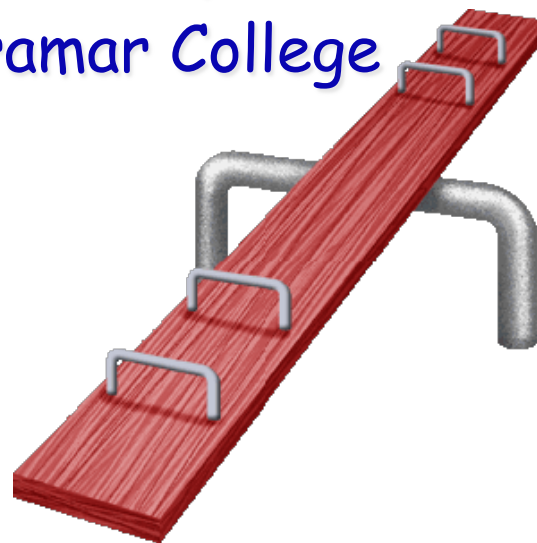


14.1 Dynamic Equilibrium, K_{eq} , and the Mass Action Expression

The Equilibrium Process



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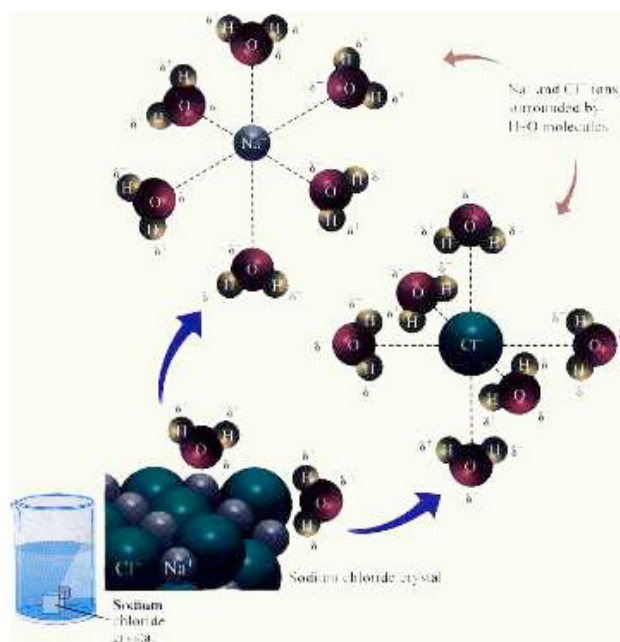
Extent of a Reaction

Chemical Reaction

Most reactions do not occur with 100% conversion to products. At the molecular, when a reaction occurs to form products, some products will back react to form reactants.

The extent of the reaction i.e., 20% or 80% can be determined by measuring concentration of each component in solution

In general the extent of the reaction is a function of the following:



Temperature, concentration and degree of **organization**, all of which are monitored by some constant value called the -
The equilibrium constant, K_{eq}

How Equilibrium is achieved

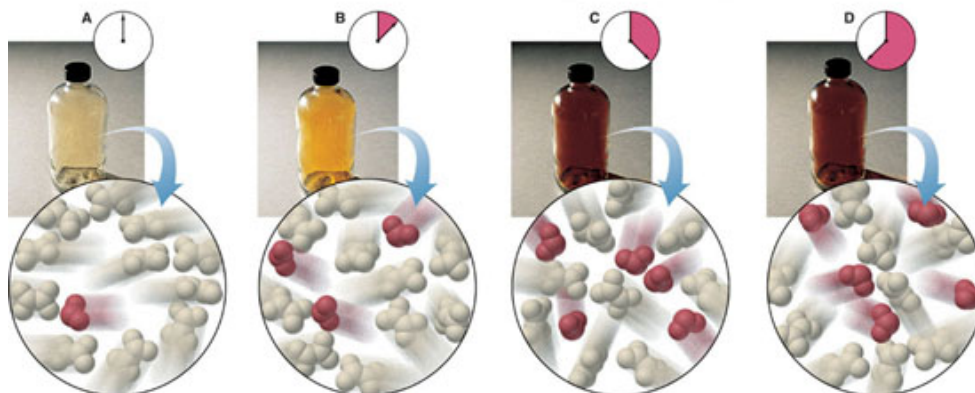
Consider the reaction $A \rightleftharpoons B$

Forward $A \rightarrow B$ $\text{rate}_f = k_f[A]$

Reverse $B \leftarrow A$ $\text{rate}_b = k_b[B]$

Overall $A \rightleftharpoons B$ $\text{rate forward } k_f[A] = \text{rate reverse } k_b[B]$

Example: $\text{N}_2\text{O}_4 \rightleftharpoons \text{NO}_2$



Effect of temperature on the $\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ equilibrium. The tubes contain a mixture of NO_2 and N_2O_4 . As predicted by Le Chatelier's principle, the equilibrium favors colorless N_2O_4 at lower temperatures. but shifts to the darker brown NO_2 at higher temperature.

Equilibrium: Mass Action Expression

When equilibrium is established, $A \rightleftharpoons B$

“ \rightleftharpoons ” illustrates that rate forward = rate reverse

$$\text{or } K_f[A] = K_b[B]$$

- Rearranging this equation yields $K_f/K_b = [B] / [A]$ which yields
- **The mass action expression** : $K_{eq} = [B] / [A]$

For any generic chemical process at equilibrium



A mass action expression can be written:

$$K_{eq} = \frac{[P]^p * [Q]^q}{[A]^a * [B]^b}$$

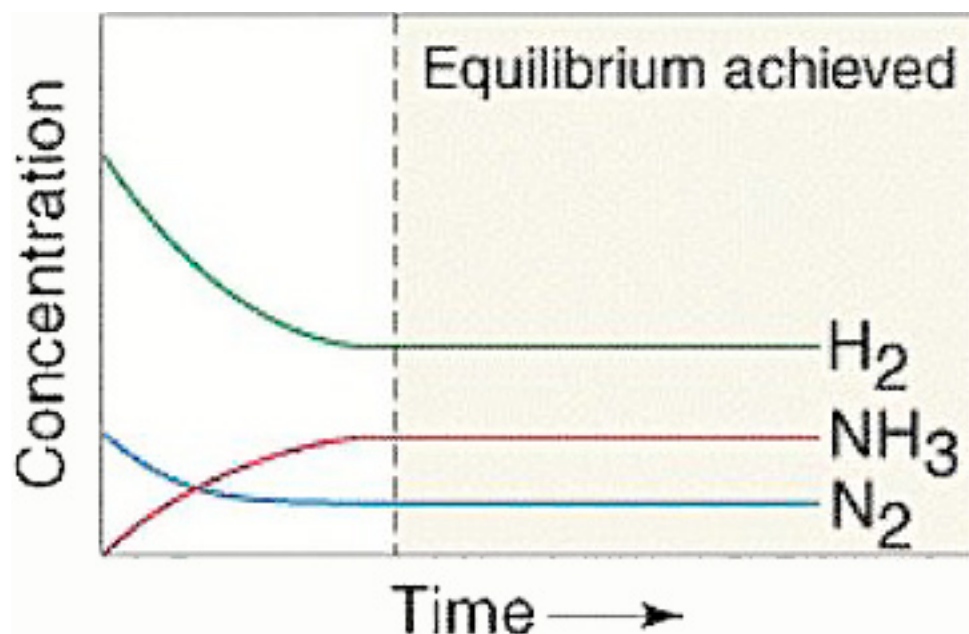
This is also referred to as the **Law of Mass Action**

Haber Process

Consider the Haber Process:



As soon as NH_3 is form, it back reacts and forms N_2 and H_2 .



**Law of Mass Action
Or
Mass Action Expression**

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

Meaning of K_{eq} : Sidebar

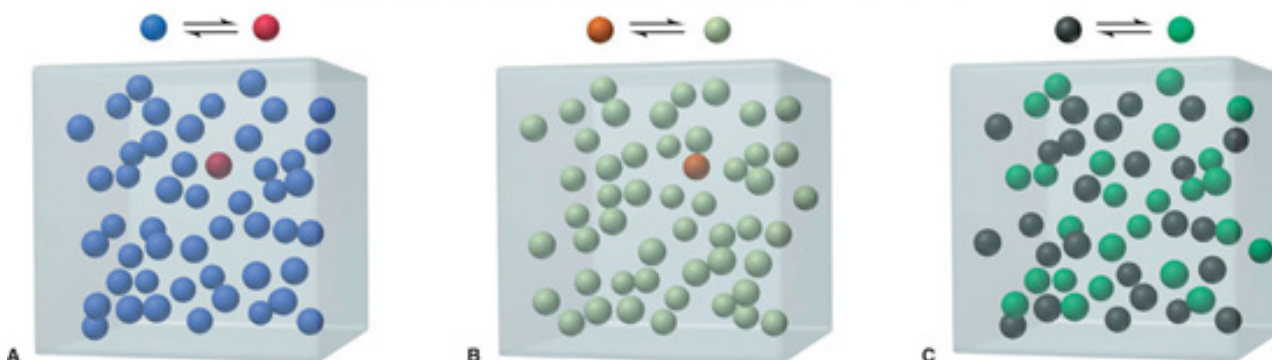
Review of Fractions

$$\frac{x}{y} < 1 \quad : \quad \text{If } x < y$$

$$\frac{x}{y} > 1 \quad : \quad \text{If } x > y$$

$$\frac{x}{y} = 1 \quad : \quad \text{If } x = y$$

- A) For $x < y$, **the denominator dominates.**
- B) For $x > y$, **the numerator dominates.**
- C) For $x = y$, **numerator and denominator are equal.**



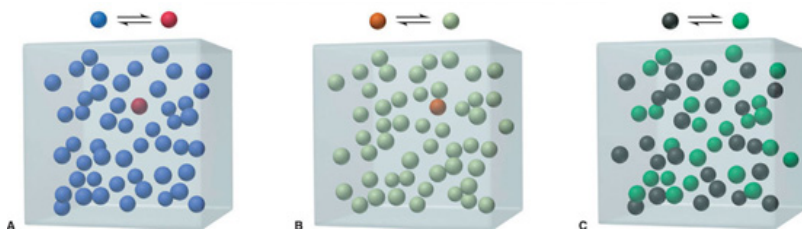
Meaning of K_{eq}

Which is favored, Reactant or Product?

$$K_{eq} = \frac{[P]^p \cdot [Q]^q}{[A]^a \cdot [B]^b} = \frac{[\text{Product}]^x}{[\text{Reactant}]^y}$$

- A) For $K_{eq} < 1$, the ratio $[\text{Product}]^x < [\text{Reactant}]^y$
- B) For $K_{eq} > 1$, the ratio $[\text{Product}]^x > [\text{Reactant}]^y$
- C) For $K_{eq} = 1$, the ratio $[\text{Product}]^x = [\text{Reactant}]^y$

- A) For $K_{eq} < 1$, at equilibrium **Reactant** is favored.
- B) For $K_{eq} > 1$, at equilibrium **Product** is favored.
- C) For $K_{eq} = 1$, at equilibrium **Product and Reactant** are equal.



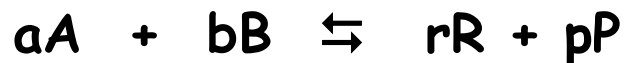
Understanding the Concept

1. What is the distinction between rates and the extent of the reaction?
2. What does the term dynamic equilibrium mean physically and at the atomic level?
3. What does the magnitude of K_{eq} mean in terms of the chemical reaction?
4. If there is no change in concentration of reactants and product at equilibrium, why is it considered dynamic?

For Reactions Not at Equilibrium

For reactions not yet at equilibrium, the Law of Mass action yield information in terms of the Reaction Quotient.

Consider the following chemical process not at equilibrium.



A reaction quotient expression can be written:

$$Q = \frac{[R]^r [P]^p}{[A]^a [B]^b}$$

Where the numerical value of Q will determine the direction the reaction will proceed.

$Q < K_{eq}$ Reaction shifts to \rightarrow Right

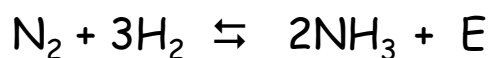
$Q > K_{eq}$ Reaction shifts to \leftarrow Left

LeChatelier's Principle (Preview)

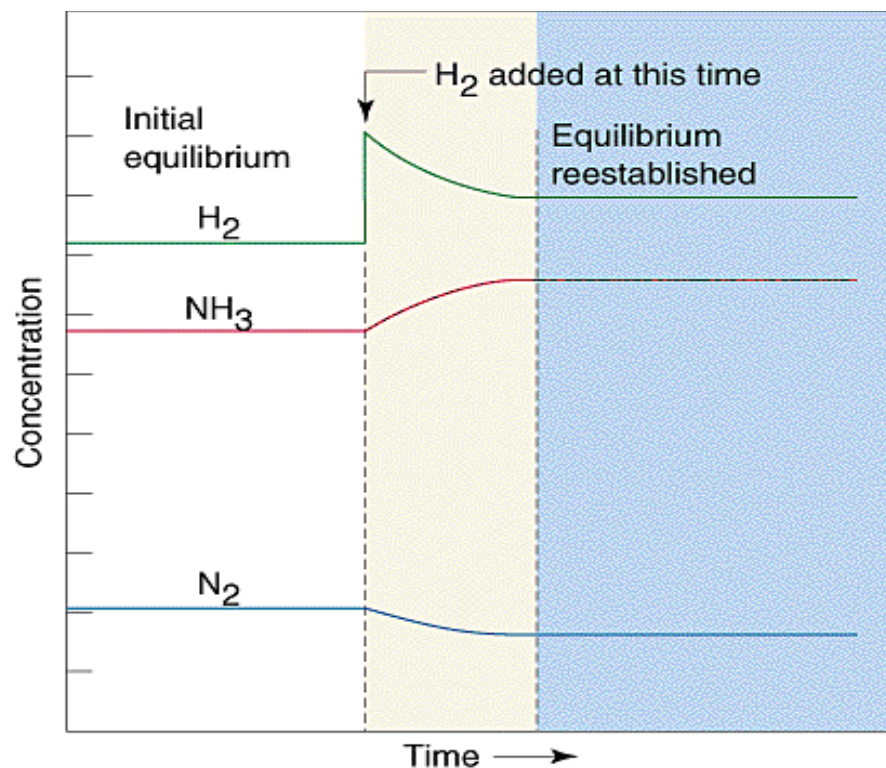
Concentration Effect

If a chemical system is at equilibrium and then a substance is added (either a reactant or product), the reaction will shift so as to re-establish equilibrium by subtracting part of the added substance. Conversely, removal of a substance will result in the reaction moving in the direction that forms more of the substance.

Consider the Haber reaction that was discussed earlier.



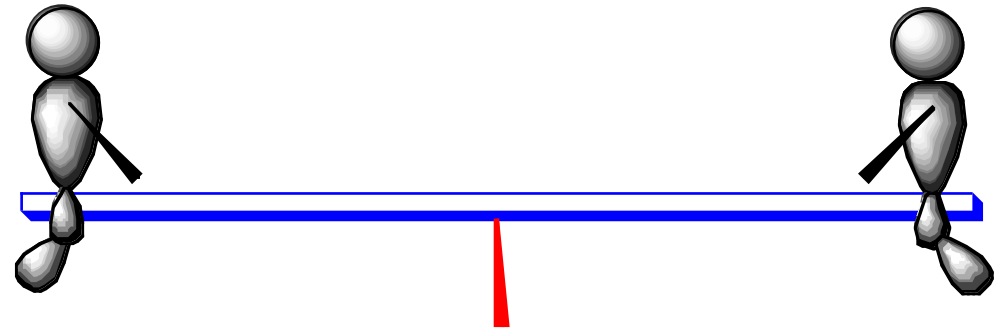
If some H_2 is added to the reaction which was at equilibrium, the system self-adjust to remove the excess H_2 by converting it to NH_3 until equilibrium is re-established; in the process some N_2 is also consumed.



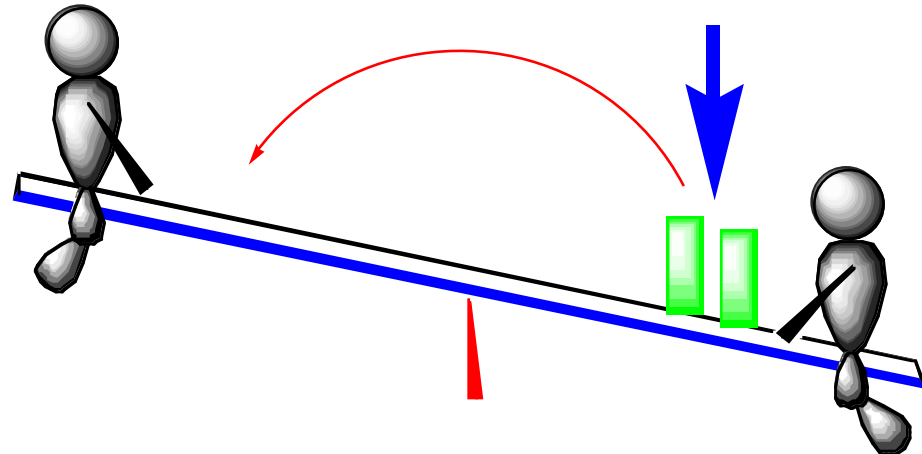
Pictorial View of LeChatelier

Teeter-Totter

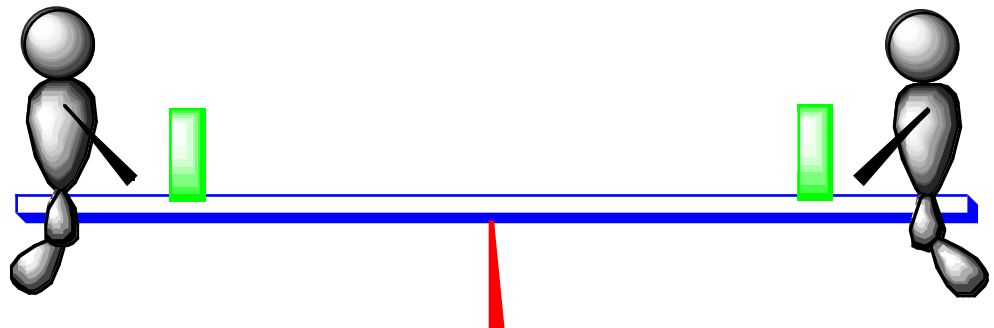
At Equilibrium



Stress applied
Self Adjust



Re-establish
Equilibrium



K_{eq} and the Q

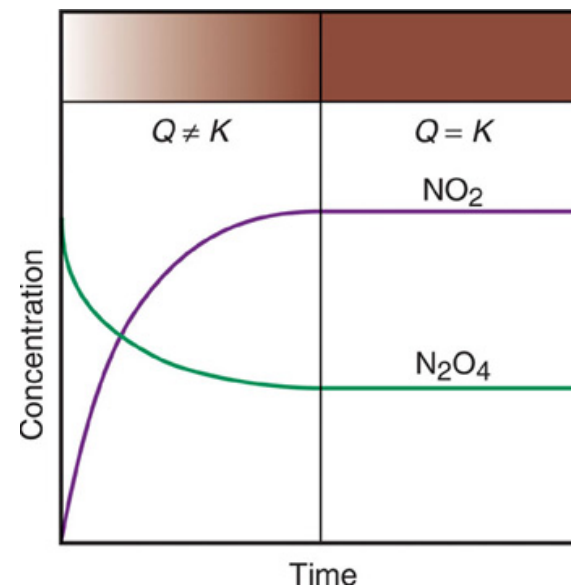
The change in Q during a reaction and its relation to K_{eq} :

Consider the reaction: $N_2O_4 \rightleftharpoons 2 NO_2$

Initial and Equilibrium Concentration Ratios for the N_2O_4 - NO_2 System at $100^\circ C$

Exp't	Initial		Ratio (Q)	Equilibrium		Ratio (K)
	$[N_2O_4]$	$[NO_2]$	$[NO_2]^2/[N_2O_4]$	$[N_2O_4]_{eq}$	$[NO_2]_{eq}$	$[NO_2]_{eq}^2/[N_2O_4]_{eq}$
1	0.1000	0.0000	0.0000	0.0491	0.1018	0.211
2	0.0000	0.1000	∞	0.0185	0.0627	0.212
3	0.0500	0.0500	0.0500	0.0332	0.0837	0.211
4	0.0750	0.0250	0.00833	0.0411	0.0930	0.210

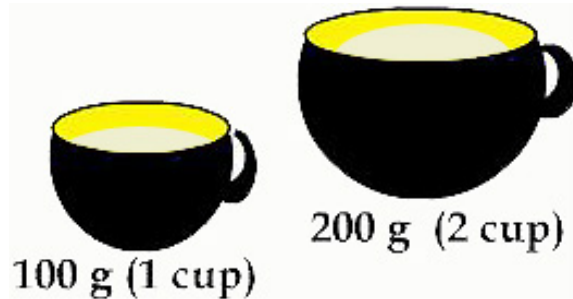
The reaction coordinate diagram shows how the concentration of N_2O_4 and NO_2 changes as the reaction approaches equilibrium. This is also reflected in Q . As the reaction proceeds to the right, N_2O_4 to NO_2 , the Q value increases, N_2O_4 becomes smaller and NO_2 becomes larger. The reaction finally reaches equilibrium at t_{eq} , at which time the concentration of N_2O_4 and NO_2 remains constant. Equilibrium is reached and the reaction quotient becomes equal to the equilibrium constant. $Q = K_{eq}$.



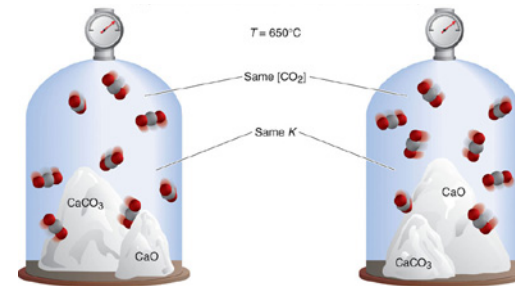
Heterogeneous Systems

The equilibrium of substances with different phases.

i.e., solid and aqueous coexisting -
Which solid is more concentrated?



Solid and gas coexisting -
Which solid is more concentrated?



Concentration of a solid is always a Constant;

Even though the two containers contain different amounts of solid solute, as long as both solids are present at a given temperature, A) the concentration of the solution is the same, B) the partial pressure of the gas is the same.

Concentration of solid remains the same (constant) !

The solid component is not taken into account in the Mass Action expression or the Reaction Quotient.

Heterogeneous Systems CaCO_3

Consider the following reaction:

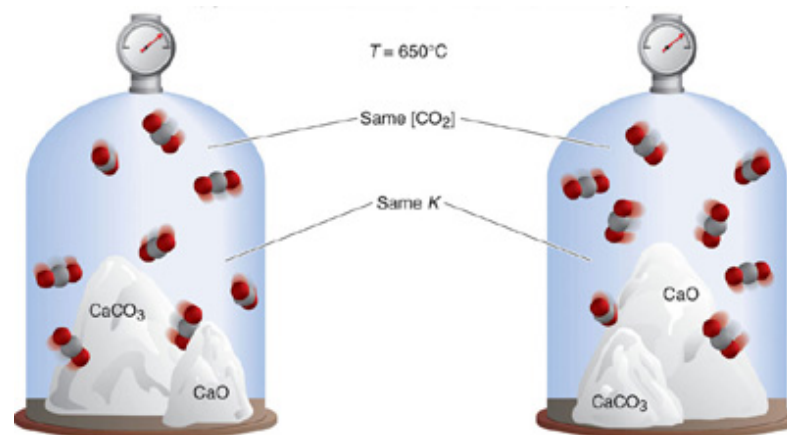


$$k_{\text{eq}} = \frac{[\text{CaO}] * [\text{CO}_2]}{[\text{CaCO}_3]}$$

but, $[\text{CaO}]$ and $[\text{CaCO}_3] = \text{Constant}$

$$k_{\text{eq}} = \frac{[\text{Constant}_1] * [\text{CO}_2]}{[\text{Constant}_2]}$$

$$k_{\text{eq}} = [\text{CO}_2]$$



The Mass Action Expression for a heterogeneous system need not take into account the concentration of the solid. Even though the two containers have different amount of solids (CaCO_3 and CaO), as long as both solids are present at the same temperature, the partial pressure of CO_2 is the same at equilibrium.

In Class exercise

The reaction is in a 10.0 L vessel. The initial concentration of $[H_2]$ is 12.0 molar and that of $[N_2]$ is 4.0 molar.

i) Sketch the change of the concentration of N_2 from 0 to 3.5 min. $T = 200\text{ K}$

ii) At 2 minutes, Q is: a) increasing b) decreasing c) not changing d) cannot be determine

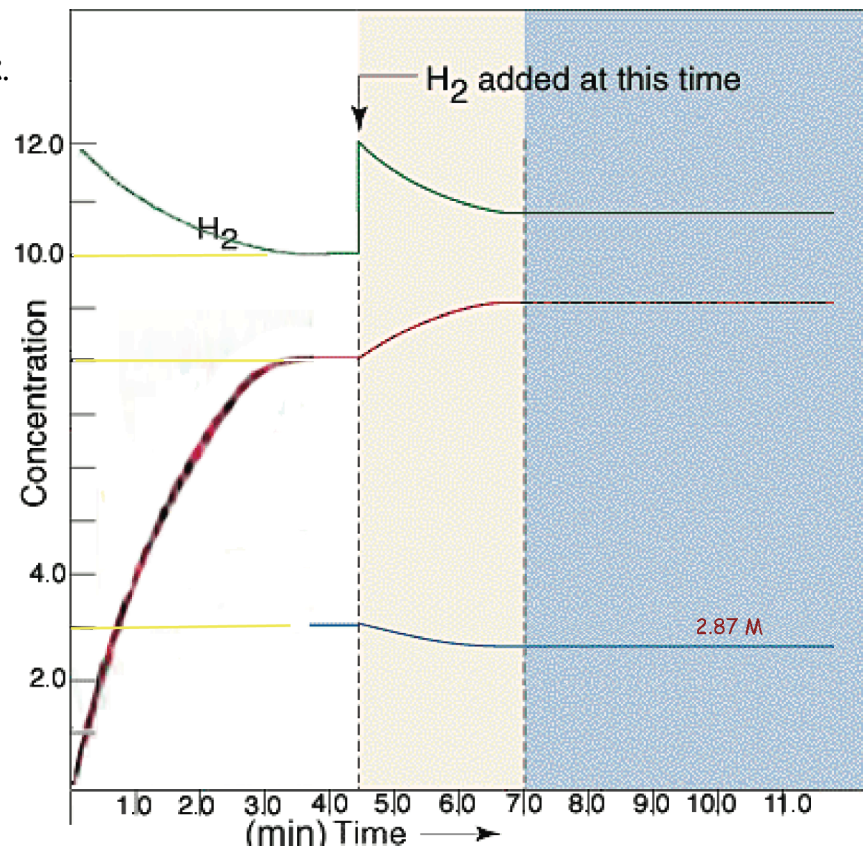
iii) At 5 minutes, Q is: a) increasing b) decreasing c) not changing d) cannot be determine

iv) Calculate the equilibrium constant at the 4.0-minute mark.

$$2.1 \cdot 10^{-2} \text{ M}^{-2}$$

v) Calculate the equilibrium constant at the 8.0-minute mark.

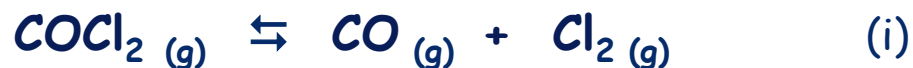
$$2.1 \cdot 10^{-2} \text{ M}^{-2}$$



K_{eq} as a Function of the Written Reaction

What is the equilibrium constant if a reaction is written in the reverse direction?

Consider,



and the reverse reaction



What is the relationship of K_{eq} between both reaction (i) & (ii)?

$$K_{eq}(\text{i}) = \frac{[\text{CO}] [\text{Cl}_2]}{[\text{COCl}_2]}$$

$$K_{eq}(\text{ii}) = \frac{[\text{COCl}_2]}{[\text{CO}] [\text{Cl}_2]}$$

hence

$$\frac{[\text{CO}] [\text{Cl}_2]}{[\text{COCl}_2]} = \left[\frac{[\text{COCl}_2]}{[\text{CO}] [\text{Cl}_2]} \right]^{-1}$$

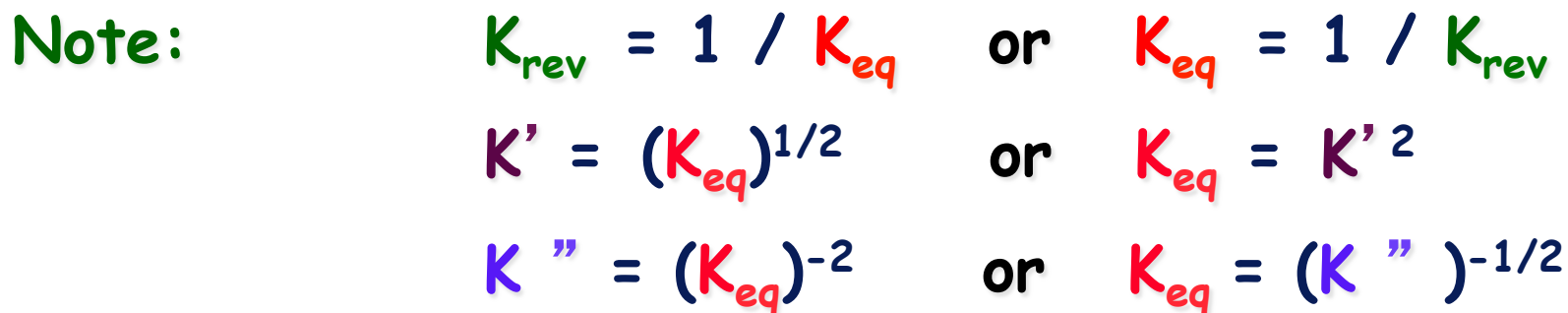
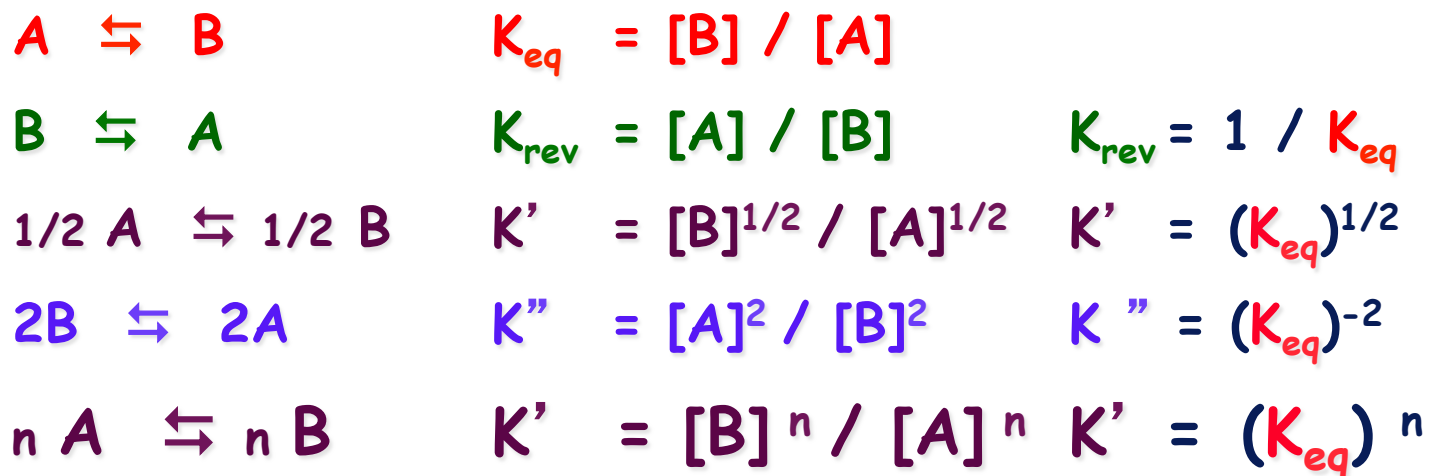
Inverse relationship -

$$K_{eq}(\text{i}) = K_{eq}(\text{ii})^{-1}$$

$$K_{\text{forward}} = \frac{1}{K_{\text{reverse}}}$$

Effects of K_{eq} and Variation of a Chem Equation

Consider the variation of a chemical reaction:



Expressing Q and Calculating K

The relationship of the Mass Expression, K_{eq} , can be extended to the Reaction Quotient, Q:

Ways of Expressing Q and Calculating K

Form of Chemical Equation	Form of Q	Value of K
Reference reaction: $A \rightleftharpoons B$	$Q_{(ref)} = \frac{[B]}{[A]}$	$K_{(ref)} = \frac{[B]_{eq}}{[A]_{eq}}$
Reverse reaction: $B \rightleftharpoons A$	$Q = \frac{1}{Q_{(ref)}} = \frac{[A]}{[B]}$	$K = \frac{1}{K_{(ref)}}$
Reaction as sum of two steps: (1) $A \rightleftharpoons C$ (2) $C \rightleftharpoons B$	$Q_1 = \frac{[C]}{[A]}$; $Q_2 = \frac{[B]}{[C]}$ $Q_{overall} = Q_1 \times Q_2 = Q_{(ref)}$ $= \frac{\cancel{[C]}}{[A]} \times \frac{[B]}{\cancel{[C]}} = \frac{[B]}{[A]}$	$K_{overall} = K_1 \times K_2$ $= K_{(ref)}$
Coefficients multiplied by n	$Q = Q_{(ref)}^n$	$K = K_{(ref)}^n$
Reaction with pure solid or liquid component, such as $A(s)$	$Q = Q_{(ref)}[A] = [B]$	$K = K_{(ref)}[A] = [B]$

Example 2: K_{eq} relationship

Consider the following equilibrium, at 480 °C:



a) What is the value of K_p for: $4\text{HCl}_{(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{Cl}_{2(g)} + 2\text{H}_2\text{O}_{(g)}$

b) What is the value of K_p : $\text{Cl}_{2(g)} + \text{H}_2\text{O}_{(g)} \rightleftharpoons 2\text{HCl}_{(g)} + 1/2 \text{O}_{2(g)}$

c) What is the value of K_c : $2\text{Cl}_{2(g)} + 2\text{H}_2\text{O}_{(g)} \rightleftharpoons 4\text{HCl}_{(g)} + \text{O}_{2(g)}$

(To be discussed later)

-
- a) This equation is the reverse of the original
 - b) This equation is half the original
 - c) This equation will be solve in the next series of slides.

Relationship Between K_c and K_p

Consider the Reaction:



$$K_p = \frac{(p_{\text{CO}}) * (p_{\text{Cl}_2})}{(p_{\text{COCl}_2})} \quad \text{or} \quad K_c = \frac{[\text{CO}] [\text{Cl}_2]}{[\text{COCl}_2]}$$

It can be shown that:

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

[RT is positive exponent (+ Δn)]

$$\text{where } \Delta n = \sum (\text{gas moles})_{\text{product}} - \sum (\text{gas moles})_{\text{reactant}}$$

Derivation K_c and K_p relationship

$$k_p = \frac{[{}_p\text{CO}] * [{}_p\text{Cl}_2]}{[{}_p\text{COCl}_2]} \quad \text{and} \quad k_c = \frac{[\text{CO}] * [\text{Cl}_2]}{[\text{COCl}_2]}$$

but $PV = nRT$

$$\text{therefore } P = \frac{nRT}{V} = \frac{n}{V}RT = [\text{conc}] * RT$$

$$k_p = \frac{[{}_p\text{CO}] * [{}_p\text{Cl}_2]}{[{}_p\text{COCl}_2]} = \frac{\{[\text{CO}] \cdot RT\} * \{[\text{Cl}_2] * RT\}}{\{[\text{COCl}_2] * RT\}}$$

$$k_p = \frac{[\text{CO}] * [\text{Cl}_2]}{[\text{COCl}_2]} * \frac{RT * RT}{RT} = \frac{[\text{CO}] * [\text{Cl}_2]}{[\text{COCl}_2]} * \frac{RT}{1}$$

$$k_p = \frac{[\text{CO}] * [\text{Cl}_2]}{[\text{COCl}_2]} * RT^{+1} = k_c * RT^{+\Delta n}$$

$$\therefore k_p = k_c * RT^{+\Delta n} \quad \text{and} \quad k_c = k_p * RT^{-\Delta n}$$

where $\Delta n = \sum(\text{gas moles})_{\text{product}} - \sum(\text{gas moles})_{\text{reactant}}$

Summary: Equilibrium constant

- The mass action expression is equal to the equilibrium constant.
- The equilibrium constant value is generally written without units.
- The equilibrium expression for a reaction is the reciprocal of that reaction when it is written in the reverse direction.
- When the balanced equation for a reaction is multiplied by a factor n , the equilibrium expression for the factored reaction is the original expression raised to the n th power.



The equilibrium constant expressed in terms of concentration, K_c , is related to the equilibrium constant expressed in terms of partial pressure, K_p , by the amount of gas moles changes during the course of the reaction.