3.1. If $-r_A = -(dC_A/dt) = 0.2$ mol/liter · sec when $C_A = 1$ mol/liter, what is the rate of reaction when $C_A = 10$ mol/liter?
Note: the order of reaction is not known.

3.1

$$-r_{A_1} = -\frac{dC_A}{dt} = 0.2 \ \frac{mol}{Lit.s} \Rightarrow C_A = 1 \ \frac{mol}{lit}$$

$$-r_{A_2} = \frac{-dC_A}{dt} = \ ? \Rightarrow C_A = 10 \ \frac{mol}{lit}$$

في هذا السؤال يجب ان يحدد رتبة التفاعل حتى يمكن حله
نفرضه firstorder -

$$-r_{A_1} = KC_A^1$$

$$0.2 = K(1)^1 \Rightarrow K = 0.2$$

$$-r_{A_2} = 0.2 * 10 = 2 \ mol/lit.s$$

3.2. Liquid A decomposes by first-order kinetics, and in a batch reactor 50% of A is converted in a 5-minute run. How much longer would it take to reach 75% conversion?

3.2

$X_A = 0.5 \Rightarrow$ time = 5 min

$X_A = 0.75 \Rightarrow$ time = ?

at first order

$$-\ln(1 - X_A) = Kt \Rightarrow -\ln(1 - 0.5) = K(5)$$

$$\therefore K = 0.1386 \ min^{-1}$$

Now for $X_A = 0.75$

$$-\ln(1 - 0.75) = 0.1386 \ (t)$$

$$\therefore t = 10 \ min$$

3.3. Repeat the previous problem for second-order kinetics. **Home work**

3.4. A 10-minute experimental run shows that 75% of liquid reactant is converted to product by a ½-order rate. What would be the fraction converted in a half-hour run?

3.4

time = 10 min ⇒ $X_A = 0.75$

time = ~~30~~ 20 min ⇒ $X_A = ?$

product by ½ order rate

ضايوجد عندي كانت المرتبة ½ لذلك ان نشتق

$$-r_A = K C_A^{0.5}$$

$$C_{A0} \frac{dX_A}{dt} = K C_{A0}^{0.5} (1 - X_A)^{0.5}$$

$$C_{A0}^{0.5} \frac{dX_A}{(1-X_A)^{0.5}} = K\,dt \qquad \text{let } \frac{K}{C_{A0}} = K'$$

$$\int_0^{X_A} (1-X_A)^{-0.5} = K' \int_0^t dt$$

$$\left. \frac{-(1-X_A)^{0.5}}{0.5} \right|_0^{X_A} = K' t$$

$$2\left[-(1-X_A)^{0.5} + 1\right] = K' t$$

for time = 10 $X_A = 0.75$

$$2\left[-(1-0.75)^{0.5} + 1\right] = K'(10)$$

$\therefore K' = 0.1$

for time = ~~30~~ 20 min

$$2\left[-(1-X_A)^{0.5} + 1\right] = 0.1 \times 20$$

⇒ $X_A = 1$

∴ in 20 min conversion is 100%

3.5. In a homogeneous isothermal liquid polymerization, 20% of the monomer disappears in 34 minutes for initial monomer concentration of 0.04 and also for 0.8 mol/liter. What rate equation represents the disappearance of the monomer?

Since the fractional disappearance is independent of initial concentration we have first order rate equation,

$\ln\left(\frac{Ca_0}{Ca}\right) = Kt$

Where, Ca = Monomer concentration

We also can find the rate constant, thus replacing values.

Case I: C_{ao}= 0.04 mol/l

$\ln(\frac{0.04}{0.8*0.04}) = k*34$

So, k= 0.00657 min^{-1}.

Case II:. C_{ao}= 0.8 mol/l

$\ln(\frac{0.8}{0.8*0.8}) = k*34$

k= 0.00657 min^{-1}.

Hence the rate of disappearance of monomer is given by,

$-r_a = (0.00657 min^{-1}) * C$

3.6. After 8 minutes in a batch reactor, reactant (C_{A0} = 1 mol/liter) is 80% converted; after 18 minutes, conversion is 90%. Find a rate equation to represent this reaction.

3.6

$C_{A0} = 1 \frac{mol}{lit}$ $\quad t = 8 min \quad x_A = 0.8$ (3)

$t = 18 min \quad x_A = 0.9$

rate eq. ? let the reaction first order

واجب

حل اخر اذا لم يعطي وظيفة

$$-r_A = -\frac{dC_A}{dt} = K C_A^n$$

$$C_A^{1-n} - C_{A0}^{1-n} = (n-1) K t$$

$$C_A = C_{A0}(1 - x_A)$$

at 8 min $C_A = 1(1 - 0.8) = 0.2 \frac{mol}{lit}$

at 18 min $C_A = 1(1 - 0.9) = 0.1 \frac{mol}{lit}$

$$(0.2)^{1-n} - (1)^{1-n} = (n-1) K (8) \quad --- (1)$$

$$(0.1)^{1-n} - (1)^{1-n} = (n-1) K (18) \quad --- (2)$$

sub. eq(1) in (2)

$$\frac{(0.2)^{1-n} - (1)^{1-n}}{(n-1)(8)} = \frac{(0.1)^{1-n} - (1)^{1-n}}{(n-1)(18)} \quad * (n-1)$$

$$\frac{(0.2)^{1-n} - (1)^{1-n}}{(0.1)^{1-n} - (1)^{1-n}} = \frac{8}{18} = 0.44$$

by try and Error when $n = 1.5$ $\quad 0.57 \neq 0.44$

when $n = 2$ $\quad 0.44 = 0.44$ ✓

sub $n = 2$ in eq 2

$$(0.2)^{1-2} - (1)^{1-2} = (2-1) K (8)$$

$$\frac{5-1}{8} = K \Rightarrow K = 0.5 \frac{lit}{mol \cdot min}$$

$$-r_A = \left[0.5 \frac{lit}{mol \cdot min}\right] C_A^2$$

3.9. The first-order reversible liquid reaction

$$A \rightleftarrows R, \quad C_{A0} = 0.5 \text{ mol/liter}, \quad C_{R0} = 0$$

takes place in a batch reactor. After 8 minutes, conversion of A is 33.3% while equilibrium conversion is 66.7%. Find the rate equation for this reaction.

3.9

first order $\quad A \underset{k_2}{\overset{k_1}{\rightleftarrows}} R \quad C_{A0} = 0.5 \quad$ 8 min

$x_{Ae} = 0.667 \Rightarrow x_A = 0.333$

$C_{R0} = 0$

$M = \frac{C_{R0}}{C_{A0}} = 0$

$$-\ln\left(1 - \frac{x_A}{x_{Ae}}\right) = \frac{M+1}{M + x_{Ae}} k_1 t$$

$$-\ln\left(1 - \frac{0.333}{0.667}\right) = \frac{0+1}{0+0.667} k_1 (8)$$

$$0.69 = 11.99\, k_1 \Rightarrow k_1 = 0.05754$$

$$\frac{k_1}{k_2} = \frac{M + X_{Ae}}{1 - X_{Ae}}$$

$$\frac{0.05754}{k_2} = \frac{0.667}{0.333} \Rightarrow k_2 = 0.02872$$

$$-r_A = 0.05754\, C_A - 0.02872\, C_R$$

3.10. Aqueous A reacts to form R ($A \rightarrow R$) and in the first minute in a batch reactor its concentration drops from $C_{A0} = 2.03$ mol/liter to $C_{Af} = 1.97$ mol/liter. Find the rate equation for the reaction if the kinetics are second-order with respect to A.

Home work

تطبيق قانون (second) فقط وإيجاد قيمة (K)

3.11. Aqueous A at a concentration $C_{A0} = 1$ mol/liter is introduced into a batch reactor where it reacts away to form product R according to stoichiometry $A \rightarrow R$. The concentration of A in the reactor is monitored at various times, as shown below:

t, min	0	100	200	300	400
C_A, mol/m³	1000	500	333	250	200

For $C_{A0} = 500$ mol/m³ find the conversion of reactant after 5 hours in the batch reactor.

3.11

$C_{A0} = 500$

form data $C_A = 500 \Rightarrow$ time = 100 min

C_A at $(\underbrace{5\,hr}_{300\,min} + 100\,min) = 200\ \frac{mol}{m^3}$

$$x_A = 1 - \frac{C_A}{C_{A0}}$$

$$= 1 - \frac{200}{500} = 0.6$$

3.12. Find the rate for the reaction of Problem 11. **Home work**

sol\ n= second order

k= 0.00001

the rate reaction $-r_A = 0.00001\, C_A^2$

3.17. An ampoule of radioactive Kr-89 (half life = 76 minutes) is set aside for a day. What does this do to the activity of the ampoule? Note that radioactive decay is a first-order process.

sol\

3.17

for 1st order $\quad x_A = ?$ after 1 day

$$-\ln \frac{C_A}{C_{A0}} = kt \qquad \frac{C_A}{C_{A0}} \text{ at } t_{1/2} = 0.5$$

$$0.6931 = k\,(76\ \text{min}) \Rightarrow k = 9.12 \times 10^{-3}\ \text{min}^{-1}$$

after 1 day (24 hr * 60 min)

$$-\ln(1 - x_A) = kt$$

$$-\ln(1 - x_A) = 9.12 \times 10^{-3}\ \text{min}^{-1} * (24 \times 6)\ \text{min}$$

$$1 - x_A = 1.979 \times 10^{-6}$$

$\therefore x_A = 0.9999$

$\Rightarrow$ conversion after 1 day is 99.99 %

3.18. Enzyme E catalyzes the transformation of reactant A to product R as follows:

$$A \xrightarrow{\text{enzyme}} R, \qquad -r_A = \frac{200 C_A C_{E0}}{2 + C_A} \frac{\text{mol}}{\text{liter} \cdot \text{min}}$$

If we introduce enzyme (C_{E0} = 0.001 mol/liter) and reactant (C_{A0} = 10 mol/liter) into a batch reactor and let the reaction proceed, find the time needed for the concentration of reactant to drop to 0.025 mol/liter. Note that the concentration of enzyme remains unchanged during the reaction.

sol\

3.18

$$-r_A = -\frac{dC_A}{dt} = \frac{200\, C_{eo} C_A}{2 + C_A} \qquad C_{eo} = 0.001 \frac{\text{mol}}{\text{lit}} \qquad C_{Ao} = 10 \frac{\text{mol}}{\text{lit}}$$

what time for $C_A = 0.025$ mol/lit

(6)

$$-\int_{C_{Ao}}^{C_A} dC_A \left(\frac{2 + C_A}{C_A} \right) = 200\, C_{eo}\, t$$

$$-\left[2 \ln C_A \Big|_{C_{Ao}}^{C_A} + C_A \Big|_{C_{Ao}}^{C_A} \right] = 200\, C_{eo}\, t$$

$$-\left[2 \ln \frac{C_A}{C_{Ao}} + C_A - C_{Ao} \right] = 200\, C_{eo}\, t$$

when $C_A = 0.025 \Rightarrow t = 169.79$ min

3.19. Find the conversion after 1 hour in a batch reactor for

$$A \rightarrow R, \quad -r_A = 3 C_A^{0.5} \frac{\text{mol}}{\text{liter} \cdot \text{hr}}, \quad C_{A0} = 1 \text{ mol/liter}$$

<u>Home work</u>

3.22. For the reaction A → R, second-order kinetics and $C_{A0} = 1$ mol/liter, we get 50% conversion after 1 hour in a batch reactor. What will be the conversion and concentration of A after 1 hour if $C_{A0} = 10$ mol/liter?

Home work

3.23. For the decomposition A → R, $C_{A0} = 1$ mol/liter, in a batch reactor conversion is 75% after 1 hour, and is just complete after 2 hours. Find a rate equation to represent these kinetics.

3.23 $C_{A0} = 1$ mol/lit

$t = 1$ hour $\Rightarrow X_A = 0.75$

$t = 2$ hour $\Rightarrow X_A = 1$

find eq. rate

$n = ?$ $K = ?$

let nth order

$C_A^{1-n} - C_{A0}^{1-n} = (n-1)Kt$

$C_A = C_{A0}(1 - X_A)$

at $X_A = 0.75$ $C_A = 0.25$

$X_A = 1$ $C_A = 0$

at 1 hour

$0.25^{1-n} - 1^{1-n} = (n-1)K(1)$ — (1)

at 2 hour $0^{(1-n)} - 1^{(1-n)} = (n-1)K(2)$ — (2)

sub (2) in (1)

$$\frac{0.25^{1-n} - 1^{1-n}}{1(n-1)} = \frac{-1^{1-n}}{2(n-1)} \quad * (n-1)$$

$n = \frac{1}{2}$

sub $n = \frac{1}{2}$ in eq (1) or (2)

$-1^{0.5} = -0.5(K)(2) \Rightarrow K = 1 \frac{mol^{1/2}}{lit^{1/2}.hr}$

$\therefore -r_A = \left[1 \frac{mol^{1/2}}{lit^{1/2}.s}\right] C_A^{\frac{1}{2}}$

3.26. Example 3.1*c* showed how to find a rate equation by using the fractional life method where F = 80%. Take the data from that example and find the rate equation by using the half-life method. As a suggestion, why not take C_{A0} = 10, 6, and 2?

Home work

3.29. Find the first-order rate constant for the disappearance of A in the gas reaction 2A → R if, on holding the pressure constant, the volume of the reaction mixture, starting with 80% A, decreases by 20% in 3 min.

3.29

$2A \rightarrow B$

0.8 - 0.4 starting with 80% A

0.2 0.2 inert

1 0.6

9

$\varepsilon_A = \frac{0.6 - 1}{1} = -0.4$

let $V_0 = 1$

V decreases by 20% in 3 min

$\Rightarrow V = 0.8 V_0$

first order variable volume

$-\ln\left[1 - \frac{\Delta V}{\varepsilon_A V_0}\right] = kt$ $\Delta V = V - V_0 = 0.8 - 1 = -0.2$

[illegible]

$-\ln\left[1 - \frac{-0.2}{-0.4}\right] = k t$

$0.693 = k\,(3\ \text{min}) \Rightarrow k = 0.231\ \text{min}^{-1}$

3.30. Find the first-order rate constant for the disappearance of A in the gas reaction A → 1.6R if the volume of the reaction mixture, starting with pure Aincreases by 50% in 4 min. The total pressure within the system stays constant at 1.2 atm, and the temperature is 25°C.

Home work
