12.10: Evaluation of Standard Molar Quantities

Some of the most useful experimentally-derived data for thermodynamic calculations are values of standard molar reaction enthalpies, standard molar reaction Gibbs energies, and standard molar reaction entropies. The values of these quantities for a given reaction are related, as we know (Eq. 11.8.21), by

$$\Delta_{\mathrm{r}} G^\circ = \Delta_{\mathrm{r}} H^\circ - T \Delta_{\mathrm{r}} S^\circ \tag{12.10.1}$$

and $\Delta_{\mathrm{r}} S^\circ$ can be calculated from the standard molar entropies of the reactants and products using Eq. 11.8.22:

$$\Delta_{\mathrm{r}} S^\circ = \sum_i \nu_i S_i^\circ \tag{12.10.2}$$

The standard molar quantities appearing in Eqs. 12.10.1 and 12.10.2 can be evaluated through a variety of experimental techniques. Reaction calorimetry can be used to evaluate $\Delta_{\mathrm{r}} H^\circ$ for a reaction (Sec. 11.5). Calorimetric measurements of heat capacity and phase-transition enthalpies can be used to obtain the value of S_i° for a solid or liquid (Sec. 6.2.1). For a gas, spectroscopic measurements can be used to evaluate S_i° (Sec. 6.2.2). Evaluation of a thermodynamic equilibrium constant and its temperature derivative, for any of the kinds of equilibria discussed in this chapter (vapor pressure, solubility, chemical reaction, etc.), can provide values of $\Delta_{\mathrm{r}} G^\circ$ and $\Delta_{\mathrm{r}} H^\circ$ through the relations $\Delta_{\mathrm{r}} G^\circ = -RT \ln K$ and $\Delta_{\mathrm{r}} H^\circ = -R \, \mathrm{d} \ln K / \mathrm{d}(1/T)$.

In addition to these methods, measurements of cell potentials are useful for a reaction that can be carried out reversibly in a galvanic cell. Section 14.3.3 will describe how the standard cell potential and its temperature derivative allow $\Delta_{\mathrm{r}} H^\circ$, $\Delta_{\mathrm{r}} G^\circ$, and $\Delta_{\mathrm{r}} S^\circ$ to be evaluated for such a reaction.

An efficient way of tabulating the results of experimental measurements is in the form of standard molar enthalpies and Gibbs energies of *formation*. These values can be used to generate the values of standard molar reaction quantities for reactions not investigated directly. The relations between standard molar reaction and formation quantities (Sec. 11.3.2) are

$$\Delta_{\mathrm{r}} H^\circ = \sum_i \nu_i \Delta_{\mathrm{f}} H^\circ(i) \qquad \Delta_{\mathrm{r}} G^\circ = \sum_i \nu_i \Delta_{\mathrm{f}} G^\circ(i) \tag{12.10.3}$$

and for ions the conventions used are

$$\Delta_{\mathrm{f}} H^\circ(\mathrm{H}^+, \mathrm{aq}) = 0 \qquad \Delta_{\mathrm{f}} G^\circ(\mathrm{H}^+, \mathrm{aq}) = 0 \qquad S_{\mathrm{m}}^\circ(\mathrm{H}^+, \mathrm{aq}) = 0 \tag{12.10.4}$$

Appendix H gives an abbreviated set of values of $\Delta_{\mathrm{f}} H^\circ$, S_{m}°, and $\Delta_{\mathrm{f}} G^\circ$ at $298.15 \, \mathrm{K}$

For examples of the evaluation of standard molar reaction quantities and standard molar formation quantities from measurements made by various experimental techniques, see Probs. 12.18–12.20, 14.3, and 14.4.