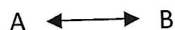


UNIT 13 – CHAPTER 12 STUDENT NOTES: CHEMICAL KINETICS

Differential Rate Law – the rate law that expresses how the rate depends on concentration

[] vs Rate * Calculated when $t = 0$

- From the following equation and information:



[A] ₀	Initial rate of the reaction (moles/liter·sec)
0.35	7.20×10^{-4}
0.70	2.90×10^{-3}
1.05	6.45×10^{-3}

- Write the expression for the rate law

$$\text{Rate} = K [A]^n$$

- Determine the order of the reaction

2/1

$$\frac{2.90 \times 10^{-3}}{7.20 \times 10^{-4}} = \frac{K [0.70]^n}{K [0.35]^n}$$

[] vs RATE
 $2^n = 4$ ($n=2$)

- Calculate the value of K

#2 $2.90 \times 10^{-3} = K [0.70]^2$
 $K = 5.92 \times 10^{-3} \text{ L/m} \cdot \text{sec}$

$$\frac{7.20 \times 10^{-4}}{2.90 \times 10^{-3}} = \frac{K [0.35]^2}{K [0.70]^2}$$

* $\log .25 \div \log .5 =$
 $-.6 \div -.3 = 2$

- Determine the rate law, solve for the order of the reaction and the value of the rate constant.



Reaction	[C] ₀	[D] ₀	[E] ₀	Initial rate (moles/liter·sec)
1	0.400	0.300	0.560	7.14×10^{-4}
2	0.100	0.500	0.200	4.55×10^{-5}
3	0.100	0.200	0.200	4.55×10^{-5}
4	0.400	0.300	0.750	1.28×10^{-3}
5	0.100	0.300	0.560	3.57×10^{-4}

* $[C] = 1/5$ RATE = $7.14 \times 10^{-4} = K [0.400]^x \cdot [0.300]^y \cdot [0.560]^z$
 $3.57 \times 10^{-4} = K [0.100]^x \cdot [0.300]^y \cdot [0.560]^z$
 $2 \quad 4 \quad 4x=2 \quad x=0.5$

$\log 2 \div \log 4 = 0.5$

* $[D] = 2/3$ RATE = $4.55 \times 10^{-5} = K [0.100]^x \cdot [0.500]^y \cdot [0.200]^z$
 $4.55 \times 10^{-5} = K [0.100]^x \cdot [0.200]^y \cdot [0.200]^z$
 $1 \quad 2.5 \quad 2.5y=1 \quad y=0$

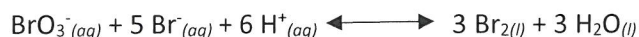
* $[E] = 4/1$ RATE = $1.28 \times 10^{-3} = K [0.400]^x \cdot [0.300]^y \cdot [0.750]^z$
 $7.14 \times 10^{-4} = K [0.400]^x \cdot [0.300]^y \cdot [0.560]^z$
 $1.79 \quad 1.34 \quad \log 1.79 \div \log 1.34 = 1.98 \quad z=2$

RATE = $K [C]^{0.5} \cdot [D]^0 \cdot [E]^2$

* $4.55 \times 10^{-5} = K [0.100]^{0.5} \cdot [0.200]^0 \cdot [0.200]^2$

$K = 3.60 \times 10^{-3}$

3. The reaction between bromate ions and bromide ions in an aqueous solution is given by the equation



The following table gives the results of 4 experiments

Reaction	$[\text{BrO}_3^-]$	$[\text{Br}^-]$	$[\text{H}^+]$	Initial rate (moles/liter·sec)
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

Calculate the rate law and the value of K for this reaction.

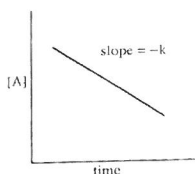
RATE LAW = $K [\text{BrO}_3^-]^1 \cdot [\text{Br}^-]^1 \cdot [\text{H}^+]^2$ $\frac{\text{M}^4}{\text{L}^4 \text{ UNITS}}$

TRIAL 1: $8.0 \times 10^{-4} = K [\cdot 10]^1 \cdot [\cdot 10]^1 \cdot [\cdot 10]^2$
DATA
 $K = 8.0 \frac{\text{L}^3}{\text{M}^3 \cdot \text{SEC}}$

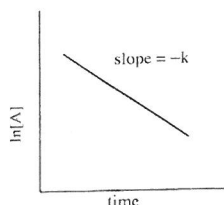
Integrated Rate Law – where the differential rate law expresses rate as a function of reaction concentration at an instant in time (hence an **instantaneous rate**); integrated rates express the reactants and concentration as a function of time.

TABLE 12.6: Summary of the Kinetics for Reactions of the Type $a\text{A} \rightarrow \text{Products}$ That Are Zero, First, or Second Order in $[\text{A}]$

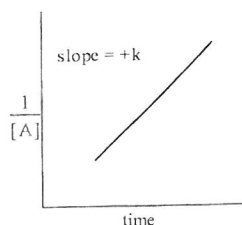
	Zeroth Order	First Order	Second Order
Rate Law:	Rate = k	Rate = $k[\text{A}]$	Rate = $k[\text{A}]^2$
Integrated Rate Law:	$[\text{A}] = -kt + [\text{A}]_0$	$\ln[\text{A}] = -kt + \ln[\text{A}]_0$ $\ln[\text{A}] - \ln[\text{A}]_0 = -kt$	$1/[\text{A}] = kt + 1/[\text{A}]_0$
Plot Needed to Give a Straight Line:	$[\text{A}]$ versus t	$\ln[\text{A}]$ versus t	$1/[\text{A}]$ versus t
Relationship of Rate Constant to the Slope of Straight Line:	Slope = $-k$	Slope = $-k$	Slope = k
Half-Life:	$t_{1/2} = [\text{A}]_0/2k$	$t_{1/2} = 0.693/k$	$t_{1/2} = 1/k[\text{A}]_0$



0 order
(-) slope



1st order
(-) slope



2nd order
(+) slope

$\text{RATE} = [\text{BrO}_3^-]^x \cdot [\text{Br}^-]^y \cdot [\text{H}^+]^z$

$\text{BrO}_3^- \nearrow \frac{1.6 \times 10^{-3}}{8.0 \times 10^{-4}} = K [\cdot 20]^x \cdot [\cdot 10]^y \cdot [\cdot 10]^z$
 $\frac{2}{2} [2]^x = 2 \rightarrow [x=1]$

$\text{Br}^- \nearrow \frac{3.2 \times 10^{-3}}{1.6 \times 10^{-3}} = K [\cdot 20]^x \cdot [\cdot 20]^y \cdot [\cdot 10]^z$
 $\frac{2}{2} [2]^y = 2 \rightarrow [y=1]$

$\text{H}^+ \nearrow \frac{3.2 \times 10^{-3}}{8.0 \times 10^{-4}} = K [\cdot 10]^x \cdot [\cdot 10]^y \cdot [\cdot 20]^z$
 $\frac{4}{4} [2]^z = 4 \rightarrow [z=2]$

Problems

1. All radioactive elements have nuclei which follow 1st order rate laws when decaying. Radon decays to polonium according to the following equation:



The first order rate constant for decay is 0.181/days. If you begin with a 5.28-gram sample of pure ^{222}Rn , how much time will be left after 1.96 days? 3.82 days?

$$1^{\text{st}} \text{ order} = \ln([A]_0/[A]) = K \cdot t$$

$$\begin{aligned} & \text{* 1.96 DAYS *} \\ \ln\left(\frac{5.28\text{g}}{[A]}\right) &= \left(\frac{0.181}{\text{DAYS}}\right) \cdot (1.96 \text{ DAYS}) \\ \frac{5.28}{[A]} &= e^{0.355} \rightarrow [A] = 3.69 \text{ Grams} \end{aligned}$$

$$\begin{aligned} & \text{* 3.82 DAYS *} \\ \ln\left(\frac{5.28\text{g}}{[A]}\right) &= \left(\frac{0.181}{\text{DAYS}}\right) \cdot (3.82 \text{ DAYS}) \\ [A] &= 2.64 \text{g} \end{aligned}$$

2. A certain 1st order reaction has a half-life of 20.0 minutes.

a) Calculate the rate constant for this reaction.

b) How much time is required for this reaction to be 75% complete?

$$\text{a) } 1^{\text{st}} \text{ ORDER: } t_{1/2} = \frac{0.693}{K} \rightarrow 20 \text{ MIN} = \frac{0.693}{K}$$

$$K = \frac{0.0347}{\text{MIN}}$$

$$\text{b) } \ln\left(\frac{[A]_0}{[A]}\right) = K \cdot T \rightarrow \ln\left(\frac{100}{25}\right) = (0.0347)(T) \quad t = 40 \text{ min}$$

3. Radioactive copper-64 decays by 1st order kinetics with a half-life of 12.8 days.

a) What is the value of K in sec⁻¹?

$$t_{1/2} = \frac{0.693}{K} \rightarrow 12.8 \text{ DAYS} = \frac{0.693}{K}$$

$$K = \frac{0.054}{\text{DAYS}} \cdot \frac{1 \text{ DAY}}{24 \text{ HRS}} \cdot \frac{1 \text{ HR}}{3600 \text{ SEC}} = \frac{6.3 \times 10^{-7}}{\text{SEC}}$$

b) A sample contains 28.0 mg of ^{64}Cu . How many decays will be produced in the first second?

$$\begin{aligned} \text{RATE} &= K[A] \\ [\text{Cu}^{64}] &= \frac{0.028 \text{ g Cu}}{63.5 \text{ g Cu}} \cdot \frac{1 \text{ mol Cu}}{1 \text{ mol Cu}} \cdot \frac{6.02 \times 10^{23} \text{ PARTICLES OF DECAY}}{1 \text{ mol Cu}} = 2.65 \times 10^{20} \text{ DECAYS} \end{aligned}$$

$$\text{RATE} = \left(\frac{6.3 \times 10^{-7}}{\text{SEC}}\right) (2.65 \times 10^{20} \text{ PARTICLES}) = \frac{1.67 \times 10^{14} \text{ DECAYS}}{\text{SEC}}$$

4. A chemist obtains a fresh sample of ^{64}Cu and measures its radioactivity. She then determines that to do the experiment she has in mind, the radioactivity cannot go below 3% of the initial measured value. How long does she have to do the experiment?

→ NO LESS THAN 3% REMAINS

How long?

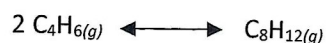
$$\begin{aligned} & \text{* SECONDS *} \\ \ln\left(\frac{100}{3}\right) &= \left(\frac{6.3 \times 10^{-7}}{\text{SECOND}}\right) \cdot t \end{aligned}$$

$$t = 5.57 \times 10^6 \text{ SECONDS}$$

$$\begin{aligned} & \text{* DAYS *} \\ \ln\left(\frac{100}{3}\right) &= \left(\frac{0.054}{\text{DAY}}\right) \cdot t \end{aligned}$$

$$t = 64.9 \text{ DAYS}$$

5. Butadiene reacts to form its dimer according to the following equation:



- 1) What is the reaction order in C_4H_6
- 2) What is the value of the rate constant for the reaction?
- 3) What is the half-life of the reaction under the conditions of this experiment?

Time ($\pm$ sec)	$[\text{C}_4\text{H}_6]$ (mol/L)
0	0.01000
1000	0.00625
1800	0.00476
2800	0.00370
3600	0.00313
4400	0.00270
5200	0.00241
6200	0.00208

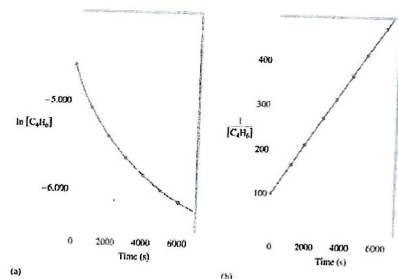
Answer

1) To decide whether the rate law for this reaction is 1st or 2nd order, we must see whether the plot of $\ln[\text{C}_4\text{H}_6]$ versus time is a straight line (2nd order). The data necessary to make these plots are as follows:

t (s)	$1/[\text{C}_4\text{H}_6]$	$\ln[\text{C}_4\text{H}_6]$
0	100	-4.605
1000	160	-5.075
1800	210	-5.348
2800	270	-5.599
3600	320	-5.767
4400	370	-5.915
5200	415	-6.028
6200	481	-6.175

The resulting plots are shown below. Since the $\ln[\text{C}_4\text{H}_6]$ versus t plot (figure a) is not a straight line, the reaction is *not* first order. The reaction is, however **second order**, as shown by the linearity of the $1/[\text{C}_4\text{H}_6]$ and $x = t$. Thus the slope of the line can be expressed as follows:

$$\text{Rate} = -\Delta[\text{C}_4\text{H}_6]/\Delta t = k[\text{C}_4\text{H}_6]^2$$



2) For a second-order reaction, a plot of $1/[C_4H_6]$ versus t produces a straight line of slope k . In terms of the standard equation for a straight line, $y = mx + b$, we have $y = 1/[C_4H_6]$ and $x = t$. Thus the slope of the line can be expressed as follows:

$$\text{Slope} = \Delta y / \Delta x = \Delta(1/[C_4H_6]) / \Delta t$$

Using the points at $t = 0$ and $t = 6200$, we can find the rate constant for the reaction:

$$k = \text{slope} = (481 - 100) \text{ L/mol} / (6200 - 0) \text{ s} = 381/6200 \text{ L/mol} \cdot \text{s} = \mathbf{6.14 \times 10^{-2} \text{ L/mol} \cdot \text{s}}$$

3) The expression for the half-life of a second-order reaction is: $t_{1/2} = 1/k[A]_0$

In this case $k = 6.14 \times 10^{-2} \text{ L/mol} \cdot \text{s}$ (from part 2) and $[A]_0 = [C_4H_6]_0 = 0.01000 \text{ M}$ (the concentration at $t = 0$). Thus

$$t_{1/2} = 1/(6.14 \times 10^{-2} \text{ L/mol} \cdot \text{s})(1.000 \times 10^{-2} \text{ mol/L}) = \mathbf{1.63 \times 10^3 \text{ s}}$$

Rate Laws: A summary

*There are two types of rate laws.

1. The **differential rate law** (often called simply the **rate law**) shows how the rate of a reaction depends on concentrations.
2. The **integrated rate law** shows how the concentrations of species in the reaction depend on time.

*Because we typically consider reactions only under conditions where the reverse reaction is unimportant, our rate laws will involve only concentrations of reactants.

*Because the differential and integrated rate laws for a given reaction are related in a well-defined way, the experimental determination of *either* of the rate laws is sufficient.

*Experimental convenience usually dictates which type of rate law is determined experimentally.

*Knowing the rate law for a reaction is important mainly because we can usually infer the individual steps involved in the reaction from the specific form of the rate law.

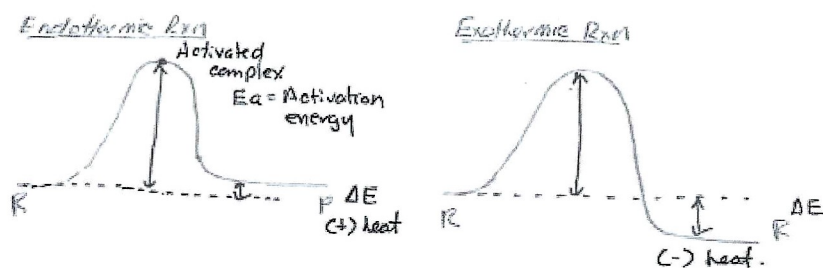
A model of chemical kinetics

Facts about rates of chemical reactions

- 1) The more concentrated the reactants, the faster the reaction.
- 2) The higher the temperature, the faster the reaction.

Collision Theory – explains why chemical reactions take place

1. Molecules must move toward each other.
2. Molecules must hit with proper orientation
3. Molecules must hit with sufficient energy.
4. Molecules will separate after the reaction occurs.



Activation Energy (E_a) – energy needed to start chemical reactions

$$\ln(K) = \frac{-E_a (1/T_k) + \ln A}{R}$$

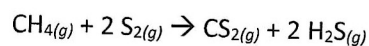
$$R = 8.3145 \text{ J/K-mol}$$

A = frequency factor (different for all reactions)

Activation energy at 2 temperatures

$$\ln[K_2/K_1] = E_a/R \cdot (1/T_1 - 1/T_2)$$

The gas-phase reaction between methane and diatomic sulfur is given by the equation



At 550°C the rate constant for this reaction is $1.1 \text{ L/mol}\cdot\text{sec}$, and at 625°C the rate constant is $6.4 \text{ L/mol}\cdot\text{sec}$. Using these values, calculate E_g for this reaction.

Solution:

The relevant data are shown in the following table:

k (L/mol · s)	T (°C)	T (K)
$1.1 = k_1$	550	$823 = T_1$
$6.4 = k_2$	625	$898 = T_2$

Substituting these values into the equation gives:

$$\ln(6.4/1.1) = (E_g/8.3145 \text{ J/K} \cdot \text{mol}) \cdot (1/823 \text{ K} - 1/898 \text{ K})$$

Solving for E_g gives:

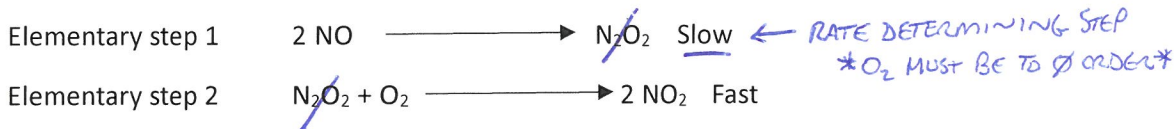
$$E_g = [(8.3145) \ln(6.4/1.1)] / (1/823 - 1/898)$$

$$E_g = 1.4 \times 10^5 \text{ J/mol}$$

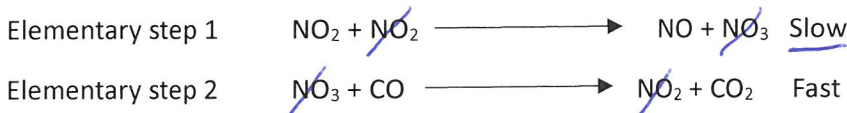
Reactions Mechanisms - For reaction mechanisms to be plausible:

1. The sum of the steps must give the overall reaction.
2. The rate law derived from the mechanism must agree with the observed mechanism (from experimental data).

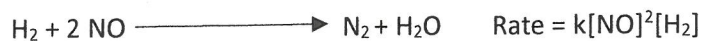
EX 1:



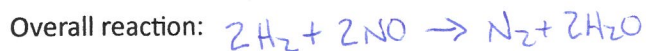
EX 2:



EX 3:

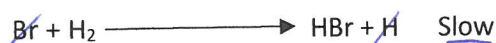


Is this a plausible mechanism?



Rate law: $\text{RATE} = k [\text{H}_2]^2 \cdot [\text{NO}]^2$ (NO)
 * SLOW STEP (RATE DETERMINING STEP) DOES NOT MATCH UP W/ EXPERIMENTAL DATA

EX 4: Mechanism:



Rate law: $\text{RATE} = k [\text{Br}_2][\text{H}_2]$
 INTERMEDIATES: H, Br

Br is a CATALYST;
 INTRODUCED AND REMAINS,
 BUT NOT PART OF THE REACTION

END OF
SECTION 3