CCXX.—*The Solubility of Sodium Fluosilicate in Aqueous Sodium Sulphate Solutions, and the Activity Coefficients of Sodium Fluosilicate and the Fluosilicate Ion.*

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In connexion with work to be published shortly, the activity coefficients of fluosilicate ion in solutions of various ionic strengths were required, and we have found it possible to determine these from measurements of the solubility of sodium fluosilicate in solutions of sodium sulphate.

The sodium fluosilicate employed was a high-grade commercial product, the purity of which was tested (*a*) by converting it into sodium sulphate by evaporation with sulphuric acid and (*b*) by titrating it with sodium hydroxide; these methods showed purities of 99·30 and 99·83% respectively. The sodium sulphate was prepared anhydrous by evaporation of solutions at the boiling point and strong ignition of the product. It was tested by direct estimation of sulphate.

Solutions of sodium sulphate were made up by weight and agitated with excess of solid sodium fluosilicate. In series A this was done at room temperature, 17°, and in series B in a thermostat at 20·8°. In the latter case, filtration was carried out in the thermostat according to the method of Campbell (J., 1930, 179), and saturation was proved by filtration after different times of contact. The filtrate was titrated hot by sodium hydroxide, prepared from well-washed sticks and standardised against succinic acid with phenolphthalein as indicator. The results are in Table I. Here $m_{Na_2SO_4}$ is the molarity (g.-mols. per 1000 g. of water) of the sodium sulphate in the solvent solution, $m_{Na_2SiF_6}$ the molarity of the sodium fluosilicate as found by titration, μ is the ionic strength, and $m_{\pm}$ is the cube root of $m^2_{Na^{\cdot}} \times m_{SiF_6''}$, where the molarities of the ions are taken stoicheiometrically (from all sources) irrespective of possible combination.

TABLE I.

$m_{Na_2SO_4}$.	$m_{Na_2SiF_6}$.	$\sqrt{\mu}$.	$-\log m_{\pm}$.	$m_{Na_2SO_4}$.	$m_{Na_2SiF_6}$.	$\sqrt{\mu}$.	$-\log m_{\pm}$.
	Series A, at 17°.				Series B, at 20·8°.		
0·000	0·0329	0·314	1·282	0·0000	0·0363	0·330	1·240
0·050	0·0143	0·439	1·209	0·0045	0·0336	0·338	1·236
0·125	0·0068	0·629	1·109	0·0050	0·0336	0·340	1·233
0·250	0·0042	0·874	0·988	0·0075	0·0320	0·344	1·233
0·375	0·0034	1·066	0·906	0·0100	0·0309	0·350	1·229
0·500	0·0029	1·229	0·842	0·0150	0·0284	0·361	1·224
				0·0250	0·0242	0·384	1·210
				0·0375	0·0201	0·416	1·191
				0·0500	0·0168	0·447	1·173

In all saturated solutions at constant temperature the activity of the salt as a whole, $a_{Na_2SiF_6}$, is constant, and it is always equal to $a^2_{Na^{\cdot}} \times a_{SiF_6''} = a^3$, where a is the geometric mean activity of the ions, usually called " the activity " of the salt. The activity coefficient γ is equal to $a/m_{\pm}$, whence we have $\log \gamma = -\log m_{\pm} + \log a$ (1) (see Brönsted and LaMer, *J. Amer. Chem. Soc.*, 1924, **46**, 555). It is to be expected that γ would be sensibly the same at the two temperatures studied, although a, like the solubility, would vary appreciably.

The variation of the activity coefficient of a salt with the ionic strength of the solution is most conveniently represented by a graph of log γ against $\sqrt{\mu}$. The course of the curve is determined from the following considerations :

(1) It begins at the origin, since γ is arbitrarily set equal to unity at infinite dilution, where $\sqrt{\mu} = 0$.

(2) The initial slope must conform to the Debye–Hückel expression (*Physikal. Z.*, 1923, **24**, 305) $\log \gamma = -0{\cdot}5Z_+Z_-\sqrt{\mu}$, where Z_+ and Z_- are, respectively, the numerical values of the valencies of the kation and anion. This, for sodium fluosilicate, becomes $\log \gamma = -\sqrt{\mu}$.

(3) For small and moderate values of $\sqrt{\mu}$ the curve should closely resemble that of any other salt of the same valency type, *e.g.*, potassium sulphate.

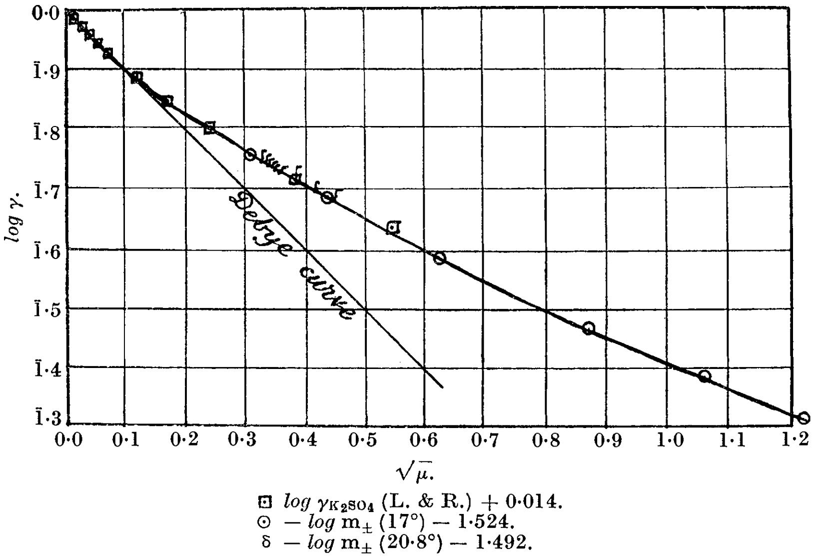
(4) In solutions of the ionic strength studied by the solubility measurements the curve must be exactly parallel to that of $-\log m_\pm$ against $\sqrt{\mu}$ in the saturated solution, as shown by equation (1).

The concentrations here studied have values of $\sqrt{\mu}$ far in excess of those for which condition (2) is valid. In consequence we have to make use of condition (3). The values of $\gamma_{K_2SO_4}$ have been calculated by Lewis and Randall ("Thermodynamics," pp. 344, 362) from freezing-point measurements. The curve obtained for log γ against $\sqrt{\mu}$ lies so closely parallel to our curves (at 17° and at 20·8°) for $-\log m_\pm(Na_2SiF_6)$ over that range of ionic strength for which both sets of figures are available, that there is no difficulty in drawing a curve for $\log \gamma_{Na_2SiF_6}$ which satisfies both the conditions (3) and (4).

There remains, however, a slight correction to be applied to the figures for potassium sulphate. The freezing-point measurements in themselves give, of course, only the *relative* activity coefficients at the concentrations studied. To adjust these to the convention that $\gamma = 1$ for the infinitely dilute solution, some extrapolation formula has to be employed to cover the range too dilute for experimental measurement. That adopted by Lewis and Randall was directly related to the freezing points but is mathematically equivalent to the postulate that, in dilute solution (up to $C = 0{\cdot}01$), $\log \gamma = -0{\cdot}931C^{0{\cdot}341}$. Remembering that for potassium sulphate $\mu = 3C$ (where C is the concentration in g.-mols. per 1000 g. of water), it is seen that this equation is entirely incompatible with that of Debye and Hückel. If Lewis and Randall's figures are used, the graph of log γ against $\sqrt{\mu}$ first falls more rapidly than the Debye–Hückel curve and then runs parallel to, but 0·014 below, it over the range $\sqrt{\mu} = 0{\cdot}025$—$0{\cdot}060$. After this it begins to slope less steeply as the range in which the experimental measurements were made is approached. Clearly, all the figures given for $\gamma_{K_2SO_4}$ should be multiplied by $1{\cdot}033$, thus making $\log \gamma$ greater by $0{\cdot}014$, in order to combine the experimental figures with the Debye–Hückel extrapolation formula.

From these considerations Fig. 1 was drawn. It shows that the points given by $\log \gamma_{K_2SO_4}$ (L. and R.) $+ 0{\cdot}014$, $-\log m_{\pm}(17^\circ) - \bar{1}{\cdot}524$, and $-\log m_{\pm}(20{\cdot}8^\circ) - \bar{1}{\cdot}492$ plotted against $\sqrt{\mu}$ afford data for drawing a smooth curve for $\log \gamma_{Na_2SiF_6}$ which satisfies all the conditions laid down.

FIG. 1.



⊡ $\log \gamma_{K_2SO_4}$ (L. & R.) $+ 0{\cdot}014$.
⊙ $-\log m_{\pm}$ (17°) $- \bar{1}{\cdot}524$.
δ $-\log m_{\pm}$ (20·8°) $- \bar{1}{\cdot}492$.

It was fortunate that series A, which was originally intended for preliminary measurements only, gave such concordant results as the smooth curve implies, since no precautions were taken as to temperature : the temperature coefficient of the solubility is quite small and the resulting $\log \gamma$ is affected only by 2% for a temperature interval of about 4°.

The values recorded in Table II were obtained by interpolation from a large-scale graph. Where the ionic strength is small, as in unsaturated solutions of sodium fluosilicate alone, the values are probably trustworthy, but for solutions of greater ionic strength, such as can only be obtained by the addition of another salt, they cannot be strictly applied unless the second salt be sodium sulphate.

Our work required a knowledge of the individual activity coefficients of the SiF_6'' ion. This we have obtained from the relationship $\gamma^3_{Na_2SiF_6} = \gamma^2_{Na^\cdot} \times \gamma_{SiF_6''}$, dividing the cube of our own values for $\gamma_{Na_2SiF_6}$ by the square of $\gamma_{Na^\cdot}$ for the corresponding ionic strength given by Lewis and Randall (*op. cit.*, p. 382). Although there are grave objections to the assumption underlying this calculation, namely, that the activity coefficients are determined *solely* by the ionic strength, yet the authors quoted have shown that such treatment affords fairly consistent numerical results and it is at present the only method open to us for getting even approximate figures.

TABLE II.

$m_{Na_2SiF_6}$.	μ.	$\log \gamma_{Na_2SiF_6} - \sqrt{\mu}$.	$\gamma_{Na_2SiF_6}$.	$\log \gamma_{SiF_6} - 2\sqrt{\mu}$.	$\gamma_{SiF_6''}$.
<0·0010	—	—	—	—	—
0·0010	0·0030	$\bar{1}$·945	0·881	$\bar{1}$·873	0·747
0·0025	0·0075	$\bar{1}$·909	0·811	$\bar{1}$·789	0·615
0·0050	0·0150	$\bar{1}$·889	0·775	$\bar{1}$·775	0·569
0·010	0·0300	$\bar{1}$·851	0·710	$\bar{1}$·675	0·473
0·0250	0·0750	$\bar{1}$·782	0·605	$\bar{1}$·526	0·336
—	0·1000	$\bar{1}$·756	0·570	1·476	0·299
—	0·2500	$\bar{1}$·652	0·449	1·228	0·169
—	0·5000	$\bar{1}$·540	0·347	—	—
—	0·7500	$\bar{1}$·470	0·295	—	—
—	1·0000	$\bar{1}$·420	0·263	—	—

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