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[TP] CO<sub>2</sub> gas at 1 atm, 25°C is heated to 1 atm, 35°C; then compressed to 75 atm, 35°C; then cooled to 75 atm, 25°C; then expanded to 65 atm, 25°C. At this point, the CO<sub>2</sub> will have undergone a phase transition ...

64% 1. once  
27% 2. twice  
9% 3. three times  
0% 4. None of the above  
0% 5. Not sure

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Lecture 9 CH131 Summer 1 2021  
Wednesday, June 9, 2021

- Phase diagrams

Chapter 11: 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,  $\Pi = RT M_c$

Next: Complete: Osmotic pressure; Ch12: Thermodynamic processes

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[TP] CO<sub>2</sub> gas at 1 atm, 25°C is heated to 1 atm, 35°C; then compressed to 75 atm, 35°C; then cooled to 75 atm, 25°C; then expanded to 65 atm, 25°C. At this point, the CO<sub>2</sub> will have undergone a phase transition ...

85% 1. once  
15% 2. twice  
0% 3. three times  
0% 4. None of the above  
0% 5. Not sure

No phase transitions!

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Supercritical fluid  $1 \text{ MPa} = 10 \text{ kPa} = 10 \text{ atm}$

Compressing a gas while keeping temperature constant will bring the gas particles closer together, making the gas denser.

7.3 MPa

0.1 MPa

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### Supercritical fluid

Heating a liquid while keeping pressure constant will move the liquid particles farther apart, making the liquid less dense.

72.9 atm  
5.1 atm  
1 atm

Pressure (not to scale)

78.5 °C -56.7 °C 31 °C  
Temperature (not to scale)

B Triple point O Critical point C Supercritical fluid

Solid Liquid Gas

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### Supercritical fluid

Above the critical pressure and critical temperature and the dense gas is indistinguishable from the less dense liquid.

72.9 atm  
5.1 atm  
1 atm

Pressure (not to scale)

78.5 °C -56.7 °C 31 °C  
Temperature (not to scale)

B Triple point O Critical point C Supercritical fluid

Solid Liquid Gas

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### Supercritical fluid

This is called the **supercritical region** and the substance there is called a **supercritical fluid**.

72.9 atm  
5.1 atm  
1 atm

Pressure (not to scale)

78.5 °C -56.7 °C 31 °C  
Temperature (not to scale)

B Triple point O Critical point C Supercritical fluid

Solid Liquid Gas

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### Supercritical fluid

Converting a liquid to a gas **across a phase boundary** always results in **abrupt density change**.

72.9 atm  
5.1 atm  
1 atm

Pressure (not to scale)

78.5 °C -56.7 °C 31 °C  
Temperature (not to scale)

B Triple point O Critical point C Supercritical fluid

Solid Liquid Gas

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### Supercritical fluid

Paths through the **supercritical region** results instead in **smooth changes in density**, and so a liquid can be converted to a gas **without abrupt density change**.

Pressure (not to scale)  
72.9 atm  
5.1 atm  
1 atm

Temperature (not to scale)  
-78.5 °C  
-56.7 °C  
31 °C

Boston University

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### Supercritical fluid

Supercritical transition of liquid Cl<sub>2</sub> ...  
<http://goo.gl/xo2jU/>

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### Phase diagrams are specific to each substance

Water

CO<sub>2</sub>

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### H<sub>2</sub>O phase diagram

Is density of liquid H<sub>2</sub>O greater than that of solid H<sub>2</sub>O? ||  
How can we tell?

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## Colligative properties *Ch 11: Solutions.*

Effect of non-volatile solute (negligible vapor pressure) ...

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## Colligative properties

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

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

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## Colligative properties

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

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

$x_1$  is the mole fraction of the solvent:  $x_1 = \frac{n_1}{n_1 + n_2}$   *$n_1 = \text{moles of solvent}$*

Pure solvent means  $x_1 = 1$  and so  $P_1 = P_1^\circ$

$x_2$  is the mole fraction of the solute:  $x_2 = \frac{n_2}{n_1 + n_2} = 1 - x_1$   *$n_2 = \text{moles of solute}$*

This is known as Raoult's law.

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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:  $T_b - T_b^\circ = i m_{\text{solute}} K_b = m_c K_b$

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## Colligative properties

$\text{NaCl}(s) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)$   
 *$i=2$ . Van't Hoff factor*

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:  $T_b - T_b^\circ = i m_{\text{solute}} K_b = m_c K_b$   *$i m_{\text{solute}} = m_c$*

$m_{\text{solute}}$  is known as a **molality**, the **moles of the solute per kg of solvent**.

$m_c$  is known as the **colligative molality** (more shortly)

Be careful to distinguish these from

**molarity  $M$** , the **moles of solute per liter of solution**.

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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:  $T_b - T_b^\circ = i m_{\text{solute}} K_b = m_c K_b$  *b.p. elevation constant*
- lowers freezing point of solvent:  $T_f^\circ - T_f = i m_{\text{solute}} K_f = m_c K_f$  *f.p. depression constant*

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## Effect of solute on vapor pressure

The vapor pressure of water at 32°C is 4.76 kPa. Calculate the vapor pressure after 68.0 g of ethylene glycol ( $M = 62.07$ ) is dissolved in 500. g of water at 32°C.

$P_1 = x_1 P_1^\circ$ ,  $\Delta P = P_1^\circ - P_1 = x_2 P_1^\circ$  (Raoult's law) *Raoult's law*

Answer: 4.58 kPa

$$x_1 = \frac{\text{moles of H}_2\text{O}}{\text{moles of H}_2\text{O} + \text{moles of gly}} = \frac{m_{\text{H}_2\text{O}}}{m_{\text{H}_2\text{O}} + m_{\text{gly}}}$$

$$P_1 = x_1 P_1^\circ$$
  

$$P_1^\circ = 4.76 \text{ kPa}$$

$$m_{\text{H}_2\text{O}} = 500. \text{ g} \times \frac{1 \text{ mole}}{18.0 \text{ g}}$$

$$m_{\text{gly}} = 68.0 \text{ g} \times \frac{1 \text{ mole}}{62.07 \text{ g}}$$

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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<sub>2</sub>SO<sub>4</sub> in water, 3 mol of particles per mol of Na<sub>2</sub>SO<sub>4</sub>, so  $i = 3$

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

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### Effect of solute on vapor pressure

$\text{Na}_3\text{PO}_4(s) \rightarrow 3\text{Na}^+(aq) + \text{PO}_4^{3-}(aq)$

The vapor pressure of water at 32°C is 4.76 kPa. Calculate the vapor pressure after 68.0 g of  $\text{Na}_3\text{PO}_4$  ( $M = 163.94$ ) is dissolved in 500. g of water at 32°C.

$P_1 = x_1 P_1^\circ$ ,  $\Delta P = P_1^\circ - P_1 = x_2 P_1^\circ$  (Raoult's law)

Answer: 4.49 kPa (not 4.69 kPa)

using  $i=4$   $\chi_2 = 1$

$X_i = \frac{m_i}{m_i + m_j}$   $i=4$

$m_2 = 4 \times \text{mole of } \text{Na}_3\text{PO}_4$

$m_{\text{Na}_3\text{PO}_4} = 68.0 \text{ g} \times \frac{1 \text{ mol}}{163.94 \text{ g}}$

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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,

- (1) the total pressure is 100.00 kPa,
- (2) there is 500. g of liquid water in the glass,
- (3) and the partial pressure of water vapor in the container is ...

25% 1. less than 4.76 kPa  
 58% 2. 4.76 kPa  
 0% 3. more than 4.76 kPa  
 17% 4. Further information required  
 0% 5. Not sure

$V=1 \text{ L}$   
 $P = 100.00 \text{ kPa}$   
 $= P_2 + P_{\text{N}_2} + P_{\text{H}_2\text{O}}$   
 500 g  $\text{H}_2\text{O}(l)$

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[TP] Then, 35.0 g of ethylene glycol is dissolved in the liquid water. After the water returns to equilibrium with its vapor, the mass of the liquid water ...

- 0% 1. will have decreased
- 0% 2. will be unchanged
- 100% 3. will have increased
- 0% 4. Further information required
- 0% 5. Not sure

$P_{\text{H}_2\text{O}} = P_{\text{H}_2\text{O}}^\circ$

pure water

35.0g of ethyl

$X_{\text{H}_2\text{O}} < 1$

$P_{\text{H}_2\text{O}} = X_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^\circ$

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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 ...

- 8% 1. higher temperature is necessary to evaporate the solute
- 0% 2. the solute particles stick to the solvent particles, analogous to van der Waals  $a$
- 38% 3. at the normal boiling point the vapor pressure of the solvent will be too low
- 8% 4. the solute vapor pressure is so low
- 0% 5. Some other reason
- 46% 6. Not sure //

$P_{\text{H}_2\text{O}}^\circ$

atm

4.76

32°C

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### Effect of solute on vapor pressure (Fig 16.4)

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### Effect of solute on vapor pressure (Fig 16.4)

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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**,  $\text{OHC}_2\text{H}_4\text{OH}$  ( $M = 62.07$ ),  $K_f = 1.86 \text{ K kg/mol}$

Freezing point depression,  $T^\circ_f - T_f = K_f m_c$

Answer: **5.24 °C**

$i \Delta T_f = i m K_f$

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

$i \Delta T_f = 1 \times \frac{525 \text{ g}}{62.07 \text{ g/mol}} \times 1.86 \frac{^\circ\text{C kg}}{\text{mol}}$

$m = \frac{525 \text{ g}}{62.07 \text{ g/mol}} \times \frac{1 \text{ mol}}{3.00 \text{ kg}} = 2.81 \text{ mol/kg}$

$\Delta T_f = 1 \times 2.81 \text{ mol/kg} \times 1.86 \frac{^\circ\text{C kg}}{\text{mol}} = 5.24 \text{ }^\circ\text{C}$

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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**,  $\text{NaCl}$  ( $M = 58.44$ ),  $K_f = 1.86 \text{ K kg/mol}$

Freezing point depression,  $T^\circ_f - T_f = K_f m_c$

Answer: **+11.1 °C**

$i = 2$

$^\circ\text{C} = \text{K} - 273$

$T_1 = ^\circ\text{C}_1 = \text{K}_1 - 273$

$T_2 = ^\circ\text{C}_2 = \text{K}_2 - 273$

$T_2 - T_1 = ^\circ\text{C} - ^\circ\text{C}$

$= (\text{K}_2 - 273) - (\text{K}_1 - 273)$

$= \text{K}_2 - \text{K}_1 - 273 + 273$

$i \Delta T_{fp} = i m K_f$

$m = \frac{\text{mol of NaCl}}{3.00 \text{ kg}}$

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### Differing vapor pressures → osmotic pressure

We have seen that solutes cause condensation of water vapor.

Initial state

Several days later

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### Differing vapor pressures → osmotic pressure

The same differing vapor pressure leads to osmotic pressure.

Initial state

Equilibrium state

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### Differing vapor pressures → osmotic pressure

The same differing vapor pressure leads to osmotic pressure.

The flow stops when the pressure ( $\Pi = Dgh$ ) due to the column height difference ( $h$ ) is equal to the vapor pressure difference ( $\Pi = P_1^o - P_1$ ).

This difference is called **osmotic pressure** and is given by

$$P_1^o - P_1 = \Pi = i c_{\text{solute}} RT = M_c RT$$

$M_c = \text{colligative molarity}$

Initial state

Equilibrium state

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### CMW recipe for osmotic pressure calculations

Osmotic pressure  $\Pi \approx i c_{\text{solute}} RT \approx M_c RT$ .

- C:** Use measured osmotic pressure,  $\Pi$ , and temperature,  $T$ , to **evaluate concentration**,  $c_{\text{solute}} = \Pi / (i R T)$ , in mol/L.
- M:** Use cell volume to express concentration in terms of **moles**,  $n = c_{\text{solute}} V$ .
- W:** Use solute mass to calculate **molecular weight**,  $M = \text{mass} / n$ .

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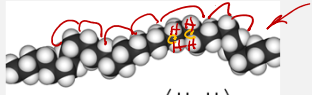


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Osmotic pressure  $\Pi = i c_{\text{solute}} R T$

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. ( $R = 8.3145 \times 10^3 \frac{\text{L Pa}}{\text{K mol}}$ )

1. C: Calculate the concentration...



$$\begin{array}{c} \text{H} & \text{H} \\ | & | \\ \text{---C---C---} \\ | & | \\ \text{H} & \text{H} \end{array}_n$$

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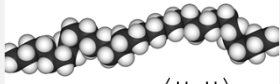
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Osmotic pressure  $\Pi = i c_{\text{solute}} R T$

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. ( $R = 8.3145 \times 10^3 \frac{\text{L Pa}}{\text{K mol}}$ )

1. C: Calculate the concentration...

$$c_{\text{solute}} = \frac{\Pi}{RT} = \frac{0.248 \times 10^3 \text{ Pa}}{8.31 \times 10^3 \frac{\text{L Pa}}{\text{K mol}} \times 298 \text{ K}}$$


$$\begin{array}{c} \text{H} & \text{H} \\ | & | \\ \text{---C---C---} \\ | & | \\ \text{H} & \text{H} \end{array}_n$$

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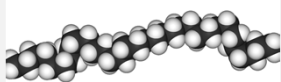
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Osmotic pressure  $\Pi = i c_{\text{solute}} R T$

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

2. M: Calculate the moles...

$$1.00 \times 10^{-4} \frac{\text{mol}}{\text{L}} \times 0.100 \text{ L} = 1.00 \times 10^{-5} \text{ mol}$$


$$\begin{array}{c} \text{H} & \text{H} \\ | & | \\ \text{---C---C---} \\ | & | \\ \text{H} & \text{H} \end{array}_n$$

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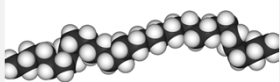
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Osmotic pressure  $\Pi = i c_{\text{solute}} R T$

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. ( $R = 8.3145 \times 10^3 \frac{\text{L Pa}}{\text{K mol}}$ )

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

2. M: Calculate the moles...  
 $10^{-5} \text{ mol}$



$$\begin{array}{c} \text{H} & \text{H} \\ | & | \\ \text{---C---C---} \\ | & | \\ \text{H} & \text{H} \end{array}_n$$

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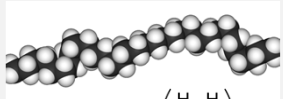
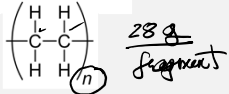
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### Osmotic pressure $\Pi = i c_{\text{solute}} R T$

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. ( $R = 8.3145 \times 10^3 \frac{\text{L Pa}}{\text{K mol}}$ )

- C:** Calculate the concentration...  
 $1.00 \times 10^{-4} \text{ mol/L}$
- M:** Calculate the moles...  
 $10^{-5} \text{ mol}$
- W:** Calculate the molecular weight ...

$$\frac{1.40 \text{ g}}{10^{-5} \text{ mol}} = 1.40 \times 10^{+5} \text{ g/mol}$$

$\frac{1.40 \times 10^5 \text{ g/mol}}{28 \text{ g/segment}}$

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