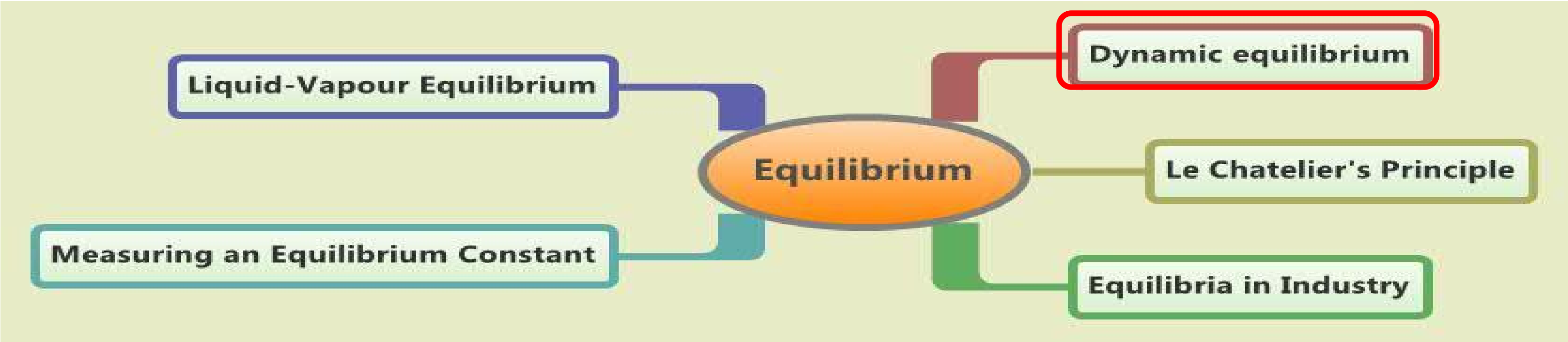
Equilibrium

Ms. Peace

Lesson 1

Dynamic Equilibrium

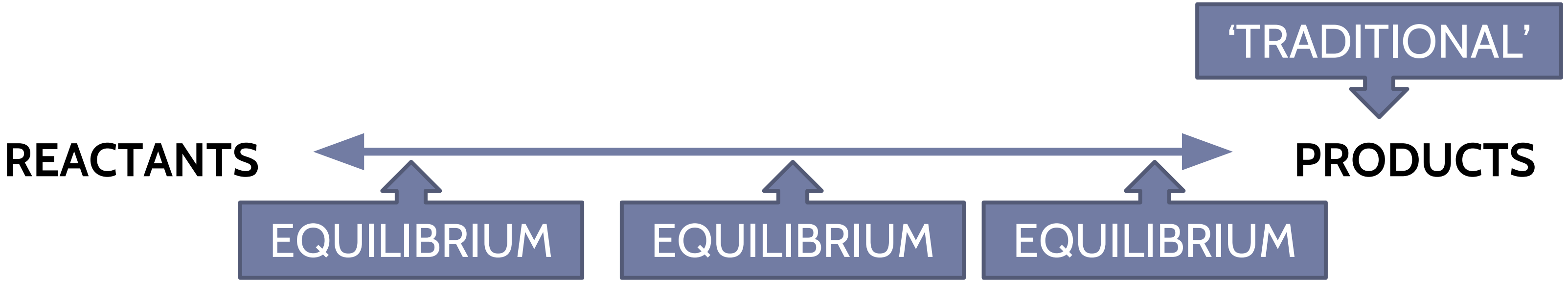
We Are Here



Main

Equilibrium

- In a ‘traditional’ reaction, all the reactants get turned into products (assuming no excess)
- A state of equilibrium is reached when the rates of the forward and reverse reactions are equal



Main

Writing Equilibrium Equations

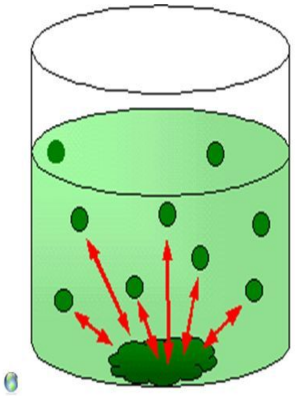
- Equilibrium reactions are written using a double arrow
  - Each of the arrows only has a single-sided head

$$\text{REACTANTS} \rightleftharpoons \text{PRODUCTS}$$

- The unit will make a lot of reference to the rate of the:
  - '**forward reaction**' (reactants becoming products)
  - '**back reaction**' (products becoming reactants)

Equilibrium and Solubility

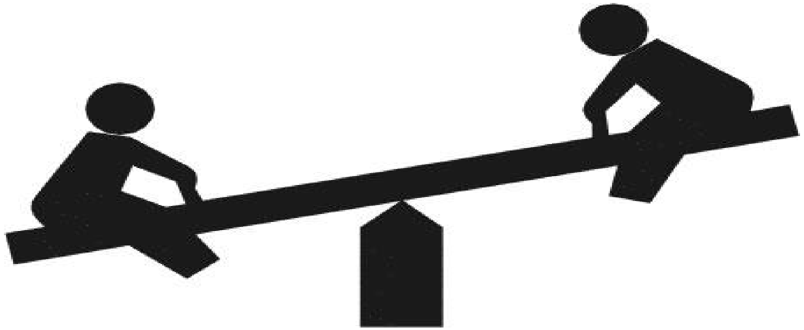
- A saturated solution in a closed system will establish a dynamic equilibrium if there is excess solid present
- The concentration of ions present in the aqueous solution will increase
- Some aqueous ions will recombine and precipitate out of solution
- When the solution becomes saturated, the rate of dissolving will equal the rate of precipitation



$$C_6H_{12}O_{6(s)} \rightleftharpoons C_6H_{12}O_{6(aq)}$$

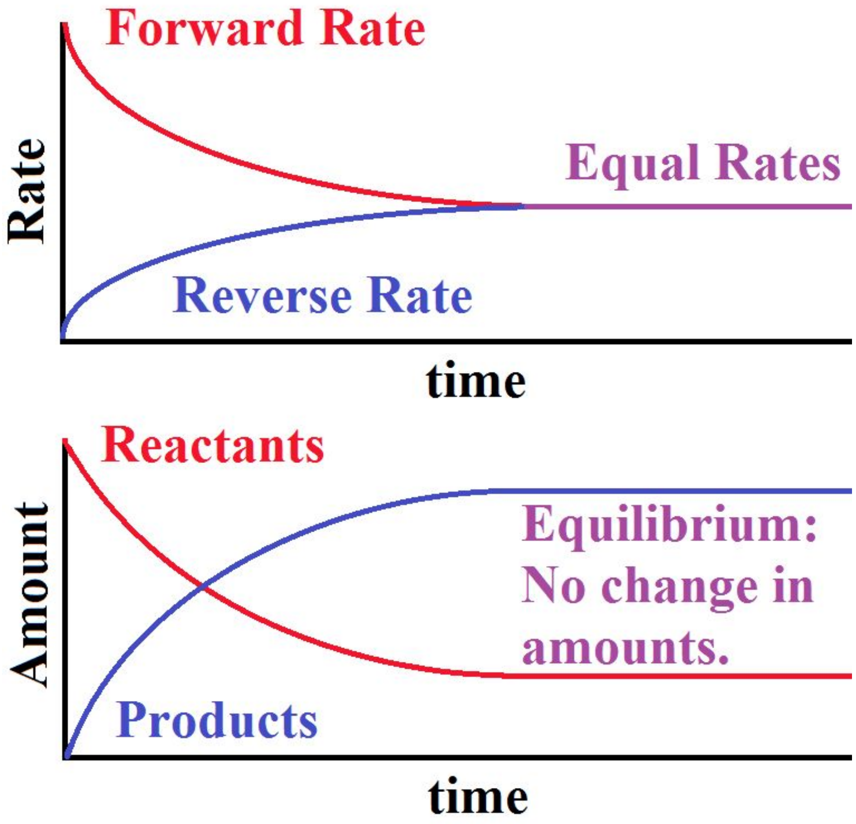
Dynamic Equilibrium

- The reaction hasn't stopped, it is still going, but the rate of the forward and back reactions are equal, so there is no overall change.



Dynamic Equilibrium

- The <u>concentration</u> of reactants and products is <u>constant</u>
  - They are NOT equal to each other
  - They are just not changing
- The rate of the forward reaction is equal to the rate of the back reaction
  - At equilibrium these are not zero…even though it looks like it on the graph



Main

Characteristics of Equilibrium

1. Properties are **constant** at equilibrium (no color change or change in density)
2. The rate of the forward reaction is **equal** to the rate of the reverse reaction
3. There is no change in concentration of reactants and products
4. Equilibrium can only be obtained in a **closed system**
5. All species in the chemical equation are present in the equilibrium reaction mixture
6. Equilibrium can be obtained from either direction
7. Changes such as temperature, pressure, or concentration of reactants or products can affect the equilibrium

Videos

Dynamic Equilibrium

Bailing Beakers

The Equilibrium Law

- The equilibrium constant describes where the position of equilibrium lies at a given temperature
- Can be used to maximize the yield of products and the profitability of industry
- The Law of Chemical Equilibrium states that at a given temperature the ratio of the concentration of products to the concentration of reactants is constant

Equilibrium Constant

$$K_c = \frac{[Products]}{[Reactants]}$$

$$wA + xB \rightleftharpoons yC + zD$$

$$K_c = \frac{[C]^y [D]^z}{[A]^w [B]^x}$$

Changes in Reaction Equation

Change in Reaction Equation	Equilibrium Constant Expression	Equilibrium Constant
Reverse the reaction	Inverse of the expression	$\frac{1}{K_c}$
Halve the coefficients	Square root of the expression	$\sqrt{K_c}$
Double the coefficients	Square the expression	K_c^2
Sum equations	Product of the expressions	$K_c = K_{c1} \times K_{c2}$

Magnitude of the Equilibrium Constant

- If K_c is large, $K_c >> 1$, at any given temperature, products are favored over reactants

- If K_c is small, $K_c << 1$, at any given temperature, the reaction is unfavorable

Writing Equilibrium Constant Expressions

- For an aqueous reaction the concentration of the solvent water does not appear in the equilibrium constant expression

- For a non-aqueous solution, water must be included in the equilibrium constant expression

Reaction Quotient

- If a system has not reached equilibrium, the ratio of concentration of product to reactants will not equal K_c
- The ratio is the reaction quotient, Q, and it helps you to determine the progress of the reaction

  as it moves toward equilibrium

  and the direction of the

  reaction that is favored

$$aA + bB \rightleftharpoons cC + dD$$

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

Main

K_c and Q

$Q>K_c$	The concentration of products is greater than at equilibrium and the reverse reaction is favored until equilibrium is reached
$Q<K_c$	The concentration of reactants is greater than at equilibrium and the forward reaction is favored until equilibrium is reached
$Q=K_c$	The system is at equilibrium and the forward and reverse reactions occur at equal rates

Lesson 2

Le Chatelier’s Principle

Main

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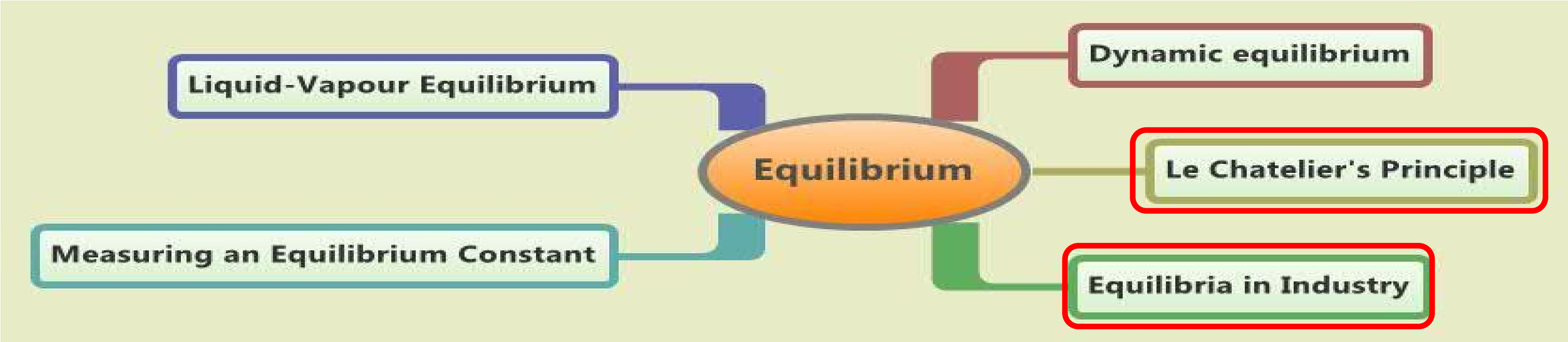


Liquid-Vapour Equilibrium
Dynamic equilibrium
Equilibrium
Le Chatelier's Principle
Measuring an Equilibrium Constant
Equilibria in Industry

Le Châtelier's Principle

- Useful tool for predicting the effect that changing conditions will have on the equilibrium position
- *"If a change is made to a system that is in equilibrium, the balance between forward and reverse reactions will shift to offset this change and return the system to equilibrium."*
- Applies to:
  - Concentration
  - Pressure
  - Temperature

Changes in Concentration

- Decrease in [Reactant] or increase in [Product]
  - Equilibrium shifts to the left
  - This has the effect of increasing [Reactant] and decreasing [Product]

- Increase in [Reactant] or decrease in [Product]
  - Equilibrium shifts to the right
  - This has the effect of decreasing [Reactant] and increasing [Product]

- **Equilibrium constant is not affected**

Changes in Pressure

- Increasing Pressure:
  - Shifts equilibrium to the side with fewest gas molecules
  - This has the effect of reducing the pressure increase
- Decreasing Pressure:
  - Shifts equilibrium to the side with more gas molecules
  - This has the effect of increasing the pressure

- Increase in pressure, decrease in volume and vice versa
- **Equilibrium constant is not affected**

Changes in Temperature

Type of Reaction	Change in Temperature	Equilibrium Position	Equilibrium Constant, K_c
Exothermic	Increase	Moves to the left, favoring reactants	Decreases
	Decrease	Moves to the right, favoring products	Increases
Endothermic	Increase	Moves to the right, favoring products	Increases
	Decrease	Moves to the left, favoring reactants	Decreases

Catalysts

- Catalysts provide alternative pathways for a reaction
- In a forward reaction, a catalyst provides sufficient energy to overcome the activation energy barrier and become products
- In a reversible reaction, the lower activation energy has the same effect on both the forward and reverse reactions

- **The position of the equilibrium will not change**
- **Equilibrium constant is not affected**

Main

How is equilibrium around us?

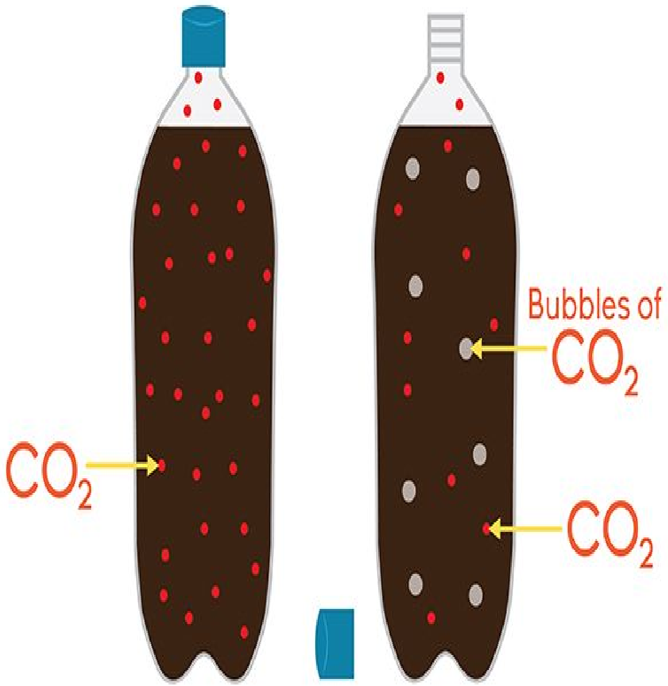
$CO_2(aq) \rightleftharpoons CO_2(g)$

When you open the can, you no longer have a closed system.
The CO_2 molecules are free to escape into the atmosphere.

This decreases the number of molecules returning to the solution.The system is no longer at equilibrium.

You are decreasing the concentration of the product.
According to Le Châtelier's Principle, the system responds by trying to replace the molecules that have escaped.
These molecules then escape into the atmosphere.

The process continues until the pop goes flat.



Haber Process

- An artificial nitrogen fixation process and is the main industrial procedure for the production of ammonia today
- Before the development of the Haber process, ammonia had been difficult to produce on an industrial scale
- Although the Haber process is mainly used to produce fertilizer today, during WWI, it provided Germany with a source of ammonia for the production of explosives

Haber Process

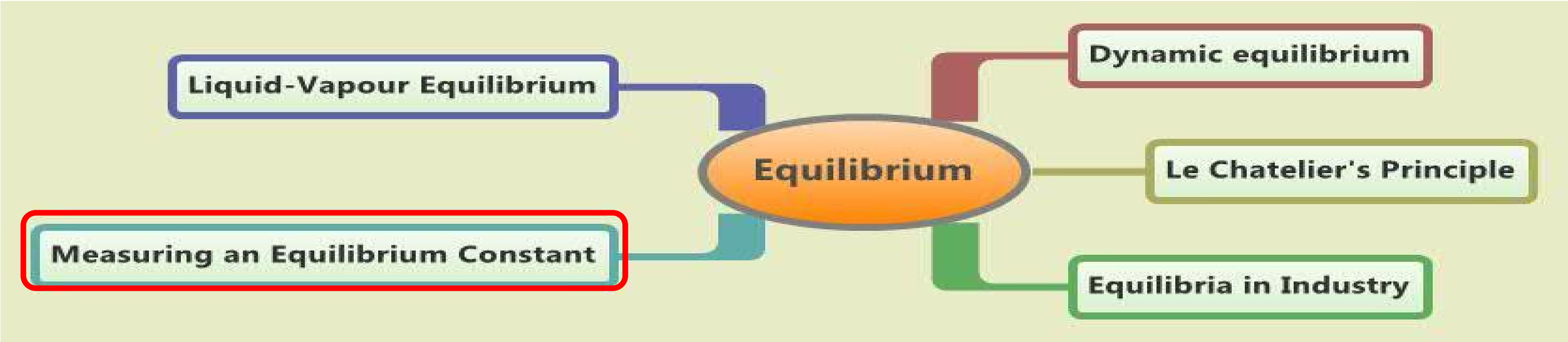
Haber Process

- The Haber process has been described as the most important chemical reaction on Earth as it has revolutionized global food production. However, it also had a large impact on weaponry in both world wars.
- How does the social context of scientific work affect the methods and findings of science? Should scientists be held morally responsible for the applications of their discoveries?

Calculation of equilibrium constants

Main

We Are Here



Main

Homologous Equilibrium Constants

When a mixture of 0.100 mol of NO, 0.051 mol of H_2, and 0.100 mol of H_2O were placed in a 1.0dm^3 flask at 300 K, the following equilibrium was established:

$$2NO(g) + 2H_2(g) \rightleftarrows N_2 + 2H_2O$$

At equilibrium, the concentration of NO was found to be 0.062 mol dm^{-3}. Determine the equilibrium constant, K_c, of the reaction at this temperature

ICE

$$2NO(g) + 2H_2(g) \rightleftarrows N_2 + 2H_2O$$

	$2NO$	$2H_2$	N_2	$2H_2O$
Initial ($mol\ dm^{-3}$)	0.100	0.051	0.00	0.100
Change ($mol\ dm^{-3}$)	-X			
Equilibrium ($mol\ dm^{-3}$)	0.062			

$0.100 - x = 0.062$

$-x = 0.062 - 0.100$

$-x = -0.038$

$x = 0.038$

Main

ICE

$$2NO(g) + 2H_2(g) \rightleftarrows N_2 + 2H_2O$$

	$2NO$	$2H_2$	N_2	$2H_2O$
Initial (mol dm^{-3})	0.100	0.051	0.00	0.100
Change (mol dm^{-3})	-0.038	-0.038	+0.019	+0.038
Equilibrium (mol dm^{-3})	0.062	0.013	0.019	0.138

Homologous Equilibrium Constants

$$2NO(g) + 2H_2(g) \rightleftarrows N_2 + 2H_2O$$

$$K_c = \frac{[N_2][H_2O]^2}{[NO]^2[H_2]^2} = \frac{[0.019][0.138]^2}{[0.062]^2[0.013]^2}$$

$K_c = 5.6 \times 10^2$

IB does not require units for K_c

Calculating Equilibrium Concentrations

The K_c for the following reaction is 6.78 at a certain temperature. The initial concentrations of NO and SO_3 were both 0.0300 mol dm^{-3}. Calculate the equilibrium concentration of each reactant and product.

$$SO_3(g) + NO(g) \rightleftarrows NO_2(g) + SO_2(g)$$

Calculating Equilibrium Concentrations

$$SO_3(g) + NO(g) \rightleftarrows NO_2(g) + SO_2(g)$$

	SO_3	NO	NO_2	SO_2
Initial (mol dm^{-3})	0.0300	0.0300	0.00	0.00
Change (mol dm^{-3})	-x	-x	+x	+x
Equilibrium (mol dm^{-3})	0.0300-x	0.0300-x	x	x

Calculating Equilibrium Concentrations

$$SO_3(g) + NO(g) \rightleftarrows NO_2(g) + SO_2(g)$$

$$K_c = \frac{[NO_2]\,[SO_2]}{[SO_3]\,[NO]} = \quad 6.78 = \frac{(x)\,(x)}{(0.0300-x)(0.0300-x)}$$

$$6.78 = \frac{(x)^2}{(0.0300-x)^2}$$

Calculating Equilibrium Concentrations

Take the square root of both sides:

$$2.60 = \frac{x}{0.0300 - x}$$

Solve for x:

$0.078 - 2.60x = x$

$0.078 = 3.60x$

$x = 0.0217$

Calculating Equilibrium Concentrations

$$SO_3(g) + NO(g) \rightleftarrows NO_2(g) + SO_2(g)$$

	SO_3	NO	NO_2	SO_2
Initial (mol dm^{-3})	0.0300	0.0300	0.00	0.00
Change (mol dm^{-3})	-.0.0217	-0.0217	+0.0217	+0.0217
Equilibrium (mol dm^{-3})	0.00830	0.00830	0.0217	0.0217

I.C.E.

ICE Video

ICE Tables

Gibbs Free Energy

Main

Gibbs Free Energy

- Gibbs free energy describes the spontaneity and temperature dependence of a reaction
- The free energy will change as reactants are converted into products
- The reaction will be spontaneous in the direction that results in a decrease in free energy (or in the direction in which the free energy value becomes more negative)

Gibbs Free Energy

Equilibrium Constant	Description	Gibbs Free Energy Change
K=1	At equilibrium; neither reactants or products favored	$\Delta G = 0$
K>1	Products favored	$\Delta G < 0$ (negative value)
K<1	Reactants favored	$\Delta G > 0$ (positive value)

- A negative ΔG indicates the reaction is spontaneous and the equilibrium concentrations of the products are larger than the equilibrium concentrations of the reactants.

Gibbs Free Energy

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G_{products} - \Delta G_{reactants} = \Delta G$$

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

Example

Consider $H_2 + I_2 \rightleftarrows 2HI$. Given that the value of ΔG at 298K for this reaction is $+1.3kJmol^{-1}$, calculate the value of the equilibrium constant.

$\Delta G = -RT\ln K$
$\Delta G = 1300 Jmol^{-1}$

*R has units of JK^{-1} the value of ΔG must be converted into $Jmol^{-1}$

$1300 = -8.31 \times 298 \times \ln K$

$$\ln K = \frac{-1300}{8.31 \times 298} = -0.525$$

Inverse function for lnx is e^x

$K = e^{-0.525}$
$K = 0.59$

The equilibrium constant is less than 1, which implies that the position of equilibrium lies closer to reactants than products, which is also consistent with value of ΔG being positive