CXCIX.—*Germanium. Part IV. The Solubility of Germanium Dioxide in Acids and Alkalis.*

By William Pugh.

The method of solubility measurements in dilute solutions of acids and alkalis, which has been employed by Wood (J., 1908, **93**, 411; 1910, **97**, 878) to determine the acid and basic dissociation constants of certain inorganic amphoteric hydroxides, is an application of the Lowenherz solubility method and appears to have led to a reasonable value for the basic dissociation constant of arsenious acid (*loc. cit.*). Now, germanium hydroxide bears a striking resemblance to arsenious hydroxide in many ways: it is a true amphoteric hydroxide; as a base, it forms a series of salts with the halogen acids; and, as an acid, it forms the germanates, the preparation and properties of some of which have already been described by the author (J., 1926, 2828). These germanates appear to be more stable and more characteristic of the element than the halogen compounds. A comparative study of their behaviour towards water indicates that germanium hydroxide is essentially an acid. In order to confirm this, quantitative measurements of the solubility of germanium dioxide in acids and alkalis were undertaken. It was hoped that these results would lead to comparative values for the acid and basic dissociation constants of germanium hydroxide.

The germanium dioxide employed was prepared from the pure disulphide by repeated treatment with concentrated nitric acid in quartz vessels and ignition at a bright red heat. The oxide, which had not been allowed to fuse, was ground with water, washed until free from sulphuric acid, and finally re-ignited.

Solubility of Germanium Dioxide in Water.—All determinations of solubility were made at 25°. A mixture of germanium dioxide and distilled water was agitated continuously in a Pyrex-glass flask in a thermostat until equilibrium was established : only after 6 days were the values obtained for the solubility concordant at 0·447 g. per 100 g. of water. The germanium dioxide in this and in all other solutions was determined by precipitating the sulphide after the addition of acid to bring the total acid concentration up to $6N$. The precipitate was then well washed with $6N$-acid saturated with hydrogen sulphide, and converted into oxide by ammoniacal hydrogen peroxide, according to the method of Johnson and Dennis (*J. Amer. Chem. Soc.*, 1925, **47**, 790).

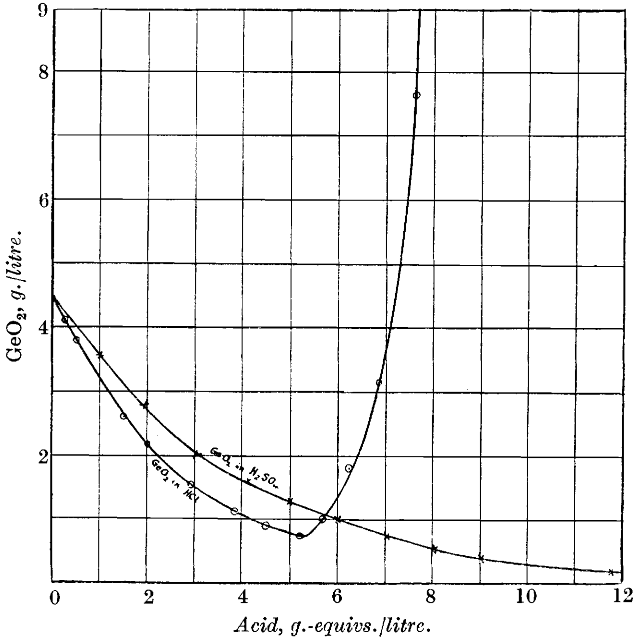
Solubility of Germanium Dioxide in Acids.—The method of determination was similar to that described above, the dioxide being mixed with acids of known concentration. Solubility measurements were made in hydrochloric and sulphuric acids. In these cases, 8—10 days were necessary to ensure complete saturation. The results are given in Table I.

TABLE I.

HCl, mols./l.	GeO_2, g./100 c.c.	HCl, mols./l.	GeO_2, g./100 c.c.	H_2SO_4, mols./l.	GeO_2, g./100 c.c.	H_2SO_4, mols./l.	GeO_2, g./100 c.c.
0·000	0·4470	4·53	0·0920	0·000	0·4470	3·50	0·074
0·25	0·4115	5·20	0·074	0·50	0·3550	4·00	0·054
0·50	0·3810	5·72	0·102	0·98	0·2805	4·50	0·041
1·50	0·2600	6·23	0·1820	1·50	0·2000	5·85	0·019
2·00	0·2185	6·85	0·3164	2·05	0·1600	7·95	0·009
2·925	0·1544	7·62	0·7660	2·52	0·1305	(95%)	0·140
3·85	0·1140			3·02	0·099		

Consideration of these figures shows that the solubility of germanium dioxide in hydrochloric acid diminishes as the concentration of acid increases, reaching a minimum at $5{\cdot}3N$-acid, and then rising rapidly with further increase in the concentration of the acid. This is more clearly seen from the curve (Fig. 1). At the concentrations falling within the first portion of the curve it is obvious that germanium hydroxide is ionising predominantly as an acid, its ionisation, and consequently its solubility, being diminished by the introduction of foreign hydrogen ions. Beyond the minimum it is equally obvious that germanium hydroxide is ionising as a base, the increase in solubility being due to the formation of increasing quantities of germanium chloride. The behaviour of germanium hydroxide is therefore parallel to that of arsenious hydroxide (Wood, *loc. cit.*), with which the minimum occurs at 3·2N-acid. It is clear, then, that the basic dissociation constant of germanium hydroxide must be much smaller than that of arsenious hydroxide, which Wood calculated to be approximately 1×10^{-14}. The same method of calculation applied to the present case does not, however, yield a trustworthy value on account of the uncertainty involved in the extrapolation of the curve.

Fig. 1.



When sulphuric acid is employed as solvent, the solubility of germanium dioxide is diminished continuously as the concentration is increased up to 16N; further, even in 95% acid the solubility has only one-third of the value it has in water. It is therefore probable that germanium sulphate is incapable of existence, at any rate in solution containing much water. The stability of any salt in water depends upon the magnitude of the dissociation constants of both acid and base. If both are small the salt may be completely decomposed by water. Thus, whilst germanium hydroxide forms with hydrochloric acid a salt which is stable in aqueous solution containing large amounts of free acid, it is not able to form a salt with the weaker sulphuric acid even in the presence of a very large excess of acid. It is doubtful whether the small increase in solubility in the 95% acid is due to salt formation.

Solubility of Germanium Dioxide in Alkali.—Since the acid dissociation constant of germanium hydroxide is probably far greater than the basic, which has already been shown to be very low, it is probable that the solubility of germanium dioxide will be increased by even small concentrations of alkali. The results obtained with solutions of caustic soda are given in Table II, in which S represents the solubility in sodium hydroxide of concentration C, and S_w that in water. It is clear that the solubility of germanium dioxide is increased over the whole range of concentration investigated. These results should, therefore, be suitable for the evaluation of the acid dissociation constant by the Lowenherz method, but actually they do not lend themselves to this treatment, for when values calculated from the table are substituted in the equation

TABLE II.

NaOH, mols./l.	GeO_2, mols./l.	$S - S_w$.	$(S - S_w)/C$.
0·00	0·0428	—	—
0·00125	0·0440	0·0012	1
0·0025	0·0483	0·0055	2·2
0·005	0·0545	0·0117	2·3
0·010	0·0675	0·0247	2·47
0·0125	0·0746	0·0318	2·54
0·025	0·1115	0·0687	2·75
0·050	0·1693	0·1265	2·53
0·100	0·2280	0·1852	1·85

$$\text{(free acid)} \times \text{(free base)}/\text{(salt)} = \text{hydrolysis constant},$$

negative values are obtained for the concentration of free base and hence for the hydrolysis constant. The explanation is found in the last column of the table, which shows that the increase in the concentration of germanium dioxide always exceeds the concentration of caustic soda. Precisely in what condition the germanium dioxide exists in solution is uncertain. All the solutions in caustic soda showed a well-defined Tyndall cone, and it is probable that the increase in solubility is due, in part at least, to a peptising action of caustic soda. It may also be that the solutions contain salts of condensed germanic acids. Salts of condensed silicic acid are known in the alkali–silica systems, and the author, in a previous communication (*loc. cit.*), has adduced some evidence of the existence of condensed germanates in the system K_2O–GeO_2; it is quite clear that there is a very close analogy between the two systems.

It is hoped to throw further light on this analogy by work at present in progress.

Summary.

(1) Measurements have been made of the solubility of germanium dioxide in solutions of hydrochloric acid, sulphuric acid, and sodium hydroxide.

(2) As an acid oxide, its solubility is repressed by hydrochloric acid, reaching a minimum at an acid concentration of $5{\cdot}3N$.

(3) There is no evidence of the existence of germanium sulphate.

(4) Solutions of germanium dioxide in caustic soda are colloidal and may also contain salts of condensed germanic acid. There is a striking resemblance between the systems alkali–germanium dioxide and alkali–silica.

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