- Chapter 15
  Chemical Equilibrium

  The Concept of Equilibrium

Chemical equilibrium occurs when a reaction and its reverse reaction proceed at the same rate.

- As a system approaches equilibrium, both the forward and reverse reactions are occurring.
- At equilibrium, the forward and reverse reactions are proceeding at the same rate.
- A System at Equilibrium

  Once equilibrium is achieved, the *amount* of each reactant and product remains constant.

- Depicting Equilibrium

  In a system at equilibrium, both the forward and reverse reactions are being carried out; as a result, we write its equation with a double arrow

- The Equilibrium Constant
- Remember both forward and reverse reactions are *elementary reactions*
- The Equilibrium Constant
- Forward reaction:

$N_2O_{4\,(g)} \longrightarrow 2\ NO_{2\,(g)}$

- Rate law:

Rate = $k_f\,[N_2O_4]$

- The Equilibrium Constant
- Reverse reaction:

$2\ NO_{2\,(g)} \longrightarrow N_2O_{4\,(g)}$

- Rate law:

Rate = $k_r\,[NO_2]^2$

- The Equilibrium Constant
- Therefore, at equilibrium

$Rate_f = Rate_r$

$k_f [N_2O_4] = k_r [NO_2]^2$

- Rewriting this, it becomes

- The Equilibrium Constant

  The ratio of the rate constants is a constant at that temperature, and the expression becomes

We learn following things from these reactions about equilibrium:

1. When a mixture of reactants and products is formed in which the concentration no longer change with time, it indicates that an equilibrium is reached.

2. For an equilibrium to occur neither reactant or product should escape.

3. At equilibrium the ratio of concentrations remains constant.

The ***Equilibrium Constant***

- To generalize this expression, consider the elementary reaction
- The Law of Mass Action expresses the relationship between the concentrations of the reactants and products present at equilibrium.

*The **equilibrium constant** expression depends only on the stoichiometry of the reaction, not on its mechanism.*

- And remember that the reactants go into the denominator.
- Kc is independent of the initial concentration of the reactants and products, but on the concentrations at the equilibrium.
- The equilibrium constant is written without a unit.
- What Are the Equilibrium Expressions for These Equilibria?
- Kc is independent of the initial concentration of the reactants:

$N_2O_{4\,(g)}$ $2\ NO_{2\,(g)}$

As you can see, the ratio of $[NO_2]^2$ to $[N_2O_4]$ remains constant at this temperature no matter what the initial concentrations of NO_2 and N_2O_4 are

Calculate the Kc for yourself.

The Equilibrium Constant

Because pressure is proportional to concentration for gases in a closed system, the equilibrium expression can also be written

- The numerical value of K_c is different than the numerical value of K_p. We must indicate the subscript c or p
- Relationship between K_c and K_p
- From the ideal gas law we know that

is nothing but molarity (moles / liter)

So for substance A we can write

P=   RT

P = [A] RT

or [A] =

- Relationship between K_c and K_p
- Relationship between K_c and K_p
- Relationship between K_c and K_p

Plugging this into the expression for K_p for each substance, the relationship between K_c and K_p becomes

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

Δn = (moles of gaseous product) − (moles of gaseous reactant)

= 2-1

= 1

$Kp = Kc\,(RT)^{\Delta n}$

So $Kp = Kc\,(RT)$

If Δ n= 0 i.e. same number of moles of gas appear in the reactant and the product then

$Kp = Kc$

As anything raised to 0 is 1

In the synthesis of ammonia from nitrogen and hydrogen,

$N_2 + 3H_2 \quad 2NH_3$

K_c= 9.60 at 300^o C. Calculate K_p

Δ n = 2 - 4 = -2

$Kp = Kc\ (RT)^{\Delta n}$

$= 9.60\ (\ .0821x\ 573)^{-2}$

$= \dfrac{9.60}{(0.0821x\ 573)^{2}} = 4.34X10^{-3}$

For the equilibrium

$2SO_3\ (g) \quad 2SO_2(g)\ +\ O_2(g)$

$K_c = 4.08x\ 10^{-3}$ at 1000K. Calculate K_p

$Kp = Kc\ (RT)^{\Delta n}$

Δn = (moles of gaseous product) − (moles of gaseous reactant)

= 3 – 2 = 1

$Kp = 4.08\ x\ 10^{-3}\ (\ 0.0821x\ 1000)$

=0. 33496 = 0.3

- Equilibrium Can Be Reached from Either Direction

It does not matter whether we start with N_2 and H_2 or whether we start with NH_3. We will have the same proportions of all three substances at equilibrium.

- What Does the Value of *K* Mean?
- If *K* >> 1, the reaction is *product-favored*; product predominates at equilibrium.
- What Does the Value of *K* Mean?
- If *K* >> 1, the reaction is *product-favored*; product predominates at equilibrium.

Because *Kc* is so small, very little NO will form at 25°C. The equilibrium lies to the left, **favoring the reactants.** Consequently, this reaction is an extremely poor choice for nitrogen fixation, at least at 25°C.

Answer: The formation of product, HI, is favored at the lower temperature because *Kp* is larger at the lower temperature.

- Manipulating Equilibrium Constants

The equilibrium constant of a reaction in the reverse reaction is the reciprocal of the equilibrium constant of the forward reaction.

- With this information the direction of the reaction needs to be specified when the equilibrium constant is given.
- Also the temperature too needs to be

given as the constant depends at the temperature.

- ***Answer:*** 2.30×10^2
- Manipulating Equilibrium Constants

The equilibrium constant of a reaction that has been multiplied by a number is the equilibrium constant raised to a power that is equal to that number.

- Manipulating Equilibrium Constants

The equilibrium constant for a net reaction made up of two or more steps is the product of the equilibrium constants for the individual steps.

- What is the difference between this and what happens to ΔH ?
- For ΔH the values are added, here they are multiplied.

- Heterogeneous Equilibrium
- The example of N_2 and H_2 to give NH_3 is a homogeneous equilibria.
- There can also be heterogeneous equilibria when the substances in the equilibrium are in different phases.

an example is the equilibrium that gets established when a substance is dissolves in water to give a saturated solution.

Example:

When a solid or liquids is encountered in a reaction its concentration is not mentioned as the concentrations of solids and liquids are essentially constant

Can you understand why?

The concentration of a solid and liquids can be derived in terms of moles per unit volume but it is not required in equilibrium constant expressions.

Remember we are referring to liquids *not*

dissolved substances.

- The Concentrations of Solids and Liquids Are Essentially Constant

  Therefore, the concentrations of solids and liquids do not appear in the equilibrium expression

  As long as some $CaCO_3$ or CaO remain in the system, the amount of CO_2 above the solid will remain the same.

The equilibrium expression for the reaction is

$$K_p=P_{CO2}$$

and $K_c= [CO_2]$

- When a solvent is involved in a equilibrium as a reactant or a product its concentration is also excluded from the equilibrium constant expression.
- But the concentration of the reactant and product has to be very low.
- The equilibrium expression will be:
- When added to $Fe_3O_4(s)$ in a closed container, which one of the following substances—$H_2(g)$, $H_2O(g)$, $O_2(g)$ —will allow equilibrium to be established in the reaction in the reaction
- Write the equilibrium-constant expression for *Kc* for each of the above
- Equilibrium Calculations
- Direct calculations:
- When the equilibrium concentrations are not known:
- We do not need to know the equilibrium concentration of all the species.
- We can use the stoichiometry of the reaction to deduce the equilibrium concentrations of the unknown ones.

1.Tabulate all the known initial and equilibriums of all the species.

2.Calculate the change of concentrations for the species for which the initial and equilibrium concentrations are known.

3. Use the stoichiometry of the reaction to calculate the changes in concentration for all other species.

4. Calculate the K_c.

- Equilibrium Calculations

Here is an example

A closed system initially containing

1.000×10^{-3} M H_2 and 2.000×10^{-3} M I_2

At 448°C is allowed to reach equilibrium.

Analysis of the equilibrium mixture shows that the concentration of HI is 1.87×10^{-3} M.

Calculate K_c at 448°C for the reaction taking place, which is

-

  What Do We Know?

- [HI] Increases by 1.87×10^{-3} *M*
- Stoichiometry tells us $[H_2]$ and $[I_2]$
  decrease by half as much
- We can now calculate the equilibrium concentrations of all three compounds…
- …and, therefore, the equilibrium constant
- Applications for Equilibrium Constants

  a. Predict the direction of the reaction

  b. To calculate equilibrium concentrations.

- The Reaction Quotient (Q)
- To calculate Q, one substitutes the initial concentrations on reactants and products into the equilibrium expression.
- Q gives the same ratio the equilibrium expression gives, but for a system that is *not* at equilibrium.
- If $Q = K$,
- If $Q > K$,
- If $Q < K$,

- Calculating equilibrium concentrations

We earlier learnt to calculate the equilibrium constant when the initial concentrations of the reactants as given.

Now we will learn to calculate the equilibrium concentrations of the various components.

- Calculating equilibrium concentrations.

For the Haber process, at 500°C. In an equilibrium mixture of the three gases at 500°C, the partial pressure of H_2 is 0.928 atm and that of N_2 is 0.432 atm. What is the partial pressure of NH_3 in this equilibrium mixture?

- Calculating equilibrium concentrations.

For the Haber process, at 500°C. In an equilibrium mixture of the three gases at 500°C, the partial pressure of H_2 is 0.928 atm and that of N_2 is 0.432 atm. What is the partial pressure of NH_3 in this equilibrium mixture?

- Le Châtelier's Principle

- Le Châtelier's Principle

"If a system at equilibrium is disturbed by a change in temperature, pressure, or the concentration of one of the components, the system will shift its equilibrium position so as to counteract the effect of the disturbance."

- Change in the Reactant or Product Concentration
- If a chemical system is in equilibrium and we add one of the substances, either a reactant or the product, the reaction will shift as to reestablish the equilibrium in a manner that the change is nullified.
- The Haber Process

The transformation of nitrogen and hydrogen into ammonia (NH_3) is of tremendous significance in agriculture, where ammonia-based fertilizers are of utmost importance.

- The Haber Process

If H_2 is added to the system, N_2 will be consumed and the two reagents will form more NH_3.

- The Haber Process

This apparatus helps push the equilibrium to the right by removing the ammonia (NH_3) from the system as a liquid.

- Effect of Volume and Pressure on
  Equilibrium
- Reducing the volume of the reaction, hence increasing the pressure causes the equilibrium to move in a direction that reduces the number of moles of gas.
- More product will be formed

What will be effect of increasing the pressure on the following reaction;

The equilibrium will have more reactant.

- The volume and pressure do not change the value of K as long as the temperature remains constant.
- The Effect of Changes in Temperature
- This is an endothermic reaction and heat is absorbed when the product is formed.

We can treat heat as one of the reactants

In an endothermic reaction

Reactant + heat → Product

In an Exothermic reaction

Reactant → Product + heat

When the temperature of a reaction is increased the reaction moves in the direction that consumes heat.

And vice versa

Endothermic reactions

Reactants + heat   Product

Increasing T

Results in more product   increases K

Endothermic reactions

Reactants + heat   Product

Increasing T

Results in more product   increases K

Exothermic reactions

Reactant Product + heat

Increasing T

results in less product reduces K

(b) The system will adjust to the removal of NO2 by shifting to the side that produces more NO2; thus, the equilibrium shifts to the right.

(b) The system will adjust to the removal of NO2 by shifting to the side that produces more NO2; thus, the equilibrium shifts to the right.

(b) The system will adjust to the removal of NO2 by shifting to the side that produces more NO2; thus, the equilibrium shifts to the right.

(b) The system will adjust to the removal of NO2 by shifting to the side that produces more NO2; thus, the equilibrium shifts to the right.

- Catalysts increase the rate of both the forward *and* reverse reactions as the activation energy of the forward and reverse reaction is lowered to the same extent .
- Equilibrium is achieved faster, but the equilibrium composition remains unaltered.

Homework question:

- Sample integrative exercise on page 657