

3.1. If  $-r_A = -(dC_A/dt) = 0.2 \text{ mol/liter} \cdot \text{sec}$  when  $C_A = 1 \text{ mol/liter}$ , what is the rate of reaction when  $C_A = 10 \text{ mol/liter}$ ?

Note: the order of reaction is not known.

3.1

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

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

في هذا السؤال يجب ان يكون رتبة التفاعل من حيث  $C_A$  حلاً  
- نفرضه first order

$$-r_{A_1} = k C_A^1$$

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

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

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

$$x_A = 0.5 \Rightarrow \text{time} = 5 \text{ min}$$

$$x_A = 0.75 \Rightarrow \text{time} = ?$$

at first order

$$-\ln(1 - x_A) = kt \Rightarrow -\ln(1 - 0.5) = k(5)$$

$$\therefore k = 0.1386 \text{ min}^{-1}$$

Now for  $x_A = 0.75$

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

$$\therefore t = 10 \text{ min}$$

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  $\frac{1}{2}$ -order rate. What would be the fraction converted in a half-hour run?

3.4

$$\text{time} = 10 \text{ min} \Rightarrow x_A = 0.75$$

$$\text{time} = \frac{20}{30} \text{ min} \Rightarrow x_A = ?$$

Product by  $\frac{1}{2}$  order rate

ضارجه كيميائية بترتيب  $\frac{1}{2}$  في السائل المتفاعل

$$-v_A = k C_A^{0.5}$$

$$C_{A0} \frac{dx_A}{dt} = k C_{A0}^{0.5} (1 - x_A)^{0.5}$$

$$C_{A0}^{0.5} \frac{dx_A}{(1 - x_A)^{0.5}} = k dt$$

$$\text{let } \frac{k}{C_{A0}^{0.5}} = k'$$

$$\int_0^{x_A} (1 - x_A)^{-0.5} dx_A = \int_0^t k' dt$$

$$\frac{-(1 - x_A)^{0.5}}{0.5} \Big|_0^{x_A} = k' t$$

$$2 [-(1 - x_A)^{0.5} + 1] = k' t$$

$$\text{for time} = 10 \quad x_A = 0.75$$

$$2 [-(1 - 0.75)^{0.5} + 1] = k' (10)$$

$$\therefore k' = 0.1$$

$$\left. \begin{array}{l} \text{for time} = \frac{20}{30} \text{ min} \\ 2 [-(1 - x_A)^{0.5} + 1] = 0.1 x_A \frac{20}{30} \\ \Rightarrow x_A = 1 \end{array} \right\}$$

$\therefore$  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,

$$\ln\left(\frac{C_{a0}}{C_a}\right) = Kt$$

Where,  $C_a$  = Monomer concentration

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

Case I:  $C_{a0} = 0.04$  mol/l

$$\ln\left(\frac{0.04}{0.8 \cdot 0.04}\right) = k \cdot 34$$

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

Case II:  $C_{a0} = 0.8$  mol/l

$$\ln\left(\frac{0.8}{0.8 \cdot 0.8}\right) = k \cdot 34$$

$k = 0.00657 \text{ min}^{-1}$ .

Hence the rate of disappearance of monomer is given by,

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

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

$$C_{A0} = 1 \frac{\text{mol}}{\text{lit}}$$

$$t = 8 \text{ min} \quad x_A = 0.8$$

$$t = 18 \text{ min} \quad x_A = 0.9$$

(3)

rate eq. ? ~~let~~ <sup>let</sup> the reaction ~~is~~ <sup>first</sup> order   
 واجب

دالة التفاضل

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

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

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

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

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

$$\text{eqn } (0.2)^{1-n} - (1)^{1-n} = (n-1)k(8) \quad \text{--- (1)}$$

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

sub. eq (1) in (2)

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

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

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

$$\text{when } n=2 \quad 0.44 = 0.44 \quad \leftarrow$$

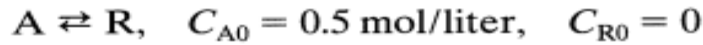
Sub  $n=2$  in eq (2)

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

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

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

### 3.9. The first-order reversible liquid reaction



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.



$$-\ln\left(1 - \frac{x_A}{x_{Ac}}\right) = \frac{M+1}{M+x_{Ac}} k_1 t \quad M = \frac{C_{R0}}{C_{A0}} = 0$$

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

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

$$\frac{k_1}{k_2} = \frac{M+x_{Ac}}{1-x_{Ac}}$$

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

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



**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:

$t, \text{ min}$	0	100	200	300	400
$C_A, \text{ mol/m}^3$	1000	500	333	250	200

For  $C_{A0} = 500$  mol/m<sup>3</sup> find the conversion of reactant after 5 hours in the batch reactor.

3.11

$$C_{A0} = 500$$

from data  $C_A = 500 \Rightarrow \text{time} = 100 \text{ min}$

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

$$\begin{aligned} X_A &= 1 - \frac{C_A}{C_{A0}} \\ &= 1 - \frac{200}{500} = 0.6 \end{aligned}$$

**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  $\chi_A = ?$  after 1 day

$$-\ln \frac{C_A}{C_{A0}} = kt$$

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

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

after 1 day (24 hr or 60 min)

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

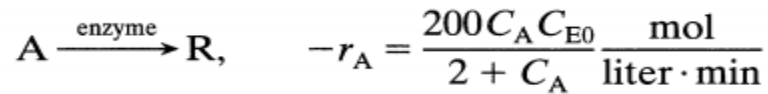
$$-\ln(1 - \chi_A) = 9.12 \times 10^{-3} \text{ min}^{-1} \times (24 \times 60) \text{ min}$$

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

$$\therefore \chi_A = 0.9999$$

$\Rightarrow$  conversion after 1 day is 99.99%

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



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

$$-r_A = -\frac{dC_A}{dt} = \frac{200 C_{E0} C_A}{2 + C_A}$$

$$C_{E0} = 0.001 \frac{\text{mol}}{\text{lit}}$$

$$C_{A0} = 10 \frac{\text{mol}}{\text{lit}}$$

what time for  $C_A = 0.025$  mol/lit

$$-\int_{C_{A0}}^{C_A} dC_A \left( \frac{2 + C_A}{C_A} \right) = 200 C_{E0} t$$

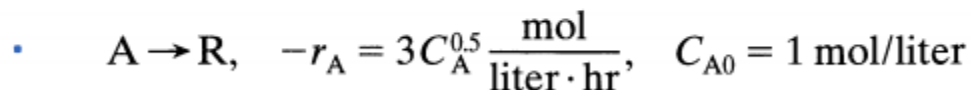
$$-\left[ 2 \ln C_A \Big|_{C_{A0}}^{C_A} + C_A \Big|_{C_{A0}}^{C_A} \right] = 200 C_{E0} t$$

$$\Rightarrow \left[ 2 \ln \frac{C_A}{C_{A0}} + C_A - C_{A0} \right] = 200 C_{E0} t$$

$$\text{when } C_A = 0.025 \Rightarrow t = 109.79 \text{ min}$$

⑥

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



Home work



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

## Home work

3.23. For the decomposition  $A \rightarrow R$ ,  $C_{A0} = 1 \text{ mol/liter}$ , 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  $C_{A0} = 1 \text{ mol/liter}$

$t = 1 \text{ hour} \Rightarrow X_A = 0.75$

$t = 2 \text{ hour} \Rightarrow X_A = 1$

find eq. rate

$n = ? \quad k = ?$

let  $n$ th order

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

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

at  $X_A = 0.75 \quad C_A = 0.25$

$X_A = 1 \quad C_A = 0$

at 1 hour

$$0.25^{1-n} - 1^{1-n} = (n-1)k(1) \quad \text{--- (1)}$$

at 2 hour  $0^{(1-n)} - 1^{(1-n)} = (n-1)k(2) \quad \text{--- (2)}$

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)

$$-1^{0.5} = -0.5(k)(2) \Rightarrow k = 1 \quad \frac{\text{mol}^{1/2}}{\text{lit}^{1/2} \cdot \text{hr}}$$

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

- 3.26. Example 3.1c 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  $C_{A0} = 10, 6, \text{ and } 2$ ?

## Home work

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

3.29



$$0.8 - 0.4$$

starting with 80% A

$$\frac{0.2}{1} \quad \frac{0.2}{0.6}$$

inert

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

9

let  $V_0 = 1$

$V$  decreases by 20% in 3 min

$$\Rightarrow V = 0.8 V_0$$

first order variable volume

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

$$\Delta V = V - V_0 = 0.8 - 1 = -0.2$$

~~$$-\ln \left[ 1 - \frac{0.2}{-0.4} \right] = kt$$~~

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

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

- 3.30. Find the first-order rate constant for the disappearance of A in the gas reaction  $A \rightarrow 1.6R$  if the volume of the reaction mixture, starting with pure A increases by 50% in 4 min. The total pressure within the system stays constant at 1.2 atm, and the temperature is  $25^\circ\text{C}$ .

## Home work