of investigators[5,6,7,8,9,10,11,12] have studied metastable double layer liquid systems and obtained S-shaped freezing point curves similar to the present one, but, with the possible exception of Faucon,[9] these investigators fail to mention the identity of the solid phases associated with the systems studied. Had they done so, perhaps, some of the systems would also be found to contain both solid solutions and metastable double layers.

Summary

1. The system iodine monochloride–acetic acid is a simple binary system in which each component depresses the freezing point of the other till a eutectic is formed.

2. The system iodine monochloride–acetic acid forms a series of solid solutions of which the liquidus is represented by an S-shaped curve. A eutectic is formed between the solid solutions and a solid phase of undetermined composition. The components also form a metastable double layer liquid system.

3. Iodine monochloride prepared for use in these researches had a freezing point 0.1° higher than the currently accepted value.

IOWA CITY, IOWA RECEIVED JULY 5, 1940

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(5) Alexjew, *Wied. Ann.*, **28**, 305 (1886).

(6) Roozeboom, *Rec. trav. chim.*, **8**, 257 (1889).

(7) Flaschner, *J. Chem. Soc.*, **95**, 668 (1909).

(8) Coehn, *Chem. Weekblad*, **7**, 277 (1910).

(9) Faucon, *Ann. chim.*, **8**, 19, 70 (1910).

(10) Baume and Georgitses, *J. chim. phys.*, **12**, 250 (1914).

(11) Sidgwick and Ewbank, *J. Chem. Soc.*, **119**, 979 (1921).

(12) Bond and Beach, THIS JOURNAL, **48**, 348 (1926).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

The Potential of the Yb^{+++}-Yb^{++} Electrode

BY GEORGE C. WALTERS[1] AND D. W. PEARCE

The determination of the oxidation potentials of the "anomalous" divalent ions of the rare earths is attended with difficulty due to the instability of these ions,[2] which react more or less rapidly with water or with H$^+$ thus

$$2Yb^{++} + 2H^+ \longrightarrow H_2 + 2Yb^{+++}$$

Because of this difficulty, as well as because of the rarity of certain of the elements involved, few quantitative data concerning the relative stability[3] of these ions are available. Due to the ready coöperation of Professor B. S. Hopkins of the University of Illinois a sample of purified Yb_2O_3, earlier prepared[4] by one of us, was kindly placed at our disposal. We wish to take this opportunity to thank Professor Hopkins for this favor.

The method used for the determination was very similar to that applied by McCoy[5] in his work with the somewhat more stable (E^0 = 0.43 v.) Eu^{++} ion. In general, the method consisted in first reducing electrolytically, to a predetermined extent, a solution of the trivalent ion to the divalent condition; an additional known amount of the trivalent ion was then added and a switch thrown to stop electrolysis and to cut into a prepared potentiometer circuit the set of auxiliary electrodes already dipping into the solution and into a standard half cell. Preliminary experiments were used to determine the approximate[6] potentiometer setting so that in the later runs only a matter of seconds for the final accurate adjustment was required.

Materials.—The chemicals used in the various analytical and electrochemical operations, sodium thiosulfate, glacial acetic acid, iodine, sodium oxalate, potassium permanganate, potassium chloride and oxalic acid, were of the C. P. or A. R. grade. Reagents and solutions were standardized by recognized standard procedures. The water was ordinary distilled water redistilled from alkaline permanganate solution.

The ytterbium sesquioxide was analyzed spectrographically and found to contain a trace of lutecium and a considerable amount of lanthanum. The atomic weight of the mixture was determined using a modified oxalate to oxide, oxalate to permanganate method.[7] This yielded the result 171.025 as the average of 172.06, 171.94, 172.13, 171.96. Disregarding the trace of lutecium present, this average gave by calculation a purity of 96.33% Yb_2O_3 (by weight) for the mixture. The ytterbic acetate solutions were prepared by dissolving weighed amounts of this oxide, previously ignited to constant weight, in hot glacial

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[1] Part of a thesis to be submitted by George C. Walters to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Master of Science in Chemistry.

[2] Pearce and Selwood, *J. Chem. Education*, **13**, 224–230 (1936).

[3] Pearce, *Chem. Rev.*, **16**, 121–147 (1935).

[4] Pearce, Naeser and Hopkins, *Trans. Electrochem. Soc.*, **69**, 557–565 (1936).

[5] McCoy, THIS JOURNAL, **58**, 1578 (1936).

[6] Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, p. 269, estimated the potential of the couple at 0.6 v.

[7] Russell and Pearce, forthcoming publication.

acetic acid, evaporating just to dryness and taking up in the required volume of solution.

Apparatus.—A 150-ml. electrolytic beaker was used as the containing vessel for the ytterbium solution. Through holes in the fiber board cover passed the various electrodes, a buret, a salt bridge and a mechanical stirrer. One glass-covered platinum wire made contact only with a mercury layer on the bottom which served as cathode during the electrolytic reduction; a platinum flag served as anode for this operation. Through two other holes passed glass-covered platinum wires, making contact with the solution, to serve as alternate electrodes in the potential measurements. These had been kept for at least one day before using in acidified ytterbium solutions which facilitated their rapid attainment of a definite potential during the measurements. A Leeds and Northrup student potentiometer–galvanometer, fitted with standard cell, and a normal calomel electrode were used in the measurement of the potential.

Reduction of the Ytterbic Ion.—As a necessary preliminary to the potential measurement, the conditions for the reduction of Yb^{+++} to Yb^{++} such as to yield a suitable concentration of the latter were determined. Twenty-five ml. of 0.0658 *N* ytterbic acetate solution, 1 *N* in acetic acid, was placed in the cell and a steady current of 0.10 amp. at 8 volts was passed for 12.0 hours. At the end of this period the current was shut off and an excess of standard iodine solution run in immediately to oxidize the reduced form. The excess of iodine was then titrated with standard sodium thiosulfate solution. The results of four such determinations gave, as an average, 81.86% reduction in this time and under these conditions.[8] This degree of reduction had to be assumed for the later reductions in which the potential was to be measured, since in these cases it was impossible to determine, with the required accuracy, both the concentration of the ytterbous ion and the potential obtained. This was due to the rapidity of the reaction of the unstable ion with the solution as commented on in the introductory remarks.

TABLE I

Sample	0.0751 *N* I_2, ml.	0.1052 *N* $Na_2S_2O_3$, ml.	Reduction, %
1	25.00	5.00	82.16
2	25.00	5.07	81.76
3	25.00	5.10	81.36
4	25.00	5.00	82.16
			Av. 81.86

Potential Measurements.—Following, then, a 12.0-hour reduction, the electrolysis was stopped, the solution simultaneously thrown into the potentiometer circuit and sufficient solid potassium chloride to make the solution 1 *N* in that constituent and a known volume of standardized ytterbic acetate solution were added. The Yb^{+++}–Yb^{++} solution thereupon became one half of the cell

Pt/Yb^{+++}, Yb^{++}, CH_3COOH, *N* KCl/*N* KCl/*N* KCl, Hg_2Cl_2/Hg

for which *E* was determined.

Various ratios of oxidized form to reduced form were used and liquid junction potentials reduced to a minimum by the presence of a high concentration of KCl in both half-cells and salt-bridge. The data are shown in Table II.

TABLE II

POTENTIAL OF THE Yb^{+++}–Yb^{++} ELECTRODE AT 23.1°

Expt.	*E* meas., v.	$C_{Yb^{++}}$ *M*	$C_{Yb^{+++}}$ *M*	E_0 calcd., v.[a]
1	0.819	0.0153	0.0748	0.578_5[b]
2	.835	.0215	.0621	$.580_8$
3	.836	.0248	.0565	$.576_0$
4	.845	.0277	.0514	$.579_8$
5	.849	.0319	.0468	$.577_8$
6	.857	.0425	.0453	$.577_6$
			Av.	.578 v.

[a] $E_0 = (E - 0.2810) + 0.05875 \log (C_{Yb^{+++}}/C_{Yb^{++}})$.

[b] Pt electrode in the Yb^{+++}–Yb^{++} soln. is charged negatively.

Discussion

The larger E_0 value for Yb^{++} $\rightleftarrows$ Yb^{+++} of 0.578 as compared to that of 0.43 for Eu^{++} $\rightleftarrows$ Eu^{+++} as determined by McCoy, substantiates an argument earlier advanced[2,3] by one of us. The lanthanide contraction, which proceeds from tighter electron binding in the second half of the rare earth group, results in greater stability for these atoms in their normal trivalent state. The tighter binding is expressed also in the decreased color of yttrium group, as compared with cerium group, trivalent ions. The stability of this valence, or the instability of the bivalence, is quantitatively expressed by the potential $M^{+3} \rightleftarrows M^{+2}$. The ytterbous and europous ions are the most stable representatives of this valence in the cerium and yttrium groups, respectively. It is next proposed to measure the potential[9] Sm^{++} $\rightleftarrows$ Sm^{+++}. This will be a very much more difficult determination since the samaric ion cannot, apparently, be reduced electrolytically in aqueous solution; the samarous ion is extremely unstable in contact with water unless it is present in a

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[8] In other cases the volume of the solution after the electrolysis was determined and the decrease from the original value used later as a correction on the concentrations of the ions present.

[9] Latimer, *loc. cit.*, has estimated E_0 = 0.8 v.

very insoluble compound. The thulous ion, for which there is only a little experimental evidence,[3] should be the most unstable of these four principal bivalent rare earth ions.

Conclusion

The oxidation potential of the Yb^{+++}–Yb^{++} electrode is $E_0 = 0.578$ v., sign on the solution. This is considerably greater than that for Eu^{+++}–Eu^{++}, $E_0 = 0.43$ v., but the Yb^{++} ion is the most stable representative of its type in the yttrium group. It is again predicted that the corresponding value for Sm^{+++}–Sm^{++} will be still larger and that for Tm^{+++}–Tm^{++} will be the largest of the four couples.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY, UNIVERSITY OF MINNESOTA]

Amperometric Titrations. VI. The Titration of Sulfate and Some Other Anions with Lead and the Reverse Titrations

BY I. M. KOLTHOFF AND YU-DJAI PAN[1]

In a previous paper[2] the amperometric titration of lead with dichromate or chromate, using the dropping mercury electrode as indicator electrode, has been described. In the present paper results obtained in the amperometric titration of sulfate with lead nitrate are presented, using the same indicator electrode as in previous work. In addition, titrations of oxalate, ferrocyanide and iodate with lead nitrate and the reverse titrations of lead with the different anions have been investigated. The present study does not exhaust the possible application of lead nitrate as a reagent in the amperometric titration of anions. Undoubtedly, several other anions which yield slightly soluble lead salts and which have not been considered in the present work can be titrated amperometrically under the proper conditions. In a subsequent paper we will deal with the titration of molybdate with lead.

Experimental.—The materials were C. P. products which had been recrystallized several times from water and dried at proper temperatures. The dried products were analyzed by standard procedures. The amperometric titrations were carried out at room temperature in the absence of oxygen. Details are given in the previous paper.[2]

Sulfate.—Some thirteen years ago Heyrovsky[3] mentioned that it should be possible to titrate sulfate with lead amperometrically (polarographically). Several years later, his student, Majer,[4] described some of these (polarometric) titrations. In order to suppress the solubility of lead sulfate, Spalenka[5] recommended carrying out the titration in a medium containing 33% ethanol. These authors did not use a simple graphical method in locating the end-point.[2] Majer's graphical method is fairly involved and requires the knowledge of the solubility of lead sulfate in the titration medium. Since this solubility varies greatly with the ionic strength of the medium, the solubility of the precipitate under the working conditions is rarely known exactly, and his procedure is of limited practical application. In our method[2] of locating the end-point a knowledge of the solubility of the precipitate is not required, and it is not necessary, as in Majer's method, to make many measurements close to the end-point.

The following study shows that the amperometric titration of sulfate, even in very dilute solutions, yields satisfactory results, and that conditions can be found under which indifferent salts do not interfere if their concentration is not too great. In Fig. 1 the results of titrations of 50 ml. of 0.01 *M* potassium sulfate with 0.1 *M* lead nitrate are given. In order to suppress maxima one drop of 0.1% methyl red solution was added to the liquid in the cell. The air from the cell was removed, as usual, with nitrogen. After each addition of reagent nitrogen was passed through for one minute, unless otherwise stated, and the current was measured. The titrations were carried out at a potential of the dropping electrode of −1.2 v., at which potential lead yields a diffusion current. All the values of the current have

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[1] From the experimental part of a thesis presented by Y. D. Pan to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the Doctor's degree (1940).

[2] I. M. Kolthoff and Y.-D. Pan, THIS JOURNAL, 61, 3402 (1939).

[3] J. Heyrovsky, *Bull. soc. chim.*, 41, 1224 (1927); Heyrovsky and S. Berezicky, *Collection Czechoslov. Chem. Commun.*, 1, 42 (1929).

[4] V. Majer, *Z. Elektrochem.*, 42, 120, 123 (1936).

[5] M. Spalenka, *Collection Czechoslov. Chem. Commun.*, 11, 146 (1939).