SOME PROPERTIES OF DEUTERIUM COMPOUNDS

with a Note on the

MUTAROTATION OF GALACTOSE.

by

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GENERAL INTRODUCTION

Since Birge and Menzel in 1931 first suggested that an isotope of hydrogen of mass two might possibly exist, chemistry has experienced the development of a new and exceedingly important field of research. Spectroscopic studies showed the existence of the heavier isotope which corresponded to a mass of two and an atomic number of unity. The problem of concentrating this heavier isotope was greatly simplified when Washburn and Urey, in the spring of 1932, reported that the water obtained from industrial electrolytic cells, which had been used for the production of oxygen and hydrogen had a markedly higher density than ordinary water. The higher density was attributed to the presence of the heavier type of water $^{2}H_2O$ and it was suggested that continued electrolysis of an aqueous solution might yield pure "heavy water" in the residual water the light hydrogen being more readily evolved than the heavy. This was actually the case and was achieved in 1933 by Lewis and Macdonald who obtained heavy water containing 70% of hydrogen in the form of the heavier isotope. Advance in this field was so rapid that within the short space of a few years water containing at least 99% of its hydrogen in the form of the isotope two, later named deuterium, could be produced commercially at a comparatively low price.

The availability and the extraordinary property of deuterium in that it is an isotopic form twice as heavy as hydrogen has resulted in extensive researches not only into the properties of its compounds but also, by virtue of its comparatively large differences in physical properties, to its use as a means of investigating the mechanisms of reactions in which hydrogen or its compounds are involved. Recent work has dealt with other methods of separation, methods of analysing isotopic mixtures, and general properties of deuterium and deuterium oxide.

In the work to be described in the following pages we are concerned with (a) the comparison of the absorption curves of anhydrous cobaltous chloride dissolved in ordinary water and in deuterium oxide, (b) the determination of the ratio of the dissociation constants of certain organic compounds in ordinary water and deuterium oxide.

Some investigations on the mutarotation of galactose are also described.

PART I.

THE ABSORPTION SPECTRUM OF COBALTOUS CHLORIDE

IN

DEUTERIUM OXIDE.

INTRODUCTION.

In 1935 Joos and Böhm (Physik. Z. 36, 826, 1935) noted that if the water of crystallisation in the compound potassium chrome selenium alum, $KCr(SeO)_4 12 H_2O$ was exchanged with deuterium oxide an appreciable displacement in the absorption lines in the spectrum was obtained. Dühm (Physik. Z. 107, 589, 1937) reported a similar displacement in the case of copper sulphate $CuSO_4 5H_2O$. Bell (Nature, 137, 534, 1936.) noticed that a solution of anhydrous copper sulphate in 99.5% deuterium oxide was a different tint to the solution in ordinary water, the former being greener. Colorimetric measurement revealed that the blue colour was noticeably less intense, viz:-

D_2O solution : H_2O solution

5.0 cm. : 4.1 cm.

Confirmation of Bell's work was forthcoming in a paper by Brodsky and Zanko (Acta Physicochemica U.R.S.S. 5, 919, 1936.) who made spectrophotometric measurements with copper sulphate in pure H_2O, 43.6% and 92.7% D_2O mixtures. These were of a preliminary nature but seemed to show that the absorption spectrum differs slightly when D_2O is present and that the amount of absorption is approximately proportional to the deuterium oxide content. These workers conclude that the difference is due to a displacement of the absorption region as in the case of potassium chrome selenium alum and that such displacement should be ascribed to the alteration of the vibration terms which results from the difference in mass of the hydrogen and deuterium atom. A similar explanation is put forward by Dühm (Z. fur physikal. Chem., <u>38</u>, 359, 1937.) to explain the change in the absorption spectra of complex chromium salts by replacement of H_2O by D_2O and NH_3 by ND_3 whilst Hein and Bähr (Z. fur physikal. Chem., <u>38</u>, 270, 1937.) report a difference in colour when silver permanganate is dissolved in deuterium oxide and ordinary water. In all cases the difference reported is very slight.

Bell as well as Brodsky and Zanko promise further communications on this subject but up to the commencement of the investigation described below such communications were not forthcoming. In the present experiment an endeavour to compare the absorption spectra of solutions of cobaltous chloride in H_2O and D_2O is made using a spectrophotometer. The absorption spectra of these solutions lie wholly in the visible region and consequently are particularly suitable for this type of experiment.

EXPERIMENTAL.

The Instrument.

The spectrophotometric readings determined during these investigations were obtained using the instrument shown in Figure I. By the combination of a wavelength spectrometer with a Hilger-Nutting Photometer any small wavelength range of the visible spectrum selected for an individual measurement can be isolated and the two beams of light entering the instrument are brought to equality by the photometric part of the apparatus on which the reading is taken which gives the measure of absorption.

The optical system of the Hilger-Nutting Photometer is shown in the accompanying diagram, Figure II. Light from a 100 c.p. Pointolite lamp for direct current enclosed in a lamp house H, which is provided with an adjustment for centring the lamp in the house, falls on two achromatic deviating prisms E, on a stand C from

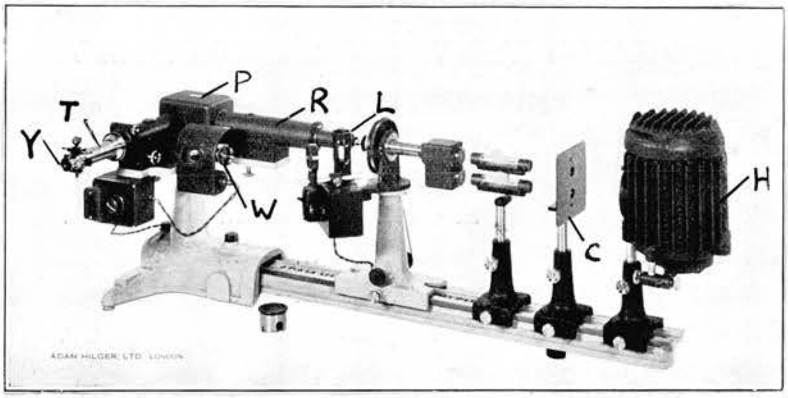


FIGURE I.

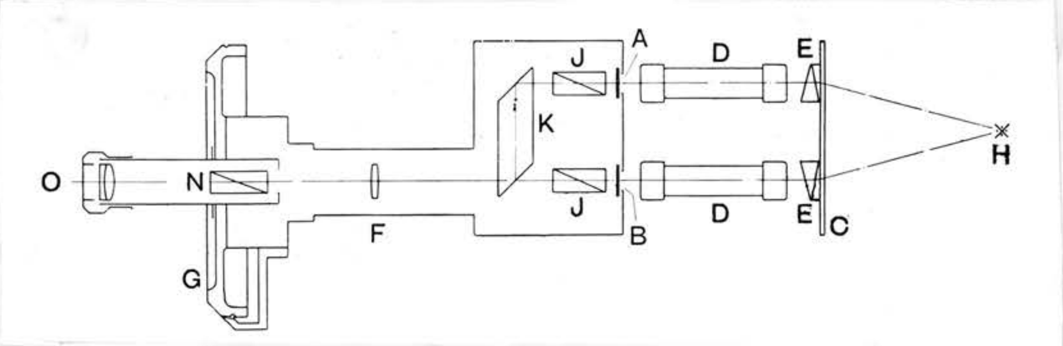


FIGURE II.

which it emerges as two axially parallel pencils. These pass through absorption cells D into the photometer through windows A and B. Two square-ended polarising prisms J whose planes of polarisation are mutually perpendicular, receive the two pencils, which are later combined to form two closely juxtaposed fields by a prism K. The object glass O focusses an image of the dividing line on the slit of the accompanying spectrometer. A third polarising prism N mounted in the circle G produces when rotated a variation in the relative intensities of the two beams such that

$$I_0/I = \tan.^2\theta$$

where I_0 = intensity of light incident upon A

I = intensity of light incident upon B

and θ = the angle through which the prism N must be rotated in order that equality of intensity may be obtained in the two fields.

The divided circle is engraved with a scale of densities as well as degrees. If a reading <u>d</u> on the "density" scale be obtained with a thickness <u>l</u> centimetres of liquid or other absorbing substance, then the extinction coefficient is d/l. Readings may also be taken on the angular scale. The density scale is derived from the angular scale by the use of the formula

$$d = 4.\log_{10}\tan\theta$$

where θ = the reading given by the angular scale.

A reading lens L is so placed that readings may be made without quitting the spectrometer eyepiece.

The spectrometer is equipped with a Constant Deviation Prism (n_D = 1.65) firmly placed on a table which is rotated by means of a micrometer screw to which is fixed a drum of duralumin W, on which the wavelength of the line under observation is read by the observer. The calibration is permanent. The telescope T and the collimator R are both rigidly fixed since to pass through the spectrum it is only necessary to rotate the prism. A prism cover P completely encloses the prism table and slow motion, and as it fits closely to the telescope and collimator bodies it provides an effective means for excluding extraneous light and for the avoidance of spurious reflection thereby producing a background to the field of extreme blackness. The slit has fine screw adjustment with a divided drum, and sliding Hartmann diaphragm. The eyepiece Y is fitted with shutters which allows a very small part of the field to be examined.

The whole assembly is securely fixed to a rigid bar which is in alignment with the collimator axis.

The Cells

The cells, shown in sketch, were parallel sided

silica cells of capacity of 1.8 mls. and length 1 cm. These small volume cells were used since the expense of deuterium oxide necessitated economy of material.

Method of Taking Measurements and Recording Results.

The substance whose absorption is to be measured is interposed in the lower beam. An identical cell containing the solvent is placed in the upper beam. The shutters in the eyepiece are set to contain a range of spectrum which should not be great enough to show any variation in brightness or hue; hence it will depend on the steepness of the edges of the absorption bands to be investigated and on the part of the spectrum under observation. The slit is set at such a width (say 1 to 4 drum divisions) that the purity of the spectrum is not marred, while sufficient light is admitted to the field of view.

On rotating the circle the two portions of the field of view are seen to alter in their relative intensities until they match exactly, and this position being attained the circle reading is noted. In the present investigations all readings were taken on the density scale.

Readings can be taken at any desired wavelength interval (read from the spectrometer drum) throughout the range of the spectrum showing absorption, the closeness of the intervals being regulated by the steepness of the absorption curve. The correctness of the wavelength setting was checked by means of sodium lamp and the comparison prism attached to the slit of the spectrometer.

All measurements are made in a darkened room and the photometer part of the apparatus is encased in a box to decrease the amount of scattered light from the lamphouse. Since the observer's eyes need to become accustomed to the comparatively dim illumination of the field of view, especially at high densities and it is important that the scales from which readings are taken should not be more brightly illuminated than is absolutely essential, if loss of sensitivity is to be avoided, a dimming switch is employed.

When taking readings a number of settings are observed, recorded and averaged as exemplified in Table I below. In general experience it is found that a number of quickly taken readings give a more accurate average than a few readings taken with long periods of viewing.

The zero reading for the density scale was adjusted and determined from time to time during these experiments.

Preparation of Solutions.

(a) Solution in H_2O

A.R. cobaltous chloride with six molecules of water was dissolved in pure water (H_2O) to a suitable concentration.

Molarity of solution = 0.4961 M.

(b) Solution in D_2O.

The deuterium oxide employed during the following experiments was obtained through Imperial Chemical Industries Ltd. from Norsk Hydro-Elektrisk Kvaelstofaktielskab and was 99.6% pure.

The A.R. cobaltous chloride hexahydrate was completely dehydrated by heating at 150°C, in an electric furnace, a specimen of the substance being contained in a Pyrex tube through which a current of dry air was passed. A small quantity was transferred to an air tight weighing bottle and the calculated weight of 99.6% deuterium oxide added.

Molarity of solution = 0.4935.

Small equivalent quantities of HCl and DCl had to be added to the respective solutions in order to hydrolyse the small quantity of hydroxide and deuteroxide formed. These solutions were very similar in appearance but a slight difference in tint was discernible the D_2O solution having a slightly more purple tinge.

Determination of Absorption Curves.

Each solution was examined by placing it in the lower beam and a reference cell containing the pure solvent in the upper beam. The absorption curve is obtained by plotting the spectrophotometer reading against the wavelength. Each reading is the average of at least four observations as is shown in Table I which is given as an example of the method of obtaining readings and the extent of the experimental error. The wavelength interval is determined by the steepness of the absorption curve.

TABLE I.

Solution (a)

λ mμ.	Spectrophotometric Readings on 'd' scale.				No. of Readings	Average	Av. Dev. from mean.
540	1.415	1.415	1.410	1.390	4	1.407	0.009
538	1.495	1.460	1.450	1.450	4	1.464	0.016
536	1.58	1.54	1.56	1.57	4	1.562	0.012
534	1.65	1.68	1.63	1.65	4	1.652	0.010
532	1.73	1.72	1.73	1.72	4	1.725	0.005
530	1.86	1.79	1.82	1.79	8	1.821	0.013
	1.84	1.82	1.82	1.83			

The reading on the density scale gives a direct value of the decadic extinction coefficient K which is defined by the equation

$$I = I_0 . 10^{-Kl}$$

where I_0 is the intensity of the incident light entering the medium, I is the intensity remaining after its subsequent passage through the path length l (in cms.) and l/K the path length passage ~~through~~ which reduces the light intensity to 1/10th. Since the density of a medium is defined by the equation

$$I = I_0 . 10^{-d}$$

we see that $d = Kl$.

and since in this particular case we are employing a cell of length 1 cm.

$d = K$.

Beer's Law states that if the absorbing substance is dissolved in a non-absorbing medium, the absorption will then be proportional to the concentration of the solution,

i.e. $$I = I_0 \,.\, \alpha^{-cl}$$

where α is a constant for the absorbing solute, c is the concentration, and the other symbols have the significance given above.

Writing $\varepsilon = K/c$

we have $$I = I_0 \,.\, 10^{-l\varepsilon c}$$

i.e. the extinction coefficient for a given wavelength of a solution of concentration c is c times that of a solution of unit concentration while for a given substance c.l is a constant for a given ratio of I/I_0. When c is expressed in gramme-molecules of absorbing substance per litre of solution, ε becomes a measure of the absorption due to a single molecule and is known as the molecular extinction coefficient.

In the present case $d = \varepsilon c$ or $\varepsilon = d/c$.

Results.

The results are given in Table II., where ε is calculated from d for various wavelengths, and the absorption curves obtained are shown in Figure III.

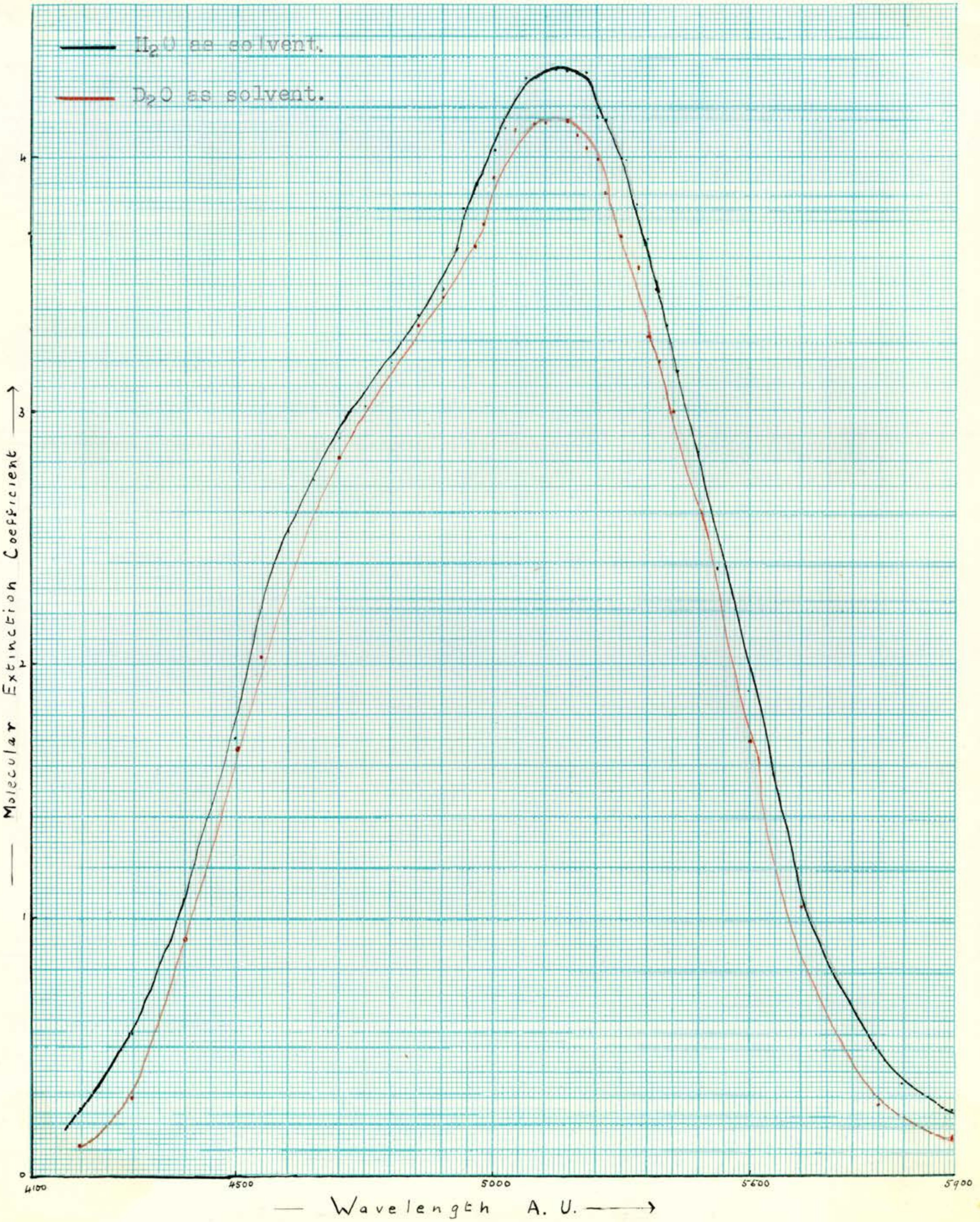
TABLE II.

Solution (a) H_2O			Solution (b) D_2O		
λ mμ.	d.	ε.	λ mμ	d.	ε.
650	0.019	0.038	650	0.061	0.124
600	0.148	0.298	600	0.088	0.178
590	0.122	0.246	590	0.069	0.140
580	0.177	0.357	575	0.134	0.272
570	0.335	0.675	560	0.514	1.042
560	0.594	1.198	550	0.837	1.696
555	0.757	1.526	540	1.252	2.537
550	0.942	1.899	535	1.476	2.990
544	1.180	2.379	532	1.577	3.196
542	1.335	2.629	530	1.627	3.293
540	1.407	2.835	528	1.752	3.550
538	1.464	2.951	526	1.809	3.666
536	1.562	3.148	525	1.820	3.689
534	1.652	3.330	524	1.838	3.726
532	1.725	3.477	522	1.899	3.850
530	1.821	3.670	520	1.950	3.952
528	1.888	3.806	518	1.976	4.033
526	1.930	3.890	516	2.075	4.084
525	1.938	3.906	514	2.040	4.134
524	1.999	4.029	512	2.034	4.122
522	2.055	4.143	510	2.040	4.134
520	2.062	4.156	508	2.036	4.127

TABLE II. (contd.)

λ mμ.	d.	ε.	λ mμ.	d.	ε.
518	2.122	4.277	506	1.975	4.003
516	2.142	4.317	504	1.966	3.985
514	2.155	4.343	502	1.922	3.895
512	2.170	4.374	500	1.934	3.920
510	2.150	4.333	498	1.840	3.729
508	2.142	4.317	496	1.795	3.639
506	2.142	4.317	494	1.732	3.612
504	2.067	4.168	492	1.728	3.502
502	2.072	4.177	490	1.705	3.455
500	1.995	4.022	488	1.678	3.401
496	1.945	3.920	485	1.648	3.340
494	1.882	3.794	484	1.575	3.193
490	1.765	3.476	480	1.563	3.167
485	1.656	3.337	476	1.512	3.065
480	1.580	3.185	470	1.390	2.817
475	1.535	3.094	464	1.350	2.736
470	1.432	2.887	460	1.183	2.463
465	1.350	2.720	450	0.819	1.660
460	1.248	2.516	440	0.445	0.902
455	1.001	2.018	430	0.144	0.292
450	0.851	1.713	420	0.053	0.107
440	0.529	1.068			
430	0.269	0.542			
420	0.125	0.252			

FIGURE III.

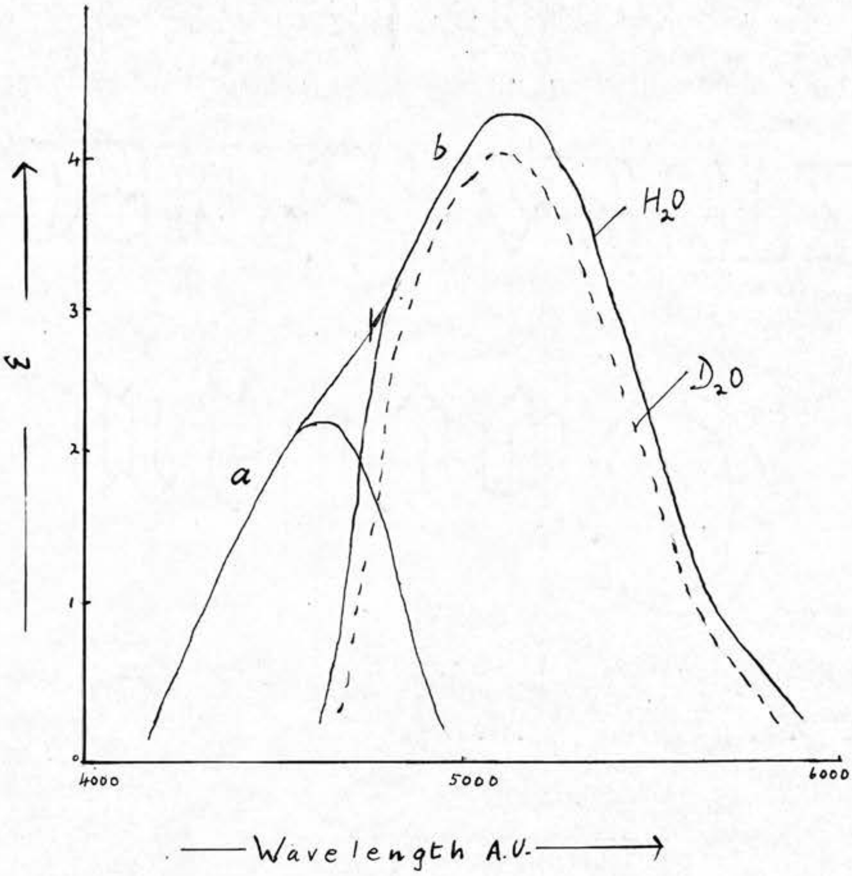

H_2O as solvent.
D_2O as solvent.
Molecular Extinction Coefficient →
0
1
2
3
4
4100
4500
5000
5500
5900
Wavelength A. U. →

DISCUSSION.

Figure III. shows the absorption curves of anhydrous cobaltous chloride dissolved in H_2O and 99.6% D_2O. These curves lie within the visible region between the wavelengths of 4000 A.U. and 6000 A.U. Distinct differences are apparent, the molecular extinction coefficient in D_2O being smaller throughout the region of absorption, and the height of the maximum is lower; up to 4900 A.U. the difference is practically insignificant, above 4900 A.U. it increases and appears to be greatest between 5300 A.U. and 5400 A.U. i.e. at lower frequencies than the maximum. These differences are of the same order of magnitude as those reported by Brodsky and Zanko (Acta Physicochemica U.R.S.S. 5, 919, 1936.) for copper sulphate in H_2O and 92.7% D_2O.

Closer examination of these curves might suggest that each is built up of two individual curves

(a) extending from 4200 A.U. - 4800 A.U. and
(b) extending from 4800 A.U. - 6000 A.U. Curve (a) does not appear to be affected by the change of solvent whilst (b) shows a decided difference. We may conclude therefore that the vibrations resulting in curve (b) involve deuterium whilst those in curve (a) do not.



F I G U R E IV.

The vibrations involved here are very complex and an analysis of them is too difficult to be attempted. A qualitative graphical representation of the ideas set down here is given in Figure IV.

The energy associated with the maximum of curve (a) is 58.5 k. cals. and that with the maximum of curve (b) is 55.6 k. cals.

PART II.

THE DISSOCIATION CONSTANTS OF SOME WEAK ACIDS

IN

DEUTERIUM OXIDE.

3

INTRODUCTION.

The tendency of a molecule to donate or accept a proton i.e. its acidity or basicity is one of its fundamental chemical properties which it exhibits in many reactive ways. The acidity constant has manifold relations to the velocity constant of many possible reactions. The introduction of deuterium has opened up new possibilities in the investigation of a large number of proton transfer processes and allowed a new kind of insight into the acidity processes. The study of acid equilibrium in both kinds of water H_2O and D_2O therefore is of importance in throwing light on the nature of the binding of the proton and deuteron in acids, in the interpretation of reaction kinetic problems in acid and base catalysis in both kinds of water, and in the treatment of ionic equilibria in both solvents.

In a gaseous molecule which may be represented by the formula $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}:H$ we may consider the potential, as a function of the distance, when the hydrogen ion is moved away from the bonding electron pair. Whatever the potential curve may be it will be almost the same for the molecule $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}:D$. Neglecting the small difference arising out of the so called electronic isotope shift we may consider the two potential curves as identical. There remains however an important difference between the two molecules in that the lowest state of vibration the deuteron, because of its greater, mass, occupies a lower position on the potential curve than the proton. Moreover on account of this the difference will be greater the more tightly the two ions are held together. Thus on account of the difference in residual energy of the two molecules the energy required to remove a deuteron by ionisation is always greater than that required to remove a proton.

Consider now the reactions in dilute aqueous solution and the relative dissociation constants of weak organic acids. If K_h is the dissociation constant of HA in H_2O and K_d is the dissociation constant of DA in D_2O, viz:-

$$HA + H_2O = H_3O^+ + A^- \quad : K_h \quad .....(1)$$

$$DA + D_2O = D_3O^+ + A^- \quad : K_d \quad .....(2)$$

we see that the ratio K_h/K_d depends on the relative magnitude of the binding forces acting on the ions when attached to the anion A^- or the neatral water molecule. Halpern (J. Chem. Physics, 3, 459, 1935.) has forwarded an approximate theory in which he assumes that the energy changes of the reactions (1) and (2) differ only by the respective residual energies, and the entropy changes are identical. He obtained the relation

$$K_h/K_d = \exp.- \frac{Fh(\nu_H^W - \nu_H^A - \nu_D^W + \nu_D^A)}{2kT} \qquad \ldots.(3)$$

where F = number of degrees of freedom of oscillation

ν_H^A = frequency of oscilllation of proton attached to the anion

ν_H^W = frequency of oscillation of proton attached to the neutral water molecule.

ν_D^A = frequency of oscillation of deuteron attached to the anion.

ν_D^W = frequency of oscillation of deuteron attached to the neutral water molecule.

h is Planck's constant, k is Boltzmann's constant and T is temperature on the Kelvin scale.

If we write $\nu_H = \sqrt{2}\,\nu_D$ on account of the difference of mass we obtain

$$K / K = \exp.- \frac{(1 - 1/\sqrt{2}).Fh(\nu_H^W - \nu_H^A)}{2kT} \qquad \ldots..(4)$$

Since ν_H increases with the binding energy, for all acids weaker than H_3O^+, K_h/K_d is positive and increases with increasing weakness of the acid.

A more quantitative development of this equation was made by Hornel and Butler (J.C.S. 1361, 1936.) who showed that if the binding energy of a proton is expressed by Morse's equation (Phys. Rev. 34, 57, 1924.)

$$Q = Q^{o}[e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}] \quad .....(5)$$

the fundemental frequency is

$$= a/\pi . (Q^{o}/M)^{\frac{1}{2}} \quad .....(6)$$

where M = reduced mass of the vibrating system

a = force constant and r = interatomic distance.

If a_W be the force constant for a proton attached to a neutral water molecule, a_A be the force constant for a proton attached to an anion, Q_W be the binding energy of a proton attached to a neutral water molecule and Q_A be the binding energy of a proton attached to an anion equation (4) becomes

$$K_h/K_d = \exp . \frac{-(1 - 1/\sqrt{2}).Fh.}{2kT\pi} \left[\frac{a_W Q_W^{o\frac{1}{2}}}{M_W^{\frac{1}{2}}} - \frac{a_A Q_A^{o\frac{1}{2}}}{M_A^{\frac{1}{2}}}\right] ..(7)$$

Making the assumption that the relation between the dissociation constant and the energy change in the dissociation is $Q_A - Q_W = -kT \log K_h$ these authors obtain a relation which may be approximated to

$$\log K_h/K_d = -(1 - 1/\sqrt{2}). \frac{\nu_H^W . h}{2kT}\left\{1 - \frac{a_A . M_W^{\frac{1}{2}}}{a_W . M_A^{\frac{1}{2}}}\left(1 - \frac{kT.\log K_h}{2Q_W^{o}}\right)\right\} ...(8)$$

Taking $\nu_H^W h/2$, the residual energy of the proton in H_3O^+ as 5.17 kg. cals./gm. mol., and Q_W^{o} = 180 kg. cals./gm. mol., and putting $M_W^{\frac{1}{2}} = M_W^{\frac{1}{2}}$ and $F = 1$ the following relation is obtained

$$\log_{10} K_h/K_d = -2.21(1 - a_A/a_w) - 0.0042\,(a_A/a_w)\log_{10}K_h \qquad \ldots\ldots(9)$$

If a_A is assumed to be the same for a series of acids the variation of K_h/K_d with K_h will be small.

It will be useful to mention at this point the results obtained by previous workers in this field. These are summarised in the accompanying Table I. The same methods which are satisfactory for the determination of such constants in ordinary water can be employed for deuterium oxide solutions. Up to date the following methods have been used

(a) the conductivity method, by Lewis and Schutz who obtained rough values for deutacetic acid and chlorodeutacetic acid in 1934;

(b) the potentiometric method with the hydrogen or quinhydrone electrode, the former by Schwarzenbach and coworkers and the latter by Korman and La Mer in 1936;

(c) the catalytic method, by Hornel and Butler on the rates of hydrolysis of acetal and ethyl orthoformate in 1936.

(d) the measurement of distribution concentrations of an acid in benzene and water, by Gross and Wischin in picric acid in 1936.

In Table I. are set out the ratios K_h/K_d. In the second column the negative logarithms of the most

TABLE I.

Acid	pK	K_H/K_d	T	Method	Ref.
1. H_3O^+	-1.74	1	-	-	-
2. Picric Acid	ca.1	4*	18°	Distribution	1
3. Oxalic Acid	1.62	1.04	15°	Catalytic	3
4. HSO_4^-	1.90	2*	20°	D_2 Electrode	2
5. $^+NH\ CH_2COOH$	2.35	2.54	20°	D_2 Electrode	4
6. H_3PO_4	2.37	1.61	20°	D_2 Electrode	4
7. $Cl-CH_2COOH$	2.85	2.7	-	Conductivity	6
8. Salicylic Acid	2.97	4.05	25°	Quinhydrone	5
9. Formic Acid	3.75	2.50	20°	D_2 Electrode	4
10. Anilinium Ion	4.60	3.07	20°	D_2 Electrode	4
11. CH_3COOH	4.75	2.87	20°	D_2 Electrode	4
12. Cacodylic Acid	6.25	3.30	15°	Catalytic	3
13. $H_2PO_4^-$	7.22	2.89	20°	D_2 Electrode	4
14. NH_4^+	9.26	3.12	20°	D_2 Electrode	4
15. $(CH_3)_3NH^+$	9.90	3.92	20°	D_2 Electrode	4
16. $^-OOC-CH_2NH_3^+$	9.90	3.41	20°	D_2 Electrode	4
17. Hydroquinone	10.0	3.36	25°	Quinhydrone	5
18. Water	15.91	5.43	20°	D_2 Electrode	4

* Rough measurements only

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1. Gross and Wischin, Trans. Far. Soc., 32, 879, 1936.
2. Drucker, Trans. Far. Soc., 33, 660, 1937.
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4. Schwarzenbach, Epprecht and Erlenmeyer, Helvetica, 19, 1292, 1936.
5. Korman and La Mer, J.A.C.S., 58, 1396, 1936.
6. Lewis and Schutz, J.A.C.S., 56, 1913, 1934.

probable value of the dissociation constants in ordinary water determined by other methods are given. Since micro-methods must be employed in these determinations, because of the expense of the solvent, unavoidable errors occur. By performing the experiments in essentially the same way in both kinds of water these errors are substantially reduced since they will largely cancel in the ratio. Nevertheless the values of K_h/K_d given in table I must not be taken as being particularly accurate, an estimate of the error might be set down as 10%.

As Table I shows the ratio K_h/K_d is greater than one in all cases and amounts to about three in all the acids. Greater deviations from this number only occur in oxalic acid, phosphoric acid and water. The first of these is much smaller and that of water is abnormally high. The value of the oxonium ion is by definition equal to one.

Originally the value of K_h/K_d was regarded as being the difference in acidity between a proton acid and a deuteron acid. This is incorrect since such a difference can only be measured by the exchange of a proton and deuteron acid in the same medium with the same base i.e. by the constants of the following equilibria,

$$DX + Y' = DY + X' \quad : K_D \qquad .....(10)$$

$$HX + Y' = HY + X' \, . \quad : K_H \qquad .....(11)$$

The ratio K_H/K_D signifies the constant of the exchange equilibrium

$$\frac{[\ HY\ ].[\ DX\ ]}{[\ HX\ ].[\ DY\ ]} \ .$$

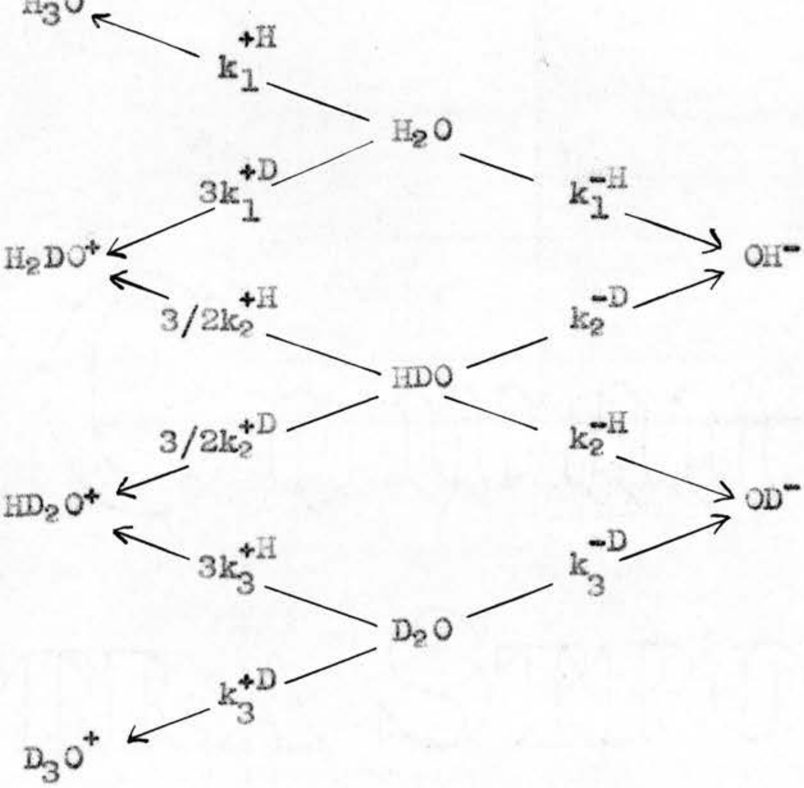
Such are accessible from direct measurement for many cases in which the acid is uncharged but the base is an negative ion.

Since both dissociations (1) and (2) will not take place in the same medium we cannot compare them without further information. We can however examine the reactions in which the deuteron acid and the proton acid react with various basic molecules such as D_2O and H_2O. It is therefore desirable at this point to consider some aspects of the equilibria existing in isotopic water mixtures. These are complicated systems containing three neutral molecules, H_2O, HOD, D_2O, four positive ions, H_3O^+, D_3O^+, H_2DO^+, HD_2O^+, and two negative ions OD^- and OH^-.

All the possible equilibria between these species can be represented by the following scheme where

$$k_1^{+H} = \frac{[H3O^+]}{\alpha_{H^+}[H_2O]} \qquad 3k_1^{+D} = \frac{[H_2DO^+]}{\alpha_{D^+}[H_2O]} \qquad \text{etc.}$$

The symbols in brackets represent the activities of the various species while α_{H^+} and α_{D^+} are the activities of proton and deuteron respectively. The numerical coefficients are statistical factors.



The ratio k_2^{+H}/k_1^{+H} is a measure of the influence of substitution of one deuterium atom in the water molecule in the reaction with a proton acid, whilst k_3^{+H}/k_1^{+H} is a measure of the substitution influence of the two deuterium atoms. k_2^{+D}/K_1^{+D} and k_3^{+D}/k_1^{+D} have the same significance for a deuteron acid.

Other known equilibria are

$$K = \frac{[HOD]^2}{[H_2O].[D_2O]} \qquad .....(12)$$

$$L = \frac{\alpha_{H^+}^2 [D_2O]}{\alpha_{D^+}^2 [H_2O]} \qquad .....(13)$$

$$M = \frac{[H_3O^+]^2 . [D_2O]^3}{[D_3O^+]^2 . [H_2O]^3} \qquad .....(14)$$

from which can be derived

$$3k_1^{+D} / 3/2k_2^{+H} = \sqrt{K.L} \qquad .....(15)$$

$$3/2k_2^{+D} / 3k_3^{+H} = \sqrt{L/K} \qquad .....(16)$$

$M = L.(k_1^{+H}/k_3^{+D})^2 = L$ if we define the proton and deuton activities by putting $k_1^{+H} = 1$ and $k_3^{+D} = 1$.

Recently Schwarzenbach (Z. fur Elektrochemie 44, 48, 1938.) suggested an assumption which permits of the theoretical calculation of these constants. This assumption is equivalent to

$$\frac{k_1^{+H}}{k_1^{+D}} = \frac{k_2^{+H}}{k_2^{+D}} = \frac{k_3^{+H}}{k_3^{+D}} \qquad .....(17)$$

by which the equations connecting these constants can be solved giving

$$\frac{k_2^{+H}}{k_1^{+H}} = \frac{k_2^{+D}}{k_1^{+D}} = \frac{2}{M^{\frac{1}{2}}K^{\frac{1}{2}}} \qquad .....(18)$$

$$\frac{k_3^{+H}}{k_1^{+H}} = \frac{k_3^{+D}}{k_1^{+D}} = \frac{1}{M^{1/3}} \qquad .....(19)$$

Taking K = 3.27 (Topley and Eyring J. Chem. Phys. 2, 220, 1934.) and L = 15.3 (Korman and La Mer J.A.C.S. 58, 1396, 1936.) Nelson and Butler (J.C.S., 957, 1938.)

find that $3/2k_2^{+H} = 1.05$ and $3k_3^{+H} = 1.21$. These values are in reasonable agreement with the constants obtained empirically by Orr and Butler (J.C.S., 330, 1937.) :- viz., $3/2k_2^{+H} = 1.05$ and $3k_3^{+H} = 1.10$. These considerations seem to justify the assumption made. This assumption also made possible the calculation of the variation of the velocity constant of acid catalysed reactions in isotopic water mixtures assuming thermodynamic equilibrium between the reaction complex and the solution. (Nelson and Butler loc. cit.)

From (18) and (19) k_2^{+H}/k_3^{+H} is found to be 0.789 and k_3^{+H}/k_1^{+H} to be 0.504. HDO and D_2O are thus less basic than H_2O and the influence of D substitution is extraordinarily high. Generally speaking therefore acids in D_2O are less dissociated than in H_2O since the solvent is less basic. Also a proton acid is less dissociated in D_2O than in H_2O quite apart from the statistical factor. This substitution effect is the same for all acids and explains the relation of the K_h/K_d values of the various acids which are set out in Table I.

If this were the only influence which existed i.e. if the proton acids were exactly dissociated by equal amounts from the deuteron acids we would obtain the same value of 1.98 (= k_1^{+H}/k_3^{+H}) for all acids. To determine the ratio of a proton acid and deuteron acid K_H/K_D we must take this influence of substitution into account :- viz ,

$$K_H/K_D = (K_h/K_d).(k_3^{+H}/k_1^{+H}) = 0.504\ K_h/K_d \quad ...(20)$$

We have assumed so far that the same simple equilibrium constant holds in D_2O and H_2O. This is only an approximation since the solvents possess different di-electric constants, that of D_2O being 1% less than that of H_2O. This is corrected for by a factor $\underline{f}$ which in those cases in which only a single charged ion participates is very small. If z is the charge on the ion $\underline{f}$ has the following values,

z =	-1	0	+1
$\underline{f}$ =	0.85	0.95	1.0

Equation (20) now reads

$$K_H/K_D = 0.504.\underline{f}.\ K_h/K_d \quad .....(21)$$

The values of K /K set out in Table II. for the acids in Table I. are calculated using equation (21) and signify the constant ratio of a proton transfer and deuteron transfer in the water molecule under equal conditions.

T A B L E II.

Acid (No. in Table I.)	1	2	3	4	5	6	7	8
K_H/K_D	1.0	1.9	0.5	0.9	1.3	0.8	1.3	1.9

Acid (No. in Table I.)	9	11	12	13	15	17	18
K /K	1.2	1.4	1.6	1.8	1.9	1.6	1.5

Recently Rule and La Mer (J.A.C.S., 60, 1974, 1938.) employing a quinhydrone electrode redetermined the ratios K_h/K_d for a number of acids and found a a steady ingrease in the ratio as the strength of the acid decreases.

Summing up we note that the accuracy acheived in the experimental work in determining these ratios has not been high and in the present state of knowledge there are three points of view which can be adopted regarding these values, (1) K_h/K_d is a function of the strength of the acid; (2) K_h/K_d is constant for acids of a given type; (3) K_h/K_d is a constant regardless of type.

The object of the work recorded below is to supplement such information and by the choice of substances endeavour to gain further insight into these equilibria.

INDICATOR-BUFFER EQUILIBRIA

If we regard an acid in the sense of Brönsted and Lowry i.e. as any molecule in the charged state which can give up a proton or deuteron the two forms of any indicator function respectively as an acid and as a base. If HI denotes the acid and I the basic form there is an equilibrium of the form

$$HI = I + H^+ \qquad \ldots\ldots(1)$$

The electric charge of the acid form HI may be positive, zero, or negative according to the nature of the indicator. The electric charge of the basic form I is always algebraically one less than that of HI.

A buffer solution can be considered likewise as being a mixture of an acid HA and a base A which control the hydrogen ion concentration according to the equation

$$HA = A + H^+ \qquad \ldots\ldots(2)$$

where the electric charge of the acid form HA may be positive, zero, or negative, whilst that of the basic form A is algebraically one less than that of HA.

Bronsted (J.C.S., <u>119</u>, 588, 1921.) has given the exact thermodynamic treatment of such equilibria. Let C = concentration and f = activity coefficients then the thermodynamic equilibrium conditions are

$$\frac{C_I . C_{H^+}}{C_{HI}} = K_{(c)HI} = K_{HI} \frac{.f_{HI}}{f_{H^+} . f_I} \qquad \ldots\ldots(3)$$

$$\frac{C_A \cdot C_{H^+}}{C_{HA}} = K_{(c)HA} = K_{HA}\frac{f_{HA}}{f_{H^+} \cdot f_A} \qquad \ldots\ldots(4)$$

where K_{HI} is the thermodynamic acid constant of the indicator and K_{HA} is the thermodynamic acid constant of the acid constitutent of the buffer. For a given temperature and solvent K_{HI} and K_{HA} are true constnats. The equilibrium concentrations products $K_{(c)HI}$ and $K_{(c)HA}$ on the other hand are not constants but depend on the concentration of electrolytes present.

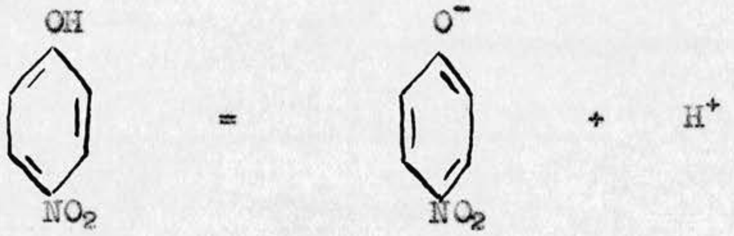
Brönsted further pointed out that we can consider double acid-base equilibrium between the indicator and the buffer instead of (1) and (2) separately* - viz.

$$HI + A = I + HA \qquad \ldots\ldots(5)$$

The thermodynamic equilibrium condition is

$$\frac{C_I \cdot C_{HA}}{C_{HI} \cdot C_A} = K_c = \frac{K_{(c)HI}}{K_{(c)HA}} = \frac{K_{HI}\, f_{HI}\, f_A}{K_{HA}\, f_I\, f_{HA}} \qquad \ldots\ldots(6)$$

The substances employed in the present investigations were nitrophenols and the indicator equilibrium may be represented as follows



I Colourless

II Yellow

Form I may be represented as HI and form II the yellow basic form with a single negative charge as I^-,

$$HI = I^- + H^+ \quad ......(7)$$

The buffers chosen for the following investigations were of the types:-

$$H_2PO_4^- = HPO_4^= + H^+ \quad ......(8)$$

and $$HAc = Ac^- + H^+ \quad ......(9)$$

The indicator-buffer equations for these combinations are

$$H_2PO_4^- + I^- = HPO_4^= + HI \quad ......(10)$$

$$HAc + I^- = Ac^- + HI \quad ......(11)$$

The thermodynamic equilibria are

$$K_c = \frac{C_{I^-}\, C_{H_2PO_4^-}}{C_{HI}\, C_{HPO_4^=}} = \frac{K_{HI}}{K_{H_2PO_4^-}} \cdot \frac{f_{HI}\, f_{HPO_4^=}}{f_{I^-}\, f_{H_2PO_4^-}} \quad ......(12)$$

and

$$K_c = \frac{C_{I^-}\, C_{HAc}}{C_{HI}\, C_{Ac^-}} = \frac{K_{HI}}{K_{HAc}} \cdot \frac{f_{HI}\, f_{Ac^-}}{f_{I^-}\, f_{HAc}} \quad ......(13)$$

From the theory of Debye and Hückel (Physik. Z. <u>21</u>, 185, 1923; <u>25</u>, 97. 1924.) the activity coefficients may be calculated according to the formula

$$-\log_{10} f_i = 0.50 \frac{Z_i^2 \sqrt{\mu}}{1 + 0.33a\sqrt{\mu}} \quad .....(14)$$

where f_i denotes the activity coefficient of the ion i of valency Z_i, μ is the ionic strength and <u>a</u> is a certain mean ionic diameter in A.U. of the given ion and other ions in the solution. A similar formula which is equally applicable at ionic strengths up to

0.1 is the following (Guggenheim J. Phys. Chem., 38, 543, 1934.)

$$-\log_{10} f_i = 0.50 \frac{Z_i^2 \sqrt{\mu}}{1+\sqrt{\mu}} + \sum_k B_{ik} C_k \qquad \ldots\ldots(15)$$

in which the coefficient of $\sqrt{\mu}$ in the denominator is given the value unity, the specific differences between various ions being taken care of by the term $\sum_k B_{ik} C_k$ where C_k denotes the concentration of the ionic species k: the quantities B_{ik} are constants, and the summation $\sum_k$ extends over all ionic species k of opposite sign to that of the species i.

Applying equation (15) to general indicator-buffer equilibria (6) we have

$$-\log_{10} \frac{f_{HI}\, f_{A}}{f_{I}\, f_{HA}} = \frac{0.50\sqrt{\mu}(Z_{HI}^2 + Z_A^2 - Z_I^2 - Z_{HA}^2)}{1+\sqrt{\mu}} + \sum_k B_{ik} C_k \qquad \ldots(16)$$

which for phosphate buffer-indicator equilibrium (12) becomes

$$-\log_{10} \frac{f_{HI}\, f_{HPO_4^=}}{f_{I^-}\, f_{H_2PO_4^-}} = \frac{1.5\sqrt{\mu}}{1+\sqrt{\mu}} + \sum_k B_{ik} C_k \qquad \ldots\ldots(17)$$

and for acetate buffer-indicator equilibrium (13) becomes

$$-\log_{10} \frac{f_{HI}\, f_{Ac^-}}{f_{I^-}\, f_{HAc}} = 0 + \sum_k B_{ik} C_k \qquad \ldots\ldots(18)$$

Taking logarithms and substituting the above relations we have from equation (12)

$$\log \frac{C_{I^-}}{C_{HI}} + \log \frac{C_{H_2PO_4^-}}{C_{HPO_4^=}} = \log K_I - \log . K_{H_2PO_4^-} + \frac{1.5\sqrt{\mu}}{1+\sqrt{\mu}} - \sum_k B_{ik} C_k$$

or

$$\log.K_I = \log\frac{C_{I^-}}{C_{HI}} + \log\frac{C_{H_2PO_4^-}}{C_{HPO_4^=}} + \log.K_{H_2PO_4^-} + \frac{1.8\sqrt{\mu}}{1+\sqrt{\mu}} - \sum_k B_{ik}C_k \quad .....(19)$$

Similarly for equation (13)

$$\log.K_I = \log\frac{C_{I^-}}{C_{HI}} + \log\frac{C_{HAc}}{C_{Ac^-}} + \log.K_{HAc} + \sum_k B_{ik}C_k \quad .....(20)$$

If we now consider the same equilibria in another solvent the equations are the same although the values are different. Thus if we are examining the dissociation constants of the substance HI in H_2O and D_2O and we designate its dissociation constant in the former by K_h and in the latter by K_d we obtain the following relations for phosphate buffer solutions provided that the ionic strength terms are equal;

$$\log K_h/K_d = \log\left(\frac{C_{I^-}}{C_{HI}}\right)_h \Big/ \left(\frac{C_{I^-}}{C_{HI}}\right)_d + \log\left(\frac{C_{H_2PO_4^-}}{C_{HPO_4^=}}\right)_h \Big/ \left(\frac{C_{D_2PO_4^-}}{C_{DPO_4^=}}\right)_d + \log\frac{K_{H_2PO_4^-}}{K_{D_2PO_4^-}} \quad .....(21)$$

and if the buffer ratio is made the same in both cases the middle term of the R.H.S. becomes zero and we have

$$\log K_h/K_d = \log\left(\frac{C_{I^-}}{C_{HI}}\right)_h \Big/ \left(\frac{C_{I^-}}{C_{HI}}\right)_d + \log\frac{K_{H_2PO_4^-}}{K_{D_2PO_4^-}} \quad .....(22)$$

The corresponding acetate buffer-indicator equilibrium gives the equation,

$$\log K_h/K_d = \log\left(\frac{C_{I^-}}{C_{HI}}\right)_h \Big/ \left(\frac{C_{I^-}}{C_{HI}}\right)_d + \log\frac{K_{HAc}}{K_{DAc}} \quad .....(23)$$

In the work to be described in the following pages determinations of the first term on the R.H.S. are made using a spectrophotometer and since the values of $\log K_{H_2PO_4^-}/K_{D_2PO_4^-}$ and $\log K_{HAc}/K_{DAc}$ are already known (Schwarzenbach, Epprecht and Erlenmeyer, Helvetica <u>19</u>, 1293, 1936.), values for K_h/K_d are obtained.

EXPERIMENTAL.

The instrument employed in obtaining the results given below was the spectrophotometer described in Part I.

As was shown in the Introduction pp. 35 - 40 if conditions were chosen suitably we have the following relations for (a) the ratio of the dissociation constants of an acid HI, which is an indicator, in H_2O and D_2O using phosphate buffers, and (b) the same ratio in acetate buffers.

$$\log K_h/K_d = \log\left(\frac{C_{I^-}}{C_{HI}}\right)_h \Big/ \left(\frac{C_{I^-}}{C_{HI}}\right)_d + \log\frac{K_{H_2PO_4^-}}{K_{D_2PO_4^-}} \quad .....(1)$$

$$\log K_h/K_d = \log\left(\frac{C_{I^-}}{C_{HI}}\right)_h \Big/ \left(\frac{C_{I^-}}{C_{HI}}\right)_d + \log\frac{K_{HAc}}{K_{DAc}} \quad .....(2)$$

where K_h = dissociation constant of HI in H_2O

K_d = dissociation constant of HI in D_2O

$K_{H_2PO_4^-}$ = dissociation constant of $H_2PO_4^-$ in H_2O

$K_{D_2PO_4^-}$ = dissociation constant of $D_2PO_4^-$ in D_2O

K_{HAc} = dissociation constant of HAc in H_2O

K_{DAc} = dissociation constant of DAc in D_2O

$(C_{I^-}/C_{HI})_h$ is the ratio of concentrations of coloured anion to undissociated HI, which is colourless, in H_2O. $(C_{I^-}/C_{HI})_d$ is the same ratio in D_2O.

The C_{I^-}/C_{HI} terms are determined experimentally as follows. A solution whose pH or pD is determined by the buffer ratio $C_{H_2PO_4^-}/C_{HPO_4^=}$ or C_{HAc}/C_{DAc} contains a concentration of HI which is suitable for examination in the spectrophotometer. Preliminary experiments are performed to determine the absorption region of the compound being investigated and a suitable wavelength chosen. A reading d' is then made on the density scale with the dilute buffer solution of HI in the lower cell. A very small quantity of strong alkali (0.01 ml. of 8N. NaOH.) sufficient to fully dissociate HI is then added and another reading d" made. d' is proportional to the concentration of the anion I^- present in the solution at the given pH or pD and d" is proportional to the concentration of the anion I^- at complete dissociation, thus

$$d' / d'' - d' = C_{I^-}/C_{HI} \qquad .....(3)$$

The conditions necessary before equations (1) and (2) are true are that (a) the ratio of $C_{H_2PO_4^-}/C_{HPO_4^=}$ be the same as $C_{D_2PO_4^-}/C_{DPO_4^=}$ in the case of the phosphate buffers and that C_{HAc}/C_{Ac^-} be the same as C_{DAc}/C_{Ac^-} in the case of acetate buffers; (b) the ionic strength of the H_2O solution be the same as the ionic strength of the D_2O solution. These conditions were acheived as far as is possible by performing the experiments in essentially the same way in both kinds of water thereby reducing the unavoidable errors considerably since these will cancel out in the ratio. Before K_h/K_d can be determined we require to know $K_{H_2PO_4^-}/K_{D_2PO_4^-}$ and K_{HAc}/K_{DAc}. These values have been determined by Schwarzenbach, Epprecht and Erlenmeyer, (Helvetica, 19, 1293, 1936.) using a deuterium electrode and are set out in Table I.

TABLE I.

Acid	-log. K_h	-log. K_d	log. K_h/K_d
$H_2PO_4^-$	7.207	7.666	0.459
CH_3COOH	4.748	5.203	0.455

The values of log K_h/K_d recorded below are obtained by means of equations (1) and (2).

Determinations made using Phosphate Buffer Solutions.

(1) O- and P- Nitrophenol.

Since the most accurate results are obtained when the acid being investigated is nearly half dissociated a pH value is chosen which will give the ratio d'/d" - d' a value approaching unity. The dissociation constants of o- and p- nitrophenol lie very close to one another and also to that of $H_2PO_4^-$ thus a buffer ratio of one was employed.

The buffer solution for these two acids was prepared by dissolving equal molar quantities of the A.R. salts Na_2HPO_4 sodium hydrogen phosphate and KH_2PO_4 potassium dihydrogen phosphate in ordinary and heavy water. Knowing the weights and densities the molarities of the heavy water solutions were calculated.

The absorption curve in both cases extends into the ultra violet from 4700 A.U. Increasing absorption takes place from 4700 A.U. to the limit of the visible region. The most suitable wavelength was found to be 4500 A.U. Each d reading was the average of ten and the zero was checked before each set of readings was made.

The nitrophenols were obtained from British Drug Houses Ltd. and subjected to several recrystallisations. The deuterium oxide was obtained from the Norsk Hydro Elektrisk Kvaelstofaktieselkab and was 99.6% D_2O.

O-Nitrophenol M.P. 45° P-Nitrophenol M.P. 114°

The results obtained are given in Table II. The values of log K_h/K_d being calculated using equation (1).

TABLE II.

Substance	Solvent	$\frac{d'}{d'' - d'}$	$\log \frac{d'}{d'' - d'}$	$\log K_h/K_d$	K_h/K_d
O-Nitrophenol	D_2O	0.5751	$\bar{1}.7598$	0.4672	2.93
	H_2O	0.5861	$\bar{1}.7680$		
P-Nitrophenol	D_2O	0.7382	$\bar{1}.8682$	0.4621	2.90
	H_2O	0.7435	$\bar{1}.8713$		

(2) M-Nitrophenol

The dissociation constant of m-nitrophenol does not come readily into the pH range of phosphate buffers. For this reason the determinations cannot be very accurate as conditions are unfavourable but the following results, given in Table III, were obtained for various buffer ratios which are indicated in the table.

The molarity of the buffer solutions was 0.1 except in those cases which are marked * where the molarity was 0.02 M.

The m-nitrophenol was obtained from British Drug Houses Ltd., and was recrystallised from benzene. M.P. 97°.

All readings were made at a wavelength of 4500 A.U.

5

TABLE III.

Solvent	$\log \frac{[Na_2HPO_4]}{[KH_2PO_4]}$	$\frac{d'}{d'' - d'}$	$\log \frac{d'}{d'' - d'}$	$\log K_h/K_d$	K_h/K_d
* D_2O	0.6870	0.1914	$\bar{1}.2819$	0.5000	3.16
H_2O	0.6870	0.2093	$\bar{1}.3227$		
D_2O	0.7102	0.175	$\bar{1}.2420$	0.4807	3.03
H_2O	0.7102	0.1835	$\bar{1}.2637$		
D_2O	0.7952	0.177	$\bar{1}.2481$	0.5070	3.21
H_2O	0.7952	0.1977	$\bar{1}.2961$		
D_2O	0.8470	0.222	$\bar{1}.3471$	0.5387	3.46
H_2O	0.8470	0.2672	$\bar{1}.4268$		
* D_2O	1.064	0.2203	$\bar{1}.3430$	0.6061	4.04
H_2O	1.064	0.3091	$\bar{1}.4901$		

(3) 3:5 Dinitrophenol.

Various buffer ratios were employed and the results are tabulated in Table IV. below.

Considerable difficulty was experienced in the preparation of this compound. It was thought likely that this compound might be obtainable most directly by the diazotisation of 3:5 dinitroaniline and boiling the resulting diazo compound with water.

No direct reference to this method was found in the literature and after preparing the 3:5 dinitroaniline by oxidising tri-nitro-toluene (Clarke and Hartman, Organic Syntheses 2, 95, 1922.) to trinitrobenzoic acid, decarboxylating to trinitrobenzene (Clarke and Hartman, Organic Syntheses 2, 93,1922.) and reducing by means of Ammonium Hydrogen Sulphide (Flurscheim, J. prakt. Chem. 71, 537, 1905.) attempts at diazotisation were made on small portions of the 3:5 dinitroaniline according to the following references;

1. Hodgson and Walker, J.C.S. 1620, 1933.
2. Manke, Organic Synthesês, 8, 80, 1928.
3. Ber. 38, 3506, 1905.
4. "The Aromatic Diazo Compounds" by Saunders.

None of these methods met with success.

The compound was prepared in the following way starting from tri-nitro-toluene. The tri-nitro-toluene (36 gm.) was mixed with concentrated sulphuric acid (360 gm.) and stirred mechanically while powdered sodium dichromate (54 gm.) was added gradually, the temperature being kept at 45-55°C during the oxidation. The mixture was poured on ice and the crude 2:4:6 trinitrobenzoic acid filtered and washed (Clarke and Hartman, Organic Syntheses 2, 95, 1922.). It is then decarboxylated by neutralising with sodium hydroxide at a temperature below 45°C, filtering off the liquid, then adding acetic acid and heating, stirring mechanically all the time, (Clarke and Hartman, Organic Syntheses, 2, 93, 1922.). The trinitrobenzene separates as a frothy layer which is filtered off and crystallised from glacial acetic acid, M.P. 120°C. The trinitrobenzene (10 gm.) was converted to the 3:5 dinitroanisole by placing it in a flask with 1.5 gm. sodium dissolved in 100 ccs. of methyl alcohol and allowing to stand at room temperature for two days. Needle shaped crystals separated from the dark red solution, (Holleman and Wilhelmy Rec. des Trav. Chem., 21, 432.). These crystals were filtered and washed. Recrystallisation from ethyl alcohol did not improve the M.P. 105°c and a 90% yield was obtained in each experiment tried. The hydrolysis of this compound was effected by heating the dinitroanisole with 4-5 moles of concentrated sulphuric acid in an open vessel maintained at a temperature of 130°C for a period of six hours, (Hantzsh, Ber., 40, 341.). Water was added to the dark brown sludge remaining and the resulting solution extracted with ether. The yellowish impure substance obtained on removing the ether gave the colour reaction but was very difficult to obtain in the pure form. This was acheived eventually by recrystallising from dilute hydrochloric acid and drying the crystals so obtained for several hours. These crystals were needle shaped and transparent giving a reasonably good melting point at 56-57°C.

This suggested a hydrated form and after trying several other methods the pure 3:5 dinitrophenol was obtained by placing these crystals in a vacuum desiccator containing phosphorus pentoxide. After several hours they became opaque giving a sharp melting point at 124°C.

All readings were made at a wavelength of 4500 A.U.

TABLE IV.

Solvent	$\log \frac{[Na_2HPO_4]}{[KH_2PO_4]}$	$\frac{d'}{d'' - d'}$	$\log \frac{d'}{d'' - d'}$	$\log K_h/K_d$	K_h/K_d
D_2O	$\bar{1}.9620$	1.636	0.2138	0.5173	3.29
H_2O	$\bar{1}.9620$	1.871	0.2721		
D_2O	0.0071	1.523	0.1826	0.4787	3.01
H_2O	0.0071	1.593	0.2023		
D_2O	0.0216	1.625	0.2108	0.5229	3.33
H_2O	0.0216	1.882	0.2747		
D_2O	0.1572	2.000	0.3010	0.5260	3.36
H_2O	0.1572	2.333	0.3680		
D_2O	0.2693	2.339	0.3681	0.5120	3.25
H_2O	0.2693	2.637	0.4211		

Mean value of K_h/K_d is 3.25.

(4) Note on the determination of K_h/K_d for the indicator Brom-Thymol-Blue.

Brode (J.A.C.S., 46, 581, 1926.) has determined the absorption spectra of certain indicators and their variation with change of hydrogen ion concentration. He found that the absorption bands of the indicators studied did not shift gradually in wavelength but merely in intensity. By using the same quantity of indicator in all solutions the hydrogen ion concentration of an unknown solution may be determined by comparing the height of the absorption band with those obtained from solutions of known hydrogen ion concentration. As the phosphate buffers used in (1) above were suitable, an examination of the behaviour of this indicator in deuterium oxide was considered worthy of investigation. The indicator Brom-Thymol -Blue is a substitution derivative of phenolsulphonphthalein whose dissociation constant is 7.01×10^{-7} i.e. its acid constituent is of a strength comparable to that of the acid constituent of the buffer.

The indicator solution was prepared as described in Clark "The Determination of Hydrogen Ions" 2nd. Edition p. 80. 0.10 gm. of the powdered indicator (obtained from British Drug Houses Ltd.) was dissolved by grinding in an agate mortar with 3.2 ml. of N/20 sodium hydroxide and making up to 25 ml. with distilled water. This gives a 0.4% solution of the dye itself. The concentration of Brom-Thymol-Blue used in these determinations was 0.5 ml. of the above 0.4% solution in 100 ml. of the buffer solution employed.

Preliminary observations revealed that the solution in the buffer solutions employed was a bluish green colour in both solvents. After the addition of alkali the colour changed to an intense blue. A rough spectrum analysis revealed that there were two main bands the one under investigation having a maximum at 6170 A.U. All readings were made at this wavelength. The molarity of the buffer solutions was 0.01 M. The results are given in Table V. Since equal quantities of primary and secondary phosphate were used to prepare the buffer solution $\log [Na_2HPO_4]/[KH_2PO_4] = 0$.

TABLE V.

Solvent	$\frac{d'}{d'' - d'}$	$\log \frac{d'}{d'' - d'}$	$\log K_h/K_d$	K_h/K_d
D_2O	0.7275	$\bar{1}.8618$	0.4301	2.69
H_2O	0.6806	$\bar{1}.8329$		

DETERMINATIONS MADE USING ACETATE BUFFER SOLUTIONS.

These solutions were prepared from A.R. reagents and carefully standardised. Fairly concentrated solutions (1.0 M.) can be prepared with all the substances employed, namely Acetic acid, Sodium Acetate and Sodium Chloride (added to obtain constant ionic strength) and the following method of investigating the behaviour of 2:4 dinitrophenol, 2:5 dinitrophenol, 2:6 dinitrophenol in deuterium oxide and determining the ratio K_h/K_d was adopted. A weighed quantity of the dinitrophenol was added to a weighed quantity of deuterium oxide giving a solution of suitable concentration for examination in the spectrophotometer. A normal solution of a suitable buffer mixture is then prepared and its density determined. A small quantity of this buffer solution is then weighed out and sufficient deuterium oxide dinitrophenol solution added to bring the normality to 0.01 M. The analogous solution in H_2O is then prepared by taking 1 ml. of the concentrated aqueous buffer solution and adding distilled water so that the normality is exactly the same as for the deuterium oxide solution.

The dinitrophenols were obtained from British Drug Houses Ltd. and recrystallisation did not improve their melting points which were sharp. The wavelength at which all readings were made was 4500 A.U.

The results obtained are summarised in Tables VI, VII, and VIII.

TABLE VI.

Results for 2:4 Dinitrophenol

Solvent	$\log \frac{[HAc]}{[NaAc]}$	$\frac{d'}{d'' - d'}$	$\log \frac{d'}{d'' - d'}$	$\log K_h/K_d$	K_h/K_d
D_2O	$\bar{1}.1746$	0.7541	$\bar{1}.8774$	0.4403	2.76
H_2O	$\bar{1}.1746$	0.7290	$\bar{1}.8627$		

TABLE VII.

Results for 2:5 Dinitrophenol

Solvent	$\log \frac{[HAc]}{[NaAc]}$	$\frac{d'}{d'' - d'}$	$\log \frac{d'}{d'' - d'}$	$\log K_h/K_d$	K_h/K_d
D_2O	0.6218	1.447	0.1606	0.4460	2.79
H_2O	0.6218	1.418	0.1516		

TABLE VIII.

Results for 2:6 Dinitrophenol

Solvent	$\log \frac{[HAc]}{[NaAc]}$	$\frac{d'}{d'' - d'}$	$\log \frac{d'}{d'' - d'}$	$\log K_h/K_d$	K_h/K_d
D_2O	1.000	1.928	0.2851	0.3807	2.40
H_2O	1.000	1.625	0.2108		

Extension of Method to the Determination of the Entropy of Ionisation

It was thought that this colorimetric method might usefully be extended to determine the entropy of ionisation of these nitrophenols and although the outcome of this work did not prove to be particularly useful it provides a good illustration of the experimental accuracy acheived in obtaining the above results.

It was felt that if values for the entropy of ionisation could be obtained for these nitrophenols it might be possible to relate them to possible resonance in the structures, (Stearn and Eyring, J. Chem. Phys., <u>5</u>, 113, 1937.). The values of entropies of ionisation so far as they have been determined have not shown any regularity, (Latimer, Chem. Rev. <u>18</u>, 349, 1936.).

If we consider the nitrophenol (HI) in an acetate buffer solution,

$$HI + Ac^- = I^- + HAc$$

the thermodynamic equilibrium is expressed by

$$K = \frac{[HI][Ac^-]}{[HAc][I^-]} = K_{HI}/K_{HAc}$$

$$= \frac{C_{HI}\ C_{Ac^-}}{C_{I^-}\ C_{HAc}} \cdot \frac{f_{HI}\ f_{Ac^-}}{f_{I^-}\ f_{HAc}}$$

where the "Cs" denote concentrations and the "fs" activity coefficients. The "Ks" are the thermodynamic equilibrium constants.

K_c was obtained as follows,

(1) C_{Ac^-}/C_{HAc} is the composition of the buffer solution which is known. C_{Ac^-} and C_{HAc} are obtained as weight concentrations.

(2) C_{HI}/C_{I^-} is obtained colorimetrically from readings on the spectrometer as described above (p. 42)

$$C_{HI}/C_{I^-} \quad = \quad d'' - d'/\,d'.$$

Values for (1) and (2) were obtained for a series of experiments in which the ionic strength (μ) was varied and by extrapolating to zero ionic strength where the activity coefficient term disappears K was determined.

$$K_c \quad = \quad K_{HI}/K_{HAc}$$

K_{HAc} has been thoroughly determined by Harned and Ehlers (J.A.C.S. <u>54</u>, 1355, 1932.) for various temperatures so that we can obtain K_{HI} for various temperatures if K_c is determined over the same temperature range.

From a knowledge of the variation of K_{HI} with temperature we can calculate the value of the entropy of ionisation as follows. From the well known thermodynamic relation we have

$$\Delta F \quad = \quad -RT \log K_{HI}$$

where ΔF is the free energy change, R the gas constant and T the temperature on the Kelvin scale. We further know that

$$\frac{d(\Delta F)}{dT} \quad = \quad \Delta S$$

where ΔS is the entropy change in the process i.e. the entropy of ionisation. Thus if we determine K_{HI} say at 25°C and 15°C we have

$$\Delta S^{25}_{15} = \Delta F_{25} \sim \Delta F_{15} / 10$$

The Determination of the Entropy of Ionisation of 2:5 Dinitrophenol

Experimental Details

The instrument employed was the spectrophotometer described above the only difference being that water jacketed polarimeter tubes were substituted for the silica cells. The rate of flow of water through the jacket, heated by passage through an electrically heated copper tube was varied by raising or lowering a constant head apparatus. This gave a rapid and accurate method of obtaining any desired temperature over the range 12 - 40°c. A thermometer dipping into the actual solution registered the temperature. The pointalite lamp was maintained at a constant voltage.

Solutions

The solutions were prepared from A.R. sodium acetate and A.R. glacial acetic acid whilst the 2:5 dinitrophenol was obtained from British Drug Houses Ltd. The melting point of the last did not improve after recrystallisation. The concentration of the 2:5 dinitrophenol in these solutions is that which is suitable for observation but it is too small to be weighed. A ratio of sodium acetate: acetic acid = 3.448 : 1 was employed as this gave convenient readings of d' and d" on the density scale. These acetate buffer solutions are apt to decay on standing at room temperature. This was avoided by adding a small amount of 2:5 dinitrophenol to the stock solution which was kept in a refrigerator.

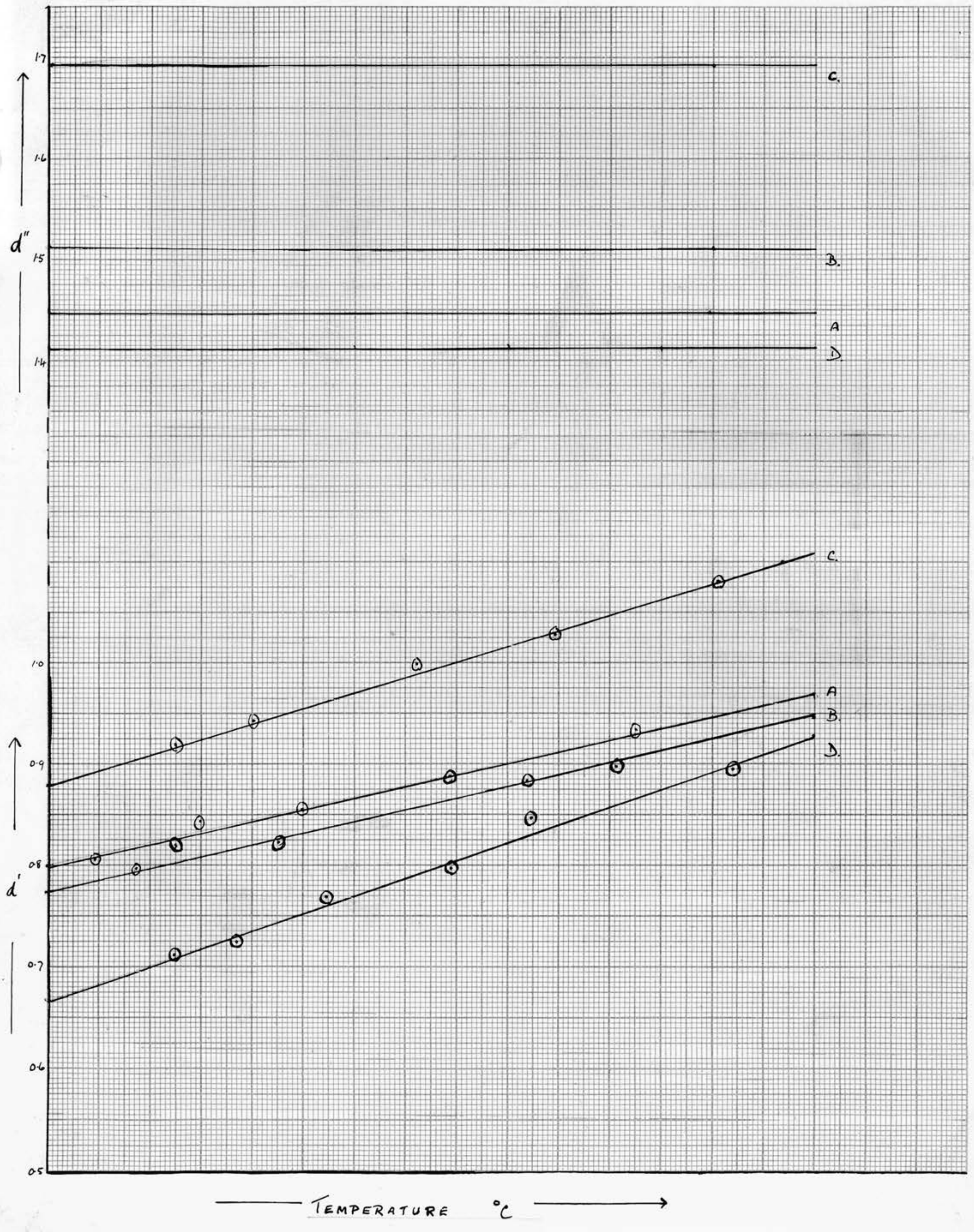
Method of obtaining readings.

In the upper beam of light is placed a control cell containing the solvent whilst the cell containing the buffer solution is placed in the lower beam. A few drops of buffer solution, to which has been added 2:5 dinitrophenol to give a fairly high concentration, are then added to give a suitable value of d' on the density scale. A series of readings (an average of ten) is taken for each of several temperatures and as the d' - temperature plot is linear the variation of d' with temperature is determined. Sufficient alkali is then added to fully dissociate the nitrophenol and d" determined. Experiments prove d" to be constant over the range of temperature investigated.

Results

Many experiments were performed and sample results are quoted for four of these experiments to illustrate the method. The experimental values for d' are plotted against the temperature in Figure I whilst the corresponding d" value is also indicated.

FIGURE I



The values of d' at 15°, 25°, and 35° are obtained from Figure I and are collected in Table IX along with the values of the ionic strength. d'_t is obtained from d' after correcting for the zero reading.

TABLE IX.

Expt. No,	Ionic Strength	T°C	d'	d'_t	d''	$d'' - d'$	$\frac{d'' - d'}{d'_t}$
A_1	0.07724	15°	0.828	0.811	1.448	0.620	0.764
A_2	0.07724	25°	0.885	0.868	1.448	0.563	0.648
A_3	0.07724	35°	0.942	0.925	1.448	0.506	0.548
B_1	0.03984	15°	0.801	0.799	1.515	0.714	0.897
B_2	0.03984	25°	0.856	0.854	1.515	0.659	0.774
B_3	0.03984	35°	0.911	0.909	1.515	0.604	0.667
C_1	0.02025	15°	0.918	0.914	1.693	0.775	0.847
C_2	0.02025	25°	0.995	0.991	1.693	0.698	0.704
C_3	0.02025	35°	1.072	1.068	1.693	0.621	0.582
D_1	0.01069	15°	0.712	0.706	1.413	0.701	0.985
D_2	0.01069	25°	0.800	0.792	1.413	0.613	0.774
D_3	0.01069	35°	0.886	0.880	1.413	0.527	0.595

The hydrogen ion concentration C_{H^+} for solutions of the above composition and ionic strength is about 0.000005 mols./ 1000 gms. H_2O. C_{NaAc} and C'_{HAc} are known from the weights of sodium acetate and acetic acid added so that taking in account the dissociation of acetic acid we obtain

$$C_{Ac^-} = C_{NaAc} + C_{H^+}$$

and $C_{HAc} = C'_{HAc} - C_{H^+}$

The values of C_{Ac^-}/C_{HAc} for the above experiments are set out in Table X along with the value of K_c calculated from

$$K_c = C_{Ac^-}/C_{HAc} \,.\, d'' - d'/\, d'_t$$

TABLE X

Experiment No.	T°C	C_{Ac^-}/C_{HAc}	$\frac{d'' - d'}{d'_t}$	K_c
A_1	15°	3.449	0.764	2.575
A_2	25°	3.449	0.648	2.236
A_3	35°	3.449	0.548	1.934
B_1	15°	3.450	0.897	3.094
B_2	25°	3.450	0.774	2.670
B_3	35°	3.450	0.667	2.301
C_1	15°	3.4518	0.847	2.924
C_2	25°	3.4518	0.704	2.431
C_3	35°	3.4518	0.582	2.009
D_1	15°	3.4554	0.985	3.402
D_2	25°	3.4554	0.774	2.674
D_3	35°	3.4554	0.595	2.055

The graph of K_c against μ is shown in Figure 2 and as is indicated by theses results, which are typical of the large number obtained, extrapolation to zero ionic strength is not an accurate process. It was because of the erratic behaviour of these results that this piece of work had to be abandoned.

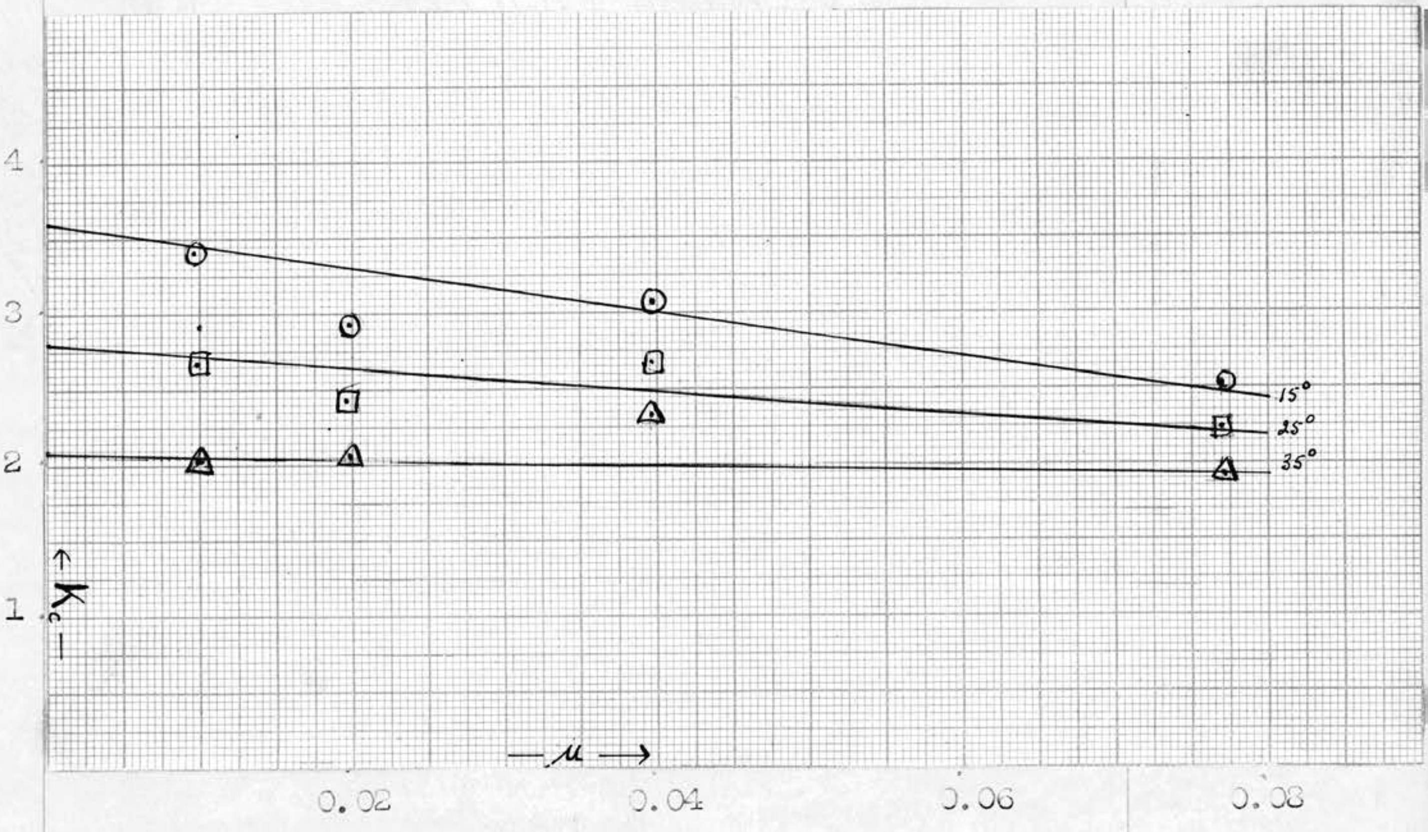


FIGURE II.

If we assume the values obtained by taking the lines drawn in Figure II we find,

$K_c^{15} = 3.6 \quad K_c^{25} = 2.8 \quad K_c^{35} = 2.1$

From Harned and Ehlers (J.A.C.S., 54, 1355, 1932.) we have

$$K^{15}_{HAc} = 1.743 \times 10^{-5} \qquad K^{25}_{HAc} = 1.753 \times 10^{-5}$$

$$K^{35}_{HAc} = 1.750 \times 10^{-5}$$

from which we can calculate that

$$K^{15}_{HI} = 6.27 \times 10^{-5} \qquad K^{25}_{HI} = 4.91 \times 10^{-5}$$

$$K^{35}_{HI} = 3.68 \times 10^{-5}$$

The corresponding values of ΔF calculated from

$$\Delta F = -2.303\ R.T \log K_{HI}$$

are

$$\Delta F^{15} = 5535 \text{ cals.} \qquad \Delta F^{25} = 5876 \text{ cals.}$$

$$\Delta F^{35} = 6250 \text{ cals.}$$

from which we have

$$\Delta S^{25}_{15} = 34.1 \text{ cals} \qquad \Delta S^{35}_{25} = 37.4 \text{ cals.}$$

Thus for the average value of the entropy of ionisation of 2:5 Dinitrophenol we obtain 35.7 cals.

DISCUSSION.

The results obtained for the series of nitrophenols and Brom-Thymol-Blue are collected in Table XI. The buffer solutions employed are shown in column two whilst details of buffer ratios etc. are given in the tables referred to in column three. In the fourth column the most probable value of K_h taken from International Critical Tables is given in each case. pK is equal to -log K_h. The last column gives the ratio for K_h/K_d as determined in the various experiments. As mentioned in the experimental section the heavy water solutions were not 100% D_2O and a correction to give the value at 100% D_2O must be made. In the case of the determinations using acetate buffers 1% H_2O was introduced to the 99.6% D_2O solution. In the case of the phosphate buffers the K_h/K_d value is that obtained using 99.6% D_2O.

TABLE XI.

Substance	Buffer	Table	K_h	pK	K_h/K_d
2:6 Dinitrophenol	Acetate	VIII	2.6×10^{-4}	3.58	2.40
2:4 Dinitrophenol	"	VI	9.6×10^{-5}	4.02	2.76
2:5 Dinitrophenol	"	VII	6.8×10^{-6}	5.17	2.79
3:5 Dinitrophenol	Phosphate	IV	2.0×10^{-7}	6.70	3.25
P - Nitrophenol	"	II	5.8×10^{-8}	7.24	2.90
O - Nitrophenol	"	II	5.6×10^{-8}	7.25	2.93
M - Nitrophenol	"	III	3.9×10^{-9}	8.41	3-4
Brom-Thymol-Blue	"	V	7.0×10^{-7}	6.15	2.69

Orr and Butler (J.C.S., 330, 1937.) have discussed the kinetic and thermodynamic activity of protons and deuterons in water - deuterium oxide solutions and the following equation is given relating the dissociation constants of weak acids in isotopic water mixtures. If we define

$$n = \frac{D}{D + H} = \text{Deuterium fraction}$$

$$K_h = \frac{[A^-]\alpha_{H^+}}{[HA]} \quad \text{the dissociation constant in pure } H_2O$$

$$K_d = \frac{[A\ ]\alpha_{D^+}}{[DA]} \quad \text{the dissociation constant in pure } D_2O$$

and the dissociation constant in water containing a fraction n of deuterium as

$$K_n = \frac{\sum H_3O^+ \, f^+[A^-]}{\sum [HA].}$$

where the quantities in square brackets represent activities, then we have the following relation,

$$K_h/K_n = 1/Q'(n) \left([H_2O]^{1/2} + \frac{K_h/K_1 \, [D_2O]^{1/2}}{\sqrt{L}} \right)$$

where

$$L = \frac{\alpha^2_{H^+}[D_2O]}{\alpha^2_{D^+}[H_2O]}$$

When $n = 1$ $1/Q'(n) = \sqrt{L}$.

Q'(n) is a function the nature of which has been established empirically by equilibrium measurements (Gross, Steiner and Süss, Trans. Far. Soc., 32, 883, 1936; Orr and Butler, J.C.S., 330, 1937.) and which can now be calculated theoretically, (Nelson and Butler J.C.S., 958, 1938.). The calculated values of Q'(n) for various values of n are shown in Figure III.

By means of this graph we obtain a series of values of Q'(n) for values of n between 0.90 and 1.00. Knowing n the deuterium fraction which is obtained from the amount of H_2O present in these mixtures $[D_2O]$ and $[H_2O]$ can be calculated (Orr and Butler J.C.S., 332, 1937.) The values of K_h/K_n, for various ratios of K_h/K_1 obtained using the above equation are shown in Table XII.

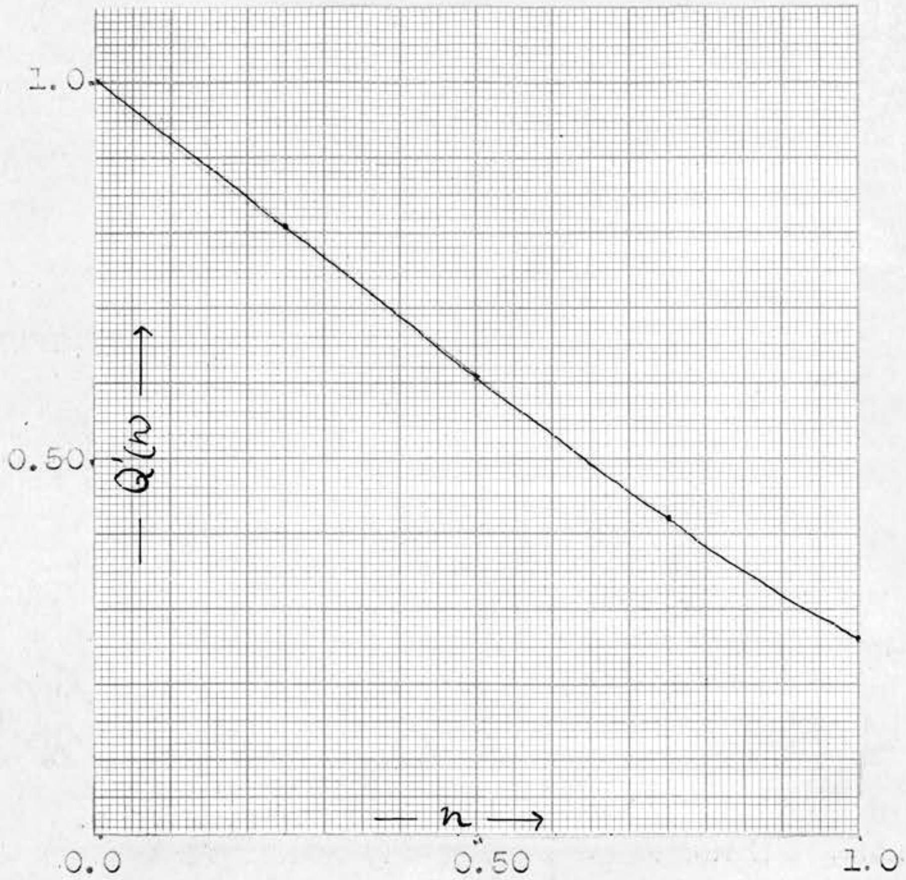


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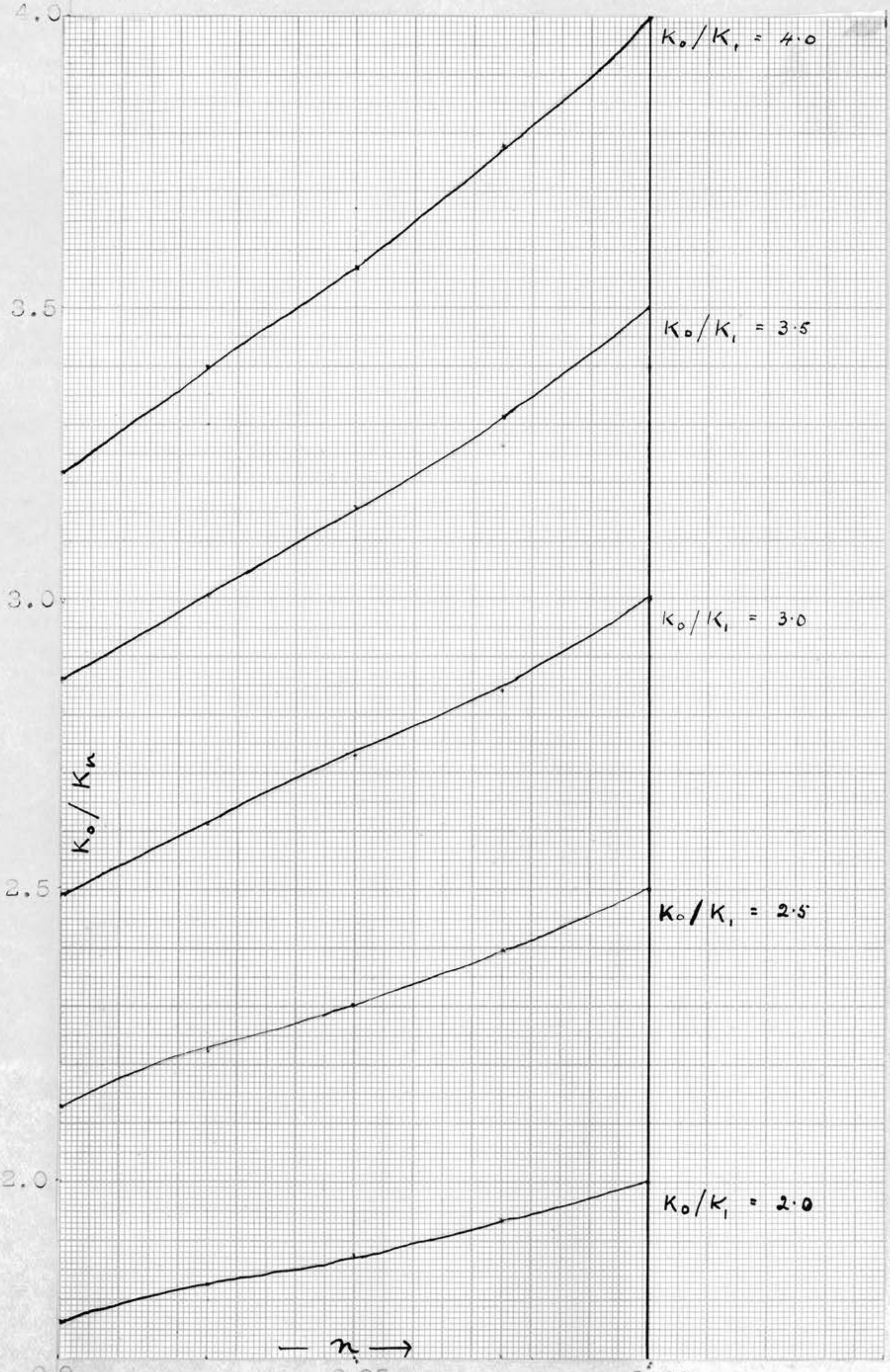
TABLE XII

n	Q'(n)	[D_2O]	[H_2O]	K_h/K_n values for K_h/K_1 equal to				
				2.0	2.5	3.0	3.5	4.0
0.90	0.322	0.901	0.1	1.766	2.13	2.496	2.86	3.22
0.925	0.305	0.926	0.075	1.828	2.226	2.615	3.01	3.40
0.95	0.290	0.95	0.05	1.875	2.301	2.73	3.155	3.57
0.975	0.275	0.975	0.025	1.935	2.399	2.84	3.315	3.77
1.00	0.260	1.00	0.00	2.00	2.50	3.00	3.50	4.00

The relation between n and the ratio K_h/K_n is shown in Figure IV.

FIGURE IV.


4.0
3.5
3.0
2.5
2.0
K_0/K_n
— n →
0.9
0.95
1.00
K_0/K_1 = 4·0
K_0/K_1 = 3·5
K_0/K_1 = 3·0
K_0/K_1 = 2·5
K_0/K_1 = 2·0

From Figure IV we readily obtain the value of K_h/K_d corrected to 100% D_2O i.e. when n = 1 by comparing the slope of the curve which would pass through the point determined for the known value of n in the solutions employed and noting where it cuts the axis. In the case of the acetate buffer solutions n was found to be 0.992 and in the case of phosphate solutions n was equal to 0.998.

The corrected values of K_h/K_d are listed in Table XIII along with the I.C.T. values for K_h.

TABLE XIII.

Substance	K_h	K_h/K_d	Corrected value K_h/K_d (100% D_2O)
2:6 Dinitrophenol	2.6×10^{-4}	2.40	2.43
2:4 Dinitrophenol	9.6×10^{-5}	2.76	2.81
2:5 Dinitrophenol	6.8×10^{-6}	2.79	2.84
3:5 Dinitrophenol	2.0×10^{-7}	3.25	3.27
P - Nitrophenol	5.8×10^{-8}	2.90	2.92
O - Nitrophenol	5.6×10^{-8}	2.93	2.95
M - Nitrophenol	3.9×10^{-9}	3-4	
Brom-Thymol-Blue	7.01×10^{-7}	2.69	2.70

Considering these results we see that in most cases the ratios K_h/K_d approximate to the value of three and comparing the ratios with the dissociation constants of the acid in water we see that with decreasing strength of acid there is an increasing value of the ratio K_h/K_d which is the result originally forecast by Halpern. It would further appear however that the factor associated with the strength of the acid is not the only one affecting the K_h/K_d ratio and the unusually high value for the meta compounds would suggest that we are dealing with a constitutive effect peculiar to the meta position in these nitrophenols.

The results for m - nitrophenol are not so reliable as the others because the phosphate buffer did not conveniently cover the pH range required in the investigation of this substance and no other buffer was available whose dissociation constant in deuterium oxide was known.

As was shown in the introduction Hornel and Butler (J.C.S., 1365, 1936.) stated that the ratio K_h/K_d is determined mainly by the force constant between the proton and the acid anion a_A rather than by the strength of the bond and the following equation relating the ratio and $-\log_{10}K_h$ was givem, (p. 26.)

$$\log_{10} K_h/K_d = -2.21(1 - a_A/a_W) - 0.0042 (a_A/a_W) \log K_h$$

The nitrophenols investigated here are all the same type of acids and we might expect to find that a_A has the same value in each case. Table XIV shows that this is true to a large extent.

TABLE XIV

Acid	$\log_{10}K_h/K_d$	$-\log_{10}K_h$	a_A/a_w
2:6 Dinitrophenol	0.381	3.585	1.17
2:4 Dinitrophenol	0.440	4.018	1.19
2:5 Dinitrophenol	0.446	5.168	1.19
3:5 Dinitrophenol	0.516	6.699	1.22
P - Nitrophenol	0.462	7.237	1.19
O - Nitrophenol	0.467	7.252	1.19

It is of interest to examine these results in conjunction with those recently obtained by Rule and La Mer, (J.A.C.S., 60, 1974, 1938.). Using a quinhydrone electrode these workers revised several values of K_h/K_d and claim a greater accuracy in so doing than had been acheived previously. As these authors use different values for K_{HAc}/K_{DAc} and $K_{H_2PO_4^-}/K_{D_2PO_4^-}$ the K_h/K_d ratios obtained in the present investigations have been recalculated using these values. These (omitting m-nitrophenol) are set out in Table XV along with the results quoted by Rule and La Mer.

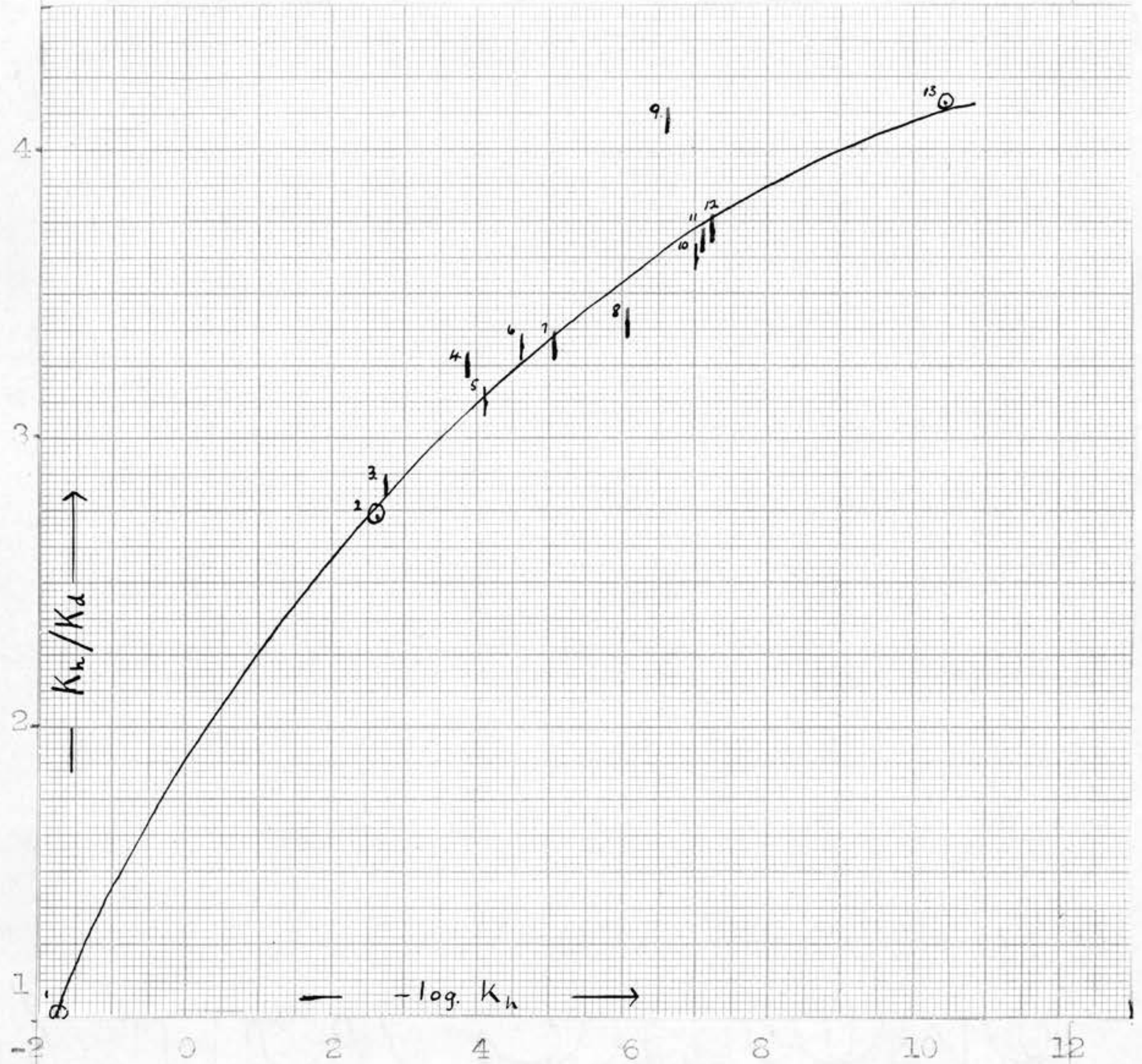
TABLE XV

No.	Acid	$-\log K_h$	K_h/K_d	Reference
1.	H_3O^+	-1.74	(1)	
2.	Chloroacetic Acid	2.76	2.74	1
3.	2:6 Dinitrophenol	3.58	2.84	
4.	2:4 Dinitrophenol	4.02	3.28	
5.	Benzoic Acid	4.21	3.13	3
6.	Acetic Acid	4.74	3.33	2
7.	2:5 Dinitrophenol	5.17	3.32	
8.	Brom-Thymol-Blue	6.15	3.40	
9.	3:5 Dinnitrophenol	6.70	4.11	
10.	$H_2PO_4^-$	7.19	3.62	3
11.	P - Nitrophenol	7.24	3.67	
12.	O - Nitrophenol	7.25	3.71	
13.	Hydroquinone	10.58	4.16	3

References

1. Lewis and Schutz, J.A.C.S., 56, 1913, 1934.
2. Korman and La Mer, J.A.C.S., 58, 1396, 1936.
3. Rule and La Mer, J.A.C.S., 60, 1974, 1938.

The curve obtained by Rule and La Mer by plotting $-\log K_h$ against $\log K_h/K_d$ is reproduced in Figure V and the values obtained in the present investigations are added. These are marked in red. The numbers refer to Table XV.



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These points lie close to the curve and would seem to support Rule and La Mer's statement that the ratios decrease as the strength of the acid increases and may become unity for acids as strong as H_3O^+.

PART III.

A NOTE

on the

MUTAROTATION OF GALACTOSE.

Introduction

Nelson (Thesis for Ph.D. Edin.) in the course of an investigation of mutarotation under various circumstances in heavy water found the catalytic coefficients of H_2O and H_3O^+, from which it appeared

that for H_2O $\quad K_{Galactose} / K_{Glucose} \quad = 2.06$

and for H_3O^+ $\quad K_{Galactose} / K_{Glucose} \quad = 1.33$

Since H_2O acts as a basic catalyst, it seemed desirable to discover whether this ratio was constant for other acids and bases. Therefore the catalytic constants of the galactose reaction with acetic and chloroacetic acids and acetate and phosphate ions were determined.

Experimental

In determining the catalytic coefficients of the following acids and bases solutions of weak acids in presence of their salts were employed, e.g. if we consider the catalysis of the mutarotation of galactose by acetic acid - acetate mixtures the catalysts will be water, acetate ion (A^-) and undissociated acetic acid (HA). The observed velocity of reaction therefore will be

$$V_{obs.} = k_{A^-}C_{A^-} + k_{HA}C_{HA} + k_{H_2O}C_{H_2O} \qquad \ldots\ldots(1)$$

where the ks are the catalytic coefficients and the Cs are the concentrations of the various species. If a solution is prepared such that the concentration of acetic acid and acetate are equal, say x, we have

$$V_{obs.} = k_{A^-}x + k_{HA}x + k_{H_2O}C_{H_2O}$$
$$= (k_{A^-} + k_{HA})x + k_{H_2O}C_{H_2O} \qquad \ldots\ldots(2)$$

If therefore $V_{obs.}$ is plotted against x the concentration of acetic acid (or acetate) the slope will give the value of $(k_{A^-} + k_{HA})$ whilst the intercept on the $V_{obs.}$ axis will give the velocity due to the water. By increasing the concentration of the acetate by a known factor, a times say, we have the relation

$$V'_{obs} = k_{A^-}a.x + k_{HA}x + k_{H_2O}C_{H_2O} \qquad \ldots\ldots(3)$$

(3) - (2)

$$V'_{obs.} - V_{obs} = k_{A^-}a.x - k_{A^-}x$$
$$= k_{A^-}x(a - 1) \qquad \ldots\ldots(4)$$

In this way k_{A^-} can be determined and since $(k_{A^-} + k_{HAc})$ has already been obtained k_{HAc} is readily found.

Kinetic Measurements

The rates of the mutarotations were observed in a Schmidt and Haensch polarimeter reading to 0.01°. Since the change in specific rotation in the conversion of α-d-galactose to the equilibrium mixture of the α and β forms is fairly large viz.:-

$$\Delta[\alpha]_D^{12.5} = 60° \quad \text{for} \quad \alpha \longrightarrow \alpha + \beta$$

a solution of about two per cent α-d-galactose was used. A quantity of the galactose was carefully weighed into a small weighing tube and cooled to 15°C in the thermostat. The solvent containing the catalysing substances was also cooled to 15°C. A carefully measured volume of the latter was then added to the α-d-galactose and the mixture thoroughly shaken until solution was complete. The solution was then speedily transferred to a narrow bore two decimetre polarimeter tube by means of a thin capillary reaching to the bottom. The polarimeter tube, previously brought to 15°C. was surrounded by a water jacket through which water from the thermostat was rapidly circulated during the experiment. A reading of the rotation was taken as soon as possible using the sodium D line. This was taken as the beginning of the reaction and thereafter r readings were taken at suitable intervals of time t mins. Table I shows the observations for a typical experiment. If we write α_t = observed rotation at time t mins. from the start of the reaction, α_∞ = rotation on completion of the reaction, we have, since the reaction is monomolecular

$$\text{Rate of reaction} \quad k = \frac{2.303 \times \log_{10}(\alpha_t - \alpha_\infty)}{t}$$

The value of k is obtained by taking the slope of the graph log $(\alpha_t - \alpha_\infty)$ - t as indicated in Figure I which is the graph obtained from figures in Table I.

TABLE I.

t mins.	Polarimeter Reading	$(\alpha_t - \alpha_\infty)$	$\log.(\alpha_t - \alpha_\infty)$		
0.0	5.65°	2.32	0.365		
2.83	5.52°	2.19	0.340		
5.26	5.44°	2.11	0.324		
7.80	5.31°	1.98	0.297		
11.43	5.21°	1.88	0.274		
15.60	5.08°	1.75	0.243		
18.17	5.04°	1.71	0.233		
21.33	4.96°	1.63	0.212		
25.25	4.85°	1.52	0.182		
29.20	4.76°	1.43	0.155		
32.88	4.68°	1.35	0.130		
38.83	4.59°	1.26	0.100		
42.27	4.48°	1.15	0.067		
48.48	4.41°	1.08	0.033		
54.75	4.28°	0.95	$\bar{1}.977$	i.e.	-0.023
61.00	4.20°	0.87	$\bar{1}.940$	"	-0.060
70.13	4.07°	0.74	$\bar{1}.869$	"	-0.131
79.72	4.00°	0.67	$\bar{1}.826$	"	-0.174
87.15	3.94°	0.61	$\bar{1}.785$	"	-0.215
97.77	3.83°	0.50	$\bar{1}.699$	"	-0.301
107.17	3.75°	0.42	$\bar{1}.623$	"	-0.377
120.85	3.69°	0.36	$\bar{1}.556$	"	-0.444
132.41	3.67°	0.34	$\bar{1}.532$	"	-0.478

Concentration of acetic acid and acetate = 0.08 M.

Temperature = 15.00 ± 0.05°

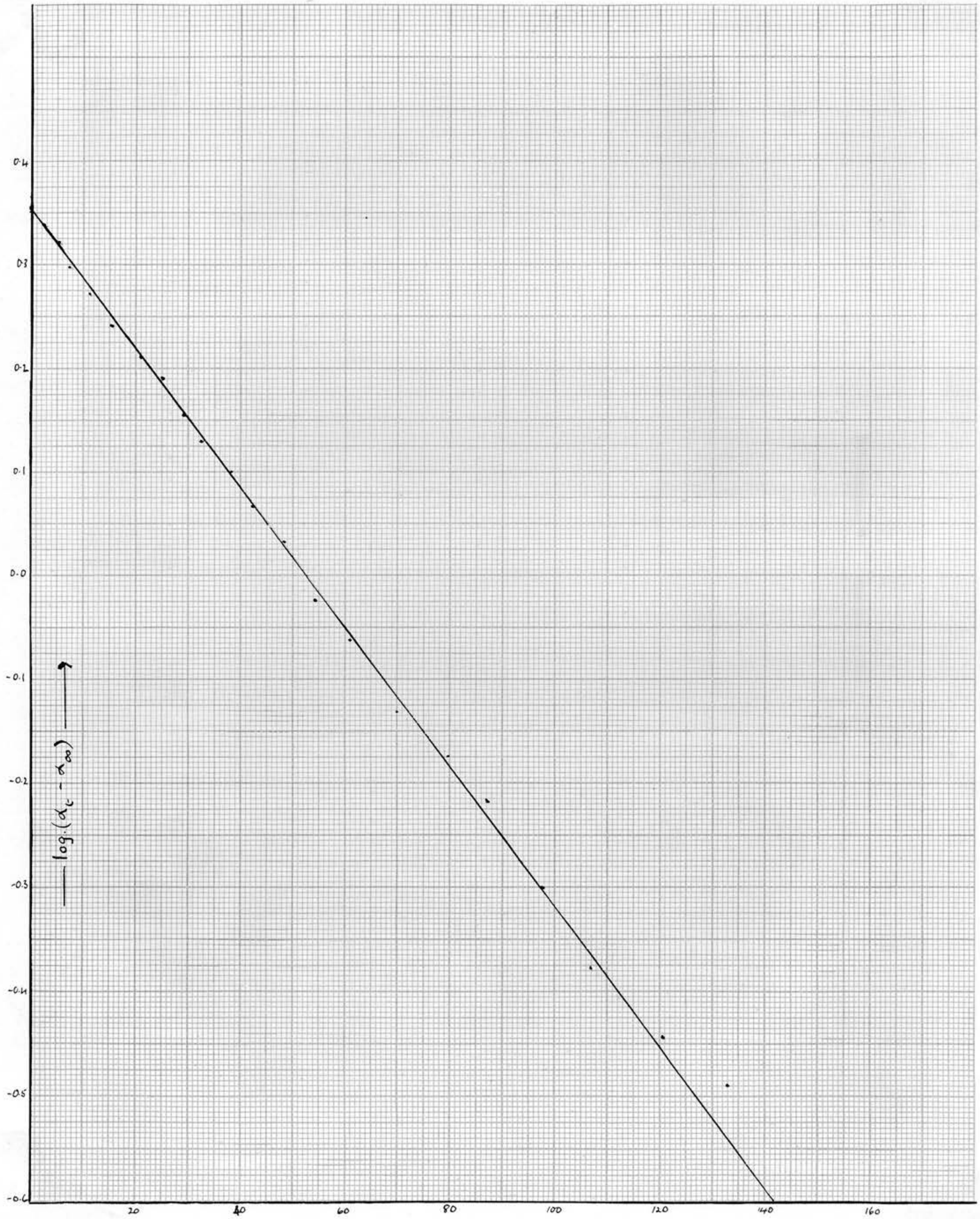
Reading after 24 hours = 3.33°

Wavelength of source of light = 5900 A.U.

Materials

The α-d-galactose was the pure commercial product and the salts and acids used were all A.R. reagents supplied by British Drug Houses Ltd. All weighing tubes, etc., were carefully cleaned using chromic acid and steam.

FIGURE I.


0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
20
40
60
80
100
120
140
160
log.($\alpha_t - \alpha_\infty$) →
t MINS. →

Results

Acetic Acid - Sodium Acetate Solutions

Using the procedure described above the rates of reactions in two series of acetic acid - sodium acetate solutions were determined. The first series were performed with solutions in which the concentrations of acetic acid and sodium acetate were identical i.e. the ratio [HAc] : [NaAc] = 1 and the second series with solutions where [HAc] : [NaAc] = 1 : 2.5. On the basis of the theory given above only one reading of the second series would be required to obtain the desired catalytic coefficients but several values of the velocity constant were made and a graph obtained to make the value as exact as possible. The results obtained are collected in Table II and the concentration - velocity graphs drawn in Figure II.

TABLE II

	$k \times 10^3$	
Concentration of Acetic Acid	HAc : NaAc 1 : 1	HAc : NaAc 1:: 2.5
0.0166 M.		13.92
0.020 M.		14.20
0.0248 M.	12.87	
0.0332 M.		15.16
0.040 M.	12.77	
0.0496 M.	13.93	
0.050 M.		16.76
0.0664 M.	14.95	
0.080 M.	15.45	
0.10 M.	16.30	21.50

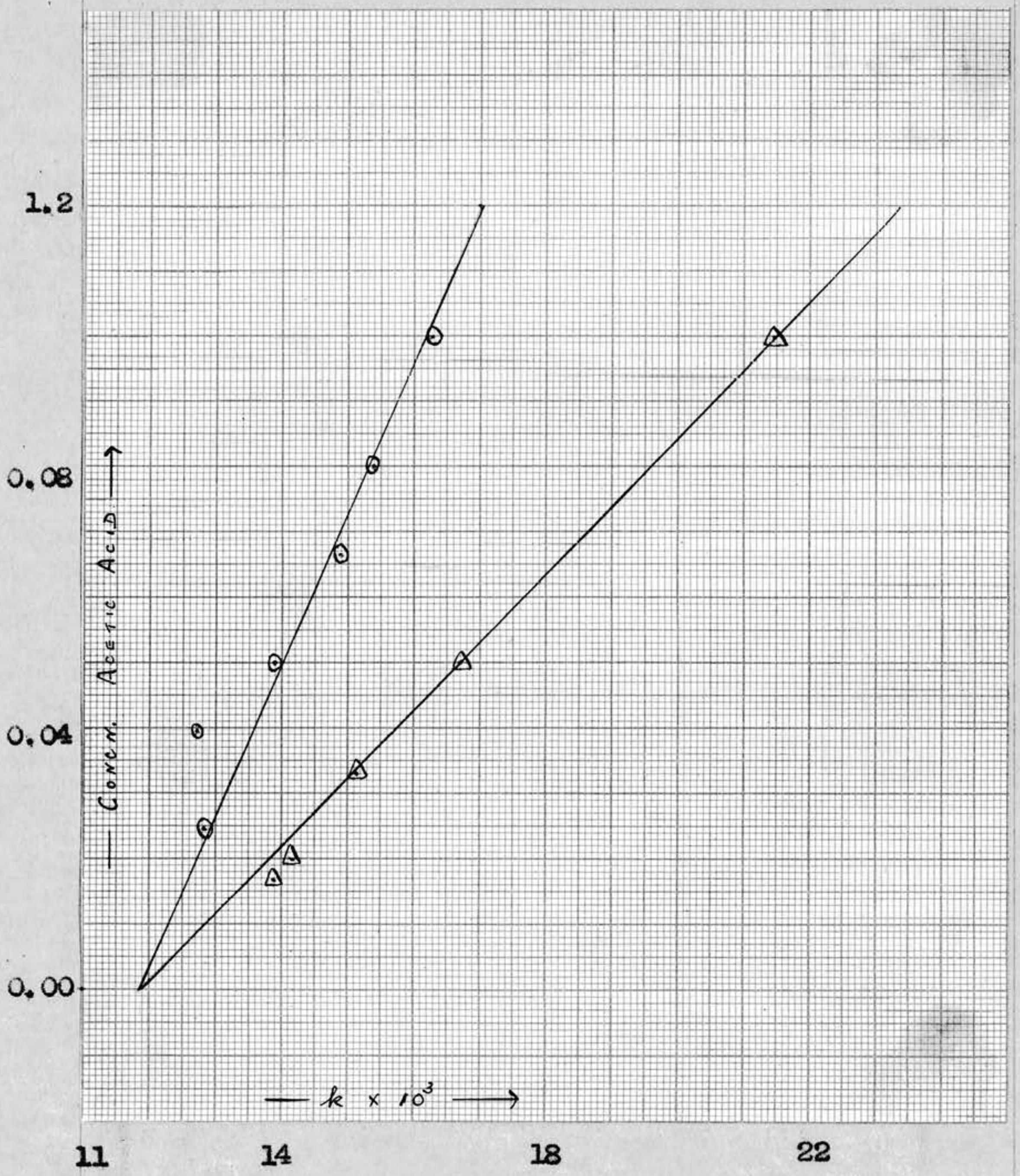


FIGURE II.

Calculation of the Catalytic Coefficients.

Applying the above equations (2) and (4) respectively to the case of acetic acid - acetate mixtures we have the relations

$$V_{obs} = (k_{Ac^-} + k_{HAc})\,x + k_{H_2O} C_{H_2O}$$

and $V'_{obs} - V_{obs} = k_{Ac^-}\,x\,(a - 1)$.

From Figure II for the value $x = 0.1$ M we have $V'_{obs.} = 21.5$ from graph B and $V_{obs.} = 16.15$ from graph A and since $a = 2.5$ we have

$$(21.5 - 16.15) \times 10^{-3} = k_{Ac^-} . 0.1 \times 1.5$$

or $k_{Ac^-} = 5.35 \times 10^{-3}/0.15$

$$= \underline{35.7 \times 10^{-3}}$$

The slope of graph A which we have already shown to be $V_{obs}/x = k_{Ac^-} + k_{HAc} = 42.6 \times 10^{-3}$

therefore $\underline{k_{HAc} = 6.9 \times 10^{-3}}$.

The two lines intersect at $k = 11.9 \times 10^{-3}$ at $x = 0$. We therefore have this as the water rate of catalysis of the mutarotation of galactose.

Phosphate Solutions

The same method was used in the case of mixtures of primary and secondary phosphates. The salts used were potassium hydrogen phosphate (KH_2PO_4) and sodium phosphate (Na_2HPO_4). The results obtained are set out in Table III and the variation of the velocity constant with concentration shown in graphs IIIa and IIIb.

The accuracy obtained in these determinations was not so high as in the other cases and the extent of the experimental error can be estimated from the figures given for duplicate experiments in Table III. In all cases good linear graphs were obtained in the determination of k. The concentration range was from 0.002 to 0.02 M.

TABLE III.

Concentration of Na_2HPO_4	$k \times 10^3$ $KH_2PO_4 : Na_2HPO_4$ 1 : 1	 $KH_2PO_4 : Na_2HPO_4$ 2.5 : 1
0.020 M.	42.47	49.78
0.016 M.	42.93	
0.014 M.	36.38	
0.012 M.	36.26	
0.010 M.	27.16	32.32, 29.51
0.008 M.	21.74	24.84
0.006 M.	22.77, 22.27, 24.79. Aver. 23.28	24.41
0.004 M.	17.28, 1802 Aver. 17.65	20.38
0.002 M.	14.55	15.92

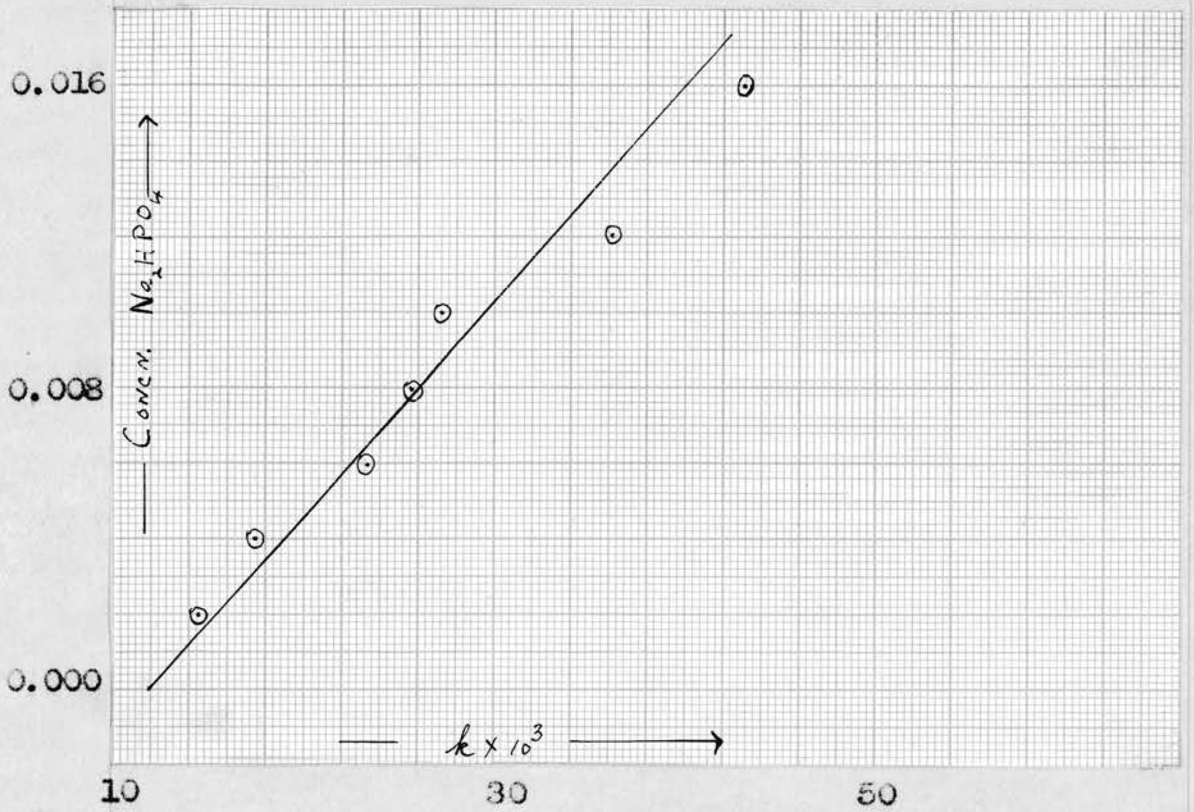


FIGURE IIIa.

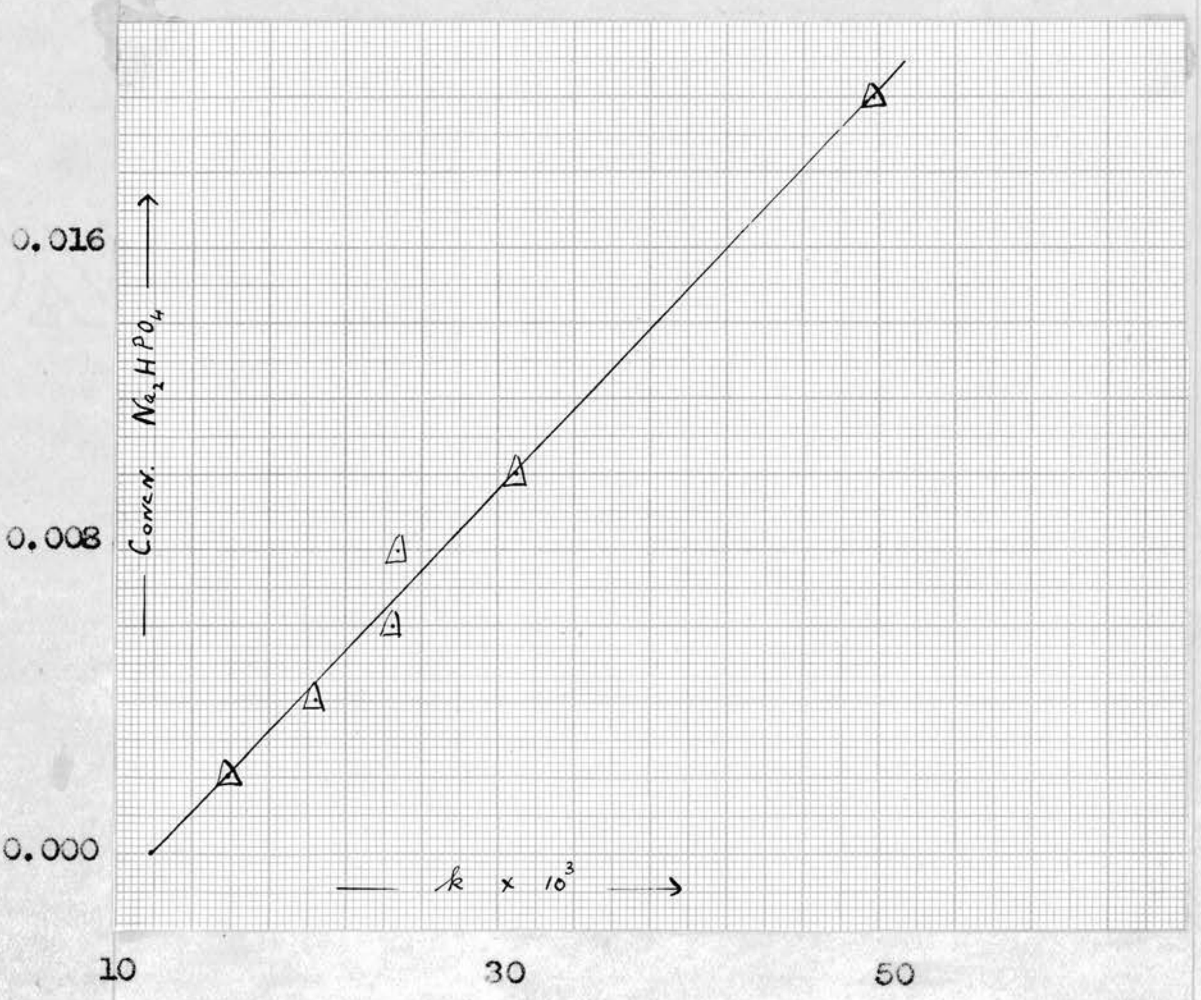


FIGURE IIIb.

Calculation of the Catalytic Coefficients.

For these phosphate solutions equations (2) and (4) respectively become

$$V_{obs.} = (k_{HPO_4^=} + k_{H_2PO_4^-})\,x + k_{H_2O}\,C_{H_2O}$$

$$V'_{obs.} - V_{obs.} = k_{H_2PO_4^-}\,.x.(a - 1)$$

Consideration of graphs IIIa and IIIb however show that $k_{H_2PO_4^-}$ must be very small and as IIIa shows the results are not so accurate for these solutions as for the acetate solutions. We come to the conclusion therefore that we would not be justified in ascribing any definite value to the $H_2PO_4^-$ ion and that the slope of graph IIIa is almost entirely due to the $HPO_4^=$ ion for which therefore we have the following figure

$$\underline{k_{HPO_4^=} = 1.77}$$

The water rate as before is 11.9×10^{-3}

Monochloroacetic Acid Solutions.

In a solution of monochloroacetic acid the observed rate of mutarotation can be represented as follows

$$V_{obs.} = V_{H_2O} + V_m + V_H + V_a$$

where V_{H_2O} is the water rate

V_m is the rate due to the undissociated acid

V_a is the rate due to the chloroacetate ion

V_H is the rate due to the hydrion.

$V_{obs.}$ was obtained for a series of concentrations of acid ranging from 0.05 M. to 0.4 M.

To determine V_m we must know the value of V_H and V_a as well as V_{H_2O} . V_{H_2O} is known from the foregoing experiments to be 11.9×10^{-3}. $V_H = k_H C_H$ where k_H is is the catalytic coefficient of the hydrion. This has been determined and has the value 502×10^{-3} (Nelson Thesis for Ph.D Edin.). C_H the concentration of hydrion is calculated from a knowledge of the dissociation constant at 15°C. This has the value $K = 1.458 \times 10^{-3}$ (Wright, J.A.C.S., 56, 314, 1934.). V_a is very small but an estimate of its value has been made assuming that

k_H/k_a in glucose reaction = k_H/k_a in galactose reaction

Since C_a is obtained from a knowledge of K and k_H is known for glucose and galactose as well as k_a in glucose $V_a = k_a C_a$ is obtained. The values of V and the calculated values of V_H and V_a are tabulated in Table IV.

$$V_m = V_{obs.} - (V_{H_2O} + V_H + V_a)$$

The plot of V_m - concentration is given in Figure IV. The slope gives the value of $k_m = 35.0 \times 10^{-3}$

TABLE IV

c		=	0.4	0.3	0.2	0.1	0.05
$V_{obs.}$	$\times 10^3$	=	36.08	29.70	26.56	21.30	19.14
V_{H_2O}	$\times 10^3$	=	11.9	11.9	11.9	11.9	11.9
Vh	$\times 10^3$	=	9.0	7.45	7.32	6.02	4.24
Va	$\times 10^3$	=	0.26	0.22	0.21	0.18	0.12
V_m	$\times 10^3$	=	14.92	10.03	7.13	3.20	2.85

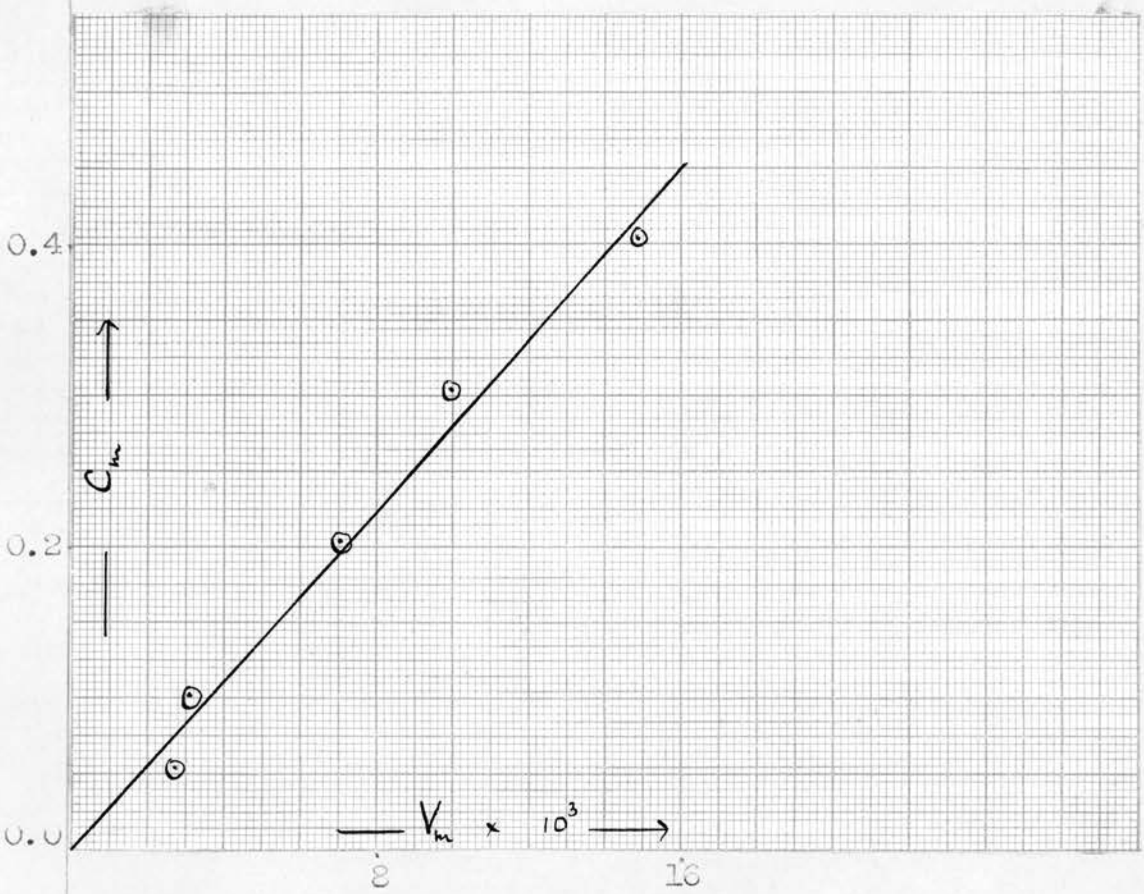


FIGURE IV.

Discussion of Results.

The results along with those obtained by Nelson (loc. cit.) are collected in Table V and the values for glucose calculated from the determinations of Smith and Smith (J.C.S. 1418, 1937.) are appended for the sake of comparison.

TABLE V.

(a) Acids.

	log K_a	k_1	k_2	k_1/k_2
H_3O^+	1.74	502×10^{-3}	243×10^{-3}	2.06
Chloroacetic Acid	-2.84	35.0×10^{-3}	18.86×10^{-3}	1.86
Acetic Acid	-4.76	6.9×10^{-3}	4.63×10^{-3}	1.49

(b) Bases.

	log K_b	k_1	k_2	k_1/k_2
H_2O	-1.74	21.5×10^{-3}	16.3×10^{-3}	1.32
Acetate	4.76	35.6×10^{-3}	44.1×10^{-3}	0.81
$HPO_4^=$	7.25	1.77	1.38	1.28

log K_a is the logarithm of the dissociation constant of the acid while log K_b is the corresponding term for the base. k_1 is the catalytic coefficient of the galactose reaction and k_2 is the catalytic coefficient of the glucose reaction.

Consideration of these results reveals that the rate of mutarotation of galactose is appreciably greater than that of glucose with acid catalysts and the ratio increases with the strength of the acid. The ratio of the rates with the base catalysed reaction appears to be rather irregular and no generalisation could be made without further data. It is to be noted in this connection that the agreement of Smith's data with the figures of Hamill and La Mer (J. Chem. Phys. 4, 395, 1936.) is not at all good and there may be some doubt about the glucose values.

SUMMARY.

1. The absorption curves of cobaltous chloride dissolved in H_2O and D_2O have been determined. Distinct differences were observed in the value of the molecular extinction coefficient.

2. A colorimetric method has been employed to determine the ratio of the dissociation constants in light and heavy water of a series of mono- and di- nitrophenols as well as the indicator Brom-Thymol-Blue. The results show that with a decrease in the acid strength there is an increase in the ratio. In the case of the meta compounds this ratio is unusually high.

3. The catalytic constants of the mutarotation of galactose with acetic and chloroacetic acids and acetate and phosphate ions have been determined and a comparison made with the corresponding values for the glucose mutarotation.

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