CHEMISTRY 225 SEMESTER 01-2007
REACTION KINETICS

1) Dinitrogen pentoxide (N_2O_5) decomposes slowly when in solution in tetrachloromethane to form nitrogen dioxide and oxygen. The reaction may be represented as follows:

$$2N_2O_5 \rightarrow 4NO_2 + 2O_2$$

In the table below are given the results of measuring the concentration of N_2O_5 at various times:

ELAPSED TIME /s	Δt /s	$[N_2O_5]$ /mol dm^{-3}	$-\Delta[N_2O_5]$ /mol dm^{-3}	REACTION RATE /mol dm^{-3} s^{-1}
0	—	2.10	—	—
100	100	1.95	0.15	
300	200	1.70		
700		1.31		
1000		1.08		
1700		0.68		
2100		0.52		
2800		0.38		

a) Plot a graph of N_2O_5 concentration ($[N_2O_5]$) against Elapsed Time. (Note: "*y*" is always plotted ***against*** "*x*".) Discuss how the concentration of N_2O_5 varies with time of reaction. Now answer the following questions from your graph.

   i) The time required for the concentration of a reagent to decrease to half its original value is known as its half-life. Determine the half-life of the N_2O_5 from your graph.

   ii) What would be the half-life of the N_2O_5 if its initial concentration were 1·08 mol dm^{-3}? Compare your two values for the half-life.

   iii) What percentage of the N_2O_5 remained after half an hour?

b) Complete the columns headed Δt and $-\Delta[N_2O_5]$ in the table. Note that the first one or two values have been inserted already to guide you.

c) Complete the column headed "Reaction Rate".

d) Draw a graph of Reaction Rate against Elapsed Time. Discuss how the Reaction Rate varies with Elapsed Time.

e) Draw a graph of Reaction Rate against $[N_2O_5]$. Is this (approximately) a straight line? Should it pass through the origin? What would a straight line graph indicate?

f) Assuming that the graph obtained in (e) above is a straight line, what Rate Law would be indicated for the decomposition of N_2O_5? Write it down as an equation.

g) Find the rate constant for the reaction by measuring the slope of your line.

2) Hydrogen reacts with nitrogen oxide in the gas phase with the production of steam and nitrogen:

$$2H_2(g) + 2NO(g) \rightarrow 2H_2O(g) + N_2(g)$$

The rate of this reaction may be followed experimentally by measuring the decrease in pressure during the reaction as 4 moles of gaseous reactants give rise to 3 moles of gaseous products. From this it is possible to calculate the rate of nitrogen production in mol dm^3 s^1.

The initial rates for a set of six experiments using different initial concentrations of reactants for this system are quoted in the table below. Study the table and then answer the following questions:

a) What is the order of reaction with respect to NO?

b) What is the order of reaction with respect to H_2?

c) What is the order of reaction with respect to N_2?

d) What is the overall order of the reaction?

e) Write down the rate law for the reaction as an equation.

EXPERIMENT	INITIAL CONCENTRATION /mol dm^{-3}		INITIAL RATE OF N_2 PRODUCTION mol dm^{-3} s^{-1}
	[NO]	[H_2]	
1	6.00×10^{-3}	1.00×10^{-3}	3.19×10^{-3}
2	6.00×10^{-3}	2.00×10^{-3}	6.36×10^{-3}
3	6.00×10^{-3}	3.00×10^{-3}	9.56×10^{-3}
4	1.00×10^{-3}	6.00×10^{-3}	0.48×10^{-3}
5	2.00×10^{-3}	6.00×10^{-3}	1.92×10^{-3}
6	3.00×10^{-3}	6.00×10^{-3}	4.30×10^{-3}

3) Hydrogen peroxide decomposes rapidly in the presence of manganese(IV) oxide to oxygen and water:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

a) Describe an experiment by which you could follow the progress of this reaction in order to study its kinetics. Draw a fully-labelled diagram of the apparatus you would use. Make clear what measurements you would make and suggest how you could determine the order of the reaction with respect to the concentration of the hydrogen peroxide.

b) Describe how you might modify your procedure in order to study the effect of:

i) temperature,

ii) mass of catalyst (manganese dioxide),

iii) particle size of catalyst,

on the rate of the reaction.

c) Sketch a graph to show how the volume of oxygen produced under constant conditions (ie. constant temperature, pressure, mass of catalyst etc.) would vary with time.

d) Using the same axes as for (c) sketch graphs to show how the volume of oxygen would vary with time if:

i) the temperature were raised somewhat.

ii) the amount of hydrogen peroxide solution were halved.

iii) the mass of catalyst were doubled.

iv) the catalyst were ground more finely.

Assume in each of the above cases that all other conditions are the same in each case.

4) a) Marble chips react readily with dilute hydrochloric acid:

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g)$$

Draw sketch graphs to show how (i) the mass of the flask and its contents, (ii) the volume of carbon dioxide produced, (iii) the concentration of the hydrochloric acid, and (iv) the rate of the reaction vary with time.

b) Dextrose exists in two forms: α-dextrose and β-dextrose. In the presence of acid α-dextrose is gradually changed into β-dextrose. Since the reaction is reversible an equilibrium mixture is eventually obtained. Given that the stoichiometry of the reaction is 1:1, and assuming that the equilibrium mixture is 50% α-dextrose, sketch a graph showing how the concentrations of these two species vary with time when a solution of pure α-dextrose is acidified.

5) A chemical reaction generates 1·0 mol dm^{-3} of product in the first minute after the reactants are mixed. In the second minute, it generates 0·5 mol dm^{-3}, and in the third minute it generates 0·25 mol dm^{-3} of product. Determine the average rate of the reaction in mol dm^{-3} s^{-1} during the first 60 seconds, during the next 60 seconds, and during the last 60 seconds. Draw a graph of concentration against time and estimate the initial rate, the rate at t=180 s. Compare the estimated initial rate with the average rate during the first minute. Comment on your results.

6) The reaction between nitrite ion (NO_2^-) and I^- in acid solution may be represented by the equation

$$2NO_2^-(aq) + 4H^+(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2NO(g) + 2H_2O(l)$$

a) i) Express the rate of reaction in terms of the rate of change of concentration of each of the dissolved species involved in the reaction (reactants and products).

ii) Write an expression showing how these rates of change of concentration are related to one another.

iii) If the rate of change of concentration of iodine is 2×10^{-3} mol dm^{-3} s^{-1}, what is the rate of change of concentration of hydrogen ions? Should it properly be represented as a negative or a positive quantity? Explain.

b) The experimental rate law for the above reaction is

$$R = k[NO_2^-][I^-][H^+]^2$$

How would the rate of the reaction be altered if

i) $[H^+]$ and $[I^-]$ were kept constant but $[NO_2^-]$ were doubled?

ii) $[I^-]$ and $[NO_2^-]$ were kept constant but $[H^+]$ were doubled?

iii) $[I^-]$ and $[NO_2^-]$ were kept constant but $[H^+]$ were halved?

iv) All concentrations were doubled?

7) For the gaseous oxidation reaction

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

state the relationship between

a) the rate of consumption of NO and

b) the rate of consumption of O_2 and

c) the rate of production of NO_2.

8) For the reaction

$$2A + B + C \rightarrow 3D + E$$

the rate of formation of E is found to double if [A] is doubled, keeping [B] and [C] constant, and is found to double if [B] is doubled keeping [A] and [C] constant. The rate is unaffected by changing [C]. Write the rate law for the reaction.

9) The rate of the reaction

$$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O$$

may be calculated by measuring the time for the first appearance of I_2 in the solution, ie. the time required for the $[I_2]$ to reach 10^{-5}M.

a) For a particular experiment in which $[H_2O_2]$ = 0.010M, $[I^-]$ = 0.010 M, and $[H^+]$ = 0.10 M, calculate the reaction rate if I_2 first appears after 5.7 seconds.

b) In a second experiment in which $[H_2O_2]$ = 0.0050 M, $[I^-]$ = 0.010 M and $[H^+]$ = 0.100 M, calculate the reaction rate if I_2 first appears after 11.5 seconds.

c) From these calculations show that the reaction rate depends upon $[H_2O_2]$ raised to the first power, ie. that R α $[H_2O_2]$

d) Given the further information that the rate law is

$$R = k[H_2O_2][H^+][I^-]$$

calculate the rate constant k.

10) a) Write down the Arrhenius law for the dependence of the rate constant for a reaction on temperature.

b) Sketch graphs showing how (i) the rate constant and (ii) the rate of reaction vary with temperature.

c) What is meant by the ***activation energy*** for a reaction?

i) Sketch a graph of energy against extent of reaction to illustrate your answer. On your graph indicate the reactants, the products and the activated complex (transition state). Also show the enthalpy change for the reaction, and the activation energy for both the forward and reverse reactions.

ii) What effect does a catalyst have on the activation energy for a reaction? Illustrate your answer by drawing a line for a catalysed reaction on your graph.

d) Sketch a graph showing how the proportion of molecules with a given energy varies with the value of this energy. What is this distribution known as? Supposing that the molecules are able to undergo a chemical reaction with activation energy E_A, mark E_A on your graph.

e) Sketch another graph (using the same pair of axes as in (d)) to show how the distribution compares at a higher temperature. Use your graph to explain why the rate of reaction is so strongly dependent on temperature.

f) Mark E_A for the same reaction in the presence of a catalyst on your graph. Use this to explain how a catalyst speeds up a reaction.

11) In the lungs, oxygen from the air is able to dissolve in blood and a constant concentration of $1{\cdot}6\times10^{-6}$ mol dm^{-3} of oxygen is maintained by continuous dissolution of oxygen from respired air. The oxygen reacts in the blood with a compound of iron called haemoglobin (abbreviated here as Hb) to yield a bright red compound, oxy-haemoglobin, HbO_2:

$$Hb + O_2 \rightarrow HbO_2$$

Since the blood is re-circulated by the heart the haemoglobin concentration is also maintained constant in the lung capillaries at 8×10^{-6} mol dm^{-3}. The rate of formation of oxy-haemoglobin, R, is described by the rate law:

$$R = k[Hb][O_2]$$

where $k = 2{\cdot}1\times10^{6}$ dm^{3} mol^{-1} s^{-1} at 37°C (the body temperature).

a) For the constant concentrations of haemoglobin and oxygen given, calculate the rate of oxy-haemoglobin formation and the rate of oxygen consumption.

b) In a sample of 200 cm^3 of blood, calculate the number of moles of oxygen consumed in this volume per second and hence per hour.

c) If the number of moles of oxygen consumed per hour were measured as a gas at 150 mmHg pressure and 37°C, what volume of oxygen would be consumed?

d) In some illnesses it is necessary that the rate of oxy-haemoglobin formation should be increased to $1{\cdot}1\times10^{-4}$ mol dm^{-3} s^{-1}. Since the haemoglobin concentration is fixed at 8×10^{-6} mol dm^{-3}, to what value must the oxygen concentration be increased? Suggest a method whereby this oxygen concentration might be attained. (Hint: the concentration of oxygen dissolved in blood is directly proportional to the partial pressure of oxygen breathed into the lungs.)

12) It is sometimes said that the rates of most simple chemical reactions "increase by a factor of 2 or 3 for every 10°C rise in temperature". Suggest reasons why reaction rate rises so rapidly with increasing temperature.