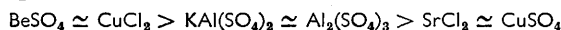


904. Water in Hydrates. Part I. Fractionation of Hydrogen Isotopes by Crystallisation of Salt Hydrates.

By R. M. BARRER and A. F. DENNY.

Isotopic fractionation of mixtures of light and heavy water during the crystallisation of stoichiometric crystallohydrates from their saturated solutions was studied. The crystallising salt hydrates gave separation factors in the probable order



In all cases crystallisation caused the mother-liquor to be enriched in heavy water. The possible significance and interpretation of the results have been considered.

WHEN hydrogen and deuterium are present in each of two phases which are in equilibrium the isotopic compositions of the phases can be expected to differ. Several investigations of this fractionation have been reported when the two phases in contact were a stoichiometric salt hydrate and its saturated aqueous solution.¹⁻³ However, it proved difficult from these studies to draw general conclusions as to the direction of the enrichment and its magnitude, and it was therefore of interest to obtain further results using this method of isotopic fractionation. It was hoped to find, *inter alia*, whether large enough separation factors can ever occur to make crystallisation a potentially interesting technique for separating hydrogen isotopes. Equilibria between light and heavy water and non-stoichiometric zeolite hydrates have recently been examined,^{4,5} so that comparison of fractionation by these and by stoichiometric hydrates merits attention.

EXPERIMENTAL

(a) *Crystallisation Procedure.*—The salts crystallised from the deuterium-enriched water were AnalaR copper sulphate, copper chloride, strontium chloride, beryllium sulphate, aluminium sulphate, and potash alum. 99.8% Deuterium oxide was supplied by Imperial Chemical Industries Limited.

Distilled water and the salt were placed in a 500 ml. flask and sufficient deuterium oxide was added to ensure the required deuterium concentration. The salt content was sufficient to saturate the solution at about 70°. The mixture was refluxed for at least 1 hr., the condenser being fitted with a calcium chloride tube. When the solution being refluxed contained aluminium sulphate or potash alum, a few drops of AnalaR sulphuric acid were added to prevent hydrolysis. The mixture was then cooled slightly, filtered into a weighed 500 ml. flask, and again refluxed for at least 30 min. The flask was allowed to cool slightly and a sample of about 3 ml. was withdrawn quickly with a drop pipette. The sample was placed in *K* (Fig. 1) which was at once sealed with *L*. The deuterium content of this solution was then determined. A second 3 ml. sample was withdrawn immediately after *K* was sealed and placed in a tared weighing bottle, which was then reweighed and the sample analysed for its salt content. All weighing bottles were fitted with B24 joints which were protected by P.T.F.E. sleeves.

The 500 ml. flask was stoppered as soon as the samples had been withdrawn and it was then weighed. The joint was always protected by a P.T.F.E. sleeve and a little Apiezon grease was smeared round the top of the stopper, after reweighing, as an additional precaution. The total weight of water and salt in the flask was now known. The flask was allowed to cool to room temperature, while being constantly shaken, and crystallisation of some of the salt occurred at this stage. Two 3 ml. samples of the mother-liquor were next withdrawn and treated in the same way as the previous two samples (*i.e.*, deuterium and salt concentrations were determined as subsequently described). As the flask had been stoppered while the solution was

¹ Day, Hughes, Ingold, and Wilson, *J.*, 1934, 1593.

² Uusitalo, *Suomen Kem.*, 1958, **31**, B, 362.

³ Teis, *Doklady Akad. Nauk S.S.S.R.*, 1954, **99**, 585.

⁴ Barrer and Fender, *J. Phys. and Chem. Solids*, 1961, **21**, 1.

⁵ Barrer and Denny, following Paper.

warm, there should be a partial vacuum inside the flask. If this was not so, the experiment was abandoned.

(b) *Determination of Salt Concentrations.*—The salts in the aqueous phase were determined as follows.⁶

CuSO_4 and CuCl_2 . The Cu^{++} ion was estimated volumetrically by the potassium iodide-sodium thiosulphate method.

BeSO_4 . Be^{++} was determined by precipitating the hydroxide and igniting it to the oxide.

$\text{Al}_2(\text{SO}_4)_3$ and $\text{KAl}(\text{SO}_4)_2$. Al^{+++} was determined gravimetrically as the 8-hydroxyquinolin adduct.

SrCl_2 . The Cl^- ion was determined volumetrically by titration with silver nitrate.

(c) *Purification of the Water.*—Since the deuterium content of the water was to be determined by a density method, the water was rigorously purified before analysis. The methods of purification and densometric analysis were slight modifications of those of Anderson *et al.*⁷ Some of the samples contained dissolved salt whereas others were mixtures of distilled and of heavy water used for calibration purposes, so that the procedure was varied according to the type of aqueous phase.

The apparatus used is shown in Fig. 1. G was first connected to C , and N and M were joined to D , the tap in M being shut. The apparatus was evacuated, the traps A and B were immersed in liquid oxygen, and tap P was then shut. If the water to be purified contained a salt it was placed in K and closed with the cap L lubricated with a little Apiezon L grease. K was next joined to M and the tap in M was carefully opened. The water was now degassed by

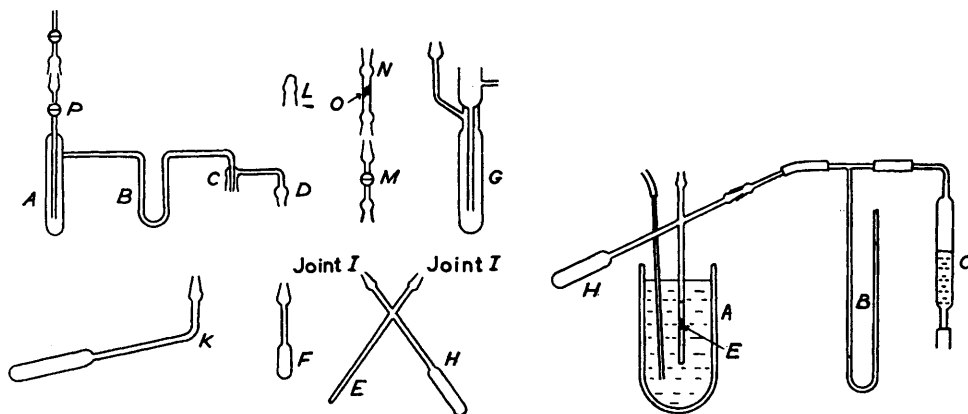


FIG. 1.

FIG. 2.

opening P momentarily until the system was evacuated. The liquid oxygen around A and B was then removed, and G was immersed in this refrigerant. The water was then allowed to distil into G from K . When almost all the water had distilled over, K was surrounded by an electric furnace and the temperature was slowly raised to about 300° . When the salt in K was completely anhydrous the tap in M was shut and the ice in G was allowed to melt. N contained a plug of glass wool, O , to prevent salt being carried over during distillation.

If the deuterated water contained no salt the sample to be purified was placed in F which was then connected to M . The water was degassed as described above and then distilled *in vacuo* to G .

After this stage the samples from both sources were treated in the same way. G , containing the water, was removed and the opening capped using L . G was so constructed that it could be used as a reflux condenser. A few mg. of AnalaR sodium peroxide were added and the mixture refluxed for 10 min. to neutralise any acids in the water. Some mg. of AnalaR potassium permanganate were then added and the mixture refluxed for a further 20 min. to oxidise any organic matter in the water. The mixture was then allowed to cool. Meanwhile both H and the cartesian diver, E , to be used in the densometric analysis of the water, had

⁶ See, *e.g.*, Vogel, "A Textbook of Quantitative Inorganic Analysis," Longmans, Third edn., 1961.

⁷ Anderson, Purcell, Pearson, King, James; Emeléus, and Briscoe, *J.*, 1937, 1492.

been thoroughly cleaned and *E* was placed in the narrow arm of *H*, closed at the top by the cap at *J*. *H* was joined to *C* by joint *I*, and *N* and *M* were replaced by fresh units *N* and *M*. *H* was then dried under vacuum, and *G* was joined to *M*, the joint being lightly lubricated as usual. Tap *P* was shut and that in *M* opened. The water was degassed as before, *A* and *B* being surrounded by liquid oxygen. This liquid oxygen was then removed from *A* and *B* and used to cool the wide limb of *H*. All the water in *G* was next distilled into *H* under vacuum, the tap in *M* was shut, and the ice in *H* allowed to melt. *H* was then connected to the apparatus shown in Fig. 2, ready for densometric analysis.

The apparatus (except *H* and *E*) was cleaned between runs with chromic-sulphuric acid mixtures followed by thorough washing with distilled water and drying. *H* and *E* were cleaned using nitric-chromic-sulphuric acid mixture, followed by thorough washing with distilled water and steaming each arm for at least 30 min. After washing and drying, joints *I* and *J* were immediately covered with tin foil.

(*d*) *Deuterium Content of the Water*.—After *H*, containing the water purified as described above, had been joined with the rest of the apparatus in Fig. 2, it was slowly tilted so that the water ran into the side arm containing the float *E*. This side arm was immersed vertically inside the Dewar vessel which served as a thermostat. The mercury level in *C* was adjusted so that a pressure of 76 cm. Hg was maintained inside *H*.

When the float *E* is stationary in the water the density of the float is the same as that of the water. The density of the water could be altered by varying the temperature of the thermostat, and is also a function of the deuterium content. The temperature at which the float remained stationary (flotation temperature) could be found quickly because the rate of movement of the float was a linear function of temperature over an interval up to 1° on either side of the flotation temperature. The temperature of the thermostat was read either on a Beckmann thermometer or, later, on a 20–32° calorimeter thermometer calibrated in 0.02° intervals. The temperature of the thermostat was adjusted until it was near the flotation temperature, and left for at least 10 min. for thermal equilibrium to be established fully. The upward or downward movement of the float was measured using a cathetometer and stopwatch and the distance moved in not less than 100 sec. was found. Two values of float velocity were measured on each side of the flotation temperature, and the linear graph then gave this flotation temperature.

The water in *H* was next poured into *F*. Distillation into *H* was repeated as described above, using the apparatus in Fig. 1. The flotation temperature was remeasured and the two values had to agree to less than 0.02° for deuterium contents up to about 12% D₂O and to within 0.06° for deuterium contents as high as 27% D₂O. Otherwise the experiment was discarded and the whole procedure repeated. Since the floats had been previously calibrated using waters of known deuterium content, prepared in a dry box, the flotation temperatures gave this content for any sample of unknown deuterium content. A change of up to 3 to 4° in the flotation temperature was caused by changing the D₂O concentration by 1% w/w.

(*e*) *Floats and Thermostat*.—The floats were made from drawn-out Pyrex glass tubing, those of the correct density being found by trial and error. The wide Dewar flask used as a thermostat had a vertical unsilvered strip down each side. Any temperature within a few degrees of room temperature could be held to within 0.01° for the duration of a densometric experiment. Stirring was effected by a slow stream of air bubbles, and temperature changes by small additions of hot or cold water. Since all of *H* in Fig. 2 was not necessarily at the same temperature as its limb containing the cartesian diver, *E*, and since there is fractionation of hydrogen and deuterium on vaporisation of water it might be thought that a time-dependence of flotation temperature would occur. However, over the time scale of the experiments no such effect was ever detected.

(*f*) *Calculation of the Separation Factor*.—The separation factor is defined as

$$\eta = \frac{(\text{D}_2\text{O})_{\text{solution}}}{(\text{H}_2\text{O})_{\text{solution}}} \bigg/ \frac{(\text{D}_2\text{O})_{\text{salt}}}{(\text{H}_2\text{O})_{\text{salt}}} \quad (1)$$

where the formulæ in parentheses denote weight per cent. of the species. In this formula only D₂O and H₂O are considered, *i.e.*, DOH is regarded as $\frac{1}{2}\text{D}_2\text{O} + \frac{1}{2}\text{H}_2\text{O}$. η can be derived from the experimental measurements as follows. If *P* denotes the mean molecular weight of a deuterium-containing water and *h* and *d* are the weight % of H₂O and D₂O in the water, then

$$P = 100 \bigg/ \left(\frac{h}{18.016} + \frac{d}{20.03} \right) \quad (2)$$

Also, if M denotes the total weight of water plus salt used in the crystallisation experiment, S is the weight of solution phase after crystallisation, m is the weight of crystals (in the anhydrous condition) in the crystallisate, N is the molecular weight of the anhydrous salt in the crystallisate, and n is the number of moles of water of hydration per mole of anhydrous salt, then

$$\text{Total wt.} = \text{Wt. of solution phase} + \text{Wt. of anhydrous crystals in crystallisate} + \text{Wt. of water of hydration}$$

$$\text{i.e.,} \quad M = S + m + mnP/N \quad (3)$$

Further, if a is the weight fraction of anhydrous salt in the hot solution (*i.e.*, when all the salt is dissolved), and b is the weight fraction of anhydrous salt in the mother-liquor after crystallisation, then

$$Ma = Sb + m \quad (4)$$

Elimination of S between (3) and (4) gives

$$m = M(a - b)/(1 - b - bnP/N) \quad (5)$$

Since all terms on the right-hand side of eqn. (4) have been determined by the analytical procedures described, m , the weight of anhydrous crystals in the crystallisate is found. This gives at once the weight, m_3 , of hydrate water as

$$m_3 = mnP/N \quad (6)$$

Also, if m_2 denotes the weight of water in the mother-liquor, and m_1 is the total mass of water in the mixture, then

$$m_1 C_1 = m_2 C_2 + m_3 C_3 \quad (7)$$

where C_1 , C_2 , and C_3 are respectively the concentrations of D_2O on the weight fraction scale in the masses m_1 , m_2 , and m_3 of water. Also

$$m_1 = M(1 - a) \quad (8)$$

and so is known, while

$$m_2 = (m_1 - m_3) = S(1 - b) \quad (9)$$

and thus can be calculated. Since, however, C_1 and C_2 are known from the densometric analysis, C_3 can be calculated from eqn. (7). Because the concentration of D_2O in the solution changes as crystallisation progresses, C_3 is an average value in the water of crystallisation. Similarly, during crystallisation C_1 changes to C_2 so that it is appropriate to use an average value $C_s = \frac{1}{2}(C_1 + C_2)$ in the formula for the separation factor η . The weight fractions can also conveniently be expressed in η as percentages, so that in this case

$$\eta = \frac{C_s}{(100 - C_s)} \bigg/ \frac{C_3}{(100 - C_3)} \quad (10)$$

While the values of C_1 , C_2 , m_1 , m_2 , and m_3 were all very accurately determined the cumulative error could be considerably larger. The maximum error is approximated by

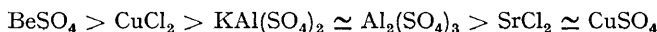
$$E = \frac{\pm x}{C_3(1 + C_3)} \left[1 + \frac{m_1 + m_2}{m_3} \right] \quad (11)$$

where $\pm x$ is the maximum error tolerated in measuring either C_1 or C_2 (the above expression assumes that errors in C_1 and C_2 were the same, which is not necessarily so). Errors recorded in Table I are these maximum tolerated errors. The actual experimental error usually approached this maximum but was sometimes considerably lower. The maximum values arise from the previously decided temperature limits within which the two measurements of flotation temperature had to agree and which can be converted into concentration units using the float calibration factor.

RESULTS

Measurements of separation factors are summarised in Table I. For the whole range of D_2O concentrations and for each salt $\eta > 1$, so that heavy water is concentrated in the aqueous

phase and light water in the crystalhydrates. No trends can be observed in the separation factors, η , with D₂O concentration, but η may vary with the salt in the sequence



In cupric sulphate and strontium chloride some of the crystal water is associated with the anion,⁸ but in all other salts it is only the cations which are co-ordinated to the water molecules. Although the solutions were constantly being shaken during the crystallisation process in order to ensure renewal of the aqueous phase in contact with the growing crystals, it is still possible that the separation factors may not represent the true equilibrium values, since the crystals grew at finite rates. To be certain that η represented equilibrium it would be necessary to show that its magnitude did not change with changes in rate of crystallisation. If this was not

TABLE I.
Enrichment factors, η_1 .

Salt	Initial D ₂ O concentration (wt. %)	Separation factor * (η)	Variance of the mean $v_m \times 10^6$	Standard deviation $\delta \times 10^3$	Student's constant t	Mean separation factor and 95% probability limit $\bar{x} \pm \sigma t$
Cupric sulphate	3.21	1.025 ± 0.014	7.38	2.717	2.37	1.022 ± 0.006
	3.86	1.024 ± 0.011				
	4.82	1.011 ± 0.008				
	7.51	1.018 ± 0.004				
	9.05	1.018 ± 0.004				
	9.61	1.017 ± 0.017				
	18.75	1.027 ± 0.018				
	18.92	1.033 ± 0.018				
Strontium chloride	9.12	1.025 ± 0.015	2.23	1.493	3.18	1.024 ± 0.005
	9.13	1.027 ± 0.015				
	25.57	1.025 ± 0.006				
	25.59	1.020 ± 0.006				
Aluminium sulphate	9.11	1.040 ± 0.020	5.23	2.287	3.18	1.035 ± 0.007
	9.57	1.033 ± 0.020				
	24.71	1.030 ± 0.015				
	25.38	1.038 ± 0.015				
Potassium aluminium sulphate	8.60	1.035 ± 0.006	4.85	2.202	2.57	1.036 ± 0.012
	18.20	1.043 ± 0.010				
	19.52	1.038 ± 0.015				
	24.68	1.031 ± 0.005				
	24.98	1.038 ± 0.005				
	26.52	1.028 ± 0.004				
Cupric chloride	8.96	1.056 ± 0.030	47.08	6.861	3.18	1.048 ± 0.022
	8.98	1.033 ± 0.025				
	25.40	1.039 ± 0.050				
	25.96	1.062 ± 0.050				
Beryllium sulphate	7.65	1.069 ± 0.006	19.40	4.405	2.57	1.055 ± 0.011
	9.15	1.061 ± 0.006				
	9.27	1.051 ± 0.005				
	18.40	1.058 ± 0.018				
	19.24	1.037 ± 0.010				
	19.39	1.054 ± 0.015				

* The \pm limits given in column 3 are the maximum tolerated errors given by eqn. (11). They are not the experimental errors.

so the separation factor would have to be obtained at various crystallisation rates and extrapolated to zero rate.

Validity of the Results.—Three different types of control experiment were conducted in order to establish the validity of the results of Table I. In these the experimental procedure already described was carried out under the following conditions: (i) a mixture of light and heavy water was used, but no salt was present (Table 2); (ii) a solution of the salt in light water was employed with no addition of heavy water (Table 3); (iii) a solution of the salt in a mixture of light and heavy water was used, but the solution was not saturated with respect to the salt at room temperature (Table 4).

In virtually all the measurements recorded in Tables 2, 3, and 4 the final purified water had a

⁸ For CuSO₄·5H₂O see, e.g., Wells, "Structural Inorganic Chemistry," O.U.P., 1945, p. 379; and for SrCl₂·6H₂O see Tovberg Jensen, *Nord Kemikermode Forh.*, 1939, 5, 201.

TABLE 2.

Blank experiments. No salt present; (D ₂ O + H ₂ O) in the mixtures.					
Initial D ₂ O concn. (wt. %)	Initial flotation temp.	Average temp.	Final flotation temp.	Average temp.	Difference of columns 4 and 5
	2-998°		2-978°		
9-22	2-982	2-990°	2-952	2-965°	-0-025°
	3-063		3-044		
9-24	3-057	3-060	3-030	3-037	-0-023
	3-063		3-043		
9-24	3-049	3-056	3-021	3-032	-0-024
	25-628		25-634		
25-04	25-580	25-604	25-556	25-595	-0-009

TABLE 3.

Blank experiments. Salt present; no D ₂ O in the mixtures.					
Salt	Initial flotation temp.	Average temp.	Final flotation temp.	Average temp.	Difference in columns 4 and 5
	2-317°		2-297°		
CuSO ₄	2-296	2-306°	2-283	3-290°	-0-016°
	2-316		2-294		
BeSO ₄	2-302	2-309	2-306	2-300	-0-009
	28-695		28-686		
Al ₂ (SO ₄) ₃	28-690	28-692	28-686	28-686	-0-006
	28-694		28-686		
KAl(SO ₄) ₂	28-679	28-686	28-686	28-686	0-000
	28-674		28-657		
CuCl ₂	28-644	28-659	28-665	28-658	-0-001
	28-654		28-674		
SrCl ₂	28-665	28-659	28-665	28-669	+0-010

TABLE 4.

No crystals present. Cupric chloride only was used; (D₂O + H₂O) in the mixture.

Initial D ₂ O concn.	Initial flotation temp.	Average temp.	Final flotation temp.	Average temp.	Difference in columns 4 and 5
	27-010°		27-000°		
9-36	26-985	26-997°	26-968	26-984°	-0-013°

flotation temperature slightly *below* but within experimental error equal to that of the water taken initially. On the other hand, in the separations of Table 1 the final flotation temperature was always *above* the initial flotation temperature. When the consistency of the present work, and the type and number of the control experiments is considered, one is justified in concluding that the separation found is indeed a function of the crystallisation process. The value of η is an average over the temperature range in which the crystals separated from the cooling mother-liquor.

DISCUSSION

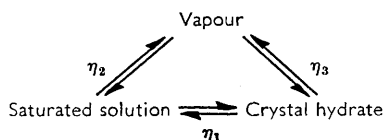
The results in Table 1 may be compared with observations of Day *et al.*,¹ of Uusitalo,² and of Teis.³ Day *et al.* reported that any separation factor must be less than 1-001 and Uusitalo that deuterium was concentrated in the crystal phase with sodium sulphate, but no fractionation was observed with strontium chloride. Teis reported concentration of deuterium in crystals of Na₂CO₃·10H₂O, Na₂SO₄·10H₂O, BaCl₂·2H₂O, and CaSO₄·2H₂O, the effect being opposite in direction to that which we have found. All these workers used heavy water concentrations less than about 2%. We have found these concentrations too small to give satisfactory results in our densometric estimations, and also there is no reference to control experiments such as those in Tables 2, 3, and 4. It is further possible that departures from equilibrium separation factors occur to variable degrees in the several studies. Recently it has been reported that all univalent ions (except the F⁻ ion) are preferentially solvated by H₂O.^{9,10} If this is also true for the multivalent ions

⁹ Swain and Bader, *Tetrahedron*, 1960, **10**, 182.

¹⁰ Gold, *Proc. Chem. Soc.*, 1963, 141.

examined and persists during actual deposition of cations on the growing crystalhydrate lattice one may readily account for the direction of the enrichment observed for the crystalhydrates in Table 1.

Some indirect evidence regarding the nearness of one of our enrichment factors to equilibrium may be obtained in the following way. Let η_1 , η_2 , η_3 denote the equilibrium separation (or enrichment) factors in the three equilibria:



In this set of equilibria, η_1 is as defined in eqn. (1), and the other fractionation factors are given by

$$\eta_2 = \frac{[\text{D}_2\text{O}]_{\text{sol.}} [\text{H}_2\text{O}]_{\text{vap.}}}{[\text{D}_2\text{O}]_{\text{vap.}} [\text{H}_2\text{O}]_{\text{sol.}}}, \quad \eta_3 = \frac{[\text{D}_2\text{O}]_{\text{salt}} [\text{H}_2\text{O}]_{\text{vap.}}}{[\text{D}_2\text{O}]_{\text{vap.}} [\text{H}_2\text{O}]_{\text{salt}}} \quad (1a)$$

We have measured a factor which will tentatively be identified with η_1 and which is then related to the other factors by

$$\eta_1 \eta_3 = \eta_2 \quad (12)$$

Combs *et al.*¹¹ found that the separation factor for salt-free ($\text{D}_2\text{O} + \text{H}_2\text{O}$) mixtures in equilibrium with their vapours could be approximated by

$$\eta^2 = p^{\circ}_{\text{H}}/p^{\circ}_{\text{D}} \quad (13)$$

where p°_{H} , p°_{D} are the vapour pressures of pure H_2O and D_2O . We will assume a similar relation to apply for a crystalhydrate containing both D_2O and H_2O in equilibrium with its vapour. The pressures p°_{H} and p°_{D} will however now denote the dissociation pressures of the crystalhydrate containing only H_2O and only D_2O , respectively. Then at 25° the results of Miles and Menzies¹² lead to $\eta_3 = 1.04$ and 1.02 respectively for the crystalhydrates of copper sulphate and of strontium chloride. Miles and Menzies also found solubilities of CuSO_4 at 25° of 1.39 and 1.29 moles of salt per 55.51 moles of pure H_2O and D_2O , respectively. They noted that the vapour pressure, p^{s}_{H} , of the saturated solution in light water was that calculated from Raoult's law, complete ionization being assumed, multiplied by a factor 1.022. With heavy water this factor was 1.03. If we assume the correctness for the saturated solution of salt in ($\text{D}_2\text{O} + \text{H}_2\text{O}$) mixtures of an equation like eqn. (13) having the form

$$\eta_2^2 = p^{\text{s}}_{\text{H}}/p^{\text{s}}_{\text{D}} \quad (13a)$$

then we calculate from the above numerical data that $\eta_2 = 1.06$. This value may be somewhat high since η tends to decrease linearly with amount of added salt.^{11,13} However, with the aid of eqn. (12) one may calculate $\eta_1 = 1.02$ in correspondence with the experimental value 1.022 ± 0.010 in Table 1. If the above extensions of eqn. (13) can be considered valid the enrichment factor we have measured would appear to be the equilibrium value. For the crystalhydrate of SrCl_2 , from η_3 and η_1 eqn. (12) gives η_2 as ~ 1.05 .

When liquid water is sorbed by zeolites^{4,5} a negligible difference was found in the uptake of pure D_2O and pure H_2O . If the zeolite is to be regarded as a concentrated solid electrolyte solution the calculations of Swain and Bader⁹ suggest that the salt-free aqueous phase should for ($\text{H}_2\text{O} + \text{D}_2\text{O}$) mixtures be enriched in D_2O and the zeolitic water in H_2O . However only a little isotope fractionation was in fact observed when ($\text{H}_2\text{O} + \text{D}_2\text{O}$)

¹¹ Combs, Googin, and Smith, *J. Phys. Chem.*, 1954, **58**, 100; Combs and Smith, *ibid.*, 1957, **61**, 441.

¹² Miles and Menzies, *J. Amer. Chem. Soc.*, 1934, **56**, 1647.

¹³ Googin and Smith, *J. Phys. Chem.*, 1957, **61**, 345.

mixtures were passed up a column of the synthetic zeolite Linde Sieve A,⁵ the D₂O being sorbed more strongly in the column. There is accordingly a factor operating in the opposite direction to that of ion solvation. Because of the restricted intracrystalline environment in which some zeolitic cations are shielded from solvation, this solvation will be less complete than in aqueous solutions. Also it is considered that hydrogen bonds are less strong than deuterium bonds¹⁴⁻¹⁶ and the zeolitic water molecules are hydrogen bonded not only to each other but also, and more particularly, to the anionic oxygens of the aluminosilicate frameworks. The greater the net anionic charge of these oxygens the stronger these bonds may be with a differential effect in favour of bonds involving deuterium. This must very nearly offset the preference of the cations to be solvated by H₂O⁹ according to our experimental observations.^{4,5} On the other hand when sorption of water occurs from the vapour phase only, the zeolites sorb heavy water preferentially, and isotopic fractionation is more easily realisable.

This and the following Paper forms part of a programme sponsored by the D.S.I.R. and the Rockefeller Foundation. One of us (A. F. D.) acknowledges a bursary from the Rockefeller Foundation. We thank Dr. E. C. Potter of the Central Electricity Research Laboratories for assistance with statistical evaluation.

PHYSICAL CHEMISTRY LABORATORIES,
IMPERIAL COLLEGE, LONDON S.W.7.

[Received, December 6th, 1963.]

¹⁴ Huggins, *J. Org. Chem.*, 1936, **1**, 407.

¹⁵ Lewis and Schutz, *J. Amer. Chem. Soc.*, 1934, **56**, 1002.

¹⁶ Wang, *J. Amer. Chem. Soc.*, 1951, **73**, 4181.
