range of substrate concentrations, and we believe that this value is accurate.

We estimate the accuracy of the results for the individual ionization constants to be ±10%, but the ratio $K_a(H_2O)/K_a(D_2O)$ is probably more accurate as many of the errors in the individual constants will cancel.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Halogen, Iron and Vanadium Potentials in Lithium Chloride–Potassium Chloride Eutectic[1]

BY H. A. LAITINEN AND J. W. PANKEY

RECEIVED AUGUST 4, 1958

Electrode potentials of chlorine, bromine, iodine, iron and vanadium systems were measured in a lithium chloride–potassium chloride eutectic at 450°. Platinum foils in contact with solutions of platinum(II) were used as reference electrodes. Halogen electrodes were prepared by the passage of vapors of the halogen around graphite indicator electrodes in eutectic solutions of the halide in question. Iron(II) and vanadium(II) ions were produced by anodic dissolution of the respective metals. The massive metals served as indicator electrodes to measure potentials at various concentrations of divalent ions. Iron(III) and vanadium(III) solutions were prepared by anodic oxidation with graphite rods of eutectic solutions of the respective divalent ions. Potentials at the graphite rods were measured at various ratios of trivalent to divalent ion concentrations. Standard potentials are given for molarity, molality and mole fraction concentration scales.

In a recent publication[2] of an electromotive force series in molten lithium chloride–potassium chloride eutectic at 450°, the potential of the chlorine–chloride electrode was included. In the present paper, the experimental details of the evaluation of this electrode are given, and several additional entries to the e.m.f. series are made.

Halogen electrodes have been studied in pure and mixed molten halides by a number of investigators[3–8] beginning with Salstrom and Hildebrand. In most studies, reversible behavior was described, although the time necessary to reach equilibrium was often of the order of one to two hours. Drossbach,[7] however, noted small overvoltages upon anodization of carbon electrodes in molten chlorides, and interpreted impedance measurements on the basis of a slow heterogeneous reaction, probably $Cl + Cl \rightarrow Cl_2$. Smirnov and co-workers[5] anodized the carbon rod electrodes to saturate them with chlorine but did not remove hydrogen chloride from the melt prior to the anodic pretreatment. Little attention has been paid to corrections for variations of the pressure. Various measurements also have been made of the decomposition potentials of halide melts. These data are not directly of concern here and are mainly of interest for comparison with values calculated from thermodynamic data for pure metal chlorides.[9] For references, the reader is referred to the thesis of the junior author.[1]

The behavior of the iron(II)–iron(0) electrode has received study in alkali metal chloride–aluminum chloride systems,[10–12] in similar bromide mixtures[13] and in sodium bromide–potassium bromide melts.[14] Iron(III) has been found to exhibit two reduction steps,[15] presumably to iron(II) and the metal.

No previous reports of the potential of the vanadium(II)-vanadium(0) electrode have apparently been made, although the electrolytic reduction of vanadium(V) oxide has been described, yielding spinels of the type $V_2O_3 \cdot MO$ where M was Fe, Mn, Co or Zn,[16] and vanadium(IV) oxide.[17] Anodization of ferrovanadium in $AlBr_3 \cdot KBr$ melts showed evidence for anodic dissolution of vanadium, but the oxidation state was not established.[17]

Experimental

Materials and Equipment. Physical Equipment.—The furnace, temperature controller, polarograph, potentiometer, constant-current source and electrolytic cell have been previously described.[2,18–20] An auxiliary furnace, operating at 500° served where required to treat equipment before insertion into the solvent. The electrolysis cell and auxiliary equipment that was used to measure the electrode potentials is illustrated in Fig. 1. All portions were of Pyrex (Corning 774) glass except as noted. Side-arm tube A was the cell, which protruded from the furnace above the level A-A.

---

(1) Sponsored in part by Office of Ordnance Research, U. S. Army. Abstracted from the Ph.D. thesis of J. W. Pankey, 1958.

(2) H. A. Laitinen and C. H. Liu, THIS JOURNAL, **80**, 1015 (1958).

(3) E. J. Salstrom and J. H. Hildebrand, *ibid.*, **52**, 4641, 4650 (1930); E. J. Salstrom, *ibid.*, **53**, 1794, 3385 (1931); **54**, 4252 (1932); **55**, 2426 (1933); J. H. Hildebrand and E. J. Salstrom, *ibid.*, **54**, 4257 (1932).

(4) S. I. Rempel and I. N. Ozeryanaya, *Zhur. Fiz. Khim.*, **25**, 1181 (1951).

(5) M. V. Smirnov, S. F. Polguyev and L. E. Ivanovski, *ibid.*, **29**, 772 (1955).

(6) M. F. Lantratov and A. F. Alabyshev, *Zhur. Priklad. Khim.*, **26**, 263, 353, 722 (1953).

(7) P. Drossbach, *Z. Elektrochem.*, **60**, 387 (1956); *J. Electrochem. Soc.*, **103**, 700 (1956).

(8) K. H. Stern, *J. Phys. Chem.*, **60**, 679 (1956).

(9) W. J. Hamer, M. S. Malmberg and B. Rubin, *J. Electrochem. Soc.*, **103**, 8 (1956).

(10) V. O. Izbekov and N. G. Chovnyk, *Mem. Inst. Chem. Ukrain. Acad. Sci.*, **4**, 57 (1937).

(11) R. G. Verdieck and L. F. Yntema, *J. Phys. Chem.*, **46**, 344 (1942).

(12) V. A. Plotnikov, E. I. Kirichenko and N. S. Fortunatov, *Zapiski Inst. Khim., Akad. Nauk (U.R.S.R.)*, **7**, 193 (1940).

(13) Y. K. Delimarskii, *J. Phys. Chem. (U.S.S.R.)*, **19**, 465 (1945).

(14) Y. K. Delimarskii, E. M. Skobets and V. D. Ryabokon, *ibid.*, **21**, 843 (1947).

(15) Y. K. Delimarskii, E. M. Skobets and L. S. Berenblyum, *Zhur. Fiz. Khim.*, **22**, 1108 (1954).

(16) J. L. Audrieux and H. Bozon, *Compt. rend.*, **228**, 565 (1949).

(17) V. A. Plotnikov and V. V. Lyulka, *Zapiski Inst. Khim., Akad. Nauk (U.S.S.R.)*, **7**, 399 (1940).

(18) W. S. Ferguson, Ph.D. Thesis, University of Illinois, 1956.

(19) H. A. Laitinen, W. S. Ferguson and R. A. Osteryoung, *J. Electrochem. Soc.*, **104**, 516 (1957).

(20) H. A. Laitinen and W. S. Ferguson, *Anal. Chem.*, **29**, 4 (1957).

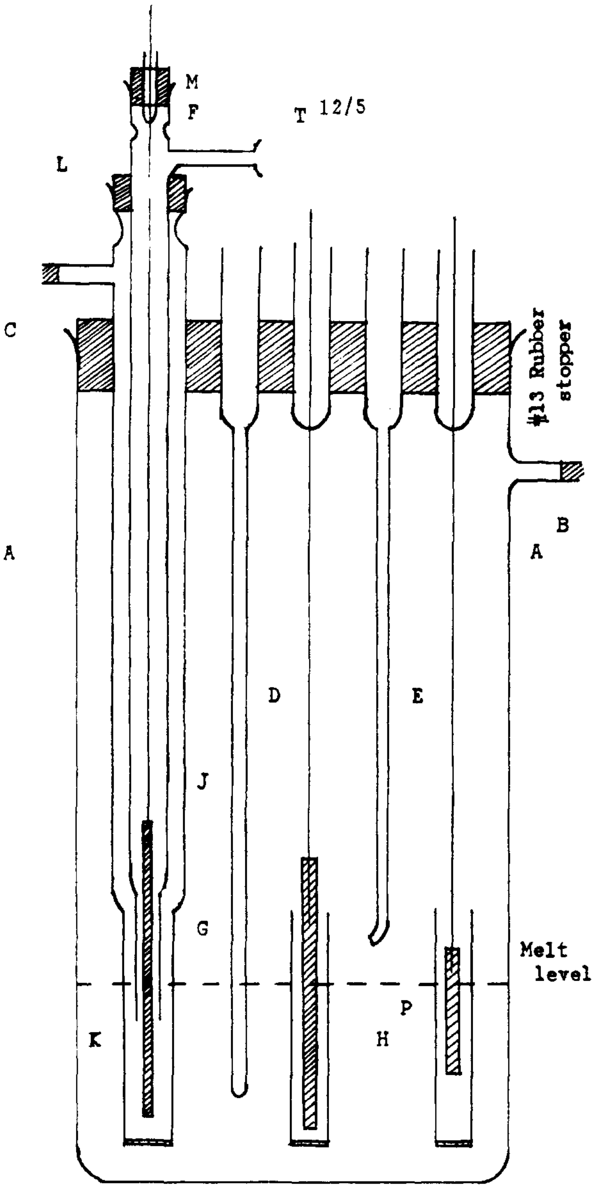

Fig. 1.—Fused salt cell and electrodes.

Tube D was the thermocouple sheath. Tubes E and F (or G) were vapor delivery tubes. Argon served where required to provide an inert atmosphere. Diffusion of moisture into the containers was prevented by $Mg(ClO_4)_2$ drying tubes at B and C, which also served as vapor effluent tubes. Excess vapors flowing from B and C were each delivered to separate glass tubes (not shown) which were immersed to the same depth into concentrated H_2SO_4. This depth amounted to only 1 cm. but tended to ensure equal vapor pressures within A and J and provided flow indicators for each gas. Equal vapor pressures inside A and J minimized contamination of other electrode systems inside A. Within cell A, the solvent was apportioned into compartments H, P and J, with fritted glass bottoms which acted as salt bridges. Compartment H containing a graphite electrode illustrates either an electrolysis electrode, a halogen–halide ion electrode or a trivalent ion–divalent ion electrode. P illustrates a compartment containing a metal–metal ion electrode. J illustrates a compartment within which may be contained an atmosphere different from that within the rest of cell A. For example, halogen vapor could be present on one side of J, argon on the other side. Vapors entered J through F, passed through G, bubbled around electrode K and out of the melt, rose and passed out through C. In use, G was immersed only 6 mm. into the solvent. The narrower portion of the delivery tube at G was 6 × 25 mm. Either graphite rods K or platinum or other metallic indicator electrodes could be accommodated concentrically inside G as long as they were 3 mm. or less in diameter. Both types of electrodes extended approximately 25 mm. below the bottom of G. L and M were 1″ lengths of black rubber tubing. The indentations in the glassware just beneath L and M helped to make vapor-tight seals and served to prevent chemical attack of the rubber. In addition, all rubber parts were coated with Kel-F No. 90 grease.

The main advantage of delivery tube G over other delivery tubes which must be beneath the surface of a liquid is that, because G is only slightly beneath the melt level, only a small volume of liquid could be inadvertently forced upward into G. Above G, there is sufficient space to contain the liquid within the heated zone of the furnace. Compartment J was easily adjusted to fit different melt levels and fused salt cells. But, if the top of J had to be opened, for example to add a solute or take a polarogram, the atmosphere within J was destroyed. Electrical contacts to all electrodes were made with platinum wires which passed through the rubber portions in glass sheaths. No evidence of corrosion of the wires by halogens was found. Glassware in contact with the solvent was boiled in $HClO_4$, rinsed and dried at 500°.

Solvent.—The solvent was the eutectic mixture of lithium chloride–potassium chloride (melting point 352°) prepared according to a procedure previously described.[18,19] Except as otherwise stated, the temperature of operation was 450°.

At the conclusion of an experiment, each compartment and its contents were removed. After cooling, the chloride content of pertinent compartments was titrated with $AgNO_3$ to determine the exact volume of solvent present in the compartment. Multiplication of the number of moles of chloride in a compartment by 55.59, the mean molecular weight of the solvent and division by 1.648, the density of the solvent at 450°[21] gave the volume of solvent in the compartment in ml. Volumes of solvent ranged from 3 to 6 ml.

By dissolution of weighed amounts of halide salts or by coulometric oxidation of metals immersed in a compartment or of ions dissolved therein, at constant current for known lengths of time, the exact amount of solute was known. Thus from the amount of solvent and solute present in a compartment, the exact concentration of a solution was known.

Chemicals.—Argon was rendered O_2-free and anhydrous by passage over hot Cu and $Mg(ClO_4)_2$. Chlorine from commercially available cylinders was dried by passage over anhydrous $Mg(ClO_4)_2$. Resublimed iodine and reagent grade bromine were used as received. The halogens were handled in all-glass delivery trains. Reagent grade KBr and KI were crushed and vacuum desiccated before use.

Reagent grade iron wire was cleaned in concentrated HCl, rinsed in deionized H_2O and in reagent grade acetone, then vacuum desiccated. Anhydrous ferrous and ferric chlorides were prepared and purified by sublimation by exposing the iron wire at elevated temperatures to anhydrous HCl and Cl_2, respectively.[22,23]

Vanadium(III) chloride was prepared by thermal decomposition of vanadium(IV) chloride which was prepared by exposing heated 99.5% vanadium metal to anhydrous chlorine.[24,25] The vanadium metal was cleaned by rapid exposure in turn to HNO_3, HCl, HF, deionized H_2O and reagent acetone, then vacuum desiccated and vented to argon.

Electrodes.—Metallic iron electrodes were fabricated by twisting reagent grade iron wire into a coil approximately $^1/_4$ in. × 2 in. Metallic vanadium electrodes were used as supplied (irregular slugs $^3/_4$ in. × $^1/_4$ in.). The iron and vanadium electrodes were cleaned in the manner just described.

Graphite rods of spectroscopic purity were used in $^1/_8$ in. and $^1/_4$ in. diameters. The former were Grade U-1 (medium) Ultra Purity Spectroscopic Graphite Electrodes from United Carbon Products, Inc., Bay City, Michigan, and the

---

(21) E. R. Van Artsdalen and I. S. Yaffe, *J. Phys. Chem.*, **59**, 118 (1955).

(22) H. Biltz and W. Biltz, "Laboratory Methods of Inorganic Chemistry." Authorized translation by W. T. Hall and A. A. Blanchard, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1928.

(23) B. R. Tarr, "Inorganic Syntheses," Vol. III, McGraw–Hill Book Co., New York, N. Y., 1950, p. 191.

(24) J. Koppel, R. Goldman and A. Kaufman, *Z. anorg. Chem.*, **45**, 346 (1905).

(25) R. C. Young and M. E. Smith, "Inorganic Syntheses," Vol. IV, McGraw–Hill Book Co., New York, N. Y., 1953, p. 128.

latter were Catalog No. L3803 Special Graphite Spectroscopic Electrodes from National Carbon Company, Cleveland, Ohio. The rods were boiled in concentrated HCl and deionized water. They were then dried at 140° and vacuum desiccated at 500°. If they were to be used as an electrolysis electrode or as an inert indicator electrode in strictly liquid systems, they were vented to and allowed to cool in dry, O_2-free argon. If the rods were to be used in a chlorine system, they were alternately vented to and flushed with the halogen and reevacuated several times while held at 500° and then allowed to cool in a flowing chlorine atmosphere. If the rods were to be used in a bromine system, they were soaked in liquid bromine. For an iodide system, the rods were vented to iodine vapors then heated and cooled in the presence of solid iodine.

Two types of platinum electrodes were used. The first of these were microelectrodes for polarographic measurements. Their method of fabrication has been reported previously.[26] Both cross-sectional and cylindrical platinum surfaces were used. Microscopic measurements were used to determine their exact projected area.

Macro platinum electrodes were used as the reference electrodes in the potential measurements. For each experiment a fresh platinum reference electrode was prepared by anodization *versus* an electrode such as H at 20 ma. constant current for known lengths of time of a 2 cm.^{2} platinum foil in a compartment of melt to generate Pt(II) coulometrically.[27] From the number of electrochemical equivalents and the volume of solvent in the compartment, the exact concentration of Pt(II) was calculated. The concentration was usually approximately 0.03 *M*. Potentials of platinum electrodes were reproducible to 1 or 2 mv. Both types of platinum electrodes were boiled in $HClO_4$ and dried before insertion into the solvent.

Potential Measurements. Chlorine–Chloride Ion Electrode.—Two identical compartments J containing 6 × $^1/_8$ in. graphite rods K were assembled, heated, evacuated and treated with chlorine, then inserted into a fused salt cell containing solvent and an argon atmosphere. While the compartments were being adjusted, chlorine flow was maintained through C. Then the solvent was forced into the chlorine compartments by turning off the argon efflux at B until the tips of each delivery tube G were barely immersed in melt. Then a minimum but steady flow of argon was maintained. Melt levels inside and outside of the compartments were equalized by adjusting the depth of immersion of J to prevent contamination by flow of solvent through the fritted disk in either direction. While chlorine was flowing at a rate of approximately 6 cm.^{3}/min., the graphite rods K were each anodized at 1 amp. for 3 minutes *versus* a graphite rod in a compartment such as H. Thus, the two chlorine electrodes were identical. Two platinum electrodes P_1 and P_2 whose concentrations of Pt(II) were subsequently found to be 0.0495 and 0.0611 *M* were fabricated. A third platinum electrode P_3 in a test-tube-like compartment (no fritted disk or other salt bridge) was inserted. The concentration of Pt(II) in P_3 was 0.0782 *M*. The potential of P_1 was frequently checked against P_2 and P_3. The average potential difference between P_1 and P_2 was 0.0097 v. which was higher than the theoretical difference of 0.0076 v. The average potential difference between P_1 and P_2 was 0.0138 v. which was slightly lower than the theoretical difference of 0.0143 v. Using the data from all three reference electrodes, the average correction to be applied to P_1 to extrapolate its potential value to 1 *M* Pt(II) was 0.0941 v. with a standard deviation of 0.0014 v.

Bromine–Bromide and Iodine–Iodide Electrodes.—The potentials of these two systems were measured in essentially identical but separate experiments. For these two systems, the platinum electrodes were held in compartments such as J by having a platinum foil at K and using argon as an inert atmosphere inside J. Various amounts of the pertinent potassium halide were placed in compartments such as H, evacuated and vented to argon then inserted into the solvent. A cold finger trap was inserted between the cell A and drying tube B to hold the halogen escaping from A. Drying tubes B and C were vented directly to the atmosphere. Several grams of halogen were dropped into E where they vaporized and replaced the argon inside A but not J. In the case of iodine the portions of A external to the furnace were heated with resistance wire. Additional halogen was added throughout the experiments. Graphite rods, cleaned, dried and treated with the pertinent halogen, were slowly inserted into the compartments containing the pertinent halide. Since large volumes of halogen had been adsorbed by the rods, sufficient halogen was released after insertion of the rods to saturate the solvent in each compartment with halogen and to ensure a halogen atmosphere in cell A. The amount of bromide in each compartment to which bromide had been added was titrated iodometrically after oxidation of the bromide to bromate with hypochlorite.[28] The concentrations of iodide were determined by a conventional potentiometric argentometric titration.

Iron(II)–Iron(0) and Vanadium(II)–Vanadium(0) Electrodes.—Weighed metallic iron and vanadium electrodes were inserted into compartments of melt such as P and anodized at constant current for various lengths of time and the weight losses were recorded. The number *n* of electrochemical equivalents per mole of metal removed was calculated and found to be 2 ± 0.02 for the average of three determinations per metal. Thus, both metals were in contact with solutions of their respective divalent ions. In this solvent, solutions of $FeCl_2$ are essentially colorless and solutions of VCl_2 are very deep violet in color. During some of the determinations of *n*, the flow of constant current was stopped during the determinations. After allowing the solutions to become homogeneous, potential measurements were taken between these metal electrodes and platinum reference electrodes. The exact amount of divalent ion was known from the coulometric data.

Iron(III)–Iron(II) and Vanadium(III)–Vanadium(II) Electrodes.—An indication that Fe(II) could not be oxidized at a platinum surface was shown by the absence of anodic waves on Fe(II) polarograms. Colorless Fe(II) solutions were changed to red solutions by the introduction of Cl_2 gas or by anodization of a graphite rod in solutions of Fe(II). Anhydrous $FeCl_3$ readily dissolved in the solvent to produce red solutions. The red color was diminished by the addition of anhydrous NaF, indicating qualitatively the formation of a fluoride complex of Fe(III).

Solutions of trivalent ions of the two metals were generated from divalent ion solutions by anodization of a graphite rod in solutions of the divalent ions. Potential measurements were taken at various times throughout the generation.

Results and Discussion

Chlorine–Chloride Electrode.—With no differentiation made between the two chlorine–chloride ion electrodes, 165 potential measurements were taken during a 20-hour period between the chloride electrodes and platinum electrode P_1 while the temperature was varied between 410 and 490°. Atmospheric pressure was 750.0 mm. The method of least squares was used to evaluate the relationship between potential and temperature. From the least squares best straight line, the predicted "best" value of the potential of the chlorine electrodes at 450° *versus* the platinum electrode P_1 was 0.4163 volt with a standard error of 0.0016 v. After correction to standard conditions, the standard potential, E^0_M, of the chlorine electrode is +0.3223 v. Several other experiments of a similar nature confirmed this value within 1 or 2 mv. The slope of potential *versus* temperature for the chlorine electrodes and platinum electrode P_1 was −0.334 mv./°C. with a standard error of 0.008 mv./°C.

Bromine–Bromide and Iodine–Iodide Electrodes.—Pertinent data and calculations are given in Tables I and II.

Least squares analysis of the data in Table I gave a value for the rate of change of potential with logarithm of bromide concentration of 0.134

---

[26] H. A. Laitinen, W. S. Ferguson and C. H. Liu, *Anal. Chem.*, **30**, 1266 (1958).

[27] R. A. Osteryoung, Ph.D. Thesis, University of Illinois, 1954.

[28] I. M. Kolthoff and H. Yutzy, *Ind. Eng. Chem., Anal. Ed.*, **9** 75 (1937).

TABLE I

POTENTIAL OF CELL Pt, Pt(II)(1 *M*), Br^-(1 *M*), C, Br_2(1 ATM.)

Bromide, mmoles	Eutectic, ml.	Concn. Br^-, *M*	*E*, v., *vs.* pt. ref.[a]	E^0_M, v.
2.13	3.25	0.637	+0.3045	+0.1749
2.47	4.16	.592	+ .3110	+ .1769
1.96	3.16	.620	+ .3039	+ .1727
2.98	4.17	.731	+ .2960	+ .1758
2.34	2.99	.783	+ .2935	+ .1767
			Av.	+ .1754
			Stand. dev.	.0054

[a] Temperature of operation was 447°. Concentration Pt(II) was 0.0384 *M*.

TABLE II

POTENTIAL OF CELL I_2(1 ATM.), C, I^-(1 *M*), Pt(II)(1 *M*), Pt

Iodide, mmoles	Eutectic, ml.	Concn. I^-, *M*	*E*, v., *vs.* Pt ref.[a]	E^0_M, v.
1.085	4.00	0.271	−0.2165	−0.1966
0.175	3.40	.0515	− .1302	− .2136
2.023	3.60	.558	− .2747	− .2096
1.975	2.95	.670	− .2900	− .2134
			Av.	− .2083
			Stand. dev.	.0080

[a] Temperature of operation was 452°. Concentration Pt(II) was 0.0382 *M*.

with a standard error of 0.014 as compared with the theoretical value at 447° of 0.1430, which was used in Table I. From Table II the least squares rate of change of potential with logarithm iodide concentration was 0.142 with a standard error of 0.008 as compared with the theoretical value at 452°, 0.1440, which was used in Table II.

Iron(II)–Iron(0) and Vanadium(II)–Vanadium(0) Electrodes.—The results of the measurements are shown in Tables III and IV. An experiment similar to the one described in Table III gave an average E^0_M of −1.178 v. with a standard deviation of 0.006 v. The average E^0_M between the latter experiment and the one described in Table III is −1.172 v., which compares favorably with the previously reported value of −1.171 v.[2] The slope of logarithm concentration Fe(II) *versus* measured potential was 0.0616 with a standard error of 0.0006 as compared with the theoretical value of 0.0717 which was used in Table III.

TABLE III

POTENTIAL OF CELL Fe, Fe(II)(1 *M*), Pt(II)(1 *M*), Pt

Anodization time, sec.[a]	Fe(II) generated, mmoles	Concn. Fe(II), m*M*	*E*, v., *vs.* Pt ref.[b]	E^0_M, v.
660	0.0684	15.58	−1.1887	−1.1559
1260	.1306	29.74	−1.1707	−1.1620
1800	.1865	42.49	−1.1621	−1.1646
2400	.2487	56.65	−1.1545	−1.1659
3000	.3109	70.82	−1.1480	−1.1663
2700	.3834	87.34	−1.1422	−1.1671
			Av.	−1.1665
			Stand. dev.	0.0040

[a] Electrode anodized at 20.00 ma. Volume of solvent present was 4.39 ml. [b] Temperature of operation was 450°. Concentration of Pt(II) was 0.0392 *M*. Equilibration time was 10 min.

From the data in Table IV, the statistical slope of potential *versus* log concentration is 0.055 with a standard error of 0.005 as compared with the theoretical value of 0.0717 which was used in Table IV.

TABLE IV

POTENTIAL OF CELL V, V(II)(1 *M*), Pt(II)(1 *M*), Pt

Anodization time, sec.[a]	V(II) generated, mmoles	Concn. V(II), m*M*	*E*, v., *vs.* Pt ref.[b]	E^0_M, v.
303	0.03140	7.930	−1.5729	−1.5285
760	.07876	19.89	−1.5387	−1.5229
1080	.1119	28.26	−1.5286	−1.5238
1800	.1865	47.11	−1.5257	−1.5368
2400	.2487	62.81	−1.5191	−1.5391
3000	.3109	78.51	−1.5140	−1.5410
3610	.3741	94.47	−1.5078	−1.5405
			Av.	−1.5332
			Stand. dev.	0.0079

[a] Electrode anodized at 20.00 ma. Volume of solvent was 3.96 ml. [b] Temperature of operation was 450°. Concentration Pt(II) was 0.0330 *M*. Equilibration time was 20 min.

Polarograms of Fe(II) and V(II) solutions are shown in Figs. 2 and 3, and curve 12, Fig. 4 curves 1 to 4, Fig. 5 and curve 4, Fig. 6. The solutions for the polarograms of Fe(II) were prepared by physical addition of anhydrous $FeCl_2$ to compartments of solvent. The polarograms of V(II) were taken on the solutions shown in Table IV and during the equilibration time. In accordance with expected behavior, as the concentration of divalent ion increased, the height of the reduction waves increased and the potential of the initial portion of the waves became less negative in value. The reduction waves at potentials more negative in value than −0.9 v. are typical of heterogeneous electroreduction processes involving the deposition of a solid metal upon an inert solid metal electrode. In most cases the reduction plateaus were followed by sharp increases of current which attained values beyond the range of the instrument. This "increasing current phenomenon" following a reduction wave was typical of solid microelectrodes when the area of an electrode is increased by deposition of a solid metal. Microscopic examination of platinum microelectrodes after cathodic polarization showed dendritic metallic deposits upon the microelectrode surfaces.

The indications are that the metals do not alloy with platinum, under the present experimental conditions. The deposits were removed easily in a short time by holding the electrode at a potential less negative than the reduction potential. Indications of essential reversibility were also obtained. When the microelectrodes were polarized to −1.9 v. to deposit the metals and then polarized toward less negative values, the rate of change of current with potential was greatest at the residual current and the current changed from positive values to negative values at the same potential.

Iron(II)–Iron(II) and Vanadium(III)–Vanadium(II) Electrodes.—A polarogram recorded after an addition of $FeCl_3$ to a compartment of melt is reproduced in curve 11, Fig. 4. The oxidation of platinum prevented observation of the initial portions of the first reduction wave and anodic waves. Curve 13, Fig. 4, illustrates the effect of adding $FeCl_3$ to a compartment containing a solution of $FeCl_2$. Thus, in the polarograms, the

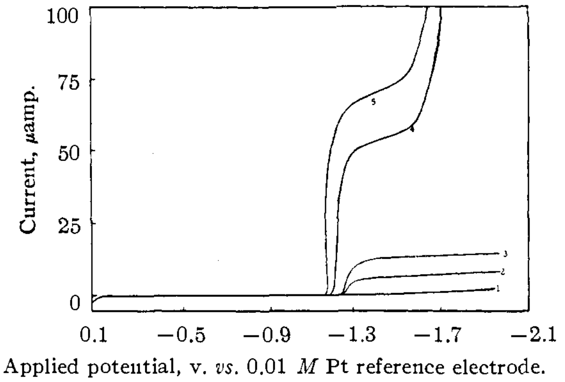

Fig. 2.—Current-voltage curves of $FeCl_2$. Area PME 2,5 = 0.66 mm.[2]; area PME 3,4 = 1.21 mm.[2] Curve 1, residual; concn. for 2, 0.00210 *M*; for 3, 0.00193 *M*; for 4, 0.00976 *M*; for 5, 0.0289 *M*.

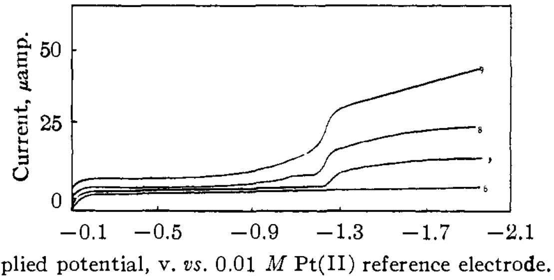

Fig. 3.—Current-voltage curves of $FeCl_3$. Area PME = 1.21 mm.[2] Curve 6, residual; concn. for 7, 0.00332 *M*; for 8, 0.00594 *M*; for 9, 0.0102 *M*.

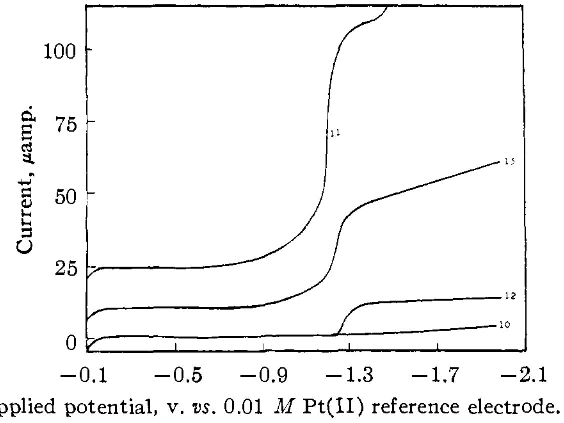

Fig. 4.—Current-voltage curves of iron chlorides. Area PME = 1.21 mm.[2] Curve 10, residual; concn. for 11, 0.0201 *M* Fe(III); for 12, 0.00255 *M* Fe(II); for 13, 0.00511 Fe(III).

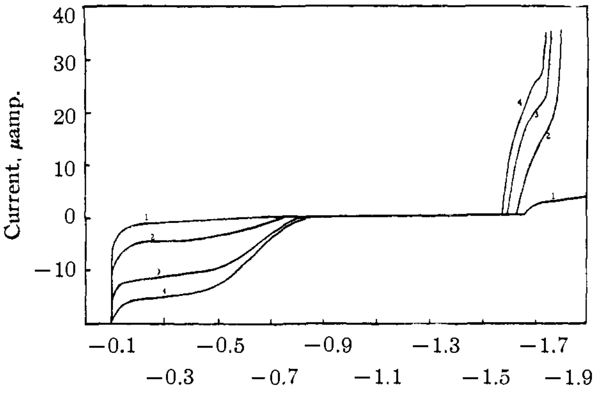

Fig. 5.—Current-voltage curves of vanadium(II) chloride. Area PME = 0.13 mm.[2] Concn. for 1, 0.00793 *M*; for 2, 0.0199 *M*; for 3, 0.0630 *M*; for 4, 0.0946 *M*. Corrected for residual current.

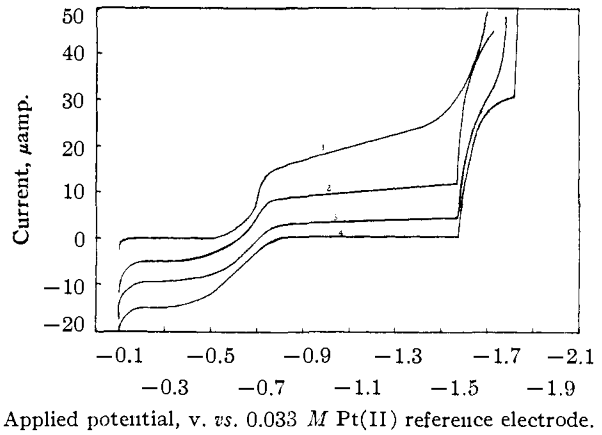

Fig. 6.—Current-voltage curves of vanadium chlorides. Area PME 1, 0.35 mm.[2]; area PME 2, 3, 4 = 0.13 mm.[2] Concn. for 1, 0.0216 *M* V(III); for 2, 0.0472 *M* V(III), 0.0474 *M* V(II); for 3, 0.0286 *M* V(III), 0.0660 *M* V(II); for 4, 0.0946 *M* V(II). Corrected for residual current.

first reduction was Fe(III) going to Fe(II). The second wave, which in some cases also showed the previously discussed "increasing current phenomenon," was Fe(II) going to Fe(0). Dendritic metallic deposits also were found on the microelectrodes.

The polarograms of V(II) show anodic waves. A polarogram of VCl_3, curve 1, Fig. 5, shows two reduction waves. The first wave began at essentially the same potential that the anodic waves of V(II) stopped. The second wave occurs at essentially the same potential as the reduction wave of V(II). Thus, the anodic waves of V(II) are V(II) going to V(III), the first cathodic wave of V(III) is V(III) going to V(II) and the last cathodic wave is V(II) going to the metal.

The data are shown in Tables V and VI. The solutions of divalent ions resulted from constant current anodization of pertinent metal electrodes

TABLE V

POTENTIAL OF CELL Pt, Pt(II)(1 *M*), Fe(II), Fe(III), C

Anodization[a] Time, sec.	Concn. Fe(III)[b] concn. Fe(II)	*E*, v., *vs.* Pt ref.[c]	$E^0{}_M$, v.
300.00	0.05739	+0.0100	+0.0818
600.00	.1218	+ .0619	+ .0868
930.00	.2023	+ .0946	+ .0879
1210.00	.2803	+ .1155	+ .0885
1500.00	.3725	+ .1328	+ .0881
2100.00	.6128	+ .1630	+ .0873
2700.00	.9551	+ .1909	+ .0876
3600.00	1.868	+ .2266	+ .0815
		Av.	+0.0862
		Stand. dev.	0.0028

[a] Electrode anodized at 10.00 ma. [b] Total concentration of Fe was 0.1275 *M*. Volume of solvent was 4.48 ml. [c] Concentration of Pt(II) was 0.0330 *M*. Equilibration time was 10 minutes.

for measured lengths of time. The V(II) solution was the final solution shown in Table IV. The least squares slope for Table V was 0.1434 in exact agreement with the theoretical value which was used in Table V. The least squares slope of log concentration ratio *versus* measured potential for Table VI was 0.1516 with a standard error of 0.0001 as compared with the theoretical value of 0.1434 which was used in Table VI.

TABLE VI

POTENTIAL OF CELL C, V(III), V(II), Pt(II)(1 *M*), Pt

Anodization[a] time, sec.	Concn. V(III)[b] concn. V(II)	*E*, v., *vs.* Pt. ref.[c]	E^0_M, v.
180.00	0.1108	−0.7824	−0.7516
360.00	.2491	− .7330	− .7526
540.00	.4269	− .6895	− .7517
720.00	.6635	− .6680	− .7487
900.00	.9945	− .6414	− .7473
1080.00	1.490	− .6135	− .7445
1260.00	2.312	− .5830	− .7414
		Av.	−0.7483
		Stand. dev.	0.0042

[a] Electrode anodized at 20.00 ma. [b] Total concentration of V was 0.09447 *M*. Volume of solvent was 3.96 ml. [c] Concentration Pt(II) was 0.0330 *M*. Temperature of operation 450°. Equilibration time was 20 minutes.

Polarograms taken after each anodization of the V(II) solution and during the equilibration time are illustrated in Fig. 5. In accordance with expected behavior the anodic wave at potentials less negative than −0.9 v. decreased and the cathodic wave between −0.9 and −1.5 v. increased as the concentration of V(II) decreased and the concentration of V(III) increased.

Vanadium(II) probably could have been oxidized at a platinum surface as easily as it was done at a graphite surface. No indication of oxidation states higher than III for vanadium was found. If V(IV) is stable in this solvent, the standard potential of V(IV), V(III) is positive to the platinum dissolution potential.

Standard potentials E^0_M, E^0_m and E^0_X, extrapolated to unit concentration on the molarity, molality and mole fraction scales, are listed in Table VII. The conversion factors for concentrations are

TABLE VII

STANDARD POTENTIALS

Electrode system	E^0_M, v.	E^0_M, v.	E^0_X, v.
V(II)–V(0)	−1.533	−1.533	−1.533
Fe(II)–Fe(0)	−1.172	−1.172	−1.172
V(III)–V(II)	−0.748	−0.764	−0.854
I_2–I^-	− .207	− .254	− .524
Pt(II)–Pt(0)	.000	.000	.000
Fe(III)–Fe(II)	+ .086	+ .070	− .020
Br_2–Br^-	+ .177	+ .130	− .140
Cl_2–Cl^-	+ .322	+ .306	+ .216

$m = m/1.648$ and $X = N/29.60$ where 1.648 is the density of the melt at 450° and 29.60 is the number of moles of solvent per liter of solvent. From the Nernst equation and the conversion factors, the correction terms from E^0_M to E^0_m and E^0_X are, respectively, $0.0311/n$ and $0.2110/n$, where n is the number of electrons involved in the electrode process. The correction term must be applied to both the electrode system in question and the platinum reference electrode. Whether the correction is added or subtracted depends upon whether the concentration of oxidant or reductant is being extrapolated. Precautions in the use of these values have been discussed previously.[2]

URBANA, ILLINOIS

[CONTRIBUTION FROM THE ISTITUTO DI CHIMICA-FISICA OF THE UNIVERSITY OF ROME]

The Conductance of Tetraethylammonium Picrate in Methanol–Water Mixtures at 25°

BY FILIPPO ACCASCINA, ALESSANDRO D'APRANO AND RAYMOND M. FUOSS[1]

RECEIVED JULY 29, 1958

The conductance of tetraethylammonium picrate in mixtures of methanol and water was measured, in order to study the transition from the case of negligible ionic association (K_A = 0.8) in water to that of moderate association (K_A = 18.9) in methanol. The data conform to the Fuoss equation for associated electrolytes, which is based on the Fuoss–Onsager equation for unassociated electrolytes, and on the hypothesis that any pair of ions in contact must be considered as not contributing to conductance for the duration of the contact. For the diameter of the sphere electrostatically equivalent to the ions, $\mathring{a}$ equals 5.31. The conductance data show the effect of the presence of the dipole in the picrate ion. The Einstein viscosity term leads to an average hydrodynamic radius of 4.27.

Introduction

Ionophores[2] (substances comprised of ions in the crystal form) in water show very slight association and their conductance curves can be reproduced by the Fuoss–Onsager equation[3] which neglects association. In solvents of dielectric constant below 20–25, association occurs to so great an extent that the modified[4–6] Ostwald dilution law can be used to analyze the data, because the Onsager square root term[7] is a satisfactory approximation to the effects of long range electrostatic forces on conductance; the higher terms in the Fuoss–Onsager equation become nearly negligible compared to the effects of pairwise association. By replacing the Bjerrum[8] definition of ion pairs by a physically more realistic one, according to which any two ions in contact are to be counted as a pair (regardless of the magnitude of their potential energy), it was possible to modify[9,10] the Fuoss–Onsager equation and to obtain a

---

(1) On sabbatical leave from Yale University, spring semester 1958. Grateful acknowledgment is made for a Fulbright Grant.

(2) R. M. Fuoss, *J. Chem. Educ.*, **32**, 527 (1955).

(3) R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 668 (1957).

(4) R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 476 (1933).

(5) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

(6) R. M. Fuoss and T. Shedlovsky, THIS JOURNAL, **71**, 1496 (1949).

(7) L. Onsager, *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1927).

(8) N. Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, No. 9 (1926).

(9) R. M. Fuoss, THIS JOURNAL, **79**, 3301 (1957).

(10) R. M. Fuoss and C. A. Kraus, *ibid.*, **79**, 3304 (1957).