COVENANT UNIVERSITY NIGERIA

TUTORIAL KIT
OMEGA SEMESTER

PROGRAMME: CHEMICAL ENGINEERING

COURSE: CHE 326
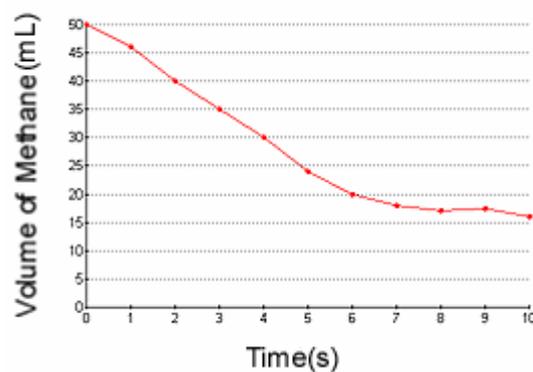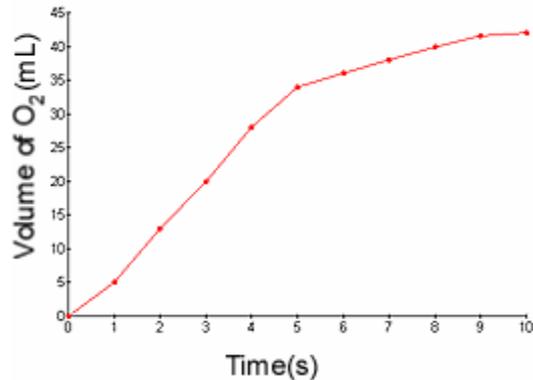
CHE326: CHEMICAL REACTION ENGINEERING I

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Use these two graphs to answer question 1.

1.) Find the reaction rate of the decomposition of methane between 3 and 7 seconds.

1b.) Find the reaction rate of the production of oxygen gas between 2 and 6 seconds.

1c.) Identify the reactant and product based on the graph.

Q2) Dinitrogen pentoxide (N_2O_5) decomposes by first order kinetics with a rate constant of 3×10^{-5} min^{-1} at 25°C.

   a. What is the half-life (in hours) for the decomposition of N_2O_5 at 25 °C.
   b. Calculate the concentration of N_2O_5 after 5 hours if the initial concentration of the pentoxide is 233 mmoles/L.
   c. How much time in seconds will elapse before the N_2O_5 concentration decreases from 233 mmoles/L to 155 mmoles/L.

3.) How does temperature affect reaction rate?

4.) Write out the rate law and explain how temperature affects the rate constant and frequency factor of a reaction

5.) What is activation energy?

6.) From first principle, derive the integrated second order rate equation for a reactant A.

7.) Explain how a catalyst works relative to activation energy.

8.) Differentiate between a batch reactor and a semi-batch reactor. With equations, give an example each of series and parallel reactions.

9.) With the given information, determine the rate law, the rate constant, and the overall reaction order.
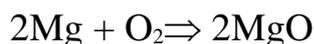
$$2Mg + O_2 \Rightarrow 2MgO \qquad\qquad Rate = k[Mg]^n[O_2]^m$$

Trial	Initial [Mg] (mol/L)	Initial [O$_2$] (mol/L)	Measured Rate (mol/L*s)
1	.10	.10	2.0x10^-3
2	.20	.10	4.0x10^-3
3	.10	.20	8.0x10^-3

10.) Consider the irreversible reaction between the reactants A and B. In one experiment, the following data were collected when the initial concentrations of A and B were 0.008 and 10 mol dm^{-3} respectively.

-r$_A$ mol/dm^3 min	8	5	2.5	1
CA* 10^{-4} mol dm^{-3}	8	6	4	2

    a. I. Write the equation for the rate of reaction of A.

       II. Use the difference between the concentrations of A and B to explain the difference between the true rate constant and the pseudo-rate constant of the reaction.

    b. Find the order with respect to A and the pseudo-rate constant K'.

    When more experiments were carried out with B still in large excess, the pseudo-rate constant k' varied with concentration of B as calculated below:

C$_{BO}$ mol/dm^3	8	5	2.5	1
K'*10^{-6} dm^3 mol^{-1} min^{-1}	8	6	4	2

Calculate the following:

    c. the order of the reaction with respect to B
    d. the overall order of the reaction
    e. true rate constant of the reaction

11a.) Find the half-life of a first-order reaction if the reaction constant, k , is 2.0x10^-3 s^{-1}.

11b.) Find the time when only 1% of reactant remains.

12.) Consider the gas phase reaction A + 2B $\longrightarrow$ C + D

If the reactor is operated at atmospheric pressure and isothermally (25 $^{\circ}$C) such that 0.66 moles of A and 0.34 moles of B were initially charged into the reactor,

    a. Draw up a stoichiometric table for the species
    b. For 20 % conversion of A, calculate the amount of B (mole or moles) in the reactor.
    c. The number of mole(s) of C at 40 % conversion of A

    d. Conversion of B at 25 % conversion of A

e. By what concentration in moles/L is C less than A at 25 % conversion of A if the initial volume of the reactor is 20 L?

13.) Find E_a using the following information:

$ClO_3^- + H_2O \Rightarrow ClO_4^- + H_2$
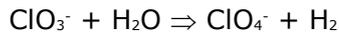
Reaction constant k, (s^{-1})	Temperature($C°$)
2.0x10^-3	25
4.0x10^-3	35
8.0x10^-3	45
1.6x10^-2	55

$$\ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln(A)$$

14.) Determine the rate constant for the second-order reaction $2A \longrightarrow 2B + C$ given that the initial concentration of A is 0.3 moles /L and that the concentration of B increased from zero to 0.010 moles/L in 20 minutes. Hint: assume constant volume

a. Determine the total pressure in the constant-volume isothermal batch reactor used to carry out this reaction at 50 % decomposition of A if the initial total pressure was 2 atm and the charge contained 10 and 90 mole percent of inert and A respectively.
b. Estimate the percent change in volume of the reactor if this reaction was carried out in a variable volume, constant-pressure, isothermal batch reactor.

15.) Find the 2nd order reaction's activation energy with the given information.

K_1=4.0L/mol*s at 37C° K_2=8.0L/mol*s at 87C°

Hint:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

16. Write the rate equations for:

a. Zero, 1st, 2nd and 3rd order reactions
b. Derive the corresponding half life equations for "a" above.
c. What is the effect of concentration on the half life for each of the equations in "b"
d. Derive the generalized half-life equation for any reaction system.

17.) State one advantage and disadvantage of the method of initial rates in the determination of the

rate equation of an isothermal homogenous reaction
b. The initial rate of reaction $2A + 2B \longrightarrow 3C + D$ is determined for different initial conditions with the results in the table below

RUN #	Reaction temp. °C	C_{AO} moles/L	C_{BO} moles/L	Initial rate D * 10^{-3} moles/L

| 1	217	0.1	0.25	1.25
2	217	0.2	0.50	10.0
3	217	0.2	0.25	2.50
4	217	0.1	0.50	5.00
5	237	0.2	0.30	5.40

(i)   Find the rate law and the rate constant for this reaction
(ii) What are the activation energy of the reaction and the pre-exponential factor

18.Mention the types of reactions and means by which we classify chemical reactions

19. Define the following terms

a. Molecularity of a reaction, conversion, order and extent of reaction
b. Given that A $\longrightarrow$ 2B + C, If pure A is fed into a reactor whose final volume is 20 litres, estimate the initial volume of this reactor for 15 % conversion of A.

20.) In the reaction between persulfate ion and iodide ion:

$$S_2O_8^{2-} (aq) + 3I^- (aq) \longrightarrow 2SO_4^{2-} (aq) + I_3^-$$
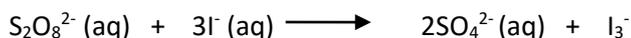
Spectophotometry was employed to determine the concentration of the tri-iodide ion. Two equimolar solutions of the persulfate ion and the tri-iodide ion are mixed in a 1:3 ratio, so that there are stoichiometric amounts of the tri-iodide and persulfate ions in the reaction solution.

a. Justify the monitoring of the products of a reaction instead of the reactants in the study of the kinetics of a reaction; any two reasons will suffice.
b. Write the equation for the rate of reaction of the persulfate ion in terms of only the concentration of the tri-iodide ion.
c. If the tri-iodide ion concentration versus time data are available, show the plot you will make to determine the overall order of the reaction by using the differential method of analysis. You may also assume that the initial concentration of persulfate ion is known.
d. The tabulated data refers to the gas phase decomposition of a reactant A. Pure A is charged at different pressures into a constant-volume isothermal batch reactor and the half life is measured.

P_0 (atm)	0.135	0.286	0.416	0.683
$t_{1/2}$ (sec)	1060	500	344	209

i.   Use the data to confirm that the reaction is second order.
ii. What is the specific rate constant of the reaction?

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1a.)

- The reaction rate is simply: the change in amount of something / Δ T.
- I know the rate law is: Δ [A] / Δ T, where [A] is the molarity.

17-35= -18

-18/4= -4.5 L/t

1b.)

- The reaction rate is simply: the change in amount of something / Δ T.
- I know the rate law is: Δ [A] / Δ T, where [A] is the molarity.

36ml-13ml / 6-3

23ml/3s = 7.7 ml/s

1c.)

- Oxygen would be the product because its reaction rate graph has a <u>positive</u> slope; the concentration of oxygen is <u>increasing</u>.
- Methane would be the reactant because its reaction rate graph has a <u>negative</u> slope; the concentration of methane is <u>decreasing</u>.

3.) Temperature increased the reaction rate. Remember for a reaction to take place, the molecules must move faster. An increase in temperature speeds up the molecules.

5.) Activation energy is the minimum amount of energy the reaction must overcome in order for the reaction to take place.

7.) A catalyst lowers the activation energy; therefore, increases the reaction rate.

9.)

$$\frac{2.0 \times 10^{-3}}{8.0 \times 10^{-3}} = \frac{k[.10][.10]}{k[.10][.20]} \qquad \frac{2.0 \times 10^{-3}}{4.0 \times 10^{-3}} = \frac{k[.10][.10]}{k[.20][.10]}$$

$$\frac{2.0 \times 10^{-3}}{8.0 \times 10^{-3}} = \frac{k[.10][.10]}{k[.10][.20]} \qquad \frac{2.0 \times 10^{-3}}{4.0 \times 10^{-3}} = \frac{k[.10][.10]}{k[.20][.10]}$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^m \qquad\qquad \frac{1}{2} = \left(\frac{1}{2}\right)^n$$

$$m=2 \qquad\qquad\qquad n=1$$

- To find the order for Mg, setup the equation like above so the concentration of oxygen cancels out.

- To find the order for O_2, simply try to cancel the concentration of Mg.
- For the rate constant, once you have the rate law, plug in any row of data from the chart and solve for k. Make sure the concentration corresponds to the measured rate.

$2.0 \times 10^{-3} = k[.10]^1[.10]^2$

k=2.0

Final rate law = $k[Mg]^1[O_2]^2$

Over all reaction order = n + m= 3

11a). Because it is a first-order reaction, the half-life equation is ln2 / k.

ln2/ 2.0×10^{-3} = 350 seconds.

I know the unit is seconds because the unit of my reaction constant is s s^{-1}.

*If the unit is $minute^{-1}$, the half life would be 350 minutes.

11b) The integrated rate law of a first order-reaction is: $\ln[A]=-kt+\ln[A]_0$

$kt=\ln[A]_0 + \ln[A]$

$kt=\ln\left[\dfrac{A_0}{A}\right]$

$kt=\ln\left[\dfrac{A_0}{A}\right] = \ln\left[\dfrac{1}{.01}\right]$

$kt=\ln 100$

$t=2300s$

13.)

Another way of looking at this equation is: y=mx+b. Looks familiar? It's the equation of a line.

$y=\ln k$; $m=-E_a/R$; $x=1/T$; $b= \ln(A)$.

slope $=-E_a/R$

Find the slope of the line when graphing $\ln k$ vs. 1/T.

(.00325-.00336)/(-5.53+ 6.21)= -6270

Remember R= 8.3145 J and convert T to kelvin.

$-6270=-E_a/R$

-6270*-8.3145= 5.21×10^4 J/mol

15.)

Make sure you change the temperature to kelvin.

37C° =300k

87C° =360k

$$\ln\left(\frac{8.0}{4.0}\right) = \frac{-E_a}{R}\left(\frac{1}{300} - \frac{1}{360}\right) \quad R = 8.3145\ J$$

The answer is 1.1x10^4 J/mol.

The rate of a particular reaction doubles when temperature changes from 27⁰C to 37⁰C. Calculate the energy of activation of the reaction.

We are given that:
When $T_1 = 27 + 273 = 300$ K
Let $k_1 = k$
When $T_2 = 37 + 273 = 310$ K
then $k_2 = 2\ k$ (doubles)
Substituting these values into the equation:
Log $(k_2 / k_1) = E_a / 2.303\ R\ \{(T_2 - T_1) / T_1\ T_2\}$

Gives

Log $(2\ k / k) = E_a / 2.303$ x 8.314 $\{(310 - 300) / 300$ x 310$\}$
Log $2 = E_a / 2.303$ x 8.314 x (10 / 300 x 310)
$E_a = 53598.6$ J mol^{-1}
$E_a = 53.6$ kJ mol^{-1}

The rate constant of a reaction is 1.2 x 10^{-3} sec^{-1} at 30⁰ C and 2.1 x 10^{-3} sec^{-1} at 40⁰ C. calculate the energy of activation of the reaction.

We are given that:
$k_1 = 1.2$ x 10^{-3} sec^{-1}
$T_1 = 30 + 273 = 303$ K
$k_2 = 2.1$ x 10^{-3} sec^{-1}
$T_2 = 40 + 273 = 313$ K

Substituting these values the equation:
Log $(k_2 / k_1) = E_a / 2.303\ R\ \{(T_2 - T_1) / T_1\ T_2\}$

Gives

Log $(2.1$ x 10^{-3} sec$^{-1}/ 1.2$ x 10^{-3} sec$^{-1})$
$= E_a / 2.303$ x 8.314 $\{(313 - 303) / 303$ x 313$\}$
Log $(2.1 / 1.2) = E_a / 2.303$ x 8.314 x (10 / 303 x 313)
$E_a = 44126.3$ J mol^{-1}
$E_a = 44.13$ kJ mol^{-1}
Hence, the energy of activation of the reaction is 44.13 kJ mol^{-1}

17a.   Advantage – it gives an approximate / quick estimate of initial rate at t = 0; disadvantage – it cannot estimate the actual initial rate of reaction especially at time t = 0

bi. $-r_A = 4 * 10^5\ C_A{}^1 C_B{}^2$

bii. $E_A = 2.3 * 10^5$ J and $k_0 = k_2 = 1.2 * 10^6$ dm^3 mol^{-2} min^{-1}

Q19.

a. molecularity – number of molecules that combine in a given reaction system to form products.

Conversion - fraction used, of the initial material fed into the reactor

Order - the index to which the concentration terms are raised in a given rate equation.

Extent of reaction – the degree of advancement of a reaction

b. $V_0 = 18.60$ L