12.3 Colligative Properties

Changes in solvent properties due to impurities



Colloidal suspensions or dispersions scatter light, a phenomenon known as the Tyndall effect. (a) Dust in the air scatters the light coming through the trees in a forest along the coast. (b) A narrow beam of light from a laser is passed through an NaCl solution (left) and then a colloidal mixture of gelatin and water (right)

Dr. Fred Omega Garces Chemistry 201 Miramar College

Phase Diagram (Revisited)



Cool

Heat



Crystalline solid

in fixed positions;

Ordered arrangement;

particles are essentially

particles close together.

Colligative Properties



It is known that:

Dissolved solute in pure liquid will change the physical property of the liquid, i.e., Density, Bpt, Fpt, Vapor Pressure This new developed property is called Colligative Property; a method of counting the number of solute in solution.



Evaporation Process

What is responsible for increasing the boiling point of water with the addition of anti-freeze (or salt)?

Evaporation occurs when molecules have sufficient energy to escape the interface of a liquid substance.

Normal Boiling Point:

Temperature at which the vapor pressure of the liquid is equal to the atmospheric pressure.

When a solute contaminates the solvent, the surface area is reduced because of the attraction between solute and solvent, thus the physical properties (i.e., vapor pressure) are altered.



A. Vapor Pressure

Vapor Pressure Reduction: Solute interferes and prevents solvent molecules from escaping into the atmosphere.



Solvent

Solution

Vapor Pressure Reduction: Expressed by Raoult's Law



Vapor pressure of $CHCl_3$ is $P^\circ = 360$ torr at $T = 40.0^\circ C$. What is the vapor pressure reduction when 10.0 g of phenol (C_6H_5OH : MW=94 g/mol) is added to 95.0 g of chloroform (MW=119.5 g/mol). What is the vapor pressure above the chloroform?

 $\chi = \frac{\text{mol phenol}}{\text{Tot. mol soln}} = \frac{(10.0 \text{ g} \cdot 1 \text{ mol}/94 \text{ g})}{(10.0 \text{ g} \cdot 1 \text{ mol}/94 \text{ g}) + (95.0 \text{ g} \cdot 1 \text{ mol}/119.5 \text{ g})} = \frac{0.106}{0.901} = 0.118$ $\Delta P = x_{\text{phenol}} \cdot P_{CHCI3}^{\circ} = 0.118 \cdot 360 \text{ torr} = 42.48 \text{ torr} = 42.5 \text{ torr}$

P_{solvent} = 360 torr - 42.48 torr = 317.52 torr = 318 torr

Normal Boiling Process

Extension of vapor pressure concept:

Normal Boiling Point: B.pt. of Substance @ 1atm When solute is added, B.pt. > Normal B.pt.

B.pt. is elevated when solute inhibits solvent from escaping.



B. Boiling Point Elevation

Boiling Point Elevation eqn.

(2) $\Delta T_b = (T_b - T_b^\circ) = m \cdot k_b$

Where, $\Delta T_b = B.pt$. Elevation

 $T_b = B.pt.$ solvent in solution

 T_b° = B.pt. of pure solvent

m = molality, $k_b = B.pt$. Constant

Some Boiling Point Elevation and Freezing Point Depression Constants						
Solvent	Normal bp (°C) pure solvent	K _b (°C/m)	Normal fp (°C) pure solvent	K _f (°C/m)		
Water Benzene Camphor Chloroform (CH ₃ Cl)	100.00 80.10 207 61.70	+0.5121 +2.53 +5.611 +3.63	0.0 5.50 179.75 - 63.5	1.86 4.90 39.7 4.70		

Normal Freezing Process

Normal Freezing Point: F.pt. of Substance @ 1atmWhen solute is added, F.pt. < Normal F.pt.F.pt. is depressed when solute inhibits solvent from escaping.

When solution freezes the solid form is almost always pure.
Depression of Freeze. pt.
Express by Freezing point depression equation

Solute particles does not fit into the crystal lattice of the solvent because of the differences in size. The solute essentially remains in solution and blocks other solvent

from fitting into the crystal lattice

during the freezing process.

Liquid phase T_f (solvent) Solid Tf (solution) phasé

C. Freezing Point Depression

Phase Diagram and the lowering of the freezing point.



Freezing pt Depression eqn.

(3) $\Delta T_f = (T_f^{\circ} - T_f) = m \cdot k_f$ Where, $\Delta T_f = f.pt.$ depression $T_f^{\circ} = f.pt.$ of pure solvent $T_f = f.pt.$ solvent in solution m = molality, $k_f = f.pt.$ Constant

Generally freezing point depression is used to determine the molecular mass of an unknown.

$$m = \Delta T_{f} = \underline{moles}_{Kg \text{ solvent}}$$

$$M.W. = \underline{mass \text{ solute}}_{molal_{soln}} \cdot Kg_{solvent} = \underline{g \text{ solute}}_{mole \text{ solute}}$$

Colligative Properties

D. Osmosis

Semipermeable membrane; water passes through membrane

- 1. Only solvent (a) allowed to pass through membrane (called osmosis)
- 2. solvent in A strikes membrane more often, solvent in B is impeded by solute (3).





- Net flow is for solvent (a) in A to migrate to B; this is referred to as osmosis.
- 4. Weight of excess volume in chamber B produce a pressure to equilibrate migration; this excess pressure is called the osmotic pressure.

Osmotic Pressure

Osmotic Pressure	13.50 Seawater contains 3.4 g NaCl per
(4) $\Pi = \underline{n R T} = M \cdot RT$	liter. Calculate the osmotic pressure of seawater at 20°C.
Where, Π = Osmotic Pressure (atm)	$\Pi = \mathbf{M} \cdot \mathbf{RT}$
n = moles	$M = 3.4 g \cdot \frac{1 \text{ mol}}{50.5} \cdot 1 \text{ L} = 0.582 \text{ M}$
T = Temp(K)	58.5 g
V = Volume (L)	Π = 0.582 <u>mol</u> • 0.0821 <u>L atm</u> • 293 K
M = Molarity (mol/L)	L mol K
R = Universal Gas Constant	
= 0.0821 <u>L· atm</u> mol·K	$\Pi = 1.4 \text{ atm}$

Osmotic pressure is the most sensitive of all colligative properties. A sugar solution of 0.0100M leads to water height of 2.35 m (7.5 ft).

Osmosis and Blood Cells

a) A red blood cell in an isotonic solution. B) The red blood cell is about to undergo hemolysis because the cell is swollen by water entering from the surrounding hypotonic solution. C) A red blood cell undergoes crenation when it is placed in a hypertonic solution



a) isotonic b)hypotonic c)hypertonic



(a) Isotonic solution (b) Hypotonic solution (c) Hypertonic solution. Osmosis and living cells. (a) A cell placed in an isotonic solution. The net movement of water in and out of the cell is zero because the concentration of solutes inside and outside the cell is the same. (b) In a hypotonic solution, the concentration of solutes outside of the cell is less than that inside. There is a net flow of water into the cell, causing the cell to swell and perhaps to burst. (c) In a hypertonic solution, the concentration of solutes outside the cell is greater than that inside. There is a net flow of water out of the cell, causing the cell to dehydrate, shrink, and perhaps die.

Dialysis



Process of cleaning blood

A solution, called the dialysate, circulates outside of the cellophane tube. This dialysate is very carefully prepared not only to be isotonic with blood but also to have the same concentrations of all the essential substances that should be left in solution in the blood. In a dialysis machine, blood from the patient runs through tubes made of a semi-porous **membrane**. Outside the tubes is a sterile solution made up of water, sugars and other components. Red and white blood cells and other important blood components are too large to fit through the pores in the membranes, but urea and salt flow through membranes into the sterile solution and are removed.



Dialysat

Colligative Property of electrolyte solution:

Property = solute concentration · constant

Colligative properties for molecular solute vs. ionic solute. Example: 1.0 m of sugar & 1.0 m of salt show different ΔT_b and ΔT_f even though the molality concentrations of the solute are identical.

Note that; $\Delta T = m \cdot K_{f,b}$ Where K is only a function of the solvent !!! Reason for the difference in colligative properties must be based on the concentration (molality, which is inherently different depending on the type of compound.

Consider the solute: Sugar ($C_6H_{12}O_6$ covalent) o 1 solute particle 0 Salt (NaCl ionic) 2 solute particle + 0 00



Fach of these beakers contains a 1 molar solution. a) 1M sugar solution has an osmolarity of 1 osm/L. b) 1M KCl solution has an osmolarity of 2 osm/L. c) 1M Na_2SO_4 solution has an osmolarity of 3 osm/L

(c)

Ionic Vs Covalent: Electrolyte Vs. Nonelectrolyte (Revisited)

Substance when dissolve can break-up to ions or stay intact. i.e., NaCl and sugar.

Type:	% ionization:	Solubility						
Electrolyte: conducts electricity.								
Strong electrolyte	100 % ionization	very soluble						
weak electrolyte	less 100% ionization	slight to very soluble						
Nonelectrolyte: Does not support electricity.								
No conduction	0 % ionization	insoluble or soluble.						

Van't Hoff factor (i)

Factor which accounts for deviation of colligative property due to electrolytic nature of solute Van't Hoff Factor (i)

Can be measured by

i = measured colligative property (from Expt)
Expected value if solute were nonelectrolyte

a) Typical non-electrolyte i.e., urea, sucrose, glucose :van' + Hoff, i = 1.
b) For electrolytic solute:

Electrolyte	ideal (i)	measured (i)	
NaCl	2	1.9	
HIO ₃	2	1.7	
MgCl ₂	3	2.7	
AICI ₃	4	3.2	

Discrepancy between real and ideal Van't Hoff (i)

Consider:

```
A|C|_3 \rightarrow A|^{+3} + 3 C|^{-1}
ideal i = 4 since four particle but in actuality
real i = 3.2
```

Why is the the measured value (3.2) lower than ideal ? -There is a strong electrostatic attraction between oppositely charged ions which causes some of the ions to be held together through ion-pair.

Note that the Van't Hoff factor parallels the ideal value when the concentration of the solution is very small. In general, large deviation from Van't Hoff factor occurs when the solute concentration is very high.

SUMMARY

All colligative property obey relationship:					
	Property	= Conc ·	Constant	•	
Property	Symbol	[Conc] [‡]	Constant		
Vapor Pressur	e ΔP	X	P°		
Boiling Point	ΔT_{b}	m	K		
Freezing Point	ΔT_{f}	m	K _f		
Osmotic Press	ure	П	Μ	R·T	

[†] Note that the concentration is dependent on the number of particles from the solute. van't Hoff factor must be considered.

Exercise

Question # 13.82:

A mixture of solid NaCl and solid sucrose, $C_{12}H_{22}O_{11}$ has an unknown composition. When 15.0 g of the mixture is dissolved in enough water to make 500 mL of solution, the solution exhibits an osmotic pressure of 6.41atm at 25°C. Determine the mass percentage of NaCl in the mixture.

What is the boiling point and melting point of the mixture? What is the molality, % mass, mole fraction and molarity of sucrose in the soln? What mass of NaCl and sucrose must be added so that the osmotic

pressure is 10 atm at 25°C?

If any of the quantity to the questions above cannot be determined, state the reason and describe what necessary information is necessary to solve the quantity.