

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 $t = 0$

1. 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}

a) Write the expression for the rate law

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

b) Determine the order of the reaction

$$\frac{2}{1} = \frac{2.90 \times 10^{-3}}{7.20 \times 10^{-4}} = \frac{K [0.70]^n}{K [0.35]^n} \rightarrow 4 = K [2]^n$$

c) Calculate the value of K

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

$$K = 5.92 \times 10^{-3} \text{ M}^{-1} \cdot \text{sec}$$

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}

$$\text{Rate} = K [C]^x \cdot [D]^y \cdot [E]^z$$

$$[C] \rightarrow \frac{1}{5} \quad \text{RATE} = \frac{7.14 \times 10^{-4}}{3.57 \times 10^{-4}} = \frac{K [0.400]^x \cdot [0.300]^y \cdot [0.560]^z}{K [0.100]^x \cdot [0.300]^y \cdot [0.560]^z} \rightarrow [4]^x = 2, \log 2 \div \log 4 = \boxed{.5} (x)$$

$$[D] \rightarrow \frac{2}{3} \quad \text{RATE} = \frac{4.55 \times 10^{-5}}{4.55 \times 10^{-5}} = \frac{K [0.100]^x \cdot [0.500]^y \cdot [0.200]^z}{K [0.100]^x \cdot [0.200]^y \cdot [0.200]^z} \rightarrow [2.5]^y = 1, \log 1 \div \log 2.5 = \boxed{0} (y)$$

$$[E] \rightarrow \frac{4}{1} \quad \text{RATE} = \frac{1.28 \times 10^{-3}}{7.14 \times 10^{-4}} = \frac{K [0.400]^x \cdot [0.300]^y \cdot [0.750]^z}{K [0.400]^x \cdot [0.300]^y \cdot [0.560]^z} \rightarrow [1.34]^z = 1.79$$

$$\log 1.79 \div \log 1.34 = 1.98 = \boxed{2} (z)$$

$$\text{RATE} = K [C]^{.5} \cdot [D]^0 \cdot [E]^2$$

$$\text{TRIAL DATA SET 3: } 4.55 \times 10^{-5} = K [0.100]^{.5} \cdot [0.200]^0 \cdot [0.200]^2$$

$$4.55 \times 10^{-5} = K (1.26 \times 10^{-2}) \rightarrow K = 3.60 \times 10^{-3}$$

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 = $K [\text{BrO}_3^-]^x [\text{Br}^-]^y [\text{H}^+]^z$ $\frac{\text{M}}{\text{L}^4 \text{ UNITS}}$

TRIAL DATA 1: $8.0 \times 10^{-4} = K [0.10]^x [0.10]^y [0.10]^z$

K = $8.0 \times 10^{-4} \frac{\text{M}}{\text{M}^4 \text{ sec}}$

RATE = $[\text{BrO}_3^-]^x [\text{Br}^-]^y [\text{H}^+]^z$
 $\text{BrO}_3^- \rightarrow \frac{2}{1}$ $\frac{1.6 \times 10^{-3}}{8.0 \times 10^{-4}} = K \frac{[0.20]^x [0.10]^y [0.10]^z}{[0.10]^x [0.10]^y [0.10]^z}$

$[2]^x = 2 \rightarrow \boxed{x=1}$

$\text{Br}^- \rightarrow \frac{3}{2}$ $\frac{3.2 \times 10^{-3}}{1.6 \times 10^{-3}} = K \frac{[0.20]^x [0.20]^y [0.10]^z}{[0.20]^x [0.10]^y [0.10]^z}$

$[2]^y = 2 \rightarrow \boxed{y=1}$

$\text{H}^+ \rightarrow \frac{4}{1}$ $\frac{3.2 \times 10^{-3}}{8.0 \times 10^{-4}} = K \frac{[0.10]^x [0.10]^y [0.20]^z}{[0.10]^x [0.10]^y [0.10]^z}$

$[2]^z = 4 \rightarrow \boxed{z=2}$

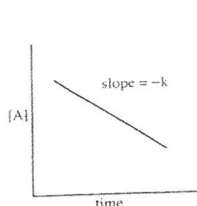
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13.1

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.

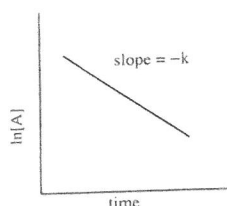
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TABLE 12.6: Summary of the Kinetics for Reactions of the Type $a\text{A} \rightarrow \text{Products}$ That Are Zero, First, or Second Order in $[\text{A}]$

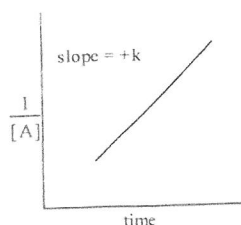
	Zeroth Order	First Order	Second Order
Rate Law:	Rate = k	Rate = $k[\text{A}]$	Rate = $k[\text{A}]^2$
Integrated Rate Law:	$[\text{A}] = -kt + [\text{A}]_0$	$\ln[\text{A}] = -kt + \ln[\text{A}]_0$ $\ln[\text{A}] - \ln[\text{A}]_0 = -kt$	$1/[\text{A}] = kt + 1/[\text{A}]_0$
Plot Needed to Give a Straight 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

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 ²²²Rn, how much sample will be left after 1.96 days? 3.82 days?

1.96 DAYS

$$\ln\left(\frac{5.28\text{g}}{[A]}\right) = (0.181/\text{DAY}) \cdot (1.96\text{ DAYS})$$

$$\frac{5.28}{[A]} = e^{(0.355)} \rightarrow [A] = 3.69\text{ Grams}$$

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

3.82 DAYS

$$\ln\left(\frac{5.28\text{g}}{[A]}\right) = (0.181/\text{DAY}) \cdot (3.82\text{ DAYS})$$

$$[A] = 2.64\text{ Grams}$$

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?

→ 75% COMPLETE MEANS 25% REMAINS!

a) 1st ORDER: $t_{1/2} = \frac{0.693}{K} \rightarrow 20\text{ MIN} = \frac{0.693}{K} \rightarrow K = \frac{0.0347}{\text{MIN}}$

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

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?

$$t_{1/2} = \frac{0.693}{K} \rightarrow 12.8\text{ DAYS} = \frac{0.693}{K} \rightarrow K = \frac{0.054}{\text{DAY}} \cdot \frac{1\text{ DAY}}{24\text{ HR}} \cdot \frac{1\text{ HR}}{3600\text{ SEC}} = \frac{6.3 \times 10^{-7}}{\text{SEC}}$$

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

$$[\text{Cu}^{64}] = \frac{28.0\text{ mg Cu}}{63.5\text{ g Cu}} \cdot \frac{1\text{ mol Cu}}{1\text{ mol Cu}} = 4.41 \times 10^{-4}\text{ mol Cu}$$

$$\text{RATE} = K[A] = \left(\frac{6.3 \times 10^{-7}}{\text{SEC}}\right) (4.41 \times 10^{-4}\text{ mol Cu}) = 2.78 \times 10^{-10}\text{ mol Cu/SEC}$$

$$\text{PARTICLES OF DECAY} = 2.78 \times 10^{-10}\text{ mol Cu/SEC} \cdot 6.02 \times 10^{23}\text{ PARTICLES/mol Cu} = 1.67 \times 10^{14}\text{ PARTICLES/SEC}$$

4. A chemist obtains a fresh sample of ⁶⁴Cu 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?

$$\ln\left(\frac{100}{3}\right) = \left(\frac{6.3 \times 10^{-7}}{\text{SEC}}\right) \cdot t$$

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

SECONDS

$$\ln\left(\frac{100}{3}\right) = \left(\frac{0.054}{\text{DAY}}\right) \cdot t$$

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

DAYS

13.2 Summary

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.

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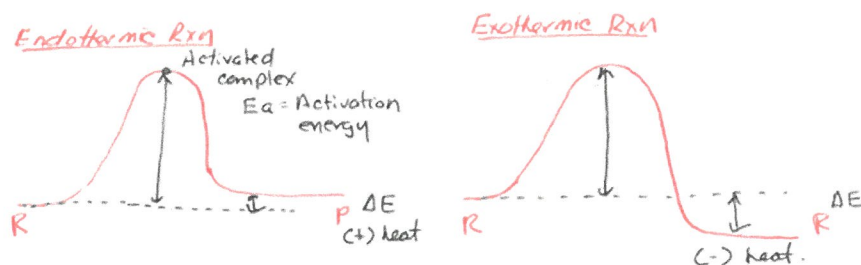
A model of chemical kinetics

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

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

A = frequency factor (different for all reactions)

we don't
use this
version
very often!

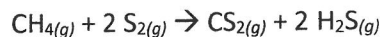
$$\ln(K) = \frac{-E_a}{R} \left(\frac{1}{T_k} \right) + \ln A$$

Activation energy at 2 temperatures

USE THIS ONE!

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

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 L/mol·sec, and at 625°C the rate constant is 6.4 L/mol·sec. Using these values, calculate E_a 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:

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

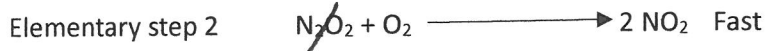
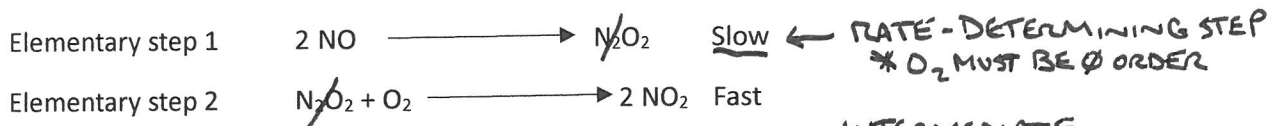
Solving for E_a gives:

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

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

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).

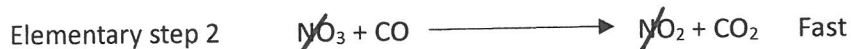
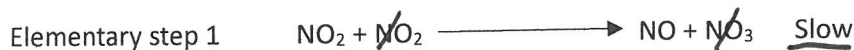


INTERMEDIATE

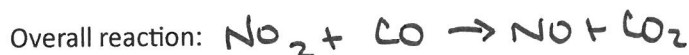
N_2O_2 IS PRODUCED, BUT THEN CONSUMED
(IMPORTANT IN IDENTIFYING MECHANISMS)



EX 2:



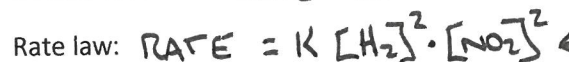
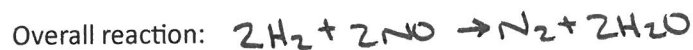
* NO_3 IS INTERMEDIATE *



EX 3:

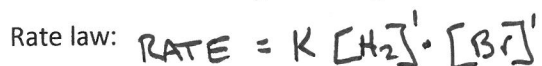


Is this a plausible mechanism?



No! *SLOW STEP DOES NOT MATCH UP W/ EXPERIMENTAL DATA - NOT A PLAUSIBLE RXN*

EX 4: Mechanism:



INTERMEDIATES: H, Br

Br is a CATALYST: INTRODUCED AND REMAINS, BUT NOT PART OF THE REACTION (2ND + 3RD) - 2Br IN 1ST + 4TH USED UP.

* RATHER THAN IT BEING PRODUCED & USED AS A REACTANT, IT IS INTRODUCED & REMAINS AS PRODUCT (LIKE IN 1ST & 4TH)

Fr 13.3

LAST PAGE OF NOTES FOR THE YEAR!
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