater ease of removing the light water from the solution, a conclusion reached by consideration of the lower vapour pressure of deuterium oxide. On the other hand, crystallisation under similar conditions of an anion-hydrated salt, requiring the formation of hydrogen bonds, should lead to a relative discrimination in favour of heavy water.

Ingold and his collaborators therefore crystallised a number of salts such as strontium chloride, lithium sulphate and copper sulphate from a very dilute solution of heavy water in ordinary water and examined, by density measurements, both the crystal water and the solution water for the deuterium content. No evidence of any discrimination was found, however, and they concluded that any structure arising out of the hydration of salts must be of a loose nature.

It was felt, however, that these results were not entirely conclusive: the solution of heavy water used was exceedingly dilute, being about 2%, and while the density measurements were made with a high degree of accuracy, the density difference to be expected, if discrimination took place, was very small.

The present work, therefore, taking advantage of the recent accessibility of pure deuterium oxide, represents a study of the problem from another angle. It was considered that a study of the properties of the pure deuterates, such as $CuSO_4,5D_2O$, etc., and a comparison with those of the corresponding hydrates might lead to evidence applicable to the question of the structure of crystalline hydrates.

It was decided to investigate the dissociation pressure relationships of the pure deuterates: it has been said by

Lembert (13) that the dissociation pressure of a crystalline hydrate is the only real measure of the strength of the linkage which binds the water molecules. From a knowledge of the dissociation pressures the heats of dissociation of the hydrates and deuterates may be calculated, and these should be of value in consideration of the structures of salt hydrates since they may give some indication of the relative stabilities.

The object of this thesis, therefore, is to show that further experimental examination of the problem of the structure of crystalline salt hydrates is now possible by comparison of the hydrates with the corresponding deuterates, and that the results of such investigations are of interest in view of structures proposed for certain types of hydrates.

11. DISCUSSION of RESULTS.

(a) Dissociation Pressures.

It was desired to examine the dissociation pressures of two groups of salts, one group believed to be cationically hydrated and the other anionically hydrated, and in the selection of suitable salts the electronic conception of the structure of hydrates was found to be a convenient guide. The simplest and most accessible examples of salts showing the two types of hydration were found in the chlorides and sulphates.

At the outset, the sulphates were therefore chosen in such a way that each has been assumed to have at least one water molecule associated with the anion, and the chlorides selected for examination were considered to have the water of crystallisation attached to the cation. Thus, for example, cobalt sulphate heptahydrate, $CoSO_4,7H_2O$, on this conception, has six of the water molecules bound by co-ordinate linkages to the cobalt atom, and the seventh linked to the sulphate ion, while in cobalt chloride hexahydrate, $CoCl_2,6H_2O$, the six water molecules form the co-ordination group around the cobalt atom.

If, now, it is assumed that hydrogen bonds are formed during anion-hydration (as shown in the illustration on p. 3) then deuterium oxide of crystallisation attached to an anion

should be relatively more strongly bound, since the deuterium bond is stronger than the hydrogen bond. In the foregoing example of cobalt sulphate and cobalt chloride, a comparison of the heptahydrate and heptadeuterate of the sulphate, and the hexahydrated and hexadeuterated chloride should indicate that the deuterium oxide of crystallisation is more difficult to remove from the sulphate than from the chloride.
No hydrogen or deuterium bonds are formed in the co-ordination group of six water molecules round the cobalt atom, but in the sulphate the seventh water molecule is linked by hydrogen bonds to the sulphate radicle, hence the effect of the introduction of deuterium oxide in place of water in this case means the formation of the stronger deuterium bonds and consequently the deuterium oxide is more strongly held.

If the dissociation pressure of a hydrate is a measure of the strength of the linkage of the water molecules, then comparison of the dissociation pressures of hydrates and deuterates should show greater differences of pressure in cases where anion-hydration has taken place.

In Table I are shown the values for the ratio of the dissociation pressure of each of the deuterates examined to that of the corresponding hydrate, the value for this ratio being the mean value over the range of temperature, usually 25—40° C, in which the dissociation pressures were determined.

Sodium bromide dihydrate and dideuterate are included in this table since these salts were examined owing to the impossibility of obtaining hydrated sodium chloride at ordinary temperatures.

Table 1.

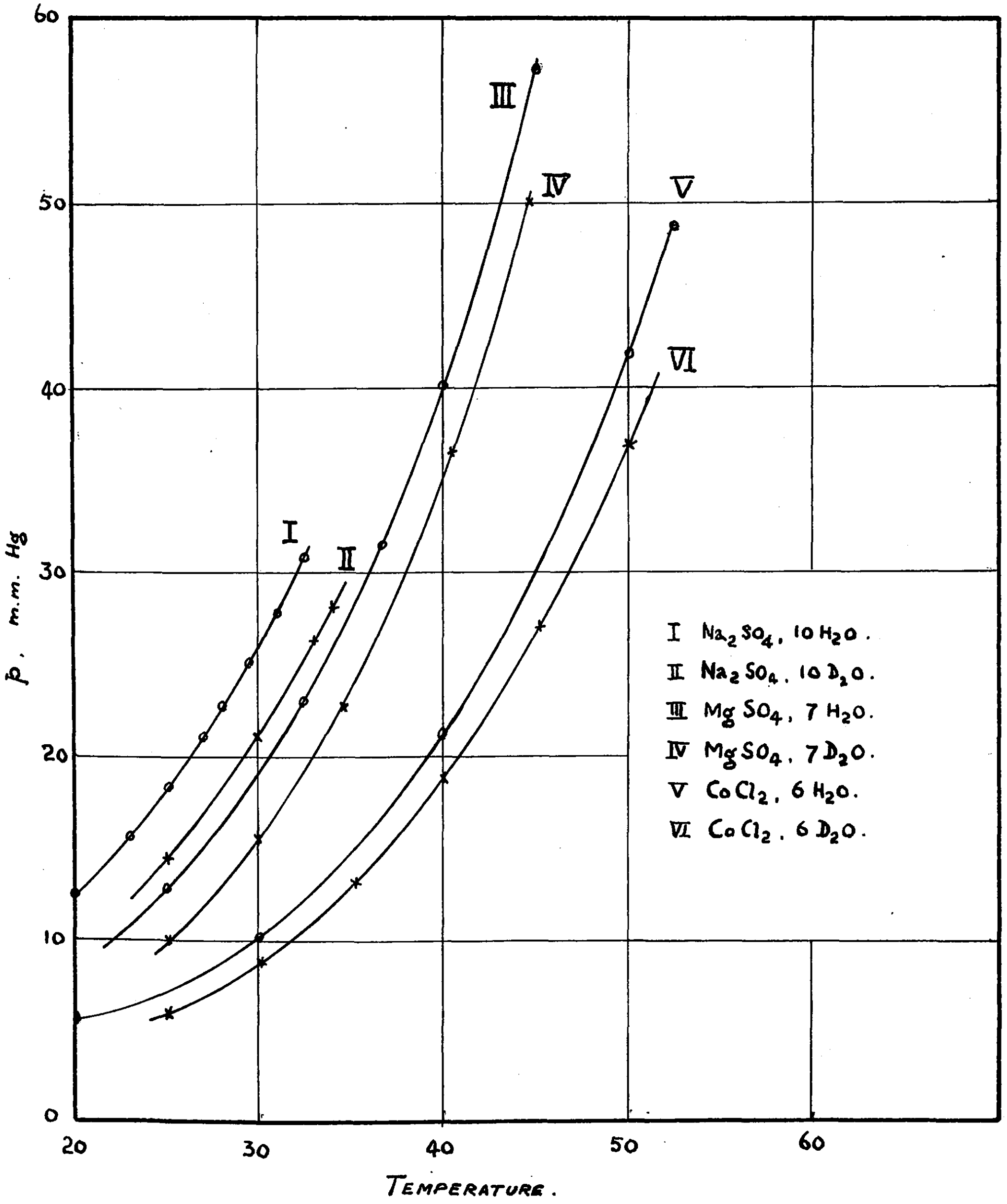
	p_D/p_H		p_D/p_H
$CuSO_4, 5D_2O$	0.844	$CuCl_2, 2D_2O$	0.929
$CuSO_4, 5H_2O$		$CuCl_2, 2H_2O$	
$Na_2SO_4, 10D_2O$	0.802	$NaBr, 2D_2O$	0.916
$Na_2SO_4, 10H_2O$		$NaBr, 2H_2O$	
$CoSO_4, 7D_2O$	0.834	$CoCl_2, 6D_2O$	0.869
$CoSO_4, 7H_2O$		$CoCl_2, 6H_2O$	
$NiSO_4, 7D_2O$	0.816	$NiCl_2, 6D_2O$	0.817
$NiSO_4, 7H_2O$		$NiCl_2, 6H_2O$	
$ZnSO_4, 7D_2O$	0.885	$SrCl_2, 6D_2O$	0.948
$ZnSO_4, 7H_2O$		$SrCl_2, 6H_2O$	
$MgSO_4, 7D_2O$	0.832	$BaCl_2, 2D_2O$	0.965
$MgSO_4, 7H_2O$		$BaCl_2, 2H_2O$	

In consideration of these results it must be remenbered that the vapour pressure of deuterium oxide is less than that of ordinary water. The values for the ratio of the two vapour pressures have been given by Farkas (14), and, for the temperatures applicable to this work, are as follows :

t	p_{D_2O}/p_{H_2O}	
20	0.87	
30	0.88	Mean value 0.885
40	0.89	
50	0.90	

The figures shown in Table 1 indicate clearly that differences in the relative dissociation pressures of hydrates and deuterates exist, and that these appear to correspond to the different types of hydration. The ratio of the dissociation pressure of the deuterate to that of the hydrate is considerably lower for the sulphates than for the chlorides. This difference is illustrated well in Fig. 1., which shows the dissociation pressure curves for the hydrate and deuterate of three of the salts, sodium sulphate, magnesium sulphate, and cobalt chloride.

Fig. 1.



60
50
40
30
20
10
0
20
30
40
50
60
p, m.m. Hg
Temperature.
I
II
III
IV
V
VI
I $Na_2SO_4, 10H_2O$.
II $Na_2SO_4, 10D_2O$.
III $MgSO_4, 7H_2O$.
IV $MgSO_4, 7D_2O$.
V $CoCl_2, 6H_2O$.
VI $CoCl_2, 6D_2O$.

The relatively lower dissociation pressures of the deuterated sulphates is in agreement with the view that in these sulphates part, at least, of the deuterium oxide of crystallisation is firmly held by deuterium bonds.

Two further examples, of a more critical nature, namely beryllium sulphate tetrahydrate and potassium fluoride dihydrate, are therefore of particular interest. In the former salt all four water molecules are considered to be co-ordinated to the beryllium atom, so that this sulphate differs from the others in having no water molecule attached to the anion. Potassium fluoride dihydrate, on the other hand, is believed to furnish an example of the hydration of the fluorine ion (Sidgwick : Electronic Theory of Valency, p 196). The ratios of the dissociation pressures of the deuterates and hydrates of these two salts are as follows :

	p_D/p_H		p_D/p_H
$BeSO_4,4D_2O$	0.899	$KF,2D_2O$	0.735
$BeSO_4,4H_2O$		$KF,2H_2O$	

It will be seen that the value for beryllium sulphate is closer to the chloride figures than to those for the other sulphates in Table 1., as would be expected. Potassium Fluoride, however, gives the lowest value yet obtained for the ratio p_D/p_H. This salt will be considered more fully in the next section, in which the heats of dissociation are discussed.

(b) Heats of Dissociation.

The dissociation pressures of hydrated salts are connected with the heat of dissociation, Q, by the relation

$$\frac{d \log p}{d T} = \frac{Q}{R T^2}$$

On integration, this can be obtained in the form

$$\frac{1}{T} = \frac{R}{Q} . \log p + C$$

Thus, if the reciprocal of the absolute temperature is plotted against the logarithm of the dissociation pressure a straight line is obtained, the slope of this line being a measure of R/Q.

The values of log p have been plotted against $10^6 \times 1/T$ for the deuterates and the corresponding hydrates, and the slopes of the lines determined. As the slope of the hydrate line gives a measure of R/Q_H, and that of the deuterate, R/Q_D, by division a value is obtained for Q_D/Q_H, i.e. the ratio of the heat of dissociation of the deuterate to the heat of dissociation of the hydrate.

Table 11 shows the values for Q_D/Q_H.

Table 11.

	Q_D/Q_H		Q_D/Q_H
$CuSO_4,5D_2O$	1.096	$CuCl_2,2D_2O$	1.012
$CuSO_4,5H_2O$		$CuCl_2,2H_2O$	
$Na_2SO_4,10D_2O$	1.086	$NaBr\ ,2D_2O$	1.032
$Na_2SO_4,10H_2O$		$NaBr\ ,2H_2O$	
$CoSO_4,7D_2O$	1.089	$CoCl_2,6D_2O$	1.053
$CoSO_4,7H_2O$		$CoCl_2,6H_2O$	
$NiSO_4,7D_2O$	1.369	$NiCl_2,6D_2O$	1.316
$NiSO_4,7H_2O$		$NiCl_2,6H_2O$	
$ZnSO_4,7D_2O$	1.086	$SrCl_2,6D_2O$	0.992
$ZnSO_4,7H_2O$		$SrCl_2,6H_2O$	
$MgSO_4,7D_2O$	1.091	$BaCl_2,2D_2O$	0.997
$MgSO_4,7H_2O$		$BaCl_2,2H_2O$	

The results in Table 11 again show the difference between the two groups of salts, the values of Q_D/Q_H for the chlorides being lower than the sulphate value. With the exception of nickel sulphate, which has a value about 20% above the mean, Q_D/Q_H for the sulphates is remarkably constant. The agreement among the chlorides is not so good ; nickel chloride, again, is an exceptional case, having a Q_D/Q_H ratio 30% above the mean value. Strontium Chloride and ~~the~~ barium chloride give values which agree closely to one another but which are rather lower than the other chloride values. It has been estimated that the experimental error in the determination of the results in Table 11 is about 2% : the difference between the mean values for the two groups of salts, excluding the nickel salts in both cases, is about 8 - 9%.

From the measurements of the vapour pressures of water and deuterium oxide (15) a similar ratio can be obtained for the two liquids. In this case Q_D/Q_H represents the ratio of the heats of vaporization of heavy and light water. The result obtained by this graphical method is 1.015, a value which is closer to the mean value of Q_D/Q_H for the chlorides than for the sulphates.

An effect such as this would be expected if the assumption that additional hydrogen or deuterium bonds are formed in anionic hydration is correct. Where there are no hydrogen bonds, as in cationic hydration, it may be legitimately expected that the ratio of the heats of dissociation of the deuterate and hydrate will have practically the same value as the ratio of the heats of vaporization of deuterium oxide and ordinary light water. The value may even be smaller, if the association of liquid deuterium oxide, and liquid water, is due to the formation of such deuterium or hydrogen bonds. On the other hand, where hydrogen bonds are formed in hydration, the effect of the greater strength of the bond to the deuterium atom should be demonstrated by a relatively greater heat of dissociation, as has been found in the case of the sulphates examined.

The cases of beryllium sulphate and potassium fluoride may now be considered. For beryllium sulphate, Q_D/Q_H has been found to be 1.002, so that it can be said that the water of crystallisation in the tetrahydrate is bound in a manner similar to that occurring in the majority of the chlorides examined. This is in agreement with the electronic view on which all four water molecules are co-ordinated to the beryllium atom.

The value of Q_D/Q_H for potassium fluoride, however, is 1.132, a value higher than that obtained for any of the other salts, with the exception of nickel sulphate and chloride. On the electronic theory this dihydrate is a clear case of anionic hydration since potassium salts are normally anhydrous. It is argued, on the same theory that the hydration of the fluorine ion may be due to the unusual strength of the covalent link between fluorine and hydrogen, which accounts for the occurrence of hydrofluoric acid as H_2F_2 and its behaviour as $H(F_2H)$. The hydration of the fluorine ion may therefore be illustrated as follows

$$F \longrightarrow H - O - H \qquad \text{analogous to} \qquad F \longrightarrow H - F$$

where the co-ordinate link to the hydrogen is unusually stable.

Naturally, in potassium fluoride dideuterate a proportionately stronger deuterium bond would be formed, so that the electronic aspect affords some explanation of the larger differences in the heats of dissociation and dissociation pressures of the hydrate and deuterate.

A further possibility remains to be considered : it may be that in certain hydrates the water of crystallisation is simply accommodated in the interstices of the crystal lattice and thus held only by the crystal forces. In a case of this type, where no structural bonds are postulated, it would be expected that the ratio of the heats of dissociation of the deuterate and hydrate would again have the same value as the ratio of the heats of vaporization of deuterium oxide and water. In certain cases, some distortion of the crystal lattice might occur, owing to the greater molecular volume of the deuterium oxide, and it would therefore be of interest if the lattice dimensions of hydrates and deuterates were determined by the usual X-Ray methods.

(c) Heats of Hydration.

From a knowledge of the dissociation pressure of a hydrate, the heat of combination of the dissociation product with liquid water can be calculated from the Clausius - Clapeyron Equation in the form

$$Q_c = 4.576 \times \frac{T_2 T_1}{T_2 - T_1} \log \frac{p_2/\pi_2}{p_1/\pi_1}$$

where p_1 and p_2 are the dissociation pressures of the hydrate at the temperatures T_1 and T_2, π_1 and π_2 being the vapour pressures of water at the same temperatures.
For example, in the case of copper sulphate, if the dissociation pressures of the pentahydrate are measured, this formula gives the heat of combination, in gm. cal., for the reaction

$$CuSO_4,3H_2O + 2H_2O\ (liq) \longrightarrow CuSO_4,5H_2O$$

The formula can, of course, also be applied to the deuterates, since the vapour pressures of deuterium oxide at different temperatures are known. The heats of combination of the hydrates and deuterates have therefore been calculated, and the mean values are shown in Table 111.

Table 111.

	Q_c	diff.
$CuSO_4,3H_2O + 2H_2O$	2992	
$CuSO_4,3D_2O + 2D_2O$	3772	780
$Na_2SO_4 + 10H_2O$	2321	
$Na_2SO_4 + 10D_2O$	2404	83
$MgSO_4,6H_2O + H_2O$	3641	
$MgSO_4,6D_2O + D_2O$	4760	1119
$CoSO_4,6H_2O + H_2O$	2204	
$CoSO_4,6D_2O + D_2O$	2916	712
$NiSO_4,6H_2O + H_2O$	1095	
$NiSO_4,6D_2O - D_2O$	4410	3315
$ZnSO_4,6H_2O + H_2O$	3205	
$ZnSO_4,6D_2O + D_2O$	4271	1066
$BeSO_4,3H_2O + H_2O$	4277	
$BeSO_4,3D_2O + D_2O$	4650	373

Table 111 (cont.)

	Q	diff.
$CuCl_2,H_2O + H_2O$	2759	
$CuCl_2,D_2O + D_2O$	2793	34
$NaBr, + 2H_2O$	3302	
$NaBr, + 2D_2O$	3333	31
$CoCl_2,2H_2O + 4H_2O$	3053	
$CoCl_2,2D_2O + 4D_2O$	3676	623
$NiCl_2,4H_2O + 2H_2O$	1654	
$NiCl_2,4D_2O + 2D_2O$	4463	2809
$SrCl_2,2H_2O + 4H_2O$	3147	
$SrCl_2,2D_2O + 4D_2O$	2597	-550
$BaCl_2,H_2O + H_2O$	1912	
$BaCl_2,D_2O + D_2O$	1449	-463
$KF, H_2O + H_2O$	3410	
$KF, D_2O + D_2O$	4201	791

No generalisation can be made from the figures in Table 111, as considerable variation is usually obtained in the values for the heats of combination calculated by this method. The most interesting feature is again the behaviour of the nickel salts, both the chloride and the sulphate showing a large difference in the heats of combination with ordinary water and with heavy water.

(d) Transition Points.

The dissociation pressure curve of a hydrate or deuterate shows a break where transition to a lower hydrate or deuterate, or to anhydrous salt, occurs. Transition points cannot, however, be determined accurately with these curves, but a more accurate determination can be made by finding the point at which the straight line obtained by plotting log p against 1/T changes its direction.

Table lV shows the transition points of several of the deuterates examined, together with the accepted figures for the transition points of the corresponding hydrates.

Taylor (16) has determined the transition point of sodium sulphate decadeuterate by a thermometric method and found it to occur at 34.48°C. This is the only example, so far, of a deuterate which has a higher transition temperature than the corresponding hydrate.

Table lV.

Transition Points.

	°C.
$Na_2SO_4,10D_2O \longrightarrow Na_2SO_4$	34.5
$Na_2SO_4,10H_2O \longrightarrow Na_2SO_4$	32.4
$MgSO_4,7D_2O \longrightarrow MgSO_4.6D_2O$	46.8
$MgSO_4,7H_2O \longrightarrow MgSO_4,6H_2O$	48.4
$CoSO_4,7D_2O \longrightarrow CoSO_4,6D_2O$	42.6
$CoSO_4,7H_2O \longrightarrow CoSO_4,6H_2O$	45.1
$NiSO_4,7D_2O \longrightarrow NiSO_4,6D_2O$	26.9
$NiSO_4,7H_2O \longrightarrow NiSO_4,6H_2O$	30.5
$ZnSO_4,7D_2O \longrightarrow ZnSO_4,6D_2O$	36.7
$ZnSO_4,7H_2O \longrightarrow ZnSO_4,6H_2O$	39.0
$NaBr,\ 2D_2O \longrightarrow NaBr$	47.7
$NaBr,\ 2H_2O \longrightarrow NaBr$	50.7
$CoCl_2,6D_2O \longrightarrow CoCl_2,2D_2O$	51.8
$CoCl_2,6H_2O \longrightarrow CoCl_2,2H_2O$	52.25
$NiCl_2,6D_2O \longrightarrow NiCl_2,4D_2O$	35.4
$NiCl_2,6H_2O \longrightarrow NiCl_2,4H_2O$	36.25

(e) Structures Suggested by X-Ray Investigations.

The results obtained for the ratios of the dissociation pressures and the heats of dissociation of the deuterates and hydrates are of interest when considered in conjunction with the results of the recent X-Ray investigations of the structures of certain hydrates. These investigations, which have so far been confined to a few hydrates, have shown definite differences in the positions and arrangements of the water molecules in different types of hydrates.

Hermann (17) has given a detailed structure for strontium chloride hexahydrate, in which the six water molecules form a highly deformed octahedron around the strontium atom. Similarly, the arrangement of water molecules in nickel sulphate hexahydrate, according to Beevers and Lipson (18) is octahedral around the nickel atom, and in beryllium sulphate tetrahydrate, which has been the subject of a complete examination by the same workers (9), the four water molecules are arranged tetrahedrally around the beryllium atom. These structures are in complete agreement with the allocation of the water molecules to the cation as suggested by Werner, and elaborated on the electronic theory of valency.

In copper sulphate pentahydrate, however, the water molecules are arranged differently. It has been found by

Beevers and Lipson (10) that four water molecules are situated round the copper atom, forming the co-ordination group, while the fifth is not co-ordinated to the copper at all. The function of the fifth water molecule does not appear to be clear, but it has been shown that, while the four co-ordinated water molecules each form three bonds, the fifth possesses four bonds forming a tetrahedron.

The structure of nickel sulphate heptahydrate is a most interesting one. According to Beevers and Schwartz (19), who have made a very complete investigation of this salt, the structure consists of octahedral groups of six water molecules around the nickel atom and an extra water molecule. The possession of this extra water molecule which is not co-ordinated to the nickel is a point of similarity with copper sulphate pentahydrate, and it seems reasonable to assume that the other examples of hepta-hydrated sulphates will have similar arrangements of water molecules, i.e. a co-ordination group of $6H_2O$ and one extra water molecule.

Although few hydrates of this type have been examined completely by X-Ray methods, the results of the present investigation seem to indicate that in salts which contain an extra water molecule, the deuterium oxide of crystallisation is relatively more firmly bound than in salts such as strontium chloride hexahydrate (or hexadeuterate) which possess no water molecules outside the co-ordination group.

It has also been shown by Beevers and Schwartz that the water molecules forming the co-ordination group in nickel sulphate heptahydrate are of two types. Four of the six water molecules make two contacts external to the co-ordination group and each of these molecules has its three bonds roughly in one plane. The remaining two co-ordinated water molecules, which are at opposite corners of the octahedron, make three external bonds, and in each case these three bonds together with that to the nickel form a tetrahedron. The seventh water molecule (not co-ordinated to the nickel atom) also makes four bonds arranged tetrahedrally, and is therefore similar to the unco-ordinated water molecule in copper sulphate pentahydrate. These workers have also shown that the co-ordination group in nickel sulphate hexahydrate is similarly constructed, two water molecules being again of the tetrahedral kind.

It is unfortunate that a complete examination such as this has not yet been carried out on the other heptahydrated sulphates as it would be of interest to see if such an arrangement of different types of water molecules inside the co-ordination group occurs in other hydrates. If this arrangement is peculiar to the nickel salt it may, in some way, account for the much larger value for Q_D/Q_H

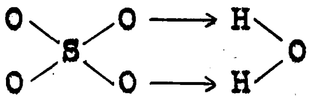
for nickel sulphate which has been found in the present work. Reference to Table 11 (p.17) will show that for nickel sulphate heptadeuterate and heptahydrate, Q_D/Q_H is 1.37, while the mean value for the other sulphates is 1.09. It will be seen also that a similarly higher value has been found for the ratio of the heats of dissociation of nickel chloride hexadeuterate and hexahydrate ; the results of an X-Ray examination of this hexahydrate would therefore be of particular value as it would be interesting to know if the same arrangement of the two types of water molecule occurred in this case also.

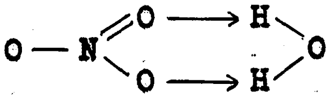
Until additional evidence is obtained, the conclusion that the relatively greater differences in dissociation pressure and heat of dissociation of certain deuterates and hydrates are due to the occurrence of tetrahedrally linked water molecules is scarcely justified.

SUMMARY

It has been shown that by comparison of the dissociation pressures and the heats of dissociation of hydrates and deuterates further evidence of the existence of different types of hydrated salts can be obtained. The differences in the relative dissociation pressures and heats of dissociation indicate that the water molecules may be bound by different types of linkage, and at present these differences appear to be in agreement with Werner's conception of hydration as interpreted by the electronic theory of valency. Recent X-Ray examination of hydrates has also shown that different types and arrangements of water molecules exist, and it has been shown that the results of the present work are in conformity with the structures suggested by the results of the X-Ray investigations.

Whether this interpretation of the differences between the various hydrates and deuterates is correct or not, it is not possible to say at present, but the results have shown that an interesting field for further investigation is opened up. It is proposed to carry out investigations of this kind on other hydrates and deuterates, for example, nitrates, as there is some evidence of hydration of the nitrate ion in a manner similar to the hydration of the sulphate ion.





More interesting examples which it is also proposed to examine are the salts which give a series of hydrates. The examination of a series of hydrates and deuterates such as

$MgSO_4,7H_2O$ $MgSO_4,6H_2O$ $MgSO_4,2H_2O$

$MgSO_4,7D_2O$ $MgSO_4,6D_2O$ $MgSO_4,2D_2O$.

may furnish information as to the relative strengths of the linkages of the various water molecules. Such a complete examination is obviously desirable before definite generalisations are made.

111. EXPERIMENTAL.

The deuterium oxide used in these experiments was obtained from the Norsk Hydroelektrisk Kvaelstofaktieselskab, and in general was of density $d_4^{20} = 1.1054$, corresponding to a deuterium oxide content of 99.95%. In a few cases, 99.4% deuterium oxide was used, this having a density $d_4^{20} = 1.1049$.

Preparation of Deuterates.

In general, the deuterates were prepared by dissolving the anhydrous salt in hot deuterium oxide and allowing the solution to crystallise. As the volume of solution in each crystallisation was, as a rule, about 1 c.c. it was necessary to use small scale apparatus.
The crystallisations were carried out in small flasks, of capacity 4 - 5 c.c., fitted with ground glass stoppers. During the crystallisations, these small flasks were allowed to stand in a large desiccator, without a drying agent, which was used for this purpose only ; solutions in ordinary water were never crystallised in the same desiccator. The crystals were filtered off, under suction on the usual type of semi-micro funnel. In all operations care was taken that the salt or solution was not exposed to moist air, so that contamination with ordinary light water was avoided as far as possible.

In certain cases where crystallisation did not take place readily, the deuterate was prepared by allowing the solution to stand over calcium chloride in a small desiccator which was constructed from a small wide-mouthed bottle having a close-fitting stopper. Freshly ignited calcium chloride was used, so that the deuterium oxide absorbed could be recovered later. If freshly heated calcium chloride was not used, the recovered deuterium oxide was always found to be considerably diluted with ordinary water.

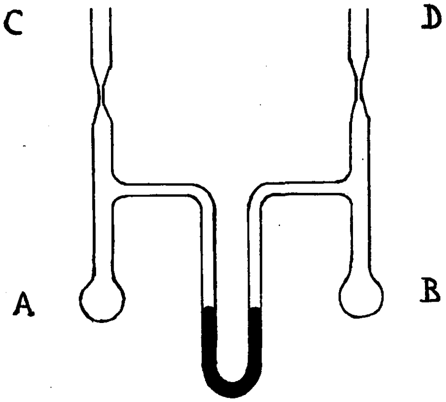
Where possible, conditions were such that the deuterate crystallised in small crystals, but before measurements of the dissociation pressures were made, the salts were finely ground, as quickly as possible, in an agate mortar.

The specimens of the deuterates, if not used immediately for dissociation pressure measurements, were kept in sealed glass tubes.

Measurement of Dissociation Pressure.

Preliminary attempts were made to construct a differential tensimeter which would give a direct reading of the difference in the dissociation pressures of the hydrate and deuterate. These were unsuccessful, the chief reason being the difficulty of evacuating both sides of the tensimeter to the same extent, as it was not desired to have the bulbs containing the hydrate and the deuterate in direct communication at any time, even during evacuation. One of simplest forms of tensimeter for this purpose was of the type shown in Fig. 2.

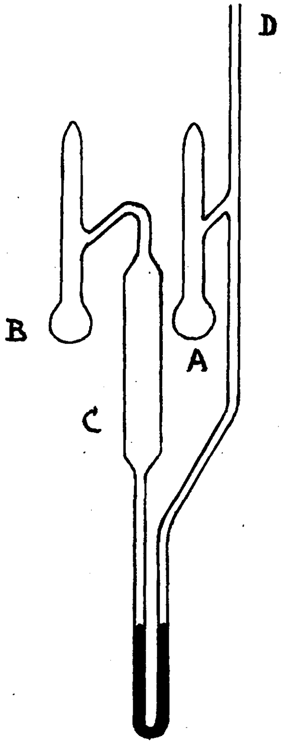
Fig. 2



The bulbs A and B contained the hydrate and the deuterate respectively. Mercury was the manometric liquid and was frozen in the U-tube of the manometer by means of solid carbon dioxide and acetone, while the apparatus was evacuated through C and D. After evacuation C and D were sealed off, and the mercury allowed to liquefy. In addition to the difficulty of obtaining equal evacuation of both sides, it was found in this case that there was a tendency for water vapour to condense on the cold mercury surfaces. Reproducible results were not obtained.

The dissociation pressures of the hydrates and deuterates were therefore measured by the static method, a modification of the Bremer - Frowein tensimeter being used. Mercury was used as the manometric liquid as the use of oils was considered to introduce a possible source of error, owing to the possibility of interchange of hydrogen atoms between the deuterium oxide vapour and the oil, should the latter contain any acidic or alcoholic hydrogen. The tensimeter had the form shown in Fig. 3.

Fig. 3.



The bulb A contained the deuterate or hydrate whose dissociation pressure was being measured, and B contained either concentrated sulphuric acid, deutosulphuric acid, or freshly fused and powdered potassium hydroxide (20).
The tensimeter was placed in a horizontal position so that the mercury flowed into the wide part of the tube at C, and the apparatus was evacuated by a mercury pump through D which was sealed after evacuation for 45 - 60 minutes.
The apparatus was then brought back to the vertical position, causing the mercury to return to the manometer tube, and a millimeter scale of mirror glass was securely strapped on to the manometer. It was then placed in the thermostat, being held vertically by a metal frame-work.

The thermostat, 17 X 17 X 40 cm., containing about 10 litres of water, had a glass front and back. It was gas heated and controlled by the usual form of toluene-mercury regulator, and was accurate to 0.05° C.
In all measurements the tensimeter was allowed to remain at the temperature of the thermostat for at least 24 hours before the reading of the pressure was made. For most salts, equilibrium was reached in 24 hours, but for a few a much longer time had to be allowed.

In the tables of measurements on the succeeding pages, temperatures, t, are given on the Centigrade scale, and the dissociation pressures, p, in ~~the~~ m.m. of mercury. The symbols, p_D and p_H represent the dissociation pressures of the deuterate and hydrate respectively.

Copper Sulphate Pentadeuterate.

Preparation : Anhydrous copper sulphate (0.5 g.) was added to deuterium oxide (1 c.c.) and dissolved by warming the solution to 80 - 90° C. On cooling, the deuterate crystallised out slowly and was filtered off after being allowed to stand overnight. It was dried as quickly as possible on porous plate.

Analysis : .1364 g. gave .0833 g. $CuSO_4$

$CuSO_4$ % = 61.1

Calc. for $CuSO_4,5D_2O$, $CuSO_4$ % = 61.5

" " $CuSO_4,5H_2O$, $CuSO_4$ % = 64.0.

The solution of copper sulphate in deuterium oxide was somewhat greener in colour than a solution in ordinary water; this difference in colour was very apparent in the solid salts $CuSO_4,5D_2O$ and $CuSO_4,5H_2O$, the former being slightly paler and greener in tint.

As it was considered possible that the difference in colour might be due simply to a difference in crystal size, the above preparation of copper sulphate pentadeuterate was repeated and a preparation of the pentahydrate, under exactly similar conditions, was carried out at the same time. Both solutions were allowed to cool at the same rate, but the difference was still apparent.

Two solutions of copper sulphate in water were prepared containing 0.45 g. and 0.55 g. $CuSO_4$ per c.c. respectively. These were allowed to cool slowly ; the stronger solution crystallised more quickly, but there was no difference in colour in the two examples of pentahydrate obtained.
As these two solutions contained respectively 10% less and 10% more copper sulphate than the solution in deuterium oxide this showed that the difference in colour between the pentadeuterate and the pentahydrate was not due to a difference in crystal size caused by a variation in the rate of crystallisation.

The colours of equimolar solutions of copper sulphate in water and in deuterium oxide were compared in a colorimeter The solutions were as follows :

Soln. A : 0.083 g. $CuSO_4$ in 5 c.c. H_2O.
Soln. B : 0.083 g. $CuSO_4$ in 5 c.c. D_2O.

It was found that a column of 5cm. of soln. B was balanced by a column of 4.1cm. of soln. A, although comparison was rather difficult owing to the greener tint of the solution in deuterium oxide.

An examination of the absorption spectra of the two solutions was attempted but the results were not satisfactory.

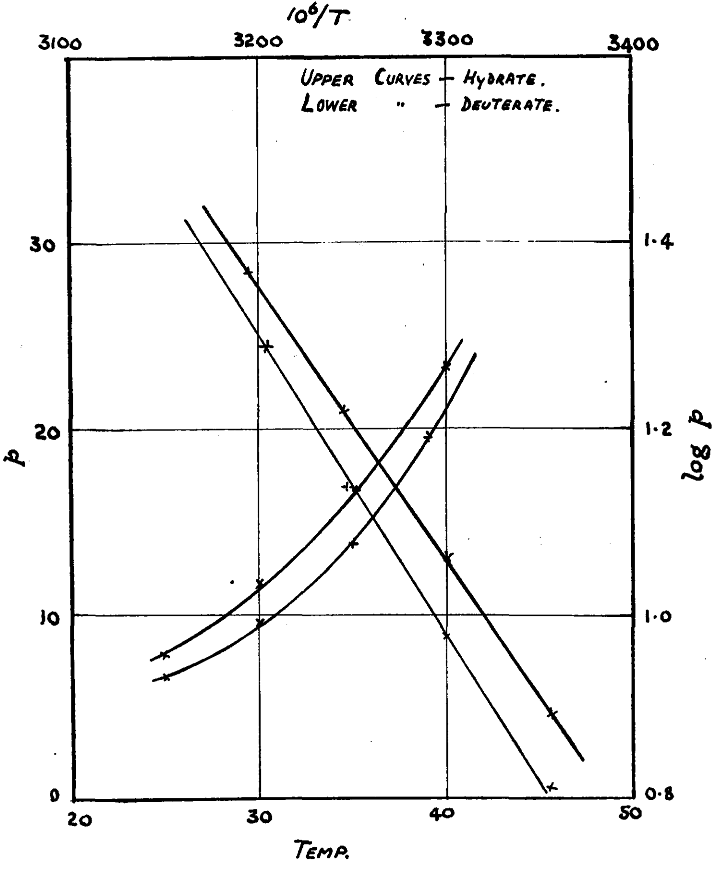
No measurement of the shift of the absorption band could be made with the apparatus available.

Dissociation Pressures : $CuSO_4,5D_2O$.

t	$10^6/T$	p.	log p.
25	3356	6.5	0.813
30	3301	9.3	0.969
35	3246	13.7	1.137
39	3205	19.4	1.288

The dissociation pressure curves and the graphs of log p against $10^6/T$ for the pentadeuterate and the pentahydrate are shown in Fig. 4. The pentahydrate graphs are drawn from the results of Carpenter and Jette (21).

Fig. 4.



Ratio of the Dissociation Pressures :

t	p_D/p_H	
25	0.833	Mean 0.844
30	0.809	
35	0.830	
40	0.905	

While this work was in progress, measurements of the dissociation pressure of the pentadeuterate were announced by Partington and Stratton (22) and by Schacherl (23). The results of the present series of measurements are in agreement with the values found by these workers.

The heats of combination for the reactions

$CuSO_4,3H_2O + 2H_2O\ (liq.) \longrightarrow CuSO_4,5H_2O$

$CuSO_4.3D_2O + 2D_2O\ (liq.) \longrightarrow CuSO_4,5D_2O$

are shown in the following table.

These values are calculated from the Clausius -Clapeyron equation in the form

$$Q_c = 4.576 \frac{T_2 T_1}{T_2 - T_1} \log \frac{p_2/\pi_2}{p_1/\pi_1}$$

	Q_c	
Temp. Range	Hydrate	Deuterate
25 - 30	3453	1974
30 - 35	2920	3972
35 - 40	2602	5550
Mean Value	2992	3772

The ratio of the heat of dissociation of the deuterate to that of the hydrate, determined from the relative slopes of the graphs of log p against $10^6/T$, has a value of 1.096.

Sodium Sulphate Decadeuterate.

Preparation : Anhydrous sodium sulphate (0.5 g.) was dissolved in deuterium oxide (1 c.c.) and the solution allowed to crystallise. The crystals were filtered off and dried quickly on porous plate.

Analysis : .0999 g. gave 0.0419 g. Na_2SO_4

Na_2SO_4 % = 41.9

Calc. for $Na_2SO_4, 10D_2O$, Na_2SO_4 % = 41.5

" " $Na_2SO_4, 10H_2O$, Na_2SO_4 % = 44.1

Dissociation Pressure : $Na_2SO_4,10D_2O$

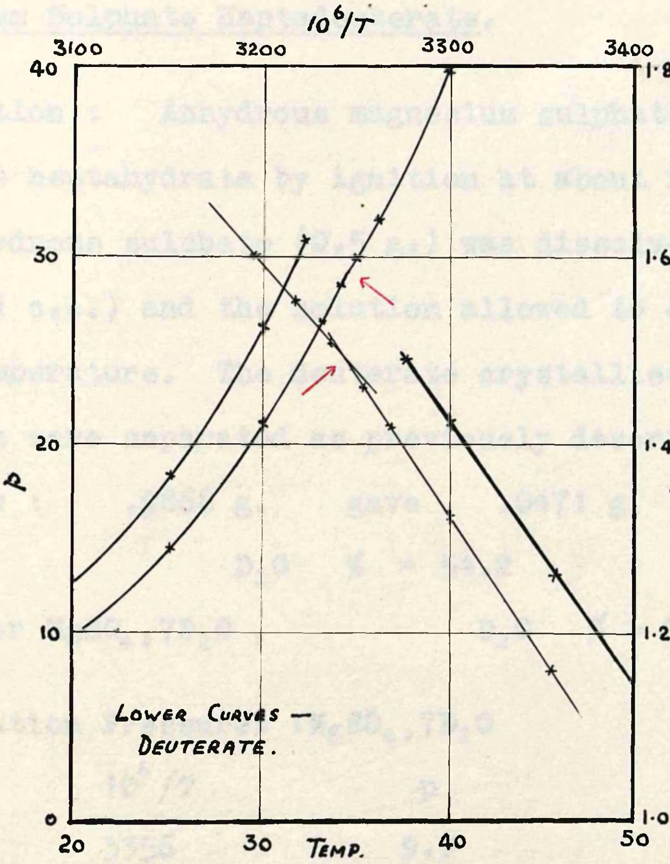
t	$10^6/T$	p	log p.
25	3356	14.5	1.161
30	3301	21.0	1.322
33	3268	26.2	1.418
34	3258	28.1	1.449
35	3246	30.0	1.477
36	3236	31.9	1.504
38	3215	35.7	1.553
40	3196	39.9	1.601

Ratio of the Dissociation Pressures :

t	p_D/p_H	
25	0.797	Mean 0.802
30	0.808	

The dissociation curves and the graphs of log p against $10^6/T$ are shown in Fig.5, the decahydrate curves being due to Wuite (24). The transition point of the decadeuterate was found to occur at $10^6/T = 3254$, corresponding to 34.5°C.

Fig. 5.



Heats of Combination :

Q_c

Temp. Range.	Hydrate	Deuterate
25 - 30	2321	2404

The ratio of the heats of dissociation of the decadeuterate and the decahydrate, determined from the log p - 10 /T graphs, has a value of 1.086.

Magnesium Sulphate Heptadeuterate.

Preparation : Anhydrous magnesium sulphate was prepared from the heptahydrate by ignition at about 200° C. The anhydrous sulphate (0.5 g.) was dissolved in deuterium oxide (1 c.c.) and the solution allowed to crystallise at room temperature. The deuterate crystallised well, and the crystals were separated as previously described.

Analysis : .0868 g. gave .0471 g. D_2O.

D_2O % = 54.2

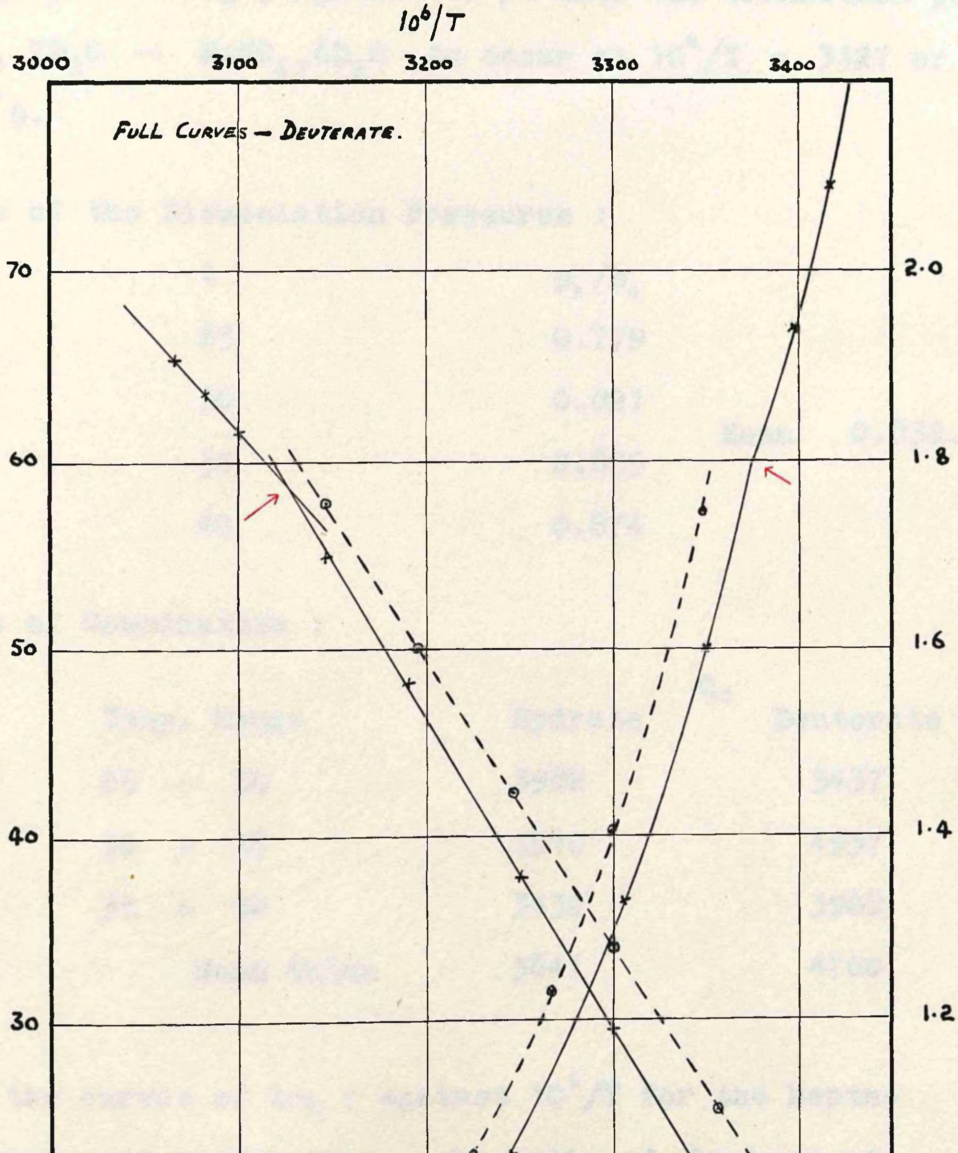
Calc. for $MgSO_4,7D_2O$, D_2O % = 53.8

Dissociation Pressures : $MgSO_4,7D_2O$

t	$10^6/T$	p	log p.
25	3356	9.9	0.996
30	3301	15.6	1.193
34.6	3251	22.7	1.356
40.5	3190	36.6	1.564
44.9	3146	50.0	1.699
49.4	3101	67.1	1.827
51.5	3082	74.5	1.872
53.2	3066	81.0	1.909

The dissociation pressure curves of the heptadeuterate and heptahydrate are shown in Fig. 6. (next page), the heptahydrate curve being that of Carpenter and Jette (21).

Fig. 6.


10⁶/T
3000
3100
3200
3300
3400
FULL CURVES — DEUTERATE.
p
70
60
50
40
30
20
10
log p
2.0
1.8
1.6
1.4
1.2
1.0
0.8
20
30
40
50
TEMP.

The graphs of log p against $10^6/T$ show the transition point $MgSO_4,7D_2O \rightarrow MgSO_4,6D_2O$ to occur at $10^6/T = 3127$ or 46.8°C.

Ratio of the Dissociation Pressures :

t	p_D/p_H	
25	0.779	
30	0.821	
35	0.855	Mean 0.832.
40	0.874	

Heats of Combination :

	Q_c	
Temp. Range	Hydrate	Deuterate
25 - 30	3982	5437
30 - 35	3510	4937
35 - 40	3432	3908
Mean Value	3641	4760

From the curves of log p against $10^6/T$ for the heptadeuterate and heptahydrate, the ratio of the heat of dissociation of the deuterate to that of the hydrate is 1.091.

Nickel Sulphate Heptadeuterate.

Preparation : Anhydrous nickel sulphate was obtained from a pure sample of the heptahydrate by dehydration for several hours at 270 - 280° C. This gave the anhydrous salt in the form of a yellowish green powder.

The anhydrous salt (0.5 g.) and deuterium oxide (1 c.c.) were introduced into a small tube which was then sealed off. This tube was then placed inside a test-tube immersed in a water-bath at 95 - 100° C. Anhydrous nickel sulphate is only slowly soluble, and about 8 hours at the above temperature were necessary before solution was complete. As was expected, a supersaturated solution was obtained on cooling, but crystallisation took place readily when the tube was opened. The crystals were separated in the usual way.

Dissociation Pressures : $NiSO_4,7D_2O$.

t	$10^6/T$	p	log p.
20.5	3407	12	1.079
25	3356	17.7	1.248
29.9	3302	25.1	1.400
34.7	3250	33.4	1.524
38.8	3207	43.0	1.634

No previous determinations of the dissociation pressure of nickel sulphate heptahydrate have been made above 25° C., the values, at this temperature, obtained by other workers are 20.69 m.m. by Schumb (25) and 21.15 m.m. by Bonnell and Burridge (26), using a dynamic method.

The dissociation pressure of the heptahydrate was therefore measured over a range of temperature for comparison with the heptadeuterate values.

Dissociation Pressures : $NiSO_4, 7H_2O$.

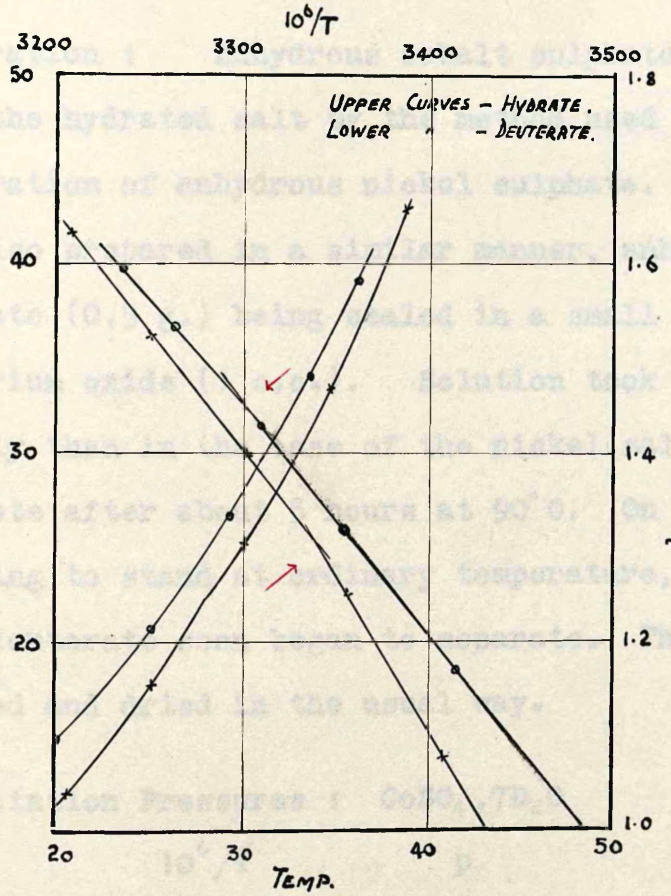
t	$10^6/T$	p	log p
25	3356	20.7	1.316
29.2	3309	26.6	1.425
33.5	3261	34.1	1.533
36.1	3235	39.2	1.593

Fig. 7, shows the dissociation pressure curves and the curves of log p against $10^6/T$.

The transition points occur as follows :

	$10^6/T$	C.
$NiSO_4, 7H_2O \longrightarrow NiSO_4, 6H_2O$	3294	30.5
$NiSO_4, 7D_2O \longrightarrow NiSO_4, 6D_2O$	3335	26.9

Fig. 7.



Ratio of the Dissociation Pressures :

t	p_D/p_H	
20	0.777	Mean 0.816
25	0.855	

Heats of Combination :

Temp. Range	Hydrate (Q_c)	Deuterate (Q_c)
20 - 25	1095	4410

From the slopes of the log p – 10^6/T curves, the ratio of the heat of dissociation of the heptadeuterate to that of the heptahydrate has the value 1.369.

Cobalt Sulphate Heptadeuterate.

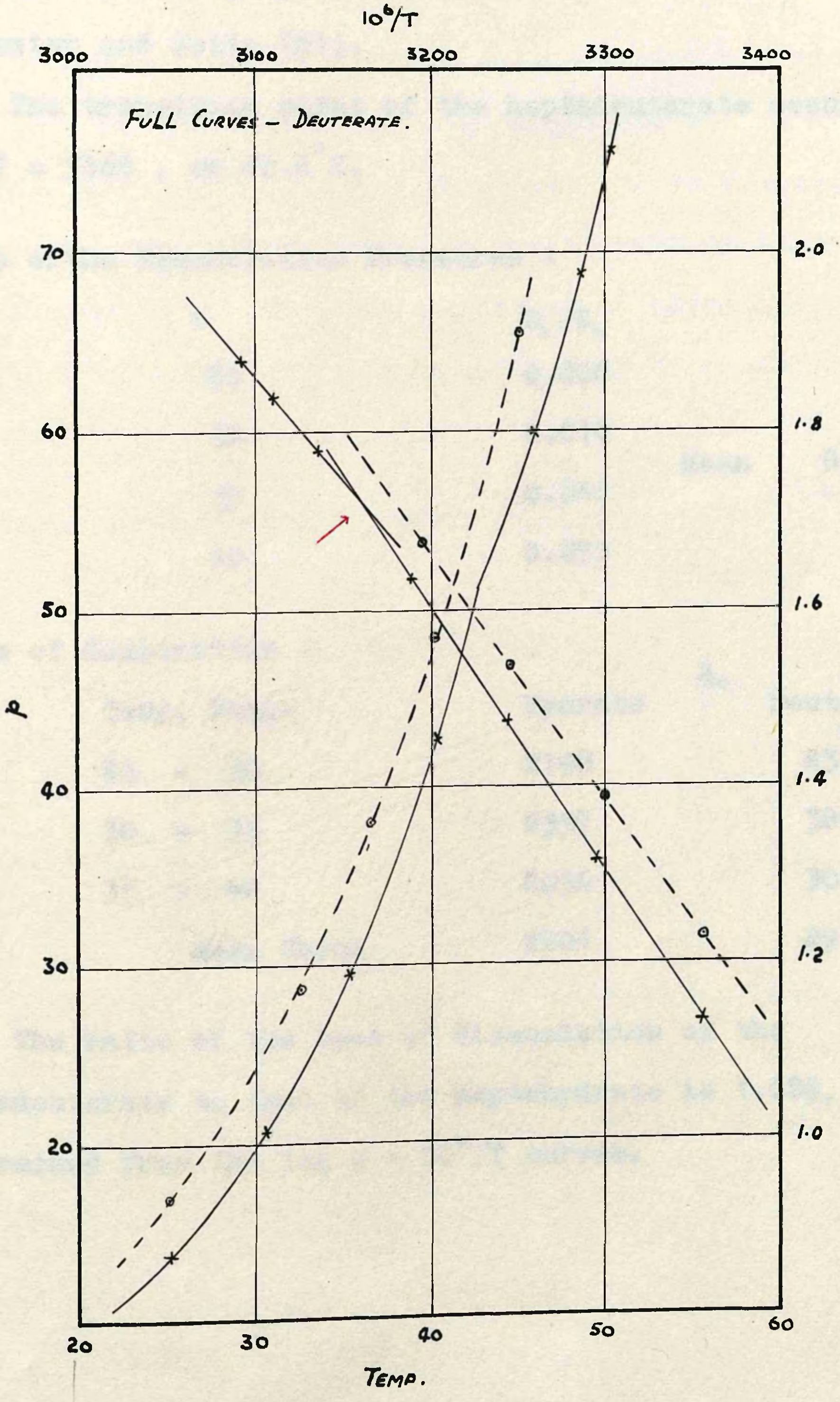
Preparation : Anhydrous cobalt sulphate was prepared from the hydrated salt by the method used in the preparation of anhydrous nickel sulphate. The deuterate was also prepared in a similar manner, anhydrous cobalt sulphate (0.5 g.) being sealed in a small tube with deuterium oxide (1 c.c.). Solution took place more quickly than in the case of the nickel salt, being complete after about 5 hours at 90° C. On cooling and allowing to stand at ordinary temperature, crystals of the heptadeuterate soon began to separate. These were removed and dried in the usual way.

Dissociation Pressures : $CoSO_4,7D_2O$

t	$10^6/T$	p	log p.
25	3356	13.7	1.137
30.5	3296	20.6	1.314
35.2	3244	29.5	1.470
40.5	3190	42.7	1.630
46.0	3134	59.9	1.777
48.5	3111	68.8	1.838
50.4	3092	75.4	1.877

On the following page (Fig.8.) are shown the dissociation pressure curves for the heptahydrate and heptadeuterate, and the log $p - 10^6/T$ curves.

Fig. 8.


$10^6/T$
3000
3100
3200
3300
3400
FULL CURVES – DEUTERATE.
70
60
50
40
30
20
2.0
1.8
1.6
1.4
1.2
1.0
p
log p
20
30
40
50
60
TEMP.

The heptahydrate graphs are drawn from the results of Carpenter and Jette (21).

The transition point of the heptadeuterate occurs at $10^6/T = 3168$, or 42.6°C.

Ratio ofthe Dissociation Pressures :

t	p_D/p_H		
25	0.806	Mean	0.834
30	0.818		
35	0.841		
40	0.873		

Heats of Combination :

	Q_c	
Temp. Range	Hydrate	Deuterate
25 - 30	2198	2338
30 - 35	2357	3222
35 - 40	2056	3088
Mean Value	2204	2916

The ratio of the heat of dissociation of the heptadeuterate to that of the heptahydrate is 1.089, determined from the log $p - 10^6/T$ curves.

Zinc Sulphate Heptadeuterate.

Preparation : Anhydrous zinc sulphate was prepared from the hydrated salt by ignition at about 250° C.
The anhydrous salt (0.8 g.) was dissolved in hot deuterium oxide (2 c.c.) and the solution was allowed to stand over calcium chloride in a small desiccator. Crystallisation took place slowly, and the crystals were separated as previously described.

Dissociation Pressures : $ZnSO_4,7D_2O$.

t	$10^6/T$	p	log p.
25	3356	13.0	1.114
29.8	3303	20.1	1.303
35.1	3245	30.0	1.477
39.8	3197	39.2	1.593
44.3	3152	49.4	1.694
47.0	3125	56.8	1.754

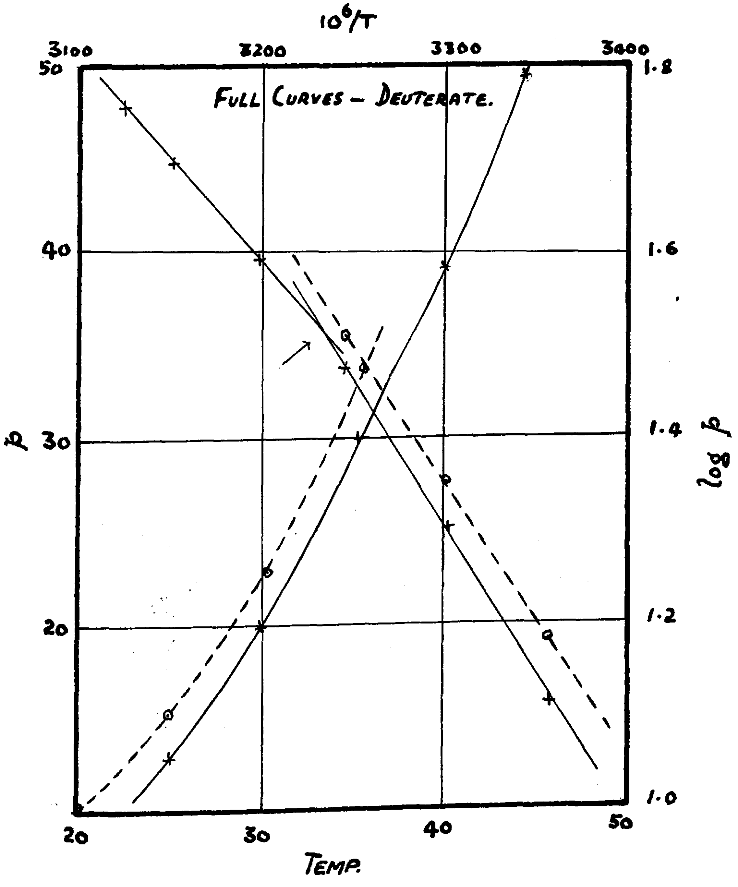
The dissociation pressures of zinc sulphate heptahydrate have been measured up to 35° C., as no values are recorded above 25° C., with the exception of the early work of Frowein (27).

Dissociation Pressures : $ZnSO_4,7H_2O$.

t	$10^6/T$	p	log p.
25	3356	15.3	1.185
30.5	3296	22.8	1.358
35.5	3241	33.5	1.525

The dissociation pressure curves, and the log p — $10^6/T$ curves for the heptahydrate and the heptadeuterate are shown in Fig. 9. The transition point of the heptadeuterate occurs at $10^6/T$ = 3228 or 36.7° C.

Fig. 9.



Ratio of the Dissociation Pressures :

t	p_D/p_H	
25	0.849	
30	0.893	Mean 0.885
35	0.913	

Heats of Combination :

Temp. Range	Q_c Hydrate	Q_c Deuterate
25 - 30	3362	4758
30 - 35	3049	3784
Mean Value	3205	4271

From the slopes of the log p — $10^6/T$ curves, the ratio of the heat of dissociation of the heptadeuterate to that of the heptahydrate is found to be 1.086.

Beryllium Sulphate Tetradeuterate.

Preparation : Tetrahydrated beryllium sulphate was prepared from the oxide by the method used by Allmand (28). As the crystallisation of this salt involves the addition of alcohol to the solution it was therefore impossible to prepare the tetradeuterate by this method owing to the exchange reaction which would take place. The anhydrous salt was therefore deuterated by allowing it to stand in contact with deuterium oxide vapour until the increase in weight showed that between three and four molecules of D_2O had been absorbed by each molecule of $BeSO_4$. For the dissociation pressure measurements the hydrated salt was prepared in a similar manner by allowing the anhydrous sulphate to stand in contact with water vapour.

The compositions of the salts were as follows :

	H_2O	D_2O
Wt. $BeSO_4$	0.7373 g.	0.9010 g.
Wt. after absorption	1.1727 g.	1.4262 g.
Composition	$BeSO_4,3.4H_2O$.	$BeSO_4,3.2D_2O$.

Dissociation Pressures : $BeSO_4,4D_2O$.

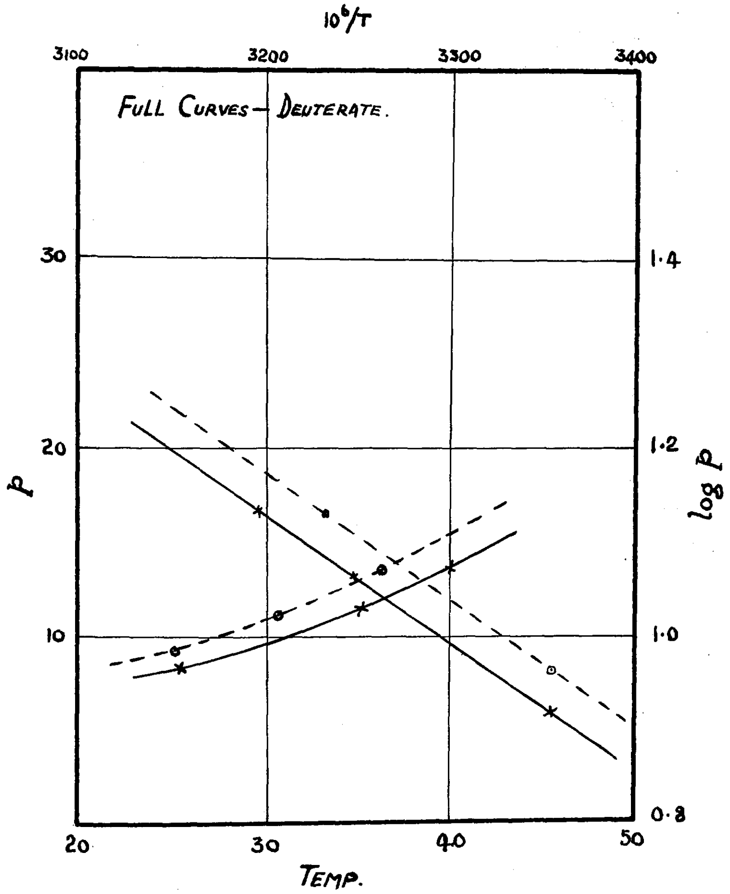
t	$10^6/T$	p	log p.
25.2	3354	8.3	0.919
35.0	3246	11.5	1.061
40.0	3196	13.6	1.134

Dissociation Pressures : $BeSO_4,4H_2O$.

t	$10^6/T$	p	log p.
25.0	3356	9.2	0.964
36.3	3232	13.5	1.130
40.0	3196	15.2	1.182

The dissociation pressure curves and graphs of log p against $10^6/T$ are shown in Fig. 10.

Fig. 10.



Ratio of the Dissociation Pressures :

t	p_D/p_H		
25	0.902		
30	0.899	Mean	0.899
35	0.899		
40	0.895		

Heats of Combination :

Temp. Range		Q_c Hydrate	Deuterate
25 - 30		4440	4930
30 - 35		4220	4310
35 - 40		4170	4710
	Mean Value	4277	4650

From the slopes of the log p — $10^6/T$ lines the ratio of the heat of dissociation of the tetradeuterate to that of the tetrahydrate has a value of 1.002.

Copper Chloride Dideuterate.

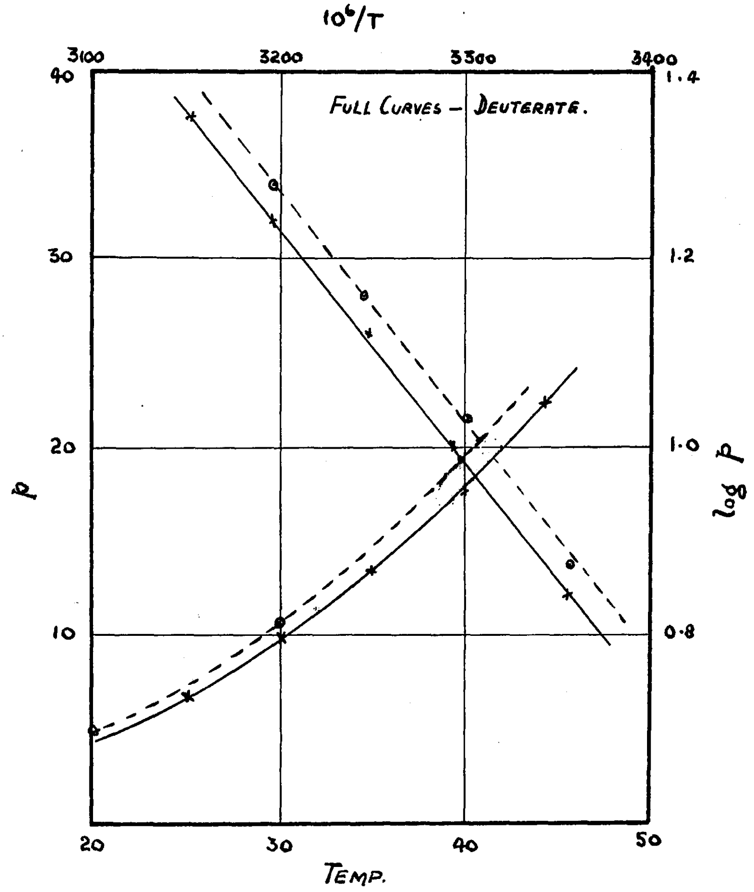
Preparation : Anhydrous copper chloride (0.8 g.) was dissolved in deuterium oxide (1 c.c.) and the brownish green solution allowed to crystallise over calcium chloride. The crystals were separated in the usual manner, but were found to be contaminated slightly with deutochloric acid, DCl. This was satisfactorily removed by drawing a current of thoroughly dried air over the finely ground salt, although a certain amount of dehydration (de-deuteration) also took place.

Dissociation Pressures : $CuCl_2,2D_2O$.

t	$10^6/T$	p	log p.
25	3356	6.9	0.839
30.7	3294	10.1	1.004
34.9	3248	13.4	1.127
40.0	3196	17.4	1.241
44.3	3152	22.2	1.346

The dissociation pressure curves of copper chloride dideuterate and dihydrate, and the graphs of log p against $10^6/T$ are shown in Fig. 11. The dihydrate curve is from the results of Derby and Yngve (29).

Fig. 11.



Ratio of the Dissociation Pressures :

t	p_D/p_H
25	0.932
30	0.944
35	0.924
40	0.915

Mean 0.929

Heats of combination :

Temp. Range	Q_c	
	Hydrate	Deuterate
25 - 30	2759	2793

The ratio of the heat of dissociation of the deuterate to that of the hydrate, found from the log $p - 10^6/T$ graphs is 1.012.

Sodium Bromide Dideuterate.

Preparation : Anhydrous sodium bromide (1.5 g.) was dissolved in deuterium oxide (1.5 c.c.) and the solution allowed to crystallise slowly. The crystals were filtered off and dried in the usual way.

Dissociation Pressures : $NaBr,2D_2O$.

t	$10^6/T$	p	log p.
20	3413	4.25	0.628
25	3356	6.9	0.839
30	3301	10.45	1.019
35	3246	15.1	1.179
40	3196	21.6	1.335
44.5	3149	30.2	1.480
49.8	3097	41.8	1.621
51.3	3084	45.0	1.653
53.8	3060	51.4	1.711

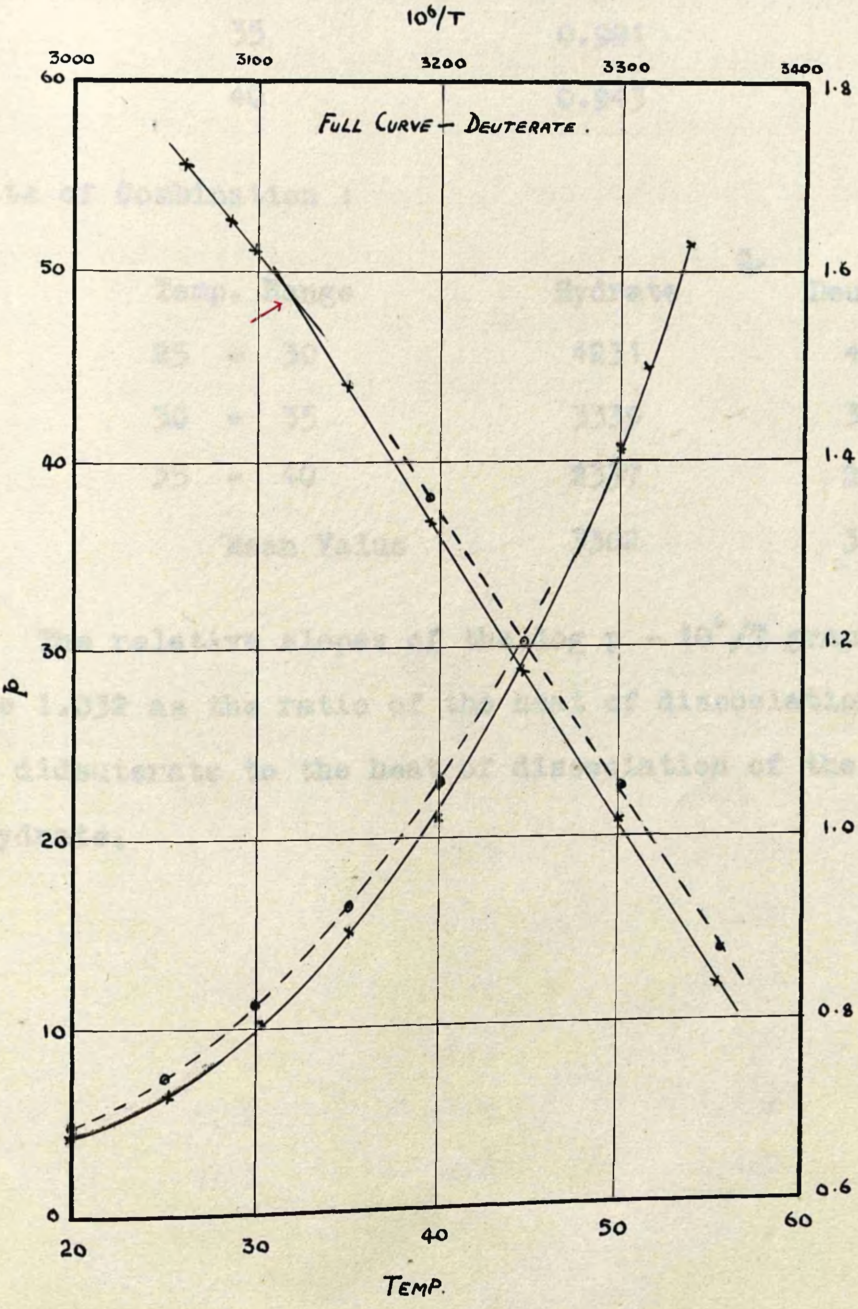
The dissociation pressures of dihydrated sodium bromide were also measured for comparison.

Dissociation Pressures : $NaBr, 2H_2O$.

t	$10^6/T$	p	log p.
20	3413	4.9	0.690
25	3356	7.5	0.875
30	3301	11.3	1.053
35	3246	16.4	1.215
40	3196	22.9	1.360

The dissociation pressure curves and the log $p - 10^6/T$ curves are shown in Fig. 12. The transition point of the dideuterate is found at $10^6/T = 3117$, or 47.7° C.

Fig. 12.



Ratio of the Dissociation Pressures :

t	p_D/p_H		
20	0.867		
25	0.920		
30	0.929	Mean	0.916
35	0.921		
40	0.943		

Heats of Combination :

Temp. Range	Q_c Hydrate	Q_c Deuterate
25 - 30	4231	4015
30 - 35	3339	3083
35 - 40	2337	2902
Mean Value	3302	3333

The relative slopes of the log p — $10^6/T$ graphs give 1.032 as the ratio of the heat of dissociation of the dideuterate to the heat of dissociation of the dihydrate.

Nickel Chloride Hexadeuterate.

Preparation : Anhydrous nickel chloride was prepared by the method of Richards (30). The hydrated salt was first dehydrated about 150° C., and, after most of the water had been removed, the salt was further heated, when a certain amount of anhydrous nickel chloride sublimed.

The anhydrous salt (0.5 g.) was dissolved in hot deuterium oxide (1 c.c.) and the solution allowed to crystallise over calcium chloride. The crystals were separated and dried in the usual manner.

Analysis :

.1738 g. gave .0913 g. $NiCl_2$.

$NiCl_2$ % = 51.2

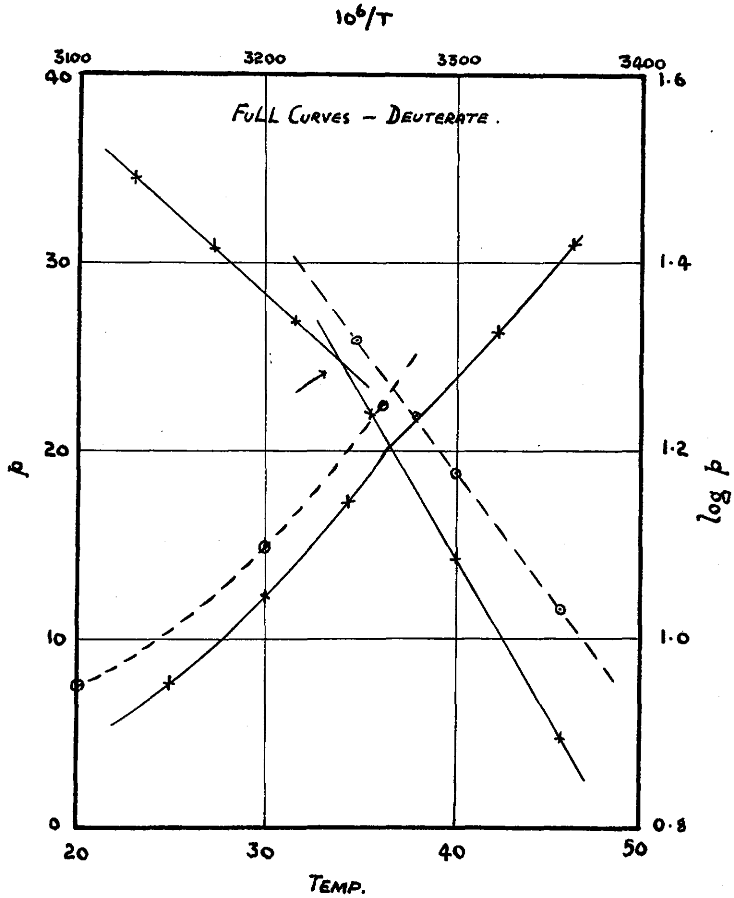
Calc, for $NiCl_2,6D_2O$, $NiCl_2$ % = 51.95.

Dissociation Pressures : $NiCl_2,6D_2O$.

t	$10^6/T$	p	log p.
24.8	3357	7.8	0.892
30.0	3301	12.2	1.086
34.3	3255	17.4	1.241
38.0	3215	21.8	1.339
42.3	3172	26.4	1.422
46.2	3132	30.9	1.490

The dissociation pressure curves for the hexadeuterate and the hexahydrate and the graphs of log p against $10^6/T$ are shown in Fig. 13. The transition point, $NiCl_2,6D_2O \rightarrow NiCl_2,4D_2O$ occurs at $10^6/T = 3242$, or 35.4° C. The hexahydrate curves are due to Derby and Yngve (29).

Fig. 13.



Ratio of the Dissociation Pressures :

t	p_D/p_H		
25	0.748		
30	0.819	Mean	0.817
35	0.885		

Heats of Combination :

	Q_c	
Temp. Range	Hydrate	Deuterate
25 - 30	1405	4263
30 - 35	1904	4663
Mean Value	1654	4463

The ratio of the heat of dissociation of the hexadeuterate to that of the hexahydrate, determined from the slopes of the log p — $10^6/T$ curves, has the value 1.316.

Cobalt Chloride Hexadeuterate.

Preparation : Anhydrous cobalt chloride was prepared from the hydrated salt by ignition at 160 - 170° C., according to Clark (31). The anhydrous chloride (0.5 g.) was dissolved in hot deuterium oxide (1 c.c.) and the solution allowed to crystallise over calcium chloride.

Analysis :

.3312 g. gave .1732 g. $CoCl_2$.

$CoCl_2$ % = 52.3

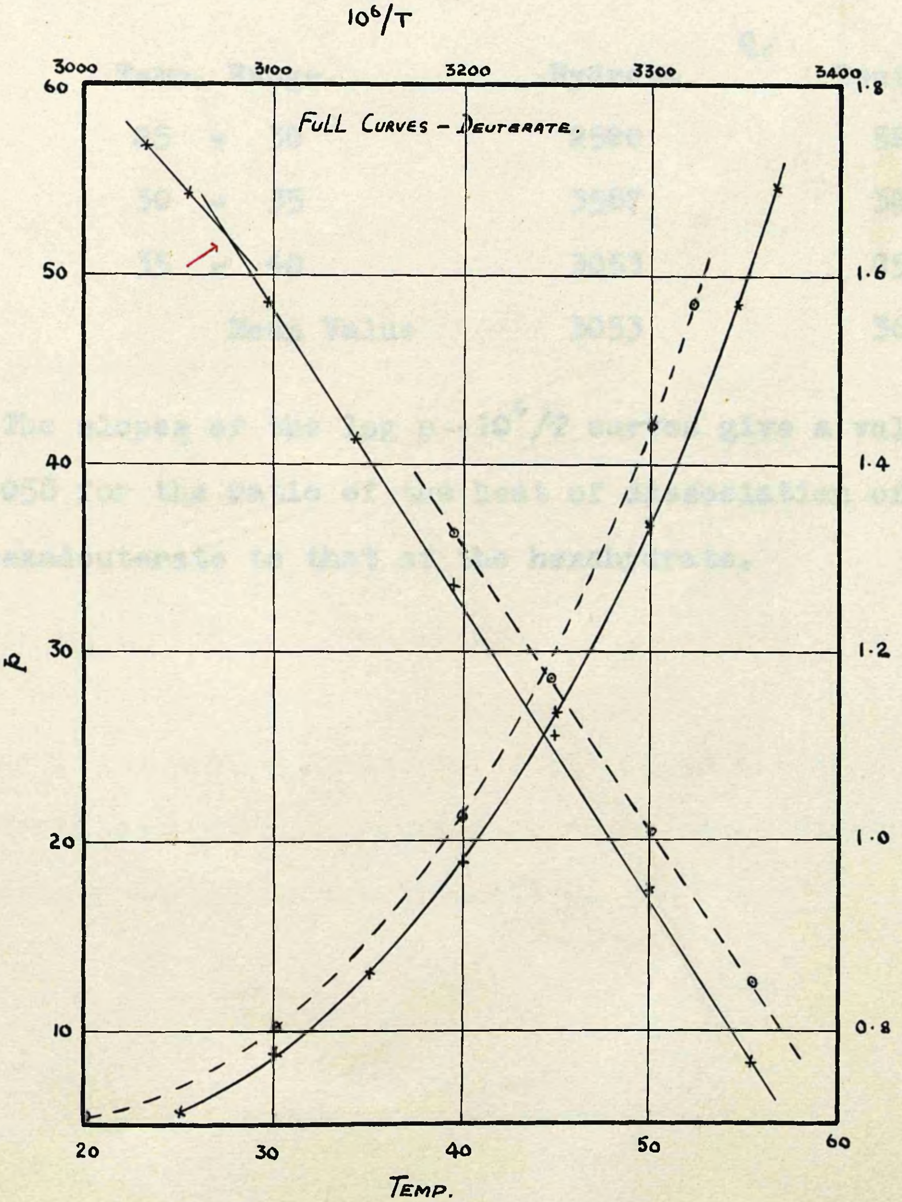
Calc. for $CoCl_2,6D_2O$, $CoCl_2$ % = 52.0.

Dissociation Pressure : $CoCl_2,6D_2O$.

t	$10^6/T$	p	log p.
25.0	3356	5.8	0.763
30.0	3301	9.1	0.959
34.9	3248	13.1	1.117
40.0	3196	18.7	1.272
45.1	3145	26.7	1.427
49.9	3096	37.0	1.568
54.5	3054	48.5	1.686
56.6	3034	54.5	1.736

Fig. 14. shows the dissociation pressure curves and the graphs of log p against $10^6/T$ for the hexahydrate and the hexadeuterate, the hexahydrate curves being drawn from the results of Derby and Yngve (29). The transition point of the hexadeuterate was found to occur at $10^6/T = 3079$, or 51.8° C..

Fig. 14.



Ratio of the Dissociation Pressures :

t	p_D/p_H		
25	0.817		
30	0.892	Mean	0.869
35	0.886		
40	0.882		

Heats of Combination :

Temp. Range.	Q_c Hydrate	Q_c Deuterate
25 - 30	2520	5279
30 - 35	3587	3228
35 - 40	3053	2523
Mean Value	3053	3676

The slopes of the log $p - 10^6/T$ curves give a value of 1.058 for the ratio of the heat of dissociation of the hexadeuterate to that of the hexahydrate.

Strontium Chloride Hexadeuterate.

Preparation : Anhydrous strontium chloride was prepared by ignition of the hexahydrate. The anhydrous salt (0.8 g.) was dissolved in deuterium oxide (1 c.c.) and the solution allowed to cool. The hexadeuterate crystallised well in long needles.

Analysis :

.1607 g. salt required 12.9 c.c. $AgNO_3$ (.0882N)

Cl % = 25.2

Calc. for $SrCl_2,6D_2O$, Cl % = 25.4.

Dissociation Pressures : $SrCl_2,6D_2O$.

t	$10^6/T$	p	log p.
25.0	3356	6.9	0.839
30.0	3301	10.7	1.029
35.0	3246	14.9	1.173
40.0	3196	20.4	1.310

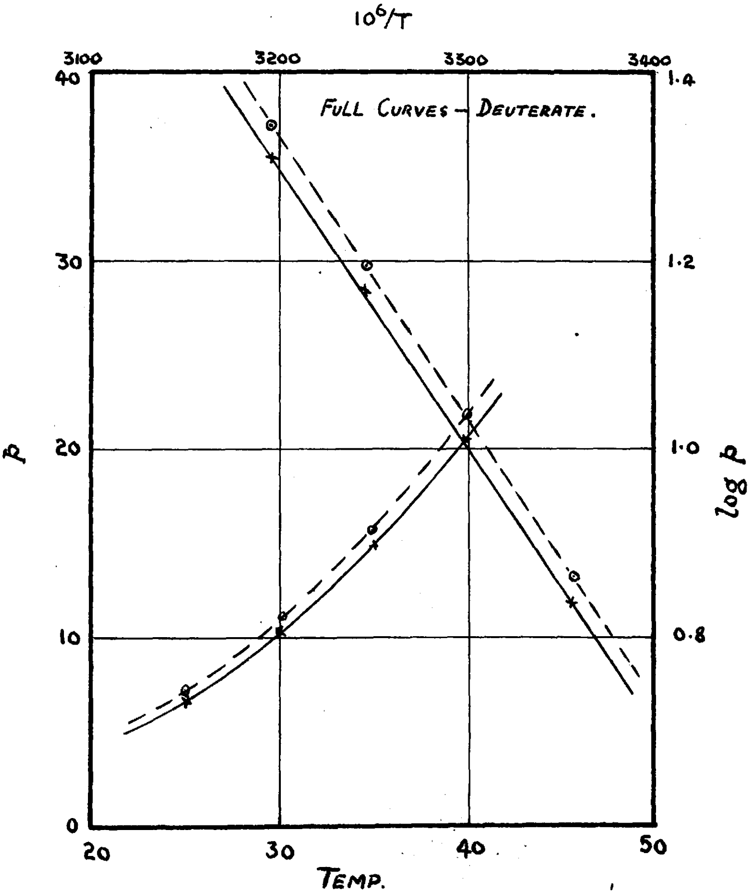
The dissociation pressures of strontium chloride hexahydrate were also determined owing to the diversity of results recorded in the literature.

Dissociation Pressures : $SrCl_2,6H_2O$.

t	$10^6/T$	p	log p.
25.0	3356	7.3	0.863
30.2	3298	11.0	1.041
35.0	3246	15.7	1.196
40.0	3196	22.0	1.342

Fig. 15 shows the dissociation pressure curves and the graphs of log p against $10^6/T$

Fig. 15.



Ratio of the Dissociation Pressures :

t	p_D/p_H		
25	0.945		
30	0.973	Mean	0.948
35	0.949		
40	0.927		

Heats of Combination :

	Q_c	
Temp. Range	Hydrate	Deuterate
25 - 30	4247	4866
30 - 35	2725	1708
35 - 40	2471	1217
Mean Value	3147	2597

From the slopes of the log p — $10^6/T$ lines the ratio of the heats of dissociation of the hexadeuterate and hexahydrate is 0.992.

Barium Chloride Dideuterate.

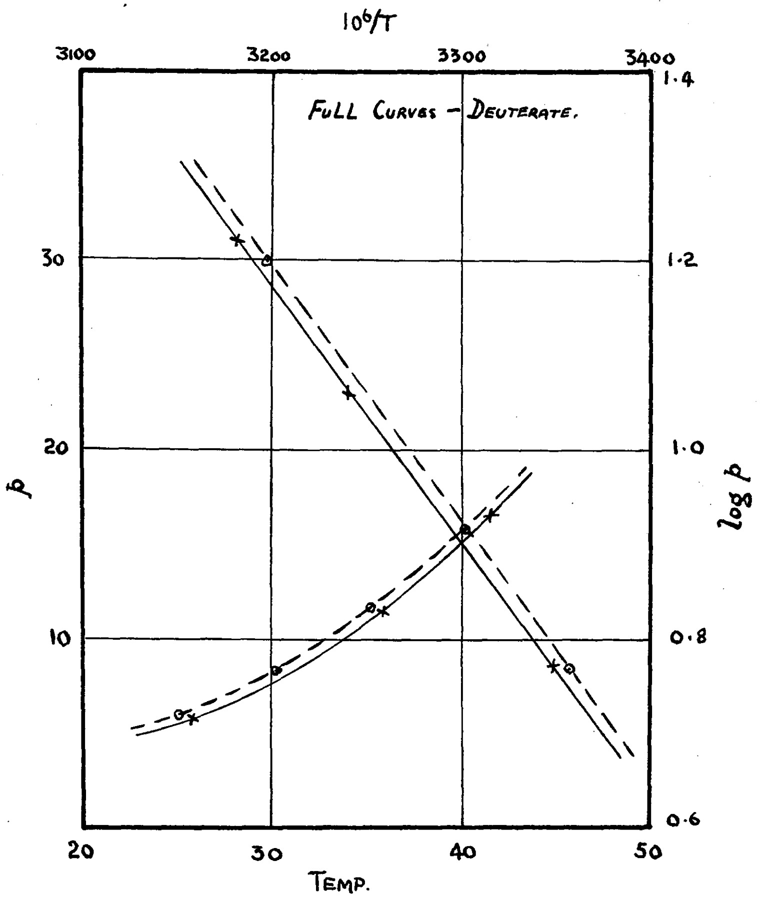
Preparation : Hydrated barium chloride was dehydrated by heating to constant weight. The anhydrous chloride (0.6 g.) was dissolved in deuterium oxide (1 c.c.) and the solution allowed to crystallise. The crystals were separated as before.

Dissociation Pressures : $BaCl_2,2D_2O$.

t	$10^6/T$	p	log p.
25.5	3350	5.9	0.771
30.0	3301	8.2	0.914
35.7	3238	11.4	1.057
41.3	3182	16.7	1.223

The dissociation pressure curves and the log $p - 10^6/T$ curves for the dideuterate and the dihydrate are shown in Fig. 16. The dihydrate curves are from the results of Baxter and Cooper (32).

Fig. 16.



Ratio of Dissociation Pressures :

t	p_D/p_H		
25	0.983		
30	0.963	Mean	0.965
35	0.957		
40	0.968		

Heats of Combination :

Temp. Range	Q_c Hydrate	Q_c Deuterate
25 - 30	1950	826
30 - 35	2400	2041
35 - 40	1386	1482
Mean Value	1912	1449

The ratio of the heats of dissociation of the dideuterate and dihydrate, from the slopes of the log p — $10^6/T$ lines, is 0.998.

Potassium Fluoride Dihydrate and Dideuterate.

Preparation : Saturated solutions of pure anhydrous potassium fluoride (neutral) in water and in deuterium oxide were allowed to stand in desiccators over calcium chloride. Well formed crystals of the dihydrate and the dideuterate separated out ; These were removed and dried as quickly as possible in the usual way.

Dissociation Pressures : $KF,2H_2O$.

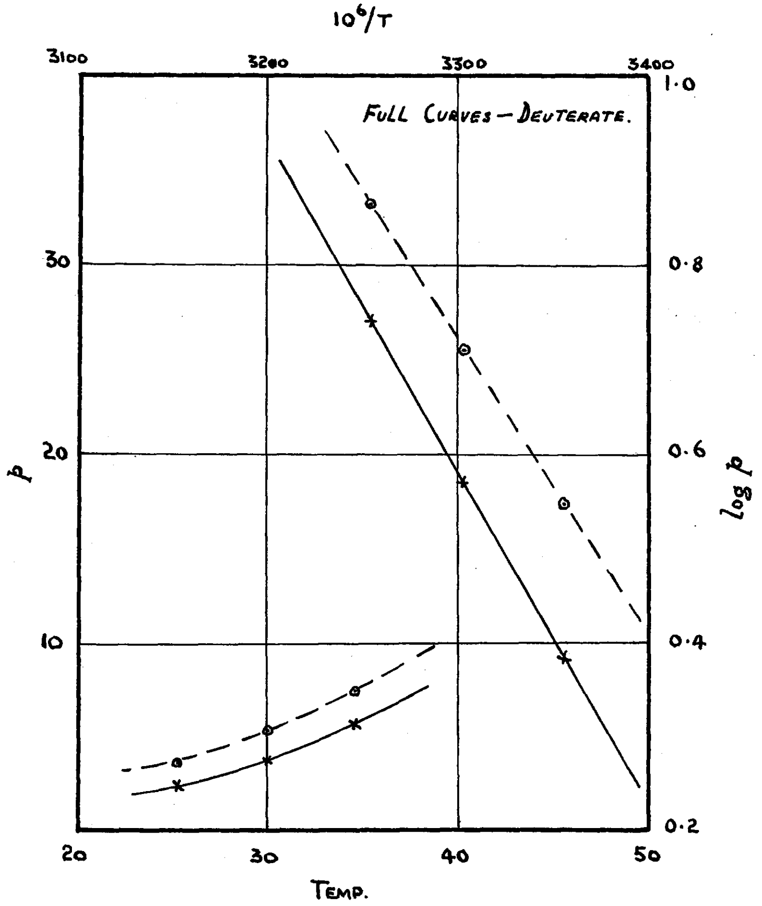
t	$10^6/T$	p	log p.
25.0	3356	3.5	0.544
29.7	3304	5.2	0.716
34.5	3253	7.3	0.863

Dissociation Pressures : KF, $2D_2O$.

t	$10^6/T$	p	log p.
24.9	3357	2.4	0.380
29.8	3303	3.7	0.568
34.3	3255	5.5	0.740

The dissociation pressure curves are shown in Fig. 17.

Fig. 17



Ratio of the Dissociation Pressures :

t	p_D/p_H		
25	0.714		
30	0.717	Mean	0.735
35	0.773		

Heats of Combination,

Temp. Range	Q_c Hydrate	Q_c Deuterate
25 - 30	4403	4148
30 - 35	2417	4253
Mean Value	3410	4201

From the slopes of the graphs of log p against $10^6/T$, the ratio of the heat of dissociation of the deuterate to that of the hydrate was found to be 1.132.

Index to Experimental Section.

1V

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PART 11.

Additional Paper.

"The PHOTOSYNTHESIS of CARBOHYDRATES in vitro with VISIBLE LIGHT."

1. HISTORICAL and THEORETICAL.

The problem of the mechanism of the assimilation of carbon dioxide by green plants and the subsequent production of carbohydrates has attracted the attention of numerous chemists and botanists, chiefly on account of the fundamental nature of the reaction and its importance in the study of plant physiology. On the chemical side, many investigators have examined the possibility of reproducing, in vitro, the photochemical reduction of carbon dioxide to formaldehyde or carbohydrates, but the results have been conflicting.

The greater part of the early work on this subject was carried out using ultra-violet light, but until 1921 few experiments of a systematic nature had been made. Since that date, however, systematic investigations of several aspects of the problem of the photosynthesis of carbohydrates have been undertaken by Baly and his collaborators, and it is with an examination of part of that work that this paper deals.

The original experiments of Baly, Heilbron, and Barker (1) on the reduction of carbon dioxide in aqueous solution to formaldehyde by illumination with ultra-violet light were subjected to considerable criticism by Porter and Ramsperger (2), Spoehr (3), Bauer (4) and others, who suggested that

the formaldehyde detected by Baly owed its origin to traces of organic impurities in the reacting substances.
On consideration of Warburg's view (5) that photosynthesis in vivo is a surface reaction, Baly suggested that the photochemical reduction of carbonic acid in vitro might also be a surface reaction, and in later experiments (6) he illuminated, with ultra-violet light, aqueous suspensions of white powders on which carbon dioxide was strongly adsorbed. It was claimed that under these conditions the photosynthesised product consisted of carbohydrate compounds instead of formaldehyde.

While the experiments with ultra-violet light were undoubtedly of importance, it was impossible to apply any of the results directly to the elucidation of the problem of photosynthesis as it occurs in green plants, since it was known that the living plant did not require ultra-violet light for photosynthetic purposes. Thus the achievement of photosynthesis in vitro by means of visible light by Baly, Stephen, and Hood (7) in 1927 represented a most interesting advance in the study of this reaction. It was stated by these workers that, by the use of visibly coloured powders capable of adsorbing carbon dioxide, such as nickel and cobalt carbonates, the photosynthesis could be effected by means of ordinary visible light, complex compounds resembling carbohydrates being obtained.

The reaction now approximated more closely to that occurring in the living plant, and it appeared probable that further investigation might yield information applicable to the problem of carbon assimilation and the photosynthesis of carbohydrates in vivo.

The experiments with nickel carbonate appeared to give the most satisfactory results, the yield being 0.07 g. carbohydrates per hour using 50g. of the nickel carbonate catalyst. An essential part of the experimental procedure was the activation of the nickel carbonate before use ; this could be achieved by exposing the carbonate to ultra-violet light for ½ - 1 hour, or by irradiation with white light for at least six hours.

Similar experiments were performed by Dhar (8) using tropical sunlight as the illumination, positive results showing the presence of formaldehyde or carbohydrates being obtained in most cases. Dhar used a wide variety of substances as the catalyst powder, including several, such as organic dyestuffs, which might be suspected of undergoing decomposition under the strong illumination used. Doubt has been cast on the accuracy of Dhar's observations by Burk (9) who considered that critical blank experiments had not been performed. This criticism seemed to be well founded.

In 1930, Baly (10) claimed that very satisfactory yields of carbohydrates could be obtained using a composite catalyst consisting of ferric oxide supported on kieselguhr which had been previously coated with alumina. The activity of this catalyst was increased by the addition, to the ferric oxide, of small quantities of thorium dioxide. Such a supported ferric oxide catalyst possessed a greater photosynthetic activity than nickel carbonate, the yield of carbohydrates being slightly more than 0.1 g. per hour using 50 g. of catalyst.

The work now described was undertaken as a critical examination of the experiments in which visible light had been used, and in the hope that, if positive results were established, information concerning the mechanism and energy considerations of the reaction might be obtained by the application of more exact methods than those hitherto employed.

In the first part of the investigation supported ferric oxide catalysts of the type described by Baly were used since their photosynthetic activity was claimed to be greater than that of nickel or cobalt carbonate.

The preparation of such catalysts was tedious and troublesome ; preliminary experiments showed that the main difficulties were the removal of calcium from the kieselguhr, and the removal of adsorbed salts and the last traces of nitric oxide from the catalyst. This last difficulty was introduced on account of the fact that the ferric oxide was produced on the catalyst by evaporation with a solution of ferric nitrate and subsequent ignition. The removal of calcium from the kieselguhr was by no means a simple matter. It was found that even after the kieselguhr had been treated for eight hours with nitric acid (50 %.) and washed for four days some calcium still went into solution as the bicarbonate when the catalyst was suspended in water through which a stream of carbon dioxide passed. This constituted a definite objection to the use of kieselguhr as a support for the catalyst. The methods used for washing the catalyst and for removing the last traces of nitric oxide were those adopted by Baly (private communication) and are described in the experimental section (p.96).

Using such supported catalysts, Baly claimed to have obtained a yield of carbohydrates amounting to 0.13 g. per hour. This result was not confirmed by the present work, no photosynthesised organic matter being obtained. The first experiments gave hopeful results, 10 - 20 m.g. of organic matter being obtained, but this was subsequently found to be dueto organic impurity in the distilled water used. Using specially purified water, and carbon dioxide carefully freed from organic impurities no photosynthesis could be detected.

Experiments were carried out using sources of illumination of widely varying intensities ; the duration of illumination was also varied. In all cases, the amount of alumina contained in the aluminated kieselguhr was 22%, since this was believed to be the optimum amount, but catalysts were prepared containing 1, 4.7, 10, 14, and 26% of ferric oxide. The ferric oxide always contained 0.64% of thorium dioxide as promoter. No evidence of photosynthesis was obtained using any of these catalysts, although cataphoresis measurements showed that these powders, when in suspension in an aqueous solution of carbon dioxide, assumed an electropositive charge. The carrying of such a charge has been claimed as an indication of a photosynthetically active catalyst (10).

While this work was in progress, Baly (10) admitted that kieselguhr was a highly unsatisfactory substance for use as a support for the catalyst. He found that, in addition to the difficulty of removing the calcium completely, dependable results were not always obtained, in fact, the results appeared to depend entirely on the type of kieselguhr used.

During the investigation of these supported catalysts it was thought that the method of preparation employed was not likely to yield a final catalyst which was quite homogeneous. Experiments were therefore performed on samples of one of the catalysts and definite evidence was obtained that these powders were not homogeneous, different fractions of the powder, separated by sedimentation, being found to contain different amounts of ferric oxide.

In a private communication Baly suggested the use of a catalyst, supported on barium sulphate, which he claimed to be photosynthetically active. The preparation of this catalyst consisted in precipitating barium sulphate in a solution containing iron alum, aluminium sulphate, and thorium nitrate, the iron, aluminium, and thorium being afterwards precipitated on the barium sulphate as hydroxides, and converted to the oxides by ignition. A test carried out with this catalyst yielded a small quantity of a yellow syrup, soluble in alcohol. Examination showed, however, that this syrup was inorganic in nature, containing ferric chloride, ammonium chloride, and hydrochloric acid. The presence of these substances was no doubt due to the inefficiency of the method of washing the freshly precipitated catalyst.

After the failure of these experiments with supported ferric oxide catalysts, it was decided to re-examine the earlier work in which nickel carbonate was used as the catalyst.

The nickel carbonate was prepared electrolytically to avoid contamination by alkali, since it had been stated (7) that even the slightest trace of alkali in the nickel carbonate was fatal to its activity as a catalyst. Before being used in photosynthesis tests, the carbonate was always activated as previously mentioned (p. 85) either by prolonged exposure to white light or by shorter irradiation with ultra-violet light.

Owing to the difficulty of deciding whether or not any slight photosynthesis of organic matter had taken place, the results of all the photosynthesis tests were determined by estimation of organic carbon in the residues after illumination, filtration, and subsequent evaporation of the solutions. The method of estimation was a "wet" oxidation method, and tests showed that it was capable of detecting, with accuracy, quantities of carbon present as carbohydrates, as small as 1 m.g..

Photosynthesis tests were carried out using approximately 5, 10, 30, and 50 g. of nickel carbonate in 1500 c.c. of water. No visible evidence of photosynthesised carbohydrate syrup was ever obtained, and tests for formaldehyde in the aqueous distillates gave negative results. Blank experiments were carried out under the same conditions as the photosynthesis tests except that the reaction vessel was kept in darkness during the experiment.

The results of the carbon estimations showed as much organic carbon occurring in the blank experiments as in the photosynthesis tests. The table of results of these estimations given in the experimental section (p. 107) indicates clearly that no photosynthetic conversion of the carbon dioxide to carbohydrates had taken place.

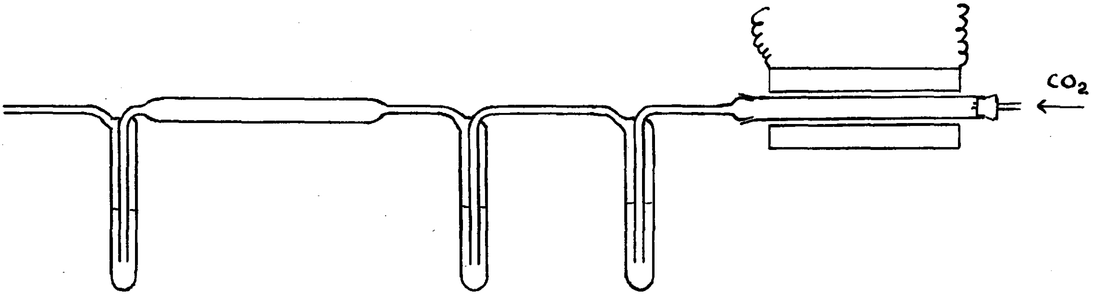
Since the completion of this work, Zscheile (11) announced his failure to repeat the experiments of Baly with nickel carbonate. In addition, Zscheile made attempts to achieve the photosynthesis using other catalysts such as platinum black, carbon, and ferric hydroxide, but these were unsuccessful.

It would appear, therefore, that, if the photosynthesis of carbohydrates in vitro has been achieved in the earlier work, the necessary conditions for the reaction have not been appreciated or observed. Until the necessary conditions are recognised it is unlikely that successful experiments will receive the confirmation which is desirable in work of this nature.

11. EXPERIMENTAL.

A few preliminary experiments were carried out using the carbon dioxide as supplied in cylinders. As this carbon dioxide is frequently obtained from the fermentation industry, it constituted a possible source of organic impurity, consequently all further experiments were performed using carbon dioxide prepared by the action of hydrochloric acid on marble. For purification the gas was passed first through a tube 12 ins. long containing copper oxide heated to redness in an electric furnace, then through a wash-bottle containing chromic acid and concentrated sulphuric acid. After passing through a second wash-bottle containing water the gas passed into a tube 10 ins. long packed with solid sodium bicarbonate, and finally into a third wash-bottle containing distilled water, from which the gas entered the reaction vessel. From the time the gas entered the combustion tube it did not come in contact with any rubber tubing or greased joints ; a ground joint, lubricated with phosphoric acid, connected the combustion tube to the rest of the purification train, and all other joints were sealed. The purification apparatus is shown diagramatically in Fig. 1.

Fig. 1.



Considerable difficulty was experienced in obtaining a satisfactory blank result. It was found that the organic matter occurring in the blank experiments was contained in the distilled water used ; this was satisfactorily removed by subjecting the water to distillation from potassium permanganate in a quartz flask connected by a ground joint to a quartz condenser. The water thus purified was stored in well-seasoned Pyrex flasks of 2l. capacity.

The reaction vessel was a rectangular glass cell 14 x 17 x 7.5 cm., having polished sides, and the following method was employed in carrying out the photosynthesis tests.

The required weight of the catalyst was suspended in 1.5 l. of distilled water in the reaction vessel and a fairly rapid stream of carbon dioxide (3 bubbles per sec.)

was passed through the suspension. The gas was, as a rule, allowed to pass for ½ - 1 hour before illumination of the vessel took place, and a steady stream was maintained throughout the entire period of illumination which varied in different experiments, from three to eight hours. After illumination, the catalyst was allowed to settle out overnight. In some cases the suspension was more stable and flocculation was assisted by warming the mixture to 60 - 70°C. After filtration from the catalyst, the water was distilled off under reduced pressure, and any residue was carefully extracted with purified absolute alcohol. The first runnings of the aqueous distillate were tested for the presence of formaldehyde by means of Schryver's test.

Kieselguhr Supported Catalysts.

Preparation : Before being used for the preparation of the catalyst, the kieselguhr was treated with a considerable excess of nitric acid (50%). The kieselguhr (50 g.) and acid (1 litre) were heated together to 80 - 90 C., and kept at that temperature for 7 - 8 hours. The greater part of the acid was removed by washing by decantation, and the kieselguhr was then transferred to a 12 inch Buchner funnel and washed with water until the washings were free from acid. This process generally took about four days. The kieselguhr was then dried at 100 C.

The preparation of the catalysts consisted in precipitating aluminium hydroxide on the kieselguhr ; after ignition to convert the hydroxide to the oxide, the powder was added to a solution of ferric nitrate containing thorium nitrate and the pasty mass evaporated to dryness. It was then ignited to produce the ferric and thorium oxides. Thereafter it was finely ground and once more ignited. The details of the method finally adopted were suggested by Baly (private communication) and were as follows.

75 g. Kieselguhr were suspended in 370 c.c. of a solution of aluminium nitrate containing 50 g. of the hexahydrate per 100 c.c.. The suspension was stirred vigorously by means of an electrically driven stirrer, and ammonia

(approx. 6N) was added drop by drop until the suspension set to a semi-solid mass. The addition of ammonia was then stopped and the stirring continued until the mass became liquid again. Ammonia was once more added until the mixture became very slightly alkaline. It was then separated into three portions and filtered on three large Buchner funnels. For washing, the cake from each funnel was suspended in about 2 litres of distilled water, disintegration of the cake being brought about by vigorous stirring. The suspension was flocculated by the addition of 4 c.c. of strong ammonia, allowed to settle, the clear liquid decanted off, and the residue filtered. This process was repeated, and then the material was dried in the steam oven at 100° C.. When thoroughly dry, the aluminated kieselguhr was roughly powdered and heated in a porcelain basin on the sand-bath for one hour. It was then transferred to a quartz tube and heated for a further half-hour at 480 - 490° C. in an electric furnace. After cooling it was finely ground in a porcelain ball-mill.

For coating with ferric oxide, a stock solution of ferric nitrate was used. This solution was accurately standardised and contained 0.0831 g. Fe_2O_3 per c.c.. The aluminated kieselguhr was evaporated to dryness with the required volume of this solution containing the calculated amount (0.6% of the Fe_2O_3) of thorium oxide in the form of the nitrate. By ignition at 475° C. for half an

hour in the electric furnace the nitrates were converted to the oxides. After being again finely ground in the ball-mill, the catalyst was transferred to a quartz tube closed at one end, and heated slowly to 400° C..
The pressure was then slowly reduced by means of a Hyvac pump until the highest vacuum was obtained. Heating was continued for a further thirty minutes. The vacuum pump was then cut off and carbon dioxide was admitted to the tube which was then allowed to cool.

In all preparations the amount of aluminium oxide precipitated on the kieselguhr was 22% and the ferric oxide always contained 0.6% of thorium dioxide.

Table 1 shows the range of catalysts used, the intensity of the light sources and their distances from the illuminated side of the reaction vessel, and the duration of the illumination.

Table 1.

wt. catalyst g.	Fe_2O_3	Light source.	Distance from cell ins.	Exposure hours.
5	1	1000 c.p.	8	3.5
10	4.7	250 watt lamp	9	7
20	4.7		9	7
10	7.5		9	7
4.5	10	1000 c.p.	8	5
20	14	250 watt lamp	12	6.5
46	14	60 " "	14	7
50	14	100 " " (½ voltage)	24	8
7.5	25	1000 c.p.	8	3

For an intensity of 1000 c.p. a Pointolite lamp was used ; in the other experiments ordinary filament lamps were used.

No evidence of the photosynthesis of organic compounds was obtained in any of these experiments.

In view of the possibility that the product of photosynthesis might remain adsorbed on the catalyst surface at the end of the experiment, the catalysts were always thoroughly extracted with hot absolute alcohol after filtration from the aqueous solution. In no experiment was any carbohydrate syrup obtained by evaporation of the alcoholic extract.

Fractionation of Catalyst by Sedimentation.

Samples of a catalyst believed to contain approximately 14% ferric oxide were separated into two extreme fractions by sedimentation.

The catalyst (30 g.) was shaken in a tall cylinder with about 500 c.c. water. It was allowed to settle for a few minutes and then the suspension was poured off, leaving behind the particles which had settled out first. This procedure was repeated on the residue. The suspension which had been poured off first was allowed to stand for about three-quarters of an hour, and then a convenient volume was pipetted off from the top. This on evaporation gave the lighter fraction of the powder.

Samples of both fractions were treated with concentrated hydrochloric acid and nitric acid, and the iron determined with standard potassium dichromate. The lighter fraction contained 13.2% of ferric oxide, and the heavier 13.96%, indicating that these powders are not homogeneous.

Cataphoretic Velocities.

Baly (10) stated that a powder which was photosynthetically active assumed a positive charge when in suspension in a saturated solution of carbonic acid, and that the cataphoretic velocity was therefore a measure of photosynthetic activity, the most active powders showing a velocity of 0.00041 cm. per sec., Experiments carried out on a kieselguhr supported catalyst containing 14% ferric oxide (believed by Baly to be the optimum amount) showed that this powder carried an electro-positive charge, and while measurements were not obtained with a high degree of accuracy, the cataphoretic velocities were found to be of the order of 0.00025 - 0.00035 cm. per sec., although it had already been shown that this powder was photosynthetically inactive. The velocities were measured in the usual manner using a potential difference of 220 volts.

Barium Sulphate Supported Catalyst.

Preparation : 100 g. Barium chloride were dissolved in 200 c.c. of hot water. 50 g. Iron alum and 50 g. ammonium alum were also dissolved in 200 c.c. of hot water and to this were added 2.6 g. thorium nitrate (hexa-hydrate). The two solutions were mixed with vigorous stirring and then boiled for about 15 minutes. Sodium carbonate (approx. 5N) was added slowly until twice the theoretical amount (370 c.c.) required for the precipitation of the iron and aluminium hydroxides had been added. The mixture was again boiled for 15 minutes, and filtered. The precipitate was washed by heating almost to the boiling point with about 2 litres of distilled water. This suspension was flocculated by the addition of 4 c.c. of strong ammonia, the supernatant liquor decanted off after settling had taken place, and the precipitate filtered. This was repeated four times, but in the final washing ammonia was not added for flocculation. The precipitate was then dried in the steam oven at 100° C for 24 hours. The ignition of the catalyst was carried out in a quartz tube, under high vacuum, the temperature being slowly raised to 300° C and maintained there for one hour. This method gave a barium sulphate supported catalyst containing 7.5% ferric oxide, 5% aluminium oxide, and 1% thorium dioxide.

Photosynthesis using Barium Sulphate Supported Catalyst.

50 g. of this catalyst were suspended in 1.5 litres of water and the photosynthesis test carried out as previously described (p. 93). The cell was illuminated for 7 hours by the light of a 100 watt lamp (at half-voltage) placed 24 ins. from the cell.

The residue after evaporation was extracted with absolute alcohol, and the alcohol distilled off. A small quantity of a yellow syrup, which charred on heating with concentrated sulphuric acid, was obtained. No charring was noticeable on heating the syrup alone, and no test for carbohydrates could be obtained. Qualitative analysis showed that the "syrup" contained ferric chloride, ammonium chloride, and hydrochloric acid. The charring with hot sulphuric acid was due to a trace of alcohol which could not be removed on the water-bath owing to the high solubility of ferric chloride in alcohol, but which could be removed on heating to 110 - 120° C..

Nickel Carbonate Catalyst.

Preparation : The nickel carbonate was prepared electrolytically as described by Baly (12). Three nickel plates 20 x 7 x 0.3 cm. were suspended in a large cylindrical vessel containing distilled water saturated with carbon dioxide. The plates were connected to a 220 volt circuit, the two outer plates being made kathodes. Two cooling coils, through which water was circulated, were suspended on either side of the central plate. By means of a variable external resistance the current was kept at 1 - 1.5 amp., and during the whole period of electrolysis, a stream of carbon dioxide was passed through the solution. The nickel carbonate, deposited from the negative plates, collected at the bottom of the cell and was filtered off, dried at 100° C., and finely powdered. It was then ready for activation.

Activation : (1) By white light.

The finely ground nickel carbonate was heated to 130 - 140° C. for three-quarters of an hour and was then spread in a thin layer on a glass plate covered by a second plate to prevent contamination by dust. This was illuminated for seven hours by a 100 watt lamp placed immediately above the plate. The catalyst was always activated just before being used in a photosynthesis test.

(2) By Ultra-violet light :

The nickel carbonate, after being heated to 130 - 140° C. as before, was spread in a thin layer on a glass plate and illuminated for three-quarters of an hour by the direct light of a mercury arc lamp placed about 9 ins. distant, the powder being stirred at intervals to expose fresh surfaces. The catalyst was used immediately after activation.

Photosynthesis Tests : For the photosynthesis tests with nickel carbonate, the following method was used. The required weight of the catalyst was suspended in 1.5 litres of distilled water and a fairly rapid stream of carbon dioxide passed in, while the cell was illuminated by the light of a 100 watt lamp at a distance of 9 ins.. Illumination was continued for two to two and a half hours. At the end of that time the undissolved nickel carbonate was removed by filtration, and the green solution, containing nickel in the form of the bicarbonate, was evaporated to dryness under reduced pressure. The solution was filtered from precipitated nickel carbonate at intervals during the evaporation. The first runnings of the aqueous distillate were in every case tested for formaldehyde.

Estimation of organic carbon in the residue was carried out by the method developed by Mills (13), a similar form of apparatus being used. The residue from the evaporation which always contained nickel carbonate was dissolved in 50 c.c. of very dilute sulphuric acid (approx. 2N), and the solution transferred to the oxidation flask and warmed to 30 - 35° C. for about half an hour while it was evacuated by the water pump. Tests made with nickel carbonate showed that this treatment effectively removed carbon dioxide arising from inorganic carbonates.

A.R. concentrated sulphuric acid (100c.c.) was added to the solution and the oxidation carried out with chromic acid solution (10 c.c.) as described by Mills. The absorption train for the carbon dioxide was on a much smaller scale, consisting of three conical flasks of 50 c.c. capacity, and the total volume of baryta solution used was 35 c.c.. Instead of weighing the precipitated barium carbonate the excess baryta was estimated by titration with standard acid, phenolphthalein being used as indicator. Blank estimations were carried out on the reagents, including the distilled water used in the photosynthesis tests. The accuracy of the method was tested by dissolving weighed amounts of sucrose in 50 c.c. of the dilute sulphuric acid and treating this solution exactly as described above.

Table 11 gives examples of the accuracy attained in these estimations.

Table 11.

Sucrose added g.	n/10HCl equiv. to CO_2 formed c.c.	Carbon	
		Found	Theor.
.0149	11.35	.0062	.0062
.0079	6.45	.0032	.0033
.0137	9.9	.0057	.0058

Photosynthesis tests were carried out using approximately 5, 10, 30, and 50 g. of nickel carbonate in 1500 c.c. water. No evidence of photosynthesised carbohydrate syrup was ever obtained, and tests for formaldehyde in the aqueous distillates gave negative results.

The blank experiments were carried out using nickel carbonate suspended in the same volume of water (1500 c.c.) and carbon dioxide was passed through for the same length of time as in the photosynthesis tests, the reaction vessel being kept in darkness.

The results of the carbon estimations in the residues from the blank experiments and from one series of the photosynthesis tests are shown in Table 111.

Experiment	Total organic carbon found g.	Reagent blank (mean)	Nett organic carbon g.
Dark blank with $NiCO_3$	.0016	.0007 (4)	.0008 (6)
"	.0017 (9)	.0007 (4)	.0010 (5)
"	.0014 (3)	.0007 (4)	.0006 (9)
<u>Photosynthesis</u>			
wt. catalyst g.			
5	.0018	.0007 (4)	.0010 (6)
10	.0015 (5)	.0007 (4)	.0008 (1)
30	.0014 (8)	.0007 (4)	.0007 (4)
50	.0014 (2)	.0007 (4)	.0006 (8)

The fact that there was no difference between the amounts of carbon found in the dark blanks and the photosynthesis tests indicated that this carbon was due to impurity in the water, nickel carbonate or carbon dioxide used It is quite possible that the whole of the carbon was contained in the distilled water used, as the value found represented an organic carbon content of less than one part per million.

111. Bibliography.

(1) J.C.S., 119, 1925, (1921).
(2) J.A.C.S., 47, 79, (1925).
(3) ibid 45, 1184, (1923)
(4) Helv. Chim. Acta, 5, 828, (1922)
ibid 6, 959, (1923)
(5) Biochem. Z., 166, 386, (1925)
(6) Proc. Roy. Soc., 116,A, 197, (1927)
(7) ibid 116A, 212, (1927)
(8) J. Phys. Chem., 29, 926, (1925)
ibid 35, 1418, (1931)
(9) J. Phys. Chem., (31) 1338, (1931)
(10) Nature, 126, 666, (1930)
Trans. Far. Soc., 27, 545, (1931)
(11) J.A.C.S., 54, 973, (1932)
(12) Proc. Roy. Soc., 122,A, 393, (1929)
(13) T, Soc. Chem. Ind., 50, 375, (1931)

AN EXPERIMENTAL INVESTIGATION CONCERNING THE PHOTOSYNTHESIS OF CARBOHYDRATES IN VITRO.

By James Bell.

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The original experiments of Baly and his co-workers[1] on the reduction of carbon dioxide in aqueous solution to formaldehyde by illumination with ultra-violet light were subjected to considerable

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[1] Baly, Heilbron and Barker, *J.C.S.*, **119**, 1025, 1921.

criticism by Porter and Ramsperger,[2] Spoehr,[3] Bauer,[4] and others, who suggested that the formaldehyde owed its origin to traces of organic impurities. Applying Warburg's view [5] that photosynthesis *in vivo* is a surface reaction, Baly later [6] illuminated aqueous suspensions of powders on which carbon dioxide was strongly adsorbed. Under these conditions he claimed that the product of the photosynthesis consisted of carbohydrate compounds instead of formaldehyde.

A most interesting advance was described in 1927, when it was stated [7] that, by the use of visibly coloured powders, such as nickel and cobalt carbonates, the photosynthesis could be effected by means of visible light. The reaction now approximated more closely to that occurring in the living plant, and it appeared probable that further investigations might lead to the elucidation of the problem of carbon assimilation and the photosynthesis of carbohydrates *in vivo.*

Experiments on similar lines have been described by Mezzadroli [8] and by Dhar.[9]

The work now described was undertaken in the hope that, by the application of more exact methods than those hitherto employed, information concerning the mechanism and energetics of the reaction would be obtained.

In a recent publication [10] Baly claimed that very satisfactory yields of carbohydrates could be obtained using a catalyst consisting of ferric oxide supported on kieselguhr which had been previously coated with alumina. Increased activity of the catalyst was obtained by the addition of small quantities of thorium dioxide to the ferric oxide. Such supported ferric oxide catalysts of varying composition have been used in the present work.

Experiments were carried out using sources of illumination of widely varying intensities; the duration of illumination was also varied. In all cases, the amount of alumina in the aluminated kieselguhr was 22 per cent., but catalysts were prepared with ferric oxide contents of 1, 4·7, 10, 14' and 26 per cent., the ferric oxide always containing 0·64 per cent. of thorium dioxide. No evidence of photosynthesis was obtained using any of these catalysts, although cataphoresis measurements showed that these powders, when in suspension in an aqueous solution of carbon dioxide, assumed an electropositive charge. The carrying of such a charge has been claimed as an indication of a photosynthetically active catalyst.

As a support for catalysts in work of this type, kieselguhr is unsatisfactory on account of the large calcium content. Complete removal of the calcium is difficult, and where mineral acid is employed for this purpose, the removal of the last traces of acid from the kieselguhr presents a further difficulty.

After the failure of these experiments with supported ferric oxide

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[2] Porter and Ramsperger, *J.A.C.S.*, **47**, 79, 1925.

[3] Spoehr, *J.A.C.S.*, **45**, 1184, 1923.

[4] Baur and Rebmann, *Helv. Chim. Acta*, **5**, 828, 1922; Baur and Büchi, *ibid.*, **6**, 959, 1923.

[5] Warburg, *Biochem. Z.*, **166**, 386, 1925.

[6] Baly, Davies, Johnson and Shanassy, *Proc. Roy. Soc.*, **116** A, 197, 1927.

[7] Baly, Stephen and Hood, *ibid.*, **116** A, 212, 1927.

[8] Mezzadroli and Gardano, *Atti Accad. Lincei* [6], **6**, 160, 1927.

[9] Dhar and Sanyal, *J. physic. Chem.*, **29**, 926, 1925; Gopala Rao and Dhar, *ibid.*, **35**, 1418, 1931.

[10] Baly, *Nature*, **126**, 666, 1930. *Trans. Far. Soc.*, **27**, 545, 1931. Discussion on Photosynthesis.

catalysts, the original work in which nickel carbonate was used as catalyst was re-examined. Electrolytically prepared nickel carbonate,[11] activated as described, was used. The experimental conditions outlined by Baly were followed as closely as his description allowed, but the results were determined by estimation of organic carbon in the residues obtained after illumination and subsequent evaporation. The method of estimation (described in experimental section) was a " wet " oxidation method, and tests showed that it was capable of detecting quantities of carbon, present as carbohydrate, as small as 1 mg.

The results indicated quite definitely that no photosynthesis of organic matter had taken place.

Experimental.

As the carbon dioxide supplied in cylinders is often obtained from the fermentation industry and therefore constitutes a possible source of organic impurity, all experiments were performed using carbon dioxide prepared from marble and hydrochloric acid. For purification the gas was passed first through a tube 12 ins. long containing copper oxide heated to redness, then through a bubbler containing chromic and sulphuric acids. After passing through a bubbler with distilled water, the gas passed into a tube 10 ins. long packed with solid sodium bicarbonate, and finally into another distilled water bubbler from which the gas entered the reaction vessel.

The reaction vessel used was a rectangular glass cell 14 × 17 × 7·5 cm., open at the top, and having polished sides; a glass plate formed a convenient cover. The method of carrying out the photosynthesis tests was as follows. The required weight of the catalyst was suspended in 1½ litres of specially distilled water in the reaction vessel and a fairly rapid stream of carbon dioxide (3 bubbles/sec.) was passed through the suspension. The gas was, as a rule, allowed to pass for half-an-hour to one hour before illumination of the vessel took place, and a steady stream was maintained throughout the period of illumination. After illumination, the catalyst suspension was allowed to settle. In some cases the suspension was more stable, and flocculation was assisted by warming to 60°-70°. After filtration from the catalyst, the water was distilled off under reduced pressure, the aqueous distillate being tested for the presence of formaldehyde by means of Schryver's test. The residues appeared to consist largely of catalyst which filtration had failed to remove. In the earlier experiments, this residue was extracted with carefully purified absolute alcohol, but this procedure was later abandoned, owing to the difficulty of removing the last traces of the alcohol, apparently adsorbed on the catalyst. The traces of alcohol gave charring with concentrated sulphuric acid, and so led to erroneous results.

Kieselguhr-Supported Catalysts.

Before being used for the preparation of the catalyst, the kieselguhr was heated for seven to eight hours with a considerable excess of nitric acid (50 per cent.) to remove the calcium. The greater part of the acid was removed by washing by decantation; the kieselguhr was then transferred to a 12-in. Buchner funnel and washed with water until

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[11] Baly and Hood, *Proc. Roy. Soc.*, **122** A, 393, 1929.

the washings were entirely free from acid, this operation generally occupying about four days. The kieselguhr was then dried.

The method of preparing the supported ferric oxide catalysts was that adopted by Baly.

The coating of the kieselguhr with aluminium hydroxide was carried out by the addition of ammonium hydroxide to a suspension of kieselguhr in aluminium nitrate solution ; the resulting aluminated kieselguhr was washed with cold water, and after being thoroughly dried, was ignited at 450° to 480°. It was then finely ground in a porcelain ball-mill, and coated with ferric oxide by evaporation with a solution of ferric nitrate as described by Baly. Before the final ignition in a vacuum, the catalyst was once more ground in the ball-mill. In all preparations, the ferric oxide contained 0·64 per cent. thorium dioxide, this being added in the form of the nitrate to the ferric nitrate solution.

Table I. gives examples of the catalysts used, the light sources, and the duration of illumination.

TABLE I.

Wt. Catalyst. g.	Fe_2O_3 %.	Light Source.	Distance from Cell. Ins.	Exposure Hours.
5	1	1000 c.p.	8	3·5
10	4·7	250 watt lamp	9	7
20	4·7		9	7
10	7·5		9	7
4·5	10	1000 c.p.	8	5
20	14	250 watt lamp	12	6·5
46	14	60 ,, ,,	14	7
50	14	100 ,, ,, (½ voltage)	24	8
7·5	26	1000 c.p.	8	3

No evidence was ever obtained that any photosynthesis had taken place. Specific tests for carbohydrates, such as the Molisch reaction, gave negative results, and the residue (if completely free from alcohol) gave no charring with concentrated sulphuric acid.

The catalysts prepared exhibited an electropositive charge when suspended in a saturated aqueous solution of carbon dioxide, and while measurements were not obtained with a high degree of accuracy, the cataphoretic velocities were found to be of the order of 0·00025 to 0·00035 cm. per sec. According to Baly[10] the most active powders show a velocity of 0·0004 cm. per sec.

Nickel Carbonate Catalyst.

The nickel carbonate was prepared electrolytically as described by Baly.[11] Three nickel plates 20 × 7 × 0·3 cm. were suspended in a large cylindrical vessel containing distilled water saturated with carbon dioxide. The plates were connected to a 220 volt circuit, in such a way that the two outer plates were made cathodes. Two cooling coils, through which water was circulated, were suspended on either side of the central plate. By means of a variable external resistance, the current was kept at 1 to 1·5 amp., and during the whole period of electrolysis a stream of pure carbon dioxide was passed through the solution. The nickel carbonate deposited at the negative plates, collected at the bottom of the cell, and was filtered off and dried at 100°. After being ground, it was heated at 130° to 140° for half an hour and once more very finely ground.

According to Baly and his collaborators,[7, 11] the nickel carbonate must be subjected to a process of activation before use as a catalyst. This may be carried out by illumination with ordinary white light, or with ultraviolet light. The nickel carbonate used in the present work was always activated by one of these methods before being used.

(*a*) *By White Light.*—The finely ground nickel carbonate was spread in a thin layer on a large glass plate covered by a second plate to prevent contamination by dust. This was illuminated for seven hours by a 100 watt metal filament lamp placed immediately above the plate. The catalyst was always activated just before being used in a photosynthesis test.

(*b*) *By Ultra-violet Light.*—Nickel carbonate was spread in a thin layer on a glass plate and illuminated for three-quarters to one hour by the direct light of a mercury arc lamp placed about 9 ins. distant, the powder being stirred at intervals to expose fresh surfaces. The catalyst was used immediately after activation.

For the photosynthesis tests with nickel carbonate, the following method was used. The required weight of the catalyst was suspended in 1500 c.c. of distilled water and a fairly rapid stream of carbon dioxide passed in, while the cell was illuminated by the light of a 100 watt lamp at a distance of 9 ins. Illumination was continued for two to two and a half hours. At the end of that time the undissolved nickel carbonate was removed by filtration, and the green solution, containing nickel in the form of the bicarbonate, was evaporated to dryness under reduced pressure. The solution was filtered from precipitated nickel carbonate at intervals during the evaporation.

Estimation of organic carbon in the residue was carried out by the method developed by Mills,[12] a similar form of apparatus being used. The residue from the evaporation which always contained nickel carbonate was dissolved in 50 c.c. of very dilute sulphuric acid, and the solution transferred to the oxidation flask and warmed to 30° to 35° for twenty to thirty minutes, while it was evacuated by the water pump. Tests showed that this effectively removed carbon dioxide arising from inorganic carbonate.

A. R. concentrated sulphuric acid (100 c.c.) was added to the solution and the oxidation carried out with chromic acid (10 c.c.) as described by Mills. The absorption train for the carbon dioxide was on a much smaller scale, consisting of conical flasks of 50 c.c. capacity, and the total volume of baryta solution was 35 c.c. Instead of weighing the precipitated barium carbonate the excess baryta was determined by titration with standard acid, phenolphthalein being used as indicator. Blank experiments were carried out on the reagents, including the distilled water used in the photosynthesis experiments. The accuracy of the method was tested by dissolving weighed amounts of sucrose in 50 c.c. of the dilute sulphuric acid and treating this solution exactly as described. Table II. gives an example of the accuracy attainable.

Photosynthesis tests were carried out using approximately 5, 10, 30, and 50 g. of nickel carbonate in 1500 c.c. water. No visible evidence of

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[12] Mills, *T. Soc. Chem. Ind.*, **50**, 375, 1931.

TABLE II.

Sucrose Added g.	N/10 HCl equiv. to CO_2 Formed c.c.	Carbon.	
		Found.	Theor.
0·0149	11·35	0·0062	0·0062
·0079	6·45	·0032	·0033
·0137	9·9	·0057	·0058

photosynthesised carbohydrate syrup was ever obtained, and tests for formaldehyde in the aqueous distillates gave negative results.

Blank experiments were carried out using nickel carbonate suspended in the same volume of water (1500 c.c.), and carbon dioxide passed through for the same length of time as in the photosynthesis tests, the reaction vessel being kept in darkness throughout this period.

The results of the carbon estimations in the residues from the blank experiments and from the photosynthesis tests are given in Table III.

TABLE III.

Experiment. Wt. Cataiyst, g.	Total Organic Carbon Found. g.	Reagent Blank (mean).	N ett Organi Carbon. g.
Dark blank with $NiCO_3$	0·0016	0·0007$_4$	0·0008$_6$
	·0017$_9$	·0007$_4$	·0010$_5$
	·0014$_3$	·0007$_4$	·0006$_9$
Photosynthetic Tests.			
5	0·0018	0·0007$_4$	0·0010$_6$
10	·0015$_5$	·0007$_4$	·0008$_1$
30	·0014$_8$	·0007$_4$	·0007$_4$
50	·0014$_2$	·0007$_4$	·0006$_8$

The fact that there is no difference betweeen the amounts of carbon found in the dark blanks and the photosynthesis tests indicates that this carbon is due to impurity in the water, nickel carbonate, or the carbon dioxide used. It is quite possible that the whole of this carbon is contained in the distilled water used, as the value found represents an organic carbon content of less than one part per million.

The results indicate quite clearly that no conversion of the carbon dioxide to carbohydrate compounds had taken place.

Summary.

The work of Baly and his co-workers on the photosynthesis of carbohydrates in visible light has been repeated, but no evidence of such photosynthesis has been found, nor the production of any formaldehyde detected.

Ferric oxide photocatalysts, supported on kieselguhr, have been used, with negative results. The catalysts were found to bear an electropositive charge when in suspension in water saturated with carbon dioxide. According to Baly this is an indication of photosynthetic activity.

Nickel carbonate has also been employed as catalyst without success, the results of these experiments being determined by estimations of organic carbon in the residues.

In conclusion, I desire to thank Professor F. G. Donnan, F.R.S., for his continued interest and advice during the course of this investigation, and Mr. C. F. Goodeve for his criticism and suggestions. I wish also to record my gratitude to the Ramsay Memorial Trustees for the award of a Glasgow Fellowship.

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PHOTOSYNTHESIS OF CARBOHYDRATES *IN VITRO*

IN a recent paper on this subject,[1] unsuccessful attempts by me to repeat the work of Baly [2] were described. It was not mentioned, however, that consideration had been given to the possibility of the failure to detect any photosynthetical sugars being due to the adsorption of these sugars on the large surfaces exposed by the catalyst powders. The catalysts were, in fact, repeatedly examined for the presence of any organic matter. The kieselguhr supported catalysts and the nickel carbonate were, after use in the photosynthetic tests, heated for some hours with water, and also with absolute alcohol, under reflux. On subsequent evaporation of the water or alcohol, no organic residue was obtained. Tests for charring with concentrated sulphuric acid on the catalysts gave negative results.

In addition, estimations of organic carbon were made, by the method described, on the nickel carbonate after use as a catalyst, but no trace of organic matter was found. Control experiments in which sucrose was estimated in presence of nickel carbonate showed that the latter did not interfere with the carbon estimation even if present to the extent of 40-50 times the weight of carbohydrate.

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[1] *Trans. Far. Soc.*, **27**, 771; 1931.
[2] *Proc. Roy. Soc.*, A, **116**, 197; 1927. *Trans. Far. Soc.*, **27**, 545; 1931.

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