

## FREE ENERGY CHARTS FOR HIGH TEMPERATURE CHEMICAL CALCULATIONS

T. B. Reed

Lincoln Laboratory, \* Massachusetts Institute of Technology  
Lexington, Massachusetts 02173

To calculate the degree of chemical reaction for



at any temperature, it is necessary to know the Gibbs free energy change

$$\Delta G(T) = \Delta H(T) - T\Delta S(T) \quad (2)$$

One can then find the concentrations of the reactants and products from the equilibrium constant  $K$

$$\Delta G = -RT \ln K \equiv -RT \ln \frac{p_M^m p_N^n}{p_A^a p_B^b} \quad (3)$$

where  $p$  is the activity of each reactant. For reactants whose standard state is gaseous at the reaction temperature,  $p$  is approximately equal to the partial pressure.

The heat capacities, and other thermodynamic properties of elements and compounds, are not simple functions of temperature and are usually presented in extensive tabulations such as JANAF Tables. However, in forming  $\Delta G$  from these properties, the non-linear terms largely cancel so that to a very good approximation

$$\Delta G(T) = \Delta \bar{H} - T\Delta \bar{S} \quad (4)$$

where now  $\Delta \bar{H}$  and  $\Delta \bar{S}$  are respectively the asymptote and slope of a plot of  $\Delta G$  vs  $T$ , and may differ by 5-10% from  $\Delta H(T)$  and  $\Delta S(T)$ . For instance, the free energy of formation of  $Al_2O_3$  varies from the straight line  $\Delta G = -402.3 + 77.2T$  by at most 0.08% between 1,000 and 2,300°K, while  $\Delta H(T)$  varies by 1.5% and  $\Delta S(T)$  varies by 5% over this range.

It is possible to summarize a great deal of the data on chemical reactions in the form of families of straight lines on plots of  $\Delta G$  vs  $T$ . Free energies of reactions for the formation of the chalcogenides, halides and hydrides, disassociation of polyatomic gases and ionization of elements are assembled here as a convenient summary of the thermodynamic data on these reactions. The straight line values of  $\Delta \bar{H}$  and  $\Delta \bar{S}$  are tabulated.

\*Operated with support from the U. S. Air Force.

A plot of  $\Delta G$  vs  $T$  has a number of advantages in the presentation of free energy data. It enables the relative reactivity of various materials to be easily visualized over a wide range of temperature. Phase changes are marked by changes in slope so that melting points and boiling points of reactants are recorded. The charts become simple nomograms in several ways. A fixed value of  $K$  lies on a line passing through the origin so that by adding one scale it is possible to read  $K$  or  $p$  for reactions involving only one gas. Other scales can be constructed to give the results of compound reactions such as hydrogen reduction of oxides. The free energy change is proportional to the emf of electrochemical reactions so that a separate scale gives this conversion.

At temperatures above  $2,000^{\circ}\text{K}$  many of the diatomic gases begin to dissociate. Above  $10,000^{\circ}\text{K}$  most molecules have dissociated to atoms and the atoms begin to ionize thermally to give electrons and ions. For dissociation and ionization at one atmosphere total pressure, it is possible to read on the free energy charts the degree of dissociation or ionization and the partial pressures of molecules, atoms, ions, and electrons. By moving the scale it is possible to read these quantities at any other total pressure. The use of the charts in measuring very high temperature is discussed.

The major source of entropy change in chemical reactions involving at least one gaseous species is the production or consumption of gas, since the entropy of a mole of gas is much higher than that of the corresponding solid or liquid. It becomes apparent on examining the charts that the entropy change is given approximately by  $\pm \Delta \bar{S} = \pm k \Delta n$ , where  $\Delta n$  is the increase in the number of moles of gas for the reaction. For the formation of the chalcogenides and halides, the constant  $k$  is approximately 40-50 e. u./mole, but is smaller for reactions involving dissociation or ionization. Provided that the reactions are all written for one mole of gas, the free energy charts then show a series of parallel lines of slope  $\Delta \bar{S}$ . From this it is seen that the relative magnitude of  $\Delta G$  is determined primarily by  $\Delta \bar{H}$  and the relative stability of oxides, sulfides, etc. stays constant over a wide range of temperatures.

The oxygen pressure at equilibrium between a metal and its oxide or between an oxide and a higher oxide provides a scale of stability toward oxidation similar to the EMF or electronegativity scale. We define "pO" as the negative log of oxygen pressure,  $-\log p_{\text{O}_2}$  (analogous to the definition of pH as the negative log of hydrogen