288. *The Decomposition of the Fluosilicate Ion in Aqueous and in Aqueous Salt Solutions.*

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Aqueous solutions of sodium fluosilicate are distinctly acid and react with alkali according to the stoicheiometric equation

$$Na_2SiF_6 + 4NaOH = 6NaF + H_2SiO_3 + H_2O \quad . \quad . \quad . \quad . \quad (1)$$

The reaction is slow and was shown by Hudleston and Bassett (J., 1921, **119**, 403), working with the acid, to be of the first order. They suggested that the mechanism was most probably a slow reaction

$$SiF_6 \longrightarrow SiF_4 + 2F' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

followed by the relatively rapid

$$SiF_4 + 3H_2O = 4HF + H_2SiO_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and neutralisation of the hydrogen fluoride produced. This is in accordance with the modern theory of hydrolysis (Sidgwick, "The Electronic Theory of Valency," 1929, pp. 156—158), according to which the SiF_6'' ion would not be open to attack since the co-ordination number of the silicon atom is fully satisfied, whereas the silicon tetrafluoride can co-ordinate two molecules of water, the silicon atom acting as acceptor, after which hydrogen fluoride would split off from the resulting complex.

If this interpretation be correct, the reaction is one which, from its simplicity, should be of considerable theoretical importance, and the present paper describes the evidence which establishes the theory on a secure basis.

EXPERIMENTAL.

The method adopted was similar to that used by Hudleston and Bassett (*loc. cit.*). Into each of a series of large test-tubes was measured the same quantity of a solution of sodium fluosilicate and six drops of phenolphthalein solution. In each tube was also placed a smaller tube containing a measured amount of alkali, insufficient for the permanent neutralisation of the fluosilicate. The outer tubes were closed by rubber bungs which carried glass rods reaching nearly to the bottom of the inner tubes, and then were brought to a constant temperature of 20·0° in a thermostat. Mixing was effected by inverting and shaking the tubes. It was greatly facilitated by the rods holding back the inner tubes from sliding up to the cork, and appeared to be complete in about 0·1 second.

At first the alkali was in excess and the solution was accordingly pink, but as further acid was produced by reactions (2) and (3) the colour faded. The time, t, from the moment of mixing to complete decolorisation was measured with a stop-watch. If the amount of fluosilicate measured into the outer tube required N c.c. of alkali for permanent neutralisation, and only a smaller quantity, n c.c., had been put into the inner tube, then at the moment when the colour just disappeared the amount of SiF_6'' present was equivalent to $(N - n)$ c.c. of alkali. Thus the fraction $(N - n)/N = R$ (say) measures the proportion of the stoicheiometrical amount of fluosilicate taken actually existing as SiF_6'' at the time t. According to the ordinary unimolecular law, $\log R$ is a linear function of t, and by extrapolating back to zero time $\log R_0$

is obtained, where R_0 is the proportion of possible fluosilicate ion actually existing as such in the original fluosilicate solution.

The underlying conception of this is that hydrogen ion is being produced at a rate which is independent of the concentration of the hydroxyl ion present, provided only that this be large enough to make the back reaction negligible. Similar log R–t relationships are possible where this is not true (*e.g.*, in the neutralisation of dichromate solutions) but confirmation in this case was obtained in the following way.

To one tube containing N c.c. of sodium fluosilicate were added n c.c. of alkali such that it took 35 seconds for the colour to fade. Then to another tube containing the same quantity, N c.c., of fluosilicate were added $(n + x)$ c.c. of alkali and, 25 seconds later, sufficient hydrochloric acid to neutralise the extra x c.c. of alkali. The colour still faded in 35 seconds from the moment of first mixing, despite the fact that for the first 25 seconds the concentration of alkali had been much greater. Thus the rate of reaction is proved to be independent of the concentration of the alkali, and the curves obtained correspond to a truly unimolecular production of hydrogen ion and cannot be interpreted on any theory which involves the hydroxyl ion entering into the slow reaction.

To eliminate the possibility that the reaction was pseudo-unimolecular, as in a hydrolysis involving the solvent water, measurements were made in mixed solvent media-water containing up to 20% of alcohol or acetone—and it was found that the rate of reaction was nearly doubled. (Our quantitative measurements of this were later found to be slightly in error owing to the effect of the solvent medium on the indicator employed, and are therefore not recorded.) This would hardly be the case if the slow reaction were itself a hydrolysis.

The final proof of the correctness of the theory arises from the fact that these reactions are reversible, giving rise to an equilibrium in solutions of sodium fluosilicate, and that the corresponding equilibrium constant can be determined over a wide range of concentration by means of the values of R_0 obtained by extrapolation as described above. Further, the addition of other salts, including fluorides, affects the concentrations of the substances involved in the equilibrium quantitatively in the way required by modern theory.

The sodium fluosilicate employed was that used by us in our solubility measurements (J., 1931, 1648). The sodium hydroxide was made from well-washed sticks, and was proved free from carbonate by its failure to give a precipitate with barium chloride. Glass vessels were used throughout, as the concentrations of hydrofluoric acid involved were extremely small and saturation with silica was in any case assured.

Since the final stage of the titration is fundamentally that of the weak hydrofluoric acid, it was to be expected that the faintest tinge of colour of phenolphthalein would indicate the stoicheiometric end-point. This was confirmed by studying with a "universal" indicator the p_H of solutions to which various amounts of alkali had been added. The greatest permanent change of p_H with quantity of alkali added occurred at the point indicated by phenolphthalein.

In each individual run N was kept the same for all the tubes; 4 or 5 values of n were adopted, usually with six tubes for each. The data for a typical run are shown below:

Run No. 40; 0·00525M-Na_2SiF_6; N = 21·07.

n.	1 + log R.	t.	t_{mean}.
9·97	0·7217	11·3, 11·1, 11·6, 11·8, 11·7, 11·9	11·5
12·94	0·5865	20·6, 20·0, 20·0, 19·7, 19·7	20·0
14·24	0·5108	25·1, 25·8, 24·6, 24·6	25·0
17·23	0·2607	40·3, 40·8, 39·4, 41·4, 39·8	40·3

From four such values of log R six values for the slope may be calculated, and the mean of these was adopted although such a method gives undue weight to any inconsistency between points which lie close together. Even so, in the whole series of 24 runs involving solutions ranging in concentration from 0·0016 to 0·0218 g.-mol./l., the mean slopes all lie within the limits 0·0154—0·0168, with a large majority around the general mean value 0·0163.

Table I shows, for each concentration studied, the mean slope obtained in this way, the mean extrapolated value of log R_0, and the equilibrium constant calculated as described below.

In calculating this constant, $K = a_{SiF_4} \times a_{F'}^2/a_{SiF_6''}$, it is convenient to think of 1 l. of solution containing stoicheiometrically m g.-mols. of sodium fluosilicate. From the velocity measurements it is determined that only R_0m g.-mols. of SiF_6'' remain as such, so that according to reaction (2), $(m - R_0m) = z$ (say) g.-mols. of silicon tetrafluoride, and $2z$ g.-ions of F′ must have been produced. But some of this tetrafluoride has been further changed according to reaction (3), producing, say, x g.-mols. of hydrogen fluoride and therefore reducing the concentration of silicon tetrafluoride to $(z - x/4)$. Finally, some of this hydrogen fluoride is ionised, producing a further quantity, say y, of F′ and, of course, y g.-ions of H˙. Thus the true concentrations of the various molecular and ionic species are

$$m_{SiF_6''} = R_0 m \quad m_{SiF_4} = (z - x/4) \quad m_{F'} = (2z + y) \quad m_{HF} = (x - y) \quad m_{H^{\cdot}} = y.$$

The constant $K = f_{SiF_4}(z - x/4) \times f_{F'}{}^2(2z + y)^2/f_{SiF} R_0 m$, where f denotes the activity coefficient of the substance indicated by the suffix, determined as given below.

The values of x and y can be determined only by an indirect method, but fortunately they prove to be fairly small compared with z although by no means negligible.

We calculate y from the p_H of the solution, assuming that no appreciable proportion of the hydrogen ion obtained from the dissociation of the hydrofluoric acid combines with the fluosilicate ion. The p_H determinations were made colorimetrically by means of methyl-orange and comparison buffer solutions of sodium hydrogen phthalate and hydrochloric acid, according to the method of Clark and Lubs (*J. Biol. Chem.*, 1926, **25**, 479). All the solutions of pure sodium fluosilicate yielded the same result, *viz.*, $p_H = 3{\cdot}6$, corresponding to the value 0·00025 for the activity of the hydrogen ion. The corresponding concentrations of the hydrogen ion should vary with the ionic strength, but the variations are small compared with the uncertainty in p_H, so a uniform value for y of 0·00027 was adopted for all the solutions of pure sodium fluosilicate.

From this it follows that $m_{F'} = 2(1 - R_0)m + 0{\cdot}00027$. The concentration of undissociated hydrogen fluoride present, $(x - y)$, may now be calculated from the dissociation constant of the acid and these concentrations of the ions, since the work of Davies and Hudleston (J., 1924, **125**, 260) has established that no complication from the formation of HF_2' is to be feared at the dilutions involved. The dissociation constant of hydrogen fluoride was calculated from the data of Dessen (*Z. physikal. Chem.*, 1922, **102**, 169), yielding $a_{HF} = 1300 a_{F'} a_{H^{\cdot}}$. It was assumed that the activity coefficient of the undissociated acid was unity, and that of the fluoride ion was taken to be the same as that of chloride ion in solutions of the same ionic strength $(= f_{KCl})$. The ionic strength was calculated simply from the stoicheiometrical concentration of the salt, since decomposition was small. Thus $m_{HF} = (x - y) = 1300 \times 0{\cdot}00025 \times f_{F'} \times (2z + y)$. In conjunction with y, this gives x, and hence $m_{SiF_4} = (z - x/4)$ is calculable.

Finally, the calculation of the constant requires a knowledge of the activity coefficients of SiF_4 and SiF_6''. The former is taken as unity since the molecule is uncharged, and to obtain the latter we made special solubility determinations (*loc. cit.*).

The results, listed in Table I, are quite free from any sign of drift, and agree within the limits of error imposed by the difficulty of determining R_0 with sufficient accuracy. This is particularly important because R_0 varies from 0·628 to 0·924, so that any error in it is magnified in the term $(1 - R_0)$ to the cube of which K is almost directly proportional. The figure, which shows the plot of log R_0 against m, and in which the curve shows the values that log R_0 should have to give a constant value of $K = 1 \times 10^{-6}$, brings out clearly the satisfactory nature of the agreement.

TABLE I.

C = concn. of Na_2SiF_6 in g.-mols./l.; k is based on common logarithms and seconds.

$C \times 10^5$.	$k \times 10^4$.	$1 + \log R_0$.	$K \times 10^6$.	$C \times 10^5$.	$k \times 10^4$.	$1 + \log R_0$.	$K \times 10^6$.	$C \times 10^5$.	$k \times 10^4$.	$1 + \log R_0$.	$K \times 10^6$.
161	162	0·7979	1·10	590	160	0·9223	1·03	1171	155	0·9511	1·35
175	158	0·8182	0·98	650	165	0·9354	0·76	1265	155	0·9350	1·24
254	163	0·8624	0·96	720	164	0·9297	1·21	1379	162	0·9596	0·95
297	157	0·8559	1·50	745	164	0·9350	1·01	1487	159	0·9578	1·25
365	160	0·8997	0·81	806	163	0·9385	1·05	1711	154	0·9556	1·97
368	165	0·8902	1·10	905	167	0·9460	0·91	1971	163	0·9736	0·60
502	159	0·9047	1·35	985	157	0·9459	1·11	1972	161	0·9723	0·70
525	164	0·9123	1·15	1047	163	0·9524	0·85	2180	157	0·9658	1·56

Measurements were then made in the presence of known concentrations of electrolytes, *viz.*, sodium chloride, sulphate, or fluoride, added to both the fluosilicate and the alkali solutions. The results are collected in Table II. It will be seen that the slopes (of the log R against t curves) all lie within the limits of the values obtained with pure fluosilicate solutions, so any effect there may be on the velocity constant lies within the experimental error. Actually, the values lie mostly below our previous mean, 0·0163, but we do not regard this difference as significant. This is in harmony with Brönsted's theory (*Z. physikal. Chem.*, 1922, **102**, 169), for in this case the rôle of " complex " must be played by an activated form of SiF_6'', and as this necessarily has the same charge as the reactant (normal SiF_6'') the velocity should be unaffected by the ionic strength of the solution.

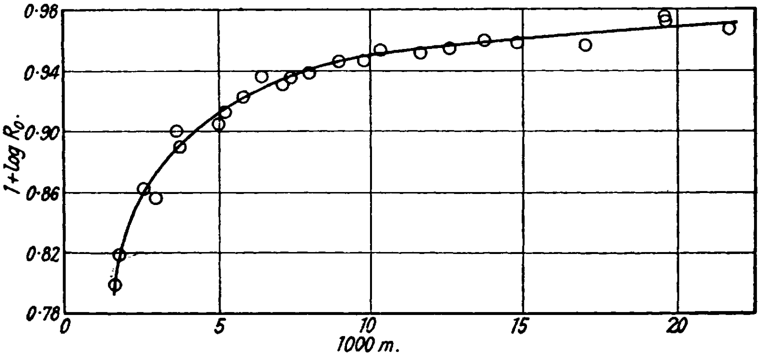

TABLE II.

C.						C.					
Na_2SiF_6.	NaCl.*	p_H.	$k \times 10^4$.	1 + $\log R_0$.	*K*.	Na_2SiF_6.	NaF.*	p_H.	$k \times 10^4$.	1 + $\log R_0$.	*K*.
0·01071	0·005	3·6	0·0159	0·9628	0·56	0·00630	0·0021	3·8	0·0155	0·9487	1·79
0·00806	0·100	3·6	0·0159	0·9516	0·78	0·00662	0·0029	3·8	0·0160	0·9655	1·14
0·00634	0·100	3·6	0·0158	0·9369	1·07	0·00654	0·0052	4·0	0·0156	0·9614	3·81
0·00175	0·200	3·6	0·0158	0·8766	0·77	0·00635	0·0085	4·0	0·0160	0·9789	—
	Na_2SO_4.*					0·00681	0·0500	?	0·0158	0·9947	—
0·00659	0·050	3·6	0·0156	0·9369	1·30						

* Added electrolyte.

On the other hand, the value of R_0 (and of R for any given value of t) is reduced by the presence of the added electrolyte. In the cases of sodium chloride and sulphate, this is simply due to the effect of the ionic strength of the solution on the activity coefficients of the ions concerned. Debye and Hückel (*Physikal. Z.*, 1923, **24**, 305) have shown that the activity coefficient of an ion is given by the equation $\log f = -0{\cdot}5Z\sqrt{\mu}$, where Z is the valency of the ion and μ is the ionic strength of the solution. Since we have $\log K = \log m_{SiF_4} + 2 \log m_{F'} - \log m_{SiF_6''} + 2 \log f_{F'} - \log f_{SiF_6''}$ (f_{SiF_4} being taken as unity), on applying the above relation we find $2 \log f_{F'} - \log f_{SiF_6''} = 1{\cdot}5\sqrt{\mu}$. Hence, the greater μ is, the smaller must be the term $\log m_{SiF_4} + 2 \log m_{F'} - \log m_{SiF_6''}$, *i.e.*, dissociation is repressed by the addition of non-participating electrolytes.

That the effect is in fair quantitative agreement is shown by the fact that the equilibrium constants, calculated exactly as before with the appropriate value for the ionic strength of the solution, are in about as good agreement as those obtained with solutions of pure sodium fluosilicate.

The effect of sodium fluoride in repressing R_0 is enormously greater than that of the previously mentioned salts because it introduces one of the products of the dissociation, *viz.*, the fluoride ion. This in itself appears to be very strong confirmation of the explanation that has been offered of the reaction. That the calculated equilibrium constant fails in the case of the more concentrated solutions is due solely to the values for the concentration of silicon tetrafluoride becoming less than the experimental error. For instance, in the presence of 0·0085*M*-sodium fluoride, it may be calculated from the known equilibrium constant that the molarity of the tetrafluoride should be 0·0003, whereas ($z - x/4$) from the experimental data is exactly zero. The discrepancy is thus actually very small, although it renders the calculation of an equilibrium constant impossible for that case. The remarkably good agreement obtained with the more dilute solutions of sodium fluoride constitutes, therefore, the most searching proof of the correctness of the postulated mechanism of the change and the essential accuracy of the method of calculation.

In the presence of sodium fluoride the p_H is slightly altered as shown in Table II. This has been taken into account in the calculation of *K*.

SUMMARY.

The reaction between sodium fluosilicate and alkali is shown to be of the first order, with a value of 0·0163 (common logarithms; seconds) for the constant at 20°.

The mechanism previously suggested by Hudleston and Bassett, that SiF_6'' slowly decomposes into SiF_4 and $2F'$, followed by rapid hydrolysis of the former, is confirmed in various ways. In particular, the velocity measurements are used to determine the initial extent of hydrolysis of the fluosilicate solutions over a range of concentration, and hence to calculate the equilibrium constant, $K = a_{SiF_4} . a_{F'}^2 / a_{SiF_6''}$, which is found to be 1×10^{-6} at 20°.

In accordance with theory, the addition of other electrolytes does not affect the velocity of change but represses the initial dissociation.

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