L.—*Equilibria of Hydrofluosilicic Acid.*

By LAWSON JOHN HUDLESTON and HENRY BASSETT.

PART I.

IN some recent work involving the use of hydrofluoric acid we found that, on titration, an appreciable time was required to obtain the true end-point. Thus, when phenolphthalein was used as

indicator, an apparently considerable excess of alkali could be run in and yet the colour would fade again after a few seconds. The acid had been supplied by a thoroughly trustworthy firm as of "A. R." standard, and it left no residue on evaporation, so that its purity was not at first doubted. However, some of the work described below was carried out with it and proved that the effect observed was due to a large proportion of hydrofluosilicic acid.

We repeated the "A. R." test ourselves. This consists (List of Reagents for Analytical Purposes with Notes indicating the Standards of Purity regarded as necessary for Analytical Work) in adding an excess of a solution of potassium chloride to the solution to be tested, when a turbidity, due to potassium silicofluoride, should be observed. However, no such turbidity appeared, doubtless owing to the formation of a colloidal solution, all the less easily detected by the eye, as vessels only of wax or platinum were admissible.

Katz (*Chem. Zeit.*, 1904, **28**, 356, 387) developed a quantitative method of determining the proportions in which these two acids might occur together in mixtures. He added potassium chloride, as in the "A. R." test, but he also added alcohol to decrease the solubility of potassium silicofluoride and then titrated the solution. The hydrofluosilicic acid was removed according to the equation $\text{H}_2\text{SiF}_6 + 2\text{KCl} = \text{K}_2\text{SiF}_6 + 2\text{HCl}$, thus liberating an equivalent quantity of hydrochloric acid. He then titrated an equal volume of the solution directly, and in this case, with phenolphthalein as indicator, the reaction took a different course, represented by the equation $\text{H}_2\text{SiF}_6 + 6\text{NaOH} = 6\text{NaF} + \text{H}_2\text{SiO}_3 + 3\text{H}_2\text{O}$. Hence, if the first titration required a c.c. of alkali and the second b c.c.,

then $\frac{3}{2}(b - a)$ was the proportion of alkali neutralised (in the

second case) by the hydrofluosilicic acid. Katz himself stated that the results were not accurate owing to the absorption of hydrofluoric acid by the colloidal precipitate, and he introduced corrective factors, which Dinwiddie (*Amer. J. Sci.*, 1916, **42**, 421) further modified. The method developed in this paper is free from these defects, though rather more lengthy. Before describing this, however, it should be mentioned that a portion of our acid was diluted until about 0.75*N* and titrated by Katz's method. The first titration required 12.90 c.c. and the second 19.00 c.c. Thus the proportion of hydrofluosilicic acid (by equivalents) was 48 per cent., or the solution contained 52 mols. of hydrogen fluoride to 8 mols. of hydrofluosilicic acid (uncorrected).

For the complete neutralisation of hydrofluosilicic acid according

to the equation $\text{H}_2\text{SiF}_6 + 6\text{NaOH} = 6\text{NaF} + \text{H}_2\text{SiO}_3 + 3\text{H}_2\text{O}$ an appreciable time is required, as mentioned by Wagner and Ross (*J. Ind. Eng. Chem.*, 1917, **9**, 1116), but, so far as we have been able to discover, no quantitative study of it has been previously made. Yet it offers another method of studying the composition of mixtures of the two acids, as indicated below. Vessels of waxed glass, or sometimes of pure wax, were used throughout the experiments. Small test-tubes containing weighed quantities of the mixed acids were placed upright in conical flasks containing measured quantities of sodium hydroxide solution coloured with a few drops of phenolphthalein. The flasks were then closed with rubber stoppers and the liquids mixed by inverting the vessel and shaking vigorously, the time from this moment until the colour (clearly visible through the wax) faded being measured by a stop-watch. The flasks were then opened and further alkali run in until the solution was permanently neutralised. It was obvious that a portion of the hydrion that the solution could ultimately furnish was produced but slowly, probably because it was "bound" in a complex. Further, if n c.c. of alkali were originally present in the flask and N c.c. were required for total, permanent neutralisation, $\frac{N-n}{N} \times 100$ was the percentage of

the total hydrion in the "bound" condition at the moment when the colour faded. This term we have denoted by C in the tables that follow. Moreover, during the period timed, the solution was alkaline, so the method allows of the study of the kinetics of the reaction: "bound" hydrion $\rightarrow$ "available" hydrion, undisturbed by any opposing reactions.

The first experiment was carried out in this way at 19.2° with the mixed acid described above, after dilution to $1.8N$, the alkali being $0.184N$. The time of fading, t , was measured in seconds.

TABLE I.

1.8N-Acid ; 0.184N-Sodium Hydroxide ; Temperature 19.2° .

$C.$ $t.$		$C.$ $t.$		$C.$ $t.$		$C.$ $t.$	
32.80	2.2	16.45	19.0	7.95	39.8	5.64	44.8
31.75	2.6	16.60	19.2	8.20	39.0	3.70	59.0
31.65	3.0	16.70	19.4	7.46	38.0	4.28	54.1
Mean	32.07 2.6	16.58	19.2	7.87	38.6	4.54	52.6

The logarithms of these values of C plotted against the times give a straight line, which is the familiar curve of a unimolecular reaction. From the four mean results six values of the velocity

constant can be calculated, and, by the help of the mean obtained, four values for the initial value of C (denoted by C_0) may then be calculated. C_0 is thus a measure of the original concentration of the "complex" present in the unneutralised acid. The values for the velocity constant (calculated for ordinary logarithms) are: 0.01694; 0.01698; 0.01668; 0.01684; 0.01707; 0.01725; mean 0.01696. Converted for natural logarithms, this becomes 0.0390. The agreement is very satisfactory. For the values of C_0 we have: 35.49; 35.10; 35.55; 35.43, the best value probably being 35.50.

In Experiment 2 these determinations were repeated with solutions brought previously to 25.0° in a thermostat. The results are given in table II, where the velocity constant and C_0 have been calculated and the deviations from the theoretical curve are shown. In the early part of the curve small errors in t cause large errors in C , whilst in the later part the reverse is the case. Hence both must be shown, and the second column gives the values of t calculated from the observed values of C , whilst the eighth column gives the values of C calculated from the observed times.

TABLE II.

1.8N-Acid; 0.184N-Sodium Hydroxide; Temperature 25.0°.
 $C_0 = 39.0$; $k = 0.0748$ (for natural logs).

Time of fading in seconds.			C.c. of alkali added.		C .		
Obs.	Calc.	Diff.	Initial.	Total.	Found.	Calc.	Diff.
5.2	4.3	+ 0.9	14.70	20.50	28.3	26.5	+ 1.8
3.8	4.3	- 0.5	15.30	21.30	28.2	29.4	- 1.2
13.2	13.2	nil	17.75	20.75	14.5	14.5	nil
13.8	13.8	nil	17.65	20.50	13.9	13.9	nil
21.0	22.2	- 1.2	18.80	20.30	7.4	8.1	- 0.7
29.0	28.6	+ 0.4	18.55	19.45	4.6	4.5	+ 0.1
33.0	33.8	- 0.8	20.15	20.80	3.1	3.2	- 0.1
33.0	32.2	+ 0.8	19.40	20.10	3.5	3.3	+ 0.2

It is unfortunate that this acid was not again checked at the lower temperature, for, in the light of subsequent work, it appears almost certain that it had become contaminated with silica. As will be seen later, it is almost certain that with a mixture of this kind C_0 is independent of the temperature (see p. 415).

A third experiment was then made with the acid diluted nearly forty times. No high degree of precision was aimed at here, and only a few determinations were made, as we wanted to determine merely whether C_0 varied greatly with dilution or not. The results are collected in table III.

TABLE III.

0.05*N*-Acid; 0.184*N*-Sodium Hydroxide; Temperature 25.0°.
 $C_0 = 35.0$; $k = 0.0640$ (for natural logs.).

Time of fading in seconds.			C.c. of alkali added.		<i>C</i> .		
Obs.	Calc.	Diff.	Initial.	Total.	Found.	Calc.	Diff.
6.4	6.5	- 0.1	4.00	5.20	23.1	23.2	- 0.1
9.2	9.5	- 0.3	4.25	5.25	19.0	10.4	- 0.4
14.0	14.0	nil	4.50	5.25	14.3	14.3	nil
19.8	20.4	- 0.6	4.75	5.25	9.5	9.8	- 0.3
31.5	30.9	+ 0.5	5.00	5.25	4.8	4.7	+ 0.1

The lower value of k obtained is satisfactorily accounted for by the smaller effect of the heat of reaction of this dilute solution, as will be shown later (see below). The theory developed in Part III of this paper, formulated many months after the measurements were made, requires that the value of C_0 should be slightly less for a very dilute solution of the mixed acid, but it is not possible to say whether this result confirms the value obtained in experiment II or not.

Further experiments were attempted at 0°, but the cooling was unsatisfactory and the results are not worth recording. They offered further evidence, however, that the value of C_0 in experiment II was too high, that is, the particular solution used had been contaminated.

The errors involved in these experiments vary very much from case to case. For instance, control experiments showed that the bulk of the liquids was mixed by this method in a fraction of a second, but the time required for the last trace of the contents of the test-tube to be completely washed out might be two seconds. Hence time readings of this order were untrustworthy; the larger values, however, were not seriously affected. Again, the end-point was not very sharp, especially for the dilute solution. For the concentrated solutions, C should be accurate to 0.25 per cent., but for the dilute solution, where a total of only 5.25 c.c. of sodium hydroxide solution was used, C could not be determined with a greater accuracy than 1 per cent. Again, the precise instant when the colour faded was difficult to determine for low values of C , because in these cases it faded so gradually, and it was difficult to see a very faint colour through the wax.

There is also the question of the rise of temperature due to the heat of the reaction. The production of 1 gram-equiv. of sodium fluoride from hydrofluoric acid and sodium hydroxide is accompanied by the production of about 16,000 cals. Thus, neglecting the

heat changes associated with the production of hydrogen fluoride from hydrofluosilicic acid, and the fact that the solution was never completely neutralised by the alkali with which it was mixed in the first instance, and also disregarding the heat absorbed by the containing vessel or lost by radiation, the maximum possible rise of temperature would be $16/V$, where V is the volume in litres containing 1 equiv. of the sodium fluoride formed. The value of this is 2.6° for the solutions in experiments 1 and 2, and 0.8° for the solution in experiment 3.

PART II.

The Product of the Action of Silicon Tetrafluoride on Water.

What was expected to be pure hydrofluosilicic acid was prepared by passing silicon tetrafluoride into water contained in vessels of either wax or silica (it was feared that glass might give rise to the production of sodium fluoride) and filtering the product from the precipitated silica through a wax funnel into a wax vessel. The silicon tetrafluoride was prepared (1) by the action of concentrated sulphuric acid on a mixture of sand and calcium fluoride, (2) by the action of concentrated sulphuric acid on potassium silicofluoride, and (3) by heating barium silicofluoride, but there was no apparent difference in the product. In all cases the solution was left in contact with the precipitated silica for at least twenty-four hours before filtering, to ensure that the concentration of any hydrofluoric acid formed should fall to its equilibrium value.

The apparatus used for the fading experiments was slightly modified. Wax cylinders were made, having for half their length a vertical wax partition, which divided the lower portion into two water-tight cells in which the acid and the alkali could be separately placed. The cylinders were closed with rubber stoppers, and, as before, mixing was secured by inverting and shaking the vessel, but the form of the apparatus allowed much more rapid washing out of both compartments. It also permitted the use of solutions of approximately equal strength, since each cell held 20 c.c., a volume that can be measured with reasonable accuracy. For the acid, pipettes of the so-called "automatic" type were made of pure wax. These are capable of considerable accuracy; for instance, in the calibration of one, three successive deliveries weighed 9.977, 10.003, and 9.898 grams respectively. The sodium hydroxide was made by placing freshly cut sodium in a platinum dish over water in a closed vessel which was then evacuated. The violence of the reaction between the water-vapour and the sodium could be easily controlled by regulating the pressure. The solution thus obtained

was diluted with freshly boiled water and stored in an iron vessel, from which it was siphoned off through a copper tube. It appeared to be completely free from silica and carbonate.

Experiment 4 was carried out in this apparatus with a solution of hydrofluosilicic acid prepared as described and filtered from the precipitated silicic acid, in order to trace the rate of decay of C throughout the length of the curve. The results were considerably less regular than those obtained previously, as the thermostat was acting irregularly. Nevertheless, as table IV shows, it is clear that the curve is logarithmic. The total alkali used in this case was only 7.8 c.c., so that C should be correct to 1 per cent.

TABLE IV.

10 c.c. of 0.3*N*-Hydrofluosilicic Acid and 0.38*N*-Sodium Hydroxide.
Temperature 15.3° (? 16.4°); $C_0 = 55.5$; $k = 0.0270$.

Time of fading.			C.c. of alkali added.		C .		
Found.	Calc.	Diff.	Initial.	Total.	Found.	Calc.	Diff.
19.4	19.8	- 0.4	5.20	7.70	32.5	32.9	- 0.4
18.6	20.4	- 1.8	5.30	7.80	32.0	33.6	- 1.6
20.0	22.9	- 2.9	5.40	7.70	29.9	32.4	- 2.5
22.0	22.4	- 0.4	5.40	7.75	30.3	30.6	- 0.3
24.0	24.0	nil	5.50	7.75	29.0	29.0	nil
4.4	3.1	+ 1.3	3.80	7.75	51.0	49.3	+ 1.7
2.8	0.9	+ 1.9	3.60	7.85	54.2	51.5	+ 2.7
3.2	1.8	+ 1.4	3.70	7.85	52.9	50.9	+ 2.0
3.0	2.7	+ 0.3	3.80	7.85	51.6	51.3	+ 0.3
5.0	3.1	+ 1.9	3.85	7.85	51.0	48.5	+ 2.5
7.0	6.6	+ 0.4	4.20	7.85	46.5	45.9	+ 0.6
4.2	4.1	+ 0.1	3.90	7.75	49.7	49.6	+ 0.1
6.4	7.9	- 1.5	4.30	7.80	44.9	46.6	- 1.7
11.0	11.8	- 0.8	4.60	7.70	40.3	41.2	- 0.9
17.0	18.0	- 1.0	5.10	7.75	34.2	35.0	- 0.8
30.0	31.2	- 1.2	5.90	7.75	23.9	24.7	- 0.8
33.4	39.7	- 6.3	6.20	7.65	19.0	22.5	- 3.5
55.4	55.5	- 0.1	6.70	7.65	12.4	12.4	nil
38.4	36.9	+ 1.5	6.20	7.80	20.5	19.7	+ 0.8
51.6	50.8	+ 0.8	6.70	7.80	14.1	13.8	+ 0.3
62.2	60.0	+ 2.2	6.85	7.70	11.0	10.4	+ 0.6
73.0	66.6	+ 6.4	6.95	7.65	9.2	7.7	+ 1.5
95.4	99.3	- 3.9	7.50	7.80	3.8	4.2	- 0.4
97.2	92.2	+ 5.0	7.30	7.65	4.6	4.0	+ 0.6
59.0	60.6	- 1.6	7.00	7.85	10.8	11.3	- 0.5
60.0	58.7	+ 1.3	7.00	7.90	11.4	11.0	+ 0.4

In experiment 5 the effect of dilution was studied with a similar preparation. Naturally the dilution was effected after filtration in each case, and, as will be seen from table V, no difference could be observed in the value of C_0 . However, as will be explained later, the concentration at which the solution was filtered from the silica did make a difference in the equilibrium values, and the value of

C_0 , therefore, was not the same as that in the previous experiment. Unfortunately, this was not realised at the time, and no record was kept of the temperatures and concentration at which the various preparations were filtered.

TABLE V.

The Effect of Dilution on the Initial Concentration of the Complex.
Temp. 15.2° ; $C_0 = 54.7$; $k = 0.025$ (for natural logs.).

18.85 c.c. of 0.32 N-Hydrofluosilicic acid and 0.323N-Sodium Hydroxide.

Time of fading.			C.c. of alkali added.		C.		
Found.	Calc.	Diff.	Initial.	Total.	Found.	Calc.	Diff.
6.8	6.3	+ 0.5	10.00	18.75	46.7	46.2	+ 0.5
10.0	12.1	- 2.1	11.00	18.50	40.5	42.6	- 2.1
16.6	17.3	- 0.7	12.00	18.60	35.5	36.1	- 0.6
20.4	23.4	- 3.0	13.00	18.70	30.5	32.9	- 2.4
30.4	31.2	- 0.8	14.00	18.70	25.1	25.6	- 0.5
40.2	40.2	nil	15.00	18.75	20.0	20.0	nil
50.6	53.1	- 2.5	16.00	18.70	14.5	15.4	- 0.9
80.0	73.1	+ 6.9	17.00	18.65	8.8	7.4	+ 1.4

18.85 c.c. of 0.15N-Hydrofluosilicic acid and 0.16N-Sodium hydroxide.

0.2	9.9	+ 0.3	10.00	17.45	42.7	42.4	+ 0.3
16.0	15.8	+ 0.2	11.00	17.45	36.9	36.7	+ 0.2
28.4	29.3	- 0.9	13.00	17.65	26.3	26.9	- 0.6
38.4	39.9	- 1.5	14.00	17.55	20.2	21.0	- 0.8
53.8	52.3	+ 1.5	15.00	17.60	14.8	14.3	+ 0.5
67.0	69.6	- 2.6	16.00	17.70	9.6	10.2	- 0.6
58.0	53.1	+ 4.9	15.00	17.55	14.5	12.8	+ 1.7

18.85 c.c. of 0.078N-Hydrofluosilicic acid and 0.087N-Sodium hydroxide.

4.8	3.4	+ 1.4	8.50	17.05	50.2	48.5	+ 1.7
9.0	8.6	+ 0.4	9.50	17.00	44.1	43.7	+ 0.4
12.4	15.3	- 2.9	10.50	16.75	37.3	40.1	- 2.8
22.0	21.3	+ 0.7	11.50	16.95	32.1	31.6	+ 0.5
26.4	28.7	- 2.3	12.50	17.95	26.7	28.3	- 1.6
45.0	41.9	+ 3.1	13.50	16.70	19.2	17.8	+ 1.4
56.6	57.8	- 1.2	14.50	16.65	12.9	13.3	- 0.4
77.4	76.9	+ 0.5	15.55	16.90	8.0	7.9	+ 0.1

In experiment 6 the effect of temperature on both the velocity constant and the value of C_0 was studied. The solution was not affected by keeping or by contamination, because some of the readings at 15° were made at the beginning of the whole experiment and the remainder at the very end, yet they lay on the same curve. The results are collected in table VI.

The usual formula for the variation of a velocity constant with temperature is $\log k = -\frac{A}{T} + C$, where T is the absolute temperature and A and C are constants. Table VI records the values of k

TABLE VI.

The Effect of Temperature on the Initial Concentration of the Complex and on the Velocity Constant.

10.0 c.c. of 0.18*N*-Hydrofluosilicic Acid and 0.12*N*-Sodium Hydroxide.

Time of fading.			C.c. of alkali added.		<i>C</i> .		
Found.	Calc.	Diff.	Initial.	Total.	Found.	Calc.	Diff.
Temp. 15.0°. $C_0 = 53.0$.			$k = 0.024$ (for natural logs).				
19.0	18.9	+ 0.1	10.20	15.40	33.7	33.6	+ 0.1
14.0	13.7	+ 0.3	9.50	15.50	38.7	37.9	+ 0.8
9.4	8.9	+ 0.5	8.80	15.40	42.8	42.3	+ 0.5
3.0	3.1	- 0.1	8.00	15.75	49.2	49.3	- 0.1
3.6	3.8	- 0.2	8.00	15.50	48.4	48.6	- 0.2
4.4	1.6	+ 2.8	7.80	15.90	50.9	47.7	+ 3.2
2.6	1.1	+ 1.5	7.60	15.70	51.6	49.8	+ 1.6
2.0	4.0	- 2.0	8.20	15.80	48.1	50.5	- 2.4
2.8	5.2	- 2.2	8.40	15.80	46.8	49.6	- 2.8
6.4	6.4	nil	8.60	15.80	45.5	45.5	nil
6.0	7.5	- 1.5	8.80	15.80	44.3	45.9	- 1.6
2.0	1.4	+ 0.6	8.00	16.40	51.2	50.5	+ 0.7
6.8	6.4	+ 0.4	9.00	16.50	45.4	45.0	+ 0.4
12.4	12.6	- 0.2	10.00	16.45	39.2	39.4	- 0.2
19.0	19.9	- 0.9	11.00	16.40	32.9	33.6	- 0.7
27.6	28.4	- 0.8	12.00	16.40	26.8	27.3	- 0.5
Temp. 25.0°. $C_0 = 57.0$.			$k = 0.075$ (for natural logs).				
2.0	1.7	+ 0.3	8.00	16.00	50.0	49.1	+ 0.9
8.4	8.1	+ 0.3	11.00	16.00	31.2	30.3	+ 0.9
6.4	5.6	+ 0.8	10.00	16.00	37.5	35.2	+ 2.3
2.2	2.7	- 0.5	8.50	15.85	46.4	48.3	- 1.9
4.4	3.8	+ 0.4	9.00	15.75	42.8	41.0	+ 1.8
4.2	4.7	- 0.5	9.50	15.85	40.0	41.6	- 1.6
5.6	5.9	- 0.3	10.00	15.80	36.7	37.4	- 0.7
9.6	10.4	- 0.8	10.50	14.30	25.6	27.7	- 2.1
8.6	8.2	+ 0.4	11.00	15.90	30.8	29.9	+ 0.9
Temp. 0°. $C_0 = 38.6$.			$k = 0.00385$ (for natural logs).				
390	393	- 3	15.00	16.40	8.5	8.6	- 0.1
720	721	- 1	16.00	16.40	2.4	2.4	nil
300	303	- 3	14.00	15.90	12.0	12.2	- 0.2
168	168	nil	13.00	16.40	20.7	20.2	+ 0.5

determined at three temperatures, and hence, by taking the equations in pairs, three values of the constant C may be obtained, namely: 29.5, 29.8 and 30.2 (mean 29.83). Thence three values of A may be determined, which in this case are 9661, 9665, and 9661 (mean 9662).

Hence, for this reaction, $\log k = -\frac{9662}{T} + 29.83$. In table VII, T , calculated by inserting in this equation the velocity constants obtained, is compared with the values recorded in the previous experiments.

TABLE VII.

Experiment	k	T obs.	T calc.	Diff.
1	0.0390	292.2	292.2	nil
2	0.0748	298.0	298.1	- 0.1
3	0.0640	298.0	296.6	+ 1.4
4	0.0270	288.3 (?)	289.0	- 0.7
5	0.0250	288.2	288.4	- 0.2
6 (a)	0.0240	288.0	288.0	nil
6 (b)	0.0750	298.0	298.1	- 0.1
6 (c)	0.00385	273.0	273.0	nil

This neglects the influence of the heat of reaction, which is a somewhat indefinite factor. Thus the maximum possible difference in temperature in experiments 2 and 3 from this cause is 1.8° (see p. 408), whilst in the above table it appears that the actual difference, as calculated from the velocity constants, in these two cases is 1.5° .

PART III.

Theoretical Discussion.

When silicon tetrafluoride is passed into water the reaction may be expressed by the equations:

The reactions must be reversible, since hydrofluosilicic acid is formed equally by the action of silicon tetrafluoride on water and of hydrofluoric acid on silica, and also hydrofluosilicic acid with sufficient alkali yields, ultimately, sodium fluoride and silicic acid. Therefore all four substances must be present in finite, even though possibly very small, concentration in these solutions. Further, these solutions, filtered from the precipitated silicic acid, on titration by Katz's method, react like pure hydrofluosilicic acid, so that the free hydrofluoric acid cannot be in excess of that required to combine with the free silicon tetrafluoride and silicic acid to form hydrofluosilicic acid. Katz's method, however, cannot detect free silicon tetrafluoride, since by the precipitation of potassium silicofluoride the equilibrium of equation (3) would be shifted completely to the right in any case.

Consider a volume, V , of a solution prepared by passing silicon tetrafluoride into water and filtering off the precipitated silicic acid. Let there be a mols. of hydrofluosilicic acid, b mols. of silicon tetrafluoride, x mols. of hydrogen fluoride, and y mols. of silicic acid present. Ultimately the solution will yield $6a + 4b + x$ eqivs. of hydron, but a fraction of this, $\frac{C_0}{100}$, will be in a form

from which it will be liberated only slowly, by a unimolecular reaction in alkaline solution. So far as the nature of this reaction is concerned, it might be the hydrolysis of silicon tetrafluoride [equation (1)], but the velocity with which this compound reacts with water in the preparation, and, still more, considerations of the equilibria involved, indicate that the slow reaction studied is not this, but the dissociation of sodium silicofluoride according to the equation $\text{Na}_2\text{SiF}_6 = 2\text{NaF} + \text{SiF}_4$, whilst the hydrolysis of silicon tetrafluoride, the neutralisation of hydrofluoric acid, and the neutralisation of hydrofluosilicic acid to produce sodium silicofluoride proceed with immeasurable rapidity. Hence, on mixing the solution with alkali,

hydrofluosilicic acid neutralises $2a$ eqivs. rapidly and a further $4a$ eqivs. slowly.

silicon tetrafluoride neutralises $4b$ eqivs. rapidly,

hydrofluoric acid neutralises x eqivs. rapidly,

and silicic acid is without action on the indicator.

The silicic acid might be present in colloidal solution, so we have no authority as yet to assume that its "active mass" is proportional to its concentration. We will therefore denote the "active mass" in this case by the formula in open brackets. The equilibrium relations corresponding with equations (1), (2), and (3) are then:

$$(1a) [\text{SiF}_4] = K_1 \times [\text{HF}]^4 \times (\text{H}_2\text{SiO}_3).$$

$$(2a) [\text{SiF}_4] \times [\text{HF}]^2 = K_2 \times [\text{H}_2\text{SiF}_6].$$

$$(3a) [\text{SiF}_4]^3 = K_3 \times [\text{H}_2\text{SiF}_6]^2 \times (\text{H}_2\text{SiO}_3).$$

Hence in the case taken we have:

$$(1b) \frac{b}{V} = K_1 \left[\frac{x}{V} \right]^4 (\text{H}_2\text{SiO}_3).$$

$$(2b) \frac{b}{a} = K_2 \left[\frac{V}{x} \right]^2$$

$$(3b) \frac{b^3}{a^2} = VK_3 (\text{H}_2\text{SiO}_3).$$

whilst

$$(4) \frac{4a}{6a + 4b + x} = \frac{C_0}{100}$$

and

$$(5) 6a + 4b + x = K_4.$$

Experiment 5 showed that V could vary fourfold without causing appreciable variation in C_0 . Hence, from equations (4) and (5), it is clear that a also is, to this extent, independent of dilution. Then, to satisfy equations (1) and (2) simultaneously, whilst at the same time having regard to the relation between the change of b and

that of x as determined by the chemical reaction, it is necessary that x should be so small that $\frac{x}{V}$ is kept constant, in spite of four-fold dilution, by the transformation of a negligible quantity of one of the other substances, so that a and b both remain sensibly constant. Then equation (3b) requires that (H_2SiO_3) shall be proportional to the concentration, that is, the "active mass" of the silicic acid can be represented in the usual way as $\frac{y}{V}$. We think it

probable that the silicic acid left after filtration is in true solution.

Hence, for solutions prepared by passing silicon tetrafluoride into water and filtering off the precipitated silicic acid, we are led to believe that, on dilution, the relative quantities of hydrofluosilicic acid, silicon tetrafluoride, and silicic acid remain sensibly unaltered, whilst the concentration of free hydrofluoric acid, which must be extremely small, is maintained constant by the hydrolysis of negligible quantities of the first two substances. This is in harmony with the fact that sodium silicofluoride is so slightly dissociated, in the sense of equations (1) and (2), that the concentration of hydrion to which it gives rise is not enough to affect methylo-range, and also with the fact that if solutions of the kind under discussion are neutralised with sufficient alkali to show the fading effect, whilst still being not completely neutralised, they show the effect again with a single drop of alkali, that is, they give rise to very little silicon tetrafluoride. It should be remembered in this connexion, however, that it is not necessary that the equilibrium constant of the sodium salt should be the same as that of the corresponding acid. While the solution is in contact with precipitated silicic acid, it must be supposed that the concentration of the latter in true solution is constant; hence equation (3b) will not, in this case, be independent of the concentration. This accounts for the different values of C_0 , obtained at the same temperature, in experiments 4, 5, and 6, which were made with different preparations filtered at different concentrations. At 15° the value of C_0 varied between 53 and 55.5. If $C_0 = 54.54$ (which is a convenient number for calculation), $a = 13.64$ (equation 4) and $b = 4.55$, since x is negligible and $6a + 4b + x = 100$ (C_0 being a percentage). Hence $\frac{b}{a} = \frac{1}{3}$. From equation (2b) $K_2 = \frac{b}{a} \left[\frac{x}{V} \right]^2$. The last term being the square of a small quantity is itself a very small quantity, so that $K_2 = \frac{1}{3}$ of a very small quantity and is itself very small. It is possible to form some estimate of its value from experiments 2 and 3. These experiments were made with the mixed acids

containing a considerable proportion of free hydrofluoric acid. Hence from equation (2b), since K_2 is small and x is here large, the concentration of silicon tetrafluoride must be very small, and great differences in its *ratio* can be brought about by transformations of negligible quantities of the other substances. Equation (2b) may be rewritten in the form $b = K_2 V^2 a / x^2$, from which it is clear that as a and x do not change appreciably, b is proportional to V^2 . If the volumes containing 100 equivs. are considered, in experiment 2, $C_0 = 39.0$ and in experiment 3, $C_0 = 35.0$. Therefore at most the silicon tetrafluoride has increased by 4 equivs. or 1 mol. for a forty-fold dilution. Hence $b + 1 = 1600 b$, or b is negligible. The dilute solution used in experiment 3 was $0.05N$, therefore the volume containing 100 equivs. was 2000 litres. Hence the composition of this solution is approximately :

$$\begin{array}{ll} \text{SiF}_4 & = 0.0005 \text{ mol. per litre.} \\ \text{H}_2\text{SiF}_6 & = 0.0045 \text{ mol. per litre.} \\ \text{HF} & = 0.021 \text{ mol. per litre.} \\ \text{therefore } K_2 & = \frac{0.0005 \times 0.0004}{0.0045} = 4 \times 10^{-5}. \end{array}$$

The data were not sufficiently accurate for this to be accepted as a final value, but it indicates the order.

It will be seen that for the stronger solutions the concentration of silicon tetrafluoride is very small, so that it should not be possible for C_0 , which is proportional to the concentration of hydrofluosilicic acid, to increase perceptibly on changing the temperature. This leads us to suppose that the solution used in experiment 2 had actually a greater silicon content than that used in experiment 1, and there is also practical reason to believe that contamination occurred.

Finally, some idea of the possible concentration of the silicic acid in solution can be obtained from a consideration of experiment 6. At 15° the value of C_0 was 53.0, hence the volume containing 100 equivs. had 13.25 mols. of hydrofluosilicic acid, whilst at 0° the value of C_0 had fallen to 38.6, so the same volume contained 9.65 mols. of hydrofluosilicic acid. Hence 3.6 mols. of the acid had been converted into silicon tetrafluoride, and therefore at the same time 7.2 mols. of hydrofluoric acid must have been produced. As K_2 is very small and there is a considerable proportion of silicon tetrafluoride, all this acid must have been converted into silicon tetrafluoride by the silicic acid present, that is, at least 1.8 mols. of silicic acid must have been present in this volume at 15° . The solution was $0.18N$, and therefore the volume containing 100 equivs. was 550 litres; hence the silicic acid must

have been present to an extent of at least 0.003 mol. per litre, apparently in true solution, since its "active mass" varied with dilution in the ordinary way.

Summary.

(1) The existing "A. R." method of testing for silica in hydrofluoric acid is shown to be inadequate.

(2) A method of measuring the proportion of hydrofluosilicic acid in mixtures of this with hydrofluoric acid is described.

(3) The rate of dissociation of sodium silicofluoride into silicon tetrafluoride and sodium fluoride has been determined, together with the formula for the variation of the velocity constant with temperature.

(4) It is shown that silicic acid can exist in solution, with an active mass proportional to its concentration, to the extent of at least 0.003 mol. per litre at 15°.

(5) The equilibria set up when silicon tetrafluoride is passed into water are discussed, and it is shown that the resulting solution contains a considerable proportion of unchanged silicon tetrafluoride.

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