Thermodynamics: A Few Selected Important Relations

Fundamental property relations or *GIBBS equations*:

$$\mathrm{d}(nU) = T\mathrm{d}(nS) - P\mathrm{d}(nV) + \sum_i \mu_i \mathrm{d}n_i$$

⬇ LEGENDRE transformation

$$\mathrm{d}(nG) = -(nS)\mathrm{d}T + (nV)\mathrm{d}P + \sum_i \mu_i \mathrm{d}n_i$$

General GIBBS-DUHEM equation:

M…molar thermodynamic quantity (homogeneous phase)

$M_i \equiv \left[\partial(nM)/\partial n_i\right]_{T,P,n_{j\neq i}}$ …partial molar thermodynamic quantity

$$\left(\frac{\partial M}{\partial T}\right)_{P,\{x_i\}} \mathrm{d}T + \left(\frac{\partial M}{\partial P}\right)_{T,\{x_i\}} \mathrm{d}P - \sum_i x_i \mathrm{d}M_i = 0$$

LEWIS-RANDALL (LR) *rule* and *HENRY's law* (HL): for liquid solutions, two components i and j, we have the *measurable* quantities:

$f_i(T,P,\{x_i\})$…fugacity of component i in solution

$f_i^*(T,P)$…fugacity of pure component i

$h_{i,j}(T,P)$…HENRY fugacity (or HENRY's law constant) of i dissolved in j

$$\lim_{x_i\to 1}\left(\frac{f_i}{x_i}\right) = \left(\frac{\mathrm{d}f_i}{\mathrm{d}x_i}\right)_{x_i=1} = f_i^*(T,P), \text{ constant } T, P$$

LR: $f_i^{\mathrm{LR}} = x_i f_i^*,\ 0 \le x_i \le 1$ basis of the most popular *ideal-solution* model

$$\lim_{x_i\to 0}\left(\frac{f_i}{x_i}\right) = \left(\frac{\mathrm{d}f_i}{\mathrm{d}x_i}\right)_{x_i=0} = h_{i,j}(T,P), \text{ constant } T, P$$

HL: $f_i^{\mathrm{HL}} = x_i h_{i,j},\ 0 \le x_i \le 1$ basis of the popular *dilute ideal-solution* model

Reality may thus be described by *activity coefficients* γ_i measuring deviations (i.e., *ratios*) of *real* $f_i(T,P,\{x_i\})$ either from LR-*idealizations* or from HL-*idealizations*:

$\gamma_i^{\mathrm{LR}}(T,P,\{x_i\}) \equiv f_i / x_i f_i^*$ ➡ $\gamma_i^{\mathrm{LR}} / \gamma_i^{\mathrm{HL}} = h_{i,j} / f_i^*$ ⬅ $\gamma_i^{\mathrm{HL}}(T,P,\{x_i\}) \equiv f_i / x_i h_{i,j}$

⬇

$$\frac{G^{\mathrm{E}}(T,P,\{x_i\})}{RT} = \sum_i x_i \ln \gamma_i^{\mathrm{LR}}(T,P,\{x_i\})$$

G^{E} is the molar *excess GIBBS energy*.