

LIQUID-VAPOR EQUILIBRIA in BINARY SYSTEMS

Chemistry BC2001x

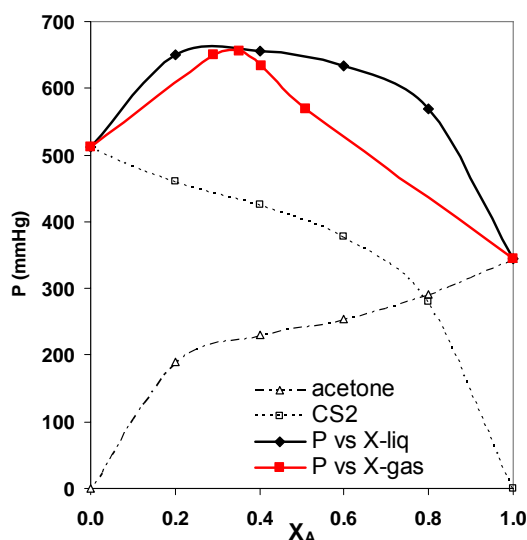
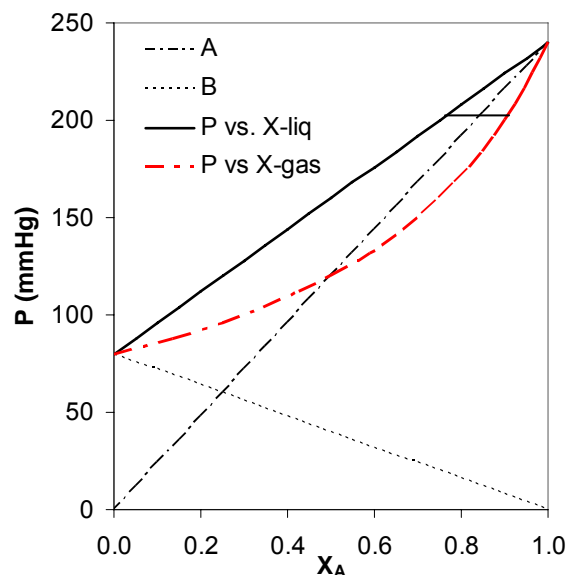
Consider a system with two components A and B; with both volatile. At a fixed temperature, P_A° is the vapor pressure of pure A, P_B° the vapor pressure of pure B. Because, in general, the composition (relative amount of A and B) differs in the liquid and gas, it is very important to distinguish them clearly: X_A^l is in the liquid, and X_A^g in the gas. In each phase $X_A + X_B = 1$, so either X_A or X_B defines the composition: as X_A goes from 0 to 1, X_B goes from 1 to 0. A graph showing P vs. X_A (or X_B) is useful to visualize the system: this is called a P - X plot.

Let P_A be the partial pressure of A and P_B the partial pressure of B in the vapor that is in equilibrium with the liquid solution. The total pressure is $P = P_A + P_B$. From the definition of partial pressures, $P_A \equiv X_A^g P$, the composition of the gas is $X_A^g = P_A/P$.

If the solution is ideal, Raoult's Law applies to both: $P_A = X_A^l P_A^\circ$, and $P_B = X_B^l P_B^\circ$. Adding, $P = X_A^l P_A^\circ + X_B^l P_B^\circ = X_A^l P_A^\circ + (1 - X_A^l) P_B^\circ = P_B^\circ + X_A^l (P_A^\circ - P_B^\circ)$. P vs. X_A^l is a straight line passing from P_B° when $X_A^l = 0$ to P_A° when $X_A^l = 1$. This line, describing pressure as a function of the liquid composition, is called the "liquidus curve".

From P_A and P_B , we can find the mole fraction of the gas at that same total pressure. A second curve, P vs. X_A^g (called the "bubble point curve"), may be drawn on the P - X plot. It meets the Raoult's law line at the ends, since liquid and gas have identical composition for pure substances. At any P value, a horizontal line (a "tie-line") may be drawn between the two curves. The ends of a tie-line describe the composition of the two phases, liquid and gas, in equilibrium at that pressure.

Example: Let $P_A^\circ = 240$ and $P_B^\circ = 80$ mmHg. Consider a liquid solution with $X_A^l = 0.75$. Raoult's Law: $P_A = (0.75)(240) = 180$ mmHg, $P_B = (0.25)(80) = 20$ mmHg, $P_{\text{tot}} = 200$ mmHg. $X_A^g = 180/200 = 0.90$ (see tie-line). The liquid is 75%, the gas 90% A: the gas is enriched in the



more volatile component ($P_A^\circ > P_B^\circ$). This diagram may be used to understand the very important separation process called **distillation**.

If the solution is not ideal, the upper (liquidus) curve is not a straight line. If it arches up, the system is exhibiting positive deviations from Raoult's law ($P_{\text{real}} > P_{\text{ideal}}$). The P vs. X^g curve is again below the liquidus curve, and may be found from P_A and P_B as above. In extreme cases, the deviation can be so large that the liquidus curve has a maximum (or minimum). When this occurs, the curves meet at the extremum. This composition is an **azeotropic mixture**: the liquid and gas have identical composition, so distillation fails to separate the components. Acetone and CS_2 form such a mixture: see the adjacent P - X diagram.