Equilibrium

In the dictionary, equilibrium is often defined as a balance.

In chemistry equilibrium is also a "balance", it is when the forward **reaction rate** is equal to the reverse **reaction rate**.

This introduces two new ideas that we have not considered before

1) Reactions are reversible.

2) Rate laws can be written for both the forward and reverse reaction.

Reversible Reactions

In “real life” most chemical reactions are reversible.

This means that products can recombine to form the original compounds.

The reactions we have studied so far have purposely not included reversible reactions to help keep things less complicated.

$$A + B \rightleftharpoons C + D$$

The arrows going both ways mean that the reaction is reversible. Given enough time, the reaction will reach equilibrium

Equilibrium

Chemical equilibrium ⇨ When the forward and reverse reaction rates are equal.

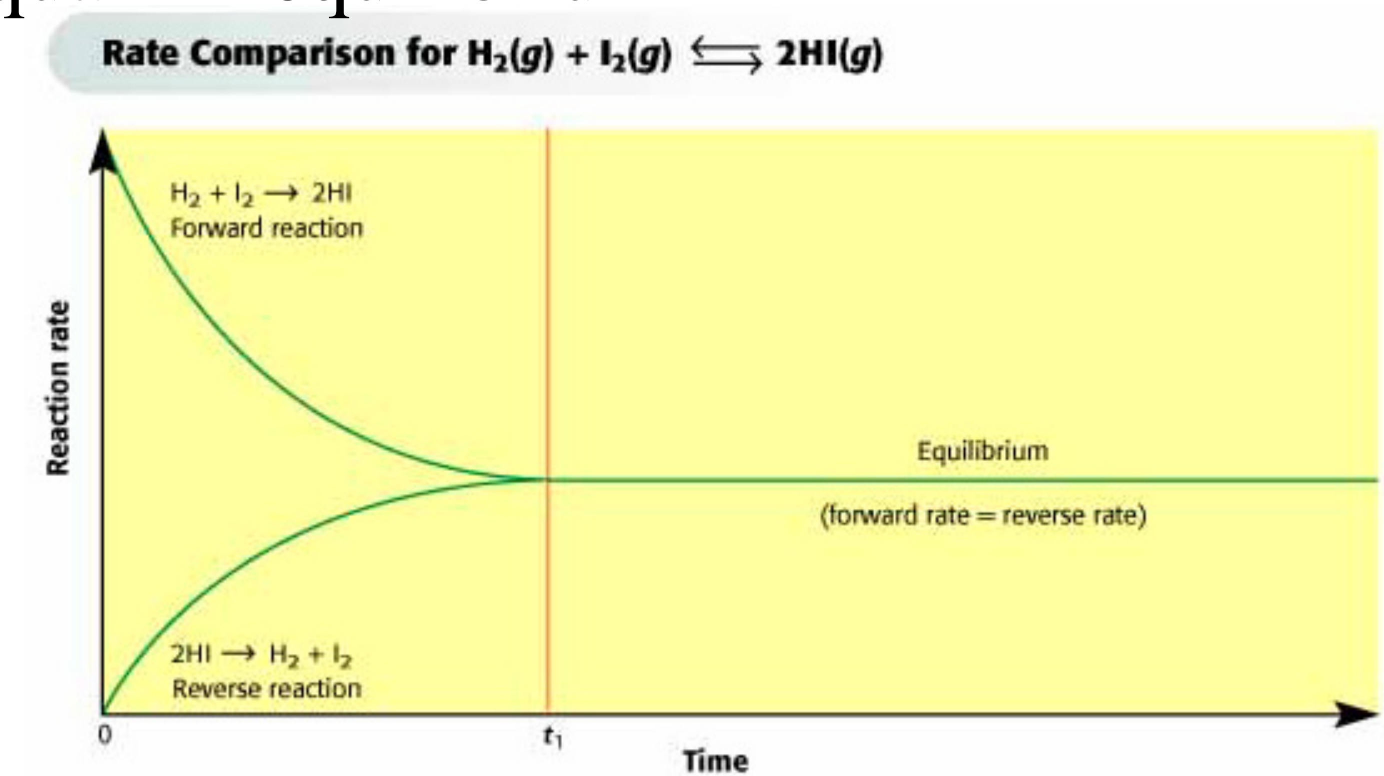
In chemical equilibrium it is the reaction rates that are "balanced", **NOT** the amounts.

As the "forward" reaction proceeds the concentration of the reactants decrease so the forward rate slows down (the rate of the reaction depends on the concentration of the reactants).

As more products are made, the concentration of the products increase so the "reverse" reaction rate increases.

Equilibrium

At some point the forward reaction will slow enough and the reverse reaction speeds up enough that the rates for the forward and reverse reaction are equal ⇨ equilibrium



Equilibrium Expression

It seems extra complicated to write two reaction rate laws for reversible reactions.

Instead we put the two rate laws together into one **equation** we call an equilibrium expression.

In the equilibrium expression the products go on top and the reactants go on the bottom.

The coefficients of the balanced equation become the exponents of the concentrations in the equilibrium expression.

Equilibrium Expression

$$wA_{(aq)} + xB_{(aq)} \leftrightharpoons yC_{(aq)} + zD_{(aq)}$$

The equilibrium expression is

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

You should notice three things

1) The K is uppercase (capital).

2) The products are on top, reactants on the bottom.

3) The coefficients of the equation are exponents.

Equilibrium Expressions

You should also remember that [ ] represent units of molarity.

This means that we are dealing with solution (aq) or gases (g).

Solids and liquids (pure substances) do not have a meaningful molarity (moles/liter)…

Solids and liquids do not change the equilibrium concentrations of other substances…

So solids and liquids **are not included** in the equilibrium expression.

Examples:

$$3H_{2\,(g)} + N_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$$

$$K = \frac{[NH_3]^2}{[H_2]^3\,[N_2]^1}$$

Examples

$$NH_{3\,(g)} + H_2O_{\,(l)} \leftrightharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$K = \frac{[NH_4^+]\,[OH^-]}{[NH_3]}$$

Equilibrium Constant for Water

$H_2O_{(l)} \leftrightharpoons H^+_{(aq)} + OH^-_{(aq)}$

$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$

Equilibrium Calculations

What is the equilibrium constant for the production of ammonia from hydrogen and nitrogen if a 2.00 L container has 2.30 moles of hydrogen, 1.50 moles of nitrogen and 0.522 moles of ammonia at equilibrium? $3H_{2\,(g)} + N_{2\,(g)} \leftrightharpoons 2NH_{3\,(g)}$

$$K = \frac{[NH_3]^2}{[H_2]^3\,[N_2]^1}$$

$$K = 0.0597\ M^{-2}$$

$$K = \frac{[0.522\ \text{moles}/2.00\text{L}]^2}{[2.30\ \text{moles}/2.00\ \text{L}]^3\,[1.50\ \text{moles}/2.00\ \text{L}]^1}$$

LeChatelier's Principle

A system at equilibrium placed under a stress will change to relieve that stress.

Whatever you do to a system in equilibrium it will try to undo.

It works in chemistry just like in economics.

The law of supply and demand ⇨ An equilibrium price occurs when the rate of supply equals the rate of demand.

If the equilibrium is disturbed (change in supply or demand) the price will change until equilibrium is re-established.

LeChatelier's Principle

There are only three things that can happen in response to supply and demand changes (stresses):

The price can go up (creating less demand and more supply),

the price can go down (creating more demand and less supply),

the price can remain constant (the amount of supply or amount of demand has no effect).

LeChatelier's Principle

The same kinds of options are available for chemical equilibrium:

The reaction can produce more products and use up reactants (shift to the right),

the reaction can produce more reactants and use up products (shift to the left),

no change - the reaction is not able to adjust for the stress or the apparent stress does not actually cause a stress on the equilibrium.

LeChatelier's Principle

Typical Stresses:

- Change in temperature
- Change in concentration
- Change in pressure (works only on gases)

Phantom Stresses:

- Adding a catalyst
- Adding or removing a pure substance (solid or liquid)

LeChatelier's Principle

Examples: $3H_{2\,(g)} + N_{2\,(g)} \leftrightharpoons 2NH_{3\,(g)}$ + heat

- Adding nitrogen would shift the reaction to the right.
- Decreasing the pressure would shift the reaction to the left.
- Increasing the temperature would shift the reaction to the left.
- Adding hydrogen would shift the reaction to the right.
- Adding a catalyst would have no effect.

LeChatelier's Principle

$$BaSO_{4\,(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

Adding barium sulfate ⇨ no effect

Adding sulfate ion ⇨ shift left

Increasing the pressure ⇨ no effect

Removing barium ion ⇨ shift right

$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]$

LeChatelier's Principle

Consider the pop you drink

$$\text{heat} + H_2CO_{3\,(aq)} \leftrightharpoons H_2O_{\,(l)} + CO_{2\,(g)}$$

Increase the pressure ⇨ shift left

Increase the temperature ⇨ shift right

Add water ⇨ no effect?

Trick question, adding water also decreases the hydrogen carbonate concentration so the reaction will shift left.

$$K = \frac{[CO_2]^1}{[H_2CO_3]^1}$$