40S Chemistry

Chemical Equilibrium

Introduction

- Very few reactions actually proceed to completion.
- Many proceed in both directions, left to right AND right to left.
- At equilibrium, the [] of both reactants and products remains constant.

Outcomes

- Define the concept of equilibrium.
- Explain solubility using the concept of solubility.
- Explain the factors affecting solubility using the concept of equilibrium.

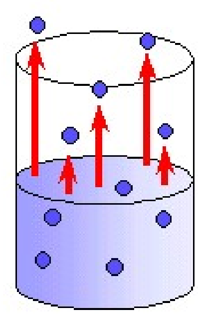
- Write chemical equations to describe solution equilibria.
- Distinguish between a system at equilibrium and one not at equilibrium.

Overview

- Defining Equilibrium
- Liquid-Vapour Equilibrium
- Solubility Equilibrium
- Physical Equilibria

Defining Equilibrium

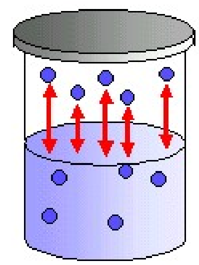
- Evaporation in open container
- Particles evaporate until all liquid has evaporated.



Open Container

Dynamic Equilibrium

- Opening sealed.
- Particles evaporate and condense at a constant rate.
- This balance is called a **dynamic equilibrium.**



Closed Container

Dynamic Equilibrium

- A state of dynamic equilibrium exists where the rate of the forward process (evaporation) is equal to the rate of the reverse process (condensation).

- Chemists use a double arrow:

$$\rightleftarrows$$

- Indicates the reaction is reversible - it proceeds both left to right and right to left.
- In a system at equilibrium, the reaction proceeds in BOTH directions simultaneously.

$$H_2O(l) \rightleftarrows H_2O(g)$$

- Notation indicates that a liquid-vapour equilibrium exists for water.

Conditions for Equilibrium

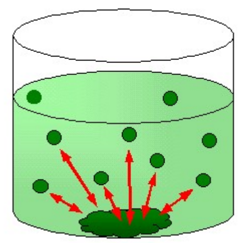
- Equilibrium can only occur in a **closed system** - no particles are allowed to enter or escape.

Solutions

- Dissolving of a solid substance in a solvent is usually a **physical process**.
- Solutions become **saturated**.
- No more solid will dissolve as long as the conditions, such as temperature remain constant.

Solution Equilibrium

- In a saturated solution, an equilibrium exists between the undissolved solute and the dissolved solute.
- It is known as **solubility equilibrium**.



- Particles dissolve at the same rate that others leave solution.
- Chemists indicate this equilibrium using the following equation:

$$\text{Sugar(s)} \rightleftarrows \text{Sugar (aq)}$$

$$C_6H_{12}O_6\ (s) \rightleftarrows C_6H_{12}O_6\ (aq)$$

Physical Equilibrium

- Any reversible physical process, in which the rate of the forward process equals the rate of the reverse process, is a **physical equilibrium**.
- Solid-liquid
- Solid-vapour
- Liquid-vapour
- Solubility

Lesson Summary

- Equilibrium occurs when the rate of the forward process = the rate of the reverse process in a reversible reaction.
- Equilibrium can only occur in a closed system.
- Equilibrium is dynamic.

- Liquid-vapour equilibrium occurs when liquid molecules enter and leave the liquid state at the same rate.
- Solution equilibria occur in saturated solutions in which solute remains undissolved.
- Physical equilibria are those occurring in physical changes.

Assignment

- Complete Chemical Equilibrium Assignment #1

Homework Answer Key

1. $I_2(s) \rightleftharpoons I_2(g)$
2. $Br_2(l) \rightleftharpoons Br_2(g)$
3. $NaCl(s) \rightleftharpoons NaCl(aq)$ sodium chloride is ionic and separates into ions in water. The equation at equilibrium would then be

   $NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$

4. At a substance's melting point there is an equilibrium between solid and liquid. The equation would be

   $Au(s) \rightleftharpoons Au(l)$

5. $H_2O(l) \rightleftharpoons H_2O(g)$

   At a substances boiling point, there is a liquid-vapour equilibrium.

40S Chemistry

Chemical Equilibrium

Introduction

- Many chemical reactions are reversible.
- Reversible reactions, under the correct conditions, can also reach equilibrium.

Outcomes

- Identify conditions required for chemical equilibrium.
- Compare and contrast chemical equilibrium.
- Propose an analogy for chemical equilibrium.
- Define the equilibrium constant and mass action expression.

- Write equilibrium law expressions from balanced chemical equations.
- Relate concentration of reactants and products to the magnitude of the equilibrium constant.
- Calculate equilibrium constant, given experimental data.

Lesson Overview

- Reversible Reactions
- Characteristics of Chemical Equilibrium
- Defining Chemical Equilibrium
- The Equilibrium Law
- The Equilibrium Constant
- Calculating Kc
- Calculating Equilibrium []

Reversible Reactions

- chemical reactions in equilibrium can only be established in a closed system.
- Consider the reaction:

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

- NO_2: brown gas present in smog.
- N_2O_4: colourless gas produced as NO_2 is exposed to UV rays.

- If NO_2 is placed in a sealed container, eventually the brown colour fades but still persists, as long as conditions remain constant.
- Fading results from production of colourless N_2O_4.
- The brownish tint indicates the presence of NO_2 in the container.
- The reaction does NOT go completely to products, but rests somewhere between.

- The equilibrium state is characterized by constant concentrations of both reactants (NO_2) and products (N_2O_4).
- The reaction is then written:

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

- The double arrow indicates the reaction is reversible. VIDEO

Characteristics of Chemical Equilibrium

In reversible reactions:

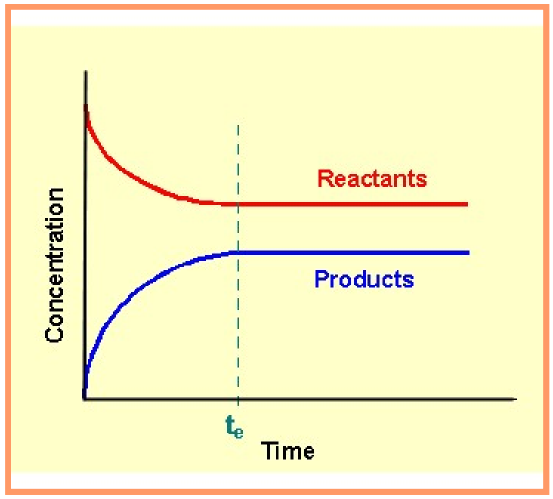
- conversion to products is the **forward reaction**
- conversion to reactants is the **reverse reaction**
- For a system at equilibrium, the rate of the forward reaction = the rate of the reverse reaction.

Defining Chemical Equilibrium

For the reaction

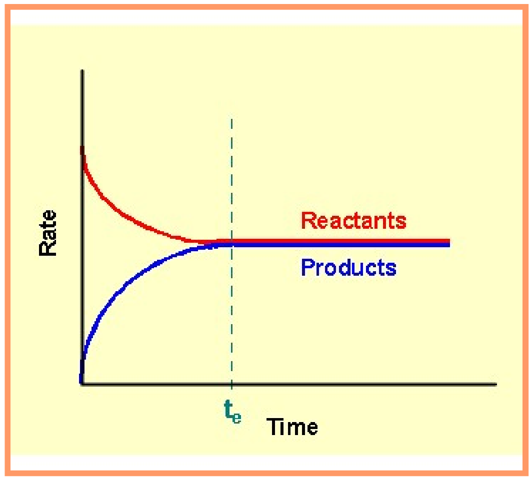
$$aA + bB \rightleftarrows cC + dD$$

- at equilibrium, the graph of concentration vs time may appear like this . . .



- At time = t_e, the concentrations of both reactants and products remain constant indefinitely.

- The concentration of products and reactants are **NOT** necessarily equal.
- The rate of conversion to products = the rate of conversion to reactants.
- This is what makes the equilibrium dynamic.
- A graph of rate vs time would appear as . . .



- At time = t_e, the rates of both forward and reverse reactions remain equal, indefinitely.

- By definition, chemical equilibrium is

"the state where the concentrations of reactants and products remain constant over time because the rate of the forward reaction is equal to the rate of the reverse reaction."

The Equilibrium Law

- Also known as the **law of mass action**.
- A relationship exists between the [reactants] and [products] at equilibrium.
- The equilibrium law is a ratio of [product] to [reactant].
- The value of this ratio is called the **equilibrium constant, k_c or k_{eq}**.

For the reaction

$$aA + bB \rightleftharpoons cC + dD$$

- the forward and reverse reactions are elementary reactions.
- $Rate_{products} = k_p[C]^c[D]^d$
- $Rate_{reactants} = k_r[A]^a[B]^b$

Therefore:

$$k_r[A]^a[B]^b = k_p[C]^c[D]^d$$

- By rearranging the expression to solve for rate constants,

$$k_r[A]^a[B]^b = k_p[C]^c[D]^d$$

Divide both sides by $[A]^a[B]^b$

$$k_r = \frac{k_p[C]^c[D]^d}{[A]^a[B]^b}$$

Divide both sides by k_p

$$\frac{k_r}{k_p} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- By rearranging the expression to solve for rate constants,

The ratio of rate constants is condensed to one constant, Kc, called the equilibrium constant.

$$\frac{k_r}{k_p} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- The law of mass action becomes

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

or

$$K_c = \frac{\text{concentration of products}}{\text{concentration of reactants}}$$

Writing the Equilibrium Law

- **Homogeneous equilibria** are those in which the reactants and products are all in the same phase, gases (g) or aqueous (aq).
- **Heterogeneous equilibria** involve reactants and products in more than one state.

- When writing the mass action expression, substances which are solids (s) or liquids (l) are omitted.
- Solids and liquids rarely change in concentration and are not included.

Example 1

Write the equilibrium law for the equation:

$$N_2(g) + 3\ H_2\ (g) \rightleftharpoons 2\ NH_3\ (g)$$

Solution:

All reactants and products are gaseous. the equilibrium law would be . . .

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Example 2

Write the equilibrium law for the equation:

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

Solution:

C is a solid and is omitted from the equilibrium law . . .

$$K_c = \frac{[CO][H_2]}{[H_2O]}$$

K_c /K_{eq}

- is the ratio of product concentrations to reactant concentrations.
- the only factor affecting K_c is temperature.
- can indicate whether products or reactants are **favoured** at equilibrium (whether there are more products or reactants at equilibrium).

Case 1:

If Kc = 1, [products] = [reactants].

Neither reactants or products are favoured.

Case 2:

If Kc > 1, the [product] > [reactant]. Products are favoured.

For example:

$A + B \rightleftharpoons C + D$ has a $Kc = 1 \times 10^5$

Mixing A and B results in almost a complete conversion to products C and D.

Case 3:

If Kc<1, the [product] < [reactant]. Reactants are favoured.

For example:

If the reaction E + F $\rightleftarrows$ G + H has a Kc = 1 x 10^{-5}

Mixing E and F results in the formation of very little G and H.

Calculating K_C

- K_C can be calculated if you are given the [reactants] and [products] at equilibrium.
- Substitute the values into the equilibrium law . . .

Example

For the reaction:

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$$

At 225°C, a 2.0 L container holds 0.040 moles of N_2, 1.5 moles of H_2 and 0.50 moles of NH_3.

If the system is at equilibrium, calculate KC.

Solution

Step 1: **Change all quantities into concentrations, mol/L.**

$$\text{Concentration} = \frac{\text{moles}}{\text{volume}} = \frac{n}{V}$$

$$C_{N_2} = \frac{0.040\ \text{moles}}{2.0\ \text{L}} = 0.020\ \text{mol/L}$$

$$C_{H_2} = \frac{1.5\ \text{moles}}{2.0\ \text{L}} = 0.75\ \text{mol/L}$$

$$C_{NH_3} = \frac{0.50\ \text{moles}}{2.0\ \text{L}} = 0.25\ \text{mol/L}$$

Step 2:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Write the equilibrium law for the reaction

Step 3:

$$K_c = \frac{(0.25)^2}{(0.020)(0.75)^3}$$

$$= \frac{0.0625}{(0.020)(0.4219)}$$

$$K_c = 7.4$$

Substitute the concentration values and calculate K. WATCH EXPONENTS!!!

Note: no units for K.

Calculating Equilibrium []

If given K_c, the concentration of one of the reactants or products can be calculated if the other values are given as well . . .

Example

For the following reaction at 210°C, the Kc is 64.0:

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$$

The equilibrium [] of N_2 and O_2 are 0.40 mol/L and 0.60 mol/L, respectively.

Calculate the equilibrium concentration of NO.

Solution

Step 1:

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

Write out the equilibrium law.

Step 2:

$$[NO]^2 = K_c[N_2][O_2]$$

$$[NO] = \sqrt{K_c[N_2][O_2]}$$

Rearrange the equilibrium law to solve for [NO].

Step 3:

$$[NO] = \sqrt{(64.0)(0.40)(0.60)} = \sqrt{15.36}$$

$$[NO] = 3.9 \text{ mol/L}$$

Lesson Summary

- Most chemical reactions are reversible.
- Chemical equilibrium can only occur in a closed system.
- Equilibrium occurs when the rate of the forward reaction equals the rate of the reverse reaction.

- At equilibrium, [products] and [reactants] remains constant.
- The Equilibrium Law, Kc, is shown by

$$K_c = \frac{[\text{products}]}{[\text{reactants}]}$$

- The Kc can be used to determine the equilibrium position.
- The equilibrium Law can be used to calculate the Kc when given [reactant] and [product].

Practice

- Write the equilibrium laws for each of the following reactions:
  - $SO_2\ (g) + NO_2\ (g) \Leftrightarrow SO_3\ (g) + NO(g)$
  - $2\ C(s) + 3\ H_2\ (g) \Leftrightarrow C_2H_6\ (g)$
  - $3\ O_2\ (g) \Leftrightarrow 2\ O_3\ (g)$
  - $MgCO_3\ (s) \Leftrightarrow CO_2\ (g) + 2\ MgO(s)$
  - $2\ Bi_3{+}(aq) + 3\ H_2S(g) \Leftrightarrow 2\ Bi_2S_3\ (s) + 6\ H{+}(aq)$
  - $I_2\ (aq) \Leftrightarrow I_2\ (s)$
  - $Cl_2\ (g) + PCl_3(g) \Leftrightarrow PCl_5(g)$

Practice

Practice

Bromine chloride, BrCl, decomposes to form bromine and chlorine.

$$2\ BrCl(g) \Leftrightarrow Cl2(g) + Br2(g)$$

At a certain temperature the equilibrium constant for the reaction is 11.1, and the equilibrium mixture contains 4.00 mol of Cl2. How many moles of Br2 and BrCl are present in the equilibrium mixture?

Practice

Find the value of K if at equilibrium there is 25.0 moles of P_4, 10.0 moles of H_2 and 5.00 moles of PH_3, in a 5.00 L container. The equation is

$$P_4(g) + 6\ H_2(g) \Leftrightarrow 4\ PH_3(g)$$

Homework Assignment

Complete *Equilibrium Assignment #2*

40S Chemistry

Solving Equilibrium Problems

Introduction

- The equilibrium law allows us to calculate the equilibrium concentrations of all species in a system.
- We can also determine if a system is at equilibrium and, if not, predict which direction it will go to achieve equilibrium.

Outcomes

- Solve equilibrium problems given initial and one equilibrium concentrations.
- Find equilibrium concentrations given initial concentrations and Kc.
- Determine the reaction quotient for a system.
- Determine if a system is at equilibrium or which reaction is favoured.

Lesson Overview

- Problem Types
- Reaction Quotient
- Predicting Equilibrium

Example

- One problem type is when the initial concentrations of some species, usually reactants are given and the equilibrium concentration of one of the products is given, calculate the equilibrium constant.

For the reaction

$$H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$$

1.00 moles of hydrogen and 1.00 moles of fluorine are sealed in a 1.00 L flask at 150°C and allowed to react.

At equilibrium, 1.32 moles of HF are present.

Calculate the equilibrium constant.

Solution

To solve this problem, it is best to set up a table recording:

initial concentrations (I)

change in concentrations (C)

equilibrium concentrations (E)

ICE for short . . .

Since the flask is 1.00L,
$[H_2] = [F_2] = 1.00$ mol/L and the initial concentration of HF is zero.

Set up the table by first rewriting the equation . . .

Insert initial concentrations

	H_2 +	F_2	$\Leftrightarrow$ 2HF
I	1.00	1.00	0
C			
E			

	H_2 +	F_2	$\Leftrightarrow$ 2HF
I	1.00	1.00	0
C	- 0.66	- 0.66	+ 1.32
E			

According to stoichiometry,

$$1.32\text{ mol/L HF}\left(\frac{1\text{ mole }H_2}{2\text{moles HF}}\right) = 0.66\text{ mol/L }H_2$$

Since the equilibrium [HF] is 1.32 mol/L, it increases by that amount. According to the stoichiometry, $[H_2]$ and $[F_2]$ will decrease by one half that amount

	H_2 +	F_2	$\Leftrightarrow$ 2HF
I	1.00	1.00	0
C	- 0.66	- 0.66	+ 1.32
E	**0.34**	**0.34**	**1.32**

Substitute the equilibrium concentrations into the equilibrium law and solve for Kc:

$$K_c = \frac{[HF]^2}{[H_2][F_2]} = \frac{(1.32)^2}{(0.34)(0.34)} = \frac{1.742}{0.1156}$$

$$K_c = 15.1$$

Example

- When given initial concentrations and the equilibrium constant, we can calculate the equilibrium concentrations of all reactants and products for many equilibrium systems.

For the reaction:

$$N_2(g) + O_2\,(g) \rightleftarrows 2\,NO(g)$$

The Kc is 6.76. If 6.0 moles of nitrogen and oxygen gases are placed in a 1.0 L container, what are the concentrations of all reactants and products at equilibrium?

Solution

Here the equilibrium concentrations are not known.

$N_2(g) + O_2(g) \rightleftarrows 2\,NO(g)$

We know from stoichiometry, as the reaction proceeds equal amounts of nitrogen and oxygen will be consumed and twice that amount of NO will be produced.

Since we do not know the amounts consumed, we will assign them a value of x and the amount of NO produced 2x.

Then, set up the "ICE" table . . .

Insert initial concentrations

	N_2 +	O_2	$\Leftrightarrow$ 2NO
I	6.0	6.0	0
C			
E			

Since we do not know the equilibrium concentrations of any of the species we insert x for the amount of N_2 and O_2 consumed and 2x for the amount of NO produced.

	N_2 +	O_2	$\Leftrightarrow$ 2NO
I	6.0	6.0	0
C	- x	-x	2x
E	6.0 - x	6.0 - x	2x

We then write out the equilibrium law and substitute these values for the concentrations:

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

substitute known values

$$6.76 = \frac{(2x)^2}{(6.0-x)(6.0-x)}$$

$$\sqrt{6.76} = \sqrt{\frac{2x^2}{(6.0-x)^2}}$$

The denominator is a square, so if we take the square root of both sides we can avoid a quadratic equation.

$$2.60 = \frac{2x}{6.0-x}$$

$$(6.0 - x)(2.60) = \left(\frac{2x}{6.0 - x}\right)(6.0 - x)$$

$$15.6 - 2.60x = 2x$$

Solve for x by eliminating the denominator.

$$15.6 = 2x + 2.60x$$

Isolate the x's

$$\frac{15.6}{4.6} = \frac{4.6x}{4.6}$$

$$3.4 = x$$

Solve for x

Since x equals the loss in concentrations of nitrogen and oxygen,

$[N2] = [O2] = 6.0 - x = 6.0 - 3.4 = 2.6$ mol/L

$[NO] = 2x = 2(3.4$ mol/L$) = 6.8$ mol/L

Therefore, at equilibrium nitrogen and oxygen are both 2.6 mol/L and the concentration of NO is 6.8 mol/L.

Homework Assignment

- Complete *Equilibrium Assignment #3*

Practice

$H_2(g) + Cl_2\,(g) \Leftrightarrow 2\ HCl(g)$ at 516°C

A student places 2.00 mol H2 and 2.00 mol Cl_2 into a 0.500 L container and the reaction is allowed to go to equilibrium at 516°C. If Keq is 76.0, what are the equilibrium concentrations of H_2, Cl_2 and HCl?

Practice

Practice

If K = 78.0 for the reaction

$$A(s) + 2\ B(g) \Leftrightarrow 2\ C(g)$$

and initially there are 5.00 moles of A and 4.84 moles of B in a 2.00 L container, how many moles of B are left at equilibrium?

Practice

Practice

Reaction Quotient

- When reactants and products are added into a container it is good to know whether equilibrium has been reached.
- If equilibrium has not been reached it is helpful to know which reaction, forward or reverse, is favoured in order for equilibrium to be achieved.

- The **reaction quotient** , Q, is used to determine this information.
- The Q is determined by using the equilibrium law and using either initial [] or those determined during experimental trials.

- To determine which reaction is favoured and in which direction the system is moving, Q is compared to Kc.
- **If Q = Kc, the system is at equilibrium**. Forward rate = reverse rate and [reactant] and [product] remain constant.

- **If Q > K, the system is NOT at equilibrium.**
- There is too much product, so the reverse reaction is favoured to bring the reactant-product ratio to equal K by increasing reactant concentration.

- **If Q < K, the system is NOT at equilibrium.**
- [Reactant] is too large, so the forward reaction is favoured.
- This results in decreasing [reactant] and increasing [product], bringing their ratio to a value equal to K.

Predicting Equilibrium

For the reaction

$$N_2(g) + O_2(g) \Leftrightarrow 2\,NO(g)$$

8.50 moles of N_2, 11.0 moles of O_2 and 2.20 moles of NO were in a 5.00 L container.

If the Kc is 0.035, are the following concentrations at equilibrium? If not, which reaction is favoured and which concentrations are increasing and which are decreasing?

Solution

Determine the [] of all species:

$$C_{N_2} = \frac{n}{V} = \frac{8.50 \text{ moles}}{5.00 \text{ L}} = 1.70 \text{ mol/L}$$

$$C_{O_2} = \frac{n}{V} = \frac{11.0 \text{ moles}}{5.00 \text{ L}} = 2.20 \text{ mol/L}$$

$$C_{NO} = \frac{n}{V} = \frac{2.20 \text{ moles}}{5.00 \text{ L}} = 0.440 \text{ mol/L}$$

Substitute the concentrations into the equilibrium law, with K replaced by Q:

$$Q = \frac{[NO]^2}{[N_2][O_2]} = \frac{(0.440)^2}{(1.70)(2.20)} = 0.0518$$

Q is greater than the value of K. This means . . .

- Since Q > K, the system is not at equilibrium. The reverse reaction is favoured and
- the [NO] is decreasing and the [oxygen] and [nitrogen] are increasing.

Lesson Summary

- How to solve problems given K and initial concentrations.
- How to use the reaction quotient to predict whether a system is at equilibrium and, if not, which reaction is favoured.

Homework Assignment

- Complete the *Equilibrium #3* worksheet

40S Chemistry

Le Chatelier's Principle

Introduction

- It is important to know the factors that will affect control the position of equilibrium.
- Chemists/chemical engineers must understand the conditions which will optimize the amount of product as well as being economical.

Outcomes

- Use Le Chatelieris Principle to explain the effects of each of the following on the position of a system at equilibrium:
  * Changing concentration
  * Changing pressure
  * Changing temperature
  * Adding a catalyst

Lesson Overview

- Le Chatelier's Principle
- Changing Concentration
- Iron-Thiocyanate Equilibrium
- Pressure Changes/Example
- Hydrogen Iodide Equilibrium
- Temperature Changes
- Nitrogen Dioxide Equilibrium
- Temperature and Kc
- Effect of a Catalyst

Le Chatelier's Principle

- Henri Louis Le Chatelier (1850 - 1936): a French chemist/mining engineer.
- In 1884 Le Chatelier proposed Le Chatelier's Principle. The principle states:

"When a system at equilibrium is subjected to a stress, the system will adjust so as to relieve the stress."

Changing Concentration

- In a system at equilibrium, a change in [products] or [reactants] present at equilibrium constitutes a stress.
- Adding more reactant, or removing product, upsets the established equilibrium.

- The stress is relieved by forming more product, or using up reactant.
- The forward reaction rate increases until equilibrium is reestablished.
- (The forward reaction is **favoured** until Kc is attained again.)
- If reactant is added or product is removed, we say that the equilibrium **"shifts to the right".**

- Adding more product, or removing reactant, causes the system to shift the equilibrium left.
- The reverse reaction is favoured until the product to reactant ratio is equal to Kc once again.

Thiocyanoiron Ion Equilibrium

A standard laboratory example for demonstrating the effect of changing concentrations on equilibria:

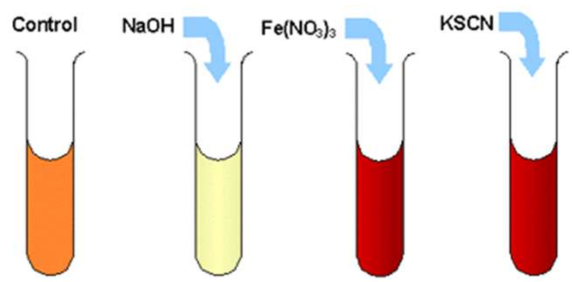
Fe^{3+} (aq) + SCN^{-}(aq) ⇔ $FeSCN^{2+}$ (aq)

pale yellow **red**

The position of equilibrium can be determined from the colour of the solution.

VIDEO

Consider the experiment below, where a control mixture is prepared with a mixture of iron (III) and thiocyanate ions. To separate test tubes of control solution, different substances are added:



- If salts containing either Fe^{3+}, SCN^- or both, the colour of the solution becomes a deeper red.
- This suggests a shift in the equilibrium to the right.
- The concentration of the thiocyanoiron ion complex, $FeSCN^{2+}$, increases, establishing a new equilibrium position.
- The system uses up some of the added reactant to counteract the change.

- When NaOH is added to the system the solution turns to a pale yellow.
- If NaOH is added to the system, the hydroxide ions combine with the iron (III) ions to produce an insoluble complex of iron (III) hydroxide.

- The colour change indicates a shift in the equilibrium to the left, reducing the $FeSCN^{2+}$ ion concentration.
- Precipitating out the iron ions reduces the iron ion concentraion.

- The system responds to the change by replacing some of the "lost" iron by favouring the reverse reaction.

Pressure Changes

- The pressure of a system can be changed by increasing or reducing the volume of the reaction container.
- Increasing the size of the container reduces the pressure.

- Decreasing the size of the container increases the pressure of the system.
- Changing the pressure of a system only affects those equilibria with gaseous reactants and/or products.

- According to Le Chatelier's Principle, increasing the pressure on a system at equilibrium causes the system to shift to reduce its pressure, by reducing the number of particles in the system.
- **That is, shift to the side with fewer molecules.**

- Decreasing the pressure on a system causes the system to shift to increase the pressure by increasing the number of particles in the container.
- **That is, shift to the side with more molecules.**

An Example of Pressure Changes

For the reaction:

$$N_2(g) + 3\ H_2\ (g) \Leftrightarrow 2\ NH_3\ (g)$$

a) What is the effect on the equilibrium if the size of the container is cut in half, but the number of particles and temperature remain unchanged?

Steps for Solving Le Chatelier's Principle Problems

- Identify the stress.
- Tell what the system does to reduce the stress.
- Indicate which concentrations increase and which ones decrease.
- Indicate whether the equilibrium shifts left, right, or has no change.

Solution

- Reducing the size of the container, increases the pressure of the system.
- According to Le Chatelier's Principle, the system will adjust to reduce pressure. The system reduces pressure by reducing the number of molecules in the container.

- This system can reduce molecules by favouring the forward reaction. There are four moles of reactants on the left (1 N_2 + 3 H_2 = 4 molecules) and only two (2 NH_3) on the right.
- The rate of the forward reaction will increase, increasing the concentration of NH_3 and reducing the concentration of N_2 and H_2.
- The equilibrium shifts right.

b) What is the effect on equilibrium if the reaction chamber is increased in volume, while keeping temperature and total number of particles constant?

Solution

- Increasing volume, while keeping other factors constant, decreases pressure.
- According to Le Chatelier's Principle, the system will adjust to increase pressure. The system does this by increasing the number of molecules in the container.

- The system increases the number of molecules in the container by shifting the equilibrium to the left, increasing the concentration of reactants. There are more gaseous reactants than products.

- The equilibrium shifts left, favouring the reverse reaction and increasing the concentration of reactants while reducing the concentration of products.

Hydrogen Iodide Equilibrium

For the following reaction

$$H_2(g) + I_2\,(g) \Leftrightarrow 2\,HI(g)$$

pressure changes would have **NO effect** on the equilibrium position.

Each side of the reaction has two moles of molecules.

There is no way to either increase or reduce the number of particles.

- In response to pressure changes, the equilibrium position remains **unchanged**.

Temperature Changes

- Increasing temperature always increases the rate of a reaction.
- Increasing temperature always increases the rate of an endothermic reaction more than the rate of an exothermic reaction.

- According to Le Chatelier's Principle, a change in temperature causes a stress on a system at equilibrium.
- The system attempts to relieve the stress by either replacing lost heat or consuming added heat.

- **To solve equilibrium problems involving heat changes, consider heat to be a product (exothermic reactions) or a reactant (endothermic reactions).**

Nitrogen Dioxide Equilibrium

The conversion of dinitrogen tetroxide to nitrogen dioxide is reversible and temperature dependent:

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

colourless **brown**

$\Delta H = +58\ kJ$

or

$$N_2O_4\ (g) + \text{heat} \Leftrightarrow 2\ NO_2\ (g)$$

VIDEO

- The forward reaction is endothermic.
- Heat is a reactant.
- Adding heat can be considered as increasing one of the reactants.
- Adding heat increases the rate of the forward reaction.

- The system attempts to remove added heat by using it up in the forward reaction.
- The reaction shifts to the right. The concentration of NO_2 increases and the concentration of N_2O_4 decreases.

- If a container holding an N_2O_4-NO_2 mixture is cooled, the system replaces lost heat by favouring the reaction which heat is a product.
- The equilibrium shifts left.
- This increases the concentration of N_2O_4 and reduces the concentration of NO_2.

- This is evident since NO_2 is a brown coloured gas, while N_2O_4 is colourless.
- As the temperature is increased the gas becomes brown and as the reaction chamber is cooled, the gas turns colourless.

Temperature and Kc

- The equilibrium constant is temperature dependent.
- In the example on the previous page, increasing temperature caused a shift in the equilibrium to the right, favouring products.

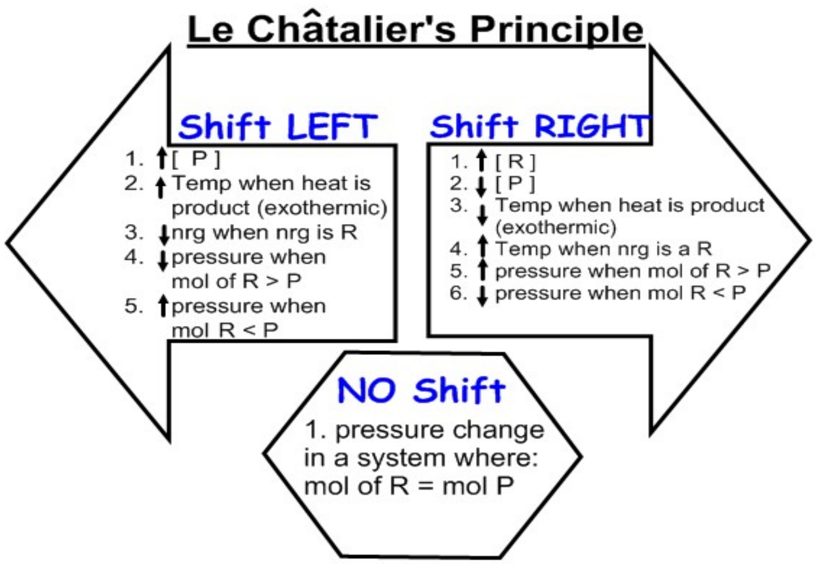
- This would cause an increase in [product] and a reduction in [reactant].
- This would result in an increase in the value of Kc.
- A decrease in temperature causes a shift to the left, reducing [product] and increasing [reactant].
- This would result in a decrease in the value of Kc.

- **Temperature is the only factor which will change the value of Kc.**

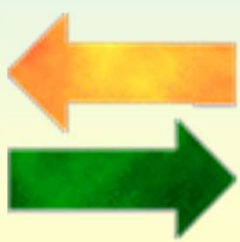
Effect of a Catalyst

- Adding a catalyst to a system decreases the activation energy of a reaction.
- This will cause the rate of a reaction to increase.
- **A catalyst lowers the activation energy of BOTH forward and reverse reactions equally.**

- Adding a catalyst to a system at equilibrium will NOT affect the equilibrium position.
- If a catalyst is added to a system which is not at equilibrium, the system will reach equilibrium much quicker since forward and reverse reaction rates are increased.



Lesson Summary



- Changing conditions of a system at equilibrium is a stress on that system.
- Le Chatelier's Principle states that when a stress is placed on a system at equilibrium, the system will respond to reduce that stress.

- We can use le Chatelier's Principle to predict the how temperature, pressure and concentration changes affect the position of equilibrium.

Homework Assignment

- Complete the *Le Chaterlier's Principle Questions* worksheet.