CYL110 2012-2013 Kinetics Tutorial 1

1. The rate of decomposition of acetaldehyde can be studied by measuring the pressure in a system at constant volume and temperature. Express the rate of reaction in terms of the rate of change of the pressure. The overall reaction is CH_3CHO (g) $\rightarrow$ CH_4 (g) + CO (g).

2. Sulphuryl chloride decomposes according to the equation $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$. Determine the order of the reaction with respect to $SO_2Cl_2(g)$ from the following initial rate data at 298 K.

$[SO_2Cl_2]_0$/mol dm^{-3}	0.10	0.37	0.76	1.22
v_0/mol dm^{-3}s^{-1}	2.24×10^{-6}	8.29×10^{-6}	1.71×10^{-6}	2.75×10^{-5}

3. A first order reaction has a rate constant of 2.24×10^{-5} s^{-1} at 320^{0}C. Calculate the half-life of the reaction. What fraction of the sample remains after being heated for 5 hrs at 320^{0}C? How long will a sample have to be heated at 320^{0}C to decompose 92% of the initial amount present. ($t_{1/2} = 3.09 \times 10^4$ s; 66.8%; 31.3h)

4. The reaction A $\rightarrow$ B is n^{th} order(where n = 1/2, 3/2, 2, 3 etc.) and goes to completion to the right. Derive the expression for the half life in terms of k, n, and $[A]_0$. ($t_{1/2} = (2^{n-1} - 1)/(n - 1)\ k\ [A]_0^{n-1}$)

5. The decomposition of acetaldehyde given in problem 1 is second order. Formulate the rate law in terms of the total pressure of the system and integrate the result to express the pressure as a function of time.

6. The definition of the rate of reaction in terms of molar concentration assumes that the volume remains constant during the course of the reaction. Derive an expression for the rate of the reaction in terms of the molar concentration of a reactant A for the case in which the volume changes during the course of the reaction.

7. Derive an integrated expression for a second-order rate law $v = k[A][B]$ for a reaction of stoichiometry 2A + 3B $\rightarrow$ P. From the expression you obtained derive the integrated expression for the second order rate law $v = k[A]^2$.

8. The second order rate constant for the alkaline hydrolysis of ethyl formate in 85% ethanol (aqueous) at 29.86 ^{0}C is 4.53 L mol^{-1} s^{-1}. (a) If the reactants are both present at 0.001 mol L^{-1}, what will be the half-life of the reaction? (b) If the concentration of one of the reactants is doubled and of the other is cut in half, how long will it take for half the reactant present at the lower concentration to react?

9. A gas reaction 2A $\rightarrow$ B is second order in A and goes to completion in a reaction vessel of constant volume and temperature with a half life of 1h. If the initial pressure of A is 1 bar, what are the partial pressures of A, of B, and the total pressure at 1h, 2h, and at equilibrium? ($p_a = 0.5$, $p_b = 0.25$; 0.33, 0.33; 0, 0.5)

10. The reaction of *cis*-2-butene to *trans*-2-butene is first order in both directions. At 25 ℃, the equilibrium constant is 0.406 and the forward rate constant is 4.21×10^{-4} s^{-1}. Starting with a sample of the pure *cis* isomer with $[cis]_0 = 0.115$ mol dm^{-3}, how long would it take for half the equilibrium amount of the *trans* isomer to form.

11. Suppose that in an industrial batch process a substance A produces the desired compound I that goes on to decay to a worthless product C, each step of the reaction being first order. At what time will I be present in greatest concentration? Calculate the maximum concentration of I.

12. Potassium-argon dating is used in geology and archeology to date sedimentary rocks. Potassium-40 decays by two different paths

$$^{40}_{19}\text{K} \rightarrow ^{40}_{20}\text{Ca} + ^{0}_{-1}e \qquad (89.3\%)$$

$$^{40}_{19}\text{K} \rightarrow ^{40}_{18}\text{Ar} + ^{0}_{1}e \qquad (10.7\%)$$

The overall half-life for the decay of potassium-40 is 1.3×10^9 y. Estimate the age of sedimentary rocks with an argon-40 to potassium-40 ratio of 0.0102.

13. Consider the decomposition of C_4H_8 according to $C_4H_8(g) \rightarrow 2C_2H_4$ (g). The rate is measured by observing the change in pressure (p) at constant T and V. (a) Express the rate of the reaction $\frac{1}{V}\frac{d\xi}{dt}$ (where ξ is the extent of the reaction in terms of $\frac{dp}{dt}$. [Hint: Initially n_0 moles of C_4H_8 is present. Express the number of moles at any times t in terms of ξ]. (b) If p_i is the pressure when C_4H_8 is completely decomposed and the reaction is first order in C_4H_8 derive the relation between p and t. (c) If k = 2.48×10^{-1} s^{-1}, calculate $t_{1/2}$. (d) What is the value of p/p_i after 2 hours? [F98]

14. The equilibrium constant for the reaction $D^+ + OD^- \rightleftharpoons D_2O$ is 4.08×10^{16} mol^{-1} dm^3. The rate constant for the reverse reaction is independently found to be 2.52×10^{-6} s^{-1}. What would the relaxation time for a T-jump experiment be? The density of D_2O is 1.04 g cm^{-3}.(1.32×10^{-4})

15. Consider the chemical reaction described by $2A \rightleftharpoons D$ with forward and reverse rate constants given by k_1 and k_{-1} respectively. Obtain an expression for the response of this system to a temperature jump and express the relaxation time in terms of the two rate constants. ($\Delta[D] = \Delta[D]_0 e^{-t/\tau}$, $\tau = 1/(4k_1[A]_{2,\text{eq}} + k_{-1})$

16. Consider the hypothetical, second order, kinetically irreversible reaction $2A \xrightarrow{k}$ Products at constant temperature and volume. Let the concentration c_t of A be given in terms of a measurable property P_t by $P_t = B\exp(b\,c_t)$ where B and b are constants depending only on temperature and t denotes the time. Derive an expression for the specific rate constant k in terms of t, P_t, B, and b. [M02]

17. Show that the ratio $t_{1/2}/t_{3/4}$, where $t_{1/2}$ is the half-life and $t_{3/4}$ is the time for the concentration of A to decrease to 3/4 of its initial value can be written as a function of n alone, and can therefore be used as a rapid assessment of the order of a reaction.

18. The oxidation of HSO_3^- by O_2 in aqueous solution is a reaction of importance to the processes of acid rain formation. The reaction $2HSO_3^- + O_2 \rightarrow 2SO_4^{2-} + 2H^+$ follows the rate law $k[HSO_3^-]^2[H^+]^2$. Given a pH of 5.6 and an oxygen molar concentration of 2.4×10^{-4} mol L^{-1} (both presumed constant), an initial HSO_3^- concentration of 5×10^{-5} mol L^{-1}, and a rate constant of 3.6×10^6 L^3 mol^{-3} s^{-1}, what is the initial rate of the reaction? How long would it take for HSO_3^- to reach half its initial concentration? [F03]

19. The first order surface reaction A (g) $\rightarrow$ A (ads) $\rightarrow$ B(g) has a rate of 1.8×10^{-4} mol dm^{-3} s^{-1}. The surface has a dimension of 1.00 cm by 3.50 cm. Calculate the rate of the reaction if the dimensions of the two sides of the surface were each doubled.

20. The rotational isomerization of a compound was studied by the T-jump method. At 20 ℃ the deviation from equilibrium attains half its value at $t = 0$ in 6.93×10^{-9} s . If the favored isomer is present to the extent of 80 %, determine the rate constants for the isomerization.