101. *Salt Hydrates and Deuterates. Part I. The Dissociation Pressures of Certain Deuterates.*

By James Bell.

It has been pointed out by Day, Hughes, Ingold, and Wilson (J., 1934, 1593), considering Werner's conception of the structure of salt hydrates and the relative stabilities of hydrogen and deuterium bonds, that salts in which the water molecules are regarded as linked to the cation should show a preference for light water when crystallised from a mixture of light and heavy water. Conversely, in the case of anion-hydration, a relative preference for heavy water should be expected. These investigators crystallised a number of salts from a dilute solution of deuterium oxide, but obtained no evidence of any preference for light or heavy water, and concluded that any structure arising out of hydration must be of a loose character.

It is probable, however, that a study of the properties of the pure deuterates and their comparison with those of the corresponding hydrates may furnish evidence applicable to the question of the structure of the hydrated salts. In the course of an extended investigation of this type, the dissociation pressures of certain deuterates have been measured over a range of temperature and compared with those of the corresponding hydrates. This communication, which is of a preliminary nature, contains the results obtained in a study of some sulphates and chlorides and hydrated sodium bromide. The transition points of the deuterates also have been determined where possible.

EXPERIMENTAL.

The dissociation pressures were measured by the tensimetric method, a modification of the Bremer–Frowein tensimeter being used. The tensimeters were immersed in a gas-heated thermostat, accurate to ± 0·05°, and in most cases 24 hours were allowed to elapse before the reading of the pressure was made. In other experiments a longer interval was necessary for the establishment of equilibrium. Mercury was used as the manometric liquid. The heavy water used in these experiments was the product of the Norsk Hydroelektrisk Kvaelstofaktieselskab and contained 99·95% of deuterium oxide.

Table I shows the results for the dissociation pressures of copper sulphate pentadeuterate, sodium sulphate decadeuterate, magnesium sulphate heptadeuterate, strontium chloride hexadeuterate, cobalt chloride hexadeuterate, nickel chloride hexadeuterate, and sodium bromide dideuterate. Values are also included for the dissociation pressures of strontium chloride hexahydrate, as there is considerable diversity in the results previously recorded, and for sodium bromide dihydrate, which does not appear to have been investigated over a range of temperature.

Transition points were determined from the graphs of log p against $10^6/T$, p being in mm. of mercury.

TABLE I.

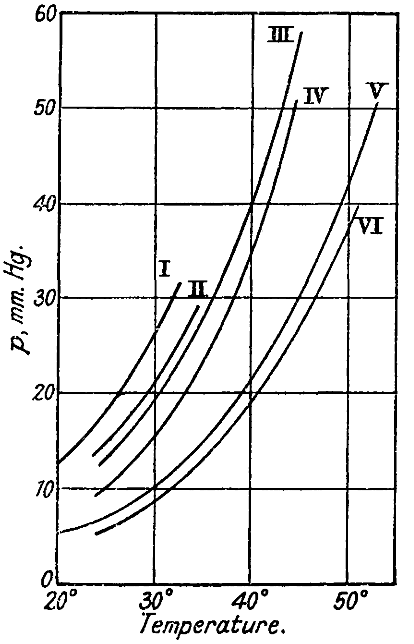
t.	*p.*	*t.*	*p.*	*t.*	*p.*	*t.*	*p.*
$CuSO_4,5D_2O$.		$MgSO_4,7D_2O$.		$SrCl_2,6D_2O$.		$NaBr,2D_2O$.	
25°	6·5	25°	9·9	25°	6·9	20°	4·25
30	9·3	30	15·6	30	10·7	25	6·9
35	13·7	34·6	22·7	35	14·9	30	10·45
39	19·4	40·5	36·6	40	20·4	35	15·1
		44·9	50·0			40	21·6
$Na_2SO_4,10D_2O$.		49·4	67·1	$SrCl_2,6H_2O$.		44·5	30·2
25	14·5	51·5	74·5	25	7·3	49·8	41·8
30	21·0	53·2	81·0	30	11·0	51·3	45·0
33	26·2			35·2	15·7	53·8	51·4
34	28·1	$CoCl_2,6D_2O$.		40	22·0		
35	30·0	25	5·8			$NaBr,2H_2O$.	
36	31·9	30	9·1	$NiCl_2,6D_2O$.		20	4·9
38	35·7	34·9	13·1	24·8	7·8	25	7·5
40	39·9	40	18·7	30	12·2	30	11·3
		45·1	26·7	34·3	17·4	35	16·4
		49·9	37·0	38	21·8	40	22·9
		54·5	48·5	42·3	26·4		
		56·6	54·5	46·2	30·9		

Discussion of Results.—The only deuterate for which values of the dissociation pressure have been previously recorded is copper sulphate pentadeuterate, Schacherl (*J. Phys. Radium*, 1935, **6**, 439; *Nature*, 1936, **138**, 406) and Partington and Stratton (*ibid.*, **137**, 1075) having investigated the change, $CuSO_4,5D_2O \rightleftharpoons CuSO_4,3D_2O + 2D_2O$. The results for the dissociation pressure in the present series of measurements are in agreement with the values reported by these workers.

Although it is impossible to make any generalisations until the dissociation pressures of many more deuterates have been examined, the results already obtained are of interest. The mean values for the ratio of the dissociation pressure of the deuterate to that of the corresponding hydrate, over a range of temperature in which these pressures were measured, are as follows :

	$CuSO_4$.	Na_2SO_4.	$MgSO_4$.	$SrCl_2$.	$NiCl_2$.	$CoCl_2$.	NaBr.
p_{D_2O}/p_{H_2O}	0·82	0·81	0·82	0·95	0·82	0·87	0·90

The relatively lower value of this ratio for the first three salts is well defined. In the figure, for example, are shown the dissociation-pressure curves for the hydrate and deuterate of three of the salts, sodium sulphate, magnesium sulphate, and cobalt chloride. The differences in pressure are clearly illustrated. For nickel chloride the ratio rises steadily from 0·75 at 25° to 0·88 at 35°, so the mean figure is probably of little value.



I, $Na_2SO_4,10H_2O$; II, $Na_2SO_4,10D_2O$;
III, $MgSO_4 7H_2O$; IV, $MgSO_4,7D_2O$;
V, $CoCl_2,6H_2O$; VI, $CoCl_2,6D_2O$.

TABLE II.

$Na_2SO_4,10H_2O \longrightarrow Na_2SO_4$	32·4°
$Na_2SO_4,10D_2O \longrightarrow Na_2SO_4$	34·48 * 34·5 †
$CoCl_2,6H_2O \longrightarrow CoCl_2,2H_2O$	52·25
$CoCl_2,6D_2O \longrightarrow CoCl_2,2D_2O$	51·1
$SrCl_2,6H_2O \longrightarrow SrCl_2,2H_2O$	61·3
$SrCl_2,6D_2O \longrightarrow SrCl_2,2D_2O$	56·5 ‡
$NiCl_2,6H_2O \longrightarrow NiCl_2,4H_2O$	36·25
$NiCl_2,6D_2O \longrightarrow NiCl_2,4D_2O$	35·9
$NaBr,2H_2O \longrightarrow NaBr$	50·7
$NaBr,2D_2O \longrightarrow NaBr$	47·7
$MgSO_4,7H_2O \longrightarrow MgSO_4,6H_2O$	48·4
$MgSO_4,7D_2O \longrightarrow MgSO_4,6D_2O$	46·8

* Taylor, *J. Amer. Chem. Soc.*, 1934, **56**, 2643.
† Present work.
‡ Miles, Shearman, and Menzies, *Nature*, 1936, **138**, 121.

The ratios of the heats of dissociation have been determined from the relative slopes of the curves of log *p* against $1/T$, and the following values found :

	$CuSO_4$.	Na_2SO_4.	$MgSO_4$.	$SrCl_2$.	$NiCl_2$.	$CoCl_2$.	NaBr.
Q_{D_2O}/Q_{H_2O}	1·09	1·08	1·09	0·99	1·31	1·05	1·03

It is proposed to study the relative dissociation pressures of the different hydrates and deuterates of the same salt, where this is possible, *e.g.*, the hepta- and hexa-hydrates and -deuterates of magnesium sulphate, for such a complete examination is obviously necessary before any conclusions regarding the structure of hydrates can be derived.

Table II shows the transition points of the deuterates where these have been determined, together with the accepted values for the corresponding hydrate transitions.

Sodium sulphate decadeuterate is the only example, so far, of a deuterate which has a higher transition point than the corresponding hydrate.

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