

Worksheet

Reaction Kinetics

This section is covered in Brown, LeMay, Bursten, Murphy, Langford and Sagatys, *Chemistry : The central science: a broad perspective*, 2nd edition, Chapter 12.

AIMS:

- To explain the factors which affect the rates of chemical reactions.
- To develop an ability to analyse experimental data to calculate reaction rates and rate constants.
- To explain how the temperature affects the rate of a reaction and to show how the effect can be predicted quantitatively.

CONTENT: Reaction rate, rate expression, order, molecularity, mechanism, concentration dependence of rate. Determination of order and calculation of reaction rate and rate constants for zero, first and second order reactions. Activation energy, Arrhenius equation, determination of activation energy and pre-exponential factor, calculation of the effect of temperature on rate constants and rates of reactions.

LEARNING OBJECTIVES - You should be able to:

1. explain what is meant by the terms: rate of reaction and indicate what general factors affect the rates of reactions;
2. write the rate of reaction in terms of any of the reactants or products given the stoichiometric equation;
3. explain the terms rate expression, rate constant, reaction order and write the rate expression for zero order, first order and second order reactions;
4. calculate initial reaction rates in terms of concentration of reactants in appropriate units;
5. explain elementary steps in chemical reactions in terms of molecular collisions or molecular dissociation;
6. distinguish between order and molecularity and elementary step and reaction mechanism;
7. use initial rates to determine reaction order (zero, first and second order reactions);
8. calculate reaction rates given a rate constant and reaction order (zero, first and second order reactions) and reactant concentrations;
9. distinguish between zero, first and second order reactions on the basis of the concentration dependence of the reaction rate;

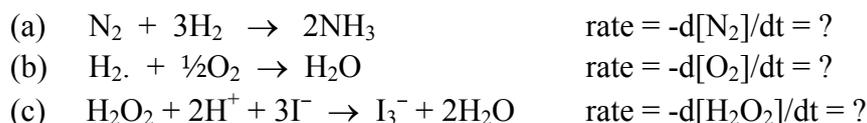
- calculate rate constants using integrated rate expressions;
- draw a typical energy profile for a reaction and describe how the temperature affects the proportion of molecules colliding with sufficient energy to react;
- explain the terms Arrhenius equation, activation energy and pre-exponential factor;
- obtain the activation energy and pre-exponential factor given the rate constant as a function of temperature by a graphical method or by calculation;
- calculate the rate constant at a particular temperature given the activation energy and the rate constant at some other temperature.

PRACTICE PROBLEMS

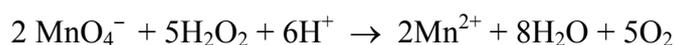
Exercises (from Brown *et al.*):

12.13	13.14	13.15	13.17	12.21
12.30	12.32	12.33	12.37	12.40
12.41	12.42	12.43	12.45	12.47
12.51	12.53			

- For each of the following reactions express the rate of change of concentration of the given reactant in terms of the rates of change of the other reactants and products:



- The reaction between MnO_4^- and H_2O_2 is as follows:



In an experiment to monitor the rate of reaction, the following results were obtained:

Time/s	0	400	800	1200	1600	2000	2400	2800
$[\text{H}_2\text{O}_2]/(\text{mol dm}^{-3})$	2.32	1.72	1.30	0.98	0.73	0.54	0.39	0.28

- Calculate the average reaction rate over each interval of 400 s.
 - Is the reaction zero order with respect to H_2O_2 ? Explain your answer.
- For the reaction $\text{H}_2(\text{g}) + 2\text{NO}(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) + \text{N}_2(\text{g})$ experiment shows that when the concentration of H_2 is halved the reaction rate is halved. Also, raising the concentration of NO by a factor of three raises the reaction rate by a factor of nine. What is the rate expression?
- The elementary reaction $\text{NO}_2\text{Cl}(\text{g}) + \text{NO}(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{NOCl}(\text{g})$ is first order with respect to NO_2Cl and NO . The energy of activation (E_a) is 28.9 kJ mol^{-1} and the frequency factor (A) is $8.3 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.
 - Write the rate law for the reaction.

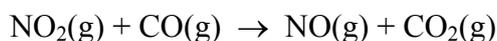
- (b) Evaluate the rate constant at 500 °C.
(c) What is the effect on the reaction rate of doubling the concentration of NO and halving the concentration of NO₂Cl?
5. The rate constant of a gas reaction was found to be $8.0 \times 10^{-5} \text{ s}^{-1}$ at 650 K. When the temperature was changed by 60 K, the **rate constant** was increased by a factor of 30.
- (a) What is the second reaction temperature?
(b) What is the order of the reaction?
(c) What is the activation energy?

Extracts from old examinations

1. The reaction $A + B \rightarrow C + D$ is found to be first order with respect to A and second order with respect to B. Write down the rate law for this reaction.

(2)

2. For the reaction



the variation of the initial rate with the initial concentration of NO₂, with the initial concentration of CO kept constant, was found to be as follows:

Experiment	[NO ₂] ₀ /mol dm ⁻³	Initial rate/mol dm ⁻³ s ⁻¹
1	0.150	0.010
2	0.300	0.040
3	0.600	0.160
4	0.900	0.360

Deduce the order of the reaction with respect to NO₂.

(4)

3. For the alkaline hydrolysis of ethyl nitrobenzoate (A) the following data were obtained at 25 °C.

Time/s	0	500	800	1500	2000
[A]/mol dm ⁻³	0.0500	0.0167	0.0119	0.0071	0.0056

Evaluate the order of the reaction and the rate constant at 25 °C.

(10)

4. The following data were obtained in the laboratory for the decomposition of NO₂,
- $$\text{NO}_2(\text{g}) \rightarrow \text{NO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$$

Time/min	0	0.50	1.0	1.5	2.0
[NO ₂]/mol dm ⁻³	0.020	0.015	0.012	0.010	0.0087

Determine whether the reaction is first order or second order, and then find the value of the rate constant.

(11)

5. Data for the reaction



is given in the table below:

Experiment	Reactant Concentration/mol dm ⁻³		Initial rate/ mol L ⁻¹ h ⁻¹
	[O ₂]	[NO]	
1	5.2 x 10 ⁻³	3.6 x 10 ⁻⁴	3.4 x 10 ⁻⁸
2	1.04 x 10 ⁻²	3.6 x 10 ⁻⁴	6.8 x 10 ⁻⁸
3	1.04 x 10 ⁻²	1.8 x 10 ⁻⁴	1.7 x 10 ⁻⁸

- (a) What is the rate law for this reaction?
(b) Calculate the rate constant, *k*, for this reaction.

(4)

6. Three mechanisms are proposed for the gas phase reaction of NO with Br₂ to give BrNO.

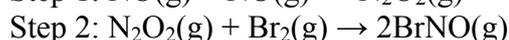
Mechanism I:



Mechanism II:



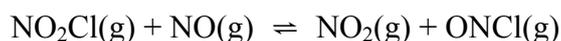
Mechanism III:



- (a) Write a balanced equation for the net reaction.
(b) What is the molecularity for step 1 in mechanism II?
(c) Identify the intermediate(s) formed in mechanism III.

(2)

7. The single step reversible reaction below has an activation energy for the forward reaction (*E_{a,f}*) of 28.9 kJ and 41.8 kJ for the reverse reaction (*E_{a,r}*).



- (a) Draw a potential energy level diagram (also known as a reaction profile diagram) for the reaction. Indicate, on your diagram, *E_{a,f}* for the forward reaction, *E_{a,r}* for the reverse reaction, and the enthalpy change (ΔH) for the reaction.

(2)

- (b) With the aid of the Arrhenius equation, show how the activation energy (*E_a*) can be determined graphically.

(2)