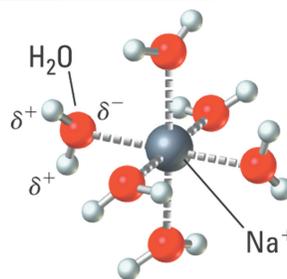


Solutes and Solution

- The first rule of solubility is “likes dissolve likes”
- Polar or ionic substances are soluble in polar solvents
- Non-polar substances are soluble in non-polar solvents

Saturation and Equilibrium



Solutes and Solution

- There must be a reason why a substance is soluble in a solvent:
 - either the solution process lowers the overall enthalpy of the system ($\Delta H_{\text{rxn}} < 0$)
 - Or the solution process increases the overall entropy of the system ($\Delta S_{\text{rxn}} > 0$)
- Entropy is a measure of the amount of disorder in a system—total entropy must increase for any spontaneous change

Solutes and Solution

- The forces that drive the dissolution of a solute usually involve both enthalpy and entropy terms
 - $\Delta H_{\text{soln}} < 0$ for most species
 - The creation of a solution takes a more ordered system (solid phase or pure liquid phase) and makes more disordered system (solute molecules are more randomly distributed throughout the solution)

Saturation and Equilibrium

- If we have enough solute available, a solution can become saturated—the point when no more solute may be accepted into the solvent
- Saturation indicates an equilibrium between the pure solute and solvent and the solution

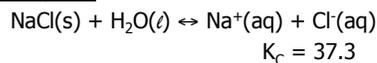
$$\text{solute} + \text{solvent} \leftrightarrow \text{solution} \quad K_C$$

Saturation and Equilibrium

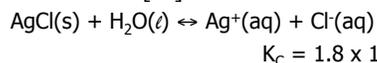
- $\text{solute} + \text{solvent} \leftrightarrow \text{solution} \quad K_C$
- The magnitude of K_C indicates how soluble a solute is in that particular solvent
- If K_C is large, the solute is very soluble
- If K_C is small, the solute is only slightly soluble

Saturation and Equilibrium

Examples:

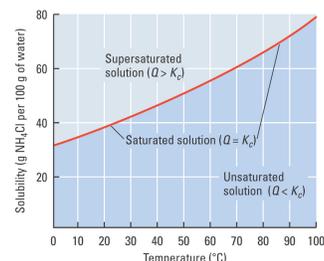


A saturated solution of NaCl has a $[\text{Na}^+] = 6.11 \text{ M}$ and $[\text{Cl}^-] = 6.11 \text{ M}$



A saturated solution of AgCl has a $[\text{Ag}^+] = 1.34 \times 10^{-5} \text{ M}$ and $[\text{Cl}^-] = 1.34 \times 10^{-5} \text{ M}$

Saturation and Equilibrium



Solubility of Gases

- When a gas is dissolved in a solvent, the process is usually exothermic:
 $\text{gas} + \text{solvent} \leftrightarrow \text{solution} \quad \Delta H_{\text{rxn}} < 0$
- In solution, the gas molecules are now in close proximity to the solvent molecules which increases the effects of the intermolecular forces and lowers the overall enthalpy of the system

Solubility of Gases

- To understand the effects of temperature on solubility, we can use LeChatelier's Principle:
 $\text{gas} + \text{solvent} \leftrightarrow \text{solution} + \text{heat}$
- Since heat appears on the product side of the chemical equilibrium, increasing the temperature will move the equilibrium toward the reactants and the gas will be less soluble

Solubility of Gases

- Pressure has no effect on the solubility of solids and liquids, but it has a significant effect on the solubility of gases
- The higher the pressure of the gas over the solution, the higher the solubility of the gas in solution
- Henry's Law:
 $S_g = k_H P_g$

Solubility of Gases

- Henry's Law:
 $S_g = k_H P_g$
 $S_g =$ solubility of gas in solution
 $k_H =$ Henry's Law constant for that gas/solvent combination
 $P_g =$ partial pressure of gas over the solution

Solubility of Gases

Example:

What is the molar concentration of N_2 in water when the partial pressure of N_2 is 600. Torr?

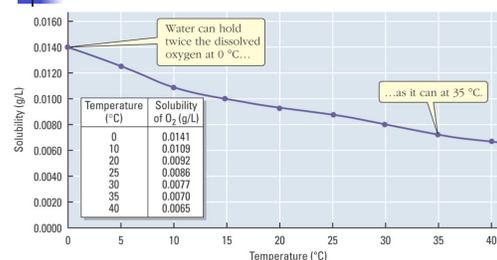
$$k_H = 8.4 \times 10^{-7} \text{ mol/L-mm Hg}$$

$$S_{N_2} = (8.4 \times 10^{-7} \text{ mol/L-mm Hg})(600. \text{ mm Hg}) = 5.04 \times 10^{-4} \text{ M}$$

What is the concentration at 20. Torr?

$$S_{N_2} = (8.4 \times 10^{-7} \text{ mol/L-mm Hg})(20. \text{ mm Hg}) = 1.7 \times 10^{-5} \text{ M}$$

Solubility of Gases



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Concentration Units

Molarity: defined as moles of solute per liter of solution

$$M = \frac{\text{moles solute}}{\text{liters of solution}} = \frac{\text{mol}}{\text{L}}$$

The volume used is the total volume of the solution, not just the volume of the solvent

Usually the volume of the solute is negligible compared to the solvent volume

Concentration Units

Molality: defined as moles of solute per mass of solvent

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

In this case, the mass is only the mass of the solvent, not the total mass of the solution

Concentration Units

Mole fraction: mole fraction is defined as the number of moles solute divided by the total number of moles of all species in the solution

$$X_A = \frac{\text{moles solute}}{\text{total moles in solution}} = \frac{n_A}{n_{\text{tot}}}$$

Mole fraction is a unitless number

Colligative Properties

- Colligative properties are a set properties that depend only on the amount of solute in a solution, and not on the chemical identity of the solute
- Colligative properties include:
 - Vapor pressure lowering
 - Freezing point depression
 - Boiling point elevation
 - Osmotic pressure

Colligative Properties

Vapor pressure lowering

- When solute is added to a pure solvent, solvent molecules are “tied up” in keeping the solute molecules in solution
- Because solvent molecules are more strongly attracted to the solute than to themselves, it requires more energy to remove them from the solution compared to the pure solvent

Colligative Properties

Vapor pressure lowering

- As a consequence, the vapor pressure of the solution is lowered
- Raoult's Law states:

$$P_1 = X_1 P_1^\circ$$

P_1 = vapor pressure of the solution

X_1 = mole fraction of solvent

P_1° = vapor pressure of the pure solvent

Colligative Properties

Vapor pressure lowering

Example: What is the vapor pressure of a saturated NaCl solution at 25 °C?

$$P^\circ = 23.76 \text{ Torr}$$

$$\rho_{\text{H}_2\text{O}} = 0.99707 \text{ g/mL}$$

$$35.7 \text{ g NaCl per } 100 \text{ mL H}_2\text{O}$$

Step 1—Determine mole fraction of solution

$$\begin{aligned} 35.7 \text{ g NaCl} / 58.443 \text{ g/mol} &= 0.611 \text{ mol NaCl} \\ (100 \text{ mL})(.9971 \text{ g/mL}) / (18.0152 \text{ g/mol}) &= 5.53 \text{ mol H}_2\text{O} \end{aligned}$$

Colligative Properties

Vapor pressure lowering

Example: What is the vapor pressure of a saturated NaCl solution at 25 °C?

Step 1—Determine mole fraction of solution

$$\begin{aligned} X_{\text{H}_2\text{O}} &= \frac{n_{\text{H}_2\text{O}}}{n_{\text{Na}^+} + n_{\text{Cl}^-} + n_{\text{H}_2\text{O}}} \\ &= \frac{5.53 \text{ mol}}{.611 \text{ mol} + .611 \text{ mol} + 5.53 \text{ mol}} = .819 \end{aligned}$$

Colligative Properties

Vapor pressure lowering

Example: What is the vapor pressure of a saturated NaCl solution at 25 °C?

Step 2—Determine vapor pressure of solution

$$P_{\text{H}_2\text{O}} = X_{\text{H}_2\text{O}} P^\circ = (.819)(23.76 \text{ Torr})$$

$$= 19.5 \text{ Torr}$$

The vapor pressure over a saturated NaCl solution is 18% lower than that of pure water

Colligative Properties

Boiling Point Elevation

- Because the vapor pressure of solution is lower than the vapor pressure of the pure solvent, the solution's boiling point will be elevated
- Remember that the boiling point is that temperature where the vapor pressure of the solution is equal to the pressure over the solution

Colligative Properties

Boiling Point Elevation

$$\Delta T_b = T_b(\text{soln}) - T_b(\text{solvent})$$

$$= K_b m$$

K_b = boiling point elevation constant

m = molality of solute

Colligative Properties

Boiling Point Elevation

Example: What is boiling point of a NaCl solution that is saturated at 25 °C?

$$K_b(\text{H}_2\text{O}) = 0.512 \text{ K kg/mol}$$

$$m = (1.22 \text{ mol solute}) / (.09771 \text{ kg H}_2\text{O})$$

$$= 12.5 \text{ m}$$

$$\Delta T_b = (12.5 \text{ mol/kg})(0.512 \text{ K kg/mol}) = 6.40 \text{ K}$$

$$T_b = 106.4 \text{ }^\circ\text{C}$$

Colligative Properties

Freezing Point Depression

- The freezing point of a solution will be lower than that of the pure solvent because the solute molecules interrupt the crystal structure of the solid solvent

$$\Delta T_f = K_f m$$

K_f = freezing pt depression constant

m = molality of solute

Colligative Properties

Freezing Point Depression

Example: Determine the freezing point of a solution that is 40% by volume ethylene glycol in water

$$K_f(\text{H}_2\text{O}) = 1.86 \text{ K kg/mol}$$

$$\rho(\text{C}_2\text{H}_6\text{O}_2) = 1.109 \text{ g/mL}$$

Colligative Properties

Freezing Point Depression

Example: Determine the freezing point of a solution that is 40% by volume ethylene glycol in water

Step 1—Assume we have 1.00 L of the solution; determine molality of ethylene glycol

$$(400 \text{ mL C}_2\text{H}_6\text{O}_2)(1.109 \text{ g/mL}) / (62.069 \text{ g/mol})$$

$$= 7.15 \text{ mol C}_2\text{H}_6\text{O}_2$$

$$m = (7.15 \text{ mol}) / (.600 \text{ kg H}_2\text{O}) = 11.9 \text{ m}$$

Colligative Properties

Freezing Point Depression

Example: Determine the freezing point of a solution that is 40% by volume ethylene glycol in water

Step 2—Determine freezing point depression

$$\Delta T_f = (11.9 \text{ m})(1.86 \text{ K kg/mol})$$

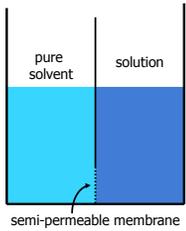
$$= 22.1 \text{ K}$$

$$T_f = -22.1 \text{ }^\circ\text{C}$$

Colligative Properties

Osmotic Pressure

- A solution is initially separated from a reservoir of pure solvent by a semi-permeable membrane
- A semi-permeable membrane allows the solvent to move through in either direction, but does not allow the solute species to pass through

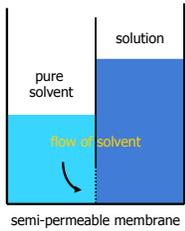


semi-permeable membrane

Colligative Properties

Osmotic Pressure

- The solvent wants to have equal concentrations on each side of the system
- The solvent will flow from the pure solvent side to the solution side of the system to minimize the concentration difference between each side of the system

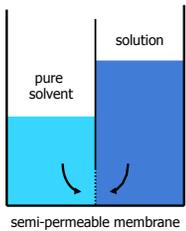


semi-permeable membrane

Colligative Properties

Osmotic Pressure

- The solution side is now higher than the solvent side which creates a pressure difference
- The increased pressure on the solution side tends to push solvent back to the pure solvent side of the system

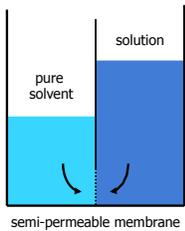


semi-permeable membrane

Colligative Properties

Osmotic Pressure

- The osmotic pressure of the solution is the pressure exerted by the solution when the system reaches equilibrium—balance between force exerted by pure solvent to equalize concentration and force exerted by increased height of solution



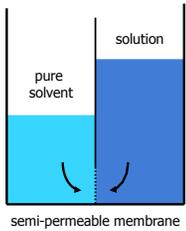
semi-permeable membrane

Colligative Properties

Osmotic Pressure

- The osmotic pressure is given by:

$$\Pi = c R T i$$
 where
 c = molar concentration
 R = gas constant
 T = temperature (in K)
 i = solute particles per unit formula



semi-permeable membrane

Colligative Properties

Osmotic Pressure

Example: Determine the osmotic pressure of a 1.00 M solution of NaCl

$$c = 1.00 \text{ mol/L} \quad i = 2 \text{ (Na}^+ \text{ and Cl}^-)$$

$$\Pi = 2(1.00 \text{ mol/L})(.08206 \text{ L atm/mol K})(298 \text{ K})$$

$$= 48.9 \text{ atm}$$