

ANALYSIS:

Procedural Questions:

1. Identify the variables (independent, dependent and controlled) in part B and part C.

Independent variable – the one and only variable changed by the experimenter (I change it)

Dependent variable – the experimenter measures this to see the effect of the change

Controlled variable – the other variables are kept the same so that we can assure that the one we changed is responsible for measured effect

Experiment 1 – part B

Independent variable – different concentrations of $\text{Na}_2\text{S}_2\text{O}_3$

Dependent variable – the time for the reaction to get to the point where the black plus sign is no longer visible - then the relative rate is calculated

Controlled variable – same concentrations of HCl

Experiment 2 – part C

Independent variable – different concentrations of HCl

Dependent variable – the time for the reaction to get to the point where the black plus sign is no longer visible - then the relative rate is calculated

Controlled variable – same concentrations of $\text{Na}_2\text{S}_2\text{O}_3$

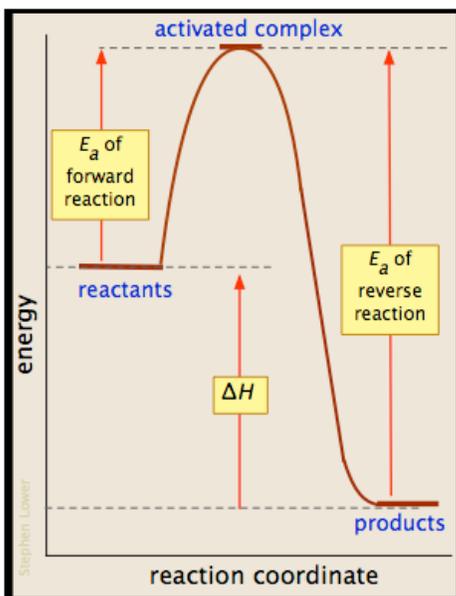
2. How is the volume of the mixture solution a controlled variable?

The total volume is 5.0 mL is the same in all the cup so that the same – the black plus sign is the same appearance suggesting the same endpoint

Concept Questions:

3. Differentiate between collisions and effective collisions. Relate collisions to the rate of a reaction.

The kinetic molecular theory – particles in constant random motion. Particles collide and transfer energy. The result may transfer cause the particles to move faster (change motion \rightarrow increase KE) or break attractions (change position \rightarrow increase PE). Effective collisions are those collisions with enough KE and at the right orientation to break bonds (attractions). The number of effective collisions per second will determine the rate of the reaction.



4. Sketch a reaction coordinate diagram (enthalpy graph) for a single step exothermic reaction. Mark the activation energy for the forward and reverse reactions and net change in enthalpy. How does activation energy affect the rate of the reaction? Which reaction would expect to be faster: the forward or the reverse?

The forward reaction has a lower activation energy, therefore the forward reaction is faster. With a lower activation energy, less energy is required to break attractions (an effective collision). A greater fraction of the collisions will meet this threshold – there will be more effective collisions per second.

The activation energy is related to the kinetics – rate of the reaction.

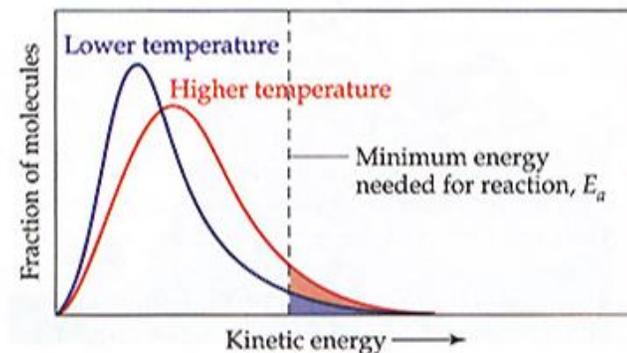
The ΔH portion of the graph is related to the thermodynamics- whether the reaction will occur.

5. Explain the effect of temperature on the rate of a reaction. Include collisions (both total number and effective collisions), activation energy and the distribution of KE (Boltzman curve) at a given temperature.

An increase temperature – by definition increase in average kinetic energy

The particles are moving faster – they will collide more often and with more KE on average.

A greater fraction of the collisions will be effective - particles with enough KE to break attractions



6. Explain the effect of a catalyst on the reaction rate.

Include collisions (both total number and effective collisions), activation energy and the distribution of KE (Boltzman curve) at a given temperature.

A catalyst changes the reaction mechanism. The result is a lower activation energy. Since less energy is required for an effective collision, a greater fraction of the collisions are effective.

7. A reaction has the following rate law: $\text{rate} = k[\text{A}]^2[\text{B}]$.

- a. What is the overall rate order of the reaction?

Second order for A and first order for B

Overall order is third order (sum of the orders – exponents)

- b. Describe the effect of each of the following changes on the rate of reaction:

- doubling the concentration of A compared to doubling the concentration of B

Second order for A and first order for B

Doubling (2x) the concentration of A leads to four times (4x) the rate – an exponential relationship

Doubling (2x) the concentration of B leads to double (2x) the rate – a linear relationship

- tripling the concentration of A compared to tripling the concentration of B

Second order for A and first order for B

Tripling (3x) the concentration of A leads to nine times (9x) the rate – an exponential relationship

Tripling (3x) the concentration of B leads to tripling (3x) the rate – a linear relationship

- reducing the concentration of A by $\frac{1}{2}$

Second order for A and first order for B

Half ($\frac{1}{2}$ x) the concentration of A leads to one-fourth ($\frac{1}{4}$ x) the rate – an exponential relationship

Half ($\frac{1}{2}$ x) the concentration of B leads to tripling half ($\frac{1}{2}$ x) the rate – a linear relationship

Additional Calculations:

8. Experimental data are listed here for the reaction $\text{A} \rightarrow 2\text{B}$ (15.20)

- a. Prepare a graph from these data, connect the points in a smooth line.

Calculate the rate of change of [B] for each 10-s interval from 0.0 to 40.0 s. Does the rate of change decrease from one time interval to the next? Suggest a reason for this result.

- b. How is the rate of change of [A] related to the rate of change of [B] in each time interval?

Calculate the rate of $\Delta[\text{A}]$ for the interval 10.0 to 20.0 s.

- c. What is the instantaneous rate when $[\text{B}] = 0.750 \text{ mol/L}$?

Time (s)	[B] (mol/L)
0.00	0.000
10.0	0.326
20.0	0.572
30.0	0.750
40.0	0.890

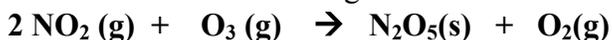
9. In the synthesis of ammonia, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$, if the $-\Delta[\text{H}_2]/\Delta t = -4.5 \times 10^{-4} \text{ mol/L min}$. What is $\Delta[\text{NH}_3]/\Delta t$? (15.19)

$-4.5 \times 10^{-4} \text{ mol H}_2$	2 mol NH_3	3.0 mol NH_3	Positive since NH_3 is a product
L min	3 mol H_2	L min	

10. In the reaction $2 \text{O}_3(\text{g}) \rightarrow 3 \text{O}_2(\text{g})$, the rate of formation of $\text{O}_2(\text{g})$ is $1.5 \times 10^{-3} \text{ mol/Ls}$. What is the rate of decomposition of $\text{O}_3(\text{g})$? (15.18)

$1.5 \times 10^{-3} \text{ mol O}_2$	2 mol O_3	$- 1.0 \text{ mol O}_3$	Negative since O_3 is a reactant
L s	3 mol O_2	L min	

11. The reaction between ozone and nitrogen dioxide at 231 K is first order in both $[\text{NO}_2]$ and $[\text{O}_3]$. (15.22)



- a. Write the rate equation for the reaction. $\text{rate} = k [\text{NO}_2] [\text{O}_3]$
 b. If the concentration of NO_2 is tripled, what will be the change in the reaction rate?
 c. What is the effect on reaction if the concentration of ozone is halved?

$3x [\text{NO}_2]$ will increase the rate by $3x$ since it is first order

$\frac{1}{2} x [\text{O}_3]$ will decrease the rate by $\frac{1}{2} x$ since it is first order

12. Nitrosyl bromide, NOBr , is formed from NO and Br_2 . (15.23) $2\text{NO}(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2 \text{NOBr}(\text{g})$

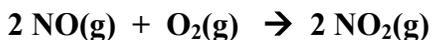
Experiments show that the second order with respect to NO and first order in Br_2 .

- a. Write the rate equation for the reaction. $\text{rate} = k [\text{NO}]^2 [\text{Br}_2]$
 b. How does the initial reaction rate change if $[\text{Br}_2]$ is changed from 0.0022 M to 0.0066 M ?
 c. How does the initial reaction rate change if $[\text{NO}]$ is changed from 0.0024 M to 0.0012 M ?

$3 x [\text{Br}_2]$ will increase the rate by $3x$ since it is first order

$\frac{1}{2} [\text{NO}]$ will decrease the rate by $\frac{1}{4}$ since it is first order

13. The data in the table are for the reaction of NO and O_2 at 660 K. (15.24)



- a. Determine the order of the reaction for each reactant.
 b. Write the rate equation for the reaction.
 c. Calculate the rate constant.
 d. Calculate the rate (in mol/Ls) at the instant when $[\text{NO}] = 0.015 \text{ M}$ and $[\text{O}_2] = 0.0050 \text{ M}$.
 e. At the instant when NO is reacting at the rate $1.0 \times 10^{-4} \text{ M/s}$, what is the rate at which O_2 is reacting and NO_2 is forming?

$[\text{NO}] \text{ (M)}$	$[\text{O}_2] \text{ (M)}$	Rate of appearance of $\text{NO}_2 \text{ (M/s)}$
0.010	0.010	2.5×10^{-5}
0.020	0.010	1.0×10^{-4}
0.010	0.020	5.0×10^{-5}

- a. Comparing exp 1 with exp 2, the $[\text{O}_2]$ is constant and the $[\text{NO}]$ is $2x$ bigger and the rate is $4x$ bigger – so this reaction is second order for NO

Comparing exp 1 with exp 3, the $[\text{NO}]$ is constant and the $[\text{O}_2]$ is $2x$ bigger and the rate is $2x$ bigger – so this reaction is first order for O_2

- b. $\text{rate} = k [\text{NO}]^2 [\text{O}_2]$

c. Using exp 1: $\text{rate} = k [\text{NO}]^2 [\text{O}_2]$ $2.5 \times 10^{-5} = k (0.01)^2 (0.01)$ solve for k . $k = 25$

d. $\text{rate} = k [\text{NO}]^2 [\text{O}_2]$ $\text{rate} = 25 (0.015)^2 (0.005) = 2.8 \times 10^{-5} \text{ M/s}$

e.

$1.0 \times 10^{-4} \text{ M NO}$	1 mol O_2	$- 5.0 \times 10^{-5} \text{ M O}_2$	Negative since O_2 is reactant and concentration increasing
s	2 mol NO	s	

$1.0 \times 10^{-4} \text{ M NO}$	2 mol NO_2	$1.0 \times 10^{-4} \text{ M NO}_2$	Positive since NO_2 is a product and concentration increasing
s	2 mol NO	s	



Data for the reaction are given in the table.

- What is the rate law of the equation?
- What is the rate constant? Include units.
- What is the initial rate in experiment 4?

	Reactant Concentration		Initial Rate Mol/L h
	CO	NO ₂	
1	5.0×10^{-4}	3.6×10^{-5}	3.4×10^{-8}
2	5.0×10^{-4}	1.8×10^{-5}	1.7×10^{-8}
3	1.0×10^{-3}	3.6×10^{-5}	6.8×10^{-8}
4	1.5×10^{-3}	7.2×10^{-5}	?

Same [CO] change [NO₂] exp 1 compared to exp 2
 $2 \times [\text{NO}_2] \rightarrow 2 \times \text{rate}$ so first order

1	5.0×10^{-4}	3.6×10^{-5}	3.4×10^{-8}
2	5.0×10^{-4}	1.8×10^{-5}	1.7×10^{-8}

Same [NO₂] change [CO] exp 3 compared to exp 1

Exp 3 1.0×10^{-3}

Exp 1 5.0×10^{-4}

$2 \times [\text{NO}_2] \rightarrow 2 \times \text{rate}$ so first order

1	5.0×10^{-4}	3.6×10^{-5}	3.4×10^{-8}
3	1.0×10^{-3}	3.6×10^{-5}	6.8×10^{-8}

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

use exp 3 $6.8 \times 10^{-8} = k (1.0 \times 10^{-3})(3.6 \times 10^{-5})$
 $k = 1.9$ need units

$$\text{rate} = k [\text{CO}][\text{NO}_2] \quad \text{rate} = 1.9 (1.5 \times 10^{-3})(7.2 \times 10^{-5}) = 2.0 \times 10^{-7}$$

15. Hypothetical reaction: $2\text{A} + \text{B} \rightarrow \text{C} + \text{D}$ General Rate Law: $\text{Rate} = k[\text{A}]^n[\text{B}]^m$

Experiment #	[A]	[B]	Reaction Time (sec)	Reaction Rate (sec ⁻¹)
1	0.10 M	0.05 M	150	6.7×10^{-3}
2	0.20 M	0.05 M	70	1.4×10^{-2}
3	0.30 M	0.05 M	50	2.0×10^{-2}
4	0.20 M	0.10 M	18	5.6×10^{-2}
5	0.20 M	0.15 M	8	0.125

- Calculate the proportional reaction rate in sec⁻¹ for each experiment.
- Determine the order with respect to A and B. Calculate the overall order of the reaction.

exp 2 compared to exp 1 diff [A] same [B] $2 \times [\text{A}] \rightarrow 2 \times \text{rate}$ so first order

verify exp 3 compared to exp 1 diff [A] same [B] $3 \times [\text{A}] \rightarrow 3 \times \text{rate}$ so first order

exp 4 compared to exp 2 diff [B] same [A] $2 \times [\text{B}] \rightarrow 4 \times \text{rate}$ so second order

verify exp 5 compared to exp 2 diff [B] same [A] $3 \times [\text{B}] \rightarrow 9 \times \text{rate}$ so second order

- Determine the rate law. $\text{rate} = k [\text{A}][\text{B}]^2$

16. Consider the reaction between nitric oxide and oxygen gas.



The following data was obtained by performing the reaction five times and varying the concentrations of the reactants. In each case, the reaction time was measured, then inverted to find the average rate.

Trial	[NO]	[O ₂]	Reaction Time (sec)	Average Rate (Msec ⁻¹)
1	0.020	0.010	35.7	0.028
2	0.020	0.020	17.5	0.057
3	0.020	0.040	8.8	0.11
4	0.040	0.020	4.4	0.23
5	0.010	0.020	71.4	0.014

a. Use this data to write the rate law for this reaction. Justify your answer using the data.

Exp 2 compared to exp 1 2x [O₂] with same [NO] → 2x rate (0.057/0.028)

Exp 3 compared to exp 1 4x [O₂] with same [NO] → 2x rate (.11/.028)

Both confirm that reaction is first order with respect to O₂.

Exp 4 compared to exp 2 2x [NO] with same [O₂] → 4x rate (0.23/0.057)

Exp 4 compared to exp 5 4x [NO] with same [O₂] → 16 x rate (0.23/0.014)

Both confirm that reaction is second order with respect to NO.

$$\text{Rate} = k [\text{NO}]^2[\text{O}_2]$$

b. Calculate the rate constant.

$$\text{Rate} = k [\text{NO}]^2[\text{O}_2] \text{ using exp 1}$$

$$0.028 = k (.02)^2(.01) \text{ so } k = 7,000 \text{ L}^2\text{mol}^{-2}\text{s}^{-1}$$