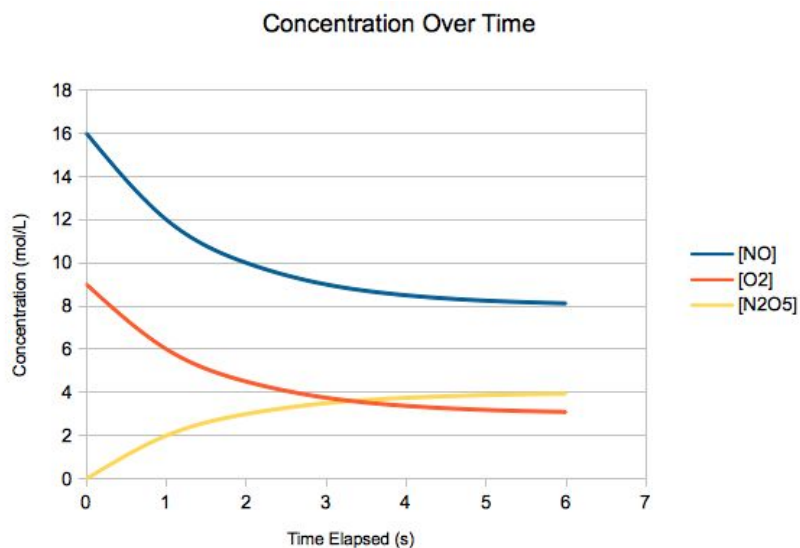


Average and Instantaneous Rates of Reaction

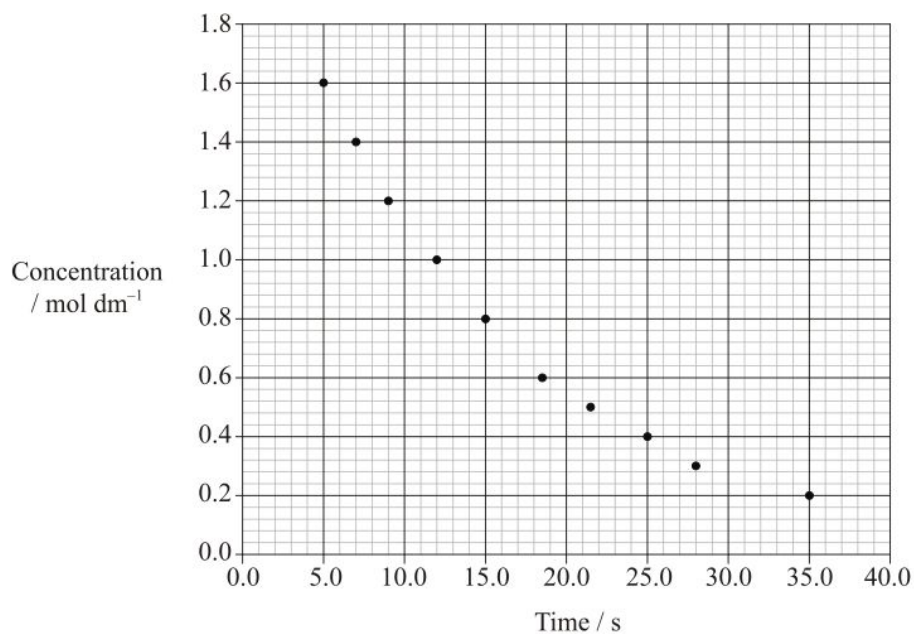
1. In the formation of N_2O_5 , four molecules of NO and three molecules of O_2 combine to form two molecules of N_2O_5 . A graph showing the concentration of each component in an industrial system is shown here.

a) What is the **average** rate of consumption of NO over the first two seconds?



b) Estimate the **instantaneous** rate of consumption of NO at 2 seconds.

2.a) For the reaction on the right, what is the average rate of reaction from 5 seconds to 25 seconds?



b) What is the instantaneous rate of reaction at 25 seconds?

Relative Rates

3. For the reaction $2 N_2O_{5(g)} \rightarrow 4 NO_{2(g)} + O_{2(g)}$, at the time when N_2O_5 is being consumed at a rate of 1.2×10^{-4} M/s:
- What is the rate at which O_2 is being formed?
 - What is the rate at which NO_2 is being produced?
4. In the Haber process, $N_2 + 3H_2 \rightarrow 2NH_3$, what rates of consumption of N_2 and H_2 correspond to production of ammonia at 0.6 moles per minute?
5. In the reaction $Mg_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$, suppose 24.3 g of Mg was consumed in 80 seconds. What is the rate of production of $H_{2(g)}$ in grams per second?

Rate Laws

- 6.a) Consider the elementary reaction: $A + B \rightarrow C$. Use the following data to determine the rate law for the reaction.

[A] (mol/L)	[B] (mol/L)	Rate (mol/L/s)
3	1	6.6
3	2	26.4
6	1	13.2

- b) Solve for k as well, and include units.
- c) What would happen to the rate of reaction if the concentration of A was halved, and the concentration of B was tripled?
7. Use the information below to determine the overall order of the reaction. Then, solve for the two unknowns.

[A] (mol/L)	[B] (mol/L)	Rate (mol/L/s)
0.144	0.291	3.456
0.288	0.291	27.648
0.144	0.873	3.456
0.432	2.052	?
?	1.526	0.384

Collision Theory and Transition State Theory

8. Use collision theory to explain why each of the following will **increase** the rate of reaction:
- Increasing Temperature
 - Adding a catalyst
 - Increasing concentration of reactants
 - Increasing the surface area of reactants
9. Draw a generic Maxwell-Boltzmann distribution, then on the same axes draw a second distribution representing the same sample at a **higher** temperature.
10. Draw a generic potential energy diagram for an endothermic reaction. Then, on the same axes draw a second distribution representing the same reaction **with a catalyst**.
11. Suggest at least three ways to **increase** the rate of the reaction between excess zinc granules and dilute hydrochloric acid:
- $$\text{Zn}_{(s)} + 2\text{HCl}_{(aq)} \rightarrow \text{ZnCl}_{2(aq)} + \text{H}_{2(g)}$$

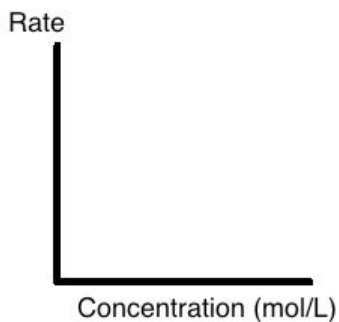
Miscellaneous

12. A reaction has the rate law $Rate = k[A][B]^2$. Which will cause the rate to increase the most?
(Multiple Choice)
- a) tripling [B]
 - b) lowering temperature
 - c) quadrupling [A]
 - d) doubling [B]
 - e) doubling [A]
13. What are the appropriate units for:
- a) Rate of reaction
 - b) k for a first-order reaction
 - c) k for a second-order reaction
 - d) k for a zeroth order reaction
 - e) k for a reaction that is 6th order overall
14. Distinguish between **catalyst**, **intermediate** and **transition state**.

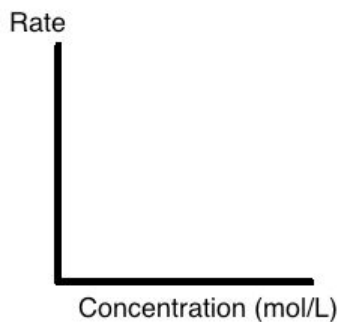
Graphs 1: Rate vs Concentration

15. Sketch graphs of Rate vs Concentration for a:

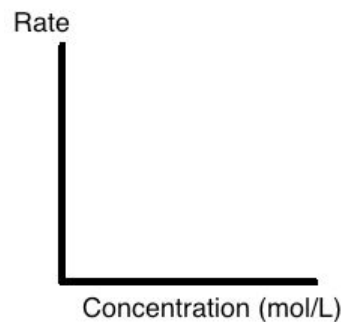
a) Zero-order reaction



b) First-Order reaction

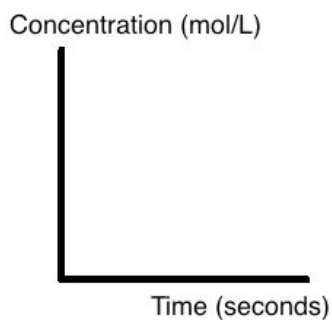


c) Second-Order reaction

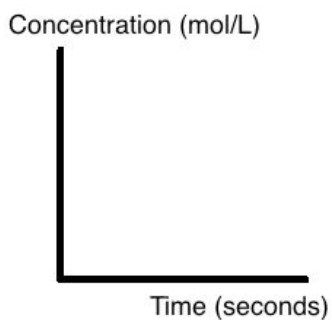


16. Sketch Graphs of Concentration vs time for:

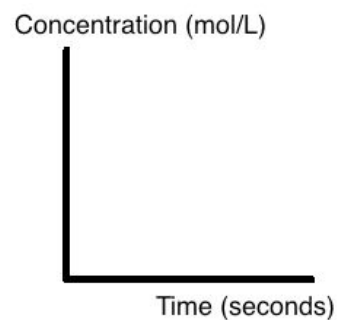
a) Zero-order reaction



b) First-Order reaction

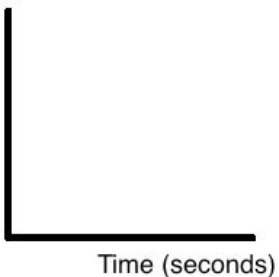


c) Second-Order reaction

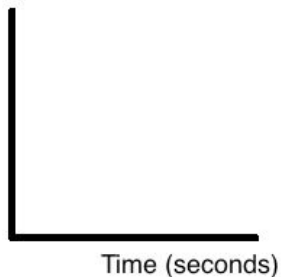


17. How can you process the *Concentration vs Time* data from Question 16 to create linear graphs?

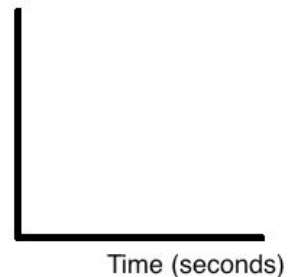
a) Zero-order reaction



b) First-Order reaction

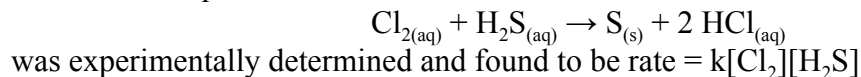


c) Second-Order reaction

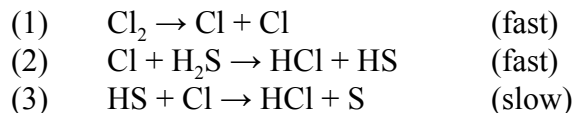


Mechanisms

18. The rate law equation for the reaction

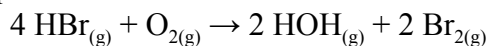


a) Explain, with two reasons, why the following mechanism is reasonable [2 marks]

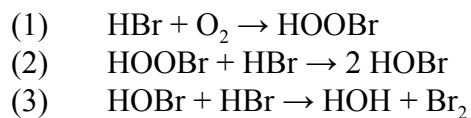


b) Indicate the molecularity of each step of the proposed mechanism [1 mark]

19. Consider the balanced equation for the oxidation of HBr.



The following mechanism has been proposed:



a) Define the term *rate determining step*. What is its significance? [1 mark]

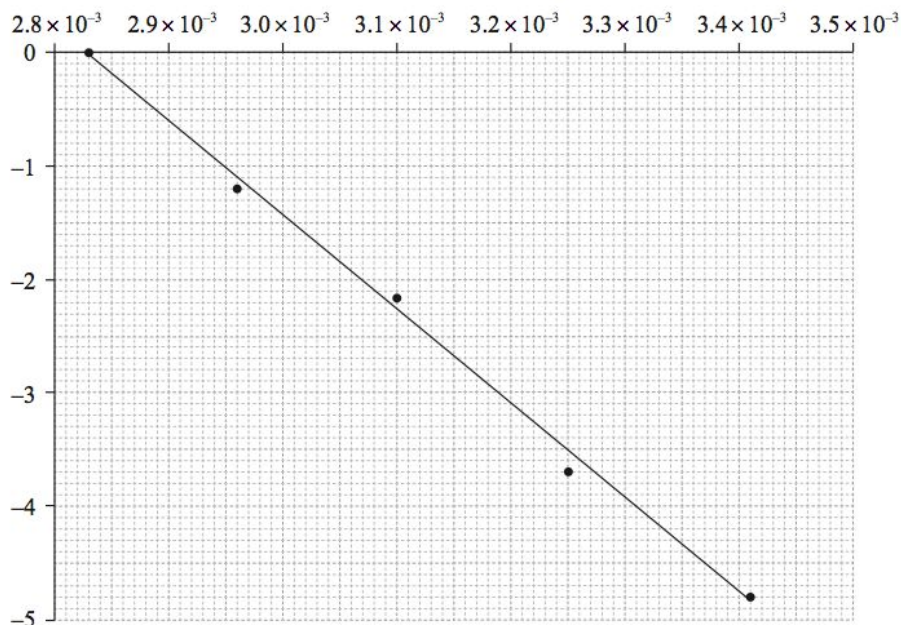
b) If the rate law equation is: rate = $k[\text{HBr}][\text{O}_2]$, which step of the mechanism must be rate determining?

Arrhenius Equation

20. The activation energy can be determined using the Arrhenius equation, $k = Ae^{\frac{-E_a}{RT}}$.

A kinetics experiment was carried out at five different temperatures. An incomplete graph, based on these results, is shown below.

- Label the axes.
- Determine the activation energy for this reaction.



21. The following rate data were obtained for the decomposition of N_2O_5 .

Temperature ($^{\circ}\text{C}$)	Rate constant (s^{-1})
35	1.4×10^{-4}
45	5.0×10^{-4}

Calculate the activation energy for the decomposition of N_2O_5 .

22. At 973 K, the rate constant for a reaction is $1.57 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$. Calculate the rate constant at 1073 K, given that the activation energy is 182 kJ/mol.

Integrated Rate Laws

$$\begin{aligned} [A] &= [A]_0 - kt \\ \ln[A] &= \ln[A]_0 - kt \\ \frac{1}{[A]} &= \frac{1}{[A]_0} + kt \end{aligned}$$

23. The following data are obtained for a reaction at 300 K.



Time (seconds)	[A] (mol/L)
0	5
20	4.44
40	3.92
60	3.46
80	3.06

- a) What is the order of the reaction?
- b) What is the rate constant (include units)?

24. Derive expressions for the half-life of a chemical reaction from the integrated rate laws for:

a) 0th order reaction

b) First order reaction

c) Second order reaction

25. The decomposition reaction $A \rightarrow B + C$ is known to be first order with respect to the reactant.

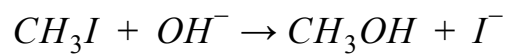
The data below was collected on the investigation of this reaction:

Time (min)	[A] (mol/L)
0	1
10	0.1

a) Calculate the rate constant, k , and attach the proper units.

b) Calculate the half-life and attach the proper units.

26. Predict the structure of the transition state between reactants and products for this reaction:



27. Define the following:

a) Activation energy

b) Activated Complex

c) Enthalpy Change

d) Kinetic Energy

e) Chemical Potential Energy

f) Rate Law

g) Rate Constant

Answers

1. In the formation of N_2O_5 , four molecules of NO and three molecules of O_2 combine to form two molecules of N_2O_5 . A graph showing the concentration of each component in an industrial system is shown here.

a) What is the **average** rate of consumption of NO over the first two seconds?

* at 0 s, $[\text{NO}] = 16 \text{ mol/L}$

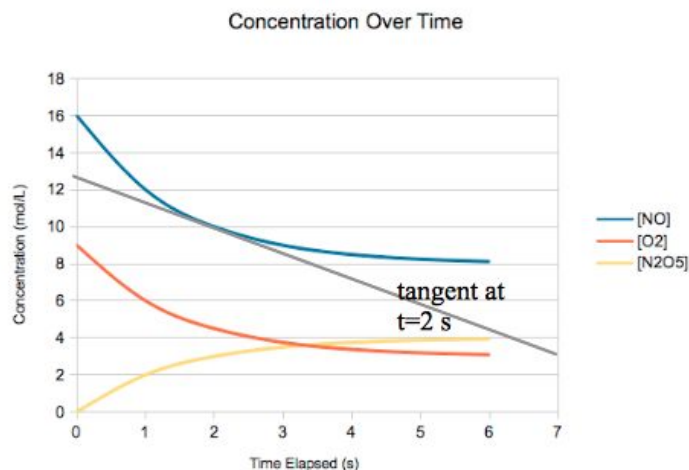
* at 2 s, $[\text{NO}] = 10 \text{ mol/L}$

$$\begin{aligned} \text{AvgRate} &= \frac{y_2 - y_1}{x_2 - x_1} = \frac{10 \frac{\text{mol}}{\text{L}} - 16 \frac{\text{mol}}{\text{L}}}{2\text{s} - 0\text{s}} \\ &= \frac{-6 \frac{\text{mol}}{\text{L}}}{2\text{s}} = -3 \frac{\text{mol}}{\text{L}\cdot\text{s}} \end{aligned}$$

b) Estimate the **instantaneous** rate of consumption of NO at 2 seconds.

Using the tangent line: At 0 s, $[\text{NO}] = 12.5 \text{ mol/L}$ and at 7 s, $[\text{NO}] = 3.5 \text{ mol/L}$.

$$\begin{aligned} \text{InstRate} &= \frac{y_2 - y_1}{x_2 - x_1} = \frac{3.5 \frac{\text{mol}}{\text{L}} - 12.5 \frac{\text{mol}}{\text{L}}}{7\text{s} - 0\text{s}} \\ &= \frac{-9 \frac{\text{mol}}{\text{L}}}{7\text{s}} = -1.289 \frac{\text{mol}}{\text{L}\cdot\text{s}} \end{aligned}$$



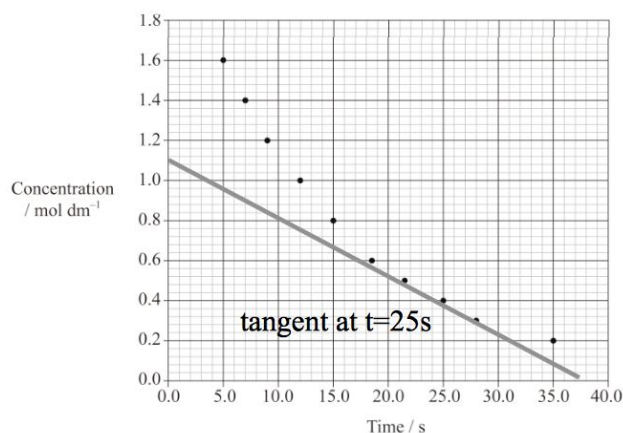
2.a) For the reaction on the right, what is the average rate of reaction from 5 seconds to 25 seconds?

At 5 s, $C = 1.6 \text{ mol dm}^{-3}$

At 25 s, $C = 0.4 \text{ mol dm}^{-3}$

$$\begin{aligned} \text{AvgRate} &= \frac{y_2 - y_1}{x_2 - x_1} = \frac{0.4 \text{ mol dm}^{-3} - 1.6 \text{ mol dm}^{-3}}{25\text{s} - 5\text{s}} \\ &= \frac{-1.2 \text{ mol dm}^{-3}}{20\text{s}} = -0.06 \frac{\text{mol dm}^{-3}}{\text{s}} \end{aligned}$$

b) What is the instantaneous rate of reaction at 25 seconds?



Using the tangent: At 0 s, $C = 1.08 \text{ mol dm}^{-3}$ and at 35 s, $C = 0.08 \text{ mol dm}^{-3}$.

$$\text{InstRate} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{0.08 \text{ mol dm}^{-3} - 1.08 \text{ mol dm}^{-3}}{35\text{s} - 0\text{s}} = \frac{-1.00 \text{ mol dm}^{-3}}{35\text{s}} = 0.02857 \frac{\text{mol dm}^{-3}}{\text{s}}$$

3. For the reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$, at the time when N_2O_5 is being consumed at a rate of $1.2 \times 10^{-4} M/s$:

a) What is the rate at which O_2 is being formed?

$$Rate(O_2) = \frac{1}{2}Rate(N_2O_5) = \frac{1}{2}(1.2 \times 10^{-4} \frac{M}{s}) = 6.0 \times 10^{-5} \frac{M}{s}$$

b) What is the rate at which NO_2 is being produced?

$$Rate(NO_2) = \frac{4}{2}Rate(N_2O_5) = \frac{4}{2}(1.2 \times 10^{-4} \frac{M}{s}) = 2.4 \times 10^{-4} \frac{M}{s}$$

4. In the Haber process, $N_2 + 3H_2 \rightarrow 2NH_3$, what rates of consumption of N_2 and H_2 correspond to production of ammonia at 0.6 moles per minute?

$$Rate(N_2) = \frac{1}{2}Rate(NH_3) = \frac{1}{2}(0.6 \frac{mol}{min}) = 0.3 \frac{mol}{min}$$

$$Rate(H_2) = \frac{3}{2}Rate(NH_3) = \frac{3}{2}(0.6 \frac{mol}{min}) = 1.8 \frac{mol}{min}$$

5. In the reaction $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$, suppose 24.3 g of Mg was consumed in 80 seconds. What is the rate of production of $H_2(g)$ in grams per second?

Rate given in g/s: $Rate(Mg) = \frac{24.3g}{80s} = 0.30375 \frac{g}{s}$

Convert to mol/s: $(\frac{0.30375g}{1s}) \times (\frac{1mol}{24.302g}) = 0.01250 \frac{mol}{s}$

Relative Rates: $Rate(H_2) = \frac{1}{1}Rate(Mg) = 0.01250 \frac{mol}{s}$

Convert to g/s: $(\frac{0.01250mol}{1s}) \times (\frac{2.0158g}{1mol}) = 0.0252 \frac{g}{s}$

6.a) Consider the elementary reaction: $A + B \rightarrow C$. Use the following data to determine the rate law for the reaction.

Rows 1 and 3:

[A] increases by a factor of 2; [B] is constant;
rate increases by factor of $13.2/6.6 = 2$; So the order of reaction with respect to A is 1

[A] (mol/L)	[B] (mol/L)	Rate (mol/L/s)
3	1	6.6
3	2	26.4
6	1	13.2

Rows 1 and 2: [B] doubles and rate quadruples, so the order of reaction with respect to B is 2

$$\text{Rate} = k[A]^1[B]^2$$

b) Solve for k as well. Use the data from any row. I choose row 3:

$$k = \frac{\text{Rate}}{[A][B]^2} = \frac{13.2 \frac{\text{mol}}{\text{L}\cdot\text{s}}}{(6 \frac{\text{mol}}{\text{L}})(1 \frac{\text{mol}}{\text{L}})^2} = \frac{13.2}{6} \frac{\text{L}^2}{\text{mol}^2\cdot\text{s}} = 2.2 \frac{\text{L}^2}{\text{mol}^2\cdot\text{s}}$$

c) What would happen to the rate of reaction if the concentration of A was halved, and the concentration of B was tripled?

Rate would change by a factor of $(\frac{1}{2})(3)^2 = 4.5$

7. Use the information below to determine the overall order of the reaction. Then, solve for the two unknowns.

Rows 1 and 2: [A] doubles; [B] is constant; rate changes by $27.648/3.456 = 8$
So order of reaction with respect to A is 3. This is because $(2)^3 = 8$.

Rows 1 and 3: [B] goes up by a factor of $0.873/0.291 = 3$; rate doesn't change
So order of reaction with respect to B is 0

$$\text{Rate} = k[A]^3.$$

$$\text{First ?} \rightarrow \frac{\text{Rate}_{\text{row4}}}{\text{Rate}_{\text{row1}}} = \frac{([A]_{\text{row4}})^3}{([A]_{\text{row1}})^3}$$

$$\frac{x}{3.456} = \frac{0.432^3}{(0.144)^3}$$

$$x = \frac{0.432^3}{(0.144)^3} (3.456) = 31.104$$

$$\text{Second ?} \rightarrow \text{Between rows 1 and 5: } \frac{\text{Rate}_{\text{row5}}}{\text{Rate}_{\text{row1}}} = \frac{([A]_{\text{row5}})^3}{([A]_{\text{row1}})^3}$$

$$\frac{0.384}{3.456} = \frac{x^3}{(0.144)^3}$$

$$x = \sqrt[3]{\left(\frac{0.384}{3.456}\right)(0.144)^3} = \sqrt[3]{0.000331776} = 0.018$$

[A] (mol/L)	[B] (mol/L)	Rate (mol/L/s)
0.144	0.291	3.456
0.288	0.291	27.648
0.144	0.873	3.456
0.432	2.052	?
?	1.526	0.384

8. Use collision theory to explain why each of the following will **increase** the rate of reaction:

a) Increasing Temperature

increases speed of molecules → more collision AND each collision is more energetic

b) Adding a catalyst

lowers activation energy → increases the probability of each collision to result in a reaction

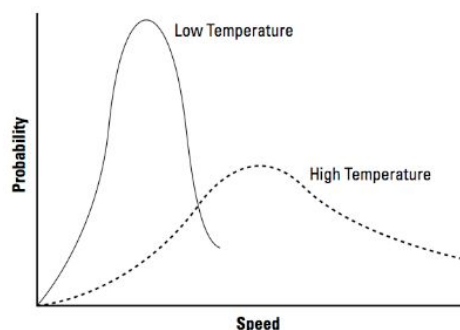
c) Increasing concentration of reactants

more collisions. Note: Concentration does not change the % effectiveness of each collision.

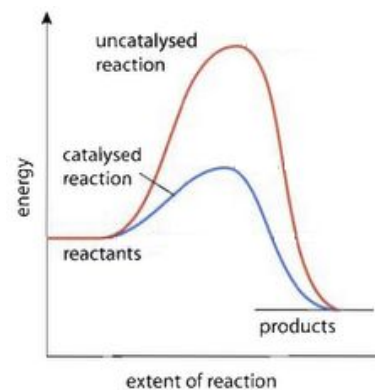
d) Increasing the surface area of reactants

more collisions. Note: Surface area does not change the % effectiveness of each collision.

9. Draw a generic Maxwell-Boltzmann distribution, then on the same axes draw a second distribution representing the same sample at a **higher** temperature.



10. Draw a generic potential energy diagram for an endothermic reaction. Then, on the same axes draw a second distribution representing the same reaction **with a catalyst**.



11. Suggest at least three ways to **increase** the rate of the reaction between excess zinc granules and dilute hydrochloric acid:

$$\text{Zn}_{(s)} + 2\text{HCl}_{(aq)} \rightarrow \text{ZnCl}_{2(aq)} + \text{H}_{2(g)}$$

grind zinc into powder (surface area); increase temperature; add catalyst; increase concentration of $\text{HCl}_{(aq)}$

12. A reaction has the rate law $Rate = k[A][B]^2$. Which will cause the rate to increase the most? (Multiple Choice)

- a) tripling [B] <-- increases rate by $3^2 = \times 9$
- b) lowering temperature <-- decreases rate
- c) quadrupling [A] <-- increases rate by $4^1 = \times 4$
- d) doubling [B] <-- increases rate by $2^2 = \times 4$
- e) doubling [A] <-- increases rate by $2^1 = \times 2$

13. What are the appropriate units for:

- a) Rate of reaction $\frac{mol}{L \cdot s}$ OR $\frac{mol}{L \cdot min}$
- b) k for a first-order reaction $\frac{L^0}{mol^0 \cdot s} = \frac{1}{s}$
- c) k for a second-order reaction $\frac{L^1}{mol^1 \cdot s} = \frac{L}{mol \cdot s}$
- d) k for a zeroth order reaction $\frac{L^{-1}}{mol^{-1} \cdot s} = \frac{mol}{L \cdot s}$
- e) k for a reaction that is 6th order overall $\frac{L^5}{mol^5 \cdot s}$

14. Distinguish between **catalyst**, **intermediate** and **transition state**.

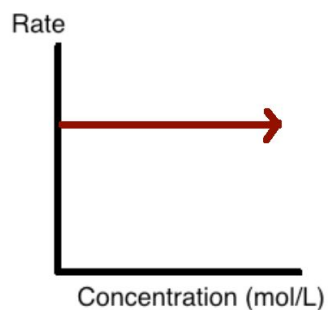
Catalyst: increases reaction rate by providing an alternative pathway for the reaction with lower activation energy. It is consumed in one step of the reaction and then regenerated later, so it does not appear in the overall reaction equation.

Intermediate: a stable product of one step of a reaction that is used up in a later step. It is a **trough** of a potential energy curve in a multi-step reaction.

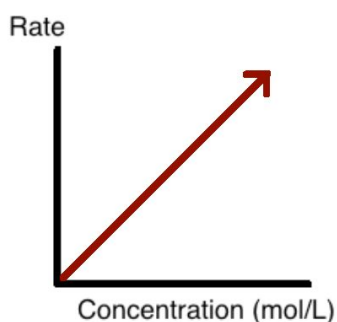
Transition State: an unstable structure that is halfway in between the reactants and products of a step of a reaction. Usually has half bonds for the bonds that are breaking and half bonds for the bonds that are forming. They are the **peaks** of a potential energy curve.

15. Sketch graphs of Rate vs Concentration for a:

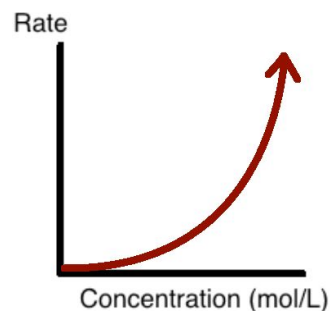
a) Zero-order reaction



b) First-Order reaction

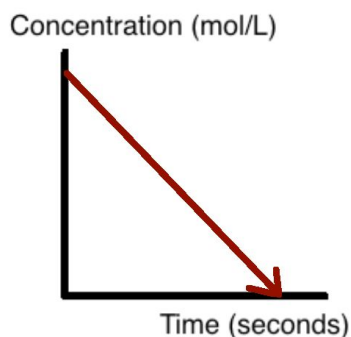


c) Second-Order reaction

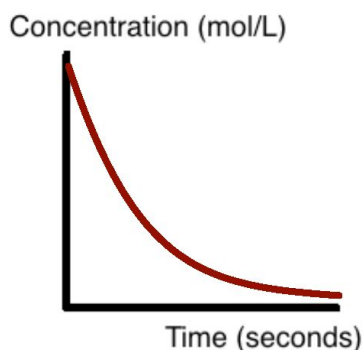


16. Sketch Graphs of Concentration vs time for:

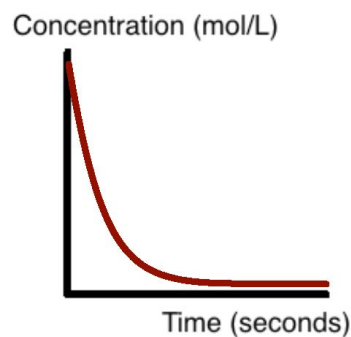
a) Zero-order reaction



b) First-Order reaction

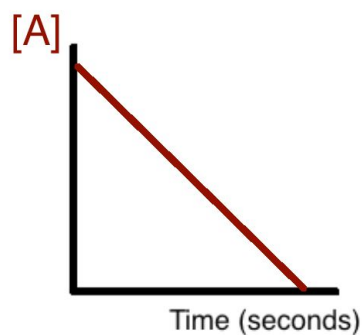


c) Second-Order reaction

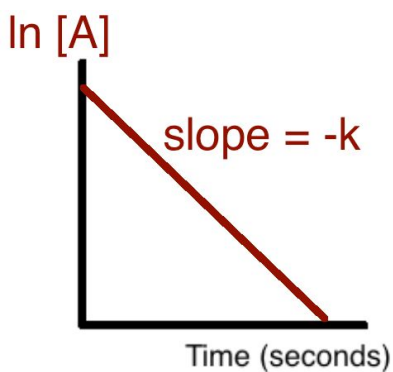


17. How can you process the *Concentration vs Time* data from Question 16 to create linear graphs?

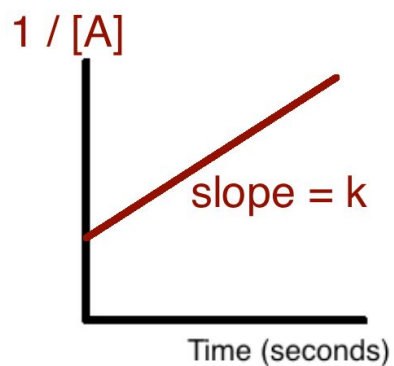
a) Zero-order reaction



b) First-Order reaction

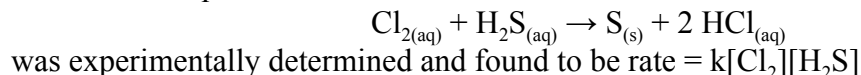


c) Second-Order reaction

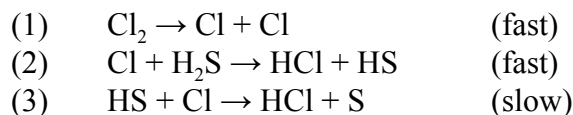


Mechanisms

18. The rate law equation for the reaction



a) Explain, with two reasons, why the following mechanism is reasonable [2 marks]



To be considered valid, a mechanism needs:

- each elementary to have *at most* three reactant molecules
- the stoichiometry of the slow step must match the rate law
- the steps of the mechanism must add up to the overall reaction

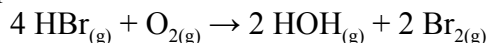
b) Indicate the molecularity of each step of the proposed mechanism [1 mark]

Step 1 is ($\text{Cl}_2 \rightarrow$) which is only one molecule .. that's **unimolecular**

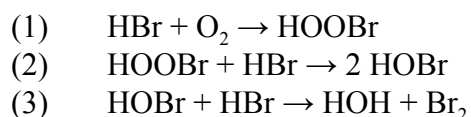
Step 2 is ($\text{Cl} + \text{H}_2\text{S} \rightarrow$) which is two molecules ... that's **bimolecular** (“dimolecular” also ok)

Step 3 is ($\text{HS} + \text{Cl} \rightarrow$) which is two molecules ... that's **bimolecular** (“dimolecular” is ok again)

19. Consider the balanced equation for the oxidation of HBr.



The following mechanism has been proposed:



a) Define the term *rate determining step*. What is its significance? [1 mark]

The *rate determining step* is the slowest step of the mechanism.

On the potential energy diagram, this step's peak is higher than all the others.

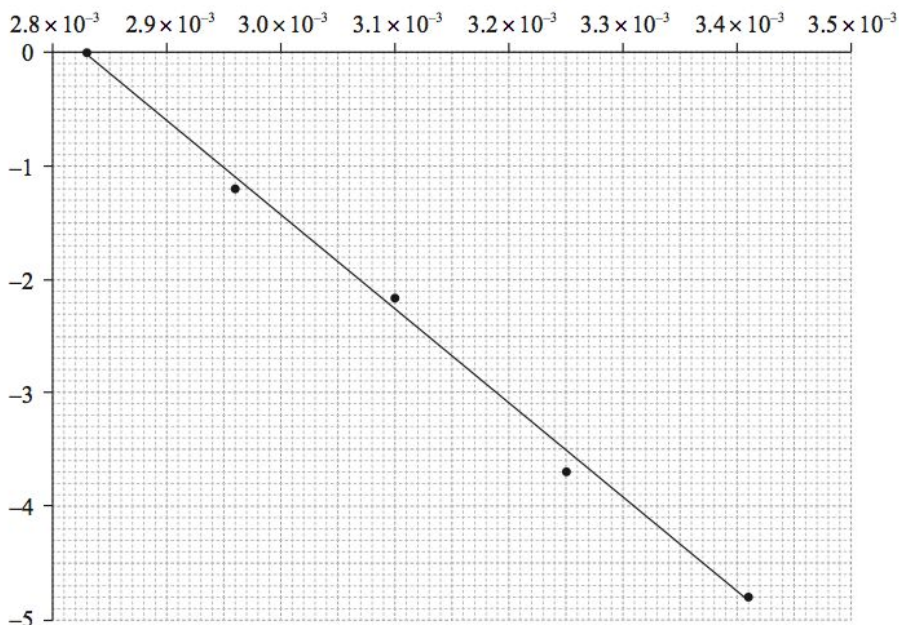
b) If the rate law equation is: rate = $k[\text{HBr}][\text{O}_2]$, which step of the mechanism must be rate determining?

The first step is ($\text{HBr} + \text{O}_2 \rightarrow$) which corresponds to $k[\text{HBr}]^1[\text{O}_2]^1$, and so the first step is the rate-determining one.

Arrhenius Equation

20. The activation energy can be determined using the Arrhenius equation, $k = Ae^{\frac{-E_a}{RT}}$.

A kinetics experiment was carried out at five different temperatures. An incomplete graph, based on these results, is shown below.



a) Label the axes.

On an Arrhenius plot, the x-axis is $1/T$ (where T is in Kelvin) and the y-axis is $\ln k$, which is unitless.

b) Determine the activation energy for this reaction.

On an Arrhenius plot, the slope of the line is $-E_a/R$.

$$\text{Here, } slope = \frac{y_2 - y_1}{x_2 - x_1} = \frac{-4.8 - 0}{(3.41 \times 10^{-3} \text{ K}^{-1}) - (2.83 \times 10^{-3} \text{ K}^{-1})} = \frac{-4.8}{5.8 \times 10^{-4}} = -8275.86 \text{ K}$$

$$\text{and so } E_a = -(slope)(R) = -(-8275.86 \text{ K})(8.314 \frac{\text{J}}{\text{mol K}}) = 68805 \frac{\text{J}}{\text{mol}} = 68.8 \frac{\text{kJ}}{\text{mol}}$$

21. The following rate data were obtained for the decomposition of N_2O_5 .

Temperature ($^{\circ}\text{C}$)	Rate constant (s^{-1})
35 = 308.15 K	1.4×10^{-4}
45 = 318.15 K	5.0×10^{-4}

Calculate the activation energy for the decomposition of N_2O_5

For questions 21 and 22, If you know that $k = Ae^{\frac{-E_a}{RT}}$, then you can use two expressions: $k_1 = Ae^{\frac{-E_a}{RT_1}}$ and $k_2 = Ae^{\frac{-E_a}{RT_2}}$, and do some mathematical manipulation to get an expression. Or, you could just memorize the end result:

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{Note: This is the same as } \ln \frac{k_2}{k_1} = \frac{-E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

which shows how rate constants change with temperature (in Kelvin)

$$\ln \frac{5.3 \times 10^{-4}}{1.4 \times 10^{-4}} = \frac{E_a}{(8.314 \frac{\text{J}}{\text{mol K}})} \left(\frac{1}{308.15 \text{ K}} - \frac{1}{318.15 \text{ K}} \right)$$

$$1.33 = \frac{E_a}{(8.314 \frac{J}{mol K})} (1.02 \times 10^{-4} K^{-1})$$

$$E_a = \frac{(1.33)(8.314 \frac{J}{mol K})}{(1.02 \times 10^{-4} K^{-1})} = 108408 \frac{J}{mol} = 108.4 \frac{kJ}{mol}$$

22. At 973 K, the rate constant for a reaction is $1.57 \times 10^{-5} M^{-1} s^{-1}$. Calculate the rate constant at 1073 K, given that the activation energy is 182 kJ/mol.

$$\ln \frac{k_2}{1.57 \times 10^{-5} M^{-1} s^{-1}} = \frac{182000 \frac{J}{mol}}{8.314 \frac{J}{mol K}} \left(\frac{1}{973 K} - \frac{1}{1073 K} \right)$$

$$\ln \frac{k_2}{1.57 \times 10^{-5} M^{-1} s^{-1}} = 2.097$$

$$\frac{k_2}{1.57 \times 10^{-5} M^{-1} s^{-1}} = e^{2.097}$$

$$\frac{k_2}{1.57 \times 10^{-5} M^{-1} s^{-1}} = 8.140$$

$$k_2 = 8.140 (1.57 \times 10^{-5} M^{-1} s^{-1})$$

$$k_2 = 1.28 \times 10^{-4} M^{-1} s^{-1}$$

23.

A 0th order reaction is linear when you plot [A] vs t

A 1st order reaction is linear when you plot ln[A] vs t

A 2nd order reaction is linear when you plot 1/[A] vs t

These can be determined from integrated rate laws, but if you're not a math fan, just memorize it.

- a) What is the order of the reaction?

My recommendation is to make two new columns in the table, and use your calculator.

Time (seconds)	[A] (mol/L)	ln [A]	1 / [A]
0	5	1.609	0.200
20	4.44	1.491	0.225
40	3.92	1.366	0.255
60	3.46	1.241	0.289
80	3.06	1.118	0.327

Which one is linear?

[A] doesn't go down by a constant amount each time (It goes down 0.56, then 0.52, then 0.46)

1/[A] doesn't go down by a constant amount each time (It goes up 0.025, then 0.30, then 0.034)

ln [A] goes down a constant amount (approximately) each time (down 0.118, then 0.125, then 0.125)

So, $\ln[A]$ vs t is linear, and the reaction is **1st order**

b) What is the rate constant (include units)?

For a first-order reaction: $\ln[A] = -kt + \ln[A]_0$

This is called the **integrated rate law** for the reaction. You can derive it, but you need to use integration, and if you don't like math, just memorize it (and the others)

So, we can just fill in the numbers we have at any given time (except 0):

$$\ln[A] = -kt + \ln[A]_0$$

$$\ln(4.44) = -k(20s) + \ln(5)$$

$$1.491 = -k(20s) + 1.609$$

$$-0.118 = -k(20s)$$

$$\frac{-0.118}{-20s} = k$$

$$0.0059s^{-1} = k$$

The answer is **0.006 s⁻¹**

24. Derive expressions for the half-life of a chemical reaction from the integrated rate laws for:

To find expressions for half-life, replace $[A]$ with $\frac{1}{2}[A]_0$, since half-life is the time it takes for the concentration to become half the original. Then, solve for t .

a) 0th order reaction

$$[A] = [A]_0 - kt$$

$$\frac{1}{2}[A]_0 = [A]_0 - kt$$

$$kt = [A]_0 - \frac{1}{2}[A]_0$$

$$kt = \frac{1}{2}[A]_0$$

$$t = \frac{[A]_0}{2k}$$

b) First order reaction

$$\ln[A] = \ln[A]_0 - kt$$

$$\ln\left(\frac{1}{2}[A]_0\right) = \ln[A]_0 - kt$$

$$\ln\left(\frac{1}{2}[A]_0\right) - \ln[A]_0 = -kt$$

$$\ln\left(\frac{[A]_0}{2[A]_0}\right) = -kt$$

$$\ln\left(\frac{1}{2}\right) = -kt$$

$$t = \frac{-\ln(1/2)}{k}$$

$$t = \frac{\ln 2}{k}$$

c) Second order reaction

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

$$\frac{1}{\frac{1}{2}[A]_0} = \frac{1}{[A]_0} + kt$$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt$$

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

$$t = \frac{1}{k[A]_0}$$

25. The decomposition reaction $A \rightarrow B + C$ is known to be first order with respect to the reactant.

The data below was collected on the investigation of this reaction:

Time (min)	[A] (mol/L)
0	1
10	0.1

a) Calculate the rate constant, k , and attach the proper units.

For a first-order reaction, $\ln[A]$ vs t is linear with slope $-k$.

At time=0, $[A]=1$ mol/L, and so $\ln[A] = \ln(1) = 0$

At time=10, $[A]=0.1$ mol/L and so $\ln[A] = \ln(0.1) = -2.303$

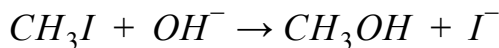
$$\text{slope} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{0 - (-2.303)}{0 - 10} = \frac{-2.303}{10} = -0.2303$$

$$\text{So } k = 0.2303 \frac{\text{L}}{\text{mol min}}$$

b) Calculate the half-life and attach the proper units.

$$\text{Half life for first-order reaction: } t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{0.2303} = 3.01 \text{ min}$$

26. Predict the structure of the transition state between reactants and products for this reaction:



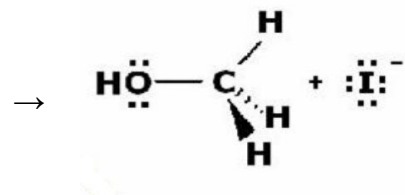
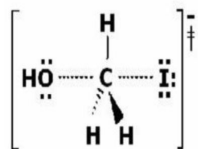
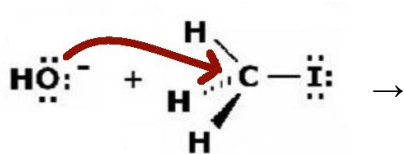
OH attacks the CH_3I

→

This is the transition state

→

I^- leaves



27. Define the following:

a) Activation energy

The minimum amount of energy that molecules need to have to react and form products.
It is the difference between the energy of the reactants and the transition state.

b) Activated Complex

The molecular structure of the transition state.

Lots of people use “transition state” and “activated complex” interchangeably ... I like to say that the transition state is the idea that the molecule can go from reactants to products (or vice versa) and the activated complex is the actual molecular structure of this half-reactant-half-product hybrid.

c) Enthalpy Change

The amount of energy released or absorbed as reactants become products.

d) Kinetic Energy

The amount of energy that manifests itself as *motion* of molecules.
This includes vibration, rotation and translation.

e) Chemical Potential Energy

Energy that *can* be released (and absorbed by something else) in the chemical reaction.

In a chemical reaction, fast-moving molecules collide and bonds can be broken. This is a conversion of kinetic energy (motion) into chemical potential energy (atoms, molecules, etc) that *can* react and release energy when new bonds are formed.

f) Rate Law

A mathematical equation that relates the rate of reaction to a coefficient (k) and the concentrations of reactants.

g) Rate Constant

The constant of proportionality (“coefficient”) found in the rate law.
Large k values belong to reactions with fast rates, since “*Rate* \propto *k*”