When is chemical equilibrium?

Why do we care?

two examples

What is happening to the acidity of the ocean?

How does ibuprofen work?

Let's look at a reaction

$$CO_2\,(aq) + H_2O(l) \longrightarrow H_2CO_3(aq)$$

what is the product?

A. carbon dioxide

B. water

C. carbonic acid

D. there are no products

Let's look at a reaction

$$CO_2\,(aq) + H_2O(l) \longleftrightarrow H_2CO_3(aq)$$

what is the product?

A. carbon dioxide

B. water

C. carbonic acid

D. there are no products because this reaction is both forward and backwards

Some reactions "go to completion"
the end up with as much product as possible

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

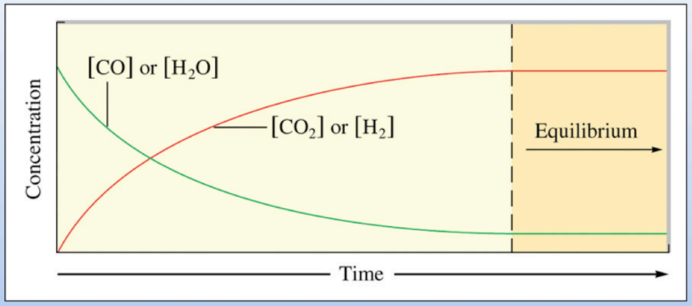
Some reactions "don't happen"
these are ones that go to completion that you have written backwards

$$2H_2O(g) \longrightarrow 2H_2(g) + O_2(g)$$

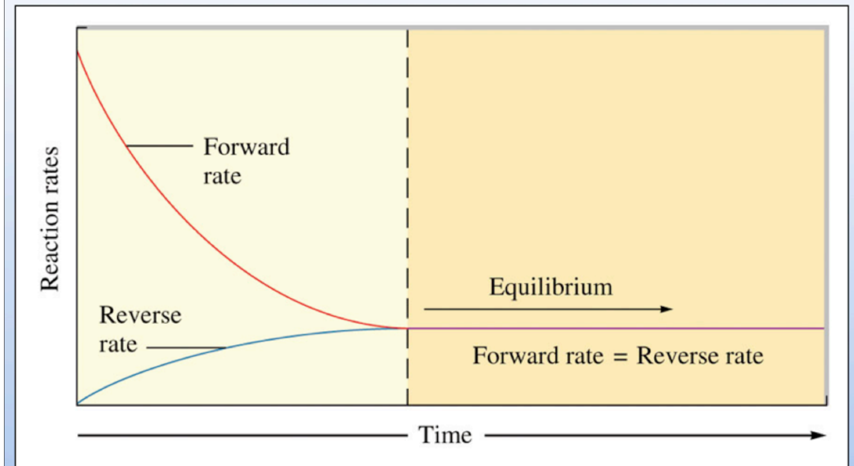
Some end up with both products and reactants
for these we want to know where they "end"
equilibrium

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

$H_2O + CO \longleftrightarrow H_2 + CO_2$



At equilibrium the ratio of the molecules stops changing



Key Idea

At equilibrium the ratio of the products to the reactants is fixed

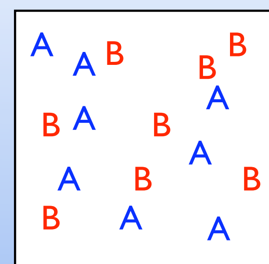
We'll give that "ratio" a name

K

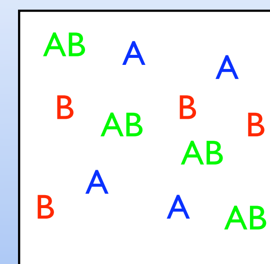
the equilibrium constant
Since it is related to equilibrium
and its a constant

Let's look at a simple reaction

A + B ⟶ AB

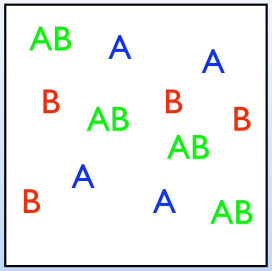


Initially 8 A and 8 B
no AB product



equilibrium 4 A, 4 B,
and 4 AB molecules

Ratio of products to reactants at equilibrium

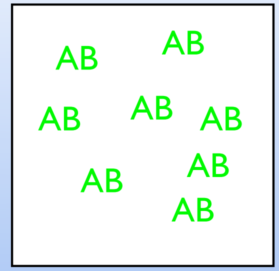


$$K = \frac{\#AB}{\#A \times \#B} = \frac{4}{4 \times 4} = \frac{4}{16} = \frac{1}{4}$$

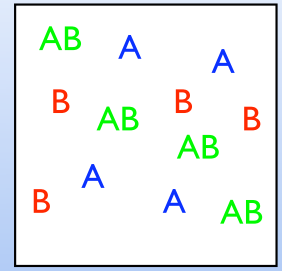
note: I just picked K = 0.25 as an example

Let's start the same reaction with all AB

$$A + B \longrightarrow AB$$

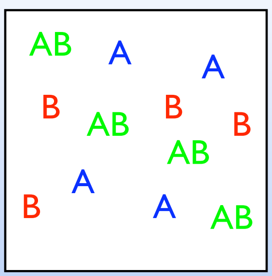


Initially 8 AB and
no A or B



equilibrium 4 A, 4 B,
and 4 AB molecules

Ratio of products to reactants at equilibrium

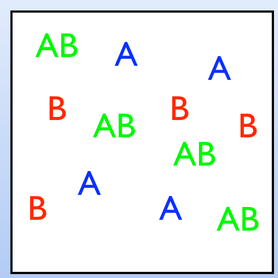


$$K = \frac{\#AB}{\#A \times \#B} = \frac{4}{4 \times 4} = \frac{4}{16} = \frac{1}{4}$$

same ratio from different starting conditions
at equilibrium the ratio will always be the same

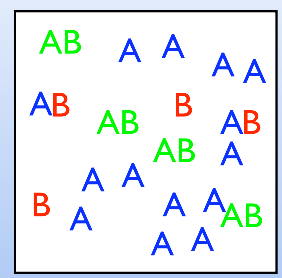
Let's mess up the equilibrium

$$A + B \longrightarrow AB$$



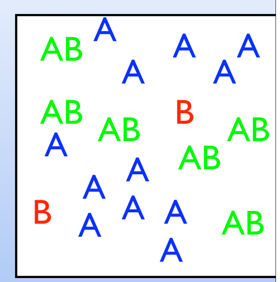
equilibrium 4 A, 4 B,
and 4 AB molecules

$$\frac{4}{4 \times 4} = 0.25$$



add 10 more A
14 A, 4 B, 4 AB

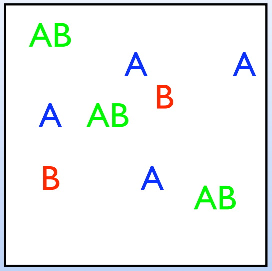
$$\frac{4}{14 \times 4} \neq 0.25$$



equilibrium
12 A, 2 B, 6 AB

$$\frac{6}{12 \times 2} = 0.25$$

Let's look at a new condition



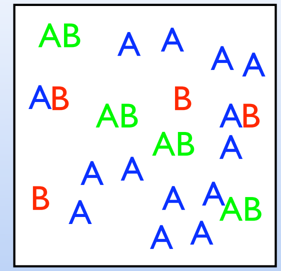
$$\frac{3}{4 \times 2} = .375 \neq 0.25$$

A. equilibrium

B. not equilibrium ←

Reaction Quotient

Ratio of Products to Reactants "now"



$$Q = \frac{4}{14 \times 4} = \frac{4}{56} = 0.071$$

$K = 0.25$

At equilibrium Q = K

Q > K "too many" products

Q < K "too many" reactants

The Reaction Quotient tell us the direction toward equilibrium

Q > K products need to go back to reactants
"reaction shifts towards reactants"

Q < K reactants need to become products
"reaction shifts towards products"

How do we write K or Q for a given reaction it is not a simple ratio

$$aA + bB \longleftrightarrow cC + dD$$

stiochiometric ratio
in balanced equation

concentrations now
in units of Molarity (mol L^{-1})

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

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

with concentrations found at equilibrium

Example

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

A. $K = \dfrac{[H_2]^3[N_2]^1}{[NH_3]^2}$

B. $K = \dfrac{[NH_3]^2}{[H_2]^3[N_2]^1}$

C. $K = \dfrac{2[NH_3]}{3[H_2][N_2]}$

D. $K = \dfrac{[2NH_3]}{[3H_2][N_2]}$

Q we now from current conditions and the balanced equation

How do we know what K is?

K is related to ΔG for the reaction

Principles of Chemistry II

$$\Delta_R G^\circ = -RT \ln K$$

$\Delta_R G^\circ < 0$ $K > 1$ favors products

$\Delta_R G^\circ > 0$ $K < 1$ favors reactants

Principles of Chemistry II

Thoughts for the day

ibuprofin + COX $\longleftrightarrow$ complex (bound together)

Initially no ibuprofin so no complex	$Q<K$
swallow the pill and some of it binds inhibiting the COX enzyme	$Q=K$
body metabolizes the ibuprofin complex comes apart	$Q>K$

Principles of Chemistry II

Thoughts for the day

If there is more CO_2 in the atmosphere
what happens to the CO_2 dissolved in the ocean?

It goes up

$$CO_2\ (aq) + H_2O(l) \longleftrightarrow H_2CO_3(aq)$$

More CO_2, now "too many reactant"
shift to products
More acid in ocean

TABLE 6.1 Results of Three Experiments for the Reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Experiment	Initial Concentrations	Equilibrium Concentrations	$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$
I	$[N_2]_0 = 1.000\ M$ $[H_2]_0 = 1.000\ M$ $[NH_3]_0 = 0$	$[N_2] = 0.921\ M$ $[H_2] = 0.763\ M$ $[NH_3] = 0.157\ M$	$K = 6.02 \times 10^{-2}\ L^2/mol^2$
II	$[N_2]_0 = 0$ $[H_2]_0 = 0$ $[NH_3]_0 = 1.000\ M$	$[N_2] = 0.399\ M$ $[H_2] = 1.197\ M$ $[NH_3] = 0.203\ M$	$K = 6.02 \times 10^{-2}\ L^2/mol^2$
III	$[N_2]_0 = 2.00\ M$ $[H_2]_0 = 1.00\ M$ $[NH_3]_0 = 3.00\ M$	$[N_2] = 2.59\ M$ $[H_2] = 2.77\ M$ $[NH_3] = 1.82\ M$	$K = 6.02 \times 10^{-2}\ L^2/mol^2$

Each equilibrium has different concentrations,
but the same value for Kc

Equilibria and Perturbations (Stress)

What happens to a system at equilibrium
if I change something like

The concentration of one of the chemicals

The Pressure

The Temperature