

ALL work must be shown to receive full credit. **Due at the beginning of lecture on Friday, September 14, 2001.**

- PS3.1. Europium metal crystallizes in a body-centered cubic unit cell. The density of europium is $5.26 \frac{\text{g}}{\text{cm}^3}$. Calculate the edge length of the unit cell and the atomic radius of europium.

Mass of the unit cell

$$\left(\frac{2 \text{ atoms}}{1 \text{ unit cell}} \right) \left(\frac{1 \text{ mol}}{6.023 \times 10^{23} \text{ atoms}} \right) \left(\frac{152 \text{ g}}{1 \text{ mol}} \right) = 5.05 \times 10^{-22} \text{ g}$$

to calculate the volume of the unit cell;

$$5.05 \times 10^{-22} \text{ g} \left(\frac{1 \text{ cm}^3}{5.26 \text{ g}} \right) = 9.60 \times 10^{-23} \text{ cm}^3 \dots$$

$$\text{edge length} = \sqrt[3]{9.60 \times 10^{-23} \text{ cm}^3} = 4.58 \times 10^{-8} \text{ cm}$$

$$r = \frac{\sqrt{3} \cdot \text{edge length}}{4} = \frac{\sqrt{3} \cdot 4.58 \times 10^{-8} \text{ cm}}{4} = 1.98 \times 10^{-8} \text{ cm}$$

- PS3.2. Aluminum crystallizes in a face-centered cubic unit cell and has a density of $2.70 \frac{\text{g}}{\text{cm}^3}$. What are the unit cell dimensions (edge length)?

Mass of the unit cell;

$$\left(\frac{4 \text{ atoms}}{1 \text{ unit cell}} \right) \left(\frac{1 \text{ mol}}{6.023 \times 10^{23} \text{ atoms}} \right) \left(\frac{27.0 \text{ g}}{1 \text{ mol}} \right) = 1.79 \times 10^{-22} \text{ g}$$

to calculate the volume of the unit cell;

$$1.79 \times 10^{-22} \text{ g} \left(\frac{1 \text{ cm}^3}{2.70 \text{ g}} \right) = 6.64 \times 10^{-23} \text{ cm}^3 \dots$$

$$\text{edge length} = \sqrt[3]{6.64 \times 10^{-23} \text{ cm}^3} = 4.05 \times 10^{-8} \text{ cm}$$

- PS3.2. 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.

There are two primary energy factors which must be considered in the solution process. The enthalpy ($\Delta H^{\circ}_{\text{solution}}$) and the entropy ($\Delta S^{\circ}_{\text{solution}}$). The first term, $\Delta H^{\circ}_{\text{solution}}$ 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, $\Delta S^{\circ}_{\text{solution}}$ is related to the mixing process and always favors solution formation. When $\Delta H^{\circ}_{\text{solution}}$ is negative (exothermic) formation of a solution is favored. So if both terms favor formation of a solution is happens.

If $\Delta H^{\circ}_{\text{solution}}$ is positive (endothermic) formation of a solution may or may not be favored depending on the relative magnitudes of $\Delta H^{\circ}_{\text{solution}}$ and $\Delta S^{\circ}_{\text{solution}}$.

Since it is a little difficult (at the moment) to get quantitative information on $\Delta H^{\circ}_{\text{solution}}$ and $\Delta S^{\circ}_{\text{solution}}$ 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.

- PS3.4. 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) ethane(g) or acetic acid(l)

Acetic acid will be more soluble than ethane because acetic acid can hydrogen bond with water. Ethane 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 ethane.

- 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 $C_6H_{12}O_6(s)$

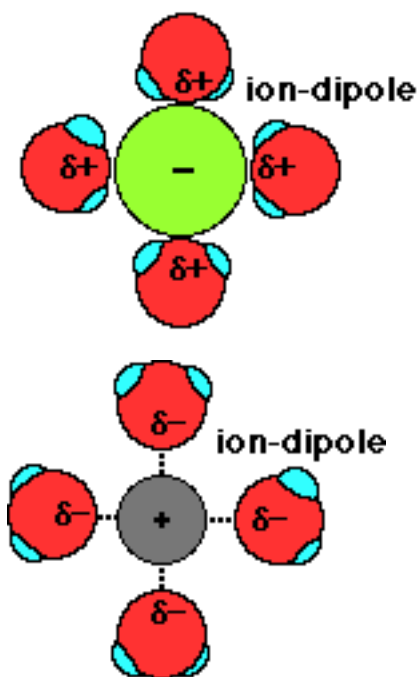
Glucose (whose formula can can also be written as $C_6H_7O(OH)_5$) will be more soluble than hexane because glucose can hydrogen bond with water. Hexane has only dispersion forces, and can not hydrogen bond with water. Another nonpolar solvent such as benzene, carbon tetrachloride or carbon disulfide would be a better solvent for hexane.

PS3.4. (CONTINUED)

d) ammonia(g) or phosphine(g)

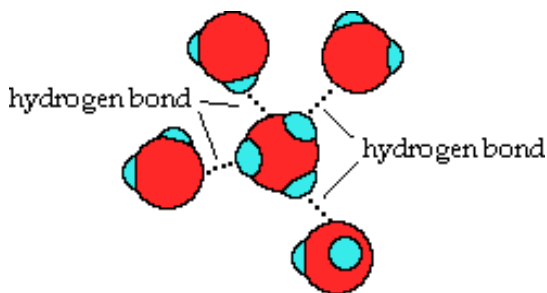
Ammonia will be more soluble than phosphine (PH₃) because ammonia can hydrogen bond with water. Phosphine is polar and can interact with water, but is not as soluble as ammonia. Another polar solvent such as dichloromethane, chloroform or acetone would be a better solvent.

PS3.5. Describe the attractive forces present when NaCl(*s*), HCl(*g*) and ethyl alcohol(*l*) (CH₃CH₂OH) 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.

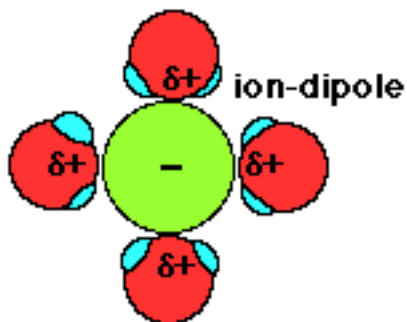
This figure shows the ion-dipole interaction between the sodium ion and the water molecules. There are two more water molecules which could have been drawn. These are located in front and behind the sodium ion. Notice the orientation of the water molecules. The δ⁻ end of the dipole is oriented towards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



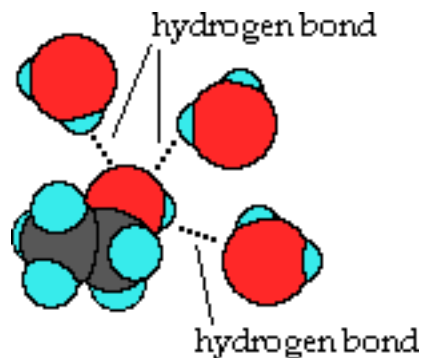
When HCl(g) dissolves in water it ionizes, i.e. it dissociates into H^+ and Cl^- ions. The water molecules solvate (surround) both ions.

However, in the case of H^+ the interaction with water is particularly strong. In fact we often think the H^+ is associated with one or more molecules of water forming an ion like H_3O^+ or H_5O_2^+ . In the image below I have elected to represent $\text{H}^+(\text{aq})$ as an H_3O^+ ion surrounded by other water molecules. All of the interactions between H_3O^+ and H_2O are hydrogen bonds.

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.



CH₃CH₂OH is a polar covalent molecule which does not ionize when added to water. The water molecules hydrate the CH₃CH₂OH molecule as shown hydrogen-bonding with -OH group. The interaction is the same for methanol.



- PS3.6. Describe how the solubility of an ionic solid can depend on temperature. Describe how the solubility of a gas can depend on temperature.
The solubility of ionic solids may increase or decrease with increasing temperature. It depends on whether the $\Delta H^{\circ}_{\text{solution}}$ is exothermic or endothermic.
The solubility of gases always decreases with increasing temperature.

PS3.7. A solution of potassium dihydrogen phosphate, KH_2PO_4 , contains 15.65 g KH_2PO_4 dissolved in 180. g water. The density of the solution is $1.058 \text{ g} \cdot \text{mL}^{-1}$. Calculate;

a) The weight percent KH_2PO_4 in the solution,

$$\text{Weight \%} = \frac{\text{grams solute}}{\text{grams solution}} \cdot 100$$

The problem states the mass of solute and solvent. Adding the mass of solute and solvent for the mass of the solution and substituting;

$$\text{Weight \%} = \frac{15.65 \text{ g } \text{KH}_2\text{PO}_4}{196 \text{ g solution}} \cdot 100 = 8.00 \%$$

b) the mol fraction of KH_2PO_4 in the solution,

$$\text{Mol fraction} = \frac{\text{mol solute}}{\text{mol solution}}$$

The mass of solute and solvent must each be converted to mol.

$$15.65 \text{ g } \text{KH}_2\text{PO}_4 \left(\frac{1 \text{ mol } \text{KH}_2\text{PO}_4}{137 \text{ g } \text{KH}_2\text{PO}_4} \right) = 0.114 \text{ mol } \text{KH}_2\text{PO}_4$$

$$180 \text{ g } \text{H}_2\text{O} \left(\frac{1 \text{ mol } \text{H}_2\text{O}}{18.0 \text{ g } \text{H}_2\text{O}} \right) = 10.0 \text{ mol } \text{H}_2\text{O}$$

Then adding the mol of solute and solvent for the mol of solution and substituting;

$$\text{Mol fraction} = \frac{0.114 \text{ mol } \text{KH}_2\text{PO}_4}{10.114 \text{ mol solution}} = 0.113$$

c) molality of KH_2PO_4 in the solution,

$$\text{Molality} = \frac{\text{mol solute}}{\text{kilogram solvent}}$$

Using the mol of solute and the (as kilograms) of solvent and substituting;

$$\text{Molality} = \frac{0.114 \text{ mol } \text{KH}_2\text{PO}_4}{0.180 \text{ kilogram } \text{H}_2\text{O}} = 0.633 \text{ molal}$$

d) the molarity of KH_2PO_4 in the solution.

$$\text{Molarity} = \frac{\text{mol solute}}{\text{liter solution}}$$

We need the volume of solution to determine the molarity. So we need the density of the solution to convert the mass of solution to a volume of solution.

$$196 \text{ g solution} \left(\frac{1 \text{ mL solution}}{1.058 \text{ g solution}} \right) = 185 \text{ mL}$$

Substituting;

$$\text{Molarity} = \frac{0.114 \text{ mol } \text{KH}_2\text{PO}_4}{0.185 \text{ liter solution}} = 0.616 \text{ molar}$$

PS3.8. An aqueous solution of methyl alcohol, CH₃OH, is 13.4 molal and has a density of 0.953 $\frac{\text{g}}{\text{mL}}$. Calculate the
a) weight percent methyl alcohol.

The solution is 13.4 molal CH₃OH. We'll assume we have 1 kilogram of water and 13.4 mol of CH₃OH.

To calculate the weight % we must convert the mol of CH₃OH to grams.

$$13.4 \text{ mol CH}_3\text{OH} \left(\frac{32.0 \text{ g CH}_3\text{OH}}{1 \text{ mol CH}_3\text{OH}} \right) = 429 \text{ g CH}_3\text{OH}$$

$$\text{Weight \%} = \frac{\text{grams solute}}{\text{grams solution}} \cdot 100$$

Adding the mass of solute and solvent for the mass of the solution and substituting;

$$\text{Weight \%} = \frac{429 \text{ g CH}_3\text{OH}}{1429 \text{ g solution}} \cdot 100 = 30.0 \%$$

b) mole fraction of methyl alcohol.

$$\text{Mol fraction} = \frac{\text{mol solute}}{\text{mol solution}}$$

The mass of solvent must each be converted to mol.

$$1000 \text{ g H}_2\text{O} \left(\frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} \right) = 55.6 \text{ mol H}_2\text{O}$$

Then adding the mol of solute and solvent for the mol of solution and substituting;

$$\text{Mol fraction} = \frac{13.4 \text{ mol CH}_3\text{OH}}{69.0 \text{ mol solution}} = 0.194$$

c) molarity of the solution.

$$\text{Molarity} = \frac{\text{mol solute}}{\text{liter solution}}$$

We need the volume of solution to determine the molarity. So we need the density of the solution to convert the mass of solution to a volume of solution.

$$1429 \text{ g solution} \left(\frac{1 \text{ mL solution}}{0.953 \text{ g solution}} \right) = 1499 \text{ mL}$$

Substituting;

$$\text{Molarity} = \frac{13.4 \text{ mol CH}_3\text{OH}}{1.499 \text{ liter solution}} = 8.94 \text{ molar}$$

- PS3.9. Describe how you would prepare the following aqueous solutions;
a) 500.00 mL of a 0.250 M CsCl solution from solid CsCl and distilled water.

To prepare a solution of a given molarity we must know the mass of solute and the final volume of solution. The mass of solute can be determined from the volume of solution and the concentration of the solution, as shown below;

$$0.500 \text{ L solution} \left(\frac{0.250 \text{ mol CsCl}}{1 \text{ L solution}} \right) = 0.125 \text{ mol CsCl}$$

$$0.125 \text{ mol CsCl} \left(\frac{168 \text{ g CsCl}}{1 \text{ mol CsCl}} \right) = 21.0 \text{ g CsCl}$$

The solution is prepared by adding 21.0 g CsCl to a 500 mL volumetric flask. Add 250 mL of water to the flask, and swirl to get all of the CsCl to dissolve. After the CsCl has dissolved add enough water to reach a final volume of 500 mLs.

- b) 145 g of a 8.5 % (by weight) solution of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ from solid sucrose and distilled water

In this case we just need to know the mass of solute and solvent that are to be added to prepare the solution. Since we know the weight % and the total mass of the solution we can determine the mass of solute and solvent;

$$145 \text{ g solution} \left(\frac{8.5 \text{ g CsCl}}{100 \text{ g solution}} \right) = 12.3 \text{ g CsCl}$$

$$145 \text{ g solution} - 12.3 \text{ g CsCl} = 132.7 \text{ g H}_2\text{O}$$

To prepare this solution 12.3 g CsCl are added to 132.7 g of H_2O and stirred.

- c) 950. g (grams of solution) of a 0.750 molal propylene glycol ($\text{C}_3\text{H}_8\text{O}_2$) solution.

This problem is very similar to part b. Although the problem wants a total mass (like part b) we are given the concentration in terms of molality, rather than weight %. If we convert molality to weight % we can do this problem just like we did in part b.

To convert 0.750 molal $\text{C}_3\text{H}_8\text{O}_2$ to weight % we can use the same approach we used in PS3.8.

The solution is 0.750 molal $\text{C}_3\text{H}_8\text{O}_2$. We'll assume we have 1 kilogram of water and 0.750 mol of $\text{C}_3\text{H}_8\text{O}_2$.

To calculate the weight % we must convert the mol of $\text{C}_3\text{H}_8\text{O}_2$ to grams.

$$0.750 \text{ mol C}_3\text{H}_8\text{O}_2 \left(\frac{76.0 \text{ g C}_3\text{H}_8\text{O}_2}{1 \text{ mol C}_3\text{H}_8\text{O}_2} \right) = 57.0 \text{ g C}_3\text{H}_8\text{O}_2$$

$$\text{Weight \%} = \frac{\text{grams solute}}{\text{grams solution}} \cdot 100$$

Adding the mass of solute and solvent for the mass of the solution and substituting;

$$\text{Weight \%} = \frac{57.0 \text{ g C}_3\text{H}_8\text{O}_2}{1057 \text{ g solution}} \cdot 100 = 5.39 \%$$

Now we can approach the problem the same way we did in part b.

$$950 \text{ g solution} \left(\frac{5.39 \text{ g C}_3\text{H}_8\text{O}_2}{100 \text{ g solution}} \right) = 51.2 \text{ g C}_3\text{H}_8\text{O}_2$$

$$950 \text{ g solution} - 51.2 \text{ g C}_3\text{H}_8\text{O}_2 = 899 \text{ g H}_2\text{O}$$

To prepare this solution 51.2 g C₃H₈O₂ are added to 899 g of H₂O and stirred.

PS3.10. A concentrated solution of NaOH in water is prepared by mixing 30.0 g NaOH with 70.0 g of water and cooled back to 25 °C . The molarity was found to be 9.975 M. Calculate

a) the molality of the solution

$$\text{Molality} = \frac{\text{mol solute}}{\text{kilogram solvent}}$$

We are given the mass of solute and solvent in the problem. We begin by determining the mol of solute;

$$30.0 \text{ g NaOH} \left(\frac{1 \text{ mol NaOH}}{40.0 \text{ g NaOH}} \right) = 0.75 \text{ mol NaOH}$$

Using the mol of solute and the (as kilograms) of solvent and substituting;

$$\text{Molality} = \frac{0.750 \text{ mol NaOH}}{0.070 \text{ kilogram H}_2\text{O}} = 10.7 \text{ molal}$$

b) the density of the solution

Density is define as;

$$\text{Density} = \left(\frac{\text{grams solution}}{\text{volume solution}} \right)$$

So we need to know this ratio. We are given the molarity of the solution as 9.975 M. Molarity is defined as;

$$\text{Molarity} = \frac{\text{mol solute}}{\text{liter solution}}$$

In this particular problem the definition is translated as;

$$\text{Molarity} = \frac{9.975 \text{ mol NaOH}}{\text{liter solution}}$$

We know that 100 grams of this solution contains 30.0 grams of NaOH (0.75 mol NaOH). Using molarity we can determine the volume of solution that contains the same number of mol of NaOH.

$$0.75 \text{ mol NaOH} \left(\frac{\text{liter solution}}{9.975 \text{ mol NaOH}} \right) = 0.0752 \text{ liters of soln}$$

So 0.75 mol NaOH are contained in 75.2 mLs of solution. Now we know the mass and the volume of solution that contain the same number of mol.

$$\text{Density} = \left(\frac{100 \text{ grams solution}}{75.2 \text{ ml solution}} \right) = 1.33 \text{ g mL}^{-1}$$

