4 The Gibbs Energy of a Reaction Mixture

- *Our focus now is using the Gibbs energy to understand equilibrium in a reaction mixture under constant pressure conditions that correspond to typical laboratory experiments*

- *For a reaction mixture containing species 1, 2, 3, . . . ,* G *is no longer a function of the variables* T *and* P *only*

- G *is written in the form* $G = G\,(T, P, n_1, n_2, n_3, \ldots)$

- *The total differential is*

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2\ldots} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2\ldots} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2\ldots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1\ldots} dn_2 + \ldots.$$

4

The Gibbs Energy of a Reaction Mixture

- *We are going to define the chemical potential,* μ_i

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j \neq n_i}$$

- *Using the notation of chemical potential, the differential form of Gibbs energy can be written as follows*

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2 \ldots} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1 n_2 \ldots} dP + \sum_i \mu_i dn_i$$

- *For a pure substance we can write* $G = n_i G_{i,m}$

- *From the definition of* $\mu_i = G_{i,m}$ *”the chemical potential is simply the molar Gibbs energy of the substance”*

4 The Gibbs Energy of a Reaction Mixture

$$dG = -S\,dT + V\,dP + \sum_i \mu_i dn_i$$

- *Note that if the concentrations do not change, all of the* $dn_i = 0$

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

- *For a binary mixture at constant* P *and* T

$$dG = \mu_1 dn_1 + \mu_2 dn_2$$

- *The integrated form of* G *is*

$$G = \mu_1 n_1 + \mu_2 n_2$$

4 The Gibbs Energy of a Reaction Mixture

$$dG = \mu_1 dn_1 + \mu_2 dn_2$$

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- *The total differential of the last equation is*

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + n_1 d\mu_1 + n_2 d\mu_2$$

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- *Because G is a state function, the previously two equations must be equal, which implies that at constant temperature and pressure*

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

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This equation states that the chemical potentials of the components in a binary solution are not independent.

$$d\mu_2 = -\frac{n_1 d\mu_1}{n_2}$$

Gibbs–Duhem equation

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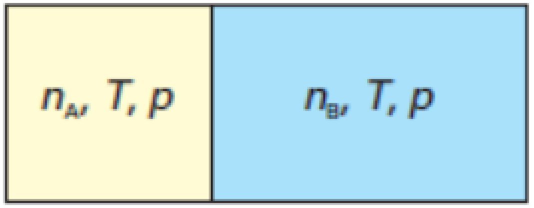
5 The Gibbs Energy of a Gas in a Mixture

6 Calculating the Gibbs Energy of Mixing for Ideal Gases

- *Let the amounts of two perfect gases in the two containers be* n_A *and* n_B*; both are at a temperature* T *and a pressure* P



- *Recall from Section 3 that the Gibbs energy of a pure ideal gas depends on its pressure as*

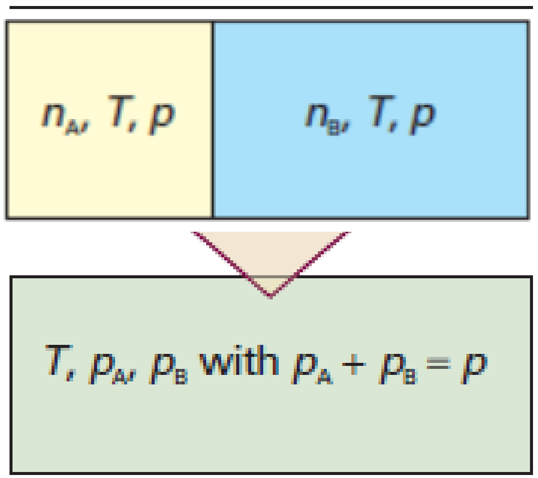
$$G(T,P) = G^\circ(T) + \int_{P^\circ}^{P} V\,dP' = G^\circ(T) + \int_{P^\circ}^{P} \frac{nRT}{P'}\,dP' = G^\circ(T) + nRT\ln\frac{P}{P^\circ}$$

- *The chemical potentials of the two pure gases are obtained by applying the definition* $\mu = G_m$

$$\mu = \mu^\circ + RT\,ln\frac{P}{P^\circ}$$

5 The Gibbs Energy of a Gas in a Mixture

6 Calculating the Gibbs Energy of Mixing for Ideal Gases



$$G_i = G_{i,A} + G_{i,B} = \ n_A G_{m,A} + n_A G_{m,B} = n_A \mu_A + n_B \mu_B$$

$$n_A \left(\mu_A^{\circ} + RT\ ln \frac{P}{P^{\circ}}\right) + n_B \left(\mu_B^{\circ} + RT\ ln \frac{P}{P^{\circ}}\right)$$

- *After mixing, the total Gibbs energy becomes*

$$G_f = n_A \left(\mu_A^{\circ} + RT\ ln \frac{P_A}{P^{\circ}}\right) + n_B \left(\mu_B^{\circ} + RT\ ln \frac{P_B}{P^{\circ}}\right)$$

5 The Gibbs Energy of a Gas in a Mixture

6 Calculating the Gibbs Energy of Mixing for Ideal Gases

- *The Gibbs energy of mixing,* ΔG_{mixing} *”*G_f *-* G_i*”*

$$\Delta G_{mixing} = n_A\, RT\, ln \frac{P_A}{P} + n_B RT\, ln \frac{P_B}{P}$$

$$P_A = x_A P$$

$$\Delta G_{mixing} = RT \sum_i n_i \ln x_i = nRT \sum_i x_i \ln x_i$$

- *Note that because all the* $x_i < 1$, *each term in the above Equation is negative, so that* $\Delta G_{mixing} < 0$ *, showing that mixing is a spontaneous process.*

5 The Gibbs Energy of a Gas in a Mixture

6 Calculating the Gibbs Energy of Mixing for Ideal Gases

$$\Delta S_{mixing} = -\left(\frac{\partial \Delta G_{mixing}}{\partial T}\right)_P = -nR\sum_i x_i \ln x_i$$

$$\Delta S = R\left(n_A \ln\frac{V_f}{V_{iA}} + n_B \ln\frac{V_f}{V_{iB}}\right) = R\left(nx_A \ln\frac{1}{x_A} + nx_B \ln\frac{1}{x_B}\right)$$

$$= -nR(x_A \ln x_A + x_B \ln x_B)$$