

Recitation: 7

10/16/03

Solutions

Open Systems: Variables: S, V, N:

$$dU = TdS - PdV + \sum_i \mu_i dn_i$$

where

$$\mu_i \equiv \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_j}$$

For the Legendre Transforms, we have:

$$\begin{aligned} H \equiv U + PV &\rightarrow dH = TdS + VdP + \sum_i \mu_i dn_i \\ F \equiv U - TS &\rightarrow dF = -SdT - PdV + \sum_i \mu_i dn_i \\ G \equiv U - TS + PV &\rightarrow dG = -SdT + VdP + \sum_i \mu_i dn_i \\ \mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_j} &= \left(\frac{\partial H}{\partial n_i} \right)_{S, P, n_j} = \left(\frac{\partial F}{\partial n_i} \right)_{T, V, n_j} = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j} \end{aligned}$$

The chemical potential, μ_i has different definitions, depending on the potential. However, the definitions are equivalent, as can be seen in the previous equation.

Using the Euler Relations:

$$\begin{aligned} U &= TS - PV + \sum_i \mu_i n_i \\ H &= TS + \sum_i \mu_i n_i \\ F &= -PV + \sum_i \mu_i n_i \\ G &= \sum_i \mu_i n_i \end{aligned}$$

Using First Law, and Euler Relation for the Energy, one can get the Gibbs-Duhem Equation:

$$SdT - VdP + \sum_i n_i d\mu_i = 0$$

The Gibbs-Duhem relation tells you that thermodynamic potentials in a system are not independent. A change in one of the potentials has to be accompanied by a corresponding change in the rest.

At constant temperature and pressure, the Gibbs-Duhem relation implies that, by knowing the thermodynamic behavior of one of the components, i of the system, it is possible to determine the behavior of the rest. To do this we have to do a *Gibbs-Duhem Integration*.

For a composite system, at constant pressure and temperature, (at mechanical and thermal equilibrium), the condition of equilibrium is such that the system minimizes its Gibbs free energy by changing its composition, n_i . For each component for which there is no constraint in its transfer across the composite system's internal boundaries, the equilibrium condition implies that:

$$\begin{array}{ccccccc} \mu_i^\alpha & = & \mu_i^\beta & = & \cdots & = & \mu_i^\phi \\ \mu_j^\alpha & = & \mu_j^\beta & = & \cdots & = & \mu_j^\phi \\ \vdots & & \vdots & & & & \vdots \\ \mu_k^\alpha & = & \mu_k^\beta & = & & = & \mu_k^\phi \end{array}$$

For all ϕ phases and k components.

Note that this equilibrium condition is valid, as long as the internal variables that can change are not coupled. For example, it is common that solids change their molar volume as their composition changes, so, in this case, the condition of all the chemical potential of i being equal in all phases is not the correct one.

When $\mu_i^\alpha > \mu_i^\beta$, and component i can pass across the α/β boundary, there will be a driving force for the mass flow of i , $\Delta\mu_i = \mu_i^\alpha - \mu_i^\beta$ until the system reaches an equilibrium state. $\mu_i^\beta = \mu_i^\alpha$. So $-dn_i^\alpha = dn_i^\beta$. Component i flows from the high chemical potential region to the low chemical potential region. The mass flow of i is parallel to *minus* the gradient of the chemical potential of component i .

Partial Molar Quantities

For any extensive quantity, Y , it is possible to define a corresponding partial quantity \bar{Y}_i :

$$\bar{Y}_i = \left(\frac{\partial Y}{\partial n_i} \right)_{P,T,n_j}$$

It is possible to define a change in the chemical potential μ_i of component i :

$$d\mu_i(P, T, x_i)_{P,T} = RT d \ln(a_i)$$

Where a_i is an *arbitrary* activity function that just makes life easier when trying to describe the thermodynamics of the system. We can integrate the previous equation on both sides, obtaining:

$$\mu_i(P, T, x_i)_{P,T} = \mu_i^*(P, T)_{P,T} + RT \ln(a_i)$$

where $\mu_i^*(T, P)$ is the reference state at the same P and T .

The standard state $\mu_i^0(T, P = 1 \text{ atm.})$ is at $P = 1 \text{ atm.}$

In general,

$$\mu_i^* - \mu_i^0 = \int_{P^0}^P \frac{\partial \mu_i}{\partial P} = \int_{P^0}^P \bar{V}_i$$

Since $\bar{V}_i \sim 0$ for condensed matter, $\mu_i^* \sim \mu_i^0$ for moderate pressures.

partial Pressures

When a gas is in equilibrium with a condensed phase, the activity of component i in the condensed phase is such that

$$a_i = \frac{p_i}{P_i}$$

where p_i is the partial pressure of component i in the gas mixture and P_i is the vapor pressure of i when you have a gas of pure component i over a condensed phase composed only of i .

In general,

$$a_i = \gamma_i x_i$$

where γ_i is called the activity coefficient of i .

Raoult's Law

$$\begin{aligned} \left. \frac{da_1}{dx_1} \right)_{x_1 \rightarrow 1} &= +1 \\ \left. \frac{d\gamma_1 x_1}{dx_1} \right)_{x_1 \rightarrow 1} &= \gamma_1)_{x_1 \rightarrow 1} + x_1 \left. \frac{d\gamma_1}{dx_1} \right)_{x_1 \rightarrow 1} = 1 \\ \left. \frac{d\gamma_1}{dx_1} \right)_{x_1 \rightarrow 1} &= 0 \\ \left. \frac{d \ln(\gamma_1)}{dx_1} \right)_{x_1 \rightarrow 1} &= 0 \\ \left. \frac{d \ln(\gamma_1)}{dx_2} \right)_{x_1 \rightarrow 1} &= - \left. \frac{d \ln(\gamma_1)}{dx_1} \right)_{x_1 \rightarrow 1} = 0 \end{aligned}$$

Henry's Law:

$$\begin{aligned} \left. \frac{da_2}{dx_2} \right)_{x_2 \rightarrow 0} &\neq \{0, \infty\} \\ \left. \frac{da_2}{dx_2} \right)_{x_2 \rightarrow 0} &= \left. \frac{d\gamma_2 x_2}{dx_2} \right)_{x_2 \rightarrow 0} = \gamma_2^\infty + x_2 \left. \frac{d\gamma_2}{dx_2} \right)_{x_2 \rightarrow 0} = \gamma_2^\infty \\ x_2 \left. \frac{d\gamma_2}{dx_2} \right)_{x_2 \rightarrow 0} &= 0 \\ x_2 \left. \frac{d \ln \gamma_2}{dx_2} \right)_{x_2 \rightarrow 0} &= 0 \end{aligned}$$

Relationship between Henry's and Raoult's Laws:

The Gibbs-Duhem Equation tells you that:

$$x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2 = 0$$

Differentiating the *Gibbs-Duhem* equation, with respect to x_2 , we have:

$$x_1 \left. \frac{d \ln \gamma_1}{dx_2} \right)_{x_2 \rightarrow 0} + x_2 \left. \frac{d \ln \gamma_2}{dx_2} \right)_{x_2 \rightarrow 0} = 0$$

If Henry's Law is obeyed $\left(x_2 \frac{d \ln \gamma_2}{dx_2}\right)_{x_2 \rightarrow 0} = 0$, then Raoult's Law has to be obeyed $\left(x_1 \frac{d \ln \gamma_1}{dx_2}\right)_{x_2 \rightarrow 0} = 0$. The opposite is not true.

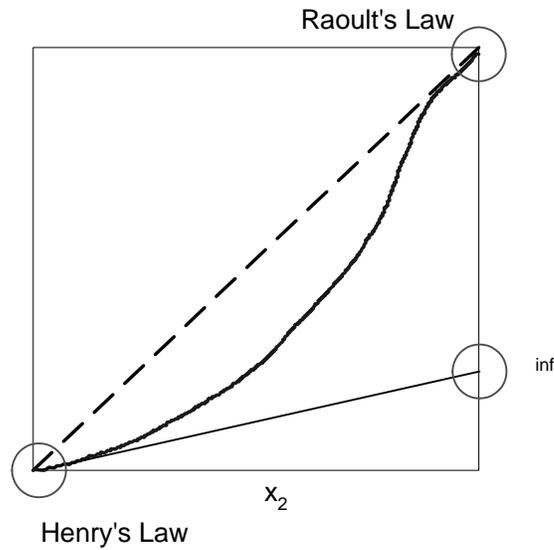


Figure 1: Raoult's Law and Henry's Law

Intercept Rule:

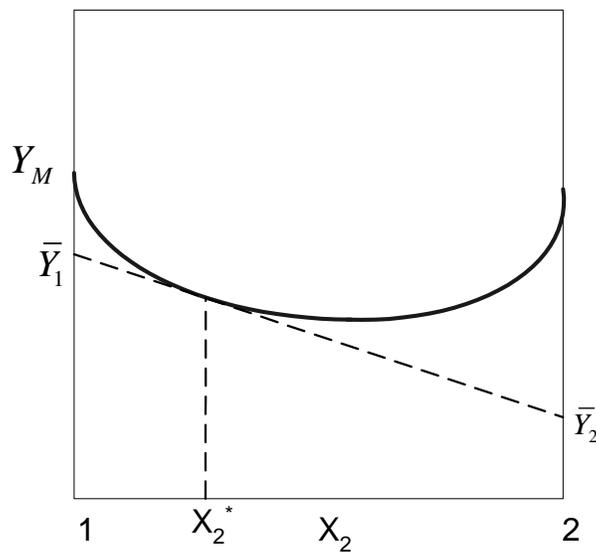


Figure 2: Intercepts Rule

Proof:

For a *molar* extensive property, Y_M , in a binary system, we have:

$$Y_M = x_1 \bar{Y}_1 + x_2 \bar{Y}_2 \quad (1)$$

If we differentiate $\frac{dY_M}{dx_2}$, considering that $x_1 + x_2 = 1$ and $dx_1 = -dx_2$:

$$\frac{dY_M}{dx_2} = -\bar{Y}_1 + \bar{Y}_2 + \left\{ x_1 \frac{\partial \bar{Y}_1}{\partial x_2} + x_2 \frac{\partial \bar{Y}_2}{\partial x_2} \right\}$$

The last term (in brackets) is equal to zero because of the Gibbs-Duhem Equation, and we have:

$$\bar{Y}_1 = \bar{Y}_2 - \frac{dY_M}{dx_2} \quad (2)$$

Substituting Eq. 2 into Eq. 1, we have:

$$Y_M = x_1 \left(\bar{Y}_2 - \frac{dY_M}{dx_2} \right) + x_2 \bar{Y}_2 \quad (3)$$

Re-arranging, we finally have:

$$\bar{Y}_2 = Y_M + x_1 \frac{dY_M}{dx_2}$$

For a Gibbs free energy, vs. composition curve, we have:

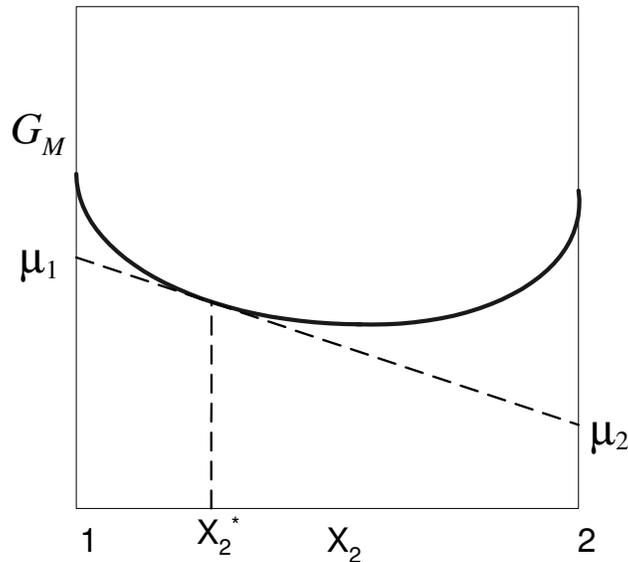


Figure 3: Intercept Rule: Molar Gibbs Energy and Chemical Potentials

Calculation of Solubility Limits:

For a system of components A and B , and assuming equilibrium between the liquid and the solid phases, the following condition must hold:

$$\begin{aligned} \mu_A^L &= \mu_A^S \\ \mu_B^L &= \mu_B^S \end{aligned}$$

Assuming that component B in the solid phase does not dissolve any A ,

$$\mu_B^L = \mu_B^{L,0} + RT \ln(x_B^L) = \mu_B^S = \mu_B^{S,0}$$

Therefore,

$$x_B^L = \exp \left[\frac{\mu_B^{S,0} - \mu_B^{L,0}}{RT} \right] = \exp \left[\frac{-\Delta H_m}{RT} \left\{ 1 - \frac{T}{T_m} \right\} \right]$$

Melting Point Depression

With the same example,

$$\Delta G_m(i) = RT \ln \left(\frac{a_i^S}{a_i^L} \right)$$

The difference in the partial molar Gibbs free energy of i is just the difference in chemical potentials.

For B , we have:

$$\Delta G_m(B) = RT \ln \left(\frac{a_B^S}{a_B^L} \right)$$
$$\frac{\Delta G_m(B)}{RT} = \ln \left(\frac{1}{1 - x_A^L} \right) \approx x_A^L$$

And

$$x_A^L = \frac{\Delta H_m(B)}{R \cdot (T_M^B)^2} \Delta T$$

A lowers the melting point of B . Since A does not dissolve in solid B , at any given temperature below the melting point of B , there is a thermodynamic driving force for forming the liquid phase, which can dissolve A .

Ideal Solution

$$a_i = x_i$$

for all i .

$$G_m = x_A \mu_A^0 + x_B \mu_B^0 + RT [x_A \ln(x_A) + x_B \ln(x_B)]$$

$$\Delta S_{mix} = -R [x_A \ln(x_A) + x_B \ln(x_B)]$$

Ideal Entropy of Mixing is always **positive**.

→ Mixing is a highly irreversible process.

$$\Delta H_{mix} = 0$$