

CHEMICAL EQUILIBRIUM

REVERSIBLE REACTIONS

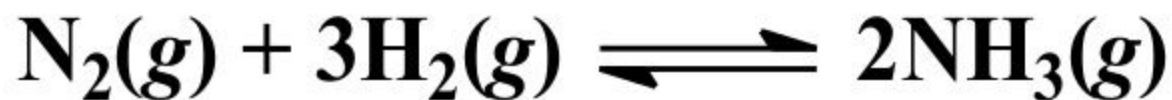
- A reaction which can go in forward & backward direction simultaneously is called reversible reaction.

Depicting Equilibrium

In a system at equilibrium, both the forward and reverse reactions are running simultaneously. We write the chemical equation with a double arrow:

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

SOME EXAMPLES OF REVERSIBLE REACTIONS



Chemical Equilibrium

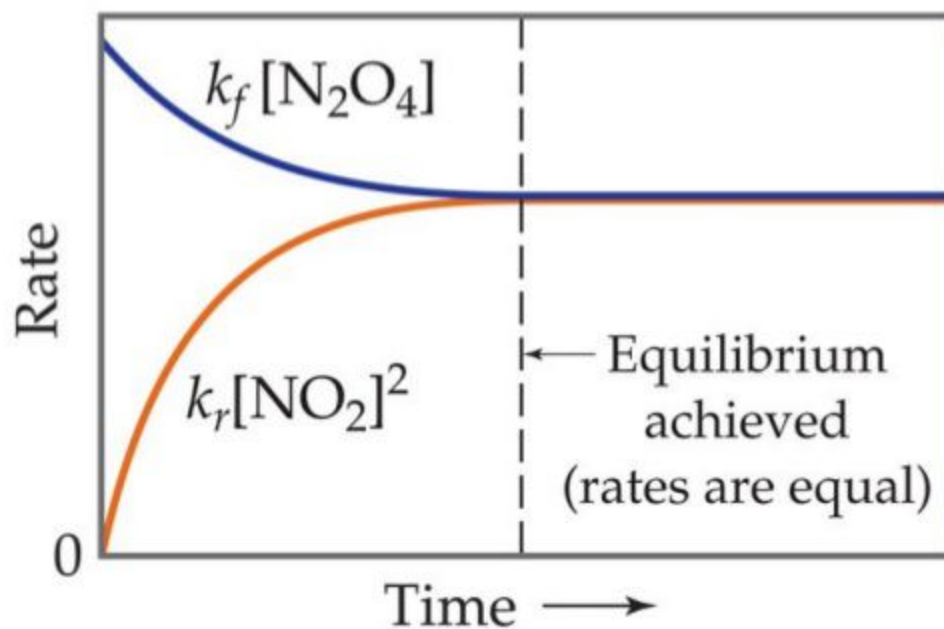
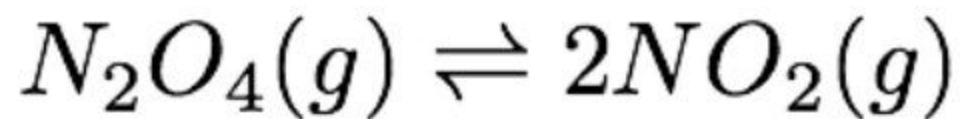
(Definitions)

A chemical system where the concentrations of reactants and products remain **constant** over time.

On the molecular level, the system is **dynamic**: The rate of change is the same in either the forward or reverse directions.

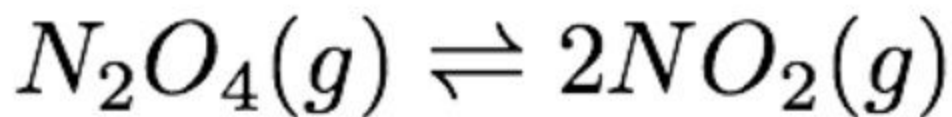
As a system approaches equilibrium, both the forward and reverse reactions are occurring.

At equilibrium, the forward and reverse reactions are proceeding at the same rate.

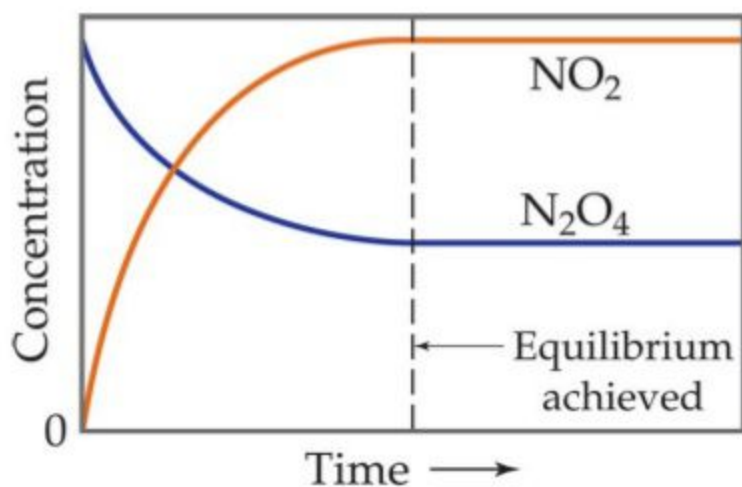


A System at Equilibrium

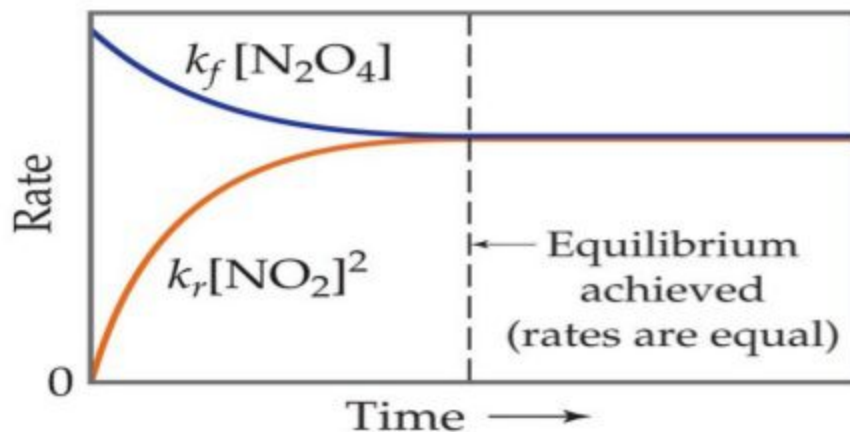
- Once equilibrium is achieved, the *amount* of each reactant and product remains constant.



Concentrations become constant



Rates become equal



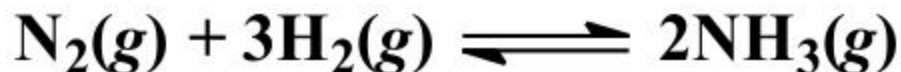
CHARACTERISTICS OF CHEMICAL EQUILIBRIUM

1- Constancy of concentrations

When a chemical reaction is established in a closed vessel at constant temperature conc. of various species in reaction mixture become constant & the reaction mixture at equilibrium is called **Equilibrium mixture** & the conc. At equilibrium is called **equilibrium conc.**

UNITS: moles/litre

2-Equilibrium can be initiated from either side



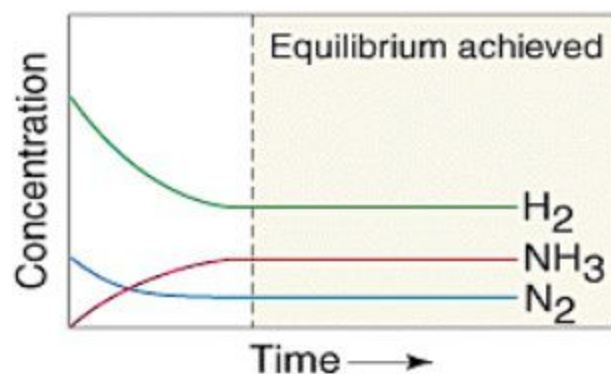
Add nitrogen and hydrogen gases together in any proportions. Nothing noticeable occurs.

Add heat, pressure and a catalyst, you smell ammonia => a mixture with constant concentrations of N_2 , H_2 and NH_3 is produced.

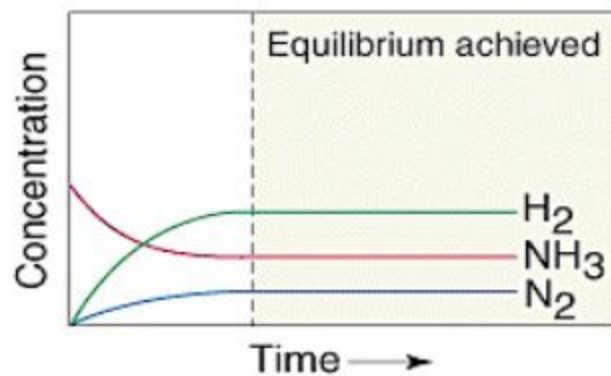
Start with just ammonia and catalyst. N_2 and H_2 will be produced until a state of equilibrium is reached.

As before, a mixture with constant concentrations of nitrogen, hydrogen and ammonia is produced.

- No matter what the starting composition of reactants and products, the same ratio of concentrations is realized when equilibrium is reached at a certain temperature and pressure.



(a)



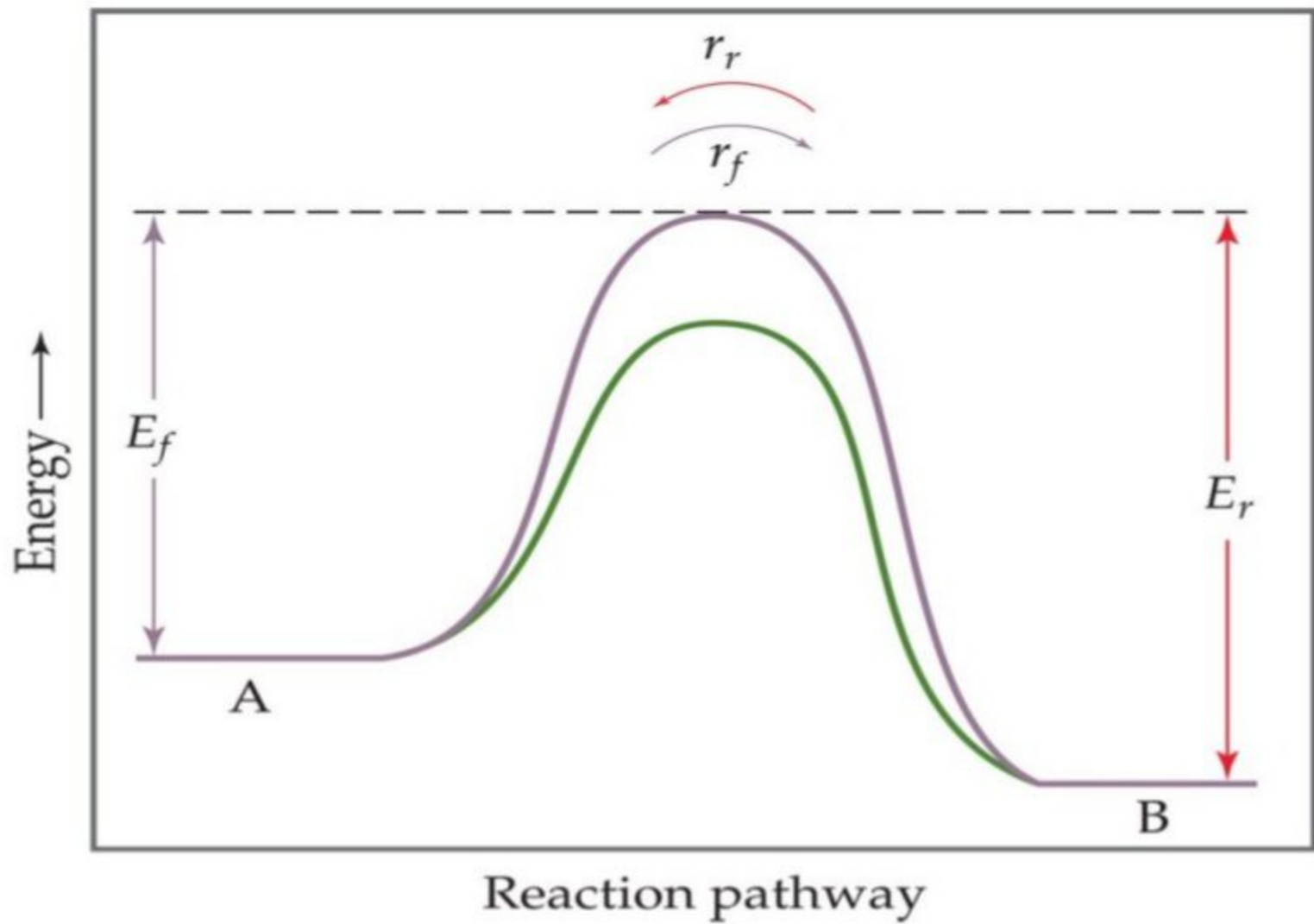
(b)

3-Equilibrium cannot be attained in open vessel

- Equilibrium can be established only if the reaction vessel is closed & no part of the reactants or products is allowed to escape out.
- In an open vessel, the gaseous reactants or products may escape out into the atmosphere leaving behind no possibility of attaining equilibrium.
- However equilibrium can be attained when all the reactants & products are in the same phase e.g, ethanol & ethanoic acid.

4-A catalyst cannot change the equilibrium point

- Catalysts increase the rate of both the forward *and* reverse reactions. Equilibrium is achieved faster, but the equilibrium composition remains unaltered. A catalyst lowers the activation energy barrier of a reaction. The diagram shows that the catalyst lowers the activation energy for the forward and reverse reactions by the same amount. Consequently a catalyst does not affect the position of the equilibrium but it does speed up the rate at which equilibrium is reached.



5-Equilibrium constant is independent of the initial conc. of reactants

6- At equilibrium the Gibbs free energy (G) is the minimum & any change taking place at equilibrium proceeds without change in free energy i.e; $\Delta G=0$

LAW OF MASS ACTION (EQUILIBRIUM EXPRESSION)

- Two Norwegian chemists, Guldberg & Waage studied experimentally a large no of equilibrium reactions. In 1864, they postulated a generalization called **LAW OF MASS ACTION** which states that:
- **“The rate of chemical reaction is proportional to the active masses of reactants”**
- **ACTIVE MASS:** means the molar conc. i.e. no. of moles per liter expressed by enclosing formula of substance in square brackets.

EQUILIBRIUM CONSTANT: EQUILIBRIUM LAW

- For a general equilibrium $aA + bB \rightleftharpoons cC + dD$
the equilibrium expression is:

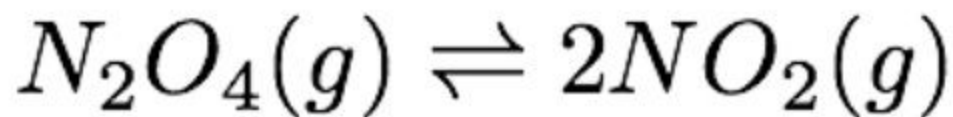
$$K = \frac{\overbrace{[C]^c [D]^d}^{\text{Products}}}{\underbrace{[A]^a [B]^b}_{\text{Reactants}}}$$

Copyright © 2008 Pearson Prentice Hall, Inc.

where **K is the Equilibrium Constant.** (Units for K will vary.)

- **EQUILIBRIUM CONSTANT** can be defined as:
- The product of equilibrium conc. Of products divided by the product of equilibrium conc. Of reactants, with each conc. Term raised to a power equal to the coefficient of substance in the balanced equation.

The Equilibrium Constant



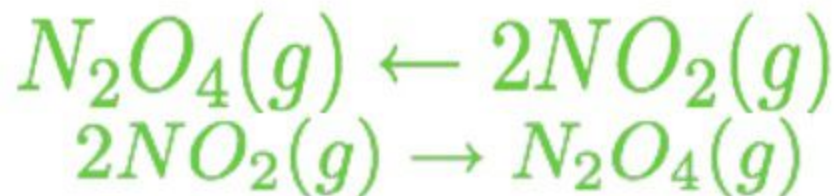
Forward reaction:



Rate law

$$rate = k_f [N_2O_4]$$

Reverse reaction:



Rate Law

$$rate = k_r [NO_2]^2$$

At equilibrium $rate_f = rate_b$

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

Rearranging gives:

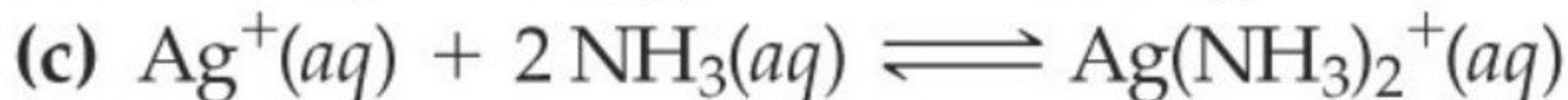
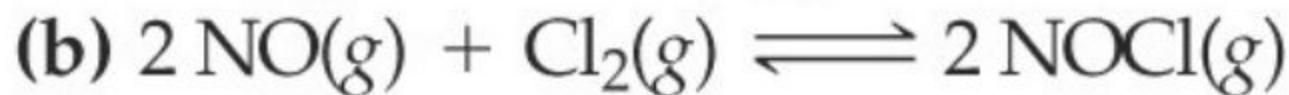
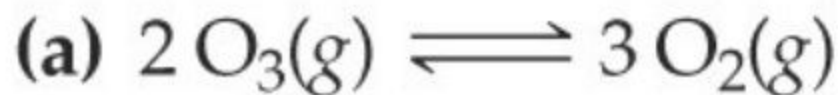
$$K_{eq} = \frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]}$$

Equilibrium Expression

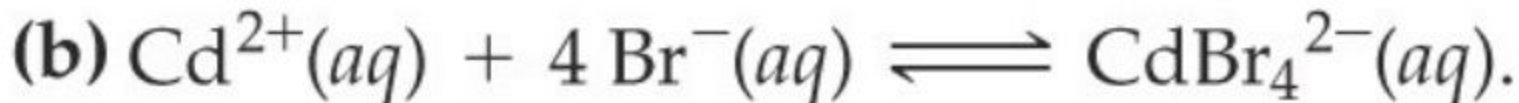
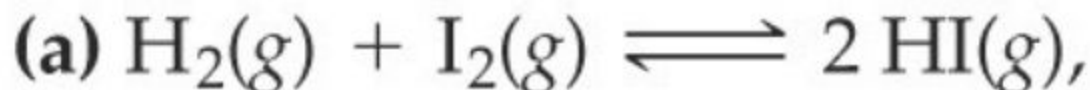
- $4 \text{NH}_3(\text{g}) + 7 \text{O}_2(\text{g}) \leftrightarrow 4 \text{NO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$
- Write the Equilibrium Expression for the reaction. The expression will have either concentration units of mol/L (M), or units of pressure (atm) for the reactants and products. What would be the overall unit for K using Molarity and atm units respectively.

$$K = \frac{[\text{NO}_2]^4 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^7}$$

SAMPLE EXERCISE: Write the equilibrium expression for K_c for the following reactions:

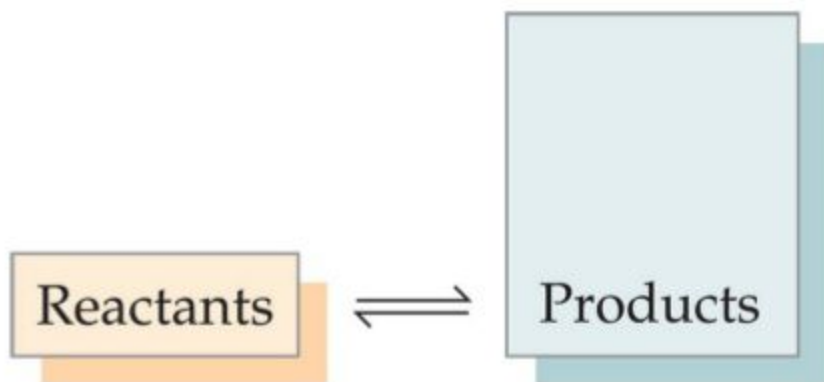


$$\text{(a) } K_c = \frac{[\text{O}_2]^3}{[\text{O}_3]^2}, \text{ (b) } K_c = \frac{[\text{NOCl}]^2}{[\text{NO}]^2[\text{Cl}_2]}, \text{ (c) } K_c = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$



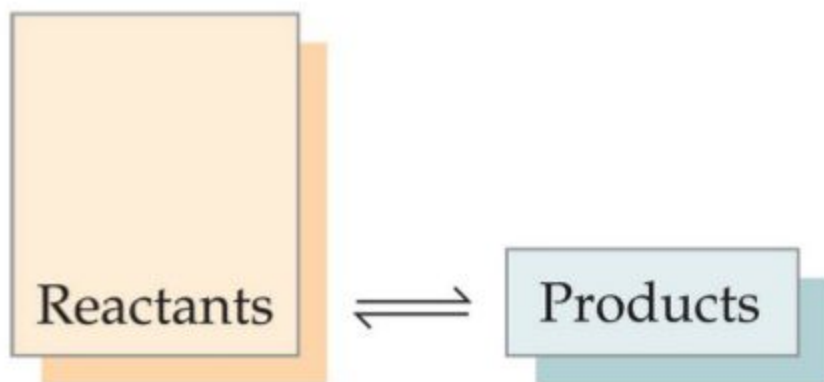
$$\text{Answers: (a) } K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}, \text{ (b) } K_c = \frac{[\text{CdBr}_4^{2-}]}{[\text{Cd}^{2+}][\text{Br}^-]^4}$$

What Does the Value of K Mean?



(a) $K \gg 1$

- If $K \gg 1$, the reaction is *product-favored*; product predominates at equilibrium.



(b) $K \ll 1$

- If $K \ll 1$, the reaction is *reactant-favored*; reactant predominates at equilibrium.

Le Chatelier's Principle

Le Chatelier's Principle:

If a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to counteract the change.



Change in concentration

Suppose you have an equilibrium established between four substances A, B, C and D:



What would happen if you changed the conditions by increasing the concentration of A?

Change in Concentration

Le Chatelier's principle says that the position of equilibrium will move in such a way as to counteract the change

- The position of equilibrium will move to **decrease** the concentration of A by reacting it with B and turning it into C + D
- The position of equilibrium moves to the right

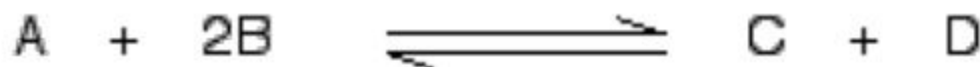


The position of equilibrium moves to the right if you increase the concentration of A.

Change in Concentration

What would happen if you changed the conditions by decreasing the concentration of A?

- Le Chatelier's principle says the position of equilibrium will move to counteract the change
- It will increase the concentration of A. C and D will react to replace the A that has been removed. The position of equilibrium moves to the left.



The position of equilibrium moves to the left if you decrease the concentration of A.

Change in Pressure

Le Chatelier's Principle with a change of pressure only applies to reactions involving gases

What would happen if you changed the conditions by increasing the pressure?

- Le Chatelier says the position of equilibrium will move in such a way as to counteract the change
- The position of equilibrium will move so that the pressure is reduced

Change in Pressure

- There are 3 molecules on the left-hand side of the equation, but only 2 on the right
- By forming more C & D from A & B, you reduce the number of molecules and the pressure decreases
- Increasing the pressure on a gas reaction shifts the position of equilibrium towards the side **with fewer molecules**



The position of equilibrium moves to the right if you increase the pressure on the reaction.

Change in Pressure

What would happen if you changed the conditions by decreasing the pressure?

- The equilibrium will move to increase the pressure by producing more molecules.
- The position of equilibrium will move towards the left-hand side of the reaction.



The position of equilibrium moves to the left if you decrease the pressure on the reaction.

Change in Pressure

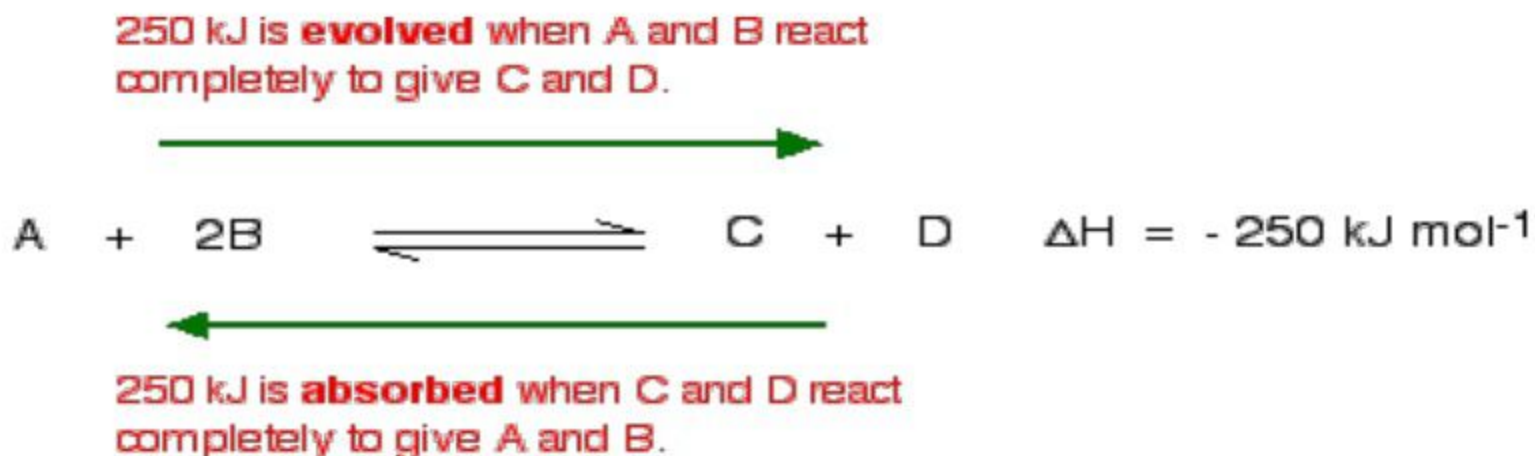
What happens if there are the same number of molecules on both sides of the equilibrium reaction?

- In this case, increasing the pressure has no effect whatsoever on the position of the equilibrium.
- With the same numbers of molecules on both sides, the equilibrium can't move in any way that will reduce the pressure again.

Change in Temperature

How does changing the temperature affect dynamic equilibrium?

For this, you need to know whether heat is evolved (exothermic) or absorbed (endothermic) during the reaction.



Change in Temperature

What would happen if you changed the conditions by increasing the temperature?

- According to Le Chatelier, the position of equilibrium will counteract the change
- That means that the position of equilibrium will move so that the temperature is reduced



Change in Temperature

If the system is in equilibrium at 300°C, and you increase the temperature to 500°C. How can the reaction counteract the change you have made?

- The *back reaction* absorbs heat. The position of equilibrium therefore moves to the left. The new equilibrium mixture contains more A and B, and less C and D.



The position of equilibrium moves to the left if you increase the temperature.

Change in Temperature

What would happen if you changed the conditions by decreasing the temperature?

- Le Chatelier's principle says that the equilibrium will move in such a way to counteract the change
- The reaction will tend to heat itself up again to return to the original temperature



Change in Temperature

The reaction will tend to heat itself up again to return to the original temperature. It can do that by favouring the **exothermic** reaction

- The position of equilibrium will move to the right.
- More A and B are converted into C and D at the lower temperature.



The position of equilibrium moves to the right if you decrease the temperature.

Change in Temperature

Summary

- Increasing the temperature of a system in dynamic equilibrium favours the **endothermic** reaction. The system counteracts the change you have made by absorbing the extra heat.
- Decreasing the temperature of a system in dynamic equilibrium favours the **exothermic** reaction. The system counteracts the change you have made by producing more heat.

Relationship between K_c , K_d , K_p and K_x .

Relation between K_c and K_p

Consider a general chemical reaction



the equilibrium expression is

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{--- (i)}$$

For reactions involving gases, it is convenient to express concentration of any gas at any given temperature in terms of its partial pressure.

So,

$$K_p = \frac{[P_c]^c [P_d]^d}{[P_a]^a [P_b]^b} \quad \text{--- (ii)}$$

From an ideal gas equation

$$PV = nRT$$

$$P = \frac{nRT}{V}$$

$$P = \frac{n}{V} RT$$

n is the number of moles of the gas occupying a volume V .

$$\text{Since } \frac{n}{V} = C$$

Therefore

$$P = CRT \quad \text{--- (iii)}$$

Now we can write that

$$P_A = C_A RT \quad P_B = C_B RT$$

$$P_C = C_C RT \quad P_D = C_D RT$$

Putting these values in equ-ii

$$K_p = \frac{(C_C RT)^c (C_D RT)^d}{(C_A RT)^a (C_B RT)^b}$$

$$K_p = \frac{(C_C) (C_D)}{(C_A) (C_B)} \cdot \frac{(RT)^{c+d}}{(RT)^{a+b}}$$

$$K_p = K_c \cdot (RT)^{(c+d) - (a+b)}$$

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

$$\Delta n = (c+d) - (a+b)$$

Δn , may be positive, negative
or zero

When $\Delta n = 0$

$$K_p = K_c$$

Relation between K_p and K_x

In order to derive a relation between ' K_p ' and ' K_x ' we take help from Dalton's law of partial pressure.

that is,

$$p = xP$$

p is the partial pressure of the gas, x is the mole fraction and P is total P .

Now,

$$P_A = x_A P$$

$$P_B = x_B P$$

$$P_C = x_C P$$

$$P_D = x_D P$$

we know that

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

therefore

$$K_p = \frac{(X_C P)^c (X_D P)^d}{(X_A P)^a (X_B P)^b}$$

$$K_p = \frac{(X_C)(X_D)}{(X_A)(X_B)} \cdot \frac{P^{(c+d)}}{P^{(a+b)}}$$

$$K_p = K_x \cdot (P)^{(c+d) - (a+b)}$$

$$K_p = K_x \cdot (P)^{\Delta n}$$

if $\Delta n = 0$

$$K_p = K_x$$

and we know that

$$K_p = K_c$$

so we can write that

$$K_p = K_c = K_x$$

Relation between K_c and K_d

Suppose we have an acid (HA) dissolved in water in a reversible manner.



K_c for this reaction is

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

At equilibrium stage, the concentration of water is almost equal as at the initial stages. Because water is taken in large excess.

to take the conc. of water as constant, and take it on the left-hand side with K_c

$$K_c [H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

$$K_c [H_2O] = K_a$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$
