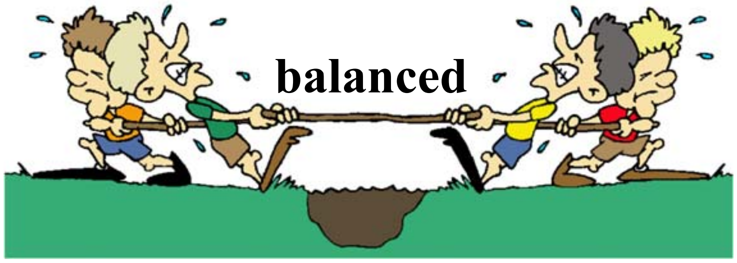
Chemical Equilibrium (Chapter 15)

1. Equilibrium.
2. Equilibrium constant (*K*).
3. Manipulating equilibrium constants.
4. Le Châtelier's Principle.

Traffic entering and leaving a city is a balance.

What is an equilibrium?

- Chemical equilibrium is the moment when a reaction and its reverse reaction proceed at the same rate.



"Equilibrium" in tug-of-war

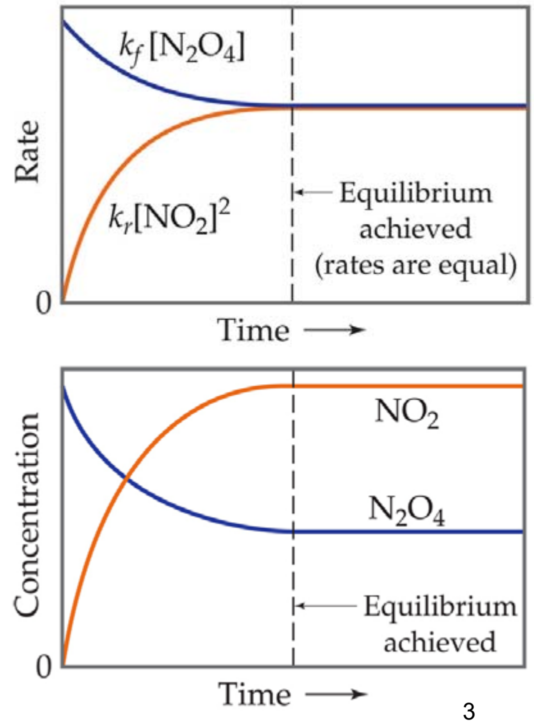
- Macroscopically, there is no concentration change for both the reactants and products.
- Microscopically, the concentrations of the reactants and products keep changing but at the same rate.

What happens at equilibrium?

$$N_2O_4 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2\ NO_2$$

At equilibrium,
the decomposition rate of N_2O_4 is equal to the combination rate of two NO_2.

Thus, both $[N_2O_4\ ]$ and $[NO_2]$ remain constant.



The equilibrium constant

$$N_2O_4 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2\ NO_2$$

Forward reaction rate: $k_f[N_2O_4]$

Reverse reaction rate: $k_r[NO_2]^2$

At equilibrium, the forward rate equals to reverse rate.

constant

$$k_f[N_2O_4] = k_r[NO_2]^2 \Rightarrow \frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]} = K$$

(for forward rxn)

The equilibrium constant (K)

- **For a reaction: $aA + bB \rightarrow cC + dD$, the equilibrium constant expression is:**

$$K = \frac{[\text{product}]}{[\text{reactant}]} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

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

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

The reactant concentrations are used in the expression.

- **This expression depends only on the stoichiometry of the reaction, not on its mechanism.**

Equilibrium can be reached from either direction

$$N_2O_4 \rightleftharpoons 2\ NO_2$$

Experiment	Initial N_2O_4 Concentration (M)	Initial NO_2 Concentration (M)	Equilibrium N_2O_4 Concentration (M)	Equilibrium NO_2 Concentration (M)	K_c
1	0.0	0.0200	0.00140	0.0172	0.211
2	0.0	0.0300	0.00280	0.0243	0.211
3	0.0	0.0400	0.00452	0.0310	0.213
4	0.0200	0.0	0.00452	0.0310	0.213

No matter what the initial concentrations of NO_2 and N_2O_4 are, we can get the same equilibrium constant.

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} \quad \textbf{(constant)}$$

Equilibrium constant for gaseous reactions

- **Pressure is proportional to concentration for gases, we may express the equilibrium expression in term of pressure:**

$$aA\ (g) + bB\ (g) \rightarrow cC\ (g) + dD\ (g)$$

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

For example, $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$

$$K_p = \frac{(P_{NO2})^2}{(P_{N2O4})}$$

Relationship between K_c and K_p

- **For an ideal gas law, we know that**

$$PV = nRT \quad \Rightarrow P = \frac{n}{V} RT$$

has a unit of mol / L, i.e., molarity (M).

- **Thus, for a substance A, we have:**

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

$$K_p = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b} = \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{c+d-a-b}$$

$$= \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{\Delta n} = K_c (RT)^{\Delta n}$$

$$\boxed{\Delta n = c + d - a - b}$$

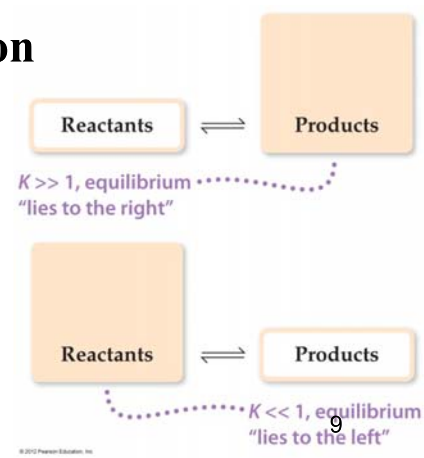
Physical meaning of the K value

- The value of K tells the compositions of the reactants and products at equilibrium.

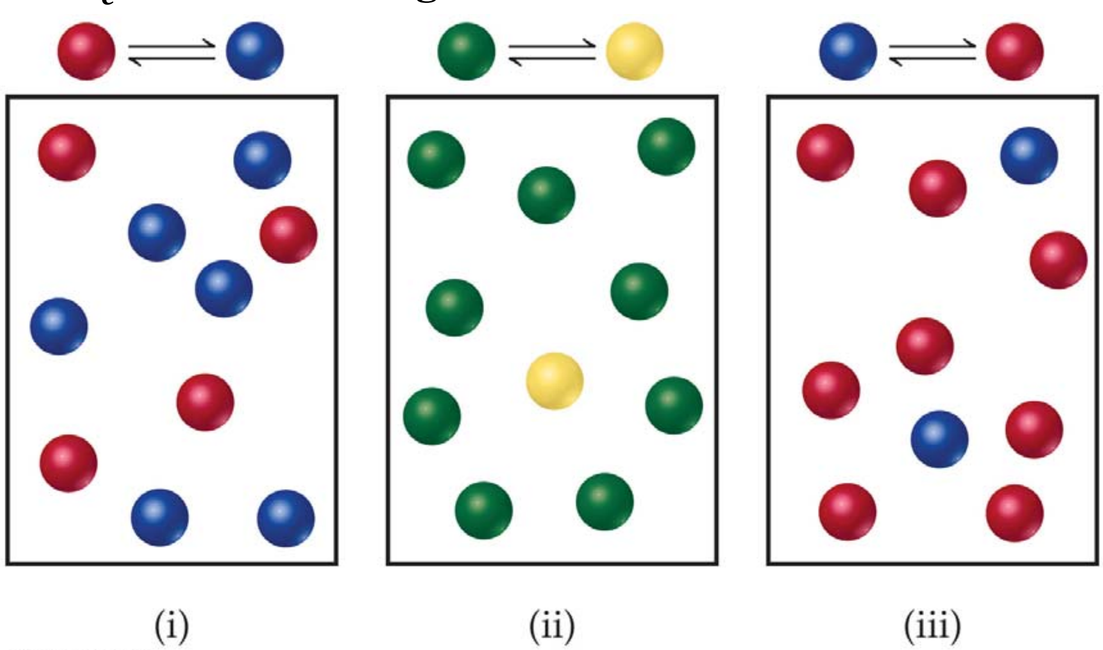
$$K = \frac{[\text{product}]}{[\text{reactant}]}$$

- If $K >> 1$, the reaction is favored on the product side; or product predominates at equilibrium.

- If $K << 1$, the reaction is favored on the reactant side; or reactant predominates at equilibrium.



The following three systems are at equilibrium, arrange the K_c in an ascending order.



Experiment 1: The 'blue Bottle' Experiment

$$\text{Methylene blue (Oxidized form – blue)} \underset{\text{Oxygen}}{\overset{\text{Glucose}}{\rightleftharpoons}} \text{Methylene blue (Reduced form – colorless)}$$

$$\text{methylene blue} + \text{glucose} \rightleftharpoons \text{methylene blue} + \text{oxygen}$$

Q. What do you expect about the value of *K* when the reaction mixture is at equilibrium? $K < 1$, $K = 1$ or $K > 1$?

Reciprocal of equilibrium constants

- **The equilibrium constant of a reaction in the reverse reaction is the reciprocal of equilibrium constant of the forward reaction.**

$$N_2O_4(g) \rightarrow 2\ NO_2(g) \qquad K_c^f = \frac{[NO_2]^2}{[N_2O_4]}$$

$$2\ NO_2(g) \rightarrow N_2O_4(g) \qquad K_c^r = \frac{[N_2O_4]}{[NO_2]^2}$$

$$\boxed{K_c^f = \frac{1}{K_c^r}}$$

Manipulating equilibrium constants

- **The equilibrium constant for a net reaction made up of two or more steps is the product of the equilibrium constants for the individual steps.**

1. $2\ NOBr(g) \rightleftharpoons 2\ NO(g) + Br_2(g)$

$$K_c^1 = \frac{[NO]^2[Br_2]}{[NOBr]^2}$$

2. $Br_2(g) + Cl_2(g) \rightleftharpoons 2\ BrCl(g)$

$$K_c^2 = \frac{[BrCl]^2}{[Cl_2][Br_2]}$$

1. $2\ NOBr(g) \rightleftharpoons 2\ NO(g) + \cancel{Br_2}(g)$

2. $\cancel{Br_2}(g) + Cl_2(g) \rightleftharpoons 2\ BrCl(g)$

(1+2) $2\ NOBr(g) + Cl_2(g) \rightleftharpoons 2\ NO(g) + 2\ BrCl(g)$

$$K_c^{1+2} = \frac{[NO]^2[BrCl]^2}{[NOBr]^2[Cl_2]} = \frac{[NO]^2[Br_2]}{[NOBr]^2} \times \frac{[BrCl]^2}{[Cl_2][Br_2]}$$

$$K_c^{1+2} = K_c^1 \times K_c^2$$

Homogenous and Heterogeneous equilibria

• **Homogenous equilibrium – all reactants and products are in the same phases.**
• **Heterogeneous equilibrium – the reactants and/or products are in the different phases.**

For example, $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ Cl^-(aq)$

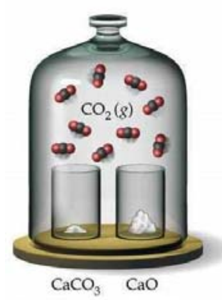
$$K_c = \frac{[Pb^{2+}][Cl^-]^2}{[PbCl_2]} = [Pb^{2+}][Cl^-]^2$$

• **The concentrations of pure solids (and liquids) is always constant during reaction. They do not appear in the equilibrium expression.**

Heterogeneous equilibria

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

Large amount of $CaCO_3$, small amount of CaO, gas pressure P



Small amount of $CaCO_3$, large amount of CaO, gas pressure still P

The concentration of a pure solid or liquid has a constant value.
If the mass of a solid is double, its volume also double.
Its concentration, which related to the ratio of mass to volume, stays the same.

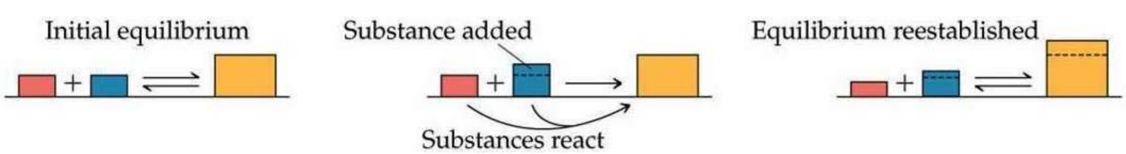
Le Châtelier's principle

- If a system at equilibrium is **disturbed** by a change in temperature, pressure, or the concentration of one of the components, the system will shift its equilibrium position so as to **counteract** the effect of the disturbance.

- This principle is to **predict** how a system at equilibrium **responds** to various changes in external conditions.

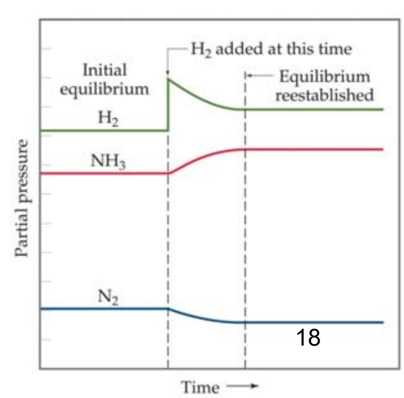
The effect of changes in [reactant] or [product]

- If a system at equilibrium and we add a substance (either product or reactant), the reaction will shift in the direction that **consumes the added substance**.



<u>The Haber process</u>

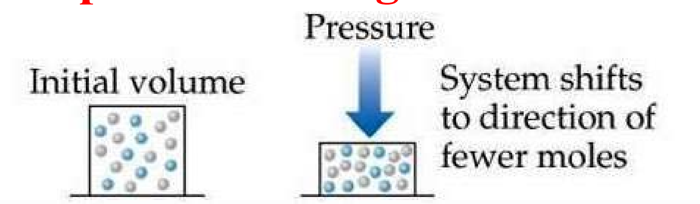
$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$$



If H_2 is added to the system, N_2 will be consumed and the reaction will form more NH_3.

The effect of changes in pressure

- At constant T, if the volume of a gaseous equilibrium mixture is reduced (i.e., increasing the pressure), this causes the system to shift in the direction that **produces less gaseous molecules**.



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

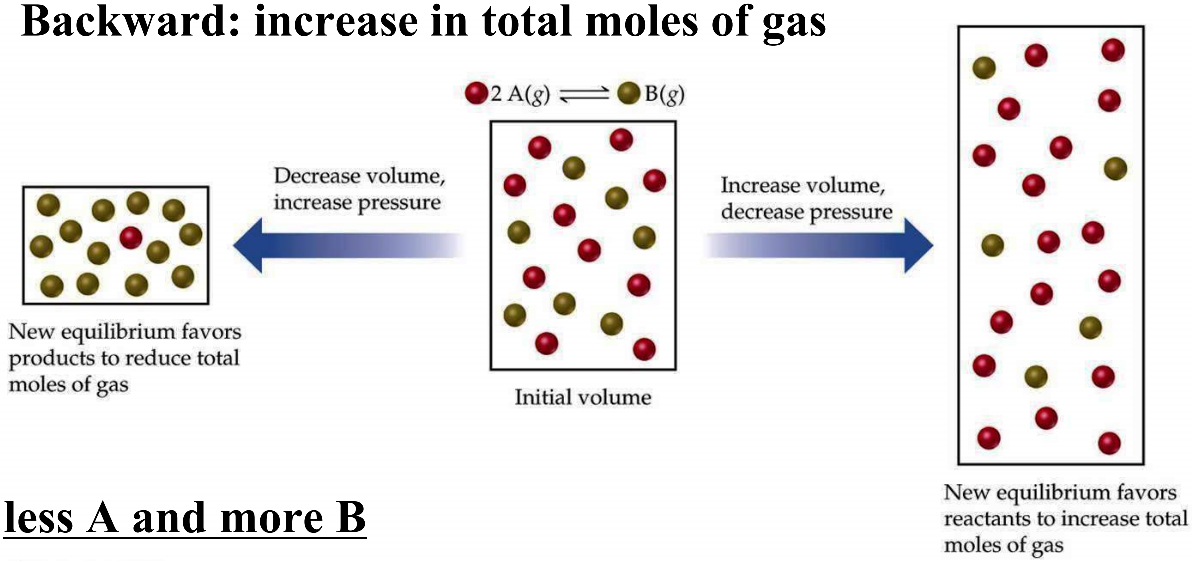
Colorless **Brown**

- **Reducing the volume at equilibrium makes the reaction mixture become colorless.**

The effect of changes in pressure

Forward: decrease in total moles of gas

Backward: increase in total moles of gas



<u>less A and more B</u>

<u>more A and less B</u>

The effect of changes in temperature

- **The effect of the temperature change to an equilibrium mixture depends on the nature of the reaction.**

$$\text{Reactants} \rightleftharpoons \text{Products} + \text{heat}$$

Forward reaction: heat is given out (exothermic).

change in enthalpy (ΔH^o) < 0.

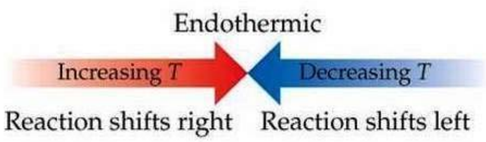
Reverse reaction: heat is absorbed (endothermic).

change in enthalpy (ΔH^o) > 0.

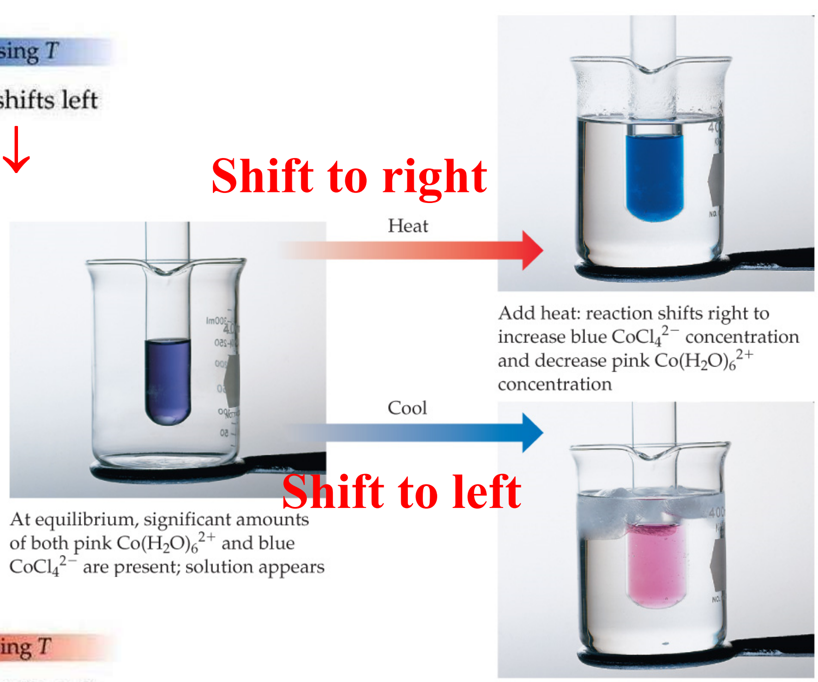
$\Delta H > 0$, endothermic reaction

$$\text{Heat} + Co(H_2O)_6^{2+}(aq) + 4\,Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6\,H_2O(l)$$

Pink Blue



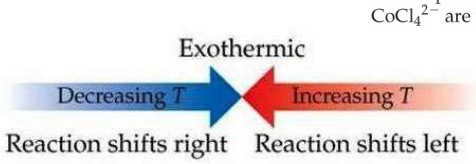
$K\uparrow$ $K\downarrow$



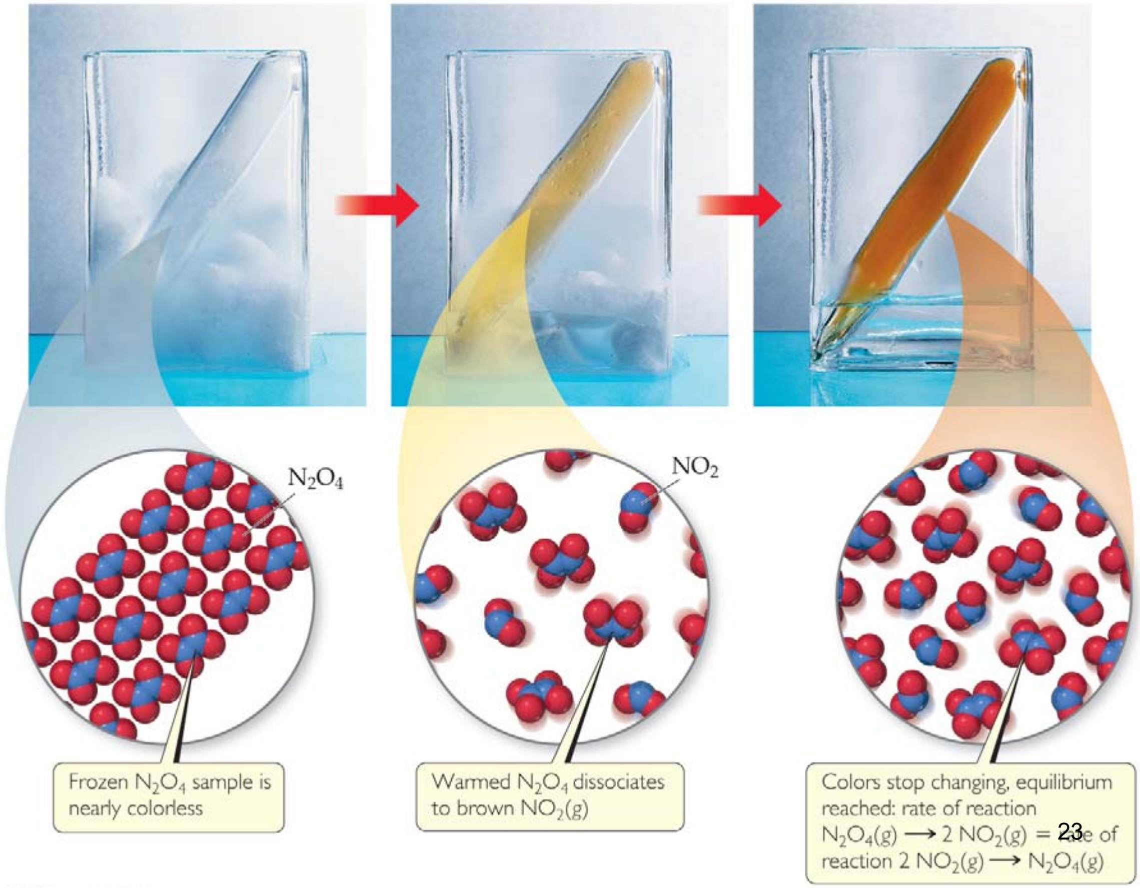
Add heat: reaction shifts right to increase blue $CoCl_4^{2-}$ concentration and decrease pink $Co(H_2O)_6^{2+}$ concentration

At equilibrium, significant amounts of both pink $Co(H_2O)_6^{2+}$ and blue $CoCl_4^{2-}$ are present; solution appears

Remove heat: reaction shifts left to decrease blue $CoCl_4^{2-}$ concentration and increase pink $Co(H_2O)_6^{2+}$ concentration



$K\uparrow$ $K\downarrow$



Exercise: Consider the equilibrium

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g) \qquad \Delta H^o = 58.0\ \text{kJ}$$

Predict in what direction the equilibrium shifts when:

(a) N_2O_4 is added;

(b) NO_2 is removed;

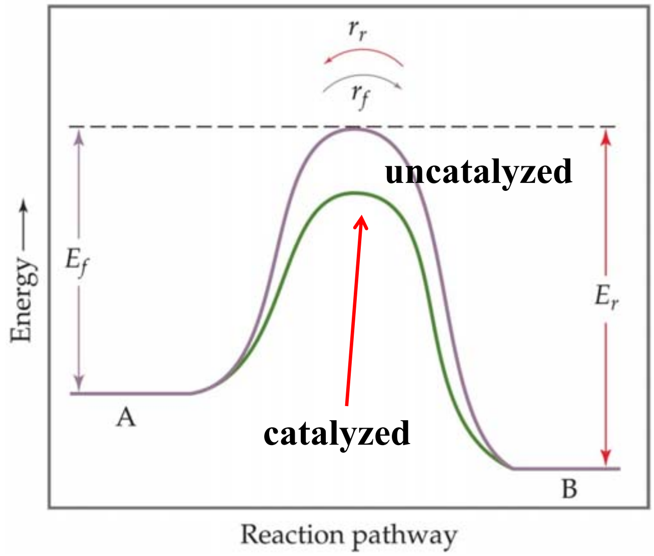
(c) The volume is increased;

(d) Total pressure is increased by addition of N_2;

(e) The temperature is decreased;

The effect of catalyst

- Catalyst speed up a reaction by providing an alternative reaction pathway of lower E_a.
- It lowers the E_a for both the forward *and* reverse reactions to the same extent.



- Catalysts increase the rate of both the forward *and* reverse reactions.
- It allows to reach the equilibrium faster, but the equilibrium composition remains unaltered.