# The Acidimetry of Hydrogen Fluoride.

By

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So far as we can find out, the acidimetry of hydrogen fluoride has not yet been particularly investigated. But it is well known that as an acid it stands apart from hydrogen chloride and other strong mineral acids. For while it even surpasses sulphuric acid in the intensity of its reaction with water and many organic substances, it yet shows such mild acidic characters, that its 'avidity' number places it in this relation among vegetable acids. Further, it not only decomposes the oxides of some metalloids, such as boron, silicon, phosphorus, and sulphur, forming fluorides possessing some degree of stability in presence of water, but also gives with potash, soda, and ammonia, salts which are alkaline to litmus.

To investigate the subject we have experimented with the following common indicators of neutralisation of acids by bases : litmus, lacmoid, methyl orange, phenacetolin, phenolphthaleïn, rosolic acid, cochineal, brazil wood, and turmeric paper. These indicators have been prepared and used in the usual way, for the most part as described in Sutton's *Volumetric Analysis*. In order to ascertain what personal difference there might be in the estimation of the particular shades of colour which indicated neutralisation we worked separately, and upon

materials all prepared by each for his own use. The first and last of the tables appended contain the results obtained by Haga, and the second those obtained by Ōsaka.

For titration in the experiments recorded in Table I and II, decinormal solutions, in the experiments given in Table III twice decinormal solutions of potassium and sodium hydroxides and of ammonia were taken. They were almost pure, containing only the merest traces of silica and alumina, but as these and also carbon dioxide when present in noticeable quantity affect the indications of some of the colour reagents, we were careful to determine for each indicator the exact titre of the alkali solution in terms of a decinormal sulphuric acid which had been standardised gravimetrically by barium chloride, thus rendering ourselves independent of the effects of any impurities present.

The hydrofluoric acid examined was purified in the following way:—Commercial "pure" hydrofluoric acid solution was distilled in a platinum retort after adding a few drops of a saturated solution of potassium permanganate and a little potassium hydroxide. The distillation went on at about 130°C. The product was found to be free from hydrochloric acid and other foreign matters. Silica was sought for by Jörgensen's chloropurpureocobaltic chloride test, and not found. Before purification the acid gave a small quantity of precipitate on standing with this reagent for three days, but the distilled acid gave none after standing for a week.

The purified acid was diluted and preserved for use in a gutta-percha bottle which had for years been holding the acid before its final purification. For each titration, a portion was weighed off in a platinum crucible with well-fitting lid, and was then washed into a large platinum dish in which the neutralisation was effected, except that in some cases the results recorded in Table I were obtained by

transferring the solution, when almost neutral, to a glass vessel, in order to observe the shade of colour more accurately.

The strength of the acid was determined gravimetrically by mixing in a platinum crucible a weighed quantity of the solution with excess of slaked lime made each time from a weighed quantity of precipitated calcium carbonate, letting the mixture stand for a night, drying, and then igniting till the weight became constant. The solution of the acid used for the trials recorded in Table I was also assayed by digesting it with precipitated and finely divided silica, and then igniting with a little sulphuric acid. The results of the two methods agreed well; they are given in the table. That used in trials recorded in Table III was assayed also by gravimetrically estimating the acid as calcium fluoride. The silica method gave in this case a low result and was rejected.

*Litmus as indicator.* Only historically and because of its universal employment for testing neutrality do we give consideration first to litmus used in titrating hydrogen fluoride. On the addition of potash or soda to dilute solution of hydrofluoric acid coloured by litmus, the red colour rapidly deepens to violet and by the time one molecule of alkali has been added the litmus has become an almost pure blue, that is, blue almost free from any violet tinge. In fact the effect upon litmus in the saturation of hydrogen fluoride with potassium hydroxide is much like that reversed of the saturation of potassium carbonate by sulphuric acid. However, by practice and by keeping before one a second vessel of water coloured by litmus of the right tint,—full blue, as it would be called—it is possible to titrate hydrofluoric acid by means of litmus. But its use is not recommended.

Blue litmus paper reddened with a solution of potassium fluoride containing a small quantity of hydrogen fluoride becomes blue again when left exposed to the air. If the paper be wetted soon after it has

become blue the red colour is generally restored. If, however, it is let dry thoroughly, subsequent moistening with water generally fails to bring back the red colour. The colouring matter seems to be modified by drying up with the fluoride. Dissolved litmus added to such a solution is also coloured red when much water is present, but becomes more and more blue on evaporating the solution, and when it has become sufficiently concentrated the greater part of the colouring matter separates out as a blue powder. This change to blue is not due to loss of hydrofluoric acid, for on addition of water the colouring matter dissolves again giving a red-coloured solution as before. A solution in which litmus paper was turned apparently permanently red and only on drying became neutral or very faintly alkaline, was in one trial found to correspond very nearly to $HK_3F_4$. Litmus paper is known to be reddened by monopotassium orthophosphate in solution and to become blue again when dried, from which it may be inferred that hydrogen fluoride, like hydrogen phosphate, is a polybasic acid, $H_2F_2$ or $H_3F_3$ or $H_4F_4$.

*Lacmoid* solution behaves essentially like litmus, the difference being that much less alkali is required to produce a bluish violet colour in a solution coloured by lacmoid than in one coloured by litmus. By titrating to a distinct blue, good results may be got with it, but it is not a desirable indicator. Lacmoid paper behaves also like litmus paper

*Phenacetolin* changes in colour somewhat gradually when near the neutrality point, but by titrating to pure purple or rose-violet free from any tinge of yellow it may be used successfully.

*Methyl orange* is quite useless for the ordinary titration of hydrogen fluoride, although it seems to find neutrality in $K_2HF_3$. The colour changes are very indefinite.

*Phenolphthaleïn* is most satisfactory as an indicator for hydrogen

fluoride, giving a very sharp colour change at the point of neutrality. It cannot of course be used with ammonia.

*Rosolic acid* is almost equal to phenolphthaleïn, but not quite so sharp in its indication. It can be used with ammonia as titrating agent, although ammonia is a little slower than the fixed alkalis in affecting this and other colours. In the case of this indicator and phenolphthaleïn the change of colour is well adapted for being observed in platinum vessels.

*Cochineal* and *brazil wood* behave alike. Either becomes violet gradually and indefinitely before the acid is neutralised, but finally it turns bluish violet. This change of colour is fairly sharp and is satisfactory for indicating neutrality. Brazil-wood paper becomes bluish violet before all the acid is neutralised and is therefore unsuitable for use.

*Turmeric* paper is satisfactory but not quite as sensitive as some of the other indicators and near the finishing point responds slowly.

It will be seen that, as in the case of the ordinary vegetable acids, the best indicator is phenolphthaleïn or, when ammonia is the titrating agent, rosolic acid.

We have yet to mention that all these indicators give satisfactory results only when the alkali solution is almost pure. The use of an impure alkali solution or of a solution which has been kept long enough in glass vessels to have taken up silica, carbonic acid, and other impurities in appreciable quantity is liable to give ill-defined and generally too-low results.

In conclusion, we have to return our thanks to Dr. Divers for his valuable suggestions in working out this paper.

## TABLE I.

Strength of the hydrofluoric acid *(a)* by lime method, 2·79%, *(b)* by silica method, 2·78%, mean 2·785%.

Of this solution from 1·2 to 2·9 grams were taken for each determination, requiring from 16 to 39 ccs. of decinormal alkali.

*Titration with Potassium hydroxide.*

| Indicator. | Colour when neutralised. | Ccs. $\frac{N}{10}$ alkali required by one gram of solution. | Mean. | Per cent. of acid found instead of 2·785. |
|---|---|---|---|---|
| **Rosolic acid.** | distinctly red. | 14·07<br>14·06 | 14·065 | 2·825 |
| **Phenolphthaleïn.** | distinctly pink. | 14·16<br>14·05 | 14·105 | 2·821 |
| **Litmus.** | pure litmus blue. | 14·11<br>13·80 | 13·955 | 2·791 |
| **Brazil wood.** | violet. | 14·11<br>14·03 | 14·07 | 2·814 |
| **Phenacetolin.** | purple. | 14·22<br>14·10 | 14·16 | 2·832 |
| **Lacmoid.** | pure lacmoid blue. | 13·99<br>14·10 | 14·045 | 2·809 |

*Titration with Sodium hydroxide.*

| Indicator. | Colour when neutralised. | Ccs. $\frac{N}{10}$ alkali required by one gram of solution. | Mean. | Per cent. of acid found instead of 2·785. |
|---|---|---|---|---|
| **Rosolic acid.** | distinctly red. | 13·90<br>13·86 | 13·88 | 2·776 |
| **Phenolphthaleïn.** | distinctly pink. | 14·00<br>13·90 | 13·95 | 2·790 |
| **Litmus.** | pure litmus blue. | 14·11<br>13·90 | 14·01 | 2·802 |
| **Brazil wood.** | violet. | 13·85<br>14·01 | 13·93 | 2·786 |
| **Phenacetolin.** | purple. | 14·04<br>13·92 | 13·98 | 2·796 |
| **Lacmoid.** | pure lacmoid blue. | 13·99<br>13·99 | 13·99 | 2·798 |

*Titration with Ammonia.*

| | | | | |
|---|---|---|---|---|
| **Rosolic acid.** | distinctly red. | 14·70<br>13·80<br>14·10 | 14·20 | 2·84 |
| **Litmus.** | pure litmus blue. | 13·62<br>13·68 | 13·66 | 2·732 |
| **Brazil wood.** | violet. | 13·85<br>14·20 | 14·025 | 2·805 |
| **Phenacetolin.** | purple. | 13·95<br>13·70 | 13·825 | 2·765 |
| **Lacmoid.** | pure lacmoid blue. | 13·60<br>13·50 | 13·55 | 2·710 |

## TABLE II.

Strength of the hydrofluoric acid by the lime method. (1) 6·29%, (2) 6·34%, (3) 6·30%, mean 6·32%. Of this solution from 0·7457 gram to 2·1622 grams were taken for each experiment, requiring from 23·3 to 68·7 ccs. of decinormal alkali.

*Titration with Potassium hydroxide.*

| Indicator. | Colour when neutralised. | Ccs. $\frac{N}{10}$ alkali required by one gram of solution. | Mean. | Per cent. of acid found instead of 6·32. |
|---|---|---|---|---|
| **Litmus.** | distinctly blue. | 32·28<br>32·42 | 32·35 | 6·47 |
| **Litmus.** | faintly blue. | 31·34<br>31·47 | 31·41 | 6·28 |
| **Rosolic acid.** | distinctly red. | 31·65<br>31·49 | 31·57 | 6·31 |
| **Phenacetolin.** | purple. | 32·31<br>31·73 | 32·02 | 6·40 |
| **Phenacetolin.** | faintly violet. | 31·94<br>30·98 | 31·46 | 6·29 |
| **Phenolphthaleïn.** | just pink. | 31·39<br>31·57 | 31·48 | 6·30 |
| **Cochineal.** | violet. | 31·14<br>31·06 | 31·10 | 6·22 |
| **Cochineal.** | faintly violet. | 30·79<br>30·79 | 30·79 | 6·16 |
| **Lacmoid.** | distinctly blue. | 31·01<br>30·84 | 30·93 | 6·19 |

*Titration with Sodium hydroxide.*

| Indicator. | Colour when neutralised. | Ccs. $\frac{N}{10}$ alkali required by one gram of solution. | Mean. | Per cent. of acid found instead of 6·32. |
|---|---|---|---|---|
| **Litmus.** | distinctly blue. | 31·93<br>32·24 | 32·09 | 6·42 |
| **Rosolic acid.** | distinctly red. | 31·87<br>31.93 | 31·90 | 6·38 |
| **Phenolphthaleïn.** | just pink | 31·92<br>31·86 | 31·89 | 6·37 |
| **Cochineal.** | violet. | 30·07<br>29·95 | 30·01 | 6·00 |
| **Phenacetolin.** | purple. | 30·52<br>30·66 | 30·59 | 6·11 |
| **Phenacetolin.** | faintly violet. | 29·71<br>29·64 | 29·68 | 5·94 |
| **Lacmoid.** | distinctly blue. | 30·07<br>29·88 | 29·98 | 6·00 |

*Titration with Ammonia.*

| Indicator. | Colour when neutralised. | Ccs. $\frac{N}{10}$ alkali required by one gram of solution. | Mean. | Per cent. of acid found instead of 6·32. |
|---|---|---|---|---|
| **Litmus.** | distinctly blue. | 32·37<br>32·86 | 32.62 | 6·52 |
| **Litmus.** | violet slightly blue. | 31·16<br>31·71 | 31·44 | 6·29 |
| **Rosolic acid.** | distinctly red. | 32·00<br>32·05 | 32·03 | 6·41 |
| **Rosolic acid.** | faintly red. | 31·74<br>31·82 | 31·78 | 6·35 |
| **Phenacetolin.** | purple. | 31·54<br>31·73 | 31·63 | 6·33 |
| **Phenacetolin.** | faintly violet. | 31·17<br>31·01 | 31·09 | 6·22 |
| **Cochineal.** | violet. | 31·26<br>31·69 | 31.48 | 6·30 |
| **Cochineal.** | faintly violet. | 30·77<br>30·85 | 30·81 | 6·16 |
| **Lacmoid.** | distinctly blue. | 31·13<br>31·12 | 31·125 | 6·22 |

## Table III.

Strength of hydrofluoric acid *(a)* by lime method, 24·93%, *(b)* by silica method, 23·98%, *(c)* by calcium fluoride method, 25·11%; mean of *(a)* and *(c)*, 25·02%.

Of this solution from 1·488 to ·7457 grams were taken for each determination, requiring from 93·23 to 45·76 ccs. of twice-decinormal alkali.

*Titration with Potassium hydroxide.*

| Indicator. | Colour when neutralised. | Ccs. $\frac{N}{5}$ alkali required by one gram of solution. | Mean. | Per cent. of acid found instead of 25·02. |
|---|---|---|---|---|
| **Rosolic acid.** | distinctly red. | 62·20<br>61·90 | 62·05 | 24·82 |
| **Phenolphthaleïn.** | distinctly pink. | 62·66<br>62·32 | 62·49 | 25·00 |
| **Litmus.** | pure litmus blue. | 61·23<br>61·54 | 61·385 | 24·55 |
| **Brazil wood.** | violet. | 61·80<br>61·76 | 61·78 | 24·71 |
| **Phenacetolin.** | purple. | 62·66<br>61·19 | 61·925 | 24·77 |
| **Cochineal.** | violet. | 62·80<br>61·49 | 62·145 | 24·86 |
| **Lacmoid.** | pure lacmoid blue. | 61·30<br>61·19 | 61·245 | 24·50 |
| **Turmeric paper.** | reddish brown. | 61·83<br>62·01 | 61·92 | 24·77 |

*Titration with Sodium hydroxide.*

| Indicator. | Colour when neutralised. | Ccs. $\frac{N}{5}$ alkali required by one gram of solution. | Mean. | Per cent. of acid found instead of 25·02. |
|---|---|---|---|---|
| **Rosolic acid.** | distinctly red. | 61·81<br>62·03 | 61·92 | 24·77 |
| **Phenolphthaleïn.** | distinctly pink. | 62·52<br>62·48 | 62·50 | 25·00 |
| **Litmus.** | pure litmus blue. | 61·36<br>61·64 | 61·50 | 24·60 |
| **Brazil wood.** | violet. | 62·73<br>62·23 | 62·48 | 24·99 |
| **Phenacetolin.** | purple. | 62·72<br>61·52 | 62·12 | 24·85 |
| **Cochineal.** | violet. | 61·63<br>61·58 | 61·605 | 24·64 |
| **Lacmoid.** | pure lacmoid blue. | 61·10<br>61·32 | 61·21 | 24·48 |
| **Turmeric paper.** | reddish brown. | 62·70<br>62·80 | 62·75 | 25·10 |

*Titration with Ammonia.*

| Indicator. | Colour when neutralised. | Ccs. $\frac{N}{5}$ alkali required by one gram of solution. | Mean. | Per cent. of acid found instead of 25·02. |
|---|---|---|---|---|
| **Rosolic Acid.** | distinctly red. | 62·10<br>62·70 | 62·40 | 24·96 |
| **Litmus.** | pure litmus blue. | 61·23<br>61·20 | 61·215 | 24·49 |
| **Brazil wood.** | violet. | 61·23<br>61·33 | 61·28 | 24·51 |
| **Phenacetolin.** | purple. | 62·66<br>61·19 | 61·925 | 24·77 |
| **Cochineal.** | violet. | 61·10<br>61·52 | 61·31 | 24·52 |
| **Lacmoid.** | pure lacmoid blue. | 61·03<br>60·99 | 61·01 | 24·40 |
| **Turmeric paper.** | reddish brown. | 62·89<br>62·34 | 61·615 | 25·05 |