

# Chapter 4: Phase Equilibrium

Equation of state for a pure (single component) gas:

ideal gas:  $PV = RT$        $V = \frac{\text{volume}}{\text{mole}}$        $nV = \text{total volume} = V^t$

Virial equation of state:

define compressibility factor ( $Z$ ) by  $Z = \frac{PV}{RT}$

- Density expansion:  $Z = 1 + B\rho + \dots$       where  $\rho = \frac{1}{V}$
- Pressure expansion:  $Z = 1 + B'P + \dots$

The pressure expansion form, which tends to be the more convenient form, is often written in terms of the coefficient for the density expansion ( $B$ ) since the coefficient is easier to predict and is the one generally measured experimentally. The following approximation is therefore often used:

$$Z = 1 + \frac{BP}{RT} \quad \begin{array}{l} B: \text{density series coefficient} \\ P: \text{pressure expansion} \end{array}$$

Prediction of  $B$ : Three parameter correlation of Pitzer and Curl

Parameters:  $P_c, T_c, \omega$  (the acentric factor)

Note:  $\omega = 0$  for inert, spherical gases. e.g. Ar etc

$$\frac{BP_c}{RT_c} = B^0(T_r) + \omega B^1(T_r)$$

$B^0(T_r) = 0.083 - \frac{0.422}{T_r^{1.6}}$

$B^1(T_r) = 0.139 - \frac{0.172}{T_r^{4.2}}$

Note:  $T_r = \frac{T}{T_c}$

Virial equation of state for a multi-component gas:

$$Z_{\text{mix}} = \frac{PV_{\text{mix}}}{RT} \quad \text{and} \quad Z_{\text{mix}} = 1 + \frac{B_{\text{mix}}P}{RT}$$

where  $B_{\text{mix}} = \sum_i \sum_j y_i y_j B_{ij}$

$B_{11} = \text{pure gas } B$   
 $B_{12} = \text{"cross" coefficient } (B_{12} = B_{21})$

Binary mixture ( $B_{\text{mix}}$ ) =  $y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22}$

Extension of Pitzer and Curl correlation to mixtures:

$$\frac{B_{ij}P_{c,ij}}{RT_{c,ij}} = B^0(T_{r,ij}) + \omega_{ij} B^1(T_{r,ij}) \quad \text{where } T_{r,ij} = \frac{T}{T_{c,ij}}$$

$\omega_{ij}, T_{c,ij}, P_{c,ij}$  are given by empirical correlations

Define fugacity (escaping tendency) for a pure gas:

$$dG_i = RT d \ln(f_i) \quad \text{and} \quad \lim_{P \rightarrow 0} \left( \frac{f_i}{P} \right) = 1$$

$f_i = P$  for an ideal gas

Fugacity coefficient (in thermo it's  $\phi$ ):  $f_i = \phi_i P$

For a gas mixture:

$$dG = RT d \ln(f)$$

$$\lim_{P \rightarrow 0} \left( \frac{f}{P} \right) = 1$$

$$f = \phi P$$

For a component in a gas mixture

$$d\bar{G}_i = RT d \ln \hat{f}_i$$

$$\lim_{P \rightarrow 0} \left( \frac{\hat{f}_i}{y_i P} \right) = 1$$

$$\hat{f}_i = \hat{\phi}_i y_i P$$

where  $\bar{G}_i$  (partial molar Gibbs energy) is:

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

Relation between  $\phi$  and  $\hat{\phi}_i$  and  $f$  and  $\hat{f}_i$

$$\left( \frac{\partial n \ln \phi}{\partial n_i} \right)_{T, P, n_j} = \ln \hat{\phi}_i \quad \left( \frac{\partial (n \ln f)}{\partial n_i} \right)_{T, P, n_j} = \ln \frac{\hat{f}_i}{x_i}$$

So that  $\ln \hat{\phi}_i$  is the partial molar property associated with  $\ln \phi$  and  $\ln \frac{\hat{f}_i}{x_i}$  is the partial molar property associated with  $\ln f$ .

Using these relations it can be shown that:  $\ln \hat{\phi}_i = \frac{P \bar{B}_i}{RT} - \left( \frac{\partial n B_{mix}}{\partial n_i} \right)_{T, P, n_j}$  ← partial molar virial coefficient

However, the above result yields complex results for  $\hat{\phi}_i$  as a function of composition. To simplify we can often use the "**Lewis Fugacity Rule**" which states that:

$$\hat{\phi}_i(T, P, y_i) = \phi_i(T, P, y_i = 1)$$

so the dependence of  $\hat{\phi}_i$  on composition is removed which leads to:

$$\hat{f}_i = y_i \phi_i P \quad \text{where } \phi_i = \exp(B_i P / RT)$$

↖ use  $\phi_i$  instead of  $\hat{\phi}_i$  here

We will show later that this is equivalent to assuming an ideal mixture of non-ideal gases.

The equation of state approach is less useful for a liquid. Instead, for a liquid, use the concept of activity.

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

← fugacity in its standard state - pure liquid at T and P of mixture

For an "ideal mixture":  $\hat{f}_i^{id} = x_i f_i^\circ$

The **activity coefficient** relates  $\hat{f}_i$  and  $\hat{f}_i^{id}$ :  $\gamma_i = \frac{\hat{f}_i}{\hat{f}_i^{id}}$  so that  $\hat{f}_i = \gamma_i x_i f_i^\circ$

## Theories for liquid phase activity coefficients:

Regular solution theory:

$$\ln \gamma_i = \frac{V_i (\delta_i - \bar{\delta})^2}{RT}$$

$V_i$  = molar volume of pure  $i$   
 $\delta_i$  = solubility parameter of pure  $i$   
 $\bar{\delta}$  = solubility parameter of the mixture

$$\delta_i = \left( \frac{\Delta U_{v,i}}{V_i} \right)^{1/2} \quad \text{where } \Delta U_{v,i} = \Delta H_{v,i} - P \Delta V_{v,i} \approx \Delta H_{v,i} - RT$$

$$\bar{\delta} = \frac{\sum_j \delta_j V_j X_j}{\sum_j V_j X_j}$$

Note that  $\frac{V_i X_i}{\sum_j V_j X_j}$  = volume fraction of component  $i$ .

Let's apply the idea of an activity coefficient to a gas mixture with the standard state being the pure real gas component at the  $T$  and  $P$  of the mixture...

$$\hat{f}_i = \gamma_i y_i \phi_i P \quad \leftarrow f_i^\circ$$

Now set  $\gamma_i = 1$  (ideal mixture) and you get (and again!) the **Lewis Fugacity Rule**. Lewis Fugacity Rule assumes that we have an ideal mixture of non-ideal gases.

## Additional relations often needed in phase equilibrium relations:

### Antoine Equation:

$$\ln(P_i^{\text{sat}}) = A_i - \frac{B_i}{T + C_i} \quad A_i, B_i, \text{ and } C_i \text{ are the Antoine Constants}$$

### Watson Equation

$$\Delta H_{v,T_2} = \Delta H_{v,T_1} \left( \frac{1 - \frac{T_2}{T_c}}{1 - \frac{T_1}{T_c}} \right)^{0.375}$$

## Liquid Phase Heat Capacity

$$\frac{C_{pL} - C_p^\circ}{R} = 2.50 + 0.430 (1 - T_r)^{-1} + \omega \left[ 2.91 + 4.28 (1 - T_r)^{1/3} T_r^{-1} + 0.290 (1 - T_r)^{-1} \right]$$

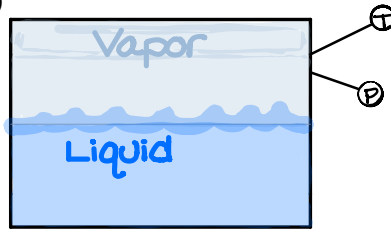
The above result is the **Lee-Kessler** "heat capacity departure function."  $C_p^\circ$  can be obtained from thermodynamic handbooks.

Note that the dependence of  $C_p$  on pressure is given by the equation of state:

$$\left( \frac{\partial C_p}{\partial P} \right)_T = -T \left( \frac{\partial^2 V}{\partial T^2} \right)_P$$

$$\text{For an ideal gas, } \left( \frac{\partial C_p}{\partial P} \right)_T = 0$$

## Vapor-Liquid Equilibrium (VLE)



Statements of equilibrium:

$$\mu_{i,v} = \mu_{i,l} \quad \text{where } \mu_i = \bar{G}_i = \text{chemical potential}$$

$$\text{or } \hat{f}_{i,v} = \hat{f}_{i,l}$$

substituting  $y_i P \hat{\phi}_i = x_i \delta_i f_i^\circ \rightarrow f_i^\circ = \text{fugacity of pure } i \text{ at } T \text{ and } P \text{ of mixture.}$

$$f_i^\circ = \underbrace{P_{i,sat} \phi_{i,sat}}_{\substack{\text{fugacity of liquid} \\ i \text{ under its own} \\ \text{vapor pressure}}} \exp \int_{P_{i,sat}}^P \frac{v_{i,l}}{RT} dP$$

vapor pressure of pure  $i$  at  $T$ :  
Poynting correction (usually  $\sim 1$ )

$$\text{Final Result: } y_i P \hat{\phi}_i = x_i \delta_i \phi_{i,sat} P_{i,sat}$$

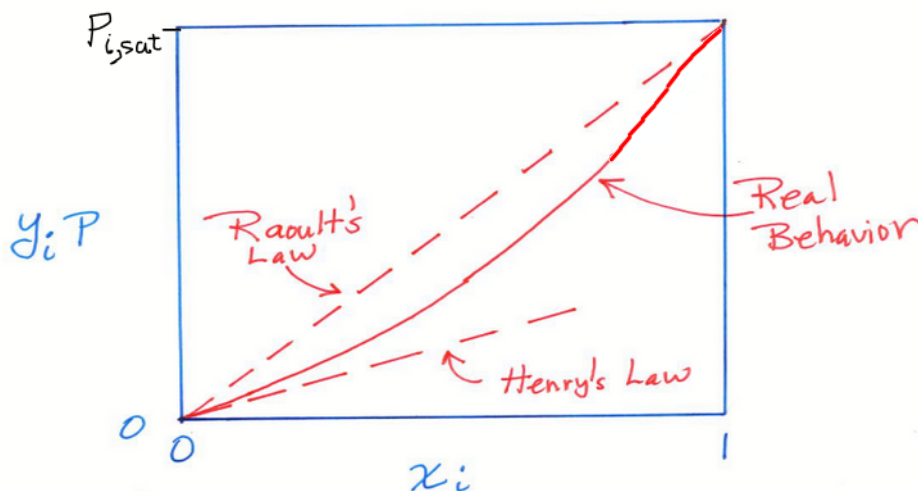
## Raoult's and Henry's Law

Select standard state for liquid so that  $\delta_i = 1$  in the concentration range of **interest**

$$\text{General equation: } y_i P \hat{\phi}_i = x_i \delta_i f_i^\circ$$

Raoult's Law:  $\delta_i = 1; \phi_i = 1; f_i^\circ = P_{i,sat}$   
vapor pressure of pure  $i$  at  $T$ .

Henry's Law:  $\delta_i = 1; \phi_i = 1; f_i^\circ = \left( \frac{y_i P}{x_i} \right)_{\lim x_i \rightarrow 0} = H_i^\circ$



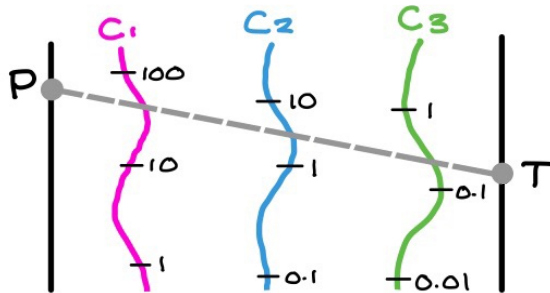
Some simple results:

$$K_i = \text{equilibrium ratio} = \frac{y_i}{x_i} \quad K_i = \frac{\gamma_i \hat{\phi}_i^{\text{sat}} P_i^{\text{sat}}}{P \hat{\phi}_i}$$

ideal mixture

For ideal gas and liquid,  $K_i$  is not a function of composition:  $K_i = \frac{P_i^{\text{sat}}}{P}$  function of temperature

If we use the Lewis Fugacity Rule and an average value of  $\gamma_i$  for each component, we will again get  $K_i$  independent of composition. These are the assumptions used to produce a **DePriester Chart**.



See wankat textbook for examples of this diagram

### Relative Volatility

$$\alpha_{ij} = \frac{\frac{y_i}{x_i}}{\frac{y_j}{x_j}} = \frac{K_i}{K_j} = \frac{\gamma_i}{\gamma_j} \frac{\hat{\phi}_i^{\text{sat}} P_i^{\text{sat}} \hat{\phi}_j}{\hat{\phi}_j^{\text{sat}} P_j^{\text{sat}} \hat{\phi}_i} = \frac{y_i}{x_i} \frac{x_j}{y_j}$$

direct dependence on P is eliminated but  $\hat{\phi}_i$  are still a function of P.

if ideal:  $\alpha_{ij} = \frac{P_i^{\text{sat}}}{P_j^{\text{sat}}}$  ← function of T only

for a binary mixture (A+B):

$$\alpha_{AB} = \frac{\frac{y_A}{x_A}}{\frac{y_B}{x_B}} \quad \text{also, } x_A + x_B = y_A + y_B = 1 \quad \text{which yields: } y_A = \frac{\alpha_{AB} x_A}{1 + (\alpha_{AB} - 1) x_A}$$

for a multi component mixture:

$$\alpha_{ij} = \frac{\frac{y_i}{x_i}}{\frac{y_j}{x_j}} \quad \text{and } \sum y_i = \sum x_i = 1 \quad \text{which yields: } y_i = \frac{\alpha_{ij} x_i}{\sum_K \alpha_{Kj} x_K} \quad \text{* can select j arbitrarily *$$

for two liquid phases in contact



$$\alpha_{ij} = \frac{\frac{x_{i1}}{x_{j1}}}{\frac{x_{i2}}{x_{j2}}} = \frac{\frac{\gamma_{i2}}{\gamma_{j2}}}{\frac{\gamma_{i1}}{\gamma_{j1}}}$$

This comes from  $\gamma_{i1} x_{i1} f_{i1}^0 = \gamma_{i2} x_{i2} f_{i2}^0$

## Phase equilibrium calculations for VLE

Consider the case where 5 components are present...

### Gibbs phase rule:

$$\text{DOF: } 2 + C - \pi \rightarrow 2 + 5 - 2 = \underline{5} \quad \begin{array}{l} C = \text{components} \\ \pi = \text{phases} \end{array}$$

Need to specify 5 independent variables in this case

### Examples:

#### 1. "Bubble T" problem

Determine boiling point temperature and composition of a vapor if pressure and liquid phase composition are specified.

Specify:  $x_1, x_2, x_3, x_4, x_5, P$  ...  $n-1$   $x_i$  are independent  
 $\uparrow$   $1 - x_1 - x_2 - x_3 - x_4$

Determine:  $y_1, y_2, y_3, y_4, y_5, T$  ... for simplicity, treat this as 6 unknowns

Equations:

$$y_1 - \frac{x_1 \hat{\gamma}_1 \phi_{1, \text{sat}} P_{3, \text{sat}}}{P \hat{\phi}_1} = 0 \quad (1)$$

$$y_2 - \frac{x_2 \hat{\gamma}_2 \phi_{2, \text{sat}} P_{3, \text{sat}}}{P \hat{\phi}_2} = 0 \quad (2)$$

$$y_3 - \frac{x_3 \hat{\gamma}_3 \phi_{3, \text{sat}} P_{3, \text{sat}}}{P \hat{\phi}_3} = 0 \quad (3)$$

$$y_4 - \frac{x_4 \hat{\gamma}_4 \phi_{4, \text{sat}} P_{4, \text{sat}}}{P \hat{\phi}_4} = 0 \quad (4)$$

$$y_5 - \frac{x_5 \hat{\gamma}_5 \phi_{5, \text{sat}} P_{3, \text{sat}}}{P \hat{\phi}_5} = 0 \quad (5)$$

$$y_1 + y_2 + y_3 + y_4 + y_5 - 1 = 0 \quad (6)$$

#### 2. "Dew P" problem

Determine the pressure and composition of liquid when a liquid is condensed from a vapor at a given temperature.

Specify:  $y_1, y_2, y_3, y_4, y_5, T$

Determine:  $x_1, x_2, x_3, x_4, x_5, P$  ... treat this as 6 unknowns

Equations:

$$x_1 - \frac{y_1 P \hat{\phi}_1}{\hat{\gamma}_1 \phi_{1, \text{sat}} P_{1, \text{sat}}} = 0 \quad (1)$$

$$x_2 - \frac{y_2 P \hat{\phi}_2}{\hat{\gamma}_2 \phi_{2, \text{sat}} P_{2, \text{sat}}} = 0 \quad (2)$$

$$x_3 - \frac{y_3 P \hat{\phi}_3}{\hat{\gamma}_3 \phi_{3, \text{sat}} P_{3, \text{sat}}} = 0 \quad (3)$$

$$x_4 - \frac{y_4 P \hat{\phi}_4}{\hat{\gamma}_4 \phi_{4, \text{sat}} P_{4, \text{sat}}} = 0 \quad (4)$$

$$x_5 - \frac{y_5 P \hat{\phi}_5}{\hat{\gamma}_5 \phi_{5, \text{sat}} P_{3, \text{sat}}} = 0 \quad (5)$$

$$x_1 + x_2 + x_3 + x_4 + x_5 - 1 = 0 \quad (6)$$