

CCXVI.—*The Action of Aqueous Hydrofluoric Acid
on Silica.*

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FOR the purpose of completing an investigation into the adsorptive power of powdered silica, it became essential to devise some trustworthy method of determining the surface of this material, a problem previously attacked by Martin, Bowes, and Christelow (*Trans. Ceramic Soc.*, 1925—1926, **25**, 51), who used the rate of dissolution of sand in hydrofluoric acid as a measure of the surface of the solid. These authors do not appear, however, to have examined the chemical mechanism of the reaction; and it is remarkable, in view of the familiar nature of the reaction, that there appears to be no record in the literature of any such investigation, which seems to be an indispensable preliminary to the special use of the reaction, and also probably a matter of general chemical interest.

E X P E R I M E N T A L.

The hydrofluoric acid used throughout was taken from the same sample of the concentrated acid, and, although not specially treated, contained a small quantity of hydrofluosilicic acid as the only detectable impurity, which had no influence on the experiments to be described. The silica was coarsely crushed and narrowly graded "Vitreosil" obtained specially from the Thermal Syndicate; 1000 particles of the material weighed almost exactly 0.5 g., the average diameter being 0.76 mm. It will be shown later that 2 g. could lose as much as 0.2 g. by solution without detectable change in surface. All vessels with which hydrofluoric acid was in contact were of vulcanite, a number of attempts to use glass coated with waxes of different kinds having proved very unsatisfactory.

The rate of dissolution of silica in *N*- and less concentrated acid (without the presence of other electrolytes) can be very conveniently and rapidly determined on the same sample of acid and silica by taking advantage of the fact that the final product of the reaction, hydrofluosilicic acid, has in aqueous solution a very much greater molecular conductivity than the reacting hydrofluoric acid. The experimental details were as follows: 50 G. of hydrofluoric acid of the desired concentration were weighed into a vulcanite tube of 60 c.c. capacity, which was then closed with a rubber stopper and clamped in a thermostat to a vertical support that was now rotated mechanically, so that the tube turned over end-wise at a standard rate of 25 times a minute. The acid having assumed the temperature of the thermostat, the rotation was stopped, and 2 g. of silica were added. After a suitable interval of stirring by rotation this was again interrupted, the stopper removed from the tube, and its place taken by another carrying a conductivity cell also of vulcanite (with ordinary platinum electrodes) of only 7 c.c. capacity. This cell was now filled with the reaction liquid by running 7 c.c. of water from a burette connected with the top of the cell, and the conductivity determined. After the liquid had been returned to the reaction tube, the cell was removed, and the stirring resumed until another reading became due. The whole operation of observing the conductivity was accomplished normally in 4 minutes. It will be proved later that the reaction of hydrofluoric acid upon silica is not of the usual type in which the thickness of a layer adherent to the solid is dependent on the rate of stirring and controls the rate of reaction. The stirring in this case serves solely to preserve a uniform composition in the liquid, and as the normal rate of reaction is low, the effect of the interruption of 4 minutes is in this respect quite negligible. There remains the slight but again

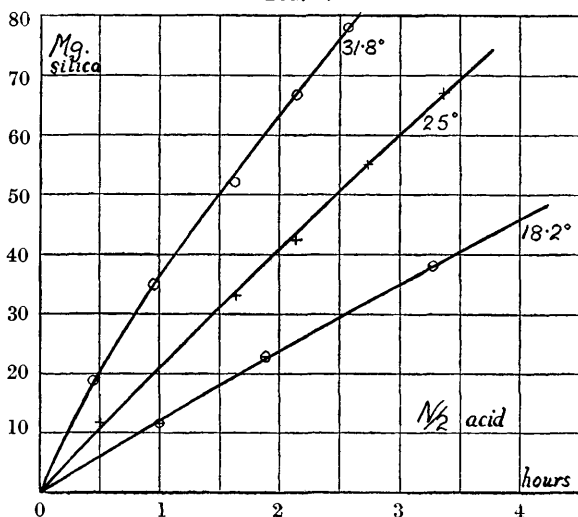
quite negligible error due to the withdrawal of a small quantity of acid from contact with the silica during the determination of conductivity. The constant (55.45) of the conductivity cell was determined at frequent intervals, but did not alter throughout the work.

Table I shows, in an abbreviated form, a specimen calibration of resistance with uptake of silica, the acid being initially of $\frac{1}{2}N$ -concentration, and the temperature 25° . In the determination of

TABLE I.

SiO ₂ (mg.) in 50 g. of acid	0.0	5.6	13.2	20.7	41.8	106.0	143.0	212.0	241.0
Resistance (ohms)	4450	4340	4170	3930	3450	2420	1990	1490	1340

FIG. 1.



conductivity, a valve oscillator was used as the source of alternating current. The setting of the minimum sound on the Wheatstone bridge was much facilitated by using a rocking slider with two contacts set 1 cm. apart, the minimum being midway between these, when each separately gave sounds of equal intensity.*

Unless otherwise stated, rates of dissolution are recorded as mg. of silica dissolved from 2 g. of silica by 50 g. of acid in one hour.

The Effect of Temperature and Rate of Stirring on the Rate of Reaction.—The temperature coefficient of a heterogeneous reaction is of great importance in deciding whether we have to deal with a diffusion mechanism as is so frequently the case in solution reactions. Fig. 1 shows the rate of reaction, determined by the conductivity

* I am much indebted to Dr. R. G. W. Norrish for suggesting this modification of the usual arrangement.

method, for three temperatures, the acid used being initially $N/2$. The rates of dissolution for equal uptake of silica, and the corresponding temperature coefficients are given in Table II, from which it appears that the latter correspond to a direct chemical action

TABLE II.

SiO ₂ , mg.	Rate of reaction at			Mean temp. coeff. for 10°.
	31.8°.	25.0°.	18.2°.	
20	34.5	19.0	11.8	2.52
40	30.0	18.5	11.7	2.35
60	27.0	18.0	11.5	2.26

unrestricted by a diffusion process. This result was independently confirmed by determining the amount of silica dissolved at 25° by N -acid, the rate of stirring being alternately 6 r.p.m. and 25 r.p.m. between successive readings (see Table III). The rate of reaction

TABLE III.

Time (mins.).	Stirring.	SiO ₂ , mg.	Rate per hour.
0		—	—
	Slow		
31		11.5	23.0
	Fast		
60		23.0	23.0
	Slow		
110		43.5	23.7
	Fast		
142		54.6	23.1
	Slow		
172		67.0	23.4

is therefore independent of the rate of stirring even when this is only barely sufficient to maintain homogeneous composition in the liquid.

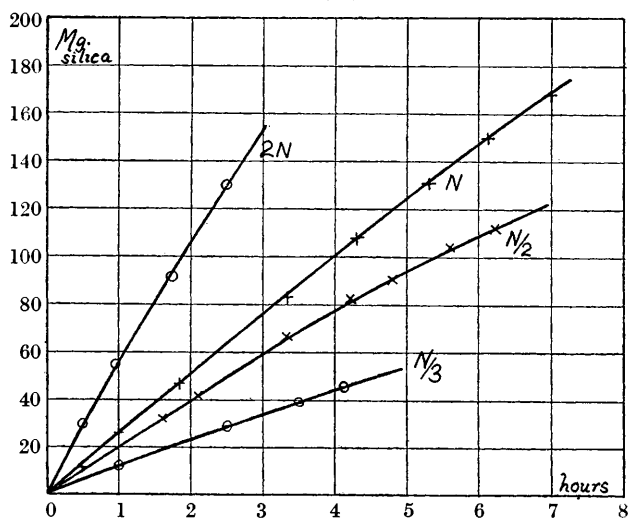
The Rate of Reaction of Hydrofluoric Acid in the Absence of Neutral Salt.—The uptake of silica plotted against time for the action of $2N$ -, N -, $\frac{1}{2}N$ -, and $\frac{1}{3}N$ -acids at 25° is shown in Fig. 2. Taking as an approximate measure of the rate, the amount of silica dissolved in one hour, we find the following :

Rate of reaction	56	26	19	12
Conc. of undissociated HF (g.-mols./l.)	1.788	0.894	0.447	0.296

The data in the second line are taken from the work of Davies and Hudleston (J., 1924, **125**, 260). While the rate decreases in approximate proportion to the undissociated hydrogen fluoride concentration between $2N$ and N , the decrease at lower concentrations is markedly less than in such proportion. Also, it will be seen from Fig. 2 that with N -acid the rate of dissolution is very nearly constant at 26.0 mg. per hour until about 140 mg. of silica have dissolved, although the concentration of the acid has up to this point fallen steadily to 0.7 of its initial value (see Table VI). Similarly $\frac{1}{2}N$ - and $\frac{1}{3}N$ -acids dissolve the solid at a rate decreasing much more gradually than the concentration of the acid.

The reaction therefore appears to receive a stimulus increasing up to a point with the amount of silica dissolved. This effect might well be due merely to an increase in the available area of the solid owing to fragmentation and etching. This possibility was tested in two ways as follows: (a) by observing the rate of dissolution of a fresh sample of silica in an acid that had already dissolved 47 mg. from a previous sample, and (b) by observing the rate up to a content of 85 mg. of silica, adding a further 2 g. of fresh solid, and then continuing the observations. In (a) the rate was quite unaltered; in (b) it was exactly doubled. These results proved that there is no measurable alteration in the available surface up to

FIG. 2.



a content in the liquid of 200 mg. of silica. We must therefore conclude that the rate of reaction is not simply related to the concentration of the hydrofluoric acid. This view is strikingly confirmed by two further series of experiments in which silica was dissolved in (a) $\frac{1}{2}N$ -acid containing $\frac{1}{2}N$ -ammonium fluoride, and (b) $\frac{1}{2}N$ -acid containing $\frac{1}{4}N$ -hydrochloric acid or $\frac{1}{2}N$ -sulphuric acid. In these experiments the conductivity method was not available owing to the prevailing high conductivity; the rate was therefore ascertained by direct weighing of the remaining silica, the hydrofluoric acid being first neutralised by pouring the contents of the reaction tube into the requisite quantity of aqueous ammonia (the high solubility of ammonium fluoride and silicofluoride renders this a simple and convenient means of arresting the action), and then

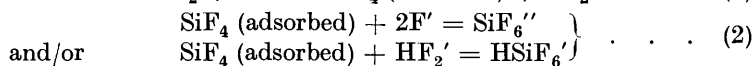
collecting and washing the silica in a Gooch crucible. The results are shown in Table IV. The composition of the liquid was calcu-

TABLE IV.

Time (mins.).	SiO ₂ , mg.	Average rate.	Initial composition.
(a) $\frac{1}{2}N$ -HF with $\frac{1}{2}N$ -NH ₄ F.			
60	35	36	$\left\{ \begin{array}{l} C_{\text{HF}_2} = 0.00057, \quad C_{\text{HF}_2'} = 0.214, \\ C_{\text{F}^-} = 0.186, \quad C_{\text{HF}} = 0.250. \end{array} \right.$
150	91		
(b) $\frac{1}{2}N$ -HF with $\frac{1}{4}N$ -HCl.			
60	9.5	10	$\left\{ \begin{array}{l} C_{\text{HF}_2} = 0.201, \quad C_{\text{HF}_2'} = 0.0021, \\ C_{\text{F}^-} = 0.0009, \quad C_{\text{HF}} = 0.500. \end{array} \right.$
180	39.0		
$\frac{1}{2}N$ -HF with $\frac{1}{2}N$ -H ₂ SO ₄ .			
60	11.0	12	(approximately as for HCl)
187	39.0		

lated on the assumption that the simple laws of chemical equilibrium would apply. The necessary constants were those obtained by Davies and Hudleston (*loc. cit.*). The above experiments seem clearly to indicate that it is the fluorine-containing ions, rather than the free hydrofluoric acid, that control the rate.

A plausible hypothesis that suggests itself may be summarised in the following equations :



There is evidence that the reaction (1) is very rapid; Baur finds the value of $C_{\text{SiF}_4} \times C_{\text{H}_2\text{O}}^2 / C_{\text{HF}}^4$ to be 163×10^7 for equilibrium in the gas phase at 104° (*Z. physikal. Chem.*, 1904, **48**, 483). We might thus assume that the rôle of the hydrofluoric acid is to maintain the surface of the silica covered with a (protective) layer of adsorbed tetrafluoride, which is in turn carried into solution as the ion SiF_6'' (or HSiF_6') after union with one of the fluorine-containing ions. The reacting ions may be adsorbed before reaction, or react by direct collision; in either case we might expect the greater part of the dissolution of the silicon tetrafluoride to be effected by the HF_2' ion, since the conjunction of one of these ions with a molecule of the tetrafluoride is stoichiometrically sufficient, while two contiguous simple fluorine ions are necessary.

If adsorption precedes reaction, then the maximum rate of reaction will only be reached when the electrokinetic potential at the surface is annihilated by the presence of excess of strong electrolyte. Fig. 3 shows the rate of uptake of silica (determined by direct weighing of the residue) by $2N$ -, N -, and $\frac{1}{2}N$ -acid at 25° in the presence of a constant high concentration (1 mol. per litre) of

ammonium sulphate; the results for these concentrations of acid without the addition of electrolyte are reproduced from Fig. 2 as broken lines for comparison. The sensitiveness of the rate of reaction to the presence of neutral salt is indicated in Table V, which shows the amount of silica dissolved in one hour at 25° by *N*-acid in the presence of varying amounts of ammonium sulphate.

FIG. 3.

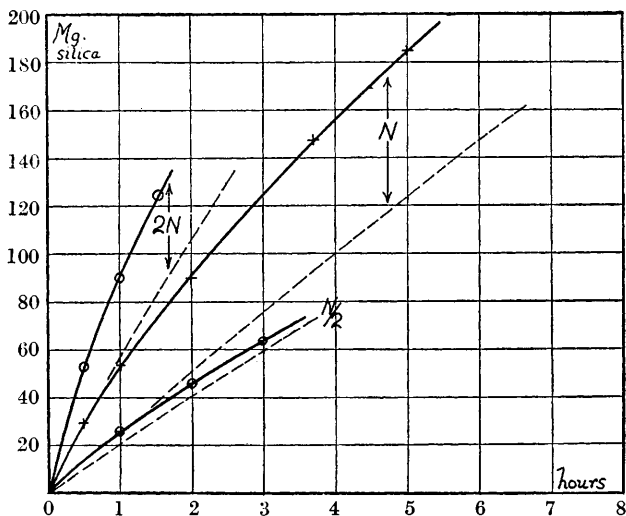


TABLE V.

$(\text{NH}_4)_2\text{SO}_4$, M.	$C_{\text{NH}_4} = 2C_{\text{SO}_4}$.	SiO ₂ , mg.
0.0	—	26.0
0.045	0.066	30.5
0.108	0.144	36.5
0.216	0.259	38.6
(1.0	—	54) from Fig. 3.

It may be observed from Fig. 3 that the accelerating effect of the electrolyte is greater the greater the rate in its absence; Table V shows, also, that for small amounts of electrolyte its effect is proportional to the concentration of the ions produced from it.

To trace what relation the rate of reaction under the above conditions bears to the concentration of the ionic species, Table VI has been prepared; it relates to a temperature of 25°. As the deductions from this table are of importance, the following summary of the method of calculation may not be superfluous. The complete equation in F' or HF_2' obtained from the classical assumptions is of the cubic order, and apart from the labour of making the numerous solutions required, it is at present uncertain how rigidly

the classical laws may apply to the case. In order to keep in closer touch with experimental values, the concentrations of hydrogen ion were first obtained from the appropriate calibration curve (*e.g.*, Table I) by effecting an approximate calculation of the molecular conductivity of the anionic species, and deducting this from the total observed molecular conductivity. Owing to the high mobility of the hydrogen ion, this procedure gives a fairly exact estimate of C_{H^+} , although the amounts of the other ions are only approximately known. The values of C_{H^+} were then used to obtain by calculation more exact values of C_{F^-} and $C_{HF_2^-}$. A second approximation on the same lines produced no material change in the first values. It is, of course, assumed throughout that the presence of the ammonium sulphate does not influence the ionic concentrations due to the hydrofluoric acid, a view that may require modification in the future.

TABLE VI.

SiO ₂ , mg., in 50 g. acid.	C_{H^+} .	C_{HF} .	C_{HF_2} .	$C_{H^+} \times C_{HF_2}$ $\times 10^5$.	Rate (with electro- lyte).	Rate/ C_{HF_2} .
N-Hydrofluoric acid.						
0	0.0584	0.870	0.0431	250	65	1510
20	0.0642	0.783	0.0382	245	56	1480
40	0.0720	0.747	0.0341	245	48	1420
60	0.0800	0.711	0.0304	244	42	1400
80	0.0870	0.675	0.0272	238	40	1470
100	0.0980	0.639	0.0251	245	34	1360
120	0.104	0.603	0.0228	240	32	1400
140	0.114	0.567	0.0207	238	30	1450
160	0.124	0.531	0.0193	235	28	1450
180	0.132	0.495	0.0176	230	27	(1540)
200	0.141	0.459	0.0159	225	26	(1640)
$\frac{1}{2}$ N-Hydrofluoric acid.						
0	0.0315	0.45	0.0218	67	30	1400
20	0.0350	0.41	0.0174	61	22	1290
40	0.0415	0.38	0.0132	55	19	1440
60	0.0460	0.34	0.0099	46	14	1410
80	0.0514	0.31	0.0075	39.5		

We may conclude from the constancy of the quotient in Col. 7 that the reaction is, as was earlier predicted, almost wholly conditioned by the reaction SiF_4 (adsorbed) + HF_2' (adsorbed) = $HSiF_6'$.

On reference to Table V, it is evident that the stimulus provided by excess electrolyte is proportional to the ionic concentration, when this is not too high. In the absence of added salt, the ionic concentration must be given by C_{H^+} . Col. 5 of Table VI shows that for N-acid the product $C_{H^+} \times C_{HF_2}$ happens to be constant up to a concentration of about 150 mg. of silica per 50 g. of acid, and then slowly decreases. The rate of reaction should therefore, as is

actually the case (see Fig. 2), be constant up to this limit and then decrease. Moreover, the above product is no longer a constant in the case of $\frac{1}{2}N$ -acid, nor is the observed rate, but reference to Col. 5 of Table VI and Col. 3 of Table II shows that the relation, rate = $k(C_H \times C_{HF_2'})$, still holds good.

The curves for $2N$ - and $\frac{1}{3}N$ -acids have not been examined in detail, but their relation in form to the other curves has shown that the same rules apply in these cases.

Though the above discussion probably presents the general features of the reaction mechanism correctly, it is not complete in detail. Thus, we cannot assume the relation, rate = $kC_{HF_2'}$ (electrolyte present), to hold quite generally. Referring to Table IV, we see that the difference in the rates of reaction is not so wide as would be expected in view of the very different proportions of HF_2' ion. Here it appears to be significant that the rate is too high with a large excess of hydrogen ion, and too low when this ion is markedly deficient. Again, in the reaction with N -acid the rate begins to show an abnormal increase when C_H has attained considerable values (values in parentheses in Col. 7 of Table VI). These discrepancies seem to point to a specific catalytic activity of the hydrogen ion. It is hoped that further examination may clear up these points, and that the use of a more extended range of neutral salts will elucidate the very marked effect of electrolytes on the main reaction process. As far as the writer can discover, this work provides the first example of this "neutral salt effect" in a heterogeneous action.

Summary.

1. The rate of reaction of dilute hydrofluoric acid on fused silica has been determined, and shown to be unrestricted by any diffusion process at the surface of the solid.

2. It is not primarily dependent on the concentration of the free hydrofluoric acid, but is proportional to that of the HF_2' ion when the reaction occurs in the presence of a large ionic concentration. When the latter is low the rate is given by the expression

$$\text{rate} = k (\text{total ionic concentration} \times C_{HF_2'}).$$

3. Some of the data obtained suggest a specific catalysis by the hydrogen ion, but this possibility has not been closely examined.

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[Received, May 16th, 1930.]