5.60 Thermodynamics & Kinetics
Spring 2008

Multicomponent Systems, Partial Molar Quantities, and the Chemical Potential

So far we've worked with fundamental equations for a closed (no mass change) system with no composition change.

$$dU = TdS - pdV \qquad\qquad dA = -SdT - pdV$$
$$dH = TdS + Vdp \qquad\qquad dG = -SdT + Vdp$$

How does this change if we allow the <u>composition</u> of the system to change? Like in a chemical reaction or a biochemical process?

• Consider Gibbs free energy of a <u>2-component</u> system $G(T,p,n_1,n_2)$

$$\Rightarrow \quad dG = \underbrace{\left(\frac{\partial G}{\partial T}\right)_{p,n_1,n_2}}_{-S} dT + \underbrace{\left(\frac{\partial G}{\partial p}\right)_{T,n_1,n_2}}_{V} dp + \underbrace{\left(\frac{\partial G}{\partial n_1}\right)_{T,p,n_2}}_{\mu_1} dn_1 + \underbrace{\left(\frac{\partial G}{\partial n_2}\right)_{T,p,n_1}}_{\mu_2} dn_2$$

We define $\boxed{\mu_i \equiv \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}}}$ as the *chemical potential* of species "i"

$\mu_i(T,p,n_j)$ is an <u>intensive</u> variable

This gives a new set of fundamental equations for <u>open</u> systems (mass can flow in and out, composition can change)

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i$$
$$dH = TdS + Vdp + \sum_i \mu_i dn_i$$
$$dU = TdS - pdV + \sum_i \mu_i dn_i$$
$$dA = -SdT - pdV + \sum_i \mu_i dn_i$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_{j\neq i}} = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j\neq i}}$$

- At equilibrium, the chemical potential of a species is the same everywhere in the system

Let's show this in a system that has one component and two parts, (for example a solid and a liquid phase, or for the case of a cell placed in salt water, the water in the cell versus the water out of the cell in the salt water)

Consider moving an infinitesimal amount dn_1 of component #1 from phase a to phase b at <u>constant T,p</u>. Let's write the change in state.

$$dn_1(T,p,\text{phase a}) = -dn_1(T,p,\text{phase b})$$

$$dG = \left[\mu_1^{(b)} - \mu_1^{(a)}\right]dn_1$$
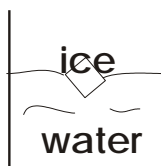
$\mu_1^{(b)} < \mu_1^{(a)} \;\Rightarrow\; dG < 0 \;\Rightarrow\;$ spontaneous conversion from (a) to (b)

$\mu_1^{(a)} < \mu_1^{(b)} \;\Rightarrow\; dG > 0 \;\Rightarrow\;$ spontaneous conversion from (b) to (a)

At equilibrium there cannot be any spontaneous processes, so

$$\boxed{\mu_1^{(a)} = \mu_1^{(b)} \;\;\text{at equilibrium}}$$

e.g. liquid water and ice in equilibrium

$\mu^{ice}(T,p) = \mu^{water}(T,p)$

at coexistence equilibrium

For the cell in a salt water solution, $\mu^{water(cell)}(T,p) > \mu^{water(solution)}(T,p)$ and the cell dies as the water flows from the cell to the solution (this is what we call osmotic pressure)

The chemical potential and its downhill drive to equilibrium will be the guiding principle for our study of phase transitions, chemical reactions, and biochemical processes

• Partial molar quantities

μ_i is the Gibbs free energy per mole of component "i", i.e. the partial molar Gibbs free energy

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}} = \mu_i = \bar{G}_i$$

$$G = n_1\mu_1 + n_2\mu_2 + \cdots + n_i\mu_i = \sum_i n_i\mu_i = \sum_i n_i\bar{G}_i$$

Let's prove this, using the fact that G is extensive.

$$G(T,p,\lambda n_1,\lambda n_2) = \lambda G(T,p,n_1,n_2)$$
$$\frac{dG}{d\lambda}(T,p,\lambda n_1,\lambda n_2) = G(T,p,n_1,n_2)$$

$$\left(\frac{\partial G}{\partial(\lambda n_1)}\right)_{T,p,\lambda n_2}\underbrace{\left(\frac{\partial(\lambda n_1)}{\partial\lambda}\right)_{T,p,\lambda n_2}}_{n_1} + \left(\frac{\partial G}{\partial(\lambda n_2)}\right)_{T,p,\lambda n_1}\underbrace{\left(\frac{\partial(\lambda n_2)}{\partial\lambda}\right)_{T,p,\lambda n_1}}_{n_2} = G$$

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

We can define other partial molar quantities similarly.

$$\left(\frac{\partial A}{\partial n_i}\right)_{T,p,n_{j\neq i}} = \bar{A}_i \quad \Rightarrow \quad A = n_1\bar{A}_1 + n_2\bar{A}_2 + \cdots + n_i\bar{A}_i = \sum_i n_i\bar{A}_i$$

partial molar Helmholtz free energy

note what is kept constant $\Rightarrow$ <u>not</u> to be confused with $\left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j\neq i}} = \mu_i$

$$\left(\frac{\partial H}{\partial n_i}\right)_{T,p,n_{j\neq i}} = \bar{H}_i \quad \Rightarrow \quad H = n_1\bar{H}_1 + n_2\bar{H}_2 + \cdots + n_i\bar{H}_i = \sum_i n_i\bar{H}_i$$

partial molar enthalpy

$$\left(\frac{\partial U}{\partial n_i}\right)_{T,p,n_{j\neq i}} = \bar{U}_i \quad \Rightarrow \quad U = n_1\bar{U}_1 + n_2\bar{U}_2 + \cdots + n_i\bar{U}_i = \sum_i n_i\bar{U}_i$$

partial molar energy

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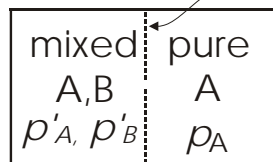Let's compare μ of a pure ideal gas to μ in a mixture of ideal gases.

• Chemical potential in a <u>pure (1-component) ideal gas</u>

From $\qquad \bar{G}(T,p) = \bar{G}^\circ(T) + RT\ln\frac{p}{p_0} \quad \Rightarrow \quad \boxed{\mu(T,p) = \mu^\circ(T) + RT\ln\frac{p}{p_0}}$

• Chemical potential in a <u>mixture of ideal gases</u>

Consider the equilibrium

Fixed Partition
permeable
only to A

mixed	pure
A,B	A
p'_A, p'_B	p_A

$$p'_A + p'_B = p_{tot}$$

At equilibrium $\quad \mu_A(mix,T,p_{tot}) = \mu_A(pure,T,p_A)$

Also
$$p_A(pure) = p_A'(mix) = p_{tot}X_A$$

Dalton's Law

So
$$\mu_A(mix,T,p_{tot}) = \mu_A(pure,T,p_{tot}X_A)$$

$$= \mu_A^o(T) + RT\ln\left(\frac{p_{tot}X_A}{p_0}\right)$$

$$= \underbrace{\mu_A^o(T) + RT\ln\frac{p_{tot}}{p_0}}_{\mu_A(pure,T,p_{tot})} + RT\ln X_A$$

$$\therefore \quad \boxed{\mu_A(mix,T,p_{tot}) = \mu_A(pure,T,p_{tot}) + RT\ln X_A}$$

Note $X_A < 1 \quad \Rightarrow \quad \mu_A(mix,T,p_{tot}) < \mu_A(pure,T,p_{tot})$

The chemical potential of A in the mixture is always less than the chemical potential of A when pure, at the same total pressure. This is at heart a reflection about entropy, the chemical potential of "A" in the mixture is less than if it were pure, under the same (T,p) conditions, because of the underlying (but hidden in this case) entropy change!