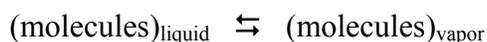


BOILING POINT AND DISTILLATION

Boiling Point

A liquid at any temperature exerts a pressure on its environment. This pressure, the *vapor pressure*, results from molecules leaving the surface of the liquid to become vapor and occurs because the molecules are in constant motion.



As a liquid is heated, its kinetic energy increases; the equilibrium shifts to the right and more molecules move into the gaseous state, thereby increasing the vapor pressure. The boiling point of a pure liquid is defined as the temperature at which the vapor pressure of the liquid exactly equals the pressure exerted on it by the atmosphere. For example, at an external pressure of 1 atm, the boiling point is reached when the vapor pressure equals 1 atm. Every pure and stable organic compound has a characteristic boiling point at one atmosphere. The boiling point of an organic compound reflects its molecular structure, specifically the type of intermolecular interactions that bind the molecules together in the liquid state.

Compound	Boiling point (°C)	Density (g/mL)
Methanol	64.7	0.79
Ethanol	78.5	0.79
Water	100.0	1.00

Distillation

Distillation is a method for separating two or more liquid compounds on the basis of boiling-point differences. The boiling point of a mixture is a function of the vapor pressures of the various components in the mixture. Consider, for example, the boiling characteristics of a mixture of water and ethanol. If water alone were present, the vapor pressure above the liquid would be due only to water. However, with water as only a fraction of the solution, the vapor pressure exerted by water (P_{water}) will correspondingly be equal to only a fraction of the vapor pressure of pure water at the same temperature

(P_{water}°), where X is the fraction of molecules of water in solution, call the mole fraction of water. The same is also true for the ethanol component.

$$P_{\text{water}} = P_{\text{water}}^{\circ} X_{\text{water}} \quad (1)$$

$$P_{\text{ethanol}} = P_{\text{ethanol}}^{\circ} X_{\text{ethanol}} \quad (2)$$

The total pressure of the solution is the sum of the partial vapor pressure of the individual components (Figure 1).

$$P_{\text{total}} = P_{\text{water}} + P_{\text{ethanol}} \quad (3)$$

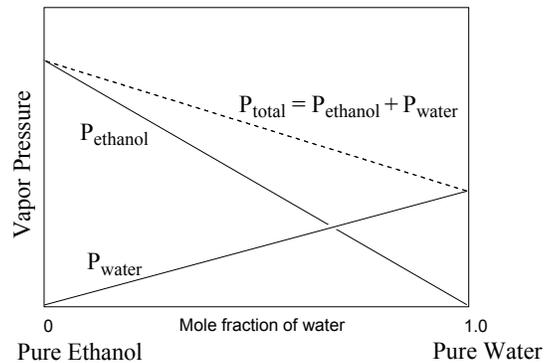


Figure 1. Vapor pressure-mole fraction diagram for ethanol-water solutions.

If Y stands for the fraction of ethanol molecules in the vapor above the solution:

$$Y_{\text{ethanol}} = P_{\text{ethanol}}/P_{\text{total}} \quad (4)$$

A single expression for the total vapor pressure can be derived easily from equations 1-4 because $X_{\text{ethanol}} + X_{\text{water}} = 1$

$$Y_{\text{ethanol}} = \frac{P_{\text{ethanol}}^{\circ} X_{\text{ethanol}}}{X_{\text{ethanol}} (P_{\text{ethanol}}^{\circ} - P_{\text{water}}^{\circ}) + P_{\text{water}}^{\circ}} \quad (5)$$

If the vapor pressures of pure water and ethanol at various temperatures and composition of the liquid are known, the fraction of ethanol in the vapor above the solution can be calculated. This calculation can be used to construct a temperature-composition diagram

(sometimes called a phase diagram) like the one shown in Figure 2. Point L_1 is the boiling point at atmospheric pressure for a solution with an initial 1:1 mole ratio of ethanol to water. To find the resulting molar composition of ethanol and water in the vapor phase follow the horizontal dotted line to point V_1 . *Note:* The mole fraction of the component with the lower boiling point is greater in the vapor than in the liquid. If the vapor at V_1 condenses, the liquid that collects will have the same composition as the vapor (V_1). Now if the condensed liquid (L_2) is revaporized, the new vapor will be even richer in ethanol. Repeating the boiling and condensing several more times allows us to obtain essentially pure ethanol.

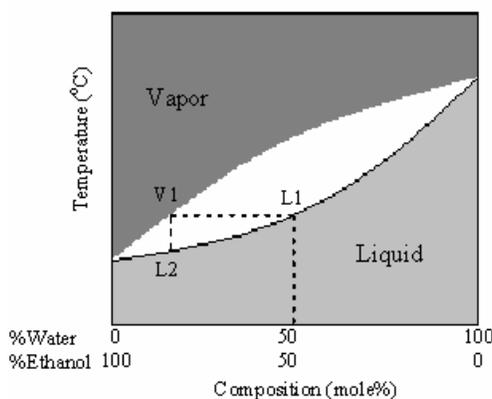


Figure 2. Temperature-Composition Diagram for ethanol/water solutions at 1.0 atm.

In a simple distillation, only one vaporization and condensation occurs, corresponding to points L_1 and V_1 in Figure 2. The liquid collected is called the distillate. Simple distillation would not effectively separate a mixture whose boiling points differ by less than 60-70°C.

Distillation Apparatus

A distillation setup usually consists of a distilling flask, a distilling head, a thermometer, a condenser and a receiving vessel. The volume of the distillation flask should be two to three times the volume of the liquid to be distilled. (If the flask is too full, liquid easily bumps over into the condenser and is not distilled. If the flask is not full enough, separation will be poor because a substantial fraction of the liquid will need to vaporize for condensation to occur.) A distilling head connects the condenser with the distilling

flask. At the branch of the distilling head should be the thermometer, which measures the temperature of the vapor gas. The condenser is a double-layered column that has cold water flowing in the outer layer. The water should flow in an opposite direction from the vapor gas flow. In this way, the vapor gas will always go from high temperature to low temperature. Teflon sleeves are used on joints so to make it easy to disconnect the setup after the distillation. Boiling chips are added to distillation flask to permit even boiling and prevent violent bumping of the solution. When the solution is heated, the molecules leave the liquid phase and enter the gas phase. The vapor reaches the thermometer and the temperature reading increases rapidly. The gaseous molecules reach the condenser and return to the liquid state and drain into the receiving flask. With each successive fraction, the temperature of the distillate vapor rises. To isolate distillate fractions of different boiling point, the experimenter must change the receiving flask at selected intervals. Distillation should be stopped by lowering the heat source before the distillation flask reaches dryness or if the temperature reading climbs above the expected boiling range or begins to drop.