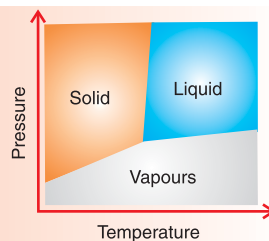


UNIT 5



Chemical Equilibrium and Phase Equilibrium

Unit Outcomes

At the end of this unit, you should be able to:

- understand how equilibrium is established;
- explain characteristics of dynamic equilibrium;
- state the law of mass action, and write an expression for equilibrium constants, K_c and K_p , from a given chemical reaction;
- apply the law of mass action to calculate K_c and K_p , the concentration and pressure of substances in equilibrium;
- understand how the reaction quotient is used to indicate the position of equilibrium;
- state Le Chatelier's principle and use it to predict and explain the effects of changes in temperature, pressure, concentration and presence of catalyst on a reaction;
- perform an activity to demonstrate the effects of changes in concentration on the position of equilibrium and to determine K_c and K_p values;
- explain how equilibrium principles are applied to optimize the production of industrial chemicals (e.g. the production of ammonia and sulphuric acid); and
- demonstrate scientific enquiry skills, observing, predicting, comparing and contrasting, communicating, asking questions and making generalizations.

MAIN CONTENTS**5.1 Chemical Equilibrium**

- Reversible and Irreversible Reactions
- Equilibrium
- Dynamic Chemical Equilibrium
- Conditions for Attainment of Chemical Equilibrium
- Characteristics of Chemical Equilibrium
- Law of Mass Action
- Factors affecting position of Chemical Equilibrium
- Equilibrium Constant
- Equilibrium Quotient
- Le Chatelier's Principle
- Chemical Equilibrium and Industry

5.2 Phase Equilibrium

- Force of Attraction, Kinetic Energy and States of Matter
- Common terms: Phase, Component and Degree of freedom
- Phase Rule
- Temperature, Pressure and Phase Changes of Pure Substance
- Phase Diagram

Start-up Activity

Form a group and perform the following activity:

1. Mix 10 mL of 0.1 mol L⁻¹ HCl solution with 10 mL of 0.1 mol L⁻¹ NaOH solution. Now, discuss each of the following questions:
 - a What is the concentration of NaCl formed?
 - b How much HCl and NaOH remain unreacted?
 - c Is the reaction complete?

2. Can you predict how much ammonia will be formed when 0.1 mol of nitrogen gas and 0.3 mol of hydrogen gas are allowed to react in a closed 2-litre flask?

Share your ideas with the rest of the class.

INTRODUCTION

In the unit on chemical kinetics you have studied about one aspect of a chemical reaction, which is the rate of the reaction. You have also studied the time taken for half the reaction to be over. However, some questions such as the following still remain. Do all reactions reach completion? If not then how much of the reactants remain unreacted, that is, what is the extent of the reaction? Why does the reaction not reach completion? Why does it attain equilibrium? These questions can be answered after studying chemical equilibrium.

In this unit, you will study about equilibrium, how it is attained, different phases in which a system can exist and stability of these phases under different conditions of temperature and pressure.

5.1 CHEMICAL EQUILIBRIUM

At the end of this section, you should be able to:

- explain reversible and irreversible reactions;
- define dynamic chemical equilibrium;
- state the necessary conditions for the attainment of equilibrium;
- describe the microscopic events that occur when a chemical system is in equilibrium;
- describe characteristics of chemical equilibrium;
- state the law of mass action;
- define equilibrium constant;
- write the equilibrium constant expression for chemical reactions that involve concentration and partial pressure;
- calculate values for equilibrium constants involving concentration and partial pressure;
- state the relationship of K_{eq} to relative amounts of product and reactants in a given reaction;

- show the relationship between K_c and K_p ;
- distinguish between homogeneous and heterogeneous reactions;
- define reaction quotient;
- use the equilibrium quotient to predict the direction of a reaction and the position of equilibrium;
- calculate equilibrium concentrations, given initial concentrations;
- determine whether the reactants or the products are favoured in a chemical reaction, given the equilibrium constants;
- list factors that affect chemical equilibrium;
- state Le-Chatelier's principle;
- use Le-Chatelier's principle to explain the effect of changes in temperature, pressure/volume, concentration and presence of a catalyst on a reaction;
- describe the effects of changes in concentration, pressure/volume and temperature on K_{eq} ;
- perform an activity to demonstrate the effects of changes in concentration and temperature on the position of equilibrium;
- perform an activity to determine K_c for esterification of organic acids;
- define optimum condition; and
- explain how Le-Chatelier's principle is applied to the Haber process for manufacturing ammonia and to the contact process for manufacturing sulphuric acid.

5.1.1 Reversible and Irreversible Reactions

Activity 5.1



Form a group and perform the following activity:

In a test tube take crushed ice. Dip a thermometer in it and note the temperature. Heat it slowly for a few seconds.

Now stop heating and place the test tube in a beaker containing large amount of crushed ice. Discuss the following questions in your group:

1. What is the temperature of crushed ice?
2. What happens when it is heated slightly?
3. What happens when it is cooled again?
4. What is the final temperature?

Share your ideas with the rest of the class.

A reversible reaction is a chemical reaction that results in an equilibrium mixture of reactants and products; for example, formation of ammonia is a reversible reaction.



Another example of reversible reaction is the formation of hydrogen iodide from hydrogen gas and iodine vapours.



Activity 5.2



Form a group and perform the following activity:

1. Take 10 mL of 0.1 M HCl solution in a test tube and dip the corner of blue and red litmus papers respectively in it. What happens?
2. In another test tube take 10 mL of 0.1 M NaOH solution and dip the corner of blue and red litmus papers respectively in it. What happens?
3. Mix the above two solutions and again test with litmus papers.
4. Dissolve a few crystals of sodium chloride in 10 mL water and test it with blue and red litmus papers. Will the resulting solution be acidic or basic? Compare the results of 3 and 4.

Share your findings with rest of the class.

Chemical reactions which proceed in only one direction are known as **irreversible reactions**. When the equation for irreversible reaction is written, a single arrow (\rightarrow) is used indicating that the reaction can proceed in only one direction.

While writing reversible reaction, double arrow (\rightleftharpoons) is used indicating that the reaction can go from reactant to product side and also from the product to the reactant side. The reaction from the reactant side to the product side is known as forward reaction and reaction from product to the reactants is known as reverse or backward reaction.

Exercise 5.1

Answer the following questions:

1. Define the terms reversible reaction and irreversible reaction.
2. Give examples of reversible and irreversible reactions.
3. Which symbol or sign is used to represent the reversibility and irreversibility of the reaction?

5.1.2 Attainment and Characteristics of Chemical Equilibrium

Equilibrium

Activity 5.3



Form a group and perform the following activity:

Take 10 mL of acetone in a test tube. Close the mouth of the test tube immediately. Clamp the test tube vertically. Mark the level of acetone with the marker. Allow it to stand for half an hour and note the level of acetone at regular intervals.

Discuss the findings with the class.

The equilibrium is *dynamic* in nature which means that although at the macroscopic level the properties do not change with time, however, at the molecular level the two processes are still taking place. So the equilibrium is attained when the rate of two opposing processes become equal.

Ice and water present together in a thermos flask at 0°C is another example of dynamic equilibrium. The equilibrium is attained when the rates of melting and freezing become equal.

The saturated solution is also an example of dynamic equilibrium. Saturated solution is a solution in which undissolved solute is in equilibrium with the solute dissolved in the solution. The molecules from undissolved solute go into the solution and equal number of solute molecules get precipitated from the solution. Therefore, the concentration of the solution remains constant.

Chemical Equilibrium

An equilibrium involving a chemical reaction is known as chemical equilibrium. When a chemical reaction takes place, the reactants are consumed and the products are formed. As a result the concentrations of reactants decrease with time and that of products increase. If the reaction is reversible in nature and it takes place in a closed vessel then the products decompose to give back reactants. After some time the concentrations of the reactants and products become constant, that is they do not change with time. This state is known as chemical equilibrium.

Chemical equilibrium is the state of the reaction when the macroscopic properties like temperature, pressure, volume and concentration of the reaction do not change with time.

Conditions for Attainment of Chemical Equilibrium

In a reversible reaction, reactant molecules react to give products and at the same time some product molecules give back reactants. The rate of reaction depends upon the concentration of reactants. The rate of forward reaction depends upon the concentration of reactants while the rate of reverse reaction depends upon the concentration of products as shown in **Figure 5.1**. Initially only the reactants are present, therefore, the rate of forward reaction is fast. The reaction in the reverse direction does not take place as no product is present. As the reaction progresses, due to the decrease in the concentration of reactants, the rate of forward reaction decreases. At the same time, due to the increase in the concentration of products, the rate of reverse reaction increases. As the reaction further progresses a stage is reached when the rate of forward reaction becomes equal to the rate of reverse reaction. When this stage is attained, the concentrations of reactants and products do not change. The reaction has attained chemical equilibrium.

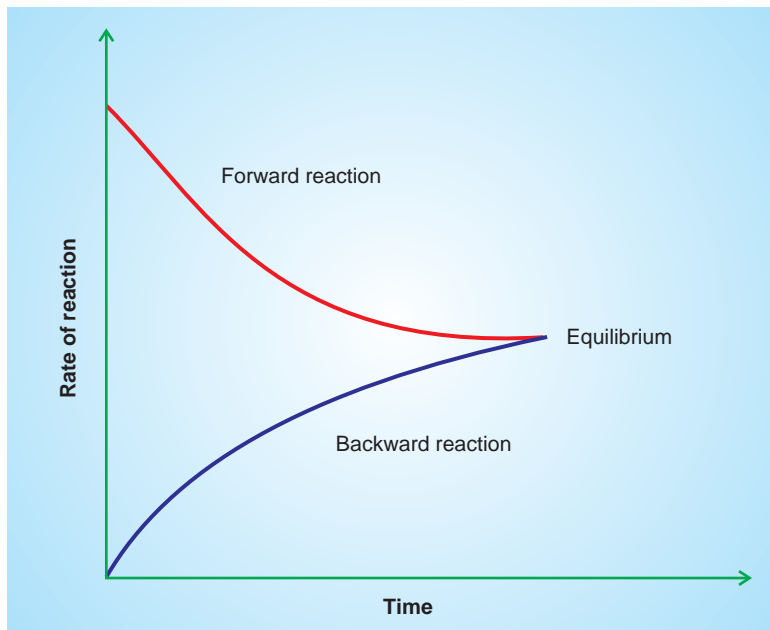


Fig 5.1 Change in the rate of reaction with time for the forward and reverse reactions.

For example, as seen earlier, formation of ammonia from nitrogen and hydrogen is a reversible process. At the start of the reaction only nitrogen and hydrogen are present. They combine to form ammonia. The rate of formation of ammonia is large. With the progress of reaction, the concentrations of nitrogen and hydrogen decrease so the rate of formation of ammonia decreases. As more and more ammonia molecules are formed, some of the molecules start decomposing to give back nitrogen and hydrogen. With the progress of reaction, the number of ammonia molecules increases, so the rate of decomposition of ammonia also increases. As the reaction proceeds, the rate of formation of ammonia decreases while the rate of decomposition of ammonia increases. A stage is reached when the two rates become equal and equilibrium is attained.



The chemical equilibrium is also dynamic in nature since the reaction does not stop at equilibrium. The macroscopic properties remain constant because the rate of forward reaction becomes equal to the rate of reverse reaction and hence no net reaction takes place.

Another example is the decomposition of dinitrogen tetraoxide to form nitrogen dioxide.



When colourless N_2O_4 is taken in a closed vessel, after some time its colour changes to brown indicating that NO_2 has been formed.

Similarly, if NO_2 is taken in a closed vessel, initially the colour is reddish brown but the colour starts fading and after some time it becomes brown. This colour change takes place because some NO_2 molecules dimerize to form N_2O_4 .

In both the cases, the final colour is same indicating that at equilibrium both N_2O_4 and NO_2 are present.

From these observations it can be concluded that the **chemical equilibrium** is attained whether the reaction is started with reactants or with products. That is, **chemical equilibrium** can be obtained from forward direction as well as reverse direction.

It should be noted that the concentrations of products and reactants are not necessarily equal at equilibrium, only the rate of forward and reverse reactions are equal.

Characteristics of Chemical Equilibrium

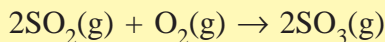
The reaction is reversible in nature.

- The reaction takes place in a closed vessel, that is, during the reaction; reactants and products are neither added nor removed from the reaction vessel.
- The rate of forward reaction is equal to the rate of reverse reaction.
- All the reactants and products are present at equilibrium.
- The macroscopic properties like temperature, pressure, volume and concentration do not change with time.
- The equilibrium is dynamic in nature.
- The state of equilibrium can be obtained from either side.
- The concentrations of reactants and products are generally not equal.
- The free energy change of the reaction is zero at equilibrium.

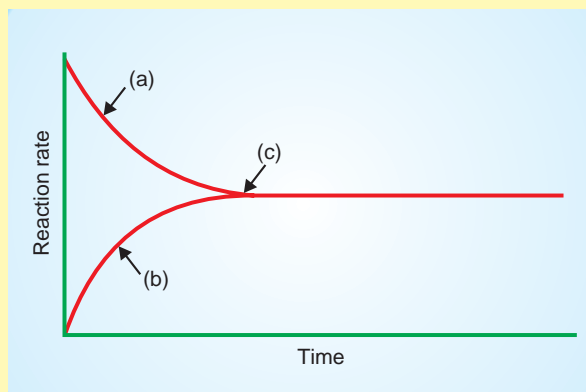
Exercise 5.2

Answers the following questions:

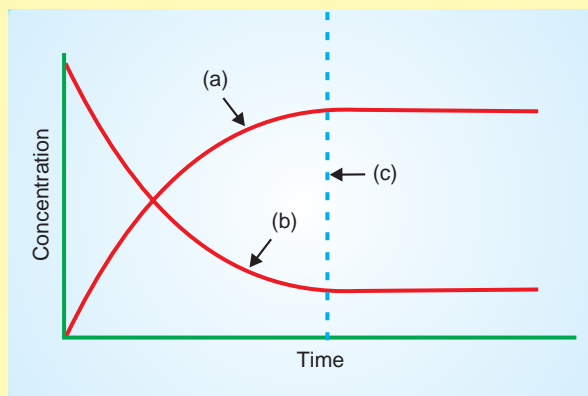
1. When a mixture of SO_2 and O_2 is introduced into a reaction vessel at a temperature of 700 K, a reaction that produces SO_3 occurs as:



- a When do we say that the system has reached chemical equilibrium? Explain your answer.
 - b Why is the equilibrium state referred to as dynamic?
 - c Write the equation that shows the presence of the three species in equilibrium.
2. Label **a**, **b** and **c** for the figure below. Explain trends of the rate of the forward reaction and the rate of the reverse reaction.



3. Label **a**, **b** and **c** for the figure shown below. Explain what happens to the concentration of the reactants and the concentration of the products.



4. What are the conditions that remain constant at equilibrium?

5.1.3 Equilibrium Expression and Equilibrium Constant

Law of Mass Action

Two Norwegian scientists **C.M. Guldberg** and **Peter Waage** studied reversible chemical reactions and gave a law characterizing the dynamic chemical equilibrium. This law is known as law of **mass action**. According to this law:

- The combining power of two reactants **A** and **B** depends upon their nature as well as their active concentrations.
- The rate at which **A** and **B** combine is directly proportional to the product of their concentration terms each raised to the power of its respective coefficient in the balanced chemical reaction.

The general equation that represents a reversible reaction is:



For the forward reaction **A** and **B** are reactants and **M** and **N** are products.

It is assumed that the reaction is homogeneous in nature, that is all the reactants and the products are present in the same state.

The rate of forward reaction (r_f) depends upon the concentrations of **A** and **B** and is given by the expression

$$r_f \propto [A]^a [B]^b \quad \text{or} \quad r_f = k_f [A]^a [B]^b$$

where $[A]$ and $[B]$ are the concentrations of **A** and **B** respectively. The rate of reverse reaction is given by the expression

$$r_b \propto [M]^m [N]^n \quad \text{or} \quad r_b = k_b [M]^m [N]^n$$

where $[M]$ and $[N]$ are the concentrations of **M** and **N** respectively. k_f and k_b are rate constants for forward and reverse reactions, respectively.

At equilibrium, the rate of forward reaction is equal to the rate of reverse reaction. Therefore,

$$r_f = r_b$$

or
$$k_f [A]^a [B]^b = k_b [M]^m [N]^n$$

k_f and k_b are constant. Therefore, the ratio of k_f to k_b is also a constant.

$$\frac{k_f}{k_b} = \frac{[M]^m [N]^n}{[A]^a [B]^b} = K_{eq}$$

The ratio of k_f and k_b is represented by K_{eq} . Since this constant represents the reaction at equilibrium it is known as equilibrium constant. $[M]$, $[N]$, $[A]$ and $[B]$ are concentrations at equilibrium.

When the concentrations are expressed in molarities, the equilibrium constant is represented by K_c .

When the reactants and the products are in the gaseous state, their concentrations can be expressed in terms of partial pressures. In such cases, the equilibrium constant is denoted by K_p .

Rules for Writing the Equilibrium Constant Expression for Homogeneous Reactions

Homogeneous reaction is a reaction in which all the reactants and the products are present in the same physical state.

For a homogeneous reaction, rules followed while writing the expression for equilibrium constant are:

- The concentrations of all the substances formed as products are written in the numerator.
- The concentrations of all the reactants are written in the denominator.

- Each concentration term is raised to the power by its respective coefficient as written in the balanced chemical reaction.

For a general reaction at equilibrium



the expression for K_c is:

$$K_c = \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

When all the reactants and the products are in the gaseous state, their concentrations can be written in terms of partial pressures. In such cases the equilibrium constant is denoted by K_p . The expression for K_p is

$$K_p = \frac{(p_M)^m (p_N)^n}{(p_A)^a (p_B)^b}$$

For the formation of ammonia,



the expression of equilibrium constant in terms of molarities is:

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

The expression of K_p is:

$$K_p = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3}$$

Exercise 5.3

Write the equilibrium constant expression for the following reactions:

1. $NH_3(g) + CH_3COOH(aq) \rightleftharpoons NH_4^+(aq) + CH_3COO^-(aq)$
2. $HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$
3. $2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$
4. $2HF(g) \rightleftharpoons H_2(g) + F_2(g)$

Units of K_c

The unit of K_c of a reaction depends upon the number of moles of the reactants and products involved in the reaction. Therefore, for a general reaction;

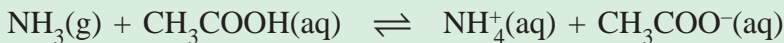


the unit of K_c will be:

$$K_c = \frac{[M]^m [N]^n}{[A]^a [B]^b} = \frac{[\text{mol L}^{-1}]^m [\text{mol L}^{-1}]^n}{[\text{mol L}^{-1}]^a [\text{mol L}^{-1}]^b} = (\text{mol L}^{-1})^{(m+n)-(a+b)}$$

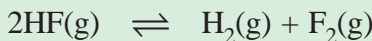
Example 5.1

1. For the reaction:



$$K_c = \frac{[\text{NH}_4^+][\text{CH}_3\text{COO}^-]}{[\text{NH}_3][\text{CH}_3\text{COOH}]} = \frac{(\text{mol L}^{-1})(\text{mol L}^{-1})}{(\text{mol L}^{-1})(\text{mol L}^{-1})} = 1$$

2. For the reaction:



$$K_c = \frac{[\text{H}_2][\text{F}_2]}{[\text{HF}]^2} = \frac{(\text{mol L}^{-1})(\text{mol L}^{-1})}{(\text{mol L}^{-1})^2} = \text{mol L}^{-1}$$

Unit of K_p

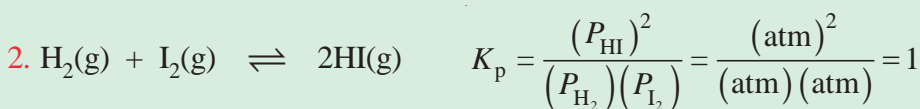
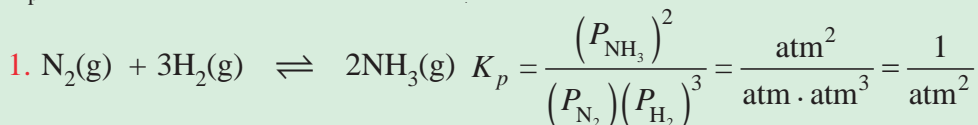
The unit of K_p is decided by the unit of pressure. If the partial pressure is expressed in atm, then the unit of K_p will be:

$$K_p = \frac{(p_M)^m (p_N)^n}{(p_A)^a (p_B)^b} = \frac{(\text{atm})^m (\text{atm})^n}{(\text{atm})^a (\text{atm})^b} = (\text{atm})^{(m+n)-(a+b)}$$

If the partial pressure is measured in kPa, then the unit of K_p will be $(\text{kPa})^{(m+n)-(a+b)}$

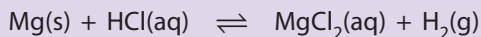
Example 5.2

K_p units for the following reactions are shown.

**Equilibrium Constant for Heterogeneous Reactions****Activity 5.4**

Form a group and discuss the following questions:

Consider the reaction



1. Identify the phases of the reactants and the products. Are the reactants and the product in the same or different phases?
2. What is the name of the equilibrium that involves such reactants and the product?

Share your ideas with the rest of the class.

In heterogeneous reactions, the reactants and products are present in more than one physical state. For example, thermal decomposition of calcium carbonate is an example of heterogeneous reaction.



Some other examples of heterogeneous reactions are

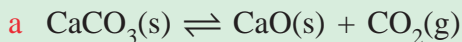


Rules for Writing the Expression for Equilibrium Constant for Heterogeneous Reaction

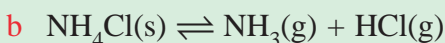
- The concentration terms of products are written in the numerator and the concentration terms of reactants are written in the denominator raised to the power of their respective coefficient in the balanced chemical equation.
- While writing the expression for K_c , the molarities of gaseous reactants and products and species present in the solution are written.
- Concentration terms of solids and pure liquids do not appear in the expression, as they are taken to be unity.
- While writing the expression for K_p , partial pressures of only the gaseous reactants and products are written in the expression for equilibrium constant.

Example 5.3

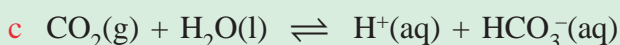
The equilibrium constant expression for some heterogeneous reactions are shown below:



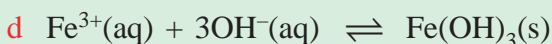
$$K_p = p_{\text{CO}_2}$$



$$K_p = (p_{\text{NH}_3})(p_{\text{HCl}})$$



$$K_c = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]}$$

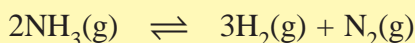


$$K_c = \frac{1}{[\text{Fe}^{3+}][\text{OH}^-]^3}$$

Exercise 5.4

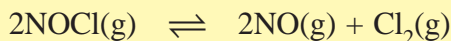
Answer the following questions:

1. 5.0 mole of ammonia were introduced into a 5.0 L reaction chamber in which it is partially decomposed at high temperatures.

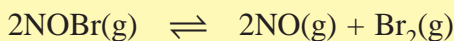


At equilibrium at a particular temperature, 80.0% of the ammonia had reacted. Calculate K_c for the reaction.

2. 1.25 mol NOCl was placed in a 2.50 L reaction chamber at 427°C. After equilibrium was reached, 1.10 moles NOCl remained. Calculate the equilibrium constant for the reaction.

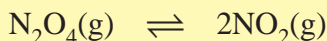


3. A sample of nitrosyl bromide was heated to 100°C in a 10.0 L container in order to partially decompose it.



At equilibrium the container was found to contain 0.0585 mol of NOBr, 0.105 mol of NO, and 0.0524 mol of Br₂. Calculate the value of K_c .

4. The brown gas NO₂ and the colourless gas N₂O₄ exist in equilibrium.



0.625 mol of N₂O₄ was introduced into a 5.00 L vessel and was allowed to decompose until it reached equilibrium with NO₂. The concentration of N₂O₄ at equilibrium was 0.0750 M. Calculate K_p for the reaction.

Relation between K_c and K_p

For the general reaction



$$K_c = \frac{[\text{M}]^m [\text{N}]^n}{[\text{A}]^a [\text{B}]^b} = \frac{C_M^m C_N^n}{C_A^a C_B^b}$$

$$K_p = \frac{(p_M)^m (p_N)^n}{(p_A)^a (p_B)^b}$$

It is assumed that all the gaseous species behave like an ideal gas. According to the ideal gas equation, the partial pressure (p) is given by

$$p = nRT / V \quad \text{and} \quad n/V = C$$

where n = amount of the gaseous species in moles

R = Gas constant

T = Temperature in kelvin

V = Volume of the reaction mixture

C = Molarity

$$\text{Thus, } p_A = n_A RT / V = C_A RT$$

$$p_B = n_B RT / V = C_B RT$$

$$p_M = n_M RT / V = C_M RT$$

$$p_N = n_N RT / V = C_N RT$$

$$K_p = \frac{(C_M RT)^m (C_N RT)^n}{(C_A RT)^a (C_B RT)^b} = \frac{C_M^m C_N^n}{C_A^a C_B^b} (RT)^{\Delta n}$$

here $\Delta n = (m + n) - (a + b)$ for gaseous species

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

When the number of gaseous reactants and products are equal then,

$$a + b = m + n$$

Therefore, $\Delta n = 0$ and hence $K_p = K_c$

Example 5.4

1. The equilibrium constant for the reaction:



is 1.8×10^{-3} kPa at 427°C . Calculate K_c for the reaction at the same temperature.

Solution:

Given: $K_p = 1.8 \times 10^{-3}$ kPa = 1.8 Nm^{-2} $T = 427^\circ\text{C} = 700 \text{ K}$.

$$R = 8.314 \text{ N m K}^{-1} \text{ mol}^{-1}$$

We know that

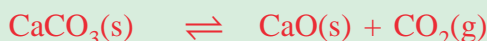
$$K_p = K_c (RT)^{\Delta n}$$

For the given reaction, $\Delta n = (2+1) - 2 = 1$

Therefore, $K_c = K_p / (RT)$

$$= \frac{1.8 \text{ Nm}^{-2}}{700 \text{ K} \times 8.314 \text{ N m K}^{-1} \text{ mol}^{-1}} = 3.09 \text{ mol m}^{-3}$$

2. What are the values of K_p and K_c at 1000°C for the reaction



if the pressure of CO_2 in equilibrium with CaCO_3 and CaO is 3.87 atm ?

Enough information is given to find K_p first. Writing the K_p expression for this heterogeneous reaction:

$$K_p = p_{\text{CO}_2} = 3.87$$

Then to get K_c , rearrange the equation,

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

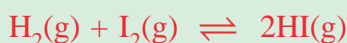
where n , the change in the number of moles of gas in the reaction is $+1$.

Calculation:

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

$$K_c = \frac{3.87}{(0.0821)(1273)} = 0.0370$$

3. At 400°C , $K_c = 64$ for the reaction



- What is the value of K_p for this reaction?
- If at equilibrium, the partial pressures of H_2 and I_2 in a container are 0.20 atm and 0.50 atm , respectively, what is the partial pressure of HI in the mixture?

Solution:

- The equation relating K_p to K_c is

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

Here the change in the number of moles of gas Δn is:

$$\Delta n = 2 \text{ mol HI} - 1 \text{ mol H}_2 - 1 \text{ mol I}_2 = 0$$

Since, $\Delta n = 0$, K_p and K_c are the same.

$$K_p = K_c(RT)^0 = K_c$$

$$K_p = K_c = 64$$

b Writing the equilibrium constant expression

$$K_p = \frac{p_{\text{HI}}^2}{p_{\text{H}_2} p_{\text{I}_2}} = 64$$

and substituting the given pressures

$$\frac{p_{\text{HI}}^2}{(0.20)(0.50)} = 64$$

the partial pressure of HI is

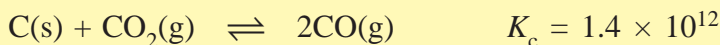
$$p_{\text{HI}} = \sqrt{(0.20)(0.50)(64)}$$

$$p_{\text{HI}} = 2.53 \text{ atm}$$

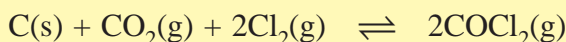
Exercise 5.5

Answers the following questions:

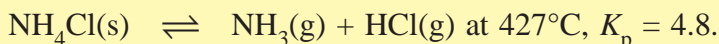
1. The following equilibrium constants were determined at 1123 K:



Write the equilibrium constant expression K_c and calculate the equilibrium constant at 1123 K for the following reaction:

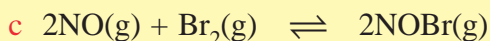
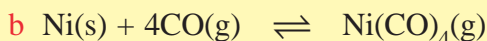
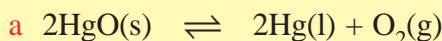


2. For the decomposition of ammonium chloride,

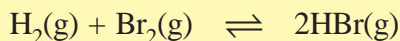


Calculate K_c for this reaction.

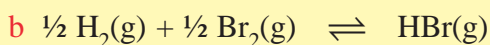
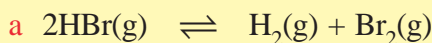
3. Write the equilibrium constant expression for the following equations:



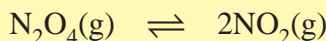
4. For the reaction:



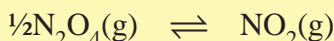
$K_p = 7.1 \times 10^4$ at 700 K. What is the value of K_p for the following reactions at the same temperature?



5. The reversible reaction:



has a value of $K_p = 0.113$ at 25°C. Determine the numerical value of K_c at 25°C for the reaction,



Is it greater than, equal to, or less than 0.113? Explain.

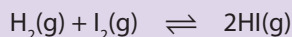
Applications of Equilibrium Constant

Activity 5.5



Form a group and discuss the following:

The equilibrium constant, K_c for the formation of hydrogen iodide from molecular hydrogen and molecular iodine in the gas phase



is 54.3 at 430°C. Suppose that in a certain experiment we place 0.243 mole of H_2 , 0.146 mole of I_2 , and 1.98 moles of HI all in a 1.00 L container at 430°C. Will there be a net reaction to form more H_2 and I_2 or more HI ?

Share your ideas with the rest of the class.

The value of equilibrium constant predicts the extent of reaction at equilibrium. It also tells about the relative concentrations of products and reactants present at equilibrium,

that is, the position of equilibrium.

Position of equilibrium: K_c can have three types of values.

Case 1: When $K_c > 1$

This indicates that the value of numerator is greater than the denominator. So the formation of products is favoured at equilibrium.

Case 2: When $K_c < 1$

This indicates that the value of numerator is less than the denominator. So the formation of products is not favoured at equilibrium.

Case 3: When $K_c = 1$

This indicates that the rate of forward reaction is equal to the rate of backward reaction.

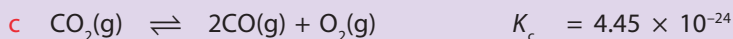
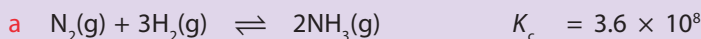
Extent of reaction: K_c value also predicts the extent of the reaction at equilibrium. Very large values of K_c indicates that the extent of the reaction is very large at equilibrium. So most of the reactants have been consumed at equilibrium. A very small value of K_c indicates that the extent of reaction is very small at equilibrium. Most of the reactants will be in the unreacted state.

Activity 5.6

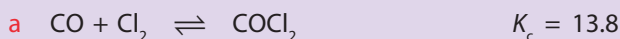


Form a group and discuss the following questions:

1. Predict whether the formation of product is favoured for the following reactions:



2. Arrange the following reactions in order of their increasing tendency to proceed towards completion (least extent to greatest extent).



Share your ideas with the rest of the class.

Reaction Quotient (Q)

Reaction quotient is the ratio of concentrations of products to the concentrations of reactants raised to the power of their respective coefficients at any stage after the start of the reaction. For the general reaction,



the expression for the reaction quotient is

$$Q = \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

$[A]$, $[B]$, $[M]$ and $[N]$ are concentrations at any stage during the reaction. At the initial stages of the reaction, the amount of product formed is low, therefore, the value of Q is small. With the progress of the reaction, since the concentration of products increases, the value of Q also increases. When the reaction attains equilibrium, Q becomes equal to the equilibrium constant.

Reaction Quotient in Terms of Molarities

When the concentrations are expressed in molarities, the reaction quotient is Q_c .

$$Q_c = \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

At equilibrium,

$$Q_c = \left\{ \frac{[M]^m [N]^n}{[A]^a [B]^b} \right\}_{\text{eq}} = K_c$$

Reaction Quotient in Terms of Partial Pressure

When the concentrations are taken in partial pressures, the reaction quotient is Q_p and is given by the expression

$$Q_p = \frac{(p_M)^m (p_N)^n}{(p_A)^a (p_B)^b}$$

At equilibrium,

$$Q_p = \left\{ \frac{(p_M)^m (p_N)^n}{(p_A)^a (p_B)^b} \right\}_{\text{eq}} = K_p$$

Application of Reaction Quotient

Reaction quotient predicts the direction of the reaction at any stage, that is for the given concentration of reactants and products. It also decides whether the reaction has attained equilibrium or not.

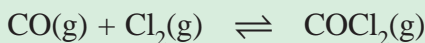
When Q is less than K , then the reaction will proceed in the forward direction and more products will be formed till the equilibrium is reached.

When Q is greater than K , then the reaction will proceed in the reverse direction and more reactants will be formed till the equilibrium is reached.

When Q is equal to K , then the reaction has attained equilibrium.

Example 5.5

At a certain temperature the reaction:



has an equilibrium constant $K_c = 13.8$. Is the following mixture an equilibrium mixture? If not, in which direction (forward or backward) will the reaction proceed to reach equilibrium? $[\text{CO}]_0 = 2.5 \text{ mol L}^{-1}$; $[\text{Cl}_2]_0 = 1.2 \text{ mol L}^{-1}$; and $[\text{COCl}_2]_0 = 5.0 \text{ mol L}^{-1}$.

Solution:

Recall that for the system to be at equilibrium $Q_c = K_c$. Substitute the given concentrations into the reaction quotient for the reaction, and determine Q_c .

$$Q_c = \frac{5 \text{ mol L}^{-1}}{(2.5 \text{ mol L}^{-1})(1.2 \text{ mol L}^{-1})} = 1.6 (\text{mol L}^{-1})^{-1}$$

Since $Q_c < K_c$ the reaction mixture is not an equilibrium mixture, and a net forward reaction will bring the system to equilibrium.

Calculating the Equilibrium Concentrations

Not only can we estimate the extent of reaction from the K_c value, but also the expected concentrations at equilibrium can be calculated from knowledge of the initial concentrations and the K_c value. In these types of problem it will be very helpful to use the following approach.

1. Express the equilibrium concentrations of all the species in terms of the initial concentrations and an unknown x , which represents the change in concentration.

- Substitute the equilibrium concentrations derived in part 1 into the equilibrium constant expression, and solve for x . The equilibrium concentration is given by: equilibrium concentration = initial concentration \pm the change due to the reaction where the **+** sign is used for a product, and the **-** sign for a reactant.
- Use x to calculate the equilibrium concentration of all the species.

Example 5.6

Let us consider the reaction between hydrogen and iodine in which 1 mole of H_2 and 2 moles of I_2 were added in 500 mL flask. First we need expressions for the equilibrium concentrations of H_2 , I_2 , and HI . Tabulating the initial concentrations as:

Concentration	H_2	+	I_2	\rightleftharpoons	2HI
Initial	1.00 mol/0.50 L		2.00 mol/0.50 L		0
Change	-		-		-
Equilibrium	-		-		-

Since the answer involves three unknowns, we will relate the concentrations to each other by introducing the variable x . Recall, that the equilibrium concentration = initial concentration \pm change in concentration. Let x = the change in concentration of H_2 . That is, let x = the number of moles of H_2 reacting per liter. From the coefficients of the balanced equation we can tell that if the change in H_2 is $-x$, then the change in I_2 must also be $-x$, and the change in HI must be $+2x$.

The next step is to complete the table in units of molarity:

Concentration	H_2	+	I_2	\rightleftharpoons	2HI
Initial (M)	2.0		4.0		0
Change (M)	$-x$		$-x$		
Equilibrium (M)	$(2.0 - x)$		$(4.0 - x)$		$+2x$

Now substitute the equilibrium concentrations from the table into the K_c expression,

$$K_c = \frac{(2x)^2}{(2.0-x)(4.0-x)}$$

and solve for x .

$$K_c = \frac{(2x)^2}{x^2 - 6.0x + 8.0} = 64$$

Rearranging, we get:

$$4x^2 = 64x^2 - 384x + 512$$

and grouping yields

$$60x^2 - 384x + 512 = 0$$

We will use the general method of solving a quadratic equation of the form

$$ax^2 + bx + c = 0$$

The root x is given by

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In this case, $a = 60$, $b = -384$, and $c = 512$. Therefore,

$$x = \frac{-(-384) \pm \sqrt{(-384)^2 - 4(60)(512)}}{2(60)}$$

$$x = \frac{384 \pm \sqrt{2.5 \times 10^4}}{120}$$

$$x = \frac{384 \pm 158}{120} = 1.9 \text{ and } 4.5 \text{ mol/L}$$

Recall that x = the number of moles of H_2 (or I_2) reacting per liter. Of the two answers (roots), only 1.9 is reasonable, because the value 4.5 M would mean that more H_2 (or I_2) reacted than was present at the start. This would result in a negative equilibrium concentration, which is physically meaningless. We therefore use the root $x = 1.9$ M to calculate the equilibrium concentrations:

$$[H_2] = 2.0 - x = 2.0 \text{ M} - 1.9 \text{ M} = 0.1 \text{ M}$$

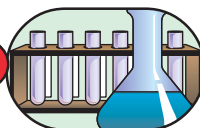
$$[I_2] = 4.0 - x = 4.0 \text{ M} - 1.9 \text{ M} = 2.1 \text{ M}$$

$[HI] = 2x = 2(1.9 \text{ M}) = 3.8 \text{ M}$. The results can be checked by inserting these concentrations back into the K_c expression to see if $K_c = 64$.

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(3.8)^2}{(0.1)(2.1)} = 68$$

Thus the concentrations we have calculated are correct. The difference between 64 and 68 results from rounding off which is to maintain the correct number of significant figures. Therefore, our result is correct only to the number of significant figures given in the problem.

Experiment 5.1



Determination of Equilibrium Constant for an Organic Acid

Objective: To determine equilibrium constant for the esterification of an acetic acid.

Apparatus: Round bottom flask, pipette, conical flask, burette, burette stand, water condenser with inlet and outlet pipes, boiling chips, clamp stand, burner, water bath.

Chemicals: 0.5 M acetic acid, 0.5 M propan-1-ol, phenolphthalein, 0.01 M NaOH solution, ice.

Procedure:

1. In a 100 mL round bottom flask, take 10.0 mL of 0.5 M acetic acid and 10.0 mL of 0.5 M propan-1-ol.
2. Add 5 drops of conc. H_2SO_4 to the solution in the round bottom flask.
3. Add a few pieces of boiling chips to the solution in the round bottom flask.
4. Attach a water condenser and reflux for 1 hour on a water bath as shown in (Figure 5.2(a)).
5. Cool the flask and its contents in an ice bath.
6. Pipette out 1.0 mL of the reaction mixture in a conical flask containing 25.0 mL of ice cold water. (Ice cold water is prepared by taking 25.0 mL of water in a conical flask and keeping on ice bath for some time).
7. Add 2 drops of phenolphthalein indicator to the solution in a conical flask.
8. Titrate the contents against 0.1 M NaOH solution as shown in (Figure 5.2(b)).
9. Repeat steps 6, 7 and 8 three times and take the average volume of NaOH consumed in titration.

Observations and analysis:

1. What is the purpose of adding small amount of H_2SO_4 to the reaction mixture at one beginning of the experiment?
2. Why do we add boiling chips to the reaction mixture before refluxing?
3. Calculate:
 - a the concentrations of reactions and products at equilibrium.
 - b the equilibrium constant for the esterification of acetic acid.

Hint: The esterification reaction is acid catalysed.

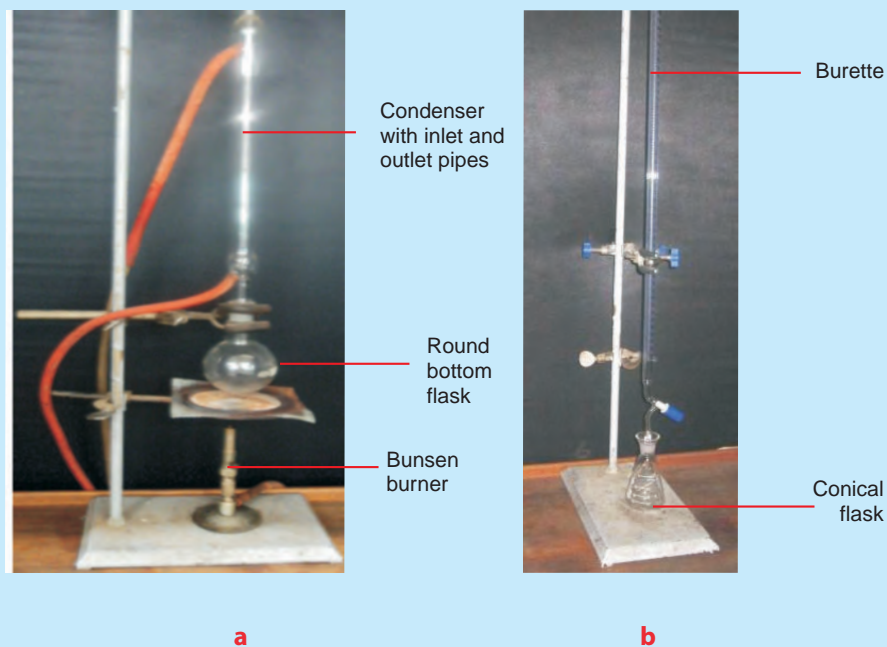
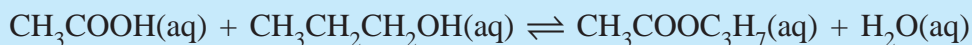


Figure 5.2 Laboratory set-up for the esterification of acetic acid.

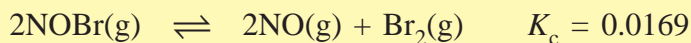
Exercise 5.6

1. For the equilibrium:



a sample of 0.25 mol N_2O_4 is allowed to dissociate and come to equilibrium in a 1.5 L flask at 100°C . What are the equilibrium concentrations of NO_2 and N_2O_4 ?

2. The decomposition of NOBr is represented by the equation:



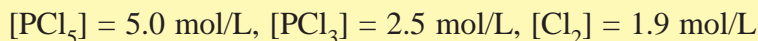
At equilibrium the concentrations of NO and Br_2 are 1.05×10^{-2} M and 5.24×10^{-3} M, respectively. What is the concentration of NOBr ?

3. The reaction:



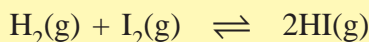
has the equilibrium constant value $K_c = 0.24$ at 300°C .

- a Is the following reaction mixture at equilibrium?



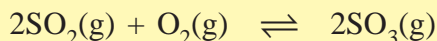
- b Predict the direction in which the system will react to reach equilibrium

4. At 400°C , the equilibrium constant for the reaction:



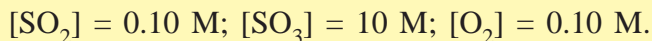
is 64. A mixture of 0.250 mol H_2 and 0.250 mol I_2 was introduced into an empty 0.75 L reaction vessel at 400°C , find the equilibrium concentrations of all components

5. At 700 K , the reaction:



has an equilibrium constant $K_c = 4.3 \times 10^6$.

- a Is a mixture with the following concentrations at equilibrium?



- b If not at equilibrium, predict the direction in which a net reaction will occur to reach a new equilibrium.

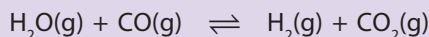
5.1.4 Changing Equilibrium Conditions–Le Chatelier's Principle

Activity 5.7



Form a group and discuss the following questions:

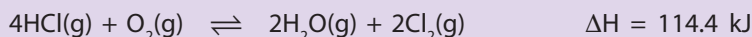
1. Consider the following reaction at 400°C :



Some amounts of H_2O , $\text{CO}(\text{g})$, $\text{H}_2(\text{g})$, and $\text{CO}_2(\text{g})$ were put into a flask so that the composition corresponded to an equilibrium mixture. A laboratory technician added

an iron catalyst to the mixture, but was surprised when no additional $\text{H}_2(\text{g})$ and $\text{CO}_2(\text{g})$ were formed even after waiting for many days. Explain why the technician should not have been surprised.

2. Equilibrium is established in the reversible reaction



Describe four changes that could be made to this mixture to increase the amount of $\text{Cl}_2(\text{g})$ at equilibrium.

3. Describe how you might be able to drive a reaction having a small value of K_c to completion.

Share your ideas with the rest of the class.

Factors Affecting the Equilibrium Constant

The equilibrium constant depends upon the following factors:

1. Temperature at which the experiment is performed.
2. The form of equations which describe the equilibrium.

For example, for the reaction



If the reaction is multiplied by 2,



the expression for K_c becomes

$$K'_c = \frac{[\text{NH}_3]^4}{[\text{N}_2]^2[\text{H}_2]^6}$$

$$K'_c = (K_c)^2$$

If the reaction is reversed, $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$

the K_c becomes

$$K''_c = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2}$$

$$K''_c = 1/K_c$$

The equilibrium constant does not depend upon the initial concentrations of the reactants. K_c and K_p are independent of pressure.

Le Chatelier's Principle

When the reaction has attained equilibrium then the temperature, pressure, volume and concentrations remain constant. These four properties are known as reaction parameters. Le Chatelier's principle describe the changes that will take place when any one of the reaction parameters are changed at equilibrium.

Statement: If any one or more of the reaction parameters is changed at equilibrium then the reaction will proceed in that direction so as to undo the change in the parameter and the equilibrium is again attained.

Le Chatelier's principle describes the effect of the change in parameters on the position of equilibrium. That is, it predicts whether the changes in reaction parameters will favour the formation of reactants or products.

Historical Note



Henry Louis Le Chatelier

Henry Louis Le Chatelier (1850-1936) was a French-Italian chemist. He is most famous for the law of chemical equilibrium which is known by his name as Le Chatelier's principle. This law is used by chemists to predict the effect of a change in conditions on a chemical equilibrium

Effect of Change in Temperature on the Position of Equilibrium

Activity 5.8



Form a group and perform the following activity to study the effect of temperature on the position of equilibrium:

Take 0.5 g of cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) in a test tube and add 10 mL of distilled water to prepare the solution. Then add 5 mL of concentrated HCl slowly to the solution. What is the colour of the solution? Now put the test tube in a beaker containing crushed ice. Note

the colour of the solution. Take out the test tube from ice bath and keep it at room temperature for 5 minutes. Note the colour of the solution.

Share your findings with the rest of the class.

According to **Le Chatelier's principle**, if the temperature of the reaction at equilibrium is increased then the reaction will proceed in that direction where heat is absorbed so as to undo the effect of heating. Similarly if the temperature of the reaction at equilibrium is lowered then the reaction will proceed in that direction where the heat is produced so that the equilibrium is again attained.

For an exothermic reaction, when the temperature is lowered, the reaction will proceed in the forward direction, since the heat produced during forward reaction will undo the effect of lowering of temperature. When the temperature is increased, then the reaction will proceed in the reverse direction where the heat is absorbed.

For an endothermic reaction, when the temperature is lowered, the reaction will proceed in the reverse direction where heat is produced so as to undo the effect of lowering of temperature. When the temperature is increased, the reaction proceeds in the forward direction.

Effect of temperature in terms of amount of reactants and products formed can be summarized as:

When the equilibrium shifts in the forward direction, then the concentration of products increases and that of reactants decreases.

So for **exothermic reactions** when the temperature is lowered, more products are formed. That is, the decrease in temperature favours exothermic reactions.

For **endothermic reactions**, when the temperature is increased, more products are formed, That is, increase in temperature favours endothermic reactions.

For example, formation of ammonia is an exothermic process.



If the temperature is lowered at equilibrium, the reaction will proceed in the **forward direction** till the new equilibrium is established. So the concentration of ammonia will

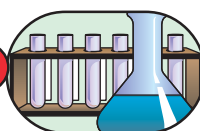
increase. If the temperature is increased at equilibrium, then the reaction will proceed in **reverse direction** which is endothermic in nature. So the concentration of ammonia will decrease.

Dissociation of dinitrogen tetroxide is endothermic in nature.



Therefore, according to Le Chatelier's principle, the formation of NO_2 is favoured by increase in the temperature at equilibrium.

Experiment 5.2



Effect of Change in Temperature on the Equilibrium Position

Objective: Determination of the effect of changes in temperature on the position of equilibrium of iodine and starch.

Apparatus: Test tubes, water bath, stands, Bunsen burner, thermometer.

Chemicals: Iodine, starch.

Procedure:

1. Add a few drops of tincture of iodine to some starch solution in a test tube. Record your observations.
2. Heat the solution to about 80°C using a water bath. Record your observation. What can we deduce from this?
3. Cool the container by placing it in an ice box. Record your observation.

Observations and analysis:

1. Explain the concept of a starch-iodine complex. Is this an example of an equilibrium reaction?
2. Which direction is exothermic and which is endothermic? How do you explain your results?
3. What can you conclude based on your observations?

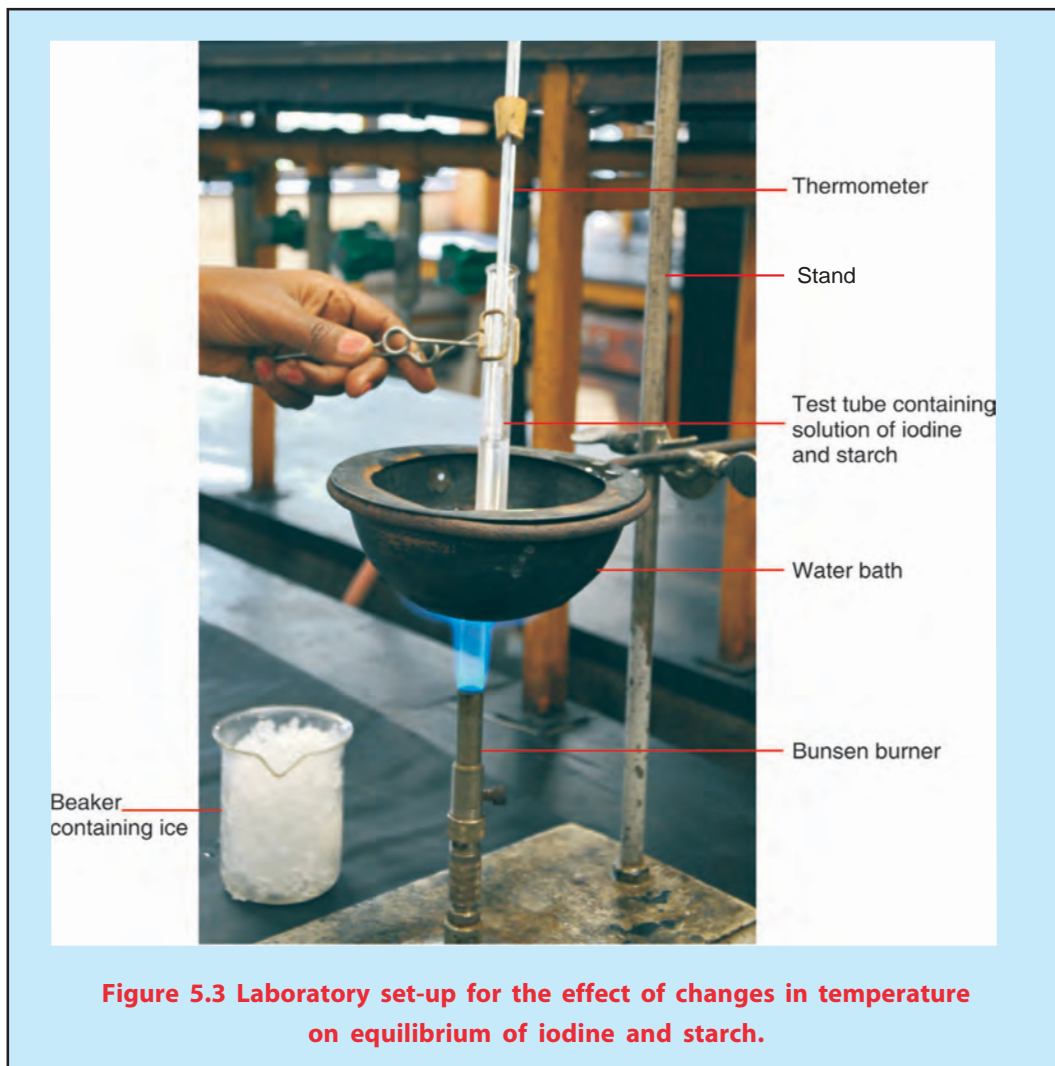


Figure 5.3 Laboratory set-up for the effect of changes in temperature on equilibrium of iodine and starch.

Effect of Change in Pressure on the Position of Equilibrium

According to Le Chatelier's principle, if the pressure at equilibrium is increased then the reaction will proceed in that direction where the pressure is reduced. Since the pressure depends upon the number of moles, on increasing the pressure the reaction will proceed in that direction where the number of moles are reduced.

If the pressure at equilibrium is decreased then the reaction will proceed in that direction where the number of moles is more.

For a general reaction,



the effect of pressure is decided by Δn .

$$\Delta n = (m + n) - (a + b)$$

If $\Delta n > 0$, that means the total moles of products is greater than the total moles of reactants. Lowering of pressure will favour the reaction in forward direction. That is, more products will be formed at equilibrium if the pressure is lowered.

If $\Delta n < 0$, that means the total moles of products is less than the total moles of reactants. Increasing the pressure will favour the reaction in forward direction. That is, more products will be formed at equilibrium if the pressure is increased.

If $\Delta n = 0$, then the change in pressure has no effect on the position of equilibrium.

For example, in the formation of ammonia,



$$\Delta n = 2 - (1 + 3) = -2$$

Therefore, an increase in pressure at equilibrium will favour the forward reaction.

For the dissociation of dinitrogen tetroxide, $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

$$\Delta n = 2 - 1 = 1$$

The decrease in pressure at equilibrium, favours the forward reaction.

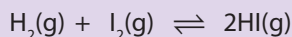
Hydrolysis of ester is not affected by the change in pressure. Why is it so?

Effect of Change in the Concentration on the Position of Equilibrium

Activity 5.9



Form a group and consider the following reaction at 400°C:



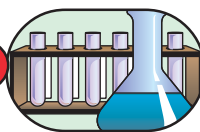
H_2 and I_2 were placed into a flask and allowed to react until equilibrium was reached. Then a small amount of H^{131}I was added. ^{131}I is an isotope of iodine that is radioactive. Discuss whether radioactive ^{131}I will remain in the HI molecule or some, or all, of it will find its way into the I_2 molecule forming $^{127}\text{I}^{131}\text{I}$.

Share your ideas with the rest of the class.

At equilibrium, on increasing the amount of a substance, the reaction proceeds in that direction where the substance is consumed. When the amount of the reactants is increased the reaction proceeds in the forward direction and when the amount of products is increased, the reaction proceeds in the backward direction.

The forward reaction is favoured if the products formed are removed from the vessel.

Experiment 5.3



Effect of Change in Concentration on Equilibrium Position

Objective: To study the effect of concentration on the position of equilibrium.

Apparatus: Test tubes (5), test tube stand, 100 mL beakers (2),

Chemicals: 0.05 M $\text{Fe}(\text{NO}_3)_3$ solution, 0.01M KSCN solution, 0.1M HNO_3 acid.

Procedure:

1. Take 5 test tubes and label them as 1, 2, 3, 4 and 5. Keep them on a test tube rack.
2. Take 50 mL of 0.05 M solution of $\text{Fe}(\text{NO}_3)_3$ in a beaker.
3. In separate beakers take 10 mL of 0.01 M KSCN solution and 20 mL of 0.1 M HNO_3 acid solution.
4. Mix the solutions according to the given table to prepare 5 different solutions.

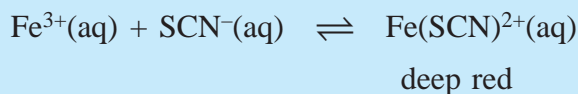
Test tube No.	Volume in mL of		
	0.05 M $\text{Fe}(\text{NO}_3)_3$	0.1 M HNO_3	0.01 M KSCN
1	1.0	4.0	1.0
2	2.0	3.0	1.0
3	3.0	2.0	1.0
4	4.0	1.0	1.0
5	5.0	0.0	1.0

- Note the colour of the solution in each test tube.
- Arrange the test tubes in the increasing order of colour intensity.

Observations and analysis:

- Which direction is exothermic and which is endothermic? How do you explain your results?
- Correlate the colour intensity with the concentration of Fe^{3+} in the test tube.

Hint: Fe^{3+} forms deep red colour complex with SCN^- ions.



- By taking different volumes of $\text{Fe}(\text{NO}_3)_3$ in the test tubes the concentration of Fe^{3+} is varied in the solution. Calculate the concentration of Fe^{3+} ions in each test tube and correlate with the colour intensity.
- In the test tube take 1.0 mL of $\text{Fe}(\text{NO}_3)_3$ solution and add 4.0 mL of HNO_3 solution followed by 1.0 mL of KSCN solution. Mix well and note the colour. Add 1.0 mL of $\text{Fe}(\text{NO}_3)_3$ solution and again note the colour of the solution.

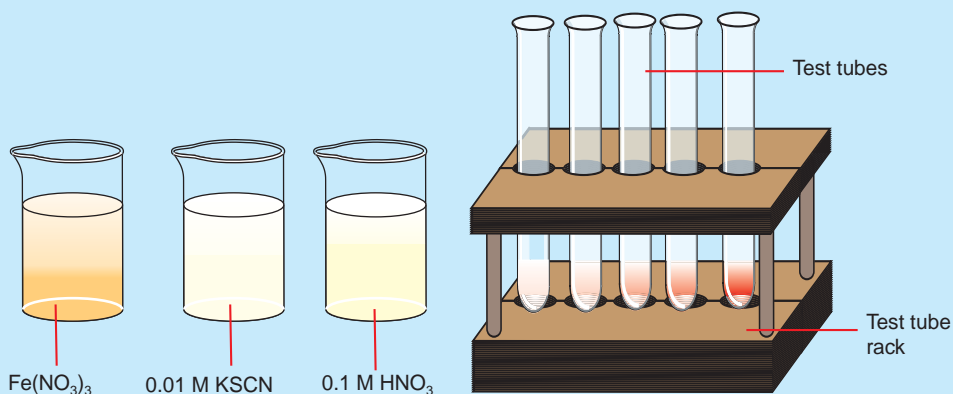


Figure 5.4 Laboratory set-up for the effect of changes in concentration on equilibrium of $\text{Fe}^{3+}(\text{aq})$ and $\text{SCN}^{-}(\text{aq})$.

Effect of Catalyst on the Position of Equilibrium

Catalyst is a substance that alters the rate of a reaction without being consumed during the reaction. The catalyst does not effect the position of equilibrium. It alters the time in which the equilibrium is attained. This is due to the fact that the catalyst changes the rate of the forward reaction and the reverse reaction by the same extent so the equilibrium is not effected.

Effect of Addition of Inert Gases on the Position of Equilibrium

When a non reactive gas is added to a reaction at equilibrium, the effect depends on various factors.

Case 1. When the non-reactive gas is added at constant volume there is no change on the position of equilibrium.

Case 2. When the non-reactive gas is added and the volume of the system changes then the effect of position is decided by the stoichiometry of the reaction.

For a general reaction,



$$\Delta n = (m + n) - (a + b)$$

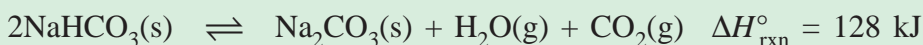
If $\Delta n < 0$, then the addition of inert gas favours the formation of the reactants.

If $\Delta n > 0$, then the addition of inert gas favours the formation of products.

If $\Delta n = 0$, then the addition of inert gas has no effect on the position of equilibrium.

Example 5.7

For the reaction at equilibrium:



state the effects (increase, decrease, no change) of the following stresses on the number of moles of sodium carbonate, Na_2CO_3 , at equilibrium in a closed container. Note that Na_2CO_3 is a solid (this is a heterogeneous equation); its concentration will remain constant, but its amount can change.

- a Removing $\text{CO}_2(\text{g})$ c Raising the temperature
b Adding $\text{H}_2\text{O}(\text{g})$ d Adding $\text{NaHCO}_3(\text{s})$.

Solution:

- a If the CO_2 concentration is lowered, the system will react in such a way as to offset the change. That is, a shift to the right will replace some of the missing CO_2 . The number of moles of Na_2CO_3 increases.
- b Addition of $\text{H}_2\text{O}(\text{g})$ exerts a stress on the equilibrium that is partially offset by a shift in the equilibrium to the left (net reverse reaction). This consumes Na_2CO_3 as well as some of the extra H_2O . The number of moles of Na_2CO_3 decreases.
- c An increase in temperature will increase the K_c value of an endothermic reaction. There is a shift to the right, and more Na_2CO_3 is formed.
- d The position of a heterogeneous equilibrium does not depend on the amount of pure solids or liquids present. The same equilibrium is reached whether the system contains 1 g of $\text{NaHCO}_3(\text{s})$ or 10 g of NaHCO_3 . No shift in the equilibrium occurs. No change in the amount of Na_2CO_3 occurs.

Optimum Conditions

The conditions that give maximum yield of the products are known as optimum conditions. These conditions are decided by the **enthalpy of reaction** and its **stoichiometry** applying Le Chatelier's principle.

1. For exothermic reactions the yield of products is increased by performing the reaction at lower temperatures.
2. For endothermic reactions the yield of products is increased by performing the reaction at higher temperatures.
3. When $\Delta n > 0$, the decrease in pressure favours the formation of products.
4. When $\Delta n < 0$, the increase in pressure favours the formation of products.

5. Removing the products from the reaction vessel shifts the equilibrium reaction in the forward direction.

5.1.5 Chemical Equilibrium and Industry

Industrial processes are designed to give maximum possible yield of the products. The conditions for carrying out the reactions are based on Le Chatelier's principle. The following processes illustrate the application of Le Chatelier's principle in the industry.

Haber Process for the Manufacture of Ammonia

In 1909 Fritz Haber established the conditions under which nitrogen, $N_2(g)$ and hydrogen, $H_2(g)$, would combine to give ammonia. This process produces ammonia with yield of approximately 10-20%. The Haber synthesis was developed into an industrial process by Carl Bosch.

The reaction between nitrogen gas and hydrogen gas to produce ammonia gas is an exothermic equilibrium reaction, releasing 92.4 kJ/mol of energy at 298K (25°C).



According to Le Chatelier's Principle:

- Increasing the pressure causes the equilibrium to move in the forward direction resulting in a higher yield of ammonia since there are more gas molecules on the left hand side of the equation (4 in total) than there are on the right hand side of the equation (1). Increasing the pressure means the system adjusts to reduce the effect of the change, that is, to reduce the pressure by having fewer gas molecules.
- Decreasing the temperature causes the equilibrium to move in the forward direction resulting in a higher yield of ammonia since the reaction is exothermic (releases heat). Reducing the temperature means the system will adjust to minimize the effect of the change, that is, it will produce more heat since energy is a product of the reaction, and will therefore produce more ammonia gas as well. However, the rate of the reaction at lower temperature is extremely slow, so a higher temperature must be used to speed up the reaction which results in a lower yield of ammonia.

The equilibrium expression for this reaction is:

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

As the temperature increases, the equilibrium constant decreases and the yield of ammonia decreases.

Temperature (°C)	K_{eq}
25	6.4×10^2
200	4.4×10^{-1}
300	4.3×10^{-3}
400	1.6×10^{-4}
500	1.5×10^{-5}

Rate Considerations:

- The use of catalyst such as an iron, speeds up the reaction by lowering the activation energy so that the N_2 bonds and H_2 bonds can be more readily broken.
- Increased temperature means more reactant molecules have sufficient energy to overcome the energy barrier to reacting (activation energy) so the reaction is faster at higher temperatures (but the yield of ammonia is lower as discussed above). A temperature range of 400 – 500 °C is a compromise designed to achieve an acceptable yield of ammonia (10-20 %) within an acceptable time period.

At 200 °C and pressure above 750 atm there is an almost 100 % conversion of reactants to the ammonia product. Since there are difficulties associated with containing larger amounts of materials at such high pressure, lower pressure of around 200 atm are used industrially. By using a pressure of around 200 atm and a temperature of about 500 °C, the yield of ammonia is 10-20 %, while costs and safety concerns during operation of the plant are minimized.

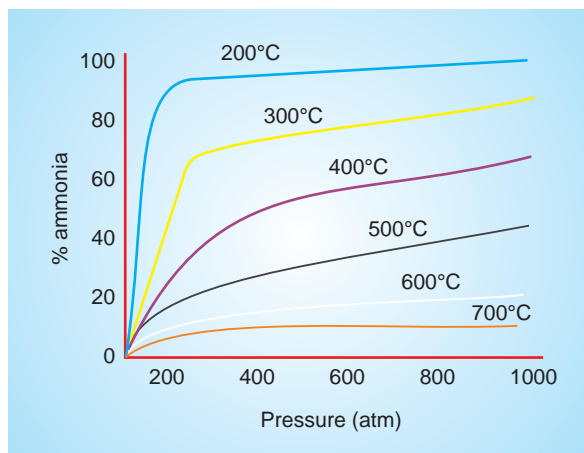


Figure 5.5 Effect of pressure on percentage yield of ammonia.

During industrial production of ammonia, the reaction never reaches equilibrium as the gas mixture leaving the reactor is cooled to liquefy and remove the ammonia. The remaining mixture of reactant gases is recycled through the reactor. The heat released by reaction is removed and used to heat the incoming gas mixture.

A flow diagram for the Haber process of manufacturing ammonia is shown below:

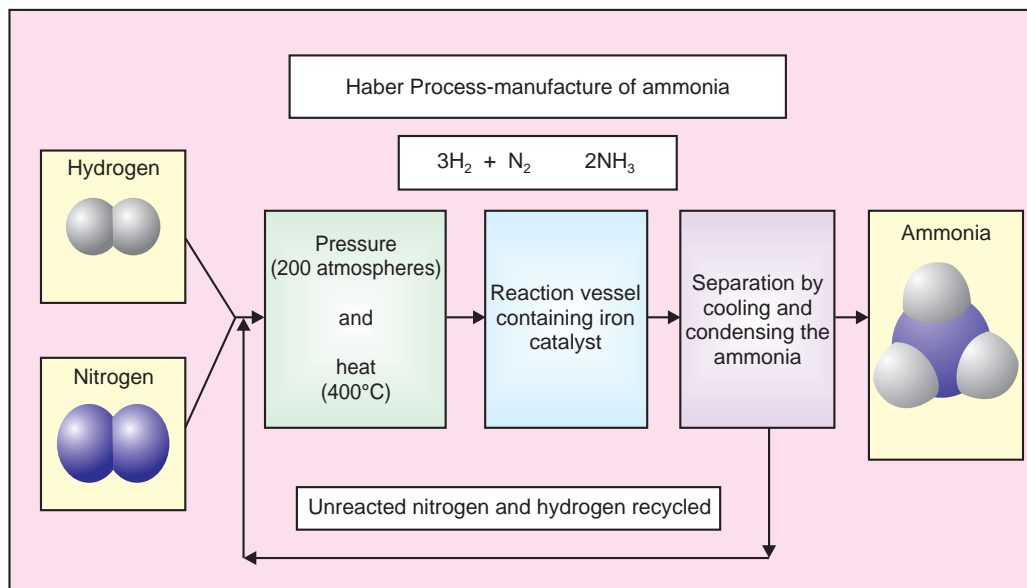
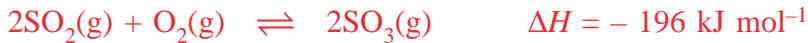


Figure 5.6 A flow scheme for Haber Process.

Contact Process for the Manufacture of Sulphuric acid

The manufacture of sulphuric acid by contact process involves the catalytic oxidation of sulphur dioxide SO_2 to sulphur trioxide SO_3 , which is a reversible reaction.



Contact Process for Production of Sulphuric Acid

Contact process involves the following steps:

- (i) Solid sulphur, $\text{S}(\text{s})$, is burned in air to form sulphur dioxide gas, SO_2 ;



- (ii) The gases are mixed with more air then cleaned by electrostatic precipitation to remove any particulate matter.
- (iii) The mixture of sulphur dioxide and air is heated to 450°C and subjected to a pressure of 101.3 - 202.6 kPa (1-2 atmospheres) in the presence of a vanadium catalyst (vanadium (V) oxide) to produce sulphur trioxide, $\text{SO}_3(\text{g})$, with a yield of 98 %.



- (iv) Any unreacted gases from the above reaction are recycled back into the above reaction.
- (v) Sulphur trioxide, $\text{SO}_3(\text{g})$ is dissolved in 98 % (18 M) sulphuric acid, H_2SO_4 , to produce disulphuric acid or pyrosulphuric acid, also known as fuming sulphuric acid or oleum, $\text{H}_2\text{S}_2\text{O}_7$.



This is done because when water is added directly to sulphur trioxide to produce sulphuric acid,



the reaction is slow and tends to form a mist in which the reaction becomes very slow.

- (vi) Water is added to the disulphuric acid, $\text{H}_2\text{S}_2\text{O}_7$, to produce sulphuric acid, H_2SO_4 .



The oxidation of sulphur dioxide to sulphur trioxide in step (iii) above is an exothermic reaction (energy is released), so according to Le Chatelier's Principle,

higher temperatures will force the equilibrium position to shift to the left hand side of the equation favouring the production of sulphur dioxide. Lower temperatures would favour the production of the product sulphur trioxide and result in a higher yield. However, the rate of reaching equilibrium at the lower temperatures is extremely low. A higher temperature means equilibrium is established more rapidly but the yield of sulphur trioxide is lower. The temperature about 450°C is a compromising situation whereby a faster reaction rate results in a slightly lower yield.

Similarly, at higher pressures, the equilibrium position shifts to the equation in which there are the least numbers of gaseous molecules.



On the left hand side of the reaction there are 3 moles of gaseous reactants, and the right hand side are 2 moles of gaseous products, so higher pressure favours the right hand side, by Le Chatelier's Principle. Higher pressure results in a higher yield of sulphur trioxide. A vanadium catalyst (vanadium (V) oxide) is also used in this reaction to speed up the rate of the reaction.

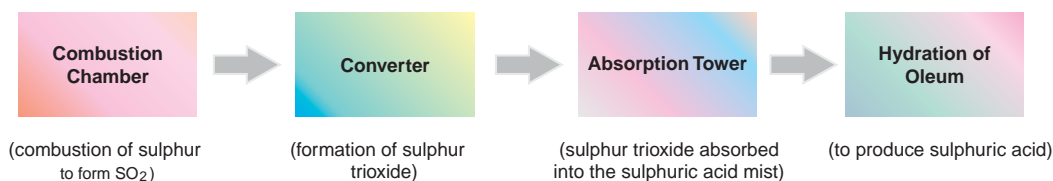


Figure 5.7 A flow scheme for Contact process.

Exercise 5.7

Answers the following questions:

1. Which compound is manufactured by Haber process?
2. What are the raw materials used in Haber process?
3. What is the role of iron in Haber process?
4. How are the reactions made to run faster in the Haber process?
5. Draw a flow chart to show what happens in the three stages of Haber process.
6. What is a mixture of H_2SO_4 and free SO_3 ?
7. What are the raw materials for making SO_2 in the contact process?
8. Why is SO_3 not directly added to make sulphuric acid?

5.2 PHASE EQUILIBRIUM

At the end of this section, you should be able to:

- explain the interplay between kinetic and potential energy that underlies the properties of the three states of matter and their phase changes;
- explain the process involved, both within a phase and through a phase change, when heat is added or removed from a pure substance;
- explain the meaning of vapour pressure and explain how phase changes are dynamic equilibrium processes;
- explain the relationship between vapour pressure and boiling point;
- describe how a phase diagram shows a phase of a substance at different conditions of pressure and temperature; and
- use a phase diagram to determine melting point, boiling point, critical temperature, critical pressure and triple point of a substance.

There are many physical processes that attain equilibrium under certain conditions. You have already performed an activity where equilibrium exists between ice and water. You also know that there are three states of **matter**, namely, solid, liquid and gas. Each substance can exist in any one state depending upon the temperature and pressure. A substance will exist in the gaseous state at high temperatures and low pressures. It will exist in solid state at low temperature and high pressure. In between the two conditions the substance will exist in the liquid state. These conditions are decided by the nature of the substance. At molecular level this can be interpreted in terms of forces of attraction and repulsion between the molecules.

5.2.1 Force of Attractions, Kinetic Energy and States of Matter

Activity 5.10



Form a group and perform the following activity:

In a test tube mix 1 mL of water with 1 mL of ethanol. Label it as **A**.

In another test tube take 1 mL of water and 1 mL of chloroform. Label it as **B**.

Discuss the following questions:

1. Find out in how many states the matter is present in test tubes **A** and **B**?
2. What is the difference between the liquids in the test tubes?

Share your ideas with the rest of the class.

In a substance the molecules are held together by the forces of attraction. At the same time each molecule possesses kinetic energy due to its motion. These two are opposing forces; forces of attraction bind the molecules together while kinetic energy tends to move the molecules apart.

- At very high temperatures, the molecules possess large kinetic energy, so

kinetic energy \gg forces of attraction

As a result, molecules are far apart, the substance does not have definite shape or volume. This state is known as **gaseous state**.

- At very low temperatures, the molecules possess small kinetic energy, so

kinetic energy \ll forces of attraction

As a result, the molecules are held together strongly and the substance has definite shape and volume. This state is known as **solid state**.

- At intermediate temperatures the kinetic energy and forces of attraction match each other, that is,

kinetic energy \approx forces of attraction

As a result, the molecules are held together, but not strongly, so that the substance has a definite volume but no definite shape. This state is known as **liquid state**.

5.2.2 Common terms: Phase, Component and Degree of Freedom

Phase: It is that part of the system which is physically and chemically homogeneous and separated from rest of the system by a discrete boundary. In this part the physical and chemical properties are uniform.

For some simple systems it is physically distinct part of the system that may be mechanically separated from other distinct parts.

The number of phases is represented by P . For example, a mixture of water and chloroform has two distinct layers, one of water and the other of chloroform (**Activity 5.5**). Therefore, there are two different **phases** although both are in the **liquid state**. Similarly, a mixture of two solids constitutes two different phases (**Activity 5.6**).

The simple rules for determining the number of phases are.

- Pure substance present in one state of matter constitutes one phase.
- Same substance present in different states of matter constitutes different phases. For example, ice and water are two different phases of H_2O .
- A mixture of gases constitutes one phase system.
- A homogeneous solution is a one phase system.
- For immiscible liquids, the number of layers formed is equal to the number of phases.
- For solids, each chemical species is a different phase. Different allotropic forms of the same substance constitute different phases. For example, diamond and graphite are different forms of carbon so they are different phases.

Component: It is the chemically distinct quantity present in the system. The number of components in a system is represented by C . When no chemical reaction takes place in the system, the number of components is equal to the total number of chemical species present in all the phases of the system. For example, an aqueous solution of sodium chloride has two components, NaCl and water.

Degree of Freedom: It is the minimum number of variables required to describe each component in each phase of the system. It is represented by F . In the case of a pure substance present in one phase, the substance can be described completely if its temperature and pressure are known. For example, if you have H_2O and you also know its temperature and pressure, then you can predict all the properties, such as, whether it is in the solid, liquid or vapour state, as well as its density, refractive index, viscosity and other properties. Since only temperature and pressure are required to describe a pure substance, the degree of freedom of pure substance is 2.

Similarly, H_2O can coexist as ice and liquid water under specific conditions of temperature and pressures only. If the temperature is known then the pressure is fixed, similarly if the pressure is known the temperature is fixed. Since only one variable is required to completely describe a pure substance simultaneously present in two phases, its degree of freedom is two.

All the three states of matter of a substance coexist (present together) at a point known as triple point. The triple point has a fixed value of temperature and pressure and no variable is required to describe the system, so the degree of freedom is zero.

Example 5.8

1. Describe the number of phases present in the following systems:

- Solution of sodium chloride in water.
- A mixture of oil and water.
- A mixture of hydrogen, oxygen and methane gases.
- A mixture of powdered sodium chloride and potassium chloride.
- Ice floating on water.

Solution:

- $P = 1$ since the solution is homogeneous.
- $P = 2$ since oil and water are immiscible and they form two layers.
- $P = 1$ since a mixture of gases is a homogeneous mixture.
- $P = 2$ since NaCl and KCl are two different chemical species present in the solid state.
- $P = 2$ since pure substance is present in two different states of matter.

2. Describe the number of components present in the following systems:

- Solution of sodium chloride in water.
- A mixture of hydrogen, oxygen and methane gases.
- Ice floating on water.

Solution:

- $C = 2$ since two chemical species are present.
- $C = 3$ since three chemical species, namely, hydrogen, oxygen and methane gas are present.
- $C = 1$ since only one chemical substance, H_2O is present.

Exercise 5.8

Determine the number of phases and components that exist in each of the following systems:

- NH_4Cl solid is placed in an evacuated chamber. After a while, some ammonia and HCl appear in the gas phase above it.

- b COCl_2 , CO and Cl_2 at equilibrium with no excess of CO or Cl_2 .
- c COCl_2 , CO and Cl_2 at equilibrium with excess of CO added (i.e., the concentrations of CO and Cl_2 are unequal).

5.2.3 Phase Rule

It is an important equation in the study of equilibrium between different phases in a system. It relates the number of phases and components to the degree of freedom by the following equation:

$$F = C - P + 2$$

This equation was given by **Josiah William Gibbs**, hence it is known as **Gibbs Phase rule equation**. This shows that the number of degrees of freedom (F) is equal to the number of components (C) minus the number of phases (P) plus the constant 2. The factor 2 stands for two parameters, namely, temperature and pressure.

Let us calculate the degree of freedom for one component system ($C = 1$). A simple example of one component is a pure substance. At a given time the pure substance can exist in one phase or more than one phases present together in equilibrium. The degree of freedom for various values of phases (1 – 4) can be calculated using the Phase rule equation.

For $P = 1$,

$$F = 1 - 1 + 2 = 2; \text{ such a system is known as } \text{bivariant system}.$$

For $P = 2$,

$$F = 1 - 2 + 2 = 1; \text{ such a system is known as } \text{monovariant system}.$$

For $P = 3$,

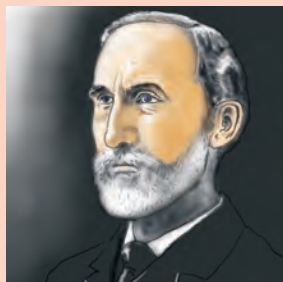
$$F = 1 - 3 + 2 = 0; \text{ such a system is known as } \text{invariant system}.$$

For $P = 4$,

$$F = 1 - 4 + 2 = -1. \text{ This system is not possible as the degree of freedom can not be negative.}$$

From this we can conclude that for one component system, at a given time, maximum of three phases can coexist in equilibrium.

Historical Note



Josiah Willard Gibbs

Josiah Willard Gibbs (1839 – 1903) was an American theoretical physicist, chemist and mathematician. He devised much of the theoretical foundation for both chemical thermodynamics and physical chemistry. He proposed Gibbs' phase rule, in the 1870s.

5.2.4 Temperature, Pressure and Phase Changes of Pure Substance

In this section, we will study how the phase of a pure substance changes when it is heated or cooled. The change in temperature may also be accompanied by the change in the pressure of system.

Changes Involved During Heating of the Pure Substance (one Component System)

When a pure substance is heated it undergoes various physical changes. These changes depend upon initial pressure at which the heating starts.

Activity 5.11



Form a group and perform the following activity:

Take 10 ice cubes in a beaker, dip a thermometer in it and start heating. Note the temperature and the physical changes taking place in the system.

Discuss the following questions in the group and afterwards share your ideas with rest of the class.

1. What happens when ice is heated?
2. Does the temperature change when the ice is melting?
3. How does the temperature vary when the ice has melted completely?
4. What will happen if water formed is further heated?



Reason for the Change in Phase on Heating

When a substance in the solid state is heated, the kinetic energy of its molecules increases and they start moving. At a higher temperature, the kinetic energy of the molecules becomes equal to the intermolecular forces of attraction, so these intermolecular forces start breaking and the liquid is formed. This temperature is known as melting point. On further heating the kinetic energy of the molecules goes on increasing and ultimately becomes much greater than the forces of attraction between the molecules. The molecules are able to overcome the forces of attraction and they start moving randomly. This is the stage when the substance gets converted into vapours.

Vapour Pressure and Boiling Point

When a liquid is taken in an evacuated closed vessel, some molecules at the surface of the liquid escape to the vapour phase. This happens when the kinetic energy of the surface molecules becomes greater than the intermolecular forces of attraction. This process is known as **vapourization**. As a result, the pressure inside the vessel starts increasing. When more and more molecules go from the liquid state to the vapour state, some molecules present in the vapour phase near the surface of the liquid go back to the liquid state. This process is known as **condensation**. The rate of condensation increases as more and more molecules go into the vapour phase. A stage comes when the rate of vapourization becomes equal to the rate of condensation and dynamic equilibrium is attained. (Refer to Activity 5.3). The pressure exerted by the vapours at this stage is known as the **vapour pressure** of the liquid.

Vapour pressure is defined as the pressure exerted by the vapours in equilibrium with the liquid at a specific temperature.

As the temperature is increased, the kinetic energy of the molecules increases, so more molecules go from liquid phase to the vapour phase. As a result the total vapour pressure increases with the increase in temperature. When the **vapour pressure** becomes equal to the **external pressure** the liquid starts boiling. The temperature at which the vapour pressure of the liquid becomes equal to its external pressure is known as **boiling point** of the liquid. When the external pressure is equal to 1 atm, the boiling point is known as **normal boiling point**.

Exercise 5.9

Calculate the degree of freedom, F for each of the following:

1. An equilibrium gas phase containing N_2O_4 and NO_2 .
2. Phosgene, CO and Cl_2 (with CO and Cl_2 derived from decomposition exclusively).
3. Phosgene, CO and Cl_2 , with excess CO added.
4. NH_4Cl , initially in an evacuated chamber, with NH_3 and HCl present from decomposition.
5. Water, water vapor and ice in equilibrium.

5.2.5 Phase diagram

A **Phase diagram** is defined as a graphical representation the conditions when two or more phases (such as vapor-liquid, liquid-solid) of a system can exist in equilibrium.

Phase Diagram for one Component System

As we know one component system has only one chemical species (pure substance) and it can be described if the temperature and pressure of the system are known. Under specific conditions of temperature and pressure, the system can exist in one phase or two or three phases may be present in equilibrium. Phase diagram for a one component system is a graph which shows the variation of pressure of the system with temperature. It gives complete information about the conditions under which the different phases of the system are stable. It also gives the information about the temperature and pressure when the system changes from one phase to another phase.

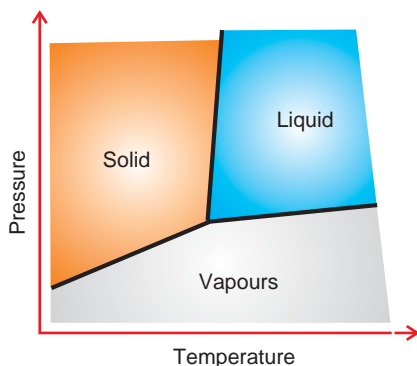


Fig. 5.8 Sketch of phase diagram of one component system.



Characteristics of a Phase Diagram for Pure Substance

- Temperature is plotted on x -axis and pressure on y -axis.
- The different regions of the graph represent different phases in which the substance can exist.
- A substance exists in solid state at low temperatures and high pressures. So the high pressure and low temperature region in the graph represents solid.
- A substance exists in vapour phase at high temperatures and low pressures, so this area in the graph represents vapour.
- The remaining area between the two regions represents liquid phase.
- The boundary between the phases is represented by a line. This line is obtained by joining the transition temperature between the two phases at different pressures. For example, the boundary between the solid and liquid phase represents points when solid changes to liquid or vice-versa. That is, it is the melting point temperatures at different pressures, so it is known as melting point curve. A boundary between liquid and vapour phase is known as **vapourization curve**. The solid and vapour phases are separated by **sublimation curve**.
- On transition line two phases are at equilibrium. For example, on melting line **(OB)** solid and liquid are in dynamic equilibrium. On boiling line **(OC)** liquid and its vapours are at equilibrium and at **sublimation temperature**, solid is in equilibrium with its vapours.
- The **boundary line** between two phases represents the two phase equilibria.
- The **slope** of the transition curves depends upon the nature of variation of transition temperature with pressure.
- A **triple point** represents three phases at equilibrium, i.e., at triple point all three phases coexist.

Phase Diagram of Pure Water

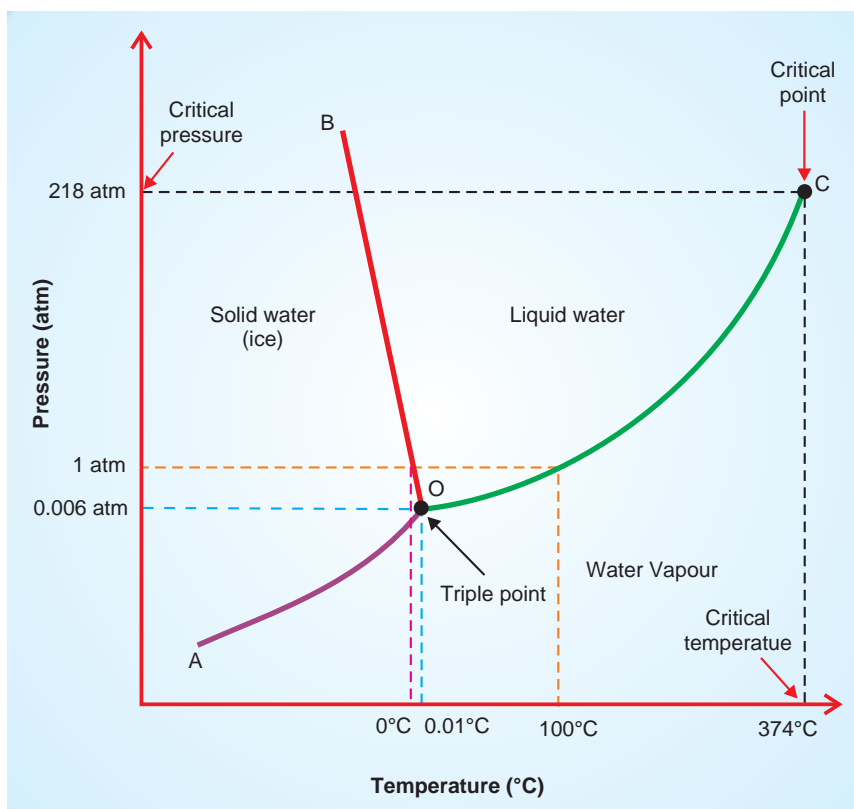


Fig. 5.9 Phase diagram of pure water.

The phase diagram for water shows three regions, namely, ice, liquid water and water vapour (Figure 5.6). Water is present in the form of ice at low temperatures and high pressures. So ice is represented by the region on the left of **AOB**. Water vapour is present at high temperatures and low pressures. So the region below **AOC** represents water vapour. Liquid water is present in the intermediate conditions. Therefore, it is represented by the region between **BOC**.

Curve **AO** is the boundary between ice and water vapour. On one side of the curve is the region representing ice; on the other side is the region representing water vapours. Along this curve, ice and vapours are present together at equilibrium, so it is known as sublimation curve. It gives the **sublimation temperature** of ice at different pressures. The slope of the curve is positive indicating that as the pressure increases, the sublimation temperature of ice also increases.

Curve **OB** represents the boundary between ice and liquid water. Along this curve water and ice exist in equilibrium, therefore it is known as fusion or melting curve. It represents the variation of melting point of ice at different temperatures. The slope of the curve is negative indicating that as the pressure is increasing the melting point of ice is decreasing.

Curve **OC** represents the boundary between water vapour and liquid water, therefore it is known as **vapourization curve**. It represents the variation of boiling point of water at different temperatures. The slope of the curve is positive indicating that as the pressure is increasing the boiling point of water is also increasing. This behaviour of decrease in melting point with increasing pressure is not common in the case of other substances. This special property is known as the **anomalous behaviour** of water.

At point **O**, ice, water and water vapour regions meet, so this point represents the **triple point** of water where all the three phases of water are at equilibrium. The temperature and pressure at triple point are 0.01°C and 0.006 atm respectively.

Point **C** represents **critical point**. At this temperature and pressure the meniscus between the liquid and the vapours disappears. **Critical temperature** is the maximum temperature at which the substance can exist in liquid state. The minimum pressure required to liquefy the vapours at critical temperature is known as **critical pressure**. For water the critical point lies at 374°C and 218 atm .

Exercise 5.10

Consider the phase diagram of pure water (Figure 5.9) and answer the following questions:

1. Under a pressure of 1 atmosphere, what is the maximum temperature at which the water can exist in liquid phase?
2. What will happen to ice if it is compressed at 0°C ?
3. What is the point at which ice, liquid water and water vapour can coexist at equilibrium? Calculate the degree of freedom at this point.
4. The triple point of CO_2 is 518 kPa at -56.6°C . Its critical point lies at 7.38 MPa at 31.1°C . The sublimation curve, fusion curve and vapourization curve have positive slope. Sketch the phase diagram of CO_2 and label it.

Applications of Phase Diagram

1. The phase diagram can be used to determine the phase of the system under the given conditions of temperature and pressure.
2. It can be used to determine the melting point, boiling point and sublimation temperature at different pressures.
3. Triple point and critical point can be determined from the phase diagram.
4. The changes taking place in a substance when it is heated at constant pressure can be predicted with the help of phase diagram.
5. The changes taking place in a substance when it is compressed at constant temperature can be predicted by phase diagram.

Unit Summary

- A system is said to be at equilibrium when its macroscopic properties like temperature, pressure, concentration and energy do not change with time without any outside help.
- The equilibrium is dynamic in nature which means that although the macroscopic properties do not change, the processes do not stop at molecular level.
- Chemical equilibrium is the state of the reaction when the macroscopic properties like temperature, pressure, volume and concentration of the reaction do not change with time.
- According to the law of mass action the rate at which A and B combine is directly proportional to the product of their concentration terms each raised to the power of its respected coefficient in the balanced chemical reaction.
- For a general reaction at equilibrium $a A + bB \rightleftharpoons mM + nN$ the expression for K_c is

$$K_c = \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

- The expression for K_p is

$$K_p = \frac{[p_M]^m [p_N]^n}{[p_A]^a [p_B]^b}$$

provided that all A, B, M and N are in gaseous state.

- The unit of K_c is $(\text{mol L}^{-1})^{(m+n)-(a+b)}$ and the unit of K_p is $(\text{atm})^{(m+n)-(a+b)}$
- $K_p = K_c(RT)^{\Delta n}$
- When $K_c > 1$ the formation of products is favoured at equilibrium.
- When $K_c < 1$, So the formation of products is not favoured at equilibrium.
- When $K_c = 1$, it indicates that the reactants and the products are present in equal amounts.
- Reaction quotient is the ratio of concentrations of products to the concentrations of reactants raised to the power of their respective coefficients at any stage after the start of the reaction.
- For the reaction, $aA + bB \rightleftharpoons mM + nN$ the expression for the reaction quotient is

$$Q = \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

- When $Q < K$, then the reaction will proceed in the forward direction and more products will be formed till the equilibrium is reached.
- When $Q > K$, then the reaction will proceed in the reverse direction and more reactants will be formed till the equilibrium is reached.
- When $Q = K$, then the reaction has attained equilibrium.
- Le Chatelier's principle gives the effect of any one or more of the reaction parameters namely, temperature, pressure or concentration on equilibrium.
- For exothermic reactions the yield of products is increased by performing the reaction at lower temperatures.
- For endothermic reactions the yield of products is increased by performing the reaction at higher temperatures.
- When $\Delta n > 0$ the decrease in pressure favours the formation of products.
- When $\Delta n < 0$ the increase in pressure favours the formation of products.

- *Removing the products from the reaction vessel shifts the reaction in the forward direction.*
- *Phase (P) is that part of the system which is physically and chemically homogeneous and separated from rest of the system by a discrete boundary.*
- *Component (C) is the chemically distinct quantity present in the system.*
- *Degree of freedom (F) is the minimum number of variables required to describe each component in each phase of the system.*
- *Gibbs Phase rule equation: $F = C - P + 2$.*
- *Vapour pressure is defined as the pressure exerted by vapours in equilibrium with the liquid at a given temperature.*
- *The temperature at which the vapour pressure of the liquid becomes equal to its external pressure is known as boiling point of the liquid.*
- *Phase diagram for a one component system is a graph which shows the variation of pressure with temperature. It gives the transition temperature between various phases.*

Check List

Key terms of the unit

- | | |
|-------------------------------|-----------------------------------|
| • <i>Chemical equilibrium</i> | • <i>Le Chateliers' principle</i> |
| • <i>Components</i> | • <i>Phase</i> |
| • <i>Critical point</i> | • <i>Phase diagram</i> |
| • <i>Critical temperature</i> | • <i>Phase equilibrium</i> |
| • <i>Degree of freedom</i> | • <i>Reaction quotient</i> |
| • <i>Equilibrium constant</i> | • <i>Sublimation curve</i> |
| • <i>Gibbs' phase rule</i> | • <i>Triple point</i> |
| • <i>Law of mass action</i> | • <i>Vaporization curve</i> |

REVIEW EXERCISE

Part I: Multiple Choice Questions

- Which of the following is correct about a reaction at equilibrium?
 - The concentrations of reactants and products are equal.
 - The system is static in nature.
 - The forward and backward rates are equal.
 - None.
- For a reaction to shift towards the product direction, which of the following condition holds true?
 - $Q_c = K_c = 0$
 - $Q_c < K_c$
 - $Q_c > K_c$
 - $Q_c = K_c$
- Given the equation $2\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g})$, the expression for K_c is:
 - $2[\text{CO}] / 2[\text{C}][\text{O}_2]$
 - $[\text{CO}]^2 / [\text{C}]^2[\text{O}_2]$
 - $[\text{CO}]^2 / [\text{O}_2]$
 - $2[\text{CO}] / [\text{O}_2]$
- In which of the following cases does the reaction go farthest towards completion:
 - $K = 10^3$
 - $K = 10^{-2}$
 - $K = 10$
 - $K = 1$
- For the reaction $\text{C}(\text{s}) + \text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g})$, the partial pressures of CO_2 and CO are 2.0 atm and 4.0 atm, respectively, at equilibrium. What is the value of K_p for this reaction?
 - 0.5 atm
 - 4.0 atm
 - 8.0 atm
 - 32.0 atm
- The equilibrium partial pressures of SO_2 , O_2 and SO_3 are 0.1 atm, 0.25 atm and 0.5 atm respectively. The equilibrium constant for the reaction $\text{SO}_3(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ is:

- a Removal of SO_2 .
- b Addition of noble gas (argon) at constant pressure.
- c Decreasing volume of the system.
- d Increasing temperature of the system.
- e Addition of a catalyst.
12. Balance the following equations and write the equilibrium constant expressions, in terms of K_c and K_p .
- a $\text{NH}_3(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
- b $\text{N}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{NH}_3(\text{g})$
- c $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

13. For the reaction at 200°C



the equilibrium constant is 3.0. Given the following information,

Species	Concentration
[A]	2.0 M
[B]	3.0 M
[C]	2.0 M

Predict the direction in which the reaction should proceed to reach equilibrium.

14. Given the reaction



what is the concentration of CO in equilibrium at 25°C in a sample of gas originally containing 1.00 mol L^{-1} of CO_2 ? For the dissociation of CO_2 at 25°C , $K_c = 2.96 \times 10^{-92}$.

15. A saturated solution of Na_2SO_4 with an excess of solid is present in equilibrium with its vapor in a closed vessel. Calculate the system's number of degrees of freedom. Also, identify the independent variables.
16. What happens to water when the pressure remains constant at 1 atm but the temperature changes from -10°C to 75°C ? (refer to phase diagram for water)?

17. 5.0 moles of ammonia were introduced into a 5.0 L reaction chamber in which it partially decomposed at high temperatures;



At equilibrium at a particular temperature, 80.0% of the ammonia had reacted. Calculate K_c for the reaction.

18. 1.25 mol NOCl was placed in a 2.50 L reaction chamber at 427°C. After equilibrium was reached, 1.10 moles of NOCl remained. Calculate the equilibrium constant K_c for the reaction.



19. A sample of nitrosyl bromide was heated to 100°C in a 10.0 L container in order to partially decompose it.



At equilibrium the container was found to contain 0.0585 mole of NOBr, 0.105 mole of NO, and 0.0524 mole of Br₂. Calculate the value of K_c .

20. The brown gas NO₂ and the colorless gas N₂O₄ exist in equilibrium.



0.625 mole of N₂O₄ was introduced into a 5.00 L vessel and was allowed to decompose until it reached equilibrium with NO₂. The concentration of N₂O₄ at equilibrium was 0.0750 M. Calculate K_c for the reaction.