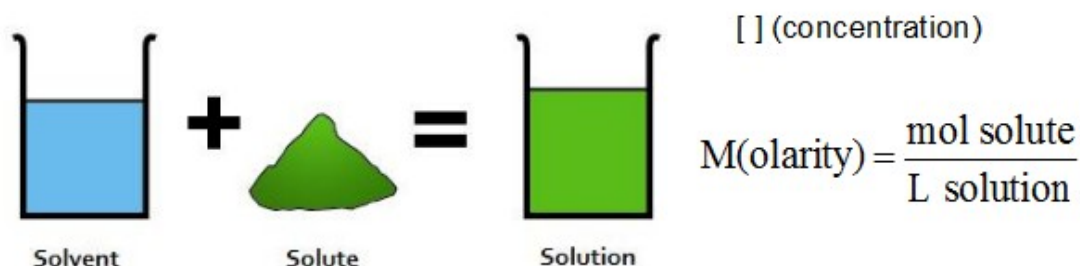


- Terminology
  - Solute** is a dissolved substance.
  - Solvent** is the most abundant part of the solution; the compound of a solution in which the other components are considered to be dissolved in.
  - Solution** is a homogenous mixture.
  - Concentration (use both links and learn from them they are great):
    - Concentration calculations: use this link <http://www.chem.purdue.edu/gchelp/howtosolveit/Solutions/concentrations.html> to learn all the different types!
    - Various examples to calculation problems and solutions: <http://www.chemteam.info/Solutions/Dilution.html>

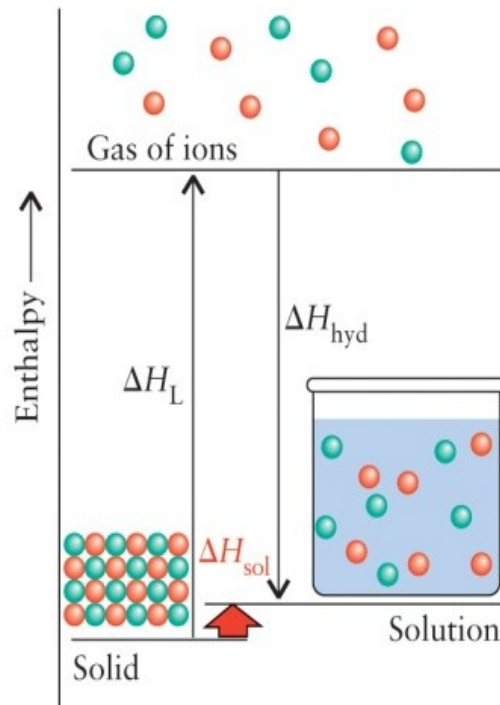


- Solubility rules (memorize):

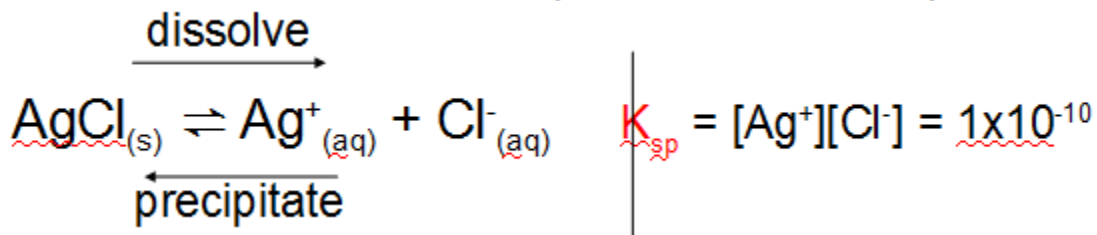
Ion	General Solubility Rule
$\text{NO}_3^-$	All nitrates are soluble
$\text{C}_2\text{H}_3\text{O}_2^-$	All acetates are soluble ( $\text{AgC}_2\text{H}_3\text{O}_2$ only moderately)
$\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$	All chlorides, bromides and iodides are soluble except $\text{Ag}^+$ , $\text{Pb}^+$ and $\text{Hg}_2^{2+}$ . ( $\text{PbCl}_2$ is slightly soluble in cold water and moderatel soluble in hot water.)
$\text{SO}_4^{2-}$	All sulfates are soluble except those of $\text{Ba}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Ca}^{2+}$ and $\text{Sr}^{2+}$
$\text{CO}_3^{2-}$ and $\text{PO}_4^{3-}$	All carbonates and phosphates are insoluble except those of $\text{Na}^+$ , $\text{K}^+$ and $\text{NH}_4^+$ . (Many acid phosphates are soluble).
$\text{OH}^-$	All hydroxides are insoluble except those of $\text{Na}^+$ and $\text{K}^+$ . Hydroxides of $\text{Ba}^{2+}$ and $\text{Ca}^{2+}$ are slightly soluble.
$\text{S}^{2-}$	All sulfides are insoluble except those of $\text{Na}^+$ , $\text{K}^+$ , $\text{NH}_4^+$ and those of the alkaline earths: $\text{Mg}^{2+}$ , $\text{Ca}^{2+}$ , $\text{Sr}^{2+}$ and $\text{Ba}^{2+}$ . (Sulfides of $\text{Al}^{3+}$ and $\text{Cr}^{3+}$ hydrolyze and precipitate as the corresponding hydroxides.
$\text{Na}^+$ , $\text{K}^+$ and $\text{NH}_4^+$	All salts of sodium ion, potassium ion and ammonium ion are soluble except several uncommon ones.

- Henry's law and gas solubility
  - Henry's law** states that the solubility of a gas is directly proportional to its partial pressure.
  - $S = k_H P$ 
    - $k_H$  = Henry's constant (temperature dependent)
    - $P$  = partial pressure of gas
  - Gases are most soluble at low temperatures and high pressures.
- Energetics and dissolving
  - 2 major steps of dissolving: solid  $\rightarrow$  gaseous ions  $\rightarrow$  dissolved aqueous ions

- (1) is **lattice enthalpy**. This is the for  $\Delta H_{\text{rxn}}$  for solid  $\rightarrow$  gas ions.  $\Delta H_L > 0$  (*endothermic*)
- (2) is **enthalpy of hydration**. This is the  $\Delta H_{\text{rxn}}$  for gas ions  $\rightarrow$  dissolved aqueous ions.  $\Delta H_{\text{hyd}} < 0$  (*exothermic*)
- **Enthalpy of solution**  $\Delta H_{\text{sol}} = \Delta H_L + \Delta h_{\text{hyd}}$ . This is the change in molar enthalpy when a substance dissolves at a constant pressure.
  - If  $\Delta H_{\text{sol}} < 0$ , the solution temperature increases since the reaction is exothermic and will release heat to the surroundings.
  - If  $\Delta H_{\text{sol}} > 0$ , the solution temperature decreases since the reaction is endothermic and will absorb heat from the surroundings.



- Solubility product constant
  - soluble vs. insoluble
    - Soluble solutes dissociate completely (“one way rxn”)
    - Insoluble solutes are in equilibrium (“two way rxn”)
  - $K_{\text{sp}}$  is the equilibrium constant for a salt dissolving in water reaction:



- $K_{\text{sp}}$  describes the saturation point of the solute; that is, it tells you the amount of products formed when the maximum amount of solid has dissolved.
- Looking at the  $K_{\text{sp}}$  value above, we can say that the solubility (s) of AgCl is  $1 \times 10^{-5}$  M.
  - The molar **solubility** of a salt (s) is the number of moles that can dissolve per L of water.
- Q and  $K_{\text{sp}}$ 
  - When  $Q = K_{\text{sp}}$ , you are at saturation point.
  - When  $Q > K_{\text{sp}}$ , there is precipitation as the reverse reaction is favored.
  - When  $Q < K_{\text{sp}}$ , there is dissolving as the forward reaction is favored.
- **Common ion effect**: decrease in the solubility of an ionic salt because there is a “common” ion present in solution already. This causes a shift to the left (precipitation).

- Example problem:  $K_{sp}$  of  $\text{Fe}(\text{OH})_2$  is  $1.6 \times 10^{-15}$ . What is the solubility of  $\text{Fe}(\text{OH})_2$  in 0.025 M  $\text{FeCl}_2$ ?

- (1) Draw an ICE box and fill in the chart:

	$\text{Fe}(\text{OH})_2 \rightarrow$	$\text{Fe}^{2+} +$	$2 \text{OH}^-$
I	XXXXXXXXXX	0.025 M	0 M
C	XXXXXXXXXX	+ x	+ 2x
E	XXXXXXXXXX	0.025 + x M	2x M

- Why is the initial concentration of  $\text{Fe}^{2+}$  0.025 M and not 0 M? Because you are adding the salt to a dissolved  $\text{FeCl}_2$  solution. Since  $\text{FeCl}_2$  will have completely dissolved, there are Fe and Cl ions in the solution and you need to account them in the ICE box.
- (2) Write out the  $K_{sp}$  equation and solve for "x." To help make the calculation easy on the DAT, ignore the "+x" value to the common ion. X = solubility

$$1.6 \times 10^{-16} = (0.025 + x)(2x)^2$$

$$1.6 \times 10^{-16} = (0.025)(4x^2)$$

$$1.6 \times 10^{-16} = 0.1x^2$$

$$(1.6 \times 10^{-16})(1.0 \times 10^{-1}) = x^2$$

$$16 \times 10^{-16} = x^2$$

$$4 \times 10^{-8} \text{ M} = x$$

- The "saturated solution problem"

- Example: What will happen if 0.05 moles of  $\text{NaCl}_{(s)}$  are added to 1 L of a saturated solution of  $\text{AgCl}$  ( $K_{sp} = 1 \times 10^{-10}$ )?
  - (1) draw out the dissolving reaction that occurs and the corresponding  $K_{sp}$
  - (2) since you are given the  $K_{sp}$  value, solve for solubility. This gives you the concentration of the Ag and Cl ions at saturation (equilibrium).
  - (3) Add 0.05 M to the Cl- concentration and calculate Q. Since  $Q > K$ ,  $\text{AgCl}$  will precipitate as the reverse reaction is favored.

## Concept Question

What will happen if 0.05 moles of  $\text{NaCl}_{(s)}$  are added to 1 L of a saturated solution of  $\text{AgCl}$  ( $K_{sp} = 1 \times 10^{-10}$ )?

A. No change

B.  $\text{AgCl}$  will dissolve

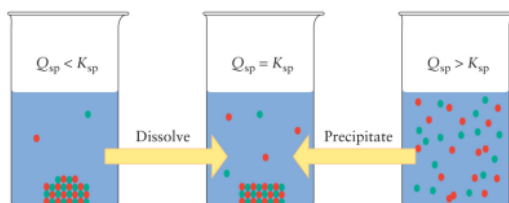
C.  $\text{AgCl}$  will precipitate



$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1 \times 10^{-10}$$

$$s = 1 \times 10^{-5}$$

$$Q = [1 \times 10^{-5}][1 \times 10^{-5} + 0.05] > K$$

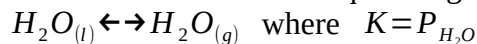


- pH change** can also affect solubility. This can only occur if an acid-base reaction can occur. Anions of weak acids will significantly be affected. This is because anions of weak acids increases pH.  $\text{A}^- + \text{H}_2\text{O} \leftrightarrow \text{OH}^- + \text{HA}$ . Lowering pH adds more  $\text{H}^+$ .  $\text{H}^+$  will react with  $\text{OH}^-$ , and lower the  $[\text{OH}^-]$ . This pushes the reaction to the right and lowers the  $[\text{A}^-]$ .  $\text{AB} \leftrightarrow \text{A}^- + \text{B}^+$ . As  $[\text{A}^-]$  goes down, this reaction is pushed to the right and solubility increases.

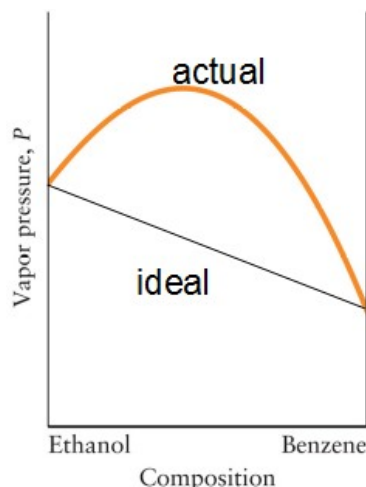
- **Colligative properties** are properties of solutions that depend on the ratio of the number of solute particles to the number of solvent particles in a solution, and not on the type of chemical species present. There are 4 colligative properties that we focus on: vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure.

- Vapor pressure and vapor pressure lowering

- **Vapor pressure** is the equilibrium constant for the liquid  $\leftrightarrow$  gas reaction.



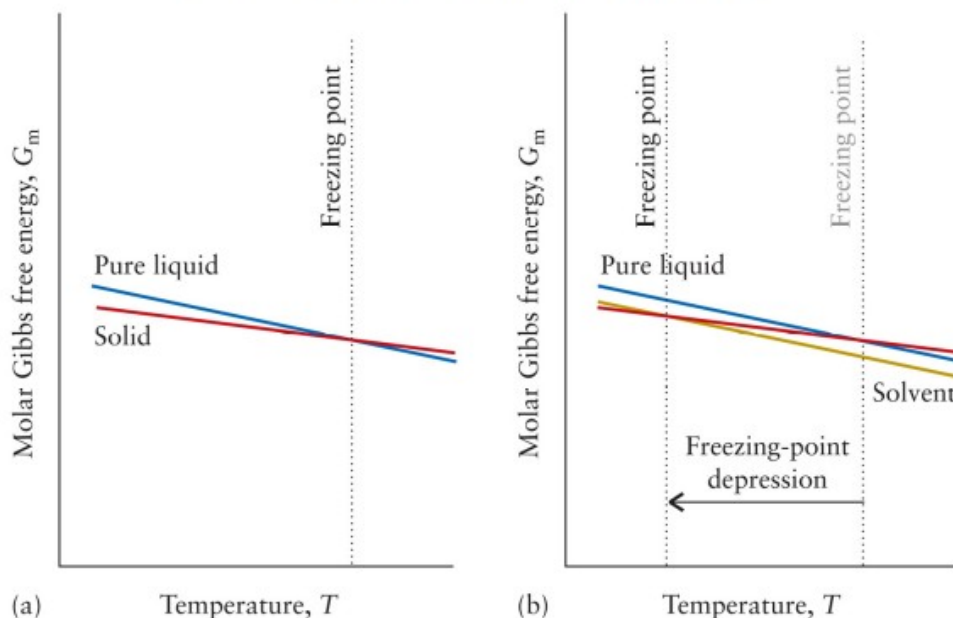
- In general, liquids boil when their vapor pressure equals the atmospheric pressure. A liquid with a higher vapor pressure boils at a lower temperature and a liquid with a lower vapor pressure boils at a higher temperature.
  - If you go to a higher altitude, atmospheric pressure decreases. Since the liquid needs to achieve a lower  $P_{\text{vap}}$  to equal  $P_{\text{atmosphere}}$ , boiling point decreases.
  - If you increase atmospheric pressure (i.e. go to a lower altitude), you increase the boiling point.
  - Unrelated but important: increasing altitude increases melting point if solid is less dense than liquid and decreases melting point if the liquid is more dense than the solid.
- The **normal boiling point** is defined as the temperature at which the vapor pressure of the liquid is 1 atm.
- What affects vapor pressure?
  - Vapor pressure decreases with increasing IMF.
  - Vapor pressure increases with increasing boiling point.
  - Vapor pressure decreases with increasing molar mass.
  - Note: vapor pressure does not depend on the surface area of a liquid.
- **Vapor pressure lowering** says that the vapor pressure of a solvent in solution is always lower than the vapor pressure of the pure solvent. This lowering is quantitatively described in Raoult's Law.
- **Raoult's Law** states that the vapor pressure of a solvent above a solution is equal to the vapor pressure of the pure solvent at the same temperature scaled by the mole fraction of the solvent present.  $P_{\text{solution}} = X_{\text{solvent}} P^{\circ}_{\text{solvent}}$ 
  - In a liquid:liquid mixture, the total vapor pressure is equal to the sum of the individual pressures:
 
$$P_{\text{vap, tot}} = P_{\text{vap, A}} + P_{\text{vap, B}}$$
  - Raoult's Law accurately describes vapor pressure lowering only in ideal solutions. Solutions are most ideal at low solute concentrations:
    - $x < 0.1$  M for **non-electrolyte** (molecular) solutions.
    - $x < 0.01$  M for **electrolyte** (ionic) solutions.
- **Azeotropes** are real liquid:liquid mixtures and deviates from Raoult's law. Two different types:
  - When the 2 liquids have dissimilar IMFs (i.e. polar + non-polar liquid):
    - $\Delta H_{\text{mix}} > 0$  so the mixing process is endothermic.
    - The mixture's boiling point decreases.
    - The total vapor pressure is higher than what Raoult's law would predict.



- When the 2 liquids have similar IMFs (i.e. 2 polar liquids):
  - $\Delta H_{mix} < 0$  so the mixing process is exothermic.
  - The mixture's boiling point increases.
  - The total vapor pressure is lower than what Raoult's law would predict.
- Boiling point elevation and freezing point depression
  - When a solute is added to a liquid, the boiling point of the resulting solution increases. **This is boiling point elevation.** In addition, the freezing point of the resulting solution decreases; this is called **freezing point depression**.
  - Quantitatively, we can describe the changes in the boiling point and the freezing point as follows:
 
$$\Delta T_f = iK_f m \text{ (freezing point depression)} \quad \Delta T_b = iK_b m \text{ (boiling point elevation)}$$
    - $m$  = molality
    - $K_f$  and  $K_b$  are constants – depends on the solvent
    - $i$  = van't hoff factor
  - The van't hoff factor ( $i$ ) expresses how many ions and particles are formed (on average) in a solution from one formula unit of solute.
    - For ionic compounds: the total number of ions that make up the compound is equal to the van't hoff factor. For example,  $i = 4$  for  $K_3PO_4$  since 3 potassium ions and 1 phosphate ion make up the compound ( $3+1 = 4$ ).
    - For molecular compounds,  $i = 1$  because they don't dissociate. For example,  $i = 1$  for  $C_6H_{12}O_6$ .
    - Treat strong acids/bases like ionic compounds because they dissociate completely! For example,  $i = 2$  for  $HBr$  ( $1 H + 1 Br = 2$ ).
    - Weak acids/bases partially dissociate. To find  $i$ , use the equation:  $i = \frac{\text{mol particles}}{\text{mol solute}}$ .
  - Gibbs vs. temperature graphs for liquid and solutions
    - Remember:  $G^\circ = -TS^\circ + H^\circ$ . We can treat this like  $y = mx + b$  and graph it. Temperature is on the x-axis and gibbs free energy is on the y-axis.
    - Freezing point depression:** The temperature at which the solid and the pure-liquid intersects (equilibrium since their gibbs values are equal) is the freezing-point. Compared to the pure liquid, the solvent has the same slope but a lower y-intercept. Therefore, the intersection between the solvent and the solid is farther to the left. This shows freezing-point depression.

## Freezing Point Depression

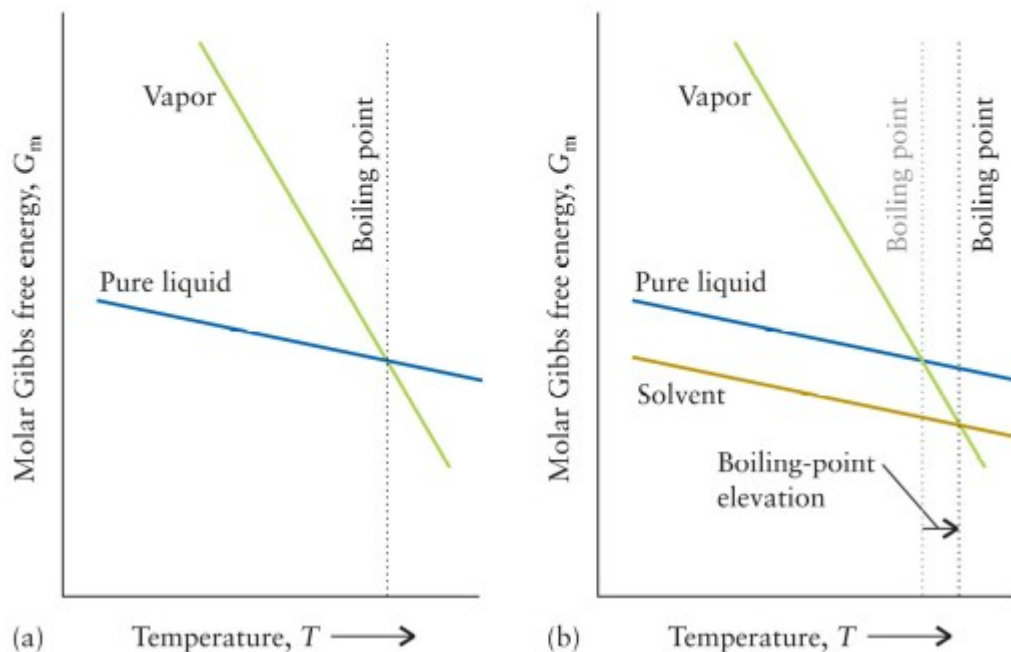
Lower T needed for solution/solid equilibrium



- Boiling point elevation: The temperature at which the vapor and the pure liquid intersect is the boiling point. Compared to the pure liquid, the solvent has the same slope but a lower y-intercept. Therefore, the intersection between the solvent and the vapor is farther to the right. This shows boiling point elevation.

# Boiling Point Elevation

raise T to reach equilibrium between solution and gas



- Osmotic pressure
  - Osmosis** is the flow of a solvent through a semipermeable membrane into a more concentrated solution. Solvent will flow until **osmotic equilibrium** is reached (occurs when the free energies of the diffusible molecules are the same on the two sides of the membrane).
  - Osmotic pressure** ( $\Pi$ ) is the pressure needed to stop the flow.
  - Hydrostatic pressure** is the pressure created by the difference in height of the columns after flow =  $\Pi$ .
  - Formula for osmotic pressure:
 
$$\Pi = iRTc$$
    - $c$  = concentration in mol/L (molarity)
    - $R = 0.08206 \frac{L \cdot atm}{K \cdot mol}$
- Real ions in water and colligative properties
  - Assuming non-ideal behavior, ions have a smaller decrease in freezing point, boiling point elevation, etc.
  - small for +/- 1 ions, moderate for +/- 2 ions, and large for +/- 3 ions.