[Contribution from the Chemical Laboratory of Harvard University]

MEASUREMENT OF OXIDATION POTENTIALS AT MERCURY ELECTRODES. III. TER- AND BIVALENT TITANIUM

By George Shannon Forbes and Lawrence Percival Hall

Received December 4, 1923

Although the normal potential of the reaction $Ti^{IV} + \ominus \rightleftarrows Ti^{III}$ is well known,[1] that of the reaction $Ti^{III} + \ominus \rightleftarrows Ti^{II}$ has not hitherto been measured. By combination of the above, the free energy of the reaction $Ti^{IV} + 2\ominus \rightleftarrows Ti^{II}$ results, for comparison with tin and lead. The value of such data is enhanced by the bare possibility of correlating them with atomic structure, with ionization potentials of vaporized elements and compounds, and with various astrophysical problems.

We found it very difficult to prepare solutions containing titanium dichloride of concentration and stability sufficient to give constant and reproducible electromotive forces and dependable analyses. Stähler's method[2] of passing mixed hydrogen and titanium tetrachloride through a cold-hot tube at 1100° and then heating the sublimate to 700° would doubtless have been satisfactory if we had taken the trouble to duplicate his apparatus. As it was, our scanty product was mostly metallic titanium. Ruff and Neumann[3] have very recently concluded that for the best yields of dichloride the temperature and pressure should be as high as possible. Reduction of trichloride with metallic titanium in solutions containing various concentrations of hydrochloric acid, and the anodic solution of the metal with various applied electromotive forces produced solutions giving little evidence of dichloride present. Finely divided material of any kind, or hydrogen bubbles, serving as nuclei for relief of gaseous supersaturation seemed to promote decomposition in the metastable system $Ti^{++} + H^{+}$, giving $Ti^{+++} + {}^1/_2\,H_2$. Instability, as would be expected, increased rapidly with hydrogen-ion concentration, 0.1 M being the limit permissible at 0°. Platinum electrodes liberated a torrent of hydrogen, but mercury with its smooth surface, constant surface energy, and high overvoltage for hydrogen[4] proved an excellent electrode for measurements, as in the investigation of the chromic-chromous potential.[5] We are indeed inclined to believe that the apparent irreversibility of the reaction $Ti^{+++} + \ominus \rightleftarrows Ti^{++}$ in water solution is due merely to the instability of the bivalent ion on cathodes, or on the surface of electronegative metals, under the conditions which prevail during attempted reductions. The bivalent ion, though a reducing agent somewhat less

---

[1] Diethelm and Foerster, *Z. physik. Chem.*, **62**, 129 (1908).

[2] Stähler and Bachran, *Ber.*, **44**, 2906 (1911).

[3] Ruff and Neumann, *Z. anorg. Chem.*, **128**, 81 (1923).

[4] Compare Lewis and Jackson, *Proc. Am. Acad.*, **41**, 399 (1906).

[5] Forbes and Richter, This Journal, **39**, 1140 (1917).

strong than chromous ion, as shown below, is incomparably more sensitive to catalytic decomposition. It is of interest to note that such an experienced investigator as Ruff[3] declared himself unable to prepare stable solutions containing dichloride. He states that hydrogen was copiously evolved, forming a turbid, black colloidal solution. Imagining that the dichloride was an exceedingly powerful reducing agent, he attempted without success to reduce to metals solutions of ferrous, chromous, and complex cobalt and nickel salts. The negative results of these experiments he took to be further evidence of the utter instability of the dichloride solutions. Consideration, however, of the normal potentials involved and the probable concentrations of the several ions in his experiments shows that dichloride could scarcely have precipitated these metals.

A satisfactory product was obtained by treating finely divided titanium in porcelain boats in a quartz tube with pure dry hydrogen chloride. This method had been tried out by Merz[6] who, however, obtained nothing but tetrachloride. We found that titanium residues recovered from previous experiments likewise yielded mostly tetrachloride. The temperature was raised, only after 24 hours' exposure to the gas at room temperature, to a maximum of 350° to 400° and kept there for about 18 hours. The metal, obtained from Professor A. Jones of Rensselaer Polytechnic Institute, had been made by the method of Nilson and Pettersson,[7] as improved by Hunter,[8a] from titanium tetrachloride and sodium in a steel bomb. The published analyses indicate a percentage purity of 99.9; a small trace of iron was present. Refining by electrolysis, distillation, etc., was obviously impossible, but we could see little reason to distrust the electromotive measurements on the ground that the metal was impure.

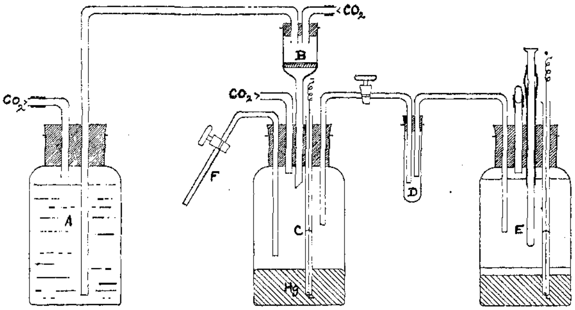

Fig. 1.—Apparatus for filtration and measurement of electromotive force.

The product, which contained both trichloride and dichloride, was purplish-black, more bulky than the metal, and turned purple in air, or if slightly warm caught fire when thus exposed. When fully cooled, and protected no doubt by adsorbed hydrogen chloride, it could be quickly transferred without detriment to a bottle of boiled water partly frozen

---

[6] Merz, *J. prakt. Chem.*, **99**, 176 (1866).

[7] Nilson and Pettersson, *Z. physik. Chem.*, **1**, 27 (1887).

[8a] Hunter, *Rensselaer Eng. Sci. Series*, **1911**, 1.

and well swept out with oxygen-free carbon dioxide. After being vigorously shaken with a solid stopper, the bottle was at once placed in position at A (Fig. 1) and the solution forced by carbon dioxide pressure through a thick asbestos filter mat at B supported by a perforated porcelain disc. At first the filtered solution was colorless, but it soon turned brown, as Stähler[2] also noted. An investigation of this color change has been begun in this Laboratory. The filtrate was collected in the half-cell C containing mercury purified by the usual treatment with acids and by distillation in a stream of air. This mercury gave no electromotive force against a sample of mercury prepared by the ignition of the oxide. D is a bridge of 4 *M* potassium chloride,[8b] and E a calomel electrode in 0.1 *M* hydrochloric acid. As the connecting tubes between C and E were not capillary, and there was some risk of contamination, this electrode was checked after each experiment against a standard calomel electrode, and any indicated correction applied. The system, full of carbon dioxide, was immersed in a tank of ice and distilled water so well insulated that zero temperature could be maintained for two days without refilling. The solutions, greenish to purplish-black, suffered little change at acid concentrations less than 0.1 *N*.

The electromotive force, read on a standard potentiometer with an Eppley standard cadmium cell, rose to a maximum within 12 minutes in one solution especially concentrated in titanium dichloride and 0.1 *N* in acid, and in 12 hours in another solution much more dilute in dichloride and acid. In the former case hydrogen bubbles formed on the mercury. The electromotive force was always slightly depressed by shaking after the maximum was reached, but quickly rose to within about 1 mv. of its former value. Apparently, therefore, all parts of the solution contained about the same concentration of dichloride and were almost equally free from oxygen. Very small quantities of air, admitted by accident or design, depressed potentials in a striking fashion.

Free hydrochloric acid previously adsorbed by the solid was always present, and in some cases we added more to the solution. It was estimated by subtracting total equivalents of titanium from total chloride determined as silver chloride. The result was too low by the amount of acid produced by the residual hydrolysis of the titanium chlorides. Increased concentration of chloride ion should raise the reducing potential of the solution by suppressing Ti^{+++} more than Ti^{++}[9] to form neutral molecules and complex ions, also by increasing the hydrolysis of Ti^{+++} more than that of Ti^{++}[9]. In harmony with this prediction, we read in *M* potassium chloride our highest reducing potential, —0.726 volt,

---

[8b] Compare Scatchard, THIS JOURNAL, **45**, 1716 (1923).

[9] Compare Peters, *Z. physik. Chem.*, **26**, 193 (1898); Chilesotti, *Z. Elektrochem.*, **12**, 173 (1906); also Ref. 1.

rapidly falling off. Increased concentration of hydrogen ion should lower the reducing potential by repressing the hydrolysis of $\mathrm{Ti^{+++}}$ more than that of $\mathrm{Ti^{++}}$[9] and also by accelerating in greater degree the decomposition of the latter. We had intended to extrapolate our potentials to zero concentration of acid, as was done in the case of the stannic-stannous potential,[10] but in the range accessible to measurement, 0.025 to 0.10 N, the observed values showed no significant trend. In 0.15 N acid the solution frothed violently, and measurements were impossible.

As soon as the maximum electromotive force was reached, two samples for analysis were forced out of the half cell by carbon dioxide pressure, through the tube F. The first was delivered into a flask filled with carbon dioxide and containing a weighed solution of standard dichromate with a large excess of sulfuric acid. The excess of dichromate was determined electrometrically[11] by standard Mohr's salt. The end-point was exceedingly sharp; total reducing power, expressed in grams of trivalent titanium $= a = 2\mathrm{Ti^{II}} + \mathrm{Ti^{III}}$. The second sample was oxidized by nitric acid or hydrogen peroxide, boiled, precipitated by ammonia in slight excess, filtered hot, washed thoroughly, and finally heated over a blast lamp in a silica crucible to constant weight. The method was checked by analyses of pure tetrachloride weighed in special bulbs which were broken under rather concentrated sulfuric acid; total grams of titanium $= b$. Under the assumption, justified below, that tetrachloride was completely reduced by dichloride in dil. hydrochloric acid, $\mathrm{Ti^{II}} = (a-b)$, and $\mathrm{Ti^{III}} = (b-\mathrm{Ti^{III}})$.

The readings of electromotive force were now extrapolated to molal or equal concentrations and referred to the normal hydrogen electrode at zero by the following hypothetical chain. $\overset{+}{\mathrm{PtH_2}} \mid \overset{+}{\mathrm{H}}M \parallel \mathrm{HCl}\ 0.1M \mid \overset{-}{\mathrm{PtH_2}} - \overset{-}{\mathrm{PtH_2}} \mid \mathrm{HCl}\ 0.1\ M \mid \mathrm{HgCl}\overset{+}{\mathrm{Hg}} - \overset{+}{\mathrm{Hg}}\mathrm{HgCl} \mid \mathrm{HCl}\ 0.1\ M \parallel \mathrm{TiCl_3} + \mathrm{TiCl_2} + \mathrm{HCl}\ 0.05\ M \mid \overset{-}{\mathrm{Hg}} - \overset{+}{\mathrm{Hg}} \mid \mathrm{TiCl_3} + \mathrm{TiCl_2} + \mathrm{HCl}\ 0.05\ M \parallel \mathrm{TiCl_2}\ M + \mathrm{TiCl_3}\ M + \mathrm{HCl}\ 0.05\ M \mid \overset{-}{\mathrm{Hg}}$.

The electromotive forces of the individual cells in the above chain are, in order: $E_1 = 0.0684 \times 273/298 = 0.0626$; $E_2 = 0.3989 - 0.0056 = 0.3933$[12]; E_3 as measured is recorded in Col. 5, Table I; E_4, in Col. 7, is $0.054 \log \mathrm{Ti^{III}}/\mathrm{Ti^{II}}$. The last column, $(E_2 - E_1) - (E_3 + E_4)$ gives the electromotive force of the cell $\overset{+}{\mathrm{PtH_2}} \mid \mathrm{H^+}\ M \parallel \mathrm{TiCl_3}\ M + \mathrm{HCl}\ 0.05\ M + \mathrm{TiCl_2}\ M \mid \overset{-}{\mathrm{Hg}}$, that is, the normal potential at 0° of the reaction $\mathrm{Ti^{III}} +$

---

[10] Compare Forbes and Bartlett, THIS JOURNAL, **36,** 2030 (1914).

[11] Forbes and Bartlett, *ibid.*, **35,** 1535 (1913). Eppley and Vosburgh, *ibid.*, **44,** 2148 (1922).

[12] Lewis, Brighton and Sebastian, THIS JOURNAL, **39,** 2245 (1917).

TABLE I

CONCENTRATIONS AND ELECTROMOTIVE FORCES

	Ti per 1000 g. solution G.	Ti^{III} per 1000 g. solution G.	Ti^{II} per 1000 g. solution G.	E_3 observed	$\frac{Ti^{III}}{Ti^{II}}$	E_4	$(E_2 - E_1) - (E_3 + E_4)$
8	1.620	1.613	0.007	0.603	230	+0.127	−0.399
9	1.967	1.621	.346	.655	4.68	+ .036	− .360
10	2.901	2.630	.271	.665	9.7	+ .053	− .387
11	5.979	2.976	3.003	.680	0.986	+ .00	− .349
12	3.241	2.757	0.484	.647	5.70	+ .041	− .357
16	2.520	1.090	1.430	.700	0.764	− .006	− .363
			Av.	.66			− .369

$\ominus \rightleftarrows Ti^{II}$ referred to the normal hydrogen electrode at 0°. The usual conventions are followed, taking at all temperatures the single potential $PtH_2 \mid H^+ M$ as zero volts, and prefixing the negative sign to the potential of an electrode process furnishing negative electrons to the normal hydrogen electrode. Also, in the absence of data concerning the degrees of dissociation, hydrolysis, and complex formation of titanium chlorides, we had to be content with the first approximation $Ti^{III}/Ti^{II} = Ti^{+++}/Ti^{++}$.

Quite obviously, the amount of bivalent titanium in a 20g. sample of Solution 8 was smaller than the probable error of the analysis, and the good agreement of the corresponding normal potential with the others is entirely accidental. Indeed, we had to exclude six experiments, likewise exceedingly dilute in bivalent titanium, where the weights of the same were calculated as negative quantities, also of four others which registered abnormally low and rapidly falling potentials. The average in the last column, −0.369 volt, would be practically the same if Solution 8 were also thrown out. This average value would tend, if anything, to be somewhat too low for the reason that none of the solutions was permanently stable. The fact, however, that maximum readings in some cases remained constant within a few millivolts for 12 hours or more, indicates that this error was not excessive.

The normal potential at 0° corresponding to the reaction $Ti^{IV} + 2 \ominus \rightleftarrows Ti^{II}$, which we will call E_{2-4}, also referred to the normal hydrogen electrode at 0°, now follows from the first law of energy: $2E_{2-4}F = E_{2-3}F + E_{3-4}F$. It must be assumed that Diethelm and Foerster's[1] value + 0.056 for the normal potential E_{3-4} is approximately the same at 0° as at 18°, and the same in 4 N sulfuric acid as in other media where the hydrolysis of the quadrivalent ion is repressed; then $2E_{2-4}F = —0.369F + 0.056F$, and $E_{2-4} = —0.16 \pm 0.01$.

We can now calculate the average concentration Ti^{IV} of the quadrivalent salt in the solution analyzed, which gave an average single potential of —0.33 volt referred to the normal hydrogen electrode.

$$—0.33 = —0.156 + 0.027 \log Ti^{IV}/Ti^{II}$$

As $Ti^{IV}/Ti^{II} = 10^{-6}$, it was clearly justifiable to disregard quadrivalent titanium in calculating the analyses.

We gratefully acknowledge a grant from the Du Pont Fund for the purchase of metallic titanium and of sundry apparatus.

Summary

A mixture of titanium trichloride and dichloride was obtained by heating the metal, presumably about 99.9% pure, in hydrogen chloride. Excluding air with carbon dioxide, it was dissolved and filtered into the cell $\overset{-}{\text{Hg}} \mid \text{TiCl}_3\ \text{TiCl}_2\ 0.05\ M\ \text{HCl} \mid 4M\ \text{KCl} \mid \text{HCl}\ 0.1M \mid \overset{+}{\text{Hg}}$. All operations were at 0°. The electromotive force gradually rose to a maximum, which was in general quite constant for a considerable time. Total titanium was determined gravimetrically and total reducing power by electrometric titration, giving the concentrations in both valences. Six cells when extrapolated to equal or molal concentrations of both valences at 0° averaged 0.700 volt with an extreme difference of 0.050 volt. The electromotive force at 0° of the chain, $\overset{+}{H_2} \mid H^+\ M \mid 4M\ \text{KCl} \mid \text{TiCl}_3\ \text{TiCl}_2 \mid \overset{-}{\text{Hg}}$, becomes —0.37 ± 0.01 when $Ti^{III} = Ti^{II}$, assuming zero potential for the normal hydrogen electrode at 0°. Acid concentrations below 0.1 *N* had but little effect on the results, but the dichloride decomposed rapidly in more concentrated acid, and the electromotive force declined rapidly.

The electromotive force of the hypothetical chain, $\overset{+}{H_2} \mid H^+\ M \mid 4\ M\ \text{KCl} \mid Ti^{IV}\ Ti^{II} \mid \overset{-}{\text{Hg}}$, is calculated to be —0.16 ± 0.01 when $Ti^{IV} = Ti^{II}$.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

THE CATALYTIC DEHYDRATION OF ETHYL ALCOHOL AND ETHER BY ALUMINA

BY ROBERT N. PEASE AND CHI CHAO YUNG

RECEIVED JULY 16, 1923

The chief purpose of the investigation recorded in the following pages was to gain information as to the kinetics of the catalytic dehydration of alcohol in the vapor phase, with formation of ether and ethylene, by a more thorough study of the reactions involved than has yet been made. Much work of a qualitative nature has been done on catalytic vapor-phase organic reactions, especially by Sabatier and his students, and many hypotheses as to their mechanisms have been evolved. It would seem, however, that only by exhaustive study of particular examples from as many points of view as possible—and that of the simpler reactions first—can satisfactory explanations be arrived at.

Among such reactions, the dehydration of alcohol stands out as one of