2. Phase Equilibrium

2.1 Review of relations for gaseous mixtures:

Partial Pressure: (P_i)

In a mixture of different gases the molecules of each gas are distributed throughout the available space and their motion contributes to the total pressure of the system.

The partial pressure of a component gas that is present in the mixture is the pressure that would be exerted by that component if it were present alone in the same volume and at the same temperature as the mixture.

For an ideal gas: $P_i = n_i \frac{RT}{V}$; V : total volume

Pure component volume: V_i

The pure component volume of a component gas that is present in a mixture of gases is the volume that would be occupied by that component if it were present alone at the same temperature and pressure as the mixture.

For an ideal Gas $V_i = n_i \frac{RT}{P}$; P : total pressure

Relation between Partial pressure, pure component volume and mole fraction:

$$\frac{P_i}{V_i} = \frac{n_i (RT/V)}{n_i (RT/P)} \Rightarrow \frac{P_i}{P} = \frac{V_i}{V}$$

$$\frac{P_i}{P} = \frac{n_i (RT/V)}{n (RT/V)} \Rightarrow \frac{P_i}{P} = \frac{n_i}{n}$$

$$\Rightarrow \quad \frac{P_i}{P} = \frac{V_i}{V} = \frac{n_i}{n} = y_i$$

Dalton's Law of Partial Pressures:

The total pressure exerted by a gaseous mixture is equal to the sum of the partial pressures of the components present in the mixture:

$$P = \sum P_i$$

Amagats Law:

The total volume occupied by a gaseous mixture is equal to the sum of the pure component volumes.

$$V = \sum V_i$$

Vapor pressure:

A vapor is a gas below its critical point. Vapor pressure is the pressure at which the liquid and vapor phases of a pure substance may exist at equilibrium at a certain temperature.

Change of vapor pressure with temperature:

Antoine Equation: (predictions of vapor pressures)

$$\ln(P) = -\frac{A}{T + C} + B$$

A, B and C are constants specific for each substance. T is the absolute temperature.

Change of vapor pressure with pressure:

Under normal conditions it is negligible.

Boiling point:

It is the temperature at which the vapor pressure of a pure liquid becomes equal to the external pressure.

Saturation:

A gaseous mixture in contact with a pure liquid is said to be saturated when the partial pressure of the liquid vapor in the mixture is equal to the vapor pressure of the liquid at a certain temperature. The vapor and liquid are at equilibrium.

Phase Rule:

For a nonchemically reactive system at heterogeneous equilibrium.

$$F = C - P + 2$$

C = Number of components (chemical species)
P = Number of phases
F = Number of degrees of freedom (variance)
= Number of intensive properties (independent variables) that must be specified to completely fix the state of the system [In this course the intensive properties are T, P and concentration].

Ex:

For a pure gas $F = 2 \Rightarrow$ T and P can be changed by small amounts without changing the state of the gas [no change in phase].

At Triple Point $P = 3 \quad \Rightarrow F = 0$

It is therefore impossible to have solid / liquid / vapor at equilibrium at conditions other than the triple point.

2.2 Vapor Liquid Equilibrium

2.2.1 Binary Vapor Liquid Equilibrium

System: vapor – Liquid mixture of components A and B.

Phase Rule: C = 2 P = 2 ⇒ F = 2

Independent variables: T, P and the concentration of one of the components in the vapor (y) and in the liquid (x).

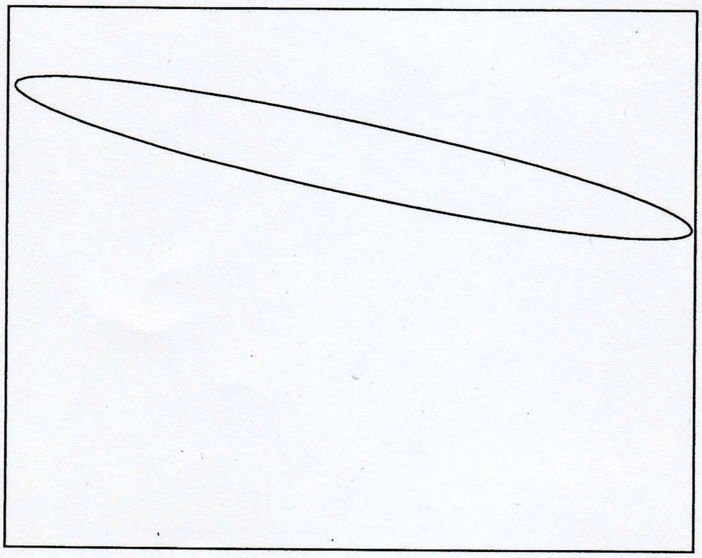
2.2.1.1 Phase equilibrium diagrams:

- Usually pressure is specified (fixed) ⇒ one independent variable remains to be fixed.
- At constant pressure four isobaric phase equilibrium diagrams involving the variables T, x and y can be constructed:

∘ T – x ∘ T – y ∘ T – x – y ∘ x – y

Constant Pressure Equilibrium:

∘ T – x ∘ T – y ∘ T – x - y diagrams:



- Liquid and vapor mixtures at equilibrium are at the same temperature and pressure and a horizontal line called a tie line joins their respective compositions.

- A mixture between two equilibrium curves such as E is a two phase mixture consisting of a liquid with composition at D and a vapor with composition at F.

  The relative amounts of equilibrium phases are given by the lever rule $\frac{MolesD}{MolesF} = \frac{\overline{EF}}{\overline{DE}}$.

- Heating a liquid mixture composition (G):

  Closed system with constant pressure. If the liquid is heated, the first bubble of vapor forms at (H) with vapor composition at (J) richer in the more volatile component (mvc). As more mixture is vaporized more vapor forms at the expense of liquid but the entire mass composition is still the same. The last drop of liquid mixture vaporizes at M and has composition at N. The boiling range of the mixture is HM.

  Open system: If a solution is boiled in an open vessel, the vapor is richer in the more volatile component. As vaporization proceeds the liquid becomes leaner. The temperature and composition of saturated liquid move along HN as vaporization (distillation) proceeds.

x vs. y diagram:

2.2.1.2 Relative volatility

The greater the distance between the equilibrium curve and the diagonal, the greater the difference in VL composition and the easier the separation.

Relative volatility is a measure of the difference between vapor and liquid composition at equilibrium. It is called separation factor.

$$\begin{aligned}\alpha &= \frac{(\text{moles A / moles B) in vapor}}{(\text{moles A / moles B) in liquid}} \\ &= \frac{y_A/(1-y_A)}{x_A/(1-x_A)} \\ &= \frac{y_A}{x_A}\frac{(1-x_A)}{(1-y_A)}\end{aligned}$$

$\alpha = 1$ no separation

$\alpha \rangle 1$ separable mixture

2.2.1.3 VLE for ideal solutions:

Characteristics of ideal solutions:

- Average inter molecular forces in the solution are unchanged upon mixing.
- No heat will be absorbed or released upon mixing.
- Volume of solution varies linearly with composition [i.e. Total solution volume equals the sum of pure component volumes].
- The total vapor pressure of solution varies linearly with composition.

Ideal solutions do not exist in reality. However, many solutions approach ideality. For example: adjacent members of homologous series of organic compounds. e.g. benzene in toluene.

Raoult's Law:

When the gas mixture in equilibrium with an ideal liquid solution also follows ideal gas law, the partial pressure of a solute gas is linearly proportional to its mole fraction in the liquid phase. The constant of proportionality being the vapor pressure of the pure species at the system temperature.

$$\underset{\substack{\nearrow \\ \text{Equilibrium partial} \\ \text{pressure}}}{P_i} = \underset{\substack{\uparrow \\ \text{vapor} \\ \text{pressure}}}{P_i^s}\ \underset{\substack{\nwarrow \\ \text{mole fraction in} \\ \text{liquid}}}{x_i}$$

It is seen that the solubility of a certain gas in an ideal solution is independent of the nature of the solvent.

For a binary mixture we have:

$$P_A = P_A^S\, x_A \qquad\qquad P_B = P_B^S\,(1 - x_A)$$

$$\begin{aligned} P_t &= P_A + P_B \\ &= P_A^S\, x_A + P_B^S\,(1 - x_A) \end{aligned}$$

$$\boxed{P_t = (P_A^S - P_B^S).\, x_A + P_B^S}$$

At constant temperature these are linear since P_A^S and P_B^S are constant.

For ideal solutions it is possible to calculate the vapor liquid equilibria from vapor pressure data of pure substances.

For Binary mixture: At a given temperature:

$x_A + x_B = 1.0$; $y_A + y_B = 1.0$

$$\boxed{x_A = \frac{(P_t - P_B^S)}{(P_A^S - P_B^S)}} \qquad y_A = \frac{P_A}{P_t} \Rightarrow \boxed{y_A = \left(\frac{P_A^S}{P_t}\right) x_A}$$

Relative volatility:

$$\alpha_{AB} = \frac{y_A}{x_A} \frac{(1 - x_A)}{(1 - y_A)}$$

$$= \frac{P_A^S x_A}{P_t x_A} \frac{(1 - x_A)}{\frac{P_B^S}{P_t}(1 - x_A)}$$

$$\therefore \quad \boxed{\alpha_{AB} = \frac{P_A^S}{P_B^S}}$$

ex. Compute the vapor liquid equilibria at constant pressure of 1 std atm for mixtures of n-heptane and n-octane.

Solution:

We need to establish t-x,y diagram at 1 atm in the temperature range between boiling points of the pure components.

At 1 atm $BP_t n\text{-}C_7 = 98.4$ °C

$BP_t n\text{-}C_8 = 125.6$ °C

$$x_A = \frac{P_t - P_B^S}{P_A^S - P_B^S} \qquad y_A = \frac{P_A^S}{P_t} x_A$$

Sample calculation

At 110 °C $P_A^S = 1050$ mm Hg $P_B^S = 484$ mm Hg

$P_t = 760$ mm Hg

$$x = \frac{760-484}{1050-484} \qquad\qquad y = \frac{1050}{760} \times 0.487$$

$$= 0.487 \qquad\qquad\qquad = 0.674$$

α_{AB}: at 110 °C

$$\alpha_{AB} = \frac{P_A^S}{P_B^S} = \frac{1050}{484} = 2.17$$

Temp. °C	P_A^S mm Hg	P_B^S mm Hg	X_A	Y_A	α_{AB}
98.4					2.28
105.0					2.25
110.0	1050	484	.487	.674	2.17
115.0					2.14
120.0					2.08
125.0					2.02

Note: α for ideal solutions does not vary considerably. An average value of α can be calculated and used.

$$\alpha_{AB} = \frac{y_A}{x_A}\frac{(1-x_A)}{(1-y_A)} \Rightarrow y_A = \alpha_{AB} x_A \frac{(1-y_A)}{(1-x_A)}$$

$$\Downarrow$$

$$y_A\left[(1-x_A) + \alpha_{AB} x_{AB}\right] = \alpha_{AB} x_A \Leftarrow y_A(1-x_A) = \alpha_{AB} x_A (1-y_A)$$

$$\Downarrow$$

$$\boxed{y_A = \frac{\alpha_{AB} x_A}{1 + x_A(\alpha_{AB} - 1)}}$$

Notes:

1. Raoult's Law can generally be applied to a component whose mole fraction in the liquid phase approaches unity or to solutions of components quite similar in chemical nature.
2. Equilibrium constant or an equilibrium distribution coefficient can be defined.

$P_i = P_i^s . x_i$ Raoult's Law

$P_i = y_i . P_t$ Dalton's Law

$$\Downarrow$$

$$K_{i,\text{Raoult}} = \frac{y_i}{x_i} = \frac{P_i^s}{P_t}$$

In general VLE data may be represented by:

$$\boxed{y_i = k_i\, x_i}$$

$K_i = f$ (T,P, composition)

It can be seen that

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{\frac{y_i}{x_i}}{\frac{y_j}{x_j}} = \frac{y_i}{x_i} . \frac{x_j}{y_j}$$

$$= \frac{y_i}{x_i} \frac{(1 - x_i)}{(1 - y_i)}$$

2.2.1.4 Actual solutions:

Miscible binary mixtures:

Few binary miscible systems obey Raoult's law throughout the complete range of concentrations. Most systems deviate from Raoult's law to a greater or lesser extent.

For real mixtures $P_i \neq P_i^s . x_i$

but instead $P_i = \gamma_i P_i^s x_i$

γ_i = activity coefficient

$$= \frac{\text{real eqm partial pressure}}{\text{ideal eqm partial pressure}} = \frac{P_i \text{ real}}{P_i^s . x_i}$$

therefore γ is a measure of the deviation from ideality

$\gamma = 1 \Rightarrow$ ideal solution

$\gamma > 1 \Rightarrow$ + ve deviation

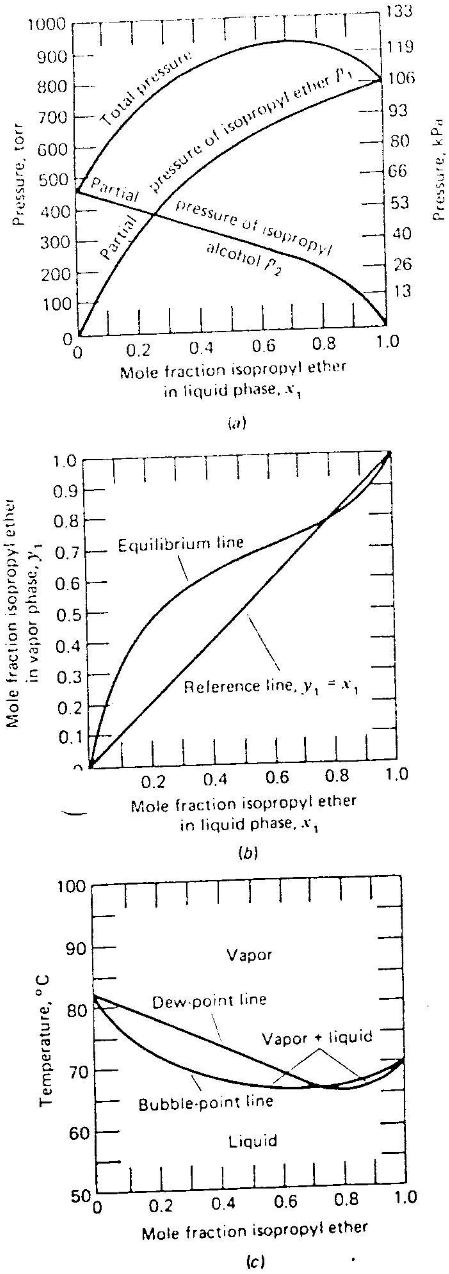


Figure 3.5. Minimum-boiling-point azeotrope, isopropyl ether–isopropyl alcohol system. (*a*) Partial and total pressures at 70°C. (*b*) Vapor-liq[illegible]ilibria at 101 kPa. (*c*) Phase diagram at 101 kPa. [Adapted from O. A. Hougen, K. M. Watson, and R. A. Ragatz, *Chemical Process Principles, Part II*, 2nd ed., John Wiley and Sons, N. Y. © (1959).]

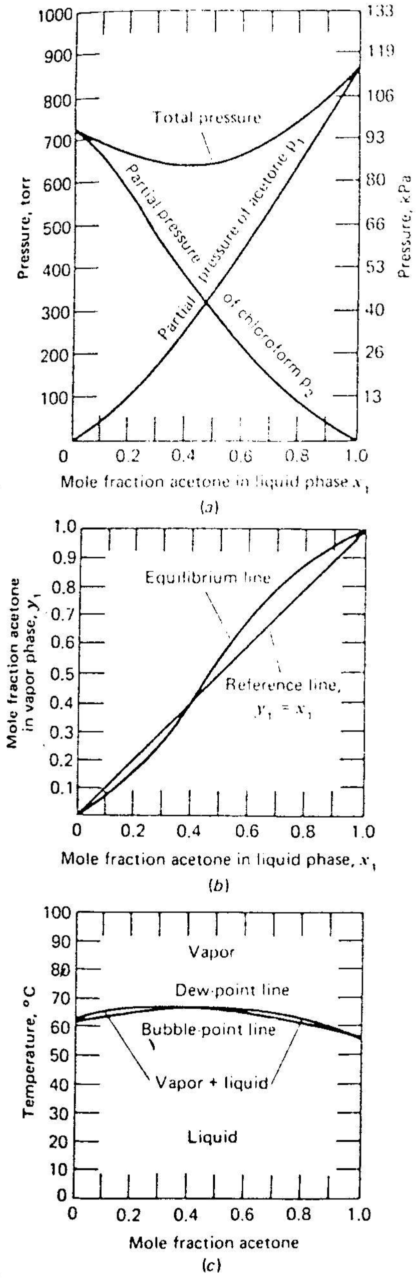


Figure 3.6. Maximum-boiling-point azeotrope, acetone–chloroform system. (*a*) Partial and total pressures at 60°C. (*b*) Vapor–liquid equilibria at 101 kPa pressure. (*c*) Phase diagram at 101 kPa pressure. [Adapted from O. A. Hougen, K. M. Watson, and R. A. Ragatz, *Chemical Process Principles, Part II*, 2nd ed., John Wiley and Sons, N. Y. © (1959).]

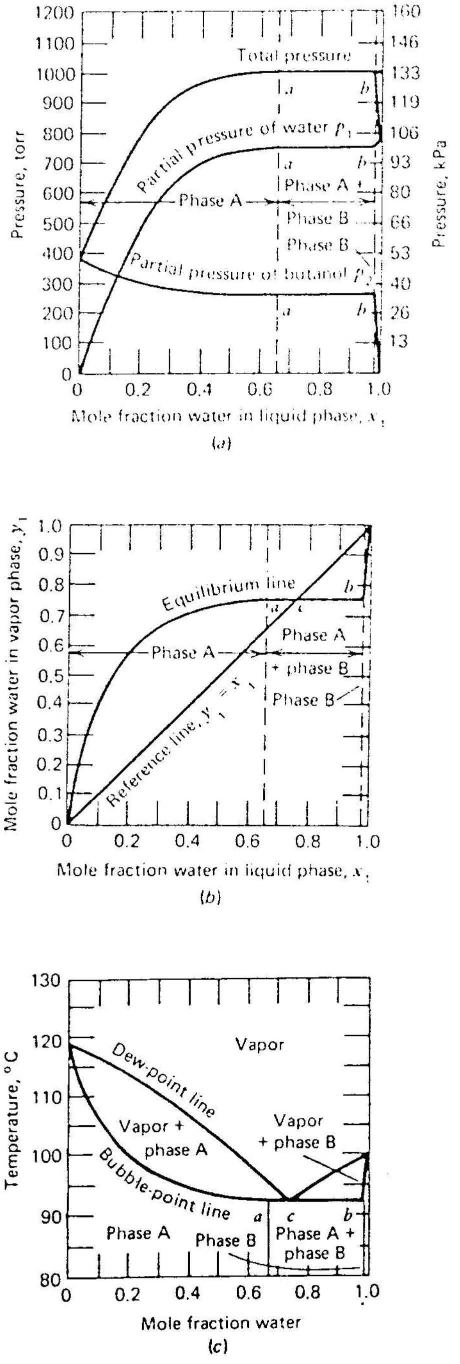


Figure 3.7. Minimum-boiling-point (two liquid phases) water–*n*-butanol system. (*a*) Partial and total pressures at 100°C. (*b*) Vapor–liquid equilibria at 101 kPa. (*c*) Phase diagram at 101 kPa pressure. [Adapted from O. A. Hougen, K. M. Watson, and R. A. Ragatz, *Chemical Process Principles, Part II*, 2nd ed., John Wiley and Sons, N.Y. © (1959).]

$\gamma < 1 \quad \Rightarrow \quad$ - ve deviation

All miscible pairs can be classified into three general types:

Type I: systems whose total vapor pressure is intermediate between those of pure components.

Ex. CCl_4 – cyclohexane
CCl_4 – benzene
Benzene – toluene
Water – methyl alcohol.

Type II: systems exhibiting a **maximum** in the total vapor pressure curve. They exhibit positive deviation from ideality and they form **minimum boiling point** mixtures.

Ex. Carbon disulfide – acetone, benzene - cyclohexane, water – ethyl alcohol.

Type III: systems exhibiting a minimum in the total vapor pressure curve. They exhibit
negative deviation from ideality and they **form maximum boiling point** mixtures.

Partially Miscible Binary Mixtures:

Some systems do not dissolve completely in all proportions. They exhibit large positive deviations (minimum boiling) [Forces of repulsion → 2 ϕ]

I. Zones:

1. all vapor
2. vapor and liquid in equilibrium with vapor richer in A
3. vapor and liquid in equilibrium with vapor richer in B
4. Liquid solution richer in B (solution of A in B)
5. Liquid solution richer in A (solution of B in A)
6. Two-phase mixtures. Each phase represents a solution of one component in the other. At constant temperature the composition of each phase is constant; however the proportions of phases are different.

II. For homogeneous liquids (zones 4 and 5), the vapor-liquid equilibrium phenomena are normal.

III. Two phase mixtures within the range KM will boil at the temperature of line KM, and they all give rise to the same vapor of composition L in equilibrium with two liquids at K and M which are also in equilibrium with each other.

IV. A two-phase mixture of average composition L which produces a vapor of the same composition is sometimes called a **heteroazeotrope.**

V. Phase rule for systems at temperature KM:

$C = 2$ $\quad P = 3$ $\quad F = C - P + 2 \Rightarrow F = 1$

∴ If pressure is set, everything else is specified.

IMMISCIBLE BINARY MIXTURES (heterogeneous solutions)

Immiscible liquids are mutually insoluble – addition of one liquid to the other does not affect the properties of either liquid. Each will behave independently and will exert its own vapor pressure corresponding to the pure liquid at a given temperature.

$$P_t = P_A^S + P_B^S$$

The mixture will boil at a certain temperature when the sum of the vapor pressures equals the external pressure. The vapor composition is:

$$y_A = \frac{P_A^S}{P_t}$$

Notes:

1. The boiling point of any mixture of two immiscible liquids is less than the boiling point of either of the two liquids.
2. Boiling point of all possible mixtures of two immiscible liquids is the same (no change in vapor pressure with composition).
3. At any boiling point, the vapor composition remains constant and is independent of overall liquid composition.

2.2.2 VLE for multi-component systems:

- Graphical presentation of more than three component systems is extremely complex.
- Many of the multi-component systems of industrial importance can be considered nearly ideal solutions. Raoult's law can be applied and vapor liquid equilibrium data can be calculated from pure component data.
- Sometimes equilibrium data can be calculated from binary mixtures data.

For multi-component systems, equilibrium data is represented by means of distribution coefficients.

For any component i

$$y_i = k_i x_I$$

For ideal solutions at moderate pressures, k_i is independent of composition. It depends only on temperature and total pressure.

At equilibrium:

$$k_i = \frac{y_i}{x_i} = \frac{p_i / p_t}{P_i / P_i^s} = \frac{P_i^s}{P_t}$$

It is also customary to choose a convenient reference component (in many cases heaviest component) to which data can be referred:

At equilibrium:

$$\alpha_{ij} = \frac{(y_i / x_i)}{(y_j / x_j)} = \frac{k_i}{k_j}$$

$$\alpha_{ij} = \frac{P_i^s / P_t}{P_j^s / P_t} = \frac{P_i^S}{P_j^S}$$

VLE For a given vapor-liquid system at equilibrium:

$$\alpha_{ij} = \frac{y_i / y_j}{x_i / x_j}$$

$$\alpha_{ij} = \frac{y_i / x_i}{y_j / x_j}$$

$$y_i = \frac{\alpha_{ij} . x_i}{(x_j / y_j}$$

$$\sum_{i=1}^{n} y_i = \sum_{i=1}^{n} \frac{\alpha_{ij} . x_i}{(x_j / y_j)} = 1$$

$$\left(\frac{x_j}{y_j} \right) = \sum_{i=1}^{n} \alpha_{ij} . x_i$$

$$\frac{y_j}{x_j} = \frac{1}{\sum \alpha_{ij} x_i}$$

$$\downarrow$$

$$\boxed{y_i = \frac{\alpha_{ij} . x_i}{\sum \alpha_{ij} . x_i}}$$

useful for Bubble
point calculation

substitute for $\frac{y_j}{x_j} = \frac{y_i}{\alpha_{ij} . x_i}$

$$x_i = \frac{y_i / \alpha_{ij}}{(y_j / x_j)}$$

$$\sum x_i = \sum \frac{y_i / \alpha_{ij}}{y_j / x_j} = 1.0$$

$$\downarrow$$

$$\left(\frac{y_j}{x_j} \right) = \sum y_i / \alpha_{ij}$$

$$\downarrow$$

$$\boxed{x_i = \frac{y_i / \alpha_{ij}}{\sum y_i / \alpha_{ij}}}$$

useful for Dew
point calculation

2.2.3 Enthalpy concentration diagrams:

Binary VLE data can also be represented by enthalpy concentration diagrams [useful in showing energy changes as well as composition changes].

Calculation of Enthalpy contents:

Liquids:

For a liquid solution:

H_L = sensible heat and heat of mixing

$H_L = C_L (t_L - t_o) M_{av} + \Delta H_S$

C_L: heat capacity of solution. For ideal solution it is the weighted average of the pure components heat capacities. (energy / mass. deg.).

M_{av}: average molecular weight.

t_L: liquid temperature (for a saturated liquid it is the bubble point).

T_o: reference temperature.

ΔH_S = heat of solution at to for the given concentration.

Saturated vapor:

We can assume pure liquids are heated separately to the dew point t_v, each vaporized at this point and vapors are mixed.

H_v = Enthalpy of Vap A + Enthalpy of Vap B.

$H_v = y\ [C_{L,A}\ (t_v - t_o)\ M_a + \lambda_A \cdot M_A] + (1-y)\ [C_{L,B}\ (t_v - t_o)\ M_B + \lambda_B]$

λ: latent heat of vaporization of pure substances at t_v [energy/mass]

C_L: heat capacity of pure liquid energy/mass deg.

2.3 Gas – Liquid systems, Henry's Law

System: Gaseous mixture A+B

A to be absorbed by liquid S

B carrier gas.

Thermodynamics variables: P, T, x_A, x_B, x_y, y_A, y_B, y_s

Degrees of freedom: $C = 3 \quad P = 2 \quad \Rightarrow F = 3 - 2 + 2 = 3$

Therefore if three variables are specified, all other variables are determined. If B is insoluble in S, and S has negligible vapor pressure, then the remaining variables are: P, T, x_A and y_A

For gases whose mole fraction in the liquid phase approaches zero, a linear equilibrium relationship may be assumed with reasonable accuracy.

Henry's Law:

$$\underset{\substack{\nearrow \\ \text{Partial pressure} \\ \text{of A}}}{P_A} = \underset{\substack{\uparrow \\ \text{Henry's} \\ \text{law constant}}}{k_h} \cdot \underset{\substack{\nwarrow \\ \text{mole fraction} \\ \text{of A in liquid}}}{x_A}$$

almost all liquids will deviate above mole fractions of 0.1.

Equilibrium constant:

$$\boxed{K_A = \frac{y_A}{x_A} = \frac{k_h}{P_t}}$$