Lecture Four:

Thermodynamics of Phase Equilibrium

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1 The Phase-Equilibrium Problem

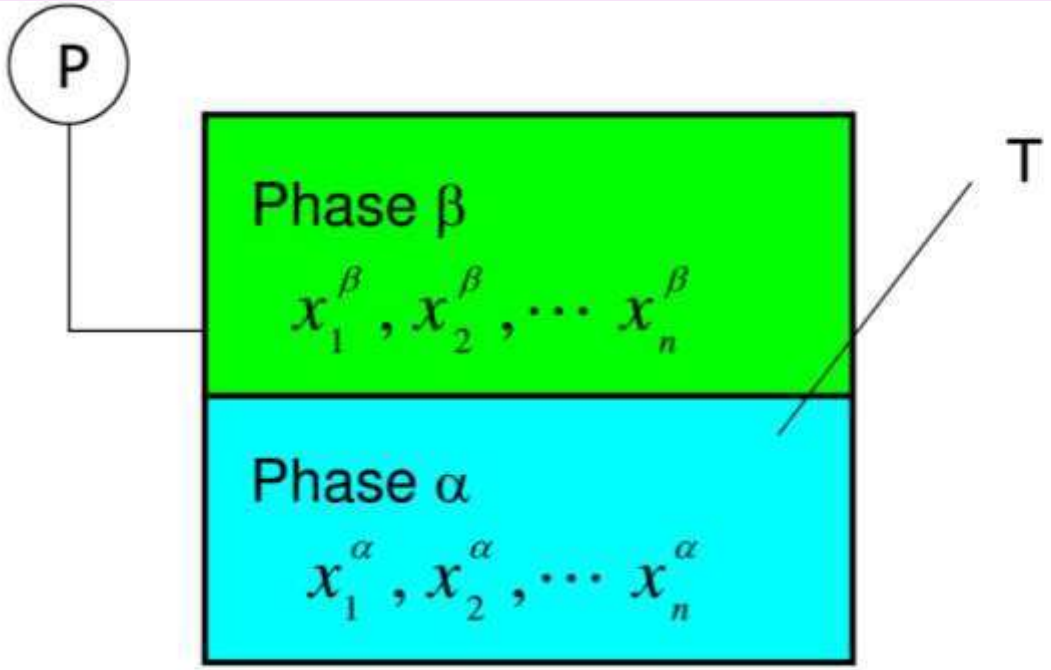
1.1 Essence of the problem

- To relate quantitatively the variables which describe states of two or more homogeneous phases at equilibirum.

- A homogeneous phase: Any region in space where the intensive properties are everywhere the same.

- Intensive properties are those which are independent of the mass, size or shape of the phase.

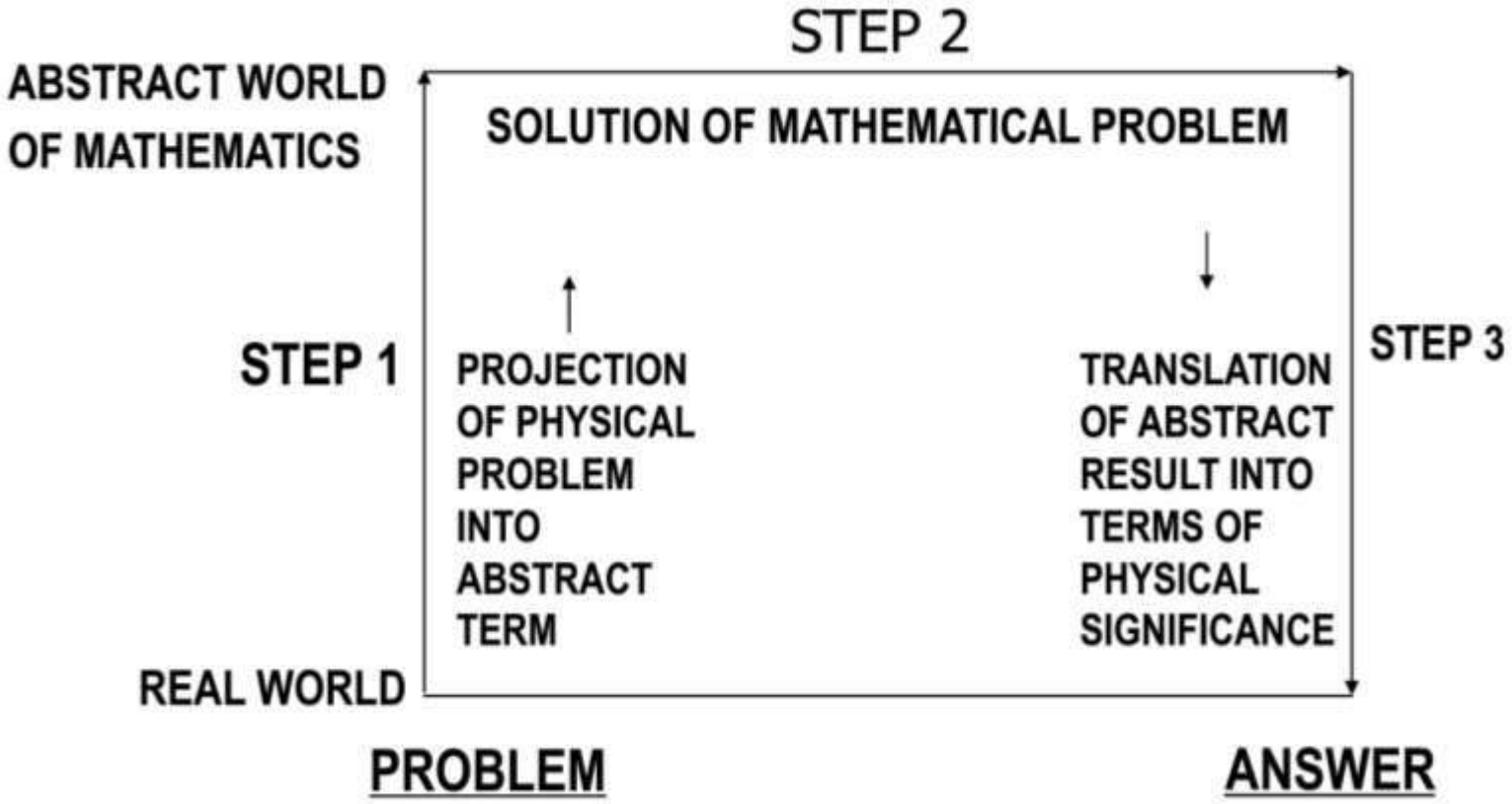
Statement of problem



Given: mole fractions $x_1^\alpha , x_2^\alpha , \cdots x_n^\alpha$ and T (or P)

Find: mole fractions $x_1^\beta , x_2^\beta , \cdots x_n^\beta$ and P (or T)

1.2 Application of Thermodynamics to Phase-Equilibrium Problems



2 Classical Thermodynamics of Phase Equilibria

2.1 Homogeneous closed system

dU=TdS-PdV

dH=TdS+VdP

dA=-SdT-PdV

dG=-SdT+VdP

fundamental property relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

Maxwell's equation

2.2 Homogeneous Open System

$$nG = g\left(P, T, n_1, n_2, \cdots, n_i, \cdots\right)$$

$$d\left(nG\right) = \left[\frac{\partial\left(nG\right)}{\partial P}\right]_{T,n} dP + \left[\frac{\partial\left(nG\right)}{\partial T}\right]_{P,n} dT + \sum_i \left[\frac{\partial\left(nG\right)}{\partial n_i}\right]_{T,P,n_j} dn_i$$

By definition the chemical potential of species i in the mixture is :

$$\mu_i = \left[\frac{\partial\left(nG\right)}{\partial n_i}\right]_{T,P,n_j} = \left[\frac{\partial G_t}{\partial n_i}\right]_{T,P,n_j}$$

$$d\left(nG\right) = \left(nV\right)dP - \left(nS\right)dT + \sum_i \mu_i dn_i$$

The chemical potential is an intensive quantity.

For one mole of solution, n=1, then

$$dG = VdP - SdT + \sum_i \mu_i dx_i$$

$$nH = nU + P(nV)$$

$$nA = nU - T(nS)$$

$$nG = nU + P(nV) - T(nS)$$

$$dU_t = d(nU) = Td(nS) - Pd(nV) + \sum_i \mu_i dn_i$$

$$dH_t = d\left(nH\right) = Td\left(nS\right) + \left(nV\right)dP + \sum_i \mu_i dn_i$$

$$dA_t = d\left(nA\right) = -\left(nS\right)dT - Pd\left(nV\right) + \sum_i \mu_i dn_i$$

$$\mu_i = \left(\frac{\partial U_t}{\partial n_i}\right)_{S_t, V_t, n_j} = \left(\frac{\partial H_t}{\partial n_i}\right)_{S_t, P, n_j} = \left(\frac{\partial A_t}{\partial n_i}\right)_{T, V_t, n_j} = \left(\frac{\partial G_t}{\partial n_i}\right)_{T, P, n_j}$$

2.3 The chemical potential and phase equilibria

- **Consider a closed system consisting of two phases in equilibrium. Each phase is an open system.**

$$d(nG)^{\alpha} = (nV)^{\alpha} dP - (nS)^{\alpha} dT + \sum_i \mu_i^{\alpha} dn_i^{\alpha}$$

$$d(nG)^{\beta} = (nV)^{\beta} dP - (nS)^{\beta} dT + \sum_i \mu_i^{\beta} dn_i^{\beta}$$

$$d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i^{\alpha} dn_i^{\alpha} + \sum_i \mu_i^{\beta} dn_i^{\beta}$$

Since the two-phase system is closed,

$$d(nG) = (nV)dP - (nS)dT$$

$$\sum_i \mu_i^{\alpha} dn_i^{\alpha} + \sum_i \mu_i^{\beta} dn_i^{\beta} = 0$$

Mass conservation requires:

$$dn_i^{\alpha} = -dn_i^{\beta}$$

$$\sum_i \left(\mu_i^{\alpha} - \mu_i^{\beta}\right) dn_i^{\alpha} = 0$$

$$\mu_i^{\alpha} = \mu_i^{\beta}$$

$$\mu_i^{\alpha} = \mu_i^{\beta} = \cdots = \mu_i^{\pi} \qquad (i = 1, 2, \cdots, N)$$

Thus, multiple phases at the same T and P are in equilibrium when the chemical potential of each species is the same in all phases.

Phase Equilibrium relationships

$$T^{(1)} = T^{(2)} = \ldots = T^{(\pi)}$$

$$P^{(1)} = P^{(2)} = \ldots = P^{(\pi)}$$

$$\mu_1^{(1)} = \mu_1^{(2)} = \ldots \mu_1^{(\pi)}$$

$$\ldots\ldots\ldots$$

$$\mu_m^{(1)} = \mu_m^{(2)} = \ldots \mu_m^{(\pi)}$$

2.4 The Phase Rule

- The variables for describing a process are
  - Extensive (depends on size of system)
  - Intensive (do not)
- The number of intensive variables that can be specified independently is called degree of freedom.
- For nonreacting systems:

$$F = 2 + (N - 1)\pi - (\pi - 1)N$$

$$= 2 - \pi + N$$

2.5 Partial properties (ponent system)

$$\overline{M}_i = \left[\frac{\partial (nM)}{\partial n_i}\right]_{T,P,n_j} = \left(\frac{\partial M_t}{\partial n_i}\right)_{T,P,n_j}$$

1. Constant T and P
2. Intensive properties
3. Partial derivative
4. Gibbs-Duhem

This equation defines the partial molar property of species i in solution, which representing the change of total property nM due to addition at constant T and P of a differential amount of species i to a finite amount of solution.

$$\mu_i \equiv \overline{G}_i$$

2.6 The Gibbs-Duhem Equation

$$nM = \mathrm{M}\left(T, P, n_1, \cdots, n_i, \cdots\right)$$

The total differential of nM is:

$$d\left(nM\right) = \left[\frac{\partial\left(nM\right)}{\partial P}\right]_{T,n} dP + \left[\frac{\partial\left(nM\right)}{\partial T}\right]_{P,n} dT + \sum_i \left[\frac{\partial\left(nM\right)}{\partial n_i}\right]_{P,T,n_j} dn_i$$

where subscript n indicates that all mole numbers are held constant, and subscript n_j that all mole numbers except n_i are held constant.

$$d\left(nM\right) = n\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + n\left(\frac{\partial M}{\partial T}\right)_{P,x} dT + \sum_i \bar{M}_i dn_i$$

Since $n_i = x_i n$

$$dn_i = x_i dn + n dx_i$$

$$d(nM) \equiv n dM + M dn$$

$$n dM + M dn = n\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + n\left(\frac{\partial M}{\partial T}\right)_{P,x} dT + \sum_i \bar{M}_i \left(x_i dn + n dx_i\right)$$

$$\left[dM - \left(\frac{\partial M}{\partial P}\right)_{T,x} dP - \left(\frac{\partial M}{\partial T}\right)_{P,x} dT - \sum_i \bar{M}_i dx_i\right] n + \left[M - \sum_i x_i \bar{M}_i\right] dn = 0$$

The only way that the left side of this equation can be zero is for each term in brackets to be zero.

$$dM = \left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \left(\frac{\partial M}{\partial T}\right)_{P,x} dT + \sum_i \bar{M}_i dx_i$$

$$M = \sum x_i \bar{M}_i$$

Multiplication by n yields the alternative expression:

$$nM = \sum_i n_i \bar{M}_i$$

$$dM = \sum_i x_i d\bar{M}_i + \sum_i \bar{M}_i dx_i$$

Comparison two equations for *dM*, yields

$$\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \left(\frac{\partial M}{\partial T}\right)_{P,x} dT - \sum_i x_i d\bar{M}_i = 0$$

This equation is called the Gibbs-Duhem equation

For the important special case of changes at constant T and P, it simplifies to:

$$\sum_i x_i d\bar{M}_i = 0 \qquad (const \quad T, P)$$

2.7 From Chemical Potential to Fugacity

$$\mu_i(T,P) = \mu_i^0 + RT \ln \frac{f_i}{f_i^0}$$

$$\mu_i^{(\alpha)} = \mu_i^{0\alpha} + RT \ln \frac{\hat{f}_i^{\alpha}}{f_i^{0\alpha}} \qquad i = 1,2,\ldots\ldots,m$$

$$\alpha = 1,2,\ldots\ldots,\pi$$

$$\mu_i^{01} + RT \ln \frac{\hat{f}_i^{(1)}}{f_i^{01}} = \mu_i^{02} + RT \ln \frac{\hat{f}_i^{(2)}}{f_i^{02}} = \ldots\ldots = \mu_i^{0\pi} + RT \ln \frac{\hat{f}_i^{(\pi)}}{f_i^{0\pi}}$$

Phase Equilibrium in terms of fugacity

$$T^{(1)} = T^{(2)} = \ldots = T^{(\pi)}$$

$$P^{(1)} = P^{(2)} = \ldots = P^{(\pi)}$$

$$\hat{f}_1^{(1)} = \hat{f}_1^{(2)} = \ldots \hat{f}_1^{(\pi)}$$

.....

$$\hat{f}_m^{(1)} = \hat{f}_m^{(2)} = \ldots \hat{f}_m^{(\pi)}$$

Fugacity coefficient and Equilibrium

$$\hat{\varphi}_i = \frac{\hat{f}_i}{Px_i} = \frac{\hat{f}_i}{P_i}$$

- Fugacities are more convenient than chemical potentials...
- ... but equilibrium is best expressed in term of fugacity coefficients
- ... which is one if the fugacity is equal to the partial pressure
- Fugacity coefficient may be considered as the correction factor to the partial pressure (effective partial pressure)

2.8 Activity

The activity of a component is defined as the ratio of the partial fugacity at system T to that at a standard state:

$$a_i = \frac{\hat{f}_i}{f_i^{o}}$$

$$a_i = \gamma_i x_i$$

activity coefficient

Equilibrium Ratios

- It is often useful to compare the behaviour of components at equilibrium. For vapour-liquid equilibrium:

$$K_i = \frac{y_i}{x_i}$$

- For liquid-liquid:

$$K_{Di} = \frac{x_i^{(1)}}{x_i^{(2)}}$$

- K_{Di} is a distribution coefficient or liquid-liquid equilibrium ratio

- For comparing components, there is the relative volatility:

$$\alpha_{ij} = \frac{K_i}{K_j}$$

If K is known, then the liquid and gas phase mole fractions can be related.

Vapour-Liquid Equilibrium

- For vapour-liquid equilibrium:

$$\overline{f_{iv}} = \overline{f_{iL}}$$ **equilibrium criterion**

$$\overline{\phi_{iv}} = \frac{\overline{f_{iv}}}{y_i P} \Rightarrow \overline{f_{iv}} = \overline{\phi_{iv}}\, y_i P$$

$$\overline{\phi_{iL}} = \frac{\overline{f_{iL}}}{x_i P} \Rightarrow \overline{f_{iL}} = \overline{\phi_{iL}}\, x_i P$$

- so that: $\overline{\phi_{iv}}\, y_i P = \overline{\phi_{iL}}\, x_i P$
- or: $\frac{y_i}{x_i} = \frac{\overline{\phi_{iL}}}{\overline{\phi_{iv}}} = K_i$

Which is called the equation of state form

Vapour-Liquid Equilibrium

activity coefficient form

$$\hat{f}_{iv} = \hat{\phi}_{iv} y_i P$$

$$\hat{f}_{iL} = \gamma_i x_i f_i^{\,0}$$

$$\hat{\phi}_i^{V} y_i P = \gamma_i x_i f_i^{\,0}$$

2.9 Fugacity of Pure Gas

$$(d\mu)_T = RTd \ln f$$

For 1 mol pure gas

$$(dG)_T = VdP = (d\mu)_T$$

$$RTd \ln f = VdP$$

For ideal gas $$RTd \ln P = VdP = \frac{RT}{P} dP$$

$$RTd (\ln f - \ln P) = \left(V - \frac{RT}{P} \right) dP$$

Fugacity of Pure Gas

Integrated to give:

$$\ln \phi = \ln \frac{f}{P} = \frac{1}{RT} \int_{P_0}^{P} \left(V - \frac{RT}{P} \right) dP$$

$$= \frac{1}{RT} \int_{P_0}^{P} V dP - \int_{\ln P_0}^{\ln P} d \ln P$$

$$\int V dP = \Delta (PV) - \int P dV$$

By using RK equation

$$\ln \frac{f}{P} = Z - 1 - \ln \left(Z - \frac{Pb}{RT} \right) - \frac{a}{bRT^{1.5}} \ln \left(1 + \frac{b}{V} \right)$$

Fugacity of Pure liquid

$$RT \ln \phi = RT \ln \frac{f_i^L}{P} = \int_0^{P_i^s} \left(V_i - \frac{RT}{P} \right) dP + \int_{P_i^s}^{P} \left(V_i^L - \frac{RT}{P} \right) dP$$

$$= RT \ln \frac{f_i^s}{P_i^s} + \int_{P_i^s}^{P} V_i^L dP - RT \ln \frac{P}{P_i^s}$$

$$f_i^L = f_i^s \exp \int_{P_i^s}^{P} \frac{V_i^L dP}{RT}$$

$$f_i^L = f_i^s \exp \left(\frac{V_i^L \left(P - P_i^s \right)}{RT} \right)$$

The exponential is known as a Poynting factor.

2.11 Fugacity of Species in Mixture

$$d\overline{G}_i = RTd \ln \hat{f}_i = \overline{V}_i dP$$

$$\lim_{P \to 0} \frac{\hat{f}_i}{y_i P} = \lim_{P \to 0} \hat{\phi}_i = 1$$

$\hat{\phi}_i$

$$RT \ln \hat{\phi}_i = \int_0^P \left(\overline{V}_i - \frac{RT}{P} \right) dP$$

$$RT \ln \hat{\phi}_i = \int_{V_t}^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \left(\frac{RT}{V_t} \right) \right] dV_t - RT \ln z_m$$

2.12 The Lewis-Randall Fugacity Rule

For pure gas i

$$\ln \phi_i = \frac{1}{RT}\int_0^P (V_i - RT)\,dP$$

For component i

$$\ln \hat{\phi}_i = \frac{1}{RT}\int_0^P \left(\bar{V}_i - RT\right) dP$$

$$\ln \frac{\hat{\phi}_i}{\phi_i} = \frac{1}{RT}\int_0^P \left(\bar{V}_i - V_i\right) dP$$

$$\hat{\phi}_i = \frac{\hat{f}_i}{y_i P} \qquad \phi_i = \frac{f_i}{P}$$

The Lewis-Randall Fugacity Rule

$$\ln \frac{\hat{f}_i}{y_i f_i} = \frac{1}{RT} \int_0^P \left(\overline{V}_i - V_i \right) dP$$

Assuming $\overline{V}_i = V_i$

$$\hat{f}_i = y_i f_i$$

or, in equivalent form, $\hat{\Phi}_i = \Phi_i$

The Lewis-Randall Fugacity Rule

For vapour-liquid equilibrium:

$$f_i^V = f_i^L$$

According to the Lewis-Randall

$$y_i f_{purei}^V = x_i f_{purei}^L$$ **Liquid phase forms an ideal mixture**

If the vapor phase can be considered to be ideal gas mixtures

$$y_i P = x_i P_i^s$$

This is called Raoult's Law

Indicating the partial pressure of a component in an ideal solution is equal to the the product of the species mole fraction and its pure component vapor pressure

2.13 Ideal Solution

$$dG_i = RTd \ln f_i$$

$$d\hat{G}_i = RTd \ln \hat{f}_i$$

$$\overline{G}_i - G_i = RT \ln \frac{\hat{f}_i}{f_i}$$

$$\overline{G}_i^{id} - G_i = RT \ln \frac{x_i f_i}{f_i} = RT \ln x_i$$

$$\Delta G^{id} = \sum_i x_i \overline{G}_i^{id} - \sum_i x_i G_i = RT \sum_i x_i \ln x_i$$

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