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## *Gases*

Because gas particles move at a high velocity and are separated by large distances, the forces acting between gas particles (intermolecular forces) tend to be negligible. It is for this reason that gases are free to expand to fill the volume of any container. Since intermolecular repulsive forces are significant only at very small distances, gases are also highly compressible.

### **4.1 Ideal Gases**

While various gases will differ in their behaviors due to small differences in intermolecular forces and molecular size, they still tend to behave much like one another; thus the concept of an ideal gas was created. An **ideal gas** is an imaginary gas which has no intermolecular forces and no molecular volume. Its properties closely approximate those of real gases under most conditions.

#### **Ideal Gas Law**

When we describe an ideal gas we are interested in four variables. These variables are listed below along with common conversion factors.

- $P$ , pressure. (1 atm = 760 mm Hg), (1 atm = 760 torr), (1 atm =  $1 \times 10^5$  Pa).
- $V$ , volume. (1 L = 1000 mL), (1 L = 1000 cm<sup>3</sup>), (1 m<sup>3</sup> = 1000 L).
- $n$ , moles. (# moles = # grams/MW).
- $T$ , temperature. ( $K = ^\circ\text{C} + 273$ ), where  $K$  is the temperature expressed in Kelvin.

The relationship of the above variables is given in the ideal gas equation below:

$$\boxed{PV = nRT}$$

where  $P$  is in atm,  $V$  is in L,  $T$  is in Kelvin.  $R$  is the gas constant which is equal to 0.082 L·atm/mol·K. (When SI units are used  $R = 8.3$  J/mol·K.)

Historically the ideal gas law was derived from a number of simpler relationships which we will explore shortly.

*example* ►

**Standard temperature and pressure, STP, is 0°C (273 K) and 1 atm.** Calculate the standard molar volume of an ideal gas at STP.

*solution:*

The **standard molar volume** is the volume occupied by one mole at 273-K and 1 atm

$$V = nRT/P, \quad V = (1)(0.082)(273)/(1) \quad V = \underline{22.4 \text{ L}} \blacklozenge$$

*question* ►

What is the density of O<sub>2</sub> gas at STP in units of g/L?

*solution:*

If we divide the MW by the standard molar volume we get:

$$\frac{32 \text{ g}}{\text{mol}} \times \frac{\text{mol}}{22.4 \text{ L}} = 1.4 \text{ g/L} \blacklozenge$$

*example* ►

What is the molecular weight of a gas that has a density of 1.25 g/L at STP?

*solution:*

To solve for the molecular weight we will need to find the number of g/mol. If we let the number of grams be 1.25, then we may use 1 L as the volume.

$$1 \text{ L} \times \frac{\text{mol}}{22.4 \text{ L}} = .0446 \text{ mol}$$

Dividing grams by moles gives, 1.25 g/.0446 mol = 28 g/mol ◆

When a gas undergoes a change from one set of conditions to another set of conditions the ideal gas law may be written in the form shown below:

$$\boxed{\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}}$$

where the subscripts 1 and 2 represent initial and final conditions, respectively. In this form of the gas constant R does not appear. When working with this equation you may use any units which are convenient for P and V, but T must be in Kelvin.

*question* ►

What will be the proportional change in the pressure of an ideal gas if its volume is doubled while at the same time the number of moles of gas is tripled, at a constant temperature of 25°C?

*solution:*

In dealing with gases undergoing a change in conditions any variable which does not change (the temperature in this case) may be ignored. Solving for the proportional change in pressure (P<sub>2</sub>/P<sub>1</sub>) gives:

$$\left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right)\left(\frac{n_2}{n_1}\right)$$

Since the volume doubles, the ratio  $V_1/V_2$  will be  $1/2$ , since the number of moles triples, the ratio of  $n_2/n_1$  will be  $3/1$ . Plugging these values in gives,

$$\left(\frac{P_2}{P_1}\right) = \left(\frac{1}{2}\right)\left(\frac{3}{1}\right) = 1.5 \blacklozenge$$

**question ►**

If 10 L of  $O_3(g)$  react completely to form  $O_2(g)$  at  $45^\circ C$  and 700 mm Hg, what volume of  $O_2(g)$  will be formed?

**solution:**

We should first write out a balanced equation:



Next it is important to recognize that since the temperature and pressure are constant, their actual values are not important to us. All we need to concern ourselves with is the relationship between the volume and the number of moles. From  $PV = nRT$  we see that  $V$  is directly proportional to the number of moles ( $V \propto n$ ), when  $T$  and  $P$  are constant. Since  $V \propto n$ , we may use the coefficients in the above equation to find the volume in the same manner as we have previously done when solving for moles.

$$10 L_{O_3} \times \frac{3 L_{O_2}}{2 L_{O_3}} = 15 L_{O_2} \blacklozenge$$

► The previous problem is an example of **Avogadro's Hypothesis** which states that for gases at the same temperature and pressure, the volume of gas is directly proportional to the number of moles of gas present.

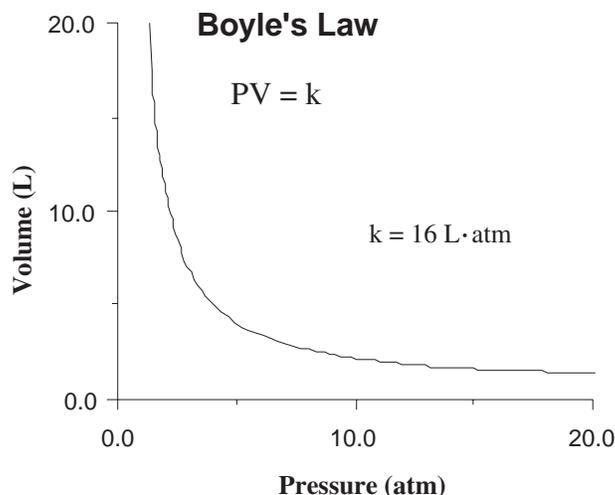
$$\boxed{\frac{V}{n} = k \text{ or } \frac{V_1}{n_1} = \frac{V_2}{n_2}}$$

In the formulas above (and those which follow)  $k$  is a constant, and the subscripts  $1$  and  $2$  represent initial and final conditions, respectively.

## Boyle's Law

Boyle's law states that a sample of gas at a constant temperature will have a volume which is *inversely* proportional to its pressure.

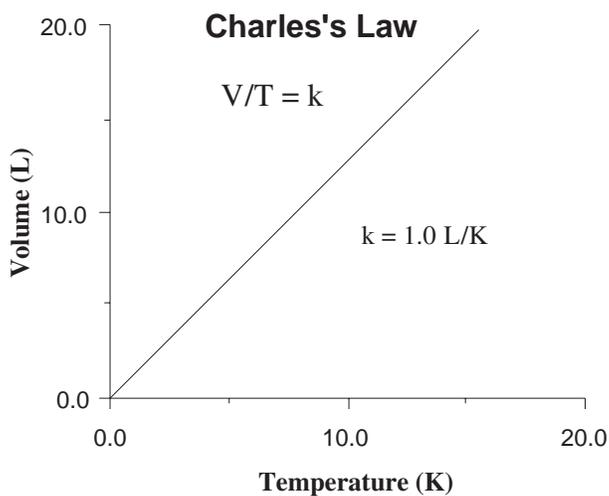
$$\boxed{PV = k \text{ or } P_1V_1 = P_2V_2}$$



### Charles's Law

Charles's law states that a sample of gas at a constant pressure will have a volume which is *directly* proportional to its temperature.

$$\frac{V}{T} = k \text{ or } \frac{V_1}{T_1} = \frac{V_2}{T_2}$$



#### question ►

In the Figure # how would the slope of the graph change if the number of moles of gas was doubled (assume no change in pressure).

#### solution:

According to Avogadro's hypothesis the volume is directly proportional to the number of moles. When the number of moles doubles the volume at each temperature also doubles. If you examine the graph carefully you should conclude that the slope must also double, from 1.0 L/K to 2.0 L/K. ♦

►Note that as a gas approaches absolute zero its volume approaches zero, and its change in volume is directly proportional to the number of moles present.

## Dalton's Law

**Dalton's law** states that when two or more gases occupy the same container each gas will contribute to the total pressure in the same manner as if it were alone. The portion of the total pressure exerted by a gas in a mixture is called its **partial pressure**. When the partial pressures of all gases are added the result will equal the total pressure,

$$P_T = P_A + P_B + P_C \dots$$

where  $P_T$  is the total pressure, and the partial pressures of various gases are listed to the right of the equal sign.

From the ideal gas law we observe that the pressure of a gas is directly proportional to the number of moles of that gas ( $P \propto n$ ). It therefore follows that the partial pressure of a gas in a mixture will be directly proportional to the fraction of moles of that gas present. The **mole fraction**,  $\chi$ , is defined as the number of moles of a gas divided by the total number of moles. When the total pressure is multiplied by a gas' mole fraction, the partial pressure of that gas is obtained:

$$\chi_A = \frac{n_A}{n_T} \quad P_A = P_T \chi_A$$

We may now rewrite the ideal gas law to give:

$$P_T = \frac{(n_A + n_B + n_C \dots)RT}{V}$$

In this equation the number of moles of all gases in a mixture are added together in order to obtain the total pressure of the mixture.

### question ►

32 g of  $\text{CH}_4$  and 32 g of  $\text{O}_2$  are both placed in a 1 L container at  $25^\circ\text{C}$ . What is the total pressure, and the partial pressures of each gas in the mixture?

### solution:

First we need to convert grams into moles,

$$32 \text{ g CH}_4 \times \frac{\text{mol CH}_4}{16 \text{ g}} = 2 \text{ mol CH}_4$$

$$32 \text{ g O}_2 \times \frac{\text{mol O}_2}{32 \text{ g}} = 1 \text{ mol O}_2$$

and temperature in to Kelvin,

$$25^\circ\text{C} + 273 = 298 \text{ K.}$$

Plugging into our new equation for ideal gas mixtures gives:

$$P_T = \frac{(2 \text{ mol} + 1 \text{ mol})(0.082 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(298 \text{ K})}{(1 \text{ L})} = 73 \text{ atm}$$

To obtain the partial pressures we simply multiply the total pressure by the mole fraction of each gas:

$$P_{\text{CH}_4} = 73 \text{ atm} \times \frac{2 \text{ mol CH}_4}{3 \text{ mol total}} = 49 \text{ atm}$$

$$P_{\text{O}_2} = 73 \text{ atm} \times \frac{1 \text{ mol O}_2}{3 \text{ mol total}} = 24 \text{ atm} \blacklozenge$$

## Kinetic Molecular Theory

The kinetic molecular theory of gases is a theoretical model of gas behavior which utilizes a number of simplifying assumptions so that real gases may be treated as ideal gases:

1. Gases are composed of particles in constant random motion.
2. Because the size of the gas particles is so small, and the distance separating them so great, the volume occupied by the gas particles will be negligible when compared to the volume of their container.
3. No appreciable intermolecular forces occur except during collisions.
4. All collisions are perfectly elastic. Kinetic energy is conserved when gas particles collide among themselves, or with the walls of the container.
5. The average kinetic energy of gas particles is directly proportional to their absolute temperature. All gases at the same temperature have the same average kinetic energy.

The relationship between the average kinetic energy per mole and the absolute temperature can be expressed as:

$$\text{KE} = \frac{3}{2}nRT \quad (\text{KE} \propto T)$$

If we set this expression equal to  $\frac{1}{2}mv^2$ , and solve for  $v$  we get:

$$v = \sqrt{\frac{3nRT}{m}}$$

Finally we may replace the terms for moles and mass with the term for molecular weight to give:

$$v_{\text{rms}} = \sqrt{\frac{3RT}{\text{MW}}}$$

where  $v_{\text{rms}}$  is called the **root mean squared speed**. (This term is not the same as the average speed, but for the MCAT the nature of the difference is not important.) *Since  $v_{\text{rms}}$  is normally expressed in m/s, the values for  $R$  and  $\text{MW}$  must also be expressed in terms of SI units.  $R = 8.3 \text{ J/mol}\cdot\text{K}$  and  $\text{MW}$  is expressed in  $\text{kg/mol}$ .*

## Graham's Law

**Diffusion** occurs when gas particles randomly migrate through space. When a bottle of perfume is opened the scent of the fragrance is gradually dispersed through out the room through the process of diffusion.

**Effusion** occurs when gas particles under pressure escape through a small orifice. An inflated balloon gradually loses pressure as the molecules of air effuse through the pores of the balloon.

The rate at which diffusion and effusion occurs is directly proportional to  $v_{\text{rms}}$ :

$$\text{rate} \propto v_{\text{rms}} \quad v_{\text{rms}} \propto \sqrt{\frac{T}{\text{MW}}} \quad \text{rate} \propto \sqrt{\frac{T}{\text{MW}}}$$

For two gases at the same temperature and pressure, the gas with the larger MW will have a smaller  $v_{\text{rms}}$  and a lower rate of diffusion and effusion. The relationship between the rate of one gas as compared to another is expressed in the equation below:

**Graham's Law**

$$\frac{\text{rate}_1}{\text{rate}_2} = \sqrt{\frac{\text{MW}_2}{\text{MW}_1}}$$

For two samples of the same gas at the same pressure but at different temperatures the following relationship holds:

$$\frac{\text{rate}_1}{\text{rate}_2} = \sqrt{\frac{T_1}{T_2}}$$

**question** ►

How will the rate of effusion of  $\text{CH}_4$  gas at 400 K compare to the rate of effusion of  $\text{O}_2$  gas at 200 K? Assume all other conditions to be identical.

**solution:**

Consolidating the formulas above using  $\text{CH}_4$  and  $\text{O}_2$  gives:

$$\frac{\text{rate}_{\text{CH}_4}}{\text{rate}_{\text{O}_2}} = \sqrt{\frac{T_{\text{CH}_4} / \text{MW}_{\text{CH}_4}}{T_{\text{O}_2} / \text{MW}_{\text{O}_2}}}$$

Substituting in for T and MW yields:

$$\frac{\text{rate}_{\text{CH}_4}}{\text{rate}_{\text{O}_2}} = \sqrt{\frac{400/16}{200/32}} = \frac{2}{1} \blacklozenge$$

► Since the above equation does not contain the gas constant R, the MW may be expressed in g/mol or in kg/mol.

## 4.2 Real Gases

One of the assumptions of the kinetic molecular theory of gases is that the gas particles are separated by large distances. Under conditions of high pressure and low temperature this assumption will no longer be true and deviations from ideal behavior will occur.

### **Deviations Due to Low Temperature**

Under conditions of low temperature gas particles are close enough together so that intermolecular attractive forces become significant. This causes the pressure of the gas to be *less* than that predicted by the ideal gas law.

## Deviations Due to High Pressure

At high pressure gas particles are close enough together to experience intermolecular attractive forces. This causes the volume of the gas to be *less* than that predicted by the ideal gas law.

Under high pressures the volume occupied by a real gas will be *greater* than that predicted for an ideal gas. At high pressures the volume occupied by the gas particles becomes a significant percentage of the total volume. Thus the total volume must be greater than predicted so as to compensate for the **excluded volume**.

## Van der Waals' Equation

The van der Waals' equation is a way of quantifying deviations from ideal gas behavior.

$$\left( P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

The term  $an^2/V^2$  is a correction to the ideal pressure. The term  $nb$  is a correction to the ideal volume. The variables  $a$  and  $b$  are specific to a particular gas and are determined experimentally. The variable  $a$  is related to intermolecular forces, and the variable  $b$  is related to the molecular volume.

## *5 Liquids, Solids, and Intermolecular Forces*

# *Liquids, Solids, and Intermolecular Forces*

The phase of a substance (gas, liquid, or solid) is determined by a balance between the ambient (outside) pressure, the energy of its intermolecular forces (IMFs), and its average kinetic energy. Increasing the pressure on a substance forces its molecules closer together. IMFs, under normal pressures, are attractive forces which bind molecules together. The ambient pressure and IMFs both tend to decrease intermolecular separation. Opposing these two forces is the average kinetic energy, which is directly proportional to the absolute temperature. As the temperature raises, molecules move more quickly and intermolecular distances tend to increase.

At a temperature greater than 100°C and 1.0 atm H<sub>2</sub>O is a gas. Because its temperature is high, the average kinetic energy of the water molecules is large enough to overcome the energy of its IMFs. Since the IMFs are unable to bind the molecules of H<sub>2</sub>O together, the distances between molecules is great, as a result H<sub>2</sub>O(g) has a low density and is readily compressible. Since there is no significant resistance to molecular motion, bulk movement of the gas (flow), and diffusion (movement of individual particles within the gas), both occur readily.

If we lower the temperature to below 100°C, the average kinetic energy of the H<sub>2</sub>O will decrease, and its IMFs will bind the molecules into a liquid state. Because the separation between molecules is reduced, liquids are virtually incompressible, and have much greater densities than gases. Although most liquids tend to flow freely, diffusion within a liquid is slow.

Below 0°C water becomes a solid as IMFs lock H<sub>2</sub>O molecules into a rigid crystalline (highly ordered) structure. As a result, H<sub>2</sub>O(s) typical of most solids, does not flow, is virtually incompressible, and has an extremely slow rate of diffusion. *Atypical* of most substances, water has a solid phase which is *less* dense than its liquid. (See *hydrogen bonding* in this chapter.)

■ Substance with weak IMFs are gases at ordinary temperatures and pressures. Substance with moderate IMFs are liquids, and those with the strongest IMFs are solids.

### 5.1 . Phase Equilibria

#### **Gas-Liquid Equilibrium**

Water at 100°C in a sealed container will exist as both a gas and a liquid. The quantity of gas and liquid will remain constant, because at 100°C the rate at which gas is formed from the liquid will be equal to the rate at which liquid is produced from the gas. A system in which competing rates are in balance is said to be in **equilibrium**. Conversion from the gas to the liquid state is called **condensation**. The process whereby a liquid forms a gas is known as **vaporization** or **evaporation**.

The pressure of a gas in equilibrium with its liquid is called the **vapor pressure** of the liquid. From the information above, we note that the vapor pressure of water at 100°C is 1.0 atm. The temperature at which a liquid has a vapor pressure equal to *1.0 atm* is called its **normal boiling point**. More generally, the **boiling point** of a liquid is that temperature at which that liquid's vapor pressure is equal to the ambient pressure.

The vapor pressure of a liquid is a measure of the tendency of that liquid to convert into a gas. Below a substance's boiling point, liquid is converted into gas through the process of evaporation. **Evaporation** occurs when individual molecules escape from the surface of a liquid. As temperature increases, vapor pressure, and evaporation, increase exponentially. At the boiling point, in an open container, the vapor pressure is large enough to overcome the confining influence of the ambient pressure. At this point boiling begins (and evaporation continues). **Boiling** occurs when large groups of molecules burst into the gas phase through out the liquid.

## Liquid-Solid Equilibrium

Water at 0°C and 1.0 atm exists as an equilibrium between liquid and solid phases. Under these conditions the rate at which liquid is converted into solid (**freezing** or **crystallization**) is equal to the rate at which solid transforms into liquid (**melting** or **fusion**). The temperature at which this equilibrium takes place is called the **melting point** or **freezing point**. The **normal freezing point** of water is 0°C (normal refers to a pressure of 1.0 atm).

During crystallization, liquid molecules having lower than average translational kinetic energies are captured by the IMFs of solid water molecules. During melting, solid water molecules with larger than average vibrational kinetic energies break free into the liquid state.

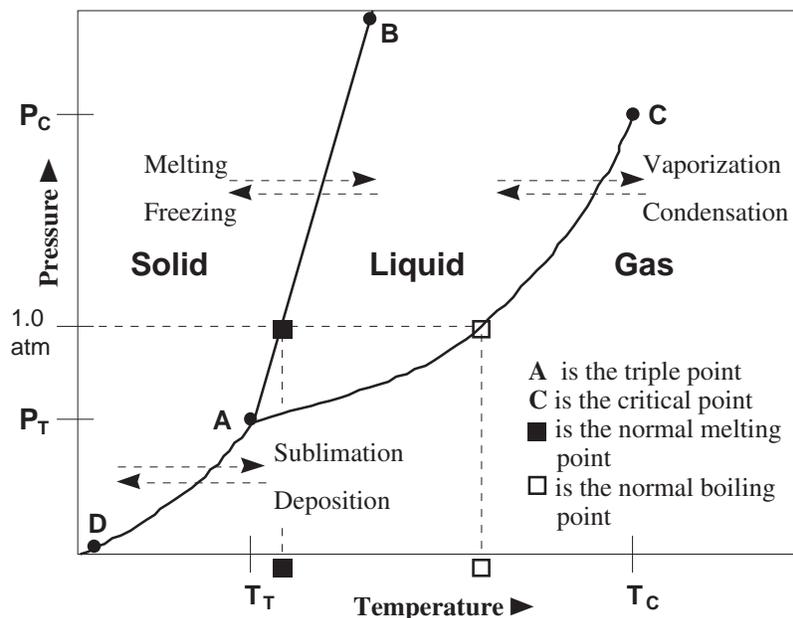
## Gas-Solid Equilibrium

Because water has comparatively large IMFs it has a liquid phase at 1.0 atm over a temperature range of from 0°C to 100°C. Carbon dioxide, however, has far weaker IMFs than water. Compounds like CO<sub>2</sub>, with weak IMFs require higher pressures to help bind molecules together into a liquid.

When solid CO<sub>2</sub> (dry ice) reaches a temperature of -78.5°C at 1.0 atm, the solid molecules break free of their IMFs and are converted directly into a gas. The process of the direct conversion of a solid into a liquid is call **sublimation**. The reverse process, of a gas converting directly into a solid is known as **deposition**.

## Phase Diagrams

The phase of a pure substance is determined by its temperature and pressure. A **phase diagram** graphically depicts this relationship. A typical diagram is shown below.

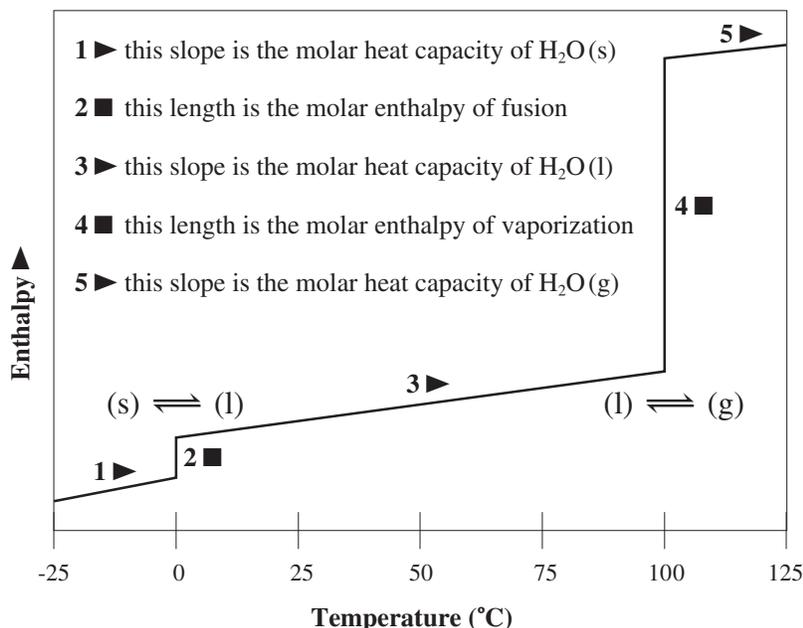


Point A is the **triple point**. At the temperature and pressure ( $T_T$  and  $P_T$ ) corresponding to the triple point all three phases of matter coexist in equilibrium. As a function of increasing pressure, the line from A to B, represents the change in melting point, the line A to C, depicts the change in the boiling point, and the line D to A, reflects the change in the sublimation point (temperature required for sublimation). Recall that the normal melting and boiling points correspond to a pressure of one atmosphere.

The liquid-gas equilibrium curve ends abruptly at point C. Beyond this point, called the **critical point**, there is no distinguishable difference between liquid and gas. The temperature and pressure corresponding to the critical point are called the **critical temperature and pressure** ( $T_C$  and  $P_C$ ). At  $T_C$  the critical pressure is required to compress a gas into a liquid. Above  $T_C$ , only the gas phase exists.

## Enthalpy Changes TIE IN W/ PHYSICS (UC)

When ice at  $-25^\circ\text{C}$  is slowly heated at 1.0 atm, the added energy results in increased molecular vibration, causing the temperature to gradually raise. At  $0^\circ\text{C}$  the temperature remains constant until all IMFs binding the ice have been broken. When only liquid remains, the added heat will once again cause an increase in temperature. At  $100^\circ\text{C}$  the temperature once again remains constant during the phase change from liquid to gas. Once no more liquid remains, the temperature of the gas begins to rise. This process is depicted in the diagram below. (See chapter *physics* for additional details)



**Figure #** Changes in the temperature of H<sub>2</sub>O as heat is added at 1.0 atm.

The flow of heat under constant pressure is called **enthalpy**,  $H$ . The above figure represents phase and temperature changes as heat is added to H<sub>2</sub>O at 1.0 atm. The diagram depicts five distinct regions of change. The portions of the graph labeled with odd numbers (diagonal lines) represent areas of temperature change. The even number regions (vertical lines) depict phase changes. The quantities of heat associated with each of these transitions has been measured and is given below (the word *molar* refers to one mole of water):

1 ► molar heat capacity of H <sub>2</sub> O(s) = $C_p$	$C_p = 37.6 \text{ J/mol}\cdot^\circ\text{C}$
2 ■ molar enthalpy of fusion = $\Delta H_{\text{fus}}$ .	$\Delta H_{\text{fus}} = 6.01 \text{ kJ/mol}$
3 ► molar heat capacity of H <sub>2</sub> O(l) = $C_p$ .	$C_p = 75.2 \text{ J/mol}\cdot^\circ\text{C}$
4 ■ molar enthalpy of vaporization = $\Delta H_{\text{vap}}$	$\Delta H_{\text{vap}} = 40.67 \text{ kJ/mol}$
5 ► molar heat capacity of H <sub>2</sub> O(g) = $C_p$ .	$C_p = 33.1 \text{ J/mol}\cdot^\circ\text{C}$

*question* ►

Do p 344 Be & Le like problem here.

*solution:*

## 5.2 . Intermolecular Forces

### Van der Waals forces

Collectively all intermolecular attractive forces not involving ions are known as **Van der Waals forces**. All Van der Waals forces involve associations between positive and negative regions of adjacent molecules. Each of these interactions acts to make molecules “sticky”. *Molecules with large IMFs thus have high boiling points, high critical points, and low vapor pressures, since more energy is necessary for them to break free into the gas phase.*

## Dispersion Forces (a.k.a. induced dipole-induced dipole)

The electron cloud which defines a molecule's surface is in constant flux as electrons orbit the nucleus. This creates short-lived dipoles (*instantaneous dipoles*) which interact with neighboring electron clouds causing them to polarize. These brief attractive interactions are known as **London dispersion forces**. While London forces are present in all molecules, they are the weakest of IMF in molecules of small molecular weight. As the molecular weight increases, dispersive forces increase, due to the presents of a larger, more easily polarized, electron cloud.

## Dipole-dipole Force

Polar molecules tend to align so that that their positive and negative poles are near each other. The resultant force of attraction is called **dipole-dipole force**. For small molecules dipole-dipole forces are stronger than dispersive forces.

## Hydrogen Bonding

For small molecules H-bonding is the strongest Van der Waals force. This interaction is not a true bond, but an example of a special form of dipole-dipole attraction. H-bonding arises when a partially negative lone pair is attracted to a partially positive hydrogen in a neighboring molecule. In order a H-bond to occur, *both* the lone pair and the hydrogen must be bound to strongly electronegative elements. These elements are: *nitrogen, oxygen, and flourine*.

Molecules with H-bonding have significantly higher boiling points than molecules of similar molecular weight that cannot H-bond. As a result HF has a higher BP than CH<sub>4</sub>. Because water has two lone pairs and two hydrogen, water is able to form two H-bonds per molecule, while HF can form only one. As a result H<sub>2</sub>O has a higher BP than HF.

The lower density of water in its solid phase is due to extensive H-bonding which creates a rigid structure of H<sub>2</sub>O molecules containing numerous empty spaces. When the temperature is increased, some H-bonds begin to break and the structure collapses into a more dense liquid state.

## IMFs Involving Ions

When an ion interacts with a nonpolar molecule it induces a short-lived dipole in this molecule. The resulting attraction is called **ion-induced dipole force**. When an ion interacts with a polar molecule a stronger attraction results. This is known as **dipole-dipole force**.

So far all IMFs discussed have been relatively weak when compared to a covalent bond. The attractive force between ions, however, is often as just as strong.. It is for this reason that **ion-ion force** (a.k.a. Coulombic force or electrostatic force) is more commonly referred to as an **ionic bond** (See Chapter#).

## Repulsive Forces

When molecules or ions approach each other, the initial forces of attraction are rapidly overcome by repulsive forces. These forces increase exponential with decreasing distance due to repulsion between electron pairs. As a result, molecule and ions behave as if they are solid objects with well defined surfaces.

# 6 Solutions

## Solutions

■ **Solutions** are homogeneous mixtures of two or more substances existing in the same phase. When a mixture is formed the component of the mixture which does not change phase is called the **solvent**. For example when salt is dissolved in water, the salt (a solid) enters the aqueous phase while the water remains a liquid. The water, therefore, is the solvent. All other components of a solution are called the **solute**. When all substances in a mixture remain in the same phase, it is customary to call the component of the mixture which is present in the largest amount the solvent, and all minor components the solute. Solutions in which water is the solvent are called **aqueous solutions**.

### 6.1 Properties of Solutions

#### Solvation

As a solute is added to a solvent the solute particles separate from one another as they are surrounded by solvent molecules. This process is called **solvation**. When solvation takes place intermolecular forces between the solute and the solvent help to stabilize the solution. It is for this reason that the general principle “like dissolves like” is useful. What this principle suggests is that polar solutes dissolve in polar solvents, while nonpolar solutes dissolve in nonpolar solvents. So if we add benzene (a nonpolar liquid) to water (a polar liquid) the result will be a heterogeneous mixture, because the benzene and water will not mix.

#### Types of Solutions

The examples which follow list various types of solutions and the relevant intermolecular forces between solute and solvent.

- Air is a mixture of  $\text{N}_2(\text{g})$  and  $\text{O}_2(\text{g})$ . There are no significant intermolecular forces for solutions of gases at ordinary temperature and pressure.
- Carbonated water is a mixture of  $\text{CO}_2(\text{g})$  and water. H-bonding is responsible for solvating the nonpolar  $\text{CO}_2$  in the polar  $\text{H}_2\text{O}$ . *Note: when H-bonding occurs “like can dissolve unlike”*
- Seawater is a mixture of  $\text{NaCl}$  and other ionic compounds dissolved in water. Ion-dipole forces predominate.
- Gasoline is a mixture of nonpolar hydrocarbons which are held in the liquid state by Van der Waals dispersive forces.

#### Solubility

**Solubility** is a measure of the quantity of solute that can be dissolved in a given mass of solvent:

$$\text{Solubility} = \frac{\text{quantity of solute}}{\text{mass of solvent}}$$

or as the quantity of solute that can be dissolved to form a given volume of solution:

$$\text{Solubility} = \frac{\text{quantity of solute}}{\text{volume of solution}}$$

The quantity of solute may be expressed in moles or in units of mass (usually grams or milligrams). The mass of solvent is typically expressed in grams, and the volume of solution in liters or milliliters.

- In the case of gas-gas mixtures all gases are infinitely soluble in each other.
- For gases dissolved in liquid the solubility is defined by Henry's law:

$$C = k \cdot P$$

Where  $C$  is the concentration of the dissolved gas in units determined by the proportionality constant  $k$ . The value of  $k$  depends upon the identity of the dissolved gas and the liquid solvent.  $P$  represents the pressure (or partial pressure) of the gas above the liquid.

Note: the the solubility of any gas above a liquid is directly proportional to the pressure of that gas. So if you open a bottle of soda, the pressure of the  $\text{CO}_2(\text{g})$  above the soda will decrease and the quantity of dissolved  $\text{CO}_2$  will gradually drop until the soda goes flat.

The solubility of gases in liquids decrease with temperature. That's why when you open a warm soda, you get a lot more fizz.

- When two liquids can be mixed in any proportions they are said to be **miscible**. An example is ethyl alcohol and water. Benzene and water do not mix, they are said to be **immiscible**.
- When a solid like  $\text{NaCl}$  is dissolved in water at  $0^\circ\text{C}$ , it is found that up to 357 g of table salt will dissolve to form a liter of salt water. Solid solutes like  $\text{NaCl}$  may be classified as **soluble** if 10 or more grams dissolve per liter of solution. **Insoluble solutes** typically have solubilities of less than 0.10 g/L. **Slightly soluble** compounds have solubilities which lie between 10 g/L and 0.10 g/L. *Note: these values are general guidelines, you may be given solubility data on the MCAT which differs in some way from the information presented above.*

## Solubilities of Ionic Compounds in Water

Some general solubility rules for salts in aqueous solution are given below:

1. Salts of group one metals ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ) and of ammonium ( $\text{NH}_4^+$ ) are soluble.
2. All nitrates ( $\text{NO}_3^-$ ) are soluble.
3. All chlorides, bromides, and iodides are soluble, except those of  $\text{Ag}^+$ ,  $\text{Pb}^+$ , and  $\text{Hg}^{2+}$ .
4. All sulfates ( $\text{SO}_4^{2-}$ ) are soluble, except those of  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}^+$ .
5. Hydroxides are insoluble except for  $\text{Ba}(\text{OH})_2$ , group one hydroxides, and  $\text{NH}_4\text{OH}$ .  $\text{Ca}(\text{OH})_2$  and  $\text{Sr}(\text{OH})_2$  are slightly soluble.
6. Carbonates ( $\text{CO}_3^{2-}$ ), phosphates ( $\text{PO}_4^{3-}$ ), sulfites ( $\text{SO}_3^{2-}$ ), and sulfides ( $\text{S}^{2-}$ ) are insoluble unless they contain group one metals or ammonium.

## 6.2 . Units of Concentration

### Mass Percent

The **mass percent**, %, of a solute is defined as the mass of solute, divided by the mass of the solution (solute plus solvent), with this quantity multiplied by 100 to give percent.

$$\%_{\text{solute}} = \frac{\text{mass}_{\text{solute}}}{\text{mass}_{\text{soln}}} \times 100$$

■ Units of concentration in parts per thousand, or parts per million (ppt or ppm) can be found by replacing the number 100 in the equation above with  $10^3$  or  $10^6$  respectively.

### Mole Fraction

The **mole fraction**,  $\chi$ , is the number of moles of one substance in a solution, divided by the total number of moles in the solution.

$$\chi_A = \frac{\text{mol}_A}{\text{mol}_{\text{soln}}}$$

The subscript  $A$  is a generic notation for any component of the solution.

■ Mole fraction is used when finding the partial pressures of gases by use of Dalton's law. (see chapter #), and will be used in this chapter to calculate vapor pressure lowering through the use of Raoult's law.

### Molality

The **molality**,  $m$ , is found by dividing the moles of solute by the kilograms of solvent.

$$m = \frac{\text{moles}_{\text{solute}}}{\text{kg}_{\text{solvent}}}$$

■ In this chapter we will see how the molality may be used determine the elevation of a solution's boiling point, and the depression of its freezing point..

### Molarity

**Molarity**,  $M$ , is defined as the moles of solute divided by the liters of solvent.

$$M = \frac{\text{moles}_{\text{solute}}}{L_{\text{soln}}}$$

■ Because the volume of a solution will change with temperature, the molarity will also vary with temperature. Although molarity is a very convenient unit of measurement it is not as precise as the previously mentioned concentration units.

#### example ►

A solution of  $\text{H}_2\text{SO}_4$  is prepared by adding 98 g of  $\text{H}_2\text{SO}_4$  to 2.0 grams of water. The resulting solution is found to have a density of 1.8 g/mL. The

MW of  $\text{H}_2\text{SO}_4$  is 98 g/mol. Calculate the mass percent, mole fraction, molality, and molarity of this solution.  $\text{H}_2\text{O}$  is the solvent.

*solution:*

►When solving for the mass percent, don't forget to add the masses of *all* components in the solution to get the total mass of the solution:

$$98 \text{ g H}_2\text{SO}_4 + 2.0 \text{ g H}_2\text{O} = 100 \text{ g of soln}$$

Now we dividing the grams of solute by the total grams and multiplying by 100 to get the mass percent of  $\text{H}_2\text{SO}_4$ :

$$\% \text{H}_2\text{SO}_4 = \frac{98 \text{ g H}_2\text{SO}_4}{100 \text{ g}_{\text{total}}} \times 100 = 98\% \blacklozenge$$

►In order to solve for the mole fraction we will need to know the moles of  $\text{H}_2\text{SO}_4$  and of  $\text{H}_2\text{O}$ :

$$98 \text{ g H}_2\text{SO}_4 \times \frac{\text{mol H}_2\text{SO}_4}{98 \text{ g}} = 1.0 \text{ mol H}_2\text{SO}_4$$

$$2.0 \text{ g H}_2\text{O} \times \frac{\text{mol H}_2\text{O}}{18 \text{ g}} = 0.11 \text{ mol H}_2\text{O}$$

Substituting these values into the formula for mole fraction gives:

$$\chi_{\text{H}_2\text{SO}_4} = \frac{1.0 \text{ mol H}_2\text{SO}_4}{1.0 \text{ mol H}_2\text{SO}_4 + 0.11 \text{ mol H}_2\text{O}} = 0.90 \blacklozenge$$

►To solve for the molality the mass of the solvent ( $\text{H}_2\text{O}$ ) must be converted into kg:

$$2.0 \text{ g H}_2\text{O} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 2.0 \times 10^{-3} \text{ kg}$$

Plugging into the equation for molality yields:

$$\frac{1 \text{ mol H}_2\text{SO}_4}{2.0 \times 10^{-3} \text{ kg H}_2\text{O}} = 500 \text{ m H}_2\text{SO}_4 \blacklozenge$$

►To obtain the molarity we will need to convert the total grams of solution into liters of solution. We'll use the density of the solution to make this conversion:

$$100 \text{ g soln} \times \frac{1 \text{ mL soln}}{1.8 \text{ g soln}} \times \frac{1 \text{ L soln}}{1000 \text{ mL soln}} = 0.056 \text{ L soln}$$

Now let's divide the moles of  $\text{H}_2\text{SO}_4$  by the liters of solution, to obtain the molarity:

$$\frac{1 \text{ mol H}_2\text{SO}_4}{0.056 \text{ L soln}} = 18 \text{ M H}_2\text{SO}_4 \blacklozenge$$

## Dilution

When water is added to an aqueous solution the molarity of that solution will decrease. This process is called **dilution**. On the MCAT it is assumed that volumes are additive, i.e., the volume of water added,  $V_A$ , plus the initial volume of the solution,  $V_1$ , will be equal to the final volume,  $V_2$ .

$$V_A + V_1 = V_2$$

When solving for the molarity resulting from a dilution the following formula may be used:

$$M_1V_1 = M_2V_2$$

where the subscript  $1$  indicates the initial conditions, and the subscript  $2$  indicates the final conditions.

### question ►

100 mL of  $H_2O$  are added to 300 mL of a 0.40 M solution of NaOH. What is the molarity of the NaOH after dilution?

### solution:

The final volume ( $V_2$ ) equals 400 mL. If we algebraically solve for  $M_2$ , and then substitute in for  $M_1$ ,  $V_1$ , and  $V_2$ , we get::

$$M_2 = \frac{M_1V_1}{V_2} = \frac{(0.40 \text{ M})(100 \text{ mL})}{(400 \text{ mL})} = 0.10 \text{ M NaOH} \blacklozenge$$

## 6.3 Electrolytes

Pure water is a poor conductor of electricity because it contains a low concentration of ions. **Electrolytes** are solutes which when dissolved in water dissociate into ions and thus produce a solution which conducts current. **Nonelectrolytes** do not form ions and therefore do not change the conductivity.

### Strong Electrolytes

Strong electrolytes dissociate completely, or nearly completely, into ions. All water soluble ionic compounds are strong electrolytes, as are all strong acids and bases (See Chapter #)

EXAMPLES OF STRONG ELECTROLYTES		
Soluble Salts*	Strong Acids	Strong Bases
NaCl	HCl	NaOH
KBr	HBr	KOH
MgCl <sub>2</sub>	HI	RbOH
KClO <sub>4</sub>	H <sub>2</sub> SO <sub>4</sub>	CsOH
Al <sub>2</sub> SO <sub>4</sub>	HNO <sub>3</sub>	Ca(OH) <sub>2</sub>
CuSO <sub>4</sub>	HClO <sub>4</sub>	Sr(OH) <sub>2</sub>
LiNO <sub>3</sub>		Ba(OH) <sub>2</sub>

\*See “Solubilities of Ionic Compounds in Water”, previously covered in this chapter.

## Weak Electrolytes and Nonelectrolytes

**Weak electrolytes** ionize only partially in aqueous solutions, while **nonelectrolytes** do not dissociate into ions at all.. All weak acids and bases, are weak electrolytes. Nonelectrolytes are typically organic compounds which are not salts, acids, or bases.\*

\*Organic salts typically contain Na, or K. Organic acids contain the carboxylic group (–COOH), and the organic bases are typically amines, which bear the –NH<sub>2</sub> group.

Examples of Weak Electrolytes		Examples of Nonelectrolytes	
HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	acetic acid	H <sub>2</sub> O	pure water
HNO <sub>2</sub>	nitrous acid	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	glucose
H <sub>2</sub> SO <sub>3</sub>	sulfurous acid	C <sub>2</sub> H <sub>5</sub> OH	ethanol
NH <sub>3</sub>	ammonia	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	ethylene glycol
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	aniline	C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	glycerol

## 6.4 Colligative Properties

Colligative properties depend on the concentration of solute particles, but *not* on identity of the solute. The colligative properties tested for on the MCAT are: boiling point elevation, freezing point depression, osmotic pressure, and vapor pressure lowering (Raoult’s law).

When evaluating colligative properties it is important to consider all solute particles present in a solution. The number of particles produced per mole of solute is represented by the van’t Hoff factor, *i*.

- For nonelectrolytes like glucose, which do not dissociate into ions, the value for *i* will be equal to one.
- For strong electrolytes like Ca(NO<sub>3</sub>)<sub>2</sub>, the value for *i* will be equal to the moles of ions formed, per mole of solute. For example, in the equation below three ions are formed per mole of Ca(NO<sub>3</sub>)<sub>2</sub>:



therefore  $i$  equals three. For NaCl and  $\text{Al}_2(\text{SO}_4)_3$ , respectively,  $i$  equals two and five.

- For weak electrolytes, like the weak acid, acetic acid ( $\text{HC}_2\text{H}_3\text{O}_2$ ), the value for  $i$  will be slightly greater than one.

The table below summarizes the above information.

Type of Solute	Behavior	Value of $i$
Nonelectrolyte	Does not dissociate in to ions	Equal to one
Strong Electrolyte	Complete dissociation into ions	Equal to the # of ions formed
Weak Electrolyte	Partially dissociates into ions	Slightly greater than one

## Boiling Point Elevation

When the vapor pressure of a liquid equals the pressure surrounding it, the liquid begins to boil. At 1.0 atm water boils at 100°C. If water is heated under greater pressure, as in a pressure cooker, the boiling point of water will be greater than 100°C.

Another way to raise the boiling point of a liquid is by add a nonvolatile solute (one that has no vapor pressure) The solute will decrease the vapor pressure of the solution, as compared to the pure liquid at the same temperature. A higher temperature will be required to achieve the same vapor pressure in the solution as in the pure liquid. The boiling point of the solution will thus elevated. The increase in the of the boiling point of the solution as compared to the pure liquid is given by  $\Delta T_b$  below:

$$\Delta T_b = i \cdot K_b m$$

where  $i$  is the van't Hoff factor,  $K_b$  is a constant which depends on the solvent, and  $m$  is the molality of the solution.

## Freezing Point Depression

When a solute is dissolved in a liquid the solute particles interfere with the attractive intermolecular forces involved in crystallization. As a result freezing occurs at a lower temperature. The depression in the freezing point as compared to that of the pure liquid is given by  $\Delta T_f$  below:

$$\Delta T_f = i \cdot K_f m$$

where  $i$  is the van't Hoff factor,  $K_f$  is a constant which depends on the solvent, and  $m$  is the molality of the solution.

### question ►

What will be the boiling and freezing point of a solution made by adding 100 g of  $\text{CaCO}_3$  (MW = 100 g/mol) to 1000 g of  $\text{H}_2\text{O}$ ?  $\Delta T_b$  and  $\Delta T_f$  for water are 1.86°C/m and 0.52°C/m, respectively.

### solution:

Since  $\text{CaCO}_3$  is a strong electrolyte,



$i$  is equal to two. The molality of the  $\text{CaCO}_3$  solution is found by dividing the number of moles of the solute by the number of kilograms of the solvent:

$$m \text{ CaCO}_3 = \frac{1.00 \text{ mol CaCO}_3}{1.00 \text{ kg H}_2\text{O}} = 1.00 \text{ m}$$

The changes in the BP and FP are:

$$\Delta T_b = (2)(0.52^\circ\text{C/m})(1.00 \text{ m}) = 1.04^\circ\text{C}$$

$$\Delta T_f = (2)(1.86^\circ\text{C/m})(1.00 \text{ m}) = 3.72^\circ\text{C}$$

*Note that although  $\Delta T_f$  is given as a positive number it should be understood to represent a negative change.*

The BP and FP are:

$$\text{BP} = 100.00^\circ\text{C} + 1.04^\circ\text{C} \quad \text{BP} = 101.04^\circ\text{C} \blacklozenge$$

$$\text{FP} = 0.00^\circ\text{C} - 3.72^\circ\text{C} \quad \text{FP} = -3.72^\circ\text{C} \blacklozenge$$

## Osmotic Pressure

Imagine a container which is divided into two halves by a semipermeable membrane. The membrane allows a solvent to freely diffuse, but does not permit a solute to pass through. When the solvent is placed in this container the height of the solvent in each half of the container will be the same. But if we add solute to the left side, we find that the water on the right side rushes through the membrane. This process where a solvent passes through a semipermeable membrane moving from higher *solvent* concentration (pure solvent in this case) into a lower *solvent* concentration is called **osmosis**.

■ The net movement of solvent is always toward the side with a higher concentration of solute.

As solvent rushes into the left side of the container the fluid level of the left side rises as that of the right side falls. Eventually the system reaches equilibrium when the pressure difference between the two sides of the container becomes so great that no farther osmosis can take place. If we now apply enough pressure to the left side, we can force the solvent back through the membrane (this is called reverse osmosis) until the levels on each side of the container are once again equal. This pressure which is required either to reverse osmosis, or to prevent it, is the **osmotic pressure**,  $\pi$ .

The osmotic pressure is typically expressed in atmospheres. It may be determined by the use of the equation below:

$$\pi = i \cdot MRT$$

where  $i$  is the van't Hoff factor,  $M$  is the molarity,  $R$  is the gas constant ( $0.082 \text{ L}\cdot\text{atm/mol}\cdot\text{K}$ ), and  $T$  is the temperature in Kelvin.

## Vapor Pressure Lowering (Raoult's Law)

When a nonvolatile solute (one with no vapor pressure) is added to a solvent, the vapor pressure of the solution will be lower than that of the pure solvent. The extent to which the vapor drops is directly proportional to the mole fraction of the *solvent*. The relationship which follows is known as Raoult's law:

$$P_A = \chi_A \cdot P_A^\circ$$

where  $P_A$  is the vapor pressure of the solution,  $\chi_A$  is the mole fraction of the solvent, and  $P_A^\circ$  is the vapor pressure of the pure solvent.

**question ►**

180 g of glucose (MW = 180 g/mol) is added to 180 g of water at 100°C. What is the vapor pressure of the resulting solution in atmospheres?

**solution:**

Recall that normal boiling begins when the vapor pressure equals 1.00 atm. Since pure water has a normal boiling point of 100°C, it must have a vapor pressure of 1.0 atm at 100°C.

Converting from grams to moles gives 1.0 mole of glucose and 10 moles of water in solution. Since the mole fraction of H<sub>2</sub>O is the moles of water divided by the total number of moles in solution we get:

$$\chi_{\text{H}_2\text{O}} = \frac{10 \text{ mol}_{\text{H}_2\text{O}}}{11 \text{ mol}_{\text{soln}}} \quad \text{So } \dots$$

$$P_{\text{H}_2\text{O}} = \frac{10 \text{ mol}_{\text{H}_2\text{O}}}{11 \text{ mol}_{\text{soln}}} \times 1.0 \text{ atm} = 0.91 \text{ atm} \blacklozenge$$

►Note that since the vapor pressure of the solution is less than 1.0 atm a temperature of greater than 100°C is required to bring this solution to a boil.

**question ►**

If the above solution is found to have a volume of 300 mL at 100°C, what would be the osmotic pressure associated with this solution as compared to pure water?

**solution:**

Recall  $\pi = i \cdot MRT$ , and M = moles of solute/liters of solution.

Since glucose is a nonelectrolyte  $i$  is equal to one. We have 1.0 mole of glucose divided by 0.300 L of solution to give a molarity of 3.3 mol/L. R is 0.082 L·atm/mol·K, and T is 100°C + 273 to give 373 K. Therefore:

$$\pi = (1)(3.3 \text{ mol/L})(0.082 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(373 \text{ K}) = 101 \text{ atm} \blacklozenge$$