CHME 312, Reaction Engineering, 2011 Spring

Final Exam, Open Text

(H. Scott Fogler, *Elements of Chemical Reaction Engineering*, 4th Ed.)

Note: For partial credit, please write your answer clearly and legibly.
For better credit, do all algebra and substitute digits, and check final figures carefully.

1. Ethane is decomposed with about 300 kJ/mol of activation energy. How fast the rate of decomposition is at 600°C comparing with that of 500°C. (15)

Sol)

- $k = A \cdot \exp\left(-\frac{E}{RT}\right)$

$$\frac{k_2}{k_1} = \exp\left[\left(\frac{E}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] = \exp\left[\left(\frac{300 \times 10^3 \text{ J}}{8.3144 \frac{\text{J}}{\text{mol} \cdot \text{K}}}\right)\left(\frac{1}{500+273} - \frac{1}{600+273}\right)\frac{1}{\text{K}}\right]$$

$$= \mathbf{210}$$

2. A converted to R, S, and T with different type of reaction order (a), (b), (c). Suppose that each reaction is elementary, S is desired product, and A is supplied at C_{A0}, determine whether you use **CSTR or PFR**, and determine whether you maintain exit **conversion at high or low** to obtain a maximum selectivity. (45)

$$\text{A}\begin{cases} \xrightarrow{1} \text{R} \\ \xrightarrow{2} \text{S (Desired)} \\ \xrightarrow{3} \text{T} \end{cases}$$

(a) $n_1 = 1$, $n_2 = 2$, $n_3 = 3$

(b) $n_1 = 2$, $n_2 = 3$, $n_3 = 1$

(c) $n_1 = 3$, $n_2 = 1$, $n_3 = 2$, where n_1, n_2, n_3 are reaction order of (1), (2), and (3), respectively.

Sol)

- $r_R = k_1 C_A^{n_1}, r_S = k_2 C_A^{n_2}\ ,\ r_T = k_1 C_A^{n_3}$

- $S_{(D/U)} = \dfrac{r_S}{r_R + r_T} = \dfrac{k_2 C_A^{n_2}}{k_1 C_A^{n_1} + k_3 C_A^{n_3}}$

(a) $n_1 = 1, n_2 = 2, n_3 = 3$

$$S_{(D/U)} = \frac{k_2 C_A^{n_2}}{k_1 C_A^{n_1} + k_3 C_A^{n_3}} = \frac{k_2 C_A^{2}}{k_1 C_A^{1} + k_3 C_A^{3}}$$ ☜ Maximum value, CSTR

(b) $n_1 = 2, n_2 = 3, n_3 = 1$

$$S_{(D/U)} = \frac{k_2 C_A^{n_2}}{k_1 C_A^{n_1} + k_3 C_A^{n_3}} = \frac{k_2 C_A^{3}}{k_1 C_A^{1} + k_3 C_A^{2}}$$ ☜ Monotonically increasing, PFR, low X_A

(c) $n_1 = 3, n_2 = 1, n_3 = 2$

$$S_{(D/U)} = \frac{k_2 C_A^{n_2}}{k_1 C_A^{n_1} + k_3 C_A^{n_3}} = \frac{k_2 C_A^{1}}{k_1 C_A^{3} + k_3 C_A^{2}}$$ ☜ Maximum value, CSTR, high X_A

3. (a) Derive the expression of **design equation** (20) and (b) determine the **reaction order** for the gas-phase decomposition of A by applying integral method. (20)

   $A \rightarrow B + 2C$

   This reaction was carried out in the laboratory in an isothermal batch system in which the total pressure was recorded at various times during the reaction and given in table. Only pure A was initially present in the reaction vessel.

Time(min)	0.0	2.5	5.0	10.0	15.0	20.0
Total Pressure (mmHg)	7.5	10.5	12.5	15.8	17.9	19.4

Sol)

1. Postulate a rate law.

   $-r_A = kC_A^{\alpha}$

2. A combination of the *mole balance* on a constant-volume batch reactor and the *rate law*

$$-\frac{dC_A}{dt} = -r_A = kC_A^{\alpha} \qquad (1)$$

Rewrite the design equation in terms of the measured variable

For the case of a constant-volume batch reactor, we recall Equations (3-26) and (3-38):

$$C_{\mathrm{A}} = \frac{N_{\mathrm{A0}}(1-X)}{V} = C_{\mathrm{A0}}(1-X) \qquad (2)$$

$$V = V_0\left(\frac{P_0}{P}\right)(1+\varepsilon X)\frac{T}{T_0}$$

For isothermal operation and constant volume ($V = V_0$, $P = P_0$)

$$X = \frac{1}{\varepsilon P_0}(P-P_0) = \frac{1}{y_{A0}\,\delta P_0}(P-P_0) \qquad (3)$$

$$X = \frac{1}{\delta P_{A0}}(P-P_0) \qquad (4)$$

By equation (2), (4)

$$C_{\mathrm{A}} = \frac{P_{\mathrm{A0}} - [(P-P_0)/\delta]}{RT}$$

Pure A initially, $y_{\mathrm{A0}} = 1$ and therefore $P_{A0} = P_0$, $\delta = 1 + 2 - 1 = 2$

$$C_{\mathrm{A}} = \frac{P_{\mathrm{A0}} - [(P-P_0)/\delta]}{RT} = \frac{P_{\mathrm{A0}} - [(P-P_0)/2]}{RT} = \frac{3P_{\mathrm{A0}} - P}{2RT} \qquad (5)$$

By equation (1), (5)

$$\frac{1}{2RT}\frac{dP}{dT} = k\left(\frac{3P_{\mathrm{A0}} - P}{2RT}\right)^{\alpha}$$

Let $k' = k(2RT)^{1-\alpha}$, then $\frac{dP}{dT} = k'(3P_{\mathrm{T0}} - P_{\mathrm{T}})^{\alpha}$ ←(a)

(b)

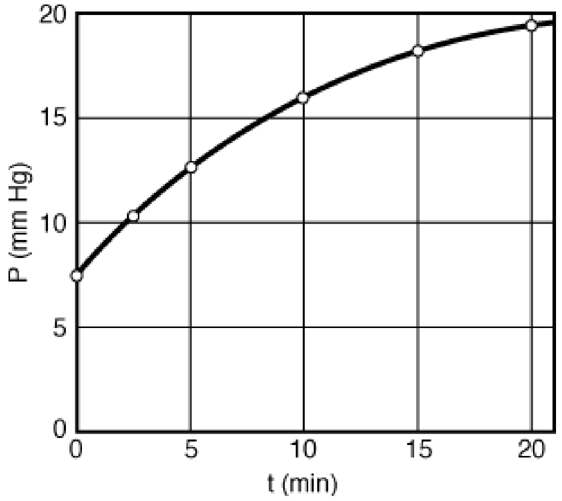
Guess 0th order, $\frac{dP}{dT} = k'$

Integrating $P_T = P_{T0} + k't$

This plot gives the right graph

Not linear!

Try 1st order



$$\frac{dP}{dT} = k'\left(3P_{T0} - P_T\right)$$

Integrating,

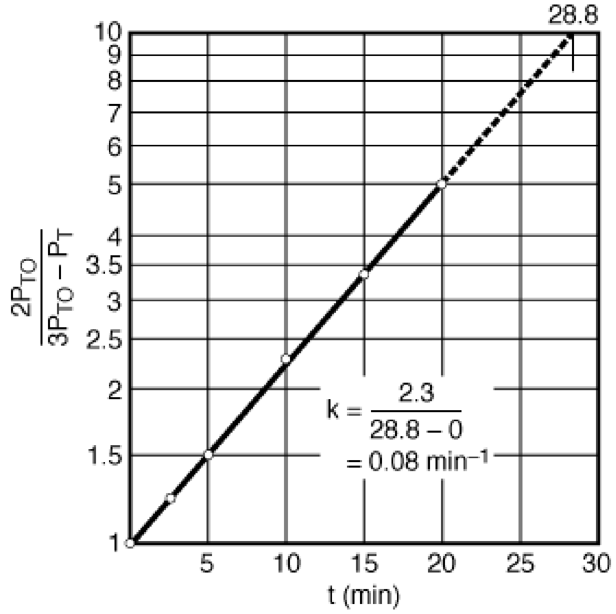
$$\ln\left(\frac{2P_{T0}}{3P_{T0} - P_T}\right) = k't$$

This plot gives the right graph

Linear!

Just in case, try 2nd order

⇒ Compare the linearity



$k = \frac{2.3}{28.8 - 0} = 0.08\ \text{min}^{-1}$

$$\frac{dP}{dT} = k'\left(3P_{T0} - P_T\right)^2$$

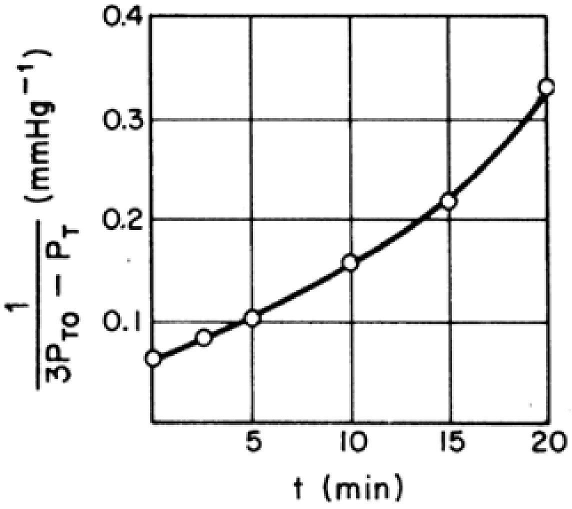
Integrating,

$$\int_{P_{T0}}^{P_T} \frac{dP_T}{(3P_{T0} - P_T)^2} = k't,$$

or $\frac{1}{3P_{T0} - P_T} - \frac{1}{2P_{T0}} = k't$

This plot gives the right graph

Not linear!



4. If adsorption constants of CO and NO are $K_{CO} = 1\ \text{atm}^{-1}$ and $K_{NO} = 3\ \text{atm}^{-1}$, what is the ratio of sites containing CO to those containing NO when the conversion is 30% and 99%? What fraction of sites is occupied by NO and by CO. The feed is equal molar in CO and NO with $P_O = 2$ atm.

Sol)

$$C_{CO\bullet S} = K_{CO}P_{CO} = K_{CO}P_{CO,0}(1-X)$$

$$C_{NO\bullet S} = K_{NO}P_{CO,0}(\theta_{NO} - X) = K_{NO}P_{CO,0}(1-X)$$

$$\text{CO to NO sites} = \frac{C_{CO\bullet S}}{C_{NO\bullet S}} = \frac{K_{CO}}{K_{NO}} = \frac{1}{3} = 0.33$$

- Fraction of CO sites.

$$\frac{C_{CO\bullet S}}{C_T} = \frac{K_{CO}P_{CO,0}(1-X)}{1 + K_{CO}P_{CO,0}(1-X) + K_{NO}P_{CO,0}(1-X)}$$

- For X=0.3

$$\frac{C_{CO\bullet S}}{C_T} = \frac{(1\ \text{atm}^{-1})(2\ \text{atm})(1-0.2)}{1 + (1\ \text{atm}^{-1})(2\ \text{atm})(1-0.2) + (5\ \text{atm}^{-1})(2\ \text{atm})(1-0.2)} = \frac{1.6}{1 + 1.6 + 8} = 0.15$$

$$\frac{C_V}{C_T} = \frac{1}{1 + (1\ \text{atm}^{-1})(2\ \text{atm})(1-0.2) + (5\ \text{atm}^{-1})(2\ \text{atm})(1-0.2)} = \frac{1}{1 + 1.6 + 8} = 0.094$$

at 20% conversion 15% of the sites are occupied by CO and 9.4% are vacant.

For X=.99

$$\frac{C_{CO\bullet S}}{C_T} = \frac{(1\ \text{atm}^{-1})(2\ \text{atm})(1-0.99)}{1 + (1\ \text{atm}^{-1})(2\ \text{atm})(1-0.99) + (5\ \text{atm}^{-1})(2\ \text{atm})(1-0.99)} = \frac{0.02}{1 + 0.02 + 0.1} = 0.18$$

$$\frac{C_V}{C_T} = \frac{1}{1 + 0.02 + 0.1} = 0.089$$

at 99% conversion 1.8% of the sites are occupied by CO and 89% are vacant.