Chapter 12

Physical Properties of Solutions

A ***solution*** is a homogenous mixture of 2 or more substances.

The ***solute*** is(are) the substance(s) present in the smaller amount(s).

The ***solvent*** is the substance present in the larger amount.

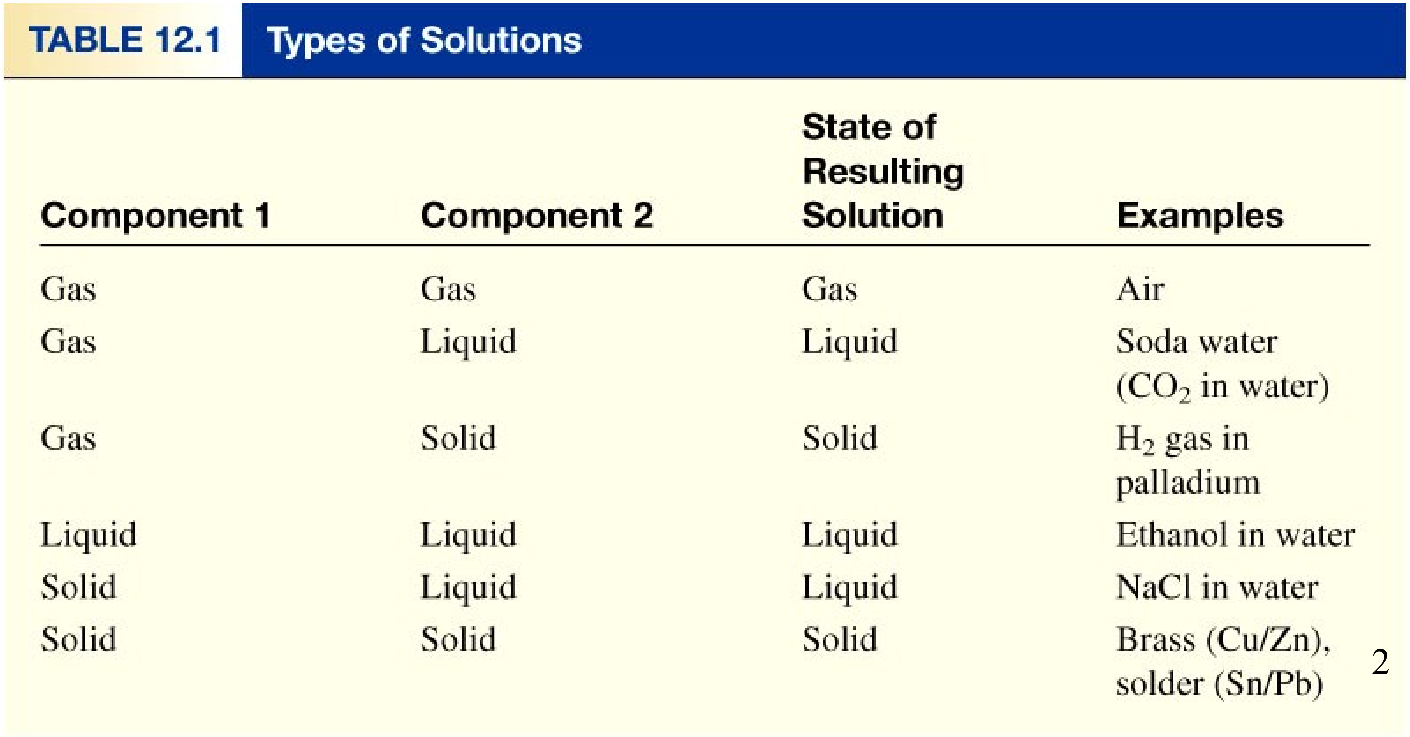
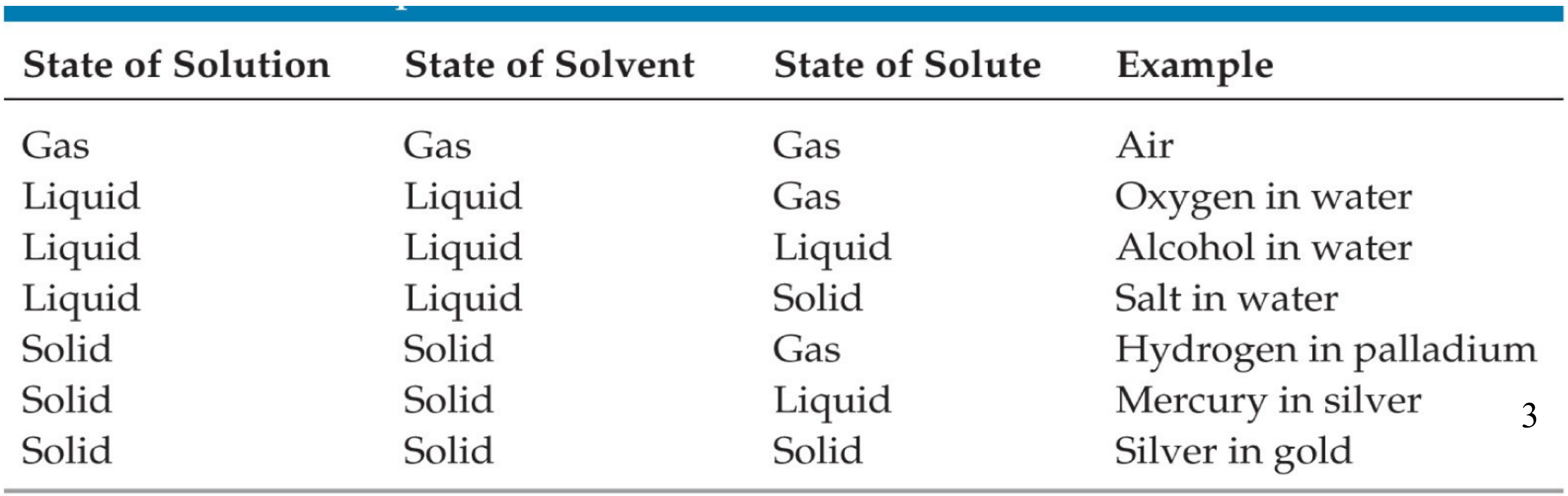


TABLE 12.1 **Types of Solutions**

Component 1	Component 2	State of Resulting Solution	Examples
Gas	Gas	Gas	Air
Gas	Liquid	Liquid	Soda water (CO_2 in water)
Gas	Solid	Solid	H_2 gas in palladium
Liquid	Liquid	Liquid	Ethanol in water
Solid	Liquid	Liquid	NaCl in water
Solid	Solid	Solid	Brass (Cu/Zn), solder (Sn/Pb)

Solutions

- Solutions are homogeneous mixtures of two or more pure substances.
- In a solution, the solute is dispersed uniformly throughout the solvent.
- The ***solute*** is(are) the substance(s) present in the smaller amount(s)
- The ***solvent*** is the substance present in the larger amount



State of Solution	State of Solvent	State of Solute	Example
Gas	Gas	Gas	Air
Liquid	Liquid	Gas	Oxygen in water
Liquid	Liquid	Liquid	Alcohol in water
Liquid	Liquid	Solid	Salt in water
Solid	Solid	Gas	Hydrogen in palladium
Solid	Solid	Liquid	Mercury in silver
Solid	Solid	Solid	Silver in gold

A ***saturated solution*** contains the maximum amount of a solute that will dissolve in a given solvent at a specific temperature.

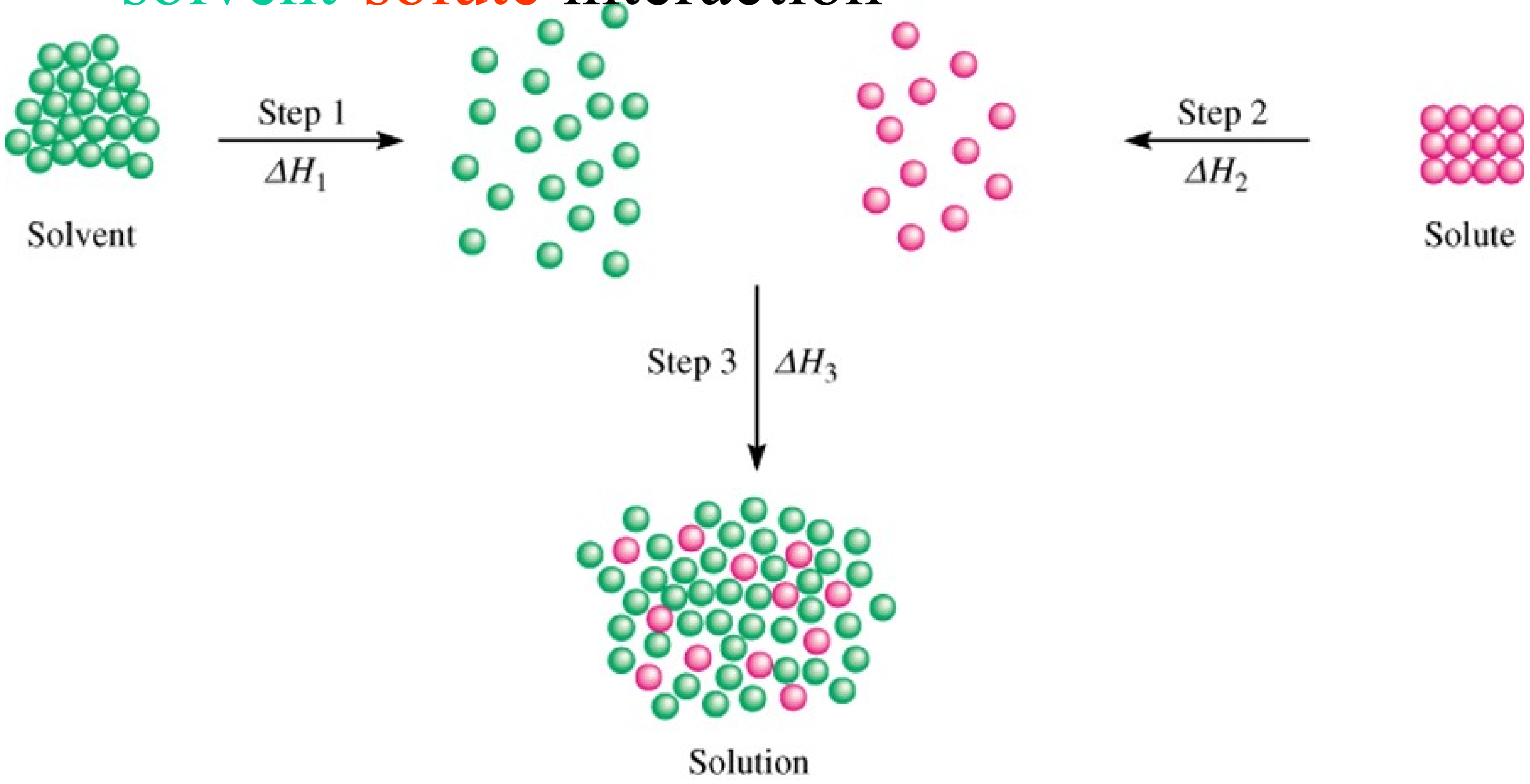
An ***unsaturated solution*** contains less solute than the solvent has the capacity to dissolve at a specific temperature.

A ***supersaturated solution*** contains more solute than is present in a saturated solution at a specific temperature.

Sodium acetate crystals rapidly form when a seed crystal is added to a supersaturated solution of sodium acetate.

Three types of interactions in the solution process:

- solvent-solvent interaction
- solute-solute interaction
- solvent-solute interaction



$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Rule of “**Like dissolves Like**”

- Use **polar** solvent for **polar** solute
- Use **Nonpolar** solvent for **nonpolar** solute

- **When strengths of intermolecular attractions are similar in solute and solvent, solutions form because net energy exchange is about the same**
- **Polar** solutes interact with and dissolve in **polar** solvents
- **H-bonding** solutes interact with and dissolve in **H-bonding** solvents

Ex. Ethanol in water

- Both are polar molecules
- Both form hydrogen bonds

“**like dissolves like**”

Two substances with similar ***intermolecular*** forces are likely to be soluble in each other.

- non-polar molecules are soluble in non-polar solvents

  CCl_4 in C_6H_6

- polar molecules are soluble in polar solvents

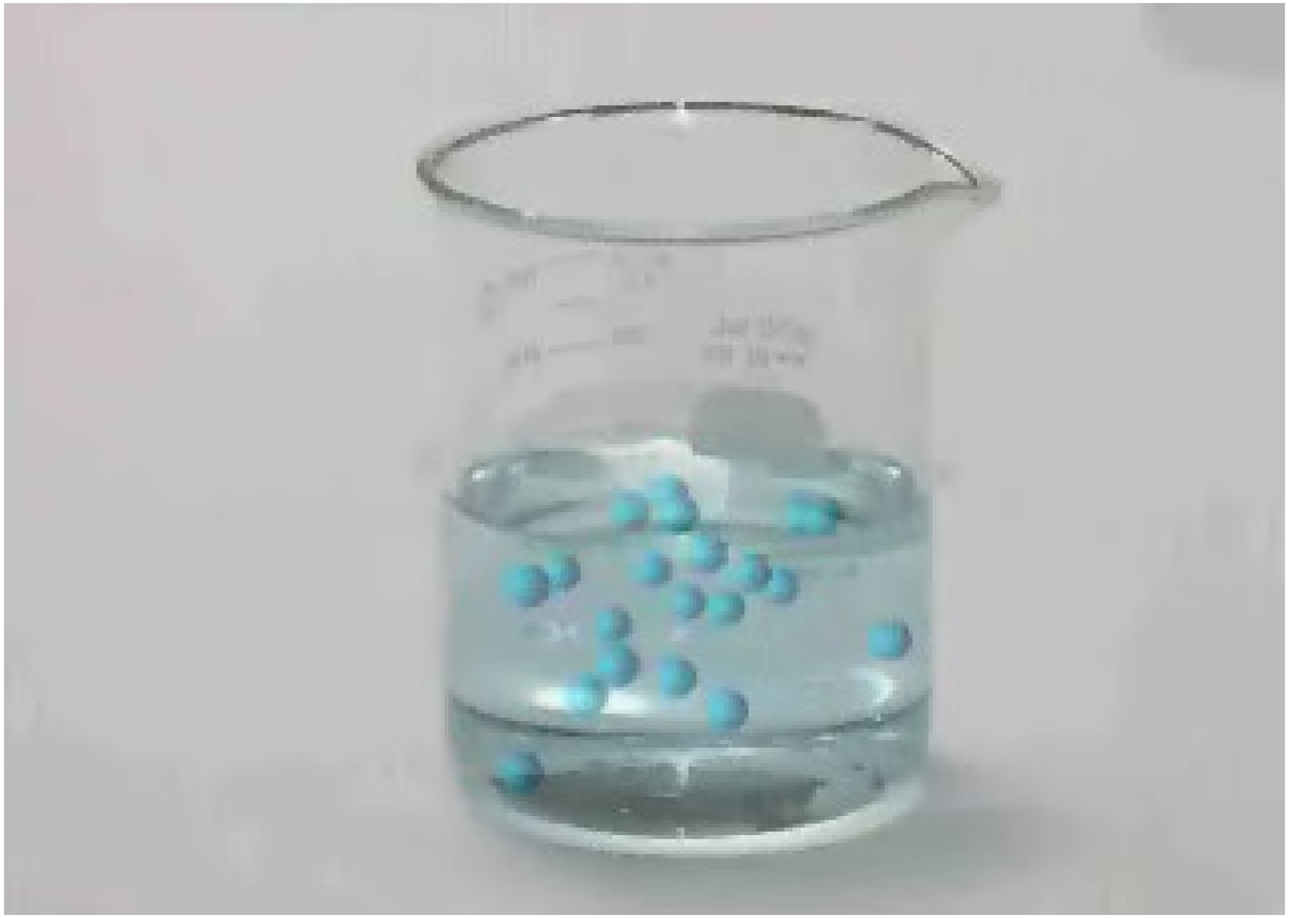
  C_2H_5OH in H_2O

- ionic compounds are more soluble in polar solvents

  NaCl in H_2O or NH_3 (*l*)

Dilution

$$M_1V_1 = M_2V_2$$



Dilution

The molarity of the new solution can be determined from the equation

$$M_c \times V_c = M_d \times V_d$$

where M_c and M_d are the molarity of the concentrated and dilute solutions, respectively, and V_c and V_d are the volumes of the two solutions.

$$M_c \times V_c = M_d \times V_d$$

$$\text{Moles solute before dilution} = \text{moles solute after dilution}$$

Examples

How many milliliters of 3.0 M H_2SO_4 are needed to make 450 mL of 0.10 M H_2SO_4 ?

$$M_{\mathrm{c}} \times V_{\mathrm{c}} = M_{\mathrm{d}} \times V_{\mathrm{d}}$$

$$3.0\ M\ x\ V_c = 0.10\ M\ x\ 450\ mL$$

$$V_c = 15\ mL$$

Concentration Units

The ***concentration*** of a solution is the amount of solute present in a given quantity of solvent or solution.

Percent by Mass

$$\% \text{ by mass} = \frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \times 100\%$$

$$= \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

Mole Fraction ***(X)***

$$X_{\text{A}} = \frac{\text{moles of A}}{\text{sum of moles of all components}}$$

Concentration Units Continued

Molarity ***(M)***

$$M = \frac{\text{moles of solute}}{\text{liters of } \boxed{\text{solution}}}$$

Molality ***(m)***

$$m = \frac{\text{moles of solute}}{\text{mass of } \boxed{\text{solvent (kg)}}}$$

Comparison of Concentration Units

- The advantage of **molarity** is that it is generally easier to measure the volume of a solution. For this reason, molarity is often preferred over molality.

- **Molality** is independent of temperature, because the concentration is expressed in number of moles of solute and mass of solvent.

- The volume of a solution typically increases with increasing temperature, so that a solution that is 1.0 M at 25 °C may become 0.97 M at 45 °C because of the increase in volume on warming.

- This concentration dependence on temperature can significantly affect the accuracy of an experiment. Therefore, it is sometimes preferable to use molality instead of molarity.

Example 12.2

A sample of 0.892 g of potassium chloride (KCl) is dissolved in 54.6 g of water.

What is the percent by mass of KCl in the solution?

Solution

We write

$$\text{percent by mass of KCl} = \frac{\text{mass of solute}}{\text{mass of soln}} \times 100\%$$

$$= \frac{0.892\ \text{g}}{0.892\ \text{g} + 54.6\ \text{g}} \times 100\%$$

$$= 1.61\%$$

To convert one concentration unit of a solution to another

Example:

Express the concentration of a 0.396 *m* glucose ($C_6H_{12}O_6$) solution in molarity? (density of solution = 1.16 g/mL)

0.396 *m* glucose ($C_6H_{12}O_6$)

i.e., there is 0.396 mole of glucose in 1000 g of the solvent.

To calculate molarity; we need to determine the volume of this solution.

First, we calculate the mass of the solution from the molar mass of glucose:

$$\left(0.396\ \cancel{\text{mol } C_6H_{12}O_6} \times \frac{180.2\text{ g}}{1\ \cancel{\text{mol } C_6H_{12}O_6}}\right) + 1000\text{ g } H_2O = 1071\text{ g}$$

The density of the solution is 1.16 g/mL

We can now calculate the volume of the solution in liters

$$\begin{aligned}\text{volume} &= \frac{\text{mass}}{\text{density}}\\ &= \frac{1071\ \text{g}}{1.16\ \text{g/mL}} \times \frac{1\ \text{L}}{1000\ \text{mL}}\\ &= 0.923\ \text{L}\end{aligned}$$

The molarity of the solution is given by

$$\begin{aligned}\text{molarity} &= \frac{\text{moles of solute}}{\text{liters of soln}}\\ &= \frac{0.396\ \text{mol}}{0.923\ \text{L}}\\ &= 0.429\ \text{mol/L} = 0.429\ M\end{aligned}$$

Examples

An aqueous solution of hydrochloric acid contains 36 % HCl by mass. (a) Calculate the mole fraction of HCl in the solution. (b) Calculate the molality of HCl in the solution.

$$\text{Moles HCl} = \frac{36\text{ g}}{36.5\text{ g mol}^{-1}} = 0.99\text{ mol}$$

$$\text{Moles H}_2\text{O} = \frac{64\text{ g}}{18\text{ g mol}^{-1}} = 3.6\text{ mol}$$

$$X_{\text{HCl}} = \frac{\text{moles HCl}}{\text{moles H}_2\text{O} + \text{moles HCl}} = \frac{0.99}{3.6 + 0.99} = 0.22$$

$$\text{Molality of HCl} = \frac{0.99\text{ mol HCl}}{0.064\text{ kg H}_2\text{O}} = 15.5\text{ m}$$

What is the molality of a 5.86 *M* ethanol (C_2H_5OH) solution whose density is 0.927 g/mL?

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} \qquad M = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Assume 1 L of solution:

5.86 moles ethanol = 270 g ethanol

927 g of solution (1000 mL x 0.927 g/mL)

mass of solvent = mass of solution – mass of solute

= 927 g – 270 g = 657 g = 0.657 kg

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} = \frac{5.86 \text{ moles } C_2H_5OH}{0.657 \text{ kg solvent}} = 8.92\ m$$

What mass of KI is required to make 500. mL of a 2.80 *M* KI solution?

$$\text{volume of KI solution} \xrightarrow{M\ \text{KI}} \text{moles KI} \xrightarrow{\mathcal{M}\ \text{KI}} \text{grams KI}$$

$$500.\ \cancel{\text{mL}} \times \frac{1\ \cancel{\text{L}}}{1000\ \cancel{\text{mL}}} \times \frac{2.80\ \cancel{\text{mol}}\ \text{KI}}{1\ \cancel{\text{L}}\ \text{soln}} \times \frac{166\ \text{g KI}}{1\ \cancel{\text{mol}}\ \text{KI}} = 232\ \text{g KI}$$

Or

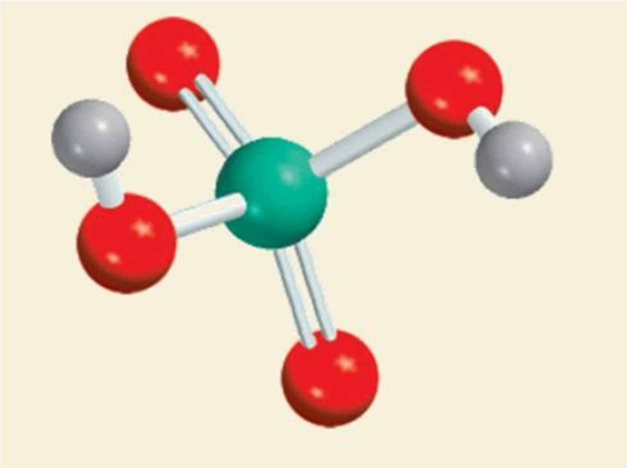
$$M = \frac{Wt(g)}{M.Wt(\frac{g}{mol})} \times \frac{1000}{V(mL)} \quad \Leftrightarrow \quad Wt(g) = \frac{M\left(\frac{mol}{L}\right) \times M.Wt\left(\frac{g}{mol}\right) \times V(mL)}{1000\ mL}$$

$$Wt(KI)(g) = \frac{2.80\left(\frac{mol}{L}\right) \times 166\left(\frac{g}{mol}\right) \times 500(mL)}{1000} = 232\ g\ KI$$

Example 12.3

Calculate the molality of a sulfuric acid solution containing 24.4 g of sulfuric acid in 198 g of water.

The molar mass of sulfuric acid is 98.09 g.



Example 12.3

Solution

The definition of molality (m) is

$$m = \frac{\text{mass of solute}}{\text{liters of solvent (kg)}}$$

First, we find the number of moles of sulfuric acid in 24.4 g of the acid, using its molar mass as the conversion factor

$$\text{moles of } H_2SO_4 = 24.4 \text{ g } \cancel{H_2SO_4} \times \frac{1 \text{ mol } H_2SO_4}{98.09 \text{ g } \cancel{H_2SO_4}}$$

$$= 0.249 \text{ mol } H_2SO_4$$

The mass of water is 198 g, or 0.198 kg. Therefore,

$$m = \frac{0.249 \text{ mol } H_2SO_4}{0.198 \text{ kg } H_2O}$$

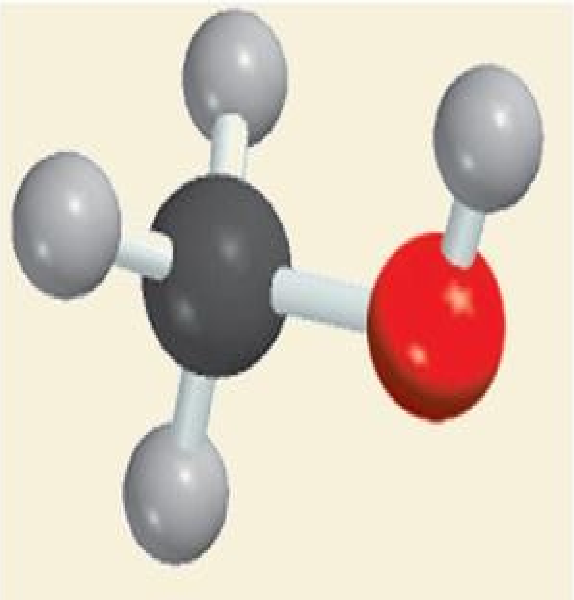
$$= 1.26\, m$$

Example 12.4

The density of a 2.45 *M* aqueous solution of methanol (CH_3OH) is 0.976 g/mL. What is the molality of the solution? The molar mass of methanol is 32.04 g.

Solution

Our first step is to calculate the mass of water in 1 L of the solution, using density as a conversion factor. The total mass of 1 L of a 2.45 *M* solution of methanol is



Example 12.4

$$1\ \cancel{\text{L}}\ \cancel{\text{soln}} \times \frac{1000\ \cancel{\text{mL}}\ \cancel{\text{soln}}}{\cancel{1}\ \cancel{\text{L}}\ \cancel{\text{soln}}} \times \frac{0.976\ \text{g}}{\cancel{1}\ \cancel{\text{mL}}\ \cancel{\text{soln}}} = 976\ \text{g}$$

Because this solution contains 2.45 moles of methanol, the amount of water (solvent) in the solution is

Mass of H_2O = mass of soln – mass of solute

$$= 976\ \text{g} - \left(2.45\ \cancel{\text{mol}}\ \cancel{\text{CH}_3\text{OH}} \times \frac{32.04\ \text{g CH}_3\text{OH}}{1\ \cancel{\text{mol}}\ \cancel{\text{CH}_3\text{OH}}}\right)$$

$$= 898\ \text{g}$$

The molality of the solution can be calculated by converting 898 g to 0.898 kg:

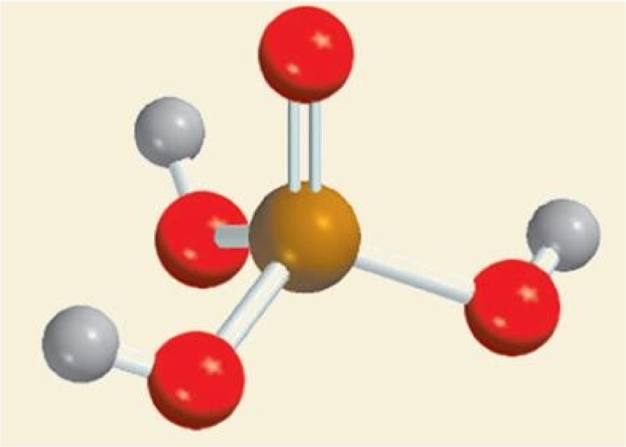
$$\text{molality} = \frac{2.45\ \text{mol CH}_3\text{OH}}{0.898\ \text{kg H}_2\text{O}}$$

$$= 2.73\ m$$

Example 12.5

Calculate the molality of a 35.4 percent (by mass) aqueous solution of phosphoric acid (H_3PO_4).

The molar mass of phosphoric acid is 97.99 g.



Example 12.5

Solution

From the known molar mass of phosphoric acid, we can calculate the molality in two steps, as shown in Example 12.3. First we calculate the number of moles of phosphoric acid in 35.4 g of the acid

$$\text{moles of } H_3PO_4 = 35.4\ \cancel{\text{g}}\ \cancel{H_3}\ \cancel{PO_4} \times \frac{1\ \text{mol } H_3PO_4}{97.99\ \cancel{\text{g}}\ \cancel{H_3}\ \cancel{PO_4}}$$

$$= 0.361\ \text{mol } H_3PO_4$$

The mass of water is 64.6 g, or 0.0646 kg. Therefore, the molality is given by

$$\text{molality} = \frac{0.361\ \text{mol } H_3PO_4}{0.0646\ \text{kg } H_2O}$$

$$= 5.59\ \text{m}$$

Question 1

Molarity is the number of …… of solute dissolved Solution

- Grams c) Milliliter
- Second d) moles

Question 2

Molality is the number of moles of ……. dissolved in 1kg solvent

a)Solvent c) Solute

b)Solution d) acid

Question 3

Molarity is the number of moles of solute dissolved 1 …… of the Solution

a)Grams c) Liter

b)Second d) moles

Question 4

A solution has a volume of 2.0 L and contains 36.0 g of glucose ($C_6H_{12}O_6$). If the molar mass of glucose is 180 g/mol, what is the molarity of the solution

a)1.0 b)1.00 c) 0.1 d) 0.01

Question 5

How many liters of 0.25 M NaCl solution must be measured to obtain 0.1 mol of NaCl

A) 1 B) 0.4 C) 2.5 D) 3.5

Question 6

What is the concentration of a solution in mol/L when 80 g of calcium carbonate, $Ca(CO_3)_2$, is dissolved in 2 L of solution? (Molecular weight of $Ca(CO_3)_2$ = 100g/mol

A) 0.4 B) 4 C) 0.004 D) 1

Question 7

A student needs to prepare 250 ml of 0.1 M of $Cd(NO_3)_2$ solution. How many grams of cadmium nitrate are required? (Molecular weight of $Cd(NO_3)_2$ = 236 g/mol

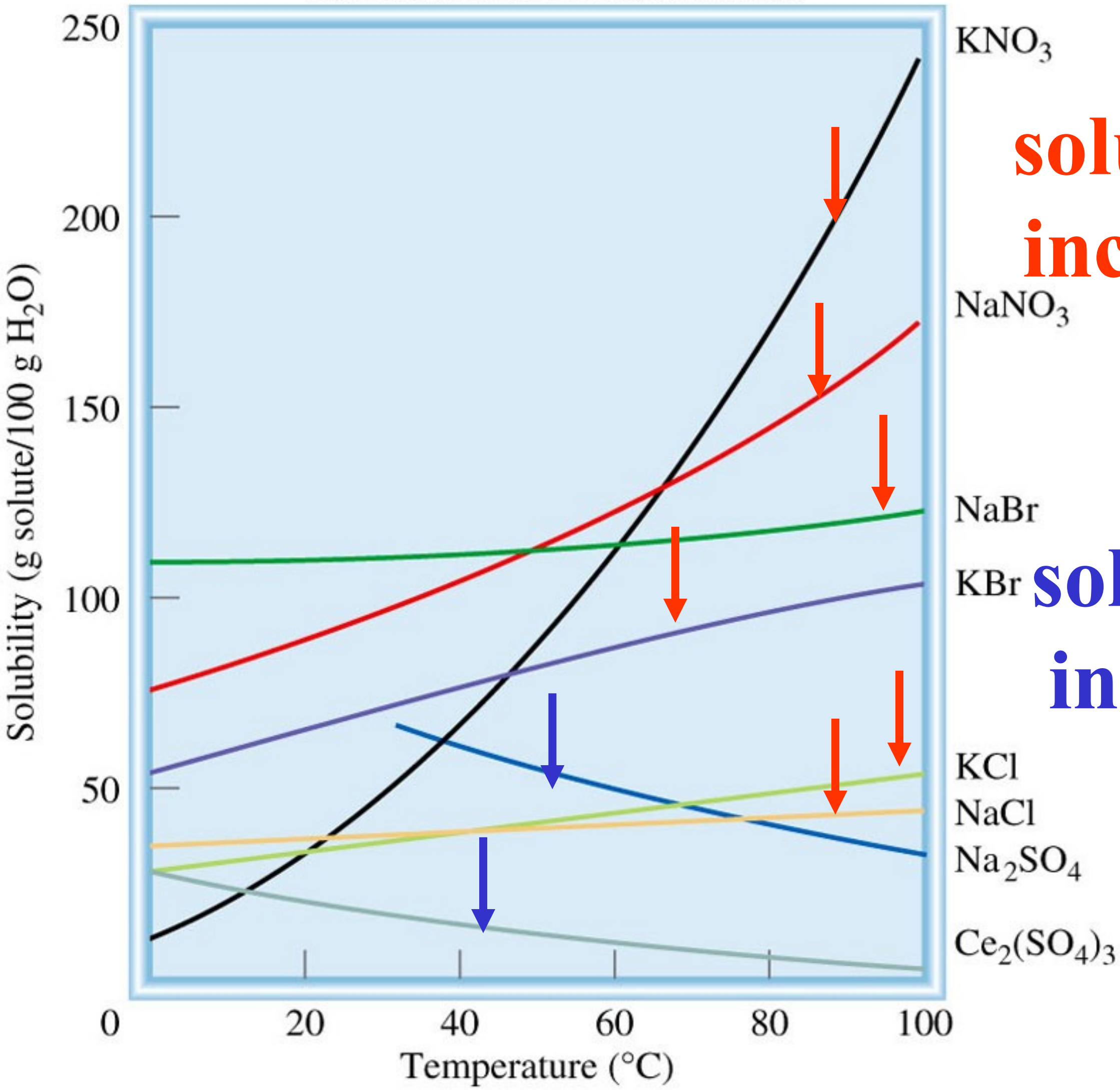
A)5.9 B) 5.1 C) 5.4 D) 5.6

The solubility of methane gas in ethanol at 25ºC and 1 atm is 0.521 mol/L.If the molarity of the gas becomes 6.25 mol/L, What is the partial pressure in (atm) at the same temperature?

A) 3.2 B) 7.6 C) 12.2 D) 9.8

Temperature and Solubility

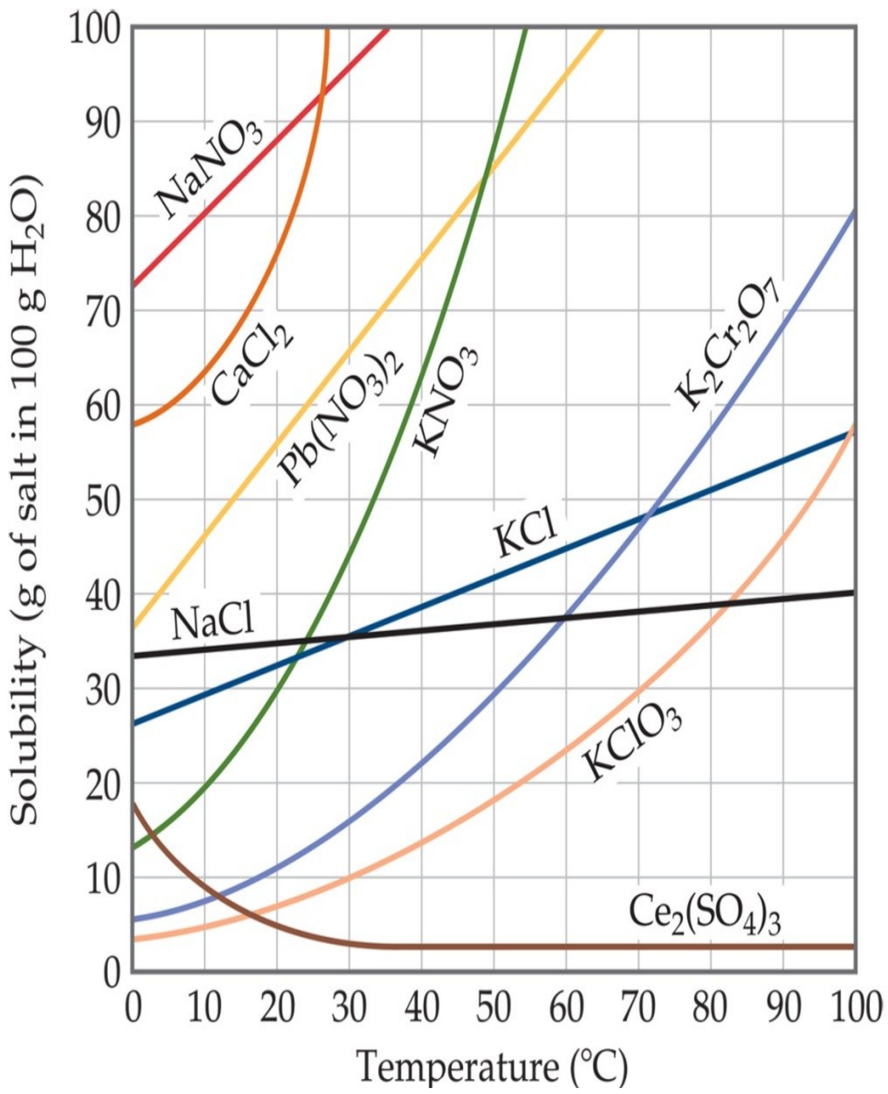
Solid solubility and temperature



solubility increases with increasing temperature

solubility decreases with increasing temperature

Temperature



Generally, the solubility of solid solutes in liquid solvents increases with increasing temperature.

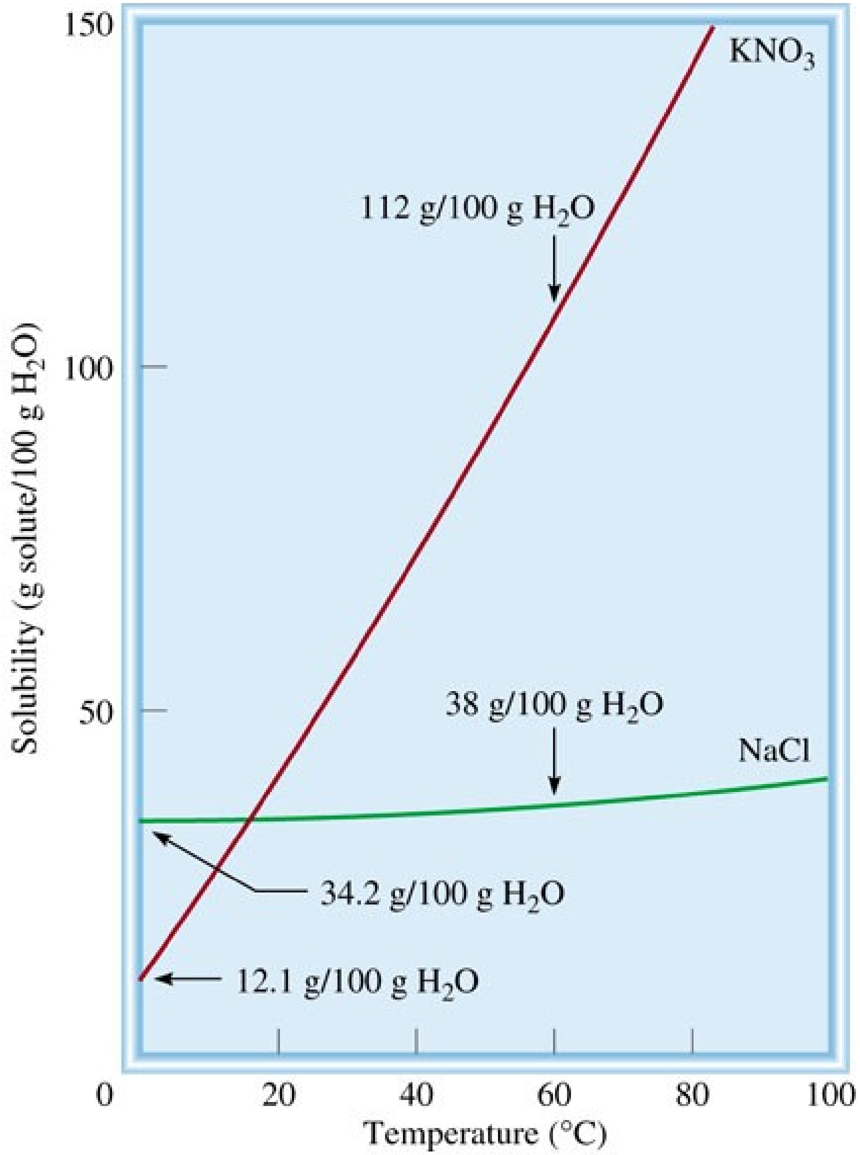
Temperature

Solid solutes: depends on balance of several factors can increase, decrease or stay the same.

Gases: solubility always *decreases* with temperature

increases

Fractional crystallization is the separation of a mixture of substances into pure components on the basis of their differing solubilities.



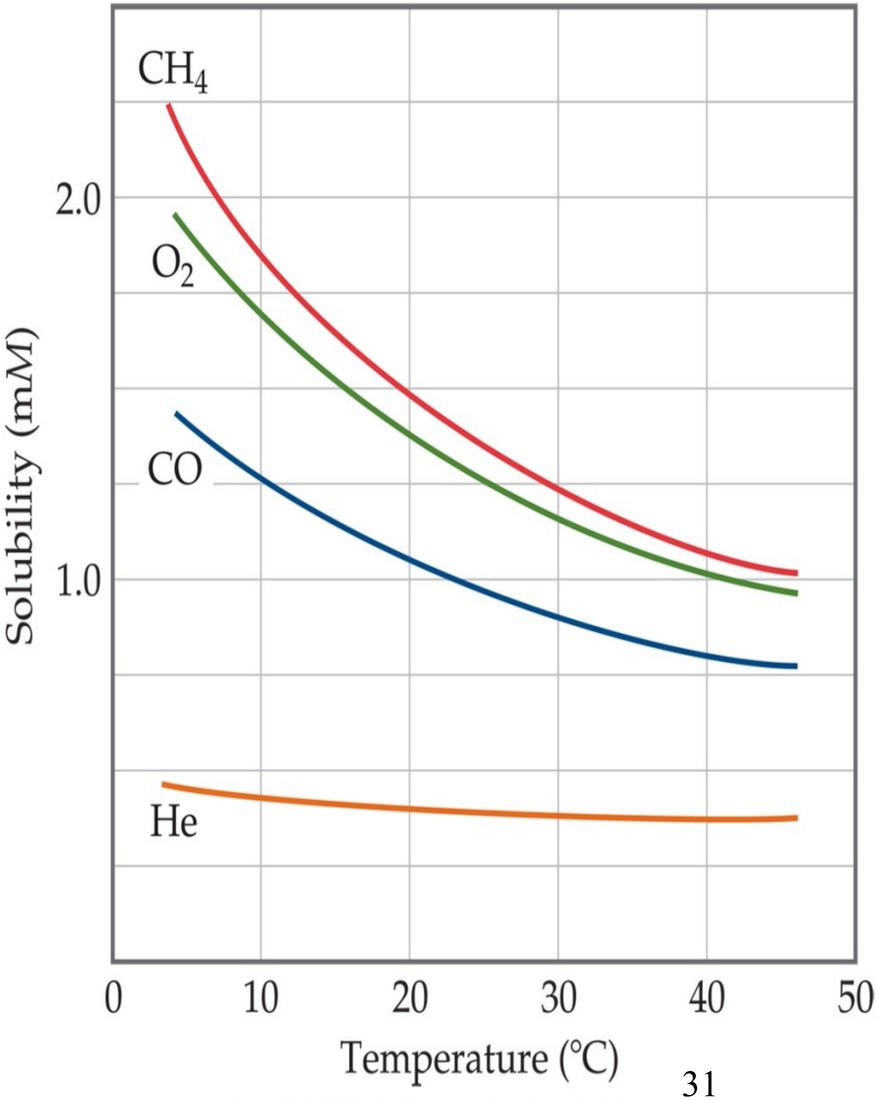
Suppose you have 90 g KNO_3 contaminated with 10 g NaCl.

Fractional crystallization:

1. Dissolve sample in 100 mL of water at 60^{0}C
2. Cool solution to 0^{0}C
3. All NaCl will stay in solution (s = 34.2g/100g)
4. 78 g of PURE KNO_3 will precipitate (s = 12 g/100g). 90 g – 12 g = 78 g

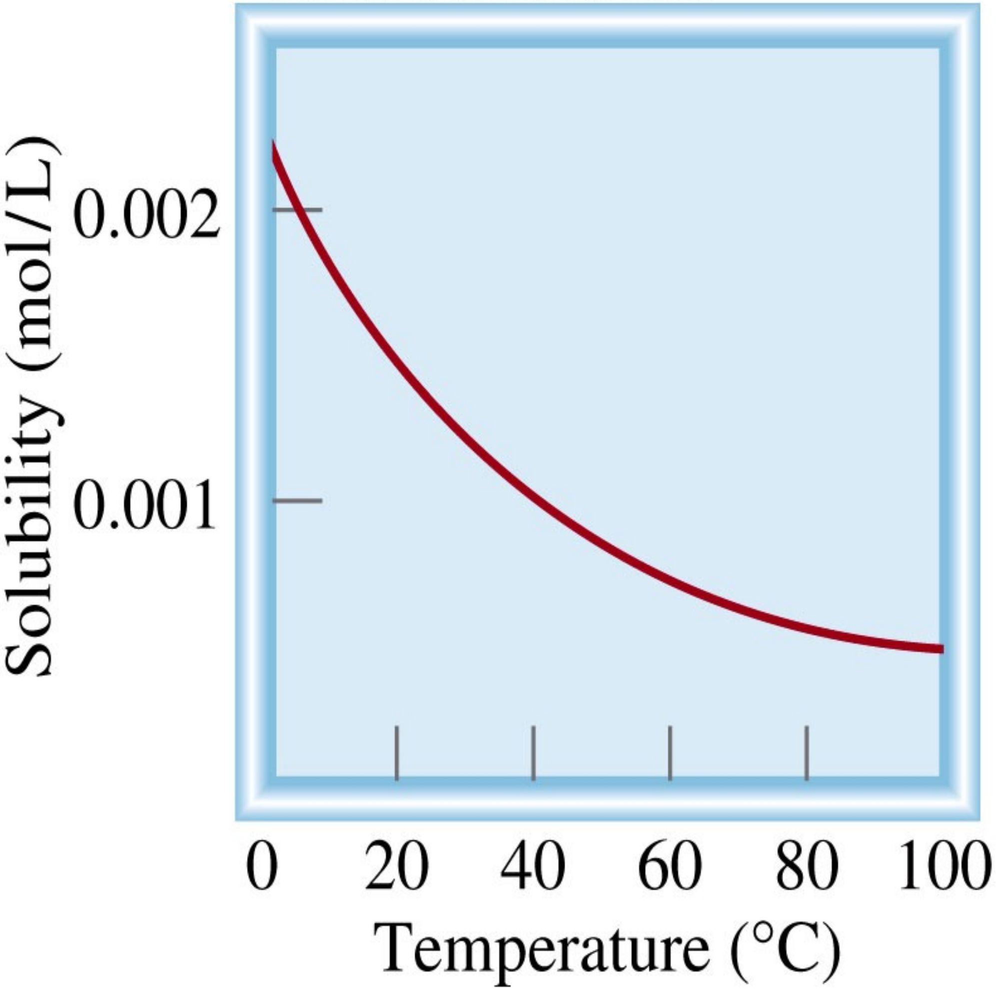
Temperature

- The opposite is true of gases. Higher temperature drives gases out of solution
  - Carbonated soft drinks are more if stored in the refrigerator.
  - Warm lakes have less O_2 dissolved in them than cool lakes.



Temperature and Solubility

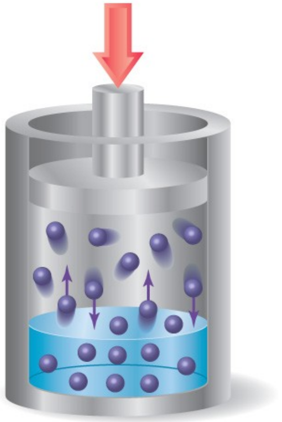
O_2 gas solubility and temperature



solubility usually decreases with increasing temperature

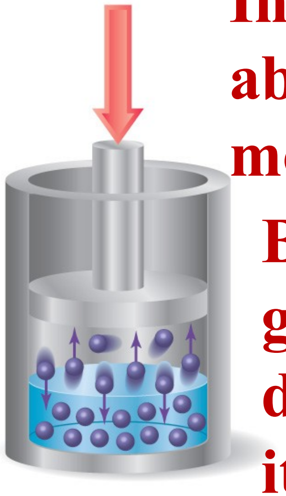
Gases in Solution

- The solubility of liquids and solids does not change appreciably with pressure.
- The solubility of a gas in a liquid is directly proportional to its pressure.



In general, the solubility of gases in water increases with increasing mass. Why?

Larger molecules have stronger dispersion forces.



Increasing pressure above solution forces more gas to dissolve.

But, the solubility of a gas in a liquid is directly proportional to its pressure.

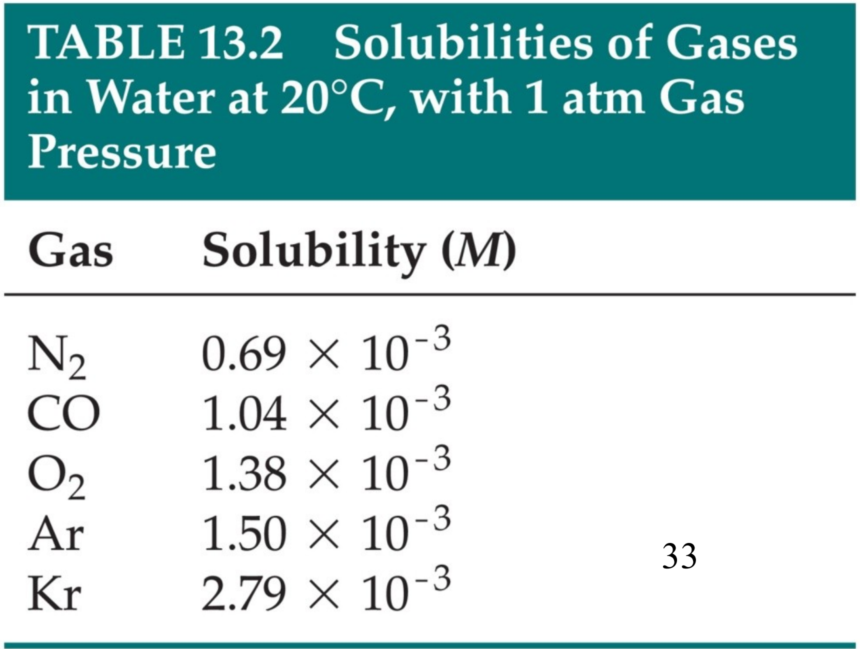


TABLE 13.2 Solubilities of Gases in Water at 20°C, with 1 atm Gas Pressure

Gas	Solubility (*M*)
N_2	0.69×10^{-3}
CO	1.04×10^{-3}
O_2	1.38×10^{-3}
Ar	1.50×10^{-3}
Kr	2.79×10^{-3}

The Effect of Pressure on the Solubility of Gases

- Most gases obey Henry's law, but there are some important exceptions.
- For example, if the dissolved gas *reacts* with water, higher solubilities can result.

The solubility of ammonia is much higher than expected because of the reaction

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Carbon dioxide also reacts with water, as follows:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

Another interesting example is the dissolution of *molecular oxygen in blood.*

$$Hb + 4O_2 \rightleftharpoons Hb(O_2)_4$$

Pressure and Solubility of Gases

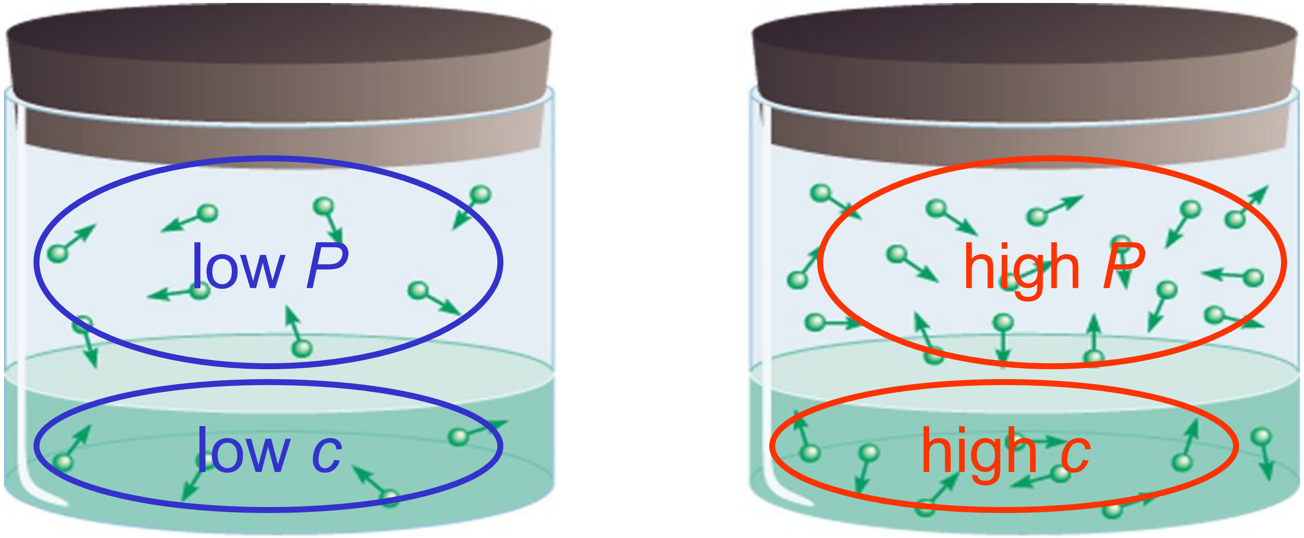
The solubility of a gas in a liquid is proportional to the pressure of the gas over the solution (***Henry's law***).

$$\boxed{c = k_H P}$$

c is the concentration (M) of the dissolved gas

P is the pressure of the gas over the solution

k_H is a constant for each gas (mol/L•atm) that depends only on temperature



Example 12.6

The solubility of nitrogen gas at 25°C and 1 atm is 6.8×10^{-4} mol/L.

What is the concentration (in molarity) of nitrogen dissolved in water under atmospheric conditions?

The partial pressure of nitrogen gas in the atmosphere is 0.78 atm.

Example 12.6

Solution

The first step is to calculate the quantity k in Equation

$$c = kP$$

$$6.8 \times 10^{-4}\ \text{mol/L} = k\,(1\ \text{atm})$$

$$k = 6.8 \times 10^{-4}\ \text{mol/L} \cdot \text{atm}$$

Therefore, the solubility of nitrogen gas in water is

$$c = (6.8 \times 10^{-4}\ \text{mol/L} \cdot \text{atm})\,(0.78\ \text{atm})$$

$$= 5.3 \times 10^{-4}\ \text{mol/L}$$

$$= 5.3 \times 10^{-4}\ M$$

The decrease in solubility is the result of lowering the pressure from 1 atm to 0.78 atm.

Colligative Properties

- Changes in colligative properties depend only on the *number* of solute particles present, not on the *identity* of the solute particles.
- Among colligative properties are
  - Vapor pressure lowering
  - Boiling point elevation
  - Melting point depression
  - Osmotic pressure

Colligative Properties of Nonelectrolyte Solutions

Colligative properties are properties that depend only on the **number** of solute particles in solution and not on the **nature** of the solute particles.

Vapor-Pressure Lowering

$$\boxed{P_1 = X_1 P_1^0}$$

Raoult's law

P_1^0 = vapor pressure of **pure** solvent

X_1 = mole fraction of the solvent

If the solution contains only one solute:

$$X_1 = 1 - X_2$$

$$P_1^0 - P_1 = \Delta P = X_2 P_1^0$$

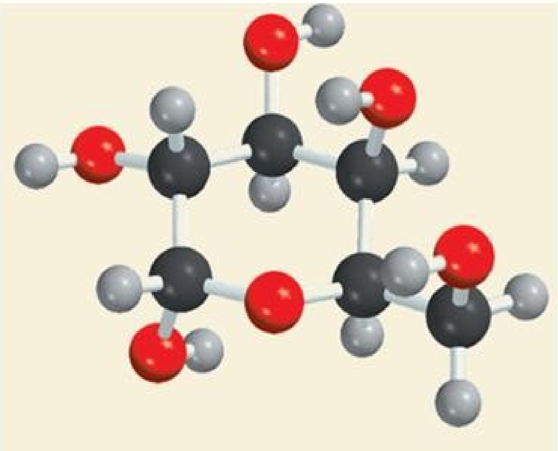
X_2 = mole fraction of the solute

Example 12.7

Calculate the vapor pressure of a solution made by dissolving 218 g of glucose (molar mass = 180.2 g/mol) in 460 mL of water at 30°C.

What is the vapor-pressure lowering?

The vapor pressure of pure water at 30°C is given in 31.82 mmHg. Assume the density of the solvent is 1.00 g/mL.



Solution

The vapor pressure of a solution (P_1) is

$$P_1\left(\text{want to calculate}\right) = X_1\left(\text{need to find}\right) P_1^{\circ}\left(\text{given}\right)$$

First we calculate the number of moles of glucose and water in the solution:

$$n_1\left(\text{water}\right) = \cancel{460}\ \cancel{\text{mL}} \times \frac{1.00\ \cancel{\text{g}}}{1\ \cancel{60^\circ}} \times \frac{1\ \text{mol}}{18.02\ \cancel{\text{g}}} = 25.5\ \text{mol}$$

$$n_2\left(\text{glucose}\right) = 218\ \cancel{\text{g}} \times \frac{1\ \text{mol}}{180.2\ \cancel{\text{g}}} = 1.21\ \text{mol}$$

The mole fraction of water, X_1, is given by

$$X_1 = \frac{n_1}{n_1 + n_2}$$

$$= \frac{25.5\ \text{mol}}{25.5\ \text{mol} + 1.21\text{mol}} = 0.955$$

From Table 5.3, we find the vapor pressure of water at 30° C to be 31.82 mmHg. Therefore, the vapor pressure of the glucose solution is

$$P_1 = 0.955 \times 31.82\ \text{mmHg}$$

$$= 31.4\ \text{mmHg}$$

Finally, the vapor-pressure lowering (ΔP)is (31.82 – 30.4) mmHg, or 1.4 mmHg.

Ex. Glycerin (using Raoult's Law)

Glycerin, $C_3H_8O_3$, is a nonvolatile nonelectrolyte with a density of 1.26 g/mL at 25 °C. Calculate the change in vapor pressure as 25 °C of a solution made by adding 50.0 mL of glycerin to 500.0 mL of water. The vapor pressure of pure water at 25 °C is 23.8 torr.

- To solve use:

$$\Delta P = X_{solute} P^{\circ}_{solvent}$$

- First we need X_{solute}, so we need mole glycerin and mole H_2O.

Ex. Glycerin (cont.)

Mole glycerin

$$50.0\text{mL } C_3H_8O_3 \times 1.26\,\frac{\text{g}}{\text{mL}} \times \frac{1\text{mol } C_3H_8O_3}{92.1\text{g } C_3H_8O_3}$$

$$= 0.684\text{mol } C_3H_8O_3$$

Mole water

$$500.0\text{mL } H_2O \times 1.00\,\frac{\text{g}}{\text{mL}} \times \frac{1\text{mol } H_2O}{18.02\text{g } H_2O} = 27.75\text{mol } H_2O$$

Mole fraction glycerin

$$X_{C_3H_8O_3} = \frac{0.684\text{mol}}{(27.75 + 0.684)\text{mol}} = 2.4\underline{0}6 \times 10^{-2}$$

$$\Delta P = X_{solute}P^{\circ}_{solvent} = \left(2.4\underline{0}6 \times 10^{-2}\right) \times 23.8\,torr$$

= 0.573 torr

Ex. Glycerin (cont.)

What is the final pressure?

- Can solve two ways:

$$\Delta P = P^{\circ}_{solvent} - P_{solution} \quad P_{solution} = P^{\circ}_{solvent} - \Delta P$$

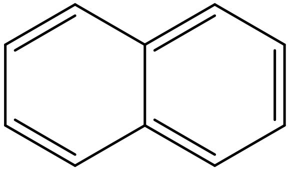
$$P_{\mathrm{soln}} = 23.8torr - 0.573torr = 23.2torr$$

- Or

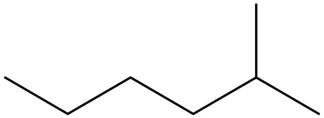
$$X_{\mathrm{H_2O}} = \frac{27.75mol}{(27.75 + 0.684)mol} = 0.9759$$

$$P_{\mathrm{solution}} = X_{\mathrm{solvent}} P^{\circ}_{\mathrm{solvent}}$$
$$= (0.9759) \times 23.8torr = 23.2torr$$

The vapor pressure of 2-methylhexane is 37.986 torr at 15°C. What would be the pressure of the mixture of 78.0 g 2-methylhexane and 15 g naphthalene, which is nearly non-volatile at this temperature?



naphthalene
$C_{10}H_8$
MM 128.17



2-methylhexane
C_7H_{16}
MM 100.2

$$\mathbf{P_{solution} = X_{solvent}P^{o}_{solvent}}$$

$$\text{mole naphthalene} = \frac{15\text{ g}}{128.17\text{ g/mol}} = 0.1\underline{1}7\text{ mol}$$

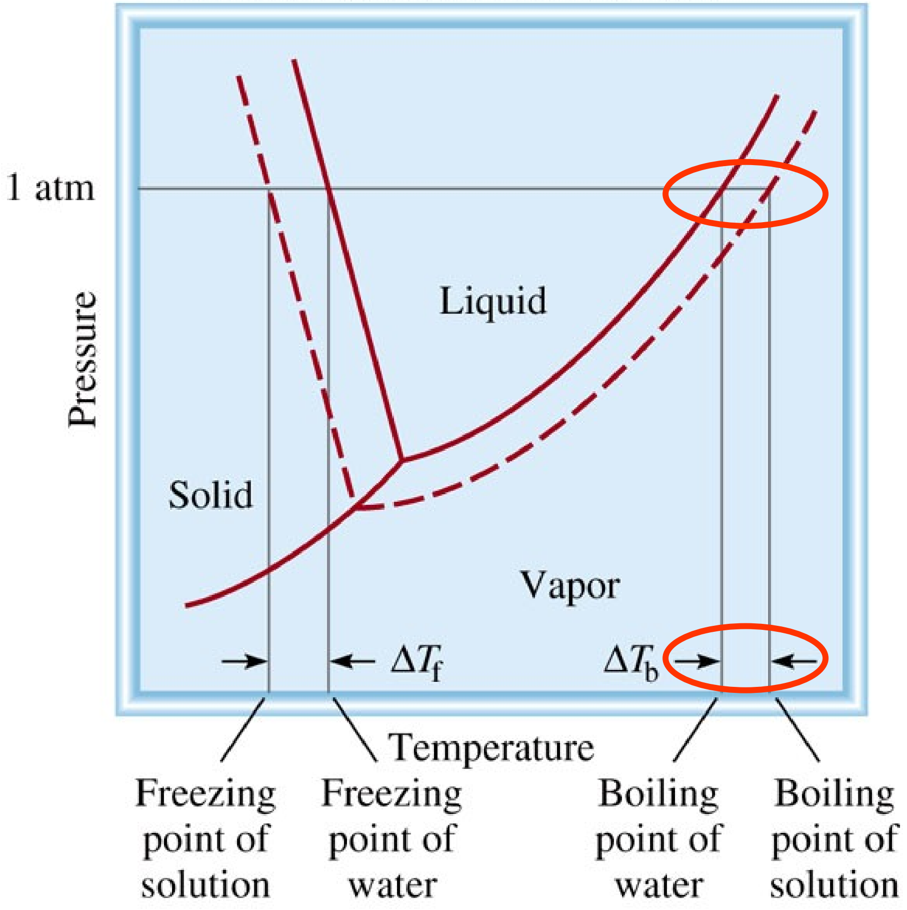
$$\text{mole 2 - methylhexane} = \frac{78.0\text{ g}}{100.2\text{ g/mol}} = 0.77\underline{8}4\text{ mol}$$

$$X_{2-\text{methylhexane}} = \frac{0.77\underline{8}4\text{ mol}}{0.77\underline{8}4\text{ mol} + 0.1\underline{1}7\text{ mol}} = 0.8\underline{6}9$$

$$P = \left(0.8\underline{6}9 \times 37.986\text{ torr}\right)$$

$$= 3\underline{3}.02\text{ torr} \mathbf{= 33\ torr}$$

Boiling-Point Elevation



$$\Delta T_b = T_b - T_b^0$$

T_b^0 is the boiling point of the pure solvent

T_b is the boiling point of the solution

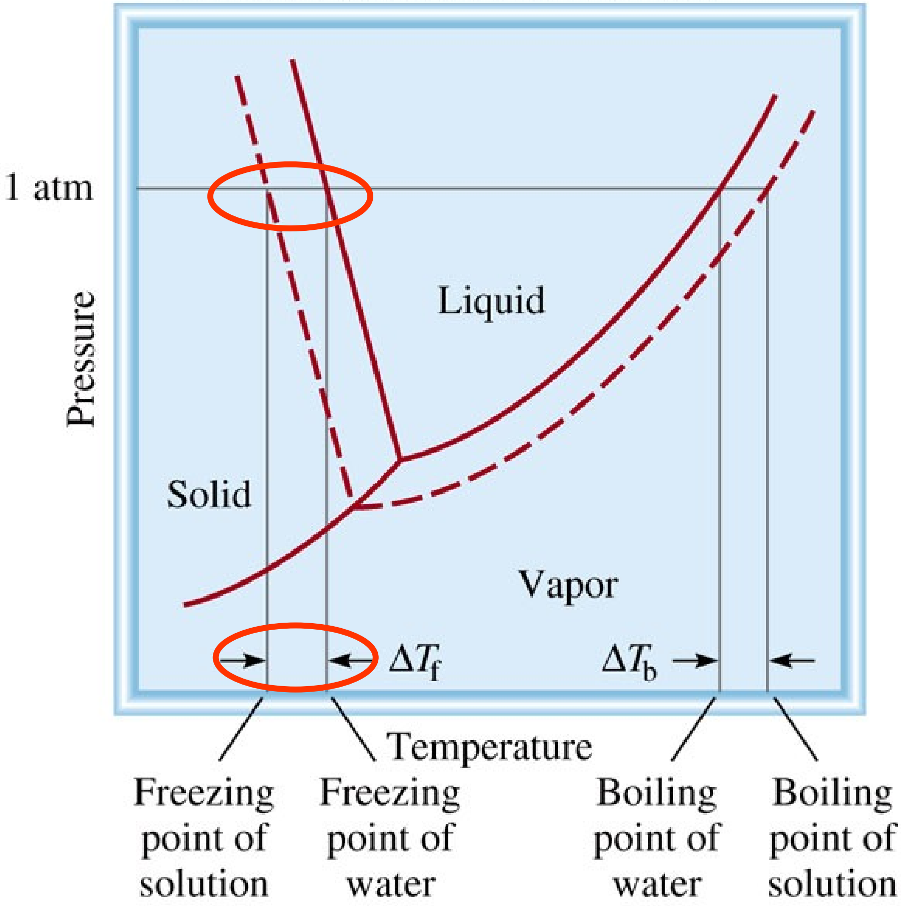
$T_b > T_b^0 \qquad \Delta T_b > 0$

$$\boxed{\Delta T_b = K_b\, m}$$

m is the molality of the solution

K_b is the molal boiling-point elevation constant (^{0}C/m) for a given solvent

Freezing-Point Depression



$$\Delta T_f = T_f^0 - T_f$$

T_f^0 is the freezing point of the pure solvent

T_f is the freezing point of the solution

$T_f^0 > T_f \qquad \Delta T_f > 0$

$$\boxed{\Delta T_f = K_f\, m}$$

m is the molality of the solution

K_f is the molal freezing-point depression constant (^{0}C/*m*) for a given solvent

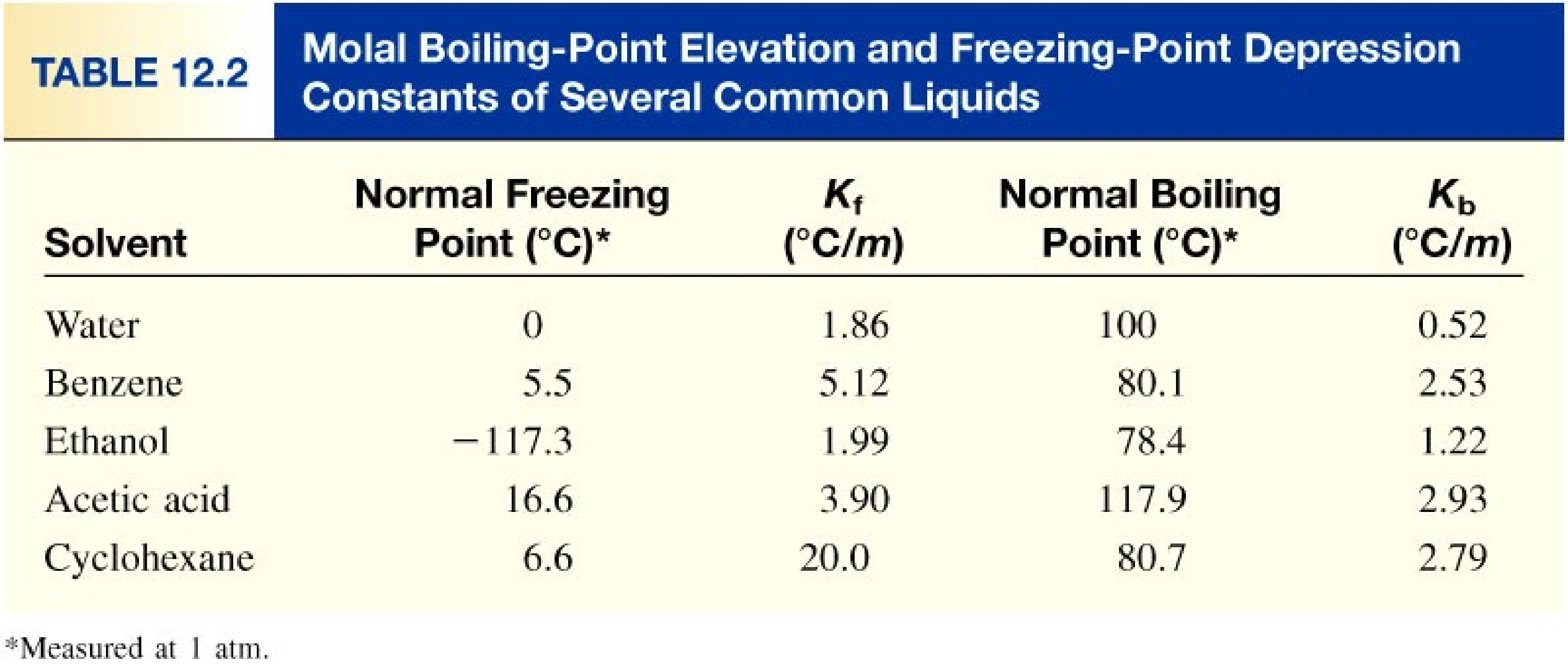


TABLE 12.2 Molal Boiling-Point Elevation and Freezing-Point Depression Constants of Several Common Liquids

Solvent	Normal Freezing Point (°C)*	K_f (°C/*m*)	Normal Boiling Point (°C)*	K_b (°C/*m*)
Water	0	1.86	100	0.52
Benzene	5.5	5.12	80.1	2.53
Ethanol	−117.3	1.99	78.4	1.22
Acetic acid	16.6	3.90	117.9	2.93
Cyclohexane	6.6	20.0	80.7	2.79

*Measured at 1 atm.

Example 12.8

Ethylene glycol (EG), $CH_2(OH)CH_2(OH)$,is a common automobile antifreeze. It is water soluble and fairly nonvolatile (b.p.197°C).

Calculate the freezing point of a solution containing 651 g of this substance in 2505 g of water.

Would you keep this substance in your car radiator during the summer? The molar mass of ethylene glycol is 62.01 g.

Solution

To solve for the molality of the solution, we need to know the number of moles of EG and the mass of the solvent in kilograms.

We find the molar mass of EG, and convert the mass of the solvent to 2.505 kg, and calculate the molality as follows:

$$651\ \cancel{\text{g}}\ \cancel{\text{EG}} \times \frac{1\text{ mol EG}}{62.07\ \cancel{\text{g}}\ \cancel{\text{EG}}} = 10.5\text{ mol EG}$$

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (Kg)}}$$

$$= \frac{10.5\text{ mol EG}}{2.505\text{ kg H}_2\text{O}} = 4.19\text{ mol EG/kg H}_2\text{O}$$

$$= 4.19\text{ m}$$

$$\Delta T_f = K_f m$$

$$= (1.86\,°\text{C}/\ m)(4.19\ m)$$

$$= 7.79°\text{C}$$

Example 12.8

Because pure water freezes at 0°C, the solution will freeze at (0 − 7.79)°C or 27.79°C.

We can calculate boiling-point elevation in the same way as follows:

$$\Delta T_b = K_b m$$

$$= (0.52°\text{C}/m)(4.19\ m)$$

$$= 2.2°\text{C}$$

Because the solution will boil at (100 + 2.2)°C, or 102.2°C, it would be preferable to leave the antifreeze in your car radiator in summer to prevent the solution from boiling.

What is the freezing point of a solution containing 478 g of ethylene glycol (antifreeze) in 3202 g of water? The molar mass of ethylene glycol is 62.01 g/mol.

$\Delta T_f = K_f\, m$ $\qquad$ K_f water = 1.86 ^{0}C/m

$$\boldsymbol{m} = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} = \frac{478\text{ g} \times \dfrac{1\text{ mol}}{62.01\text{ g}}}{3.202\text{ kg solvent}} = 2.41\ m$$

$$\Delta T_f = K_f\, m = 1.86\ ^0\text{C}/m \times 2.41\ m = 4.48\ ^0\text{C}$$

$$\Delta T_f = T_f^0 - T_f$$

$$T_f = T_f^0 - \Delta T_f = 0.00\ ^0\text{C} - 4.48\ ^0\text{C} = -4.48\ ^0\text{C}$$

Automotive antifreeze consists of ethylene glycol, $CH_2(OH)CH_2(OH)$, a nonvolatile nonelectrolyte. Calculate the boiling point and freezing point of a 25.0 mass % solution of ethylene glycol in water.

Moles of ethylene glycol = 250 g/62.1 g mol^{-1} = 4.03 mol

$$\text{Molality} = \frac{4.03\ \text{mol}}{0.75\ \text{Kg}} = 5.37\ \text{m}$$

$$\Delta T_b = K_b \bullet m = (0.51\ ^{o}\text{C/m})(5.73\ \text{m}) = 2.7\ ^{o}\text{C}$$

$$\Delta T_f = K_f \bullet m = (1.86\ ^{o}\text{C/m})(5.73\ \text{m}) = 10.0\ ^{o}\text{C}$$

Boling point = (normal bp of solvent) + ΔT_b

= 100 ^{o}C + 2.7 ^{o}C = 102.7 ^{o}C

Freezing point = (normal fp of solvent) - ΔT_f

= 0 ^{o}C - 10 ^{o}C = -10 ^{o}C

Glycerin ($C_3H_8O_3$) is a nonvolatile nonelectrolyte with a density of 1.26 g/mL at 25°C. Calculate the vapor pressure at 25°C of a solution made by adding 50.0 mL of glycerin to 500.0 mL of water. The vapor pressure of pure water at 25°C is 23.8 torr (Appendix B).

- What is the freezing point in (^{o}C) of an aqueous Solution made by dissolving 60 g of (CH_4N_2O) (nonelectrolyte) in 1000g of water? K_f of water = 1.86 $^{o}C/m$

A) -6.21 B) -8.95 C) -1.86 D) -12.30

- The boiling point in (^{o}C) of an aqueous solution of a non electrolyte solute that has a freezing point of -13.6 ^{o}C, is: (K_f of water = 1.86 $^{o}C/m$ K_b of water = 0.52 $^{o}C/m$)

A) 108.5 B) 103.8 C) 101.4 D) 105.3

Example 12.10

A 7.85-g sample of a compound with the empirical formula C_5H_4 is dissolved in 301 g of benzene.

The freezing point of the solution is 1.05°C below that of pure benzene.

What are the molar mass and molecular formula of this compound?

Solution

The sequence of conversions for calculating the molar mass of the compound is freezing - point depression → molality → number of moles → molar mass

Our first step is to calculate the molality of the solution. From Equation (12.7) and Table 12.2 we write

$$\text{molality} = \frac{\Delta T_\text{f}}{K_\text{f}} = \frac{1.05°\text{C}}{5.12°\text{C}/m} = 0.205\, m$$

Because there is 0.205 mole of the solute in 1 kg of solvent, the number of moles of solute in 301 g, or 0.301 kg, of solvent is

$$0.301\,\text{kg} \times \frac{0.205\,\text{mol}}{1\,\text{kg}} = 0.0617\,\text{mol}$$

Example 12.10

Our first step is to calculate the molality of the solution. From Equation (12.7) and Table 12.2 we write

$$\text{molality} = \frac{\Delta T_\text{f}}{K_\text{f}} = \frac{1.05°\text{C}}{5.12°\text{C}/m} = 0.205\ m$$

Because there is 0.205 mole of the solute in 1 kg of solvent, the number of moles of solute in 301 g, or 0.301 kg, of solvent is

$$0.301\,\text{kg} \times \frac{0.205\,\text{mol}}{1\,\text{kg}} = 0.0617\,\text{mol}$$

Example 12.10

Thus, the molar mass of the solute is

$$\begin{aligned}\text{molar mass} &= \frac{\text{grams of compound}}{\text{moles of compound}} \\ &= \frac{7.85\text{ g}}{0.0617\text{ mol}} = 127\text{ g/mol}\end{aligned}$$

Now we can determine the ratio

$$\frac{\text{molar mass}}{\text{empirical molar mass}} = \frac{127}{64\text{ g/mol}} \approx 2$$

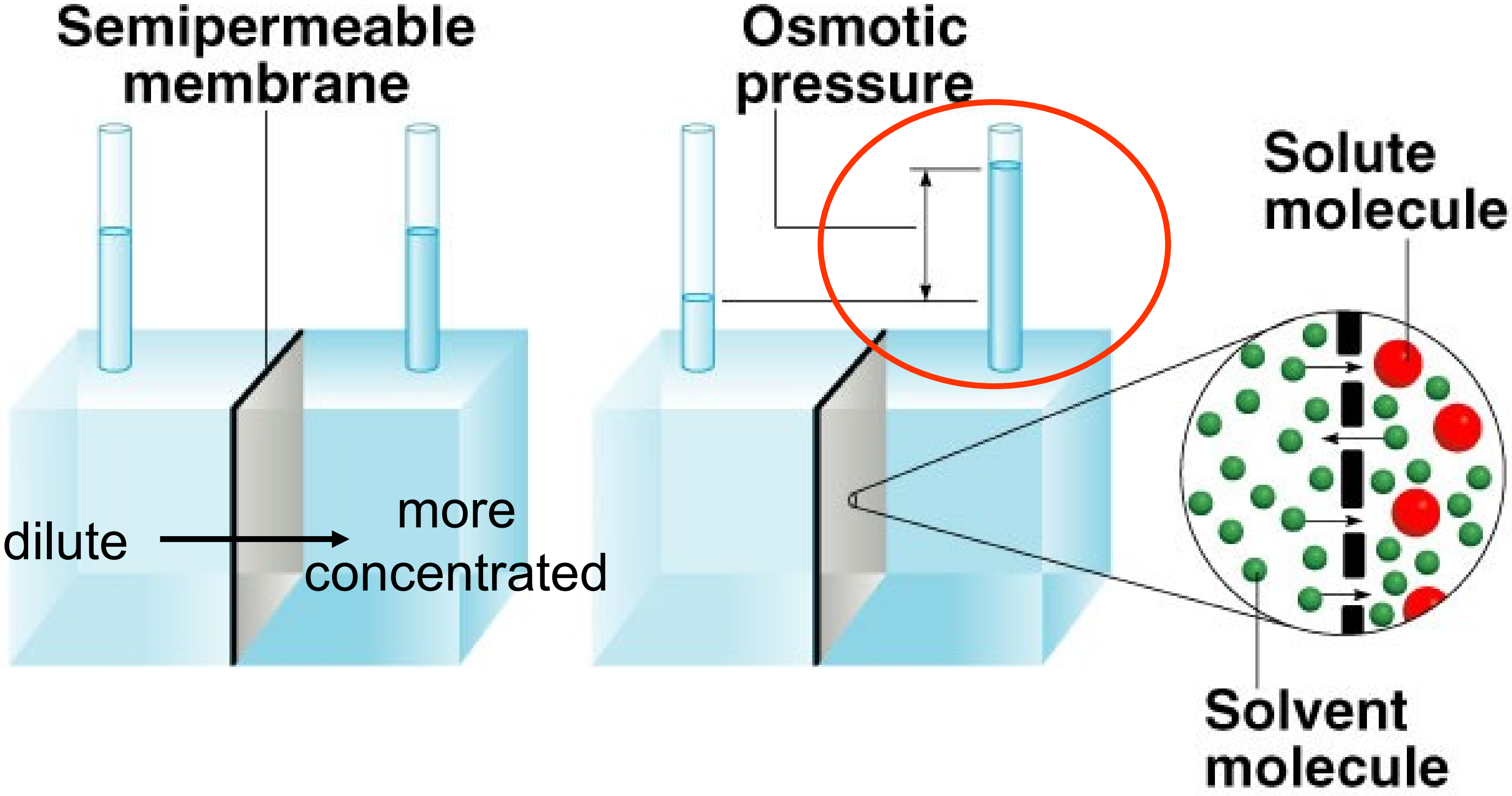
Therefore, the molecular formula is $(C_5H_4)_2$ or $C_{10}H_8$ (naphthalene).

Osmotic Pressure (π)

Osmosis is the selective passage of solvent molecules through a porous membrane from a dilute solution to a more concentrated one.

A ***semipermeable membrane*** allows the passage of solvent molecules but blocks the passage of solute molecules.

Osmotic pressure (π) is the pressure required to stop osmosis.



Osmotic Pressure

The pressure required to stop osmosis, known as osmotic pressure, π, is

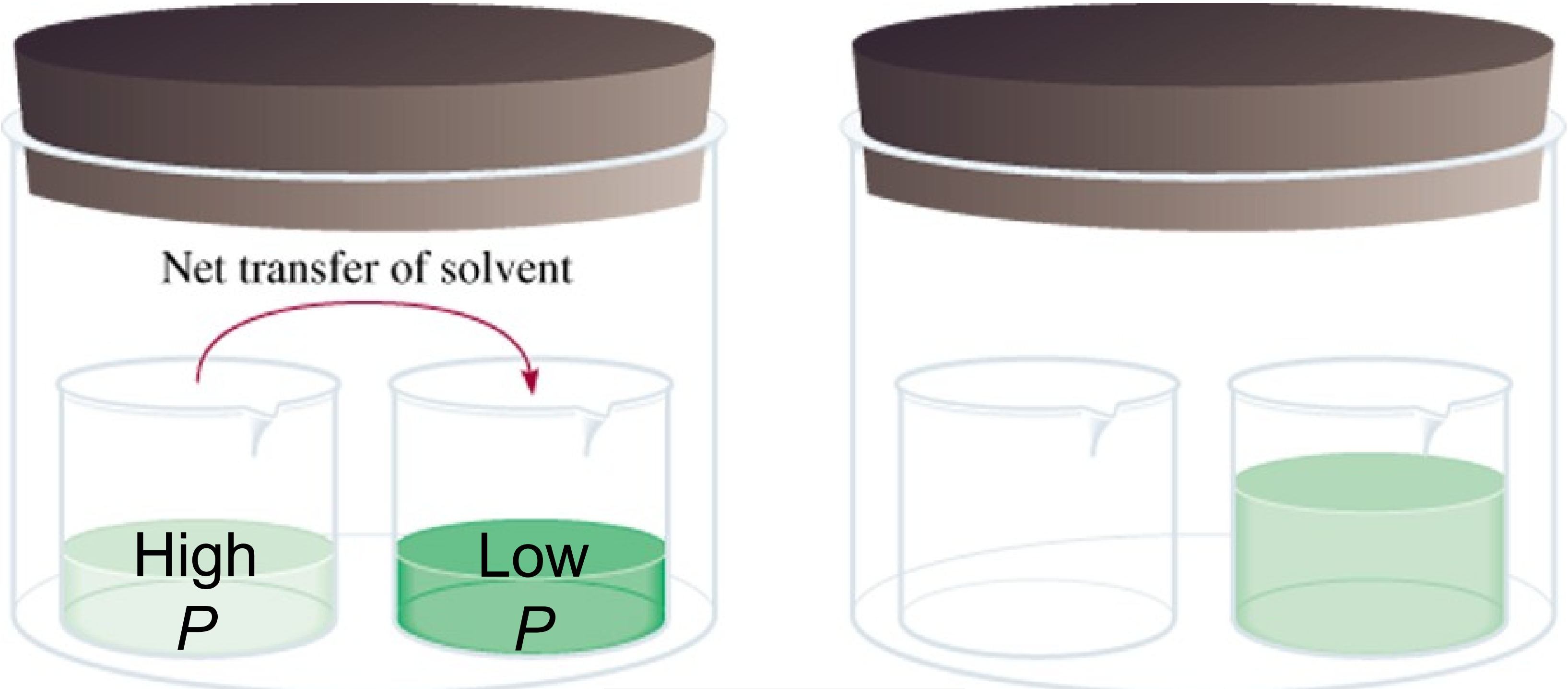
$$\pi V = nRT$$

$$\pi = \left(\frac{n}{V}\right)RT = M\,RT$$

where M is the molarity of the solution.

If the osmotic pressure is the same on both sides of a membrane (i.e., the concentrations are the same), the solutions are isotonic.

Osmotic Pressure (π)



$$\boxed{\pi = MRT}$$

M is the molarity of the solution

R is the gas constant

T is the temperature (in K)

The average osmotic pressure of blood is 7.7 atm at 25 °C. What molarity of glucose ($C_6H_{12}O_6$) will be isotonic with blood?

$$\Pi = MRT$$

$$M = \frac{\Pi}{RT} = \frac{7.7\ \text{atm}}{\left(0.0821\ \frac{\text{L-atm}}{\text{mol-K}}\right)(298\ \text{K})} = 0.31\ M$$

- A 250 mL solution containing 21.4 g of a on electrolyte substance in toluene had an osmotic pressure of 0.055 atm at 27 ºC. The molar mass in *(g/mol)* of this substance is:

A) 15 x10^4

B) 3.8 x10^4

C) 1.8 x10^3

D) 3.2 x10^3

Example 12.11

A solution is prepared by dissolving 35.0 g of hemoglobin (Hb) in enough water to make up 1 L in volume.

If the osmotic pressure of the solution is found to be 10.0 mmHg at 25°C, calculate the molar mass of hemoglobin.

Solution

The sequence of conversions is as follows:

$$\text{osmotic pressure} \rightarrow \text{molality} \rightarrow \text{number of moles} \rightarrow \text{molar mass}$$

$$\pi = MRT$$

$$M = \frac{\pi}{RT}$$

$$= \frac{10.0\text{mmHg} \times \dfrac{1\,\text{atm}}{760\,\text{mmHg}}}{(0.0821\,\text{L}\cdot\text{atm}/\text{K}\cdot\text{mol})(298\,\text{K})}$$

$$= 5.38 \times 10^{-4}\,M$$

The volume of the solution is 1 L, so it must contain 5.38×10^{-4} mol of Hb.

We use this quantity to calculate the molar mass:

$$\text{moles of Hb} = \frac{\text{mass of Hb}}{\text{molar mass of Hb}}$$

$$\text{molar mass of Hb} = \frac{\text{mass of Hb}}{\text{moles of Hb}}$$

$$= \frac{35.0\text{ g}}{5.38 \times 10^{-4}\,\text{mol}}$$

$$= 6.51 \times 10^{4}\text{ g/mol}$$

Summary - Colligative Properties of Nonelectrolyte Solutions

Colligative properties are properties that depend only on the number of solute particles in solution and not on the nature of the solute particles.

Vapor-Pressure Lowering $P_1 = X_1 P_1^0$

Boiling-Point Elevation $\Delta T_b = K_b m$

Freezing-Point Depression $\Delta T_f = K_f m$

Osmotic Pressure (π) $\pi = MRT$

Colligative Properties of Electrolyte Solutions 1

$$0.1\,m\ \text{NaCl solution} \rightarrow \quad 0.1\,m\ \text{Na}^{+}\ \text{ions}\ \&\ 0.1\,m\ \text{Cl}^{-}\ \text{ions}$$

Colligative properties are properties that depend only on the **number** of solute particles in solution and not on the **nature** of the solute particles.

$$0.1\ m\ \text{NaCl solution} \rightarrow \qquad 0.2\ m\ \text{ions in solution}$$

$$\textbf{\textit{van't Hoff factor}}\left(\textbf{\textit{i}}\right) = \frac{\text{actual number of particles in soln after dissociation}}{\text{number of formula units initially dissolved in soln}}$$

	***i* should be**
nonelectrolytes	**1**
NaCl	**2**
$\mathbf{CaCl_2}$	**3**
$\mathbf{AaCl_3}$	**4**

Colligative Properties of Electrolyte Solutions 2

- **Boiling-Point Elevation** $$\Delta T_{\mathrm{b}} = iK_{\mathrm{b}}m$$
- **Boiling-Point Depression** $$\Delta T_{\mathrm{f}} = iK_{\mathrm{f}}m$$

Osmotic Pressure (π) $$\pi = iMRT$$

Table 12.3 The van’t Hoff Factor of 0.0500 *M* Electrolyte Solutions at 25°C

Electrolyte	***i* (Measured)**	***i* (Calculated)**
Surcose*	1.0	1.0
HCl	1.9	2.0
NaCl	1.9	2.0
$MgSO_4$	1.3	2.0
$MgCl_2$	2.7	3.0
$FeCl_3$	3.4	4.0

*Source is a nonelectrolyte. It is listed here for comparison only.

EXAMPLE 12.12

The osmotic pressure of a 0.010 *M* potassium iodide (KI) solution at 25°C is 0.465 atm. Calculate the van't Hoff factor for KI at this concentration.

Strategy Note that KI is a strong electrolyte, so we expect it to dissociate completely in solution. If so, its osmotic pressure would be

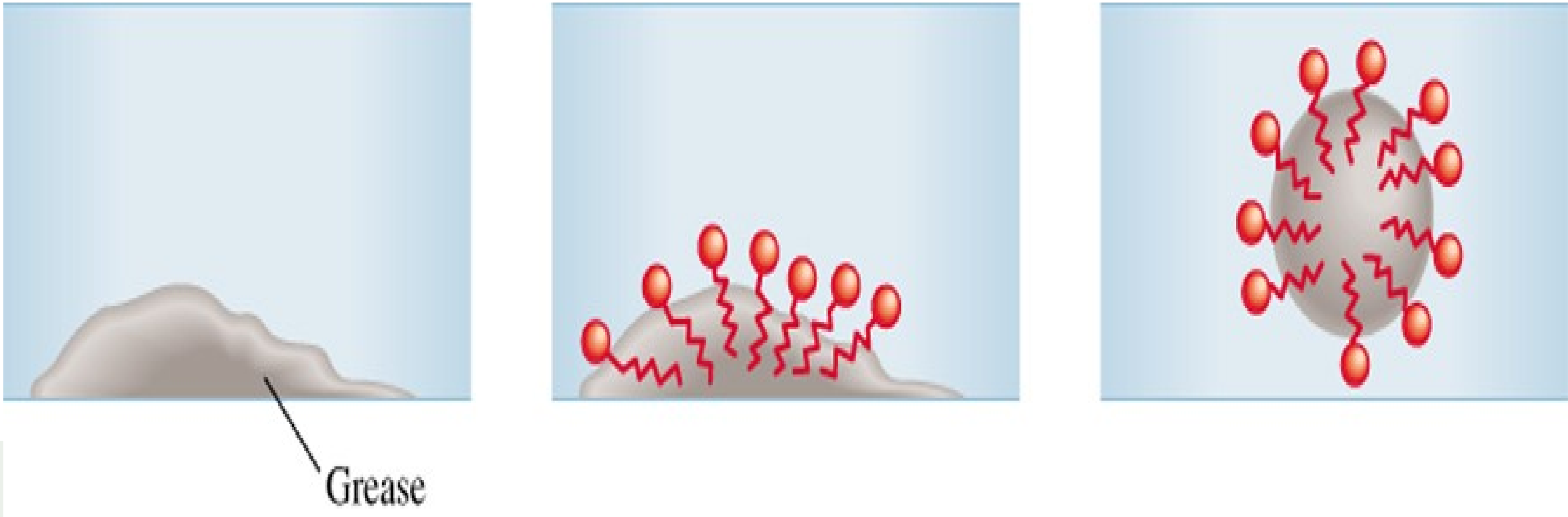
$$2(0.010\,M)(0.0821\ \text{L}\cdot\text{atm/K}\cdot\text{mol})(298\ \text{K}) = 0.489\ \text{atm}$$

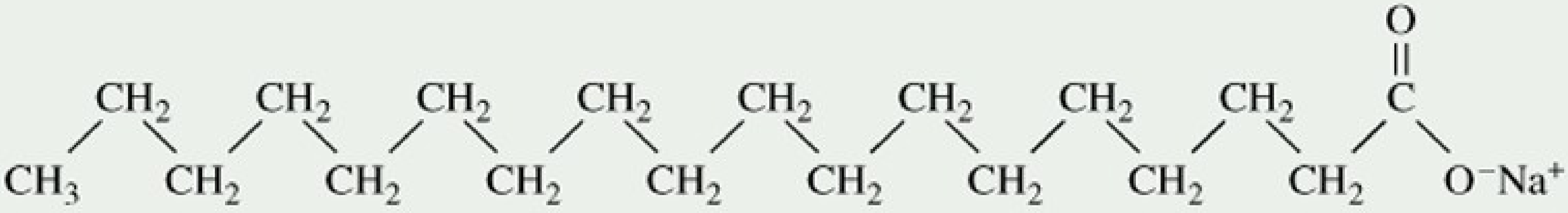
However, the measured osmotic pressure is only 0.465 atm. The smaller than predicted osmotic pressure means that there is ion-pair formation, which reduces the number of solute particles (K^+ and I^- ions) in solution.

Solution From Equation (12.12) we have

$$\begin{aligned} i &= \frac{\pi}{MRT} \\ &= \frac{0.465\ \text{atm}}{(0.010\,M)(0.0821\ \text{L}\cdot\text{atm/K}\cdot\text{mol})(298\ \text{K})} \\ &= \boxed{1.90} \end{aligned}$$

The Cleansing Action of Soap



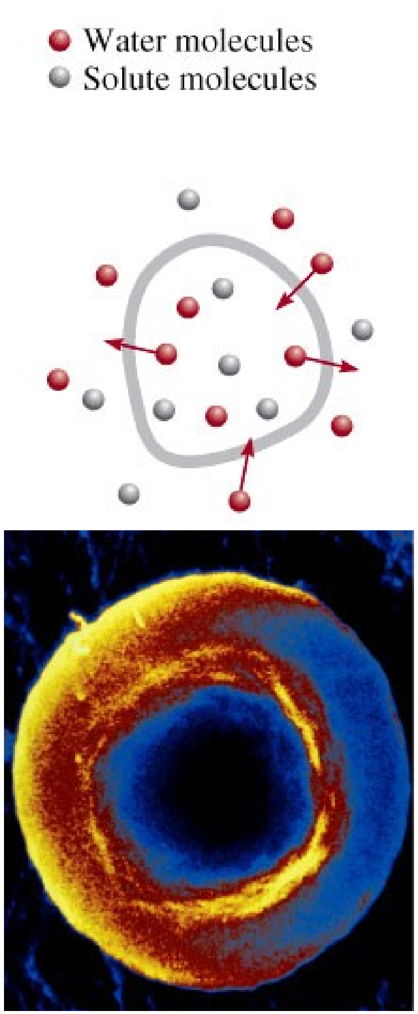


$$\mathrm{CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^-Na^+}$$

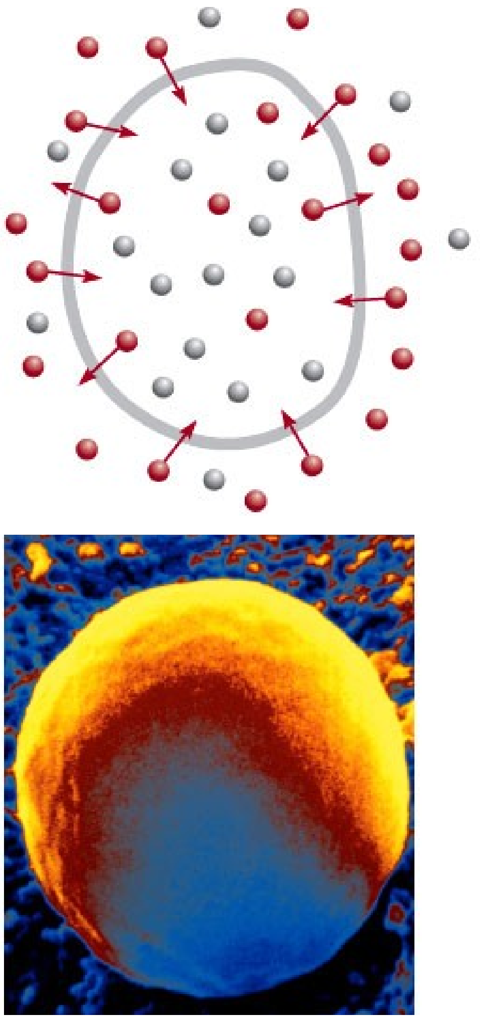
Sodium stearate ($C_{17}H_{35}COO^-Na^+$)

(a)

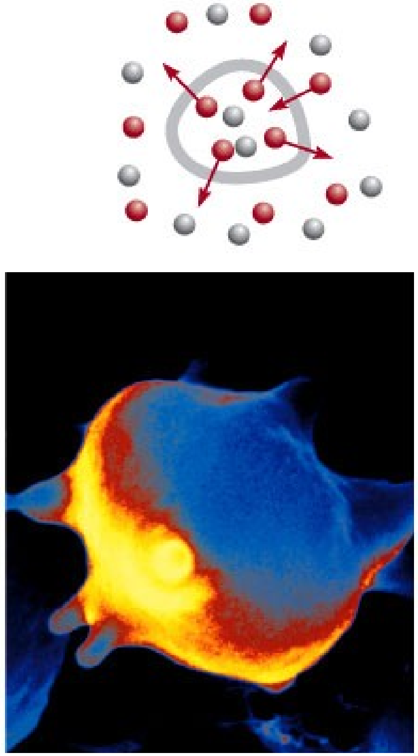
A cell in an:



isotonic
solution



hypotonic
solution



hypertonic
solution