

## Phase Diagrams of Some Sodium and Potassium Salts in Light and Heavy Water

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Phase diagrams for fluorides, chlorides, bromides, iodides, nitrates, sulphates, and carbonates of sodium and potassium with  $D_2O$  and  $H_2O$  have been determined in the range from eutectic temperature to  $60^\circ C$ . Generally the relative solubility is less in  $D_2O$ , but there are some exceptions in cases of a hydrate as the solid phase. The freezing point depression for freezing of ice is often somewhat smaller in the case of  $D_2O$ .

The first note on salt solubility in  $D_2O$  was published in 1933, soon after the discovery of deuterium and the first isolation of  $D_2O$ . It referred to the solubility of  $NaCl$  and  $BaCl_2$  at  $25^\circ C$ .<sup>1</sup> Later on several investigations of salt solubility in  $D_2O$  have been published. The most important are:  $KCl$  from 0 to  $180^\circ C$ ,<sup>2</sup>  $NaCl$ ,  $NaBr$ ,  $NaI$ ,  $KBr$ ,  $KI$ ,  $Na_2SO_4$ ,  $BaCl_2$ ,  $CdI_2$ , and  $HgCl_2$  from 0 to over  $100^\circ C$ ,<sup>3</sup>  $CdSO_4$   $-1$  to  $70^\circ C$ ,<sup>4</sup>  $CuSO_4$  and  $SrCl_2$  0 to over  $100^\circ C$ ,<sup>5</sup>  $MnSO_4$  99 to  $138^\circ C$ ,<sup>6</sup>  $AgClO_3$ ,  $TiClO_4$ ,  $KMnO_4$ ,  $TiNO_3$ ,  $K_2Cr_2O_7$  5 to  $35^\circ C$  and  $CsNO_3$ ,  $KAg(CN)_2$ ,  $KClO_3$ ,  $NaBrO_3$ ,  $Na_2C_2O_4$ ,  $Hg(CN)_2$  at  $5^\circ C$  and  $PbCl_2$  at  $25^\circ C$ ,<sup>7</sup>  $KCl$ ,  $KBr$ ,  $KI$ ,  $KIO_3$ ,  $K_2SO_4$ ,  $KReO_4$ ,  $K_3Fe(CN)_6$  at  $25^\circ C$ <sup>8</sup> and  $KNO_3$ ,  $KMnO_4$  and  $KSCN$  at  $25^\circ C$ .<sup>9</sup>

According to these early measurements the solubility of a salt in one mole  $D_2O$  is nearly always less than in one mole  $H_2O$ . The relative difference in solubility varies much with temperature and is generally larger at low temperatures. Therefore measurements performed at a single temperature have a rather limited value. Almost no work has been done below  $0^\circ C$ , where the largest effects are to be expected. In the first investigations only small amounts of  $D_2O$  were available and it was necessary to use experimental methods which permitted repeated use of the heavy water but did not give the highest accuracy.

The aim of the present work was to measure the relative solubility of a number of common salts in  $H_2O$  and  $D_2O$  in the range from  $60^\circ C$  down to eutectic temperature. Partly this was done in order to corroborate and, if possible, improve earlier data, but chiefly in order to investigate a larger number of salts and to make measurements in the range of interest below  $0^\circ C$ .

Solubility depends in a sensitive way upon the interaction between solute and solvent. Data of solubility in heavy water may therefore possibly contribute to a deeper understanding of the structure of water and its solutions. Moreover  $D_2O$  is nowadays so important that accurate data of its ability to dissolve common salts ought to be available.

In most cases a few points on the curve of freezing of ice have been determined in order to obtain more complete phase diagrams.

## EXPERIMENTAL

*Chemicals.* Twice distilled natural water and heavy water (99.7–99.98 mole %  $D_2O$ ) were used. The salts were from E. Merck and of *p.a.* quality except in the following cases. Sodium bromide was Mallinckrodt analytical reagent. Potassium fluoride, "Baker Analyzed" reagent, was recrystallized as  $KF \cdot 2H_2O$  in polythene vessels, dehydrated in a vacuum desiccator and finally dried in an oven. All salts were carefully dried before preparing solutions with  $D_2O$ .

*Temperature control.* Commercial thermostats or cryostats were used. Generally the temperature could be kept constant within  $\pm 0.01^\circ C$ .

*Temperature measurement.* Mercury thermometers graduated in  $0.1^\circ C$  and readable to  $0.01^\circ C$  were used. They were compared with certified normals at every 10 degrees.

*Phase equilibrium.* In test tubes with a ground stopper 5–10 ml  $D_2O$  or  $H_2O$  were contacted with a suitable amount of salt to obtain a saturated solution and some excess of solid phase. Efficient stirring was provided by a magnetic stirrer or by rotating the tube in an oblique position in the thermostat bath. The time of contact was generally 2–3 h, in some cases, particularly with viscous solutions and at low temperature, considerably more. In preliminary tests with KCl at  $30^\circ C$  equilibrium within experimental error was obtained in 10 min.

*Sampling.* Samples were taken after stopping the stirring and letting the solid settle. If necessary the pipet was heated to avoid premature crystallization of salt. The sample volume was generally between 0.3 and 1 ml.

*Analysis.* The samples were evaporated, dried at about  $200^\circ C$  and weighed. Sodium and potassium carbonates were determined by titration with acid.

*Protection against exchange between  $D_2O$  and air humidity.* No precautions were taken except working rapidly and avoiding unnecessary access of air. This was estimated to be sufficient.

*Eutectic, transition and melting temperatures.* These were in some cases measured directly in a conventional way by taking the temperature of a sample in a tube surrounded by a larger air-filled tube in a bath of about the same temperature.

## Estimated accuracy

Considering errors of reading, stem correction and the calibration of the normal thermometers, the absolute accuracy of temperatures measured is probably better than  $0.1^\circ C$ .

Errors in salt content due to weighing errors are 0.04 % of the sample weight or less. An agreement within 0.08 % between samples taken after different times of contact has been considered as evidence of the attainment of equilibrium.

Total impurities in the salts, according to certificates, are generally less than 0.1 % and are not believed to seriously affect the solubility except in rare cases.

The important thing in the present work was to determine the relative solubility in  $D_2O$  compared to  $H_2O$  with good accuracy. Therefore measurements with  $D_2O$  and  $H_2O$  have been performed in the same way with the same apparatus, and generally simultaneously. In this way errors due to inaccuracy of temperature and largely also systematic errors, *e.g.* due to evaporation in connection with sampling or to impurities in the salts, are eliminated. Only accidental experimental and analytical errors will remain.

## Presentation of data

For a direct comparison of salt contents it is convenient to give them as g salt/100 g H<sub>2</sub>O (=L<sub>H</sub>) or g salt/111.17 g D<sub>2</sub>O (=L<sub>D</sub>) *i.e.* in both cases per 5.55 mole water. From a theoretical point of view it may be better to give them as moles of salt per mole H<sub>2</sub>O or D<sub>2</sub>O or as mole fraction. In the tables data have been interpolated to the nearest whole degree near the point of measurement. For comparisons it is also convenient to use the relative solubility  $r(D/H)=L_D/L_H$ .

The diagrams are drawn as solubility diagrams but could, of course, just as well have been given as conventional phase diagrams with the temperature on the ordinate axis.

## RESULTS AND COMMENTS

The results are given in Tables 1–14. Some characteristic phase diagrams are given in Figs. 1–7. Experimental points are not featured in these diagrams since they do not visibly deviate from the curves. The diagrams for NaF, NaNO<sub>3</sub>, KBr, KI, KNO<sub>3</sub>, and K<sub>2</sub>SO<sub>4</sub> are of a similar type to that for KCl.

*Tables 1–14.* In the following tables are given corresponding values of temperature (°C) and salt concentration, expressed as L<sub>H</sub> (g salt/100 g H<sub>2</sub>O) or L<sub>D</sub> (g salt/111.17 g D<sub>2</sub>O), and when appropriate in the *b* tables also the relative solubility  $r(D/H)=L_D/L_H$ .

*Table 1a.* System NaF–H<sub>2</sub>O

Solid phase NaF: 60, 4.31; 40, 4.23; 30, 4.19; 20, 4.17; 0, 4.12  
 Solid phase ice: –1.71, 2.22  
 Solid phase NaF+ice: –3.10, 4.11

*Table 1b.* System NaF–D<sub>2</sub>O

Solid phase NaF: 60, 4.21, 0.977; 40, 4.13, 0.977; 30, 4.11, 0.981; 20, 4.07, 0.976; 0, 4.03, 0.978  
 Solid phase ice: 2, 2.39  
 Solid phase NaF+ice: 0.75, 4.03

*Table 2a.* System NaCl–H<sub>2</sub>O

Solid phase NaCl: 60, 36.97; 40, 36.41; 20, 35.89; 0, 35.59; –10, 35.61  
 Solid phase NaCl·2H<sub>2</sub>O: –2, 34.88; –10, 32.70; –16, 30.96; –20, 30.14; –21, 29.84  
 Solid phase ice: –5, 8.72; –10, 16.47; –15, 22.96; –21, 29.94  
 Solid phase NaCl+NaCl·2H<sub>2</sub>O: 0.03, 35.57  
 Solid phase NaCl·2H<sub>2</sub>O+ice: –21.11, 29.80

*Table 2b.* System NaCl–D<sub>2</sub>O

Solid phase NaCl: 60, 35.47, 0.959; 40, 34.74, 0.954; 20, 33.72, 0.940; 0, 33.04, 0.928; –10, 33.00, 0.927  
 Solid phase NaCl·2D<sub>2</sub>O: –6, 32.83, 0.972; –10, 31.76, 0.971; –15, 30.43, 0.974  
 Solid phase ice: –1, 8.46; –5, 14.84; –10, 22.36; –15, 28.72  
 Solid phase NaCl+NaCl·2D<sub>2</sub>O: –5.50, 33.00  
 Solid phase NaCl·2D<sub>2</sub>O+ice: –16.47, 30.07

*Table 3a.* System NaBr–H<sub>2</sub>O

Solid phase NaBr·2H<sub>2</sub>O: 40, 107.5; 0, 80.3; –10, 75.5; –20, 71.4; –27, 69.0  
 Solid phase NaBr·5H<sub>2</sub>O: –22, 70.7; –24, 65.9; –27, 61.8  
 Solid phase ice: –10, 28.19; –20, 48.02; –27, 60.7  
 Solid phase NaBr·5H<sub>2</sub>O+ice: –27.07, 61.5  
 Solid phase NaBr·2H<sub>2</sub>O+ice: –30.79, 67.8  
 Solid phase NaBr·2H<sub>2</sub>O+NaBr·5H<sub>2</sub>O: –21.56, 70.8

Table 3b. System NaBr-D<sub>2</sub>O

Solid phase NaBr·2D<sub>2</sub>O: 40, 106.7, 0.992; 0, 78.7, 0.980; -10, 73.4, 0.971; -20, 68.7, 0.961  
 Solid phase NaBr·5D<sub>2</sub>O: -24, 67.2, 1.019; -24.4, 66.8; -24.8, 66.1  
 Solid phase ice: -6, 28.28; -16, 50.1; -22, 61.3  
 Solid phase NaBr·5D<sub>2</sub>O+ice: -24.62, 66.0  
 Solid phase NaBr·2D<sub>2</sub>O+ice: -25.30, 66.8  
 Solid phase NaBr·2D<sub>2</sub>O+NaBr·5D<sub>2</sub>O: -23.64, 67.4

Table 4a. System NaI-H<sub>2</sub>O

Solid phase NaI·2H<sub>2</sub>O: 60, 256.9; 40, 206.9; 20, 178.9; 0, 160.4; -10, 152.0  
 Solid phase NaI·5H<sub>2</sub>O: -12.40, 148.6; -16, 127.2; -24, 102.0; -30, 90.3  
 Solid phase ice: -10, 38.95; -20, 67.0; -30, 89.0  
 Solid phase NaI·5H<sub>2</sub>O+ice: -30.26, 89.5  
 Solid phase NaI·2H<sub>2</sub>O+ice: -12.32, 150.5

Table 4b. System NaI-D<sub>2</sub>O

Solid phase NaI·2D<sub>2</sub>O: 60, 263.8, 1.026; 40, 208.1, 1.005; 20, 177.9, 0.996; 0, 157.5, 0.981; -10, 149.1, 0.980; -12.40, 147.9  
 Solid phase NaI·5D<sub>2</sub>O: -16, 131.0, 1.029; -26, 100.1  
 Solid phase ice: -6, 38.95; -16, 65.6; -26, 91.5  
 Solid phase NaI·5D<sub>2</sub>O+ice: -27.84, 96.2  
 Solid phase NaI·2D<sub>2</sub>O+NaI·5D<sub>2</sub>O: -13.68, 146.3

Table 5a. System NaNO<sub>3</sub>-H<sub>2</sub>O

Solid phase NaNO<sub>3</sub>: 60, 124.1; 50, 115.0; 40, 105.6; 30, 97.0; 20, 88.2; 10, 80.2; 0, 73.0; -10, 65.5; -15, 62.3  
 Solid phase ice: -6, 18.82; -10, 33.32; -14, 47.91; -17, 59.6  
 Solid phase NaNO<sub>3</sub>+ice: -17.45, 61.1

Table 5b. System NaNO<sub>3</sub>-D<sub>2</sub>O

Solid phase NaNO<sub>3</sub>: 60, 124.5, 1.003; 50, 114.1, 0.995; 40, 104.6, 0.993; 30, 95.7, 0.991; 20, 87.1, 0.989; 10, 79.0, 0.985; 0, 71.4, 0.977; -10, 63.7, 0.972; -12, 62.5  
 Solid phase ice: -1, 14.86; -6, 34.13; -10, 49.93; -12, 57.9; -13.6, 63.8  
 Solid phase NaNO<sub>3</sub>+ice: -13.11, 61.7

Table 6a. System Na<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O

Solid phase Na<sub>2</sub>SO<sub>4</sub>·7H<sub>2</sub>O: 7, 27.05; 5, 24.73; 0, 19.43  
 Solid phase Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O: 2, 5.12  
 Solid phase ice: -3, 13.77  
 Solid phase Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O+ice: -1.12, 4.28

Table 6b. System Na<sub>2</sub>SO<sub>4</sub>-D<sub>2</sub>O

Solid phase Na<sub>2</sub>SO<sub>4</sub>·7D<sub>2</sub>O: 10, 25.90; 5, 19.99, 0.808; 0, 15.11, 0.777  
 Solid phase Na<sub>2</sub>SO<sub>4</sub>·10D<sub>2</sub>O: 2, 3.89, 0.760  
 Solid phase ice: 0.5, 16.11  
 Solid phase Na<sub>2</sub>SO<sub>4</sub>·10D<sub>2</sub>O+ice: 2.69, 4.20

*Table 7a.* System Na<sub>2</sub>CO<sub>3</sub>-H<sub>2</sub>O

Solid phase Na<sub>2</sub>CO<sub>3</sub>·H<sub>2</sub>O: 60, 46.05; 50, 47.28; 44, 48.15; 40, 48.85; 30, 50.44  
 Solid phase Na<sub>2</sub>CO<sub>3</sub>·7H<sub>2</sub>O: 35, 49.12; 34, 47.93; 32, 45.60; 30, 43.27; 25, 38.20; 20, 33.80;  
 10, 26.23; 0, 19.85; -4, 17.55  
 Solid phase Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O: 32.7, 48.46; 32.4, 47.06; 31.6, 44.07; 30, 39.35; 25, 29.03;  
 20, 21.85; 15, 16.48; 10, 12.33; 5, 9.21; 0, 6.84  
 Solid phase ice: -5, 16.01; -2, 5.88  
 Solid phase Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O+ice: -2.06, 6.04

*Table 7b.* System Na<sub>2</sub>CO<sub>3</sub>-D<sub>2</sub>O

Solid phase Na<sub>2</sub>CO<sub>3</sub>·D<sub>2</sub>O: 60, 44.54, 0.967; 50, 46.07, 0.974; 44, 47.00, 0.976; 40, 47.74,  
 0.977; 30, 49.70, 0.985  
 Solid phase Na<sub>2</sub>CO<sub>3</sub>·7D<sub>2</sub>O: 36, 49.04; 35, 47.65; 0.970; 34, 46.36; 0.967; 32, 44.06, 0.966;  
 30, 41.82, 0.966; 25, 36.75, 0.962; 20, 32.25, 0.954; 10, 24.45, 0.932; 0, 17.71, 0.892  
 Solid phase Na<sub>2</sub>CO<sub>3</sub>·10D<sub>2</sub>O: 36.3, 50.73; 35, 44.56; 32, 35.87; 30, 31.53, 0.801; 25, 22.94,  
 0.790; 20, 17.00, 0.778; 15, 12.51, 0.759; 10, 9.12, 0.740; 5, 6.65, 0.722; 0, 4.76, 0.696  
 Solid phase ice: -1, 17.15; 0, 13.15; 2, 5.67  
 Solid phase Na<sub>2</sub>CO<sub>3</sub>·10D<sub>2</sub>O+ice: 2.01, 5.48

*Table 8a.* System KF-H<sub>2</sub>O

Solid phase KF: 60, 141.1; 50, 139.9; 40, 139.2  
 Solid phase KF·2H<sub>2</sub>O: 40, 131.7; 30, 104.9; 20, 91.4; 10, 82.4  
 Solid phase KF·4H<sub>2</sub>O: 18, 72.0; 10, 53.6; 0, 42.71; -10, 35.10; -20, 29.05  
 Solid phase ice: -5, 8.34; -12, 18.09; -20, 26.89  
 Solid phase KF+KF·2H<sub>2</sub>O: 41.40, 139.2  
 Solid phase KF·2H<sub>2</sub>O+KF·4H<sub>2</sub>O: 18.07, 89.7  
 Solid phase KF·4H<sub>2</sub>O: 18.72, 80.6  
 Solid phase KF·4H<sub>2</sub>O+ice: -21.40, 28.29

*Table 8b.* System KF-D<sub>2</sub>O

Solid phase KF: 60, 139.5, 0.988; 50, 138.9, 0.992; 40, 138.2, 0.992  
 Solid phase KF·2D<sub>2</sub>O: 40, 121.1, 0.919; 30, 100.5, 0.957; 20, 88.7, 0.969  
 Solid phase KF·4D<sub>2</sub>O: 18, 63.2, 0.878; 10, 50.1, 0.936; 0, 40.37, 0.945; -10, 33.23, 0.947;  
 -16, 29.63  
 Solid phase ice: -1, 8.37; -8, 18.45; -16, 27.58  
 Solid phase KF+KF·2D<sub>2</sub>O: 44.25, 138.2  
 Solid phase KF·2D<sub>2</sub>O+KF·4D<sub>2</sub>O: 20.69, 89.3  
 Solid phase KF·4D<sub>2</sub>O: 21.28, 80.6  
 Solid phase KF·4D<sub>2</sub>O+ice: -17.28, 28.89

*Table 9a.* System KCl-H<sub>2</sub>O

Solid phase KCl: 60, 45.54; 50, 43.37; 40, 40.57; 30, 37.57; 20, 34.51; 10, 31.10; 0, 27.83;  
 -6, 25.58; -10, 24.47  
 Solid phase ice: -3, 7.07; -6, 14.09; -10, 23.75  
 Solid phase KCl+ice: -10.66, 24.29

*Table 9b.* System KCl-D<sub>2</sub>O

Solid phase KCl: 60, 42.74, 0.938; 50, 40.31, 0.929; 40, 37.50, 0.924; 30, 34.31, 0.913;  
 20, 30.96, 0.896; 10, 27.28, 0.877; 0, 23.63, 0.848; -6, 21.36, 0.834  
 Solid phase ice: 0, 8.85; -2, 13.84  
 Solid phase KCl+ice: -5.33, 21.52

*Table 10a.* System KBr—H<sub>2</sub>O

Solid phase KBr: 60, 86.2; 50, 81.9; 40, 76.3; 30, 71.2; 20, 65.9; 10, 59.6; 0, 53.75; -10, 47.06  
Solid phase ice: -4, 15.73; -8, 29.94; -10, 37.53  
Solid phase KBr+ice: -12.60, 45.20

*Table 10b.* System KBr—D<sub>2</sub>O

Solid phase KBr: 60, 79.8, 0.925; 50, 75.2, 0.918; 40, 69.5, 0.910; 30, 64.0, 0.895; 20, 58.0, 0.879; 10, 51.3, 0.860; 0, 44.52, 0.823; -10, 36.87, 0.783  
Solid phase ice: -1, 17.16; -4, 30.67  
Solid phase KBr+ice: -6.73, 39.67

*Table 11a.* System KI—H<sub>2</sub>O

Solid phase KI: 60, 177.0; 50, 168.9; 40, 161.0; 30, 153.6; 20, 145.9; 10, 136.0; 0, 127.8; -10, 117.5; -16, 111.4; -21, 106.1  
Solid phase ice: -5, 25.61; -10, 46.71; -15, 74.8; -20, 98.3; -21, 102.6  
Solid phase KI+ice: -21.69, 105.4

*Table 11b.* System KI—D<sub>2</sub>O

Solid phase KI: 60, 165.1, 0.932; 50, 156.4, 0.926; 40, 147.9, 0.918; 30, 139.2, 0.905; 20, 130.1, 0.891; 10, 119.3, 0.876; 0, 108.3, 0.850; -10, 96.6, 0.821  
Solid phase ice: -1, 26.17; -6, 51.9; -13, 88.4  
Solid phase KI+ice: -13.77, 91.7

*Table 12a.* System KNO<sub>3</sub>—H<sub>2</sub>O

Solid phase KNO<sub>3</sub>: 60, 110.7; 50, 85.8; 40, 64.1; 30, 45.96; 20, 31.68; 10, 20.90; 0, 13.16; -2.7, 11.59  
Solid phase ice: -1, 4.28; -2, 7.64  
Solid phase KNO<sub>3</sub>+ice: -2.87, 11.47

*Table 12b.* System KNO<sub>3</sub>—D<sub>2</sub>O

Solid phase KNO<sub>3</sub>: 60, 107.3, 0.969; 50, 82.0, 0.955; 40, 60.3, 0.940; 30, 42.31, 0.920; 20, 28.37, 0.895; 10, 18.12, 0.867; 3, 12.97; 1, 11.69  
Solid phase ice: 3, 2.97; 2, 7.23; 1, 12.08  
Solid phase KNO<sub>3</sub>+ice: 1.03, 11.71

*Table 13a.* System K<sub>2</sub>SO<sub>4</sub>—H<sub>2</sub>O

Solid phase K<sub>2</sub>SO<sub>4</sub>: 60, 18.19; 50, 16.50; 40, 14.81; 30, 12.99; 20, 11.19; 10, 9.22; 0, 7.33; -1, 7.07  
Solid phase ice: -1, 4.81  
Solid phase K<sub>2</sub>SO<sub>4</sub>+ice: 1.59, 6.93

*Table 13b.* System K<sub>2</sub>SO<sub>4</sub>—D<sub>2</sub>O

Solid phase K<sub>2</sub>SO<sub>4</sub>: 60, 17.21, 0.946; 50, 15.50, 0.939; 40, 13.81, 0.932; 30, 11.96, 0.920; 20, 10.07, 0.900; 10, 8.05, 0.873; 3, 6.70  
Solid phase ice: 2.5, 5.79  
Solid phase K<sub>2</sub>SO<sub>4</sub>+ice: 2.37, 6.56

Table 14a. System K<sub>2</sub>CO<sub>3</sub>-H<sub>2</sub>O

Solid phase K<sub>2</sub>CO<sub>3</sub>·3/2H<sub>2</sub>O: 60, 128.6; 40, 119.0; 30, 115.2; 20, 111.6; 0, 106.4; -10, 105.6; -15, 103.0; -20, 102.6; -32, 104.8; -36, 106.0

Solid phase K<sub>2</sub>CO<sub>3</sub>·5H<sub>2</sub>O: -6, 105.8; -7, 103.8; -10, 97.0; -15, 88.2; -20, 82.4; -25, 76.6; -31, 71.1; -36, 67.1

Solid phase ice: -38, 70.0; -28, 58.8; -19, 46.31; -10, 29.43; -4, 13.35

Solid phase K<sub>2</sub>CO<sub>3</sub>·5H<sub>2</sub>O+ice: -36.04, 67.1

Table 14b. System K<sub>2</sub>CO<sub>3</sub>-D<sub>2</sub>O

Solid phase K<sub>2</sub>CO<sub>3</sub>·3/2D<sub>2</sub>O: 60, 125.1, 0.973; 40, 115.9, 0.975; 30, 112.5, 0.977; 20, 109.5, 0.981; 0, 105.2, 0.988; -10, 103.4, 0.979; -31, 104.5; -32, 106.3

Solid phase K<sub>2</sub>CO<sub>3</sub>·5D<sub>2</sub>O: -6, 105.2, 0.994; -7, 102.2, 0.985; -10, 96.0, 0.989; -15, 87.1, 0.988; -20, 80.8, 0.980; -25, 75.7, 0.989; -31, 70.4, 0.989

Solid phase ice: -32, 70.6; -23, 61.1; -15, 48.31; -5, 28.04; 0, 13.38

Solid phase K<sub>2</sub>CO<sub>3</sub>·5D<sub>2</sub>O+ice: -31.53, 69.9

The transition point NaCl·2D<sub>2</sub>O—NaCl was difficult to determine directly and its value -5.50°C was taken from the diagram.

For NaBr the transition NaBr·5H<sub>2</sub>O—NaBr·2H<sub>2</sub>O was found to be at -21.56°C by direct measurement and -22.0°C from the diagram; Landolt-Börnstein<sup>10</sup> gives -24.0°C from a diagram composed of data from several authors. Values above 50°C in the present diagram are taken from Eddy and Menzies.<sup>3</sup>

In the case of Na<sub>2</sub>SO<sub>4</sub> we have made only few measurements. Other values needed for the diagram have been taken from Eddy and Menzies.<sup>3</sup>

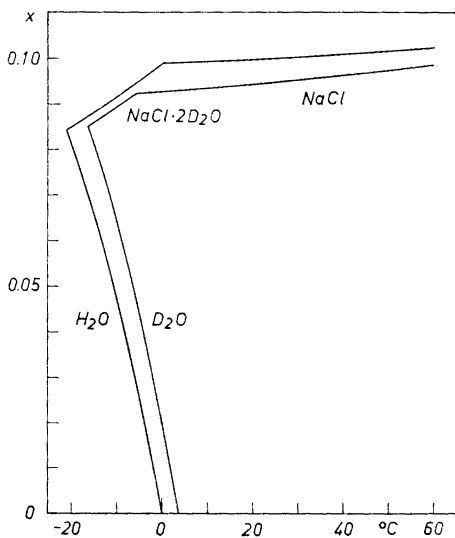


Fig. 1. System NaCl-H<sub>2</sub>O and NaCl-D<sub>2</sub>O,  $x$ =mole fraction NaCl.

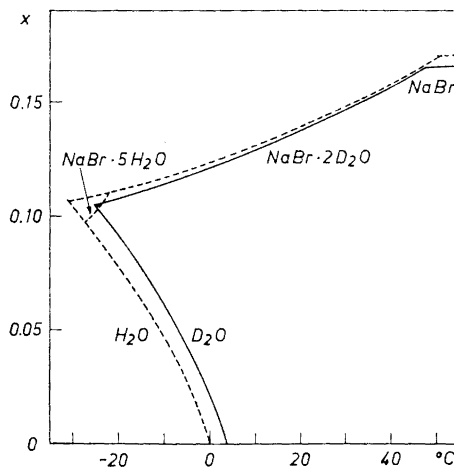


Fig. 2. Systems NaBr-H<sub>2</sub>O and NaBr-D<sub>2</sub>O,  $x$ =mole fraction NaBr.

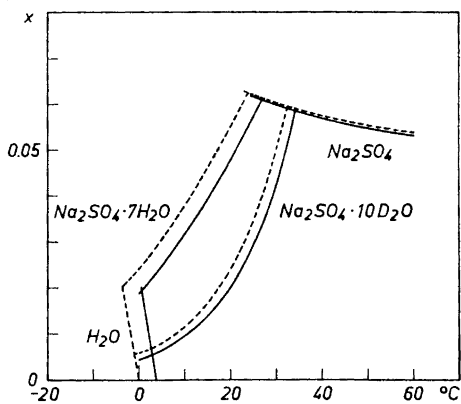


Fig. 3. Systems  $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4\text{-D}_2\text{O}$ ,  $x$ =mole fraction  $\text{Na}_2\text{SO}_4$ .

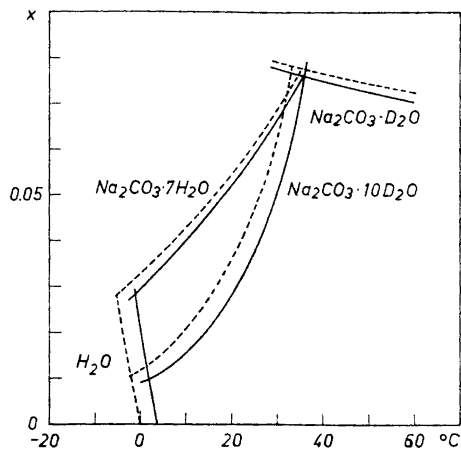


Fig. 4. Systems  $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$  and  $\text{Na}_2\text{CO}_3\text{-D}_2\text{O}$ ,  $x$ =mole fraction  $\text{Na}_2\text{CO}_3$ .

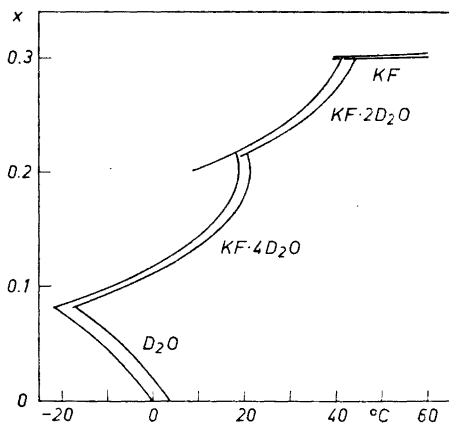


Fig. 5. Systems  $\text{KF-H}_2\text{O}$  and  $\text{KF-D}_2\text{O}$ ,  $x$ =mole fraction  $\text{KF}$ .

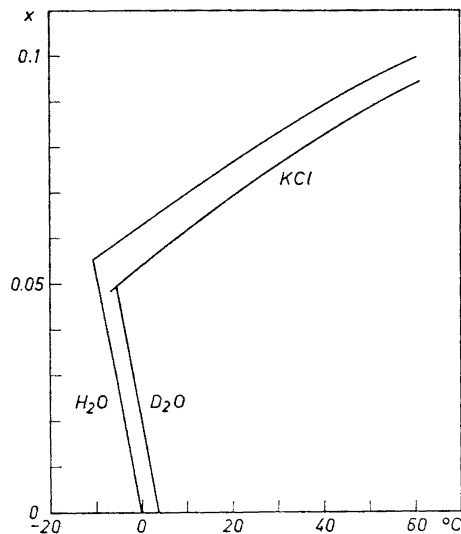


Fig. 6. Systems  $\text{KCl-H}_2\text{O}$  and  $\text{KCl-D}_2\text{O}$ ,  $x$ =mole fraction  $\text{KCl}$ .

For  $\text{K}_2\text{SO}_4$  the existence of a monohydrate,  $\text{K}_2\text{SO}_4\cdot\text{H}_2\text{O}$ , below  $+9.7^\circ\text{C}$  has been claimed.<sup>11</sup> No such hydrate was observed here, and no special effort was made to find it. Our value for the relative solubility of  $\text{K}_2\text{SO}_4$  at  $25^\circ\text{C}$  ( $r(\text{D}/\text{H})=0.910$ ) differs considerably from a published<sup>8</sup> value (0.795).



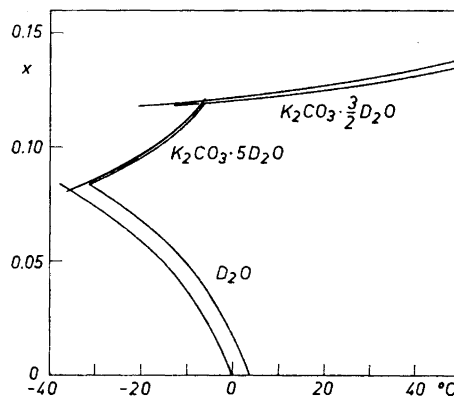


Fig. 7. Systems  $K_2CO_3-H_2O$  and  $K_2CO_3-D_2O$ ,  $x$ =mole fraction  $K_2CO_3$ .

The eutectic points for  $K_2CO_3 \cdot 5aq$  were difficult to determine because of the rather high viscosity of the solutions at such low temperatures, and may be somewhat inaccurate. The hydrate  $K_2CO_3 \cdot 5aq$ <sup>12</sup> was earlier considered to be a hexahydrate.<sup>13</sup>

#### DISCUSSION

Any treatment of differences in solubilities or phase diagrams in systems of salt with  $D_2O$  or  $H_2O$  must reasonably rest upon conceptions of the structure of the pure water and the saturated solutions. Water is generally considered to have a highly ordered structure, which is more or less broken down by the presence of dissolved salts or by increasing temperature.

*Anhydrous salts.* Heavy water is considered to have a stronger and more developed structure than light water.<sup>14,15</sup> Therefore it can better resist the breaking down connected with the formation of a solution and the result is that salts are generally less soluble in  $D_2O$ . As the structure breaking effect increases with the ion diameter,<sup>15</sup> it is to be expected that salts of large ions will differ most in solubility in  $H_2O$  and  $D_2O$ . With increasing temperature the ordered structure is more and more broken down,  $D_2O$  and  $H_2O$  become more similar, and the solubility differences will gradually vanish.

*Salt hydrates.* If the solid phase is an anhydrous salt the solubility difference depends only on isotopic effects in the solution. If the solid phase is a hydrate it will contain  $H_2O$  if it is in equilibrium with ordinary water and  $D_2O$  if it is in equilibrium with heavy water. In the latter case it may be termed a deuterate. The hydrate and the deuterate will have different stabilities because of isotopic effects and this will contribute to the difference in solubility, which may be quite different for different hydrates and anhydrous salts. An example illustrating this is afforded by  $NaBr$ , Fig. 2. At the transition  $NaBr \cdot 2aq$  to  $NaBr$  the solubility differences are clearly unequal and at the transition  $NaBr \cdot 5aq$  to  $NaBr \cdot 2aq$  they are even of opposite sign. The diagrams for  $Na_2SO_4$  and  $Na_2CO_3$  also provide good examples. A knowledge of the atomic arrangement and binding conditions may contribute to an understanding of the isotopic effects.

in the hydrate and the mechanism by which they contribute to the solubility differences.

Knowledge of the hydrate structure may be useful in another context. Consider  $\text{KF} \cdot 4\text{H}_2\text{O}$ , the structure of which is known.<sup>16</sup> It is composed of  $\text{K}^+$  and  $\text{F}^-$  ions, both octahedrally surrounded by  $\text{H}_2\text{O}$ , while  $\text{H}_2\text{O}$  is tetrahedrally surrounded either by two  $\text{F}^-$ , one  $\text{K}^+$  and one  $\text{H}_2\text{O}$  or by one  $\text{F}^-$ , two  $\text{K}^+$  and one  $\text{H}_2\text{O}$ . It has a congruent melting point and it is probable that on melting many of the features of the crystal structure are preserved, since essentially the same binding forces and molecular and ionic radii are operative in both the crystal and the melt. It is also to be expected that even in dilute solutions the more stable structure elements are preserved. An example of this is afforded by  $\text{Eu}(\text{H}_2\text{O})_6(\text{NO}_3)_3$ , where the octahedrally coordinated ion  $\text{Eu}(\text{H}_2\text{O})_6^{3+}$  has been observed in the crystal hydrate and in solution.<sup>17</sup> An extensive knowledge of salt hydrate structures may therefore be of assistance in understanding salt-water solution structures which are less accessible by direct experiment.

*Ice as solid phase.* For the same molar concentration the freezing point depression in  $\text{D}_2\text{O}$  should be less than in  $\text{H}_2\text{O}$  because of the larger heat of melting of  $\text{D}_2\text{O}$  ( $\Delta H = 1.501$  kcal/mole for  $\text{D}_2\text{O}$  and 1.4363 kcal/mole for  $\text{H}_2\text{O}$ ).

Using the following formula for the freezing point depression  $\Delta T$

$$\log x = \frac{\Delta H}{R} \cdot \frac{\Delta T}{T^2}$$

where  $x$  is the mole fraction solute,  $R$  the gas constant and  $T$  the melting point of the pure solvent, the following ratio is obtained for the same mole fraction

$$(\Delta T)_{\text{D}_2\text{O}} / (\Delta T)_{\text{H}_2\text{O}} = 0.984$$

Actually, the relative freezing point depressions in  $\text{D}_2\text{O}$  are often even smaller. One reason may be that the salts are considerably associated and more so in  $\text{D}_2\text{O}$  than in  $\text{H}_2\text{O}$ .

The question of the structure of salt solutions, solubilities and their isotopic effects is certainly a complicated one, and it would be premature to attempt a more detailed discussion, based on present limited data. However, relations undoubtedly exist and, if they become understood, phase equilibrium data for salt- $\text{D}_2\text{O}$  systems will no doubt increase our knowledge of saltwater solutions.

In an AE-report<sup>18</sup> this work is presented with more complete tables, containing weight percent and mole fraction data, and with diagrams for all the salt-water systems.

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