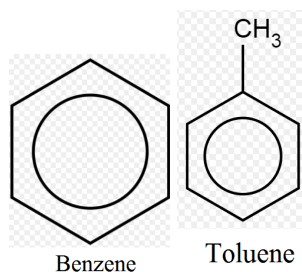


24.1: Ideal Solutions - Raoult's Law

When two substances whose molecules are very similar form a liquid solution, the vapor pressure of the mixture is very simply related to the vapor pressures of the pure substances. Suppose, for example, we mix 1 mol benzene with 1 mol toluene as shown in the figure below.



The mole fraction of benzene, X_b , and the mole fraction of toluene, X_t , are both equal to 0.5. At 79.6°C the measured vapor pressure of this mixture is 516 mmHg, slightly less than 517 mmHg, the average of the vapor pressures of pure benzene (744 mmHg) and of pure toluene (290 mmHg) at the same temperature.

It is easy to explain this behavior if we assume that because benzene and toluene molecules are so nearly alike, they behave the same way in solution as they do in the pure liquids. Since there are only half as many benzene molecules in the mixture as in pure benzene, the rate at which benzene molecules escape from the surface of the solution will be half the rate at which they would escape from the pure liquid. In consequence the partial vapor pressure of benzene above the mixture will be one-half the vapor pressure of pure benzene. By a similar argument the partial vapor pressure of the toluene above the solution is also one-half that of pure toluene. Accordingly, we can write

$$P_b = \frac{1}{2} P_b^* \quad (24.1.1)$$

and

$$P_t = \frac{1}{2} P_t^* \quad (24.1.2)$$

where P_b and P_t are the partial pressures of benzene and toluene vapors, respectively, and P_b^* and P_t^* are the vapor pressures of the pure liquids. The total vapor pressure of the solution is

$$P = P_b + P_t = \frac{1}{2} P_b^* + \frac{1}{2} P_t^* = \frac{P_b^* + P_t^*}{2} \quad (24.1.3)$$

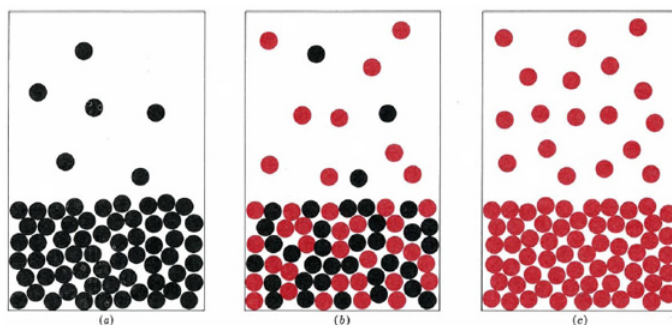


Figure 24.1.1: Vapor-liquid equilibria for (a) pure toluene; (b) a mixture of equal amounts of toluene and benzene; and (c) pure benzene. In the solution (b) only half the molecules are benzene molecules, and so the concentration of benzene molecules in the vapor phase is only half as great as above pure benzene. Note also that although the initial amounts of benzene and toluene in the solution were equal, more benzene than toluene escapes to the gas phase because of benzene's higher vapor pressure.

The vapor pressure of the mixture is equal to the mean of the vapor pressures of the two pure liquids.

We can generalize the above argument to apply to a liquid solution of any composition involving any two substances A and B whose molecules are very similar. The partial vapor pressure of A above the liquid mixture, P_A , will then be the vapor pressure of

pure A , P_A^* , multiplied by the fraction of the molecules in the liquid which are of type A , that is, the mole fraction of A , X_A . In equation form

$$P_A = X_A P_A^* \quad (24.1.4)$$

Similarly for component B

$$P_B = X_B P_B^* \quad (24.1.5)$$

Adding these two partial pressures, we obtain the total vapor pressure

$$P = P_A + P_B = X_A P_A^* + X_B P_B^* \quad (24.1.6)$$

Liquid solutions which conform to Eqs. 24.1.4 and 24.1.6 are said to obey **Raoult's law** and to be **ideal mixtures** or **ideal solutions**.

In addition to its use in predicting the vapor pressure of a solution, Raoult's law may be applied to the solubility of a gas in a liquid. Dividing both sides of Equation 24.1.4 by P_A^* gives

$$X_A = \frac{1}{P_A^*} \times P_A = k_A \times P_A \quad (24.1.7)$$

Since the vapor pressure of any substance has a specific value at a given temperature, Equation 24.1.7 tells us that the mole fraction X_A of a gaseous solute is proportional to the partial pressure P_A of that gas above the solution.

For an ideal solution the proportionality constant k_A is the reciprocal of the vapor pressure of the pure solute at the temperature in question. Since vapor pressure increases as temperature increases, k_A , which is $1/P_A^*$, must decrease. Thus we expect the solubility of a gas in a liquid to increase as the partial pressure of gas above the solution increases, but to decrease as temperature increases. Equation 24.1.7 is known as **Henry's law**. It also applies to gaseous solutes which do not form ideal solutions, but in such cases the Henry's-law constant k_A does not equal the reciprocal of the vapor pressure.

The video below shows the effect of varied pressure on the amount of CO_2 dissolved in soda. The amount of dissolved CO_2 is monitored by a pH indicator. The more dissolved CO_2 , the lower the pH (the more red the solution). Watch the video to find out how the solubility of CO_2 is related to the pressure, paying particular attention to the color of the solution.



In actual fact very few liquid mixtures obey Raoult's law exactly. Even for molecules as similar as benzene and toluene, we noted a deviation of 517 mmHg – 516 mmHg, or 1 mmHg at 79.6°C. Much larger deviations occur if the molecules are not very similar. These deviations are of two kinds. As can be seen from Figure 24.1.2, a plot of the vapor pressure against the mole fraction of one component yields a straight line for an ideal solution. For non-ideal mixtures the actual vapor pressure can be larger than the ideal value (positive deviation from Raoult's law) or smaller (negative deviation). Negative deviations correspond to cases where attractions between unlike molecules are greater than those between like molecules.

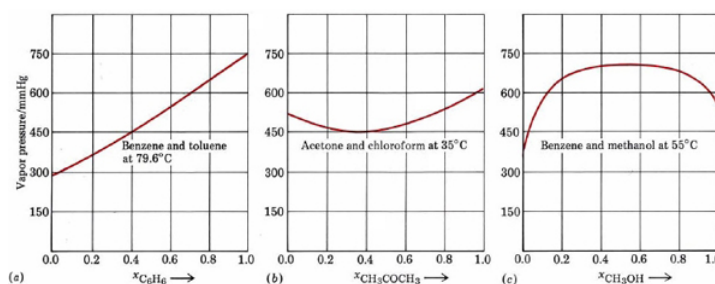
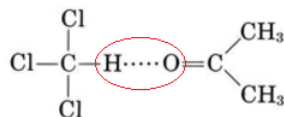


Figure 24.1.2: Deviations from Raoult's law. (a) When Raoult's law is obeyed, a plot of vapor pressure against mole fraction yields a straight line. This is nearly true for the benzene and toluene mixture at 79.6°C. (b) A mixture of acetone and chloroform shows negative deviations from Raoult's law at 35°C, indicating that the two different molecules prefer each other's company to their own. (c) The opposite behavior is shown at 55°C by a benzene-methanol mixture where the polar and nonpolar molecules prefer the company of their own kind.

In the case illustrated below, acetone (CH_3COCH_3) and chloroform (CHCl_3) can form a weak hydrogen bond:



Because of this extra intermolecular attraction, molecules have more difficulty escaping the solution and the vapor pressure is lower. The opposite is true of a mixture of benzene and methanol. When C_6H_6 molecules are randomly distributed among CH_3OH molecules, the latter cannot hydrogen bond effectively. Molecules can escape more readily from the solution, and the vapor pressure is higher than Raoult's law would predict.

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