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SF CH 2201: Chemical Kinetics.

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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.
They are made available to Trinity SF Chemistry students to assist them in their revision of the Chemical kinetics lectures delivered by Dr Lyons in the Michaelmas Term.

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 19^0C and 1.38 x 10^{-3} L mol^{-1} s^{-1} at 37^0C. 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

$$S + E \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \overset{k_2}{\longrightarrow} P + S$$
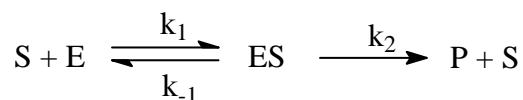
where ES represents the enzyme/substrate complex. The reaction rate R is given by $R = k_2[ES]$.

(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 $R = \dfrac{k_c[E]_\Sigma[S]}{K_M + [S]}$ where $k_c = k_2$ is the catalytic rate constant and $K_M = \dfrac{k_{-1} + k_2}{k_1}$ 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:

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

$$A^- + HA \; \xrightarrow{k_2} \; P$$
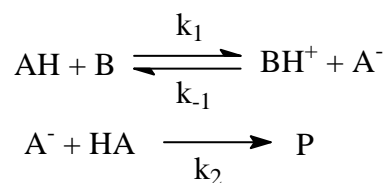
where AH represents acetone and A^- is the carbanion. Use the steady state approximation to determine the concentration of the carbanion, and hence derive the rate equation for the formation of the product .

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 $k = A \exp\left[-\dfrac{E_A}{RT} \right]$. 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^{3}mol^{-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 $\dfrac{1}{c_t} = kt + \dfrac{1}{c_0}$, 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 $H^+(aq) + OH^-(aq) \underset{k'}{\overset{k}{\rightleftharpoons}} H_2O(\ell)$ is 1.4 x 10^{11} dm^{3}mol^{-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: $-\dfrac{dc}{dt} = kc^2$ 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 $\tau_{1/2} = \dfrac{\ln 2}{k}$ 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

$-\dfrac{dc}{dt} = kc^2$, that the half life is given by $\tau_{1/2} = \dfrac{1}{kc_0}$ where c_0 denotes

the initial concentration of reactant.

(b)   A rate constant is measured as 2.78×10^{-4} dm^{3}mol^{-1}s^{-1} at 292 K
and 3.38×10^{-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

$\tau_{1/2} = \dfrac{\ln 2}{k}$ 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) $\rightarrow$ $CHCl_3$(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
10^5rate /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

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

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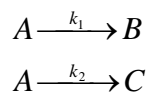
where k_1 and k_2 are first order rate constants. Assume the initial condition that at time t = 0, the concentration of A is a_0 and the concentrations of both B and C are zero.

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:

$$A\,(g) + S \;\xrightleftharpoons[k_{-1}]{k_1}\; A\,(ads)$$

$$B\,(g) + S \;\xrightleftharpoons[k_{-2}]{k_2}\; B\,(ads)$$
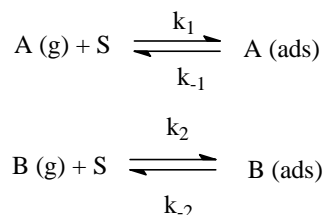
where S represents a surface site, and k_1, k_{-1} denote the rate constants for adsorption and desorption of A and k_2, k_{-2} are the corresponding values for B. Let p_A and p_B denote the partial pressures of the gases A and B, and let θ_A, θ_B represent their surface coverages.

(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:

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

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

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

(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

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

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 $L^{-1}s^{-1}$	2.78×10^{-5}	5.0×10^{-5}	8.33×10^{-5}	1.67×10^{-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:

$$A \xrightarrow{\ k_1\ } B \xrightarrow{\ k_2\ } C$$
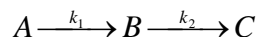
where the absorption step exhibits first order kinetics with a rate constant k_1 and the metabolic oxidation exhibits zero order kinetics with a rate constant k_2.

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 $t_m = \dfrac{1}{k_1} \ln\left(\dfrac{k_1 [A]_0}{k_2} \right)$, 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:

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

$$E + I \overset{K_I}{\rightleftharpoons} EI$$
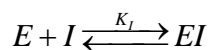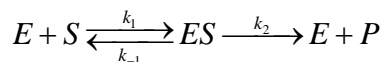
where E denotes the enzyme, S is the substrate, P is the product and ES denotes the enzyme – substrate complex. Here the inhibitor competes with substrate for free enzyme binding sites. K_I represents the equilibrium constant for the inhibitor binding reaction.

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

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

where [I] denotes the inhibitor concentration.

Note that the Michaelis constant given by $K_M = \dfrac{k_{-1} + k_2}{k_1}$ 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 mol^{-1}, determine the rate constant and half life at a temperature of 1100 K.

Foundation Scholarship Examination 2010

(a)   Derive a relationship between the change in Gibbs energy ∆G and the potential of a galvanic cell E. Use this latter relationship coupled with the Gibbs-Helmholtz equation $\Delta H = \Delta G - T\left(\dfrac{\partial \Delta G}{\partial T}\right)_P$ 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 ∆G, ∆H and ∆S at 298 K for the cell reaction $A^{2+} + P \rightarrow A + P^{2+}$.