CHEMICAL ENGINEERING THERMODYNAMICS II (0905323)

02. EXAMPLES OF SIMPLE EQUILIBRIA

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Outline

- The Equilibrium Criteria
- Simplest Phase Equilibria: Water and Steam
- Hierarchy of Phase Equilibria: Air-Water
- Raoult's Law
- Henry's Law
- The General two-Phase Equilibria Calculation
- Limitations of Raoult's and Henry's Laws

The Equilibrium Criteria

- For a system composed of *C* components and *p* phases the following criteria must, **simultaneously**, be satisfied for equilibrium to be established:
  1. Thermal equilibrium

$$T^{(1)} = T^{(2)} = \cdots = T^{(p)}$$

  2. Mechanical equilibrium

$$P^{(1)} = P^{(2)} = \cdots = P^{(p)}$$

  3. Chemical equilibrium

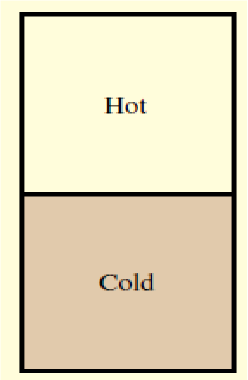
$$f_i^{(1)} = f_i^{(2)} = \cdots = f_i^{(p)}, \quad i = 1, 2, \cdots, C$$

$$\mu_i^{(1)} = \mu_i^{(2)} = \cdots = \mu_i^{(p)}, \quad i = 1, 2, \cdots, C$$

Thermal Equilibria

- Any system at equilibrium is an isothermal system; and unless it is in an adiabatic container (which exists only in theory and in thermodynamics textbooks), it is at the same temperature as its surroundings.

$$\left(\frac{\partial T}{\partial x}\right) = \left(\frac{\partial T}{\partial y}\right) = \left(\frac{\partial T}{\partial z}\right) = \left(\frac{\partial T}{\partial t}\right) = 0$$

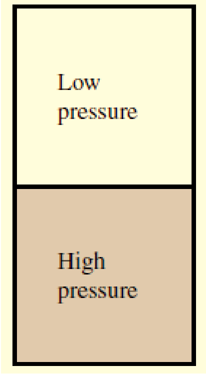


If two parts of a system are at different temperatures and are in thermal contact with each other, then there will be a spontaneous change as heat flows from hot to cold. So this is not an equilibrium system.

Mechanical Equilibria

- In the absence of restraining gravity, spring, electrostatic, magnetic, osmotic or surface forces, at equilibrium the system must be at a uniform pressure

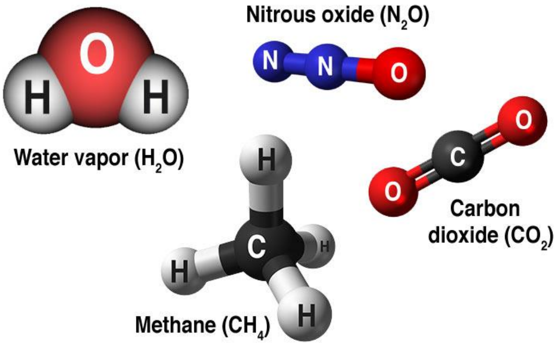
$$\left(\frac{\partial P}{\partial x}\right)=\left(\frac{\partial P}{\partial y}\right)=\left(\frac{\partial P}{\partial z}\right)=\left(\frac{\partial P}{\partial t}\right)=0$$



If two parts of system are in contact and do not have the same pressure, then a spontaneous process will occur unless the difference in pressure is opposed by gravity, a spring, or surface tension.

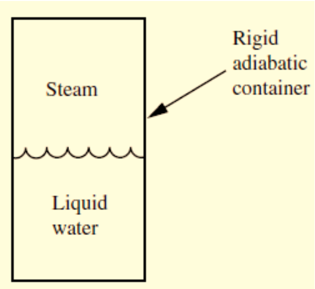
Distinction Between Vapor and Gas

- A gas is any substance in the gaseous state, which means that it will expand as needed to fill any container in which it is placed. Solids and liquids do not do that.
- A vapor is a gas that is at a temperature below its critical temperature. This means that if a vapor is compressed at a constant temperature it will turn into a liquid



Simplest Phase Equilibria: Water and Steam

- For pure water and steam to be in equilibrium (without air mixed in) the pressure of the gas must equal the vapor pressure of the liquid.
  - If the pressure of the gas is less than the vapor pressure of the liquid, then the liquid will boil, expelling gas.
  - If the pressure of the gas is greater than the vapor pressure of the liquid, then the gas will condense into the liquid.
- If these processes occur in a closed container, then they will continue until the two pressures (and temperatures) become the same, at which time we will have phase equilibrium.



Antoine equation

Hierarchy of Phase Equilibria: Air-Water

- At temperatures near room temperature and 1 bar pressure there will be a liquid and a gas, as there was for pure water, but that there will be air dissolved in the water, and water vapor dissolved in the gas.

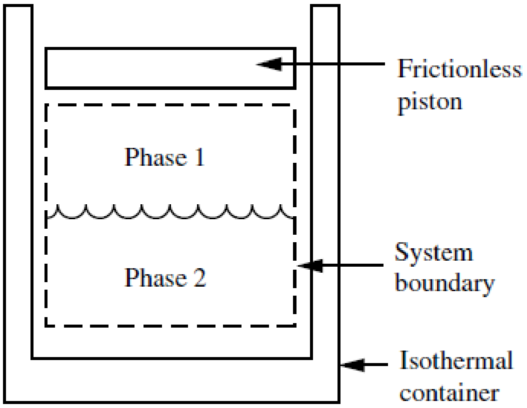
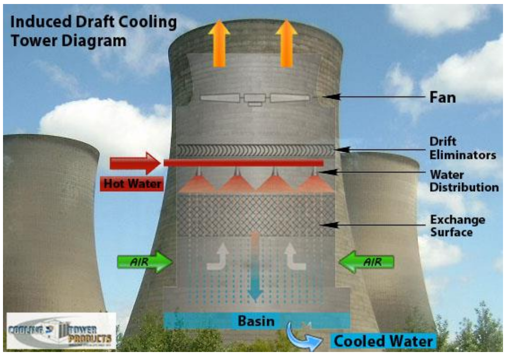


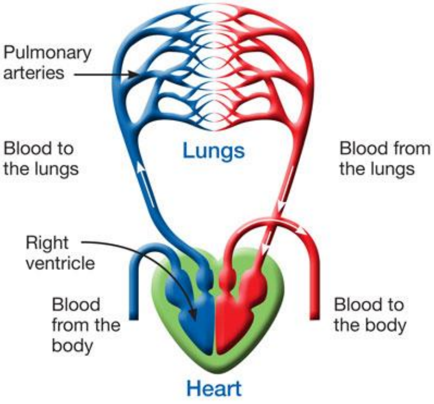
FIGURE 3.5 Two phases (mostly air and mostly water) in equilibrium in a piston and cylinder arrangement, at constant temperature.

Most physical separation processes (distillation, crystallization, evaporation, drying) utilize this difference in composition between equilibrium phases to separate one chemical from another.

Importance of Air-Water Mixtures

- The amount of oxygen dissolved in the water is small, but it is needed for almost all life on this planet All living things conduct their biochemical business in dilute solutions of various materials in water; most need dissolved oxygen to conduct that biochemical business.
  - We regularly oxygenate our fish bowls to provide the oxygen, dissolved in the water, that the fish must have to live.
- Our blood and that of most animals has chemicals in it (ours is hemoglobin in our red blood cells, which gives our blood its red color) that increase the equilibrium amount of oxygen dissolved in it making us much more efficient animals than we would be otherwise.
  - That dissolved oxygen makes iron and steel rust. Oxygen-free water will not rust iron or steel; the feed water for boilers is treated to remove the dissolved oxygen.





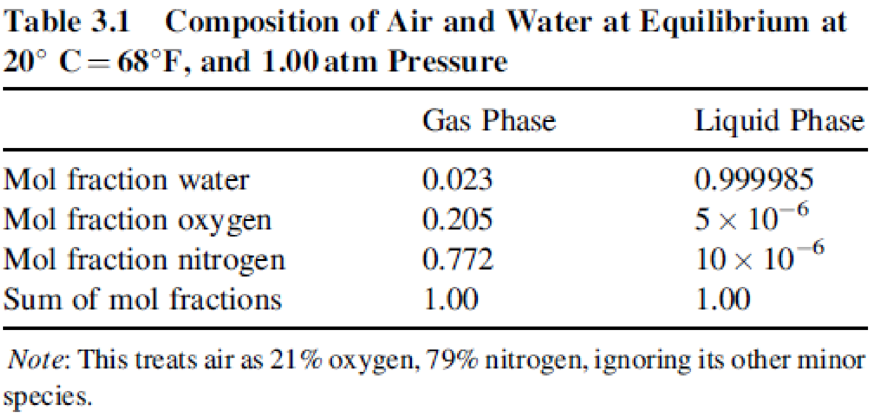


Table 3.1 Composition of Air and Water at Equilibrium at 20° C = 68°F, and 1.00 atm Pressure

	Gas Phase	Liquid Phase
Mol fraction water	0.023	0.999985
Mol fraction oxygen	0.205	5×10^{-6}
Mol fraction nitrogen	0.772	10×10^{-6}
Sum of mol fractions	1.00	1.00

Note: This treats air as 21% oxygen, 79% nitrogen, ignoring its other minor species.

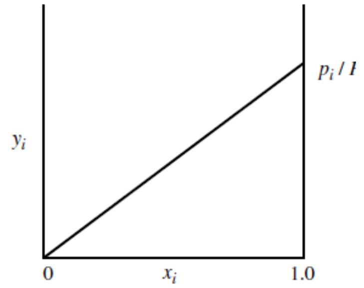
Raoult's Law

- For gas–liquid (gas-solid) equilibrium for each chemical species present, the partial pressure in the gas is equal to the partial vapor pressure in the liquid.

$$y_i P = x_i P_i^{\text{vap}}, \quad i = 1, 2, \cdots, C$$

$$x_i P_i^{\text{vap}}(T) = y_i P = P_i$$

$$\sum_{i=1}^{C} x_i P_i^{\text{vap}}(T) = \sum_{i=1}^{C} P_i = P$$



Raoult's law has a very simple geometrical interpretation. There is a corresponding plot for species j, species k, and so on.

Example 3.1 Estimate the mol fraction of water vapor in air in equilibrium with water at 20°C = 68°F and one atmosphere pressure.

$$y_i = \frac{x_i p_i}{P} \qquad (3.5)$$

Here we have a ternary mixture of nitrogen, oxygen, and water. If we let the subscript *i* stand for water, we can say that

$$x_{\text{water}} = 1 - x_{N_2} - x_{O_2} \qquad (3.B)$$

but we know from experience that the mol fractions of dissolved N_2 and O_2 in liquid water are quite small, so that we are safe in saying that $x_{\text{water}} \approx 1$. Later we must check to see that this approximation is satisfactory, which we do in Example 3.2. From any steam table we may look up the value of the vapor pressure of water at 20°C, finding $p_{\text{water}} = 0.023$ atm. We use this value in Eq. 3.5, with the total pressure, $P = 1.00$ atm, finding $y_{\text{water}} \approx 0.023$. ■

Henry’s Law

- We cannot use Raoult’s law to find the equilibrium vapor pressures of pure liquid nitrogen and oxygen at 298.15 K, because that is above the critical temperature of these materials (154.8K for oxygen, 126.2K for nitrogen, see Table A.1);
  - they cannot exist as pure liquids at this temperature.
- The experimental measurements of the solubility of gases like oxygen and nitrogen in liquids like water show that we can still use the equivalent of Raoult’s law, but in place of **the liquid vapor pressure** we must use a **“pseudo vapor pressure,”** determined not from measuring the vapor pressure of the pure liquid as we did for water, but rather from the measured gas solubility data.
  - This pseudo vapor pressure is called the Henry’s law constant.

Henry’s Law

- It is found empirically that, in very dilute region

$$\boxed{P_i = H_i x_i}$$

  - Known as **Henry’s law**, where H_i is known as Henry’s constant from a **particular system** and **temperature**.
  - Of particular importance for sparingly soluble gases and solids.
  - H_i is a strong function of temperature.
    - For gases the usual trend is to rise with increasing temperature ⇨ decreasing solubility.
    - For solids the usual trend is to decrease with increasing temperature ⇨ increasing solubility.

TABLE 8.1 Henry's Law Constants for Various Gases in Water at 25°C

Gas	$\mathcal{H}_i$ [bar]
Ar	35,987.9
Br_2	74,686.8
H_2	70,381.1
N_2	87,365.0
O_2	44,253.9
H_2S	54,991.8
CO	58,487.0
CO_2	1,651.9
CH_4	41,675.8
C_2H_2	1,342.2
C_2H_4	11,522.0
C_2H_6	30,525.9

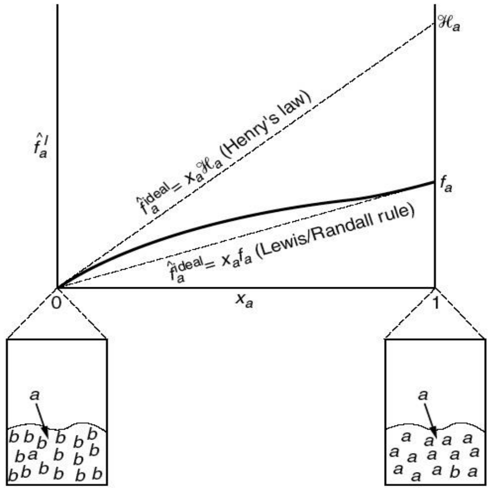


Figure 7.5 Fugacity of a binary liquid mixture. Also shown are ideal solution reference states based on *a-a* interactions (Lewis/Randall rule) and *a-b* interactions (Henry's law).

Example 3.2 Estimate the concentration of oxygen dissolved in water when air and water are at equilibrium at 20°C = 68°F and one atmosphere pressure. From Example 3.1 we know that $y_{water} = 0.023$, so that $Y_{N_2} + Y_{O_2} = 1 - 0.023 = 0.977$. The oxygen is 0.21 mol fraction of this mix, so that

From Table A.3 we look up the Henry's law constant for oxygen in water at 20°C, finding $H = 40{,}100$ atm. Then, by direct substitution in Eq. 3.6,

$$x_{oxygen} = \frac{y_{oxygen} \cdot P}{H_{oxygen}} = \frac{0.205 \cdot 1 \text{ atm}}{40{,}100 \text{ atm}} = 5 \times 10^{-6} \qquad (3.D)$$

This is the value shown in Table 3.1 as the mol fraction of oxygen dissolved in water at equilibrium at this temperature and pressure. By the same logic we find that

$$y_{N_2} = 0.79 \cdot 0.977 = 0.772 \qquad (3.E)$$

and

$$x_{nitrogen} = \frac{y_{nitrogen} \cdot P}{H_{nitrogen}} = \frac{0.772 \cdot 1 \text{ atm}}{80{,}400 \text{ atm}} = 10 \times 10^{-6} \qquad (3.F)$$

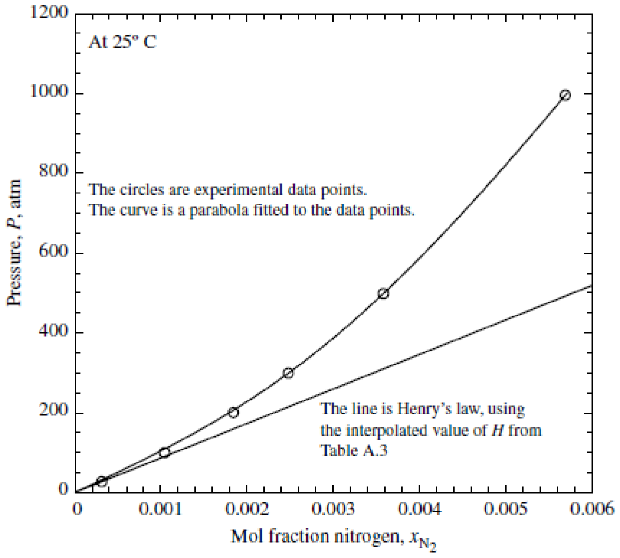


FIGURE 3.9 Experimental data [1] for the solubility of nitrogen gas in water at 25°C on P-x coordinates, compared to a Henry's law estimate of the same data, using an interpolated Henry's law constant from Appendix A.3.

The General two-Phase Equilibria Calculation

- Solution was based on liquid being practically pure water and that the concentration of water vapor in air was small.
- In general, for solutions involving more than two species we will not know this, and will have as many species equilibrium equations to solve simultaneously as there are species present, normally by trial and error.
- Before the age of computers this calculation was a giant pain, but our computers now do it for us quickly and easily.

- The three equilibrium equations

$$y_{\text{water}}\, P = x_{\text{water}}\, p_{\text{water}} \qquad (3.\text{H})$$

$$y_{\text{oxygen}}\, P = x_{\text{oxygen}}\, H_{\text{oxygen}} \qquad (3.\text{I})$$

$$y_{\text{nitrogen}}\, P = x_{\text{nitrogen}}\, H_{\text{nitrogen}} \qquad (3.\text{J})$$

- A set of three equations with six unknowns.
- We have two additional equations that say that the mole fractions in each phase sum to 1.0, making this a system of five equations and six unknowns.
- Additional relation is $(y_{\text{nitrogen}}/y_{\text{oxygen}})$= 0.79/0.21, independent of how much water vapor is dissolved in the air.

Example 3.3 Repeat the calculation of Table 3.1, using the above six equations, and not making the simplifications previously used.

Inserting numerical values, we have

$$\begin{aligned}
y_{\text{water}} \cdot 1\ \text{atm} &= x_{\text{water}} \cdot 0.023\ \text{atm} \\
y_{\text{oxygen}} \cdot 1\ \text{atm} &= x_{\text{oxygen}} \cdot 40{,}100\ \text{atm} \\
y_{\text{nitrogen}} \cdot 1\ \text{atm} &= x_{\text{nitrogen}} \cdot 80{,}400\ \text{atm} \\
y_{\text{water}} + y_{\text{oxygen}} + y_{\text{nitrogen}} &= 1 \qquad (3.\text{K}) \\
x_{\text{water}} + x_{\text{oxygen}} + x_{\text{nitrogen}} &= 1 \\
\frac{y_{\text{oxygen}}}{y_{\text{nitrogen}}} &= \frac{0.21}{0.79} = 0.266
\end{aligned}$$

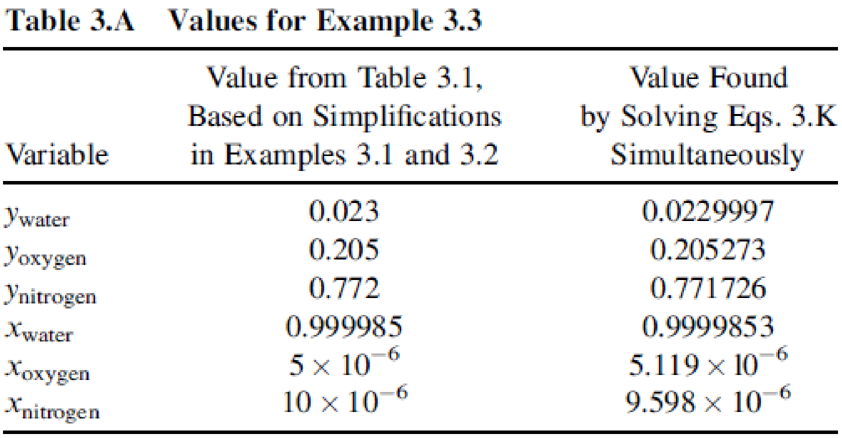
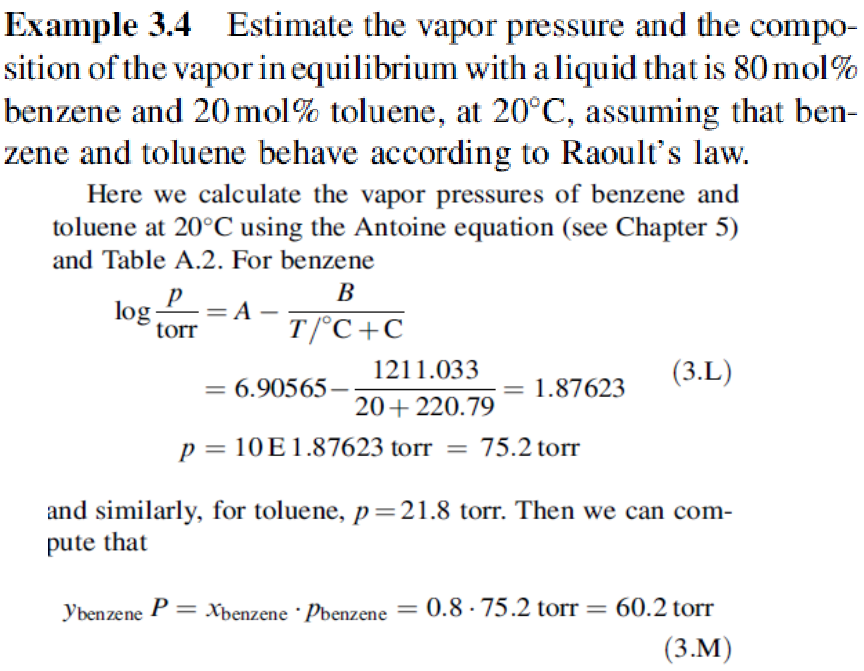


Table 3.A Values for Example 3.3

Variable	Value from Table 3.1, Based on Simplifications in Examples 3.1 and 3.2	Value Found by Solving Eqs. 3.K Simultaneously
y_{water}	0.023	0.0229997
y_{oxygen}	0.205	0.205273
y_{nitrogen}	0.772	0.771726
x_{water}	0.999985	0.9999853
x_{oxygen}	5×10^{-6}	5.119×10^{-6}
x_{nitrogen}	10×10^{-6}	9.598×10^{-6}



Example 3.4 Estimate the vapor pressure and the composition of the vapor in equilibrium with a liquid that is 80 mol% benzene and 20 mol% toluene, at 20°C, assuming that benzene and toluene behave according to Raoult's law.

Here we calculate the vapor pressures of benzene and toluene at 20°C using the Antoine equation (see Chapter 5) and Table A.2. For benzene

$$\log \frac{p}{\text{torr}} = A - \frac{B}{T/^{\circ}\text{C} + C}$$

$$= 6.90565 - \frac{1211.033}{20 + 220.79} = 1.87623 \qquad (3.L)$$

$$p = 10\,\text{E}\,1.87623 \text{ torr} = 75.2 \text{ torr}$$

and similarly, for toluene, $p = 21.8$ torr. Then we can compute that

$$y_{\text{benzene}} P = x_{\text{benzene}} \cdot p_{\text{benzene}} = 0.8 \cdot 75.2 \text{ torr} = 60.2 \text{ torr} \qquad (3.M)$$

and correspondingly for toluene, $y_{\text{toluene}} P = 0.2 \cdot 21.8 = 4.36$ torr. If we add these two values we will have

$$y_{\text{benzene}} P + y_{\text{toluene}} P = (y_{\text{benzene}} + y_{\text{toluene}})P = 64.6 \text{ torr} \tag{3.N}$$

But we know that $y_{\text{benzene}} + y_{\text{toluene}}$ must equal 1.00, so the total pressure must be 64.6 torr. To find either mol fraction in the gas phase we observe that the mol fraction of any species is equal to that species' partial pressure divided by the total pressure, so the two mol fractions are $60.2/64.6 = 0.932$ and $4.36/64.6 = 0.068$. ■

Example 3.5 Estimate the concentration of benzene in air that is saturated with benzene at 20°C.

This repeats Example 3.1, with the vapor pressure of benzene taken from Example 3.4. Thus,

$$y_i = \frac{x_i p_i}{P} = \frac{1.00 \cdot 75.2 \text{ torr}}{760 \text{ torr}} = 0.099 \approx 0.1 \approx 10\% \tag{3.O}$$

which is the value shown in Section 1.1. ■

Example 3.6 At what temperature will the benzene–toluene mixture in Ex. 3.4 have a vapor pressure of one atmosphere? (That is, what is the normal boiling point temperature for this mixture?) Assume that both species obey Raoult's law.

Writing the Raoult's law expression for each species, adding them, and grouping terms we have

$$(y_{\text{benzene}} + y_{\text{toluene}})P = x_{\text{benzene}} \cdot p_{\text{benzene}} + x_{\text{toluene}}\, p_{\text{toluene}} \tag{3.P}$$

The terms on the left of the equation are known, (1·1 atm) = 1 atm, and the two mol fractions on the right are known. The two pure species vapor pressures on the right depend on temperature alone (see Chapter 5, or Figure 1.8, which shows such a curve for water). In principle we can substitute the vapor pressure equations for benzene and toluene in the above equation and solve. But in practice the useful vapor pressure equations always involve logarithms, and equations containing two different logarithms have no analytic solutions, so this is inherently a trial-and-error problem. Using the Antoine equation and Table A.2 for each pure species vapor pressure and guessing values of T we may compute Table 3.B and we see that 84.377°C the vapor pressure is 760 torr = 1 atm. (We should not believe the computed temperature to more than 3 significant figures, but the value shown makes the calculated value of $P = 760.00$ torr.) From Raoult's law we see that the mol fractions in the

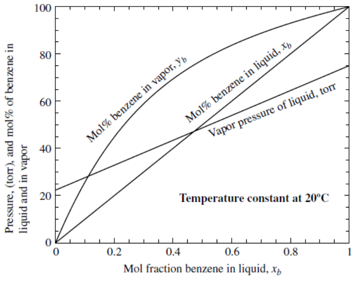


FIGURE 3.11 Computed liquid vapor pressure and vapor mol% benzene, according to Raoult's law, for a mixture of benzene and toluene at a constant temperature of 20°C. (Here we use mol percent instead of mol fraction on the ordinate so that both curves plot on the same scale.) The line for mol% benzene in the liquid is shown because it is traditionally shown in this type of diagram.

Table 3.B Solution to Example 3.6

Guessed T (°C)	p_{benzene} (torr) Calculated from the Antoine Equation	p_{toluene} (torr) Calculated from the Antoine Equation	P (torr) Calculated from Eq. 3.P
80	757.7	291.5	664.4
83	830.3	323.0	728.8
84.377	865.4	338.3	**760.0**
86	908.3	357.1	798.0
90	1021.0	407.1	898.2

$$\begin{aligned} y_b &= \frac{x_b p_b}{P} = \frac{0.8 \cdot 865.4\ \text{torr}}{760\ \text{torr}} = 0.911 \\ y_t &= \frac{x_t p_t}{P} = \frac{0.2 \cdot 338.3\ \text{torr}}{760\ \text{torr}} = 0.089 \end{aligned} \tag{3.Q}$$

This solution was done intuitively. Formally, the set of equations we are solving is

$$\begin{aligned} x_b + x_t &= 1.00 \\ y_b + y_t &= 1.00 \\ y_b &= \frac{x_b p_b}{P} \\ y_t &= \frac{x_t p_t}{P} \\ \frac{p_b}{\text{torr}} &= 10\,\text{E}\left(6.90565 - \frac{1211.003}{T/{}^\circ\text{C} + 220.79}\right) \\ \frac{p_t}{\text{torr}} &= 10\,\text{E}\left(6.95334 - \frac{1343.943}{T/{}^\circ\text{C} + 219.337}\right) \\ P &= 760\ \text{torr} \\ x_b &= 0.8 \end{aligned} \tag{3.R}$$

■

Uses and Limits of Raoult's and Henry's laws

- In a dilute solution of any kind, Raoult's law will apply satisfactory to the **solvent**, but probably not to the solute.
- If solute and solvent are chemically similar, like benzene and toluene, then Raoult's law will apply satisfactorily for both solute and solvent, over the whole range of possible concentrations at modest pressures.
- If the solute and solvent interact strongly chemically (for example, solutions of strong acids, such as H_2SO_4, and bases, such as NaOH in water), then Raoult's law gives poor estimates of the behavior.
- Henry's law is useful for the solution of most gases in water, except for gases that interact chemically with water, such as HC1, NH_3, and SO_2.

- Henry's law is widely used for liquids that are strongly immiscible with water, such as mercury and hydrocarbons, in which the minuscule amount of the other material dissolved in water behaves as if it had first vaporized and then dissolved as a gas in the water.
- Henry's law can also be used for small amounts of gases dissolved in liquids other than water.

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