

some of the several polar structures which may be written for these molecules. The moment of *N*-methylbenzothiazolethione shows that contributions from structures involving polarity in the thiazole ring raise the moment only a little above the large value calculated from the normal group moments. The large moments of 2-mer-

captobenzothiazole and 4- and 6-methylmercaptobenzothiazole as compared to the small moment of 2-methylmercaptobenzothiazole show that the former substances exist mainly in the lactam form with the hydrogen on the nitrogen rather than on the sulfur.

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

The Potential of the Ytterbic-Ytterbous Ion Electrode

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According to Walters and Pearce,¹ the ytterbic-ytterbous ion electrode potential is -0.578 volt (negative charge on electrode). Although this value is in essential agreement with the prediction of Latimer,² several considerations throw doubt on its validity.

First, the value of Walters and Pearce would lead to the prediction that ytterbic ions should be reducible by zinc (normal potential -0.76 volt). However, a series of experiments³ by W. A. Taebel⁴ in this Laboratory failed to verify this prediction. Over fifty attempts to reduce aqueous ytterbic chloride solutions by shaking with zinc dust, liquid zinc amalgams and solid amalgamated zinc using various concentrations of hydrochloric acid in the presence and absence of ammonium sulfate, over a temperature range of 0° to 100° failed to give any evidence of reduction. Passage of ytterbic chloride solutions through a Jones reductor into a standard iodine solution showed no measurable reduction of the iodine. Attempts to catalyze the reduction by the presence of other oxidation-reduction systems likewise failed.

Second, it was pointed out in a previous publication⁵ that the polarographic half-wave potential for the reduction of trivalent ytterbium or europium ions to the corresponding divalent ion should be very nearly equal to the normal electrode potential, provided that the reduction process at the dropping mercury electrode is reversible. The half-wave potential for europium was found to

be in agreement with the normal potential given by McCoy.⁶ The half-wave potential for ytterbium, however, was found to be -1.169 volts referred to the normal hydrogen electrode.⁵ Logarithmic analysis of the current voltage curves showed only slight deviations from the theoretical slope (based on reversible electrode behavior) for both europium and ytterbium.

Third, the determinations of Walters and Pearce were made by using a platinum indicator electrode in solutions containing ytterbic and ytterbous ions in a $1 N$ potassium chloride, $1 N$ acetic acid medium. The platinum electrode in such a solution can possess a hydrogen electrode function and assume a potential determined partly by hydrogen ions and partly by the ytterbium. It is well known that divalent ytterbium reacts fairly rapidly in acid solution to produce hydrogen and trivalent ytterbium. Kolthoff and Miller⁷ have shown that when two different potential determining systems exist in the same solution and are not in oxidation-reduction equilibrium, the potential of an electrode in the solution is a function of the potentials of both systems and also depends upon the relative concentrations of the potential-determining substances. The resulting potential, lying between the individual potentials of the two systems and not characteristic of either system, is called a mixed potential.

The dropping mercury electrode, owing to its high hydrogen over-voltage, should be a suitable indicator electrode for the ytterbic-ytterbous systems in solutions of moderate acidity. Preliminary experiments showed that solutions of divalent ytterbium are too unstable to permit accurate polarographic measurements. The step-

(1) G. C. Walters and D. W. Pearce, *THIS JOURNAL*, **62**, 3330 (1940).

(2) W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, New York, N. Y., 1938, p. 269.

(3) Unpublished experiments, private communication.

(4) Present address, Westinghouse Electric and Manufacturing Co., Bloomfield, N. J.

(5) H. A. Laitinen and W. A. Taebel, *Ind. Eng. Chem., Anal. Ed.*, **13**, 825 (1941).

(6) H. N. McCoy, *THIS JOURNAL*, **58**, 1578 (1936).

(7) I. M. Kolthoff and C. S. Miller, *ibid.*, **62**, 2171 (1940).

wise anodic dissolution of ytterbium from a dropping ytterbium amalgam electrode was therefore studied to determine the reversibility of the ytterbic-ytterbous ion system at a mercury surface.

Experimental

A comparison of a dropping mercury electrode with a platinum microelectrode was made to show the possibility of mixed potential behavior with the latter. Figure 1 (curves A, B and C) shows the current-voltage curves obtained by use of a platinum microelectrode in the manner previously described.⁸ These curves show that the evolution of hydrogen occurs more readily at a platinum than at a mercury electrode. The difference in behavior of the two electrodes is shown by curves A and D for the acetic acid-potassium chloride medium used by Walters and Pearce, and by curves B and F for 0.1 *N* ammonium chloride solution. Curve E shows that the reduction of ytterbic ions takes place without interfering ammonium ion reduction at a dropping mercury electrode, whereas in acetic acid-potassium chloride solution (curve D), hydrogen discharge would interfere.

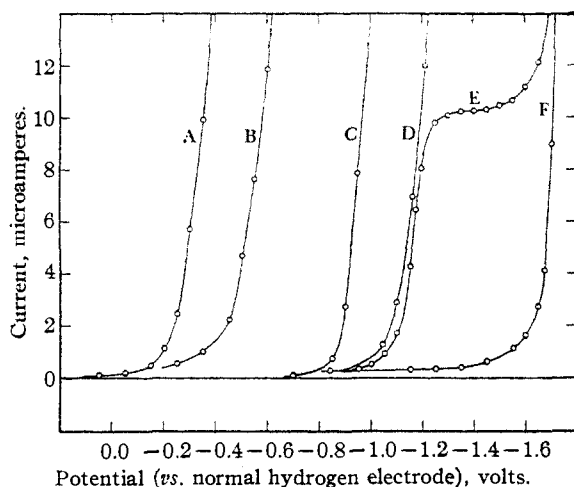


Fig. 1.—Comparison of platinum microelectrode with dropping mercury electrode, platinum microelectrode in: A, 1 *N* acetic acid, 1 *N* KCl; B, 0.1 *N* NH_4Cl ; C, 0.1 *N* KCl, 0.01 *N* KOH. Dropping mercury electrode in: D, 1 *N* acetic acid, 1 *N* KCl; E, 0.003 *M* YbCl_3 , 0.1 *N* NH_4Cl ; F, 0.1 *N* NH_4Cl .

It is apparent that if the mercury electrode shows a reversible ytterbic-ytterbous potential, the platinum electrode in any aqueous solution must give an erroneous value in the direction of more positive potential. On the other hand, the potential of the europic-europous electrode, as measured by McCoy⁹ is reliable on this basis because of its less negative value (-0.43 volt) and the fact that the measurements were made in solutions of relatively low acidity (small concentration of formic acid), with relatively great (0.1 *M*) concentrations of europium.

A dilute ytterbium amalgam, free of sodium or potas-

(8) H. A. Laitinen and I. M. Kolthoff, *J. Phys. Chem.*, **45**, 1061 (1941).

sium, was prepared by a modification of the method described by McCoy.⁹ A solution containing 6.0 g. of ytterbic acetate and 20 g. of citric acid was made alkaline with freshly prepared, sodium-free, tetramethylammonium hydroxide and diluted to 200 ml. A dilute ytterbium amalgam was prepared by electrolyzing the solution for three hours, using a current of 1 ampere (current density 0.05 amp./sq. cm.) and 100 ml. of mercury provided with mechanical stirring as a cathode. The solution was kept near room temperature by water cooling. The amalgam was drawn off, washed with water and with absolute alcohol, and stored under an atmosphere of pure, dry nitrogen. Portions of the amalgam were diluted about tenfold with freshly redistilled mercury and introduced in a nitrogen atmosphere into a dropping electrode reservoir. The final diluted amalgams contained approximately 0.001% ytterbium and were found to remain constant in composition (determined from the magnitude of the anodic current) for a period of two weeks. Current-voltage curves were determined by the usual polarographic technique¹⁰ with the amalgam dropping into air-free solutions of 0.1 *N* ammonium chloride and 0.1 *N* potassium chloride. Nearly identical results were obtained with the two different solutions. An external saturated calomel reference electrode was used in a cell of the type previously described.¹¹ The resistance of the cell was so low (500 ohms) that corrections for iR drop were negligibly small.

Current-voltage measurements were made with a Fisher Electropode and a Heyrovsky Polarograph. Residual current measurements were made by replacing the amalgam by pure mercury using the same capillary. All curves described below have been corrected for residual current.

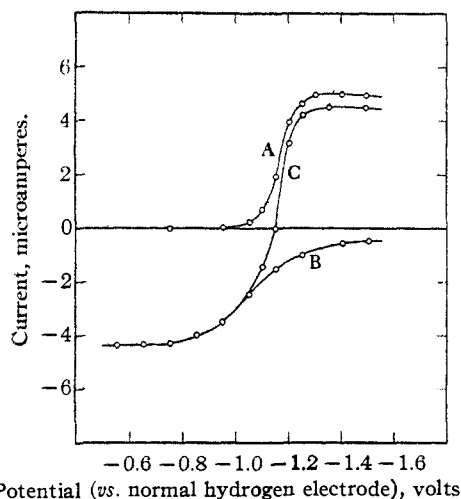


Fig. 2.—Reduction of Yb^{+++} and oxidation of Yb^{++} : A, dropping mercury electrode in 0.0015 *M* YbCl_3 , 0.1 *N* NH_4Cl ; B, dropping Yb amalgam electrode in 0.1 *N* NH_4Cl ; C, dropping Yb amalgam electrode in 0.0015 *M* YbCl_3 , 0.1 *N* NH_4Cl ; all curves corrected for residual current

(9) H. N. McCoy, *THIS JOURNAL*, **63**, 1622 (1941).

(10) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.

(11) J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

A typical set of curves using a medium of 0.1 *N* ammonium chloride is shown in Fig. 2. Curve A shows the reduction of 0.0015 *M* ytterbic chloride on a mercury surface, and differs from curve E, Fig. 1, only in having been made with an ytterbium solution of half the concentration. Curve B shows the anodic dissolution of ytterbium from a dilute amalgam, and curve C shows the result of dropping the amalgam into 0.0015 *M* ytterbic chloride in 0.1 *N* ammonium chloride.

Discussion

The anodic dissolution of ytterbium from a dropping amalgam occurs in two steps, resulting in a double anodic wave. The first wave corresponds to the process $\text{Yb(Hg)} \rightarrow \text{Hg} + \text{Yb}^{++} + 2e^-$. Its beginning occurs at a potential more negative than the reduction of ammonium or potassium ions and is therefore not shown in Fig. 2. The second wave corresponds to the transition from divalent to trivalent ytterbium and should have the same half-wave potential as the reduction wave of trivalent to divalent ytterbium on a mercury surface, if both processes are strictly reversible.

In Fig. 2, the two anodic steps are evident, although the magnitude of the diffusion current in the first anodic wave is much less than the expected two-thirds of the total anodic current. In a previous publication⁵ evidence was given for a reaction between ytterbous ions at the dropping electrode surface with water or hydrogen ions in the solution. The reduction of the ytterbic ions thus produced causes a cathodic (positive) current which compensates a part of the first anodic wave. In effect, a catalytic hydrogen discharge can occur at potentials at which divalent ytterbium can exist at the electrode surface.

The curve obtained by plotting $\log i/(i_d - i)$ against the electrode potential for curve B (Fig. 2) is a straight line of slope 0.200 volt rather than the theoretical 0.059 volt (at 25°) calculated for a reversible electrode process. Apparently the oxidation process $\text{Yb}^{++} \rightarrow \text{Yb}^{+++} + e^-$ is less

reversible on a dropping amalgam surface than the corresponding reduction process (curve A) which shows a logarithmic slope of 0.066 volt.⁵ The half-wave potential of curve B is -1.05 volts, whereas the corresponding value for the reduction process is -1.169 volts. The half-wave potential of the composite curve C is -1.154 volts.

Since the oxidation process was not found to be strictly reversible, attempts to establish an exact value of the ytterbic-ytterbous potential by this method were abandoned. However, it can be stated that the value must lie between -1.05 and -1.69 volts, the latter value being considerably more probable than the former, because of the closer approach to reversible electrode behavior. The value of -1.15 volts obtained from the composite curve is suggested as the most probable normal potential.

Summary

The accepted value of the ytterbic-ytterbous ion electrode potential is criticized on the basis of chemical and electrochemical evidence. It is pointed out that erroneous results will in general be obtained with a platinum indicator electrode in solutions of ytterbic and ytterbous salts because of mixed potential behavior.

The anodic dissolution of ytterbium from dilute dropping amalgams has been studied, and compared with the reduction of trivalent ytterbium on a mercury surface. It is concluded that the potential of the ytterbic-ytterbous ion electrode must lie between the values of -1.05 and -1.169 volts with the latter value being considerably more probable because of a closer approach to reversibility. The half-wave potential obtained with an ytterbium amalgam dropping into an ytterbic salt solution is -1.15 volts. This value is suggested as the most probable value of the normal potential of the ytterbic-ytterbous ion electrode.

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