AP* Chemistry
CHEMICAL EQUILIBRIA: GENERAL CONCEPTS

THE NATURE OF THE EQUILIBRIUM STATE: Equilibrium is the state where *the rate of the forward reaction is equal to the rate of the reverse reaction.* At these conditions, concentrations of all reactants and products remain constant with time once equilibrium has been established at constant temperature. In stoichiometry, we assumed chemical systems "went to completion". A chemist would be quick to point out that the vast majority of chemical reactions do not go to completion; they just have very large *K* values! Never, ever forget that equilibrium is TEMPERATURE DEPENDENT.

Reactions are reversible. This is indicated by double arrows. $\rightleftarrows$

- **Dynamic equilibrium**--$\rightleftarrows$ indicates that the reaction is proceeding in the forward and in the reverse direction simultaneously and once equilibrium is established, the *rate* of each direction is equal. This also keeps the *concentration* of reactants and products constant (which is not to be confused with "equal").
- The nature and properties of the equilibrium state are the same, no matter what the direction of approach.
- Examples: Look at the following plot of the reaction between steam and carbon monoxide in a closed vessel at a high temperature where the reaction takes place rapidly.

THE EQUILIBRIUM POSITION

Whether the reaction lies far to the right (favors products) or to the left (favors reactants) depends on three main factors:

- Initial concentrations (more collisions--faster reaction)
- Relative energies of reactants and products (nature goes to minimum energy)
- Degree of organization of reactants and products (nature goes to maximum disorder)
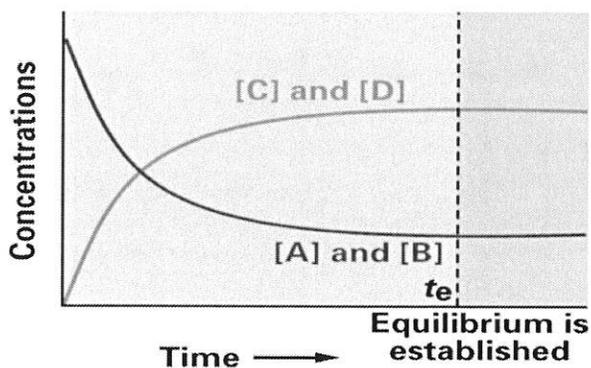
The significance of *K*:

K > **1** means that the reaction **favors the products** at equilibrium

K < **1** means that the reaction **favors the reactants** at equilibrium

THE EQUILIBRIUM EXPRESSION: A general description of the equilibrium condition proposed by Gudberg and Waage in 1864 is known as the Law of Mass Action. Equilibrium is temperature dependent, however, it does not change with concentration or pressure.

- **equilibrium constant expression**--for the general reaction
  $$aA + bB \rightleftarrows cC + dD$$
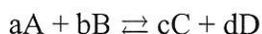
Equilibrium constant: $\quad K = \dfrac{[C]^c[D]^d}{[A]^a[B]^b} \quad$ * Note* K, K_c, K_{eq} may all be used here!

The product concentrations appear in the numerator and the reactant concentrations in the denominator.
Each *concentration is raised to the power of its stoichiometric coefficient in the balanced equation.*
- [ ] indicates concentration in Molarity (mol/L)
- K_c--is for concentration (aqueous)
- K_p--is for partial pressure (gases)
- "K" values are often written without units

- USING EQUILIBRIUM CONSTANT EXPRESSIONS
- **Pure solids**--do not appear in expression—you'll see this in K_{sp} problems soon!
- **Pure liquids**--do not appear in expression—$H_2O(l)$ is pure, so leave it out of the calculation
- **Water**--as a pure liquid or reactant, does not appear in the expression. (55.5 M will not change significantly)
  - o Weak acid and weak base equations are heterogeneous [multi-states of matter; pure liquid and aqueous components] equilibria.

  - o Solubility of salts also fits into this category. The initial solid component has a constant concentration and is therefore left out of the equilibrium expression.

Exercise 1   **Writing Equilibrium Expressions**

Write the equilibrium expression for the following reaction:

$$4\ NH_3(g) + 7\ O_2(g) \rightleftarrows 4\ NO_2(g) + 6\ H_2O(g)$$
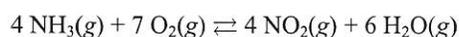
Exercise 2   **Equilibrium Expressions for Heterogeneous Equilibria**

Write the expressions for K and K_p for the following processes:

a. The decomposition of solid phosphorus pentachloride to liquid phosphorus trichloride and chlorine gas.

b. Deep blue solid copper(II) sulfate pentahydrate is heated to drive off water vapor to form white solid copper(II) sulfate.

- CHANGING STOICHIOMETRIC COEFFICIENTS

  when the stoichiometric coefficients of a balanced equation are multiplied by some factor, the K is raised to the power of the multiplication factor (K^n). Thus, $2x$ is K squared; $3x$ is K cubed; etc.
- REVERSING EQUATIONS

  take the reciprocal of K $(1/K)$
- ADDING EQUATIONS

  multiply respective Ks $(K_1 \times K_2 \times K_3 \ldots)$

Exercise 3   **Calculating the Values of K**

The following equilibrium concentrations were observed for the Haber process at 127°C:

$$[NH_3] = 3.1 \times 10^{-2} \text{ mol/L}$$
$$[N_2] = 8.5 \times 10^{-1} \text{ mol/L}$$
$$[H_2] = 3.1 \times 10^{-3} \text{ mol/L}$$

a. Calculate the value of K at 127°C for this reaction.

b. Calculate the value of the equilibrium constant at 127°C for the reaction:
$$2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)$$

c. Calculate the value of the equilibrium constant at 127°C for the reaction given by the equation:
$$\tfrac{1}{2}\,N_2(g) + \tfrac{3}{2}\,H_2(g) \rightleftharpoons NH_3(g)$$
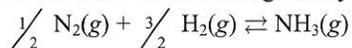
The following results were collected for two experiments involving the reaction at 600°C between gaseous sulfur dioxide and oxygen to form gaseous sulfur trioxide:

	Experiment 1		Experiment 2	
Initial	Equilibrium		Initial	Equilibrium
$[SO_2]_0 = 2.00\ M$	$[SO_2] = 1.50\ M$		$[SO_2]_0 = 0.500\ M$	$[SO_2] = 0.590\ M$
$[O_2]_0 = 1.50\ M$	$[O_2] = 1.25\ M$		$[O_2]_0 = 0$	$[O_2] = 0.0450\ M$
$[SO_3]_0 = 3.00\ M$	$[SO_3] = 3.50\ M$		$[SO_3]_0 = 0.350\ M$	$[SO_3] = 0.260\ M$

Show that the equilibrium constant is the same in both cases.

- K_c & K_p--**NOT INTERCHANGEABLE!** $\boldsymbol{K_p = K_c(RT)^{\Delta n}}$
  where Δn is the change in the number of moles of gas going from reactants to products:

- Δn = total moles gas produced − total moles gas reacting
  - R = universal gas law constant   0.0821 L atm/ mol K
  - T = temperature in Kelvin

- $Kc = Kp$ **if** the number of moles of gaseous product = number of moles of gaseous
  reactant since $(RT)^{\Delta n} = (RT)^0 = 1$

- $K_p = K_c(RT)^{\Delta n}$ is often referred to as the "politically correct" (pc) equation to help you remember the
  order of the Ks in the equation!

Exercise 5   **Calculating Values of K_p**

The reaction for the formation of nitrosyl chloride

$$2\ NO(g) + Cl_2(g) \rightleftarrows 2\ NOCl(g)$$
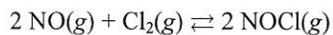
was studied at 25°C. The pressures at equilibrium were found to be

$$P_{NOCl} = 1.2\ atm$$
$$P_{NO} = 5.0 \times 10^{-2}\ atm$$
$$P_{Cl2} = 3.0 \times 10^{-1}\ atm$$

Calculate the value of K_p for this reaction at 25°C.

Exercise 6   **Calculating K from K_p**

Using the value of K_p obtained in Sample Exercise 13.4, calculate the value of K at 25° C for the reaction:

$$2\ NO(g) + Cl_2(g) \rightleftarrows 2\ NOCl(g)$$

Chemical Equilibria: General Concepts
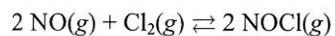
- MAGNITUDE OF K--what does it mean anyway? When greater than one, formation of products is favored. When less than one, formation of reactants is favored.

    Can you...
    1. ...write an equilibrium constant expression?
    2. ...tell how K is changed if the stoichiometric coefficients are changed on an equation?
    3. ... tell how to find K for a summary equation?
    4. ...tell how K depends on the way equilibrium concentrations are expressed and how to convert K in terms of K_c vs. K_p?
    5. ...explain what K is telling you about a reaction?

THE REACTION QUOTIENT
For use when the system is NOT at equilibrium.
For the general reaction

$$aA + bB \rightleftharpoons cC + dD$$
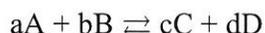
$$\text{Reaction quotient} = Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Q_c has the appearance of K but the concentrations are *not necessarily* at equilibrium.

1. **If $Q < K$, the system is not at equilibrium:** Reactants $\rightarrow$ products to make $Q = K$ at equil.
2. **If $Q = K$, the system is at equilibrium.**
3. **If $Q > K$, the system is not at equilibrium:** Reactants $\leftarrow$ products to make $Q = K$ at equil.
Quite useful for predicting what will happen under special conditions.

Exercise 7	Using the Reaction Quotient

For the synthesis of ammonia at 500°C, the equilibrium constant is 6.0×10^{-2}. Predict the direction in which the system will shift to reach equilibrium in each of the following cases:

a. $[NH_3]_0 = 1.0 \times 10^{-3} \, M;$ $[N_2]_0 = 1.0 \times 10^{-5} \, M;$ $[H_2]_0 = 2.0 \times 10^{-3} \, M$

b. $[NH_3]_0 = 2.00 \times 10^{-4} \, M;$ $[N_2]_0 = 1.50 \times 10^{-5} \, M;$ $[H_2]^0 = 3.54 \times 10^{-1} \, M$

c. $[NH_3]_0 = 1.0 \times 10^{-4} \, M;$ $[N_2]_0 = 5.0 \, M;$ $[H_2]_0 = 1.0 \times 10^{-2} \, M$

SOME CALCULATIONS WITH THE EQUILIBRIUM CONSTANT
General steps for solving equilibrium problems.

1. Set up "**R**ICE" TABLE—write a balanced reaction, place **i**nitial **c**oncentrations into the table, determine the **c**hange in initial concentrations in terms of x, calculate the **e**quilibrium concentration expressions ($0.25\ M - x$).

    R = write a balanced reaction for the predominant reacting species
    I = fill in the initial concentrations
    C = determine the change that is taking in place in terms of x
    E = express the equilibrium concentrations in terms of x

2. Set up the equilibrium expression and set it equal to its value, if given.
3. Celebrate if you are given equilibrium concentrations! Just skip down to the "E" line and fill them in. You may be asked to work backwards to determine the "change" in equilibrium.
4. If you are given a K value, then use it to solve for x and use x to calculate the equilibrium concentrations.

    Hints:
    - Look for very small K values (where $K < 10^{-5}$), "x" may be negligible.
    - If "x" is large enough to impact the equilibrium values, then you must subtract it from the initial concentration. Your math will be simplified if the problem is a perfect square. If not, you must use the quadratic formula. You are allowed to use your calculator with a solver or program for solving the quadratic.
    - If none of the initial concentrations are zero, then Q must be calculated first to determine the direction of the shift before following the above general steps.

Exercise 8	Calculating Equilibrium Pressures I

Dinitrogen tetroxide in its liquid state was used as one of the fuels on the lunar lander for the NASA Apollo missions. In the gas phase it decomposes to gaseous nitrogen dioxide:

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$$
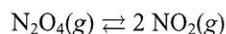
Consider an experiment in which gaseous N_2O_4 was placed in a flask and allowed to reach equilibrium at a temperature where $K_p = 0.133$. At equilibrium, the pressure of N_2O_4 was found to be 2.71 atm. Calculate the equilibrium pressure of $NO_2(g)$.

Exercise 9   **Calculating Equilibrium Pressures II**

At a certain temperature a 1.00-L flask initially contained 0.298 mol $PCl_3(g)$ and 8.70×10^{-3} mol $PCl_5(g)$. After the system had reached equilibrium, 2.00×10^{-3} mol $Cl_2(g)$ was found in the flask. Gaseous PCl_5 decomposes according to the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Calculate the equilibrium concentrations of all species and the value of K.

Exercise 10   **Calculating Equilibrium Concentrations I**

Carbon monoxide reacts with steam to produce carbon dioxide and hydrogen. At 700 K the equilibrium constant is 5.10. Calculate the equilibrium concentrations of all species if 1.000 mol of each component is mixed in a 1.000-L flask.

Exercise 11   **Calculating Equilibrium Concentrations II**

Assume that the reaction for the formation of gaseous hydrogen fluoride from hydrogen and fluorine has an equilibrium constant of 1.15×10^2 at a certain temperature. In a particular experiment, 3.000 mol of each component was added to a 1.500-L flask. Calculate the equilibrium concentrations of all species.

Exercise 12   **Calculating Equilibrium Pressures**

Assume that gaseous hydrogen iodide is synthesized from hydrogen gas and iodine vapor at a temperature where the equilibrium constant is 1.00×10^2. Suppose HI at 5.000×10^{-1} atm, H_2 at 1.000×10^{-2} atm, and I_2 at 5.000×10^{-3} atm are mixed in a 5.000-L flask. Calculate the equilibrium pressures of all species.

EXTERNAL FACTORS AFFECTING EQUILIBRIA

- **Le Chatelier's Principle**: If a stress is applied to a system at equilibrium, the position of the equilibrium will shift in the direction which reduces the stress.

- Shifts occur to reestablish equilibrium positions. Think about K! Generally, $\dfrac{[products]}{[reactants]}$

- Adding or removing a reagent causes the equilibrium to shift to reestablish K.
  As long as you milk a "mamma" cow, she keeps making more milk!

- Increasing pressure causes the equilibrium to shift to the side containing the fewest number of moles of gas. The converse is also true.

- Adding a catalyst to a reaction has causes no shift and has NO EFFECT on K. It just causes equilibrium to be established faster!

- Changing the temperature is a lot like adding or removing a "reactant or product". Well, as long as you think of *heat energy* as a "reactant" or "product".

Think of it this way:

ENDOTHERMIC: $A + B \rightleftharpoons C + D$ $+\Delta H$ value (heat is added into the system $\therefore$ heat is a reactant)

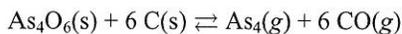Rewrite: $A + B + heat \rightleftharpoons C + D$

EXOTHERMIC: $A + B \rightleftharpoons C + D$ $-\Delta H$ value (heat is lost from the system $\therefore$ heat is a product)

Rewrite: $A + B \rightleftharpoons C + D + heat$
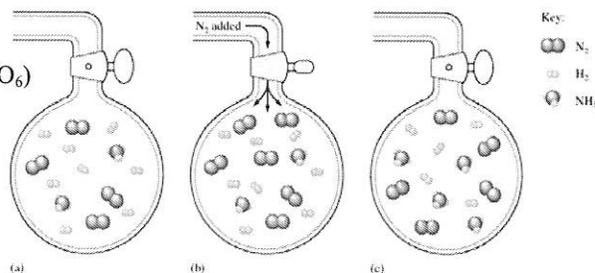

Exercise 13	Using Le Chatelier's Principle I

Arsenic can be extracted from its ores by first reacting the ore with oxygen (called *roasting*) to form solid As_4O_6, which is then reduced using carbon:

$$As_4O_6(s) + 6\ C(s) \rightleftharpoons As_4(g) + 6\ CO(g)$$

Predict the direction of the shift of the equilibrium position in response to each of the following changes in conditions.

a. Addition of carbon monoxide
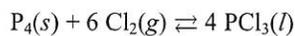**b.** Addition or removal of carbon or tetraarsenic hexoxide (As_4O_6)
**c.** Removal of gaseous arsenic (As_4)

Exercise 14　　　　　　　　　**Using Le Chatelier's Principle II**

Predict the shift in equilibrium position that will occur for each of the following processes when the volume is reduced.
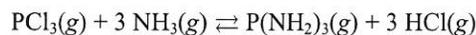
a. The preparation of liquid phosphorus trichloride by the reaction:

$$P_4(s) + 6\ Cl_2(g) \rightleftharpoons 4\ PCl_3(l)$$

b. The preparation of gaseous phosphorus pentachloride according to the equation:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$
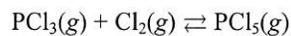
c. The reaction of phosphorus trichloride with ammonia:

$$PCl_3(g) + 3\ NH_3(g) \rightleftharpoons P(NH_2)_3(g) + 3\ HCl(g)$$

Exercise 15　　　　　　　　　**Using Le Chatelier's Principle III**

For each of the following reactions, predict how the value of K changes as the temperature is increased.

a. $N_2(g) + O_2(g) \rightleftharpoons 2\ NO(g)$ 　　　　　$\Delta H° = 181\ kJ$

b. $2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$ 　　　　$\Delta H° = -198\ kJ$