

GENERAL CHEMISTRY

Chapter 6

Chemical Kinetics

1

Kinetics

- ❖ Kinetics is the study of how fast chemical reactions occur.
- ❖ There are 4 important factors which affect the rates of chemical reactions:
 - ✓ reactant concentration,
 - ✓ temperature,
 - ✓ action of catalysts, and
 - ✓ surface area.

2

Reaction Rates

- The speed of a reaction is defined as the change that occurs per unit time.
 - It is determined by measuring the change in concentration of a reactant or product with time.
 - The speed the of the reaction is called the **reaction rate**.
- For a reaction $A \rightarrow B$:

$$\begin{aligned}\text{Average rate} &= \frac{\text{change in number of moles of B}}{\text{change in time}} \\ &= \frac{\Delta(\text{moles of B})}{\Delta t}\end{aligned}$$

- Suppose A reacts to form B. Let us begin with 1.00 mol A.

3

Reaction Rates

- At $t = 0$ (time zero) there is 1.00 mol A and no B present.
- At $t = 10$ min, there is 0.54 mol A and 0.26 mol B.
- At $t = 20$ min, there is 0.30 mol A and 0.70 mol B.
- Calculating,

$$\begin{aligned}\text{Average rate} &= \frac{\Delta(\text{moles of B})}{\Delta t} \\ &= \frac{(\text{moles of B at } t = 10) - (\text{moles of B at } t = 0)}{10 \text{ min} - 0 \text{ min}} \\ &= \frac{0.26 \text{ mol} - 0 \text{ mol}}{10 \text{ min} - 0 \text{ min}} = 0.026 \text{ mol/min}\end{aligned}$$

4

Reaction Rates

❖ For the reaction $A \rightarrow B$ there are two ways of measuring rate:

- ✓ the speed at which the products appear (i.e. change in moles of B per unit time), or
- ✓ the speed at which the reactants disappear (i.e. the change in moles of A per unit time).

$$\text{Average rate with respect to A} = \ominus \frac{\Delta(\text{moles of A})}{\Delta t}$$

- The equation, when calculating rates of reactants, is multiplied by -1 to compensate for the negative concentration.

5

Reaction Rates and Stoichiometry

- In general :



$$\text{Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

- For the reaction:



$$\text{Rate} = -\frac{\Delta[C_4H_9Cl]}{\Delta t} = \frac{\Delta[C_4H_9OH]}{\Delta t}$$

6

Reaction Rates and Stoichiometry

The rate-law expression for a reaction in which A, B, . . . are reactants:

$$\text{rate} = k[\text{A}]^x[\text{B}]^y \dots$$

- ✓ The constant **k**: the specific rate constant (or **the rate constant**) for the reaction at a particular temperature
- ✓ **x and y**: **no** necessary **relationship to the coefficients** in the balanced chemical equation for the overall reaction and **must be determined experimentally**.

7

Reaction Rates and Stoichiometry

- ✓ x and y are usually integers or zero but are occasionally fractional or even negative.
- ✓ A **power of one** means that the **rate is directly proportional** to the concentration of that reactant.
- ✓ A **power of two** means that the rate is directly **proportional to the square** of that concentration.
- ✓ A **power of zero** means that the **rate does not depend on the concentration** of that reactant, so long as some of the reactant is present.

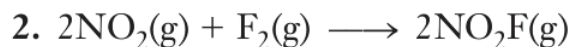
8

Reaction Rates and Stoichiometry



$$\text{rate} = k[\text{NO}]^2$$

second order in NO; second order overall

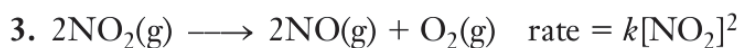


$$\text{rate} = k[\text{NO}_2][\text{F}_2]$$

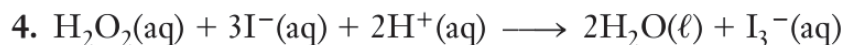
first order in NO_2 and first order in F_2 ;
second order overall

9

Reaction Rates and Stoichiometry



second order in NO_2 ;
second order overall



$$\text{rate} = k[\text{H}_2\text{O}_2][\text{I}^-]$$

first order in H_2O_2 and first order in I^- ;
zero order in H^+ ; second order overall

10

Reaction Rates and Stoichiometry

- For the reaction



we note

- as $[\text{NH}_4^+]$ doubles with $[\text{NO}_2^-]$ constant the rate doubles,
- as $[\text{NO}_2^-]$ doubles with $[\text{NH}_4^+]$ constant, the rate doubles,
- We conclude $\text{rate} \propto [\text{NH}_4^+][\text{NO}_2^-]$.

- Rate law:

$$\text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-]$$

- The constant k is the rate constant.

11

Reaction Rates and Stoichiometry

- For a general reaction with rate law

$$\text{Rate} = k[\text{reactant 1}]^m[\text{reactant 2}]^n$$

we say the reaction is m th order in reactant 1 and n th order in reactant 2.

- The overall order of reaction is $m + n + \dots$

12

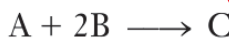
Reaction Rates and Stoichiometry

- A reaction is zero order in a reactant if the change in concentration of that reactant produces no effect.
- A reaction is first order if doubling the concentration causes the rate to double.
- A reaction is n th order if doubling the concentration causes an 2^n increase in rate.
- Note that the rate constant does not depend on concentration.

13

Reaction Rates and Stoichiometry

Example:



Experiment	Initial [A]	Initial [B]	Initial Rate of Formation of C
1	$1.0 \times 10^{-2} M$	$1.0 \times 10^{-2} M$	$1.5 \times 10^{-6} M \cdot s^{-1}$
2	$1.0 \times 10^{-2} M$	$2.0 \times 10^{-2} M$	$3.0 \times 10^{-6} M \cdot s^{-1}$
3	$2.0 \times 10^{-2} M$	$1.0 \times 10^{-2} M$	$6.0 \times 10^{-6} M \cdot s^{-1}$

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

$$\text{rate}_1 = k[A]_1^2[B]_1 \quad \text{or} \quad k = \frac{\text{rate}_1}{[A]_1^2[B]_1}$$

$$k = \frac{1.5 \times 10^{-6} M \cdot s^{-1}}{(1.0 \times 10^{-2} M)^2(1.0 \times 10^{-2} M)} = 1.5 M^{-2} \cdot s^{-1}$$

14

Concentration Change with Time

First Order Reactions

- Goal: convert rate law into a convenient equation to give concentrations as a function of time.

$$\begin{aligned}\text{Rate} &= -\frac{\Delta[A]}{\Delta t} = k[A] \\ \ln[A]_t - \ln[A]_0 &= -kt \\ \ln\left(\frac{[A]_t}{[A]_0}\right) &= -kt\end{aligned}$$

15

Half-Life Reactions

First Order Reactions

- Half-life is the time taken for the concentration of a reactant to drop to half its original value.
- For a first order process, half life, $t_{1/2}$ is the time taken for $[A]$ to reach $\frac{1}{2}[A]_0$.
- Mathematically defined by:

$$t_{1/2} = -\frac{\ln\left(\frac{1}{2}\right)}{k} = \frac{0.693}{k}$$

- The half-life for a 1st order reactions depends only on k

16

Compound A decomposes to form B and C in a reaction. At 25°C, the specific rate constant for the reaction is 0.0450 s⁻¹. What is the half-life of A at 25°C?

$$t_{1/2} = \frac{\ln 2}{ak} = \frac{0.693}{1(0.0450 \text{ s}^{-1})} = 15.4 \text{ s}$$

17

Concentration Change with Time

Second Order Reactions

- Goal: convert rate law into a convenient equation to give concentrations as a function of time.

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

18

Half-Life Reaction

Second Order

- Mathematically defined by:

$$t_{1/2} = \frac{1}{k[A]_0}$$

- A second order reaction's half-life depends on the initial concentration of the reactants

19

EXAMPLE 16-7

Compounds A and B react to form C and D in a reaction . The rate constant at 30°C is 0.622 **liter per mole per minute**. What is the half-life of A when $4.10 \times 10^{-2} \text{M}$ A is mixed with excess B?



20

The Arrhenius Equation

- Arrhenius discovered most reaction-rate data obeyed the Arrhenius equation:

$$k = Ae^{-E_a/RT}$$

- k is the rate constant, E_a is the activation energy, R is the gas constant (8.314 J/K-mol) and T is the temperature in K.
- A is called the frequency factor.
 - A is a measure of the probability of a favorable collision.
- Both A and E_a are specific to a given reaction.

21

$$\begin{aligned}
 k &= A e^{-\frac{E_a}{RT}} \\
 \ln k &= \ln A - \frac{E_a}{RT}
 \end{aligned}
 \quad \left\{ \begin{array}{l} \text{Van't Hoff eq.} \\ \ln \frac{k_{T_1}}{k_{T_2}} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \\ \text{From exp at } T_1 \rightarrow k_{T_1} \end{array} \right.$$

$$\begin{aligned}
 \text{at } T_1: & \ln k_{T_1} = \ln A - \frac{E_a}{RT_1} \\
 \text{at } T_2: & \ln k_{T_2} = \ln A - \frac{E_a}{RT_2}
 \end{aligned}$$

$$\ln \frac{k_{T_1}}{k_{T_2}} = -\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Arrhenius Eq.

→ find out k_{T_2} at T_2

22

$$k = A e^{-\frac{E_a}{RT}} ; \ln k = \ln A - \frac{E_a}{R \cdot T}$$

at T_1 : $\ln k_{T_1} = \ln A - \frac{E_a}{R \cdot T_1}$

T_2 : $\ln k_{T_2} = \ln A - \frac{E_a}{R \cdot T_2}$

Arrhenius eq.

$$\ln \frac{k_{T_1}}{k_{T_2}} = - \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$\rightarrow 8.314 \frac{J}{mol \cdot K}$
 $\rightarrow 15 \frac{kJ}{mol}$

Vant' Hoff: $\ln \frac{k_{T_1}}{k_{T_2}} = - \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

$\rightarrow 8.314 \frac{J}{mol \cdot K}$