Chem 1515.001 - 006
Problem Set #5
Spring 2002

Name_____

TA's Name _____

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ALL work must be shown to receive full credit. **Due by 1:00 p.m. on Friday, February 22, 2002.**

PS5.1. Describe all the energy changes which must be considered in the solution process. Indicate the types of interactions which are important in the solution process and discuss what conditions favor and do not favor formation of a solution.

Based on Gibbs-Helmholtz equation,
$$\Delta G^{\bullet}_{solution} = \Delta H^{\bullet}_{solution} - T\Delta S^{\bullet}_{solution}$$
There are two primary energy factors which must be considered in the solution process. The $\Delta H^{\bullet}_{solution}$ and $\Delta S^{\bullet}_{solution}$. The first term, $\Delta H^{\bullet}_{solution}$ depends on three steps; the energy required to separate the solute particles, the energy required to separate the solvent particles, and the energy released when new solute-solvent interactions form. The second term, $\Delta S^{\bullet}_{solution}$ is related to the mixing process and generally always favors solution formation. When $\Delta H^{\bullet}_{solution}$ is negative (exothermic) formation of a solution is favored. So if both terms favor formation of a solution is happens.
If $\Delta H^{\bullet}_{solution}$ is positive (endothermic) formation of a solution may or may not be favored depending on the relative magnitudes of $\Delta H^{\bullet}_{solution}$ and $\Delta S^{\bullet}_{solution}$.
Since it is a little difficult (at the moment) to get quantitative information on $\Delta H^{\bullet}_{solution}$ and $\Delta S^{\bullet}_{solution}$ we used a simple rule to help us predict solution formation. 'like dissolves like'. This rule is interpreted in terms of the intermolecular attractive forces between the pure solute and pure solvent particles. If they are similar we can expect a solution to form when the two components are mixed. If the forces are dissimilar we would predict no solution formation, i.e. a heterogeneous mixture.

PS5.2. Which substance of each of the following pairs is likely to be more soluble in water? Explain each choice and, for the less soluble of each pair, suggest a better solvent.

a) ammonia(g) or carbon dioxide(g)
   Ammonia, NH_3, will be more soluble than carbon dioxide, CO_2, because ammonia can hydrogen bond with water. Carbon dioxide has only dispersion forces, and can not hydrogen bond with water. Another nonpolar solvent such as benzene, carbon tetrachloride or carbon disulfide would be a better solvent for carbon dioxide.

b) chlorine(g) or hydrogen chloride(g)
   Hydrogen chloride will be more soluble than chlorine because hydrogen chloride is a polar covalent compound which when dissolved in water dissociates into ions. Chlorine has only dispersion forces, and can not hydrogen bond with water. Another nonpolar solvent such as benzene, carbon tetrachloride or carbon disulfide would be a better solvent for chlorine.
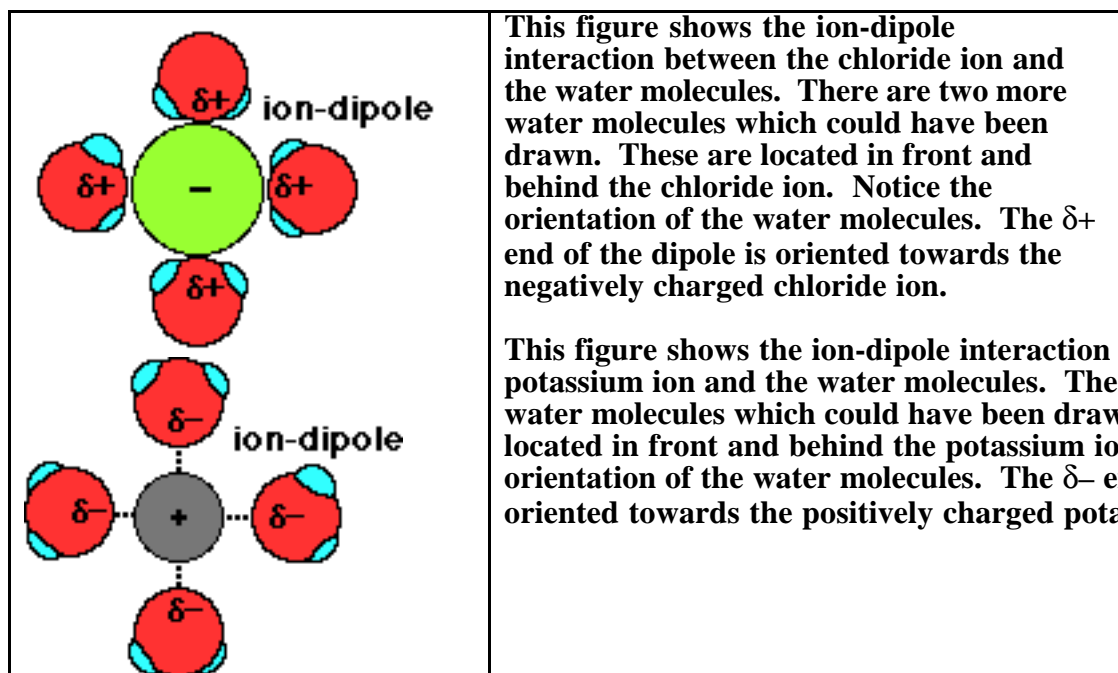
c) hexane(g) or $C_6H_{12}O_6$(s)
   Glucose will be more soluble than hexane because glucose can hydrogen bond with water. Hexane has only dispersion forces, and can not hydrogen bond with water. Another nonpolar solvent such as benzene, carbon tetrachloride or carbon disulfide would be a better solvent for hexane.
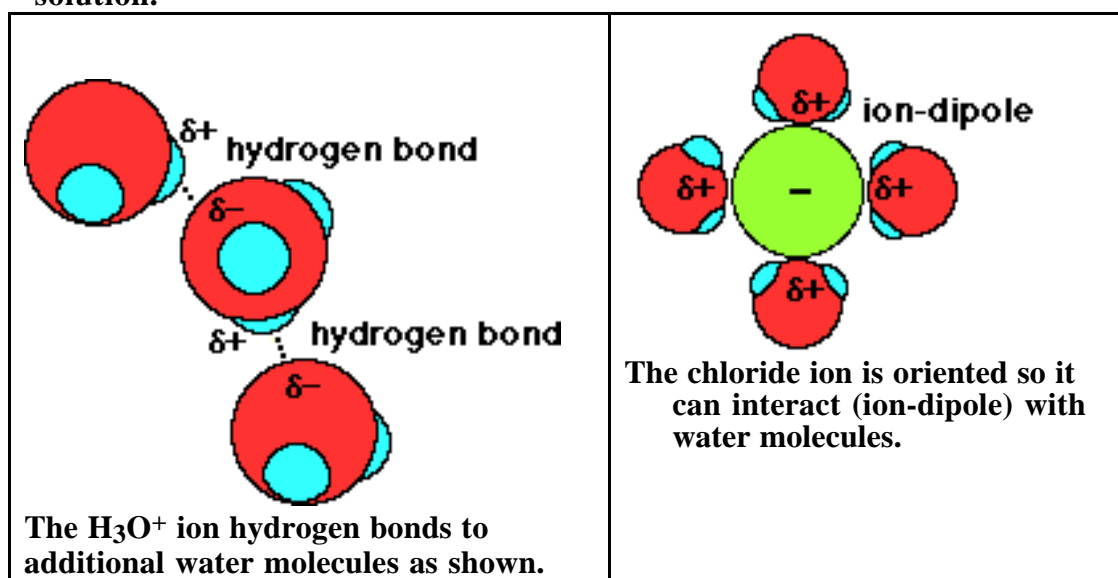
d) capric acid(s) ($CH_3(CH_2)_8COOH$) or acetic acid(l)

Both capric acid and acetic acid can hydrogen bond with water. However, capric acid has a much larger hydrocarbon group bonded to the –COOH group. The hydrocarbon portion is nonpolar and has dispersion forces. The larger this portion of the molecule becomes (the more carbon atoms), the less soluble the substance will be in water. Generally around 4 carbons is the break point where the solubility changes. Another nonpolar solvent such as capric acid, carbon tetrachloride or carbon disulfide would be a better solvent for ethane.
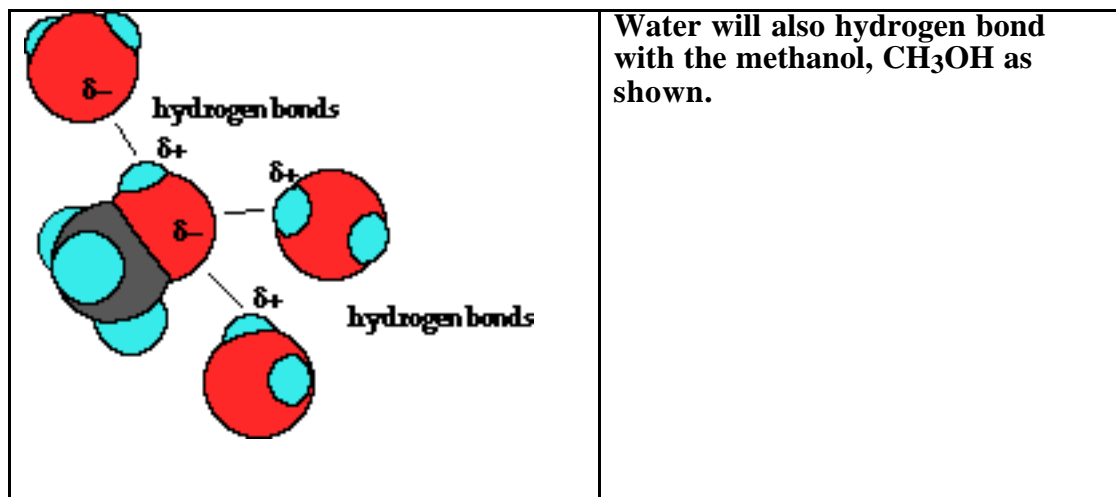
PS5.3. Describe the attractive forces present when KCl(s), HCl(g) and methanol(l) dissolve in water. Use the space below to sketch diagrams depicting at the atomic level how each of the three substances interact with water molecules.

This figure shows the ion-dipole interaction between the chloride ion and the water molecules. There are two more water molecules which could have been drawn. These are located in front and behind the chloride ion. Notice the orientation of the water molecules. The δ+ end of the dipole is oriented towards the negatively charged chloride ion.

This figure shows the ion-dipole interaction b potassium ion and the water molecules. Ther water molecules which could have been drawn located in front and behind the potassium ion orientation of the water molecules. The δ– en oriented towards the positively charged potas

HCl(g) is a polar covalent molecule. When added to water hydrogen chloride complete to form H+ and Cl– ions. These species are hydrated by water. The H+ exists as H3O solution.

The H3O+ ion hydrogen bonds to additional water molecules as shown.

The chloride ion is oriented so it can interact (ion-dipole) with water molecules.

PS5.3. Continued.

| | Water will also hydrogen bond with the methanol, CH_3OH as shown. |

PS5.4. Consider the spontaneous, room temperature, solution process when a solid, or liquid solute is added to a liquid solvent.

a) If ΔH is positive what must be happening in terms of the entropy change for the solution process to be spontaneous?

Based on Gibbs-Helmholtz equation,
$$\Delta G^{\bullet}_{solution} = \Delta H^{\bullet}_{solution} - T\Delta S^{\bullet}_{solution}$$
If ΔH is positive the solution process is endothermic. Since ΔS is generally + the relative magnitude of $T\Delta S$ must be larger than ΔH. When this happens the $T\Delta S$ is more negative compared to ΔH and the the difference will be negative so ΔG is negative.

b) If ΔS is negative, what must be happening in terms of the enthalpy change for the process to be spontaneous?

Based on Gibbs-Helmholtz equation,
$$\Delta G^{\bullet}_{solution} = \Delta H^{\bullet}_{solution} - T\Delta S^{\bullet}_{solution}$$
If ΔS is negative the solution process is producing more order. This can happen when the substance orders the water molecules more. This can happen when some ionic compounds ddissolve in water. Very small ions with high charge will order the water molecules that hydrate thee ions. This is not the usual when an ionic substance dissolves in water. So if the solution is more ordered, ΔH must be exothermic so the ΔH term is more important than the $T\Delta S$ term.

PS5.5. A concentrated solution of lactose, $C_{12}H_{22}O_{11}$, contains 114.6 g $C_{12}H_{22}O_{11}$ dissolved in 929 g water. The density of the solution is 1.043 g·mL^{-1}. Calculate;

a) The weight percent $C_{12}H_{22}O_{11}$ in the solution,

$$\frac{\text{mass } C_{12}H_{22}O_{11}}{\text{mass soln}} \times 100$$
$$\frac{114.6 \text{ g}}{1043.6 \text{ g soln}} \times 100 = 11.0 \text{ \%}$$

PS5.5. Continued.

b) the mol fraction of $C_{12}H_{22}O_{11}$ in the solution,

$$114.6 \text{ g } C_{12}H_{22}O_{11} \left(\frac{1 \text{ mol } C_{12}H_{22}O_{11}}{342 \text{ g}}\right) = 0.335 \text{ mol } C_{12}H_{22}O_{11}$$

$$929 \text{ g } H_2O \left(\frac{1 \text{ mol}}{18.0 \text{ g}}\right) = 51.6 \text{ mol } H_2O$$

$$\chi = \frac{\text{mol } C_{12}H_{22}O_{11}}{\text{mol soln}}$$

$$\chi = \frac{0.335 \text{ mol}}{51.6 \text{ mol} + 0.335 \text{ mol}} = 0.00645$$

c) molality of $C_{12}H_{22}O_{11}$ in the solution,

$$\frac{\text{mol } C_{12}H_{22}O_{11}}{\text{kg } H_2O}$$

$$\frac{0.335 \text{ mol } C_{12}H_{22}O_{11}}{0.929 \text{ kg}} = 0.361 \text{ molal}$$

d) the molarity of $C_{12}H_{22}O_{11}$ in the solution.

$$1043.6 \text{ gm soln} \left(\frac{1 \text{ mL}}{1.043 \text{ g}}\right) = 1000 \text{ mL}$$

$$\frac{\text{mol } C_{12}H_{22}O_{11}}{\text{L soln}} = \text{molarity}$$

$$\frac{0.335 \text{ mol } C_{12}H_{22}O_{11}}{1.00 \text{ L}} = 0.335 \text{ molar}$$

PS5.6. An aqueous solution of sulfuric acid is 2.238 molal and has a density of $1.124 \frac{\text{g}}{\text{mL}}$. Calculate the

$$\frac{2.238 \text{ mol } H_2SO_4}{1 \text{ kg } H_2O}$$

$$2.238 \text{ mol } H_2SO_4 \left(\frac{98.0 \text{ gm } H_2SO_4}{1 \text{ mol}}\right) = 219 \text{ g } H_2SO_4$$

a) weight percent sulfuric acid.

$$\frac{219 \text{ g } H_2SO_4}{219 \text{ g } H_2SO_4 + 1000 \text{ g } H_2O} \text{ x } 100 = 18.0\%$$

b) mole fraction of sulfuric acid.

$$1,000 \text{ g } H_2O \left(\frac{1 \text{ mol}}{18.0\text{g}}\right) = 55.6 \text{ mol } H_2O$$

$$\text{mole fraction } H_2SO_4 = \frac{\text{mol } H_2SO_4}{\text{mol soln}} = \frac{2.238 \text{ mol}}{2.238 \text{ mol} + 55.6 \text{ mol}} = 0.0387$$

c) molarity of the solution.

$$\frac{\text{mol } H_2SO_4}{\text{Liter soln}} = \text{molarity} \qquad 1219 \text{ g soln} \left(\frac{1 \text{ mL}}{1.124 \text{ g}}\right) = 1.08 \text{ L}$$

$$= \frac{2.238 \text{ mol}}{1.08 \text{ Liters}} = 2.06 \text{ molar}$$

PS5.7. Describe how you would prepare the following aqueous solutions;

a) 250.00 mL of a 0.425 M $Mg(NO_3)_2$ solution.

$$0.250 \text{ L} \left(\frac{0.425 \text{ mol } Mg(NO_3)_2}{1 \text{ Liter}} \right) = 0.106 \text{ mol}$$

$$0.106 \text{ mol } Mg(NO_3)_2 \left(\frac{148.3 \text{ g}}{1 \text{ mol } Mg(NO_3)_2} \right) = 15.8 \text{ gm } Mg(NO_3)_2$$

Add 15.8 gm $Mg(NO_3)_2$ to a 250 mL volumetric flask. Add about 200 mLs of water and stir the mixture until all of the $Mg(NO_3)_2$ dissolves. Then add enough water until the final volume of solution is 250 mLs. (Note: we do not have to worry about how much water is added, only the final volume.)

b) 126 g of a 5.11 % (by weight) solution of KCl.

$$126 \text{ g soln} \left(\frac{5.11 \text{ g KCl}}{100 \text{ g soln}} \right) = 6.44 \text{ g of KCl}$$

126 g – 6.44 g = 121 g are water.
We need 126 g of solution, 6.44 g is and 121 g are water. Place 121 g of water and 6.44 g of KCl into a 250 mL beaker aand stirr until dissolved.

c) 275. g (grams of solution) of a 0.120 molal propylene glycol ($C_3H_8O_2$) solution.

$$\frac{0.120 \text{ mol } C_3H_8O_2}{1 \text{ kg } H_2O}$$

$$0.120 \text{ mol } C_3H_8O_2 \left(\frac{76.0 \text{ gm}}{1 \text{ mol}} \right) = 9.12 \text{ gm } C_3H_8O_2$$

$$275 \text{ gm soln} \left(\frac{9.12 \text{ g } C_3H_8O_2}{9.12 \text{ g} + 1000 \text{ g}} \right) = 2.49 \text{ gm } C_3H_8O_2$$

275 gm soln - 2.49 g $C_3H_8O_2$ = 273 g H_2O

Add 2.49 g $C_3H_8O_2$ to 273 g H_2O and stir.

PS5.8. A solution of glucose, $C_{12}H_{22}O_{11}$, in water is prepared by mixing 85.0 g $C_{12}H_{22}O_{11}$ with 446 g of water. The molarity was found to be 0.944 M. Calculate
a) the molality of the solution

$$85.0 \text{ g } C_{12}H_{22}O_{11} \left(\frac{1 \text{ mol}}{342 \text{ gm } C_{12}H_{22}O_{11}} \right) = 0.249 \text{ mol } C_{12}H_{22}O_{11}$$

$$\frac{0.249 \text{ mol } C_{12}H_{22}O_{11}}{0.446 \text{ kg } H_2O}$$

$$= 0.557 \text{ molal}$$

b) the density of the solution

$$\text{density} = \frac{\text{mass solution}}{\text{vol solution}}$$

1 liter of solution contains 0.944 mol of $C_{12}H_{22}O_{11}$. To determine the mass of solution in 1 liter of solution, then

$$0.944 \text{ mol of } C_{12}H_{22}O_{11}\left(\frac{342.0 \text{ g}}{1 \text{ mol}}\right) = 322 \text{ g solute } (C_{12}H_{22}O_{11})$$

$$322 \text{ g solute}\left(\frac{446 \text{ g } H_2O + 85.0 \text{ g } C_{12}H_{22}O_{11}}{85.0 \text{ g } C_{12}H_{22}O_{11}}\right) = 2017 \text{ g solution}$$

$$\text{density} = \frac{2017 \text{ g solution}}{1000 \text{ mL solution}} = 2.017 \frac{g}{mL}$$

PS5.9.   A solution of a compound called potassium acid phthate, is prepared by dissolving 0.234 g in 100 mLs of water. This solution is then reacted with exactly 10.25 mLs of a 0.137 M NaOH solution. Calculate the molar mass of KHP (potassium acid phthalte).

$$KHP + NaOH \rightarrow KNaP + H_2O$$
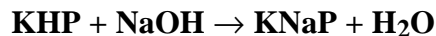
According to the chemical equation 1 mol of KHP reacts with 1 mol of NaOH.

$$10.25 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)\left(\frac{0.137 \text{ mol}}{1 \text{ L}}\right) = 0.00140 \text{ mol NaOH}$$

$$0.00140 \text{ mol NaOH}\left(\frac{1 \text{ mol KHP}}{1 \text{ mol NaOH}}\right) = 0.00140 \text{ mol KHP}$$

$$\left(\frac{0.234 \text{ g KHP}}{0.00140 \text{ mol}}\right) = 166 \text{ g mol}^{-1}$$