

Separation of Heavy Water in Phase Equilibria Involving Pure Water or Salt-Water Systems

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Separation factors for deuterium on equilibration of ice or vapour with liquid water and with some salt solutions have been determined, and also factors for equilibrium between some salt hydrate crystals and their saturated solutions. Some separation factors have been calculated from vapour pressures and known thermodynamic data. Comparisons are made with data from other authors.

For equilibrium in the system ice-vapour-solution the three separation factors are found to be closely compatible which lends support to the claim that the experimental measurements are fairly reliable.

The separation factor for the freezing of ice from a salt solution may be considerably larger than that for freezing from pure water.

With liquid water and vapour in equilibrium heavy water favours the liquid¹ and with liquid and ice in equilibrium it favours the ice.² A separation factor for equilibrium between two phases a and b is defined in the usual way

$$\alpha_b^a = \frac{N_a}{1-N_a} \cdot \frac{1-N_b}{N_b} \quad (1)$$

where N_a and N_b are mole fractions of deuterium in the phases a and b. If heavy water is enriched in phase a, α_b^a is larger than one. Solid, liquid and vapour phases are indicated by s, l, and v.

If all three phases are in equilibrium the following relation must hold true

$$\alpha_v^s = \alpha_l^s \times \alpha_v^l \quad (2)$$

This permits a check of experimental determinations against each other or the calculation of one α if the other two are known.

The separation effect on evaporation is known to be generally smaller for salt solutions than for pure water.³ Then it must be expected from eqn. (2)

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that freezing of ice from a salt solution will give a larger effect than freezing from water.

The present work comprises the direct determination of separation factors for equilibria vapour-liquid and ice-liquid for pure water and for solutions of KCl, KBr, KI, NaCl, LiNO₃, and Ca(NO₃)₂ in the range from 0°C to eutectic temperature. Comparisons have been made with published results and calculations with the aid of known physical and thermodynamic data. A few determinations of deuterium separation factors upon crystallization of salt hydrates have also been made.

EQUILIBRIUM LIQUID-VAPOUR

Pure water above 0°C. The separation factor α_v^1 for pure water of normal deuterium content has been determined by Merlivat, Botter and Nief⁴ by mass spectrometric analysis of samples of liquid and vapour. It has been determined for water containing 50 % D₂O by Combs, Googin and Smith,⁵ using a vapour entrainment method.

The separation factor may also be calculated from vapour pressure data

$$\alpha_v^1 = \frac{P_{H_2O}}{P_{HDO}} = \sqrt{\frac{P_{H_2O}}{P_{D_2O}}} \quad (3)$$

if it is assumed that the water species form ideal solutions, that the vapour pressure of HDO is the geometric mean of those of H₂O and D₂O, and that the equilibrium constant for H₂O + D₂O = 2 HDO is 4.00 in the liquid phase. These assumptions are not quite true and it is possible that the separation factor α_v^1 varies a little with the deuterium concentration.

Vapour pressures of D₂O have been determined by Niwa and Shimasaki,⁶ Kiss, Jakly and Illy,⁷ Jones,⁸ and Combs *et al.*⁵

In the present work α_v^1 for water has been determined by the distillation of water containing about 10 mole % D₂O at temperatures in the range 3–20°C. The chief purpose was to test the experimental procedure, which was also used for salt solutions below 0°C. The results are given in Table 1. Rayleigh distillation corrections⁹ have been applied in this and all other cases, where appropriate.

Table 1. Separation factor α_v^1 for deuterium on equilibration between water and vapour, determined by distillation from water containing about 10 mole % D₂O.

Temperature °C	Distillation velocity g cm ⁻² h ⁻¹	Amount distilled %	α_v^1
20.4	0.25	3.8	1.0839
9.8	0.24	4.9	1.0976
3.4	0.25	7.5	1.1074
3.4	0.18	5.5	1.1075
3.0	0.24	7.3	1.1082
3.0	0.21	7.2	1.1080
3.0	0.27	7.2	1.1086

We have also calculated α_v^1 with eqn. (3) from some of our own measurements of vapour pressure given in Table 2.

Table 2. Vapour pressures of H₂O and D₂O. Separation factor α_v^1 according to eqn. (3).

Temperature °C	$P_{\text{H}_2\text{O}}$ mm Hg	$P_{\text{D}_2\text{O}}$ mm Hg	α_v^1
20.01	17.55	14.96	1.083
15.04	12.82	10.81	1.089
9.90	9.15	7.65	1.093
4.84	6.47	5.35	1.100

Present data and data from other authors are shown in Fig. 1. The agreement is only moderate. It is not surprising that the values of α_v^1 calculated from vapour pressures do not fully agree with those directly determined, but they ought to have agreed better between themselves. The disagreement between the direct determinations may perhaps partly be ascribed to the different concentrations of D₂O used. There does not seem to exist any systematic

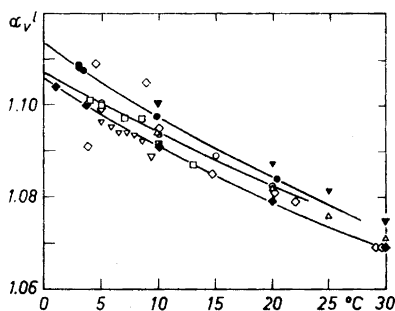


Fig. 1. Separation factor α_v^1 for equilibrium between liquid water and vapour. Open symbols refer to values calculated from vapour pressures, solid symbols to values determined by distillation.

Jones³ \diamond ; Merlivat *et al.*⁴ \blacklozenge ; Niwa *et al.*⁶ \square ; Combs *et al.*⁵ \blacktriangledown ; \blacktriangle ; Kiss *et al.*⁷ ∇ ; present work \bullet \circ .

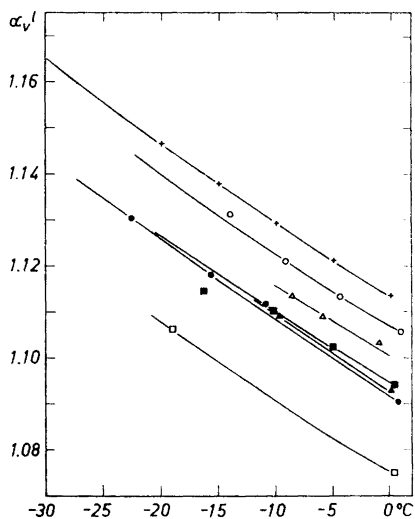


Fig. 2. Separation factor α_v^1 for equilibrium between vapour and saturated solutions, determined in the present work by distillation.

Calculated for supercooled water $+$; KCl Δ ; KBr \blacktriangle ; KI \square ; NaCl \blacksquare ; LiNO₃ \circ ; Ca(NO₃)₂ \bullet .

investigation of the effect of D₂O content on the separation factor α_v^1 , but Narten has announced a prospective investigation.¹⁰ Distillation as performed here seems to be a precise and reproducible method for the determination of α_v^1 . However, considering the difference between the present results and those of Merlivat *et al.*,⁴ a small systematic error cannot be excluded.

Pure water below 0°C. Separation factors, α_v^1 , for supercooled water have been calculated with eqn. (3), using vapour pressures calculated by the Clausius-Clapeyron formula. The following heats of vapourization have been used for $t^\circ\text{C}$.

H₂O: $\Delta H = 10.767 - 0.0102 t$ kcal/mole

D₂O: $\Delta H = 11.155 - 0.0122 t$ kcal/mole

For results, see Table 3 and Fig. 2.

Table 3. Calculated vapour pressures for liquid H₂O and D₂O below 0°C, and separation factor α_v^1 .

Temperature °C	$P_{\text{H}_2\text{O}}$ mm Hg	$P_{\text{D}_2\text{O}}$ mm Hg	α_v^1
3.82		4.91 ^b	
0	4.579 ^a	3.685	1.1135
-5	3.160	2.509	1.1212
-10	2.147	1.680	1.1293
-35	1.433	1.104	1.1378
-20	0.940	0.714	1.1465

^a From *Handbook of Chemistry and Physics*.¹¹

^b The calculation is based on this figure in order to have agreement of α_v^1 with the experimental value at 0°C. According to Kirshenbaum¹ the value should be 5.05 mm Hg, from the measurements of Table 2 we get 4.97 mm Hg at 3.82°C.

Salt solutions at about 0°C and below. Googin and Smith³ have determined separation factors for a considerable number of salt solutions by distillation, but only at 27°C. Niwa and Shimasaki⁶ have determined vapour pressures over saturated solutions of KCl in H₂O and D₂O between 0 and 10°C, and Higuchi¹² over saturated Na₂SO₄ in H₂O and D₂O at 20–50°C. From these pressures α_v^1 can be calculated with eqn. (3) with the limitations already mentioned.

Distillations have now been performed from solutions of salts in about 10 mole % D₂O. In the cases of KCl, KBr, and KI the solutions were saturated (excess of solid salt), in the other cases there was no solid in order to avoid withdrawing part of the water as a crystal hydrate. Results are given in Table 4, in which α_v^1 also has been calculated for saturated solutions, and in Fig. 2.

Table 4. The separation factor α_v^1 for equilibrium between salt solutions and vapour. Water containing about 10 mole % D_2O used.

Salt	Temperature °C	Salt con- centration ^b % by weight	Distillation velocity g cm ⁻² h ⁻¹	α_v^1 experimental	α_v^1 for saturated solution
KCl	- 8.6	<i>a</i>	0.27	1.1134	
	- 5.9	<i>a</i>	0.30	1.1089	
	- 1.0	<i>a</i>	0.25	1.1033	
KBr	- 9.7	<i>a</i>	0.25	1.1087	
	+ 0.1	<i>a</i>	0.21	1.0927	
KI	- 19.0	<i>a</i>	0.16	1.1061	
	+ 0.4	<i>a</i>	0.14	1.0746	
NaCl	- 16.3	21.4	0.20	1.1172	1.1146
	- 10.2	23.4	0.16	1.1108	1.1104
	- 5.0	23.8	0.20	1.1038	1.1023
	+ 0.4	24.6	0.17	1.0954	1.0941
LiNO ₃	- 14.0	28.7	0.15	1.1310	1.1312
	- 9.2	29.7	0.19	1.1211	1.1212
	- 4.4	31.1	0.12	1.1134	1.1136
	+ 0.9	32.2	0.11	1.1055	1.1057
Ca(NO ₃) ₂	- 22.6	49.2	0.12	1.1266	1.1304
	- 15.7	47.6	0.11	1.1167	1.1181
	- 10.9	46.1	0.14	1.1120	1.1119
	+ 0.7	47.4	0.09	1.0981	1.0904

^a saturated at the indicated temperature.

^b mean concentration during the experiment.

According to Googin and Smith³ the lowering of α_v^1 in the presence of a salt is proportional to the salt concentration, expressed as mole fraction N of the anion

$$\Delta\alpha_v^1 = -kN \quad (4)$$

The constant k , however, is dependent on the temperature.

Present data for k are given in Fig. 3, which also gives data from Googin and Smith³ and some calculated from vapour pressures given by Niwa and Shimasaki.⁶ Only in the case of KBr there is a considerable disagreement. Knowing k α_v^1 can be calculated for every salt concentration in the temperature range investigated. In view of the values of $\Delta\alpha_v^1$, which are generally small, and the possible experimental errors, too much weight should not be laid on the k values and their temperature dependence. Accurate k values are not needed for deriving α_v^1 for saturated solutions.

EQUILIBRIUM SOLID-VAPOUR

The separation factor, α_v^s , for the equilibrium ice-vapour cannot easily be determined experimentally because of the slow diffusion in the ice. It can, however, be obtained from vapour pressures, using eqn. (3).

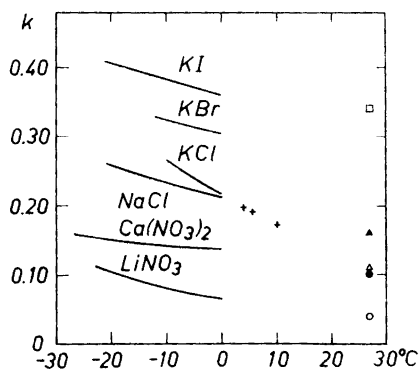


Fig. 3. Factor k according to eqn. (4). Curves are from the present work. For comparison: + data for KCl from Niwa and Shimasaki;⁶ remainder Δ KCl, \blacktriangle KBr, \square KI, \circ LiNO_3 , and \bullet $\text{Ca}(\text{NO}_3)_2$ are from Googin and Smith.³

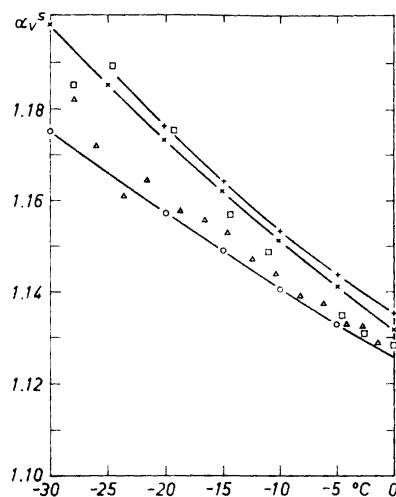


Fig. 4. Separation factor α_v^s for equilibrium between ice and vapour. Data from Merlivat *et al.* are experimental, the others are calculated from data of vapour pressures taken from several authors. Calculated, Table 5 +; Merlivat *et al.*¹⁶ \times ; Kiss *et al.*⁷ Δ ; Matsuo *et al.*¹³ \square ; calculated from Niwa *et al.*⁶ \circ .

Vapour pressures over solid D_2O have been determined by Kiss *et al.*⁷ and Matsuo *et al.*¹³ Niwa and Shimasaki⁶ give data between 1 and 3°C, which may be extrapolated.

Vapour pressures over ice have been calculated here by the Clausius-Clapeyron formula, using known data for heats of melting of ice¹⁴ and specific heats¹⁵ of ice and vapour to obtain ΔH for the transition ice-vapour. The results are given in Table 5 and Fig. 4.

Table 5. Calculated vapour pressures for solid H_2O and D_2O , and separation factors α_v^s and α_1^s .

Temperature °C	$P_{\text{H}_2\text{O}}$ mm Hg	$P_{\text{D}_2\text{O}}$ mm Hg	α_v^s	α_1^s
3.82		4.91 ^b		
0	4.579 ^a	3.545	1.1354	1.0197
-5	3.011	2.297	1.1438	1.0201
-10	1.949	1.461	1.1532	1.0212
-15	1.241	0.914	1.1641	1.0231
-20	0.776	0.560	1.1759	1.0256

^a From *Handbook of Chemistry and Physics*.¹¹

^b See note to Table 3.

Recently direct determinations of the separation factor for ice-vapour and vapour-supercooled water in equilibrium have been made by Merlivat and Nief.¹⁶

EQUILIBRIUM ICE-LIQUID

Pure water-ice. Direct determinations of the separation factor, α_1^s , on freezing of ice from water were performed by Posey and Smith² who, with 18 mole % D₂O at +0.7°C, obtained $\alpha_1^s=1.0211\pm 0.0007$ by extrapolation to zero freezing velocity. Kuhn and Thürkauf,¹⁷ with 10 mole % D₂O at +0.4°C, obtained $\alpha_1^s=1.0171\pm 0.0005$. They calculated a theoretical value of 1.0188. Weston¹⁸ derived an expression, giving α_1^s as a function of the temperature. For 0°C $\alpha_1^s=1.0192$ is obtained.

Using eqn. (2), we obtain with the calculated values of α_v^1 and α_v^s (Tables 3 and 5) the α_1^s given in Table 5. Of course the values below 0°C are hypothetical, as the liquid cannot be maintained in equilibrium with the ice.

A single freezing experiment with 10 mole % D₂O was performed, intending to give a suspension of ice. However, the ice separated as a continuous layer on the wall. The result was $\alpha_1^s=1.0187$ (without correction for possibly entrained water).

Table 6. Separation factor α_1^s obtained by directional freezing of water containing about 10 % D₂O at about +0.4°C.

Amount frozen %	Freezing velocity g cm ⁻² h ⁻¹	α_1^s	Remark
36.4	0.41	1.0195	
41.3	0.46	1.0196	
43.6	0.44	1.0194	
52.6	0.53	1.0196	
43.7	0.39	1.0195	
54.4	0.48	1.0197	
51.7	0.48	1.0198	
50.3	0.35	1.0198	Siliconized tubes
40.6	0.28	1.0198	
47.8	0.45	1.0204	
46.5	0.46	1.0200	Very narrow space between ice and stirrer
49.9	0.44	1.0199	
50.2	0.45	1.0200	

A number of experiments with directional freezing gave the results shown in Table 6. The method seems to work well with pure water.

All data, direct experimental and calculated, seem to agree on the value $\alpha_1^s=1.020\pm 0.001$. This value can be approached experimentally only by slow freezing and good stirring.

Salt solutions-ice. Two experimental procedures were used, freezing of ice as a suspension, and directional freezing, in the hope of discovering whether one method was more suitable or convenient than the other.

When separating the suspended ice, part of the solution remained in the ice, and part of the ice melted and mixed the solution. These amounts were determined and corrected for. The results of a number of experiments are given in Table 7.

Table 7. Separation factor, α_1^s , on freezing a suspension of ice from salt solutions.

Salt	Temperature range °C	Mean tempera- ture °C	Freezing velocity % ice/h ^a	Amount frozen % ^a	Adhering solvent % ^b	Molten ice % ^c	α_1^s
KBr	— 2.5 to — 3.6	— 3.0	14.3	25.1	3.0	4.5	1.023
	— 2.5 to — 3.4	— 3.0	12.9	23.7	2.5	4.6	1.021
	— 6.2 to — 8.1	— 7.1	9.4	22.7	3.4	4.8	1.031
	eutectic		11.0	22.1	6 ^d	5 ^d	1.038 ^e
KI	— 3.0 to — 4.0	— 3.5	11.9	23.8	2.5	8.6	1.022
	— 6.1 to — 8.4	— 7.2	9.6	28.9	4.0	4.1	1.030
	— 11.0 to — 16.3	— 13.6	9.0	35.9	2.7	4.4	1.041
	— 10.5 to — 14.7	— 12.6	16.4	30.0	4.2	6.5	1.040
	eutectic		22.7	34.1	8 ^d	8 ^d	1.061 ^f
NaCl	— 8.8 to — 11.7	— 10.3	8.7	21.8	5.9	1.0	1.028

^a Calculated on the initial amount of water.

^b Solvent water as % of total water in the separated solid fraction.

^c Calculated on the amount of ice before centrifugation.

^d Estimated, direct determination not possible.

^e Uncorrected value 1.0354.

^f Uncorrected value 1.0534.

In the case of directional freezing the liquid phase can be separated without any melting of ice. However, the amount of solution enclosed in the solid phase is rather large and erratic, so there may be some uncertainty in the applied corrections, particularly as the salt concentration in the solution varies during the course of the experiment. Experimental results are given in Table 8. It is to be observed that in the cases of eutectic freezing the amount of solution enclosed within the ice cannot be determined. In order to obtain, after corrections, α_1^s values equal to those expected from eqn. (2) and distillation results, it would be necessary to assume the following entrainment of solvent water in the ice: for KCl 9–12 %, for KBr 2.5 % and for KI 8–11 %. These amounts are quite reasonable compared to those which could be experimentally determined.

All results for α_1^s , those determined by direct freezing and those calculated from α_v^1 of distillation experiments, are shown in Figs. 5 a–c. The freezing values seem to be slightly lower. But on the whole the agreement is good, except for $\text{Ca}(\text{NO}_3)_2$, indicating that the data are largely reliable. It cannot be said for certain which freezing method gives the best results. The freezing of ice as a suspension is, however, much quicker and experimentally simpler, and the phase separation could perhaps be improved so as to avoid any melting of the ice.

Table 8. The separation factor α_1^s on directional freezing of ice from salt solutions. Water containing about 10 mole % D_2O used.

Salt	Temperature range °C	Mean tempera- ture °C	Amount frozen % ^a	Freezing velocity g cm ⁻² h ⁻¹	Adhering solvent % ^c	α_1^s
KCl	eutectic	-10.2	54.3	0.11	<i>b</i>	1.0282
	»	-10.2	51.8	0.11	<i>b</i>	1.0292
	»	-10.2	44.1	0.12	<i>b</i>	1.0298
KBr	eutectic	-12.0	35.7	0.08	<i>b</i>	1.0386
	- 4.8 to - 7.1	- 6.0	27.4	0.07	13.7	1.0300
	- 4.7 to - 7.0	- 5.9	28.0	0.08	14.7	1.0295
	- 3.0 to - 4.8	- 3.9	35.4	0.08	3.8	1.0285
	- 3.0 to - 5.0	- 4.0	37.7	0.09	5.8	1.0270
KI	eutectic	-21.0	34.3	0.16	<i>b</i>	1.0547
	»	-21.0	35.9	0.16	<i>b</i>	1.0553
	»	-21.0	31.3	0.13	<i>b</i>	1.0564
	»	-21.0	35.7	0.15	<i>b</i>	1.0568
	- 9.2 to -13.8	-11.5	27.5	0.14	13.3	1.0412
NaCl	- 9.5 to -14.3	-11.9	28.7	0.14	13.2	1.0410
	- 15.0 to -17.2	-16.1	10.6	0.08	18.4	1.0354
	- 14.8 to -17.4	-16.1	11.9	0.09	26.8	1.0380
	- 12.2 to -17.4	-14.8	24.2	0.11	10.8	1.0337
	- 12.0 to -18.0	-15.0	26.6	0.12	13.3	1.0343
	- 5.2 to - 7.7	- 6.5	26.9	0.25	20.4	1.0272
	- 5.0 to - 7.6	- 6.3	27.9	0.25	24.0	1.0265
	- 12.0 to -17.6	-14.8	25.3	0.07	23.1	1.0266
LiNO ₃	- 13.8 to -18.2	-16.0	15.7	0.11	26.7	1.0237
	- 13.6 to -21.0	-17.3	24.3	0.08	32.8	1.0322
Ca(NO ₃) ₂	- 15.2 to -22.8	-19.0	23.6	0.08	39.8	1.0318

^a Calculated on initial amount of water.

^b Cannot be determined, the α_1^s is uncorrected.

^c Calculated as % of the total water in the solid fraction.

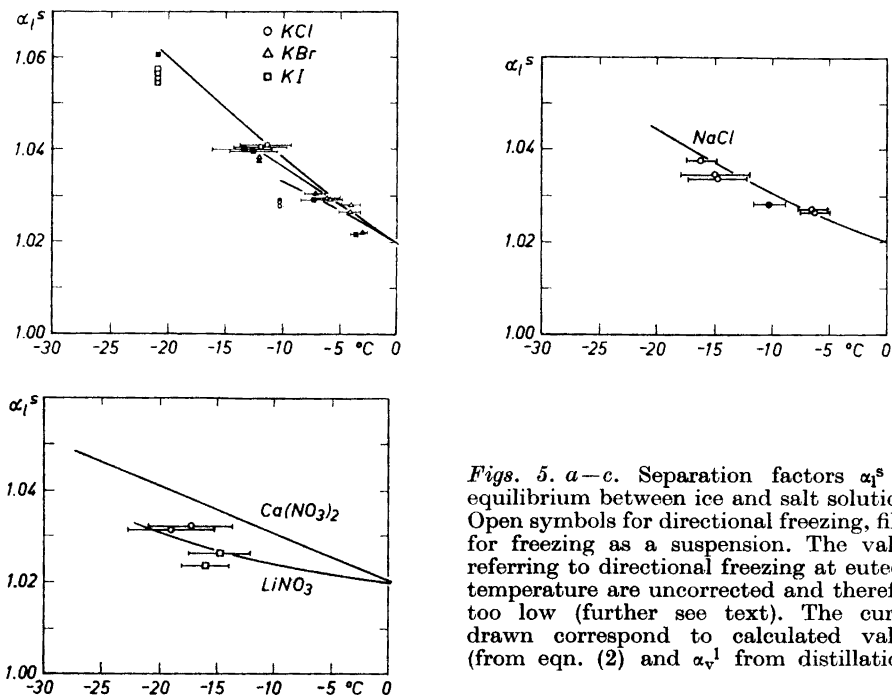
EQUILIBRIUM SALT HYDRATE-SOLUTION

The separation of hydrogen isotopes in salt hydrates has been observed or claimed¹⁹⁻²² but accurate data of separation factors are only given in two papers.^{23,24} The statements are, however, conflicting about the phase into which D_2O enriches.

The separation phenomenon in this case must be closely related to that of other phase equilibria involving salt-water solutions and it was considered of interest to collect some more data, some relating to salt used in the other parts of this work.

Considering the slow diffusion of water in the crystals the only practical experimental method is to grow crystals slowly from solution, assuming equilibrium at the crystal surface but no diffusion in its interior parts.

The present experiments, which are few and may be considered preliminary, have been performed by the slow growing of large crystals and in two cases as directional freezing of congruently melting hydrates. The results are given



Figs. 5. *a-c*. Separation factors α_1^s for equilibrium between ice and salt solutions. Open symbols for directional freezing, filled for freezing as a suspension. The values referring to directional freezing at eutectic temperature are uncorrected and therefore too low (further see text). The curves drawn correspond to calculated values (from eqn. (2) and α_v^1 from distillation).

Table 9. Separation of D_2O on crystallization of salt hydrates. $\alpha > 1$ means enrichment of D_2O in the hydrate.

Salt	Temperature range °C	α
$CuSO_4 \cdot 5aq$	26.0 to 14.0	0.978
$Na_2SO_4 \cdot 10aq$	26.5 to 25.5	1.014
$LiNO_3 \cdot 3aq$	25.1 to 24.3 ^a	1.012
	24.3 to 23.5 ^a	1.020
	16.1 to 14.7 ^a	1.016
	14.7 to 11.6 ^a	1.021
	7.3 to 4.2	1.017
	30.0 ^b	1.008
$Ca(NO_3)_2 \cdot 4aq$	26.0 to 23.8	1.009
	24.2 to 22.7	1.010
	13.5 to 8.0	1.011
	42.9 ^b	1.005

^a Performed consecutively.

^b The congruent melting point.

in Table 9 and Fig. 6. In two pairs of consecutive experiments for $\text{LiNO}_3 \cdot 3\text{aq}$ the results of the second (continued crystallisation from the residual solution from the first) were unreasonably higher than those of the first. We have no obvious explanation; perhaps it is accidental. Unfortunately there was no time for further experiments.

The present result for $\text{CuSO}_4 \cdot 5\text{aq}$ agrees with that of Barrer and Denny²³ who, however, used a larger temperature range. Enrichment of D_2O in $\text{Na}_2\text{SO}_4 \cdot 10\text{aq}$ is to be expected from vapour pressure measurements over $\text{Na}_2\text{SO}_4 \cdot 10\text{D}_2\text{O}$ and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ by Higuchi.¹²

It might be thought that α_v^s for salt hydrates could be calculated from the vapour pressures of the H and D forms using eqn. (3) followed by the application of eqn. (2) in order to obtain the corresponding α_1^s . Many hydrates, however, lose water in steps and it is very probable that the relative vapour

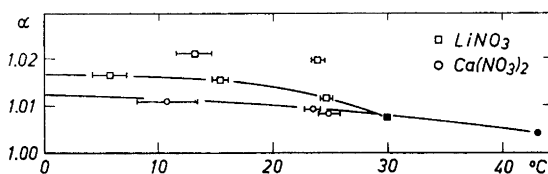


Fig. 6. Separation factor for D_2O on equilibration between salt hydrate and solution, using water containing about 10 mole % D_2O .

pressure ($P_{\text{D}_2\text{O}}/P_{\text{H}_2\text{O}}$) for different pairs of hydrates will differ. Moreover, even in cases where only one hydrate exists water molecules can be bound in different ways in the crystal and the enrichment of deuterium may differ in the different positions. Accordingly no simple relationship is to be expected between enrichment in the salt hydrates and relative vapour pressure over the isotopic forms of the salt hydrate.

Still vapour pressure measurements over salt hydrates may give some idea of what effects may be expected, and we may refer to papers by Bell.^{25,26} According to him the relative volatility of D_2O from a hydrate is sometimes lower and sometimes higher than from liquid water.

If water is bound in the hydrate chiefly by its oxygen it is to be expected that D_2O will enrich in the solution. But if it is bound by a larger number of hydrogen bonds in the crystal, D_2O will probably enrich in the crystal. So even if things are complicated, there may be interesting relations between crystal structure and binding forces on the one hand and enrichment of D_2O on the other.

CONCLUSIONS

Isotopic effects for D_2O in equilibrium between phases (vapour, pure liquid or solution, ice, salt hydrates) can either be determined directly in experiments or calculated from published data, for example from vapour pressures of the pure H_2O and D_2O systems.

Separation factors calculated from vapour pressures may be somewhat wrong because H_2O and D_2O do not form perfectly ideal solutions. Further, the vapour pressures at low temperatures are small and it will be difficult and time-consuming to determine them with the necessary accuracy. Particularly it is difficult to measure vapour pressures over salt hydrates.

Distillation below room temperature from water or salt solutions seems to be an accurate and rather simple direct method. It may have some systematic errors but they are small and may perhaps be further reduced by experimental modifications.

For the freezing of ice from salt solutions two methods have been used, suspension and directional freezing. They both give rise to difficulties in separation of the phases. They have about the same accuracy but freezing as a suspension is simpler and quicker.

The growing of large crystals of salt hydrates is probably an accurate method. Unfortunately it is also very slow. Growing the crystals as a suspension would be more convenient, but then there is the difficulty of phase separation and correction for entrained solution.

DISCUSSION

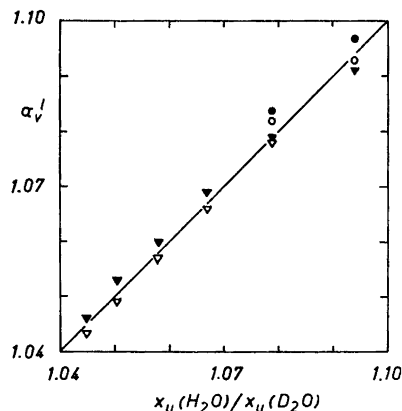
The hydrogen isotope effect in the systems under consideration must be associated to a relatively high degree with the formation of hydrogen bonds. In ice all hydrogen atoms are engaged in hydrogen bonding. In the vapour there are no such bonds. Liquid water has chiefly an ice-like structure, but with several hydrogen bonds broken. In salt solutions in general, further hydrogen bonds are broken.

It may be assumed that the isotopic effect is a function of the difference in degree of hydrogen bonding in the two phases. For equilibrium between a condensed phase and vapour the effect may be considered, at least qualitatively, to give measure of the extent of hydrogen bonding in the condensed phase.

It may be concluded that the strongest separation effect in phase equilibria involving water will be between ice and vapour ($\alpha=1.135$ at 0°C , $\alpha=1.20$ at -30°C). For equilibrium between two condensed phases α is always expected to be considerably lower, since it is unlikely that a condensed phase has very few hydrogen bonds.

Nemethy and Scheraga²⁷ have suggested a model for liquid water and used IR data to estimate the mole fraction of free (not hydrogen bonded) water molecules, x_u . This mole fraction increases with temperature and, at a given temperature, is larger for H_2O than for D_2O . We have observed that their ratios of free molecules in H_2O and D_2O , $x_u(\text{H}_2\text{O})/x_u(\text{D}_2\text{O})$, at given temperatures in the range $10-60^\circ\text{C}$, correspond closely to the separation factors α_v at the same temperatures as demonstrated in Fig. 7. We have no ready explanation for this feature but the relationship is rather striking and it seems appropriate to draw attention to it.

Fig. 7. Separation factor α_v^l for water as a function of the ratio of mole fractions of free water molecules in light and heavy water, $x_u(\text{H}_2\text{O})/x_u(\text{D}_2\text{O})$, at corresponding temperatures in the range 10–60°C as estimated by Nemethy and Scheraga.²⁷ Data from present work \circ ; data from Merlivat *et al.* ∇ ; open symbols represent data calculated from vapour pressure, filled symbols represent data from distillation experiments.



Water and water solutions are complicated systems from a structural point of view. They have been investigated by many methods, but the results are difficult to interpret and often more or less discordant. Determination of isotopic effects in phase equilibria may contribute to the understanding of these systems.

EXPERIMENTAL

Chemicals. Salts of *pro analysi* quality were used without further purification. The water was triple distilled, first from acid permanganate, then from NaOH and at last without additions.

Distillation. A round-bottomed flask, with a thermometer well dipping in the liquid, was used. It was connected by an adapter to a U-shaped condenser, which on the other side had a tube with stopcock for evacuation. The walls of the flask were hydrophobated with dimethyldichlorosilane. In this way the separation factors were found to be about 0.008 higher than with an untreated flask, in which liquid climbs the walls by surface tension and evaporates without adequate mixing with the bulk of the liquid.

Before distillation the liquid was deaerated by repeated freezing, evacuation, and melting.

The flask with about 110 ml water or solution was placed in a bath regulated by a cryostat to within $\pm 0.1^\circ\text{C}$ at $1.5\text{--}2^\circ\text{C}$ above the desired distillation temperature. The liquid was stirred with a magnetic stirrer as vigorously as possible without splashing. The distillation rate was regulated by the temperature of the bath around the condenser. The desired distillation temperature in the flask was reached in about 5 min, corresponding to 5–10 % of the total distillation time, and it could be kept within about $\pm 0.1^\circ\text{C}$. After about 8 g of water had distilled, dry air was admitted and samples from the distillate and the residue were taken.

Analysis. The content of D_2O was determined by a float method according to Baertschi and Thürkau²⁸ on samples completely distilled twice in vacuum.

Accuracy. Float temperatures could be determined within 0.01°C . Comparing two samples this corresponds to a probable error within ± 0.0005 for the separation factor. The absolute content of D_2O was determined within $\pm 0.02\%$ with a 10 ml pycnometer. At 10 % D_2O this corresponds to an error of ± 0.0002 in α . For 1°C change in distillation temperature α changes about 0.0015. The distillation separation factor for H_2^{18}O was measured for some of the salt solutions and was found to be the same as for pure water, $\alpha = 1.01$. As the natural abundance of ^{18}O is only 0.2 %, this corresponds to an error of 0.002 % D_2O or 0.0002 in α . Totally a single determination of α for D_2O should be correct

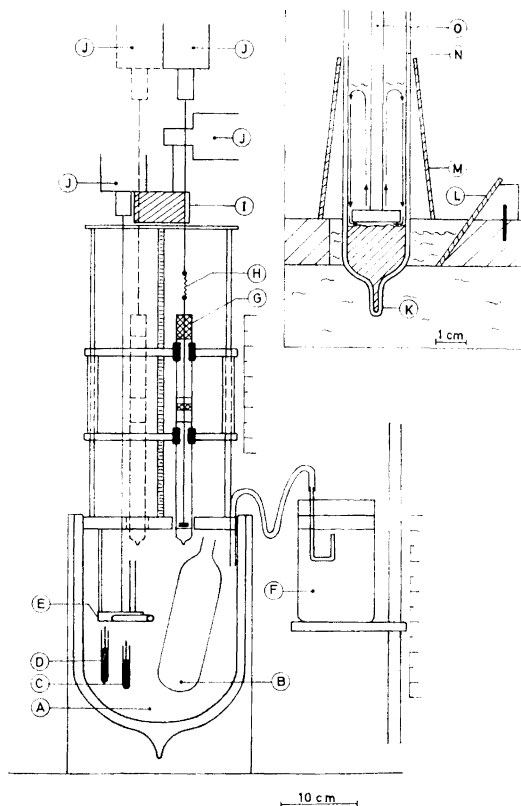


Fig. 8. Apparatus for directional freezing. A: A seven litre Dewar vessel. B: Dip cooler of cryostat Rheinische TK 1. C: Contact thermometer for the cryostat. D: Thermometer. E: Centrifugal pump for efficient stirring. F: Constant level arrangement. G: Slide bearing of vulcan fibre. H: Wire helix connection to damp vibrations. I: Reduction gear 100:1. J: Laboratory stirrer, continuously variable 15–1700 r.p.m. K: Tip for seeding. L: Mirror. M: Temperature shield for work below -10°C . N: Experimental tube, cross-sectional area 3 cm^2 . O: Stirrer of stainless steel, with 6 inclined holes of 1 mm diameter, to obtain good circulation.

to within ± 0.001 , and it was found that repeated determinations generally agreed within this limit.

There are possibly systematic errors in the distillation. If the stirring is insufficient or the diffusion in the liquid is too slow, D_2O will enrich locally and a too low separation factor will result. If the surface is colder than the rest of the liquid the separation factor tends to be too high. If the distillation rate is too high the separation factor may also be too high. Estimating according to Kucherov and Rikenglaz²⁹ we obtain an error of about 0.0025 at the rate $0.2\text{ g cm}^{-2}\text{ h}^{-1}$.

Freezing of ice as a suspension. The partial freezing of salt solutions was performed in a stainless steel beaker, cooled in a glass sleeve, and under efficient stirring. After 2–4 h a sample of the liquid was taken and analysed for salt in order to determine how much ice had formed. Ice and solution were separated by a short centrifugation (4 min at

4000 g) in vessels precooled to the freezing temperature. Samples of the solution and the melted ice were analysed for salt in order to determine the amount of solution adhering to the ice and the amount of ice which had melted during the centrifugation. From samples of the ice and the solution water was distilled and analysed for D_2O as already described.

Directional freezing. An apparatus according to Fig. 8 was used to lower tubes with water or salt solution slowly into a cold bath. The following experimental conditions were used. The solution in each tube was prepared from about 14 g water with about 10 mole % D_2O . The bath temperature was about $5^\circ C$ below the pertinent freezing point. The lowering velocity was $1-2 \text{ mm h}^{-1}$, corresponding to 10–20 h for freezing half the amount of water and the stirrer velocity in the tubes 1400 rpm. The intention was to have a strong shearing in the liquid near the ice surface and the distance between the ice surface and the stirrer should be small, preferably $\leq 1 \text{ mm}$. This was possible in the case of pure water, but not with salt solutions, in which it had to be 2–10 mm in order to avoid the formation of suspended ice.

The phases were separated by sucking off the liquid through a capillary, and the water was analysed for D_2O as already described or, in some cases of a small amount of sample, by the falling drop method.³⁰ The solid phase was analysed for salt in order to estimate the amount of solution adhering to it.

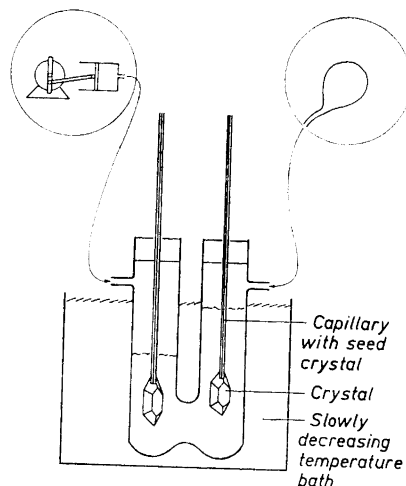


Fig. 9. Arrangement for growing large crystals of salt hydrates.

Growing crystals of salt hydrates. A U-tube as in Fig. 9 was used for growing large crystals. The amount of solution was about 200 ml, prepared from water containing about 10 mole % D_2O . A slowly oscillating air pressure provided mild but efficient stirring. The temperature was continuously and slowly lowered so that in 2–3 days crystals with 5–8 g hydrate water had formed. In the case of $CuSO_4 \cdot 5aq$ the salt separated as a number of smaller crystals on the bottom and at the walls of the tube.

Crystallization of $LiNO_3 \cdot 3aq$ and $Ca(NO_3)_2 \cdot 4aq$ at their congruent melting point was performed as directional freezing with the apparatus already described (Fig. 8).

Water from the crystals and from the remaining solution was recovered, purified, and analysed as described above.

Auxiliary data. Solubilities and eutectic temperatures for the salts in water containing 10 % D_2O were needed. They were obtained by interpolating data for H_2O and D_2O taken from Landolt-Börnstein¹⁴ and from Holmberg.³¹ Data for $LiNO_3$ and $Ca(NO_3)_2$ in D_2O were not available and had to be determined (see Tables 10 and 11).

Table 10. Equilibria of LiNO₃ solutions with LiNO₃·3aq or ice (light and heavy water).

Solvent	Solid phase	Temperature °C	Weight % LiNO ₃
H ₂ O	ice	- 6.24	10.06
	»	- 14.36	18.20
	»	- 16.68	20.03
	eutectic	- 22.74	24.28
	LiNO ₃ ·3H ₂ O	- 14.26	27.37
	»	- 10.47	28.76
	»	- 4.12	31.31
D ₂ O	»	+ 4.08	34.06
	eutectic	- 19.06	23.28
	LiNO ₃ ·3D ₂ O	- 9.88	26.24
	»	+ 0.17	30.11

Table 11. Equilibrium between Ca(NO₃)₂·4aq and its solution in light and heavy water.

Solvent	Temperature °C	Weight % Ca(NO ₃) ₂
H ₂ O	- 4.95	48.3
	- 11.0	46.7
	- 15.6	45.7
	- 24.9	43.2
	- 26.3	42.9
	eutectic = - 27.83	
D ₂ O	- 4.95	45.3
	- 11.0	43.6
	- 15.6	42.4
	- 22.2	40.8
	eutectic = - 23.33	40.7

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