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Energies of Solution of Silica in Water and HCl

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THE solubilities of silica in water and acid at various temperatures evidently depend upon the energies of association and dissociation of the various ions present, energies which are derivable from the solubilities by thermodynamic analysis. Recent determinations by Harned¹ of the dissociation constant of water at various temperatures, by Hitchen² of the solubility of silica through a range of elevated temperatures, and by Lenher and Merrill³ on its solubility in solutions of hydrochloric acid of 0 to 20 percent concentration appear to be of sufficient precision to warrant such reductions but none such seems to have been made. The work was done for its bearing on problems concerned with the solubilities of silicates in general and is here summarized to save needless repetition. Many of the associations involved, such as that of water molecules for its ions and of silica molecules for each other (polymerization), represent energies negligible in comparison with those considered.

With the ionization constant K_w of water known for a range of temperatures, the energy necessary to separate H and OH ions in water may be readily calculated in calories per mole. Hitchen's data on solubility in water likewise give the heat of solution of silica in water. From the depression of solubility by acid the work done by the acid may be calculated. A comparison of these three energies is of interest.

Harned's observed values of K_w are given in Table I with values for 70 and 90°C added, calculated from

$$\log_e K_w = -11038.1/T - 7.13954 \log_e T - 0.023892T + 84.8291 \quad (1)$$

which, with the relation $E = -Rd \log K/d(1/T)$ and $R = 1.9864$, gives

$$E_k = -21926 + 14.182T + 0.047460T^2, \quad (2)$$

values of which are also given in Table I.

¹ Herbert S. Harned, J. Frank. Inst. **225**, 642 (1938).

² C. S. Hitchen, *The Solubility of Silica in Water*, Bulletin 364 of the British Institute of Mining and Metallurgy (January, 1935).

³ V. Lenher and H. B. Merrill, J. Am. Chem. Soc. **39**, 2630 (1917).

Hitchen's data on silica solubility S in grams per liter and heat of solution E_s in calories per mole are also given in Table I.

$$\log S = -8168.78/T - 35.7430 \log T + 0.045306T + 215.8447, \quad (3)$$

$$E_s = -16226.47 + 71.0000T - 0.090000T^2. \quad (4)$$

It is to be noted that $E_w - E_s$ is sensibly constant, 6800 cal./mole. However, each molecule of SiO_2 takes on two molecules of H_2O before dispersing as a solution. Since $E_w - E_s$ is much more nearly constant than $2E_w - E_s$, it is to be inferred that most of the energy change is due to the first H_2O taken on during the hydration of the

TABLE I. Dissociation constants of water and solubilities of silica in water, with energies.

T	K_w	E_k	S	E_s	E_w	$E_w - E_s$
0	0.1133	-14511	0.110	-3547	10187	6640
15	0.4503	13898	.153	3240	10013	6773
30	1.468	13265	.202	2975	9844	6869
50	5.474	12386	.270	2680	9605	6925
70	16.16	11470	.337	2456	9361	6905
90	39.31	10519	.409	2311	9107	6796

$K_w \times 10^{-14}$, dissociation constant of water (Harned).

S , solubility of silica in water in grams per liter (Hitchen).

E_k , calories per mole to separate H and OH in H_2O .

E_s , net heat of solution of SiO_2 in H_2O in calories per mole.

E_w , energy of association of H_2O molecules with each other in liquid (cal./mole). Internal latent heat.

silica, the second H_2O differing little in energy from the solvent. The useful energy equation (not exact) is therefore $E_w = E_s + 6800$ cal./mole of water.

DEPRESSION OF SILICA SOLUBILITY BY ACID

The solubility of silica in hydrochloric acid of various concentrations determined by Lenher and Merrill in 1917, falls off in a smooth curve from 418 p.p.m. in pure water to 25 p.p.m. in 20 percent acid. No attempt at a thermodynamic treatment of their determinations appears ever to have been made, nor even to formulate them in a specific law. Such discussion and formulation seem well worth while in view of their fundamental bearing on the problem of the solubility of silicates in general. The data of Lenher and Merrill are given in Table II.

TABLE II. Solubility of silica in HCl solutions.

Acid percent	Silica dis- solved	S_0/S	\log S_0/S	Acid percent	Silica dis- solved	S_0/S	\log S_0/S
	p.p.m.				p.p.m.		
0.0	418	1.000	0.0	7.6	230	1.8174	0.5974
1.2	408	1.0245	.0242	9.3	190	2.2000	0.7885
3.0	374	1.1176	.1111	10.0	182	2.2967	0.8315
3.8	354	1.1808	.1662	13.6	112	3.7321	1.3170
5.3	302	1.3841	.3251	15.8	88	4.7500	1.5581
6.3	268	1.5597	.4445	18.6	58	7.2069	1.9750

The depression in solubility ($S_0 - S$) is related to the acid causing it but the graph of $\log (S_0 - S)$ against \log (acid concentration) has a definite though slight curvature. $RT \log (S_0/S)$ is the work (in cal./mole) done in depressing the silica concentration from S_0 to S . A graph shows an excellent linear relation between this energy and HCl concentration, the equation for which is

$$\begin{aligned}\log (S_0/S) &= 0.1179 \text{ HCl} - 0.3031 \\ &= 0.1179 (\text{HCl} - 2.57).\end{aligned}$$

The work done by a mole of HCl is

$$RT \log (S_0/S)$$

divided by the molar concentration of acid. The graph of this work per mole plotted against acid concentrations consists of two straight lines, steep at lower, nearly flat at higher concentrations, meeting in a rounded shoulder at about 7 percent (2 molar) HCl. It does not recall any familiar properties of this acid but is clearly descriptive of the competition of HCl and $\text{Si}(\text{OH})_4$ ions for water. The actual energies involved are small; at 9.3 percent HCl, for example, a liter of solution contains 2.55 moles of HCl, 0.0032 mole of SiO_2 , and $RT \log (S_0/S)$ is 569 cal./mole of SiO_2 or 223 cal./mole HCl. Even this small amount of extra energy is sufficient to halve the solubility of the silica and indicates the delicacy of the balance between free and associated ions.

Data on the solubility of pure silica in water and HCl solutions have been formulated and reduced to energy as a step in the study of the solubility of the silicates. Two new relations developed may prove to be of general interest.