CEN 207 Physical Chemistry

Text book:

Atkins' Physical Chemistry, Peter Atkins, Julio de Paula, James Keeler, 11th Edition, Oxford University Press.

Reference books

. Physical Chemistry, Robert J. Silbey, Robert A. Alberty, Moungi G. Bawendi

. Physical Chemistry, Ira N. Levine

The thermodynamic description of mixture

Partial molar Gibbs energy (remember: $G = n_J G_{J,m}$; $\mu_J = G_{J,m}$)

From the definition

$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,ń}$$ (Chemical potential)

$$G = n_A\mu_A + n_B\mu_B$$

$$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \cdots$$

Fundamental equation of chemical thermodynamics

At constant p and T

$$dG = \mu_A dn_A + \mu_B dn_B + \cdots$$

Under the same conditions

$$dG = dw_{add.max} = d\mu_A dn_A + \mu_B dn_B + \cdots$$

The thermodynamic description of mixture

The wider significance of the chemical potential

$$G = U + pV - TS \rightarrow U = -pV + TS + G \rightarrow dU = -pdV - Vdp + SdT + TdS + dG$$

$$dU = -pdV - Vdp + SdT + TdS + (Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \cdots)$$

$$dU = -pdV + TdS + +\mu_A dn_A + \mu_B dn_B + \cdots$$

At constant V and S

$$dU = \mu_A dn_A + \mu_B dn_B + \cdots$$

$$\mu_J = \left(\frac{\partial U}{\partial n_J}\right)_{S,V,\acute{n}}$$ IN THE SAME WAY;

$$\mu_J = \left(\frac{\partial H}{\partial n_J}\right)_{S,p,\acute{n}} \qquad \mu_J = \left(\frac{\partial A}{\partial n_J}\right)_{T,V,\acute{n}}$$

The Gibbs-Duhem Equation

$G = n_A\mu_A + n_B\mu_B$ The total Gibbs energy of a binary mixture

$dG = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B$

At constant p and T, the term $n_A d\mu_A + n_B d\mu_B$ must be equal to zero.

$n_A d\mu_A + n_B d\mu_B = 0$ This equation is a special case of the Gİbbs-Duhem Equation.

$\sum_J n_J d\mu_J = 0$ Gİbbs-Duhem Equation.

For a binary mixture, if one chemical potential increases, then the other must decrease;

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A$$

For partial molar volume,

$$\sum_J n_J dV_J = 0 \quad dV_B = -\frac{n_A}{n_B} dV_A$$

The thermodynamics of mixture

a) The Gibbs energy of mixing of perfect gases

n_A, T, p	n_B, T, p	→	T, p_A, p_B with $p_A + p_B = p$

$$G_m(p) = G_m^\theta + RTln\left(\frac{p}{p^\theta}\right) \qquad \mu = G_m$$

$\mu = \mu^\theta + RTln\left(\frac{p}{p^\theta}\right) = \mu^\theta + RTlnp$ variation of chemical potential with pressure (perfect gas)

μ^θ : the standard chemical potential

$G_i = n_A\mu_A + n_B\mu_B = n_A(\mu_A^\theta + RTlnp) + n_B(\mu_B^\theta + RTlnp)$ *initial. After mixing* $p_A + p_B = p$

$$G_f = n_A(\mu_A^\theta + RTlnp_A) + n_B(\mu_B^\theta + RTlnp_B)$$

$$G_i - G_f = \Delta_{mix}G = n_A RTln\frac{p_A}{p} + n_B RTln\frac{p_B}{p} \Rightarrow \Delta_{mix}G = nRT\ (x_A ln x_A + x_B ln x_B)$$

Gibbs energy of mixing (perfect gas).

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The thermodynamics of mixture

Other thermodynamic mixing functions

$\left(\frac{\partial G}{\partial T}\right)_p = -S$ from this, for a mixture of perfect gases initially at the same pressure;

$\Delta_{mix}S = -\left(\frac{\partial \Delta_{mix}G}{\partial T}\right)_p = -nR(x_A lnx_A + x_B lnx_B)$ (entropy of mixing, for perfect gas at constant T and p)

Note: lnx<0, it follows that $\Delta_{mix}S > 0$ for all compositions.

Enthalpy of mixing;

$$\Delta G = \Delta H - T\Delta S$$

$$nRT\ (x_A lnx_A + x_B lnx_B) = \Delta_{mix}H - T\big(-nR(x_A lnx_A + x_B lnx_B)\big)$$

$\Delta_{mix}H = 0$ (enthalpy of mixing, for perfect gas at constant T and p)

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