Note on the Crystal Lattice of Samarium Sulphate OctoHydrate

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Additional information on J. Chem. Phys.

LETTERS TO THE EDITOR

Mixtures of Deuterium and Protium Oxides as Ideal Solutions

In several recent papers[*][1] calculations have been made of equilibria involving the three forms of water molecules with the hydrogen isotopes of masses 1 and 2. In all such calculations it has been necessary to assume that in the liquid state the various species form ideal solutions. The only pertinent evidence is Luten's observation[2] that the molecular volume of mixtures of H_2O and D_2O does not vary linearly with the mole fraction, whence Luten deduces that the solutions are not ideal. However, the argument is not cogent since the existence of the intermediate molecule HDO introduces another variable and actually, if the molecular volume of HDO is assumed to be the geometric mean of the molecular volumes of H_2O and D_2O, one can deduce from equations of the type set out by Lewis and Cornish[3] that the square root of the molecular volume should vary as the mole fraction.

In order to obtain more direct evidence of the extent to which such mixtures deviate from ideal solutions it was decided to determine the composition of the vapor in equilibrium with mixtures of known composition. The method used was that employed by McBain, Pollard and Wynne-Jones[4] for determining the partial pressures of aqueous solutions of p-toluidine. The composition of the liquid was determined by means of a Pulfrich refractometer using a differential prism with which small differences of refractive index could be determined to 0.000005 of a unit. Since the difference in n_{20}^D between H_2O and D_2O is 0.00462[5] and Luten[2] has shown that the refractive index is a linear function of the mole fraction, the mole fraction could be determined to approximately 0.001. Duplicate experiments agreeing to this limit of accuracy were made with 10 and 50 percent D_2O and the results are given in Table I.

The last column gives the mole ratio of D_2O in the liquid divided by the value for the vapor.

On the assumption that $K=4$ for the equilibrium $H_2O + D_2O = 2HDO$ and that $p_{HDO} = (p_{H_2O} p_{D_2O})^{\frac{1}{2}}$ it follows from the equations of Lewis and Cornish that for ideal solutions $R = (p_{H_2O}/p_{D_2O})^{\frac{1}{2}}$ and from the data of Lewis and

TABLE I.

Liquid		Vapor		
Mole fraction	Mole ratio	Mole fraction	Mole ratio	R
0.1196	0.1359	0.1097	0.1232	1.10₄
0.4917	0.967	0.4667	0.8755	1.10₆

MacDonald[6] the value of R should be 1.07. Topley and Eyring have calculated that the actual value of K is 3.26 but the introduction of this value instead of 4 has no perceptible effect on the result. The difference between 1.07 and 1.10 is definitely greater than the experimental error and the discrepancy may be the result of the assumption that p_{HDO} is the geometric mean of p_{H_2O} and p_{D_2O} or it may indicate a slight deviation from ideal behavior: in the latter event the activity coefficients need not differ from unity by more than 2 percent to account for the results. It is evident that these mixtures approximate rather closely to ideal solutions and that for most purposes no appreciable error is introduced by assuming ideal behavior.

<div align="right">W. F. K. WYNNE-JONES</div>

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* Inter alia.
[1] Topley and Eyring, J. Chem. Phys. **2**, 217 (1934).
   Crist and Dalin, J. Chem. Phys. **2**, 735 (1934).
   Farkas and Farkas, Trans. Faraday Soc. **30**, 1071 (1934).
[2] Luten, Phys. Rev. **45**, 161 (1934).
[3] Lewis and Cornish, J. Am. Chem. Soc. **55**, 2616 (1933).
[4] McBain, Pollard and Wynne-Jones, Colloid Symposium **6**, 57 (1928).
[5] Taylor and Selwood, J. Am. Chem. Soc. **56**, 998 (1934).
[6] Lewis and MacDonald, J. Am. Chem. Soc. **55**, 3057 (1933).

Note on the Crystal Lattice of Samarium Sulphate Octo-Hydrate

At the suggestion of Professor Ivar Waller of the University of Uppsala I undertook a determination of the samarium positions in the crystal lattice of the sulphate octo-hydrate. As the results may be of some value in connection with various paramagnetic problems, it was decided to publish the information obtained. Unfortunately it proved impossible to fix the positions of sulphur, oxygen and water because of the many degrees of freedom involved and also because of the small scattering powers.

The crystals used were borrowed from Dr. S. Freed of the Chemistry Department of this University.

The dimensions of the monoclinic unit cell were found to be: $a = 20.30 \pm 0.06$A; $b = 6.76 \pm 0.03$A; $c = 13.53 \pm 0.05$A; $\beta = 118°16'$. There are four molecules per cell and the space group is $A2/c(C_{2h}^6)$. The eight samarium atoms are lying in general positions: $\pm(xyz) \pm (\frac{1}{2}-x, y, \frac{1}{2}-z) \pm (x+\frac{1}{2}, \frac{1}{2}-y, z) \pm (x, y+\frac{1}{2}, z+\frac{1}{2})$. Four of the sulphur atoms must lie on

the twofold axes, while all other atoms probably occupy eightfold positions. Disregarding the hydrogen atoms there are thus 37 degrees of freedom in the structure.

The determination of the three parameters for the samarium atoms was made by means of Laue photographs taken parallel to the c axis and perpendicularly to the c face. In this manner several hundreds of first order reflections were recorded.

For the great majority of reflections the observed intensity may be attributed to the samarium atoms alone. There are two reasons: In the first place the scattering power of samarium is great, and secondly, there are as many as 34 parameters for sulphur, oxygen and water, so that the chance of getting appreciable contribution from these atoms is small.

By using the data from the Laue photographs it was possible to fix the samarium parameters with considerable accuracy:

$x = 0.106 \pm 0.003$; $y = 0.025 \pm 0.006$; $z = -0.231 \pm 0.003$.

The closest distance between two samarium atoms is 5.08A. Around any given one of the samarium atoms there are 18 others at distances less than 10A, namely:

1 at	5.08A	2 at	7.08A
1	5.51	4	7.57
1	6.13	1	9.10
1	6.48	3	9.12
2	6.76	2	9.16

A great many of the lanthanides form octo-hydrated sulphates which are isomorphous with the samarium salt. As the axial ratios change very little throughout the series, the interatomic distances can be calculated with sufficient accuracy from the known distances in the samarium compound and the molecular volume. Thus the distances in the gadolinium salt are 0.2 percent smaller than in the samarium compound, in the erbium salt 1.1 percent smaller and in the neodymium salt 0.7 percent greater.[1]

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February 4, 1935.

[1] The molecular volumes are given in G. v. Hevesy: Zeits. f. anorg. Chemie 147, 217; 150, 68 (1925).