Process Chem and Pharmaceutical Engineering 1

Background of Separation Process

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http://ocw.ump.edu.my/course/view.php?id=350#section-4

Chapter Description

- Aims
  - Solve problems related to extraction process by applying the formula relevant to specific unit operations

- Expected Outcomes
  - Explain the criteria in multiphase system, phase diagram and phase transition
  - Describe the types of separation process

- References
  - Mass Transfer and Separation Processes: Principles and Applications, Diran Basmadjian, CRC Press, 2^{nd} Edition, 2007.

Phase Equilibria

- Phase equilibria plays a crucial role in determining overall mass transfer rates.

- In processes involving single-film resistances, equilibrium compositions or pressures constitute the anchor of the driving force responsible for the transport of the mass.

- The driving forces: C* - C or P* - P
- Where C* = equilibrium compositions

  P* = partial pressure
- Transport will continue only as long as the two quantities are unequal and will come to halt when C* = C and P* = P. The two phases are then said to be in equilibrium.

- Phase equilibria also appear in processes involving two- film resistances in series.

Phase Equilibria

- Another important aspect of phase equilibria rests on the fact that they determine certain maximum or minimum quantities associated with the process
- For example, a liquid evaporates into an enclosure. By allowing the process to proceed to equilibrium (i.e., to full saturation), we are able to determine the maximum amount of liquid that will have evaporated or the minimum mass of air that can accommodate that amount of vapour
- Equilibrium determines the driving potential of the process and sets upper and lower limits to the enrichment/ depletion attainable and the material inventory involved
- Equilibrium can be viewed as one of two key players in mass transport- the other being the transport coefficients
- By ignoring the effect of transport resistance and allowing the two phases to come to equilibrium
- The device in which this step is carried out is termed an equilibrium or ideal stage

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Single- Component Systems: Vapor Pressure

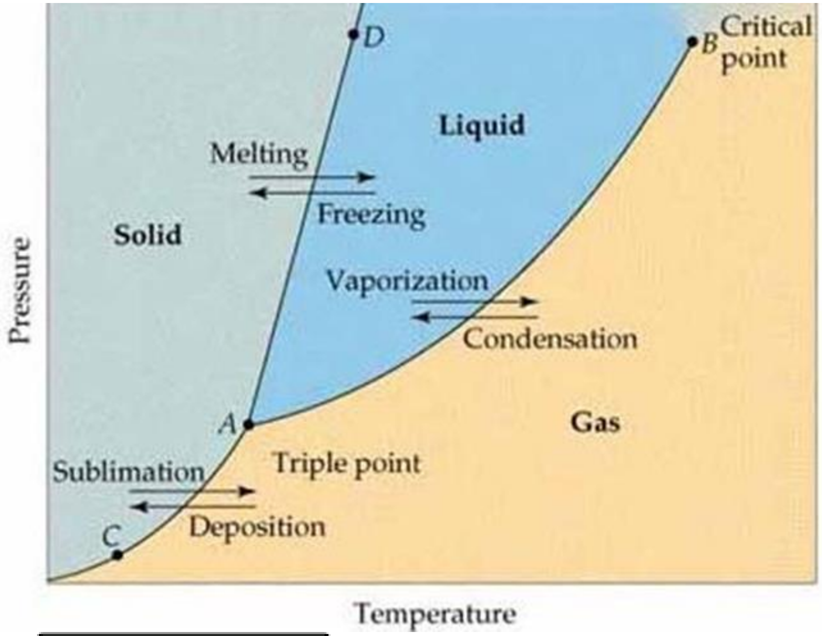
- Most pure substances that we are familiar that can exist in solid, liquid and vapour phases

- The principal exceptions are high- molecular- weight solid compounds, such as proteins, carbohydrates and polymers; which decompose before they can pass into the liquid/ vapour phase.

- The wider class of substances, is capable of existing in all three phases. Their behaviour is best illustrated by means of a pressure-temperature phase diagram

Phase Diagram of A Pure Substance

- The diagram is divided into three regions representing the solid phase (S), the liquid phase (L) and the vapour phase (V)
- The dividing boundaries between these regions are:
- Curve A: the melting point/ freezing point curve B; the sublimation which separates the solid and vapour phases
- Curve C: the vapour pressure or boiling point, which is the dividing line between liquid and vapour phases
- Normal melting point (NMP) Normal boiling point (NBP) - prevail at a pressure of 1 atm or101.3 kPa
- The pair Pt- Tt marks the triple point and represents the conditions under which all three phases can coexist. For water, the pressure and temperature values are 0.006 atm and 0.01°C respectively



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Phase Diagram of A Pure Substance

- Suppose, now, that a liquid sealed in a container and in equilibrium with its vapour is heated up starting from room temperature.
- As the temperature is raised, liquid passes into the vapour phase, thus increasing the density of the latter, while the liquid undergoes expansion with attendant decrease in density
- A point is eventually reached where the densities of the two phases become identical and the two phases merge into a single entity. The specific condition (Pc – Tc) at which this occurs is termed the critical point of the system
- Beyond it (i.e., above the critical temperature Tc), a substance can exist only as a vapour and no liquefaction can occur, no matter how high the pressure is raised.
- For water, this point is reached at a temperature of 374.4°C and a corresponding pressure of 219.5 atm
- Note that while a substance can exist only as a gas above the critical temperature, its density is nevertheless high enough that it can also qualify as a quasi- liquid.
- This dual behaviour has certain advantages that are exploited in a process termed supercritical fluid extraction.

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Phase Diagram of a Pure Substance

- In consideration of the equilibrium between liquid and vapour. The aim is to establish a quantitative relation for the curve C in Fig. a. (i.e., for the vapour pressure of the liquid in the interval between the triple point Tt and the critical temperature Tc)
- The starting point is given by the Clausius- Clapeyron equation, which is the thermodynamic expression of phase equilibrium for a pure substance:
- $\frac{dP^0}{dT} = \frac{\Delta H}{t\Delta V}$
- Here ΔH and ΔV denote the molar enthalpy and volume changes that occur during the passage from one phase to another. Above equation is confined to pure substances but is otherwise quite general and capable of expressing the transition between any two of the phases.
- Thus, for a passage from the solid to the liquid phase, ΔH will represent the latent heat of fusion, while ΔV denotes the difference between liquid and solid molar volumes. The derivative, which appears on the left side of the equation, gives the slope at any point of the phase boundary curve B or C.

Phase Diagram of a Pure Substance

- The above equation is integrated:
- $\ln P^0 = A - \frac{\Delta H_v}{RT} \quad \frac{lnP_2^0}{lnP_1^0} = \frac{\Delta H_v}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
- These equations are based on the following three assumptions:
- - constant latent heat ΔHv
- - validity of ideal gas law
- Negligible condensed phase molar volume: $\Delta V \approx V_{vapour}$

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Phase Diagram of a Pure Substance

- Variations of ΔHv with temperature are often considered negligible over a wide range of T but a thermodynamic requirement.
- All three assumptions tend to break down with increasing pressure, with the deviations escalating as the critical point is approached
- At the critical temperature, both ΔV and ΔH vanish, both equations are invalid. Antoine equation has proved to be particularly successful:
- $\log P^0 = A - B/(T + C)$
- Where
- P^0 = liquid vapour pressure (mmHg)
- T = temperature (C)
- A,B,C = Antoine constant

Phase Diagram of A Pure Substance

- The log P-inverse temperature relation is not unique to vapour-liquid and vapour-solid equilibria. It applies equally well to gas-liquid and gas-liquid equilibria, provided assumptions 1 to 3 and the concentration in the condensed phase is assumed to be constant.
- For gas absorption (at constant liquid-phase concentration C)
- $\ln\left(\frac{P_2}{P_1}\right)c = \frac{\Delta H_{ads}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
- Because the heat of values of solution in water and of adsorption (ΔH abs and ΔH ads) cluster about a value of 25 kJ/mol for the most common gases, except very low-boiling species, the following guideline emerges from both equations:

For each 20°C increase in temperature, the partial pressure of the dissolved or adsorbed gas approximately doubles

Multicomponent Systems: Distribution of a Single Component

- Vapour- liquid equilibria of mixtures and other similar multicomponent systems involving the appearance of several solutes in each phase
- They include the equilibrium of a single gas with a liquid solvent or a solid (gas absorption and adsorption), and the distribution of solutes between a liquid solution and an immiscible solvent (liquid extraction) or solid (liquid-phase adsorption)
- Although more than one component may be present in both phases, the appearance of other components does not affect the distribution of the principal component under consideration
- Thus, in gas absorption, solvent vapour is present in the gas phase but does not interfere in any way with the distribution of the main solute
- Similarly, in liquid extraction, the two solvents may not be perfectly immiscible, but this does not significantly affect the distribution of the solute

Multicomponent Systems: Gas-Liquid Equilibria

- Gases of both a benign and a toxic nature are taken up or released by bodies of water.

- On the industrial scale, both valuable and objectionable gases are often selectively removed or recovered by gas absorption or gas scrubbing

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Gas-Liquid Equilibrium Isotherm

- The phase equilibrium between a gas and a liquid solvent is usually expressed in terms of the amount absorbed or liquid-phase concentration as a function of gas pressure
- The concentration of the dissolved gas is seen to increase with pressure and it does so indefinitely (i.e., no limiting saturation value is attained)
- This is in contrast to gas-solid and liquid-solid adsorption equilibria in which the solid surface ultimately becomes saturated with solute
- An increase in temperature, diminishes the solubility of the gas and hence its concentration
- The slope of this linear portion is termed the Henry’s constant H, and the phase equilibrium in this range is said to follow Henry’s Law, given by: $P = HC$
- Here P is the gas pressure usually expressed in kilopascal (kPa) and C is the concentration of the dissolved gas (mol/L or mol/m^3)

Gas-Liquid Equilibrium Isotherm

- Henry's constants at 25°C for some common gases are displayed in the following table. Note that large values of H denote low solubility and vice versa

- The validity of equation P = HC for these gases extends to several atmospheres and in the case of permanent gases such as H_2, O_2 and N_2

Example: Carbonation of a Soft Drink

- It is common practice in the soft drink industry to carbonate drinks by dissolving a fixed volume of CO2 in the liquid, rather than by applying a prescribed pressure to the contents. That volume is set at three to five times the volume of the liquid contents
- Consider a standard 1.5L soft drink bottle with a headspace of 5%. The task is to calculate the pressure in the bottle after carbonation and the consumption of CO_2 in a plant bottling 10000 containers per day. We assume a CO_2 charge equal to 5L.
- Taking account of the 5% headspace and assuming a bottling temperature of 298 K together with a molar volume of STP of 22.4L, this leads to a CO_2 volume of
- $VCO_2 = 5000 – (0.05 \times 5000) = 4750\ L/m^3$

or equivalently,

- $C = (4750/22.4)(273/298)$ moles CO_2/m^3
- Apply this value to Henry's Law to obtain,
- $P = HC = 2.9(4750/22.4)(273/298)$ or 563 kPa
- To this value has to be added the initial air pressure of 100 kPa, which brings the total pressure in the container to slightly above 6.5 atm. To obtain this result in 10000 bottles of 1.5 L each, one requires a CO_2 volume of:
- VCO2 = 10000 x 1.425 x 5L

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Example: Carbonation of a Soft Drink

- The headspace of 0.075 L was subtracted from the total bottle volume of 1.5 L. The corresponding mass of CO_2 in the carbonated drink (mCO_2)d is given by:
- $(mCO_2) = \frac{1000\ x\ 1.425\ x5\left(\frac{273}{298}\right)M}{22.4}$, M = molar mass of CO_2 = 44
- $(mCO_2) = 128$ kg
- The amount of CO_2 in the headspace is a small fraction of this value and is given by:
- $(mCO_2)h = 1000\frac{PV}{RT}M = \frac{1000x5.63x10^5x0.075x10^{-3}x44}{8.314\ x\ 298}$
- $(mCO_2)h =$7499 g = 7.5 kg
- Thus, a total of 135 kg of CO_2 will be required in the daily operation of the plant.

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Liquid and Solid Solubilities

- Another example of a binary system in which one component is considered to be confined to one phase involves the solubility of liquids and solids in a solvent
- The confined species here is the solvent, which is in contact with a second phase containing a pure liquid or solid. At equilibrium the solvent phase has become saturated with the dissolved species or solute and no further dissolution takes place. The concentration corresponding to this state is termed the solubility of the liquid or solid.
- A listing of the solubility in water of a number of solutes, mostly organic in nature, appears in the following table. Sodium nitrate and glucose show high values of close to 50% as expected, while solubilities of DDT and mercury are measured in ppb
- The amounts dissolved may be considerable and their presence in discharged process water must be accounted for.

Solubilities of Liquids and Solids in water at 25 ^{o}C

Substance	Solubility (g/L water)
Chloroform	11
Carbon tetrachloride	0.8
Diethyl ether	75
N-Hexane	0.15
N-Octane	66 x 10^{-4}
Benzene	1.8
Toluene	0.52

Example: Discharge of Plant Effluent into a River

- In the case of process water saturated with benzene being discharged into a river. The question to be addressed is whether the diluting effect of the river flow is sufficient to reduce the effluent concentration to within permissible limits and if not, how much of the offending substance has to be removed to meet environmental standards.

- Consider an effluent discharge of 150 L/min and a river flow that varies seasonably from 23000 L/s to 50000 L/s. Because of the regulatory limit has to be met at all times during the year, the lower summer flow rate of 23000 L/s must be used. The standard used by US EPA, which set the maximum permissible level of benzene in drinking water at 0.05 mg/l or 5 ppb. The effluent is assumed to be saturated with benzene at the solubility level of 1.8 g/L (1.8 x 106 ppb)

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Example: Discharge of Plant Effluent into a River

- By commencing with a mass balance around the juncture of effluent and river flow shown in the figure and assume the contents of the envelope to be well mixed and to have attained a steady state. Thus,

Rate of benzene in – Rate of benzene out = 0

$$QeCe - (Qe + Qr)Cr = 0$$

where the subscripts e and r refer to effluent and river, respectively and Q denotes volumetric flow rates.

- Substituting the given data into this equation, we obtain

$$(150/60)1.8 \text{ x } 106 - [(150/60) + 23000]Cr = 0$$

- Solving for Cr yields a downstream river concentration of

$$C_r = \frac{4.5\,x10^8}{23002.5} = 195 \text{ ppb}$$

- With the allowable concentration set at 5 ppb, the required fractional removal R is given by:

$$R = \frac{1-5}{196} = 0.974$$

- In other words, slightly more than 97% of the benzene in the plant effluent will have to be removed. It is likely that an adsorption purification process using activated carbon can be used to achieve this goal

Fluid-Solid equilibria: The Langmuir isotherm

- In gas- liquid equilibria, it is considered that a gas is absorbed into and comes into equilibrium with a liquid solvent. This process of absorption, in which the solute gas permeates the entire body of the liquid, differs from adsorption
- Here the solute also penetrates the porous structure of the solid and the process is therefore initially at least similar to absorption. However, the solute molecules come to rest on the walls of the porous structure and remain confined there in dynamic equilibrium with the surrounding pore pace
- Thus, while permeation of the solid structure takes place, the solute molecules are not uniformly dispersed but are rather localized on the internal surface of the solid matrix

Difference between Absorption and Adsorption

- There is a further distinction to be made between the two processes
- In adsorption, the surface area available for accommodating solute molecules is limited and finite. Here an increase in pressure or a solute concentration will lead to complete coverage by a ‘monolayer’ or saturation of the surface. On reaching this state, no further adsorption can take place. This is indicated by the asymptotic saturation capacity shown by the isotherm in the phase diagram.
- An exception occurs when the solute gas is within reach of a state of condensation. The solute may then form multiple adsorbed layer or multilayers and fill the entire pore space by condensation (capillary condensation)

Langmuir Adsorption Isotherm

- In his derivation, Langmuir postulated that the adsorption equilibrium was the result of two rate processes, equal in magnitude but opposite in direction. There were the rate of adsorption, which was taken to be proportional to solute pressure or concentration and the available free surface area and a desorption rate, which varied directly with the fractional surface coverage.

Moisture Adsorption Isotherms

- Although the great majority of adsorbed solutes show Langmuir-type behaviour, a considerable number of substances exhibit inflecting isotherms. This is particularly the case with vapours in the vicinity of saturation
- The graph shows moisture isotherms on a variety of adsorbents. Zeolitic sorbents are the only ones among them which display Langmuir-type behaviour. They are most effective at low humidities where they show a substantial uptake of water. Silica gel and activated alumina have high uptakes at higher humidities, where they exceed zeolite capacities by factors of two or more. Carbon, because of its hydrophobic nature, has only limited affinity for water.

Types of Separation Process

- Vapour- Liquid
- Distillation
- Liquid- Liquid
- Solvent extraction
- Solid- Liquid
- Drying
- Sedimentation
- Membrane Separation
- Microfiltration
- Ultrafiltration

Conclusion of The Chapter

- This chapter discussed about phase equilibria, single component systems: vapour pressure, phase diagram of a pure substance, multicomponent system, isotherms and absorption and adsorption

Mass Transfer and Separation Processes: Principles and Applications, Diran Basmadjian, CRC Press, 2nd Edition, 2007