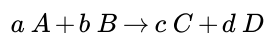


11.9: The Standard Entropy and the Gibbs Free Energy of Formation

Given $\Delta_f G^\circ$ for all of the species involved in a reaction, we can calculate the difference between the Gibbs free energies of formation of the pure separate products and those of the pure separate reactants. We call this difference the **standard Gibbs free energy change** for the reaction, $\Delta_r G^\circ$. A standard Gibbs free energy of formation is the standard Gibbs free energy change for the reaction that forms a substance from its elements. Likewise, from the absolute entropies, S° , of the reactants and products, we can calculate the standard entropy change for the reaction, $\Delta_r S^\circ$. In doing so, we utilize the thermochemical cycle that we introduced to calculate $\Delta_r H^\circ$ from the values of $\Delta_f H^\circ$ for the reacting species. For



we have

$$\Delta_r G^\circ = c \Delta_f G^\circ (C) + d \Delta_f G^\circ (D) - a \Delta_f G^\circ (A) - b \Delta_f G^\circ (B)$$

and

$$\Delta_r S^\circ = c S^\circ (C) + d S^\circ (D) - a S^\circ (A) - b S^\circ (B)$$

We use $\Delta_f G_A^\circ (HIG^\circ)$ to denote the Gibbs free energy of one mole of a gas in its hypothetical ideal-gas standard state. Because the fugacity of the ideal gas standard state is 1 bar, $f_A (HIG^\circ) = P^\circ$, the Gibbs free energy of a gas at unit fugacity becomes the Gibbs free energy change for the formation of the substance in its hypothetical ideal gas standard state. For an ideal gas, unit fugacity occurs at a pressure of one bar. For real gases, the standard state of unit fugacity occurs at a real-gas pressure that is, in general, different from one bar.

The Gibbs free energy of the gas at any other pressure, $\bar{G}_A (P)$, becomes identical to the difference between the Gibbs free energy of the gas in that state and the Gibbs free energy of its constituent elements in their standard states at the same temperature. This convention makes the Gibbs free energy of the elements the “zero point” for the Gibbs free energy of the gas. As indicated in Figure 4, the Gibbs free energy of the gas at any pressure, P, becomes

$$\begin{aligned} \bar{G}_A (P) &= \Delta_f G_A^\circ (HIG^\circ) + RT \ln \left(\frac{f_A (P)}{f_A (HIG^\circ)} \right) \\ &= \Delta_f G_A^\circ (HIG^\circ) + RT \ln \left(\frac{f_A (P)}{P^\circ} \right) \end{aligned}$$

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