[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE SOLUBILITY OF IODINE PENTOXIDE IN SULFURIC ACID

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Solutions of iodine pentoxide in concentrated, and particularly in fuming, sulfuric acid oxidize carbon monoxide rapidly at room temperatures and at the same time undergo a marked change in color, which affords a sensitive test for this substance.[1] Preliminary to a study of the reaction involved in this oxidation, we have determined the solubility of iodine pentoxide in sulfuric acid of various concentrations. In the course of these determinations certain unexpected phenomena were observed, and particularly on their account it has seemed desirable to present the following brief statement of our results and observations.

Method.—Mixtures of an excess of iodine pentoxide (5–8 g.) with 100–150 cc. of the various solutions of sulfuric acid, contained in 200cc. bottles having carefully ground stoppers and tightly fitting protective caps, were rotated end over end in a water thermostat, which maintained a temperature of 24.77 ± 0.005°. The rotation was just fast enough to allow complete draining of the dead space in the neck at each revolution.

Materials.—The iodine pentoxide was very pure, having been made by the chloric acid method.[2] It was taken from a large, carefully preserved sample several years old, whose water content had originally been 0.55%, corresponding to 10.7% conversion into iodic acid (HIO_3). Some additional moisture may have been taken up, but this small amount of water could have had no perceptible effect on the water content of the sulfuric acid used, and in any case redistribution of the water between the iodic anhydride and the sulfuric acid would be expected.

The solutions of sulfuric acid were made up by weight from a large stock sample of pure sulfuric acid, rigorously protected from all access of moisture, even during the withdrawal of acid. The concentration of this stock acid was ascertained by comparison of a diluted, weighed sample with a solution of *N* hydrochloric acid, whose concentration had been established by gravimetric analysis.

Sampling.—The samples for analysis were withdrawn by means of a special filter-pipet. The filter consisted of a plug of asbestos wool packed in a bulb 1 cm. in diameter on an extension tube, which was attached to the tip of the pipet by a ground-glass joint. In use, the pipet was operated by means of an efficient water pump; when it had been filled above the mark, the extension tube was removed, and the pipet used in the ordinary fashion.

Because of the considerable viscosity of the more concentrated solutions and the extreme fineness of the solid suspension after prolonged agitation, the filter plug had to be very carefully prepared. The asbestos was first finely shredded, thoroughly purified by boiling with a mixture of chromic and sulfuric acids and then with conc. hydrochloric acid, and finally was ignited to a red heat in air. It was packed in place, a little at a time, by gentle tamping with a bent glass rod. In use, the suction had to be applied gently to avoid excessive packing and a consequent impermeability of the filter.

Analysis.—The filtered 10-, or with the more dilute solutions, 20cc. samples were made up to 250 cc. or 500 cc., respectively. Aliquot portions were then treated with an

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[1] Lamb, Bray and Frazer, *J. Ind. Eng. Chem.*, **12**, 213 (1920). Hoover, *ibid.*, **13**, 770 (1921).

[2] Lamb, Bray and Geldard, THIS JOURNAL, **42**, 1636 (1920).

excess of potassium iodide, and titrated with an approximately 0.1 *N* solution of sodium thiosulfate.

Results.—With 50–78% solutions of sulfuric acid constant values of the solubilities were rapidly established, as indicated by Table I, where the number of grams of iodine pentoxide per liter, present in solutions of 50.0, 60.0, 75.0 and 78.0% sulfuric acid, are collected.

TABLE I

GRAMS OF IODINE PENTOXIDE PER LITER OF SULFURIC ACID OF VARIOUS CONCENTRATIONS

Temperature = 24.77°

Time Days	Conc. H_2SO_4	50.0%	60.0%	75.0%	78.0%
1		48.86	34.84	19.46	...
2		...	...	19.46	...
3		...	...	19.54	...
5		54.82	34.68	19.44	...
9		54.82	34.58	...	18.73
12		54.74	34.50	...	...
19		...	...	...	18.63
22		...	34.77	...	18.63
26		...	...	...	18.63
Av.		54.79	34.68	19.48	18.66

It can also be seen from this table that there is at first a rapid, and then a slow, *decrease* in concentration of the iodine pentoxide as the concentration of the sulfuric acid increases.

With acids of higher concentrations (82–96%) definite initial values of the solubilities are also rapidly established, as shown by the results collected in Table II.

TABLE II

GRAMS OF IODINE PENTOXIDE PER LITER OF SULFURIC ACID OF VARIOUS CONCENTRATIONS

Temperature = 24.77°

Time Hours	Conc. H_2SO_4	82.0%	86.0%	90.30%	95.96%	95.96%
1		19.51[a]	20.98[a]	22.63[a]	...	...
2		19.60	21.03	22.80	22.94	23.15
4		19.78	21.08	22.66	23.22	23.56
6		19.87	21.07	22.62	23.07	23.40
24		19.70	21.07	22.60	...	...
Av.		19.74	21.04	22.67	23.08	23.37

[a] These determinations were made independently of the others on fresh samples of sulfuric acid.

Here, there is evidently a slight *increase* in the solubility of the iodine pentoxide with increasing concentration of the sulfuric acid.

However, with these more concentrated acids an unexpected and interesting phenomenon appears. A slow decrease from the definite initial solubilities takes place, extending over many days. Thus, with 82%

acid after intervals of 1, 2, 3, 5, and 7 days, concentrations of 18.91, 18.76, 18.66, 18.57 and 18.57 g., respectively, of iodine pentoxide per liter were found. With the higher concentrations of sulfuric acid these changes become much more pronounced. They can be appreciated best by reference to Fig. 1, where the curves represent the change in the concentration of the iodine pentoxide with time for various concentrations of sulfuric acid.

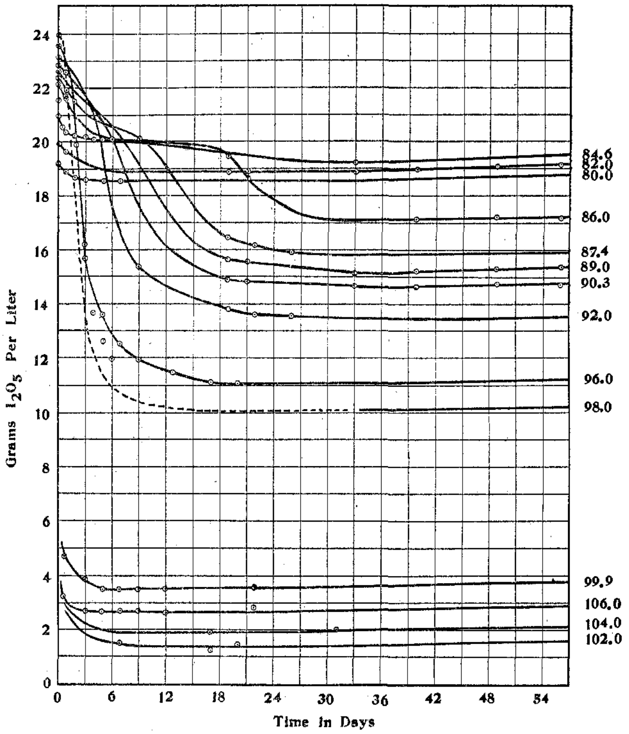

Fig. 1.

It can be seen that with 80, 82 and 84.6% acids a slight decrease from the initial solubilities occurs, apparently complete in 10–20 days. With 86 and 87.4% acids the decrease becomes considerable, while with 96 and 98% acids the concentrations drop rapidly to less than $^1/_2$ their initial values. With still higher concentrations the decrease is so rapid and so great that no initial values were obtained.

It should be pointed out that in all cases substantial constancy is attained within 40 days, but that a slight increase thereafter is invariably evident whenever the measurements have covered a longer interval.[3]

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[3] This effect was particularly evident in two runs with 82.0 and 89.0% acids lasting 81 days. The former gave 19.63, the latter 15.53 g. of iodine pentoxide per liter; the former 0.50, the latter 0.14 g. greater than the value at 56 days.

These values after 40 days we have considered "final," and have collected them in Table III, along with the "initial" values obtained from Fig. 1. Both sets of data have been plotted in Fig. 2.

TABLE III

INITIAL AND FINAL SOLUBILITIES OF IODINE PENTOXIDE IN SULFURIC ACID OF VARIOUS CONCENTRATIONS

Temperature = 24.77°

Conc. H_2SO_4 %	Solubility I_2O_5. G. per liter		Conc. H_2SO_4 %	Solubility I_2O_5. G. per liter	
	Initial	Final		Initial	Final
50.0	54.79	54.79	89.0	22.1	15.1
60.0	34.68	34.68	90.3	22.7	14.5
75.0	19.48	19.48	92.0	23.4	13.5
78.0	18.66	18.66	96.0	(23.2)	11.0
79.6	19.0	18.5	98.0	(22.0)	9.5
82.0	19.9	18.8	99.9		3.48
84.6	20.5	19.3	102.0[a]	..	1.28
86.0	21.0	17.1	104.0	..	1.90
87.4	21.5	15.8	106.0	..	2.67

[a] This percentage represents weights of 100% H_2SO_4 equivalent to 100 g. of the acid in question. The 106.5% of acid, therefore, contained 29.0% of free SO_3.

Fig. 2 is particularly instructive. It shows that the solubility curve of iodine pentoxide falls rapidly with increasing concentration of sulfuric acid until about 77% acid is reached. From this point the "initial" solubility curve rises, at first slowly and then rapidly, and is evidently a continuation of the falling curve just mentioned. Presumably then, the same solid phase is present along both branches, and is characterized by a minimum solubility at 77%. At this point, however, another curve makes its appearance, namely, the one representing the "final" solubilities. The distance between these two curves and the rapidity of change to the "final" curve increase as the concentration of the acid increases. Beyond 98% this change becomes so rapid that no initial observations were made. Indeed, the points at 96 and 98% acid, responsible for the downward bend of the "initial" curve beyond 94%, are doubtless vitiated by this same effect, and should presumably be considerable higher, as indicated by the dotted continuation of the "initial" curve.

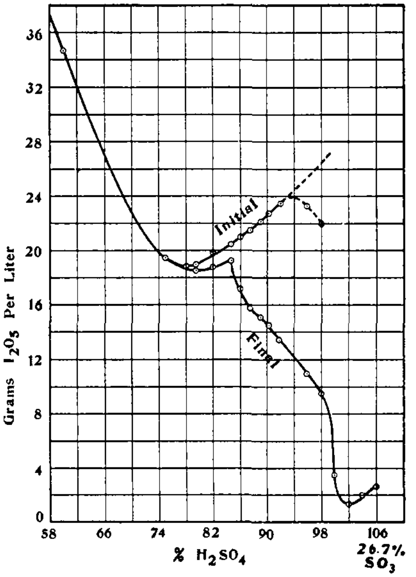

Fig. 2.

The "final" curve also exhibits a minimum solubility; in this case at about 103% acid.

The peculiar hump in the "final" solubility curve may be interpreted in two ways. The simpler and perhaps more plausible interpretation would be that the portion of the "final" curve between 77 and 85% acid, just before the sudden downward break, represents the solubility of one substance, while the remainder of the "final" curve represents the solubility of a third substance. The alternative explanation would be that there is no sharp break at 85%, and that this elevated portion of the "final" curve is fictitious because of the slow transformation in these more dilute acids of the solid substance responsible for the "initial" curve, into that responsible for the "final" curve. In other words, this portion of the curve does not represent the true equilibrium, which would presumably be a smooth continuation of the lower portion of the curve. The fact that this transformation did not go to completion, for instance, in the experiments with 82% acid lasting 81 days, but instead a slight *increase* in solubility took place from 30 days on, does not exclude this explanation, for a similar increase in the solubility over long periods was observed in *all* the concentrated acids.

The nature of the various solid phases can only be guessed at, but it appears reasonable to suppose that they may differ only in water content. That phase responsible for the "initial" curve might well be iodic acid HIO_3; that for the hump anhydro iodic acid,[4] HI_3O_8, and that for the remainder of the "final" curve iodine pentoxide. On this basis, the increasingly rapid dehydration of the iodic acid (HIO_3) in the more concentrated solutions of sulfuric acid could readily be understood.

Summary

The solubility of iodine pentoxide has been determined in various solutions of sulfuric acid of 50–106% concentration at 24.77°, and has been found to decrease up to 77% sulfuric acid; from there on, the initial solubility rises. However, a slow transformation of the solid phase begins at this point, with the formation of a less soluble solid substance. This substance, too, exhibits a minimum solubility at about 104% acid. There is also evidence of still a third solid substance in equilibrium with acids of intermediate concentrations. A plausible explanation is that the main solubility curve (the initial curve) represents the solubility of iodic acid (HIO_3), while the second and probably third curves represent solubilities of iodine pentoxide and of anhydro iodic acid (HI_3O_8).

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[4] Groschuff, *Z. anorg. Chem.*, **47**, 331 (1905).