Chemical Equilibrium – a dynamic state in which the rate of the forward reaction and the rate of the reverse reaction in a system are equal (the concentration of the products and reactants remains constant but not equal)

EQUILIBRIUM EXPRESSIONS

Equilibrium Constant \( K_{eq} \) – a value which relates the concentration of products with the concentration of reactants in a chemical reaction (units depend on the reaction and are usually not used)

Also known as “\( K_c \)” (concentration equilibrium constant)

and “\( K_p \)” (pressure equilibrium constant)

or simply “\( K \)”

For the reaction:

\[
\begin{align*}
wA & \quad + \quad xB \\ & \quad \leftrightarrow \\ yC & \quad + \quad zD
\end{align*}
\]

the equilibrium constant expression would be:

\[
K_c = \frac{[C]^y[D]^z}{[A]^w[B]^x}
\]

If the reverse reaction occurs:

\[
K'_c = \frac{1}{K_c}
\]

If the original reaction is multiplied by some factor “n”:

\[
K'_c = K_c^n
\]

For a 2-step reaction with \( K_{c1} \) and \( K_{c2} \) as equilibrium constants for each step:

\[
K_{c-\text{overall}} = K_{c1} \times K_{c2}
\]
Pressures can also be used in equilibrium expressions:

$$K_p = \frac{(P_C)^y (P_D)^z}{(P_A)^w (P_B)^x}$$

**NOTE:**

$$K_c = K_p$$

if the # of moles of gaseous reactant = the # of moles of gaseous product

**OTHERWISE:**

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

where “$\Delta n$” = # moles gaseous products – # moles gaseous reactants

Also note: Concentrations of pure solids and pure liquids are not included in equilibrium expressions because they are constant

In addition: If $K>>1$, then the equilibrium is shifted to the right (favoring products)

If $K<<1$, then the equilibrium is shifted to the left (favoring reactants)

**EXAMPLE:** Give the equilibrium constant expressions for the following reactions:

$$4\text{NH}_3(g) + 7\text{O}_2(g) \leftrightarrow 4\text{NO}_2(g) + 6\text{H}_2\text{O}(g)$$

$$\text{CaCO}_3(s) \leftrightarrow \text{CaO}(s) + \text{CO}_2(g)$$
EXAMPLE: Consider the reaction

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

3.00 mol NOCl, 1.00 mol NO, and 2.00 mol Cl\(_2\) are mixed in a 10.0-L flask. After the system has reached equilibrium, the concentrations at 35°C are observed to be:

\[
\begin{align*}
[\text{Cl}_2] &= 1.52 \times 10^{-1} \text{ M} \\
[\text{NO}] &= 4.00 \times 10^{-3} \text{ M} \\
[\text{NOCl}] &= 3.96 \times 10^{-1} \text{ M}
\end{align*}
\]

Calculate the value of “K” for this reaction at 35°C:

\[
K = \frac{[\text{NO}]^2 [\text{Cl}_2]}{[\text{NOCl}]^2}
\]

Calculate the value of “K” for the reverse reaction:

\[
K' = \frac{[\text{NOCl}]^2}{[\text{NO}]^2 [\text{Cl}_2]}
\]

Calculate the value of “K” for the reaction:

\[ \text{4NOCl}(g) \leftrightarrow \text{4NO}(g) + \text{2Cl}_2(g) \]

Calculate the value of “\(K_p\)” for the reaction in part “a”:
**Fig. 1**

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

**Fig. 2**

The forward process: \( A + B \rightarrow C + D \) decreases in rate, as time increases.

At equilibrium, the forward and reverse rates become equal. 
\( A + B \rightleftharpoons C + D \)

The reverse process: \( C + D \rightarrow A + B \) increases in rate, as time increases.
Le Chatelier’s Principle – When a stress is applied to a system the equilibrium will shift in the direction that will relieve that stress.

\[ 2\text{NH}_3 \leftrightarrow \text{N}_2 + 3\text{H}_2 \]

If a reaction shifts in the direction that *favors the products* as written in a chemical equation, it is referred to as a *shift right* (ie. the reaction proceeds in the forward direction):

If a reaction shifts in the direction that *favors the reactants* as written in a chemical equation, it is referred to as a *shift left* (ie. the reaction proceeds in the reverse direction):

**Changes in Concentration**

*Increasing the concentration of a reactant will shift the reaction to the right (ie. to the opposite side)*
*Increasing the concentration of a product will shift the reaction to the left (ie. to the opposite side)*
*A change in concentration of a reactant or product will not change the value of “K_c”*
*A change in the concentration of a pure solid or a pure liquid will not affect equilibrium*

\[ \text{H}_2\text{CO}_3(\text{aq}) + \text{heat} \leftrightarrow \text{H}_2\text{O}(l) + \text{CO}_2(\text{g}) \]

**Changes in Temperature**

*Increasing the $T^\circ$ of an exothermic reaction will shift the reaction to the left (“K_c” will decrease)*
*Decreasing the $T^\circ$ of an exothermic reaction will shift the reaction to the right (“K_c” will increase)*
*Increasing the $T^\circ$ of an endothermic reaction will shift the reaction to the right (“K_c” will increase)*
*Decreasing the $T^\circ$ of an endothermic reaction will shift the reaction to the left (“K_c” will decrease)*

\[ \text{H}_2\text{CO}_3(\text{aq}) + \text{heat} \leftrightarrow \text{H}_2\text{O}(l) + \text{CO}_2(\text{g}) \]
Changes in Pressure

*Only affects systems having a gaseous reactant and/or product

*Increasing pressure shifts the reaction to the side with the fewest number of moles of gas
*Decreasing pressure shifts the reaction to the side with the greatest number of moles of gas
*Pressure change has no effect on reactions in which #moles gaseous reactant = #moles gaseous product

*Adding an inert gas does not affect equilibrium

*Pressure changes will not affect the value of “Kc”

\[ \text{H}_2\text{CO}_3(aq) + \text{heat} \leftrightarrow \text{H}_2\text{O}(l) + \text{CO}_2(g) \]

Addition of a Catalyst

*Adding a catalyst has no effect on equilibrium (it just causes the reaction to reach equilibrium faster)

EXAMPLE: Consider the reaction

\[ 2\text{NO}_2(g) \leftrightarrow \text{N}_2(g) + 2\text{O}_2(g) + \text{heat} \]

A vessel contains nitrogen dioxide, nitrogen, and oxygen at equilibrium. Predict how each of the following stresses will shift the reaction. In addition, determine the effect on the concentration of oxygen in the container as well as the value of “Kc”.

<table>
<thead>
<tr>
<th>Direction of shift</th>
<th>∆ [oxygen]</th>
<th>∆ Kc</th>
</tr>
</thead>
</table>
* nitrogen dioxide is added
* nitrogen is removed
* helium is added
* the temperature is increased
* the pressure is decreased
* a catalyst is added
* the volume of the container is halved
EQUILIBRIUM: THE REACTION QUOTIENT

The Reaction Quotient (Q) is determined in the same manner as “K_c”, but is not at equilibrium.

The reaction quotient used values for concentrations of substances at points other than equilibrium.

*If Q > K . . . . . . the concentration of products is too high; the reaction will shift left to reach equilibrium

*If Q < K . . . . . . the concentration of products is too low; the reaction will shift right to reach equilibrium

*If Q = K . . . . . . the system is at equilibrium

EXAMPLE: For the synthesis of ammonia, the value of “K” is $6 \times 10^{-2}$ at 500°C. In an experiment, 0.50 mol of nitrogen, $1.0 \times 10^{-2}$ mol of hydrogen, and $1.0 \times 10^{-4}$ mol of ammonia are mixed at 500°C in a 1.0-L flask. In which direction will the system proceed to reach equilibrium?

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
EQUILIBRIUM: THE RICE METHOD

SOLVING EQUILIBRIUM PROBLEMS

Use the *RICE Method*:

1. Write the balanced “Reaction” with the corresponding equilibrium expression.

2. Set up a chart that includes “Initial Concentrations” (all values must be in mol/L).

3. Add the “Changes in Concentration” in terms of “x” to the chart.

4. Add the “Equilibrium Concentration” in terms of “x” to the chart.

5. Substitute the equilibrium concentration terms into the equilibrium expression and solve.

PROBLEMS WITH SMALL EQUILIBRIUM CONSTANTS (“Neglecting x”)

EXAMPLE: Consider the reaction

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

At 35°C the equilibrium constant is \(1.6 \times 10^{-5}\). In an experiment in which 1.0 mol of NOCl is placed in a 2.0-liter flask, what are the equilibrium concentrations? How many grams of NOCl remain in the flask?
EXAMPLE: Calculate the number of moles of chlorine produced at equilibrium in a 10.0-L flask when 2.0 mol of phosphorus pentachloride is heated to 150°C. ($K_c = 4.10 \times 10^{-6}$)

\[ \text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g) \]
EQUILIBRIUM: THE RICE METHOD REVISITED

OTHER TYPES OF EQUILIBRIUM PROBLEMS

EXAMPLE: At 700 K, carbon monoxide reacts with water to form carbon dioxide and hydrogen. The equilibrium constant for this reaction is 5.10. Consider an experiment in which 0.500 mol of carbon monoxide and 0.500 mol of water vapor are mixed together in a 0.500-L flask. Calculate the concentrations of all species at equilibrium.

EXAMPLE: When solid ammonium carbamate sublimes, it dissociates completely into ammonia and carbon dioxide according to the equation

\[ \text{N}_2\text{H}_6\text{CO}_2\text{(s)} \leftrightsquigarrow 2\text{NH}_3\text{(g)} + \text{CO}_2\text{(g)} \]

At 25°C, experiment shows that the total pressure of the gases in equilibrium with the solid is 0.116 atm. What is the equilibrium constant for the reaction?
EXAMPLE: The equilibrium constant, $K_p$, for $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$ is 0.15 at 25°C. If the pressure of N$_2$O$_4$ at equilibrium is 0.85 atm, what is the total pressure of the gas mixture (N$_2$O$_4$ + NO$_2$) at equilibrium?
EXAMPLE: For the synthesis of hydrogen fluoride from hydrogen and fluorine, 3.000 mol of hydrogen and 6.000 mol of fluorine are mixed in a 3.000-L flask. The equilibrium constant for the reaction at this temperature is $1.15 \times 10^2$. Calculate the equilibrium concentration of each component.