

## Chemical Engineering Department

### Unit Operation Branch

#### Reactor Design for Undergraduated Students

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#### Typical Questions and Answers

Q1) When a concentrated urea solution is stored it slowly condenses to biuret by the following elementary reaction:



To study the rate of condensation a sample of urea ( $C = 20 \text{ mol/L}$ ) is stored at  $100^\circ\text{C}$  and after 7 hr 40 min we find that 1 mol% has turned into biuret. Find the rate equation for this condensation reaction. [Data from W. M. Butt, *Pak. J. Ch. E.*, **1**, 99 (1973).]

Q2) The thermal decomposition of hydrogen iodide



is reported as follows:

T, deg. C	508	427	393	356	283
K, cm <sup>3</sup> /mol.s	0.1059	0.0031	0.000588	$80.9 \times 10^{-6}$	$0.942 \times 10^{-6}$

Find the complete rate equation for this reaction.

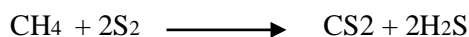
Q3) The Rate of a gaseous irreversible reaction  $\text{A} \longrightarrow \text{B}$  at  $450 \text{ K}$  is 33 times its rate value at  $400 \text{ K}$ . If the frequency factor in Arrhenius equation is  $5 \times 10^{10} \text{ 1/sec}$ . At what temperature will the reaction have a half-life of 1 min.

Q4) A gas-phase reaction  $\text{A} + \text{B} \longrightarrow \text{C}$  is to be conducted in a 10-L (initially) isothermal batch reactor at  $25^\circ\text{C}$  at constant pressure. The reaction is second-order with respect to A, with  $k_A = 0.023 \text{ L/mol s}$ . Determine the time required for 75% conversion of 5 mol A.

Q5) Consider a liquid-phase, first-order reaction  $\text{A} \longrightarrow \text{C}$ , occurring in a reactor of volume  $V$ , with a specified shut down-time,  $t_d$ . The reactor initially contains 5 moles of pure A. Determine the reaction time which maximizes the production rate of C (i.e.,  $Pr(C)$ ), given  $k_A = 0.021 \text{ 1/min}$ , and  $t_d = 30 \text{ min}$ ; and calculate the maximum value of  $Pr(C)$ .

Q6) At elevated temperatures, acetaldehyde ( $\text{CH}_3\text{CHO}$ , A) undergoes gas-phase decomposition into methane and carbon monoxide. The reaction is second-order with respect to acetaldehyde, with  $k_A = 22.2 \text{ L/mol} \cdot \text{min}$  at a certain  $T$ . Determine the fractional conversion of acetaldehyde that can be achieved in a 1500-L CSTR, given that the feed rate of acetaldehyde is  $8.8 \text{ kg/min}$ , and the inlet volumetric flow rate is  $2.5 \text{ m}^3/\text{min}$ . Assume  $T$  and  $P$  are unchanged.

Q7) A gas-phase reaction between methane (A) and sulfur (B) is conducted at  $600^\circ\text{C}$  and  $101 \text{ kPa}$  in a PFR, to produce carbon disulfide and hydrogen sulfide.



The reaction is first order with respect to each reactant, with  $k_B = 12 \text{ m}^3/\text{mole} \cdot \text{h}$  (based upon the disappearance of sulfur). The inlet molar flow rates of methane and sulfur are  $23.8$  and  $47.6 \text{ mol/h}$ , respectively. Determine the volume ( $V$ ) required to achieve 18% conversion of methane, and the resulting residence or space time.

Q8) At present we have 90% conversion of a liquid feed ( $C_{A0} = 10 \text{ mol/L}$ ) to our plug flow reactor with recycle of product ( $R = 2$ ). If we shutt off the recycle stream, by how much will this lower the processing rate of our feed to the same 90% conversion. The reaction kinetics is first order.

(1)

A1) Since the reaction is elementary the stoichiometric equation shows that the reaction is 2nd order. So from the definition of the reaction rate,

$$(-r_A) = -\frac{\Delta C}{\Delta t} = K C_A^2$$

$$\text{or } K = -\frac{\Delta C}{\Delta t} \cdot \frac{1}{C_A^2} = \frac{-0.2 \text{ mol/lit}}{7 \frac{2}{3} \text{ hr}} \cdot \frac{1}{(19.9 \text{ mol/lit})^2}$$

$$= 6.6 \times 10^{-5} \text{ lit/mol} \cdot \text{hr}$$

$$\therefore -r_{\text{NH}_2\text{-CO-NH}_2} = 6.6 \times 10^{-5} C_{\text{NH}_2\text{-CO-NH}_2}^2 \text{ } \frac{\text{mol}}{\text{lit} \cdot \text{hr}}$$

A2) Depending on the units of the rate constant, the kinetics of the reaction is 2nd order,

$$(-r_A) = K C_A^2 = K_0 e^{-E/RT} C_A^2$$

$$K = K_0 \exp(-E/RT)$$

$$\text{or } \ln K = \ln K_0 - \frac{E}{R} \left( \frac{1}{T} \right) \dots (*)$$

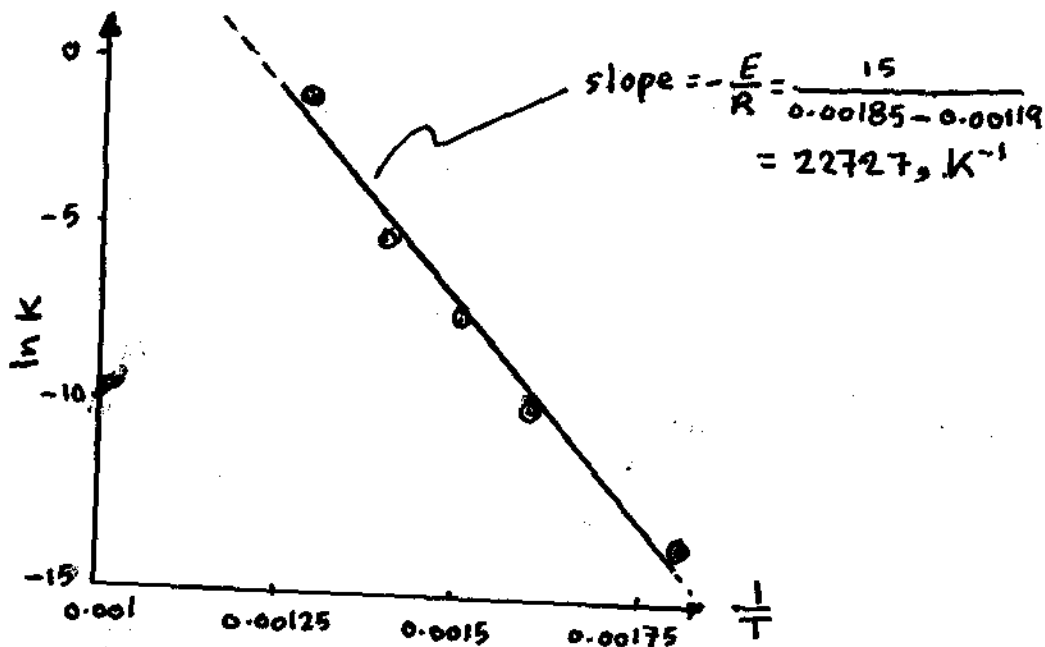
So to find the values of  $K_0$  and  $E/R$ , one must plot  $\ln K$  vs.  $1/T$ . The slope gives  $E/R$  and the intercept gives  $K_0$ , as follows:

First let us tabulate,

$T, K$	$1/T, K^{-1}$	$K$	$\ln K$
780	0.00128	0.1059	-1.697
700	0.00143	0.0031	-5.776
660	0.00150	0.0005	-7.438
630	0.00154	$80.9 \times 10^{-6}$	-9.422
550	0.00183	$0.94 \times 10^{-6}$	-13.875

Next plot  $\ln K$  vs.  $1/T$

(2)



To find the value of  $K_0$  take the second data point from equation (\*),

$$\ln K_0 = \ln K - \frac{E}{R} \left( \frac{1}{T} \right)$$

$$= 5.776 - 22727 \left( \frac{1}{700} \right) = 38.244$$

$$\text{or } K_0 = \exp(38.244) = 4.06 \times 10^{16}$$

So for the temperature range covered in the reported data,

$$-r_{HI} = 4.06 \times 10^{16} \exp\left(\frac{-22727}{T}\right) C_A^2, \quad \frac{\text{mol}}{\text{cm}^3 \cdot \text{s}}$$

A3)

$$\ln \frac{K_2}{K_1} = \frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{33 K_1}{K_1} = \frac{E}{0.082} \left( \frac{1}{400} - \frac{1}{450} \right)$$

$$E = 956.66 \quad \text{cal/mol}$$

For 1st order reaction (units of rate constant is  $\text{s}^{-1}$ )

$$t_{1/2} = \frac{\ln 2}{K}$$

$$K = \frac{\ln 2}{60 \text{ s}} = 0.011 \text{ s}^{-1}$$

(3)

$$K = A e^{-E/RT}$$

$$0.011 = 5 \times 10^{10} e^{\frac{-956.66}{0.082 T}}$$

$$2.2 \times 10^{-13} = e^{\frac{-11666.6}{T}}$$

$$T = 399 \text{ K}$$

A4)

The time required for a constant pressure batch reaction is given by,

$$t = N_{A0} \int_0^x \frac{dx}{(-r_A)V} \quad \text{--- (1)}$$

In this expression, both  $(-r_A)$  and  $V$  vary and must be related to  $x$ , as follow:

$$V = V_0(1 + \epsilon X)$$

$$\epsilon = y_{A0} \delta = 1 \times (1 + 1 - 1) = 1$$

$$\therefore V = V_0(1 + X) \quad \text{--- (2)}$$

From the units of the rate constant, the kinetics is a 2nd order reaction.

$$(-r_A) = K C_A^2 \quad \text{--- (3)}$$

$$\text{For gas-phase, } C_A = C_{A0} \frac{1-X}{1+\epsilon X} = C_{A0} \frac{1-X}{1+X}$$

Substitute into eqn. (3)

$$(-r_A) = K \left[ C_{A0} \frac{1-X}{1+X} \right]^2 \quad \text{--- (4)}$$

Substitute eqns. (2) and (4) into (1) to obtain,

$$t = \frac{N_{A0}}{K V_0 C_{A0}^2} \int_0^{0.75} \frac{dx}{\left[ \frac{1-X}{1+X} \right]^2 (1+X)}$$

(4)

$$t = \frac{1}{K C_{A_0}} \int_0^{0.75} \frac{(1+x) dx}{(1-x)^2} \quad \text{--- (5)}$$

$$C_{A_0} = \frac{N_{A_0}}{V_0} = \frac{5 \text{ mol}}{10 \text{ L}} = 0.5 \text{ mol/L}$$

To evaluate the integral part of eqn (5),

Let  $\alpha = 1-x$ , then  $x = 1-\alpha$ , and  $dx = -d\alpha$

$$\int_1^{0.25} \frac{\alpha-2}{\alpha^2} d\alpha = \int_1^{0.25} \left[ \frac{1}{\alpha} - \frac{2}{\alpha^2} \right] d\alpha = \ln(0.25) + 6 = 4.61$$

Therefore

$$t = \frac{1}{0.023 \times 0.5} (4.61) = 400 \text{ s}$$

A5) From the definition of the reaction rate for A,

$$(-r_A) = -\frac{dC_A}{dt} = C_{A_0} \frac{dx}{dt}$$

The rate law of 1st order kinetics,

$$C_{A_0} \frac{dx}{dt} = K C_A = K C_{A_0} (1-x)$$

$$\frac{dx}{dt} = K(1-x) \quad \text{--- (1)}$$

Integrate eqn (1) to obtain,

$$x = 1 - e^{-Kt} \quad \text{--- (2)}$$

Substitute eqn. (2) into (1)

$$\frac{dx}{dt} = K e^{-Kt} \quad \text{--- (3)}$$

The number of moles of C produced after a complete time cycle for one batch is,

$$P_r(C) = \frac{\text{no. of moles C produced}}{(\text{reaction time} + \text{shutdown time})}$$

(5)

$$r(c) = \frac{x C_{A0} V}{t + t_d} \quad \text{--- (4)}$$

differentiate eqn. (4) w.r.t  $t$ ,

$$\frac{dr}{dt} = C_{A0} V \left[ \frac{(t + t_d) \frac{dx}{dt} - x}{(t + t_d)^2} \right] \quad \text{--- (5)}$$

for maximum value, let eqn (5) equal zero,

$$(t + t_d) \frac{dx}{dt} - x = 0 \quad \text{--- (6)}$$

Substitute eqns. (2) and (3) into (6), we have

$$(t + t_d) K e^{-Kt} - (1 - e^{-Kt}) = 0 \quad \text{--- (7)}$$

Equation (7) can be solved by trial. For  $t_d = 30$  min and  $K = 0.021 \text{ min}^{-1}$ . We obtain  $t = 45$  min. Then from eqn. (2),  $x = 0.612$  for maximum  $r(c)$ , and from eqn. (4) with  $N_{A0} = 5 \text{ mol}$ ,  
 $r(c) = 2.45 \text{ mol/h}$

A6)

The reaction is,  $\text{CH}_3\text{CHO (A)} \rightarrow \text{CH}_4\text{ (B)} + \text{CO (C)}$

From CSTR design eqn. and the given rate law,

$$x = \frac{(-r_A)V}{F_{A0}} = \frac{K C_A^2 V}{F_{A0}} \quad \text{--- (1)}$$

$$C_A = \frac{F_A}{V} \quad \text{--- (2)}$$

$$F_A = F_{A0}(1 - x) \quad \text{--- (3)}$$

$$V = V_0(1 + \varepsilon X) \frac{T}{T_0} \cdot \frac{P_0}{P} \quad \text{--- (4)}$$

since  $T$  and  $P$  unchanged,  
 eqn. (4) becomes,

$$V = V_0(1 + \varepsilon X) \quad \text{--- (5)}$$

$$\varepsilon = y_{A0} \delta = 1(1 + 1 - 1) = 1 \quad \text{--- (6)}$$

Substitute eqns. (2), (3), (5) and (6) into (1)

$$x = \frac{K F_{A0} V}{V_0^2} \frac{(1 - x)^2}{(1 + x)^2} = \frac{22.2 \times 200 \times 1500}{(2500)^2} \frac{(1 - x)^2}{(1 + x)^2}$$

(6)

$$X = 1.066 \frac{(1-X)^2}{(1+X)^2} \quad \text{--- (7)}$$

Eqn. (7) rearranged to give the following cubic polynomial equation.

$$X^3 + 0.934X^2 + 3.132X - 1.066 = 0 \quad \text{--- (8)}$$

eqn. 8 has 3 roots, but only one is positive and acceptable which is,

$$X = 0.304$$

A7)

Since  $F_{A0} = \frac{1}{2} F_{B0}$

$$\therefore C_{A0} = \frac{1}{2} C_{B0} \quad \text{--- (1)}$$

The rate law with respect to B is,

$$(-r_B) = K_B C_A C_B = K_B \left(\frac{1}{2} C_B\right) C_B$$

$$(-r_B) = K_B \frac{C_B^2}{2} \quad \text{--- (2)}$$

The design eqn. of PFR,

$$V = F_{B0} \int_0^{x_B} \frac{dx_B}{(-r_B)} \quad \text{--- (3)}$$

$$C_B = C_{B0} (1 - x_B) \quad \text{--- (4)}$$

Substitute eqns. (2) and (4) into (3).

$$V = F_{B0} \int_0^{x_B} \frac{dx_B}{\frac{K_B C_{B0}^2}{2} (1 - x_B)^2}$$

$$V = \frac{2 F_{B0}}{K_B C_{B0}^2} \int_0^{x_B} \frac{dx_B}{(1 - x_B)^2} = \frac{2 F_{B0}}{K_B C_{B0}^2} \left[ \frac{x_B}{1 - x_B} \right]$$

$$C_{B0} = \frac{y_{B0} P}{R T_0} = \frac{0.66(1)}{0.082(873)} = 9.22 \times 10^{-3} \frac{\text{mol}}{\text{L}} = 9.22 \frac{\text{mol}}{\text{m}^3}$$



(7)

$$V = \frac{2(47.6)}{12 \times (9.22)^2} \cdot \frac{0.18}{0.82} = 0.02 \text{ m}^3$$

$$\text{space time} = \frac{V}{V_0} = \frac{0.02}{\frac{47.6}{9.22}} = 0.004 \text{ h}$$

A8)

The design eqn. of a PFR with recycle is:

$$V = (R+1) F_{A0} \int_{\frac{R}{(R+1)} x_{Af}}^{x_{Af}} \frac{dx_A}{(-r_A)} \quad \text{--- (1)}$$

In terms of concentration eqn (1) becomes:

$$V = -(R+1) \frac{F_{A0}}{C_{A0}} \int_{\frac{C_{A0} + R C_{Af}}{R+1}}^{C_{Af}} \frac{dC_A}{(-r_A)} \quad \text{--- (2)}$$

for 1st order reaction (i.e.,  $-r_A = K C_A$ )

$$K\tau = (R+1) \ln \frac{C_{A0} + R C_{Af}}{(R+1) C_{Af}} \quad \text{--- (3)}$$

$$K\tau = (2+1) \ln \frac{10 + 2(1)}{(2+1) 1} = 3 \ln 4 \quad \text{--- (4)}$$

without recycle:

$$V = - \frac{F_{A0}}{C_{A0}} \int_{C_{A0}}^{C_{Af}} \frac{dC_A}{K C_A}$$

$$K\tau = \ln \frac{C_{A0}}{C_{Af}} = \ln 10 \quad \text{--- (5)}$$

Divide eqn. (4) by (5).

$$\frac{(K\tau)_{\text{with recycle}}}{(K\tau)_{\text{without recycle}}} = \frac{3 \ln 4}{\ln 10} = 1.8 = \frac{V_{\text{without recycle}}}{V_{\text{with recycle}}}$$

So, without recycle is better.