

## CEN 207 Physical Chemistry

### Text book:

Atkins' Physical Chemistry, Peter Atkins, Julio de Paula, James Keeler, 11<sup>th</sup> 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

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

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

$$dG = V dp - S dT + \mu_A dn_A + \mu_B dn_B + \dots$$

Fundamental equation of chemical thermodynamics

At constant  $p$  and  $T$

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

Under the same conditions

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

## The thermodynamic description of mixture

The wider significance of the chemical potential

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

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

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

At constant V and S

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

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

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

## 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 Gibbs-Duhem Equation.

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

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

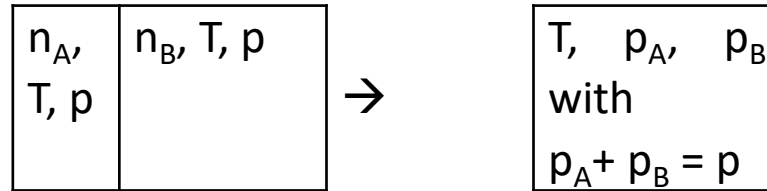
$$d\mu_B = -\frac{n_A}{n_B} d\mu_A$$

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



$$G_m(p) = G_m^\theta + RT \ln \left( \frac{p}{p^\theta} \right) \quad \mu = G_m$$

$$\mu = \mu^\theta + RT \ln \left( \frac{p}{p^\theta} \right) = \mu^\theta + RT \ln p \quad \text{variation of chemical potential with pressure (perfect gas)}$$

$\mu^\theta$  : the standard chemical potential

$$G_i = n_A \mu_A + n_B \mu_B = n_A (\mu_A^\theta + RT \ln p) + n_B (\mu_B^\theta + RT \ln p) \quad \text{initial. After mixing } p_A + p_B = p$$

$$G_f = n_A (\mu_A^\theta + RT \ln p_A) + n_B (\mu_B^\theta + RT \ln p_B)$$

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

Gibbs energy of mixing (perfect gas).

# 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;

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

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

Enthalpy of mixing;

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

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

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