ART. II.—*On the Rate of Solution of Silver in Chromic Acid*; by R. G. VAN NAME and D. U. HILL.

(Contributions from the Kent Chemical Laboratory of Yale Univ.—cexxvi.)

In a recent study of the rates of solution of metals in oxidizing solutions, the results of which have already been published in this Journal,¹ it was found that when two or more metals under like conditions dissolved at different rates, these rates could be brought into closer agreement by increasing the acidity. The only exception to this empirical rule was observed in the case of silver dissolving in a chromic acid solution containing sulphuric acid. When the sulphuric acid was 0.25 molar the ratio of the rate of solution of cadmium to that of silver was found to be 1.64, while in the presence of 5 molar sulphuric acid this ratio was 2.19, a larger difference in the stronger acid. A conspicuous feature of the experiments with silver in the 5 molar sulphuric acid was the fact that the initial velocity constant of the series was much higher than the succeeding ones, as seen in the following example:²

$$k = 1.53 \quad 1.26 \quad 1.20 \quad 1.18 \quad 1.21 \quad 1.23 \quad 1.25$$

This was not the case in the 0.25 molar acid, though the constants showed a slight tendency to decrease as the experiment progressed.

On account of these peculiarities the case seemed to merit a further investigation, which has now been carried out, with the results described below. For this work no changes were made in the apparatus, experimental conditions, or procedure described in the former article. All experiments were at 25°.

At the outset it seemed possible that the effects noted might be due in part to the formation of an interfering coating on the dissolving disk of metal, and as chlorine might act in this manner great care was taken to have the reagents used free from traces of chloride. Later, however, it was found that the addition of small amounts of hydrochloric acid (two or three drops) to the solution at the beginning of the experiment had no measurable effect upon the reaction velocity, since the silver ions

¹ Vol. xlii, 301, 1916.² Table X, Exp. 18.

entering the solution quickly precipitated all the chloride in the body of the liquid, and so rendered it innocuous. On the other hand a larger amount of chloride (1 cm³ of strong hydrochloric acid in 600 cm³ of solution) soon produced a coating of silver chloride on the disk, and the reaction velocity dropped to zero in a few minutes. Following are the velocity constants obtained in an experiment under these conditions, the duration of the reaction periods being ten minutes each, and the normal value of k about 1.95.

$$k = 1.08 \quad 0.09 \quad -0.04 \quad -0.02 \quad 0.12 \quad -0.02 \quad 0.02$$

Further evidence against the hypothesis that coatings on the disk were responsible for the irregularities noted in experiments under normal conditions, was obtained by removing the disk after each reaction period and immersing it for several minutes in strong ammonia before replacing it. This procedure was employed in a number of experiments, but produced no appreciable change in the velocity constants.

The possibility that the depression of the reaction velocity might be caused by the accumulation of silver salt in the solution was also investigated. Such an effect could not, of course, be due to a simple displacement of the equilibrium, as in the case of silver in ferric sulphate,³ because the reaction between chromic acid and metallic silver is not reversible, but might be produced in some other way. It was found, however, that no measurable change in the reaction velocity was produced by dissolving in the solution at the outset two grams of silver sulphate, an amount considerably larger than that produced during an average experiment. Three successive experiments which illustrate this point are recorded in Table I.

TABLE I.
Silver (Sample A) in Chromic Acid.

Sulphuric acid 5 molar.							
Exp. 1.	$k = 2.20$	2.11	1.88	1.83	2.08	1.92	1.95
Exp. 2.	$k = 2.27$	2.07	1.78	1.90	1.79	1.95	1.88
Exp. 3.	Two grams of Ag ₂ SO ₄ added at outset.						
	$k = 2.12$	1.88	1.90	2.02	1.93	1.97	1.99
							Av. 1.97

At an early stage of the work it became clear that the cause of the variations lay in the metal itself. Two

³ Loc. cit. p. 310.

samples of silver were used, designated below as Samples A and B, respectively, both obtained from the firm which had furnished the sample used in the former investigation. The rates of solution of these three specimens were all very different, Sample A giving an average velocity of about 1.95, and Sample B of 1.60, under conditions where 1.22 had been obtained in the former work. Moreover, the same sample gave different results according to the amount of metal which had been removed in the preliminary treatment with nitric acid, for the outer layer, owing probably to differences in physical structure produced by the greater stresses undergone in the process of rolling, generally showed a much higher rate of solution than the metal beneath. The following experiment illustrates the behavior of a silver disk which had had only a very light etching with nitric acid before the experiment. After the fourth reaction period (each of 10 minutes) this disk was removed and another disk substituted which had been cleaned as usual with boiling caustic soda, but had undergone no subsequent etching with acid.

Silver, Sample B. Sulphur acid 5 molar.

$k = 2.23 \quad 1.62 \quad 1.68 \quad 1.64; \text{ (new disk) } 2.24 \quad 2.02 \quad 1.87$

The high initial value of k , followed by a more or less rapid fall to a comparatively constant final rate, is characteristic. It was only this final rate which was in any way definite and reproducible, and even this often varied considerably for samples cut from different parts of the same sheet. The more serious initial irregularities could of course be avoided by strong preliminary treatment with nitric acid.

For these reasons, in attempting to compare rates of solution of silver in the 0.25 and 5 molar acid we have found it best to use the same disk first in one solution for three or four reaction periods and then in the other. The results of a series of experiments so conducted, in each of which the solution was changed either once or twice, are recorded in Table II.

According to these figures the reaction is about 2.9 times more rapid in the weak than in the strong acid, while the former investigation gave a value of about 3.5 for this ratio. The new result is undoubtedly more correct as the older one was obtained before the sources of

TABLE II.

Silver (Sample B) in Chromic Acid.

Reaction periods usually 10 minutes with 5 molar H_2SO_4 ,
and 7 minutes with 0.25 molar H_2SO_4 .

	H_2SO_4									Average
1	5.0 molar		1.72	1.74	1.57					1.68
	0.25 molar		4.92	4.71	4.71	4.59	4.81			4.75
2	5.0 molar		1.63	1.46	1.57					1.55
	0.25 molar		4.59	4.50	4.81	4.27	4.67	4.53	4.49	4.55
3	0.25 molar		5.03	5.22	4.91	5.07				5.06
	5.0 molar		1.69	1.51	1.47	1.69	1.44	1.52	1.50	1.55
4	5.0 molar		1.63	1.62	1.54	1.63	1.55			1.59
	0.25 molar		4.36	4.69	4.61	4.82	4.94	4.89	4.76	4.73
	5.0 molar		1.79	1.68	1.60	1.53				1.63
5	0.25 molar		4.74	4.75	4.67	4.78				4.74
	5.0 molar		1.63	1.65	1.44	1.65				1.59
	0.25 molar		4.50	4.20	4.38	4.57				4.41

error were fully understood. The mean value of the constant k is 4.70 for the weaker, and 1.60 for the stronger acid. Combination of these results with those formerly obtained for cadmium under like conditions, gives for the ratio $\text{Cd}:\text{Ag}$ the value 1.50 in the 0.25 molar acid, and 1.67 in the 5 molar acid. This still constitutes an exception to the empirical rule that the agreement should be closer in the stronger acid, but the exception is a much less conspicuous one than the former results indicated.

Considering these results from the standpoint of the diffusion theory the most interesting and important fact brought out is the proof of the existence in the case of silver of such large differences in the rate of solution depending upon the physical state of the metal. In the light of that theory we can distinguish, as shown in the former article, two classes of cases, those in which the reaction velocity is determined entirely by the rate of diffusion, and those in which the chemical stage of the reaction also exerts its influence upon the observed result. Differences in the physical state of the metal could affect the reaction velocity in the former case only in so far as they produced considerable variations in the roughness of the surface, for theory and experience alike go to show that slight variations would be without appreciable effect. Moreover, such changes would account, in general, only for an increasing reaction velocity, since it is only in the rarest cases that the surface of the metal would grow smoother as it dissolved, while the progres-

sive changes in the rate of solution of silver observed in the present work, have nearly always been in the opposite direction,—that of decreasing reaction velocity. They are therefore of a kind which would be expected to occur, if at all, only in the cases of the second class, that is, in those in which the rate of the chemical reaction proper has an influence upon the result. As was shown in our former article, it is to this class that the case of silver in chromic acid belongs.

The opposite proposition should also be true. Variations in the rate dependent upon the physical state of the metal and not caused by roughness or impurities should not occur in cases where the rate is governed solely by diffusion. On this point the evidence is rather limited. In our work on the rates of solution of metals we have usually confined our experiments with a given metal to specimens cut from one and the same sheet, so that the conditions were not very favorable for detecting variations of the kind in question, but so far as our experience goes, it confirms the truth of the above proposition. One case, however, which is clearly of the first class, has been much more fully investigated. This is the reaction between cadmium and dissolved iodine, which has been the subject of several papers from this laboratory.⁴ Although the cadmium used in these investigations was rolled out into sheets in small quantities at various times, and without any attempt at uniformity of treatment, no characteristic differences were observed in the rates of solution of the numerous different samples so prepared, nor between the behavior of the superficial and the interior layers of metal in a single specimen.

⁴ This Journal, 32, 207, 1911; 36, 543, 1913; 43, 449, 1917.