

Solubility of Solids

- "Like dissolves like" a pretty good rule!
- A dirty secret:

Despite the often unwritten implication of textbooks, it is very difficult to make quantitative predictions regarding solubility! Why?









Henry's Law

Solubility (*s*) of a gas in a liquid is proportional the the partial pressure of the gas:

 $s = k_{\rm H} P$

- ♦ Henry's constant, k_H, depends on the strength of solvent-solute intermolecular forces and temperature.
- E.g., $k_{\rm H}$ for O₂ in water is 1.3×10^{-3} mol·L⁻¹·atm⁻¹ at 20 °C. Is the number of O₂ molecules per liter greater in water or in air?

Boiling, Vapor Pressures

• The boiling point of a substance is temperature at which the equilibrium vapor pressure of the gas over the liquid reaches 1.0 atm.

Water here is made to "boil" at 55 °C by reducing the pressure below 1.0 atm.











Phase Equilibria

- For molecules or ions dissolved in solution, equilibria involve concentrations. For gases, equilibria involve pressures.
- When a solid or liquid is in equilibrium with a gas, the "concentration" of the condensed phase = 1.0. Also, when a solid is in equilibrium with dissolved species, the "concentration" of the solid = 1.0.

Gas-Liquid and Gas-Solid Equilibria

 \bullet H₂O(ℓ) \rightleftharpoons H₂O(g); CO₂(s) \rightleftharpoons CO₂(g) $K_P = P_{CO_2}$

$$K_P = P_{H_2O}$$

- ◆ recall: When gases are nearly ideal (usually OK), activity is numerically equal to pressure.
- There is no "concentration" of $H_2O(l)$ or $CO_2(s)$ in these expressions. As long as at least some $H_2O(l)$ or $CO_2(s)$ are present, the equilibrium vapor pressures of the gases will not not depend on how much of the condensed phases there are.

Vapor Pressure, Quantitative Relationship $H_2O(l) \rightleftharpoons H_2O(g)$

• Now we can get the relationship between pressure and the "boiling temperature".

♦ **K** =
$$P_{H_{2O}} = \exp\{-\Delta G_{vap}/RT\} \Rightarrow$$

In P_{H2O} ≈ -∆G°_{vap}/RT
(see page 395 and Sections 9.2 and 9.3 in your text- read carefully about the relationship between K and ∆G)

Temperature Dependence of K_{eq}

- $K = \exp\{-\Delta G/RT\}$ \Rightarrow $\ln K = -\Delta G/RT$ • $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \Rightarrow \ln K \approx -(\Delta H^{\circ}/RT) + (\Delta S^{\circ}/R)$
- $\ln (P_2/P_1) \approx -(\Delta H^\circ/R)(1/T_2 1/T_1)$ a form of the van't Hoff equation, Sec. 9.11 Usually called the Clausius-Clapeyron equation
- Assume, as you have before, that ΔH and ΔS don't change much as a function of temp. (ΔH ≈ ΔH°; ΔS ≈ ΔS°), then a plot of the temperature dependence of K will give us ΔH and ΔS.