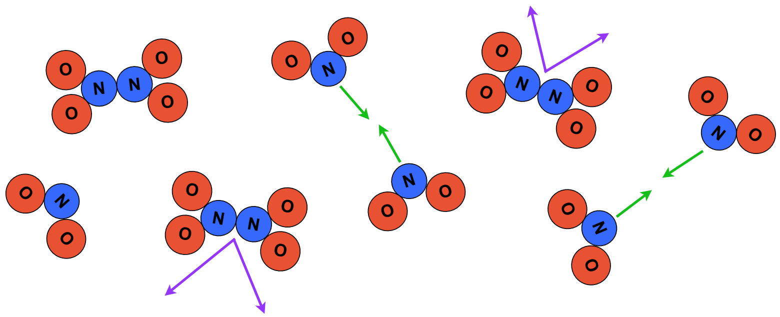
Chemical Equilibrium

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



Some reactions proceed to completion

A chemical reaction is said to go to ***completion*** if the reaction proceeds until all of the limiting reactant or reactants is used up

Examples:

Dissolution of a soluble salt

$$NaCl(s) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq)$$

Dissociation of a strong acid

$$HNO_3(l) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$

Combustion

$$CH_4(g) + 2\ O_2(g) \longrightarrow CO_2(g) + 2\ H_2O(g)$$

Reversible reactions

Many reactions do ***not*** proceed to completion

-- instead they approach an ***equilibrium*** state in which both reactants and products are present

This occurs because the reaction is ***reversible***

-- the products formed by the reaction can themselves react to form the original reactants

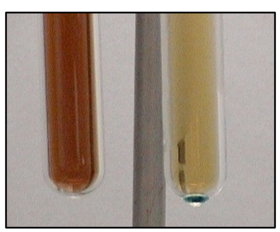
***Example:* Nitrogen dioxide / dinitrogen tetroxide**

$2\ NO_2\ (g) \xrightarrow{\text{combination}} N_2O_4\ (g)$

red-brown colorless

$2\ NO_2\ (g) \xleftarrow{\text{decomposition}} N_2O_4\ (g)$

red-brown colorless



Reversible reactions

In a ***reversible*** reaction, the products formed by the reaction can themselves react to form the original reactants

***Example:* NO_2 – N_2O_4 combination / decomposition**

$2\ NO_2\ (g) \xrightarrow{\text{combination}} N_2O_4\ (g)$ **forward reaction**

$N_2O_4\ (g) \xrightarrow{\text{decomposition}} 2\ NO_2\ (g)$ **reverse reaction**

$2\ NO_2\ (g) \rightleftharpoons N_2O_4\ (g)$ **combined equation for forward and reverse reactions**

Definition of *equilibrium*

General definition:

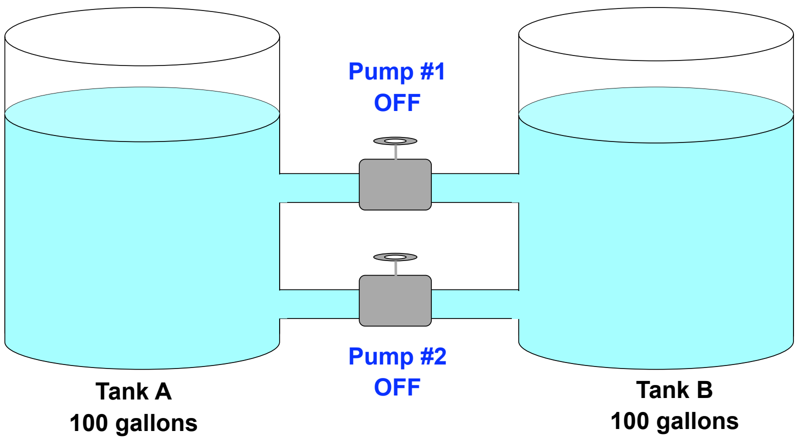
equilibrium -- a state of balance

Technical definition:

equilibrium -- a dynamic state in which two or more opposing processes are taking place at the same time and at the same rate

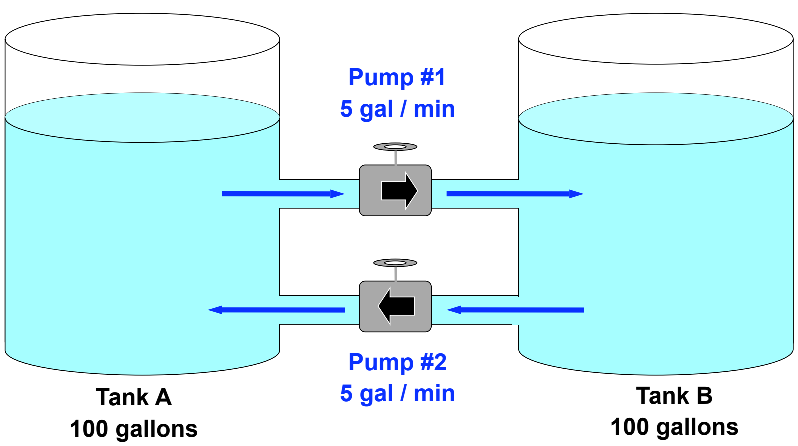
The concept of equilibrium

The system is in a state of **static equilibrium**
-- no water is flowing and the volume of water in both tanks is constant



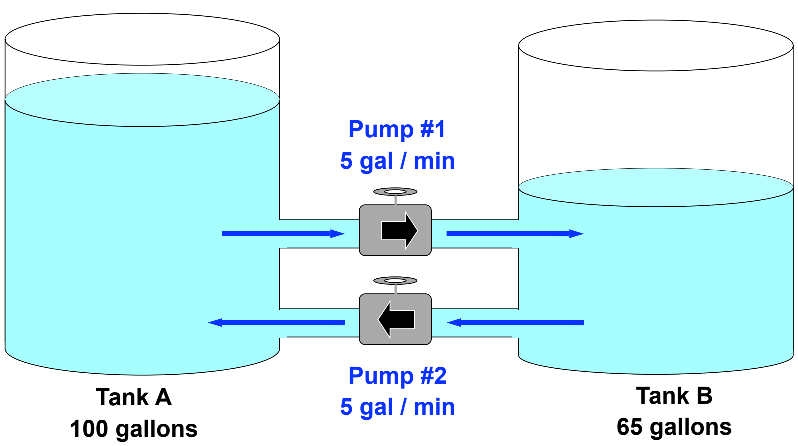
The concept of equilibrium

The system is in a state of **dynamic equilibrium** -- water is flowing in and out of both tanks, but the volume of water in both tanks is constant



The concept of equilibrium

Note: For the system to be at equilibrium, the amounts of water in each tank can be different -- but the ***flow rates*** have to be the same



Definition of *equilibrium*

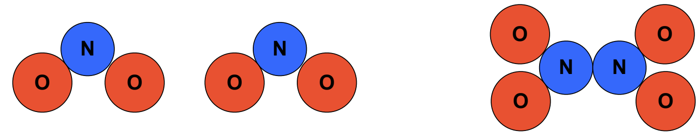
Chemical definition:

chemical equilibrium -- for a reversible reaction, a dynamic state in which the *rate* of the forward reaction *is exactly equal to* the *rate* of the reverse reaction

Note: The *concentrations* of reactants and products do **not** have to be equal

Examples of chemical equilibrium

Many chemical reactions



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

	$2\,NO_2(g)$	$N_2O_4\,(g)$
Initial:	1.00 mol	0 mol
Equilibrium at 298 K:	0.047 mol	0.48 mol

At equilibrium, the *rate* of the forward reaction is equal to the *rate* of the reverse reaction

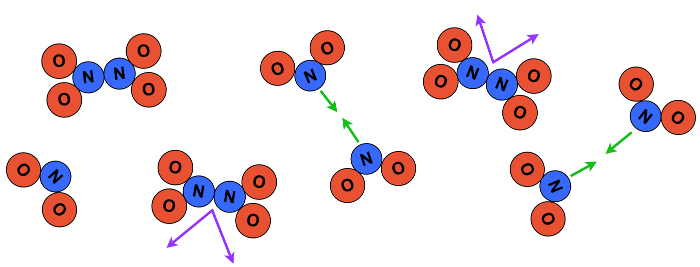
(but the *concentrations* of products and reactants are **not** equal)

Examples of chemical equilibrium

Reversible chemical reaction

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

At equilibrium: *Rate* of forward reaction = *Rate* of reverse reaction



NO_2 molecules are *combining* to form N_2O_4 at the same ***rate*** that N_2O_4 molecules are *decomposing* to form NO_2

Reaction rates

- Every chemical reaction has a rate, or speed, at which it proceeds
  - *-- some are fast, some are very slow*
- The rate of a reaction is dependent of the chemical and physical properties of the reactants (and catalysts, if any are present)
- The rate of a reaction varies under different conditions
  - *-- concentration of reactants*
  - *-- temperature*
  - *-- volume (if gases are involved)*

The rate of a reaction is proportional to the concentration of the reactants

Rates of forward and reverse reactions

Example: Formation / decomposition of hydrogen iodide

$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$

As the forward reaction proceeds, the concentration of the reactants *decreases*

-- the rate of the forward reaction therefore *decreases*

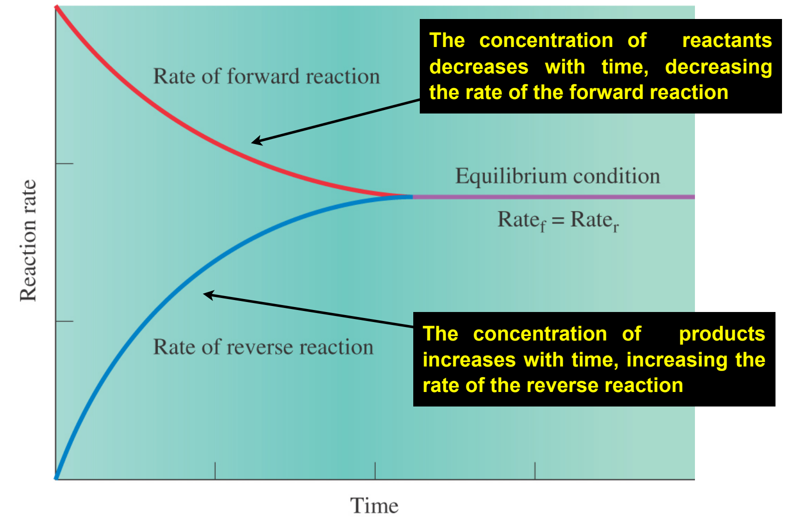
As the forward reaction proceeds, the concentration of the products *increases*

-- the rate of the reverse reaction therefore *increases*

Eventually, a point is reached where the rate of the forward reaction is equal to the rate of the reverse reaction

-- when this occurs, the system has reached a state of ***equilibrium***

Rates of forward and reverse reactions



Equilibrium constants

For a system at ***equilibrium:***

- the rates of the *forward* and *reverse* reactions are equal
- the concentrations of the reactants and products are constant

The **equilibrium constant** (K_{eq}) is a value representing the unchanging concentrations of the reactants and the products in a chemical reaction at equilibrium

Equilibrium constants

For the general reaction:

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

The expression for the equilibrium constant is:

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

- The quantities in brackets are the concentrations of each substance in moles / liter
- The superscripts a, b, c, and d are the coefficients from the balanced chemical equation
- For any reaction, the value of K_{eq} will vary with temperature (25°C is assumed unless stated otherwise)

Equilibrium constants

For the general reaction:

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

The expression for the equilibrium constant is:

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

IMPORTANT

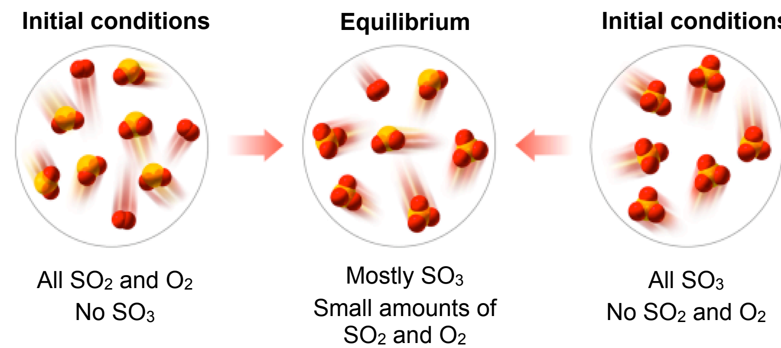
Pure solids and liquids are ***not*** included in the expression for the equilibrium constant

-- *i.e.*, only gases and aqueous substances appear in the expression for the equilibrium constant

Reaching equilibrium

For the reaction: $2\ SO_2 + O_2 \rightleftharpoons 2\ SO_3$

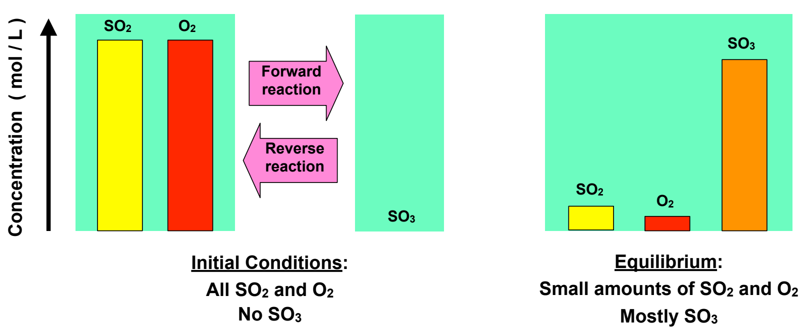
Flasks filled initially with *only* SO_2 and O_2 or *only* SO_3 will both reach the same equilibrium state



Equilibrium can favor the products or reactants

For the reaction: $2\ SO_2 + O_2 \rightleftharpoons 2\ SO_3$

- Equilibrium is reached after most of the forward reaction has occurred
- The equilibrium for this reaction favors the products



Equilibrium can favor the products or reactants

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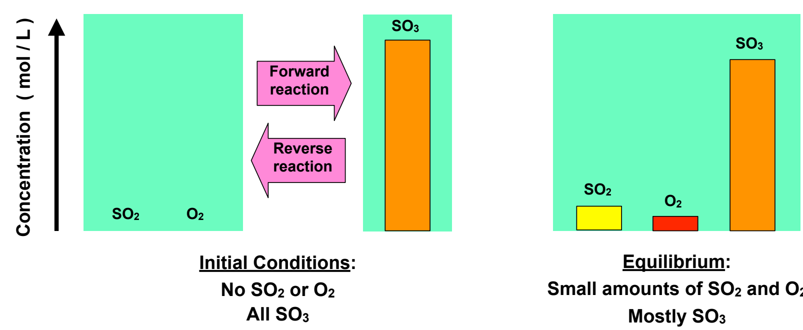


Equilibrium constants

$$2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3$$

$$K_{eq} = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

Large amounts

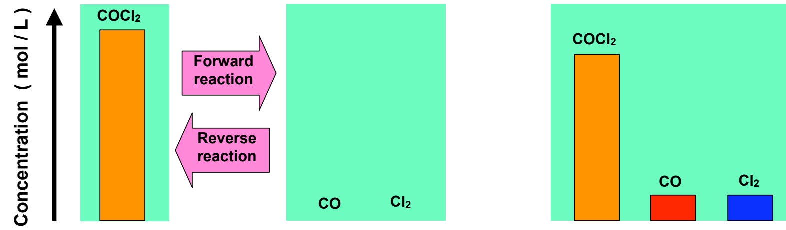
Small amounts

- Equilibrium is reached after most of the forward reaction has occurred
- $[SO_3]^2 \gg [SO_2]$ and $[O_2]$
- The equilibrium for this reaction favors the **products**
- $K_{eq} \gg 1$

Equilibrium can favor the products or reactants

For the reaction: $COCl_2 \rightleftharpoons CO + Cl_2$

- Equilibrium is reached after very little of the forward reaction has occurred
- The equilibrium for this reaction favors the reactants



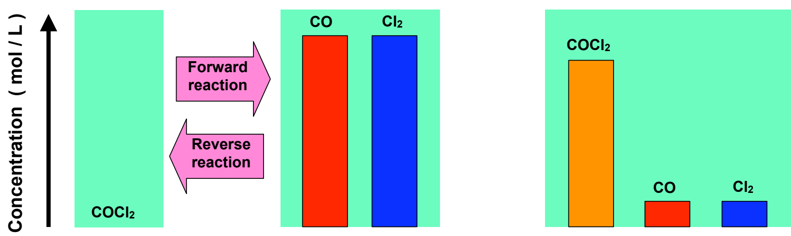
Initial Conditions: All $COCl_2$, No CO or Cl_2

Equilibrium: Mostly $COCl_2$, Small amounts of CO and Cl_2

Equilibrium can favor the products or reactants

For the reaction: $COCl_2 \rightleftharpoons CO + Cl_2$

- Equilibrium is reached after very little of the forward reaction has occurred
- The equilibrium for this reaction favors the reactants



Initial Conditions: No $COCl_2$, All CO and Cl_2

Equilibrium: Mostly $COCl_2$, Small amounts of CO and Cl_2

Equilibrium constants

$$COCl_2 \rightleftharpoons CO + Cl_2$$

$$K_{eq} = \frac{[CO]\,[Cl_2]}{[COCl_2]}$$

Small amounts

Large amount

- Equilibrium is reached after very little of the forward reaction has occurred
- $[CO]$ and $[Cl_2] \ll [COCl_2]$
- The equilibrium for this reaction favors the **reactants**
- $K_{eq} \ll 1$

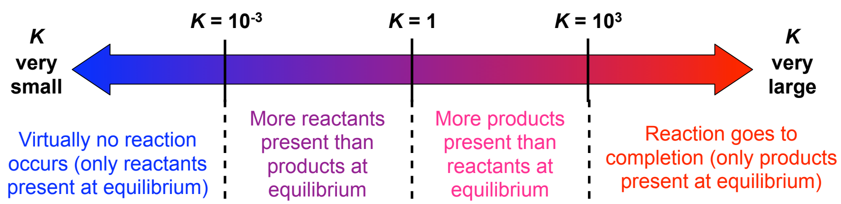
Value of equilibrium constant indicates whether products or reactants are favored

$$aA + bB \rightleftharpoons cC + dD \qquad K_{eq} = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

Products favored: Large K_{eq}

Reactants favored: Small K_{eq}

Products/reactants roughly equal: $K_{eq} \approx 1$



Equilibrium constants

Example: Write the equilibrium constant expression for:

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

The expression for the equilibrium constant is:

$$K_{eq} = \frac{[NH_3]^2}{[H_2]^3\,[N_2]}$$

Equilibrium constants

Example: Consider the following reaction:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Calculate the value of K_{eq} for the reaction based on the following equilibrium concentrations of products and reactants at 300°C:

$[PCl_5] = 0.030$ mol/L

$[PCl_3] = 0.97$ mol/L

$[Cl_2] = 0.97$ mol/L

Equilibrium constants

Example: Consider the following reaction:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Calculate the value of K_{eq} for the reaction based on the following equilibrium concentrations of products and reactants at 300°C:

Step 1: Write the expression for the equilibrium constant

$$K_{eq} = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]}$$

Equilibrium constants

Example: Consider the following reaction:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Calculate the value of K_{eq} for the reaction based on the following equilibrium concentrations of products and reactants at 300°C:

Step 2: Plug in the concentration values and solve for K_{eq}

$$K_{eq} = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]} = \frac{(0.97)(0.97)}{(0.030)} = 31$$

- **Which of these reactions proceeds to completion?**
- **Which of these reactions has more products than reactants present at equilibrium?**
- **Which of these reactions has more reactants than products at equilibrium?**

	K_{eq} (at 25°C)
$3\,H_2(g) + N_2(g) \rightleftharpoons 2\,NH_3(g)$	5.9×10^{5}
$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$	1.0×10^{-14}
$CO(g) + 2\,H_2(g) \rightleftharpoons CH_3OH(g)$	10.5

Homework assignment

Chapter 7 Problems:

7.52, 7.54, 7.55, 7.56, 7.57, 7.58, 7.59, 7.60, 7.61