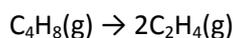


SKKK3233 - Physical Chemistry for Engineer

Assignment 05 – Elementary Chemical Kinetics

Instruction : Write down the basis of calculation and assumptions (if any) clearly. **BOX** the final answer(s)

- 1) Consider the first-order decomposition of cyclobutane at 438°C at constant volume:



- Express the rate of the reaction in terms of the change in total pressure as a function of time.
- The rate constant for the reaction is $2.48 \times 10^{-4} \text{ s}^{-1}$. What is the half-life?
- After initiation of the reaction, how long will it take for the initial pressure of C_4H_8 to drop to 90% of its initial value?

$$(\text{Ans: } \frac{1}{2RT} \frac{dP_t}{dt}, 2.79 \times 10^3 \text{ s}, 425 \text{ s})$$

- 2) Solve the following:

- What are the inherent assumptions in the Langmuir model of surface adsorption?
- The adsorption of nitrogen on mica measured at different pressures is as follows

$V_{\text{ads}} (\text{cm}^3 \text{g}^{-1})$	$P (\text{Torr})$
0.494	2.1×10^{-3}
0.782	4.6×10^{-3}
1.16	1.3×10^{-3}

Langmuir equation can be written as

$$\frac{1}{V_{\text{ads}}} = \frac{1}{KV_m} \left(\frac{1}{P} \right) + \frac{1}{V_m}$$

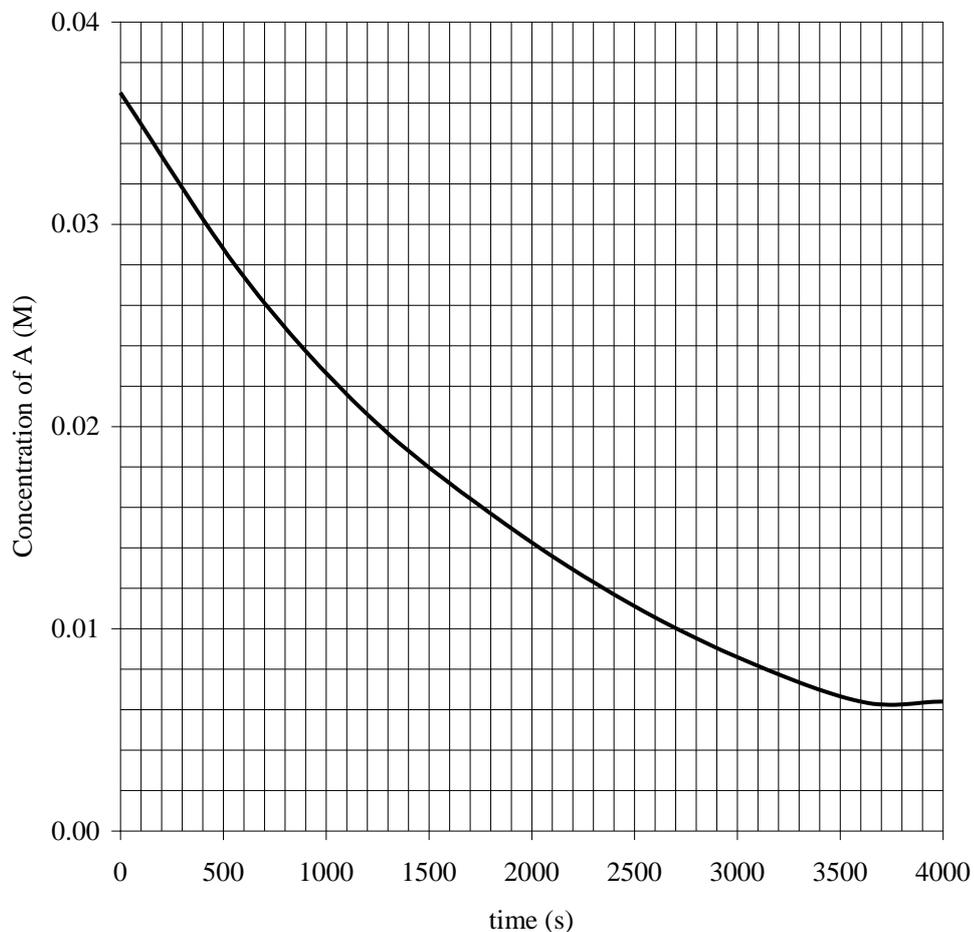
where V_m is the maximum adsorption and K is equilibrium constant.

Using Langmuir isotherm, determine the

- Langmuir parameters
- Fractional coverage, θ at each pressure.

Fractional coverage, θ is defined as ratio of adsorbed volume to the volume of maximum absorption

$$(\text{Ans: } 1.56 \text{ cm}^3 \text{g}^{-1}, 2.21 \text{ torr}^{-1}, 0.317, 0.501, 0.744)$$



- a) From the figure, estimate the values of rate constant and reaction order for the degradation of A.
 b) If the degradation of A at 100°C gives a four times higher rate constant than that at 25°C, determine the value of activation energy, E_a .

(Ans: $4.9 \times 10^{-4} [A]^{0.98}$, 17.082 kJ/mol)

- 3) The following data were obtained for the gas-phase decomposition of nitrogen dioxide at 300 °C,

Time (s)	[NO ₂] (M)
0	0.01000
50	0.00787
100	0.00649
200	0.00481
300	0.00380

- a) Determine whether the reaction is first or second order in NO₂.
 b) What is the reaction rate constant for this disappearance of NO₂.
 c) If the initial concentration of NO₂ in a closed vessel is 0.0500 M, what is the remaining concentration after 0.500 h?

(Ans: $0.543 \text{ M}^{-1} \text{ s}^{-1}$, $1.0 \times 10^{-3} \text{ M}$)

- 4) The following table shows the rate constants for the rearrangement of methyl isonitrile at various temperatures:

Temperature (°C)	k (s ⁻¹)
189.7	2.52 x 10 ⁻⁵
198.9	5.25 x 10 ⁻⁵
230.3	6.30 x 10 ⁻⁴
251.2	3.16 x 10 ⁻³

- (a) From these data, calculate the activation energy for the reaction.
(b) What is the value of the rate constant at 430.0 K and at 280 °C?

(Ans: 160 kJ/mol, 1.0x10⁻⁶ s⁻¹, 2.2 x 10⁻² s⁻¹)

- 5) Consider the following reaction: $\text{Br}_2(\text{aq}) + \text{HCOOH}(\text{aq}) \rightarrow 2\text{Br}^-(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{CO}_2(\text{aq})$ The reaction is initiated, and the following data are obtained:

Time (s)	[Br ₂] (M)
0.0	0.0120
50.0	0.0101
100.0	0.00846
150.0	0.00710
200.0	0.00596
250.0	0.00500
300.0	0.00420
350.0	0.00353
400.0	0.00296

Determine the rate constant, *k* for this reaction?

(Ans: 3.50 x 10⁻³ s⁻¹)

DUE DATE: 10TH JANUARY 2016