Chemistry, The Central Science, 10th edition Theodore L. Brown; H. Eugene LeMay, Jr.; and Bruce E. Bursten

## Chapter 13 <br> Properties of Solutions

## Solutions

- Solutions are homogeneous mixtures of two or more pure substances.
- In a solution, the solute is dispersed uniformly throughout the solvent.

| 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 |

## Solutions

The intermolecular forces between solute and solvent particles must be strong enough to compete with those between solute particles and those between
 solvent particles.

## How Does a Solution Form?

As a solution forms, the solvent pulls solute particles apart and surrounds, or solvates, them.


## Solvated NaCl



If an ionic salt is soluble in water, it is because the iondipole interactions are strong enough to overcome the lattice energy of the salt crystal.

## Energy Changes in Solution

- Simply put, three processes affect the energetics of the process:
> Separation of solute particles
$\Delta \mathrm{H}_{1}$ ( this is always endothermic)
$>$ Separation of solvent particles $\Delta \mathrm{H}_{2}$ ( this too is always endothermic)
> New interactions between solute and solvent $\Delta \mathrm{H}_{3}$ ( this is always exothermic)
The overall enthalpy change associated with these three processes:
$\Delta \mathrm{H}_{\text {solv }}=\Delta \mathrm{H}_{1}+\Delta \mathrm{H}_{2}+\Delta \mathrm{H}_{3}$

$\Delta H_{1}$ : Separation of solute molecules

$\Delta H_{2}$ : Separation of solvent molecules
- The process solution formation can be either endo or exothermic
- Hot packs use $\mathrm{MgSO}_{4}$ and cold packs use $\mathrm{NH}_{4} \mathrm{NO}_{3}$ and water.
- The solvent solute interactions must be strong enough to make $\Delta \mathrm{H}_{3}$ comparable in magnitude to $\Delta H_{1}+\Delta H_{2}$
- So NaCl will not dissolve in nonpolar liquids as the attraction between the ions and the nonpolar solvent will not compensate for the energies required to separate the ions.


## Energy Changes in Solution

The enthalpy
change of the
overall process
depends on $\Delta H$ for
each of these steps.

## Why Do Endothermic Processes Occur?

Things do not tend to occur spontaneously (i.e., without outside intervention) unless the energy of the system is lowered.

## Why Do Endothermic Processes Occur?



# Yet we know that in some processes, like the dissolution of $\mathrm{NH}_{4} \mathrm{NO}_{3}$ in water, heat is absorbed, not released. 

## Enthalpy Is Only Part of the Picture

The reason is that increasing the disorder or randomness (known as entropy) of a system tends to lower the energy of the system.

(b)

## Enthalpy Is Only Part of the Picture

So even though enthalpy may increase, the overall energy of the system can still decrease if the system becomes more disordered.

(b)

## Favorable Entropy Changes

- The process occurring at a constant temperature in which the randomness in space or the entropy of the system increases tend to occur spontaneously
- Free Energy dictate spontaneity
$\Delta G=\Delta H-T \Delta S$
An large increase in entropy can overcome the positive enthalpy change


## Student, Beware!



Just because a substance disappears when it comes in contact with a solvent, it doesn't mean the substance dissolved.

## Student, Beware!



- Dissolution is a physical change-you can get back the original solute by evaporating the solvent.
- If you can't, the substance didn't dissolve, it reacted.
- The above example is the reaction of nickel with HCl resulting in the formation of $\mathrm{NiCl}_{2}$


## Types of Solutions



- Saturated
> Solvent holds as much solute as is possible at that temperature.
> Dissolved solute is in dynamic equilibrium with solid solute particles.


## Types of Solutions

- Unsaturated
$>$ Less than the maximum amount of solute for that temperature is dissolved in the solvent.



## Types of Solutions



- Supersaturated
$>$ Solvent holds more solute than is normally possible at that temperature.
$>$ These solutions are unstable; crystallization can usually be stimulated by adding a "seed crystal" or scratching the side of the flask.


## Factors Affecting Solubility

## Solute Solvent Interaction

- Chemists use the axiom "like dissolves like":
$>$ Polar substances tend to dissolve in polar solvents.
>Nonpolar substances tend to dissolve in nonpolar solvents.


Hydrogen bond



## The more similar the intermolecular attractions, the more likely one substance is to be soluble in another.

## Glucose (which has hydrogen bonding) is very soluble in water, while cyclohexane (which only has dispersion forces) is not.



- Vitamin A is soluble in nonpolar compounds (like fats).
- Vitamin C is soluble in water.



Vitamin A

## TABLE 13.3 Solubilities of Some Alcohols in Water and in Hexane*

| Alcohol | Solubility <br> in $\mathrm{H}_{2} \mathrm{O}$ | Solubility <br> in $\mathrm{C}_{6} \mathrm{H}_{14}$ |
| :--- | :--- | :--- |
| $\mathrm{CH}_{3} \mathrm{OH}$ (methanol) | $\infty$ | 0.12 |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}$ (ethanol) | $\infty$ | $\infty$ |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ (propanol) | $\infty$ | $\infty$ |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ (butanol) | 0.11 | $\infty$ |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ (pentanol) | 0.030 | $\infty$ |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ (hexanol) | 0.0058 | $\infty$ |
| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ (heptanol) | 0.0008 | $\infty$ |

[^0]
## Gases in Solution

- In general, the solubility of gases in water increases with increasing mass as the attraction between the gas and the solvent molecule is mainly dispersion forces.
- Larger molecules have stronger dispersion forces.

TABLE 13.2 Solubilities of Gases in Water at $20^{\circ} \mathrm{C}$, with 1 atm Gas Pressure

Gas Solubility ( $M$ )

| $\mathrm{N}_{2}$ | $0.69 \times 10^{-3}$ |
| :--- | :--- |
| CO | $1.04 \times 10^{-3}$ |
| $\mathrm{O}_{2}$ | $1.38 \times 10^{-3}$ |
| Ar | $1.50 \times 10^{-3}$ |
| Kr | $2.79 \times 10^{-3}$ |

## Effect of Pressure

- The solubility of solids and liquids is not affected by pressure.
- However the solubility of gases is greatly affected by pressure.


## Gases in Solution



- The solubility of a gas in a liquid is directly proportional to its pressure.



## Henry's Law

$$
\begin{aligned}
& S_{g} \propto P_{g} \\
& S_{g}=k P_{g}
\end{aligned}
$$

where

- $S_{g}$ is the solubility of the gas;
- $k$ is the Henry's law constant for that gas in that solvent at that temperature
- $P_{g}$ is the partial pressure of the gas above the liquid.


Calculate the concentration of $\mathrm{CO}_{2}$ in a soft drink that is bottled with a partial pressure of $\mathrm{CO}_{2}$ of 4.0 atm over the liquid at $25^{\circ} \mathrm{C}$. The Henry's law constant for $\mathrm{CO}_{2}$ in water at this temperature is $3.1 \times 10-2 \mathrm{~mol} / \mathrm{L}-\mathrm{atm}$.

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$$
S_{\mathrm{CO}_{2}}=k \mathrm{P}_{\mathrm{CO} 2}=\left(3.1 \times 10^{-2} \mathrm{~mol} / \mathrm{L}-\mathrm{atm}\right)(4.0 \mathrm{~atm})=0.12 \mathrm{~mol} / \mathrm{L}=0.12 \mathrm{M}
$$

Calculate the concentration of $\mathrm{CO}_{2}$ in a soft drink after the bottle is opened and equilibrates at $25^{\circ} \mathrm{C}$ under a $\mathrm{CO}_{2}$ partial pressure of $3.0 \times 10^{-4} \mathrm{~atm}$. The Henry's law constant for $\mathrm{CO}_{2}$ in water at this temperature is $3.1 \times 10^{-2} \mathrm{~mol} / \mathrm{L}-\mathrm{atm}$.

Answer: $9.3 \times 10^{-6} \mathrm{M}$

## Temperature



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

## Temperature

- The opposite is true of gases:
> Carbonated soft drinks are more "bubbly" if stored in the refrigerator.
$>$ Warm lakes have less $\mathrm{O}_{2}$ dissolved in them than cool lakes.



## How to read a solubility curve

1. How much KCl would be able to dissolv in 100 g of water at $50^{\circ} \mathrm{C}$ ?
2. At $40^{\circ} \mathrm{C}$, exactly 64 g of an unknov salt dissolved in 100 g of water. What is the likely identity of the unknown?
3. At what temperature could you full dissolve 80 g of NaCl in 200 g of water?
4. At $60^{\circ} \mathrm{C}, 30 \mathrm{~g}$ of $\mathrm{KClO}_{3}$ are dissolved in 100 g of water. Is the solution undersaturated, saturated or supersaturated?


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- How would this affect the marine life if the water temperature goes up.....
- Implications of global warming....


## Ways of Expressing Concentrations of Solutions

## There are many ways to express concentration mathematically

- Weight percent = mass of component per total mass (expressed as a percentage)
- Mole fraction = moles of component per total moles (expressed as a value between 0 and 1)
- Molarity = moles of solute per liter of solution
- Molality = moles of solute per kg of solvent


## Mass Percentage

Mass $\%$ of $A=\frac{\text { mass of } A \text { in solution }}{\text { total mass of solution }} \times 100$

## Parts per Million and Parts per Billion

Parts per Million (ppm)
For dilute solutions

$$
\mathrm{ppm}=\frac{\text { total mass of solution }}{\text { m }} \times 10^{6}
$$

Parts per Billion (ppb)
For even more dilute solutions

$$
\mathrm{ppb}=\frac{\text { mass of } \mathrm{A} \text { in solution }}{\text { total mass of solution }} \times 10^{9}
$$

(a) A solution is made by dissolving 13.5 g of glucose $\left(\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}\right)$ in 0.100 kg of water. What is the mass percentage of solute in this solution?

Mass $\%$ of glucose $=\frac{\text { mass glucose }}{\text { mass soln }} \times 100=\frac{13.5 \mathrm{~g}}{13.5 \mathrm{~g}+100 \mathrm{~g}} \times 100=11.9 \%$

A 2.5-g sample of groundwater was found to contain $5.4 \mu \mathrm{~g}$ of $\mathrm{Zn}^{2+}$ What is the concentration of $\mathrm{Zn}^{2+}$ in parts per million?

$$
\mathrm{ppm}=\frac{\text { mass of solute }}{\text { mass of soln }} \times 10^{6}=\frac{5.4 \times 10^{-6} \mathrm{~g}}{2.5 \mathrm{~g}} \times 10^{6}=2.2 \mathrm{ppm}
$$

## Mole Fraction ( $X$ )

$$
X_{\mathrm{A}}=\frac{\text { moles of } \mathrm{A}}{\text { total moles in solution }}
$$

- In some applications, one needs the mole fraction of solvent, and in others solutemake sure you find the quantity you need!
- A in that case will be the solvent.
(a) Calculate the mass percentage of NaCl in a solution containing 1.50 g of NaCl in 50.0 g of water.
(a) A commercial bleaching solution contains 3.62 mass \% sodium hypochlorite, NaOCl . What is the mass of NaOCl in a bottle containing 2500 g of bleaching solution?


## Molarity ( $M$ )

## $M=\frac{\text { mol of solute }}{L \text { of solution }}$

- You will recall this concentration measure from Chapter 4.
- Because volume is temperature dependent, molarity can change with temperature.


## Molality ( $m$ )

$$
m=\frac{\text { mol of solute }}{\mathrm{kg} \text { of solvent }}
$$

Because both moles and mass do not change with temperature, molality (unlike molarity) is not temperature dependent.

Example (from p. 546)
A commercial bleach solution contains 3.62 mass \% NaOCI in water. Calculate
(a) the molality,
(b) the mole fraction of NaOCl ,
(c) the mole fraction of $\mathrm{H}_{2} \mathrm{O}$ in the solution.
(a) molality:
$3.62 \%$ means 3.62 g NaOCl in 96.38 g water.
$3.62 \mathrm{~g} \times \underset{74.5 \mathrm{~g} \mathrm{NaOCl}}{\mid \text { mole }}=0.048590$ moles
$0.04859 \mathrm{~mol}=0.504 \mathrm{~m}$
0.09638 Kg solv
(b) Mole fraction:

## Changing Molarity to Molality



If we know the density of the solution, we can calculate the molality from the molarity, and vice versa.

## A solution contains 5.0 g of toluene $\left(\mathrm{C}_{7} \mathrm{H}_{8}\right)$ and 225 g of benzene

 and has a density of $0.876 \mathrm{~g} / \mathrm{mL}$. Calculate the molarity of theSolve: The number of moles of solute is

$$
\text { Moles } \mathrm{C}_{7} \mathrm{H}_{8}=\left(5.0 \mathrm{~g} \mathrm{C}_{7} \mathrm{H}_{8}\right)\left(\frac{1 \mathrm{~mol} \mathrm{C}_{7} \mathrm{H}_{8}}{92 \mathrm{~g} \mathrm{C}_{7} \mathrm{H}_{8}}\right)=0.054 \mathrm{~mol}
$$

The density of the solution is used to convert the mass of the solution to its volume:

$$
\text { Milliliters soln }=(230 \mathrm{~g})\left(\frac{1 \mathrm{~mL}}{0.876 \mathrm{~g}}\right)=263 \mathrm{~mL}
$$

Molarity is moles of solute per liter of solution:

$$
\text { Molarity }=\left(\frac{\text { moles } \mathrm{C}_{7} \mathrm{H}_{8}}{\text { liter soln }}\right)=\left(\frac{0.054 \mathrm{~mol} \mathrm{C}_{7} \mathrm{H}_{8}}{263 \mathrm{~mL} \mathrm{soln}}\right)\left(\frac{1000 \mathrm{~mL} \text { soln }}{1 \mathrm{~L} \text { soln }}\right)=0.21 \mathrm{M}
$$

## Colligative Properties

- Changes in colligative properties depend only on the number of solute particles present, not on the identity of the solute particles.
- How would the ionic compounds and covalent compounds behave.....


## Colligative Properties

- Among colligative properties are
>Vapor pressure lowering
>Boiling point elevation
$>$ Melting point depression
>Osmotic pressure


## Vapor Pressure

Because of solutesolvent intermolecular attraction, higher concentrations of nonvolatile solutes<br>make it harder for solvent to escape to the vapor phase.


(b)

## Vapor Pressure

# Therefore, the vapor pressure of a solution is lower than that of the pure solvent. 


(b)

## Raoult's Law

- The partial pressure exerted by solvent vapor above the solution, $\mathrm{P}_{\mathrm{A}}$, equals to the product of the mole fraction of the solvent in the solution, Xa , times the vapor pressure of the pure solvent.


## Raoult's Law

$$
P_{\mathrm{A}}=X_{\mathrm{A}} P_{\mathrm{A}}^{\circ}
$$

where

- $X_{\mathrm{A}}$ is the mole fraction of compound A
- $P_{A}^{\circ}$ is the normal vapor pressure of $A$ at that temperature

NOTE: This is one of those times when you want to make sure you have the mole fraction of the solvent.

Glycerin $\left(\mathrm{C}_{3} \mathrm{H}_{8} \mathrm{O}_{3}\right)$ is a nonvolatile nonelectrolyte with a density of $1.26 \mathrm{~g} / \mathrm{mL}$ at $25^{\circ} \mathrm{C}$. Calculate the vapor pressure at $25^{\circ} \mathrm{C}$ of a solution made by adding 50.0 mL of glycerin to 500.0 mL of water. The vapor pressure of pure water at $25^{\circ} \mathrm{C}$ is 23.8 torr (Appendix B).

- The vapor pressure of pure water at $110^{\circ} \mathrm{C}$ is 1070 torr. A solution of ethylene glycol and water has a vapor pressure of 1.00 atm at $110^{\circ} \mathrm{C}$. Assuming that Raoult's law is obeyed, what is the mole fraction of ethylene glycol in the solution

Only ideal solutions obey Raoult's law.
Real solutions best approximate ideal behavior when:
a. Solute concentration is low
b. Solute and solvent have similar molecular size
c. And they have similar type of intermolecular attractions

When is Raoult's law not obeyed:
When the solution is not ideal.
a. When the intermolecular forces between the solvent-solvent and solute-solute are stronger than the ones between the solvent and solute.
Then the vapor pressure would be higher than predicted.

## Deviation from Raoul's Law

- When the attraction between the solvent and the solute is very strong then the vapor pressure would be lower than that predicted by the Raoul's law.
When do you expect a situation like this to happen ....
- When the solvent and the solute start forming hydrogen bonds.
- We will ignore these departures from the ideal solutions for this chapter while doing the numerical problems.
- But we still need to understand the concept and be able to explain them in the test.


## Boiling Point Elevation and Freezing Point Depression

Nonvolatile solute-solvent interactions also cause solutions to have higher boiling points and lower freezing points than the pure solvent.


- The boiling point of a liquid is the temperature at which its vapor pressure equals 1 atm (ref. Chapter 11).


## Boiling Point Elevation

The change in boiling point is proportional to the number of particles of solute in the solution and therefore the molality of the solution:

$$
\Delta T_{b}=K_{b} \cdot m
$$

$\Delta T b$ is added to the normal boiling point of the solvent.
and where $K_{b}$ is the molal boiling point elevation constant, a property of the solvent.

|  | Normal <br> Soiling <br> Point <br> $\left({ }^{\circ} \mathrm{C}\right)$ | $\mathrm{K}_{b}$ <br> $\left({ }^{\circ} \mathrm{C} / m\right)$ | Normal <br> Freezing <br> Point <br> $\left({ }^{\circ} \mathrm{C}\right)$ | $\mathrm{K}_{f}$ <br> $\left({ }^{\circ} \mathrm{C} / m\right)$ |
| :--- | :---: | :--- | :---: | :---: |
| Water, $\mathrm{H}_{2} \mathrm{O}$ | 100.0 | 0.51 | 0.0 | 1.86 |
| Benzene, $\mathrm{C}_{6} \mathrm{H}_{6}$ | 80.1 | 2.53 | 5.5 | 5.12 |
| Ethanol, $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}$ | 78.4 | 1.2 | -114.6 | .99 |
| Carbon tetrachloride, $\mathrm{CCl}_{4}$ | 76.8 | 5.02 | -22.3 | 29.8 |
| Chloroform, $\mathrm{CHCl}_{3}$ | 61.2 | 3.6 | -63.5 | .68 |

For water $K_{b}$ is $0.51^{\circ} \mathrm{C} / \mathrm{m}$
This means that a $1 \mathrm{molal}(\mathrm{mol} / \mathrm{Kg}$ solv) aqueous solution of any nonvolatile substance would boil $0.51^{\circ} \mathrm{C}$ higher than water.

- The boiling point elevation is proportionate to the concentration of the solute particles.

When a substance that produces two ions (such as NaCl ) upon dissolving into water, it has twice the effect of a substance that does not dissociate, like sugar.

So if a 1 m solution of NaCl is taken it would have 2 m ions in it.

The elevation of boiling point would therefore be

$$
2 \mathrm{~m} \times 0.51 \mathrm{C} / \mathrm{m}=1^{\circ} \mathrm{C}
$$

- For this reason it is important to know if the solute is an electrolyte or not


## Freezing Point Depression

- When a solution freezes, pure solvent crystallize out of solution.
- The solute particles are not normally soluble in the solid phase of the solvent.
- When an aqueous solution freezes, pure ice crystals are formed.
- recrystallization is an important tool used for Isolation/separation/purification
- The part of the phase diagram that represents solid-gas boundary is the same for solution and the pure solvent
- As the solution has a lower vapor pressure, the triple point has moved down.

- The line representing the solid liquid line rises nearly vertically up from the triple point.
- As the triple point of a solution is lower than the solvent the freezing point too, is lower.



## Freezing Point Depression

- The change in freezing point can be found similarly:

$$
\Delta T_{f}=K_{f} \cdot m
$$

- $\Delta T_{f}$ is subtracted from the normal freezing point of the solvent.
- Here $K_{f}$ is the molal freezing point depression constant of the solvent.


## Boiling Point Elevation and Freezing Point Depression

Note that in both equations, $\Delta T$ does
$\Delta T_{b}=K_{b} \cdot m$ not depend on what the solute is, but only on how many particles are dissolved.

$$
\Delta T_{f}=K_{f} \cdot m
$$

Automotive antifreeze consists of ethylene glycol $\left(\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}_{2}\right)$, a nonvolatile nonelectrolyte. Calculate the boiling point and freezing point of a 25.0 mass \% solution of ethylene glycol in water.

$$
\begin{gathered}
\left(\frac{250 \mathrm{~g} \mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}_{2}}{750 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}}\right)\left(\frac{1 \mathrm{~mol} \mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}_{2}}{62.1 \mathrm{~g} \mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}_{2}}\right)\left(\frac{1000 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}}{1 \mathrm{~kg} \mathrm{H}_{2} \mathrm{O}}\right) \\
\text { Molality }
\end{gathered}=\frac{\text { moles } \mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}_{2}}{\text { kilograms } \mathrm{H}_{2} \mathrm{O}}: 子 \begin{aligned}
& \text {. } \\
& =5.37 \mathrm{~m}
\end{aligned}
$$

We can now use Equations 13.11 and 13.12 to calculate the changes in the boiling and freezing points:

$$
\begin{aligned}
\Delta T_{b} & =K_{b} m \\
\Delta T_{f} & =K_{f} m=\left(0.51^{\circ} \mathrm{C} / m\right)(5.37 m)=2.7^{\circ} \mathrm{C} \\
\left.{ }^{\circ} \mathrm{C} / m\right)(5.37 m) & =10.0^{\circ} \mathrm{C}
\end{aligned}
$$

Calculate the freezing point of a solution containing 0.600 kg of $\mathrm{CHCl}_{3}$ and 42.0 g of eucalyptol $\left(\mathrm{C}_{10} \mathrm{H}_{18} \mathrm{O}\right)$, a fragrant substance found in the leaves of eucalyptus trees. (See Table 13.4.)

List the following aqueous solutions in order of their expected freezing point: $0.050 \mathrm{~m} \mathrm{CaCl}_{2}, 0.15 \mathrm{~m} \mathrm{NaCl}, 0.10 \mathrm{~m} \mathrm{HCl}, 0.050$ $m \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}, 0.10 m \mathrm{C}_{12} \mathrm{H}_{22} \mathrm{O}_{11}$.
$0.050 \mathrm{~m} \mathrm{CaCl}_{2} \Rightarrow 0.050 \mathrm{~m}$ in $\mathrm{Ca}^{2+}$ and 0.10 m in $\mathrm{Cl}^{-} \Rightarrow 0.15 \mathrm{~m}$ in particles

$$
\begin{aligned}
& 0.15 \mathrm{~m} \mathrm{NaCl} \Rightarrow 0.15 \mathrm{~m} \mathrm{Na}^{+} \text {and } 0.15 \mathrm{~m} \text { in } \mathrm{Cl}^{-} \Rightarrow 0.30 \mathrm{~m} \text { in particles } \\
& 0.10 \mathrm{~m} \mathrm{HCl} \Rightarrow 0.10 \mathrm{~m} \mathrm{H}^{+} \text {and } 0.10 \mathrm{~m} \text { in } \mathrm{Cl}^{-} \Rightarrow 0.20 \mathrm{~m} \text { in particles }
\end{aligned}
$$

$0.050 m \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2} \Rightarrow$ weak electrolyte $\Rightarrow$ between 0.050 m and 0.10 m in particles

$$
0.10 \mathrm{~m}_{12} \mathrm{H}_{22} \mathrm{O}_{11} \Rightarrow \text { nonelectrolyte } \Rightarrow 0.10 \mathrm{~m} \text { in particles }
$$

Because the freezing points depend on the total molality of particles in solution, the expected ordering is

$$
0.15 \mathrm{~m} \mathrm{NaCl} \text { (lowest freezing point), }
$$

0.10 m HCl ,
$0.050 \mathrm{~m} \mathrm{CaCl}_{2}$,
$0.10 m \mathrm{C}_{12} \mathrm{H}_{22} \mathrm{O}_{11}$, and
$0.050 \mathrm{~m} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$, (highest freezing point).

## Colligative Properties of Electrolytes

Since these properties depend on the number of particles dissolved, solutions of electrolytes (which dissociate in solution) should show greater changes than those of nonelectrolytes.


## Colligative Properties of Electrolytes

However, a 1 M solution of NaCl does not show twice the change in freezing point that a 1 M solution of methanol does.


## van't Hoff Factor



## One mole of NaCl in water does not really give rise to two moles of ions.

## van't Hoff Factor



## Some $\mathrm{Na}^{+}$and $\mathrm{Cl}^{-}$ reassociate for a short time, as ion pairs so the true concentration of particles is somewhat less than two times the concentration of NaCl .

## The van't Hoff Factor

- Reassociation is more likely at higher concentration.
- Therefore, the number of particles present is concentration dependent.

|  | Concentration |  |  |  |
| :--- | :---: | :---: | :---: | :---: |
| Compound | $\mathbf{0 . 1 0 0} \mathbf{m}$ | $\mathbf{0 . 0 1 0 0} \mathbf{m}$ | $\mathbf{0 . 0 0 1 0 0} \mathbf{m}$ | Limiting <br> Value |
| Sucrose | 1.00 | 1.00 | 1.00 | 1.00 |
| NaCl | 1.87 | 1.94 | 1.97 | 2.00 |
| $\mathrm{~K}_{2} \mathrm{SO}_{4}$ | 2.32 | 2.70 | 2.84 | 3.00 |
| $\mathrm{MgSO}_{4}$ | 1.21 | 1.53 | 1.82 | 2.00 |

## The van't Hoff Factor

## We modify the previous equations by multiplying by the van't Hoff factor, $i$

|  | Concentration |  |  |  |
| :--- | :---: | :---: | :---: | :---: |
| Compound | $\mathbf{0 . 1 0 0} \mathbf{m}$ | $\mathbf{0 . 0 1 0 0} \mathbf{m}$ | $\mathbf{0 . 0 0 1 0 0} \boldsymbol{m}$ | Limiting |
| Value |  |  |  |  |
| Sucrose | 1.00 | 1.00 | 1.00 | 1.00 |
| NaCl | 1.87 | 1.94 | 1.97 | 2.00 |
| $\mathrm{~K}_{2} \mathrm{SO}_{4}$ | 2.32 | 2.70 | 2.84 | 3.00 |
| $\mathrm{MgSO}_{4}$ | 1.21 | 1.53 | 1.82 | 2.00 |

Concentration

$$
i=\frac{\Delta T_{f}(\text { measured })}{\Delta T_{f}(\text { calculated })}
$$

- If the van't hoff factor is not given use the ideal value in calculation


## Osmosis

- Some substances form semi permeable membranes, allowing some smaller particles to pass through, but blocking other larger particles.
- In biological systems, most semi permeable membranes allow water to pass through, but solutes are not free to do so.


## Osmosis



In osmosis, there is net movement of solvent from the area of higher solvent concentration (dilute solution) to the area of lower solvent concentration (concentrated solution).

## Osmotic Pressure

- The pressure required to stop osmosis, known as osmotic pressure, $\pi$, is

$$
\pi=\left(\frac{n}{V}\right) R T=M R T
$$

Where n is the moles of solute
and $M$ 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.

The average osmotic pressure of blood is 7.7 atm at $25^{\circ} \mathrm{C}$. What concentration of glucose $\left(\mathrm{C}_{6} \mathrm{H1}_{2} \mathrm{O}_{6}\right)$ will be isotonic with blood?

$$
\begin{aligned}
\pi & =M R T \\
M & =\frac{\pi}{R T}=\frac{7.7 \mathrm{~atm}}{\left(0.0821 \frac{\mathrm{~L}-\mathrm{atm}}{\mathrm{~mol}-\mathrm{K}}\right)(298 \mathrm{~K})}=0.31 \mathrm{M}
\end{aligned}
$$

What is the osmotic pressure at $20^{\circ} \mathrm{C}$ of a 0.0020 M sucrose $\left(\mathrm{C}_{12} \mathrm{H}_{22} \mathrm{O}_{11}\right)$ solution?

What is the osmotic pressure at $20^{\circ} \mathrm{C}$ of a 0.0020 M sucrose $\left(\mathrm{C}_{12} \mathrm{H}_{22} \mathrm{O}_{11}\right)$ solution?

Answer: 0.048 atm, or 37 torr

## Osmosis in Blood Cells

- If the solute concentration outside the cell is greater than that inside the cell, the solution is hypertonic.
- Water will flow out of the cell, and crenation results.



## Osmosis in Cells

- If the solute concentration outside the cell is less than that inside the cell, the solution is hypotonic.

- Water will flow into the cell, and hemolysis results.


## Applications of osmosis

- Food preservation
- Dialysis

Dialysis works on the principles of the diffusion and osmosis of solutes and fluid across a semi permeable membrane

# Molar Mass from Colligative Properties 

We can use the
effects of a colligative property such as osmotic pressure to determine the molar mass of a compound.

> 125 mg of an alkaline earth metal chloride ( $\mathrm{XCl}_{2}$ ) dissolved in enough water to make 50.0 mL of solution at $298^{\circ} \mathrm{C}$ has an osmotic pressure of 1.16 atm . Identify the alkaline earth metal.

Use the measured osmotic pressure to determine the molar concentration of dissolved particles.

Use the molarity of dissolved particles, and knowledge of the compound formula, to determine the molarity of the compound.

Use the molarity of the compound and the volume of solution to determine the number of moles of compound in solution.

Use the number of moles of compound and the number of grams of compound in solution to determine molar mass.

Knowing molar mass, determine the identity of the alkaline earth chloride.

Because the freezing points depend on the total molality of particles in solution, the expected ordering is 0.15 m NaCl (lowest freezing point), $0.10 \mathrm{mHCl}, 0.050 m \mathrm{CaCl}_{2}, 0.10 \mathrm{~m}_{12} \mathrm{H}_{22} \mathrm{O}_{11}$, and $0.050 m \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$, (highest freezing point).

Solve: From Equation 13.11 we have

$$
\text { Molality }=\frac{\Delta T_{b}}{K_{b}}=\frac{0.357^{\circ} \mathrm{C}}{5.02^{\circ} \mathrm{C} / \mathrm{m}}=0.0711 \mathrm{~m}
$$

Thus, the solution contains 0.0711 mol of solute per kilogram of solvent. The solution was prepared using $40.0 \mathrm{~g}=0.0400 \mathrm{~kg}$ of solvent $\left(\mathrm{CCl}_{4}\right)$. The number of moles of solute in the solution is therefore

$$
\left(0.0400 \mathrm{~kg} \mathrm{CCl}_{4}\right)\left(0.0711 \frac{\mathrm{~mol} \text { solute }}{\mathrm{kg} \mathrm{CCl}_{4}}\right)=2.84 \times 10^{-3} \mathrm{~mol} \text { solute }
$$

The molar mass of the solute is the number of grams per mole of the substance:

$$
\text { Molar mass }=\frac{0.250 \mathrm{~g}}{2.84 \times 10^{-3} \mathrm{~mol}}=88.0 \mathrm{~g} / \mathrm{mol}
$$

Camphor $\left(\mathrm{C}_{10} \mathrm{H}_{16} \mathrm{O}\right)$ melts at $179.8^{\circ} \mathrm{C}$, and it has a particularly large freezing-point-depression constant, $K f=40.0^{\circ} \mathrm{C} / \mathrm{m}$. When 0.186 g of an organic substance of unknown molar mass is dissolved in 22.01 g of liquid camphor, the freezing point of the mixture is found to be $176.7^{\circ} \mathrm{C}$. What is the molar mass of the solute?

## Colloids:

## Suspensions of particles larger than individual ions or molecules, but too small to be settled out by gravity.

| Phase <br> of Colloid | Dispersing <br> (solventlike) Substance | Dispersed <br> (solutelike) Substance | Colloid Type | Example |
| :--- | :--- | :--- | :--- | :--- |
| Gas | Gas | Gas | - | None (all are solutions) |
| Gas | Gas | Liquid | Aerosol | Fog |
| Gas | Gas | Solid | Aerosol | Smoke |
| Liquid | Liquid | Gas | Foam | Whipped cream |
| Liquid | Liquid | Liquid | Emulsion | Milk |
| Liquid | Liquid | Solid | Sol | Paint |
| Solid | Solid | Gas | Solid foam | Marshmallow |
| Solid | Solid | Liquid | Solid emulsion | Butter |
| Solid | Solid | Solid | Solid sol | Ruby glass |

Solutions

## Tyndall Effect



- Colloidal suspensions can scatter rays of light.
- This phenomenon is known as the Tyndall effect.



## Colloids in Biological Systems

Some molecules have a polar, hydrophilic (water-loving) end and a nonpolar, hydrophobic (waterhating) end.


## Colloids in Biological Systems



Sodium stearate is one example of such a molecule.

## Colloids in Biological Systems

These molecules can aid in the emulsification of fats and oils in aqueous solutions.



[^0]:    *Expressed in mol alcohol $/ 100 \mathrm{~g}$ solvent at $20^{\circ} \mathrm{C}$. The infinity symbol indicates that the alcohol is completely miscible with the solvent.

