

CHEMICAL EQUILIBRIUM



CONCEPT NOTES

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02. What is Chemical Equilibrium?
03. The Equilibrium Constants
04. The LeChâtelier Principle

CHEMICAL EQUILIBRIUM

Section - 1

INTRODUCTION

Chemical change is one of the two central concepts of chemistry, the other being the study of **structures**. Chemical change occurs when the atoms that make up one or more substances rearrange themselves in a way so that new substances are formed. These substances are called the **components** of the chemical reaction system; those components that decrease in quantity are called **reactants**, while those that increase are products. A given chemical reaction system is defined by a balanced net chemical equation which is generally written as



The first thing we need to know about a chemical reaction represented by such a balanced chemical equation is whether it can actually even take place. In principle at least as long as the reactants and products are all substances capable of an independent existence, the answer to this is 'yes'. However, this affirmative answer needs to be qualified by the following two considerations:

- (1) Does the reaction take place to a sufficient extent to produce useful (or even detectable) quantities of products?

This question has actually got to do with the thermodynamics (energetics) of the reaction, which determines its **tendency** to occur. The study of equilibrium will address this question. Later on, we'll also see that the tendency of a reaction to occur can be predicated entirely, from the properties of the reactants and products using the laws of thermodynamics.

Note that this consideration does not take into account the mechanistic details of how the atoms rearrange themselves as the reactants are transformed into products.

- (2) What is the mechanism of the reaction?

What happens, at the atomic or molecular level, when reactants are transformed into products? What **intermediate** species are involved? This is the **kinetic** view of chemical change, and unlike the macroscopic thermodynamical aspects above, cannot be predicated by theory, and must be inferred from the results of experiments. The variable we generally observe that relates to the **kinetics** of a reaction is the **rate** at which it takes place. These rates can be extremely high (for example, a mole per microsecond) or extremely low (for example, a mole per year), and they are frequently almost zero. The rate of a given reaction can be highly influenced by factors such as particle size, the presence of a catalyst, or in some cases even the shape of the container!

To summarize, there are two aspects to any chemical reaction:

Energetics

- Deals with the tendency of the reaction to occur
- Can be predicted entirely from theory based on the laws of thermodynamics

Kinetics

- Deals with what is actually happening the atomic/molecular level-**how** the reaction is proceeding
- Generally described by the rate (or the rate law) at which the reaction occurs.

It is important to understand that the energetics and kinetics of a reaction are not dependent upon each other. A reaction that is thermodynamically possible but for which no reasonably rapid mechanism is available is said to be **kinetically limited**. Conversely, one that occurs rapidly but only to a small extent is, **thermodynamically limited**.

There are often ways of getting around both kinds of limitations. For example, a kinetically limited reaction can be speeded up by the use of a catalyst. These and other considerations are a few aspects of industrial chemistry.

Section - 2

WHAT IS CHEMICAL EQUILIBRIUM

Let's first consider the more general term "equilibrium". This basically refers to what we might term as a "balance of force". For example, most of you are familiar with mechanical equilibrium, of which the following is a simple example.

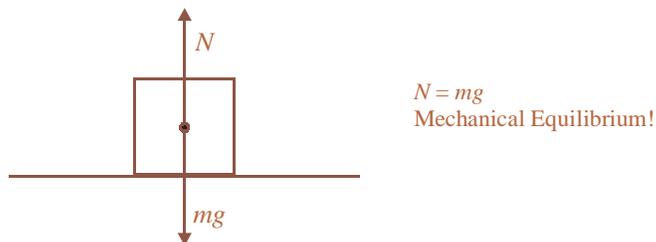


Fig - 01

Thermal equilibrium is another example: When two objects are brought into contact, heat will flow from the warmer object to the cooler one until their temperatures become identical. Thermal equilibrium is a "balance of forces" in the sense that temperature is a measure of the tendency of an object to lose thermal energy. For example, a metallic object at room temperature will feel cool to your hand when you first pick it up because the thermal sensors in your skin detect a flow of heat from your hand into the metal, but as the metal approaches the temperature of your hand, this sensation diminishes.

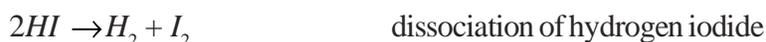
Let us now try to understand the concept of chemical equilibrium. When a chemical reaction takes place in a container which prevents the entry or escape of any of the substances involved in the reaction, the quantities of these components change as some are consumed and others are formed. Eventually, this change will come to an end, after which the composition will remain unchanged as long as the system remains undisturbed. The system is then said to be in its **equilibrium state**, or more simply, at **equilibrium**. Thus, we can say that

A chemical reaction is in equilibrium when there is no tendency for the quantities of reactants and products to change

We now try to understand an important issue with regard to the concept of equilibrium. The **direction** in which we write chemical reaction (and thus which components are considered reactants and which are products) is arbitrary. For example:



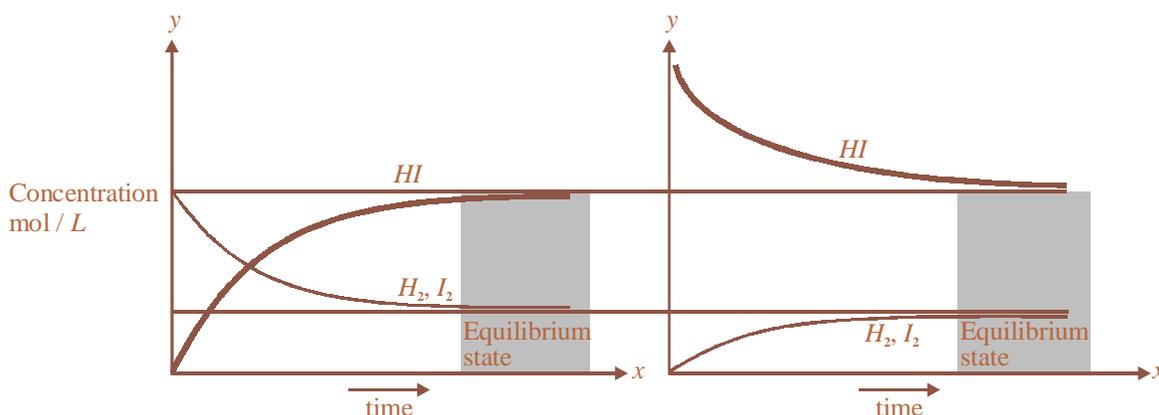
and



represent the same chemical reaction system in which the roles of the components are reversed: **both yield the same mixture of components when the change is completed**

Let us elaborate more on this very important point: it makes no difference whether we start with two moles of HI or one mole each of H_2 and I_2 ; once the reaction has run to completion, the quantities of these components will be the same. Thus, in general we can say that the composition of a chemical reaction system will tend to change in a direction that brings it closer to its equilibrium composition. Once this equilibrium composition has been attained, no further change in the quantities of the components will occur as long as the system remains undisturbed.

Let us understand this concept graphically, using the same example we were discussing earlier. The two diagrams below show how the concentrations of the three components of a chemical reaction change with time (under the conditions in which this particular reaction is carried out, the time scale is typically 10 to 100 minutes.) Note in each case, which components have zero initial concentrations, and so are “products”, while those components with non-zero initial concentrations are “reactants”. These two cases represent the same chemical reaction system, but with the reactions occurring in opposite directions. And most importantly, at equilibrium, the concentrations of all components are identical.

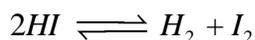


The equilibrium state is independent of the direction from which it is approached. Whether we start with an equimolar mixture of H_2 and I_2 (left) or a pure sample of HI (right, using twice the initial concentration of HI to keep the number of atoms the same). The composition will be the same once equilibrium is attained (shaded regions).

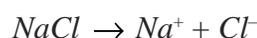
The time required to reach equilibrium is highly variable (from microseconds to centuries) and depends on the mechanism of the reaction and on the temperature.

Fig - 02

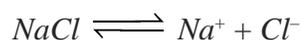
This discussion brings us to an important aspect regarding chemical reactions: **reversibility**. A chemical equation of the form $A \rightarrow B$ represents the transformation of A into B , but it does **not** imply that **all** of the reactants will be converted into products, or that the reverse action $B \rightarrow A$ cannot occur. In general, both processes can be expected to occur, resulting in an equilibrium mixture containing all the components of the reaction system (i.e., both reactants and products). If the equilibrium state is one in which significant quantities of both reactants and products are present (as in the HI example above), we generally term the reaction **incomplete** or **reversible**, and emphasize this by writing the reaction as



These are reactions for which the equilibrium composition contains no significant amount of the reactants; such reactions are said to be **complete**. For example, $NaCl$ (almost) entirely dissolves in water to give Na^+ and Cl^- ions. The reverse reaction, namely the combination of Na^+ and Cl^- to regenerate $NaCl$, is negligible. We thus write this reaction as



rather than



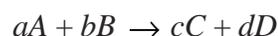
although principally, the latter is not wrong.

Thus, in principal, **all** chemical reactions are reversible, but its reversibility may not be observable if the fraction of products in the equilibrium mixture is very small, or if the reverse reaction is kinetically inhibited.

In light of this concept of reversibility, what exactly, then, is happening when a system attains chemical equilibrium? Do all reactions cease to occur? No!

To understand this, we consider what is termed as the **law of mass** action:

Let the reaction under consideration be of the form

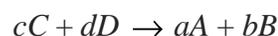


This law tells us that the rate of the (forward) reaction r_f will be

$$r_f = k_f [A]^a [B]^b$$

where k_f is a constant known as the (forward) rate constant and the quantities in the square brackets represent concentrations at any given time (actually, active masses, but at this level, we think of $[A]$ and $[B]$ as concentrations; for example, having the units of mol L^{-1}). Note that r_f varies with the concentrations, so as the latter vary with time, so does r_f .

By the same taken, the rate of the backward reaction

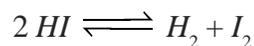


at any given point in time will be

$$r_b = k_b [C]^c [D]^d$$

where k_b is the (backward) rate constant and $[C]$ and $[D]$ represent the concentrations at that time.

Let us apply the law of mass action on the system



and see what happens, as we approach equilibrium.

Suppose that initially we have only HI in our container, then obviously only the forward reaction can take place, with initial rate

$$r_f = k_f [HI]_0^2$$

where $[HI]_0$ is the initial HI concentration. (In case of gases, concentrations are specified in terms of partial pressures, but this is something we'll talk about later).

As the forward reaction starts generating H_2 and I_2 , the rate of the backward reaction $H_2 + I_2 \rightarrow 2HI$ starts picking up, so that HI starts regenerating. With further progress of time, more H_2 and I_2 is generated, leading to still further increase in the backward reaction (production of HI), so that a time comes when

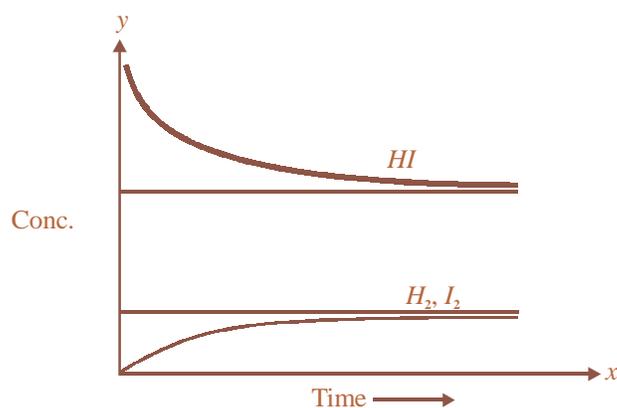
The rate of HI dissociation in the forward reaction = The rate of HI regeneration in the backward direction

OR

The rate of H_2, I_2 production in the forward direction = The rate of H_2, I_2 consumption in the backward direction

OR (simply)

The rate of forward reaction = The rate of backward reaction



As HI conc. decreases, the rate of forward reaction decreases, while simultaneously, the rate of backward reaction rises, so conc. of H_2 and I_2 increase

Fig - 03

Mathematically, at equilibrium we have (for the general system):

$$k_f [A]^a [B]^b = k_b [C]^c [D]^d$$

$$\Rightarrow \frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{k_f}{k_b} = K$$

where the constant ratio k_f/k_b has been written as K , and is termed the **equilibrium constant** of the reaction. Thus, at equilibrium, the ratio

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

known as the quotient ratio of the reaction, becomes fixed and equal to K .

At equilibrium,

$$Q = K$$

Before equilibrium is attained, i.e., when the forward reaction is still proceeding at a faster rate than the backward reaction, we will have

$$k_f [A]^a [B]^b > k_b [C]^c [D]^d$$

or

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} < \frac{k_f}{k_b} = K$$

Thus,

Before equilibrium is attained, $Q < K$

If, for some reason the system overshoots the equilibrium position so that the backward reaction rate becomes greater than the forward reaction rate, we will have $Q > K$.

To summarize

- At equilibrium the rates of forward and backward reactions become equal, so that

$$Q = \frac{k_f}{k_b} = K$$

- Chemical equilibrium is dynamic, that is, reactions are very much taking place in the system, but the rates of the opposing forward and backward reactions are exactly balanced, so **visibly**, no change appears to occur in a system in an equilibrium state.
- Equilibrium can be attained **starting from either side**. This is very well illustrated in Fig...02. that describes the $2HI \rightleftharpoons H_2 + I_2$ system.

Example - 1

A chemical system described by



is in equilibrium

Describe qualitatively what will happen if to the reaction container, the product C is added from the outside so as to increase its concentration

Solution: Initially, when at equilibrium, the forward and reverse reaction rates will be exactly balanced:

$$r_f = r_b$$

where $r_f = k_f[A][B]$ and $r_b = k_b[C][D]$. When $[C]$ is abruptly increased, r_b will exhibit a sudden jump, and we'll have

$$r_b > r_f$$

So that the system will no longer be in equilibrium. The backward reaction will proceed at a faster rate.

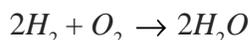
However, this 'mismatch' will only be temporary. As the reverse reaction proceeds, more of $[A]$ and $[B]$ will be generated than in the previous equilibrium position, so that r_f will rise, whereas r_b will decrease. Eventually, r_f and r_b will match so that we'll have **a new equilibrium position**.

We say that "the equilibrium has shifted to the left". This shift is an example of the application of LeChâtelier's principle, which we'll soon encounter. ◀

Example - 2

How can we tell whether a chemical system is at equilibrium?

- Solution:**
- If we observe some change taking place - a change in color, emission of gas bubbles, the appearance of a precipitate or the release of heat, we can definitely say that the system is not at equilibrium
 - However, the **absence** of any sign of change **does not** by itself establish that the reaction is at equilibrium - for no reaction might be occurring at all, because of being inhibited kinetically. For example, the reaction



is highly favored thermodynamically, evident by the observation that hydrogen so easily 'burns'; but this reaction is so inhibited kinetically that it will not start without an ignition. You can store H_2 and O_2 in the same container indefinitely without any observable change occurring - you'll certainly not call that equilibrium (in the dynamic sense we have discussed about)

- It is however almost always the case that once a reaction actually starts, it will continue on its own until reaches equilibrium, so if we can observe the change as it occurs and see it slow down and stop, we can be reasonably certain that the system is in equilibrium. This is generally the most common criterion used by chemists.

- Another experimental way of testing for equilibrium is by causing a small **disturbance** say, abruptly increase the concentration of one of the components, for example, so that a temporary mismatch is created between r_f and r_b , and equilibrium is temporarily disrupted - this will result in an observable change in the composition of the system as it moves towards its new equilibrium state. Temperature changes will also shift the equilibrium, as we'll see while discussing the LeChâtelier's principle.

If carrying out any of these operations fails to produce an observable change, then it is likely that the reaction is kinetically inhibited, so that there is no question of equilibrium. ◀

Section - 3

THE EQUILIBRIUM CONSTANTS

As discussed in the previous section, the equilibrium constant k_{eq} was obtained as:

$$K_{eq} = \frac{k_f}{k_b}$$

This is a constant for a given temperature. If the reaction is



then at equilibrium, we say that

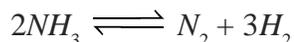
$$k_{eq} = \frac{k_f}{k_b} = \frac{[P_1]^{p_1} [P_2]^{p_2} \dots}{[R_1]^{r_1} [R_2]^{r_2} \dots}$$

We said earlier that $[A]$ represents the activity of the component A , which we thought of as (molar) concentration in the previous section. For reactions in aqueous solution activities are indeed taken to be the molar concentrations.

However, any concentration-like term can be used to represent activity, including mole fraction and molality, and so we have different equilibrium constants utilizing different forms of activity.

For example, when $[A]$ represents molar concentration, then K_{eq} is denoted as K_c , 'c' implying concentration.

Let us try writing K_c for the system



Suppose that initially, we had x moles of NH_3 present in a closed vessel of volume V . At equilibrium, we will have the following compositions:

Moles	NH_3 $x-y$	N_2 $\frac{y}{2}$	H_2 $\frac{3y}{2}$
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where we've assumed that NH_3 has decreased by some y moles, so that according to the reaction coefficients,

$\frac{y}{2}$ moles of N_2 and $\frac{3y}{2}$ moles of H_2 will be generated.

The corresponding concentrations, in the units mol/L, will be:

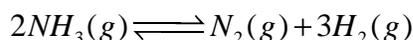
$$\text{Conc:} \quad \frac{NH_3}{\frac{x-y}{v}} \quad \frac{N_2}{\frac{y}{2v}} \quad \frac{H_2}{\frac{3y}{2v}}$$

Thus,

$$\begin{aligned} K_c &= \frac{[N_2][H_2]^3}{[NH_3]^2} \\ &= \frac{\frac{y}{2v} \cdot \left(\frac{3y}{2v}\right)^3}{\left(\frac{x-y}{v}\right)^2} \\ &= \frac{27}{16v^2} \frac{y^4}{(x-y)^2} \end{aligned}$$

When the reaction components are gases (as in the system above), it is preferred to write the equilibrium constant in terms of **partial pressures** rather than **concentrations**. The equilibrium constant in such a case will be denoted as K_p .

Let us write K_p for the system for which we just wrote K_c :



where we've explicitly shown now that all the components are gases. We assume the same molar compositions at equilibrium as obtained above.

Now, suppose the total pressure (in the vessel or wherever the reaction is taking place) at equilibrium is P_{Tot} . You will recall that the partial pressure p_A of any component A in a gaseous mixture is

$$p_A = \chi_A P_{Tot}$$

where χ_A is the mole fraction of A .

For the molar composition

$$\frac{NH_3}{x-y}, \quad \frac{N_2}{\frac{y}{2}}, \quad \frac{H_2}{\frac{3y}{2}},$$

we have the total number of moles as

$$n = x - y + \frac{y}{2} + \frac{3y}{2} = x + y$$

Thus,

$$\chi_{NH_3} = \frac{x-y}{x+y}, \quad \chi_{N_2} = \frac{y}{2(x+y)}, \quad \chi_{H_2} = \frac{3y}{2(x+y)},$$

So that,

$$p_{NH_3} = \left(\frac{x-y}{x+y}\right)P, \quad p_{N_2} = \left(\frac{y}{2(x+y)}\right)P, \quad p_{H_2} = \left(\frac{3y}{2(x+y)}\right)P; \quad \text{where } P \text{ is the total pressure } (P_{Tot})$$

Finally, we can now write K_p as follows:

$$\begin{aligned}
 K_p &= \frac{P_{N_2} \cdot P_{H_2}^3}{P_{NH_3}^2} \\
 &= \frac{\left(\frac{y}{2(x+y)}\right) \left(\frac{3y}{2(x+y)} P\right)^3}{\left(\frac{x-y}{x+y} P\right)^2} \\
 &= \frac{27}{16} \frac{y^4}{(x^2 - y^2)^2} P^2
 \end{aligned}$$

You may wish to compare the expression for K_p obtained above with the one for K_c obtained earlier: This contains P , the total pressure, while K_c contained V , the volume of the vessel.

We'll later on see how K_c and K_p can be related, you may try that now note that concentrations and partial pressures can be related like this:

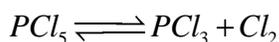
$$[A] = \frac{n_A}{V} = \frac{p_A V}{RT} = \frac{p_A}{RT}$$

Note: There are other forms in the equilibrium constant can be written; eg: K_x, K_m . However, it is important to appreciate one significant fact about all these forms: they are only approximately correct, working best at low concentrations or pressures. The only equilibrium constant that is truly “constant” (except that it too varies with temperature!) is expressed in terms of activities, which can be thought of as “effective concentrations”, that allow for interaction between molecules. In practice, this distinction between activities and concentrations/partial pressures etc only becomes important for equilibria involving gases at very high pressures or ionic solutions with relatively high concentrations.

For our purposes, activities can safely represented by concentrations and partial pressures, which is what we'll do!

Example - 3

For the system



write K_p and K_c assuming that

- (1) the reaction starts with 1 mol of PCl_5

- (2) at equilibrium, x moles of PCl_5 have dissociated
 (3) the vessel volume is V
 (4) the equilibrium (total pressure is P)

Solution: The equilibrium compositions are

	PCl_5	PCl_3	Cl_2	
Moles	$1-x$	x	x	Total = $1+x$
Conc.	$\frac{1-x}{V}$	$\frac{x}{V}$	$\frac{x}{V}$	
Past. press	$\frac{1-x}{1+x}P$	$\frac{x}{1+x}P$	$\frac{x}{1+x}P$	

Thus, we have

$$\begin{aligned}
 K_p &= \frac{P_{PCl_3} P_{Cl_2}}{P_{PCl_5}} = \frac{\left(\frac{x}{1+x}P\right)\left(\frac{x}{1+x}P\right)}{\left(\frac{1-x}{1+x}P\right)} \\
 &= \frac{x^2}{1-x^2}P \\
 K_c &= \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\frac{x}{V} \cdot \frac{x}{V}}{\frac{1-x}{V}} \\
 &= \frac{x^2}{(1-x)V}
 \end{aligned}$$

Example - 4

Calculate the volume percent of Cl_2 at equilibrium in PCl_5 under a total pressure of 1.5 atm. K_p is known to be 0.202.

Solution: The relative percentage of reactants product, at equilibrium will be the same for given reaction conditions, no matter which side we start from and with how much initial reactants and products. Thus, we can use the expression for K_p in the previous example:

$$\begin{aligned}
 K_p &= \frac{x^2}{1-x^2}P \\
 \Rightarrow \quad 0.202 &= \frac{x^2}{1-x^2} \times (1.5)
 \end{aligned}$$

$$\Rightarrow x = 0.343$$

$$\Rightarrow \text{Volume percentage of } Cl_2 = \frac{x}{1+x} = \frac{0.343}{1.343} = 25.5\%$$

Note: Is the expression for K_p dimensionally correct? What unit should K_p have? Do the unit depend on the particular reaction

Example - 5

The **degree of dissociation** α is a frequent parameter used while dealing with equilibria:

$$\alpha = \frac{\text{no. of moles of the reactant dissociated}}{\text{no. of moles of the reactant present initially}}$$

For example,

	$2NH_3 \rightleftharpoons N_2 + 3H_2$		
Initial	x	0	0
At equilibrium	$x - y$	$\frac{y}{2}$	$\frac{3y}{2}$

α for NH_3 will be $\frac{y}{x}$

Suppose that 0.1 mol of PCl_5 is placed in a 3L vessel containing Cl_2 at 0.5 atm and 250°C. What will be α for PCl_5 . ($K_p = 1.78$)

Solution: Initially, we have 0.1 mol of PCl_5 . Suppose x moles dissociate when equilibrium is attained. The initial moles of Cl_2 will be

$$\begin{aligned} n_{Cl_2/\text{initial}} &= \frac{PV}{RT} \quad (\text{gas law}) \\ &= \frac{0.5 \times 3}{0.082 \times 523} \\ &= .035 \end{aligned}$$

At equilibrium, we have the following compositions:

	PCl_5	\rightleftharpoons	PCl_3	+	Cl_2	
Moles	$0.1 - x$		x		$.035 + x$	Total = $0.135 + x$
Past. Press	$\frac{0.1 - x}{0.135 + x} P$		$\frac{x}{0.135 + x} P$		$\frac{.035 + x}{0.135 + x} P$	

Thus,

$$K_p = \frac{P_{PCl_3} \cdot P_{Cl_2}}{P_{PCl_5}} \quad \dots (1)$$

$$\begin{aligned} \Rightarrow 1.78 &= \frac{\frac{x(0.035+x)}{(0.135+x)^2}}{0.1-x} P \\ &= \frac{0.135+x}{(0.1-x)(0.135+x)} \frac{x(0.035+x)}{P} \quad \dots (2) \end{aligned}$$

The total pressure P is given by the gas law:

$$\begin{aligned} P_{Tot} V &= n_{Tot} RT \\ \Rightarrow P_{Tot} &= \frac{(0.135+x)RT}{V} \quad \dots (3) \end{aligned}$$

Using (3) in (2), we have

$$1.78 = \frac{x(0.035+x)}{(0.1-x)} \frac{RT}{V} \quad \dots (4)$$

from where we can calculate x to be 0.0574.

An alert reader might have realized that this route to get to x is unnecessarily long; we should have worked with partial pressures from the beginning itself instead of calculating moles:

	PCl_5	\rightleftharpoons	PCl_3	+	Cl_2	
Init PP	0		0		0.5	PP: partial pressure
Equilibrium PP	$\frac{(0.1-x)RT}{V}$		$\frac{xRT}{V}$		$\frac{xRT}{V} + 0.5$	

Make sure you properly understand the entries in the last row. We now have (using (1)):

$$1.78 = \frac{\left(\frac{xRT}{V}\right)\left(\frac{xRT}{V} + 0.5\right)}{\frac{(0.1-x)RT}{V}} \quad \dots (5)$$

you can verify that this is the same as (4); there is no need to calculate moles first - we can directly deal with partial pressures.

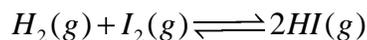
Finally,

$$\alpha = \frac{x}{0.1} = 0.574 \quad \text{or } 57.4\%$$



Example - 6

1, 2, 3 moles respectively of H_2 , I_2 and HI are taken together in a 1-litre flask. The equilibrium system is



for which K_c is 50 at 710 K. What will be the concentrations of each species at equilibrium?

Solution: We can assume that x moles each of H_2 and I_2 have dissociated, and $2x$ moles of HI formed, when equilibrium is attained:

	H_2	+	I_2	\rightleftharpoons	$2HI$	
Moles at eq.	$1-x$		$2-x$		$3+2x$	$V = 1L$
Conc. at eq.	$\frac{1-x}{1}$		$\frac{2-x}{1}$		$\frac{3+2x}{1}$	

Thus,

$$K_c = 50 = \frac{(3+2x)^2}{(1-x)(2-x)}$$

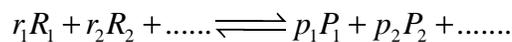
$$\Rightarrow x \approx 0.7$$

$$\Rightarrow [H_2] = 0.3, [I_2] = 1.3, [HI] = 4.4$$

Example - 7

Relate K_p and K_c for a system where all components are gaseous.

Solution: Let the system be



Remember that $[A]$ and p_A for any component A are related as

$$[A] = \frac{p_A}{RT}$$

Thus,

$$\begin{aligned}
 K_c &= \frac{[P_1]^{r_1} [P_2]^{r_2} \dots}{[R_1]^{r_1} [R_2]^{r_2} \dots} = \frac{\left(\frac{p_{P_1}}{RT}\right)^{r_1} \left(\frac{p_{P_2}}{RT}\right)^{r_2} \dots}{\left(\frac{p_{R_1}}{RT}\right)^{r_1} \left(\frac{p_{R_2}}{RT}\right)^{r_2} \dots} \\
 &= \frac{(p_{P_1})^{r_1} (p_{P_2})^{r_2} \dots}{(p_{R_1})^{r_1} (p_{R_2})^{r_2} \dots} \left(\frac{1}{RT}\right)^{(r_1+r_2+\dots)-(r_1+r_2+\dots)}
 \end{aligned}$$

If we denote by Δn the difference in the total moles (stoichiometric) between the left and right sides of the equilibrium equation, i.e., if

$$\Delta n = \underbrace{(p_1 + p_2 + \dots)}_{\text{PRODUCTS}} - \underbrace{(r_1 + r_2 + \dots)}_{\text{REACTANTS}}$$

then,

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

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

This is an important relation and should be committed to memory. Note that partial pressures are generally specified in atmospheres, concentrations in mol L^{-1} and temperatures in K , so the units for R should accordingly be atm-L/mol-K . ($R = 0.082 \text{ atm-L/mol-K}$)

Finally, note that K_p and K_c are the same if $\Delta n = 0$. Also you may have noticed that no units are specified with K_p and K_c , which is the norm, although they obviously do have units:

$$K_c : (\text{mol} \cdot \text{L}^{-1})^{\Delta n} \quad K_p : (\text{atm})^{\Delta n}$$

Before discussing more examples, some comments need to be made regarding particular cases that come up in equilibria situations.

- (1) The equilibria we have been considering till now are **homogenous**, that is, each component is of the same phase, for example all aqueous or all gaseous.

Equilibria that have components in more than one phase are called heterogenous. For example:



is a heterogenous equilibrium. How do we write its K ? Well, that is simply: we use partial pressures for all gaseous components and molar concentrations for all aqueous components. Since K written in such a manner can neither be called K_c nor K_p , we may denote it by K_{pc} :

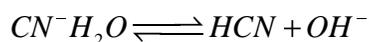
$$K_{pc} = \frac{[\text{OH}^-] p_{\text{CO}_2}}{[\text{HCO}_3^-]}$$

This is therefore in a sense a “hybrid” equilibrium constant

- (2) Substances whose concentrations undergo no significant change in a chemical reaction do not appear in equilibrium constant expressions. How can the concentration of a reactant or product not change when a reaction involving that substance takes place? There are two general cases to consider.

(a) The substance is also the solvent

This happens all the time in acid-base chemistry. For example, for the system



we write

$$K = \frac{[HCN][OH^-]}{[CN^-]} \quad \dots (1)$$

rather than

$$K = \frac{[HCN][OH^-]}{[CN^-][H_2O]} \quad \dots (2)$$

Why? Water is both the solvent and a reactant, and the amount of water consumed for this reaction is so minute (because the K for this particular reaction is small) that any change in the concentration of H_2O from that of pure water (55.6 mol L^{-1}) will be negligible.

How about the equilibrium that is setup when acetic acid and ethanol are mixed ?



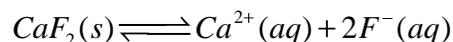
For this system, $[H_2O]$ must be present in the expression for K since it is being generated as a product whose concentration cannot be assumed to be constant. However, if the reaction is assumed to take place between dilute aqueous solutions of the acid, then we can throw out $[H_2O]$ since it will hardly vary.

One final point for emphasis: the expression for K_{eq} will still be given by (2) (it will contain **all** reactants and products, even if they have constant concentrations, like H_2O in this case), but it is preferred to have an equilibrium constant with only variable quantities. Thus,

$$K_c = \frac{[HCN][OH^-]}{[CN^-]}$$

(b) The substance is a solid (or a pure liquid) phase

This is most frequently seen in solubility equilibria, but there are many other reactions in which solids are directly involved:



These are heterogenous equilibrium, and the argument here is that concentration is only meaningful when applied to a substance within a single phase. Thus, the term $[CaF_2]$ would refer to the “**concentration of calcium fluoride within the solid CaF_2** ”, which is a constant depending on the molar mass of CaF_2 and the density of that solid. The concentrations of the two ions will be independent of the quantity of solid CaF_2 in contact with the water; in other words, the system can be in equilibrium as long as any CaF_2 at all is present.

For this system, we should therefore write

$$K_c = [Ca^{2+}][F^-]^2$$

Let us compare the expressions for K_{eq} , K_p and K_c for a few systems to make our discussion clearer:

	K_{eq}	K_c	K_p
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	$\frac{[CaO][CO_2]}{[CaCO_3]}$	$[CO_2]$	p_{CO_2}
$Na_2SO_4 \cdot 10H_2O \rightleftharpoons Na_2SO_4(s) + 10H_2O(g)$	$\frac{[Na_2SO_4][10H_2O]}{[Na_2SO_4 \cdot 10H_2O]}$	$[H_2O]^{10}$	$p_{H_2O}^{10}$
$I_2(s) \rightleftharpoons I_2(g)$	$\frac{[I_2(g)]}{[I_2(s)]}$	$[I_2(g)]$	p_{I_2}
$A(g) + B(aq) \rightleftharpoons C(s) + D(g)$	$\frac{[C][D]}{[A][B]}$	$\frac{[D]}{[A][B]}$	—

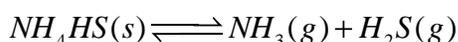
For the last reaction, instead of using K_c we can use K_{pc} defined as

$$K_{pc} = \frac{p_D}{p_A [B]}$$

you may now appreciate why we use K_c/K_p instead of K_{eq} whenever they aren't the same: the expressions for the former are simpler, and we don't have to worry about including constant terms in our numerical calculations. ◀

Example - 8

The dissociation of solid NH_4HS in a closed container produces a pressure of 1.12 atm at 105°C. Calculate K_p for the equilibrium



Solution: It should be obvious that at equilibrium, the partial pressures for NH_3 and H_2S will be equal since both will be equi-molar:

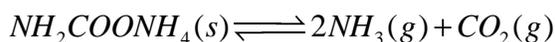
$$p_{NH_3} = p_{H_2S} = p = \frac{P_{Tot}}{2} = \frac{1.12}{2} = 0.56 \text{ atm}$$

Thus,

$$K_p = p_{NH_3} \cdot p_{H_2S} = (0.56)^2 = 0.3136 \quad \blacktriangleleft$$

Example - 9

Consider the following equilibrium system that has been established in a closed vessel.



NH_3 is now added so that the partial pressure of NH_3 at the new equilibrium position is equal to the original total pressure. What is the ratio of the total pressure at the new equilibrium to that of the original total pressure?

Solution: If P is the original total pressure, then

$$p_{NH_3} = \frac{2}{3}P, \quad p_{CO_2} = \frac{1}{3}P$$

are the original partial pressures. Thus,

$$\begin{aligned} K_p &= p_{NH_3}^2 \cdot p_{CO_2} \\ &= \frac{4}{27}P^3 \end{aligned}$$

Now, when NH_3 is added, we have

$$\begin{aligned} p_{NH_3, \text{new}} &= P \\ \Rightarrow K_p &= \frac{4}{27}P^3 = p_{NH_3, \text{new}}^2 \times p_{CO_2, \text{new}} = P^2 p_{CO_2, \text{new}} \\ \Rightarrow p_{CO_2, \text{new}} &= \frac{4}{27}P \\ \Rightarrow p_{Tot, \text{new}} &= P + \frac{4}{27}P = \frac{31}{27}P \\ \Rightarrow \frac{p_{Tot, \text{new}}}{P} &= \frac{31}{27} \end{aligned}$$

Example - 10

25 mL of H_2 and 18 mL of I_2 produce 30.8 mL of HI of equilibrium, when heated in a closed container. What is the degree of dissociation of HI at the same temperature?

Solution: We will use volume directly as a measure of concentrations for this example (why is this justified?). Thus, at equilibrium, the volumes are:



i.e., $H_2 \leftrightarrow 9.6 \text{ mL}$, $I_2 \leftrightarrow 2.6 \text{ mL}$, $HI \leftrightarrow 30.8 \text{ mL}$

no. of moles will be proportional to the volume of the gas (P and T are constant)

Thus,

$$K_c (\text{not } K_p) = \frac{30.8^2}{9.6 \times 2.6} = 38.01$$

Now, let us consider the dissociation of HI at the same temperature:

	$2HI \rightleftharpoons H_2 + I_2$		
Init. mols	1	0	0
Moles at eq	$1-x$	$\frac{x}{2}$	$\frac{x}{2}$

Thus,

$$K'_c = \frac{1}{K_c} = \frac{\frac{x}{2} \cdot \frac{x}{2}}{(1-x)^2} = \frac{x^2}{4(1-x)^2} = \frac{1}{38.01}$$

$$\Rightarrow x = 0.245$$

$$\Rightarrow \alpha = 24.5\%$$

Did you understand why K'_c , the equilibrium constant for the dissociation reaction is the reciprocal of K_c , the equilibrium constant for the reaction in (1)? This should be obvious; if not, write K_c and K'_c explicitly and verify for yourself.

Also, we have directly used moles instead of molar concentrations in the second calculation. Is that justified? Make sure you proceed only when you'r clear about these point.

Let us briefly summarize what we've covered till now, before closing this section.

- $K_{eq} = \frac{k_f}{k_b}$, the expression for K_{eq} when written in terms of activities, includes all the reactants and products.
- K_c : equilibrium constant written using concentrations; all constant concentrations (solid/solvent etc) are not included.
- K_p : equilibrium constant written using partial pressures; all constant concentrations are not included.

- Q : reaction coefficient; For the system



Q at any point in time be given by

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

At equilibrium,

$$Q = K$$

If the system is yet to attain equilibrium (is still to the 'left'), we have

$$Q < K, \quad \left\{ \begin{array}{l} \text{Product conc. 'too low', net reaction} \\ \text{proceeds to right} \end{array} \right\}$$

while if the system has overshoot the equilibrium position (from the 'left' to the 'right'), we have

$$Q > K \quad \left\{ \begin{array}{l} \text{Product conc. 'too high', net} \\ \text{reaction proceeds to left} \end{array} \right\}$$

you can say that K is the special value that Q attains when equilibrium is established.

- $K_p = K_c(RT)^{\Delta n}$, where Δn signifies the stoichiometric change in the number of moles. For $\Delta n = 0$, $K_p = K_c$
- As we've seen, changes in pressure or concentration at equilibrium may shift the equilibrium position, but they do not change K_p or K_c , which depend only on temperature. If a reaction is subjected to temperature changes, the equilibrium position and the equilibrium constant both generally change. In fact, the change is governed by the Van't Hoff equation:

$$\log K_{T_2} - \log K_{T_1} = \frac{\Delta H^\circ}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

where ΔH° is the standard heat of the reaction (at constant pressure). Thus, the change in K is governed by ΔH° :

$\Delta H^\circ > 0$ (endothermic) : K increases with increase in temp.

$\Delta H^\circ < 0$ (exothermic) : K decreases with increase in temp.

we'll read more about how temperature effects equilibria positions in the next section. ◀

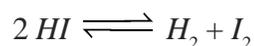
Section - 4

THE LeCHÂTELIER PRINCIPLE?

If a reaction is at equilibrium and we alter the conditions so as to create a new equilibrium state, then the composition of the system will tend to change until that new equilibrium state is attained. (We say “tend to change” because if the reaction is kinetically inhibited, the change may be too slow to observe or it may never take place.) In 1884, the French chemical engineer and teacher Henri LeChâtelier (1850-1936) showed that in every such case, the new equilibrium state is one that partially reduces the effect of the change that brought it about. This law is known as the *LeChâtelier principle*. His original formulation was somewhat more complicated, but a reasonably useful paraphrase of it reads as follows:

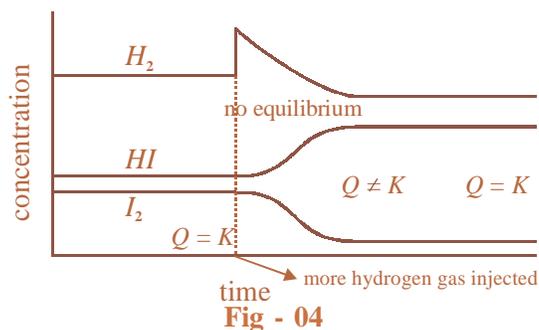
LeChâtelier principle: If a system at equilibrium is subjected to a change of pressure, temperature, or the number of moles of a substance, there will be a tendency for a net reaction in the direction that tends to reduce the effect of this change.

To see how this works (and you must do so, as this is of such fundamental importance that you simply cannot do any meaningful Chemistry without a thorough working understanding of this principle), look again the hydrogen iodide dissociation reaction



Consider an arbitrary mixture of these components at equilibrium, and assume that we inject more hydrogen gas into the container. Because the H_2 concentration now exceeds its new equilibrium value, the system is no longer in its equilibrium state, so a net reaction now ensues as the system moves to the new state. The LeChâtelier principle states that the net reaction will be in a direction that tends to reduce the effect of the added H_2 . This can occur if some of the H_2 is consumed by reacting with I_2 to form more HI ; in other words, a net reaction occurs in the reverse direction. Chemists usually simply say that “the equilibrium shifts to the left”.

To get a better idea of how this works, carefully examine the diagram below which follows the concentrations of the three components of this reaction as they might change in time (the time scale here will typically be about an hour). The following table contains several examples showing how changing the quantity of a reaction component can shift an established equilibrium



Disruption and restoration of equilibrium. At the left, the concentrations of the three components do not change with time because the system is at equilibrium. We then add more hydrogen to the system, disrupting the equilibrium. A net reaction then ensues that moves the system to a new equilibrium state (right) in which the quantity of hydrogen iodide has increased; in the process, some of the I_2 and H_2 are consumed. Notice that the new equilibrium state contains more hydrogen than did the initial state, but not as much as was added; as the LeChâtelier principle predicts, the change we made (addition of H_2) has been partially counteracted by the “shift to the right”.

The following table contains several examples showing how changing the quantity of a reaction component can shift an established equilibrium.

System	Change	Result
$CO_2 + H_2 \rightarrow H_2O(g) + CO$	A drying agent is added to absorb H_2O	Shift to the right. Continuous removal of a product will force any reaction to the right.
$H_2(g) + I_2(g) \rightarrow 2HI(g)$	Some nitrogen gas is added to the container	No change; N_2 is not a component of this reaction system
$NaCl(s) + H_2SO_4(l) \rightarrow Na_2SO_4(s) + HCl(g)$	Reaction is carried out in an open container	Because HCl is a gas that can escape from the system, the reaction is forced to the right. This is the basis for the commercial production of hydrochloric acid
$H_2O(l) \rightarrow H_2O(g)$	Water evaporates from an open container	Continuous removal of water vapor forces the reaction to the right, so equilibrium is never achieved
$HCN(aq) \rightarrow H^+(aq) + CN^-(aq)$	The solution is diluted	Shift to right; the product $[H^+]$ $[CN^-]$ diminishes more rapidly than does $[HCN]$
$AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq)$	Some $NaCl$ is added to the solution	Shift to left due to increase in Cl^- concentration. This is known as the <i>common ion effect</i> on solubility
$N_2 + 3H_2 \rightarrow 2NH_3$	A catalyst is added to speed up this reaction	No change. Catalysts affect only the rate of a reaction; they have no effect at all on the composition of the equilibrium state.

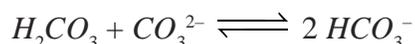
An interesting Example

The LeChâtelier principle in physiology: hemoglobin and oxygen transport. Many of the chemical reactions that occur in living organisms are regulated through the LeChâtelier principle. Few of these are more important to warm-blooded organisms than those that relate to aerobic respiration, in which oxygen is transported to the cells where it is combined with glucose and metabolized to carbon dioxide, which then moves back to the lungs from which it is expelled.



The partial pressure of O_2 in the air is 0.2 atm, sufficient to allow these molecules to be taken up by hemoglobin (the red pigment of blood) in which it becomes loosely bound in a complex known as oxyhemoglobin. At the ends of the capillaries which deliver the blood to the tissues, the O_2 concentration is reduced by about 50% owing to its consumption by the cells. This shifts the equilibrium to the left, releasing the oxygen so it can diffuse into the cells.

Carbon dioxide reacts with water to form the weak acid H_2CO_3 which would cause the blood acidity to become dangerously high if it were not promptly removed as it is excreted by the cells. This is accomplished by combining it with carbonate ion through the reaction



which is forced to the right by the high local CO_2 concentration within the tissues. Once the hydrogen carbonate (bicarbonate) ions reach the lung tissues where the CO_2 partial pressure is much smaller, the reaction reverses and the CO_2 is expelled.

Carbon monoxide poisoning. Carbon monoxide, a product of incomplete combustion that is present in automotive exhaust and cigarette smoke, binds to hemoglobin 200 times more tightly than does O_2 . This blocks the uptake and transport of oxygen by setting up a competing equilibrium



Air that contains as little as 0.1 percent carbon monoxide can tie up about half of the hemoglobin binding sites, reducing the amount of O_2 reaching the tissues to fatal levels. Carbon monoxide poisoning is treated by administration of pure O_2 which promotes the shift of the above equilibrium to the left. This can be made even more effective by placing the victim in a hyperbaric chamber in which the pressure of O_2 can be made greater than 1 atm.

Changes in temperature: Effect on equilibria?

Virtually all chemical reactions are accompanied by the liberation or uptake of heat. If we regard heat as a “reactant” or “product” in an endothermic or exothermic reaction respectively, we can use the LeChâtelier principle to predict the direction in which an increase or decrease in temperature will shift the equilibrium state. Thus for the oxidation of nitrogen, an endothermic process, we can write



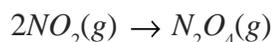
Suppose this reaction is at equilibrium at some temperature T_1 and we raise the temperature to T_2 . The LeChâtelier principle tells us that a net reaction will occur in the direction that will partially counteract this change, meaning that the system must absorb some of this additional heat, and the equilibrium will shift to the right.

(Nitric oxide, the product of this reaction, is a major air pollutant which initiates a sequence of steps leading

to the formation of atmospheric smog. Its formation is an unwanted side reaction which occurs when the air (which is introduced into the combustion chamber of an engine to supply oxygen) gets heated to a high temperature. Designers of internal combustion engines now try, by various means, to limit the temperature in the combustion region, or to restrict its highest-temperature part to a small volume within the combustion chamber.)

Changes in pressure: Effect on equilibria?

You will recall that if the pressure of a gas is reduced, its volume will increase; pressure and volume are inversely proportional. With this in mind, suppose that the reaction



is in equilibrium at some arbitrary temperature and pressure, and that we double the pressure, perhaps by compressing the mixture to a smaller volume. From the LeChâtelier principle we know that the equilibrium state will change to one that tends to counteract the increase in pressure. This can occur if some of the NO_2 reacts to form more of the dinitrogen tetraoxide, since two moles of gas is being removed from the system for every mole of N_2O_4 formed, thereby decreasing the total volume of the system. Thus increasing the pressure will shift this equilibrium to the right.

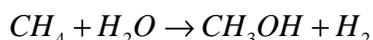
It is important to understand that changing the pressure will have a significant effect only on reactions in which there is a change in the number of moles of gas. For the above reaction, this change $\Delta n_g = (n_{\text{products}} - n_{\text{reactants}}) = 1 - 2 = -1$. In the case of the nitrogen oxidation reaction described previously, $\Delta n_g = 0$ and pressure will have no effect.

The volumes of solids and liquids are hardly affected by the pressure at all, so for reactions that do not involve gaseous substances, the effects of pressure changes are ordinarily negligible. Exceptions arise under conditions of very high pressure such as exist in the interior of the Earth or near the bottom of the ocean. A good example is the dissolution of calcium carbonate $CaCO_3(s) \rightarrow Ca^{2+} + CO_3^{2-}$. There is a slight decrease in the volume when this reaction takes place, so an increase in the pressure will shift the equilibrium to the right, so that calcium carbonate becomes more soluble at higher pressures. The skeletons of several varieties of microscopic organisms that inhabit the top of the ocean are made of $CaCO_3$, so there is a continual rain of this substance toward the bottom of the ocean as these organisms die. As a consequence, the floor of the Atlantic ocean is covered with a blanket of calcium carbonate. This is not true for the Pacific ocean, which is deeper; once the skeletons fall below a certain depth, the higher pressure causes them to dissolve. Some of the seamounts (undersea mountains) in the Pacific extend above the solubility boundary so that their upper parts are covered with $CaCO_3$ sediments.

The effect of pressure on a reaction involving substances whose boiling points fall within the range of commonly encountered temperature will be sensitive to the states of these substances at the temperature of interest.

Example - 11

The commercial production of hydrogen is carried out by treating natural gas with steam at high temperatures and in the presence of a catalyst (“steam reforming of methane”):



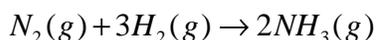
Given the following boiling points: CH_4 (methane) = -161°C , $H_2O = 100^\circ\text{C}$, $CH_3OH = 65^\circ\text{C}$, $H_2 = -253^\circ\text{C}$, predict the effects of an increase in the total pressure on this equilibrium at 50° , 75° and 120°C .

temp	equation	Δn_g	shift
50°	$CH_4(g) + H_2O(l) \rightarrow CH_3OH(l) + H_2(g)$	0	none
75°	$CH_4(g) + H_2O(l) \rightarrow CH_3OH(g) + H_2(g)$	+1	to left
120°	$CH_4(g) + H_2O(g) \rightarrow CH_3OH(g) + H_2(g)$	0	none

For reactions involving gases, only changes in the partial pressures of those gases directly involved in the reaction are important; the presence of other gases has no effect.

The Haber process

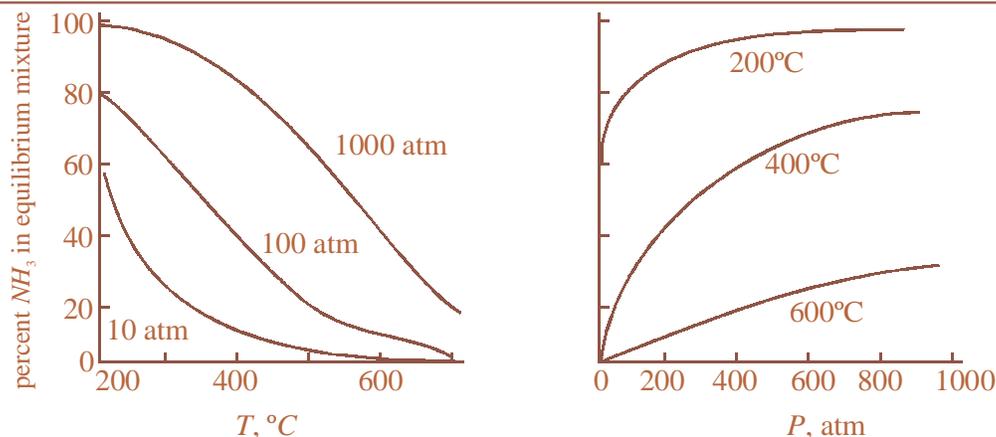
The Haber process for the synthesis of ammonia is based on the exothermic reaction



The LeChâtelier principle tells us that in order to maximize the amount of product in the reaction mixture, it should be carried out at high pressure and low temperature. However, the lower the temperature, the slower the reaction (this is true of virtually all chemical reactions). As long as the choice had to be made between a low yield of ammonia quickly or a high yield over a long period of time, this reaction was infeasible economically.

Although nitrogen is a major component of air, the strong triple bond in N_2 makes it extremely difficult to incorporate this element into species such as NO_3^- and NH_4^+ which serve as the starting points for the wide variety of nitrogen-containing compounds that are essential for modern industry. This conversion is known as *nitrogen fixation*, and because nitrogen is an essential plant nutrient, modern intensive agriculture is utterly dependent on huge amounts of fixed nitrogen in the form of fertilizer. Until around 1900, the major source of fixed nitrogen was the $NaNO_3$ (Chile saltpeter) found in extensive deposits in South America. Several chemical processes for obtaining nitrogen compounds were developed in the early 1900's, but they proved too inefficient to meet the increasing demand.

Although the direct synthesis of ammonia from its elements had been known for some time, the yield of product was found to be negligible. In 1905, Fritz Haber (1868-1934) began to study this reaction, employing the thinking initiated by LeChâtelier and others, and the newly-developing field of thermodynamics that served as the basis of these principles. From the LeChâtelier law alone, it is apparent that this exothermic reaction is favored by low temperature and high pressure. However, it was not as simple as that: the rate of any reaction increases with the temperature, so working with temperature alone, one has the choice between a high product yield achieved only very slowly, or a very low yield quickly. Further, the equipment, and the high-strength alloy steels need to build it, did not exist at the time. Haber solved the first problem by developing a catalyst that would greatly speed up the reaction at lower temperatures. The second problem, and the development of an efficient way of producing hydrogen, would delay the practical implementation of the process until 1913, when the first plant based on the Haber-Bosch process (as it is more properly known, Bosch being the person who solved the major engineering problems) came into operation. The timing could not have been better for Germany, since this country was about to enter the First World War, and the Allies had established a naval blockade of South America, cutting off the supply of nitrate for the German munitions industry.



Bosch's plant operated the ammonia reactor at 200 atm and 550 $^{\circ}C$. Later, when stronger alloy steels had been developed, pressures of 800-1000 atm became common. The source of hydrogen in modern plants is usually natural gas, which is mostly methane:



The Haber-Bosch process is considered the most important chemical synthesis developed in the 20th century. Besides its scientific importance as the first large-scale application of the laws of chemical equilibrium, it has tremendous economic and social impact; without an inexpensive source of fixed nitrogen, the intensive crop production required to feed the world's growing population would have been impossible. In 1918, Haber was awarded the Nobel Prize in Chemistry in recognition of his work.

Let us now summarize all the important cases of the application of LeChâtelier's principle you can expect to deal with:

(1) **Effect of addition or removal of reactants/products**

At constant volume, when more reactant is added to (or product removed from) an equilibrium mixture, the reaction moves in the forward direction and attains a new equilibrium position. Conversely, when more product is added to (or more reactant removed from) the equilibrium mixture, the reaction moves in the backward direction.

(2) **Effect of change in volume**

Suppose an equilibrium system containing gaseous components is set up in a container. Let Δn denote the change in the number of moles (stoichiometrically calculated from the balanced reaction). The effect of volume change depends on Δn :

$\Delta n = 0$ Equilibrium isn't affected

$\Delta n > 0$ With increase in volume, equilibrium shifts to the right
(with decrease, the shift is towards the left)

$\Delta n < 0$ With increase in volume, equilibrium shifts to the left
(with decrease, the shift is towards the right)

Can you see how LeChâtelier's principle justifies these three observations.

(3) **Effect of change in pressure**

$\Delta n = 0$ No change

$\Delta n > 0$	Increase pressure \rightarrow left shift Decrease pressure \rightarrow right shift
$\Delta n < 0$	Increase pressure \rightarrow right shift Decrease pressure \rightarrow left shift

(4) Effect of addition of inert gas

Inert gas can be added to the equilibrium either at constant pressure or at constant volume. If you add inert gas at constant pressure, volume will obviously increase, while addition of the inert gas at constant volume (for example, by injecting the inert gas in the closed container) means an increase in pressure. Now, addition of inert gas at constant volume will not shift the equilibrium at all: this is because there is no change in the concentrations/partial pressures of the components in this case. For addition of inert gas at constant pressure, we again consider three cases:

$\Delta n = 0$	No change
$\Delta n > 0$	Right shift
$\Delta n < 0$	Left shift

Once again, make sure you understand how the LeChâtelier's principle leads to these conclusions.

(5) Effect of addition of catalyst

Chemical equilibrium is a dynamic process in which the forward and reverse reactions are continually opposing each other in a dead heat.

Although it is the **ratio** $\frac{k_f}{k_r}$ that determines K , the magnitudes of these two rate constants makes a difference; if they are small (or in some cases close to zero), then the reaction is kinetically inhibited and equilibrium position will be achieved very slowly. When they are large, equilibrium is achieved quickly.

However, note that the ratio $\frac{k_f}{k_r}$ or K remains the same, implying that the equilibrium 'position' is still the same. A catalyst simply speeds up the attainment of the equilibrium position by increasing both k_f and k_r ; a catalyst will have no effect on $\frac{k_f}{k_r}$.

(6) Effect of temperature change

By the Van't Hoff equation, for an endothermic (forward) reaction, K increases with increase in temperature, so equilibrium shifts to the right. For an exothermic (forward) reaction, K decreases with increase in temperature. This is consistent with what the LeChâtelier's principle would predict: with temperature increase, the net reaction moves in that direction where the effect of the temperature increase is opposed, i.e., where heat is absorbed.

For example, the system



would shift to the right if you were to increase the temperature, since the (forward) reaction is endothermic

Conclusion

EQUILIBRIUM CONSTANT AND FREE ENERGY CHANGE

As you might recall from your studies on thermodynamics, free energy of a system characterises its total intrinsic (electrostatic) potential energy. It is the change in free energy at a given temperature that tells whether a reaction will occur or not at that given temperature.

The system always tends to move towards a direction where its free energy decreases, since that would imply higher attractive forces and consequently more stability. Let us see how an equilibrium is established from a free energy perspective.

Initially, when you mix the reactants, the forward reaction starts taking place since the free energy lowers as more of the products are formed. Eventually, a stage is reached when the free energy can't decrease anymore: at this juncture, equilibrium is established and we say that the free energy change at equilibrium is **zero**.

The free energy change is represented by ΔG in general and ΔG° under a standard set of conditions which you may refer to in the chapter on thermodynamics. Thus, we can summarize this discussion as follows:

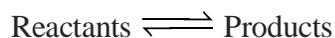
$$\Delta G = (\text{Total free energy of products}) - (\text{Total free energy of reactants})$$

$$\Delta G < 0 \quad \Rightarrow \quad \text{reaction moves in the forward direction since the free energy lowers that way}$$

$$\Delta G > 0 \quad \Rightarrow \quad \text{reaction moves in the backward direction since it is the backward direction now where the free energy will lower.}$$

$$\Delta G = 0 \quad \Rightarrow \quad \text{reaction is at equilibrium; the free energy won't lower further.}$$

It might seem evident that the equilibrium constant for a system at a given temperature must somehow be related to the free energy change ΔG at that temperature. As an example, let the system be



and let ΔG be the free energy change corresponding to the forward direction. The more negative ΔG is, the more we can expect the equilibrium to lie on the right. The more positive ΔG , the more we can expect equilibrium to lie to the left. If ΔG is 0, we can expect the reaction to proceed, in a sense, 'halfway'.

In fact, there exists a precise relation between ΔG and K :

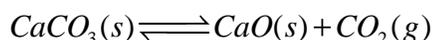
$$\Delta G^\circ = -RT \ln K$$

We will sometimes use this relation in solving numerical problems.

MISCELLANEOUS EXAMPLES

Example - 12

The partial pressure of CO_2 in the reaction



is 0.773 mm at 500°C. Calculate K_p at 600°C for the above reaction, assuming that ΔH° for the reaction is 43.2 K cal mol⁻¹ and does not vary much in the temperature range of interest.

Solution: The expression for K_p will simply be:

$$\begin{aligned} K_p &= p_{CO_2} \\ &= 0.773 \text{ mm at } 500^\circ\text{C} \end{aligned}$$

Let the equilibrium constant at 600°C be represented by k'_p . Using the Van't Hoff's equation, we have

$$\log \frac{k'_p}{k_p} = \frac{\Delta H^\circ}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right); \quad \begin{array}{l} T_1 = 500^\circ\text{C} = 773\text{K} \\ T_2 = 600^\circ\text{C} = 873\text{K} \end{array}$$

Using $\Delta H^\circ = 43200 \text{ cal mol}^{-1}$ and $R = 1.98 \text{ cal deg}^{-1} \text{ mol}^{-1}$ (we have to make sure all the quantities have consistent units), we obtain

$$\begin{aligned} \log \frac{k'_p}{k_p} &= \frac{43200}{2.303 \times 1.98} \left(\frac{1}{773} - \frac{1}{873} \right) \\ \Rightarrow K'_p &= 19.6 \text{ mm} \end{aligned}$$

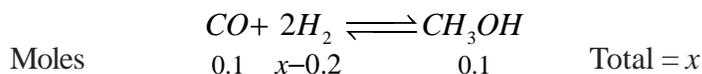
Example - 13

For the reaction $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$, H_2 is introduced into a five-litre flask at 327°C, containing 0.2 mole of $CO(g)$ and a catalyst, until the pressure is 4.92 atm. At this point 0.1 mol of CH_3OH is formed. Calculate K_p and K_c for this system.

Solution: During the entire “ H_2 -introduction” process, assume that x moles of H_2 were added to the system. By the time “ H_2 - introduction” process is stopped, 0.1 mole of CH_3OH is formed.

Note that special emphasis has been laid on telling us that there is a catalyst present, which means that the attainment of equilibrium is rapid. Thus, as more H_2 is introduced, the new equilibrium position is quickly attained, so when addition of H_2 is stopped, the CH_3OH moles given as 0.1 mol should be taken as the equilibrium value.

At equilibrium, therefore:



This is because to produce 0.1 mol of CH_3OH , 0.1 mol of CO and 0.2 mol of H_2 must be utilized.

The total pressure, P , at equilibrium is 4.92 atm; and the total moles at equilibrium are x :

$$\begin{aligned} PV &= xRT \\ \Rightarrow x &= \frac{PV}{RT} = \frac{4.92 \times 5}{0.0821 \times 600} = 0.5 \end{aligned}$$

Thus, at equilibrium, the respective moles are

$$x_{\text{CO}} = 0.1 \quad x_{\text{H}_2} = 0.3 \quad x_{\text{CH}_3\text{OH}} = 0.1$$

Finally,

$$K_p = \frac{\left(\frac{0.1}{0.5} P\right)}{\left(\frac{0.1}{0.5} P\right) \left(\frac{0.3}{0.5} P\right)^2} \quad \text{why?}$$

$$= \frac{25}{9 P^2}$$

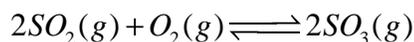
$$= 0.1147 \text{ atm}^{-2}$$

$$K_c = \frac{K_p}{(RT)^{\Delta n}} \quad \left(\text{or } K_c \text{ can also be calculated by evaluating the molar concentrations} \right)$$

$$= 277.8 \text{ (mol L}^{-1}\text{)}^{-2}$$

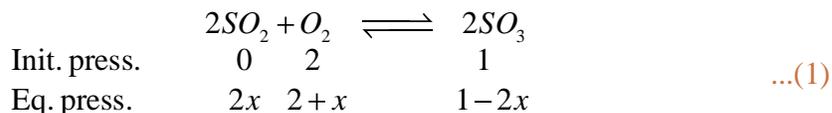
Example - 14

The equilibrium constant K_p of the system



is 900 atm at 800 K. A mixture containing SO_3 and O_2 having initial partial pressures of 1 and 2 atm respectively is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at 800 K.

Solution: We will directly work in terms of partial pressures here (rather than moles):



Now, an alert reader might have noticed that the units specified for K_p are “atm”, but for the reaction system written in the way it is, $\Delta n = -1$, which means the K_p mentioned is actual for the system



However, this is not a problem; the K_p for (1) will be simply the reciprocal of the K_p for (2), Thus, for (1), we get:

$$K_p = \frac{1}{900} = \frac{(1-2x)^2}{(2x)^2 (2+x)}$$

$$\Rightarrow x = 0.475$$

$$P_{SO_3} = 1 - 2x = 0.05 \text{ atm}$$

$$P_{SO_2} = 2x = 0.95 \text{ atm}$$

$$P_{O_2} = 2 + x = 2.475 \text{ atm}$$

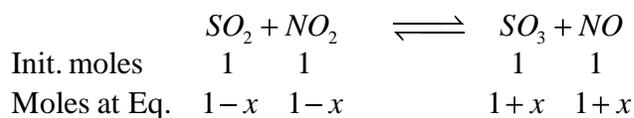
Example - 15

At a certain temperature, K_c is 16 for the system



If we take one mole of each of the four gases in a one - litre container, What would be the equilibrium concentration of NO and NO_2 ?

Solution: The problem is evidently quite simply:



Since $V = 1L$, the concentrations at equilibrium are the same as the moles at equilibrium. Thus,

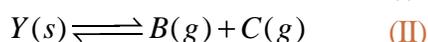
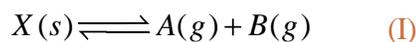
$$K_c = \frac{(1+x)^2}{(1-x)^2} = 16$$

$$\Rightarrow x = 0.6$$

$$\Rightarrow [NO] = 1.6 \text{ mol L}^{-1}, [NO_2] = 0.4 \text{ mol L}^{-1}$$

Example - 16

Two solids X and Y dissociate into gaseous products as follows:



At a given temperature T , the pressure over X is 40 mm while that over Y is 60 mm. What will be the total pressure over a mixture of X and Y ?

Solution: For the first system I, we have

$$p_A = p_B = \frac{40\text{mm}}{2} = 20\text{mm} \quad (\text{why?})$$

$$\Rightarrow K_{pI} = 400\text{mm}^2$$

Similarly,

$$K_{pII} = 900\text{mm}^2$$

Now, when X and Y are mixed what happens? The pressure of B will be due to both the systems.

Assume $p_A = x_A$ and $p_C = x_C$. Thus, $p_B = x_A + x_C$

$$\Rightarrow K_{pI} = x_A(x_A + x_C) = 400$$

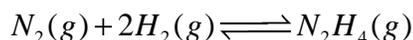
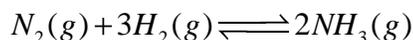
$$K_{pII} = x_C(x_A + x_C) = 900$$

$$\Rightarrow \frac{x_A}{x_C} = \frac{4}{9} \Rightarrow x_A = 11.1\text{mm}, \quad x_C = 24.97\text{mm}$$

$$\begin{aligned} \Rightarrow P_{Tot} &= x_A + (x_A + x_C) + x_B \\ &= 72.15\text{mm} \end{aligned}$$

Example - 17

In a vessel, two equilibria are simultaneously established:

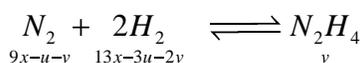
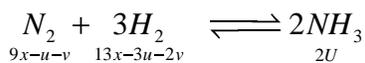


Initially, the vessel contains N_2 and H_2 in the molar ratio 9:13. The equilibrium pressure is $7P_0$, and $p_{NH_3} = P_0$, $p_{H_2} = 2P_0$. Find K_p 's for both the system.

Solution: Since the initial molar ratio $m_{N_2} : m_{H_2} = 9 : 13$, the initial partial pressures will be in the same ratio, so we let

$$p_{N_2, \text{init}} = 9x, \quad p_{H_2, \text{init}} = 13x$$

Now, consider the compositions at equilibrium (we have to consider both equilibria simultaneously):



where U, V correspond to N_2 utilized in the first and second systems. Since the total pressure and equilibrium is $7P_0$, and we know p_{NH_3} and p_{H_2} , we have

$$p_{NH_3} = 2u = P_0 \Rightarrow u = \frac{P_0}{2}$$

$$p_{H_2} = 13x - 3u - 2v = 2P_0 \Rightarrow 13x - 2v = \frac{7P_0}{2}$$

$$p_{Tot} = (9x - u - v) + (13x - 3u - 2v) + (2u) + (v)$$

$$= 9x - 2u + (13x - 2v)$$

$$= 9x - P_0 + \frac{7P_0}{2} = 7P_0 \quad (\text{given})$$

$$\Rightarrow x = \frac{P_0}{2}$$

$$\Rightarrow v = \frac{3P_0}{2}$$

Finally, to evaluate K_{p_1} and K_{p_2} , we note that

$$p_{N_2} = 9x - u - v = \frac{5}{2}P_0$$

$$p_{H_2} = 13x - 3u - 2v = 2P_0$$

$$p_{NH_3} = 2u = P_0$$

$$p_{N_2H_4} = v = \frac{3P_0}{2}$$

$$\Rightarrow K_{p_1} = \frac{(p_{NH_3})^2}{p_{N_2} \cdot (p_{H_2})^3} = \frac{P_0^2}{\frac{5}{2}P_0 \cdot (2P_0)^3} = \frac{1}{20P_0^2}$$

$$\text{and } \Rightarrow K_{p_2} = \frac{p_{N_2H_4}}{p_{N_2} \cdot (p_{H_2})^2} = \frac{\frac{3}{2}P_0}{\frac{5}{2}P_0 \cdot (2P_0)^2} = \frac{3}{20P_0^2}$$

Can you infer from the initial data that the fact that K_{p_2} is greater than K_{p_1} should have been expected! 

Example - 18

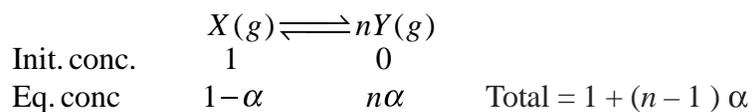
Consider the gaseous system in a closed vessel:



Let the degree of dissociation for this be α . Let the vapour densities of the system be D_0 and D_{eq} initially and at equilibrium respectively. Show that

$$\alpha = \frac{D_0 - D_{eq}}{(n-1)D_{eq}}$$

Solution: Let us start with 1 mol of $X(g)$ initially, and let the volume of the vessel be VL .



Recall that vapour density is inversely proportional to the number of moles (why?; in fact,

$V.D. = \frac{PV}{2n}$). Thus,

$$\frac{D_0}{D_{eq}} = \frac{1 + (n-1)\alpha}{1}$$

$$\Rightarrow \alpha = \frac{1}{n-1} \left(\frac{D_0}{D_{eq}} - 1 \right)$$

which is the desired result. ◀

EXERCISE

[OBJECTIVE]

Q. 1 For a gaseous reversible reaction, which of the following expressions is correct?

- (a) $K_c = K_p (RT)^{\Delta n}$ (b) $K_p = K_c + \Delta n RT$
 (c) $K_p = K_x (P)^{\Delta n}$ (d) $K_p = K_c (RT / \Delta n)$

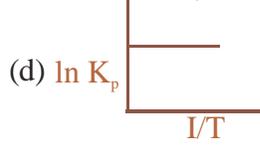
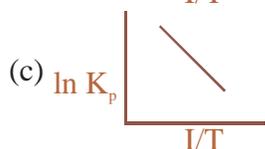
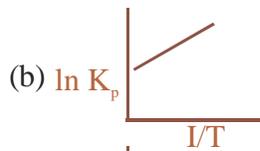
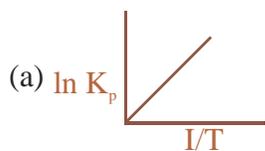
Q. 2 Sulphide ion reacts with solid sulphur to form $S_2^{2-}{}_{(aq)}$ and $S_3^{2-}{}_{(aq)}$ with equilibrium constants 12 and 132 respectively. The equilibrium constant for the formation of $S_3^{2-}{}_{(aq)}$ and $S_2^{2-}{}_{(aq)}$ and sulphur is

- (a) 132×12 (b) $1/11$
 (c) 11 (d) none of these

Q. 3 On heating $CaCO_3$ in open container, the formation of lime commences, at temperature when K_p of the reaction $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ is:

- (a) 1 atm (b) < partial pressure of CO_2 in the air
 (c) = partial pressure of CO_2 in the air (d) none of these

Q. 4 An exothermic reaction is represented by the graph:



Q. 5 The equilibrium constant for the dissociation of water at elevated temperature takes place as:

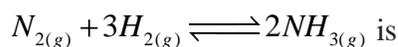
$H_2O_{(g)} \rightleftharpoons H_{2(g)} + \frac{1}{2} O_{2(g)}$. If α is the degree of dissociation at equilibrium pressure P atm, then K_p is given by:

- (a) $K_p = \alpha^3 \left(\frac{P}{2} \right)^{1/2}$ (b) $K_p = \frac{\alpha^3 P^{3/2}}{(1-\alpha)(2+\alpha)}$
 (c) $K_p = \frac{\alpha^{3/2} P^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$ (d) $K_p = \frac{\alpha^3 P^{1/2}}{(1+\alpha)(2-\alpha)^{1/2}}$

Q. 6 Equilibrium constant K_p for the reaction $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ is 0.82 atm at $727^\circ C$. If 1 mole of $CaCO_3$ is placed in a closed container of 20 L and heated to this temperature, what amount $CaCO_3$ would dissociate at equilibrium?

- (a) 0.2 g (b) 80 g
 (c) 20 g (d) 50 g

Q. 7 28 g of N_2 and 6.0 g of H_2 are heated over a catalyst in a closed 1 L flask at 450°C . The entire equilibrium mixture required 500 ml of 1.0 M H_2SO_4 for neutralization. The value of K_c for the reaction:



- (a) $1.69 \text{ mol}^2 \text{ L}^{-2}$ (b) $0.03 \text{ mol}^2 \text{ L}^{-2}$
 (c) $0.59 \text{ mol}^{-2} \text{ L}^2$ (d) $0.06 \text{ mol}^{-2} \text{ L}^2$

Q. 8 Vapour density of the equilibrium mixture of the reaction $SO_2Cl_2 \rightleftharpoons SO_{2(g)} + Cl_{2(g)}$ is 50.0. Percent of extent of dissociation of SO_2Cl_2 is:

- (a) 33.33 (b) 35.0
 (c) 30.0 (d) 66.67

Q. 9 If the enthalpy of a reversible reaction is $8.314 \text{ kJ mol}^{-1}$ over the temperature range $400 - 500 \text{ K}$, the value of $\ln K_{500} / K_{400}$ for the reaction is

- (a) 1.0 (b) 2.0
 (c) 2.5 (d) 0.5

Q. 10 Equilibrium constant for the reaction $CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_5_{(l)} + H_2O_{(l)}$ is 4.0. The mole fraction of the ester present at equilibrium on mixing 120.0 g of CH_3COOH and 92.0 g of C_2H_5OH will be

- (a) .1000 (b) 0.250
 (c) 0.333 (d) 0.667

Q. 11 K_p of the reaction : $N_{2(aq)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ is affected by:

- (a) increasing the volume of reaction vessel
 (b) introducing helium gas keeping total pressure constant
 (c) introducing a catalyst
 (d) changing the temperature.

Q. 12 A plot of Gibbs energy of a reaction system *versus* the extent of reaction has

- (a) positive slope before equilibrium (b) negative slope after equilibrium
 (c) a maximum at equilibrium (d) a minimum at equilibrium

Q. 13 At constant pressure, addition of helium to the reaction system: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

- (a) favours the formation of ammonia (b) reduces the formation of ammonia
 (c) reduces the dissociation of ammonia (d) does not affect the position of equilibrium

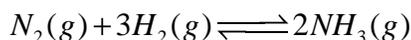
Q. 14 Ice and water are placed in a closed container at a pressure of 1 atm and temperature 273.15 K . If pressure of the system is increased to 2 atm while keeping temperature constant, which of the following would be the correct observation?

- (a) The liquid phase disappears completely (b) The amount of ice decreases
 (c) The solid phase (ice) disappears completely (d) Volume of the system increases

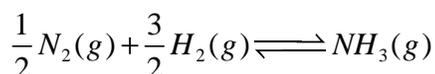
- Q. 15** K_p for the process $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}_{(s)} \rightleftharpoons \text{CuSO}_4 \cdot 3\text{H}_2\text{O}_{(s)} + 2\text{H}_2\text{O}_{(g)}$ is $1.21 \times 10^{-4} \text{ atm}^2$ at certain temperature. If aqueous tension at that temperature is 30 torr, then at what relative humidity of air will $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ effloresce?
 (a) 50% (b) 40%
 (c) 30% (d) Below 28%
- Q. 16** At temperature $T\text{K}$, K_p for the reaction of CO_2 with excess of hot graphite to form CO is 9 atm. Calculate the mole % of CO in the equilibrium mixture of gases
 (a) 20% (b) 25% (c) 60% (d) 75%
- Q. 17** For a reaction the free energy change, $\Delta G = -RT \ell_n K_p + RT \ell_n Q_p$ where $K_p =$ equilibrium constant, $Q_p =$ reaction quotient for the reaction to be in equilibrium state
 (a) $\frac{Q_p}{K_p} > 1$ (b) $\frac{Q_p}{K_p} < 1$
 (c) $\frac{Q_p}{K_p} = 1$ (d) $Q_p K_p = 1$
- Q. 18** In an aqueous solution of 1L, when the reaction $2\text{Ag}_{(aq)}^+ + \text{Cu}_{(s)} \rightleftharpoons \text{Cu}_{(aq)}^{2+} + 2\text{Ag}_{(s)}$ reaches equilibrium, $[\text{Cu}^{2+}] = xM$ and $[\text{Ag}^+] = yM$. If volume of solution is doubled by adding water, then at equilibrium
 (a) $[\text{Cu}^{2+}] = \frac{x}{2}M, [\text{Ag}^+] = \frac{y}{2}M$ (b) $[\text{Cu}^{2+}] > \frac{x}{2}M, [\text{Ag}^+] > \frac{y}{2}M$
 (c) $[\text{Cu}^{2+}] < \frac{x}{2}M, [\text{Ag}^+] > \frac{y}{2}M$ (d) $[\text{Cu}^{2+}] < \frac{x}{2}M, [\text{Ag}^+] < \frac{y}{2}M$
- Q. 19** A reversible reaction is endothermic in forward direction. Then which of the following is correct?
 (a) $\ell_n K$ versus $1/T$ will be a straight line with negative slope
 (b) $\frac{d}{dT} \ell_n K > 0$
 (c) A plot of $d \ell_n K$ against $1/T^2$ will have positive slope
 (d) all
- Q. 20** In a 10L closed vessel, the equilibrium $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ is maintained at certain temperature. If K_c for this reaction is 100 L mol^{-1} and number of moles of SO_2 and SO_3 at equilibrium are in the ratio of 1:2, molar concentration of O_2 will be
 (a) 0.4 mol L^{-1} (b) 0.04 mol L^{-1}
 (c) 0.004 mol L^{-1} (d) 0.002 mol L^{-1}

[SUBJECTIVE]
LEVEL - I

- Q. 1** One mole of nitrogen is mixed with three moles of hydrogen in a 4-litre container. If 0.25 per cent of nitrogen is converted to ammonia by the following reaction:



calculate the equilibrium constant K_c . What will be the value of K_c for the following equilibrium?



- Q. 2** The equilibrium constant of the reaction $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$ at $100^\circ C$ is 50. If a one-litre flask containing one mole of A_2 is connected to a two-litre flask containing two moles of B_2 , what amount of AB will be formed at $373 K$?

- Q. 3** At a certain temperature, equilibrium constant (K_c) is 16 for the reaction



If we take one mole of each of all the four gases in a one litre container, what would be the equilibrium concentration of NO and NO_2 ?

- Q. 4** N_2O_4 is 25% dissociated at $37^\circ C$ and 1 atm pressure. Calculate (i) K_p and (ii) the percentage dissociation at 0.1 atm and $37^\circ C$.

- Q. 5** The equilibrium constant K_p of the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is 900 atm^{-1} at $800 K$. A mixture containing SO_3 and O_2 having initial partial pressures of 1 atm and 2 atm, respectively, is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at $800 K$.

- Q. 6** For the reaction $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$, hydrogen gas is introduced into a five-litre flask at $327^\circ C$ containing 0.2 mol of $CO(g)$ and a catalyst until the pressure is 4.92 atm. At this point, 0.1 mol of $CH_3OH(g)$ is formed. Calculate the equilibrium constants K_p and K_c .

- Q. 7** $HgO(s)$ dissociates according to the equation $HgO(s) \rightleftharpoons Hg(g) + \frac{1}{2}O_2(g)$. The dissociation pressure is 0.51 atm at $693 K$. Calculate K_p for the reaction.

- Q. 8** At $70^\circ C$ and 1 atm, N_2O_4 is 66% dissociated into NO_2 . What volume will 10 g N_2O_4 occupy under these conditions?

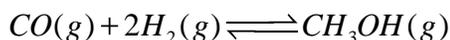
- Q. 9** The values of K_c° for the reactions $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$ and $NO(g) + \frac{1}{2}Br_2(g) \rightleftharpoons NOBr(g)$ are 2.4×10^{30} and 1.4, respectively at $300 K$. Calculate the value of K_c for the reaction $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) + \frac{1}{2}Br_2(g) \rightleftharpoons NOBr(g)$.

- Q. 10** The following data for the reaction $2Na(g) \rightleftharpoons Na_2(g)$ equilibrium have been observed. Equilibrium pressure = 1 atm; Mass per cent of $Na = 71.3$; Mass per cent of $Na_2 = 28.7$ Calculate K_p for the reaction.

LEVEL - II

Q. 1 One mole of N_2 and 3 mole of PCl_5 placed in 100-litre vessel are heated to $227^\circ C$. The equilibrium pressure is 2.05 atm. Assuming ideal behaviour, calculate the degree of dissociation of PCl_5 and K_p for the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$.

Q. 2 0.15 mol of CO taken in a 2.5 L flask maintained at 705 K along with a catalyst so that the following reaction takes place



Hydrogen is introduced until the total pressure of the system is 8. atm at equilibrium and 0.08s; mol of methanol is formed. Calculate (a) K_p and K_c and (b) the final pressure if the same amount of CO and H_2 as before are used, but with no catalyst so that the reaction does not take place.

Q. 3 At temperature T , a compound $AB_2(g)$ dissociates according to the reaction $2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$ with a degree of dissociation, x , which is small compared with unity. Deduce the expression for x in terms of the equilibrium constant, K_p and the total pressure P .

Q. 4 For the reaction $Ag(CN)_2^- \rightleftharpoons Ag^+ + 2 CN^-$, the equilibrium constant at $25^\circ C$ is 4.0×10^{-19} . Calculate the silver ion concentration in a solution which was originally 0.10 molar in KCN and 0.03 molar in $AgNO_3$.

Q. 5 For the reaction $NH_3(g) \rightleftharpoons \frac{1}{2} N_2(g) + \frac{3}{2} H_2(g)$ show that the degree of dissociation of NH_3 is given as $\alpha = \left(1 + \frac{3\sqrt{3} p}{4 K_p} \right)^{-1/2}$ where p is the equilibrium pressure. If K_p of the above reaction is 78.1 atm at $400^\circ C$, determine the value of K_c .

Q. 6 H_2S dissociates according to the equation $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$. If α is the degree of dissociation of H_2S , show that K_p of the reaction is given as

$$K_p = \frac{\alpha^3 p}{2(1-\alpha)^2(1+\alpha/2)}$$

At $1125^\circ C$, the value of the α found to be 0.31 when the equilibrium pressure is 1 atm. Determine the values of K_p and K_c .

Q. 7 $COCl_2$ gas dissociates according to the equation $COCl_2 \rightleftharpoons CO + Cl_2$. When $COCl_2$ is heated to $724 K$ at 1 atm, the density of gas mixture at equilibrium was found to be $1.162 g L^{-1}$. Calculate (a) the degree of dissociation and (b) K_p of the reaction.

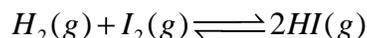
Q. 8 N_2O_4 dissociates according to the equation $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. When 0.578 g of N_2O_4 was introduced into a one litre flask maintained at 308 K, the equilibrium pressure was 0.238 atm. Calculate (a) the degree of dissociation, and (b) K_p of the reaction.

Q. 9 $PCl_5(g)$ dissociates according to the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. At $523 K$, $K_p = 1.78$ atm. Find the density of the equilibrium mixture at a total pressure of 1 atm.

Q. 10 Sulphur trioxide dissociates on heating $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$. A sample of 0.63 g of SO_3 is placed in a 1.0 L container and heated to a temperature of 1100 K. The equilibrium total pressure at this temperature is 1.0 atm. Calculate (a) degree of dissociation of SO_3 and (b) K_p and K_c of the reaction.

TRY YOURSELF - I

Q. 1 Consider the system



Assume that we start with 'a' moles of H_2 and 'b' moles of I_2 , and at equilibrium 'x' moles of H_2 and I_2 have been utilized. What will be the expression for K_p ?

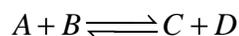
Q. 2 At 27°C and 1 atm, N_2O_4 is 20% dissociated into NO_2 .

Find

(a) K_p

(b) the percentage dissociation at 27°C and at a total pressure of 0.1 atm

Q. 3 Let the equilibrium constant for the systems

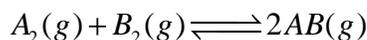


be K_1 and K_2 respectively. What will be the equilibrium constants for the following systems?

(a) $C + D \rightleftharpoons A + B$ (b) $\frac{1}{2}A + \frac{1}{2}B \rightleftharpoons \frac{1}{2}C + \frac{1}{2}D$ (c)



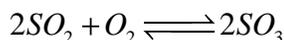
Q. 4 The equilibrium constant for



at 100°C is 50. If a one-litre flask containing one mole of A_2 is connected to a two-litre flask containing two moles of B_2 , how many moles of AB will be formed at 373 K ?

Q. 5 In terms of K_p , what is the pressure necessary to obtain 50% dissociation of PCl_5 at 250°C ?

Q. 6 A mixture of SO_2 , SO_3 and O_2 is maintained in a 10 L flask at a certain temperature at which $K_c = 100$:



Calculated m_{O_2} if $m_{SO_3} : m_{SO_2}$ equals

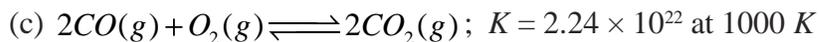
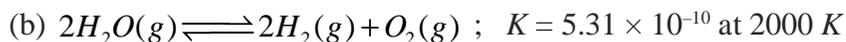
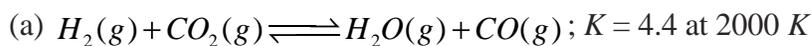
(a) 1

(b) 2

where m_x stands for number of moles of X

Q. 7 For the reaction $Br_2 \rightleftharpoons 2Br$, the equilibrium constants at 327°C and 527°C are respectively 6.1×10^{-12} and 1.0×10^{-7} . Is this reaction endothermic or exothermic?

Q. 8 Consider the following data:



Is the third reaction endothermic or exothermic?

Q. 9 A mixture of air at 1.0 bar and 2000 K was passed through an through an electric arc to produce nitric oxide:



What fraction of O_2 will be converted at equilibrium?

Q. 10 Consider this system :



This initial pressures are $p_{CO} = 342\text{ mm}$, $p_{Cl_2} = 352\text{ mm}$ and the total pressure at equilibrium is 440 mm .

What is the percentage dissociation of $COCl_2$ at 400°C at 1 atm ?

TRY YOURSELF - II

Q. 1 Interpret the following in light of the LeChâtelier's principle:

- (a) Melting of ice is favored by increase in temperature and increase in pressure
- (b) Solids which absorb heat on dissolution in water, will show increased solubilities with increasing temperatures.
- (c) For the system



there is no effect on equilibrium with changing pressures, but high temperature favors the forward reaction.

Q. 2 For the system $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, it is known that $K_c = 0.00466$ at 298 K. A one-litre container initially containing 0.8 moles of N_2O_4 was allowed to reach equilibrium. Now suppose the volume is suddenly halved, keeping the temperature same. Use the LeChâtelier's principle to figure out how the equilibrium position will shift. Calculate $[N_2O_4]$ and $[NO_2]$ at the new equilibrium positions

ANSWER

T. Y - 1

- Ans. 1** $K_p = \frac{4x^2}{(a-x)(b-x)}$
Ans. 2 (a) $K_p = 0.17$, (b) 55%
Ans. 3 (a) $\frac{1}{K_1}$, (b) $\sqrt{K_1}$, (c) $K_1 K_2$
Ans. 4 1.86
Ans. 5 $3 K_p$
Ans. 6 (A) 0.1 (b) 0.4
Ans. 7 endothermic
Ans. 8 exothermic
Ans. 9 2 %
Ans. 10 20.6%

T. Y - 2

- Ans. 2** [equilibrium will shift to the left ;
 $[N_2O_4] = 1.557 \text{ M}$, $[NO_2] = 0.086 \text{ M}$]

EXERCISE (OBJECTIVE)

1. (c) 2. (c) 3. (c) 4. (b) 5. (b) 6. (c)
 7. (c) 8. (b) 9. (d) 10. (c) 11. (d) 12. (d)
 13. (b) 14. (c) 15. (d) 16. (d) 17. (c) 18. (c)
 19. (d) 20. (b)

SUBJECTIVE

LEVEL - I

1. $K_c = 1.49 \times 10^{-5} (\text{mol L}^{-1})^{-2}$
 $K_c' = 3.86 \times 10^{-3} (\text{mol L}^{-1})^{-1}$
 2. 1.868 mol.
 3. $[\text{NO}] = 1.6 \text{ mol L}^{-1}$.
 $[\text{NO}_2] = 0.4 \text{ mol L}^{-1}$.
 4. (i) $K_p = 0.267 \text{ atm}$
 (ii) 63 %
 5. $P(\text{SO}_2) = 0.023 \text{ atm}$
 $P(\text{O}_2) = 2.0115 \text{ atm}$
 $P(\text{SO}_3) = 0.977 \text{ atm}$
 6. $K_c = 27.78 (\text{mol L}^{-1})^{-2}$
 $K_p = 0.115 \text{ atm}^{-2}$
 7. $K_p = 0.14 \text{ atm}^{3/2}$
 8. $V = 5.08 \text{ L}$
 9. $K_c = 9.04 \times 10^{-16}$
 10. $K_p = 0.24 \text{ atm}^{-1}$

LEVEL - II

1. $\alpha = 0.333$
 $K_p = 0.205 \text{ atm}$.
 2. (a) $K_c = 150.85 (\text{mol L}^{-1})^{-2}$
 $K_p = 0.045 \text{ atm}^{-2}$
 (b) $P_0 = 12.20 \text{ atm}$
 3. $x = \left(\frac{2K_p}{P} \right)^{1/3}$
 4. $[\text{Ag}^+] = 7.5 \times 10^{-18} \text{ M}$.
 5. $K_c = 1.413 \text{ mol L}^{-1}$
 6. $K_p = 2.71 \times 10^{-2} \text{ atm}$
 $K_c = 2.39 \times 10^{-4} \text{ mol L}^{-1}$
 7. (a) $\alpha = 0.433$
 (b) $K_p = 0.231$
 8. (a) 0.5
 (b) 0.319
 9. $\rho = 2.70 \text{ g L}^{-1}$
 10. (a) $\alpha = 0.81$
 (b) $K_p = 5.26 \text{ atm}$
 $K_c = 5.82 \times 10^{-2} \text{ mol L}^{-1}$