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Ollscoil Átha Cliath | The University of Dublin

# SF Physical Chemistry 2001-2013.

# SF CH 2201: Chemical Reaction Kinetics.

**Professor Mike Lyons.**

**School of Chemistry**
**Trinity College**
**Dublin 2.**

**melyons@tcd.ie**

**A compendium of past examination questions set on Chemical Reaction Kinetics.**

This booklet has been produced to provide SF Chemistry students with a full selection of problems in chemical kinetics set by the author since 2001**.** These problems have appeared in Annual, Supplemental and Foundation Scholarship examination papers in Physical Chemistry set by the Examination Board of the School of Chemistry, University of Dublin, Trinity College. As such these problems reflect the standard set for the exam. They were originally available to Trinity SF Chemistry students to assist them in their revision of the 5 CH2201 Chemical Reaction Kinetics lectures delivered by Prof. Lyons in the first semester. They are now being made available to the current CH2201 class as a useful learning and revision tool even though CH2201 is now being given by another member of the Physical Chemistry Faculty. Please note that model answers are not provided.

## Annual and Supplemental Exam Questions.

### SF Chemistry 2001.

### Annual.

(a) What do you understand by the terms *reaction rate* , *rate constant* and *activation energy* ? Indicate, using a suitable example how the rate constant and activation energy of a reaction could be determined.

(b) The rate constant for the first order decomposition of $N_2O_5$ in the reaction $N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ is k = 3.38 x $10^{-5}$ $s^{-1}$ at 298K. What is the half life of $N_2O_5$ ? What will be the total pressure, initially 500 Torr for the pure $N_2O_5$ vapour, (a) 10 s, (b) 10 min after initiation of the reaction?

### Supplemental.

(a) Write down the Arrhenius equation relating the rate constant k and the activation energy $E_A$ . Explain the terms used in the equation.

(b) Describe how the activation energy could be measured experimentally and indicate how the data could be manipulated graphically to obtain a numerical estimate of $E_A$ .

(c) A rate constant is 1.78 x $10^{-4}$ L $mol^{-1}$ $s^{-1}$ at $19^0$C and 1.38 x $10^{-3}$ L $mol^{-1}$ $s^{-1}$ at $37^0$C. Evaluate the activation energy for the reaction.

### SF Chemistry 2002.

### Annual.

The kinetics of many enzyme reactions may be described in terms of the Michaelis-Menten mechanism . If S represents the substrate molecule and E is the enzyme then a simple form of the Michaelis-Menten mechanism is

$$S + E \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} P + S$$

where ES represents the enzyme/substrate complex. The reaction rate R is given by $R = k_2[ES]$.

(a) Use the steady state approximation to evaluate the enzyme/substrate complex concentration [ES] and hence show that the rate of product formation R is given by $R = \frac{k_c[E]_\Sigma[S]}{K_M + [S]}$ where $k_c = k_2$ is the catalytic rate constant and $K_M = \frac{k_{-1} + k_2}{k_1}$ is the Michaelis constant. Note that the total enzyme concentration is given by $[E]_\Sigma = [E] + [ES]$ where [E] represents the concentration of free enzyme. Provide an interpretation of $K_M$ and $k_c$.

(b) Make a rough labeled sketch of the way that the reaction rate varies with substrate concentration. What form does the reaction rate take when (i) the substrate concentration $[S] << K_M$ , and (ii) the substrate concentration $[S] >> K_M$ ?

**Supplemental**

(a) What do you understand by the terms (i) reaction rate, (ii) rate constant, (iii) reaction order and (iv) activation energy ?

(b) Given a set of values of reactant concentration versus time, outline how you would determine whether the reaction exhibited first order kinetics or second order kinetics.

(c) The following data have been obtained for the decomposition of $N_2O_5(g)$ at 340 K according to the reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$. Determine the order of the reaction, the rate constant and the half life.

| $[N_2O_5]$/M | 1.0 | 0.705 | 0.497 | 0.349 | 0.246 | 0.173 |
|---|---|---|---|---|---|---|
| t/min | 0 | 1 | 2 | 3 | 4 | 5 |

**SF Chemistry 2003.**

**Supplemental**

(a) Outline, using a specific example, the use of the steady state approximation in the analysis of complex reaction mechanisms. Under what conditions will the steady state approximation be valid?

(b) The condensation reaction of acetone $(CH_3)_2CO$ in aqueous solution is catalysed by bases B, which react reversibly with acetone to form the carbanion $C_3H_5O^-$ . The carbanion then reacts with a molecule of acetone to give the product P. A simplified version of the reaction mechanism is as follows:

$$AH + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} BH^+ + A^-$$

$$A^- + HA \xrightarrow[k_2]{} P$$

where AH represents acetone and $A^-$ is the carbanion. Use the steady state approximation to determine the concentration of the carbanion, and hence derive the rate equation for the formation of the product .

**SF Chemistry 2004.**

**Annual.**

(a) The manner that the rate constant for a chemical reaction varies with temperature is often described by the Arrhenius equation which takes the form $k = A\exp\left[-\frac{E_A}{RT}\right]$. Briefly explain the significance of the parameters A and $E_A$. Indicate how these parameters can be related to a simple physical model based on collisions between molecules

(b) Given that the rate constant for the gas phase reaction $H + O_2 \rightarrow OH + O$ is 4.7 x $10^{10}$ $cm^3mol^{-1}s^{-1}$ at 1000 K and that the activation energy is 66.5 kJ $mol^{-1}$ , determine the value of the bimolecular rate constant at 2000 K.

**Supplemental.**

A reaction is known to exhibit first order kinetics. At 300 K the concentration of reactant is reduced to one half of its initial value after 5000 s. In contrast at 310 K the concentration is halved after 1000 s. Use this information to calculate:

(a) the rate constant for the reaction at 300 K

(b) the time required for the reactant concentration to be reduced to one quarter of its initial value at 310 K

(c) the activation energy of the reaction.

**SF Chemistry 2005.**

**Annual**

(a) What do you understand by the term half life as used in chemical kinetics?

(b) Derive an expression for the half life of a first order reaction.

(c) The half life of a first order reaction is 24 days.

  (i) Calculate the rate constant for the reaction .

  (ii) The time taken for 75% of the reactant to decay.

**Supplemental.**

(a) Provide a concise definition of activation energy. Describe, including any pertinent theoretical equations, how the activation energy of a chemical reaction may be experimentally determined.

(b) The activation energy for the decomposition of benzene diazonium chloride is 99 kJ mol$^{-1}$. At what temperature will the rate constant be 10% greater than that at 298 K?

## SF Chemistry 2006.

### Annual.

(a) A reactant A undergoes first order kinetics. Show that the time variation of the reactant concentration c at any time t is given by $c = c_0 e^{-kt}$ where $c_0$ is the initial concentration of the reactant and k is the rate constant. Hence derive an expression for the half life $\tau_{1/2}$ of the reaction.

(b) For a particular first order reaction at 300 K, the concentration of reactant is reduced to one half of its initial value after 5000 s. At 310 K, the concentration is halved after 1000 s. Calculate:

(i) the rate constant for the reaction at 300 K,

(ii) the time required for the concentration to be reduced to one quarter of its initial value at 310 K

(iii) the activation energy of the reaction.

### Supplemental.

(a) What do you understand by the term half life as used in chemical kinetics? Derive an expression for the half life of a first order reaction. Write down an expression for the half life of a second order reaction.

(b) The half life of a first order reaction is 100 s. Calculate the rate constant and determine what fraction will have reacted after 250 s.

## SF Chemistry 2007.

### Annual

(a) Consider the following bimolecular reaction A(aq) + B(aq)→ Products. Write down the rate equation for this reaction assuming that the concentrations of A and B are equal. Integrate this rate equation and show that the concentration $c_t$ of the reactant at any time t depends on time according to $\frac{1}{c_t} = kt + \frac{1}{c_0}$, where k denotes the bimolecular rate constant and $c_0$ represents the reactant concentration initially. Hence derive an expression for the half life of the reaction.

(b) The rate constant k for the reaction described by $H^+(aq) + OH^-(aq) \underset{k'}{\overset{k}{\rightleftarrows}} H_2O(\ell)$ is 1.4 x $10^{11}$ $dm^3mol^{-1}s^{-1}$. Calculate the half life of this reaction if the initial conditions are $[H^+]_0=[OH^-]_0$ = 0.1 M.

### Supplemental

(a) What do you understand by the terms half life and activation energy. Briefly outline how the activation energy of a chemical reaction may be experimentally measured.

(b) A rate constant is 1.78 x $10^{-4}$ L $mol^{-1}s^{-1}$ at $20^0$C and 1.38x $10^{-3}$ $Lmol^{-1}s^{-1}$ at $37^0$C. If the initial reactant concentration is 0.1 M, estimate the activation energy for the reaction and the half life of the reaction at $37^0$C. What is the order of the reaction?

## SF Chemistry 2008.

### Annual.

(a) A reaction follows first order kinetics.

(i) Show that the integrated form of the rate equation is given by $kt = \ln\left(\frac{c_0}{c_0 - x}\right)$ where $c_0$ denotes the initial reactant concentration , k denotes the first order rate constant, and x represents the concentration reacted at time t.

(ii) If y denotes the fraction of reactant reacted at time t show that $kt = \ln\left(\frac{1}{1-y}\right)$.

(iii) Derive an expression for the half life for a first order reaction and use this result to show that in a first order reaction the time taken for the reactant concentration to drop by three quarters of its initial value is double that for the initial concentration to drop by one half.

(b) Ethyl ethanoate and sodium hydroxide in solution in an ethanol water mixture at 303 K exhibit a hydrolysis reaction. In an experiment in which 0.05 M of each reactant were present at time t = 0, the half life was found to be 1800 s, and the time required for three quarters of the initial concentration of either reactant to react was 5400 s. Deduce the order of the reaction and calculate the rate constant. At what time was 10% reaction complete?

### Supplemental.

(a) Define the term half life.

(b) Derive an expression for the half life of a reaction which obeys second order kinetics assuming that the rate equation takes the following form: $-\frac{dc}{dt} = kc^2$ with c = $c_0$ at t = 0.

(c) If a reaction exhibits second order kinetics show that the time required for three quarters of the initial reactant concentration to react , $\tau_{1/4}$ , is three times the half life $\tau_{1/2}$ .

**SF Chemistry 2009**

**Annual**

(a) Show by suitable integration of the first order rate equation that the half life $\tau_{1/2}$ is independent of the initial reactant concentration $c_0$ and is given by $\tau_{1/2} = \frac{\ln 2}{k}$ where k denotes the first order rate constant. What are the units of k?

(b) The Arrhenius parameters which define the Arrhenius equation for the decomposition reaction of cyclobutane $C_4H_8(g) \rightarrow 2C_2H_4(g)$, are ln(A/s$^{-1}$)=15.6 and $E_A$ = 261 kJmol$^{-1}$. Determine the ratio of the half lives of cyclobutane at the temperatures 293 K and 773 K.

**Supplemental**

(a) Shown by suitable integration of the second order rate equation $-\frac{dc}{dt} = kc^2$, that the half life is given by $\tau_{1/2} = \frac{1}{kc_0}$ where $c_0$ denotes the initial concentration of reactant.

(b) A rate constant is measured as 2.78 x 10$^{-4}$ dm$^3$mol$^{-1}$s$^{-1}$ at 292 K and 3.38 x 10$^{-3}$ dm$^3$mol$^{-1}$s$^{-1}$ at 310 K. Use the Arrhenius equation to evaluate the pre-exponential factor and activation energy of the reaction.

## SF Chemistry 2010

### Annual

(a) Define the term half life $\tau_{1/2}$ as used in chemical kinetics. Show by integrating the first order rate equation that the half life is given by $\tau_{1/2} = \frac{\ln 2}{k}$ where k denotes the first order rate constant.

(b) Trichloroethanoic acid is readily decarboxylated in aqueous solution according to the following reaction: $CCl_3COOH$ (aq) → $CHCl_3$(aq) + $CO_2$(g). The reaction kinetics were monitored by monitoring the volume V of $CO_2$ released as a function of time. The following data was obtained during a typical kinetic run.

| V/cm$^3$ | 2.25 | 8.30 | 14.89 | 31.14 | 40.04 |
|---|---|---|---|---|---|
| t/min | 330 | 1200 | 2400 | 7760 | ∞ |

Show that the reaction exhibits first order kinetics, determine the rate constant and the half life of the reaction, and calculate the time taken for the initial concentration of $CCl_3COOH$ to fall by 25 %.

### Supplemental

(a) Define the terms rate constant, reaction order, activation energy, and half life as used in chemical kinetics. Describe how the activation energy may be experimentally determined using equations where pertinent.

(b) The following kinetic data were found for the reaction A → B + C

| | Experiment 1 | Experiment 2 | Experiment 3 | Experiment 4 |
|---|---|---|---|---|
| $10^5$rate /moldm$^{-3}$min$^{-1}$ | 0.30 | 3.80 | 62.20 | 475 |
| $10^2$[A] /moldm$^{-3}$ | 0.50 | 1.78 | 7.22 | 19.90 |

Explaining your reasoning, determine the order of the reaction with respect to reactant A and hence evaluate the rate constant.

Show that your conclusions are consistent with the following data for the same reaction at the same temperature.

| $10^3$[A] /moldm$^{-3}$ | 10 | 8.05 | 6.75 | 5.0 |
|---|---|---|---|---|
| t/min | 0 | 200 | 400 | 800 |

**SF Chemistry 2011**

**Annual.**

(a) Define the terms activation energy and rate constant. Write down the Arrhenius equation which describes the variation of the rate constant with temperature. Discuss how the rate constant and activation energy of a chemical reaction which exhibits first order kinetics may be determined using experimental measurements and theoretical analysis.

(b) Provide a brief description of the collision theory of gas phase chemical reactions and compare the theoretical expression for the rate constant derived using this theory with the empirical Arrhenius equation.

(c) The rate constant for the bromination of propanone as a function of temperature is outlined in the following table. Show that the tabulated data obey the Arrhenius equation and evaluate the activation energy of the reaction and the pre-exponential factor A.

| $10^8$k/s$^{-1}$ | 4.53 | 59.3 | 197 | 613 |
|---|---|---|---|---|
| T/$^0$C | 90 | 110 | 120 | 130 |

**Supplemental**

(a) Explain how a catalyst serves to enhance the rate of a chemical reaction. What is the difference between heterogeneous and homogeneous catalysis?

(b) Outline the various steps involved in a typical catalytic reaction involving a species in the gas phase and a solid catalyst surface.

(c) Derive the Langmuir adsorption isotherm which predicts the way in which the surface coverage $\theta$ of an adsorbed gas molecule varies with the partial pressure of the reactant species in the gas phase. Use the expression derived for $\theta$ to construct a theoretical expression for the reaction rate of the adsorbed molecule on the catalyst surface, assuming that the transformation of the adsorbed species A exhibits first order kinetics, $A_{ads} \xrightarrow{k} \text{Products}$.

## SF 2201 Chemistry 2012

### Annual

(a) What is meant by the term reaction order as used in chemical kinetics? What is zero order kinetics? Derive an expression for the variation of reactant concentration with respect to time for a reaction which exhibits zero order kinetics. How can this expression be used graphically to evaluate the rate constant?

(b) The decomposition of ammonia on a platinum surface at 1129 K occurs according to the following reaction: $2\ NH_3\ (g) \rightarrow N_2(g) + 3\ H_2(g)$. It occurs via zero order kinetics. Use the following kinetic data which report the variation of ammonia concentration in the gas phase with time t to evaluate the rate constant  for the reaction at 1129 K.

| $10^3[NH_3]$/M | 2.10 | 1.85 | 1.47 | 1.23 | 0.86 | 0.57 | 0.34 |
|---|---|---|---|---|---|---|---|
| t/s | 0 | 200 | 400 | 600 | 800 | 1000 | 1200 |

Suggest why the reaction exhibits zero order kinetics with respect to the concentration of ammonia in the gas phase.

### Supplemental

(a) The elementary reaction between ethanol ($CH_3CHO$) and ·OH radicals $CH_3CHO + \cdot OH \rightarrow CH_3CO\cdot + H_2O$ was studied at T = 298 K by laser flash photolysis, using laser induced fluorescence to detect the radical concentration [·OH] as a function of time. In this experiment  the ethanol concentration $[CH_3CO]$ was $3.3 \times 10^{-7}$M and this concentration was much higher that the concentration of hydroxyl radicals [·OH]. The following data for the concentration of hydroxyl radicals relative to their concentration at zero time was obtained.

| $[\cdot OH]/[\cdot OH]_0$ | 1.0 | 0.55 | 0.31 | 0.16 | 0.09 | 0.05 | 0.03 | 0.01 |
|---|---|---|---|---|---|---|---|---|
| $t/10^{-3}$s | 0 | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 | 1.2 | 1.5 |

(i) Write a rate equation for the reaction

(ii) Show that, under the described conditions, the reaction follows pseudo-first order kinetics

(iii) Determine the pseudo first order rate constant k′.

(b) The investigation was repeated a number of times, each time using a different concentration of ethanol, $[CH_3CO]_0$. A value for k′ was found in each case. Use the tabulated results presented below to confirm that the reaction is first order with respect to ethanol and determine the second order rate constant k for the reaction.

| $[CH_3CHO]_0/10^{-7}$M | 1.2 | 2.4 | 4.0 | 5.1 |
|---|---|---|---|---|
| $k'/10^3 s^{-1}$ | 1.12 | 2.10 | 3.65 | 4.50 |

**CH2201 Kinetics . 2013.**

**Annual**

(a) Define the terms rate constant, reaction order, half life and activation energy.

(b) Briefly outline how the rate constant measured at room temperature and the activation energy of a first order chemical reaction could be experimentally measured. You should indicate any equations and graphical procedures that you would need to apply in order to get a numerical value for the first order rate constant and the activation energy.

(c) Derive an expression for the half life of a first order chemical reaction.

(d) When cyclopropane (CP) is heated to 750 K in a closed container it isomerizes to form propene. The reaction was monitored using infrared spectroscopy and the following data obtained. Use this data to show that the reaction follows first order kinetics, evaluate the rate constant at 750 K and determine the half life of the reaction.

| t/min | 0 | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
|---|---|---|---|---|---|---|---|---|
| $10^3$[CP]/M | 1.50 | 1.23 | 1.01 | 0.68 | 0.46 | 0.31 | 0.21 | 0.14 |

**Supplemental**

(a) Define the term activation energy and write down the mathematical relationship between rate constant k and activation energy $E_A$. What are the units of activation energy?

(b) The rate constant for the hydrolysis of bromoethane in alkaline solution $C_2H_5Br\ (aq) + OH^-(aq) \rightarrow C_2H_5OH\ (aq) + Br^-(aq)$ was measured at different temperatures. Use the results in the following table to find a value for the activation energy of the reaction.

| T/K | 298 | 301 | 304 | 307 | 310 | 313 | 316 | 319 |
|---|---|---|---|---|---|---|---|---|
| $10^5k$/ $M^{-1}s^{-1}$ | 8.5 | 13 | 19 | 25 | 37 | 51 | 70 | 96 |

(c) The main mechanism for removing methane from the atmosphere is the reaction with hydroxyl radicals $CH_4 + OH^\cdot \rightarrow CH_3^\cdot + H_2O$. The activation energy for the reaction is 19.5 kJ $mol^{-1}$. Calculate the ratio of the rate constants for the reaction at the earth's surface (T = 295 K) and at the top of the troposphere (where T = 220 K).

## Foundation Scholarship Questions.

### Foundation Scholarship Physical Chemistry 2001.

A common reaction mechanism involves branching, the formation of more than one product from a single reactant. Consider the following reaction mechanism in which reactant A forms either B or C

$$A \xrightarrow{k_1} B$$
$$A \xrightarrow{k_2} C$$

where $k_1$ and $k_2$ are first order rate constants. Assume the initial condition that at time t = 0, the concentration of A is $a_0$ and the concentrations of both B and C are zero.

Derive an expression for the rate of loss of reactant species A with respect to time, and integrate this expression using the initial condition given to show that the concentration of A at any time t is given by

$$a(t) = a_0 \exp\left[-(k_1 + k_2)t\right]$$

Derive an expression for the half life of species A.

If b(t) denotes the concentration of product species B at any time t, show that

$$\frac{db}{dt} = k_1 a_0 \exp\left[-(k_1 + k_2)t\right]$$

Integrate the latter equation, noting that b = 0 when t = 0 to obtain an expression for b(t). Show that the product ratio $b/c$ at any time t is given by

$$\frac{b}{c} = \frac{k_1}{k_2}$$

## Foundation Scholarship Physical Chemistry 2002.

The competitive adsorption of two gases onto a solid surface is of considerable fundamental importance in catalysis. Consider the following adsorption equilibria:

$$\mathrm{A\,(g) + S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A\,(ads)}$$

$$\mathrm{B\,(g) + S} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{B\,(ads)}$$

where S represents a surface site, and $k_1$, $k_{-1}$ denote the rate constants for adsorption and desorption of A and $k_2$, $k_{-2}$ are the corresponding values for B. Let $p_A$ and $p_B$ denote the partial pressures of the gases A and B, and let $\theta_A$, $\theta_B$ represent their surface coverages.

(a) Set up expressions for the rate of adsorption and desorption for species A and B, and show that at equilibrium, the following expressions are obtained for gases A and B respectively:

$$\frac{\theta_A}{1-\theta_A-\theta_B} = K_A p_A \quad \text{and} \quad \frac{\theta_B}{1-\theta_A-\theta_B} = K_B p_B$$

where $K_A = k_1/k_{-1}$ and $K_B = k_2/k_{-2}$ represent the adsorption equilibrium constants for the gases A and B. Hence show that the surface coverages are given by

$$\theta_A = \frac{K_A p_A}{1+K_A p_A + K_B p_B} \quad \text{and} \quad \theta_B = \frac{K_B p_B}{1+K_A p_A + K_B p_B}$$

(b) Assume that the adsorbed molecules can react in a bimolecular manner with a rate constant k, on the surface to form an adsorbed product C which can subsequently desorb. If the bimolecular reaction process is rate determining show that the rate of product formation can be expressed as

$$\frac{dc}{dt} = \frac{kK_A K_B p_A p_B}{(1+K_A p_A + K_B p_B)^2}$$

What form would the rate equation adopt if (i) reactant A is strongly adsorbed while reactant B is only weakly adsorbed, and (ii) both reactants were weakly adsorbed ? Provide a brief interpretation of these limiting forms of the rate equation.

**Foundation Scholarship Physical Chemistry 2003.**

(a) Describe briefly how enzymes catalyse chemical reactions. What do you understand by the terms Michaelis constant $K_M$ and catalytic rate constant $k_C$ as applied to describe the kinetics of an enzyme catalysed reaction.

(b) Show how you can use the steady state approximation to derive an expression for the rate of an enzyme catalysed reaction in terms of the concentration of the substrate.

(c) How can this expression be transformed in to a linear form which can be used to graphically evaluate the Michaelis constant and the catalytic rate constant for an enzyme reaction.

(d) The following data outlining the variation of the rate of reaction R with the substrate concentration [S]were obtained for an enzyme catalysed reaction at 273.5 K and pH 7. The total concentration of the enzyme $[E]_\Sigma$ was 2.3 nmol $L^{-1}$.

| [S]/mmol $L^{-1}$ | 1.25 | 2.5 | 5.0 | 20 |
|---|---|---|---|---|
| Rate R/ mol $L^{-1}s^{-1}$ | $2.78 \times 10^{-5}$ | $5.0 \times 10^{-5}$ | $8.33 \times 10^{-5}$ | $1.67 \times 10^{-4}$ |

Use this data to graphically evaluate the Michaelis constant $K_M$ and the catalytic rate constant $k_C$ for the enzyme catalysed reaction. Estimate a value for the catalytic efficiency of the enzyme which is given by $k_C/K_M$ .

## Foundation Scholarship Physical Chemistry 2004.

The kinetics of ethanol absorption in the human body followed by the metabolic oxidation of ethanol by the enzyme LADH (Liver Alcohol Dehydrogenase) can be mathematically described in terms of a consecutive reaction sequence of the type:

$A \xrightarrow{k_1} B \xrightarrow{k_2} C$

where the absorption step exhibits first order kinetics with a rate constant $k_1$ and the metabolic oxidation exhibits zero order kinetics with a rate constant $k_2$.

Write down the rate equations for the time rate of decay of reactant A and the rate of formation of species B and C. Integrate these expressions using the assumption that at zero time $[A]=[A]_0, [B]=[C]=0$, and show that the time variation for the species concentrations are given by:

$$[A]_t = [A]_0 \exp[-k_1 t]$$
$$[B]_t = [A]_0 \{1-\exp[-k_1 t]\} - k_2 t$$
$$[C]_t = k_2 t$$

Show that the intermediate species B will exhibit a maximum concentration at a time given by $t_m = \frac{1}{k_1}\ln\left(\frac{k_1[A]_0}{k_2}\right)$, and determine the value of the maximum concentration $[B]_m$ at this time.

**Foundation Scholarship 2005.**

(a) Briefly explain what is meant by the half life of a chemical reaction. Derive the expression for the half life of a reaction which exhibits (i) first order kinetics and (ii) second order kinetics.

A substance A may decompose by either first or second order kinetics. If we assume that both reactions have the same half life for same initial concentration of A (which we label $a_0$), calculate an expression for the ratio of the first order rate to the second order rate initially, and at the time of one half life.

(b) The decomposition of an organic aldehyde at 773 K produced the following kinetic data

| | | | |
|---|---|---|---|
| Initial pressure $P_0$/ mmHg | 200 | 400 | 600 |
| Half life $t_{1/2}$ / s | 800 | 400 | 267 |

Determine the order of the reaction and the rate constant at this temperature.

**Foundation Scholarship 2006.**

The kinetics of enzyme biocatalysis of substrates is described when inhibition by a species I occurs by the modified Michaelis-Menten scheme:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES \xrightarrow{k_2} E + P$$

$$E + I \overset{K_I}{\rightleftarrows} EI$$

where E denotes the enzyme, S is the substrate, P is the product and ES denotes the enzyme – substrate complex. Here the inhibitor competes with substrate for free enzyme binding sites. $K_I$ represents the equilibrium constant for the inhibitor binding reaction.

Using the steady state approximation applied to the ES complex, and noting the mass balance expression $[E]_0 = [E] + [ES] + [EI]$, show that the Michaelis-Menten reaction rate when inhibitor is present is given by

$$v = k_2[ES] = \frac{v_{\max}[S]}{[S] + K'_M}$$

In the latter expression the maximum reaction rate is

$$v_{\max} = k_2[E]_0$$

and the modified Michaelis constant is given by

$$K_M{}' = \left(1 + K_I[I]\right)K_M$$

where [I] denotes the inhibitor concentration.

Note that the Michaelis constant given by $K_M = \frac{k_{-1} + k_2}{k_1}$ is that obtained for the enzyme biocatalytic reaction when the inhibitor concentration is zero.

## Foundation Scholarship 2007.

In the homogeneous decomposition of nitrous oxide $N_2O$ to form nitrogen and oxygen, it is found that at constant temperature the time needed for half the reaction to be completed ($\tau_{1/2}$) is inversely proportional to the initial pressure ($p_0$) of $N_2O$. On varying the temperature the following results were obtained.

| Temperature/K | 967 | 1030 | 1085 |
|---|---|---|---|
| $P_0$/Torr | 294 | 360 | 345 |
| $\tau_{1/2}$ /s | 1520 | 212 | 53 |

You should note that 1 atm = 760 Torr = 101.325 kPa, and you may assume that $N_2O$ behaves as an ideal gas.

Deduce the reaction order and calculate:

(i) the rate constant k for the reaction at 967 K expressed in units of $dm^3mol^{-1}s^{-1}$.

(ii) The mole fraction of nitrogen in the reaction mixture at time $\tau_{1/2}$.

(iii) The activation energy of the reaction.

## Foundation Scholarship 2008.

(a) Assume that a reaction obeys the following rate equation:

$$-\frac{dc}{dt} = kc^n$$

where k denotes the rate constant and n is the reaction order. Show that the integrated form of the rate equation is given by

$$\frac{1}{c^{n-1}} = (n-1)kt + \frac{1}{c_0^{n-1}}$$

where $c_0$ denotes the initial concentration of the reactant at time t = 0. Show further that the half life of the reaction $\tau_{1/2}$ is given by

$$\tau_{1/2} = \frac{2^{n-1}-1}{(n-1)kc_0^{n-1}}$$

Indicate how the latter equation may be used to graphically analyze experimental data to estimate the reaction order n.

(b) When the initial concentration of a reactant obeying the rate equation outlined in part (a) was changed from 0.502 mol dm$^{-3}$ to 1.007 mol dm$^{-3}$, the half life dropped from 51 s to 26 s at 298 K. What is the order n of the reaction and estimate a numerical value for the rate constant k. What are the units of k ?

## Foundation Scholarship 2009.

The decomposition of a gas phase reactant A into gaseous products P and Q proceeds according to the reaction stoichiometry: $A(g) \rightarrow P(g) + Q(g)$, and has been studied by measurement of the pressure increase in a constant volume system. Starting with an initial pressure of 112 torr of pure A at 713 K, the following *total* pressure p was measured at the times t stated:

| t/min | 15 | 30 | 45 | 60 | 75 |
|---|---|---|---|---|---|
| p/torr | 136 | 155 | 170 | 181 | 191 |

(a) Derive a suitable expression for the integrated rate equation by which the tabulated data can be analysed to confirm that the reaction exhibits first order kinetics.

(b) Calculate the rate constant and the half life of the reaction.

(c) If the activation energy of the reaction is given by 120 kJ $\text{mol}^{-1}$, determine the rate constant and half life at a temperature of 1100 K.

## Foundation Scholarship 2009 (MEGL).

1. (a) A common reaction mechanism in chemical kinetics involves the formation of more than one product from a single reactant. Hence we consider the following reaction

$$A \xrightarrow{k_1, E_{A1}} X$$

$$A \xrightarrow{k_2, E_{A,2}} Y$$

Where $k_1$, $E_{A1}$, $k_2$ and $E_{A2}$ represent the rate constants and activation energies for the two possible reaction steps. Let $E_{A\Sigma}$ represent the observed activation energy for the disappearance of the reactant species A and assume that it is defined by $E_{A\Sigma} = -R\dfrac{d\ln k_\Sigma}{d\left(1/T\right)}$ where T denotes the absolute temperature, R is the gas constant and

$k_{\Sigma} = k_1 + k_2$ represents the observed rate constant. Show that the observed activation energy is given by the following expression:

$$E_A = \frac{k_1 E_{A1} + k_2 E_{A2}}{k_1 + k_2}$$

(b) The product ratio r depends on the ratio of the rate constants for the parallel reaction steps according to the expression: $r = \frac{c_X}{c_Y} = \frac{k_1}{k_2}$ where $c_X, c_Y$ denote the concentrations of the product species X and Y. Assuming that each step obeys the Arrhenius equation derive a simple expression for the product ratio in terms of the activation energies and pre-exponential factors of the two steps. The product ratio changes with temperature depending on which of the activation energies $E_{A1}$ or $E_{A2}$ is larger. Predict how r changes with increasing temperature (i) if $E_{A1} > E_{A2}$ and (ii) if $E_{A1} < E_{A2}$. Hence propose a general rule which will describe the influence of temperature on the rates of competing reactions.

## Foundation Scholarship Examination 2010

(a) Derive a relationship between the change in Gibbs energy ΔG and the potential of a galvanic cell E. Use this latter relationship coupled with the Gibbs-Helmholtz equation $\Delta H = \Delta G - T\left(\frac{\partial \Delta G}{\partial T}\right)_P$ to derive expressions which enable the enthalpy change and entropy change of a reaction to be measured by making measurements of the cell potential E as a function of temperature T.

(b) The following E versus T data was obtained for a Galvanic cell in which the cathode reaction is $A^{2+} + 2e^- \rightarrow A$ and the anode reaction is $P \rightarrow P^{2+} + 2e^-$.

| E/V | 1.0352 | 1.0335 | 1.0330 | 1.0317 | 1.0304 | 1.0280 |
|---|---|---|---|---|---|---|
| T/K | 295.0 | 300.5 | 303.5 | 307.9 | 313.9 | 322.6 |

Determine the values of ΔG, ΔH and ΔS at 298 K for the cell reaction $A^{2+} + P \rightarrow A + P^{2+}$.

**Foundation Scholarship Examination 2011**

The rates of many bimolecular reactions in solution may be described by the following mechanism. The reactants A and B approach one another via molecular diffusion and associate to form an encounter complex AB (with a rate constant $k_D$). This complex can then either revert back via dissociation to reactants (with a rate constant $k'_D$) or undergo chemical transformation and decompose to form products P (with a rate constant $k_R$. Use the steady state approximation applied to the encounter complex AB to show that the net reaction rate R is given by: $R = kc_A c_B = \frac{k_R k_D}{k_R + k'_D} c_A c_B$ where $c_A$ and $c_B$ denote the concentrations of A and B respectively and k denotes a composite rate constant given by: $k = \frac{k_R k_D}{k_R + k'_D}$.

(a) Derive expressions for :

i. the reaction rate for the situation where the rate of chemical reaction to form products P is much faster than the rate at which the encounter complex breaks up to revert to reactants.

ii. The reaction rate for the opposite case where the rate of chemical transformation is much slower than the rate of encounter complex dissociation to reform reactants. This is called an activation controlled process.

iii. Interpret these two limiting cases in terms of barrier heights and energy diagrams

(b)

The air bags in cars are inflated when a collision triggers the explosive highly exothermic decomposition of sodium azide $NaN_3$ to generate $N_2$ gas and solid Na according to: $2NaN_3(s) \rightarrow 2Na(s) + 3\,N_2(g)$. A typical driver side air bag contains about 50 g of $NaN_3$. Determine the volume of $N_2$ gas that would be produced by the decomposition of 50 g of sodium azide at 85°C and 1.0 atm pressure.

**Foundation Scholarship Examination 2012.**

(a) What is the function of a catalyst. Discuss the principles by which an enzyme catalyst operates.

(b) Derive, using the Quasi Steady State Approximation, the Michaelis-Menten equation which relates the rate of the enzyme reaction to the concentration of the substrate in the solution, sketch the shape of the rate versus substrate concentration curve and derive useful limiting expressions for the reaction rate in the limit of very low and very high substrate concentrations.

(c) Indicate how the Michaelis-Menten equation may be linearized to obtain useful kinetic parameters such as the catalytic rate constant $k_{cat}$ and the Michaelis constant $K_M$. How can the ratio $k_{cat}/K_M$ (the catalytic efficiency) be interpreted. Is the linearization of enzyme kinetic data the best approach to adopt in order to derive numerical values for the latter parameters?

(d) The enzyme carbonic anhydrase catalyses the hydration of $CO_2$ in red blood cells to give bicarbonate ion according to : $CO_2(g) + H_2O\ (l) \rightarrow HCO_3^-\ (aq) + H^+(aq)$. The following data were obtained for the reaction measured at pH 7.1 and at T = 273.5 K. The enzyme concentration was estimated as 2.3 nmol dm$^{-3}$.

| $[CO_2]$/mmol dm$^{-3}$ | 1.25 | 2.50 | 5.0 | 20.0 |
|---|---|---|---|---|
| Rate/mmol dm$^{-3}$ s$^{-1}$ | $2.78 \times 10^{-2}$ | $5.0 \times 10^{-2}$ | $8.33 \times 10^{-2}$ | 0.167 |

Determine the catalytic efficiency of the enzyme at 273.5 K.

**Foundation Scholarship 2013 . Chemical Kinetics.**

(a) Define the terms rate constant k and half life $\tau_{1/2}$ as used in Chemical kinetics.

(b) Assume that a reaction A + B → products occurs by second order kinetics and that the rate constant is given by k. The differential rate equation is given by $-\frac{dc_A}{dt} = k\,c_A c_B$.

(i) Show that a general expression for the concentration $c_A$ as a function of time t is given by: $c_A = \frac{b_0 - a_0}{\frac{b_0}{a_0}\exp\left[\left(b_0 - a_0\right)kt\right] - 1}$

where $a_0$ and $b_0$ denote the initial concentrations of reactants A and B respectively and are related to the reactant concentrations remaining at any time t via $c_A = a_0 - x,\ c_B = b_0 - x$ where x denotes the amount of reactant consumed at any time t. (hint: the following relationship is useful to note: $\int \frac{dx}{\left(a_0 - x\right)\left(b_0 - x\right)} = \frac{1}{b_0 - a_0}\ln\left(\frac{b_0 - x}{a_0 - x}\right) + C$ where C is a constant of integration).

(ii) Show that in the limiting case when $a_0 = b_0$ then $c_A = \frac{1}{\frac{1}{a_0} + kt}$

(iii) Show that in the limiting case where $b_0 >> a_0$ (pseudo first order kinetics) then $c_A = a_0 \exp\left[-b_0 kt\right]$.

(iv) Show that in the general case where $a_0 \neq b_0$ the half life is given by: $\tau_{1/2} = \frac{\ln\left(2 - \frac{a_0}{b_0}\right)}{\left(\frac{b_0}{a_0} - 1\right)}\left\{\frac{1}{ka_0}\right\}$ and that in the special case where $b_0 >> a_0$, $\tau_{1/2} \cong \frac{\ln 2}{kb_0}$.