

throughout the reaction. The reaction is reversible with a rate equation which over the concentration range of interest, can be written

$$-r_A = K_f C_A C_B - K_r C_M C_N$$

At the operating temperature of 100°C , the rate constants have the values:

$$K_f = 8.0 \times 10^{-6} \text{ m}^3/\text{kmol}\cdot\text{s}, K_r = 2.7 \times 10^{-6} \text{ m}^3/\text{kmol}\cdot\text{s}$$

The reaction mixture will be discharged when the conversion of the acetic acid is 30%. A time of 30 min is required between batches for discharging, cleaning, and recharging.

Determine the volume of the reactor required.

Solution

$$C_A = C_{A_0} - x C_{A_0} \quad ; \quad C_B = C_{B_0} - \frac{b}{a} x C_{A_0}$$

$$C_M = C_{M_0} + \frac{m}{a} x C_{A_0} \quad ; \quad C_N = C_{N_0} + \frac{n}{a} x C_{A_0}$$

From the reaction eqn., $a = b = m = n$ & $C_{M_0} = 0$

$$(-r_A) = K_f (C_{A_0} - x C_{A_0})(C_{B_0} - x C_{A_0}) - K_r x C_{A_0}(C_{N_0} + x C_{A_0})$$

$$t = C_{A_0} \int_0^{x_f} \frac{dx}{(-r_A)}$$

$$t = C_{A_0} \int_0^{0.3} \frac{dx}{K_f (C_{A_0} - x C_{A_0})(C_{B_0} - x C_{A_0}) - K_r x C_{A_0}(C_{N_0} + x C_{A_0})} \quad \text{--- (*)}$$

$$M_{wt}(\text{CH}_3\text{COOH}) = 60$$

$$M_{wt}(\text{C}_2\text{H}_5\text{OH}) = 46$$

$$M_{wt}(\text{H}_2\text{O}) = 18$$

Basis: 1 m³ of reaction mixture.

$$C_{E_0} = \frac{500/46}{1} = 10.9 \frac{\text{Kmol}}{\text{m}^3} ; C_{A_0} = \frac{250/60}{1} = 4.2 \frac{\text{Kmol}}{\text{m}^3}$$

$$1000 \text{ Kg} - 500 \text{ Kg} - 250 \text{ Kg} = 250 \text{ Kg H}_2\text{O initially in } 1 \text{ m}^3$$

$$C_{N_0} = \frac{250}{18} = 16.4 \text{ Kmole/m}^3$$

$$t = 4.2 \int_0^{0.3} \frac{dx}{[8 \times 10^{-6} (4.2 - x)(10.9 - x) - 2.7 \times 10^{-6} \times 4.2 \times (16.4 + x)]}$$

To evaluate the integral numerically, use Simpson's rule of 3 points.

$$t_r = C_{A_0} \left[\underbrace{\frac{h}{3} (f(x)_0 + 4f(x)_1 + f(x)_2)}_{\text{Simpson's rule}} \right]$$

X	-r _A	$\frac{1}{(-r_A)} = f(x)$
0	366×10^{-6}	2730 = f(x) ₀
0.15	264×10^{-6}	3780 = f(x) _{0.15}
0.3	226×10^{-6}	4410 = f(x) _{0.3}

$$t_r = 4.2 \left[\frac{0.15}{3} (2730 + 4 \times 3780 + 4410) \right]$$

$$= \underline{4674.6 \text{ sec}}$$

$$t_{\text{total}} = t_r + t_s = 4674.6 + 30 \times 60$$

$$= \underline{6474.6 \text{ sec}}$$

$$\text{no. of batches carried out per day} = \frac{24 \times 60 \times 60}{6474.6} \approx 13$$

$$\begin{aligned} \text{Ethyl acetate produced per day per m}^3 &= X_{A0} \times M_{ut} \times \text{no. of batches} \\ &= 0.3 \times 4.2 \times 88 \times 13 \\ &= 1441.4 \text{ kg/day} \cdot \text{m}^3 \end{aligned}$$

$$\begin{aligned} \text{Volume of reactor} &= \frac{\text{Total production per day}}{\text{production per day per m}^3} \\ &= \frac{10000 \text{ kg/day}}{1441.4 \text{ kg/day} \cdot \text{m}^3} = 6.937 \text{ m}^3 \\ &\approx 7 \text{ m}^3 \end{aligned}$$

Batch reactor - Nonisothermal operation

If the temperature is not constant but varies during the course of reaction, then the rate of reaction ($-r_A$) will be a function of temperature as well as concentration,

$$-r_A = [k(T)] [f(C_A, C_B, \dots)]$$

The temperature at any stage is determined by Energy balance. During reaction, there is no material flow into or out of a batch reactor. However there may be a flow of heat to or from the reactor by heat transfer.

In the case of a jacketed vessel or one with an internal coil, the heat transfer coefficient will

be largely dependent on agitator speed which usually held constant. Thus, assuming that the viscosity of the liquid does not change appreciably, which is reasonable in many cases (except for some polymerisation), the heat transfer coefficient may be taken as constant. If heating is effected by condensing saturated steam at constant pressure, $T_c(T_a)$ is constant. If cooling is carried out with water, the rise in temperature of the water may be small, if the flow rate is large, and $T_c(T_a)$ again taken as constant.

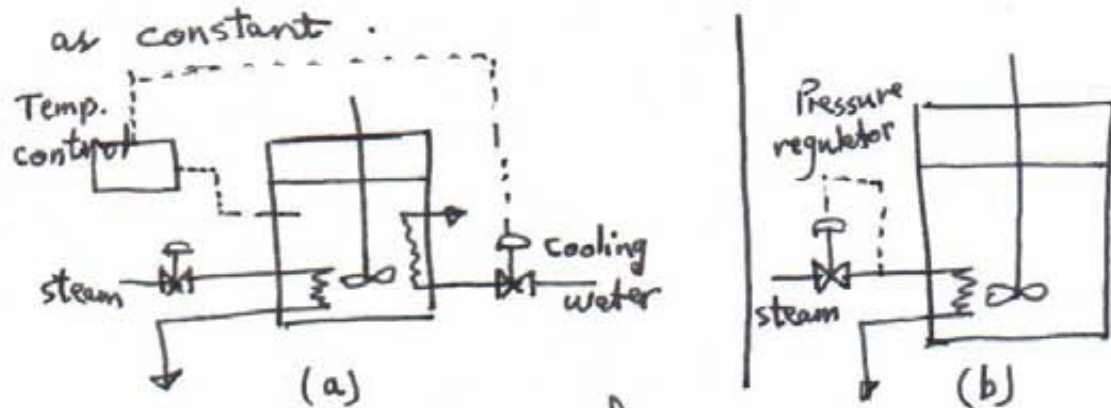


Fig. () Methods of operating batch reactor.

(a) Isothermal operation of an exothermic reaction, heating to give required initial temperature, cooling to remove heat of reaction

(b) Non-isothermal operation, simple scheme

$$UA(T_a - T) - \Delta H_R(T)(-r_A V) = V \cdot \sum C_{p_j} C_j \frac{dT}{dt}$$

Rate of heat flow out by heat transfer Rate of heat released by Chem. reaction Rate of heat accumulated

where A : heat transfer area (m^2)

U : overall heat transfer ($J/s \cdot m^2 \cdot K$)

ΔH_R = enthalpy change in the reaction per mole of A reacting.

T = temp. of the reaction mixture (K)

$\sum C_{p_i} C_j$ = sum of heat capacities (specific heats \times conc.) of the reaction mixture and the reactor itself.

For a reaction $A + B \rightarrow C + D$

$$\sum C_{p_i} C_j = C_{pA} C_A + C_{pB} C_B + C_{pC} C_C + C_{pD} C_D$$

For Adiabatic Operation

$$Q = 0, \quad U A (T_a - T) = 0$$

$$-\Delta H_R(T) (-r_A) V = V \sum C_{p_i} C_j \frac{dT}{dt}$$

$$-r_A = \frac{dC_A}{dt}; \quad X = \frac{C_{A0} - C_A}{C_{A0}} = 1 - \frac{C_A}{C_{A0}}$$

$$dX = -\frac{dC_A}{C_{A0}}; \quad \frac{dX}{dt} C_{A0} = -\frac{dC_A}{dt}$$

The heat released by the reaction is retained as sensible heat in the reactor. Thus for reaction at $V = \text{const.}$

$$-\Delta H_R(T) \left(-\frac{dC_A}{dt} \right) V = V \sum C_{p_i} C_j \frac{dT}{dt}$$

$$-\Delta H_R(T) C_{A0} \frac{dX}{dt} = \sum C_{p_i} C_j \frac{dT}{dt}$$

$$-\Delta H_R(T) C_{A0} \int_0^X dX = \sum C_{p_i} C_j \int_{T_0}^T dT$$

$$\boxed{[-\Delta H_R(T)] C_{A0} X = \sum C_{p_i} C_j (T - T_0)}$$

at certain time

$$\Delta H_R(T) = \Delta H_R^0(T_R) + \Delta \bar{C}_p (T - T_R)$$

$$\Delta \bar{C}_p = [C_{pC} + C_{pD}] - [C_{pA} + C_{pR}]$$

T_0 : initial temp. $\Leftarrow T_R$: reference temp.

If the density and specific heat of the reaction mixture are constant throughout, the adiabatic energy balance eqn. becomes

$$-\Delta H_R(T) C_{A0} X = \rho_{\text{mix}} C_{p\text{mix}} (T - T_0)$$

Example: 1.3 Adiabatic operation

Acetic anhydride is hydrolysed by water in accordance with the reaction: $(\text{CH}_3\text{CO})_2\text{O} + \text{H}_2\text{O} \rightleftharpoons 2\text{CH}_3\text{COOH}$

In a dilute aqueous solution where a large excess of water is present, the reaction is irreversible and pseudo first-order with respect to the acetic anhydride. The variation of the pseudo first-order rate constant with temp. is as follows:

Temp. ($^{\circ}\text{C}$)	15	20	25	30
Rate constant (s^{-1})	0.00134	0.00188	0.00263	0.00351

A batch reactor for carrying out the hydrolysis is charged with an anhydride solution containing 0.3 kmol/m^3 at 15°C . The specific heat and density of the reaction mixture are $3.8 \text{ kJ/kg}\cdot\text{K}$ and 1070 kg/m^3 respectively, and may be taken as constant throughout the course of reaction. The reaction is exothermic, the heat of reaction per kmole of anhydride being 210000 kJ/kmol

If the reactor is operated adiabatically, estimate the time required for the hydrolysis of 80% of the anhydride.

Solution

We may most conveniently take the adiabatic heat balance over the unit volume, i.e. 1 m^3 of reaction mixture. Thus integrating eqn. with the temperature T_0 when $x=0$.

$$-\Delta H_R C_{A0} X = \rho_{\text{mix}} C_{p\text{mix}} (T - T_0) \quad \text{unit volume}$$

$$210000 \times 0.3 \times X = (1070)(3.8)(T - T_0)$$

$$(T - T_0) = 15.6 X \quad \text{————— (1-3-1)}$$

Thus, if the reaction went to completion ($X=1$), the adiabatic temp. rise would be 15.6°C .

For a pseudo first order reaction, the rate eqn. is

$$-r_A = K C_A = K C_{A0} (1 - X)$$

$$t = C_{A0} \int_0^{X_f} \frac{dx}{-r_A} = \frac{C_{A0}}{C_{A0}} \int_0^{0.8} \frac{dx}{K(1-x)}$$

$$t = \int_0^{0.8} \frac{dx}{K(1-x)} \quad \text{————— (1-3-2)}$$

(i) For isothermal operation, $T = \text{const.}$, $K = \text{constant}$

$$t = \frac{1}{K} \int_0^{0.8} \frac{dx}{(1-x)}$$

ii) For Nonisothermal operation, $T \neq \text{const}$, $K \neq \text{const}$
 it can't take K out of the integral $\Rightarrow t = \int \frac{dx}{K(1-x)}$

To evaluate this integral using numerical evaluation.

From EB we find $x = f(T)$
 Arrhenius eqn. gives $K = f(T)$ } \rightarrow we get x at any K
 $\frac{1}{K(1-x)} = f(x)$

conversion	Temp. rise ($T - T_0$), K	Temp. K	K s^{-1}	$\frac{1}{K(1-x)} = f(x)$
0	0	288	0.00134	746 = $f(x)_0$
0.4	6.2	294.2	0.00205	813 = $f(x)_{0.4}$
0.8	12.5	300.5	0.00305	1630 = $f(x)_{0.8}$

Using Simpson's one-third rule (three points)

$$\int_{x_0}^{x_2} f(x) dx = \frac{h}{3} [f(x)_0 + 4f(x)_1 + f(x)_2]$$

$$h = \frac{x_2 - x_0}{2} = 0.4$$

$$= \frac{0.4}{3} [746 + 4(813) + 1630]$$

$$t = \underline{\underline{750 \text{ s}}}$$

Equilibrium Conversion

The highest conversion that can be achieved in reversible reaction is equilibrium conversion (X_e).

To calculate X_e , set $(-r_A) = 0$.

Example 1.4 Calculating the adiabatic Equilibrium Temp. For the elementary liquid-phase reaction,



make a plot of equilibrium conversion as a function of temperature. $[X_e = f(T), X_{EB} = f(T)]$.

Determine the adiabatic equilibrium temperature and conversion when pure A is fed to the reactor at a temperature of 300 K.

$$H_A^\circ(298\text{ K}) = -40000 \text{ cal/mol}$$

$$H_B^\circ(298\text{ K}) = -60000 \text{ cal/mol}$$

$$C_{PA} = C_{PB} = 50 \text{ cal/mol} \cdot \text{K}$$

$$K_e = 100000 \text{ at } 298\text{ K}$$

Solution

$$\begin{aligned} 1* \quad (-r_A) &= r_{Af} - r_{Ar} = K C_A - K' C_B \\ (-r_A) &= K \left(C_A - \frac{K'}{K} C_B \right) = K \left(C_A - \frac{C_B}{K_e} \right) \quad \dots (E1-4-1) \end{aligned}$$

$$2* \quad \text{At equilibrium, } -r_A = 0, \text{ so } C_{Ae} = C_{Be} / K_e$$

$$\therefore C_{A0}(1 - X_e) = C_{A0} X_e / K_e$$

3* Solving for X_e gives,

$$X_e = \frac{K_e(T)}{1 + K_e(T)} \quad (E1-4.2)$$

(31)

4x Equilibrium Constant: Calculate ΔC_p , then $K_e(T)$

$$\Delta \bar{C}_p = C_{pB} - C_{pA} = 50 - 50 = 0 \text{ cal/mol.K}$$

For $\Delta C_p = 0$, the equilibrium constant varies with temp. (Van't Hoff's equation)

$$K_e(T) = K_e(T_1) \exp \left[\frac{\Delta H_R^0}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \dots (E1-4-3)$$

$$\Delta H_R^0 = H_B^0 - H_A^0 = 20000 \text{ cal/mol}$$

$$K_e(T) = 100000 \exp \left[\frac{-20000}{1.987} \left(\frac{1}{298} - \frac{1}{T} \right) \right]$$

$$K_e(T) = 100000 \exp \left[-33.78 \left(\frac{T-298}{T} \right) \right] \dots (E1-4.4)$$

Substituting eqn (E1-4.4) into (E1-4.2)

$$X_e = \frac{100000 \exp \left[-33.78 (T-298)/T \right]}{1 + 100000 \exp \left[-33.78 (T-298)/T \right]} \dots (E1-4.5)$$

The calculations are shown in Table (1-4-1)

<u>T</u>	<u>K_e</u>	<u>X_e</u>
298	100000	1.00
350	661.6	1.00
400	18.17	0.95
425	4.14	0.8
450	1.11	0.53
475	0.34	0.25
500	0.12	0.11

For the reaction carried out adiabatically, the energy balance reduces to:

$$X_{EB} = \frac{\sum \theta_i C_{p,i} (T - T_0)}{-\Delta H_R} = \frac{C_{pA} (T - T_0)}{-\Delta H_R} \dots (E1-4.6)$$

Table (E1-4.2) shows the calculation of eqn. (E1-4.6)

T	300	400	500	600
X_{EB}	0	0.25	0.5	0.75

Data from Tables (E1-4.1) & (E1-4.2) are plotted in Figure (E1-4.1)

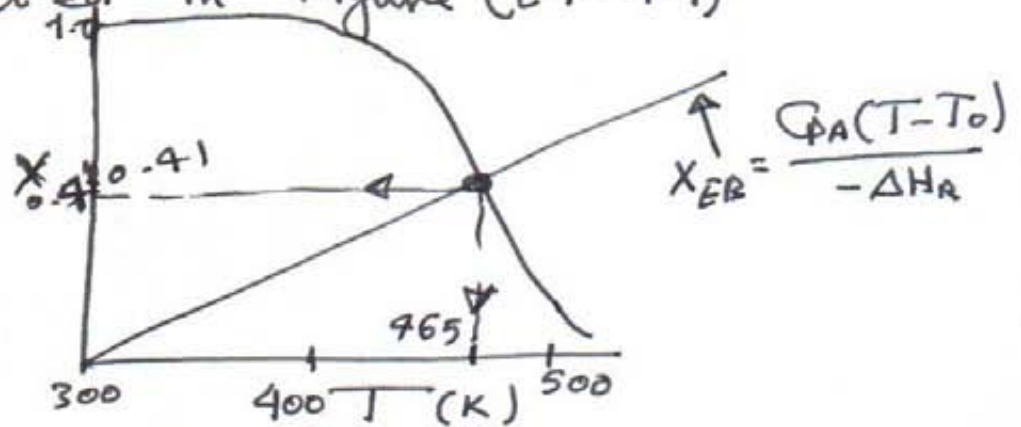


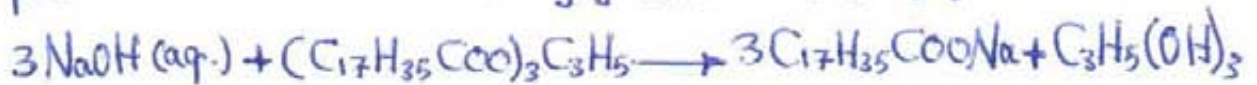
Fig. (E1-4.1)

For a feed temp. of 300 K,
 the adiabatic equilibrium temp. = 465 K
 the adiabatic equilibrium conversion = 0.41

3- Stoichiometric Table.

3- (A) Batch system:

Ex. The saponification reaction for the formation of soap from aqueous caustic soda and glycerol stearate is:



Set up a stoichiometric table expressing the concentration of each species in terms of its initial concentration and the conversion. Consider the reaction to occur in a batch system.

Sol.



Since this is a liq.-phase reaction, the density ρ is to be considered constant, therefore $V = V_0$

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X)$$

$$\theta_B = \frac{C_{B0}}{C_{A0}}; \theta_C = \frac{C_{C0}}{C_{A0}} \text{ and } \theta_D = \frac{C_{D0}}{C_{A0}}$$

Species		Initially	Change	= Change	Remaining	Concentration
NaOH	A	N_{A0}	$-N_{A0}X$	$-N_{A0}X$	$N_{A0}(1-X)$	$C_{A0}(1-X)$
$(\text{C}_{17}\text{H}_{35}\text{COO})_3\text{C}_3\text{H}_5$	B	N_{B0}	$-\frac{b}{a}N_{A0}X$	$-\frac{1}{3}N_{A0}X$	$N_{A0}(\theta_B - \frac{X}{3})$	$C_{A0}(\theta_B - \frac{X}{3})$
$\text{C}_{17}\text{H}_{35}\text{COONa}$	C	N_{C0}	$+\frac{c}{a}N_{A0}X$	$N_{A0}X$	$N_{A0}(\theta_C + X)$	$C_{A0}(\theta_C + X)$
$\text{C}_3\text{H}_5(\text{OH})_3$	D	N_{D0}	$+\frac{d}{a}N_{A0}X$	$\frac{1}{3}N_{A0}X$	$N_{A0}(\theta_D + \frac{X}{3})$	$C_{A0}(\theta_D + \frac{X}{3})$
Water	I	N_{I0}			N_{I0}	C_{I0}
		N_{T0}			N_{T0}	

3-⑧ Flow system:

This system is applied for the tubular reactor (PFR) and the backmix reactor (CSTR).

$$C_A \left(\frac{\text{mol}}{\text{m}^3} \right) = \frac{F_A \left(\frac{\text{mol}}{\text{s}} \right)}{V \left(\frac{\text{m}^3}{\text{s}} \right)} = \frac{\text{molar flow rate}}{\text{volumetric flow rate}}$$

$$C_A = \frac{F_{A0} - F_{A0}X}{V} = \frac{F_{A0}(1-X)}{V} \quad \dots 3-(1)$$

$$C_B = \frac{F_B}{V} = \frac{F_{B0} - \left(\frac{b}{a}\right)F_{A0}X}{V} \quad \dots 3-(2)$$

$$C_C = \frac{F_C}{V} = \frac{F_{C0} + \left(\frac{c}{a}\right)F_{A0}X}{V} \quad \dots 3-(3)$$

$$C_D = \frac{F_D}{V} = \frac{F_{D0} + \left(\frac{d}{a}\right)F_{A0}X}{V} \quad \dots 3-(4)$$

multiply eqns (2), (3) and (4) by $\frac{F_{A0}}{F_{A0}}$ to obtain:

$$F_B = F_{A0} \left(\theta_B - \frac{b}{a}X \right) \quad \dots 3-(5)$$

$$F_C = F_{A0} \left(\theta_C + \frac{c}{a}X \right) \quad \dots 3-(6)$$

$$F_D = F_{A0} \left(\theta_D + \frac{d}{a}X \right) \quad \dots 3-(7)$$

$$\text{where } \theta_B = \frac{F_{B0}}{F_{A0}} = \frac{C_{B0}V_0}{C_{A0}V_0} = \frac{C_{B0}}{C_{A0}} = \frac{y_{B0}}{y_{A0}}$$

and θ_C , θ_D and θ_I are defined similarly.

For liquids, the volume change with reaction is negligible when no phase changes are taking place.

Consequently, we can take:

$$V = V_0$$

$$\text{Then } C_A = \frac{F_{A0}}{V_0} (1-X) = C_{A0}(1-X) \quad \dots 3-(8)$$

$$C_B = C_{A0} \left(\theta_B - \frac{b}{a}X \right) \quad \dots 3-(9)$$

$$C_C = C_{A0} \left(\theta_C + \frac{c}{a}X \right) \quad \dots 3-(10)$$

$$C_D = C_{A0} \left(\theta_D + \frac{d}{a}X \right) \quad \dots 3-(11)$$

3-C Volume change with reaction

Most gaseous reactions undergo volume changes, for example the synthesis of ammonia:



C_A , C_B and C_C can be determined by expressing the volume (V) for a batch system or volumetric flow rate (U) for a flow system as a function of conversion: $V = f_1(x)$; $U = f_2(x)$

To derive the relations, starting from equation of state.

$$PV = Z N_T R T \quad \text{--- C- (1)}$$

where:

P = total pressure (kPa) , 1 atm = 101 kPa

Z = compressibility factor

V = volume (dm^3)

N_T = total number of moles (mole)

R = gas constant $0.082 \frac{\text{atm} \cdot \text{dm}^3}{\text{gmol} \cdot ^\circ\text{K}} = 8.314 \frac{\text{kPa} \cdot \text{dm}^3}{\text{gmol} \cdot ^\circ\text{K}}$

at time = 0 (initial condition)

$$P_0 V_0 = Z_0 N_{T0} R T_0 \quad \text{--- C- (2)}$$

Divide (1) on (2)

$$\frac{PV}{P_0 V_0} = \frac{Z N_T R T}{Z_0 N_{T0} R T_0}$$

$$V = V_0 \left(\frac{P_0}{P} \right) \left(\frac{N_T}{N_{T0}} \right) \left(\frac{T}{T_0} \right) \left(\frac{Z}{Z_0} \right) \quad \text{--- C- (3)}$$

$$N_T = N_{T0} + \delta N_{A0} X \quad \text{--- C- (4)}$$

where $\delta = (c) - (a+b)$

Divide both sides of equation (4) on N_{T0}

$$\frac{N_T}{N_{T0}} = 1 + \delta \frac{N_{A0}}{N_{A0}} X = 1 + \delta Y_{A0} X \quad \dots \text{C-(5)}$$

Define ϵ = change in total number of moles when reaction is completed

$$\epsilon = Y_{A0} \delta \quad \dots \dots \dots \text{C-(6)}$$

Substitute (6) into (5)

$$\frac{N_T}{N_{T0}} = 1 + \epsilon X \quad \dots \dots \dots \text{C-(7)}$$

Substitute (7) into (3)

$$V = V_0 \left(\frac{P_0}{P} \right) \left(\frac{T}{T_0} \right) \left(\frac{Z}{Z_0} \right) (1 + \epsilon X) \quad \dots \text{C-(8)}$$

The compressibility factor will not change significantly $\Rightarrow Z = Z_0$

Equation (8) becomes

Volume of gas for batch reaction \rightarrow
$$V = V_0 \left(\frac{P_0}{P} \right) \left(\frac{T}{T_0} \right) (1 + \epsilon X) \quad \dots \text{C-(9)}$$

Gas phase volumetric flow rate \rightarrow
$$V = V_0 \left(\frac{P_0}{P} \right) \left(\frac{T}{T_0} \right) (1 + \epsilon X) \quad \dots \text{C-(10)}$$

$$C_j = \frac{F_j}{V} \quad \dots \dots \dots \text{C-(11)}$$

where j any component in the reaction mixture.

$$C_j = \frac{F_{j0} (\theta_j + \nu_j X)}{V}$$

$$C_j = \frac{F_{j0} (\theta_j + \nu_j X)}{V_0 \left(\frac{P_0}{P} \right) \left(\frac{T}{T_0} \right) (1 + \epsilon X)}$$

$$C_j = C_{j0} \frac{(\theta_j + \nu_j X)}{(1 + \epsilon X)} * \left(\frac{P}{P_0} \right) * \left(\frac{T_0}{T} \right) \quad \dots \text{C-(12)}$$

Equation (12) represent the gas-phase concentration as function of conversion (37)

For the reaction in a flow system (volume change):



$$V_A = 1, V_B = \frac{b}{a}, V_C = \frac{c}{a} \text{ and } V_D = \frac{d}{a}$$

$$\theta_A = \frac{N_{A0}}{N_{A0}}, \theta_B = \frac{N_{B0}}{N_{A0}}, \theta_C = \frac{N_{C0}}{N_{A0}} \text{ and } \theta_D = \frac{N_{D0}}{N_{A0}}$$

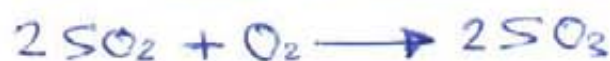
$$C_A = C_{A0} \frac{(1-X)}{(1+\varepsilon X)} * \left(\frac{P}{P_0}\right) \left(\frac{T_0}{T}\right) \quad \text{---E-(13)}$$

$$C_B = C_{A0} \frac{(\theta_B - V_B X)}{(1+\varepsilon X)} * \left(\frac{P}{P_0}\right) \left(\frac{T_0}{T}\right) \quad \text{--- C-(14)}$$

$$C_C = C_{A0} \frac{(\theta_C + V_C X)}{(1+\varepsilon X)} * \left(\frac{P}{P_0}\right) \left(\frac{T_0}{T}\right) \quad \text{--- C-(15)}$$

$$C_D = C_{A0} \frac{(\theta_D + V_D X)}{(1+\varepsilon X)} * \left(\frac{P}{P_0}\right) \left(\frac{T_0}{T}\right) \quad \text{--- C-(16)}$$

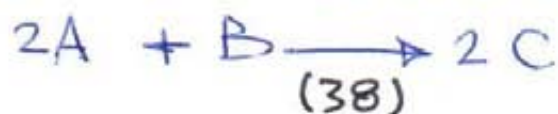
Ex. A mixture of 28% SO_2 and 72% air is charged to a flow reactor in which SO_2 is oxidised



- Set up a stoichiometric table using only the symbols (i.e., θ_i, C_i)
- Prepare a stoichiometric table evaluating numerically when the total pressure is 1485 kPa and the temperature is constant at 227°C .

Sol.

- Taking SO_2 as the basis of calculation



Species	Symbol	Initially	Change	= Change	Remaining
SO ₂	A	F _{A0}	-F _{A0} X	-F _{A0} X	F _A = F _{A0} (1-X)
O ₂	B	F _{B0} = θ _B F _{A0}	$-\frac{b}{a} F_{A0}X$	$-\frac{F_{A0}X}{2}$	F _B = F _{A0} (θ _B - $\frac{X}{2}$)
SO ₃	C	0	$+\frac{c}{a} F_{A0}X$	+F _{A0} X	F _C = F _{A0} X
N ₂	I	F _{I0} = θ _I F _{A0}	—	—	F _I = F _{I0} = θ _I F _{A0}
		F _{T0}			F _T = F _{T0} - $\frac{F_{A0}X}{2}$

- (b) Initially 72% of the total number of moles is air, containing 21% O₂ and 79% N₂

$$F_{O_{SO_2}} = F_{A0} = 0.28 F_{T0} ; F_{O_{O_2}} = (0.72)(0.21) F_{T0} = F_{B0}$$

$$\theta_B = \frac{F_{B0}}{F_{A0}} = \frac{0.72(0.21) F_{T0}}{0.28 F_{T0}} = 0.54$$

$$\theta_{I(N_2)} = \frac{F_{I0}}{F_{A0}} = \frac{0.72(0.79) F_{T0}}{0.28 F_{T0}} = 2.03$$

$$C_A = \frac{F_A}{V} = \frac{F_{A0}(1-X)}{V} ; V = V_0(1+\epsilon X) \frac{P_0}{P} \left(\frac{T}{T_0} \right)$$

For isothermal operation (T = T₀) → $\frac{T}{T_0} = 1$

For isobaric operation (ΔP = 0) → $\frac{P_0}{P} = 1$

$$\therefore C_A = \frac{F_{A0}}{V_0} \times \frac{1-X}{1+\epsilon X} = C_{A0} \frac{1-X}{1+\epsilon X}$$

C_{T0} = total concentration of components

$$C_{T0} = \frac{P_0}{RT_0} = \frac{1485 \text{ kPa}}{8.314 \frac{\text{kJ}}{\text{mol} \cdot \text{K}} \times 500 \text{ K}} = 0.1 \frac{\text{mol}}{\text{dm}^3}$$

$$\epsilon = y_{A0} \delta = 0.28 \left(1 - \frac{1}{2} - 1 \right) = -0.14$$

$$C_A = 0.1 \frac{1-X}{1-0.14X} \quad \frac{\text{mol}}{\text{dm}^3}$$

$$C_B = C_{A0} \frac{\theta_B - \frac{1}{2}X}{1+\sum X} = 0.1 \frac{(0.54-0.5X)}{1-0.14X} \quad \frac{\text{mol}}{\text{dm}^3}$$

$$C_C = \frac{C_{A0} X}{1+\sum X} = \frac{0.1 X}{1-0.14X} \quad \frac{\text{mol}}{\text{dm}^3}$$

$$C_I = \frac{C_{A0} \theta_I}{1+\sum X} = \frac{0.1(2.03)}{1-0.14X} \quad \frac{\text{mol}}{\text{dm}^3}$$

Species	X=0	X=0.5	X=0.75
SO ₂	C _A =0.1	C _A =0.054	C _A =0.028
O ₂	C _B =0.054	C _B =0.031	C _B =0.018
SO ₃	C _C =0	C _C =0.054	C _C =0.084
N ₂	C _I =0.203	C _I =0.218	C _I =0.227
	C _T =0.357	C _T =0.357	C _T =0.357

4.3 Tubular Reactors

Gas phase reactions are carried out primarily in tubular reactors. By assuming that there are no radial gradients in either temperature, velocity, or concentration, we model the flow in the reactor as plug flow.

After multiplying both sides of the tubular reactor design equation (1-10)

$$- \frac{dF_A}{dV} = -r_A \quad \dots (2-14)$$

For a flow system, F_A has previously been given in terms of the entering molar flow rate F_{A0} and the conversion X

$$F_A = F_{A0} - F_{A0}X \quad \dots (2-10)$$

Substituting eqn. () into (), gives the differential form of the design equation for a plug flow reactor (PFR)

$$F_{A0} \frac{dX}{dV} = -r_A \quad \dots (2-15)$$

We now separate the variables and integrate with the limits $V=0$ when $X=0$ to obtain the PFR volume necessary to achieve a specified conversion X

$$V = F_{A0} \int_0^X \frac{dX}{-r_A} \quad \dots (2-16)$$

To carry out the integrations in the batch and PFR design equations () and () - as well as to evaluate the CSTR design equation () - , we need to know how the reaction rate $-r_A$ varies with the concentration (hence conversion) of the reacting species,

where

V = volume of PFR, m^3
 F_{A0} = rate of feed of A in moles per time.
 X = conversion of A, percentage or fraction.
 r_A = rate of reaction, $kmol/m^3 \cdot s$

i) If the mass flow rate of A (\dot{m}) in kg/s is given, to calculate F_{A0} we need only to divide the value of (\dot{m}) by the molecular weight of A.

ii) If the production rate is given, to calculate F_{A0} , $F_{A0} = \frac{(\dot{m}_{\text{product}})}{X \cdot M_{wt \text{ product}}}$

$$V = V_0 C_{A0} \int \frac{dX}{-r_A}$$

$$\tau = \frac{V}{V_0} = C_{A0} \int \frac{dX}{-r_A} \quad \text{---- (2-17)}$$

Space time (τ) : time needed to treat (i.e., process) one reactor volume of feed measured at specified conditions $= C_{A0} \int_0^X \frac{dx}{(-r_A)}$

\bar{t} = mean residence time of flowing material in the reactor

$$\bar{t} = \frac{V}{V_0} = \frac{C_{A0} V}{F_{A0}} \quad \text{--- (2-18)}$$

For constant density system (all liquids and constant density gases)

$$\tau = \bar{t} = \frac{V}{v} \quad \text{--- (2-19)}$$

Space velocity $= \frac{1}{\tau}$ = number of reactor volumes of feed measured at specified conditions which can be treated in unit time $\cdot \left(\frac{1}{\text{time}}\right)$

Examples

A space-time of 2 min means that every 2 minutes one reactor volume of feed at specified conditions is being treated by the reactor.

A space-velocity of 5 hr^{-1} means that five reactor volumes of feed at specified conditions are being fed into the reactor per hr.

Example (4.3.): PFR (2nd order reaction)

1- PFR design equation: $V: F_{A0} \int_0^x \frac{dx}{-r_A}$

2- Substituting the rate law for special case of a second order reaction gives:

$$V: F_{A0} \int_0^x \frac{dx}{K C_A^2}$$

3- For constant-temperature and constant pressure gas-phase reactions, the concentration is expressed as a function of conversion.

$$C_A = C_{A0} \frac{1-X}{1+\varepsilon X}$$

4- and then substituted into the design eqn.

$$V: F_{A0} \int_0^x \frac{(1+\varepsilon X)^2}{K C_{A0}^2 (1-X)^2} dx$$

5- The entering (initial) concentration C_{A0} can be taken outside the integral sign since it is not a function of conversion and also the specific reaction rate constant may be considered constant since the reaction is carried out isothermally.

$$V: \frac{F_{A0}}{K C_{A0}^2} \int_0^x \frac{(1+\varepsilon X)^2}{(1-X)^2} dx$$

6- From the integral equations in Appendix A-2, Fogler, we find that

$$V: \frac{V_0}{K C_{A0}} \left[2\varepsilon(1+\varepsilon) \ln(1-X) + \varepsilon^2 X + \frac{(1+\varepsilon)^2 X}{1-X} \right] \quad \text{--- (4-20)}$$

7- If we divide both sides of Equation (4-20)

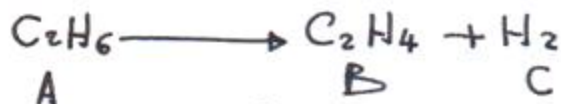
by the cross sectional area of the reactor, A_c , we obtain the following equation relating reactor length to conversion)

$$L = \frac{V_0}{K C_{A_0} A_c} \left[2\varepsilon(1+\varepsilon) \ln(1-X) + \varepsilon^2 X + \frac{(1+\varepsilon)^2}{1-X} \right] \quad \text{--- (4-21)}$$

Example (4.4) Producing 150×10^3 tonn per Year in a PFR : Design of a Full-Scale Tubular Reactor.

Ethylene ranks fourth in the USA of chemicals produced and it is number one organic chemical produced each year. Determine the PFR volume necessary to produce 150×10^3 tonn of ethylene a year from cracking a feed-stream of pure ethane. The reaction is irreversible and elementary. We want to achieve 80% conversion of ethane, operating the reactor isothermally at 1100 K at a pressure of 6 atm. The rate constant at 1000 K is 0.072 s^{-1} and the activation energy (E) is 82 Kcal/gmol.

Solution



The molar flow rate of ethylene (C_2H_4) exiting the reactor is :

$$F_B = 150 \times 10^6 \frac{\text{Kg}}{\text{year}} \times \frac{1 \text{ year}}{365 \text{ day}} \times \frac{1 \text{ day}}{24 \text{ h}} \times \frac{1 \text{ h}}{3600 \text{ s}} \times \frac{1 \text{ kmol}}{28 \text{ Kg}} = 0.17 \frac{\text{Kmol}}{\text{s}}$$

$$F_B = X F_{A_0} \Rightarrow F_{A_0} = \frac{F_B}{X} = \frac{0.17}{0.8} = 0.212 \frac{\text{Kmol}}{\text{s}}$$

(45)

$$(-r_A) = k C_A \quad , \quad k_1 (\text{at } 1000 \text{ K}) = 0.072 \text{ s}^{-1}$$

To estimate k_2 at 1100 K :

$$\ln \frac{k_1}{k_2} = \frac{E}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{0.072}{k_2} = \frac{82 \times 10^3}{1.987} \left(\frac{1}{1100} - \frac{1}{1000} \right)$$

$$k_2 = 3.06 \text{ s}^{-1}$$

$$\varepsilon = y_{A_0} \delta = 1 * (1 + 1 - 1) = 1$$

$$C_{A_0} = \frac{y_{A_0} P}{R T_0} = \frac{1 * 6}{0.082 * 1100} = 0.066 \frac{\text{kmol}}{\text{m}^3}$$

$$V = \frac{F_{A_0}}{k C_{A_0}} \int_0^{0.8} \frac{dx}{\left(\frac{1-x}{1+\varepsilon x} \right)} = \frac{F_{A_0}}{k C_{A_0}} \int_0^{0.8} \frac{dx}{\left(\frac{1-x}{1+x} \right)}$$

$$V = \frac{F_{A_0}}{k C_{A_0}} * F(x)$$

To evaluate $F(x)$ use:

(a) Integral forms of Fogler, 1809

$$\int \frac{dx}{\left(\frac{1-x}{1+\varepsilon x} \right)} = (1+\varepsilon) \ln \frac{1}{1-x} - \varepsilon x$$

$$F(x) = (1+1) \ln \frac{1}{1-0.8} - 0.8 = 2.42$$

$$V = \frac{0.212}{3.06 * 0.066} * 2.42 = \underline{\underline{2.54 \text{ m}^3}}$$

(b) Simpson's rule

x	$\left(\frac{1-x}{1+\varepsilon x} \right)$	$\left(\frac{1+x}{1-x} \right) = f(x)$
0	1	$1 = f(x)_0$
0.4	0.43	$2.33 = f(x)_{0.4}$
0.8	0.11	$9.1 = f(x)_{0.8}$

$$F(x) = \frac{0.4}{3} [1 + 4 * 2.33 + 9.1] = 2.58$$

$$V = \underline{\underline{2.7 \text{ m}^3}}$$

$$\% \text{ error} = \frac{2.7 - 2.54}{2.7} * 100 = 17.5 \%$$

4.4 Pressure Drop in Reactors

In gas-phase reactions, the concentration of the reacting species is proportional to the total pressure and consequently, proper accounting for the effects of pressure drop on the reaction system can, in many instances be a key factor in the success or failure of the reactor operation.

While in liquid-phase reactions, the concentration of reactants is insignificantly affected by even relatively large changes in the total pressure.

Consequently, we can totally ignore the effect of pressure drop on the rate of reaction when sizing chemical reactors.

4.4-1 Pressure Drop and the Rate law

For an ideal gas, the concentration of reacting species is :

$$C_i = \frac{F_i}{V} = \frac{F_{A0} (\theta_i + V_i X)}{V_0 (1 + \epsilon X) (P_0/P) (T/T_0)} \quad \dots (4-22)$$

For isothermal operation ($T = T_0$)

$$C_i = C_{A0} \left(\frac{\theta_i + V_i X}{1 + \epsilon X} \right) \left[\frac{P}{P_0} \right] \quad \dots (4-23)$$

We now substitute for the ratio P/P_0 in terms of volume V or the catalyst weight, W , to account for pressure drop.

We then combine the conc., the rate law, and design equation.

For example, the first-order isomerization reaction



is being carried out in a packed-bed reactor, the differential form of the mole balance equation in terms of catalyst weight is ($P \neq P_0$)

$$F_{A0} \frac{dX}{dW} = -r_A' \quad \frac{\text{gram moles}}{\text{gram catalyst} \cdot (\text{min})}$$

The rate law is $-r_A' = K C_A$

From stoichiometry for gas-phase reactions,

$$C_A = C_{A0} \left(\frac{1-X}{1+\epsilon X} \right) \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right)$$

And the rate law can be written as

$$-r_A = K C_{A0} \frac{1-X}{1+\epsilon X} \frac{P}{P_0} \frac{T_0}{T} \quad \dots (4-24)$$

Note from equation (4-24) the the larger the pressure drop (from frictional losses), the smaller the reaction rate. Combining eqn. (4-24) with the mole balance and assuming isothermal operation,

$$F_{A0} \frac{dX}{dW} = \frac{K C_{A0} (1-X)}{(1+\epsilon X)} \frac{P}{P_0}$$

Dividing by F_{A0} ,

$$\frac{dX}{dW} = \frac{K}{V_0} \left(\frac{1-X}{1+\epsilon X} \right) \frac{P}{P_0} \quad \dots (4-25)$$

The R.H.S is a function of only conversion