

## 11.8: A General Strategy for Expressing the Thermodynamic Properties of a Substance

The equations we develop in Sections 11.7 and 11.8 express the differences  $\Delta_f H_A^\circ (HIG^\circ) - \bar{H}_A(P)$ ,  $\Delta_f S_A^\circ (HIG^\circ) - \bar{S}_A(P)$ , and  $\Delta_f G_A^\circ (HIG^\circ) - \bar{G}_A(P)$  between thermodynamic functions for one mole of a gas at two different pressures and the same temperature. They follow from the properties of gases and the relationships that result when we express the enthalpy, entropy, and Gibbs free energy as functions of temperature and pressure. Because  $\Delta_f H_A^\circ (HIG^\circ)$ ,  $\Delta_f S_A^\circ (HIG^\circ)$ , and  $\Delta_f G_A^\circ (HIG^\circ)$  are measured relative to the constituent elements of substance  $A$  at the same temperature,  $\bar{H}_A(P)$ ,  $\bar{S}_A(P)$ , and  $\bar{G}_A(P)$  are the differences in these properties between the real substance at pressure  $P$  and temperature  $T$  and the real constituent elements in their standard states at the same temperature.

We have just found a way to express the thermodynamic functions of a pure real gas at any pressure and temperature. This development shows us the way toward a broader goal. Ultimately, we want to be able to express—and to find the values of—the thermodynamic functions of any substance in any system at any temperature and pressure.

*Our goal is to create a scheme in which the enthalpy, the entropy, or the Gibbs free energy of any substance in any arbitrary state is equal to the change in that thermodynamic property when the substance is produced, in that state, from its pure, separate, constituent elements, in their standard states at the same temperature.*

The scheme we create uses two steps to convert the constituent elements into the substance in the arbitrary state. The elements are first converted into the pure substance in its standard state at the same temperature. The substance is then taken from its standard state to the state it occupies in the arbitrary system, at the same temperature. While straightforward in principle, finding changes in thermodynamic properties for this last step is often difficult in practice.

The value of the Gibbs free energy of substance  $A$  in any arbitrary system,  $\bar{G}_A$ , becomes equal to the sum of its Gibbs free energy in the standard state,  $\Delta_f G_A^\circ$ , and the Gibbs free energy change when the substance passes from its standard state into its state in the arbitrary system,  $\Delta \bar{G}_A$ . That is,

$$\bar{G}_A = \Delta_f G_A^\circ + \Delta \bar{G}_A$$

and  $\bar{G}_A$  is the same thing as the Gibbs free energy change when the substance is formed, as it is found in the arbitrary system, from its constituent elements. The same relationships apply to the enthalpies and entropies of these states:

$$\bar{H}_A = \Delta_f H_A^\circ + \Delta \bar{H}_A$$

and

$$\bar{S}_A = \Delta_f S_A^\circ + \Delta \bar{S}_A$$

Measuring the differences  $\Delta \bar{H}_A$ ,  $\Delta \bar{S}_A$ , and  $\Delta \bar{G}_A$  become important objectives—and major challenges—in the study of the thermodynamics of chemical systems.

In Section 11.6, we find the changes that occur in the enthalpy, entropy, and Gibbs free energy when one mole of a pure gas is taken from its real gas state at any pressure to its hypothetical ideal-gas standard state, at the same temperature. In Chapter 13, we extend this development to express the thermodynamic properties of any mixture of ideal gases in terms of the properties of the individual pure gases. As a result, we can find the equilibrium position for any reaction of ideal gases from the thermodynamic properties of the individual pure gases. This application is successful because we can find both  $\Delta_f G_A^\circ$  and  $\Delta \bar{G}_A$  for an ideal gas at any pressure. Beginning in Chapter 14, we extend this success by finding ways to measure  $\Delta \bar{G}_A$  for the process of taking  $A$  from its standard state as a pure substance to any arbitrary state in which  $A$  may be only one component of a solution or mixture.

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