

Physical Chemistry

Lecture 34 Colligative Properties of Solutions

Colligative properties

- ◆ Solution properties that reflect the number of particles in solution
 - Vapor-pressure lowering
 - Freezing-point depression
 - Boiling-point elevation
 - Osmotic pressure
- ◆ Historically used to determine molar properties, especially molar mass

Vapor-pressure lowering

- ◆ By Raoult's law

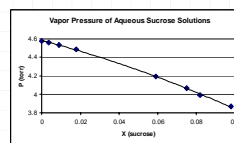
$$P_{\text{solvent}} = a_{\text{solvent}} P_{\text{solvent}}^{\bullet} = \gamma_{\text{solvent}} X_{\text{solvent}} P_{\text{solvent}}^{\bullet}$$

- ◆ By difference, solution vapor pressure is lower than that of pure solvent in a way that depends on the solute concentration (or activity)

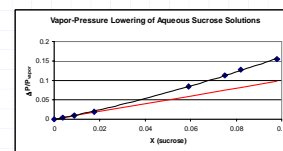
$$\begin{aligned} \Delta P_{\text{solvent}} &= (1 - a_{\text{solvent}}) P_{\text{solvent}}^{\bullet} = (1 - \gamma_{\text{solvent}} X_{\text{solvent}}) P_{\text{solvent}}^{\bullet} \\ &\equiv (1 - X_{\text{solvent}}) P_{\text{solvent}}^{\bullet} = X_{\text{solute}} P_{\text{solvent}}^{\bullet} \end{aligned}$$

- ◆ Knowing solute weight added and an independent determination of X_2 (from vapor pressure) gives a means to calculate the molar mass

Vapor-pressure lowering of aqueous sucrose solutions



X (sucrose)	P (torr)
0	4.579
0.0036	4.562
0.0089	4.536
0.0177	4.489
0.059	4.195
0.075	4.064
0.082	3.994



Freezing-point depression

- ◆ Solutions freeze below the freezing point of the pure solvent

$$\Delta T_f = T_f^{\bullet} - T_f(m)$$

- ◆ Temperature lowering depends on the concentration

$$\Delta T_f = K_f \phi(m) m$$

- ◆ Freezing-point-depression constant depends on solvent thermodynamic parameters

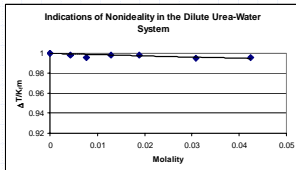
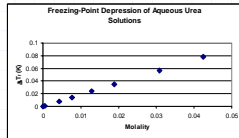
$$K_f = \frac{M_{\text{solvent}} R T_f^{\bullet 2}}{\Delta_f H}$$

Freezing-point-depression constants

Solvent	K_f (K/molal)
Water	1.86
Formic acid	2.77
Acetic acid	3.90
Benzene	5.12
Urethane	5.14
N-methylacetamide	5.77
Phenol	7.27
Diphenylamine	8.60
Benzophenone	9.80
Ethylene dibromide	11.8
Cyclohexane	20.0
Camphor	40.0

Freezing-point depression of dilute aqueous urea solutions

- In very dilute solutions, ΔT is almost a linear function of the molality, m



Molality	ΔT (K)
0	0
0.000538	0.001002
0.004235	0.007846
0.007645	0.01413
0.012918	0.02393
0.01887	0.03496
0.03084	0.05696
0.04248	0.0785

Boiling-point elevation

- Solutions boil at temperatures above the boiling point of the pure solvent
- Temperature elevation depends on solute concentration
- Boiling-point-elevation constant depends on thermodynamic parameters of the solvent
- Must extrapolate to low concentrations, as with freezing-point depression, to obtain linear behavior

$$\Delta T_b = T_b(m) - T_b^*$$

$$\Delta T_b = K_b \phi(m) m$$

$$K_b = \frac{M_{\text{solvent}} RT_b^{*2}}{\Delta_v H}$$

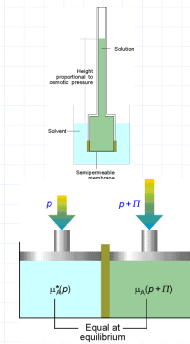
Boiling-point-elevation constants

Solvent	K_b (K/molal)
Water	0.512
Methanol	0.83
Ethanol	1.22
Acetone	1.71
Diethyl ether	2.02
Benzene	2.53
Cyclohexane	2.79
Acetic acid	3.07
n-Octane	4.02
Carbon tetrachloride	5.03

Osmotic pressure of a solution

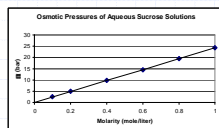
- Solvent separated by a semipermeable membrane from a solution
- Pressure drop across the membrane due to chemical-potential difference

$$\Pi = c RT \phi(c)$$



Osmotic pressure of aqueous solutions

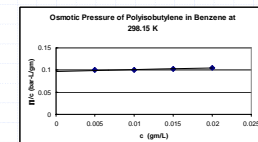
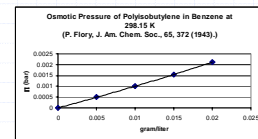
- Osmotic pressure linear in the concentration
- Could use slope of plot versus weight concentration to determine molecular weight
- In many cases, not linear in concentration
 - Must extrapolate Π/c to infinitely low concentration to determine molecular weight



Molality	Π (bar)
0.1	2.62
0.2	4.87
0.4	9.75
0.6	14.6
0.8	19.4
1	24.3

Determining polymer molar mass by osmotic pressure

- Classical method for determining molar mass of large molecules
- Limiting slope = RT/M
 - Determined from intercept of second plot
- For this isobutylene sample
 - $M = 25.3$ kg/mol



Osmotic-pressure examples

- ◆ Isotonic solutions injected into the body
 - If the solution is not the right salt concentration, the cells will expand and . .
- ◆ Salting to protect meat from bacterial spoilage
 - Bacteria on meat die because the water gets sucked out of the cells by osmosis
- ◆ Determination of polymer molar mass

Summary

- ◆ Colligative properties depend on the number of particles in solution
 - Vapor-pressure lowering
 - Freezing-point depression
 - Boiling-point elevation
 - Osmotic pressure
- ◆ Historically used to measure molar mass
- ◆ Have to extrapolate to low concentration for ideal behavior