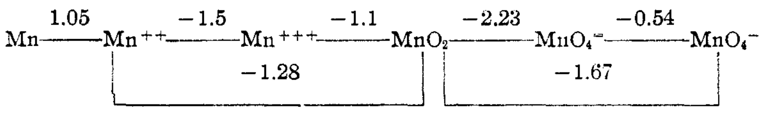
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Oxidation Potential–Free Energy Diagrams

BY ARTHUR A. FROST

A new type of diagram is presented which shows both free energy and oxidation potential data conveniently. Standard free energy is plotted against the oxidation state for an element. The standard oxidation potential is the negative slope of the line joining any two states forming a couple.

Oxidation potential diagrams have been used, particularly by Latimer,[1] to summarize the chemical interrelations of the oxidation states of a given element. As an example take the case of manganese in acid solution



The numbers are the standard oxidation potentials in volts for each couple indicated, with reference to the H_2–H^+ couple.

This type of diagram, although of great value, is often confusing because of the lack of additivity of potentials. The potential for a given two-electron process is the average of the potentials of the two successive one-electron processes. More generally, a weighted average must be used if successive processes involve unequal numbers of electrons.

Now the oxidation potential, $\mathcal{E}$, is related to the free energy change in the reaction ΔF, through the formula

$$\Delta F = -n\mathfrak{F}\mathcal{E}$$

where n is the number of equivalents reacting and $\mathfrak{F}$, the Faraday. Since free energy is a conservative quantity it appears that the oxidation potential diagram might conveniently be replaced by a free energy diagram similar to a spectroscopic energy level diagram. For example, the manganese relations would appear as in Fig. 1.

Free energy	Oxidation state	Formula
+5.47 e.v.	+7	MnO_4^-
+4.93	+6	$MnO_4^{=}$
⋮	⋮	⋮
+0.46	+4	MnO_2
0	0	Mn
−0.6	+3	Mn^{+++}
•	•	•
−2.10	+2	Mn^{++}

Fig. 1.—Manganese free energy level diagram.

The standard free energy scale attached is in terms of electron volts as the unit. This is convenient since the difference between two energy levels for one-electron processes gives the oxidation or reduction potential. The zero of free energy is taken as usual as that of the uncombined element. For ions such as Mn^{++} and Mn^{+++} the $\Delta F°$ of the level is the standard free energy of formation, but for any molecule or ion containing oxygen the $\Delta F°$ is that for the formation of the species minus the $\Delta F°$ of formation of a number of molecules of water equal to the number of oxygen atoms in the molecule or ion. Or, stated more generally, the $\Delta F°$ to be used is the $\Delta F°$ for the half-reaction in going from the element to the reduced or oxidized form under consideration. In case the formula involves more than one atom of the element which is oxidized or reduced the $\Delta F°$ is to be calculated per atom.

The oxidation states, as shown in the center column of Fig. 1, are not in order with the levels in the case of manganese nor are they for most metals. The diagram immediately indicates that Mn^{++} is the stable state of manganese in acid solution, in relation to the H_2–H^+ couple, and that MnO_4^- is the most unstable state. However, a fault of this type of diagram is that the oxidation potential for any given couple is not immediately obvious. For our units of electron volts for free energy $\Delta F° = -n\mathcal{E}°$ or $\mathcal{E}° = -\Delta F°/n$. It is necessary to divide the free energy differences between levels by the number of electrons involved. For example, to predict a value for the standard oxidation potential of the couple $Mn^{++} \rightarrow MnO_4^-$ the result will be

$$\mathcal{E}° = -[5.47 - (-2.10)]/_5 = -1.51 \text{ volts}$$

Since in working with this free-energy diagram it may be inconvenient to make even this simple calculation when potentials are desired, and since the oxidation states are out of order, the following two-dimensional free energy oxidation state diagram was devised. Figure 2 shows the standard free energies, as calculated above for the manganese states, plotted against oxidation state. This diagram has the advantage of showing free energy and oxidation state conveniently and furthermore of giving a simple presentation of oxidation potentials for the various couples inasmuch as *the oxidation potential is the negative slope of the line joining two points* because $\mathcal{E} = -\Delta F/n$ and ΔF is the ordinate and n is the difference in oxidation state number. The steepness of the line for a given couple is a measure of the tendency for the couple to react in the direction yielding the product at the lowest free energy. A positive slope means a tendency for the couple to oxidize H_2 to H^+ while a negative slope shows a tendency toward reduction. Actually with this diagram no thought need be given to the meaning of a positive or negative potential or to the convention that is being used. One only need remember a simple analogy to the motion of a particle in a gravitational field. Consider the "curve" of the diagram as the profile

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[1] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938.

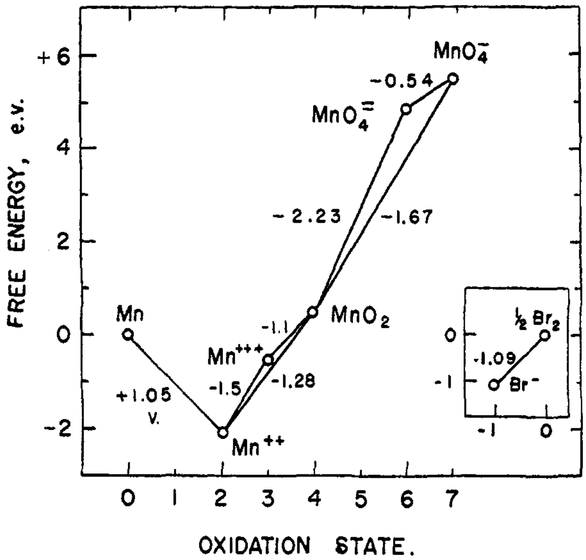

Fig. 2.—Manganese free energy–oxidation state diagram for acid solution.

of two hills and a valley. The force is given by the negative of the slope and is greater in magnitude the greater the slope. The tendency for a reaction to occur depends on the slope rather than directly on the decrease in energy. The downhill direction indicates unequivocally whether the oxidation state should increase or decrease with a particular couple.

When the other couple involved in the reaction is not H_2–H^+ the tendency for reaction must be judged by the relative values of the slopes of the two couples. Consider, for example, the couple Br^-–Br_2 with an oxidation potential of -1.09 volts. This couple would appear on a bromine free energy oxidation state diagram with a positive slope of 1.09. This slope being less than the slopes for both the Mn^{++}–MnO_2 and MnO_2–MnO_4^- couples it is evident that both MnO_2 and MnO_4^- are capable of oxiding Br^- to Br_2.

The question of the stability of aqueous solutions is easily answered by a glance at the diagram. First of all, reduction of water to hydrogen may occur if a couple such as Mn–Mn^{++} has a greater negative slope than about -1 volt allowing an overvoltage of about 0.5. For oxidation of water to evolve oxygen gas a slope of about $+1.5$ volts is required, realizing that an overvoltage or extra potential is required to provide free energy of activation for an otherwise slow reaction. Therefore, any couples with slopes greater in magnitude than these values would indicate instability. These rules must be applied with caution inasmuch as many potentials are functions of the *p*H. In particular, when there is a change in the number of oxygen atoms as in going from Mn^{++} to MnO_2 or MnO_2 to MnO_4^-, but not for the couple $MnO_4^=$ to MnO_4^-, an increase in *p*H favors the state with more combined oxygen (see Fig. 3).

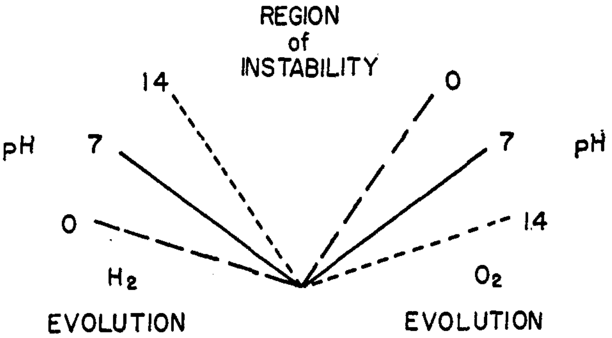

Fig. 3.—Instability in aqueous solution.

Stability with respect to disproportionation is also easily answered by a glance at the diagram. If the curve has a maximum it is obvious that simultaneous oxidation and reduction of the form located at that point would take place spontaneously. But other cases are more common such as is evidenced by Mn^{+++} and $MnO_4^=$. Disproportionation will tend to occur if the ΔF of the molecule or ion under consideration lies above the straight line joining the two neighboring forms. This is true because the free energy of the products of such a reaction may be calculated to be that given by the point on the line directly below. On the other hand MnO_2, which has a free energy below that which would correspond to the intersection of a straight line joining Mn^{++} and MnO_4^- with the $+4$ ordinate, is formed from a solution containing these two as reactants.

A possible criticism of this free energy oxidation state diagram as a competitor of the simpler oxidation potential diagram is that the slopes may not be as easily or accurately recognized as are the direct numerical values of the oxidation potentials. These values can be put opposite the lines associated with various couples but it also should be realized that they could just as well be omitted since the diagrams serve only a semiquantitative purpose as an aid in the descriptive chemistry of the elements. To make quantitative predictions it would be necessary to make corrections for concentration or activity and also to realize that the rate of reaction may be of suprene importance in determining what reaction will be observed.

These diagrams may have their usefulness extended by including curves for different *p*H's or by plotting members of the same group together.

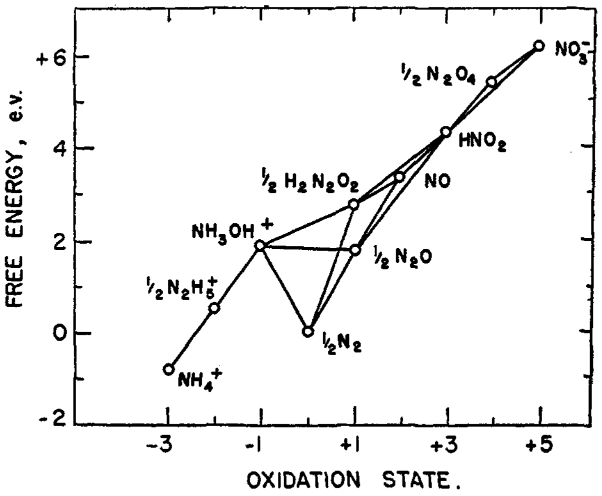

Fig. 4.—Nitrogen free energy–oxidation state diagram fo nitrogen acid solution.

Also if sufficient data were available it would be a simple matter to include rate information by showing free energies of activation as free energy humps[2,3] associated with each couple.

An additional example of a free energy oxidation state diagram calculated, using data from Latimer, is shown in Fig. 4.

The author wishes to acknowledge helpful discussions of this idea with many of his colleagues at Northwestern University.

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(2) Bancroft and Magoffin, *J. Franklin Inst.*, **224**, 283 (1937).

(3) Remick, THIS JOURNAL, **69**, 94 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF METALLURGY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Thermodynamic Properties of Liquid Ternary Cadmium Solutions[1]

BY JOHN F. ELLIOTT AND JOHN CHIPMAN

The ternary systems cadmium–lead–bismuth, cadmium–lead–antimony and cadmium–lead–tin have been investigated by electrode-potential methods over the temperature interval of 380 to 600°. The properties ΔF^x, ΔS^x, ΔH, $\Delta \bar{F}_i^x$, $\bar{L}_i$ and activities are computed for the three ternary solutions and the lead–tin binary solution at 500°. They are best summarized by reference to the appropriate figures in the text.

Up to the present time, thermodynamic studies of liquid alloys containing more than two components have been concentrated on very small portions of the multicomponent field. Consequently highly specific information has been accumulated and little is known regarding the general thermodynamic behavior of multicomponent metallic systems. Recently Darken[2] has clarified the treatment of tertiary systems by showing that a molal thermodynamic property (and in turn the corresponding partial molal quantities) may be computed for the whole of an isobaric, isothermal, single-phase ternary system if the partial molal property of one component is known over the ternary field. Compositions represented by a line with constant ratio of component 1 to component 3 crossing the ternary field to the apex of pure component 2 are treated as a binary system. Darken has demonstrated that the familiar methods for determining partial molal properties are applicable to this pseudo-binary system.

This paper describes an electrochemical study of three ternary metallic systems in the liquid phase and utilizes Darken's methods to determine the molal and partial molal properties, free energy, heat of solution and entropy. The electrode-potential method described in a previous paper[3] was used to evaluate the thermodynamic properties of cadmium for several pseudo-binary lines crossing each of the ternary fields in the systems cadmium–lead–bismuth, cadmium–lead–antimony and cadmium–lead–tin. The properties of the component binary systems are taken from the earlier paper and from other published data.

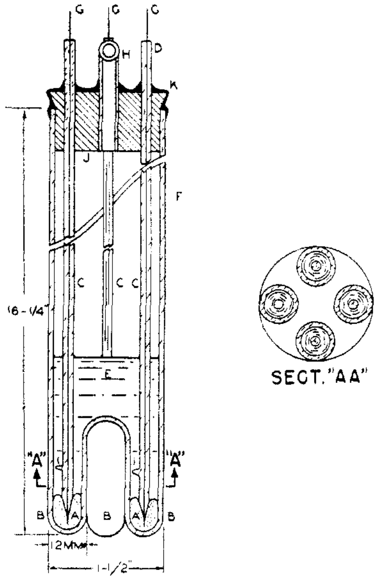

Fig. 1.—Design of cell.

Experimental Method

The experimental technique, equipment and materials will be described only briefly, as they have been discussed in considerable detail in the preceding paper.[3] The electrode-potential measurements were obtained from four-legged Pyrex-glass cells (Fig. 1). The cathode alloys were placed in three of the four legs and the pure anode, the most electropositive metal in the alloys, was placed in the fourth. Liquid electrolyte, the eutectic mixture of lithium and potassium chlorides containing about 5% of the chloride of the most electropositive metal, was poured in the cell. The system was sealed and evacuated to degas the electrodes and electrolyte. Subsequently the lower portion of the cell was placed in a lead-bath and the potentials between the cathodes and anode were obtained for five to six temperatures between 380 and 600°. Measurements above 575° were discarded since unsteady readings were noted occasionally near 600°. The estimated limit of error in the data is approximately 0.05 mv. for potentials below 10 mv. and 0.10 mv. for those above.

Cadmium–Lead–Bismuth Solution

Two master binary alloys with the atomic ratios of lead to bismuth of 1.974:1.000 and 1.000:2.000 were prepared. (For convenience these alloys will subsequently be called Series 1 and 2, respectively, and the atomic ratios of lead to bismuth will be approximated by the figures 2:1 and 1:2.) Pure bismuth and lead were alloyed at 350° under an eutectic cover of potassium and lithium chlorides and then sticks of the alloys were chill cast. Subsequent analyses of the alloys and of electrodes prepared from the alloys showed that there was no significant segregation during casting.

The cell electrodes were prepared by alloying in the cell legs previously weighed sticks of cadmium and master alloys. Preparing the electrodes in this manner gave two series of alloys which cross the ternary field from the base binary

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[1] This paper is based upon a thesis submitted by John F. Elliott in partial fulfillment of the requirements for the degree of Doctor of Science at the Massachusetts Institute of Technology.

[2] L. S. Darken, THIS JOURNAL, **72**, 2909 (1950).

[3] J. F. Elliott and J. Chipman, *Trans. Faraday Soc.*, **47**, 138 (1951).