Name ___________________________________Chem 162, Section: _______Group Number: ______

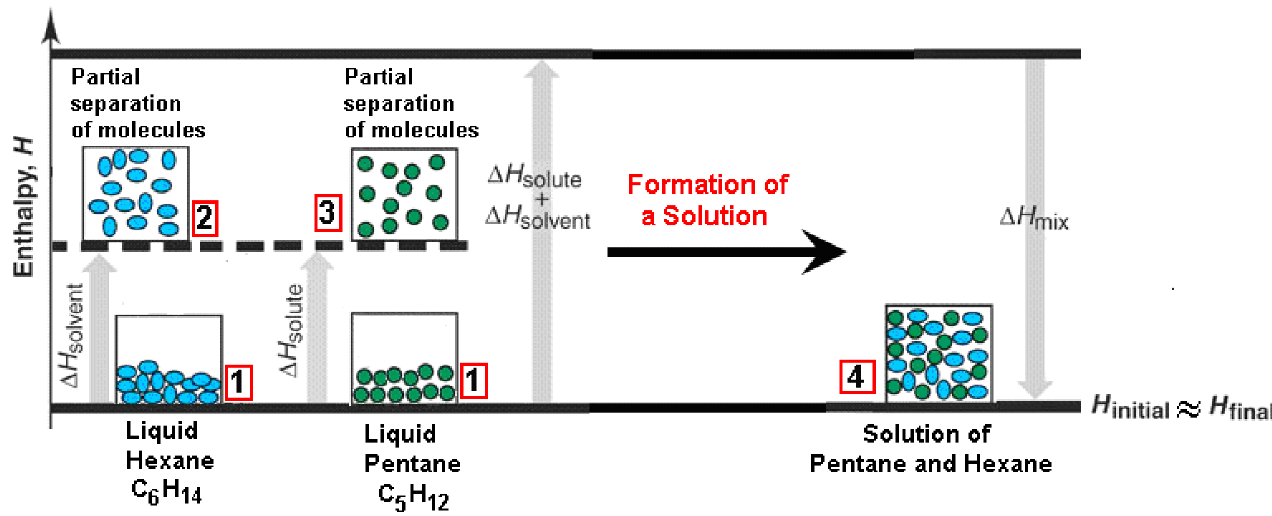
ALE 22. Principles of Solubility

(Reference: 13.3 *Silberberg 5th edition*)

Why don't oil and water mix?

The Model: Formation of an Ideal Solution

For a solution to form the solvent and solute particles must be attracted to each other—"like dissolves like." Moreover, when a solution forms the solute particles and solvent particles must partially separate from each other. The following ethalpy-level diagram represents the hypothetical step-by-step formation of a solution between hexane (C_6H_{14}, represented by) and pentane (C_5H_{12}, represented by).



Key Questions

1a. What type(s) of intermolecular forces hold pentane molecules together in a sample of liquid pentane? (Circle all that apply.)

Dispersion forces Dipole-dipole Hydrogen bonding

b. What type(s) of intermolecular forces hold hexane molecules together in a sample of liquid hexane? (Circle all that apply.)

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c. In a solution of hexane and pentane, what intermolecular forces hold hexane molecules to pentane molecules and to other hexane molecules? (Circle all that apply.)

Dispersion forces Dipole-dipole Hydrogen bonding

2. At **1** we have a sample of liquid hexane and a sample of liquid pentane. At **4** we have a solution of hexane and pentane. Explain what is occurring to intermolecular forces and enthalpy (i.e. heat) between:

   a. **1** and **2**?

   b. **1** and **3**?

   c. **2** and **3** when mixed?

3. What does the above enthalpy-level diagram suggest about the relative strengths of intermolecular forces in the separated (pure) solvent and solute and in the solution? (Circle your response.)

   i) The sum of the intermolecular forces in liquid hexane and in liquid pentane is weaker than the intermolecular forces in a solution of hexane and pentane.

   ii) The sum of the intermolecular forces in liquid hexane and in liquid pentane is the same in strength as the intermolecular forces in a solution of hexane and pentane.

   iii) The sum of the intermolecular forces in liquid hexane and in liquid pentane are stronger than the intermolecular forces in a solution of hexane and pentane.

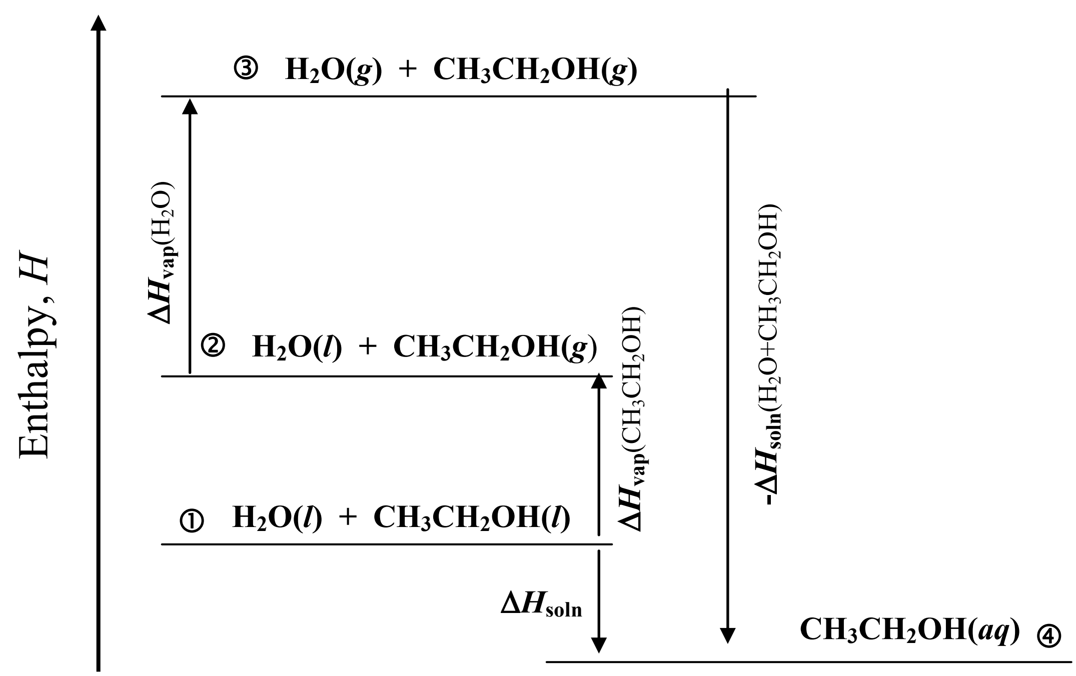
4. Which of the following reasons explains why hexane and pentane spontaneously mix to form a solution? (Circle all that apply.)

   A. The solution is less disordered than the separated solvent and solute.
   B. The solution is more disordered than the separated solvent and solute.
   C. The heat of solution is endothermic.
   D. The heat of solution is exothermic.

The Model: The Formation of a Non-Ideal Solution

Considering the formation of a solution between hexane and pentane, because the intermolecular forces before and after mixing have virtually the same strength, hexane and pentane mix together to form what is called an **ideal solution**. *Ideal solutions are, however, very rare*!

An example of a **non-ideal solution** is that of water and ethanol (CH_3CH_2OH). Consider the following energy-level diagram for the formation of a solution between water and ethanol:



Key Questions

5. Consider the enthalpy-level diagram for the formation of a solution between water and ethanol. The arrow for the heat of solution is pointing downward from level ① to ④. What is the thermodynamic significance of this? (Circle your response.)

   i) The mixture is more stable than the separated components and the solution process is endothermic.

   ii) The mixture is less stable than the separated components and the solution process is endothermic.

   iii) The mixture is more stable than the separated components and the solution process is exothermic.

   iv) The mixture is less stable than the separated components and the solution process is exothermic.

6. A process (such as the mixing of two components to become a solution) *tends to be* spontaneous if *either* of the following conditions is met: (1) the final state is more disordered than the initial state; or (2) heat is transferred from the system to the surroundings. Why do water and ethanol mix to form a solution? (Circle all that apply.)

   A. The solution is less disordered than the separated solvent and solute.
   B. The solution is more disordered than the separated solvent and solute.
   C. The heat of solution is endothermic.
   D. The heat of solution is exothermic.

7. Draw the Lewis structures of water and of ethanol.

   Water: Ethanol:

8a. What intermolecular forces of attraction hold water molecules together in a sample of liquid water?

(Circle all that apply.) Dispersion force Dipole-dipole Hydrogen bonding

b. What intermolecular forces of attraction hold ethanol molecules together in a sample of liquid ethanol?(Circle all that apply.)

   Dispersion forces Dipole-dipole Hydrogen bonding

c. What intermolecular forces of attraction hold water molecules and ethanol molecules together in an aqueous solution of ethanol? (Circle all that apply.)

   Dispersion forces Dipole-dipole Hydrogen bonding

9. An adage that often helps us predict solubilities is “like dissolves like”. Look back to Questions 3 and 8, and from them explain what is meant by “like dissolves like”.

10. “Oil and water don’t mix.” You are probably familiar with that adage. An oil is a hydrocarbon, like hexane, but longer chain of carbon atoms saturated with hydrogen. But hexane and water don’t mix for the exact same reason.

   a. Draw the Lewis structure for n-hexane, C_6H_{14}.

10b. What intermolecular forces of attraction hold water molecules and hexane molecules together in an aqueous solution of hexane?

10c. The strength of dispersion forces is proportional to how much surface area two neighboring molecules' electron clouds can overlap. Compare the strength of dispersion forces between a molecule of water and a molecule of hexane to the strength of dispersion forces between two molecules of hexane. Circle the following statement that is most accurate:

i) The sum of the intermolecular forces in liquid hexane and in liquid water is weaker than the intermolecular forces in a solution of hexane and water.

ii) The sum of the intermolecular forces in liquid hexane and in liquid water is stronger than the intermolecular forces in a solution of hexane and water.

10d. Sketch an enthalpy-level diagram in the style of that on *page 2* for the hypothetical formation of a solution of water and hexane from the mixing of liquid water and liquid hexane. Show the levels for when liquid water and liquid hexane are ***unmixed***, for when the ***molecules are separated***, and for when the components are ***mixed together***. Draw the arrows for and label all ΔH's, including ΔH_{soln}.

10e. Using the energy-level diagram, explain why water and hexane do not mix to form a solution. (Keep in mind Question 6.)

What determines if the heat of solution for a solid with a liquid is exo- or endothermic?

Model: the Major Factors that influence the Heat of Solution

When a solution forms between a solid and a liquid or between a liquid and another liquid, the following three things must happen:

1. Solute particles partially separate from each other—this is *always* an endothermic process!

   solute (aggregated) + heat → solute (separated) $\Delta H_{solute} > 0$

2. Solvent particles partially separate from each other—this is *always* an endothermic process!

   solvent (aggregated) + heat → solvent (separated) $\Delta H_{solvent} > 0$

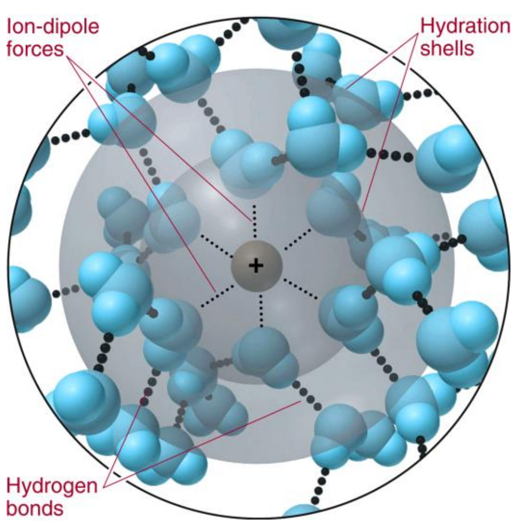
3. Solute and solvent particles mix—this is *always* an exothermic process!

   solute (separated) + solvent (separated) → Solution (solute solvated) + heat $\Delta H_{solvation} < 0$

$$\Delta H_{solution} = \Delta H_{solute} + \Delta H_{solvent} + \Delta H_{solvation}$$

If the solute is a solid, then the energy needed to separate the solute particles in step 1, above, would be the lattice energy (i.e. ΔH_{solute} = lattice energy). If the solute is an ionic solid and the solvent is water, then the heat of solvation ($\Delta H_{solvation}$) is called the heat of hydration, $\Delta H_{hydration}$.

Hydration Shells Around an Aqueous Cation



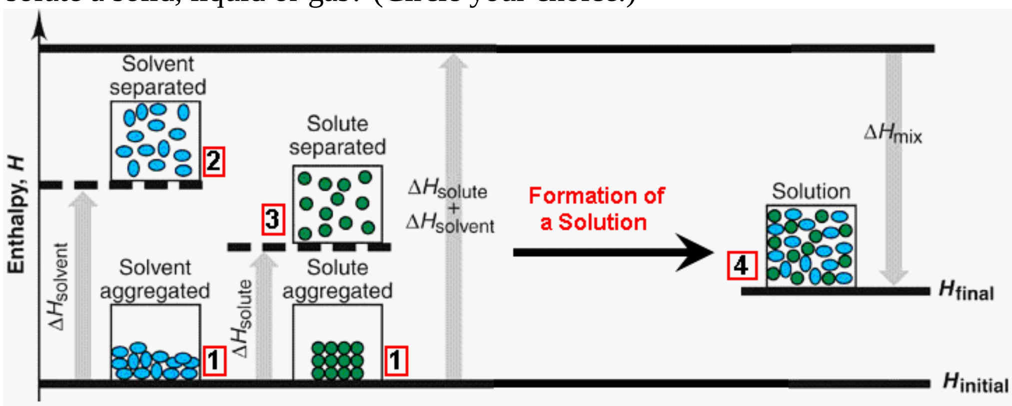
Trends in Ionic Heats of Hydration

Ion	Ionic Radius (pm)	ΔH_{hydr} (kJ/mol)
Group 1A(1)		
Li^+	76	−510
Na^+	102	−410
K^+	138	−336
Rb^+	152	−315
Cs^+	167	−282
Group 2A(2)		
Mg^{2+}	72	−1903
Ca^{2+}	100	−1591
Sr^{2+}	118	−1424
Ba^{2+}	135	−1317
Group 7A(17)		
F^-	133	−431
Cl^-	181	−313
Br^-	196	−284
I^-	220	−247

11. Why is the $\Delta H_{soln} = 0$ for solutions between gases?

12. A mixture of $CaCl_2$ and NaCl are often used to salt roads in the winter. Why is the dissolving of calcium chloride, $CaCl_2$, in water exothermic?

13. Refer to the enthalpy diagram below involving a solute dissolving in a liquid solvent when answering the following questions.
    a. Indicate with an arrow in the diagram below the enthalpy change the represents the enthalpy of solution and then label the arrow ΔH_{soln} and its appropriate value: 0, < 0 or > 0
    b. Will the temperature of the increase or decrease as the solute mixes with the solvent? (Circle your choice.)
    c. Is the heat of solution of the endothermic or exothermic? (Circle your choice.)
    d. Is the solute a solid, liquid or gas? (Circle your choice.)



14. When solid ammonium nitrate, NH_4NO_3, dissolves in water the solution becomes extremely cold—hence NH_4NO_3 is used in chemical cold packs.
    a. Is the dissolving of ammonium nitrate endothermic or exothermic? (Circle your choice.)
    b. Is the combined magnitude of $\Delta H_{lattice}$ of ammonium nitrate and $\Delta H_{solvent}$ larger or smaller than the combined $\Delta H_{hydration}$ of the ions? Explain.
    c. Given the answer to part (a), why does ammonium nitrate dissolve in water?

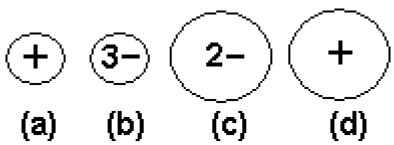
15. Why is ΔH_{soln} always exothermic (negative) for solutions between gases and liquids?

16a. Use the following data to calculate the combined heats of hydration for the ions in sodium acetate, $CH_3COO^-Na^+$: $\Delta H_{lattice}$ = -763 kJ/mol ΔH_{soln} = 17.3 kJ/mol

16b. Which ion, Na^+ or CH_3COO^-, do you think contributes more to the answer in part (a)? Why?

17a. What is meant by "the charge density" of an ion? What two properties of an ion affect the charge density of an ion?

b. Below are 2-D representations of four different ions. Arrange the ions in order of ***increasing charge density***. Assume the following ***sphere*** radii: a = b; c = d; the radius of (a) & (b) is half that of (c) & (d). ***Hint***: $V_{sphere} = 4/3\pi r^3$



c. Arrange the ions depicted in part b, above, in order of increasing hydration energies, $\Delta H_{hydration}$.

18a. Refer to the table of hydration energies on page 5. Which ions in groups 1A and 7A have nearly the same charge densities?

b. Compare the hydration energies of the two ions in part a, above, and explain why they are different.

19. Circle the ion in each pair that has the ***smaller*** $\Delta H_{hydration}$—use the periodic table and your knowledge of periodic trends in atomic radius and the relative sizes of ions to answer this question.

a.) Br^- or I^-

b.) Sc^{3+} or Ca^{2+}

c.) Br^- or K^+

d.) S^{2-} or Cl^-

e.) Sc^{3+} or Al^{3+}