

Lecture 8 CH131 Summer 1

Tuesday, June 4, 2019

- Relative boiling points

Ch11: Solutions

- Vapor pressure lowering, $P_1 = x_1 P_1^\circ$
- Boiling point elevation, $T_b - T_b^\circ = K_b m_c$
- Freezing point depression, $T_f^\circ - T_f = K_f m_c$
- Osmotic pressure, $\Pi = RTM_c$

Next lecture: Begin ch12: Thermodynamic processes and thermochemistry



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Relative boiling points

Effects of

- Dispersion — *always, but weak*
- Dipole-dipole interaction — *polar molecules, moderate*
- Hydrogen bonding — *N-H, O-H, F-H; strongest*

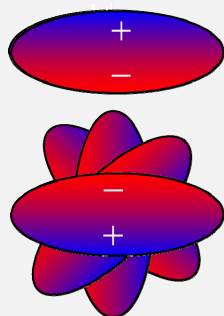


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Dipole can be attractive or repulsive

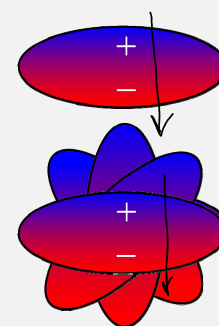


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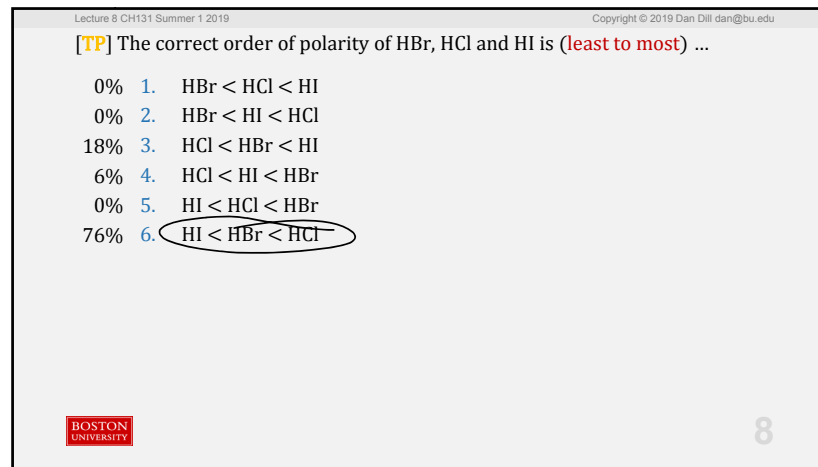
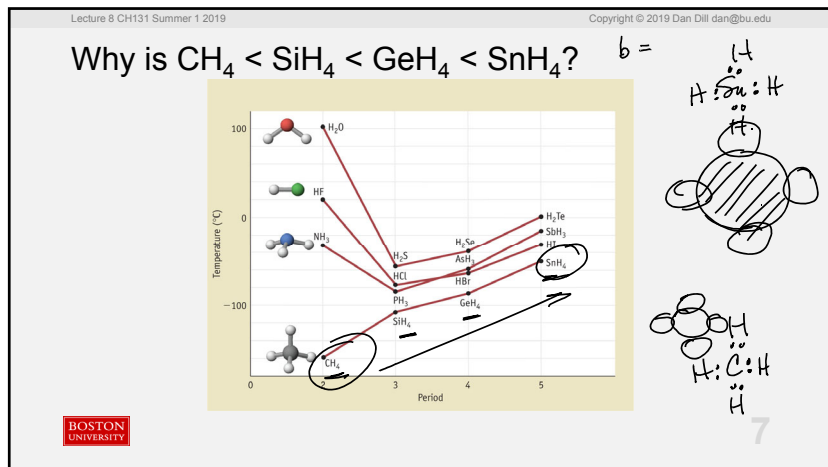
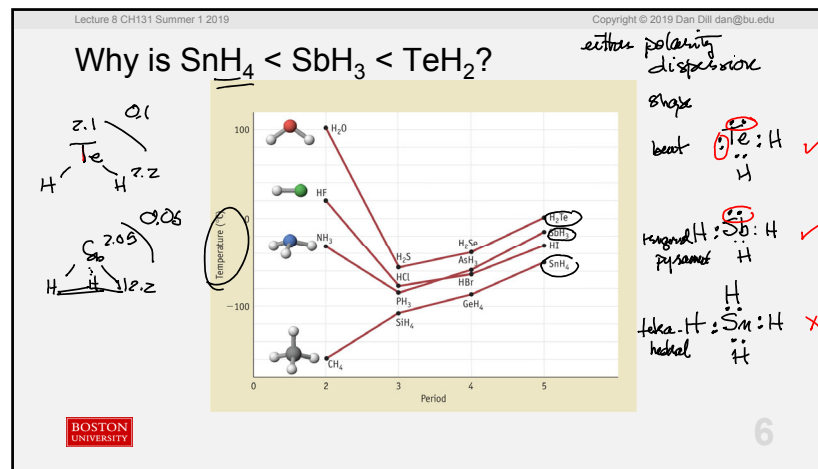
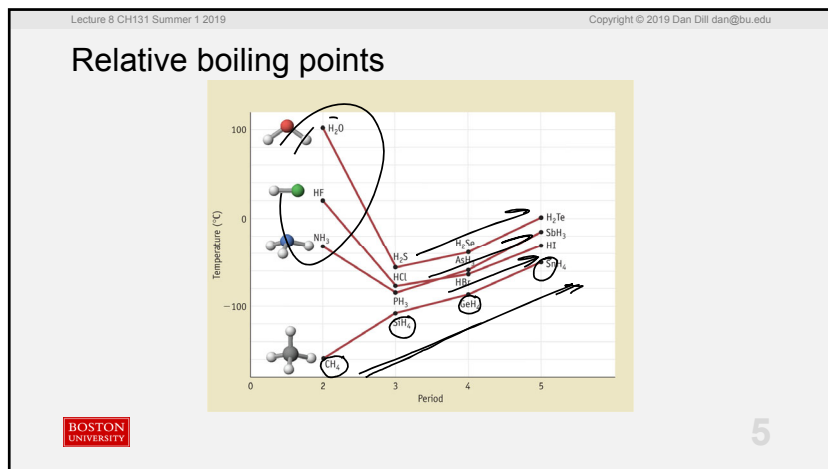
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Dispersion always attractive



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[TP] The correct order of **boiling point** of HBr, HCl and HI is (**lowest to highest**) ...

- 0% 1. HBr < HCl < HI
- 0% 2. HBr < HI < HCl
- 31% 3. HCl < HBr < HI *observed*
- 6% 4. HCl < HI < HBr
- 13% 5. HI < HCl < HBr
- 50% 6. HI < HBr < HCl *expect*

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Why is HCl < HBr < HI?

Temperature (°C) vs Period

Handwritten Lewis structures for HCl and HI showing lone pairs on the halogen atoms.

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Why is NH₃ > PH₃ < AsH₃ < SbH₃?

Temperature (°C) vs Period

Handwritten Lewis structures for SbH₃, AsH₃, PH₃, and NH₃ with arrows indicating boiling point trends.

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Why is OH₂ > FH > NH₃?

Temperature (°C) vs Period

Handwritten Lewis structures for H₂O, HF, and NH₃ with notes on hydrogen bonding and dipole-dipole interactions.

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Colligative properties

Non-volatile solute (negligible vapor pressure) ...

- lowers vapor pressure of solvent: $P_1 = x_1 P_1^0$, $\Delta P = P_1^0 - P_1 = x_2 P_1^0$

$x_1 = \frac{\text{mole fraction}}{\text{mol of solvent}} = \frac{2.8 \text{ kPa}}{0.96 \times 3 \text{ kPa}}$
 $x_1 = \frac{\text{mol of solvent}}{\text{mol of solvent} + \text{mol of solute}}$

$\text{NaCl}(s) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)$
 $1 \text{ mol} \rightarrow 1 \text{ mol} \quad 1 \text{ mol}$

$x_1 = \frac{55 \text{ mol}}{55 + 2} = 0.96$

$1 \text{ L of H}_2\text{O} = 1000 \text{ g} \times \frac{1 \text{ mol}}{18 \text{ g}} = 55 \text{ mol}$
 $1 \text{ mol of NaCl in 1 L of water}$

$P_1^0 = 3 \text{ kPa}$
 25°C

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- lowers vapor pressure of solvent: $P_1 = x_1 P_1^0$, $\Delta P = P_1^0 - P_1 = x_2 P_1^0$
- raises boiling point of solvent: $T_b - T_b^0 = i m_{\text{solute}} K_b = m_c K_b$

$i = \# \text{ of mol of solute particles in solution / mol of solute}$
 NaCl: $i = 2$
 Sugar: $i = 1$
 CaCl_2 : $i = 3$

$m = \text{molality} = \frac{\text{mol of solute}}{\text{kg of solvent}}$
 $K_b = \text{boiling point elevation constant}$

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Effect of solute on vapor pressure (Fig 16.4)

Freezing-point curve of solution
 Freezing-point curve of pure water
 Vapor-pressure curve of pure water
 Vapor-pressure curve of solution

Freezing-point depression
 Depressed freezing point
 Normal freezing point
 Boiling-point elevation
 Normal boiling point
 Elevated boiling point

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The more particles, the greater the effect

Sugar in water, 1 mol of particles per mol of sugar, so $i = 1$

NaCl in water, 2 mol of particles per mol of NaCl, so $i = 2$

Na_2SO_4 in water, 3 mol of particles per mol of Na_2SO_4 , so $i = 3$

$\text{Na}_2\text{SO}_4(s) \rightarrow 2 \text{Na}^+(aq) + \text{SO}_4^{2-}(aq)$

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Colligative properties

Non-volatile solute (negligible vapor pressure) ...

- lowers vapor pressure of solvent: $P_1 = x_1 P_1^\circ$, $\Delta P = P_1^\circ - P_1 = x_2 P_1^\circ$
- raises boiling point of solvent: $T_b - T_b^\circ = i m_{\text{solute}} K_b = m_c K_b$
- lowers freezing point of solvent: $T_f^\circ - T_f = i m_{\text{solute}} K_f = m_c K_f$

$$i m_{\text{solute}} = m_c$$

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Freezing point example

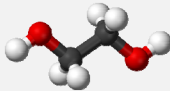
Calculate the freezing point of 3.00 kg of water to which has been added 525 g of ethylene glycol, $\text{OHC}_2\text{H}_4\text{OH}$, $K_f = 1.86 \text{ K kg/mol}$

Answer: -5.24°C

$$T_f^\circ - T_f = m_c K_f$$

$$m_c = \frac{1 * 525 \text{ g} / 62.1 \text{ g/mol}}{3.00 \text{ kg}}$$

$$T_f^\circ - T_f = \frac{(525/62.1) \text{ mol}}{3.00 \text{ kg}} * 1.86 \text{ K kg/mol}$$

$$= 5.25 \text{ K}, \quad \left. \begin{array}{l} T_f = -5.25^\circ\text{C} \\ T_f = 0^\circ\text{C} \end{array} \right\}$$


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Freezing point example again

Calculate the freezing point of 3.00 kg of water to which has been added 525 g of sodium chloride, NaCl , $K_f = 1.86 \text{ K kg/mol}$

Answer: -11.1°C

$$\text{NaCl} = 58.4 \text{ g/mol}$$

$$T_f^\circ - T_f = \frac{2 * 525 \text{ g} / 58.4 \text{ g/mol}}{3.00 \text{ kg}} * 1.86 \text{ K kg/mol}$$

$$= 11.1$$

$$T_f = -11.1^\circ\text{C}$$

$\text{NaCl(s)} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

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[TP] A non-volatile solute lowers the vapor pressure of the solvent. This in turn means the boiling point of the solvent **must** increase. Why? Because ...

- 0% 1. higher temperature is necessary to evaporate the solute
- 35% 2. the solute particles stick to the solvent particles, analogous to van der Waals a
- 65% 3. at the normal boiling point the vapor pressure of the solvent will be too low
- 0% 4. the solute vapor pressure is so low
- 0% 5. Some other reason

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[TP] The vapor pressure of water at 32 °C is 4.76 kPa. A glass of water is sealed in a 1.00 L container filled with air at 32 °C. After the water comes to equilibrium with the air in the container, the total pressure is 1 bar and there is 500. g of liquid water in the glass, and the partial pressure of water vapor in the container is ...

- 12% 1. less than 4.76 kPa
 88% 2. 4.76 kPa
 0% 3. more than 4.76 kPa
 0% 4. Further information required



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[Quiz] Then, 35.0 g of ethylene glycol if dissolved in the liquid water. After the water returns to equilibrium, the mass of the liquid water ...

- 35% 1. will have decreased
 0% 2. will be unchanged
 65% 3. will have increased
 0% 4. Further information required



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Effect of solute on vapor pressure

The vapor pressure of water at 32 °C is 4.76 kPa. A glass of water is sealed in a container filled with air at 32 °C. After the water comes to equilibrium with the air in the container, the total pressure is 1.00 bar, there is 500. g of liquid water in the glass, and the volume of the container in addition to the glass and liquid water is 1.00 L

Then 35.0 g of ethylene glycol if dissolved in the water.

Calculate change in the mass of the liquid water after it has returned to equilibrium.

Answer: The mass of liquid water will increase by 0.000673 g



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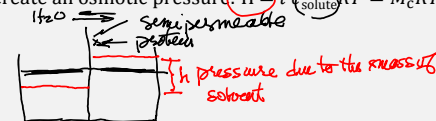
Colligative properties

Non-volatile solute (negligible vapor pressure) ...

- lowers vapor pressure of solvent: $P_1 = x_1 P_1^0$, $\Delta P = P_1^0 - P_1 = x_2 P_1^0$
- raises boiling point of solvent: $T_b - T_b^0 = i m_{\text{solute}} K_b = m_c K_b$
- lowers freezing point of solvent: $T_f^0 - T_f = i m_{\text{solute}} K_f = m_c K_f$

If solute cannot pass through a membrane ...

- the solvent will create an osmotic pressure: $\Pi = i \frac{M_{\text{solute}}}{V_{\text{solution}}} RT = M_c RT$



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Roadmap of osmotic pressure calculations

Osmotic pressure $\Pi = i c R T$. $c = \frac{\text{mol of solute}}{\text{L of solution}} = \text{molarity}$

1. Use measured osmotic pressure, Π , and temperature, T , to **evaluate concentration** $c = \Pi / (i R T)$, in mol/L.
2. Use cell volume to express concentration in terms of **moles**, $n = c V$.
3. Use solute mass to calculate **molar mass**, $M = \text{mass}/n$.

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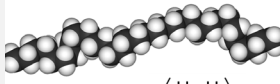
Osmotic pressure $\Pi = i c R T$

1.40 g of polyethylene ($i = 1$) dissolved in 100. mL of benzene generates an osmotic pressure of 0.248 kPa at 25 °C. Calculate the molar mass of the polyethylene.

1. Calculate the concentration...

$$c = \frac{\Pi}{R \cdot T} = \frac{248 \text{ Pa} \cdot \text{K} \cdot \text{mol}}{8.314 \text{ Pa} \cdot 10^3 \cdot \text{L} \cdot 298 \text{ K}}$$

Handwritten: $\frac{1}{\text{K mol}}$

$$= 1.00 \times 10^{-4} \text{ mol/L}$$


$$\left(\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{H} \quad \text{H} \end{array} \right)_n$$

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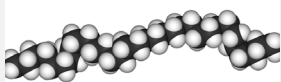
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Osmotic pressure $\Pi = i c R T$

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1. Calculate the concentration...
 $1.00 \times 10^{-4} \text{ mol/L}$



$$\left(\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{H} \quad \text{H} \end{array} \right)_n$$

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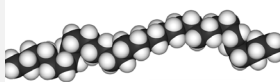
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Osmotic pressure $\Pi = i c R T$

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1. Calculate the concentration...
 $1.00 \times 10^{-4} \text{ mol/L}$
2. Calculate the moles...

$$\frac{1.00 \times 10^{-4} \text{ mol}}{\text{L}} \times \frac{100 \text{ mL} \times 1 \text{ L}}{1000 \text{ mL}}$$

$$= 1.00 \times 10^{-5} \text{ mol}$$


$$\left(\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{H} \quad \text{H} \end{array} \right)_n$$

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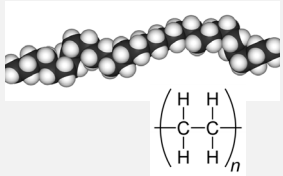
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Osmotic pressure $\Pi = i c R T$

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1. Calculate the concentration...
 $1.00 \times 10^{-4} \text{ mol/L}$
2. Calculate the moles...
 $1.00 \times 10^{-5} \text{ mol}$



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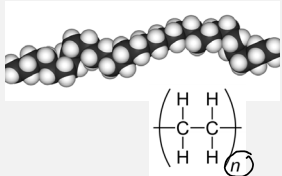
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Osmotic pressure $\Pi = i c R T$

1.40 g of polyethylene ($i = 1$) dissolved in 100. mL of benzene generates an osmotic pressure of 0.248 kPa at 25 °C. Calculate the molar mass of the polyethylene.

1. Calculate the concentration...
 $1.00 \times 10^{-4} \text{ mol/L}$
2. Calculate the moles...
 10^{-5} mol
3. Calculate the molar mass...
 $\frac{1.40 \text{ g}}{1.00 \times 10^{-5} \text{ mol}} = 1.40 \times 10^5 \text{ g/mol}$ *Handwritten note: How many n?*



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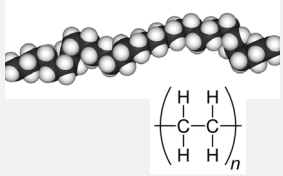
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Osmotic pressure $\Pi = i c R T$

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1. Calculate the concentration...
 $1.00 \times 10^{-4} \text{ mol/L}$
2. Calculate the moles...
 10^{-5} mol
3. Calculate the molar mass...
 $1.40 \times 10^5 \text{ g/mol}$



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