

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ATOMIC WEIGHT OF IODINE. THE ANALYSIS OF IODINE PENTOXIDE

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Introduction and Summary

In an earlier investigation by Baxter and Tilley¹ the ratio of silver to iodine pentoxide was found to be 0.646225, whereas on the basis of the more probable values of the atomic weights of silver and iodine,² 107.880 and 126.932, the ratio should be 0.646251. This puzzling discrepancy is in small part explained by the recent discovery in this Laboratory by Mr. A. C. Titus³ that the very porous iodine pentoxide, made by a process of double efflorescence from iodic acid, possesses the property of adsorbing air to the extent of 0.001%. The experimental ratio of silver to iodine pentoxide is thus raised to 0.646231, leaving a discrepancy between this value and that to be expected of 0.003%.

In the hope of discovering the cause of the discrepancy, and at the same time of obtaining a direct determination of the ratio of the atomic weights of iodine and oxygen, we have completed a series of analyses of iodine pentoxide by simple decomposition and weighing the iodine. This has already been done by Guichard,⁴ but the results of his experiments were less concordant than could be desired and were subject to an uncertain correction for moisture retained by the iodine pentoxide.⁵ The outcome of our work was unexpected, for we have found the ratio of iodine to iodine pentoxide to be almost 0.005% smaller than that corresponding to the modern value for the atomic weight of iodine, 126.932. Thus both this investigation and that on the ratio of silver to iodine pentoxide indicate that iodine pentoxide produced by dehydration of iodic acid contains less iodine (and more oxygen) than corresponds to the theoretical formula; for aside from the fact that the modern value for the atomic weight of iodine rests on several well-established ratios to silver and the other halogens, in order to reconcile the experimental values of the ratios of silver and iodine to iodine pentoxide with the theoretical values would necessitate an *increase* in the atomic weight of iodine of 0.005 unit in the former case and a *decrease* of 0.03 unit in the latter.

The Preparation of Iodine Pentoxide.—No pains were spared in the

¹ Baxter and Tilley, *THIS JOURNAL*, 31, 201 (1909).

² Baxter, *ibid.*, 32, 1591 (1910).

³ This investigation will soon be published.

⁴ Guichard, *Compt. rend.*, 159, 185 (1914).

⁵ Baxter, *THIS JOURNAL*, 37, 411 (1915).

purification of this substance, and advantage was taken of much experience in this Laboratory in the purification of iodine and iodic acid.

Three kilograms of commercial iodine were distilled in portions from solution in concentrated aqueous potassium iodide. In this way the greater portion of chlorine and bromine were removed. A portion of the product was converted to potassium iodate by boiling with alkaline permanganate, and the iodate was converted to iodide at an elevated temperature. The remainder of the iodine was again distilled in portions from a concentrated solution of this potassium iodide. Thus the purification effected in the first distillation was made more nearly complete since the iodide was purer. Centrifugal rinsing of the product with pure water removed the greater part of any potassium iodide solution which might have accompanied the iodine vapor as spray.

Since iodine which has been purified merely by distillation from aqueous solution leaves a residue of organic matter when sublimed, this impurity was next removed by combustion in oxygen. The iodine was placed in a 20-mm. quartz tube connected at one end with a supply of carefully purified oxygen. Beyond the iodine the quartz tube was constricted to half diameter at two points, in such a way as to provide two compartments several centimeters long. The constrictions were filled with coils of platinum wire. The iodine was then sublimed in a current of oxygen into the first compartment through the first constriction which was heated to redness. A second sublimation followed, from the first to the second compartment, while the second constriction was heated. The twice sublimed material was then melted in the second compartment and poured into a vessel of pure water. The first distillation yielded a small amount of brownish residue, but the second yielded none. The presumption seems justified that organic impurities, even cyanogen, were removed in this treatment.

The iodine was next converted into potassium iodate by oxidation with potassium permanganate which had been twice recrystallized. Since this oxidation proceeds through the iodide, a small amount of potassium hydroxide was added to start the reaction. At first this latter was made by igniting a portion of the purified permanganate; later a portion of the alkaline solution resulting in the main reaction was used. Iodine and permanganate were mixed and boiled with an alkaline solution, sufficient iodine being used to complete the reaction with the permanganate. The solution of the iodate after standing was decanted from the precipitate of manganese dioxide, clarified by centrifugal settling and filtration through a sintered glass filter, and evaporated until saturated with potassium iodate. After the crystals had been removed, the mother liquor was further evaporated and a second crop obtained. All the potassium iodate was then once recrystallized.

The potassium iodate was converted into barium iodate by precipitation with barium hydroxide which had been twice recrystallized. Boiling hot normal solutions of both were used in the precipitation, the hydroxide being very slightly in excess. After standing for some time the precipitate was washed by decantation until the washings were nearly or quite free from alkali. In order to increase the efficiency of each washing the precipitates were centrifugally settled. The precipitate was then dried in platinum over an electric heater, and was found to weigh 2630 g. or about 45% of the theoretical yield from the original 3 kilograms of iodine.

The final step in the series was the conversion of the barium iodate into iodic acid by metathesis with distilled sulfuric acid. A hot concentrated solution of a slight excess of sulfuric acid was added to the barium iodate suspended in hot water and the mixture was digested for several days in Pyrex flasks. After the supernatant solutions had been decanted, they were evaporated in platinum dishes. The precipitates were washed by decantation and the washings after evaporation in pyrex flasks were added to the main solutions. Since a small amount of suspended barium sulfate still remained, the solu-

tions were filtered through a platinum sponge crucible into platinum dishes and after evaporation on electric heaters, were allowed to crystallize. The ordinary method of fractional crystallization was then followed as indicated in Fig. 1, where the crystal fractions are carried to the left, the mother liquors to the right. Because of the slowness with which equilibrium is established, each crystallization required several days. In the early steps of the process each fraction was divided into two or more portions for convenience and safety. Just before each final crystallization the solution was filtered through platinum sponge, although no insoluble matter could be detected. As soon as the crystallization process was commenced the material came into contact only with platinum.

In spite of these efforts the iodic acid at first possessed the peculiar odor which has been noted elsewhere.⁶ This gradually disappeared from the purer fractions and was almost if not quite absent from each final crystal fraction.

Since sulfuric acid was present in the original solution, it was important to determine how rapidly this was eliminated in the crystallization. The usual test for sulfate is not sensitive enough for the purpose on account of the large amount of iodic acid necessarily present. A better method was found by heating the iodic acid in a current of air at 200–250° and passing the air through pure water, which was then tested for sulfate in the usual manner. In this way it was found possible to detect with certainty 0.2 mg. of sulfuric acid in 5 g. of iodic acid. Using this method the

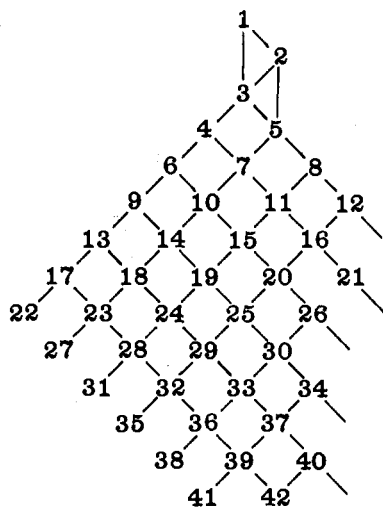


Fig. 1.

mother liquor 40 was found to contain 0.05–0.10 g. of sulfuric acid, while none could be detected in mother liquor 42.

Further tests for sulfate were combined with tests for non-volatile matter by decomposing 5-g. portions of the final crystal fractions in weighed platinum or quartz boats and determining the weights of the residues.

Fraction	Boat	Sulfate, mg.	Residue, mg.
41	Pt	0.03	-0.02
41	Pt	0	+ .07
31	Quartz	0	.00
22	Quartz	0	+ .03

Spectroscopic tests in a copper arc, using a Féry quartz spectrograph, failed to indicate the presence of barium except in the first mother liquor.

This evidence indicates that the purification by crystallization proceeded

⁶ Baxter and Tilley, *THIS JOURNAL*, 31, 203 (1909).

rapidly and that the final crystal fractions must have been very nearly if not quite pure.

In all the foregoing operations the usual precautions in precise work were taken. Water was doubly distilled, first from alkaline permanganate, then from a trace of sulfuric acid, with tin condensers. Especial care was taken to insure protection from dust and fumes. Crystals were centrifugally drained either in an all porcelain centrifuge or in platinum Gooch crucibles.⁷ Pyrex glass vessels were employed in the earlier operations, nothing but platinum during the crystallization of the iodic acid.

The Quantitative Decomposition of Iodine Pentoxide

The method of analysis consisted first in preparing iodine pentoxide for weighing by careful dehydration of iodic acid. The pentoxide was then decomposed by heating to about 400° in a weighed quartz reaction vessel which contained hot silver to prevent escape of iodine, and finally the weight of the iodine was determined. Water retained by the pentoxide was collected in a weighed absorbing tube and subtracted from the weight of the iodine pentoxide, as was also a correction of 0.001% for adsorbed air.

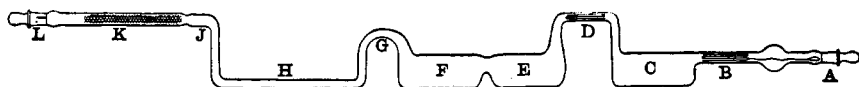


Fig. 2.

Since the possible accuracy of the process was limited by the weight of oxygen liberated, which constitutes less than one-quarter of the weight of the pentoxide, comparatively large quantities of pentoxide were used in each experiment, usually over 40 g. Necessarily the reaction tube was of considerable size and weight. After various preliminary experiments with a reaction tube made of pyrex glass, the final tube of fused quartz was constructed as indicated in Fig. 2. The air current entered through the ground joint A which was provided with a carefully ground stopper. At B was placed a coil of platinum wire which could be heated to redness from the outside. The tube D connecting the decomposition chamber C, 30 × 75 mm., which served to contain the iodine pentoxide during the initial weighing, and the iodine condensation chambers E and F, contained a coil of platinum wire which was heated to redness during an experiment. Condensation of iodine was made as complete as possible in H and the small amount of uncondensed iodine was collected in K upon metallic silver heated to about 600° by means of a removable resistance coil. During an analysis E, F and H were immersed in an ice-bath. A weighed U-tube containing resublimed phosphorus pentoxide was attached by a ground joint at L, which also was provided with a carefully ground stopper. Be-

⁷ Baxter, *THIS JOURNAL*, 30, 286 (1908).

cause of limitation of space in the balance case the apparatus was bent back on itself at D, G and J, so that the inlet A and the outlet L were not far apart. The weight of the empty system was 143 g. In order to avoid any effect from changing atmospheric conditions between the initial and final weighings, a counterpoise was provided of very nearly the same construction. The weight and volume of the counterpoise were made very nearly the same as those of the tube by adjusting with pieces of platinum and silver wire, and of quartz, the weight of the counterpoise being slightly less than that of the tube. In the early experiments the counterpoise was of pyrex glass, but in the later ones a quartz counterpoise was used.

The method of weighing consisted in hanging the tube and counterpoise on opposite sides of a No. 9 Troemner balance of 500-g. capacity and sensitive to 0.02 mg. or less, and finding the difference in weight necessary to bring the system to the zero point of the empty balance taken directly afterward. The balance room was kept at constant temperature within two degrees so that variations of the ratio of the balance arms were avoided. The balance case was provided with two dishes containing a few milligrams of impure radium bromide to dispel electrostatic charges. During a portion of the time fused potassium hydroxide also was placed in the balance case, although no apparent benefit resulted from this.

In spite of these precautions many difficulties were experienced in weighing the tube, and more time was spent in overcoming these than in the actual analyses. Part of the difficulty undoubtedly resulted from surface effects on the quartz, for this material is notoriously troublesome in this respect. Uncertainty from this source eventually was eliminated by standardizing the preliminary treatment. That finally adopted consisted in wiping the surface with dilute hydrochloric acid, rinsing with water and wiping with a damp cloth just before placing on the balance. The counterpoise was wiped with a damp cloth at the same time. The weighing was carried out only after some hours, usually twelve to fourteen.

A far more troublesome irregularity was eventually traced to diffusion of water vapor from the outside into the tube, thus displacing the heavier air and causing a loss in weight. The amount of water vapor found in the tube, initially filled with dry air and allowed to stand, corresponded closely with the loss in weight of the tube which took place during this period when the difference in density of air and water vapor was taken into consideration. This loss in weight in one case amounted to 0.75 mg. in two days, even when the tube was closed except for narrow grooves in the stoppers necessary for equalization of pressure within and without. How much of this was due to simple diffusion and how much to small fluctuations in temperature is difficult to determine. The effect was considerably more noticeable in the late spring and summer months when most of

the experiments were carried out than in the early spring when the preliminary ones were performed.

The difficulty was largely overcome by providing the tube with a stopper grooved for only half its length. The groove could be connected with the outside at will by turning the stopper until the groove registered with a small opening in the socket. In this way the tube could be kept essentially sealed until shortly before the weighing, when connection with the outside could be established by turning the stopper.

Even with the new stopper moisture was found very slowly to enter the tube, to the extent of 0.20 mg. in twenty hours, on an average as determined in four concordant experiments. With uniform treatment the reaction tube whether empty or containing iodine pentoxide or iodine would always be affected to the same extent, so that the weight of oxygen would not be affected if it were not for the fact that this water was collected in the phosphorus pentoxide tube. It is obvious that the weight of water collected in each experiment must be corrected for the water diffusing into the reaction tube.

The moisture content of the iodine pentoxide was found by passing the oxygen which resulted from the decomposition through a counterpoised U-tube containing resublimed phosphorus pentoxide. Iodine pentoxide which has been formed by dehydration of iodic acid at the temperature used in our experiments has been found to contain from 0.0025 to 0.0062% of moisture according to the method of preparation and time of heating.⁶ In order to avoid the uncertainty involved in applying an average correction, the water was collected in each experiment. Since experience has shown the practical impossibility of securing absolute blanks in a water determination, the rate of gain of the phosphorus pentoxide tube was found in the air stream utilized in our experiments. The following table gives the results of these experiments.

Duration, hours	H ₂ O found, mg.	H ₂ O found per hour, mg.
3	0.09	0.03
3	.13	.04
2.75	.11	.04
2	.08	.04
1.5	.09	.06
	Average	.04

The air stream itself was cleansed and dried by passing through a train containing the following agents: hot copper oxide, aqueous silver nitrate, aqueous potassium hydroxide, fused potassium hydroxide, concentrated sulfuric acid, phosphorus pentoxide, sintered glass filter. The system was constructed wholly of glass with dry, ground-glass connections.

To prepare iodine pentoxide from iodic acid, crystals of the latter were powdered in an agate mortar, usually together with a small proportion of

the first phase formed in the dehydration, $\text{HIO}_3 \cdot \text{I}_2\text{O}_5$, since the water is then given off at a comparatively low temperature ($80\text{--}110^\circ$) by efflorescence without melting, and moisture retained by the final product somewhat reduced.⁸ The powder contained in platinum boats was placed in a quartz tube connected with the train for purifying and drying air and surrounded by an aluminum block furnace.⁹ The temperature of the furnace was first maintained at $100\text{--}110^\circ$ as long as water appeared to be given off and then was raised to $200\text{--}210^\circ$ to expel the remaining water of composition. Finally the material was heated to 240° , the highest temperature found by Baxter and Tilley to be safe, for about three hours. In many cases the product remained perfectly white, in others, especially if the temperature exceeded 240° or the period of heating was longer, a slight brownish tint appeared. Even when the iodic acid was free from odor, the iodine pentoxide made from it always possessed the peculiar odor which has been noted before.

In the meantime the quartz reaction tube had been prepared for weighing by passing a current of dry air through it and, after the treatment described on page 972 and standing for fourteen hours, was weighed. By means of a platinum thistle tube extending into the decomposition chamber C the iodine pentoxide was introduced without contaminating the inlet tube. The platinum coil B was then replaced. Dry air was then passed through the tube, while usually at the same time the chamber C was warmed to about 100° . If C was warmed the air entered at L so that iodine formed by incipient decomposition of the pentoxide could not come into contact with the silver. After cooling with the air current running, the tube was treated and weighed after fourteen hours as in the first weighing. After some time, about six hours, the quartz tube was rapidly attached both to the air line and to the phosphorus pentoxide tube, which also had been weighed. A second phosphorus pentoxide tube was used to protect the weighed tube from back diffusion of moisture. The chambers F and E were surrounded with ice and water and the tube K containing silver was surrounded by an electrically heated sleeve. The platinum coils B and D were heated to redness by Méker burners and the ground connections were cooled with wet cotton wicks. Then an air current was started and the chamber C was cautiously heated with a flame until decomposition of the iodine pentoxide proceeded slowly and uniformly. Usually about two hours were required for complete decomposition. Care was necessary to avoid rapid decomposition since the pentoxide itself was likely to be blown about if the reaction proceeded too rapidly. The hot platinum coils served the purpose of decomposing powdered material which might have been expelled from the decomposition chamber. Clog-

⁸ Baxter and Tilley, Ref. 6, p. 210.

⁹ Baxter and Coffin, *Proc. Am. Acad.*, **44**, 184 (1909).

ging of the system with condensed iodine was likely to occur and was remedied by judicious use of a flame.

When decomposition was complete the ice-water bath was transferred to the tube H and the iodine sublimed from E, where the greater part originally condensed, to F where it was eventually fused. Except for the silver the whole system was then allowed to come to room temperature. Next the phosphorus pentoxide tube was removed, the stopper inserted at L, and the silver in K allowed to cool while at the same time the dry air was maintained inside at atmospheric pressure so that no moist air was forced in during the cooling. Finally, after it had been disconnected and the stopper inserted at A, the system was prepared for weighing as usual and weighed fourteen hours later. The experiment was completed by the weighing of the phosphorus pentoxide tube.

Although a considerable quantity of silver iodide was formed on the inner end of the silver column, the outer end remained untarnished. Furthermore, tests for free iodine in the air which passed through the system during an analysis were negative. It therefore is unlikely that any iodine was lost in the air current.

After an experiment the decomposition tube was attached to the air train in the reverse fashion by the joint L and cleaned by subliming the iodine into a pyrex flask. A very slight residue was allowed to accumulate in C (see page 970).

Weights were calibrated by the Richards substitution method, just before and just after the analytical work was carried out. In only two cases was the correction of an individual weight found to vary by 0.02 mg. in this interval, although differences of 0.01 mg. were found in the case of more than half the weights. In computing vacuum corrections the following densities were assumed:

Air (0° and 760 mm.)	0.001293
Weights	8.3
I ₂ O ₅	4.799 ¹⁰
I ₂	4.94 ¹¹

Results

The following table presents the data for all analyses which were completed except one. Of these, three are subject to known errors, Nos. 1, 2 and 6. In one experiment, not included in the table, the procedure was so changed that it was impossible to determine the weight of the pentoxide or that of the water with certainty.

The weights of iodine pentoxide given in the third column have been corrected by subtracting 0.001% for adsorbed air. Since the iodine was chiefly in the form of a fused mass, with a relatively small proportion of

¹⁰ Baxter and Tilley, Ref. 6.

¹¹ "International Critical Tables," Vol. III, p. 21.

crystals of considerable size, the surface exposed was small and adsorption of air must have been at a minimum.

TABLE I
THE RATIO OF IODINE TO IODINE PENTOXIDE

Analy- sis	Crys- tal frac- tion	I ₂ O ₅ ^a in vacuum, g.	H ₂ O, ^b g.	H ₂ O, %	Corr. wt. of I ₂ O ₅			Ratio I ₂ :I ₂ O ₅	Ratio I ₂ :O ₅
					in vacuum, g.	I ₂ in vacuum, g.	O ₂ in vacuum, g.		
1	35	23.43598	0.00071	0.0030	23.43527	17.81810	5.61717	0.760311	3.17208
2	35	25.53039	.00215	.0084	25.52824	19.40949	6.11875	.760314	3.17213
3	35	42.46100	.00195	.0046	42.45905	32.28337	10.17568	.760341	3.17260
4	35	46.13494	.00186	.0040	46.13308	35.07899	11.05609	.760344	3.17264
5	22	46.22744	.00163	.0035	46.22581	35.14741	11.07840	.760342	3.17261
6	27	21.05743	.00181	.0086	21.05562	16.00913	5.04649	.760326	3.17233
7	27	22.07691	.00037	.0017	22.07654	16.78564	5.29090	.760338	3.17255
8	27	41.89153	.00179	.0043	41.88974	31.85032	10.03942	.760337	3.17253
9	41	42.71467	.00201	.0047	42.71266	32.47602	10.23664	.760337	3.17253
Average								.760332	3.17244
Average of Analyses 3, 4, 5, 7, 8, 9								.760340	3.17259
Extreme deviation of Analyses 3, 4, 5, 7, 8, 9								.000007	0.00011

^a Less a correction of 0.001% for adsorbed air.

^b Less a correction of 0.20 mg. for moisture diffused into the system before weighing and of 0.04 mg. per hour of duration of the experiment. See pages 968 and 973.

In Analysis 1 iodine vapor was lost from the tube owing to plugging with condensed iodine. In Analysis 2 a crack developed in the tube and in addition, owing to overheating, silver iodide sublimed from the silver section. In Analysis 6 a stopcock in the system was accidentally left open so that owing to insufficient pressure iodine was lost by back diffusion. In Analysis 7 the quantity of material was made about half the size of that usually employed in the hope that a constant error might be uncovered.

One other correction remains to be discussed. The air in the decomposition tube must have been nearly saturated with iodine vapor at the time of weighing and therefore the weight of the tube was less than it should be by the weight of air displaced by the iodine. Since the vapor pressure of iodine at 25° is 0.3 mm.¹² and the interior volume of the tube about 200 ml., the air displaced is 0.08 ml. under average conditions and the weight of iodine too small by 0.10 mg. The effect of applying this correction is to raise the observed ratios of iodine to oxygen and iodine pentoxide by 0.001 and 0.0003%, respectively, to 3.17262 and 0.760342.

The values for these ratios to be expected from the atomic weight of iodine now considered most probable, 126.932, are 3.17330 and 0.760381, differences of 0.021 and 0.005%. The difference between the observed values and those to be expected corresponds to a difference in the atomic weight of iodine of -0.027. In other words the atomic weight of iodine calculated from our experimental results is 126.905. It is difficult to believe that this value is correct. On the basis of the more probable value 126.932 the computed deficiency in iodine obtained experimentally amounts

¹² Baxter, Hickey and Holmes, THIS JOURNAL, 29, 127 (1907).

to 0.0015 g. with a 40-g. sample of iodine pentoxide. This deficiency is far greater than the apparent experimental error.

The atomic weight of iodine calculated from the corrected experimental ratio of silver to iodine pentoxide, 0.646231, found by Baxter and Tilley, is 126.937, on the basis of the atomic weight 107.880 for silver. The coincidence is striking that the discrepancy in the composition of iodine pentoxide, though a little more than half as large, is in the same direction as that indicated by our experiments.

By combining the experimental ratios of silver and iodine to iodine pentoxide the ratio of iodine to silver is found to be 1.176579 and the atomic weight of iodine 126.929 on the basis of $Ag = 107.880$. This value for iodine differs very little from that found by direct comparison with silver, 126.932.

The percentage of iodine in iodine pentoxide is apparently too small, the percentage of oxygen too large. If the extra oxygen is wholly or in part in the form of a higher oxide, the oxidizing power of the iodine pentoxide should be too large. In a subsequent paper will be described a comparison of arsenic trichloride with iodine pentoxide in which it appears that this is the case. If the apparent excess of oxygen indicated by our work, 0.005%, is wholly in the form of the heptoxide, the proportion of the latter would be ten times as large.

We cannot avoid the conclusion, therefore, that iodine pentoxide of normal composition is difficult if not impossible to prepare and that conclusions based upon its actual composition are not sufficiently reliable for work of high precision.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

SALT AND MEDIUM EFFECTS ON THE TEMPERATURE COEFFICIENT OF VELOCITY OF DECOMPOSITION OF DIACETONE ALCOHOL¹

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The hydroxide-ion catalysis of diacetone alcohol has recently been investigated by Åkerlöf,² who determined the influences of different hydroxides at various concentrations and both weak and strong hydroxides in salt solutions upon the reaction rate. Further, results were obtained by him which showed the effects on this reaction rate of addition of some alcohols and other organic solvents to the aqueous hydroxide solutions. Results contained in this investigation demonstrate the influences of the

¹ The present study constitutes a part of a thesis presented to the Graduate School of Yale University as partial fulfilment of the requirements of the degree of Doctor of Philosophy, 1930.

² Åkerlöf, *THIS JOURNAL*, **48**, 3046 (1926); **49**, 2955 (1927); **50**, 733 (1928).