

Separations in Chemical Engineering

Separations (gas from a mixture of gases, liquids from a mixture of liquids, solids from a solution of solids in liquids, dissolved gases from liquids, solvents from gases partially/completely saturated with solvents) are important in chemical process industries because they comprise large portion (up to 90%) of capital and operating expenditure.

All separations involve either bringing a phase (physically separable mass) containing the mixture to be separated with another phase into which the desired species gets distributed or creating another phase into which the desired species gets concentrated. The distribution or concentration continues till the two phases reach equilibrium after which there is no *net* transfer of the species. At equilibrium, the two phases get saturated with the species.

Examples of Separations

Absorption: A gas (or gases) from a mixture of gases is absorbed into a liquid that is brought into contact with the mixture. Separation depends on solubility of the gas or gases that are absorbed.

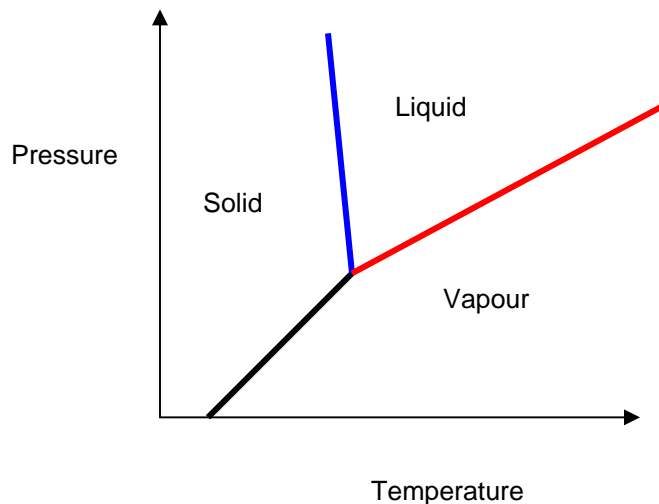
Distillation: A mixture of liquid is heated and a vapour phase is created. The vapour phase is enriched with the species with low boiling point or higher volatility; this phase is cooled and condensed to obtain a liquid phase concentrated with more volatile species.

Liquid extraction: A mixture of liquids is agitated with another immiscible or partially miscible liquid vigorously and then the two liquid phases are allowed separate. The desired species distributes between the two liquid phases.

Adsorption: A gas or gases from a mixture of gases or a liquid (or liquids) from a mixture of liquids is bound physically to the surface of a solid.

Crystallization: A solid comes out of the solution and forms crystals when the temperature of a solution containing the solid is lowered.

Single Component Phase Equilibrium



It is represented by a plot between temperature (on x-axis) and pressure on y-axis. Points on red boundary indicate vapour pressure and temperature; those on blue boundary represent pressure and melting point temperature; those on black boundary are pressure and sublimation temperature.

Normal boiling point is the temperature at which vapour pressure becomes equal to one atmosphere (a point on red boundary).

Vapour pressure is the pressure of vapour in equilibrium with its own liquid or solid. Imagine an evacuated in which a liquid is taken and a temperature is maintained. The maximum pressure recorded at this temperature is the vapour pressure of the liquid at that temperature. Vapour is a strong function of temperature rising exponentially with it. Vapour pressure is also the measure the volatility; the higher the vapour pressure the higher is the volatility.

Vapour pressure can be estimated in the following ways:

$$\text{Clausius Clapeyron equation: } \ln p^* = -\frac{\Delta \hat{H}_v}{RT} + B$$

Where p^* is vapour pressure, $\Delta \hat{H}_v$ is latent heat of vapourization, T is temperature, R is gas constant and B is a constant. Knowing the values of variables and constants on RHS, we could calculate vapour pressure.

$$\text{Antoine equation: } \log_{10} p^* = A - \frac{B}{T + C}$$

Where p^* is vapour pressure, T is temperature, A , B and C are constants. The constants are available in any standard text book or in Perry's Chemical Engineering hand book. *Note the units of p^* and T before plugging in the values.*

Cox charts: Because of importance of vapour pressure in chemical engineering calculations, plots called Cox charts have been prepared. In this graph, vapour pressure is plotted against temperature. Again, standard text books should have this chart.

Gas-liquid Systems: One condensable component

When temperature of a gas containing a solvent is lowered at constant temperature, the solvent condenses. The temperature at which first droplet of the solvent forms is called dew point temperature. At this temperature, if Raoult's is applied:

$$p_i = yP = p^*$$

Where p_i is partial pressure of the solvent, P is total pressure, y is mole fraction of the solvent in the gas. According to above equation, solvent in a gas condenses whenever its partial pressure equals vapour pressure.

At temperatures higher than dew point temperature, partial pressure is less than vapour pressure and the vapour in the gas is called super heated vapour. $p_i = yP < p^*$

The difference between the temperature of the gas and its dew point temperature is called degrees of superheat.

Few terms are useful in making material balance calculations involving condensable species. They are:

$$\text{Relative humidity} = \frac{p_i}{p_i^*} \times 100$$

$$\text{Molal humidity} = \frac{p_i}{P - p_i^*} = \frac{\text{moles of vapour}}{\text{moles of vapour - free (dry) gas}}$$

$$\text{Absolute humidity} = \frac{p_i M_i}{(P - p_i^*) M_{dry}} = \frac{\text{mass of vapour}}{\text{mass of vapour - free (dry) gas}}$$

$$\text{Percentage humidity} = \frac{p_i / (P - p_i)}{p_i^* / (P - p_i^*)} \times 100$$

The information on saturation of a gas could be obtained from values of any of the four terms defined above. For example, if relative humidity is 90% at 30°C at 1 atm, it means the partial pressure is 0.9 times the vapour pressure at 30°C. This piece of information could be used to find mole fraction of the solvent, which could be calculated by estimating the vapour pressure at 30°C using, say Antoine's equation.

Henry's law

This law describes the equilibrium between a non-condensable gas and a liquid in which the gas is sparingly soluble (mole fraction of the gas in liquid is close to zero). Examples of some sparingly soluble gases: CO₂, O₂, N₂, CH₄, C₂H₆

$$p_i = Hx_i$$

p_i is partial pressure of the gas above liquid, H is Henry's law constant and x_i is mole fraction of the gas in the liquid. Units of H are atm/mole fraction; of course other units for pressure could be used.

Vapour Liquid Equilibrium

When a mixture of liquids (liquid A, liquid B, liquid C and so on) is heated at a constant pressure, at a certain temperature first bubble of vapour forms; this temperature is called bubble point temperature. The mole fractions of all components A, B, C and so on in the bubble add up to unity. Using Raoult's law, we have:

$$\frac{x_A P_A^*}{P} + \frac{x_B P_B^*}{P} + \frac{x_C P_C^*}{P} + \dots = 1$$

Where x is mole fraction and p^* is vapour pressure and P is total pressure.

You could imagine, lowering the pressure of the liquid keeping the temperature constant, the pressure at which first bubble of vapour forms is called bubble point pressure. The above equation could be used to find pressure for a given temperature.

If a vapour contains more than one condensable component (say A, B, C etc.) and when the temperature is lowered, at a certain temperature first droplet of liquid forms; this temperature is called dew point temperature. When this happens, the mole fractions of all components in the drop should add up to unity. Applying Raoult's law and summing up the mole fractions in the drop, we have:

$$\frac{y_A P}{P_A^*} + \frac{y_B P}{P_B^*} + \frac{y_C P}{P_C^*} + \dots = 1$$

Similar to bubble point pressure, dew point pressure is the pressure to which the vapour must be subjected at a constant temperature so that first drop of liquid forms. Above equation could be used to estimate the dew point pressure for a given temperature

Liquid Extraction

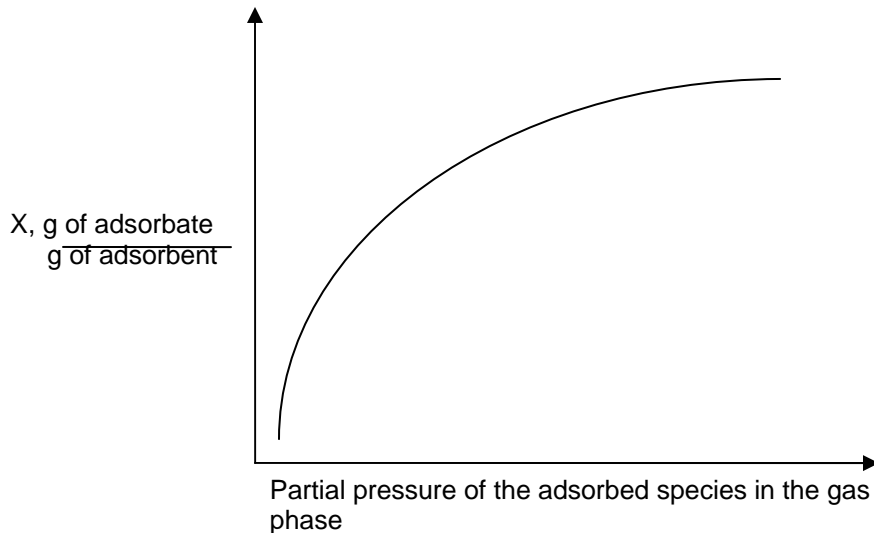
To separate a species from a liquid A, another liquid B, which is immiscible or partially miscible with the mixture is added to the mixture and mixed vigorously. After mixing, when allowed to settle, two phases form and the species to be separated distributes between the phases. One of the phases would be rich in A and the other rich in B. If A and B are immiscible, they do not distribute.

We will consider only immiscible liquids. The distribution of the species between the two phases is determined by a distribution coefficient, K , defined as the ratio of mass fraction of species in one phase to its mass fraction in other phase.

$$K = \frac{\text{mass fraction of the species in one phase}}{\text{mass fraction of species in other phase}}$$

Adsorption

This is a process in which a gas or gases from a mixture of gases adsorb on the surface of a solid. It applies to a mixture of liquids also. The species that gets attracted to the solid is called adsorbate and the solid is called adsorbent. An adsorbent has an affinity for an adsorbate. Adsorption is not used extensively but nevertheless an important operation.



When a mixture of gases is brought in contact with an adsorbent and if we wait for long time, the system reaches equilibrium. That is the gas phase is in equilibrium with the solid phase. This equilibrium is represented by plotting partial pressure of the species in the gas phase against ratio of the amount of species absorbed to the amount of adsorbent. The plot is generated by making an experiment in which a certain partial pressure of the adsorbate in the gas phase is maintained and then X is measured. We could repeat this experiment for several values of the partial pressure and generate the complete curve. All the experiments are done at a temperature and therefore the curve is called an isotherm. These curves are called Langmuir-adsorption isotherms.

Engineers are always interested in fitting equations to experimental data in order to reduce experimentation. Langmuir-adsorption isotherms can be represented by the following equation:

$$X = \frac{aK_L p^*}{1 + K_L p^*}$$

where a and K_L are constants obtained by fitting experimental data to the above equation.

Knowing one quantity, either X or p^* , other quantity can be found if the equation for adsorption is given.

Test Your Understanding

- Air contains 7.0 mole% water at 35°C and 755 mm Hg. What is the dew point temperature? What pressure air must be subjected to at 35°C to condense water?
- How can you condense a solvent in partially saturated gas?
- Explain vapour pressure in your own words to a 10th class student.
- Henry's law constant for ethane in water at 20°C is given as 1460 atm cc/mol. Convert it to the units of atm/mole fraction (*Hint*: Ethane is sparingly soluble in water with its mole fraction close to zero).
- What is bubble point temperature of 40.0 mole% benzene and 60.0 mole% toluene mixture at a pressure of 1 atm. Get Antoine constants for benzene and toluene from Appendix B of the text book.
- Calculate the dew point temperature of a vapour containing 40.0 mole% benzene and 60.0 mole% toluene at 1 atm. Get Antoine constants for benzene and toluene from Appendix B of the text book.
- What do you conclude about the bubble point and dew point temperatures estimated in questions 4 and 5.
- Plot bubble point temperature Vs. mole fraction of benzene (varying from 0 to 1.0) and explain the plot. Also, plot dew point temperature Vs. mole fraction of benzene.
- What is distribution coefficient? Benzene and hexane are being considered to extract acetic acid from aqueous mixture. K for benzene is 0.098 and that for hexane is 0.017. For the same extent of extraction of acetic acid, would you need more of benzene or hexane? Explain.
- Can partial pressure of a solvent in a gas at a given temperature be greater than its vapour pressure at that temperature?
- Explain how Langmuir adsorption isotherms are generated in your own words.
- If a gas mixture containing 10.0 mole% water in air is brought in contact with silica gel, the gel adsorbs water. If you wish to determine the amount of adsorbent to reduce the water content to 1.0 mole%, you would obtain a value of X corresponding to 10.0 mole% or 1.0 mole%? Why?