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APPLIED THERMODYNAMICS IN HIGH TEMPERATURE REFRACTORIES SYSTEMS

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### Author

Searcy, Alan W.

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REFRACTORIES SYSTEMS**

**Berkeley, California**

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Alan W. Searcy

July 16, 1965

APPLIED THERMODYNAMICS IN HIGH TEMPERATURE REFRACTORIES SYSTEMS\*

Alan W. Searcy

Inorganic Materials Research Division, Lawrence Radiation Laboratory,  
and Department of Mineral Technology, College of Engineering,  
University of California, Berkeley, California

July 16, 1965

Perhaps there is no more appropriate way to begin this lecture on applications of thermodynamics to studies of high temperature chemistry than by repeating a statement of the first and second laws of high temperature chemistry which I first suggested for the guidance of frequently frustrated high temperature scientists and engineers at a conference in 1959:<sup>1</sup> (1) at high temperatures everything reacts with everything else, and (2) the higher the temperature, the more seriously everything reacts with everything else.

These "laws" can be viewed as the factitious hybrid that results from crossing the laws of thermodynamics with bitter experience. And because continual evaluation of experience in terms of the laws of thermodynamics provides the best single avenue for expanding our understanding of high temperature reactions, the first and second laws of high temperature chemistry provide the theme for one of the two principal sections of this lecture: a discussion in simple thermodynamic terms of how and why equilibria in chemical and physical processes change with temperature.

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\*Presented as an educational lecture before the Electrothermics and Metallurgy Division of the The Electrochemical Society, San Francisco, May 11, 1965.

The other principal section of the lecture is dependent in part on the first. This second section describes the development for high temperature use of something equivalent to the familiar activity series, which has a value in facilitating systematic prediction and understanding of aqueous reactions that is thoroughly appreciated by all electrochemists. Most of the ideas of this lecture have been presented at greater length and with an extensive list of references in one of several recent papers.<sup>2-4</sup>

The Exponential Increase in Disorder with Temperature<sup>4</sup>

If complete equilibrium could be established at absolute zero for any set of chemical elements, the maximum number of phases formed would be predictable by the phase rule. Any changes in the proportions of the various elements present at that temperature would change the relative proportions of the phases present but would not change the composition of any of the phases--that is at absolute zero, Dalton's Law of Definite Proportions is obeyed.\*

Why Dalton's law is obeyed at absolute zero is readily understood in terms of thermodynamics plus experience: at absolute zero, thermodynamics tells us that the stable phase, or set of phases, will be that phase, or those phases, in proportions and at the compositions that have the minimum possible enthalpy of formation per gram atom of material, i. e., the maximum bond energy per atom. Experience teaches us that

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\*Scientific caution requires that I admit that this statement, while widely accepted, is unproved, and I can conceive of possible exceptions. These exceptions, however, are not important to the line of argument here developed.

enthalpies of formation per gram atom vary in such a way that lower values of the enthalpy of formation per gram atom are obtained by changing the proportions of the phases than by varying the compositions of the individual phases.

Thermodynamics further tells us that at any temperature above absolute zero the state of maximum stability is no longer that of minimum enthalpy but that of minimum free energy per gram atom. Now, the free energy change for any process is related to the enthalpy change for the process by

$$\Delta F = \Delta H - T\Delta S, \quad (1)$$

where  $\Delta F$  is the free energy change,  $\Delta H$  is the enthalpy change,  $T$  is the absolute temperature, and  $\Delta S$  is the entropy change.

The entropy change in any process is a reflection of the change in order that characterizes the process. Experience, amply bolstered and explained by statistical mechanical theory, teaches us that all disordering events such as order-disorder transitions, fusion, vaporization, and solution of one substance in another produce an increase in entropy. Experience again teaches us that for any given process, changes in entropies and enthalpies with temperature are relatively small and tend to cancel with respect to their effect on the free energy. Accordingly, we can for qualitative discussions treat both entropy and enthalpy as independent of temperature.

We then see by reference to Eq. (1) that any equilibrium changes that occur as the result of an increase in temperature are characterized by an increase in total entropy, i.e., increased disorder, at the expense

of an increase in the enthalpy, i. e., a decrease in the total bond energy per atom. Thus, for example, a reversible transition from a low temperature to a higher temperature modification of a solid is accompanied by an increase in entropy and enthalpy. The italicized rule which I first saw applied by Buerger<sup>5,6</sup> in reference to crystallographic changes is valid for all equilibrium changes. I have called it the principle of successive entropy states.

As a more specific example of the principle, the heat of the reaction between  $\alpha$ -iron saturated with oxygen and magnetic iron oxide saturated with iron to form wustite (approximately FeO) at 570°C must necessarily be endothermic (Fig. 1). On the other hand, we cannot know without experimental measurements whether the reaction of Fe<sub>2</sub>O<sub>3</sub> with iron to form wustite is exothermic or endothermic because iron and Fe<sub>2</sub>O<sub>3</sub> are not at equilibrium at any temperature.

Another implication of Eq. (1) is that any reaction that occurs exothermally during heating is necessarily irreversible. For example, if we heat silicon with graphite to high temperatures we may observe a highly exothermic reaction to form silicon carbide. This reaction must be irreversible at and near the temperature at which it is observed. Furthermore, because the reaction is highly exothermic, we can be confident that silicon carbide will remain stable with respect to decomposition back to elemental silicon and carbon on cooling to any lower temperature. No reasonable changes of  $\Delta H$  or  $\Delta S$  for the reaction with temperature could be sufficient to reverse the equilibrium at lower temperatures. We cannot be sure, however, that silicon carbide may not be unstable at low temperatures relative to decomposition to silicon



and some presently unknown silicon carbide phase such as  $\text{SiC}_2$  or to carbon and some presently unknown phase such as  $\text{Si}_2\text{C}$ .

By introducing now the definition of activity in terms of free energy, we place ourselves in a position to explore the implications of Eq. (1) to the effect of temperature upon the equilibrium solubilities of one phase in another and upon the equilibrium concentration of defects such as vacancies and interstitial atoms. The activity  $a_i$  of any component  $i$  can be defined by the equation  $RT \ln a_i = \overline{\Delta F}_i$ , where  $R$  is the gas constant and  $\overline{\Delta F}_i$  is the difference between the partial molal free energy of component  $i$  and the partial molal free energy when component  $i$  is in its standard state. Now if two components  $L$  and  $M$  react to form one gram atom of solution in which the mole fraction of  $L$  is  $X_L$ , for the reaction  $X_L L + (1 - X_L)M = L_{X_L} M_{(1 - X_L)}$ ,  $\Delta F = X_L \overline{\Delta F}_L + (1 - X_L) \overline{\Delta F}_M = X_L RT \ln a_L + X_M RT \ln a_M$ . This same expression can be used to describe the free energy change even if the composition  $L_{X_L} M_{X_M}$  corresponds to an intermediate phase, or for that matter even if it corresponds to the composition of a two-phase mixture of stable intermediate phases. We need only choose to retain the pure components as the standard states and express the activity of each component accordingly.

Suppose now that it happens that component  $L$  and component  $M$  of a two-phase system form no intermediate phases and are only very slightly soluble in each other. If the system is brought to equilibrium,  $L$  dissolves enough  $M$  and  $M$  dissolves enough  $L$  so that  $a_L(L_{\text{sat}}) = a_L(M_{\text{sat}})$  and  $a_M(L_{\text{sat}}) = a_M(M_{\text{sat}})$ , where  $M_{\text{sat}}$  means  $M$ -phase saturated with  $L$  and  $L_{\text{sat}}$  means  $L$ -phase saturated with  $M$ .

In dilute solid solutions, generally up to at least 1 at.% solute, Henry's law behavior is closely approximated by the solute and Raoult's law behavior is approximated by the solvent. Focusing our attention on the activity of component L, we see that  $RT \ln a_{L(M_{\text{sat}})} = RT \ln a_{L(L_{\text{sat}})} = \overline{\Delta F}_L = \overline{\Delta H}_L - T\overline{\Delta S}_L$ , where  $\overline{\Delta H}_L$  and  $\overline{\Delta S}_L$  are the partial enthalpy and partial entropy that correspond to  $\overline{\Delta F}_L$ . But for low solubilities  $a_{L(L_{\text{sat}})} = X_{L(L_{\text{sat}})} \cong 1$  so that  $RT \ln a_{L(L_{\text{sat}})} \cong 0$  and  $\overline{\Delta S}_L$  can be written as  $-R \ln X_{L(M_{\text{sat}})} + \overline{\Delta S}_{L(M_{\text{sat}})}^e$ , where  $-R \ln X_{L(M_{\text{sat}})}$  is a configurational contribution to the partial entropy which statistical mechanical considerations demonstrate we should expect for dilute solutions and  $\overline{\Delta S}_{L(M_{\text{sat}})}^e$  is any other entropy change that may accompany the transfer of L to the saturated solution of L in M. Thus,  $RT \ln a_{L(M_{\text{sat}})} \cong 0 \cong \overline{\Delta H}_L(M) - T [ -R \ln X_{L(M)} + \overline{\Delta S}_{L(M)}^e ]$  so that finally we get by rearranging and writing in exponential form

$$X_{L(M_{\text{sat}})} = e^{-\overline{\Delta H}_L(M)/RT} e^{\overline{\Delta S}_{L(M)}^e/R} \quad (2)$$

But  $a_{L(M_{\text{soln}})} = \gamma^\circ X_{L(M_{\text{soln}})}$ , where  $\gamma^\circ$  is the activity coefficient. But  $\gamma^\circ$  is independent of composition over the Henry's law range, and because here  $a_{L(M_{\text{sat}})} \cong 1$ ,  $\gamma^\circ = 1/X_{L(M_{\text{sat}})}$  so that the product  $e^{\overline{\Delta H}_L(M)/RT} e^{-\overline{\Delta S}_{L(M)}^e/R}$  must be a constant equal to  $\gamma_L^\circ$ . For this product to be independent of composition (but, of course, dependent on temperature), both  $\overline{\Delta H}_L(M)$  and  $\overline{\Delta S}_{L(M)}^e$  must be independent of composition in the Henry's law range. Finally, since  $X_{L(M)} = a_{L(M)}/\gamma^\circ$  we can write

$$X_{L(M)} = a_{L(M)} e^{-\overline{\Delta H}_L(M)/RT} e^{\overline{\Delta S}_{L(M)}^e/R} \quad (3)$$

This expression tells us that for dilute solutions if we know the activity we can predict the temperature variation of solubility just as we can do when the activity is unity so that if one or more intermediate phases of known stability are formed we can still predict the variation of solubility with temperature. The slope of a plot of  $-R \ln X_{L(M)}$  vs  $1/T$  at constant solute activity is the partial heat of solution of the solute in the solvent and the intercept should be the excess partial entropy of solution. Determination of the solubility at two temperatures allows prediction of the solubility over a range of temperatures.

We can now see why at high temperatures everything reacts with everything else and why the higher the temperature the more seriously everything reacts with everything else. Each stable phase is in a minimum enthalpy state at absolute zero so that the enthalpy of reaction of these stable phases to form solid solutions is always positive. Equation (3) requires that mutual solubilities of phases that mix endothermally will increase with temperature.

If the partial enthalpy of solution of one solid in the other is high, the actual level of solution may remain low, but it must be finite at any finite temperature. Any transformation of one of the solids to a higher temperature modification necessarily results in a lower bond energy per atom so that the partial enthalpy of solution of the second phase in this high temperature modification is usually (but not always\*)

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\* For example, solution of carbon in transition metals requires the carbon to occupy interstitial sites in the metal lattice. The solubility of carbon in  $\delta$ -iron is decreased over that in  $\gamma$ -iron because the unfavorable strain energy that must be overcome to place carbon atoms on the more sterically crowded sites in  $\delta$ -iron is greater than the small favorable energy of transition between  $\gamma$ - and  $\delta$ -iron.

decreased over that in the lower temperature modification. The entropy change that characterizes solution of the second phase in the high temperature modification of the first solid is usually little different from that in its low temperature modification. Equation (2) tells us that a lower partial enthalpy of solution in the high temperature modification coupled with an unchanged entropy will result in an increased solubility. Fusion of either phase further weakens the average bond energy per atom in that phase, which favors an increased solution for the liquid. Again, solubility of the second phase in the molten phase is usually higher than in the solid.

The concentration of vacancies and of free electrons and electron holes in semiconductors (provided that the energies are high enough so that Boltzmann's statistics are applicable<sup>7</sup>) are governed by Eq. (2) since the activity may be considered unity for each of these lattice constituents at equilibrium. The enthalpy of formation of vacancies and the enthalpy required to free electrons or create electron holes are all positive. So an exponential increase in concentration of each with temperature can be expected.

Neither Eq. (2) nor Eq. (3) is strictly applicable for interstitial solutions but a similar expression can be used at concentrations low enough to allow application of Henry's law. Among interstitial solutions are solutions of hydrogen, carbon, nitrogen, boron, and oxygen in transition metals. Atoms that have left their regular lattice sites to occupy interstitial positions can also be viewed as being in interstitial solution in the parent lattice.

For a dilute interstitial solution of L in M, the equation that governs the solubility limit is

$$X_{L(M_{\text{sat}})} = \theta a_L e^{-\overline{\Delta H}_{L(M)}/RT} e^{\overline{\Delta S}_{L(M)}^e/R}, \quad (4)$$

where  $\theta$  is the ratio of the number of interstitial positions that may be occupied by solute atoms to the number of regular lattice positions. Values of  $\theta$  are 1 for octahedral sites in close packed lattices, 2 for tetrahedral sites in close packed lattices, 3 for octahedral sites in body centered cubic lattices, and 6 for tetrahedral sites in body centered cubic lattices.<sup>8</sup>

Measurements of solubility of a solute at known activity and two or more different temperatures are required to predict the temperature variation of solubility by means of Eqs. (3) or (4). If, however, the solubility at any known solute activity has been measured at one temperature only, a reasonable estimate of the temperature variation of the solubility can usually still be made because the partial excess molal entropies of solution in the Henry's law range are to a good approximation dependent only upon the kind of substance dissolved. For example, the partial excess entropy of solution of a solid solute in a metal phase can be assumed equal to  $0 \pm 2$  cal/deg/g atom and the partial excess entropy of interstitial solution of  $H_2$  gas in a metal phase is about  $-15 \pm 2$  cal/deg/1 g atom of hydrogen.

#### Activity Series for High Temperature Reactions<sup>2,3</sup>

The activity series for prediction of reactions in aqueous solutions is a powerful generalization from thermodynamics; the electromotive

force for a given half reaction is nothing more nor less than the free energy per mole of electrons exchanged. Certainly, we would like to be able to use the activity series or a thermodynamic generalization similar to it to predict the course of high temperature reactions. But it is quickly apparent that the aqueous activity series itself is not a reliable guide for predictions of high temperature reactions. For example, although the heavier alkali metals such as rubidium and cesium stand above aluminum and titanium in the aqueous activity series, rubidium and cesium oxide are readily reduced at high temperatures by aluminum and titanium.

We require a new series that describes the relative activities of the elements toward oxygen. In fact, since the different metallic elements differ in their relative reactivities toward the various nonmetals, we require a separate activity series for the metals toward each nonmetal. Furthermore, because free energy of reactions are dependent upon temperature through Eq. (1), we require a means of incorporating the effect of temperature into our high temperature activity series. Fortunately, neither of these new problems proves to be difficult to solve. Let us consider first the matter of the temperature dependence.

As we have seen from Eq. (1) the change in the free energy of the reaction with temperature is a function of the magnitude of the entropy of the reaction. Entropies of reactions depend almost exclusively on broad classes of reaction and very little upon particular compounds within the classes. Trouton's rule is the most familiar example of the generalizations that can be made about entropies for a class of reactions:

the entropy of vaporization of normal substances at their standard boiling points is approximately 22 cal/deg/mole of gas. Richards' rule tells us that the entropies of fusion for metals are approximately 2 to 3 cal/deg/g atom.

Various other classes of reactions are as regular in their entropies as are vaporization or fusion. Table I shows average entropies and average deviations from these averages for various classes of reactions. Note that the largest single factor that determines the entropy is the number of gas molecules that are formed or consumed in a reaction. For any reaction in which one solid metallic element displaces another from its solid compound,  $\Delta S$  for the overall reaction is approximately zero. For example, the entropy of the reaction  $\text{Ca(s)} + 1/2 \text{O}_2(\text{g}) = \text{CaO(s)}$  is -24.6 cal/deg, the entropy of the reaction  $2/5 \text{Ta(s)} + 1/2 \text{O}_2(\text{g}) = 1/5 \text{Ta}_2\text{O}_5(\text{s})$  is 21.6, and the entropy of the reaction  $\text{Ca(s)} + 1/5 \text{Ta}_2\text{O}_5(\text{s}) = 2/5 \text{Ta(s)} + \text{CaO(s)}$  is the difference between these values, 3.0 cal/deg. Neglect of the entropy introduces about  $3 \cdot T$  calories error per gram atom of oxygen exchanged.

Because the entropy of reactions that involve only solid reactants and reaction products is always close to zero, the free energies are approximated by the difference between the enthalpies of formation of the products of the reaction and of the reactants at any temperature for which all reactants and products remain solids.

For displacement reactions involving only solids, the enthalpy of formation per gram atom of nonmetal can play the role that the emf does in the activity series. For example, we can subtract the enthalpy of formation of  $1/5 \text{Ta}_2\text{O}_5$ , -97.7 kcal, from the enthalpy of formation of

CaO, -151.8 kcal, to obtain -54.1 kcal, the enthalpy of the displacement reaction of the paragraph above, and this enthalpy approximates the free energy of the reaction.

Furthermore, because the enthalpies of formation per gram atom of any particular nonmetal are regularly arranged in respect to the position of the metals in the periodic table, an arrangement of the enthalpies of formation in the form of the periodic table provides a convenient means for organizing high temperature activity information.<sup>9</sup> For example, Fig. 2 illustrates such an arrangement for solid oxides. In Fig. 2 for each element the oxide which has the most negative enthalpy of formation per gram of oxygen atom is listed with that enthalpy. Usually when a given metal forms more than one solid oxide, the one of most negative enthalpy of formation per gram atom of oxygen is the oxide of highest metal content.

The most stable oxides are arrayed along a diagonal that extends from lithium through calcium and the lanthanide elements to thorium. Oxide stabilities fall off in either direction from this diagonal, though a second less prominent stability maximum is found in oxides of gallium, tin, and lead. Simply by qualitatively noting the position of an element relative to the band of maximum stability, one can predict its approximate position in the activity series for metals relative to oxygen. For example, titanium which lies closer than vanadium or chromium to the band of maximum stability will displace vanadium and chromium from their oxides at high temperatures. This qualitative prediction can be proved and semiquantitative use of the activity series for metals relative to oxygen can be illustrated by subtracting



the enthalpy of formation of chromous oxide per gram atom from that of titanium monoxide. Thus, for  $\text{Ti(s)} + 1/3 \text{Cr}_2\text{O}_3(\text{s}) = \text{TiO(s)} + 2/3 \text{Cr(s)}$   $\Delta H = -124.0 - (-90.9) = -33.1$  kcal. The actual free energy of this reaction at  $1000^\circ\text{K}$  is  $-31.3$  kcal and at  $1500^\circ\text{K}$  is  $-30.7$  kcal.

Obviously the same kinds of limitations that apply in use of the aqueous activity series must be expected for our high temperature activity series. For example, if titanium is heated with an excess of chromium oxide, titanium dioxide rather than titanium monoxide can be expected as the reaction product, just as in aqueous solutions iron metal may be oxidized to the +3 state in the presence of an excess of oxidizing agent despite the fact that the emf for the overall oxidation reaction to that state is less than that for oxidation to  $\text{Fe}^{+2}$ .

Similarly, reactions may occur that cannot be predicted from the activity series alone. For example, if silica is equilibrated with aluminum metal the reaction products may be alumina and elemental silicon, but if excess silica is present the alumina will react with this silica to form mullite.

Qualitative predictions of displacement reactions from enthalpies of formation of the solid compound from the solid elements are usually dependable even if a reactant or a product of the displacement reaction happens to be a liquid at the temperature of interest so long as the other reactants and products are relatively insoluble in the liquid phase. However, if either a reactant or product is a gas under the conditions of the experiment or can vaporize out of the reaction mixture, the effect of the entropy of reaction upon the free energy cannot be neglected. Sodium is a poor reducing agent for oxides at high

temperatures in part because its oxides have relatively low enthalpies of formation, but also because the element itself is highly volatile. Carbon, silicon, and germanium, on the other hand, are all excellent reducing agents for oxides because the monoxides of these elements, while having relatively small enthalpies of formation in comparison to the stable solid oxides of other elements, have entropies of formation of about +21.5 cal/deg/g atom of oxygen compared to -22 cal/deg/g atom of oxygen for the solid oxides.

By taking entropies as well as the enthalpies into account, we can incorporate these elements which have important gaseous oxides into our oxide activity series. For the reaction  $1/4 \text{Fe}_3\text{O}_4(\text{s}) + \text{C}(\text{s}) = 3/4 \text{Fe}(\text{s}) + \text{CO}(\text{g})$ ,  $\Delta H_{298} = -26.4 - (-67.0) = +40.6$  kcal while  $\Delta S_{298} \cong +21.5 - (-22) = 44$  cal/deg. And  $\Delta F^\circ \cong 40,600 - 44T$  so that at  $1000^\circ\text{K}$  or above the reaction has a negative standard free energy even though the enthalpy is positive.

A particularly convenient form of high temperature activity series was demonstrated by Ellingham in 1944.<sup>10</sup> Ellingham plotted free energies of formation per gram atom of nonmetal vs temperature. Figure 3 shows an Ellingham plot for a few selected oxides.

(It is apparent that those oxides which lie toward the bottom of Fig. 3 are stable relative to reduction by the elements with oxides that lie higher in the figure. The free energy change for displacement of one element from the oxide of another can be obtained by finding the difference between the free energies at the desired temperature. For example, at  $1000^\circ\text{K}$  for the reaction  $2/3 \text{Al}(\ell) + \text{ZnO}(\text{s}) = 1/3 \text{Al}_2\text{O}_3(\text{s}) + \text{Zn}(\ell)$ ,  $\Delta F \cong -110 - (-60) = -50$  kcal.

Notice that just as the emf of half reactions for solution reactions are affected by concentrations of reactants or products, the free energies of formation of oxides are affected by pressures of reactants or products. The entries on the plot are free energies for oxygen reacting at one atmosphere pressure. The line labeled  $P_{\text{CO}} = 10^{-3}$  atm is displaced from that labeled  $P_{\text{CO}} = 1$  atm by  $RT \ln 10^{-3}$ .

The Ellingham plot clearly illustrates some points about the effect of entropies on relative stabilities with changing temperature. The curves for solid oxides are all nearly parallel below the melting points of the metals since the intercept for each curve at  $T = 0^\circ\text{K}$  is the heat of formation at  $0^\circ\text{K}$ . It is apparent that for a displacement reaction involving only solid reactants and products the difference in free energy of products and reactants is little different from the difference between the enthalpies of products and reactants.

The stabilities of solid oxides decrease with temperature because the number of moles of gas is decreased, and the entropy accordingly increased, by the reaction  $m/n \text{M}(\text{s}) + 1/2 \text{O}_2(\text{g}) = 1/n \text{M}_m\text{O}_n(\text{s})$ . The free energy of formation of carbon dioxide changes little with temperature because the number of gas molecules is unchanged by the reaction  $\text{C}(\text{s}) + \text{O}_2(\text{g}) = \text{CO}_2(\text{g})$ . The stability of  $\text{CO}(\text{g})$  increases with temperature because the reaction  $\text{C}(\text{s}) + 1/2 \text{O}_2(\text{g}) = \text{CO}(\text{g})$  involves a net increase in the number of moles of gas and a corresponding increase in entropy.

Activity series for metallic elements relative to other nonmetals can be developed in exactly the manner that we have illustrated for metals relative to oxygen. When the series that result are examined,

the most stable fluorides are found to be on the same band across the periodic table as are the most stable oxides, while the most stable chlorides, bromides, iodides, sulfides, and selenides are displaced from that band toward the lower left-hand corner of the periodic table, and the most stable nitrides and carbides are displaced slightly to the right in the periodic table from the band of stable oxides. Thus, there is a gratifying and understandable pattern in high temperature stabilities which emerges when chemical experience is evaluated in terms of thermodynamics. We could extend the analysis farther and develop activity series for nonmetals relative to various metals--but a prudent professor never extends his lecture beyond the hour, to do so is to waste wisdom, or at least to waste effort.

When I outlined for one of my graduate students what I planned to cover in this talk he remarked, "Oh yes, the first half of your course in High Temperature Materials." There is a distressing germ of truth to his statement.

Perhaps I have flown over a bit too much ground. I can only plead that a scan from the air is the best means for discerning the main features of the terrain. I hope that this paper may provide perspective that will be helpful to some of you in pursuing in depth topics that have been skimmed over here.

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| Reaction type                          | Number of examples | Average $\Delta S^\circ_{298}$ (eu) |
|--|--------------------|-------------------------------------|
| $(2/n)M_mN_n(s) = (2m/n)M(s) + N_2(g)$ | 7                  | $45.2 \pm 2.0$                      |
| $(2/n)M_mO_n(s) = (2m/n)M(s) + O_2(g)$ | 64                 | $44.4 \pm 2.6$                      |
| $(2/n)M_mS_n(s) = (2m/n)M(s) + S_2(g)$ | 19                 | $43.0 \pm 4.2$                      |
| $(2/n)MF_n(s) = (2/n)M(s) + F_2(g)$    | 22                 | $39.3 \pm 3.2$                      |
| $(2/n)MCl_n(s) = (2/n)M(s) + Cl_2(g)$  | 22                 | $36.5 \pm 2.4$                      |
| $(2/n)MBr_n(s) = (2/n)M(s) + Br_2(g)$  | 9                  | $35.5 \pm 2.4$                      |
| $(2/n)MI_n(s) = (2/n)M(s) + I_2(g)$    | 6                  | $37.3 \pm 2.4$                      |
| $2M(s) + O_2(g) = 2MO(g)$              | 18                 | $41.2 \pm 4.1$                      |
| $2M(s) + F_2(g) = 2MF(g)$              | 14                 | $41.6 \pm 6.5$                      |
| $M(s) + O_2(g) = MO_2(g)$              | 17                 | $3.5 \pm 2.1$                       |
| $M(s) + F_2(g) = MF_2(g)$              | 8                  | $5.9 \pm 3.2$                       |
| $Z_2(g) + X_2(g) = 2ZX(g)$             | 62                 | $3.6 \pm 2.5$                       |
| $Z_2(g) = 2Z(g)$                       | 15                 | $23.9 \pm 3.0$                      |

<sup>a</sup> From Kelley and King (1961) and Stull *et al.* (1962).

Table I. Entropies of various classes of reactions.

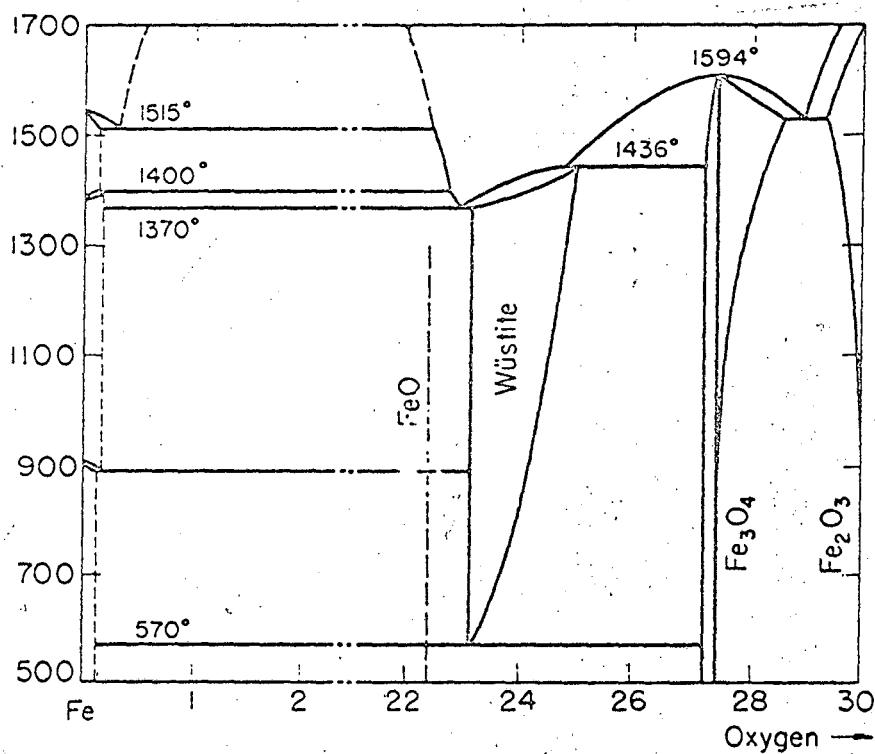


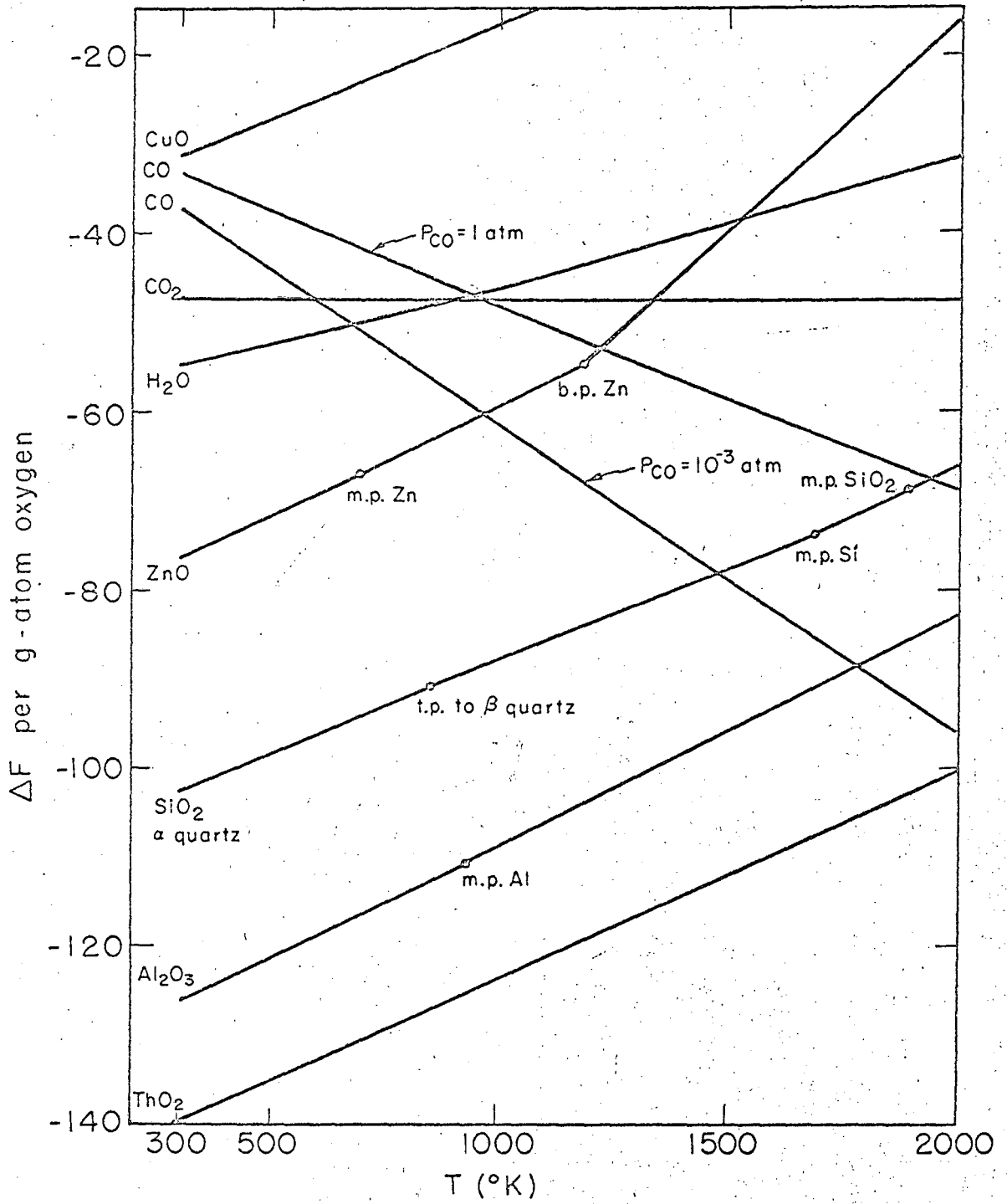
Fig. 1. The Fe-Fe<sub>2</sub>O<sub>3</sub> phase diagram.



|                   |        |                                |                                |                                |                                |                  |                                |                                |                                |                                |                                |                                |                                |                                |                                |                                |    |  |  |                  |                                |                 |    |    |
|-------------------|--------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|----|--|--|------------------|--------------------------------|-----------------|----|----|
| Li <sub>2</sub> O | BeO    | B <sub>2</sub> O <sub>3</sub>  |                                |                                |                                |                  |                                |                                |                                |                                |                                |                                |                                |                                |                                |                                |    |  |  | C                | N <sub>2</sub> O <sub>5</sub>  | O               | F  | Ne |
| -142.4            | -143.1 | -101.8                         |                                |                                |                                |                  |                                |                                |                                |                                |                                |                                |                                |                                |                                |                                |    |  |  |                  | -2.0                           |                 |    |    |
| Na <sub>2</sub> O | MgO    | Al <sub>2</sub> O <sub>3</sub> |                                |                                |                                |                  |                                |                                |                                |                                |                                |                                |                                |                                |                                |                                |    |  |  | SiO <sub>2</sub> | P <sub>4</sub> O <sub>10</sub> | SO <sub>3</sub> | Cl | Ar |
| -99.4             | -143.8 | -133.5                         |                                |                                |                                |                  |                                |                                |                                |                                |                                |                                |                                |                                |                                |                                |    |  |  | -108.8           | -72.0                          | -36.8           |    |    |
| K <sub>2</sub> O  | CaO    | Sc <sub>2</sub> O <sub>3</sub> | TiO                            | VO                             | Cr <sub>2</sub> O <sub>3</sub> | MnO              | Fe <sub>3</sub> O <sub>4</sub> | CoO                            | NiO                            | Cu <sub>2</sub> O              | ZnO                            | Ga <sub>2</sub> O <sub>3</sub> | GeO <sub>2</sub>               | As <sub>2</sub> O <sub>3</sub> | SeO <sub>2</sub>               | Br                             | Kr |  |  |                  |                                |                 |    |    |
| -86.4             | -151.8 | -149.0                         | -124.0                         | -103.2                         | -90.9                          | -92.0            | -67.0                          | -57.1                          | -57.3                          | -40.4                          | -83.3                          | -86.0                          | -64.5                          | -52.3                          | -27.5                          |                                |    |  |  |                  |                                |                 |    |    |
| Rb <sub>2</sub> O | SrO    | Y <sub>2</sub> O <sub>3</sub>  | ZrO <sub>2</sub>               | NbO <sub>2</sub>               | MoO <sub>2</sub>               | TcO <sub>2</sub> | RuO <sub>2</sub>               | Rh <sub>2</sub> O <sub>3</sub> | Pd                             | Ag <sub>2</sub> O              | CdO                            | In <sub>2</sub> O <sub>3</sub> | SnO <sub>2</sub>               | Sb <sub>2</sub> O <sub>3</sub> | TeO <sub>2</sub>               | I <sub>2</sub> O <sub>5</sub>  | Xe |  |  |                  |                                |                 |    |    |
| -79.0             | -144.4 | -148.5                         | -130.8                         | -95.5                          | -70.4                          | -51.7            | -28.3                          | -22.8                          | -22.9                          | -7.2                           | -61.2                          | -73.7                          | -69.4                          | -56.9                          | -38.9                          | -8.5                           |    |  |  |                  |                                |                 |    |    |
| Cs <sub>2</sub> O | BaO    | La <sub>2</sub> O <sub>3</sub> | HfO <sub>2</sub>               | Ta <sub>2</sub> O <sub>5</sub> | WO <sub>2</sub>                | ReO <sub>3</sub> | OsO <sub>4</sub>               | IrO <sub>2</sub>               | Pt                             | Au <sub>2</sub> O <sub>3</sub> | Hg <sub>2</sub> O              | Tl <sub>2</sub> O              | PbO                            | BiO                            | PoO <sub>2</sub>               | At                             | Rn |  |  |                  |                                |                 |    |    |
| -76.0             | -139.0 | -142.9                         | -133.0                         | -97.7                          | -70.5                          | -48.7            | -23.5                          | -20.0                          |                                | -0.3                           | -22.0                          | -43.2                          | -52.5                          | -50.0                          | -30.3                          |                                |    |  |  |                  |                                |                 |    |    |
| Fr                | RaO    | Ac <sub>2</sub> O <sub>3</sub> |                                |                                |                                |                  |                                |                                |                                |                                |                                |                                |                                |                                |                                |                                |    |  |  |                  |                                |                 |    |    |
|                   | -130.0 | -148.0                         |                                |                                |                                |                  |                                |                                |                                |                                |                                |                                |                                |                                |                                |                                |    |  |  |                  |                                |                 |    |    |
|                   |        |                                | Ce <sub>2</sub> O <sub>3</sub> | Pr <sub>2</sub> O <sub>3</sub> | Nd <sub>2</sub> O <sub>3</sub> | Pm               | Sm <sub>2</sub> O <sub>3</sub> | Eu                             | Gd <sub>2</sub> O <sub>3</sub> | Tb                             | Dy <sub>2</sub> O <sub>3</sub> | Ho <sub>2</sub> O <sub>3</sub> | Er <sub>2</sub> O <sub>3</sub> | Tm <sub>2</sub> O <sub>3</sub> | Yb <sub>2</sub> O <sub>3</sub> | Lu <sub>2</sub> O <sub>3</sub> |    |  |  |                  |                                |                 |    |    |
|                   |        |                                | -142.3                         | -145.6                         | -14.3                          |                  | -144.6                         |                                | -144.6                         |                                | -148.6                         | -149.9                         | -151.2                         | -150.5                         | -144.6                         | -149.6                         |    |  |  |                  |                                |                 |    |    |
|                   |        |                                | ThO <sub>2</sub>               | Pa                             | UO <sub>2</sub>                | NpO <sub>2</sub> | PuO <sub>2</sub>               | Am <sub>2</sub> O <sub>3</sub> | Cm                             | Bk                             | Cf                             | Es                             | Fm                             | Md                             |                                | Lw                             |    |  |  |                  |                                |                 |    |    |
|                   |        |                                | -146.6                         |                                | -129.6                         | -123.0           | -123.0                         | -140.0                         |                                |                                |                                |                                |                                |                                |                                |                                |    |  |  |                  |                                |                 |    |    |

Fig. 2. Heats of formation per gram atom of oxygen for solid oxides.

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Fig. 3. The stabilities of oxides as a function of temperature.

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