Elective physical chemistry

Fourth stage/College of Education for Pure Sciences

Asst.Prof.Dr.Fedaa AL-Taie

chemical equilibrium

- **chemical equilibrium,** the state where the concentrations of all reactants and products remain constant with time.
- Any chemical reactions carried out in a closed vessel will reach Equilibrium.
- For some reactions the equilibrium position so favors the products that the reaction appears to have gone to completion.
- We say that the equilibrium position for such reactions lies far to the right (in the direction of the products). For example, hydrogen and when gaseous oxygen are mixed in stoichiometric quantities and react to form water vapor, the reaction proceeds essentially to completion. The amounts of the reactants that remain when the system reaches equilibrium are so tiny as to be negligible. By contrast, some reactions occur only to a slight extent.

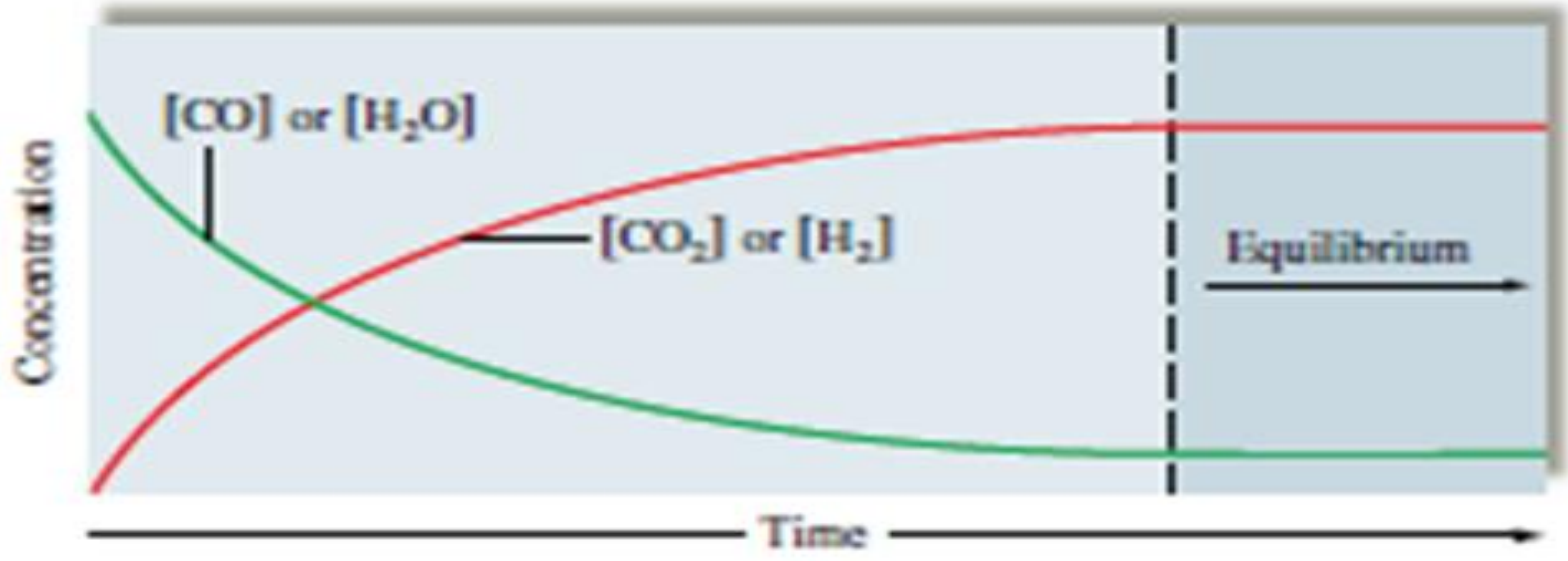
For example, when solid CaO is placed in a closed vessel at25C the decomposition to solid Ca and gaseous O2 is virtually undetectable. In cases like this, the equilibrium position is said to lie *far to the left* (in the direction of the reactants). In this chapter we will discuss how and why a chemical system comes to equilibrium and the characteristics of equilibrium. In particular, we will discuss how to calculate the concentrations of the reactants and products present for a given system at equilibrium.

The Equilibrium Condition

- Since no changes occur in the concentrations of reactants or products in a reaction systemat equilibrium, it may appear that everything has stopped. However, this is not the case. On the molecular level, there is frantic activity. Equilibrium is not static but is a highly *dynamic* situation. The concept of chemical equilibrium is analogous to the flow of cars across a bridge connecting two island cities. Suppose the traffic flow on the bridge
- To see how this concept applies to chemical reactions, consider the reaction between steam(H2O) and carbon monoxide(CO) in a closed vessel at a high temperature where the reaction takes place rapidly:

$H2O_{(g)} + CO_{(g)} \rightleftharpoons H2_{(g)} + CO2_{(g)}$

Assume that the same number of moles of gaseous CO and gaseous H2O are placed in a closed vessel and allowed to react.

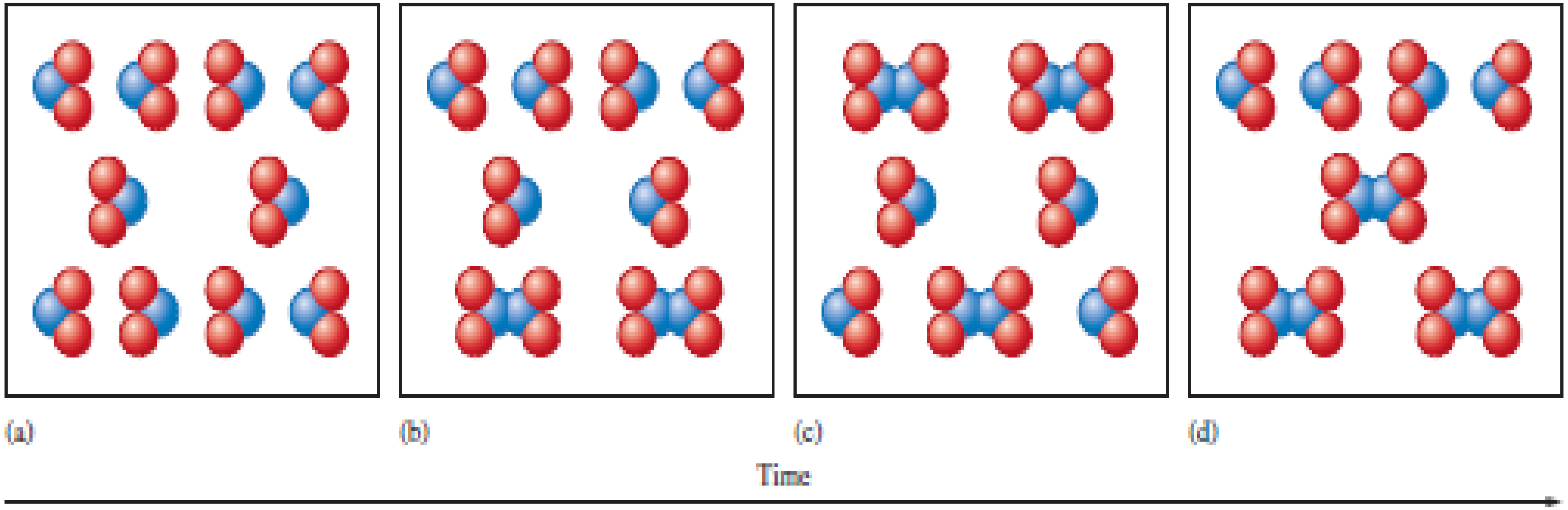


figure(1) The changes in with time for the reaction:

H2O(g) + CO(g) ⇌ H2(g)+ CO2(g)

when equimolar quantities of H2O(g)and CO(g)are mixd.

- When CO and H2O are mixed,they immediately begin to react to form H2 and CO2. which leads to a decrease in the concentrations of the reactants, but the concentrations of the products, and in same time increasing the product concentrations. Beyond a certain time, the concentrations of reactants and products no longer change—equilibrium has been reached . Note that although the equilibrium position lies far to the right, the concentrations of reactants never go to zero; the reactants will always be present in small but constant concentrations.
-



FIGURE(2)

FIGURE(2):(a) H_2O and CO are mixed in equal numbers and begin to react (b) to form CO_2 and H_2. After time has passed, equilibrium is reached (c)and the numbers of reactant and product molecules then remain constant over time (d).

- In the beginning the concentrations of H2O and CO are lowered by the forward reaction .
- As the concentrations of the reactants decrease reaction slows down.
- As the forward reaction proceeds, the concentrations of H2 and CO2 build up,and the rate of the reverse reaction increases as the forward reaction slows down .
- Eventually, the concentrations reach levele where the rate of the forward concentrations reaction equals the rate of the reverse reaction.The system has reached equilibrium .
- th equilibrium position of a reaction is determined by many factors:
- 1-The initial concentrations.
- 2- The relative energigies of the reactants and products.
- 3- The relative degree of “organization” of the reactants and products.

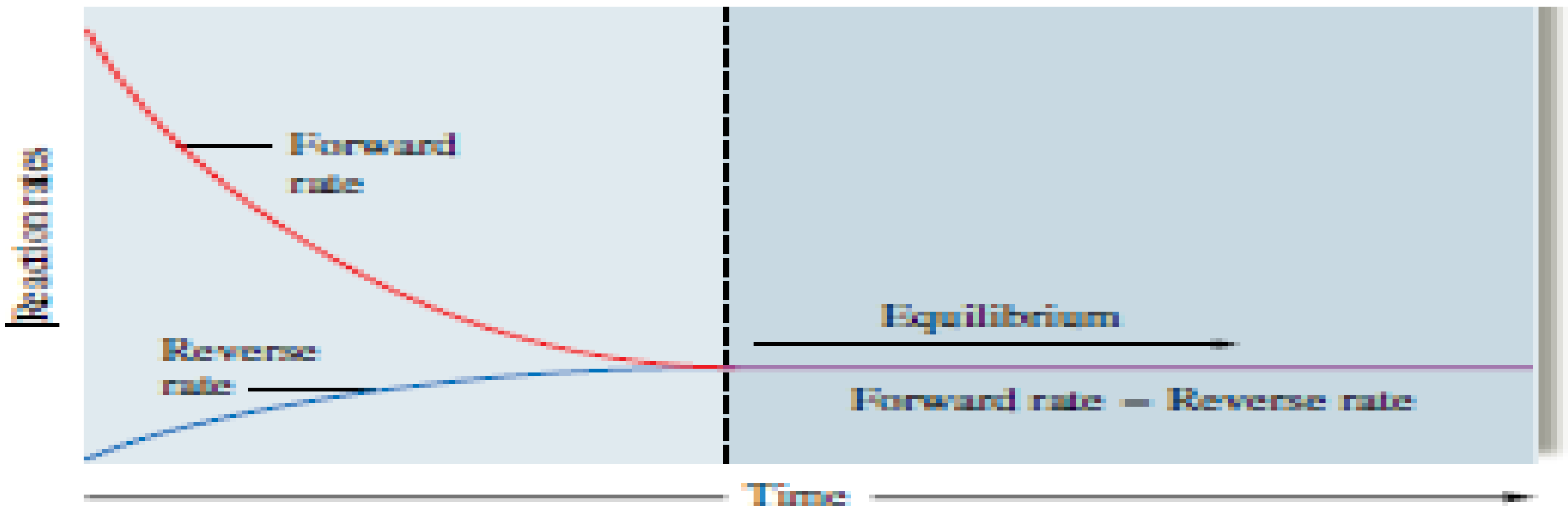


FIGURE 3

The changes with time in the rates of forward and reverse reactions for

$H_2O(g) + CO_2(g) \rightleftharpoons H_2(g) + CO_2(g)$

when equimolar quantities of $H_2O(g)$ and $CO(g)$ are mixed.

The rates do not change in the same way with time because the forward reaction has a much larger rate constant than the reverse reaction.

The Characteristics of Chemical Equilibrium :

- To explore the important characteristics of chemical equilibrium, we will consider the synthesis
- of ammonia from elemental nitrogen and hydrogen:
-
- $N_2(g) + 3H_2 \rightleftharpoons 2NH_4(g)$
- When gaseous nitrogen, hydrogen, and ammonia are mixed in a closed vessel at 25ºC,no apparent change in the concentrations occurs over time, regardless of the original amounts of the gases. Why? There are two possible reasons why the concentrations the
- reactants and products of a given chemical reaction remain unchanged when mixed.
- 1. The system is at chemical equilibrium.
- 2. The forward and reverse reactions are so slow that the system moves toward equilibrium at a rate that cannot be detected.
-
- In this case the second reason is true(N2 has very strong triple bond and H2 has strong single bond which implies the need for high activation energy) and catalyst is required to move reaction at detectable rate:

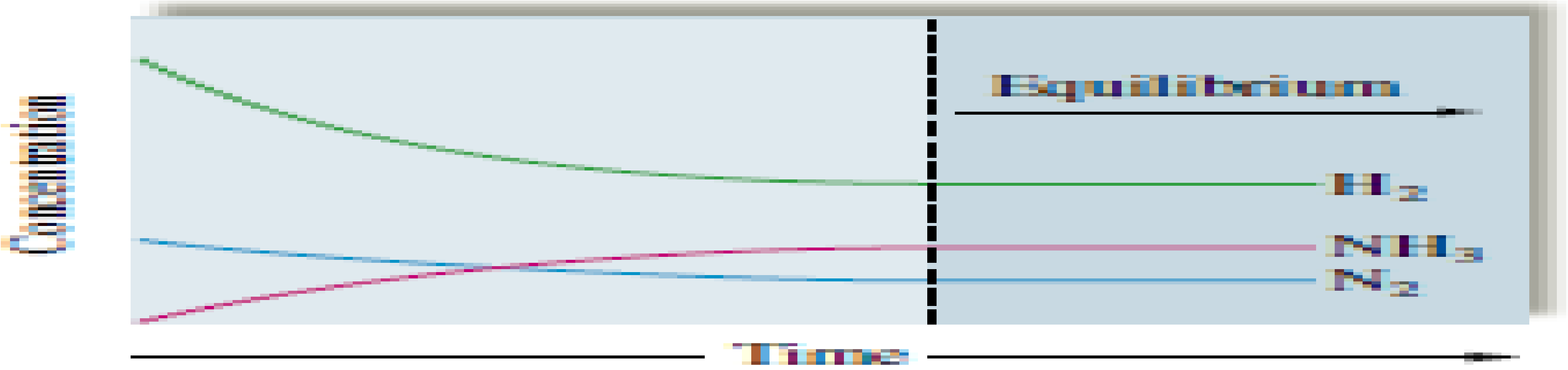


FIGURE 4 •

A concentration profile for the reaction •

•

$\mathrm{N2}(g)+ 3\mathrm{H2} \rightleftharpoons 2\mathrm{NH3}(g)$ •

•

when only **N2**(*g*) and **H2**(*g*) are mixed initially. •

•

•

Thank you all

Elective physical chemistry

Fourth stage/College of Education for Pure Sciences

Asst.Prof.Dr.Fedaa AL-Taie

The Equilibrium Constant:

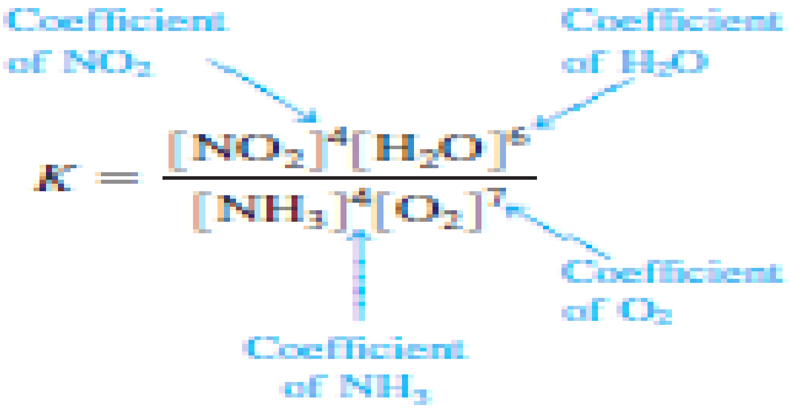
- Science is fundamentally empirical—it is based on experiment.
- The development of the equilibrium concept is typical. From their observations of many chemical reactions, two Norwegian chemists, CatoMaximilian Guldberg (1836–1902) and Peter Waage (1833–1900),
- proposed in (1864)the **law of mass action** as a general description of the equilibrium condition.
- Guldberg and Waage postulated that for a reaction of the type:
- $jA + kB \rightleftharpoons iC + mD$
- where A, B, C, and D represent chemical species and *j*, *k*, *l*, and *m* are their coefficie in the balanced equation.
- the law of mass action is represented by the following

equilibriumexpression:

$$K = \frac{[C]^l[D]^m}{[A]^j[B]^k}$$

The square brackets indicate the concentrations of the chemical species at equilibrium and K is a constant called the equilibrium constant.

- Writing Equilibrium Expressions
- Example 1 : Write the equilibrium expression for the following reaction:
- Solution : $4NH3(g) + 7O2(g) \rightleftharpoons 4O2(g) + 6H2O(g)$



$$K = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7}$$

Calculating the Values of K

Example 1: The following equilibrium concentrations were observed for the Haber process at 127°C:

L/[NH3]=3.1X10^{-2} mol

L/[N2]=8.5X10^{-1} mol

L/[H2]=3.1X10^{-3} mol

a. Calculate the value of *K* at for this reaction.

b. Calculate the value of the equilibrium constant at for the reaction.

$NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

c. Calculate the value of the equilibrium constant at for the reaction given by the equation $N_2(g) + 3H_2 \rightleftharpoons 2NH_3(g)$

$\frac{1}{2}N_2(g) + 3/2\ H_2(g) \rightleftharpoons NH_3(g)$

Solution •

a. The balanced −equation for the Haber process is Thus •

$N2(g) + 3H2 \rightleftharpoons 2NH3(g)$ •

•

$K = \frac{[NH3]^2}{[N2][H2]^3} = \frac{(3.1\ X10^{-2})^2}{(8.5\ X\ 10^{-1})^2 X (3.1\ X10^{-3})} = 3.8\ X10^4$ •

Note that *K* is written without units. •

B-The equilibrium expression is •

$K' = \frac{[N2][H2]^3}{[NH3]^2}$ •

which is the reciprocal of the expression used in part a. Therefore •

$K' = \frac{[N2][H2]^3}{[NH3]^2} = \frac{1}{K'} = \frac{1}{3.8\ x\ 10^4} = 2.6\ x\ 10^{-5}$ •

c. We use the law of mass action: •

$K'' = \frac{[NH3]^2}{[N2][H2]^3}$ •

If we compare this expression to that obtained in part a, we see that since •

$$\frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = \left(\frac{[NH_3]^2}{[N_2][H_2]^3}\right)^{1/2}$$

$$K'' = K^{1/2}$$

Thus

$$K'' = K^{1/2} = (3.8 \times 10^4)^{1/2} = 1.9 \times 10^2$$

We can draw some important conclusions from the results . For a reaction of the form

$$jA + kB \rightleftharpoons lC + mD$$

the equilibrium expression is

$$K = \frac{[C]^l[D]^m}{[A]^j[B]^k}$$

If this reaction is reversed, then the new equilibrium expression is

$$K' = \frac{[A]^j[B]^k}{[C]^l[D]^m} = \frac{1}{K}$$

If the original reaction is multiplied by some factor n to give

$$njA + nkB \rightleftharpoons nlC + nmD$$

the equilibrium expression becomes

$$K'' = \frac{[C]^{nl}[D]^{nm}}{[A]^{nj}[B]^{nk}} = K^n$$

Conclusions About the Equilibrium Expression:

1- The equilibrium expression for a reaction is the reciprocal of that for the reaction written in reverse.

2- When the balanced equation for a reaction is multiplied by a factor *n*, the equilibrium expression for the new reaction is the original expression raised to the n^{th} power. Thus $K_{\text{new}} = (K_{\text{original}})^n$.

3- *K* values are customarily written without units.

- The law of mass action provides a remarkably accurate description of all types of chemical equilibriats.
- The equilibrium constant *K* always has the same value at a given temperature. *regardless of the amounts of* reactants of products that are present *initially.*
- **equilibrium position is a** set of equilibrium concentrations.
- For a reaction , at a given temperature, there are many equilibrium position but only one equilibrium constant ,K.
- For exampale,the following table shows a results of three experiments for the reaction:
- $N_2(g) + 3H_2 \rightleftharpoons 2NH_3(g)$

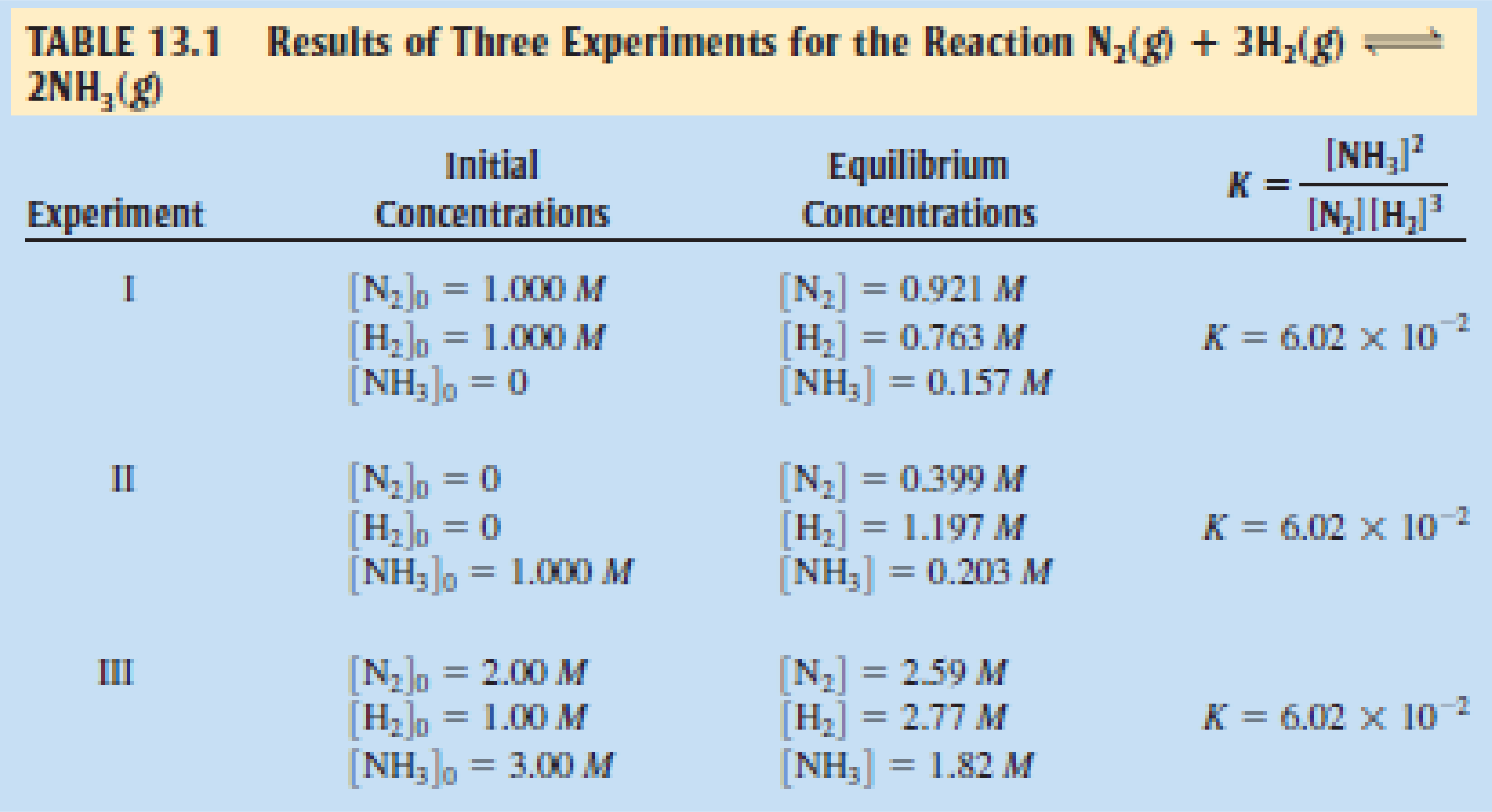
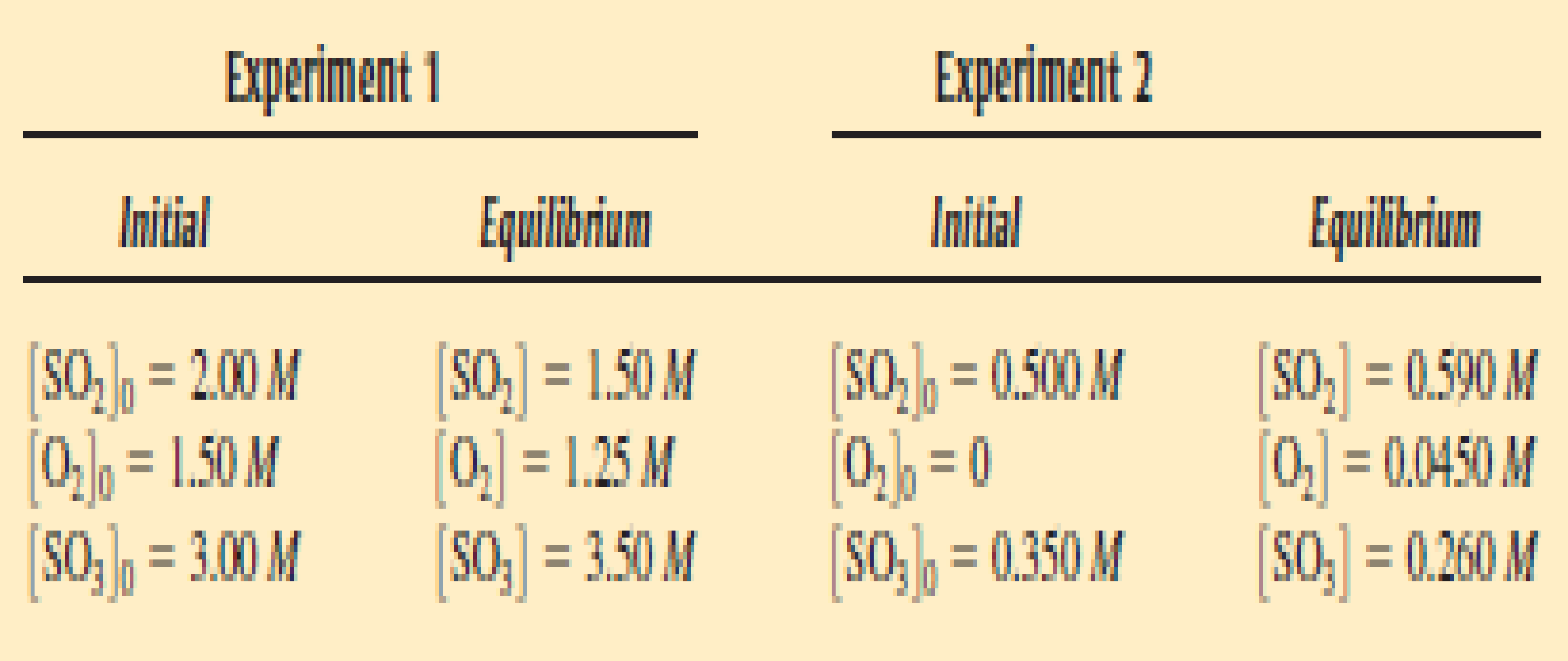


TABLE 13.1 Results of Three Experiments for the Reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

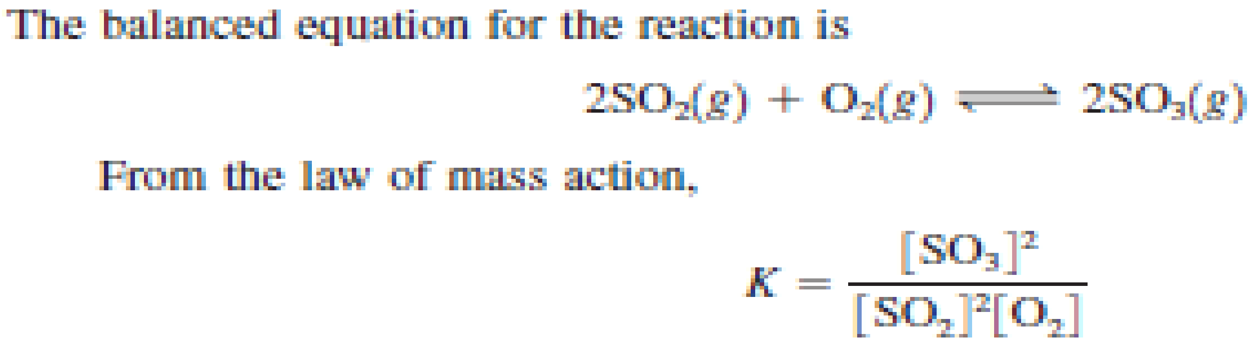
Experiment	Initial Concentrations	Equilibrium Concentrations	$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$
I	$[N_2]_0 = 1.000\ M$ $[H_2]_0 = 1.000\ M$ $[NH_3]_0 = 0$	$[N_2] = 0.921\ M$ $[H_2] = 0.763\ M$ $[NH_3] = 0.157\ M$	$K = 6.02 \times 10^{-2}$
II	$[N_2]_0 = 0$ $[H_2]_0 = 0$ $[NH_3]_0 = 1.000\ M$	$[N_2] = 0.399\ M$ $[H_2] = 1.197\ M$ $[NH_3] = 0.203\ M$	$K = 6.02 \times 10^{-2}$
III	$[N_2]_0 = 2.00\ M$ $[H_2]_0 = 1.00\ M$ $[NH_3]_0 = 3.00\ M$	$[N_2] = 2.59\ M$ $[H_2] = 2.77\ M$ $[NH_3] = 1.82\ M$	$K = 6.02 \times 10^{-2}$

- The equilibrium constant, which depends on the ratio of the concentrations, remains the same.
- Each set of equilibrium concentrations is called an equilibrium position.
-
- Example: 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.
Solution:



The balanced equation for the reaction is

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

From the law of mass action,

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

For Experiment 1 $K1=((3.50)^2)/((1.50)^2(1.25))=4.36$

For Experiment 2, $K2=((0.260)^2)/((0.590)^2(0.0450))=4.36$

Thank you all

Elective physical chemistry

Fourth stage/College of Education for Pure Sciences

Asst.Prof.Dr.Fedaa AL-Taie

Dissociation constant:

What is Ka?

The acid ionisation constant, Ka, is the equilibrium constant for chemical reactions in an aqueous solution involving weak acids. The magnitude of acid dissociation is predicted using Ka’s numerical value.

What is pKa?

- The pKa value is a number that describes the acidity of a specific molecule. The strength of an acid is determined by how tightly a proton is held by a Bronsted acid.
- In chemistry, the terms pH, pKa, pKb, Ka, and Kb are used to characterise how acidic or basic a solution is, as well as to measure the strength of acids and bases. Although the pH scale is the most commonly used indicator of acidity and basicity, pKa, pKb, Ka, and Kb are more accurate predictors of acid andbase strength and reactions. Here are definitions for each term, as well as basic formulas for calculating them and an explanation of how they differ.

Understanding Ka and pKa

The acid dissociation constant is Ka. The – log of this constant is pKa. The general equation for acid dissociation is:

$HA + H_2O \rightleftharpoons A^- + H_3O^+$

Where,

$Ka = [H3O^+][A^-]/ [HA]$

$pKa = – \log Ka$

At half the equivalence point,

$pH = pKa = – \log Ka$

Because an acid dissociates primarily into its ions, a high Ka value implies a powerful acid. A high Ka value indicates that the reaction arrow promotes product formation. A low Ka value, on the other hand, indicates that just a little amount of acid dissociates, indicating a weak acid. A low Ka value indicates that the reaction prefers the reactants above the products. The Ka values of most weak acids range from 10^{-2} to 10^{-14}.

- The same information is provided by pKa, but in a different format. The stronger the acid, the lower the pKa value. Alternatively, the weaker the acid, the higher the pKa value. The pKa value of weak acids is usually between 2 and 14.

Converting From pKa to Ka

The conversion of pKa to Ka is given below.
pKa = – log Ka

– pKa = log Ka

$10^{-(pKa)}$ = Ka

Ka = $10^{-(pKa)}$
Consider the reactions below.

$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^{-}(aq)$
$Ka = [A^–][H_3O^+] / [HA]$

We can calculate the Keq (equilibrium constant) or Ka of a reversible acid-base reaction. The temperature is the only variable that affects the Ka.

The ability of a strong acid to completely dissociate in an aqueous solution distinguishes it from a weak acid. If the acid-base reaction favoured the left (greater [HA]), the concentrations of both [A–] and [H3O+] would be lower, resulting in a lower Ka value. As a result, the stronger the acid is, the greater the Ka. The weaker the acid, the lower the Ka.

pKa = – log[Ka]

As a result, the lower the pKa, the more powerful the acid. The weaker the acid, the greater the pKa.

Thanks

Elective physical chemistry

Fourth stage/College of Education for Pure Sciences

Asst.Prof.Dr.Fedaa AL-Taie

Frequently Asked Questions on Ka to pKa

Q1 Does Ka equal pKa?

Similar to pH, the value of Ka can also be represented as pKa. pKa = -log Ka. The larger the pKa, the weaker the acid. pKa is a constant for each conjugate acid and its conjugate base pair.

Q2 What is the relationship of pKa and Ka?

- The smaller the value of Ka, the larger the value of pKa, the weaker the acid. If the pH of a solution of a weak acid and the pKa are known, the ratio of the concentration of the conjugate base to the concentration of the acid may be calculated.

Q3 What is the relationship between Ka and pH?

The Ka is the acid dissociation constant, and thus it is what determines how strong the acid is. Stronger acids dissociate to a greater extent and produce lower pH values.

Q4 What is a pKa in chemistry?

- pKa is a measure of the tendency of a molecule or ion to keep a proton, H+, at its ionisation centre(s). It is related to the ionisation capabilities of chemical species. More precisely – pKa is the negative log base ten of the Ka value (acid dissociation constant). The lower the value of pKa, the stronger the acid and the greater its ability to donate its protons.

Q5 How do you calculate Ka from pKa?

- To create a more manageable number, chemists define the pKa value as the negative logarithm of the Ka value: pKa = -log Ka. If you already know the pKa value for acid and you need the Ka value, you find it by taking the antilog.

Thanks

Thanks

Elective physical chemistry

Fourth stage/College of Education for Pure Sciences

Asst.Prof.Dr.Fedaa AL-Taie

How to calculate pKa

pKa is the criterion used to determine the acidity of the molecule. It is used to measure the acid strength. The lesser the pKa is, the molecule would hold proton less tightly; hence the more potent the acid will be.

Numerous parameters can determine the pKa value. Few of them are enlisted below.

pKa from Ka or Molarity

pKa from pH

pKa from the titration curve

pKa from Ka or Concentration

.

Consider dissociation of acid HX

$HX \leftrightharpoons H^+ + X^-$

For the above equation, Ka would be

$Ka=[X-][H+][HX]$

We know that Ka and pKa are related.

pKa= – logKa

pKa from Ka or Concentration

$pKa = -log[X-][H+][HX]$

$pKa = log[HX]\backslash[X-][H+]$

Here, the quantities in the brackets symbolise the concentration.

Thus we can quickly determine the pKa value if the concentration of reactants and products or Ka are known.

pKa from pH

- From the Henderson equation of acidic buffer, we can quickly determine the value of pKa from the pH.
- pH = pKa + log {[salt] / [Acid]}
- Let [salt] / [Acid] be equal to 10 then,
- pH = pKa + log 10
- pH = pKa + 1
-

Let [salt] / [Acid] be equal to 1 / 10 then,

$pH = pKa + \log 1 / 10$

$pH = pKa + \log 1 - \log 10$

$pH = pKa - 1$

Thus we can quickly determine the pKa value if the pH of the solution is known.

pKa from the Titration Curve

- pKa value can be determined by the titration curve.
- To calculate the pKa of the solution, firstly, we will determine the equivalence point and then find the pH of the solution. pKa of the solution is equivalent to the pH of the solution at its equivalence point.
- Hence we can quickly determine the value of pKa by using a titration curve.
-
- $pH = pKa + \log 1 / 10$
- $pH = pKa + \log 1 – \log 10$
- $pH = pKa – 1$
- Thus we can quickly determine the pKa value if the pH of the solution is known.

•

Thanks