KINETICS OF THE OXIDATION OF VANADIUM(II) AND VANADIUM(III) IONS BY PERCHLORATE ION^{1a}

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Kinetic studies of the oxidation of V(II) and V(III) ions by perchlorate ion were carried out at 49.9°, leading to the following rate laws in the initial concentration range 0.050–0.15 f VCl₂, 0.0035–0.078 f VCl₃, 0.53–1.99 f ClO₄⁻, 0.17–1.67 f H⁺, μ adjusted to 2.5 with NaCl and NaClO₄, $-d(V^{++})/dt = k_1(V^{++})(ClO_4^{-}) + 2k_2(V^{++})(ClO_4^{-})$, and in the absence of V(II) ion, $-d(V^{+++})/dt = k_2(V^{+++})(ClO_4^{-})$. The latter rate law agrees with that found by Sugimoto. A decrease in the average hydrogen ion concentration from 1.65 to 0.11 f gave an approximately 25% decrease in the value of k_1 and a twofold decrease in the value of k_2 . The former effect is not much larger than the estimated experimental error (15%), and may arise from specific electrolyte effects in maintaining constant ionic strength. At (H⁺) = 1 f, $k_1 = 1.3 \times 10^{-3}$ mole⁻¹ liter min.⁻¹. Although the variation of k_2 with hydrogen ion concentration appears to be sigmoidal, a rough resolution of k_2 may be effected into two terms, $k_2 = k_2' + k_2''(H⁺)$, with $k_2' = 0.17 \times 10^{-3}$ mole⁻¹ liter min.⁻¹ and $k_2'' = 0.1 \times 10^{-3}$ mole⁻² liter² min.⁻¹. The rate-determining step in the V(II)–ClO₄⁻ reaction is suggested to involve transfer of an oxygen atom from ClO₄⁻ to V⁺⁺, or possibly to be an electron transfer from V⁺⁺ to ClO₄⁻. The absorption spectrum of V(ClO₄)₂ in aqueous HClO₄ was obtained. VCl₂ solutions 0.1-1 f in HCl are only slowly oxidized by hydrogen ion (or water) even at 50°, although oxidation by oxygen is fairly rapid at 25°.

As is well known, aqueous perchlorate ion is remarkably inert at ordinary temperatures toward many reducing agents, including even such strong reductants as sodium amalgam, zinc and iron(II) ion. At room temperature perchlorate ion is reduced to chloride ion in aqueous acid solutions at a measurable rate by titanium(III),^{2,3} vanadium (III),² chromium(II),^{2,3} molybdenum(III),³ ruthenium(III)⁴ and europium(II)⁵ ions. Bromide ion in the presence of ruthenium(III, IV)⁶ and osmium(IV)⁷ catalysts and tin(II) ion with molybdate catalyst⁸ also reduce perchlorate ion under these conditions. However, only five kinetic investigations of oxidation by aqueous perchlorate ion appear to have been reported,^{3,6-9} three of which involve catalyzed reactions.

Sugimoto⁹ carried out a kinetic study of the vanadium(III)-perchlorate reaction, for which the over-all reaction may be represented by

 $8V^{+++} + ClO_4^- + 4H_2O \longrightarrow 8VO^{++} + Cl^- + 8H^+$ (1) At 50° the oxidation of vanadium(III) ion, V⁺⁺⁺ (hydrated), was first order in vanadium(III) and in perchlorate ion, with a complex dependence on hydrogen ion concentration, the nature of which may have been obscured by failure to control the ionic strength of the reaction solutions (ionic strength, μ , varied from 0.65 to 3.5).

We have undertaken a kinetic study of the vanadium(II)-perchlorate reaction, as well as a reinvestigation of the vanadium(III)-perchlorate reaction, not only to extend the knowledge of the kinetic behavior of perchlorate ion as an oxidant, but also to gain information about perchlorate

(1) (a) Adapted from a portion of the Ph.D. thesis of William R. King, Jr., University of California, Los Angeles, June, 1952; (b) Filtrol Corporation, Los Angeles, California.

(2) V. Rothmund, Z. anorg. Chem., 62, 109 (1909).

(3) G. Bredig and J. Michel, Z. physik. Chem., 100, 124 (1922).

(4) P. Wehner and J. C. Hindman, J. Am. Chem. Soc., 72, 3911 (1950). Ru(IV) is reported to be inert toward 1 f HClO₄ at 25° and to reduce ClO₄⁻ to Cl⁻ slowly in 6 f HClO₄ at 75°.

(5) D. J. Meier and C. S. Garner, THIS JOURNAL, 56, 853 (1952).

(6) W. R. Crowell, D. M. Yost and J. M. Carter, J. Am. Chem. Soc., 51, 786 (1929).

(7) W. R. Crowell, D. M. Yost and J. D. Roberts, *ibid.*, **62**, 2176 (1940).

(8) G. P. Haight, Jr., and W. F. Sager, ibid., 74, 6056 (1952).

(9) R. Sugimoto, M.S. thesis, University of California, Los Angeles, 1941.

oxidation of vanadium(II) and vanadium(III) ions which was of interest in connection with a study¹⁰ of isotopic exchange reactions.

Preliminary experiments with vanadium(II) perchlorate solutions initially free of chloride ion demonstrated that chloride ion is produced according to the stoichiometry of equation 2

$$8V^{++} + ClO_4^- + 8H^+ \longrightarrow 8V^{+++} + Cl^- + 4H_2O$$
 (2)

The study of the kinetics of this reaction was complicated by the fact that the vanadium(III) produced by this reaction reacts at a comparable rate with perchlorate ion by equation 1, forming vanadyl ion, VO^{++} , which reacts instantaneously with vanadium(II) ion to produce vanadium(III) ion

$$VO^{++} + V^{++} + 2H^{+} \longrightarrow 2V^{+++} + H_2O$$
 (3)

Experimental

Chemicals.—Stock solutions of vanadium(II) chloride were prepared by electrolytic reduction of a mixture of vanadium(V) oxide (made by igniting recrystallized ammonium metavanadate) and 0.7 f hydrochloric acid, the cell having a mercury cathode and an anode compartment separated by a porous cup. In addition to oxygen, chlorine was liberated at the anode, necessitating the addition of more hydrochloric acid during the reduction. Vanadium(IV) perchlorate solution was prepared from vanadium(IV) perchlorate solution (1.6 f in HClO₄) by reduction with zine amalgam at 0.5°; the vanadium(IV) perchlorate solution was made by refluxing a mixture of purified vanadium(V) oxide, perchloric acid and formic acid, adsorbing the resulting solution on Ion-X cation-exchange resin, washing out the excess formic acid with water, then eluting the vanadium-(IV) with 4 f perchloric acid. The stock solutions were analyzed for dipositive and tripositive vanadium by a modification of the method devised by Ramsey¹¹ for the determination of vanadium(III). Total vanadium (IV) with ammonium peroxydisulfate, followed by titration at 50° with cerium(IV) sulfate solution standardized against arsenic(III) acid, using o-phenanthroline iron(II) sulfate indicator. For the determination of total reducing equivalents a separate aliquot was delivered into an excess of sodium metavanadate solution (0.3 f in sulfuric acid), which oxidizes all the vanadium to vanadium(IV) and reduces the metavanadate to the same state in an amount dependent upon the amounts of +2 and +3 vanadium present; the vanadium(IV) sulfate. From the results of these two titra-

(10) W. R. King, Jr., and C. S. Garner, J. Am. Chem. Soc., 74, 3709 (1952).

(11) J. B. Ramsey, ibid. 49, 1138 (1927).

tions the concentrations of vanadium(II) and vanadium(III) were calculated (ca. 10% of the vanadium was present as vanadium(III) at the time of use in the rate runs). The hydrogen ion concentration was determined indirectly by a gravimetric determination of the chloride concentration, assuming that neither vanadium(II) ion nor vanadium(III) ion is hydrolyzed to any extent in these solutions.¹²

Because of the ease of air oxidation of vanadium(II) and vanadium(III), all solutions were prepared from water redistilled from an alkaline permanganate solution in an all-Pyrex still and freed from oxygen by passage of a stream of oxygen-free nitrogen through the water. All solutions were stored in all-Pyrex closed-buret systems,¹³ under an atmosphere of oxygen-free nitrogen. The latter was prepared by passage of high purity tank nitrogen through a continuously regenerated chromium(II) chloride solution.¹⁴ The perchloric acid was C.P. grade, redistilled at 5 mm.

The perchloric acid was C.P. grade, redistilled at 5 mm. pressure. C.P. sodium perchlorate was found to contain chlorate and iron(III) ions, and was purified by recrystallization from water until negative tests for these impurities were obtained (KSCN test for Fe(III), and $Ag^+ + NO_2^$ for ClO_3^-). C.P. hydrochloric acid and C.P. sodium chloride were tested and found satisfactory without further purification. Sodium metavanadate solution was prepared by boiling recrystallized ammonium metavanadate with the stoichiometric amount of C.P. sodium carbonate.

Procedure.—Appropriate volumes of standardized solutions of perchloric acid, sodium perchlorate, hydrochloric acid, sodium chloride and water were delivered from their respective storage burets into a closed previously evacuated reaction vessel equipped with a buret. A calculated volume of standardized vanadium(II) chloride solution was similarly transferred to a second vessel, and both vessels were brought to temperature in a thermostated oil-bath maintained at $49.9 \pm 0.1^{\circ}$. Then the two solutions were mixed by interconnecting the two vessels and forcing the vanadium(II) chloride solution into the reaction vessel with nitrogen. The transfer was quantitative inasmuch as the inside of the vessel containing the vanadium(II) solution was coated with Beckman "Silicote" and was not wet by the solution.



Fig. 1.—Comparison of absorption spectra of hydrated V⁺² and V⁺³ ions in HClO₄, 25°: curve I, 0.07 f V(ClO₄)₂, 0.5 f HClO₄, $\mu = 0.7$; curve II, 0.073 f V(ClO₄)₃, 0.38 f HClO₄, 0.56 f NaClO₄, $\mu = 1.4$ (Furman and Garner, ref. 15).

The change in vanadium(II) concentration with time was followed by removing the reaction vessel momentarily from the oil-bath, immersing the tip below the surface of an excess of sodium metavanadate solution (0.3 f in sulfuric acid), and delivering a 5-ml. aliquot from the buret (another aliquot was delivered 0.5 minute later into a second metavanadate

(14) H. W. Stone and E. R. Skavinski, Ind. Eng. Chem., Anal. Ed., 16, 111 (1944).

solution for a duplicate analysis). Titration with cerium-(IV) sulfate, as outlined above, together with a knowledge of the total vanadium concentration, permitted calculation of the vanadium(II) concentration at that time. Two other less satisfactory methods of following the change in vanadium(II) concentration were tried. In one case, the vanadium(II) was caused to react with α, α' -dipyridyl to form a green complex, the color intensity of which was determined spectrophotometrically. In the other case, attempts were made to follow the decrease in the absorption of light by the vanadium(II) ion itself, but the absorption spectra of vanadium(II) and vanadium(III) ions were found to be too similar to make this convenient. Figure 1 gives a comparison of these spectra, the spectrum of the vanadium(III) ion being taken from the paper of Furman and Garner.¹⁶ In some experiments the rate of the vanadium(III)-perchlorate reaction was followed in the absence of vanadium-(IV).

In some experiments the rate of the vanadium(III)-perchlorate reaction was followed in the absence of vanadium-(II) by using reaction mixtures which had stood until all the vanadium(II) had reacted, the change in vanadium(III) concentration being followed by titration as above. **Calculation of Reaction Rates.**—Vanadium(II) titers of the reaction aliquots were plotted against time on large-

Calculation of Reaction Rates.—Vanadium(II) titers of the reaction aliquots were plotted against time on largescale graph paper for each run, the points falling on a smooth curve. Slopes were measured at various points on each curve with a Bausch and Lomb tangent meter, these values (multiplied by suitable factors) giving the rate of disappearance of vanadium(II) ion, $-d(V^{++})/dt$. Similar treatment was given the data for the vanadium(III)-perchlorate reaction. All concentrations are expressed in moles per liter of solution of 49.9°, and the time is given in minutes.

of solution of 49.9°, and the time is given in minutes. Normally the order of reaction with respect to a particular species can be determined by varying the concentration of this species while holding that of all others constant. This procedure was not possible here, but an equivalent method was used by calculating the slopes from the various curves as a function of time for various fixed concentrations of all species but the particular one. A plot of such slopes versus the concentration of the particular species then allowed determining the order of reaction with respect to that species. The data of all such plots were treated by the least squares method. The over-all error in the values of the rate constants is estimated to be 15%.

Results

Stability of Vanadium(II) Chloride Solutions.---Although vanadium(II) ion, V++ (hydrated), is thermodynamically capable of reducing hydrogen ion (or water) in acid solutions (V⁺⁺ = V⁺⁺⁺ + e^- , E = +0.255 volt¹⁶ at 25° on the Latimer scale), we find that vanadium(II) chloride solutions 0.5–1 f in hydrochloric acid, prepared as described above, are comparatively inert with respect to oxidation by hydrogen ion even at 50°. Solutions 0.5 f in hydrochloric acid retained their vanad-ium(II) titer to within 1% for a month at 25°, and only a 13% decrease in vanadium(II) concentration was found for a 1 f hydrochloric acid solu-tion kept at 50° for 36 days. The gas above a solution ca. 0.05 f in vanadium(II) chloride and 0.1 f in hydrochloric acid which had been kept at 50° for 3 days showed no trace of hydrogen when examined in a mass spectrometer. (However, hydrogen is rapidly evolved when a platinum wire is immersed in these vanadium(II) solutions.) Consequently, no correction to the rate data is required for oxidation of vanadium(II) by hydrogen ion or water.

Dependence of Rate of Vanadium(II)–Perchlorate Reaction on Vanadium(II) and Vanadium(III) Concentrations.—To find the order with respect to vanadium(II), $-d(V^{++})/dt$ was determined at fixed concentrations of vanadium(III), perchlorate

(15) S. C. Furman and C. S. Garner, J. Am. Chem. Soc., 72, 1785 (1950).

(16) G. Jones and J. H. Colvin, *ibid.*, 66, 1573 (1944).

⁽¹²⁾ S. C. Furman and J. T. Denison, private communication, estimated the hydrolysis constant for V⁺⁺⁺ to be of the order of 2×10^{-3} at 25°.

⁽¹³⁾ H. W. Stone, Anal. Chem., 20, 749 (1948).

SUMMARY OF KINETIC RATE RUNS AT 49.9°, $\mu = 2.5^{\circ}$					
(H +), <i>f</i>	(ClO4 ⁻),	$(V^{+_2}), f$	$(V^{+3}), f$	$k_1 \times 10^3$, mole ⁻¹ l. min. ⁻¹	$k_2 \times 10^{s}$, mole ⁻¹ 1. min, ⁻¹
1.65	1.50	0.050	0.0035	. 1.33	0.35
1.62	1.50	. 100	.0071	1.39	. 32
1.60	1.50	. 150	.0106	1.44	.35
0.98	1.50	.050	. 0035	1.27	. 25
. 95	1.50	. 100	.0071	1.21	. 28
.68	0.532	. 100	.0071	ь	Ь
. 65	1.50	. 100	.0071	1.10	. 26
. 65	1.99	. 100	.0071	1.10	.25
.11	1.50	. 100	.0071	1.10	.17
1.62	1.49	0	.0784	• •	.30
0.94	1.49	0	.0784	• •	.23
. 65	1.49	0	.0784		.23
.11	1,49	0	.0784	• •	.19

TABLE I SUMMARY OF KINETIC RATE RUNS AT 49.9°, $\mu = 2.5$

^a All concentrations are initial values, except (H⁺) for which the average value is given. ^b This run was used solely to gain an additional point on the (ClO_4^-) dependence plot.

ion, and hydrogen ion (the latter varied ca. 3% in a given run), and these slopes were plotted against the vanadium(II) concentration. The linearity of the plot, shown in Fig. 2, indicates first-order dependence on vanadium(II) ion concentration.

Figure 2 also gives a plot of $-d(V^{++})/dt$ at fixed concentrations of vanadium(II), perchlorate ion and hydrogen ion against vanadium(III) concentration and shows that the reaction is first order in vanadium(III) ion.

Dependence of Rate of Vanadium(II)-Perchlorate Reaction on Perchlorate Ion Concentration.— Plots of $-d(V^{++})/dt$ against perchlorate ion concentration (varied from 0.53 to 1.99 f) at various fixed values of vanadium(II) concentration were made. Figure 3 displays some typical plots. The linearity of the curves and the fact that each curve extrapolates to the origin within the experimental error indicates that the entire rate expression is first order in perchlorate ion with no significant terms independent of perchlorate ion concentration.

The results presented allow the formulation of the rate expression as

$$-d(V^{++})/dt = k_1(V^{++})(ClO_4^{-}) + 2k_2(V^{+++})(ClO_4^{-})$$
(4)

where any hydrogen ion dependence is included in the rate constants k_1 and k_2 . The first term expresses the rate of disappearance of vanadium(II) due to direct reaction with perchlorate ion, and the second term gives the rate of disappearance because of reaction with the product (\dot{VO}^{++}) of the concurrent reaction between vanadium(III) and perchlorate ions according to equations 1 and 3. Values of the rate constants are given in Table I. It is assumed that the concentrations of chloro-complexed and hydrolyzed species of vanadium(II) and vanadium(III) are negligible. Lingane and Meites¹⁷ have shown that the polarographic half-wave potential for the reduction of vanadium(III) ion to vanadium(II) ion remains constant within the experimental error $(\pm 0.002$ volt) when the perchlorate medium is replaced by chloride medium (1 f acid). Furman and Garner¹⁵ found that the absorption spectrum of vanadium (III) perchlorate solutions was not measurably

(17) J. J. Lingane and L. Meites, J. Am. Chem. Soc., 70, 2525 (1948).

altered by the addition of chloride ion until the Cl⁻ concentration was at least twenty times the total vanadium concentration. The hydrolysis constant for the presumably more hydrolyzed V⁺⁺⁺ ion is only ca. 7×10^{-3} at 50°, estimated from an approximate value¹² for the hydrolysis constant at room temperature and the heat of hydrolysis.¹⁵



Fig. 2.—Effect of vanadium(II) and vanadium(III) ion concentrations on rate of oxidation of vanadium(II) ion, $(\text{ClO}_4^-) = 1.50 \ f, \ (\text{H}^+)_0 = 1.62 \ f, \ 49.9^\circ, \ \mu = 2.5$: curve I, $(\text{V}^{+_3}) = 0.041 \ f;$ curve II, $(\text{V}^{+_2}) = 0.035 \ f.$



Fig. 3.—Effect of perchlorate ion concentration on rate of oxidation of vanadium(II) ion, $(H^+)_{\nu} = 0.70 f$, 49.9°, $\mu = 2.5$: curve I, $(V^{+2}) = 0.080 f$; curve II, $(V^{+2}) = 0.75 f$, curve III, $(V^{+2}) = 0.050 f$.

Order of Rate of Vanadium(III)-Perchlorate Reaction with Respect to Reactants.-From runs made in the absence of vanadium(II), rate plots were prepared by plotting the logarithm of vanadium(III) concentration versus time for fixed concentrations of perchlorate ion and hydrogen ion. A typical plot is shown in Fig. 4. The linearity of these plots demonstrates the first-order dependence on vanadium(III) concentration. First-order dependence on perchlorate ion concentration was demonstrated by the fact that the entire rate expression (vanadium(II) present also) was found to be first order in perchlorate ion. These findings are in agreement with the rate law developed by Sugimoto⁹ for the vanadium(III)-perchlorate reaction, namely

$$-d(V^{+++})/dt = k_2(V^{+++})(ClO_4^{-})$$
(5)

where the hydrogen ion dependence is included in the rate constant k_2 . Intercomparison of our values of k_2 with Sugimoto's values is presented below.



Fig. 4.—Representative semi-logarithmic plot of vanadium(III) ion concentration against time, vanadium(III)perchlorate reaction, $(\text{ClO}_4^-) = 1.49 \ f$, $(\text{H}^+)_0 = 0.63 \ f$, 49.9° , $\mu = 2.5$.

Hydrogen Ion Dependence.—The data of Table I show that a fifteen-fold variation in hydrogen ion concentration is associated with an approximately 25% change in the value of k_1 and a twofold change in k_2 , the latter holding both in the presence and absence of vanadium(II) ion. In view of the experimental error of ca. 15% the relatively small variation in the values of k_1 may be due to a specific electrolyte activity effect arising from the substitution of sodium ion for hydrogen ion in maintaining constant ionic strength, rather than being due to an actual hydrogen-ion dependence. The larger variation in values of k_2 suggests that there is a hydrogen ion-dependent term in the rate expression, as was proposed by Sugimoto⁹ for the vanadium(III)perchlorate reaction. In order to examine this and to permit intercomparison of our data with Sugimoto's, the values of k_2 were plotted against hydrogen ion concentration, both for the vanadium (II)-perchlorate and vanadium(III)-perchlorate reactions. These curves, although actually sigmoidal, may be treated as roughly linear, permitting an approximate resolution of k_2 into two terms

$$k_2 \cong k_2' + k_2''(\mathrm{H}^+)$$
 (6)

Table II gives the average values of k_2' and k_2'' so determined. In view of the experimental errors and the approximations made in computing these values, the agreement is satisfactory.

Catalysis by Light.—Some of the reactions were allowed to proceed for 30% of the run time in darkness; all others were carried out with normal laboratory illumination. There was no noticeable difference in the rate curves for the dark and light runs.

TABLE II

Dependence of k_2 on Hydrogen Ion Concentration (49.9°, $\mu = 2.5$) $k_2' \times 10^3$, $k_2'' \times 10^3$.

nole - 1. mi	n1 mole -2 l.2 mi	in1 Source
0.17	0.10	V(II) runs (King and Garner)
0.18	0.07	V(III) runs (King and Garner)
0.24	0.15	V(III) runs (Sugimoto ⁹) ^a
° 50.0°;	ionic strength	permitted to vary from 0.65 to 3.5.

Temperature Coefficient.—All experiments were performed at 49.9°. However, Furman and Garner¹⁸ have observed that 0.1 f vanadium(III) perchlorate solutions develop amounts of chloride ion detectable by silver nitrate test in approximately one week at 0°.

Discussion

The mechanism proposed by Sugimoto⁹ for the vanadium(III)-perchlorate reaction, equations 1, 5 and 6, assumes that there are two reaction paths, one dependent on hydrogen ion, the other independent. He gave for the acid-independent path

$$V^{+++} + ClO_4^- + H_2O \xrightarrow{k_2'} VO_2^+ + ClO_3^- + 2H^+$$
(rate determining) (7)

$$V^{+++} + ClO_3^- \longrightarrow \text{ products (rapid)}$$
 (8)

$$V^{+++} + VO_2^+ \longrightarrow 2VO^{++} \text{ (rapid)} \tag{9}$$

and for the reaction which is assumed to be first order in hydrogen ion

$$H^+ + ClO_4 - \longrightarrow HClO_4 (rapid equilibrium)$$
 (10)

$$V^{+++} + HClO_4 + H_2O \xrightarrow{^{n_2}} VO_2^+ + ClO_3^- + 3H^+$$

(rate determining) (11)

followed by equations 8 and 9. The uncertain nature of the hydrogen ion dependence of the reaction rate makes it difficult to formulate a satisfying detailed mechanism for the reaction.

Ignoring the possibility of a small hydrogen ion term in the rate expression, at least two satisfactory mechanisms may be formulated which are consistent with the rate expression for the vanadium (II)-perchlorate reaction: (1) an oxygen atom is transferred from ClO_4^- to (hydrated) V⁺⁺ in the rate-determining step

$$V^{++} + ClO_4 \xrightarrow{\kappa_1} VO^{++} + ClO_3 \xrightarrow{} (rate determining)$$
(12)
$$3V^{++} + ClO_3 \xrightarrow{} 3VO^{++} + Cl \xrightarrow{} (rapid)$$
(13)

$$^{++} + VO^{++} + 2H^{+} \longrightarrow 2V^{+++} + H_{2}O \text{ (rapid)} (14)$$

We found that ClO_3^- reacts rapidly with an excess of V⁺⁺ in acid solution, and VO⁺⁺ reacts rapidly with V⁺⁺ as shown in equation 16. (2) An electron is transferred from V⁺⁺ to ClO_4^- in the ratedetermining step

$$V^{++} + ClO_4^- \xrightarrow{k_1} V^{+++} + ClO_4^-$$
 (rate determining) (15)

⁽¹⁸⁾ S. C. Furman and C. S. Garner, J. Am. Chem. Soc., 74, 2333 (1952).

$$7V^{++} + 3ClO_4^{--} + 16H_2O \longrightarrow 7V(OH)_4^{+} + 3Cl^{--} + 4H^{-}$$
(rapid) (16)

$$2V^{++} + V(OH)_4^{+} + 4H^{+} \longrightarrow 3V^{+++} + 4H_2O$$
(rapid) (17)

The unknown intermediate, ClO₄⁻, was invoked

by Bredig and Michel³ in the mechanism they suggested for the weakly acid-dependent path of the titanium(III)-perchlorate reaction. In the absence of further data, the simpler oxygen atom transfer process seems more probable.

THE GALLIUM-INDIUM SYSTEM

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The specific resistances of solid and liquid gallium and indium and their alloys have been determined. From the results of these resistance measurements, the phase diagram for the gallium-indium system has been redetermined. The diagram is not in close accord with others in the literature.

The phase diagram for the gallium-indium system has been studied previously.^{2,3} The study of de Boisbaudran was limited to four alloys. He predicted a concave liquidus curve. French, Saunders and Ingle made a thorough study of this system. These investigators also found the liquidus curve to be concave over the whole concentration range. However, the liquidus curves of the two investigators are not compatible with one another as reference to Fig. 2 will show.

The purpose of this research was to reinvestigate the gallium-indium system. Accordingly, electrical resistance-temperature measurements of various alloys covering the complete concentration range have been made and from these data the gallium-indium phase diagram has been deduced.

Materials. Indium.—The indium was a grant from the Anaconda Mining Company of Great Falls, Montana. Their assay claimed a purity of 99.97%. Spectrographic analysis showed the presence of very small amounts of tin and copper. The indium was used without further purification.

Gallium.—The gallium was of the Eagle Picher brand and was purified, with slight modifications, by a method in the literature.⁴ Spectrographic analysis indicated the complete absence of foreign elements. Since the supply of gallium was limited, it was necessary to reclaim and reuse the gallium from the gallium-indium alloys. After purification, spectrographic analysis indicated the same purity as before.

spectrographic analysis indicated the same purity as before. Mercury.—The mercury used for the calibration of test cells had been carefully distilled.

Apparatus.—A Leeds and Northrup high precision standard resistance was used in the experiments. This unit was certified by the National Bureau of Standards as having a resistance of 1.0004 ohms at 25° when carrying a current of 1 ampere. The unit had a pair of current carrying and potential measurement leads.

Three Everready Air Cells connected in parallel furnished the current for the measurements.

Potential drops were measured with a Type B Rubicon potentiometer using a Rubicon No. 3402 Spotlight galvanometer as the indicating instrument.

nometer as the indicating instrument. The test cells were of Pyrex tubing 40-cm. long and were sealed at one end. The current carrying and potential measurement leads sealed in the cell were of tungsten wire. The two end current carrying leads were placed 30 cm. apart. The potential measurement leads were each 2.5 cm.

(1) Abstracted from the thesis of Sidney M. Selis presented to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the Ph.D. degree.

(2) L. de Boisbaudran, Compt. rend., 100, 701 (1885).

(3) S. J. French, B. J. Saunders and G. W. Ingle, THIS JOURNAL, 42, 265 (1938).

(4) J I. Hoffman, Bur Standards J. Research, 13, 665 (1934).

from the current carrying leads as suggested by Thomas.⁵ The tubing used in the construction of the cells ranged from 4-mm. tubing with standard wall thickness to small bore, heavy walled capillary tubing with an inside diameter of 2 mm. and an outside diameter of 9 mm. The reason for using heavy-walled tubing was that the gallium-rich alloys expanded on freezing and in doing so, tended to break the test cells.

The control of temperature was maintained by the use of two baths, water and oil. The water-bath was used for temperatures up through 50°, and the oil-bath for temperatures over 50°. In the water-bath, resistance measurements could be made at temperatures known to within $\pm 0.01^{\circ}$. The thermometer used in this bath was checked against a similar one calibrated at the National Bureau of Standards. In the oil-bath, the temperature could be controlled to within $\pm 0.05^{\circ}$. The thermometer used in the oil-bath was checked against Anschütz thermometers calibrated at the National Bureau of Standards.

Experimental Method.—The measuring circuit consisted of a series arrangement of the current source, standard resistance, cell, rheostat and a d.c. ammeter. Measurements consisted of reading the potential drops across the standard and unknown resistances as the current passed through them. It is apparent that connections between resistances and potentiometer must be made at points within the leads linking the several series components; otherwise the resistances of these leads would give rise to errors in the measurement of potential differences. If the current passing through the main series circuit is about one ampere, then the small amount of current shunted through the potentiometer will result in a negligible error.

The current passing through the two resistances (*i.e.*, standard and unknown) in series must be the same, *i.e.*, $I_x = I_e$. By use of Ohm's law, one obtains

$$R_{\mathbf{x}} = E_{\mathbf{x}}(R_{\mathbf{s}}/E_{\mathbf{s}}) \tag{1}$$

where E_s and E_x are the potential drops and R_s and R_x are the resistance values of the standard resistance and the unknown resistance, respectively.

A very convenient approach to studying alloy resistance is in terms of specific resistance. The cell constant, C, for converting measured resistance to specific resistance may be calculated by the use of equation 2

$$C = \rho/R \tag{2}$$

where ρ is the specific resistance and R is the measured resistance.

One of the cells was calibrated using mercury⁶ as a standard over the temperature range of 20 to 157° and the cell constant *C* was constant within 0.2%. The cell constants for the other seven cells used in this research were determined at one temperature only.

Alloys were prepared by melting weighed amounts of the

(5) We acknowledge our indebtedness to Dr. J. L. Thomas of the National Bureau of Standards for his advice on these electrical resistance studies.

(6) T. I. Edwards, Phil. Mag., Series 7, 2, 1 (1926)