CHEMICAL EQUILIBRIA: GENERAL CONCEPTS

THE NATURE OF THE EQUILIBRIUM STATE: Equilibrium is the state where the concentrations of all reactants and products remain constant with time. (in stoichiometry, we dealt with equations that went to completion; often equilibrium equations are going to fall short of this goal)

Reactions are reversible. This is indicated by double arrows. ≈

! dynamic-- <---> indicates that the reaction is proceeding in the forward and in the reverse direction and once equilibrium is established, the rate of each direction is equal. This keeps the concentration of reactants and products 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.

\[ \text{H}_2\text{O(g)} + \text{CO(g)} \rightleftharpoons \text{H}_2\text{(g)} + \text{CO}_2\text{(g)} \]

THE EQUILIBRIUM POSITION: Whether the reaction lies far to the right or to the left 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

\[ \text{aA + bB} \rightleftharpoons \text{cC + dD} \]

Equilibrium constant: \[ K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]

* 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
"[ ] indicates concentration in Molarity
"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_{2}O (l) is pure, so leave it out of the calculation

Water--as a liquid or reactant, does not appear in the expression. (55.5M will not change significantly)

Weak acid and weak base equations are heterogeneous [multi-states of matter; pure liquid and aqueous components] equilibria. Water is a pure liquid component (55.5M) in these reactions and is left out.

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:

4NH_{3}(g) + 7O_{2}(g) \rightleftharpoons 4NO_{2}(g) + 6H_{2}O(g)

K = \frac{[NO_{2}]^{4}[H_{2}O]^{6}}{[NH_{3}]^{4}[O_{2}]^{7}}

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.

A: K = [Cl_{2}]
K_p = P_{Cl_{2}}

B: K = [H_{2}O]^{5}
K_p = P_{H_{2}O}^{5}
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 \((K^n)\). 2x is K squared; 3x is K cubed; etc.

REVERSING EQUATIONS
" take the reciprocal of K \((1/K)\)

ADDING EQUATIONS
" multiply respective K=\((K_1 \times K_2 \times K_3 \ldots)\)

### Exercise 3
Calculating the Values of K

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

\[
\begin{align*}
[NH_3] &= 3.1 \times 10^{-2} \text{ mol/L} \\
[N_2] &= 8.5 \times 10^{-1} \text{ mol/L} \\
[H_2] &= 3.1 \times 10^{-3} \text{ mol/L}
\end{align*}
\]

**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:

\[
2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)
\]

**c.** Calculate the value of the equilibrium constant at 127°C for the reaction given by the equation:

\[
\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)
\]

A: \(K = 3.8 \times 10^4\)  
B: \(K' = 2.6 \times 10^5\)  
C: \(K'' = 1.9 \times 10^2\)
Exercise 4  

Equilibrium Positions

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:

<table>
<thead>
<tr>
<th>Experiment 1</th>
<th>Experiment 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>Equilibrium</td>
</tr>
<tr>
<td>[SO₂]₀ = 2.00 M</td>
<td>[SO₂] = 1.50 M</td>
</tr>
<tr>
<td>[O₂]₀ = 1.50 M</td>
<td>[O₂] = 1.25 M</td>
</tr>
<tr>
<td>[SO₃]₀ = 3.00 M</td>
<td>[SO₃] = 3.50 M</td>
</tr>
</tbody>
</table>

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

\[ K_1 = 4.36 \]
\[ K_2 = 4.32 \]

\[ K_c \neq K_p \text{--NOT INTERCHANGEABLE!} \]

\[ K_p = K_c (RT)^{\Delta n} \]

where \( \Delta n \) is the change in the number of moles of gas going from reactants to products:

\[ \Delta n = \text{total moles gas prod. - total moles gas reactants} \]

\[ R = \text{universal gas law constant} \ 0.0821 \text{ L atm/ mol K} \]

\[ T = \text{temperature in Kelvin} \]

\[ K_c = K_p \text{ if the number of moles of gaseous product = number of moles of gaseous reactant.} \]
Exercise 5  Calculating Values of \( K_p \)

The reaction for the formation of nitrosyl chloride

\[
2\text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{NOCl}(g)
\]

was studied at 25°C. The pressures at equilibrium were found to be

\[
\begin{align*}
P_{\text{NOCl}} &= 1.2 \text{ atm} \\
P_{\text{NO}} &= 5.0 \times 10^{-2} \text{ atm} \\
P_{\text{Cl}_2} &= 3.0 \times 10^{-1} \text{ atm}
\end{align*}
\]

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

\[= 1.9 \times 10^3\]

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:

\[
2\text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{NOCl}(g)
\]

\[= 4.6 \times 10^4\]
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 eq. 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 Kc vs. Kp?
5. tell what K is telling you about a reaction?

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

For the general reaction
\[ aA + bB \rightarrow cC + dD \]
the reaction quotient is
\[ Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]

This has the appearance of K but the concentrations are not necessarily at equililibrium.

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 \( \rightarrow \) 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 \( 6.0 \times 10^{-2} \). Predict the direction in which the system will shift to reach equilibrium in each of the following cases:

a. \([\text{NH}_3]_0 = 1.0 \times 10^{-3} \text{ M}; \quad [\text{N}_2]_0 = 1.0 \times 10^{-5} \text{ M}; \quad [\text{H}_2]_0 = 2.0 \times 10^{-3} \text{ M}\)

b. \([\text{NH}_3]_0 = 2.00 \times 10^{-4} \text{ M}; \quad [\text{N}_2]_0 = 1.50 \times 10^{-5} \text{ M}; \quad [\text{H}_2]_0 = 3.54 \times 10^{-1} \text{ M}\)

c. \([\text{NH}_3]_0 = 1.0 \times 10^{-4} \text{ M}; \quad [\text{N}_2]_0 = 5.0 \text{ M}; \quad [\text{H}_2]_0 = 1.0 \times 10^{-2} \text{ M}\)

A: shift left
B: no shift
C: shift right
SOME CALCULATIONS WITH THE EQUILIBRIUM CONSTANT

General steps for solving equilibrium problems.
A. Write a balanced equation. (* do stoichiometry first in moles if needed.)
B. Set up equilibrium expression.
C. Set up RICE diagram.
   ARICE TABLES—reaction, initial concentration, change in concentration, equil. concentration! Never Fails!!
   
   \[
   \begin{align*}
   R &= \text{write a balanced reaction for the predominant reacting species} \\
   I &= \text{fill in the initial concentrations} \\
   C &= \text{what change is taking in place} \\
   E &= \text{equilibrium concentrations}
   \end{align*}
   \]
D. Fill in initial concentrations.
E. Calculate change in concentration using coefficients or information in the problem.
F. Solve for equilibrium concentrations.
G. Substitute equilibrium concentrations into the K expression and calculate.
H. Tricks:
   1. Look for very small K values (where \( K < 10^{-5} \)) , "x" may be negligible.
      You must check validity by plugging "x" over original concentration.
      It must be less than 5% of the original concentration to be valid.
   2. If "x" is necessary, then see if the problem may be a perfect square and thus, ease
      the steps of solving. (Sometimes you must use the quadratic formula!)
   3. 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:

\[
\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)
\]

Consider an experiment in which gaseous N\(_2\)O\(_4\) was placed in a flask and allowed to reach equilibrium at a temperature
where \( K_p = 0.133 \). At equilibrium, the pressure of N\(_2\)O\(_4\) was found to be 2.71 atm. Calculate the equilibrium pressure of
NO\(_2\)(g).

\[
= 0.600
\]
Exercise 9  Calculating Equilibrium Pressures II

At a certain temperature a 1.00-L flask initially contained 0.298 mol PCl₃(g) and 8.70 X 10⁻³ mol PCl₅(g). After the system had reached equilibrium, 2.00 X 10⁻³ mol Cl₂(g) was found in the flask. Gaseous PCl₅ decomposes according to the reaction

$$\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$$

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

$$\begin{align*}
[\text{Cl}_2] &= 2.00 \times 10^{-3} \text{ M} \\
[\text{PCl}_3] &= 0.300 \text{ M} \\
[\text{PCl}_5] &= 6.70 \times 10^{-3} \text{ M} \\
K &= 8.96 \times 10^{-2}
\end{align*}$$

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.

$$\begin{align*}
[\text{CO}] &= [\text{H}_2\text{O}] = 0.613 \text{ M} \\
[\text{CO}_2] &= [\text{H}_2] = 1.387 \text{ M}
\end{align*}$$
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 $1.15 \times 10^2$ 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.

$$[\text{H}_2] = [\text{F}_2] = 0.472 \, M$$  
$$[\text{HF}] = 5.056 \, M$$

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 $1.00 \times 10^2$. Suppose HI at $5.000 \times 10^{-1}$ atm, H$_2$ at $1.000 \times 10^{-2}$ atm, and I$_2$ at $5.000 \times 10^{-3}$ atm are mixed in a 5.000-L flask. Calculate the equilibrium pressures of all species.

$$P_{\text{HI}} = 4.29 \times 10^{-1} \, \text{atm}$$  
$$P_{\text{H}_2} = 4.55 \times 10^{-2} \, \text{atm}$$  
$$P_{\text{I}_2} = 4.05 \times 10^{-2} \, \text{atm}$$
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 Q!

! Temperature—exothermic Δ heat is a product; endothermic Δ heat is a reactant.

Adding or removing a reagent—shift tries to reestablish Q.

Pressure—increase favors the side with the least # of gas moles; the converse is also true.

(a) mixture at equilibrium  (b) volume is suddenly decreased  (c) new equilibrium position

Catalysts—NO EFFECT on K; just gets to equilibrium faster!
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 $\text{As}_4\text{O}_6$, which is then reduced using carbon:

$$\text{As}_4\text{O}_6(\text{s}) + 6\text{C}(\text{s}) \leftrightarrow \text{As}_4(\text{g}) + 6\text{CO}(\text{g})$$

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 ($\text{As}_4\text{O}_6$)
- **c.** Removal of gaseous arsenic ($\text{As}_4$)

![Diagram](image_url)

**A:** shift left  
**B:** no shift  
**C:** shift right

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:
  $$\text{P}_4(\text{s}) + 6\text{Cl}_2(\text{g}) \leftrightarrow 4\text{PCl}_3(\text{l})$$

- **b.** The preparation of gaseous phosphorus pentachloride according to the equation:
  $$\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \leftrightarrow \text{PCl}_5(\text{g})$$

- **c.** The reaction of phosphorus trichloride with ammonia:
  $$\text{PCl}_3(\text{g}) + 3\text{NH}_3(\text{g}) \leftrightarrow \text{P(NH}_2)_3(\text{g}) + 3\text{HCl}(\text{g})$$

**A:** shift right  
**B:** shift right  
**C:** no shift
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.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H^\circ$</th>
<th>Prediction</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$</td>
<td>$181\text{ kJ}$</td>
<td>A: increases</td>
</tr>
<tr>
<td>b. $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$</td>
<td>$-198\text{ kJ}$</td>
<td>B: decreases</td>
</tr>
</tbody>
</table>