13. *Salt Hydrates and Deuterates. Part II. Correlation of Heats of Dissociation and Structure.*

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Heats of dissociation of a number of salt hydrates and deuterates, calculated from dissociation-pressure measurements, show that the work required to remove deuterium oxide molecules from a deuterate is greater than that required for the removal of the water molecules from the corresponding hydrate. This may be regarded as further evidence that the water in a normal hydrate is bound by ordinary covalent or van der Waals forces and not by special resonance linkages such as hydrogen bonds.

The effect of the hydrogen bond in oxalic acid dihydrate is illustrated by a study of the dissociation pressures of $H_2C_2O_4,2H_2O$ and $D_2C_2O_4,2D_2O$, that of the latter being the greater. The heats of dissociation of the hydrate and deuterate are in this case almost identical, indicating a weakening of the hydrogen bond on the introduction of deuterium.

The isotope effect is also illustrated by the greater molecular volume of $D_2C_2O_4,2D_2O$; in the salt hydrates a contraction of molecular volume takes place on replacement of the H_2O by D_2O.

Determination of the molecular volumes of KH_2PO_4 and KD_2PO_4 again illustrates the presence of the hydrogen bond.

It is suggested that expansion of the molecular volume on the substitution of hydrogen by deuterium may indicate the presence of hydrogen bonds, but the converse is not necessarily true.

IN Part I (J., 1937, 457) it was shown that differences occur in the ratios of the dissociation pressures of certain salt deuterates to those of the corresponding hydrates. Further hydrates and deuterates have since been examined, and the heat relationships for the dissociation processes calculated. The results of the present measurements are summarised in Table I, in which are included the hydrates $NiSO_4,7H_2O$, $ZnSO_4,7H_2O$, and $KF,2H_2O$, for which comparable results were not available.

TABLE I.

Dissociation pressures (in mm. Hg).

Temp.	20°.	25°.	30°.	35°.	40°.
$NiSO_4,7D_2O$	11·6	17·7	—	—	—
$NiSO_4,7H_2O$	14·8	20·7	27·9	—	—
$CoSO_4,7D_2O$	—	13·7	19·8	28·6	41·4
$ZnSO_4,7D_2O$	—	13·0	19·9	29·7	—
$ZnSO_4,7H_2O$	—	15·3	22·4	32·2	—

Temp.	25°.	30°.	35°.	40°.
$CuCl_2,2D_2O$	6·9	9·8	13·4	17·4
$BaCl_2,2D_2O$	5·8	8·2	11·3	15·2
$KF,2D_2O$	2·4	3·8	5·8	—
$KF,2H_2O$	3·5	5·3	7·5	—

The relationship connecting vapour pressure and temperature is of the form $\log p = A - B/T$, and Table II gives the values of A and B for all salts so far examined, together with those of the heat of dissociation, L, obtained by multiplying the coefficient B by 4·575 (Miles and Menzies, *J. Amer. Chem. Soc.*, 1938, **60**, 87). For some of the hydrates, the measurements reported by other workers have been used.

TABLE II.

	A.		*B*.		*L*, kg.-cals.	
	Hyd.	Deut.	Hyd.	Deut.	Hyd.	Deut.
$CuSO_4,5H_2O$	10·78	11·02	2948	3045	13·49	13·93
$Na_2SO_4,10H_2O$	10·1	10·97	2626	2922	12·01	13·38
$CoSO_4,7H_2O$	10·45	11·09	2748	2967	12·57	13·57
$MgSO_4,7H_2O$	11·47	12·35	3090	3474	14·14	15·7
$ZnSO_4,7H_2O$	11·12	12·18	2959	3298	13·54	15·09
$NiSO_4,7H_2O$	10·48	12·36	2730	3310	12·48	15·15
$CuCl_2,2H_2O$	9·06	9·62	2435	2616	11·14	12·22
$CoCl_2,6H_2O$	10·42	12·09	2852	3337	13·05	14·76
$NiCl_2,6H_2O$	10·21	12·45	2740	3442	12·53	15·75
$BaCl_2,2H_2O$	9·35	9·85	2629	2719	12·02	12·44
$SrCl_2,6H_2O$	10·34	11·4	2807	3149	12·84	14·4
$NaBr,2H_2O$	11·03	11·23	3029	3095	13·86	14·17
$KF,2H_2O$	10·73	12·18	3037	3516	13·91	16·08

Ubbelohde (*Trans. Faraday Soc.*, 1936, **32**, 525) has shown that the effect of the substitution of deuterium for hydrogen is dependent on the nature of the linkage involved, and has discussed the effect for ionic and covalent linkages. In ionic compounds such as lithium hydride where hydrogen is present as a negative ion comparatively large contractions of the lattice dimensions are found on substituting deuterium for hydrogen (Zintl and Harder, *Z. physikal. Chem.*, 1935, *B*, **28**, 478). In covalent compounds the most important effect is believed to arise from a change in the minimum distance of approach of the molecules (van der Waals's *b*). The normal effect expected when only van der Waals and Coulomb forces are operative is again a contraction of the lattice.

If, therefore, the water molecules in a salt hydrate are considered as bound by covalent or van der Waals forces, the effect of replacing the water by deuterium oxide will normally be a contraction of the crystal lattice spacings, and consequently the removal of the deuterium oxide molecules will require a larger amount of work. The values for the heat of dissociation, *L*, shown in Table II indicate clearly that such an increase in the work of removal is found. This increase is greater than can be accounted for by the difference in the heats of vaporisation of water and deuterium oxide, which is about 0·3 kg.-cal. for the temperature range of these experiments. The extent of the increase varies but it is not yet possible to connect this variation with any particular effect.

While this work was in progress, Robertson and Ubbelohde (*Nature*, 1937, **139**, 504) described the results of a preliminary *X*-ray examination of deutero-oxalic acid dideuterate, $D_2C_2O_4,2D_2O$. Its structure showed an expansion of certain spacings when compared with that of oxalic acid dihydrate, the expansion reaching a maximum near the direction of the hydrogen bond connecting a water molecule to a carbonyl oxygen atom. This effect was tentatively explained by assuming that the resonance associated with the hydrogen bond would be less complete in the deuterium compound.

Hence an examination of the dissociation pressures of $D_2C_2O_4,2D_2O$ and $H_2C_2O_4,2H_2O$ seemed of particular interest in connection with the results already obtained for the salt hydrates. Measurements of these pressures (in mm. Hg) have therefore been made over a range of temperature as follows :

Temp.	25·0°.	30·3°.	35·0°.	39·5°.	40·3°.
$D_2C_2O_4,2D_2O$	3·2	4·7	6·8	9·0	9·9
$H_2C_2O_4,2H_2O$	2·8	4·3	6·3	8·4	9·1

These results differ from all others in this work in that the dissociation pressure of the deuterated acid is greater than that of the hydrated acid, the mean value for p_{D_2O}/p_{H_2O} being 1·09. The dissociation pressure–temperature relationships are expressed by the equations

$$D_2C_2O_4,2D_2O : \log p = 10{\cdot}27 - 2910/T$$
$$H_2C_2O_4,2H_2O : \log p = 10{\cdot}45 - 2983/T$$

and the heats of dissociation, calculated as before, are found to be 13·3 and 13·6 kg.-cals. respectively, showing that the work of removal of D_2O is in this case slightly less than that of H_2O. A second set of independent observations gave values of 13·25 and 13·5 kg.-cals.

Huggins (*J. Org. Chem.*, 1936, **1**, 407) considers that the deuterium bond should be stronger than the hydrogen bond, but the above result can be suitably explained by assuming a weakening of the bond on replacement of the hydrogen by deuterium, as was suggested by the work of Robertson and Ubbelohde which has since been extended (*Proc. Roy. Soc.*, 1939, *A*, **170**, 222). It appeared possible that the expansion effect which they noticed might be more simply illustrated by comparison of the molecular volumes of $D_2C_2O_4,2D_2O$ and $H_2C_2O_4,2H_2O$. The densities of these two acids were therefore determined by flotation and the molecular volume of the former has been found to be about 2% greater than that of the ordinary acid, providing unequivocal evidence of an expansion effect.

Density measurements were extended to other compounds, and a similar but smaller expansion was found in comparing the molecular volumes of KD_2PO_4 and KH_2PO_4, so the presence of hydrogen bonds, as suggested by Bernal and Megaw (*Proc. Roy. Soc.*, 1935, *A*, **151**, 382), is again associated with the greater molecular volume of the deuterium compound.

The values for the molecular volumes (*V*) are shown in Table III, along with the results of similar measurements made on certain salt hydrates and deuterates. The density measurements reported in this table are, in all cases, the mean values of several determinations on different samples. It will be seen that the molecular volumes in most cases showed the expected small contraction on the replacement of the water by deuterium oxide, although in others this appears to be too small to be detected.

TABLE III.

	$d_{4^\circ}^{20^\circ}$.	*V*.	Diff., %.		$d_{4^\circ}^{20^\circ}$.	*V*.	Diff., %.
$H_2C_2O_4,2H_2O$	1·650	76·4	+2·3	$CoSO_4,7H_2O$	1·939	144·9	—
$D_2C_2O_4,2D_2O$	1·688	78·2		$CoSO_4,7D_2O$	2·038	144·7	
KH_2PO_4	2·319	58·6	+1·4	$CoCl_2,6H_2O$	1·918	124·1	—
KD_2PO_4	2·324	59·4		$CoCl_2,6D_2O$	2·013	124·1	
$CuSO_4,5H_2O$	2·272	109·9	−0·7	$SrCl_2,6H_2O$	1·954	136·3	−0·4
$CuSO_4,5D_2O$	2·379	109·1		$SrCl_2,6D_2O$	2·051	135·8	
Li_2SO_4,H_2O	2·051	62·2	−1·8				
Li_2SO_4,D_2O	2·127	61·1					

Such measurements of molecular volumes appear to constitute a simple method of detecting the presence of hydrogen bonds which lead to a small expansion of molecular volume on the replacement of the hydrogen by deuterium, whereas the normal effect is a small contraction. It must be emphasised that the method cannot be regarded as infallible, for an expansion due to the isotope effect in a hydrogen bond might be offset by a contraction of certain dimensions elsewhere in the molecule, but it is suggested that the method will be of use in the selection of suitable compounds for further examination by other methods. In this connection an example of particular interest is furnished by acetaldehyde and paraldehyde. The molecular volumes, calculated from the density measurements of Zanetti and Sickling (*J. Amer. Chem. Soc.*, 1936, **58**, 2034), show a small contraction of 0·4% for $CD_3\cdot CDO$ as compared with $CH_3\cdot CHO$, but for the polymerised compounds the effect is in the opposite direction, the molecular volume of $(CD_3\cdot CDO)_3$ being about 0·5% greater than that of $(CH_3\cdot CHO)_3$.

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