# CHEM 116 – Honors and Majors General and Analytical Chemistry I

2 Exams, 6 Quizzes, 7 Labs, 9 Weeks HWK - 595 points (1245 in course)

EII: AVE = 108 (72%) Range: 49 - 148

EI: AVE = 87 (58%)

| | |
|---|---|
| Q1 6.0 | Q5 6.5 |
| Q3 4.2 | Q6 6.1 |
| Q4 7.8 | Q7 6.1 |

| | | |
|---|---|---|
| E1 19 | E5 16 | L5 18 |
| E2 17 | E7 12*** | |
| L3 18 | SP 17 | |

Class Averages

| | | |
|---|---|---|
| EXAM | 195 | 65% |
| QZ | 37 | 61% |
| LAB | 118 | 84% |
| HWK | 73 | 77% |

Course Grade Estimate

| | |
|---|---|
| A | 75% |
| B | 65% |
| C | 50% |
| D | 40% |

**class average 72.1%**

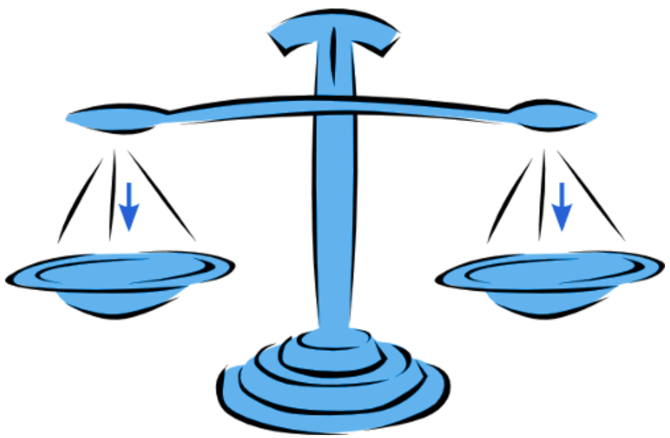
**GPA 3.1**

**7+**

# Chemical Equilibrium Z Ch 6

"When a system is in chemical equilibrium, a change in one of the parameters of the equilibrium produces a shift in such a direction that, were no other actors involved in this shift, it would lead to a change of opposite sign in the parameter involved."

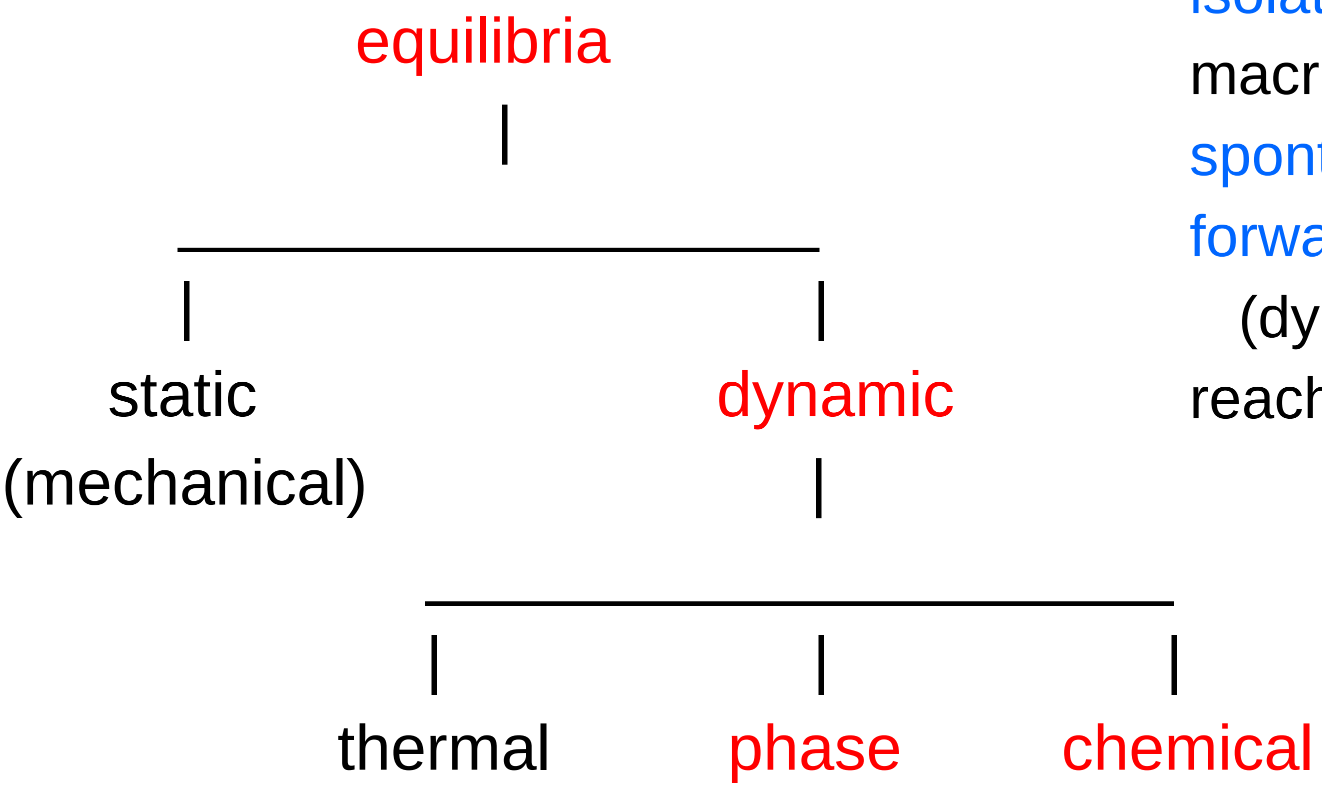
**Henri Louis Le Châtelier, 1888**



**6.1 The Equilibrium Condition**
**6.2 The Equilibrium Constant**
**6.3 Equilibrium Expressions Involving Pressures**
**6.4, 6.9 The Concept of Activity and Equilibria Involving Real Gases (See Harris 8-2)**
**6.5 Heterogeneous Equilibria**

**Please check your grades on Blackboard – Friday is drop date – talk with me FIRST!**

# The Equilibrium Condition




**attributes of equilibrium**

isolated from outside interference

macroscopic properties constant

spontaneously reach equilibrium state

forward rate = reverse rate
(dynamically balanced)

reached from products or reactants

# The Equilibrium Condition

Our emphasis will be on chemical equilibria but occasionally we will encounter phase equilibria

phase boundaries in a phase diagram; colligative properties examine phase equilibria in mixtures, primarily in liquids

steady state - system with macrosopic concentrations not changing with time but it is not at equilibrium; rather than a dynamic balance between forward and reverse processes a steady state is achieved by competiton between a process that supplies components and another process that removes components; common for chemical reactions in biological systems

# Arrows of Chemistry – Different Equilibrium Constants

reaction

$Ag^+(aq)$ + $Cl^-(aq)$ $\rightarrow$ $AgCl(s)$

resonance

O = S – O $\leftrightarrow$ O – S = O

equilibrium

$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$

**equilibrium constant, *K***

$K$ - concentration ($K_c$) Zumdahl/Harris

$K_P$ - pressure

$K_a$ - ionization of weak acid

$K_b$ - ionization of weak base

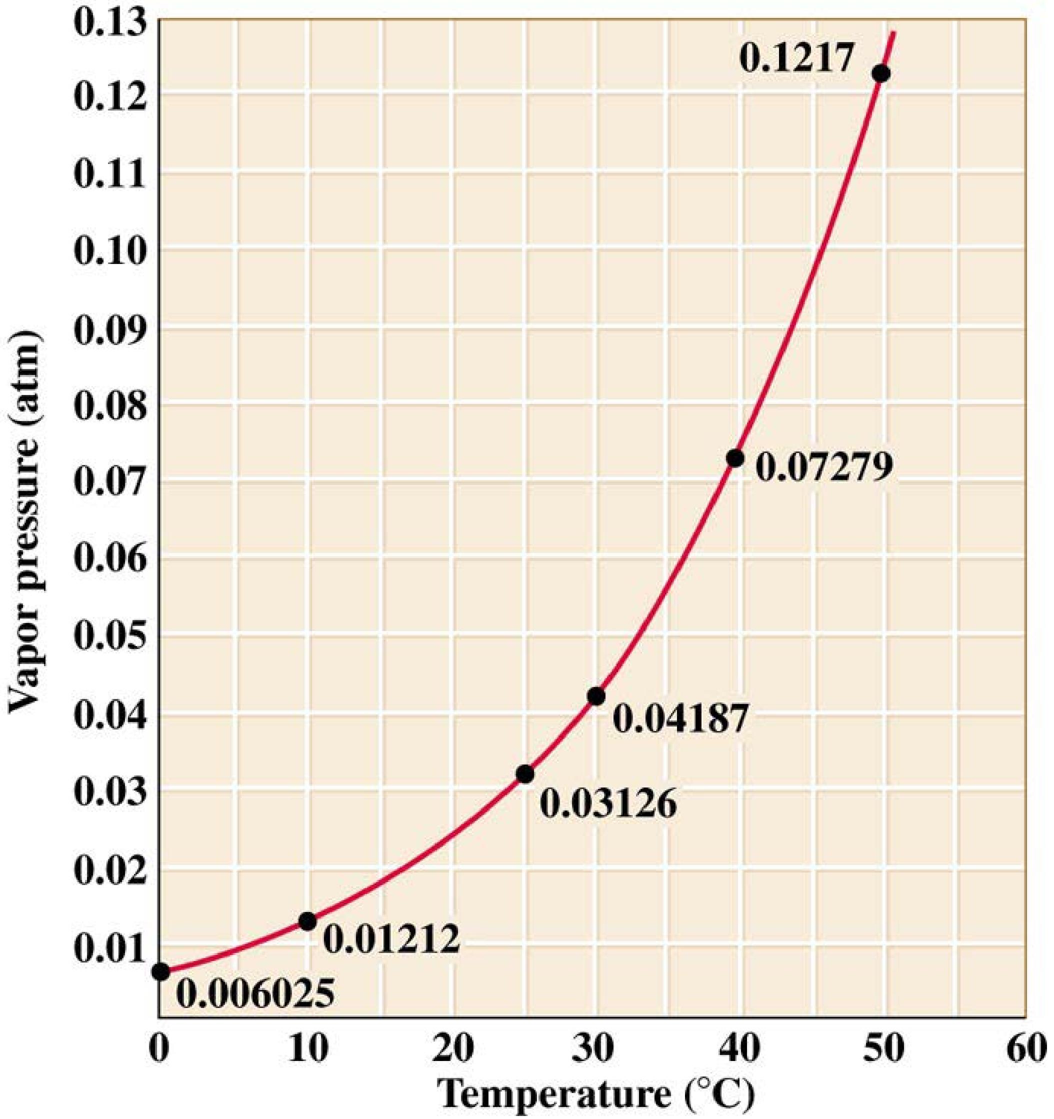
$K_{sp}$ - dissolution of slightly soluble salt

# Phase Equilibria

Phase Equilibria

$H_2O(s) \rightleftharpoons H_2O(l)$

$CO_2(s) \rightleftharpoons CO_2(g)$




**Vapor pressure of water as a function of temperature**

# The Equilibrium Constant

## Law of Mass Action

For aA + bB <=> cC + dD the equilibrium constant *K* is

$$K = \frac{\mathcal{A}^{c}_{C}\ \mathcal{A}^{d}_{D}}{\mathcal{A}^{a}_{A}\ \mathcal{A}^{b}_{B}}$$

where $\mathcal{A}^{a}_{A}$ is the activity (Zumdahl p. 178, 194; Harris p. 164) of species A raised to its stoichiometric coefficient a. Expression for activity depends upon how composition is expressed.

molarity ($K$), $\mathcal{A}_A = \gamma_A[A] / [ref]$ [ref] = 1 M

pressure ($K_P$), $\mathcal{A}_A = \gamma_A P_A / P_{ref}$ $P_{ref}$ = 1 atm (bar)

$\mathcal{A}$ = 1 for pure liquids, solids

Reference composition is usually 1, insures equilibrium constant is unitless; $\gamma$ is the activity coefficient, where deviations from ideal gas or solution found.

$\gamma$ = 1 ideal gas, ideal solution (obeys Raoult's law)

# The Equilibrium Constant

**EX 1.** At 1000 K the equilibrium gas mixture contains 0.562 atm $SO_2$, 0.101 atm $O_2$, and 0.332 atm $SO_3$. What is $K_P$ ?

| | $2\,SO_2(g)$ | + | $O_2(g)$ | $\rightleftharpoons$ | $2\,SO_3(g)$ |
|---|---|---|---|---|---|
| EQ | 0.562 | | 0.101 | | 0.332 |

$$K_P = \frac{\mathcal{A}^2_{SO3}}{\mathcal{A}^2_{SO2}\ \mathcal{A}_{O2}} = \frac{(P_{SO3})^2}{(P_{SO2})^2\ P_{O2}}$$

$$= (0.332)^2 / (0.562)^2(0.101) = 3.46$$

# The Equilibrium Constant – $K$ and $K_P$

**EX 2.** At 250°C the equilibrium concentrations are $[PCl_3] = [Cl_2] = 0.280$ M and $[PCl_5] = 1.885$ M for

| | $PCl_3(g)$ | + | $Cl_2(g)$ | $\rightleftharpoons$ | $PCl_5(g)$ |
|---|---|---|---|---|---|
| EQ | 0.280 | | 0.280 | | 1.885 |

$$K = \frac{[PCl_5]}{[PCl_3][Cl_2]} = (1.885) / (0.280)^2 = \mathbf{24.0}$$

$PV = nRT \Rightarrow P = (n/V)RT = MRT$

$$= \frac{P_{PCl5} / RT}{(P_{PCl3} / RT)\ (P_{Cl2} / RT)} = K_P / RT = 24.0 / (0.082)(250+273) = 0.056$$

$$K = K_P\ (RT)^{\Delta n} \qquad \text{where } \Delta n = n_{prod} - n_{react}$$

# Heterogeneous Equilibria

**EX 4.** What is thc value of $K$ if an equilibrium mixture contains 1.0 mol Fe, l.0 × $10^{-3}$ mol $O_2$, and 2.0 mol $Fe_2O_3(s)$ in a 2.0-L container'?

| | $4\ Fe(s)$ | $+$ | $3\ O_2(g)$ | $\rightleftharpoons$ | $2\ Fe_2O_3(s)$ |
|---|---|---|---|---|---|
| EQ | 1.0 / 2.0 | | $1.0 \times 10^{-3}$ / 2.0 | | 2.0 / 2.0 |

$$K = 1 / [O_2]^3 = 1 / (0.50 \times 10^{-3})^3$$

$$= \mathbf{8.0 \times 10^9}$$

# Relationship of *K* 's of Related Equilibria

$K_P = 55.6$ for $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$

**EX 5.** For the above reaction ($K_P = P^2_{HI} / P_{H2}\, P_{I2}$) what is $K_P$ for:

*a*) $2\,H_2(g) + 2\,I_2(g) \rightleftharpoons 4\,HI(g)$

multiply all coefficients by $n$ => $K_{new} = K_o^{\,n}$

b) $2\,HI(g) \rightleftharpoons H_2(g) + I_2(g)$

reverse reaction (multiply by -1) => $K_{new} = K_o^{-1} = 1 / K_o$

c) $\frac{1}{2}\,H_2(g) + \frac{1}{2}\,I_2(g) \rightleftharpoons HI(g)$

multiply all coefficients by $n = \frac{1}{2}$ => $K_{new} = K_o^{\,1/2} = \sqrt{K_o}$