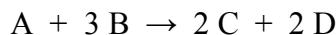


REVIEW QUESTIONS

Chapter 13

1. Consider the reaction shown below:



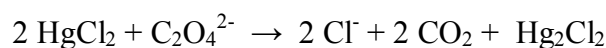
- a) Express the rate of this reaction in terms of concentrations of A, B, C and D.

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{1}{3} \frac{\Delta[B]}{\Delta t} = \frac{1}{2} \frac{\Delta[C]}{\Delta t} = \frac{1}{2} \frac{\Delta[D]}{\Delta t}$$

- b) At some point in the reaction $[B]=0.9986 \text{ M}$ and 13.20 minutes later $[B]=0.9746$. Based on this data, what is the average rate of the reaction during this time in Ms^{-1} ?

$$\text{Rate} = -\frac{\Delta[B]}{\Delta t} = -\frac{(0.9746 \text{ M}) - (0.9986 \text{ M})}{13.20 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}}} = 3.030 \times 10^{-5} \text{ Ms}^{-1}$$

2. The following data was collected for the reaction shown below:



Expt.	$[\text{HgCl}_2]$ M	$[\text{C}_2\text{O}_4^{2-}]$ M	Initial Rate M min^{-1}
1	0.105	0.15	1.8×10^{-5}
2	0.105	0.30	7.1×10^{-5}
3	0.052	0.30	3.5×10^{-5}

Determine the rate law for this reaction.

$$\text{Rate} = k [\text{HgCl}_2]^x [\text{C}_2\text{O}_4^{2-}]^y$$

Compare experiments 2 and 3:

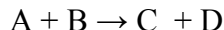
With $[\text{C}_2\text{O}_4^{2-}]$ constant, as $[\text{HgCl}_2]$ is halved, rate is halved.
Therefore rate is first order with respect to $[\text{HgCl}_2]$; $x = 1$

Compare experiments 1 and 2:

With $[\text{HgCl}_2]$ constant, as $[\text{C}_2\text{O}_4^{2-}]$ is doubled, rate increases by 4 times.
Therefore rate is second order with respect to $[\text{C}_2\text{O}_4^{2-}]$; $y = 2$

$$\text{Rate} = k [\text{HgCl}_2] [\text{C}_2\text{O}_4^{2-}]^2$$

3. The following data was collected for the reaction shown below:



Expt.	[A] M	[B] M	Initial Rate M s ⁻¹
1	0.185	0.133	3.35 x 10 ⁻⁴
2	0.185	0.266	1.35 x 10 ⁻³
3	0.370	0.133	6.75 x 10 ⁻⁴
4	0.370	0.266	????

a) Determine the rate law for this reaction.

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

Compare experiments 1 and 3:

**With [B] constant, as [A] is doubled, rate is doubled.
Therefore rate is first order with respect to [A]; x = 1**

Compare experiments 1 and 2:

**With [A] constant, as [B] is doubled, rate increases by 4 times.
Therefore rate is second order with respect to [B]; y = 2**

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

b) Calculate the value of k for this reaction.

Insert data from any experiment into the rate equation to calculate k

$$k = \frac{\text{Rate}}{[A][B]^2} = \frac{3.35 \times 10^{-4} \text{ Ms}^{-1}}{(0.185 \text{ M})(0.133 \text{ M})^2} = 0.102 \text{ M}^{-2} \text{ s}^{-1}$$

c) Calculate the rate of experiment 4.

$$\begin{aligned} \text{Rate} &= k [A][B]^2 = (0.102 \text{ M}^{-2} \text{ s}^{-1})(0.370 \text{ M})(0.266 \text{ M})^2 \\ \text{Rate} &= 2.67 \times 10^{-3} \text{ Ms}^{-1} \end{aligned}$$

Or

Since both [A] and [B] are doubled compared to experiment 1, rate would be expected to be 8 times rate in experiment 1. Therefore

$$\text{Rate (expt 4)} = 8 \times (3.35 \times 10^{-4} \text{ Ms}^{-1}) = 2.68 \times 10^{-3} \text{ Ms}^{-1}$$

4. The thermal decomposition of N_2O_5 to form NO_2 and O_2 is a first order reaction. The rate constant for the reaction is $5.1 \times 10^{-4} \text{ s}^{-1}$ at 318 K. Calculate the half-life of this reaction.

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5.1 \times 10^{-4} \text{ s}^{-1}} = 1400 \text{ s or } 23 \text{ min}$$

5. The thermal decomposition of phosphine (PH_3) to phosphorus and hydrogen gas is a first order reaction, with a half-life of 35 s at 680°C .
- a) Calculate the rate constant for this reaction.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{35 \text{ s}} = 0.0198 \text{ s}^{-1}$$

- b) Calculate the time required for 95% of phosphine to decompose.

$$\begin{aligned} \log \frac{[A_t]}{[A_0]} &= -\frac{kt}{2.303} \\ \log \frac{0.05}{1} &= -\frac{(0.0198 \text{ s}^{-1})(t)}{2.303} \\ -1.30(2.303) &= -0.0198 t \\ t &= 151 \text{ s} \end{aligned}$$

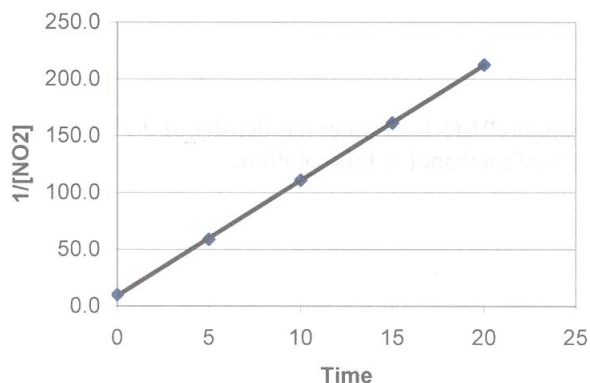
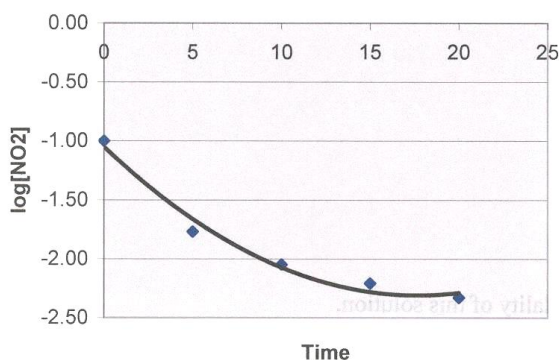
6. The rate constant for the 2nd order reaction shown below is 0.54 M^{-1} at 300°C . How many seconds would it take for the concentration of NO_2 to decrease from 0.62 M to 0.28 M?

$$\begin{aligned} \frac{1}{[A_t]} &= kt + \frac{1}{[A_0]} \\ \frac{1}{0.28} &= (0.54) t + \frac{1}{0.62} \\ 0.54 t &= 3.57 - 1.61 = 1.96 \\ t &= \frac{1.96}{0.54} = 3.6 \text{ s} \end{aligned}$$

7. The gas phase decomposition of NO_2 to form NO and O_2 was studied at 383°C and the following data was collected:

Time (s)	$[\text{NO}_2], \text{M}$	Log $[\text{NO}_2]$	$1/[\text{NO}_2]$
0.0	0.100	-1.00	10.0
5.0	0.017	-1.77	58.8
10.0	0.0090	-2.05	111.1
15.0	0.0062	-2.21	161.3
20.0	0.0047	-2.33	212.8

Determine the order of this reaction with respect to $[\text{NO}_2]$ and calculate the rate constant.



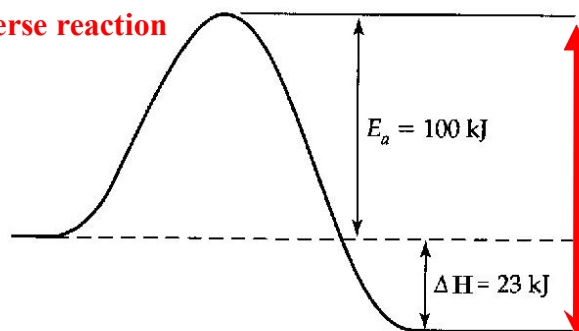
**Plot a graph of $\log[\text{NO}_2]$ vs. time and $1/[\text{NO}_2]$ vs. time.
Since plot of $1/[\text{NO}_2]$ vs. time give a straight line, this reaction is second order with respect to $[\text{NO}_2]$**

The rate constant, k , is the slope of the plot.

$$k = \frac{212.8 - 10.0}{20.0 - 0} = 10 \text{ M}^{-1}\text{s}^{-1}$$

8. The reaction $2 \text{N}_2\text{O}_5 \rightarrow 4 \text{NO}_2 + \text{O}_2$ has an activation energy of 100 kJ/mol and an enthalpy of -23 kJ/mol . Sketch a potential energy diagram for this reaction and determine the activation energy for the reverse reaction?

The activation energy for the reverse reaction is 123 kJ



9. The activation energy for a certain reaction is 76.7 kJ/mol. How many times faster will the reaction occur at 50°C compared to 0°C?

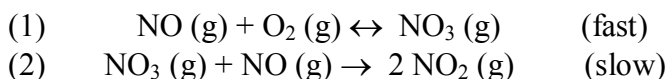
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{76.7 \times 10^3 \text{ J/mol}}{(2.303)(8.314 \text{ J/mol}\cdot\text{K})} \left(\frac{1}{273 \text{ K}} - \frac{1}{323 \text{ K}} \right)$$

$$= (4.006 \times 10^3) (0.003663 - 0.003096) = 2.27$$

$$\frac{k_2}{k_1} = 10^{2.27} = 186$$

The reaction at 50°C will occur 186 times faster than at 0°C.

10. The reaction $2 \text{NO} (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2 \text{NO}_2 (\text{g})$ was studied and the following mechanism was proposed:



Determine the rate law based on this mechanism.

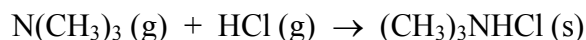
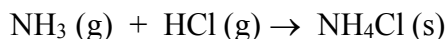


$$[\text{NO}_3] = \frac{k_1}{k_{-1}} [\text{NO}][\text{O}_2]$$

Substituting into reaction (2)

$$\text{Rate} = \frac{k_2 k_1}{k_{-1}} [\text{NO}][\text{NO}][\text{O}_2] = k [\text{NO}]^2 [\text{O}_2]$$

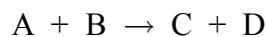
11. Assuming the activation energies are equal, which of the following reactions will occur at a higher rate at 50°C? (Hint: What factors affect the rate of a reaction)



At 50°C, both NH_3 and $\text{N}(\text{CH}_3)_3$ would have the same kinetic energy, but since $\text{N}(\text{CH}_3)_3$ has a larger molar mass than NH_3 , its molecules would have lower average speed, leading to lower collision frequency and lower reaction rates.

Also, since $\text{N}(\text{CH}_3)_3$ is a more complex molecule, it would probably have lower orientation probability, reducing its reaction rate even further.

12. The following rate data was collected for the reaction shown below:



Exp. #	[A] (M)	[B] (M)	Initial Rate (M/min)
1	0.50	1.50	4.2×10^{-3}
2	1.50	1.50	1.3×10^{-2}
3	3.00	3.00	5.2×10^{-2}

Determine the Rate Law and calculate the rate constant (k) for this reaction.

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

Compare experiments 1 and 2:

**With [B] constant, as [A] is tripled, rate is tripled.
Therefore rate is first order with respect to [A]; $x = 1$**

Compare experiments 2 and 3:

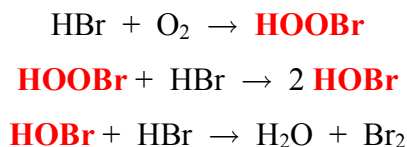
As [A] and [B] are both doubled, rate increases by 4 times. Factoring the effect of A (doubling rate since it is first order) the effect of B would be doubling of rate due to doubling of concentration.

Therefore rate is first order with respect to [B]; $y = 1$

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

$$k = \frac{\text{Rate}}{[A][B]} = \frac{1.3 \times 10^{-2} \text{ Mmin}^{-1}}{(0.150 \text{ M})^2} = 5.8 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1}$$

13. The following mechanism has been proposed for reaction of HBr with O₂ to form H₂O and Br₂

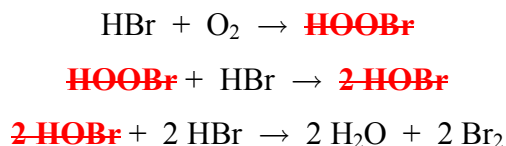


- a) Identify all reaction intermediates in this reaction.

Reaction intermediates are HOBr and HOB_r

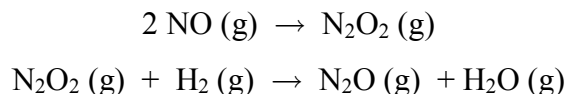
- b) Write a balanced overall equation for this reaction. (Hint: you may have to multiply all the coefficients of an elementary reaction before adding)

Multiply the third equation by 2 and add all equations:



overall equation

14. The following mechanism has been proposed for the reaction of NO with H₂ to form N₂O and H₂O.



The observed rate law for this reaction is: Rate = k [NO]² [H₂]. If the proposed mechanism is correct, what can we conclude about the relative speeds of the first and the second steps?

If the first reaction was the slow step, Rate = k₁ [NO]²

If the second reaction was the slow step, Rate = k₂ [N₂O₂] [H₂]

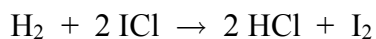
Since N₂O₂ is an intermediate it cannot be in the rate law, therefore

From first reaction: k₁ [NO]² = k⁻¹ [N₂O₂] and [N₂O₂] = $\frac{k_1}{k_{-1}}$ [NO]²

Substituting for [N₂O₂]: Rate = $\frac{k_1 k_2}{k_{-1}}$ [NO]² [H₂] = k [NO]² [H]

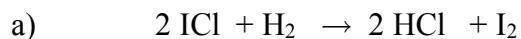
Since the predicted rate law for the second assumption matches the observed rate law, it is correct.

15. The reaction below has been studied and the following experimental rate law determined:

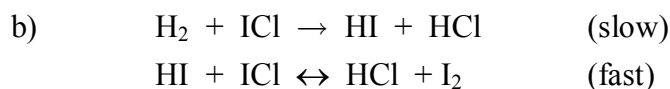


$$\text{Rate} = k [\text{H}_2][\text{ICl}]$$

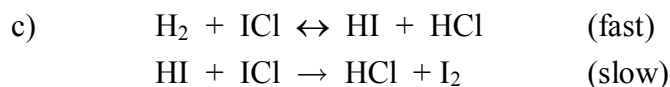
Three mechanisms have been proposed for this reaction. Predict the rate law based on each mechanism and determine which is consistent with the experimental rate law?



$$\text{Rate} = k [\text{ICl}]^2 [\text{H}_2]$$



$$\text{Rate} = k [\text{H}_2] [\text{ICl}]$$



$$\text{Rate} = k_2 [\text{HI}] [\text{ICl}]$$

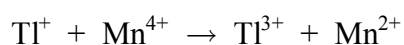
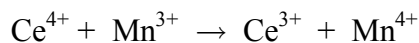
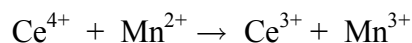
$$\text{From first reaction: } k_1 [\text{H}_2] [\text{ICl}] = k_{-1} [\text{HI}] [\text{HCl}]$$

$$[\text{HI}] = \frac{k_1 [\text{H}_2] [\text{ICl}]}{k_{-1} [\text{HCl}]}$$

$$\text{Substituting for [HI]: } \text{Rate} = \frac{k_2 k_1 [\text{H}_2] [\text{ICl}]^2}{k_{-1} [\text{HCl}]} = k \frac{[\text{H}_2][\text{ICl}]^2}{[\text{HCl}]}$$

The predicted rate law from mechanism (b) matches the observed rate law, therefore mechanism (b) is correct.

16. The following mechanism has been proposed for the catalyzed oxidation of thallium (I) by cerium (IV):



- a) Identify the catalyst and the intermediates in this mechanism.

Since Mn^{2+} is used in the first step and generated in the last step, it is the catalyst.

Mn^{3+} and Mn^{4+} are both generated in one step and used in another step, therefore they are intermediates.

- b) Determine the overall equation for this reaction.



- c) Explain why the reaction would be slow without the catalyst.

Without a catalyst, this reaction would be termolecular which would be expected to occur very slowly