

Reaction Rates

Reactions can be fast or slow.

Expressing rxn rates in quantitative terms:

$$\text{Average rate} = \frac{\Delta \text{quantity}}{\Delta t}$$

Example: Reaction data for the reaction between butyl chloride (C₄H₉Cl) and water is given below. Calculate the average reaction rate over this time period expressed as moles of C₄H₉Cl consumed per liter per second.

$$\text{Average rate} = \frac{\Delta \text{quantity}}{\Delta t} = \frac{[\text{C}_4\text{H}_9\text{Cl}]_{\text{final}} - [\text{C}_4\text{H}_9\text{Cl}]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}} = \frac{0.100 \text{ M} - 0.220 \text{ M}}{4.00 \text{ s} - 0.00 \text{ s}} = -0.0300 \frac{\text{mol}}{\text{L}\cdot\text{s}}$$

Table 17-1: Molar Concentration

[C ₄ H ₉ Cl] at t=0.00 s	[C ₄ H ₉ Cl] at t=4.00 s
0.220 M	0.100 M

Collision Theory:

- Atoms, ions and molecules must collide in order to react.
- Reacting substances must collide with the correct orientation.
- Reacting substances must collide with sufficient energy to form the activated complex.

Activation energy and reaction: Only collisions with enough energy to react form products

Does ΔG tell us anything about rxn rate? Yes (No)

- If a reaction is spontaneous, it does not follow that it is fast or slow.
- Thus, a new branch of chemistry... *kinetics*

Factors affecting reaction rates:

- 1) nature of reactants : Some elements/compounds are more reactive than others
- 2) concentration : As concentration ↑, frequency of collisions ↑, and therefore rxn rate ↑
- 3) Pressure (gases only) : For gases, ↑ pressure creates the same effect as ↑ concentration
- 4) surface area : As surface area ↑, rxn rate ↑
- 5) temperature : Generally, ↑ temp = ↑ rate

Why? Higher temp = faster molecular motion = more collisions and more energy per collision = faster rxn

- 6) catalysts : Adding a catalyst speeds up the rxn by lowering the activation energy

Catalyst: a substance that speeds up the rate of a reaction without being consumed in the reaction.

- Provides an easier way to react
- Lowers the activation energy

Enzyme = biological catalyst

Reaction Rate Laws

- The equation that expresses the mathematical relationship between the rate of a chemical reaction and the concentration of reactants is a **rate law**.

For the reaction: A → B

$$\text{Rate} = k[A]$$

* k is a constant specific to this reaction

Rate Laws and Reaction Order

- The **reaction order** for a reactant defines how the rate is affected by the concentration of that reactant.
- The overall reaction order of a chemical reaction is the sum of the orders for the individual reactants in the rate law.
- The rate law for most reactions has the general form...

$$\text{Rate} = k[\text{reactant 1}]^m[\text{reactant 2}]^n \dots$$
- The exponents m and n are called reaction orders. Their sum ($m + n$) is called the overall reaction order.
- For the reaction $aA + bB \rightarrow \text{products}$

$$\text{Rate} = k[A]^m[B]^n$$
- Only if the rxn between A and B happens in a *single step* (with a single activated complex... which is *unlikely*) does $m=a$ and $n=b$.
- Thus, the values of m and n must be determined experimentally !!!
- Rate laws cannot be predicted by looking at a balanced chemical equation.

Finding the rate law

- The most common method for experimentally determining the differential rate law is the method of initial rates.
- In this method several experiments are run at different initial concentrations and the instantaneous rates are determined for each at the same value of time (as near $t = 0$ as possible)

Example: $A + B \rightarrow C$

Exp #	Initial [A]	Initial [B]	Rate (M/s)
1	.100 M	.100 M	4×10^{-5}
2	.100 M	.200 M	4×10^{-5}
3	.200 M	.100 M	16×10^{-5}

From this data, find the form of the rate law: $\text{Rate} = k[A]^m[B]^n$ $\text{Rate} = k[A]^2$

1) Calculate m

$$\frac{\text{Rate 3} = 16 \times 10^{-5}}{\text{Rate 1} = 4 \times 10^{-5}} = \frac{k[.200]^m \cdot [.100]}{k[.100]^m \cdot [.100]}$$

$$4 = \frac{[.200]^m}{[.100]^m}$$

$$4 = 2^m$$

$$m = 2$$

2) Calculate n

$$\frac{\text{Rate 2} = 4 \times 10^{-5}}{\text{Rate 1} = 4 \times 10^{-5}} = \frac{k[.100]^m \cdot [.200]^n}{k[.100]^m \cdot [.100]^n}$$

$$1 = \frac{[.200]^n}{[.100]^n}$$

$$1 = 2^n$$

$$n = 0$$

3) Calculate k

$$k = \frac{\text{rate}}{[A]^2[B]^0} = \frac{4 \times 10^{-5}}{[.100]^2} = 4 \times 10^{-3}$$

$$\boxed{\text{Rate} = 4 \times 10^{-3} [A]^2}$$

$$\text{Rate} = k[A]^m[B]^n$$

$$\text{Rate} = k[A]^2[B]^0$$

$$\text{Rate} = k[A]^2$$

Knowing rate laws and rate orders helps us predict how the reaction will proceed over time

Application: Radioactive decay is a first order reaction; Half life is constant over time; Allows us to date fossils, etc.

Reaction Mechanisms

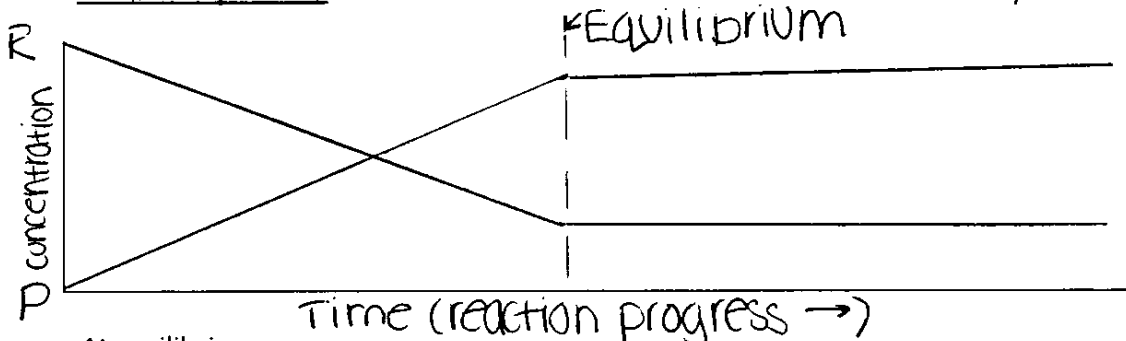
- Most chemical reactions consist of a sequence of two or more steps (or simpler reactions). These add together to create the overall reaction equation.
- Generally, some steps will be fast and others will be slow.
- The slow step is the rate determining step.

Chemical Equilibrium (Ch. 12)

REVERSIBLE REACTIONS do not go to completion & can occur in either direction:



Chemical equilibrium exists when the forward & reverse rxns. occur at exactly the same rate



At equilibrium:

- if there are more products than reactants, the products are said to be favored
- if there are more reactants than products, the reactants are said to be favored

The Equilibrium Constant, K_{eq}

-for the reaction: $aA + bB \rightleftharpoons cC + dD$ at equilibrium, the constant, K_c or K_{eq} :

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

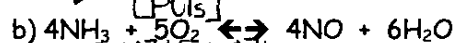
[] denotes concentration

K_{eq} is a measure to extent to which a reaction occurs; it varies with temperature.

Ex: Write the K_{eq} expression for:



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



$$K_{eq} = \frac{[NO]^4 [H_2O]^6}{[NH_3]^4 [O_2]^5}$$

Ex: One liter of the equilibrium mixture from example (a) was found to contain 0.172 mol PCl_3 , 0.086 mol Cl_2 , and 0.028 mol PCl_5 . Calculate K_{eq} .

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \quad K_{eq} = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(0.172M)(0.086M)}{(0.028M)} = 0.63$$

When $K_{eq} > 1$, most reactants will be converted to products.

When $K_{eq} < 1$, most reactants remain unreacted.

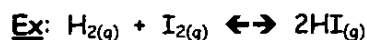
Reaction Quotient (Q) is calculated the same as K_{eq} , but the concentrations are not necessarily equilibrium concentrations.

Comparing Q with K_{eq} enables us to predict the direction in which a rxn will occur to a greater extent when a rxn is NOT at equilibrium.

When: $Q < K$: Forward reaction predominates - "reaction proceeds to the right (until equilibrium is reached)"

$Q = K$: System is at equilibrium

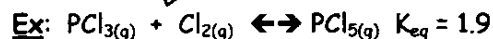
$Q > K$: Reverse reaction predominates - "reaction proceeds to the left" (until equilibrium is reached)



K_{eq} for this reaction at 450°C is 49. If 0.22 mol I_2 , 0.22 mol H_2 , and 0.66 mol HI are put into a 1.00 L container, would the system be at equilibrium? If not, what must occur to establish equilibrium?

$$Q = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.66 \text{ M})^2}{(0.22 \text{ M})(0.22 \text{ M})} = \boxed{9.0}$$

$Q < K_{eq}$; forward reaction predominates until equilibrium is reached



In a system at equilibrium in a 1.00 L container, we find 0.25 mol PCl_5 , and 0.16 mol PCl_3 . What equilibrium concentration of Cl_2 must be present?

$$K_{eq} = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]}$$

$$1.9 = \frac{(0.25 \text{ M})}{(0.16)[\text{Cl}_2]}$$

$$[\text{Cl}_2] = \boxed{0.82 \text{ M}}$$

Factors Affecting Equilibrium (Ch. 12)

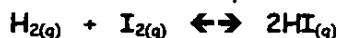
• When a system is at equilibrium, it will stay that way until something changes this condition.

• **Le Chatelier's Principle:**

When a change ("stress") is applied to a system at equilibrium, the system will shift its equilibrium position to counteract the effect of the disturbance.

- Factors affecting equil. include changes in:
 - concentrations (of reactants or products)
 - temperature
 - pressure

• **Changes in Concentration:** consider this reaction at equilibrium:



What will happen to the equilibrium if we:

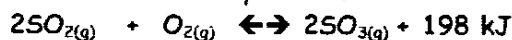
-add some H_2 ?
Reaction shifts to the right (forms more products)

-remove some H_2 ?
Reaction shifts to the left (forms more reactants)

****when a substance is added, the stress is relieved by shifting the equil. in the direction that consumes some of the added substance.**

****when a substance is removed, the rxn that produces that substance occurs to a greater extent**

• **Changes in Temperature** - consider this rxn at equilibrium:



What will happen to the equilibrium if we:

-increase the temperature?
Reaction shifts to the left (forms more reactants)

-decrease the temperature?
Reaction shifts to the right (forms more products)

****increasing the temp. always favors the rxn that consumes heat, and vice versa.**

Changes in Pressure- consider this rxn at equilibrium:



What will happen to the equilibrium if we:

-increase the pressure?

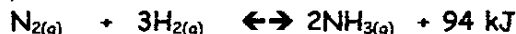
Reaction shifts to the right (forms more product)

-decrease the pressure?

Reaction shifts to the left (forms more reactants)

****increasing the pressure favors the rxn that produces fewer moles of gas, and vice-versa.**

Example: consider the rxn at equilibrium:



How would the equil. be influenced by:

a) increasing the temp.: ←

b) decreasing the temp.: →

c) increasing the pressure: →

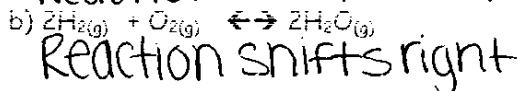
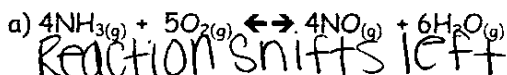
d) adding more H₂: →

e) removing some NH₃: →

f) decreasing the pressure: ←←

g) adding a catalyst: no change in equilibrium position

Example: How will an increase in pressure affect the equilibrium in :



Example: How will an increase in temperature affect the equilibrium in:

