

# CH 302 Unit 1 Review 2

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SOLUTIONS AND COLLIGATIVE PROPERTIES

# Physical Equilibrium Road Map

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**The theme of Unit One is the thermodynamics of phase changes and how creating a solution increases the stability of the liquid phase**

1. Quantifying phase changes using enthalpy, entropy, and free energy
2. Vapor Pressure: concepts, calculations, and its relationship to boiling and IMFs
3. Phase Diagrams: identifying the most stable phase of a substance at a given temperature and pressure
4. Thermodynamics associated with creating a solution
  - Does it dissolve?
  - Temperature dependence of dissolution
5. Colligative Properties: the increased stability of a solution changes the physical properties accordingly
  - Vapor pressure lowering, freezing point depression, boiling point elevation, and osmotic pressure



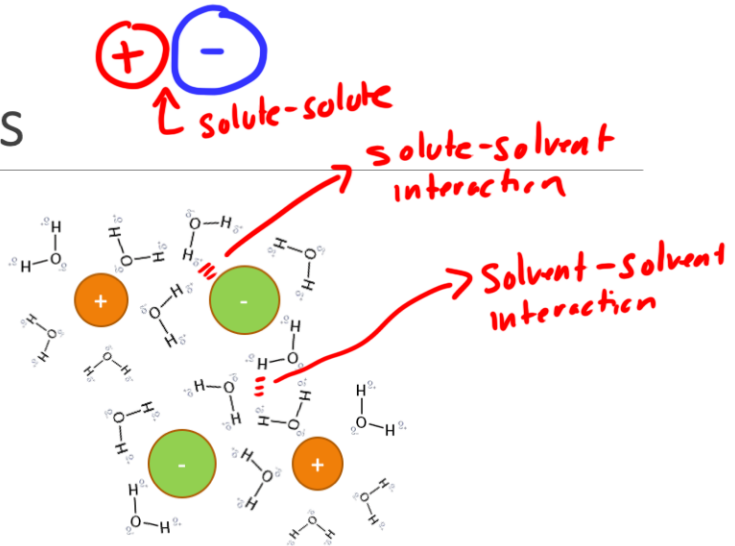
# Solutions

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DEFINITIONS, CONCENTRATION UNITS, LIKE-DISSOLVES-LIKE,  
ENTHALPY OF A SOLUTION

# Reviewing Solutions

- A solution is a homogenous mixture consisting of a solute (can be gas, liquid, or solid) dissolved in a liquid solvent.
- Whether a solute dissolves in a liquid solvent or not depends on basic thermodynamics: if the solution is more stable than the solute + solvent individually, the free energy of solution will be negative.



What does this mean? It means that if you dissolve a solute into a solvent, you are making a solution with a lower free energy.

$$\Delta G = \Delta H - T\Delta S \quad (+) \rightarrow \text{entropy-driven}$$

# Enthalpy of Salt Solution

$$\Delta H_{\text{solution}} = \Delta H_{\text{lattice}} + \Delta H_{\text{solvation}}$$

$\neq$

Always +

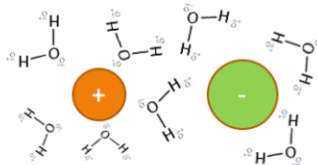
Always -

Step one: Lattice Energy breaks apart ionic solute (bonds breaking)

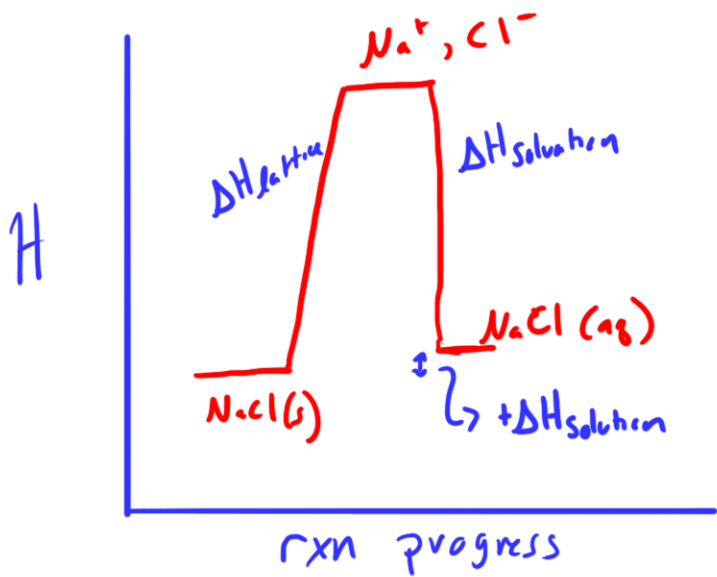


+  $\Delta H_{\text{lattice}}$  (positive value)  
Bonds breaking = endothermic

Step two: Solvation Energy is released when solvent dissolves positive and negative charges (bonds forming)



+  $\Delta H_{\text{solvation}}$  (negative value)  
Bonds forming = exothermic



\* if  $|\Delta H_{\text{lattice}}| > |\Delta H_{\text{solvation}}|$ :

$$\Delta H_{\text{solution}} > 0$$

\* if  $|\Delta H_{\text{lattice}}| < |\Delta H_{\text{solvation}}|$ :

$$\Delta H_{\text{solution}} < 0$$

# Thermodynamics of Solution



## Salt Dissolving in Water

$$\Delta H_{\text{solution}} = \Delta H_{\text{lattice energy}} + \Delta H_{\text{solvation}} \approx 0^*$$

$$\left[ \Delta S_{\text{solution}} = S_{\text{(aqueous)}} - S_{\text{(solid)}} = \text{Positive} \right]$$

$$\Delta G_{\text{solution}} = \Delta H_{\text{solution}} - T\Delta S_{\text{solution}} = \text{Negative}$$

$$(-) \quad \Delta G_{\text{solution}} = (0^*) - T(+)$$

Dissolution of salt is typically an entropy-driven process, favored at high temperatures

## Gas Dissolving in Water

$$\Delta H_{\text{solution}} = \Delta H_{\text{lattice energy}} + \Delta H_{\text{solvation}} = \text{Negative} \text{ exo}$$

$$\Delta S_{\text{solution}} = S_{\text{(aqueous)}} - S_{\text{(solid)}} = \text{Negative}$$

↳ unfavourable

$$\Delta G_{\text{solution}} = \Delta H_{\text{solution}} - T\Delta S_{\text{solution}} = \text{Negative}$$

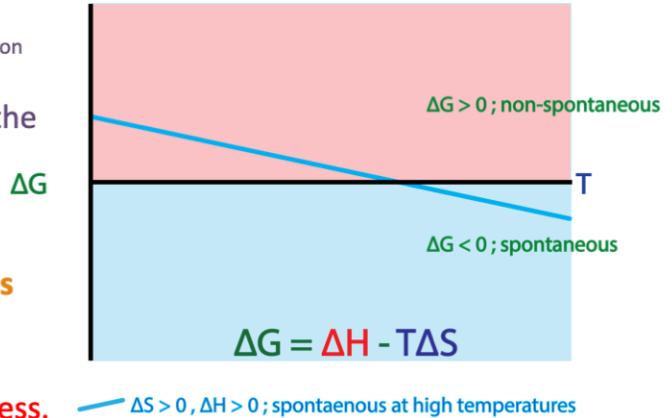
$$\Delta G_{\text{solution}} = (-) - T(-)$$

Dissolution of gas is typically an enthalpy-driven process, favored at low temperatures and high pressures

\*  $\Delta H_{\text{solution}}$  is 0 for an ideal solution. For your typical salts, it is slightly endothermic. There are examples of both endothermic AND exothermic solid dissolution processes

# Free Energy of a Salt Dissolving in Water: $+\Delta H$ , $+\Delta S$

- The majority of salts have a positive  $\Delta H_{\text{solution}}$
- In this class, we focus on situations where the  $\Delta S_{\text{solution}}$  is positive (solid to aqueous is a positive entropy change)
- **Dissolution is favored at high temperatures for all salts dissolving in water.**
- **Why? Dissolution is an entropy driven process.**

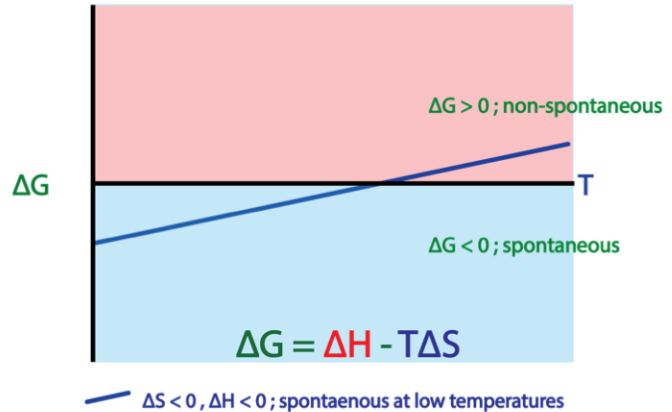






## Free Energy of a Gas Dissolving in Water: $-\Delta H$ , $-\Delta S$

- For a gas dissolving in liquid, the reaction is exothermic ( $\Delta H_{\text{solution}} < 0$ ) because there is **no lattice energy** and a negative solvation energy.
- There is a negative change in entropy ( $\Delta S < 0$ ) because you are going from gas to aqueous
- Therefore, dissolution is favored at low temperatures. Henry's Law also states that gas dissolution is favored at high pressures.
- **Why? Dissolution of a gas is an enthalpy driven process!**



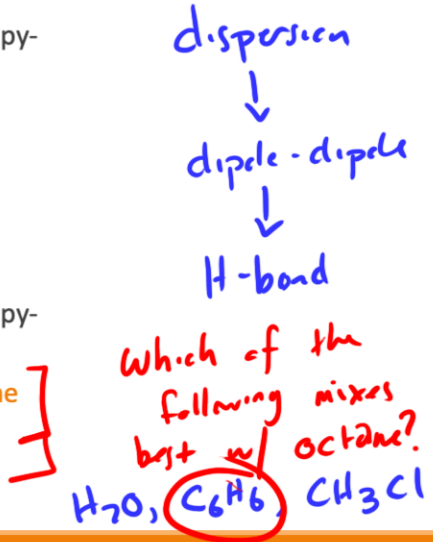
# Liquids Mixing (wrong title)

Like the dissolution of a solid, liquids mixing is typically an entropy-driven process, favored at high temperatures:

$$\Delta G_{\text{solution}} = \Delta H_{\text{solution}} - T\Delta S_{\text{solution}} = \text{Negative}$$
$$\Delta G_{\text{solution}} = (+) - T(+)$$

Like the dissolution of a solid, liquids mixing is typically an entropy-driven process. There are two important points here:

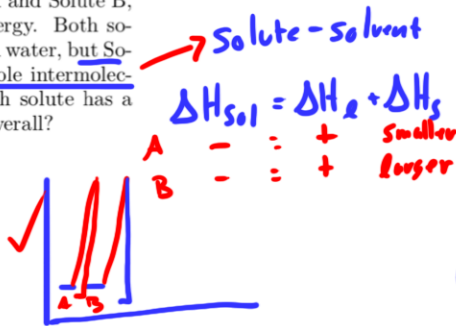
1. Enthalpy is important when mixing two liquids. Matching the IMF's of two liquids MINIMIZES the  $\Delta H$  term.
2. Increasing temperature increases solubility



# Dissolution Concept Checks

Consider two solutes, Solute A and Solute B, that have the same lattice energy. Both solutes dissolve exothermically in water, but Solute A creates weaker ion-dipole intermolecular forces with water. Which solute has a more exothermic dissolution overall?

1. Not enough information
2. Solute A
3. They are equal
4. Solute B



In the lab, you have a collection of liquids you keep under the fume hood: water, isopropyl alcohol, chloroform, diethyl ether, and dichloromethane. If you want to make a binary liquid, which of the following explains the two steps you can take to make sure this process occurs spontaneously? Note: all of these liquids will mix endothermically if they are miscible.

1. Maximize  $\Delta H_{sol}$  by selecting two liquids with similar intermolecular forces; Increase the temperature
2. Maximize  $\Delta S_{sol}$  by selecting two liquids with similar intermolecular forces; Minimize  $\Delta H_{sol}$  by decreasing the temperature
3. Minimize  $\Delta H_{sol}$  by selecting two liquids with similar intermolecular forces; Increase the temperature
4. Select two liquids with very different intermolecular forces; Decrease the temperature
5. Minimize  $\Delta H_{sol}$  by selecting two liquids with similar intermolecular forces; Decrease the temperature

1)  $T \uparrow$

2)  $\Delta H$   
Small  
↓  
like-dissolves-like

# Colligative Properties

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DECREASING THE FREE ENERGY RESULTS IN A MORE STABLE LIQUID SOLUTION

Solvent-specific  $\rightarrow P_A^{\circ}, K_f, K_b$  Solute-unspecific  
Concentration-specific  
 $\rightarrow i \cdot m$

## Colligative Property Summary

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Vapor Pressure Lowering (Raoult's Law):

- Solves for **the new vapor pressure** ( $P_A$ ) of a solution, based on the **mole fraction of the solvent** ( $X_A$ )
  - $P_A = X_A P_A^{\circ}$

Freezing Point Depression:

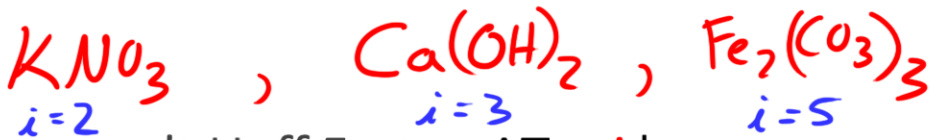
- Solves for the **negative change in the freezing point** ( $\Delta T_f$ ), based on the **molality of the solute** ( $m$ )
  - $\Delta T_f = i k_f m$

Boiling Point Elevation:

- Solves for **the positive change in the boiling point** ( $\Delta T_b$ ), based on **the molality of the solute** ( $m$ )
  - $\Delta T_b = i k_b m$

Osmotic Pressure:

- Solves for the pressure exerted by a fluid to restore osmotic equilibrium, based on **the molarity of the solute** ( $M$ )
  - $\Pi = iMRT$



van't Hoff Factor,  $\Delta T_f = i k_f m$

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- Colligative properties depend on the number of effective solute concentration, which can be more than just the given concentration.
- Why? in the case of electrolytes (salts), colligative properties depend on the concentration of ions rather than the initial amount of the solid salt.
- We make this "correction" by using the Van't Hoff Factor (i) in our colligative properties calculations
- The Van't Hoff Factor is the total number of solute species in solution divided by the moles of solute dissolved

effective  $m$   
↓  
 $i \cdot m$

# Introduction to Solutions

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- Some of the concentration units you should know for solutions are (gchem fundamentals chapter):

- **Molarity (M): moles of solute per liter solution (mol/L)**

$$M = \frac{\text{mol}}{L}$$

- **Molality: moles of solute per kilogram solvent (mol / kg)**

$$m = \frac{\text{mol}}{\text{kg}}$$

- **Mole Fraction: moles of a particular species per total moles of solution / mixture (dimensionless)**

$$X_A = \frac{\text{mol}_A}{\text{mol}_{\text{total}}}$$

$A+B$

$$\frac{\text{moles A}}{\text{moles B} + \text{moles A}}$$

# Colligative Properties: Units

$\rightarrow 2 K^+ \rightarrow 1 CrO_4^{2-}, i=3$

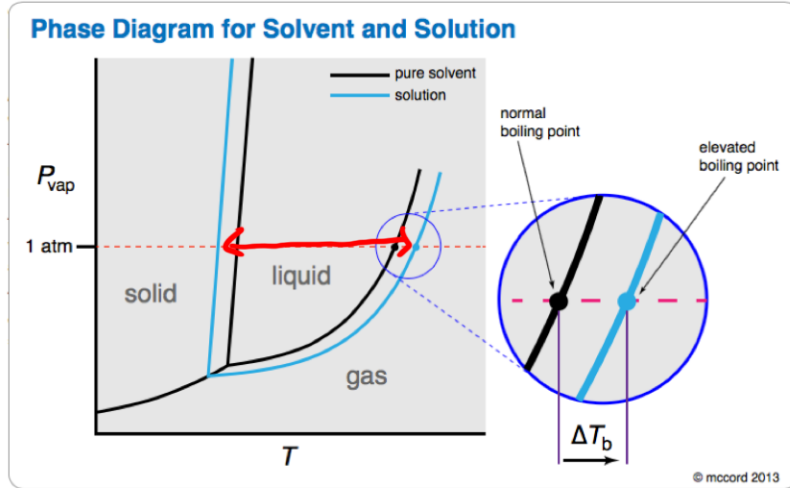
You have 0.2 moles of  $K_2CrO_4$  in 834 mL aqueous solution. What is the effective molarity of ions in this solution?

$$\frac{\text{mol solute}}{\text{L solution}} = \frac{0.2 \text{ mol solute} \times \frac{3 \text{ mol total species}}{\text{mol solute dissolved}}}{0.834 \text{ L}} = 0.719 \text{ M}$$



# Boiling Point Elevation, Freezing Point Depression

- Creating a solution from a pure solvent lowers the free energy of your substance in the liquid phase.
- This has four effects that we call the **colligative properties**
- You can see in the diagram to the right that the liquid phase is favored in a larger range of temperatures



# Boiling Point Elevation, Freezing Point Depression

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- Using the following equations, you are solving for the change in the freezing point or boiling point. **Remember: you are solving for a change ( $\Delta T_f$  is always negative,  $\Delta T_b$  is always positive) and you are NOT solving for the final temperatures.**

## Freezing Point Depression:

Solves for the **negative change in the freezing point** ( $\Delta T_f$ ), based on the **molality of the solute** ( $m$ )

$$\Delta T_f = i k_f m$$

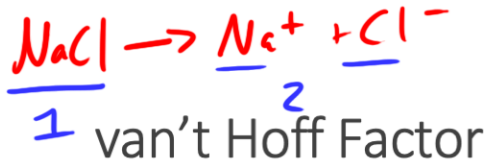
$$0^\circ - (+)$$

## Boiling Point Elevation:

Solves for the **positive change in the boiling point** ( $\Delta T_b$ ), based on the **molality of the solute** ( $m$ )

$$\Delta T_b = i k_b m$$

$$(+)+ 100^\circ\text{C}$$



$\Delta T_b = i k_b m$   
same

Which of the following solutions has the same boiling point as 0.6 M Sucrose?

- organic,  $i = 1$
- a.  $0.6 \text{ M NaCl} \times 2 = \underline{1.2 \text{ M}}$
- b.  $0.2 \text{ M Na}_2\text{SO}_4 \times 3 = \underline{0.6 \text{ M}}$

Which of the following solutions has the highest boiling point?

- a.  $0.6 \text{ M NaCl} \times 2$
- b.  $0.2 \text{ M Na}_2\text{SO}_4 \times 3$

# Vapor Pressure Lowering

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- Vapor Pressure is **lower when a liquid is more stable**. Therefore, it should make sense that when you create a lower free energy solution from a pure solvent, the vapor pressure goes down.
- **Mathematically, vapor pressure lowering looks like this:**

## Vapor Pressure Lowering (Raoult's Law):

Solves for **the new vapor pressure** ( $P_A$ ) of a solution, based on the **mole fraction of the solvent** ( $X_A$ ) and the vapor pressure of the pure solvent ( $P^\circ_A$ )

$$P_A = X_A P^\circ_A$$

You **WILL** have to account for electrolytes in the “total moles” of this mole fraction term, even though you don’t see a van’t Hoff Factor here.

# Vapor Pressure Lowering – Mixing Volatile Liquids

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- The vapor pressure of a binary liquid (A + B) must take into account the vapor pressure of both liquids.
- **Mathematically, this follows Dalton's Law of Partial Pressures:**

**Vapor Pressure Lowering (Raoult's Law) + Dalton's Law:**

$$P_A = X_A P_A^\circ$$

$$P_B = X_B P_B^\circ$$

$$P_{\text{total}} = P_A + P_B$$

# Vapor Pressure Lowering: Mixing Liquids

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Consider two liquids, A and B. Liquid A has a vapor pressure of 200 torr. Liquid B has a vapor pressure of 400 torr. Calculate the vapor pressure when the concentrations of A and B are equal.

$$X_A = X_B = 0.5$$

Vapor Pressure Lowering (Raoult's Law):

Solves for **the total vapor pressure**

$$P_A = X_A P_A^\circ$$

$$P_B = X_B P_B^\circ$$

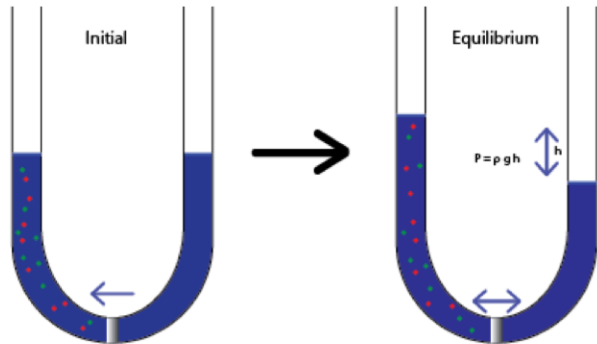
$$P_{\text{total}} = P_A + P_B$$

$$\begin{aligned} & (0.5)(200 \text{ Torr}) \\ & + (0.5)(400 \text{ Torr}) \\ & = 300 \text{ Torr} \end{aligned}$$

Dalton's Law  
(CH301)

# Osmotic Pressure

- **Osmotic pressure is the pressure exerted by a fluid to restore osmotic equilibrium.**
- The basic idea is that fluid will flow from the less concentrated to the high concentrated side of a semipermeable membrane (only allows the flow of the solvent; blocks solute).
- Again, this property is due to the fact that the solution is lower in energy. **This is why water flows toward the solution (going from high to low energy).**



$$\Pi = iMRT$$

# Colligative Properties Challenge

Catalase (a liver enzyme) dissolves in water. A 14 mL solution containing 0.166 g of catalase exhibits an osmotic pressure of 1.2 Torr at 20°C. What is the molar mass of catalase?

$$\Pi = iMRT$$

$$\Pi = 1.2 \text{ Torr} = 0.00158 \text{ atm}$$

$$i = 1$$

$$R = 0.08206 \frac{\text{L atm}}{\text{mol K}}$$

$$T = 20^\circ\text{C} + 273 = 293$$

1) Find  $M$

$$M = \frac{\Pi}{iRT} = 0.00006567 \frac{\text{mol}}{\text{L}}$$

2) Find MW ( $\frac{\text{g}}{\text{mol}}$ )

$$\text{MW} = \frac{0.166 \text{ g}}{0.0006567 \frac{\text{mol}}{\text{L}} \times 0.014 \text{ L}}$$

$$= \underline{\hspace{2cm}} \frac{\text{g}}{\text{mol}}$$