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THE OXIDATION POTENTIAL OF THE PENTAVALENT- TRIVALENT COLUMBIUM SYSTEM. II

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Introduction

During our study of the reduction of columbic acid at a mercury electrode¹ the behavior of the reduced columbium upon reoxidation to the pentavalent state indicated that the trivalent columbium might possess a rather high reducing potential. Consequently, inasmuch as the literature contained no potential measurements whatever upon the pentavalent-trivalent columbium system, it was deemed worth while to make a study of this phase of the chemistry of columbium.

Apparatus

On account of the oxidation of a reduced columbium solution by contact with the air, it was necessary to devise and construct an hermetically sealed apparatus in which measurements could be made and solutions could be introduced, withdrawn and transferred. In an apparatus described below, which provided an atmosphere of hydrogen, the measurements were made. Platinum electrodes were first tried but the results were so inconstant and non-reproducible that, as with Forbes and Bartlett² in their measurement of the stannic-stannous potential and Forbes and Richter³ in their determination of the chromic-chromous potential, they were abandoned and the mercury electrodes were employed instead. Forbes and Bartlett and Forbes and Richter concluded from their experimental work that with the mercury electrodes results were more quickly obtained, irregularities due to surface energy of the electrode were less pronounced and deviations due to traces of oxygen in the system were almost eliminated. Besides, mercury has, as an important and as an additional property in its favor, a free surface upon which hydrogen has a high overvoltage. Also it does not appreciably react with sulfuric acid of the concentrations used in these experiments when the solutions are at room temperature.

Mercury Electrode.—The mercury electrode employed in the measurement of oxidation potentials is shown in Fig. 1. It consists of a wide-mouthed bottle of 250cc. capacity, closed with a rubber stopper provided with seven holes through which, respectively, pass a glass tube with a

¹ Kiehl and Hart, *THIS JOURNAL*, **50**, 1608 (1928).

² Forbes and Bartlett, *ibid.*, **36**, 2030 (1914).

³ Forbes and Richter, *ibid.*, **39**, 1140 (1917).

sealed-in platinum wire to make contact with the mercury on the bottom of the cell, a glass tube to furnish a stream of hydrogen, two burets to introduce the reduced and unreduced solutions, respectively, a glass tube leading into a bottle to act as a water seal to release the excess of hydrogen, a glass tube for the withdrawal of an analytical sample, and finally a glass tube to act as a salt bridge connecting the solution to be measured with the saturated calomel cell.

The instruments, the arrangement and the method used to measure the electromotive force were described by Hansen and one of us.⁴

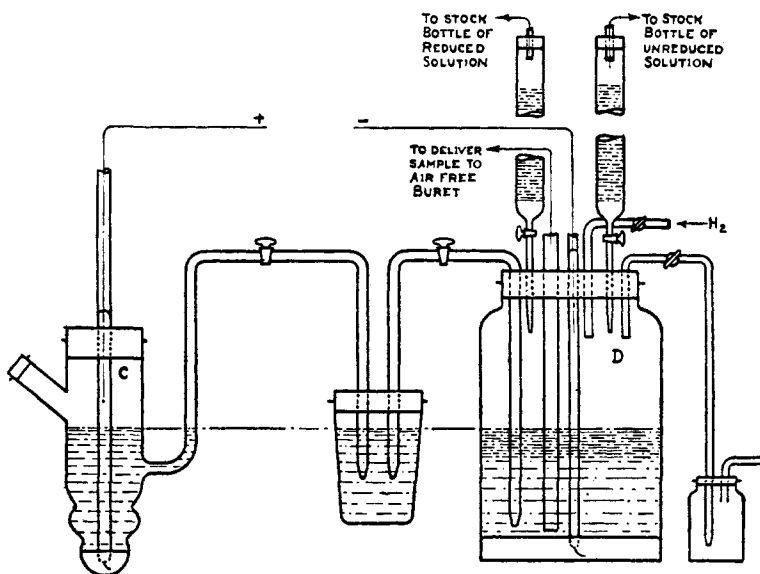


Fig. 1.

Experimental

Preparation of Solutions.—Solutions containing both pentavalent and trivalent columbium were prepared as follows. A solution of approximately 0.025 M Cb_2O_5 in the desired concentration of sulfuric acid was prepared and reduced completely to the trivalent state by the method previously described by us.¹ About one-half of this reduced solution was transferred to a stock bottle and reoxidized to the pentavalent state by passing purified air through it until the blue color disappeared. The excess oxygen was removed by a stream of hydrogen. This procedure insured the same sulfate concentration in the reduced as in the unreduced solution. This solution furnished the pentavalent columbium used below in the measurements.

Before the required amounts of the two solutions were introduced into bottle D, Fig. 1, the air was swept out by a stream of hydrogen. The whole system, including stock bottles, pipet for withdrawal of samples and titrating system used previously by us,¹ was connected hermetically and operated in an atmosphere of hydrogen. After the complete apparatus was ready, measured quantities of the solutions of trivalent

⁴ Kiehl and Hansen, *THIS JOURNAL*, **48**, 2802 (1926).

and pentavalent columbium sufficient to make a total of 100 cc. and to give the required reduction were introduced into bottle D of Fig. 1 through the burets connected to the stock bottles. In this manner the approximate amount of reduction was secured.

The bottle D was connected to the saturated calomel-saturated potassium chloride half-cell C by a glass-stoppered siphon tube leading through an intermediate solution of saturated potassium chloride at 25°. The value of this electrode at 25° according to Fales and Mudge⁵ is 0.5266 volt. The system was placed in a Freas electrically regulated thermostat at 25° and the electromotive force measurements were made by the null method with the standard apparatus previously mentioned. Wherever rubber connections were employed, they were covered with collodion.

After several hours, the potential assumed a value which remained constant within ± 0.0003 of a volt, provided no leakage of air occurred. This was considered to be the potential of the combination at equilibrium for this particular system. Furthermore, this value remained the same whether the solution was stirred or not, whereas violent fluctuations occurred if the solution was stirred before a constant value was obtained. For further assurance of the equilibrium potential a trace of mercuric chloride, a test generally used, was introduced into the system. The trivalent columbium reduced the mercuric mercury to the mercurous condition and free mercury, a reaction which lowered the potential considerably. The original potential before the introduction of the mercuric chloride was restored after it stood for a short time unless equilibrium was not reached.

After the equilibrium potential was recorded, 25 cc. of the equilibrium solution was delivered into a 250cc. Erlenmeyer flask previously swept by hydrogen and the amount of reduced columbium was determined by a standard potassium permanganate solution as heretofore.¹ The value thus obtained, in general, agreed closely with the amount of reduced solution originally added, so practically no oxidation had taken place during the transfer of solutions.

After each electromotive force measurement, the bottle D was thoroughly cleaned and dried. Fresh mercury prepared by the method of Hulett⁶ was then introduced to serve as the electrode for the next measurement.

Tables I, II and III contain the results obtained with 0.024 molar solutions of Cb_2O_5 in approximately three molar, six molar and ten molar sulfuric acid, respectively.

TABLE I

RESULTS OF EXPERIMENTS

Expt.	0.0240 M Cb_2O_5 . Temperature, 25°. 3.14 M sulfuric acid			Reduction, %	Obs. e.m.f., v. ^a	Normal ox. potential, E_0 , v. ^b	$^{\circ}K \times 10^{13}$	Time, hours
	-25 cc. of 0.02 M $KMnO_4$, cc.	Total Cb_2O_5 , g.	Reduced Cb_2O_5 , g.					
1	2.40 ^d	0.1595	0.0016	1.0	-0.3125	-0.3714	2.6	14
2	4.76 ^d	.1595	.0032	2.0	-.3225	-.3724	2.4	26
3	11.86 ^d	.1595	.0075	5.0	-.3348	-.3725	2.4	17
4	23.42 ^d	.1595	.0156	9.8	-.3443	-.3727	2.3	65
5	46.56 ^d	.1595	.0311	19.5	-.3551	-.3733	2.2	25
6	7.11	.1595	.0475	29.8	-.3618	-.3728	2.3	31
7	9.53	.1595	.0636	39.9	-.3681	-.3734	2.2	28
8	11.92	.1595	.0795	49.8	-.3735	-.3736	2.2	12
9	11.95	.1595	.0798	50.0	-.3730	-.3730	2.4	17

⁵ Fales and Mudge, *THIS JOURNAL*, **42**, 2434 (1920).

⁶ Hulett, *Z. physik. Chem.*, **33**, 611 (1900).

TABLE I (Concluded)

Expt.	—25 cc. of columbium solution—			Reduction, %	Obs. e.m.f., v. ^a	Normal ox. potential, E ₀ , v. ^b	^c K × 10 ¹³	Time, hours
	0.02 M KMnO ₄ , cc.	Total Cb ₂ O ₅ , g.	Reduced Cb ₂ O ₅ , g.					
10	14.30	.1595	.0954	59.8	— .3782	— .3731	2.3	41
11	16.65	.1595	.1111	69.7	— .3840	— .3733	2.2	16
12	19.06	.1595	.1271	79.7	— .3908	— .3732	2.2	18
13	21.46	.1595	.1431	89.8	— .4014	— .3735	2.2	12
14	21.92	.1595	.1462	91.7	— .4045	— .3737	2.1	13
15	22.64	.1595	.1510	94.7	— .4102	— .3732	2.2	21
16	23.41	.1595	.1561	97.9	— .4211	— .3721	2.3	37
						Mean	2.3	
Duplicate								
1	7.20	.1603	.0480	30	— .3622	— .3731	2.3	36
2	12.01	.1603	.0801	50	— .3732	— .3732	2.2	45
3	16.80	.1603	.1120	70	— .3845	— .3736	2.2	23
4	21.58	.1603	.1439	90	— .4012	— .3731	2.3	49
						Mean	2.2	

^a Against sat. calomel-sat. KCl cell as zero.^b Referred to the sat. calomel-sat. KCl electrode as zero.^c $K = [\text{Cb}^{+++}]_e / [\text{Cb}^{++++}]_e$.^d 0.002 M KMnO₄ was employed for these titrations.TABLE II
RESULTS OF EXPERIMENTS0.0241 M Cb₂O₅. Temperature, 25°. 5.91 M sulfuric acid

Expt.	—25 cc. of columbium solution—			Reduction, %	Obs. e.m.f., v. ^a	Normal ox. potential, E ₀ , v. ^b	^c K × 10 ¹⁴	Time, hours
	0.02 M KMnO ₄ , cc.	Total Cb ₂ O ₅ , g.	Reduced Cb ₂ O ₅ , g.					
1	11.84 ^d	0.1606	0.0079	4.9	— 0.3464	— 0.3844	9.3	18
2	24.52 ^d	.1606	.0164	10.0	— .3570	— .3850	8.9	15
3	47.68 ^d	.1606	.0318	19.8	— .3668	— .3847	9.1	12
4	7.20	.1606 _k	.0480	29.9	— .3742	— .3851	8.8	27
5	9.56	.1606	.0638	39.7	— .3795	— .3849	9.0	15
6	12.02	.1606	.0802	49.9	— .3848	— .3848	9.0	19
7	12.04	.1606	.0803	50.0	— .3850	— .3850	8.9	47
8	14.38	.1606	.0959	59.7	— .3902	— .3854	8.6	18
9	16.82	.1606	.1121	69.8	— .3969	— .3862	8.1	10
10	19.21	.1606	.1282	79.8	— .4029	— .3854	8.6	17
11	21.61	.1606	.1441	89.7	— .4111	— .3834	10.8	25
12	22.86	.1606	.1524	94.9	— .4227	— .3852	8.8	23
						Mean	8.9	
Duplicate								
1	47.72 ^d	.1606	.0318	20	— .3672	— .3850	8.9	31
2	12.04	.1606	.0803	50	— .3845	— .3845	9.3	52
3	16.87	.1606	.1125	70	— .3973	— .3864	8.0	28
4	22.89	.1606	.1527	90	— .4117	— .3836	9.9	17
						Mean	9.0	

^a Against sat. calomel-sat. KCl cell as zero.^b Referred to the sat. calomel-sat. KCl electrode as zero.^c $K = [\text{Cb}^{+++}]_e / [\text{Cb}^{++++}]_e$.^d 0.002 M KMnO₄ was employed in the titrations.

TABLE III
RESULTS OF EXPERIMENTS

0.0240 M Cb₂O₅. Temperature, 25°. 9.87 M sulfuric acid

Expt.	—25 cc. of columbium solution—			Reduction, %	Obs., e.m.f., v. ^a	Normal ox. potential, E ₀ , v. ^b	^c K × 10 ¹⁴	Time, hours
	0.02 M KMnO ₄ , cc.	Total Cb ₂ O ₅ , g.	Reduced Cb ₂ O ₅ , g.					
1	2.40 ^d	0.1602	0.0016	1.0	−0.3663	−0.4252	3.9	12
2	11.90 ^d	.1602	.0079	5.0	−.3878	−.4255	3.8	17
3	23.93 ^d	.1602	.0160	10.0	−.3975	−.4256	3.7	15
4	7.18	.1602	.0479	29.9	−.4155	−.4264	3.4	64
5	9.57	.1602	.0638	39.8	−.4208	−.4261	3.6	13
6	11.98	.1602	.0800	50.0	−.4265	−.4265	3.5	32
7	14.37	.1602	.0958	59.8	−.4314	−.4263	3.5	36
8	19.21	.1602	.1280	79.9	−.4444	−.4267	3.4	17
9	21.56	.1602	.1439	89.8	−.4545	−.4256	3.7	51
10	22.80	.1602	.1521	94.9	−.4645	−.4270	3.4	18
11	23.75	.1602	.1584	98.9	−.4834	−.4258	3.7	15
						Mean	3.6	
Duplicate								
1	7.22	.1602	.0481	30	−.4153	−.4262	3.6	29
2	11.99	.1602	.0800	50	−.4270	−.4270	3.4	33
3	19.26	.1602	.1285	80	−.4440	−.4262	3.6	17
4	21.62	.1602	.1442	90	−.4548	−.4267	3.4	20
						Mean	3.5	

^a Against sat. calomel-sat. KCl cell as zero.

^b Referred to sat. calomel-sat. KCl electrode as zero.

^c $K = [Cb^{+++}]_e/[Cb^{++++}]_e$.

^d 0.002 M KMnO₄ was employed in the titrations.

All concentrations have been expressed in terms of Cb₂O₅ from which the solutions were always prepared. The analytical results in the tables are expressed in grams of Cb₂O₅ in 25 cc. because the total columbium content in the solution was so determined gravimetrically.

TABLE IV
RESULTS OF EXPERIMENTS

0.013 M Cb₂O₅. Temperature, 25°. 3 M sulfuric acid

Expt.	—25 cc. of columbium solution—			Degree of reduction, %	Obs., e.m.f., v. ^a	Normal ox. potential, E ₀ , v. ^b	^c K × 10 ¹³	Time, hours
	0.02 M KMnO ₄ , cc.	Total Cb ₂ O ₅ , g.	Reduced Cb ₂ O ₅ , g.					
1	11.84 ^d	0.0794	0.0079	10.0	−0.3440	−0.3721	2.4	31
2	35.53 ^d	.0794	.0237	29.9	−.3620	−.3729	2.3	12
3	59.52 ^d	.0794	.0397	50.0	−.3725	−.3725	2.4	75
4	8.32	.0794	.0555	69.9	−.3839	−.3731	2.3	35
5	10.75	.0794	.0717	90.3	−.4012	−.3727	2.3	15
						Mean	2.3	

^a Against sat. calomel-sat. KCl cell as zero.

^b Referred to sat. calomel-sat. KCl electrode as zero.

^c $K = [Cb^{+++}]_e/[Cb^{++++}]_e$.

^d 0.002 M KMnO₄ was employed in these titrations.

The Effect of a Change of Total Columbium Content.—In Tables I, II and III the total columbium content was the same in each case. To determine what effect a change in the concentration would make, a solution of one-half the total concentration used above was prepared in a 3 *M* sulfuric acid solution. The results recorded in Table IV show that in solutions of such low concentrations of columbium in the presence of such high concentrations of sulfuric acid there is but little change in the normal oxidation potential.

Table V contains the data from which the curves in Fig. 2 were constructed. It contains the ratio of the concentrations, the logarithm of the ratio and the corresponding electromotive force measurement for the three different acid concentrations, respectively.

TABLE V
RATIOS AND LOGARITHMIC RELATIONS
0.0240 *M* Cb_2O_5

3.14 <i>M</i> H_2SO_4			5.91 <i>M</i> H_2SO_4			9.87 <i>M</i> H_2SO_4		
A	B	C	A	B	C	A	B	C
0.01	-2.00	-0.3125	0.05	-1.29	-0.3464	0.01	-2.00	-0.3663
.02	-1.69	-.3225	0.11	-0.95	-.3570	.05	-1.28	-.3878
.05	-1.28	-.3348	.25	-.61	-.3668	.11	-0.95	-.3975
.10	-0.96	-.3443	.43	-.37	-.3742	.43	-.37	-.4155
.24	-.62	-.3551	.66	-.18	-.3795	.66	-.18	-.4208
.42	-.37	-.3618	1.00	.00	-.3850	1.00	.00	-.4265
.66	-.18	-.3681	1.48	.17	-.3902	1.49	.17	-.4314
1.00	.00	-.3730	2.31	.36	-.3969	3.98	.60	-.4444
1.49	.17	-.3782	3.95	.60	-.4029	8.80	.94	-.4545
2.30	.36	-.3840	8.71	.94	-.4111	18.86	1.27	-.4645
3.93	.59	-.3908	18.61	1.27	-.4227	89.90	1.95	-.4834
8.81	.94	-.4014						
11.05	1.04	-.4045						
17.86	1.25	-.4102						
45.62	1.67	-.4211						

A = $[\text{Cb}^{+++}]/[\text{Cb}^{++++}]$. B = $\log [\text{Cb}^{+++}]/[\text{Cb}^{++++}]$. C = Obs. e.m.f., volts.

Discussion

In all the electrical potential measurements the probable error found experimentally was plus or minus one-half millivolt. The observed voltage represents the average of several readings taken after the system had reached equilibrium.

The potential was referred to a saturated calomel-saturated potassium chloride cell as zero to which it became progressively more negative as the acid concentration increased. With a large negative potential trivalent columbium may be classed, therefore, as a strong reducing agent within the range of our experiments.

By assuming that the degree of ionization and the activity were the same for both states of columbium, calculations of the normal oxidation

potential tabulated in Tables I, II, III and IV were made by use of the⁷ well-known equation

$$E = E_0 - \frac{RT}{nF} \times \ln \frac{C''}{C'}$$

developed from the Nernst formula. When the ratio of the concentrations was unity, the observed potential became the normal potential.

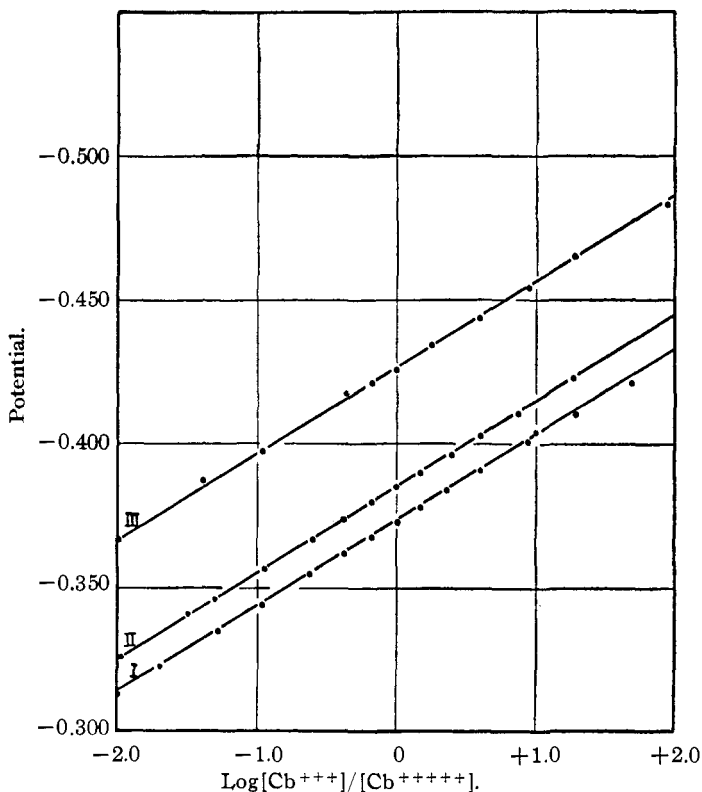


Fig. 2.—I, 0.024 M Cb_2O_5 in 3.14 M H_2SO_4 ; II, 0.024 M Cb_2O_5 in 5.91 M H_2SO_4 ; III, 0.024 M Cb_2O_5 in 9.87 M H_2SO_4 ; temperature, 25°.

By this value the valence of three for the reduced form determined by us¹ was confirmed. At 25° the final equation used for the calculations was

$$E = E_0 - 0.0295 \log \frac{[Cb^{+++}]}{[Cb^{+++++}]}$$

By use of the formula

$$\log K = \frac{E_0}{0.0295}$$

derived from the above relations, the average value of equilibrium con-

⁷ Peters, *Z. physik. Chem.*, **26**, 193 (1898).

starts for the system in three sulfuric acid concentrations, 3.14 *M*, 5.91 *M* and 9.87 *M* were found to be, respectively, 2.3×10^{-13} , 8.9×10^{-14} and 3.6×10^{-15} .

During the process of measurement, the potentials at extreme reduction were made and the extent of reduction determined by titration in the usual manner. In the 3.14 *M*, 5.91 *M* and 9.87 *M* sulfuric acid, respectively, the average corresponding potentials were -0.4580 , -0.4795 and -0.5090 , with the values of 99.87, 99.94 and 99.83% in order for the determined reduction.

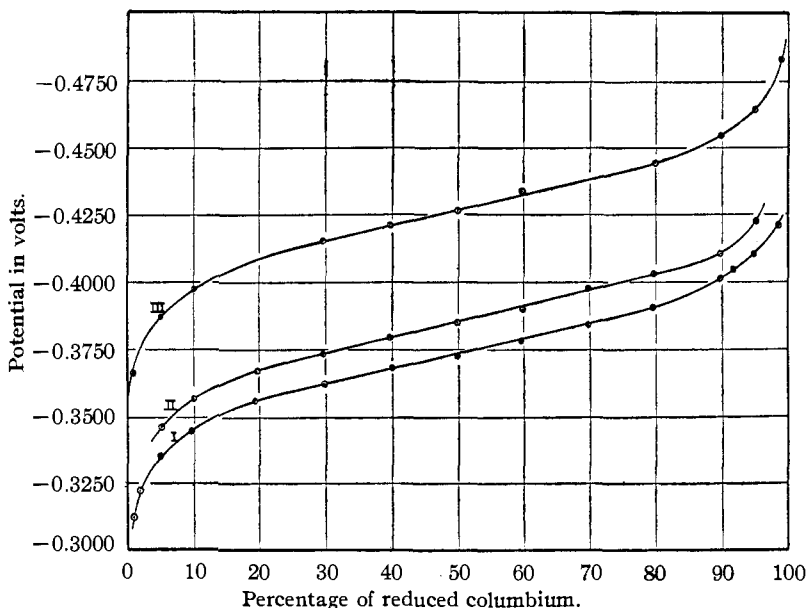


Fig. 3.—I, 3.14 *M* H₂SO₄; II, 5.91 *M* H₂SO₄; III, 9.87 *M* H₂SO₄; 0.024 *M* Cb₂O₆; temperature, 25°.

In Fig. 2 the data collected in Table V were used to construct nearly straight lines, the slopes of which are very nearly identical for the three acid concentrations and agree very closely with that of the ideal, 0.0295. The slopes for the system in the three acid concentrations were calculated also. Their average values were, respectively, for 3.14 *M* sulfuric acid, 0.0294; for 5.91 *M* sulfuric acid, 0.0293 and for 9.87 *M* sulfuric acid 0.0296. The plotted values were, respectively, 0.0298, 0.0295 and 0.0300 approximately.

When the percentage of reduced columbium is plotted against the corresponding potential, a set of curves set forth in Fig. 3 was obtained. These curves are similar in form and character to those obtained by Peters⁷ in the ferric-ferrous system.

Summary

1. The oxidation-reduction potentials of the pentavalent-trivalent columbium system were measured with a mercury electrode in an atmosphere of hydrogen at 25°. Three concentrations of sulfuric acid, 3.14 *M*, 5.91 *M* and 9.87 *M* were used. The concentration of columbium in Tables I, II, III and V expressed as Cb_2O_5 was 0.024 *M*. In Table IV it was 0.012 *M*.

2. The trivalent columbium was found to be a strong reducing agent which increased markedly as the concentration of acid increased.

3. A valence of three was confirmed for the reduced state.

4. The average calculated normal electrode potentials for the three concentrations of acid, respectively, are: -0.3730, -0.3849 and -0.4261.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

PHOTOCHEMICAL STUDIES. VII. THE PHOTOCHEMICAL DECOMPOSITION OF FORMIC ACID LIQUID AND VAPOR

BY W. N. HERR AND W. ALBERT NOYES, JR.

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The fact that formic acid decomposes under the influence of ultra-violet radiation has been known for many years. Thiele¹ found that the product of photochemical decomposition of the anhydrous acid was largely carbon dioxide, together with small amounts of oxygen, carbon monoxide and other gases. Berthelot and Gaudechon² state that long wave lengths (250 to 350 μ) cause the formation of water and carbon monoxide, while shorter wave lengths cause the formation of carbon dioxide and hydrogen. Allmand and Reeve,³ in a recent careful investigation of the photochemical decomposition of formic acid in aqueous solution, find that wave lengths below 350 μ are effective and that practically the only gas formed is carbon dioxide. They think that the hydrogen (which would be formed simultaneously) is used in reducing formic acid to formaldehyde and other products. These authors also made accurate studies of the quantum efficiency and found the latter to be nearly independent of concentration but to depend on the wave length, being greater for short wave lengths.

Little work has been done on the photochemical decomposition of formic acid vapor. Ramsperger and Porter⁴ have made a study of the absorption spectrum. They find that two types of molecule, HCOOH and $(\text{HCOOH})_2$, exist in the vapor state and that each absorbs below about

¹ Thiele, *Ber.*, **40**, 4914 (1907).

² Berthelot and Gaudechon, *Compt. rend.*, **151**, 478 (1910).

³ Allmand and Reeve, *J. Chem. Soc.*, **129**, 2852 (1926).

⁴ Ramsperger and Porter, *THIS JOURNAL*, **48**, 1267 (1926).