Computer Aided Process Engineering CL303

Module-1

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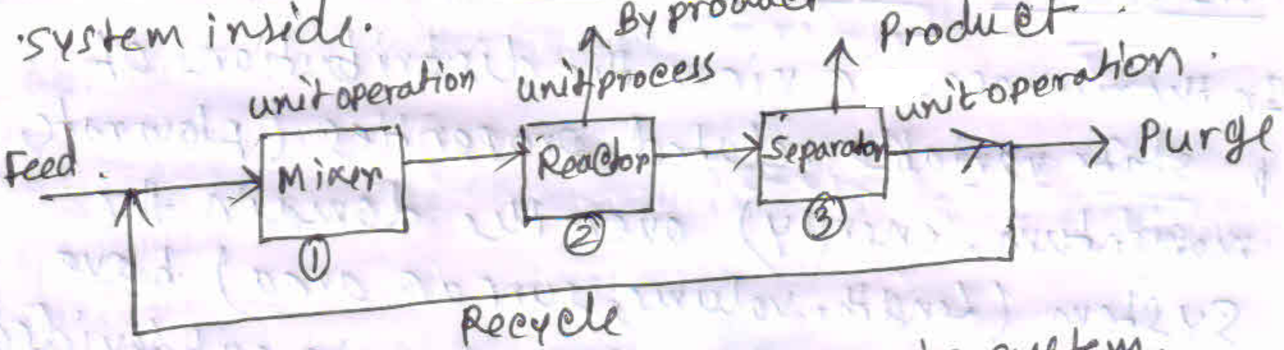
CAPE Lecture

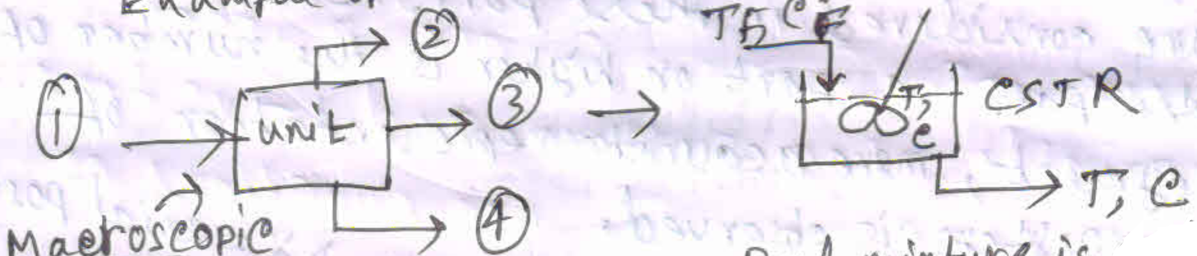
Macroscopic view of a system

It is the view of a bulk-system, where state variables related properties like, flow rate, compositions, pressure, temperature or energy of the system remains constant/unchanged over the complete domain (length, volume, surface area) of the same. It is considered as a black box where we can observe the outcome of the system such as changes of streams (outlet, inlet) properties of the system. One is unable to depict the mechanisms of the system inside.



Multiple unit Macroscopic system.

Example of Macroscopic system



Feed mixture is homogeneously mixed in the reactor and reacted in such a way that there is no change in property all over the volume of the reactor. outlet concentration and T are same reactor T & C.

Conservation of property.

unsteady state conservation equation.

Accumulation of mass, energy, momentum/or property = Property in − Property out + generation of property.

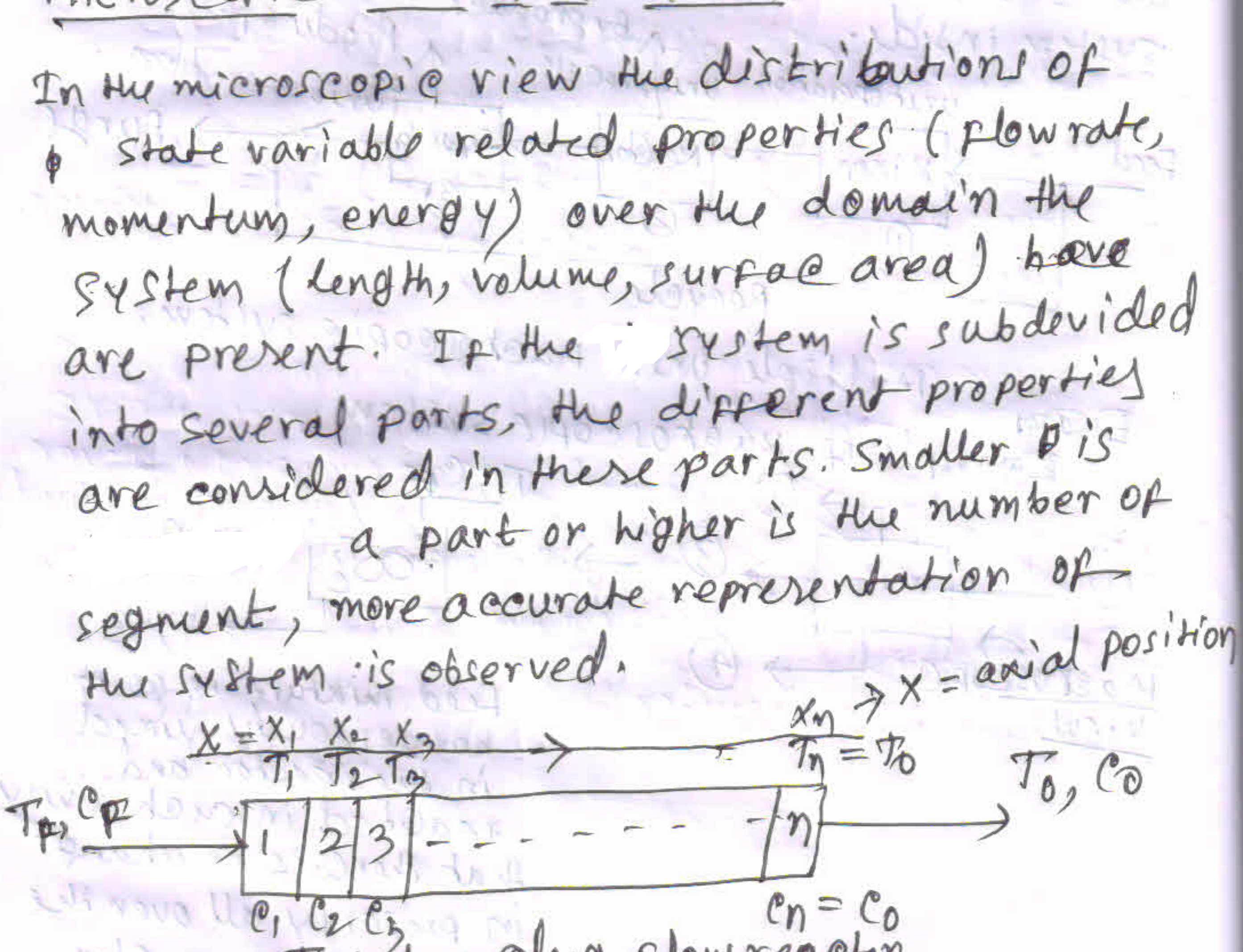
at Steady State

Accumulation of property/state variables = 0.

Property in − Property out + generation of property = 0

Microscopic view of ~~a~~ system.

In the microscopic view the distributions of state variable related properties (flow rate, momentum, energy) over the domain the system (length, volume, surface area) ~~have~~ are present. If the system is subdevided into several parts, the different properties are considered in these parts. Smaller ϕ is a part or higher is the number of segment, more accurate representation of the system is observed.



Tubular plug flow reactor

Other examples are a long heatexchanger, distillation column, fluidzed or and packed bed reactors where the microscopic view is essential.

The distributions of property in microscopic view is represented by distribution coefficients and the partial differential terms.

Heat transfer → $k \frac{\partial^2 T}{\partial x^2}$. (k = Thermal conductivity)

Mass transfer → $D \frac{\partial^2 T}{\partial x^2}$ (D = Diffusion coeffient).

Momentum transsfer → $\mu \frac{\partial^2 v}{\partial x^2}$ (μ = viscosity)

→ Molecular mode of transport

Heat transfer → $v \frac{\partial T}{\partial x}$ (v = velocity, T = Temperature)

Species transfer → $v \frac{\partial C}{\partial x}$ (C = species concentration)

momentum transfer → $v \frac{\partial V}{\partial x}$

→ Bulk mode of transport

∴ overall transport = Bulk transport + Molecular transport.

State variable

It is the variable, that defines physical state of a system.

State variable can be T, P, V, C. etc.

In a CSTR (continuous stirred tank reactor) state variables are T, C.

The unsteady state of a system can be represented by the state variable as.

$$\frac{dS_1}{dt} = f_1(S_1, S_2, \ldots S_n)$$

$$\frac{dS_2}{dt} = f_2(S_1, S_2, \ldots S_n)$$

$$\vdots$$

$$\frac{dS_n}{dt} = f_n(S_1, S_2, \ldots S_n)$$

where, $S_1, S_2, \ldots S_n$ are n state variables of a system and t is time. $f_1, f_2, \ldots f_n$ are functions of the state variables.

Flow sheet simulation based on Material balance equation

It is based on ↘
Conservation of mass.

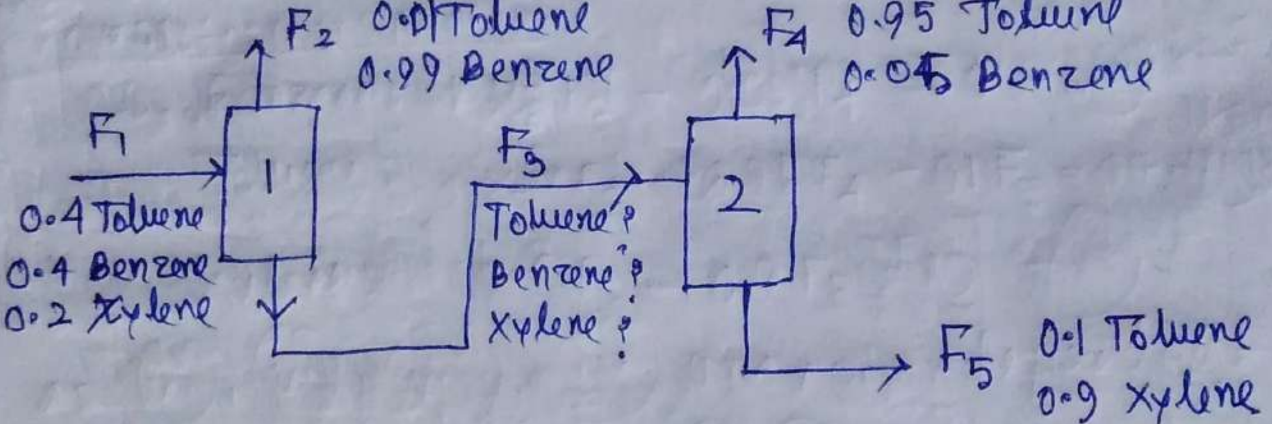
Rate of Accumulation of Mass = Rate of Mass in − Rate of Mass out

at steady state, Rate of accumulation of Mass = 0.

∴ Rate of Mass in − Rate of Mass out = 0

1st case study

Material balance equation without chemical reaction



consider the series of unit operations.
(generally two separation columns).

a F_1, F_2, F_3, F_4, F_5 are molar flow rate of five streams. (in kmol/hr). These variables are unknowns.

compositions given in the figure are mole fraction

b In the 3rd stream of molar flow rate F_3, compositions of toluene, Benzene and xylene are unknowns.

Assume these are x_B^3 = Mole fraction of benzene in 3rd stream

x_T^3 = Mole fraction of toluene in 3rd stream.

x_X^3 = Mole fraction of xylene in 3rd stream.

Total unknown variables = 5 + 3
= 8

Consider material balance equations of unit 1.

Overall material balance: $F_1 = F_2 + F_3$ [in = out rate of mass]

or $F_1 - F_2 - F_3 = 0$ — (i) ✓ I.

Composition material balance or species material balance.

~~Benzene: $F_1 0.4 + F_2 0.99$~~

Benzene: $0.4F_1 - 0.99F_2 - x_B^3 F_3 = 0$ — (ii) ✓ I

Toluene: $0.4F_1 - 0.01F_2 - x_T^3 F_3 = 0$ — (iii) ✓ I

Xylene: $0.2F_1 - x_X^3 F_3 = 0$ — (iv)

If you add (ii), (iii), (iv) equations, the equation (i) will be formed. So all 4 equations are not independent equation. Any three, 3 equation of 4 equations are independent.

So independent set of equations are (ii), (iii), (iv) or (i), (ii), (iv) or (i), (ii), (iii) or (i), (iii), (iv) any one set can be taken.

Take (i), (ii), (iii) ⇒ where variables are

$F_1, F_2, F_3, x_B^3, x_T^3, x_X^3$ = (6) no. of variables.

Another one independent equation is

$\Sigma x^3_{B,T,X} = 1$ ⇒ $x_B^3 + x_{\cancel{B}T}^3 + x_X^3 = 1$.

⇒ $x_B^3 + x_T^3 + x_X^3 - 1 = 0$ — (v) I is called composition equation.

Total independent equation = 3 + 1 = (4)

↳ (i), (ii), (iii) & (v)

Degree of freedom of unit ①

is, DOF_1 = no. of variable − no. of equations

$= ~~4~~\ 6 - 4$

$= 2 > 0$

So, 2 no. of bassis is required to fix the system of unit 1.

Consider Material balance equations of unit 2

Overall balance $F_3 - F_4 - F_5 = 0$ — (vi) ✓ I

Comosition or species.

Benzene: $x_B^3 F_3 - 0.05 F_4 = 0$ — (vii) ✓ I

Toluene: $x_T^3 F_3 - 0.95 F_4 - 0.1 F_5 = 0$ — (viii) I

Xylene: $x_X^3 F_3 - 0.9 F_5 = 0$ — (ix)

as (vi), (vii), (viii), (ix) are not independent equations. [sum of (ix), (vii), (viii) gives equation (vi)]

Take independent set as.

(vi), (vii), (viii).

And $\Sigma x^3_{T,B,X} = 1$ is common in both unit.

So total independent equations are

(i), (ii), (iii), (v), (vi), (vii), (viii) → (7)

Writing those independent equations

$F_1 - F_2 - F_3 = 0$ – (i) — ①

$0.4F_1 - 0.99F_2 - X_B^3 F_3 = 0$ – (ii) — ②

$0.4F_1 - 0.01F_2 - X_T^3 F_3 = 0$ – (iii) — ③

$X_B^3 + X_T^3 + X_X^3 - 1 = 0$ – (v) — ④

$F_3 - F_4 - F_5 = 0$ – (vi) — ⑤

~~$X_T^3 F_3$~~ $X_B^3 F_3 - 0.05 F_4 = 0$ (vi) — ⑥

$X_T^3 F_3 - 0.95 F_4 - 0.1 F_5 = 0$ (viii) — ⑦

Variables

F_1 – ①

F_2 – ②

F_3 – ③

F_4 – ④

F_5 – ⑤

X_B^3 – ⑥

X_T^3 – ⑦

X_X^3 – 8

∴ Degree of freedom of the system

DOF_{sys} = no. of variable – no. of equation

= 8 – 7 = ①

∴ 1 basis will be taken to fix the system.

Take $F_1 = 100$ kmol/hr Basis.

Solve ⑦ equations with ⑦ variable.

The equation is nonlinear as $X_B^3 F_3$, $X_T^3 F_3$ and $X_X^3 F_3$ terms are multiplied by two unknowns.

If the solution set is formed by all linear equation, it can be solved by a matrix solution (using linear algebra) ✓ This will be performed

If one of ~~be~~ these equations is nonlinear, it will be solvable by Newton method. [iterative method]

$$X_{new} = X_{old} - [J]^{-1}_{old}[f_{old}] \quad \boxed{\text{iterative method}}$$

dimension

X_{old} = old value of solution matrix. $\underline{7\times1}$ matrix

$$X_{old} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \\ x_6 \\ x_7 \end{bmatrix}_{old}$$

at first an inital guess of this set is chosen.

$x_1 = F_2$ $\quad x_6 = x_T^3$

$x_2 = F_3$ $\quad x_7 = x_X^3$

$x_3 = F_4$

$x_4 = F_5$

$x_5 = x_B^3$

⇒ variables

X_{new} = new value of solution matrix [it will be calculated]

J = Jacobian matrix

$$J = \begin{bmatrix} \frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} & \cdots & \frac{\partial f_1}{\partial x_7} \\ \frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2} & \cdots & \frac{\partial f_2}{\partial x_7} \\ \vdots & \vdots & & \vdots \\ \frac{\partial f_7}{\partial x_1} & \frac{\partial f_7}{\partial x_2} & \cdots & \frac{\partial f_7}{\partial x_7} \end{bmatrix}_{old}$$

$\underline{7\times7}$ matrix.

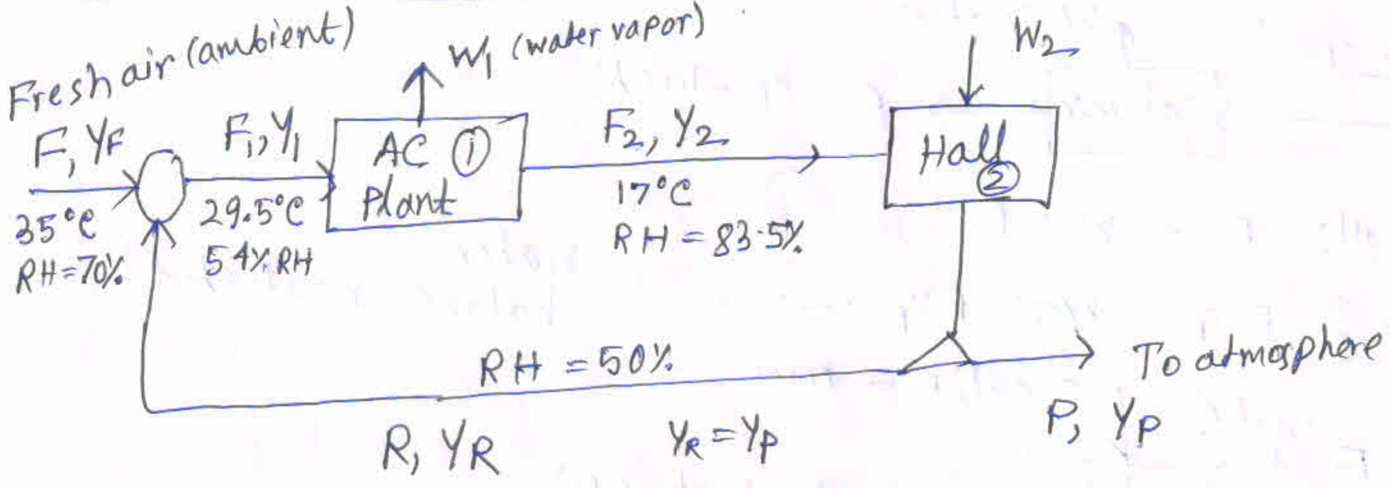
$$f_{old} = \begin{bmatrix} f_1 \\ f_2 \\ f_3 \\ f_4 \\ f_5 \\ f_6 \\ f_7 \end{bmatrix}_{old}$$

$f_1, f_2 \cdots f_7$ are function values of the equations. $\underline{7\times1}$ Matrix

Function is the term in the left hand side of all equations.

When the method converges, $\underline{f_{old}} \rightarrow 0 \approx \underline{10^{-10}}$ for 10^{th} order accuracy

Air conditioning plant (AC plant)



RH { Relative humidity).

Y = ~~Relative~~ Absolute molar humidity of air stream at specific, T & P.

F = Flowrate of air stream (kmol/hr).

F = Flowrate of air stream (dry basis)

Y is in kmol of water/kmol of dry air

~~Mixture~~ Mixer before AC plant.

overall: $F + R = F_1$ — (i)

water $F\frac{Y_F}{1+Y_F} + R\frac{Y_R}{1+Y_R} = F_1\frac{Y_1}{1+Y_1}$ — (ii)

AC plant

overall: $F_1 = W_1 + F_2$ — (iii)

water: $F_1\frac{Y_1}{1+Y_1} = W_1 + F_2\frac{Y_2}{1+Y_2}$ — (iv)

Hall overall: $F_2 + W_2 = R + P$. — (v)

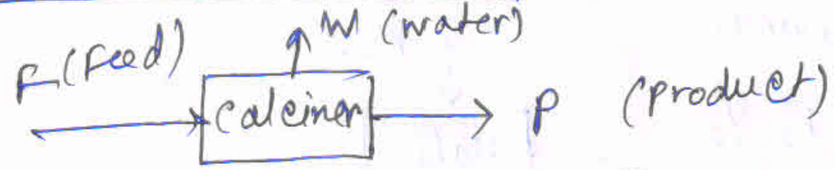
$F_2\frac{Y_2}{1+Y_2} + W_2 = (R+P)\frac{Y_R}{1+Y_R}$. — (vi)

$F, F_1, F_2, W_1, W_2, R, P$ } unknow flowrates ⑦

$Y_F, Y_1, Y_2, Y_R(Y_P)$ · are known. as $Y = F(\overset{\smile}{T}, \overset{\smile}{RH})$.
$\quad\quad\downarrow$ known $\searrow$ known.

∴ DOF = 7−6 = ① Take Basis $F = 50$ kmol/hr.

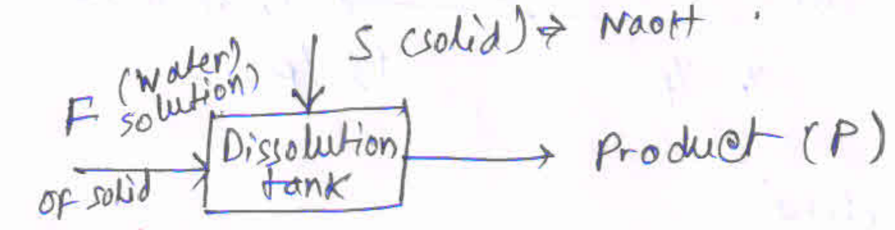
Two component systems



Overall: $F = W + P$ — (i)

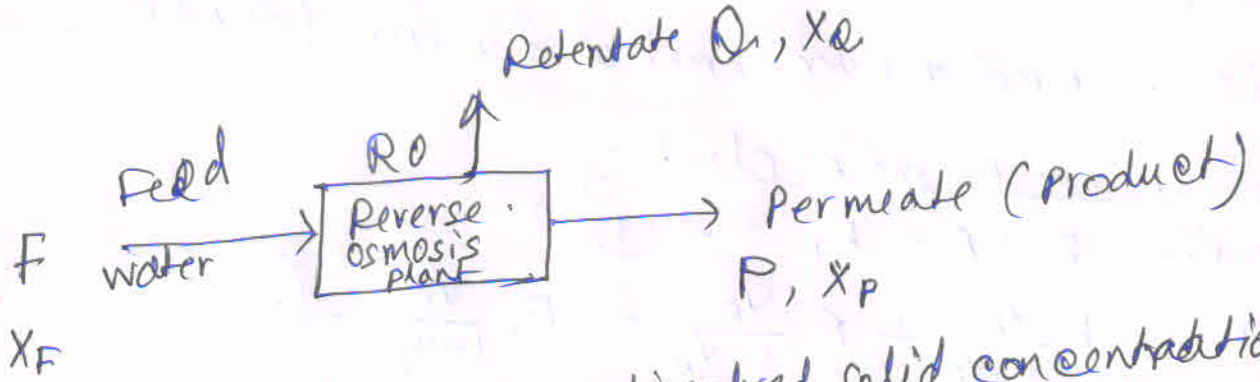
solid: $FX_F = PX_P$ — (ii)

} water balance neglected)



$F + S = P$

NaOH: ~~Feed~~ $FX_F = S + PX_P$. (water balance neglected)



X_F, X_Q, X_P are dissolved solid concentrations in feed, retentate and ~~feed~~ perpeate respectively.

Overall: $F = Q + P$

Dissolved solid $FX_F = QX_Q + PX_P$.

Solution of Multiple separators

$$\text{Initial guess } x_{old} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \\ x_6 \\ x_7 \end{bmatrix} = \begin{bmatrix} F_2 = 500 \\ F_3 = 500 \\ F_4 = 250 \\ F_5 = 250 \\ x_B^3 = 0.1 \\ x_T^3 = 0.5 \\ x_X^3 = 0.5 \end{bmatrix}$$

Using Matlab fsolve solver, the system can be solved. After 8 iterations a solution set can be obtained with Fval $< 10^{-8}$ (accuracy of 10^{-9}).

The solution set is $\Rightarrow F_2 = 384.16$ kmol/hr.

$F_3 = 615.83$ kmol/hr

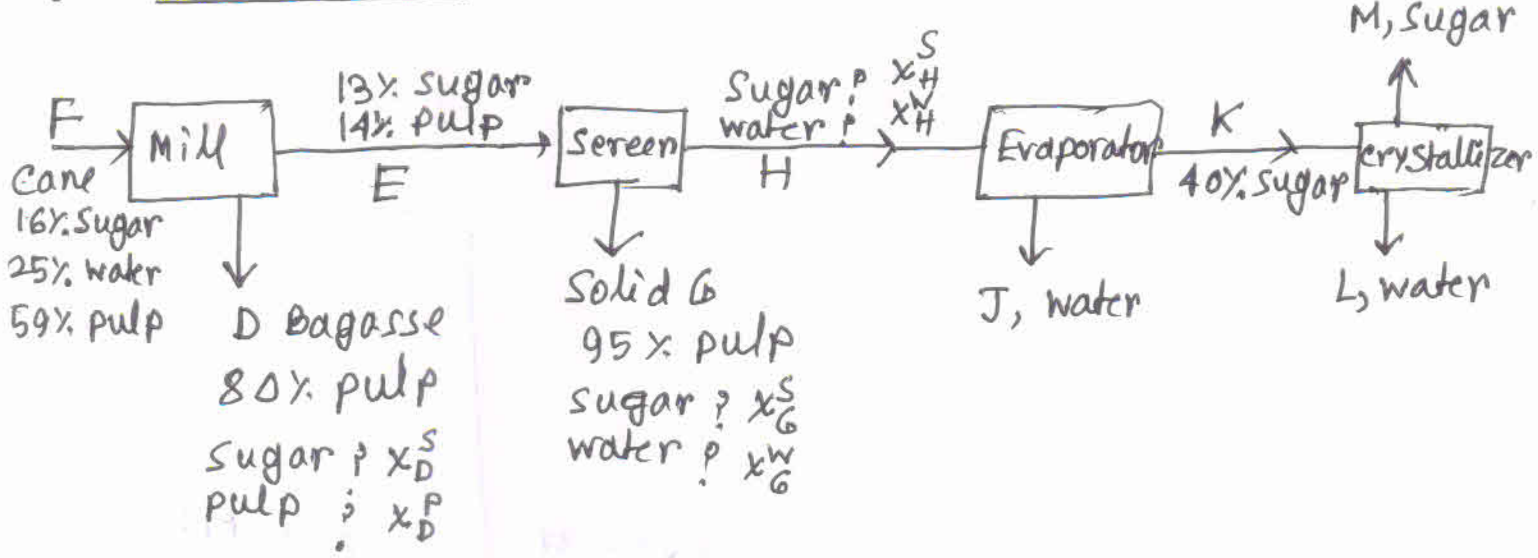
$F_4 = 222.22$ kmol/hr

$F_5 = 393.61$ kmol/hr

$x_B^3 = 0.03195$; $x_T^3 = 0.6432$.

$x_X^3 = 0.3247$

~~Sugar~~ sugarplant



Sugar plant

Mill

P: $0.8D + 0.14E - F \times 0.59 = 0$ — (i)

S: $x_D^S D + E\,0.13 - F \times 0.16 = 0$ — (ii)

W: $x_D^W D + 0.73E - F \times 0.25 = 0$ — (iii)

$x_D^S + x_D^W - 0.2 = 0$ — (iv)

P = Pulp
S = Sugar
W = water

Screen

P: $0.14E - G \times 0.95 = 0$ — (v)

S: $0.13E - H x_H^S - G x_G^S = 0$ — (vi)

W: $0.73E - H x_H^W - G x_G^W = 0$ — (vii)

$x_H^S + x_H^W = 1.$ — (viii)

$\boxed{x_G^S + x_G^W - 0.05 = 0 \;\text{— (ix)}} \rightarrow$ Excluded Equation

Evaporator

W: $H x_H^W - J - 0.6K = 0$ — (x)

S: $H x_H^S - 0.4K = 0$ — (xi)

after degree of freedom analysis
↓
solve with
12 equations
12 variable.

Crystallizer.

S: $0.4K - M = 0$ — (xii)

W $0.6K - L = 0$ — (xiii)

No. of equation (13)   DOF = 2.

No of variable 15.

take basis $F = 1000$ kg/hr.

$x_G^S = 0.025$; $x_G^W = 0.025$.

∴ No. of variable will be $15 - 3 =$ (12)

No. of equation " " $13 - 1 =$ (12)

equation no. (ix) will be excluded.

① D, E ②, x_D^S ③, x_D^W ④, G ⑤, H ⑥

x_H^S ⑦

x_H^W — ⑧

J — ⑨

K ⑩

L — ⑪

M — ⑫

variables

```
                                         Norm of      First-order   Trust-region
 Iteration  Func-count     f(x)          step         optimality    radius
     0          8         81987.6                     1.71e+005               1
     1         16         14433.3              1             168               1
     2         24         14105.1            2.5            59.3             2.5
     3         32         13301.3           6.25             156            6.25
     4         40         11395.1         15.625            95.6            15.6
     5         48         7274.63        39.0625             476            39.1
     6         56         1016.96        97.6562       3.26e+003            97.7
     7         64        0.904809        57.6007             822             244
     8         72    7.43783e-018     0.00144689       1.55e-006             244
     9         80     1.9387e-026   5.13622e-009          7e-011             244

Equation solved.

fsolve completed because the vector of function values is near zero
as measured by the default value of the function tolerance, and
the problem appears regular as measured by the gradient.

<stopping criteria details>


x =

  1.0e+002 *

   3.841607565011821
   6.158392434988180
   3.936170212765958
   2.222222222222220
   0.006432821497121
   0.000319577735125
   0.003247600767754


fval =

  1.0e-012 *

                   0
  -0.113686837721616
   0.056843418860808
                   0
  -0.056843418860808
                   0
                   0

>>
```

```
                                         Norm of      First-order   Trust-region
 Iteration  Func-count     f(x)          step         optimality    radius
     0          13          134650                       8.25e+004               1
     1          26         70552.2              1        3.63e+004               1
     2          39         53514.9            2.5        2.09e+004             2.5
     3          52         47392.8           6.25        8.98e+003            6.25
     4          65           41421         15.625        5.22e+003            15.6
     5          78         30128.2        39.0625        2.13e+003            39.1
     6          91         10327.9        97.6562           4e+003            97.7
     7         104         176.054        149.133        6.41e+003             244
     8         117    4.16314e-005        13.6244              2.7             373
     9         130      1.011e-023    1.1736e-005        8.76e-010             373

Equation solved.

fsolve completed because the vector of function values is near zero
as measured by the default value of the function tolerance, and
the problem appears regular as measured by the gradient.

<stopping criteria details>


x =

  1.0e+002 *

   6.818181818181818
   3.181818181818182
   0.001740000000000
   0.000260000000000
   0.468899521531101
   2.712918660287110
   0.001481481481482
   0.008518518518518
   1.708133971291866
   1.004784688995215
   0.401913875598086
   0.602870813397129


fval =

  1.0e-011 *

  -0.011368683772162
   0.099475983006414
  -0.099475983006414
                   0
   0.000710542735760
  -0.120325971408874
  -0.161537450082960
                   0
   0.161293201017543
   0.120792265079217
```

```
                     0
                     0

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Material Balance With Chemical Reactions

Module-1

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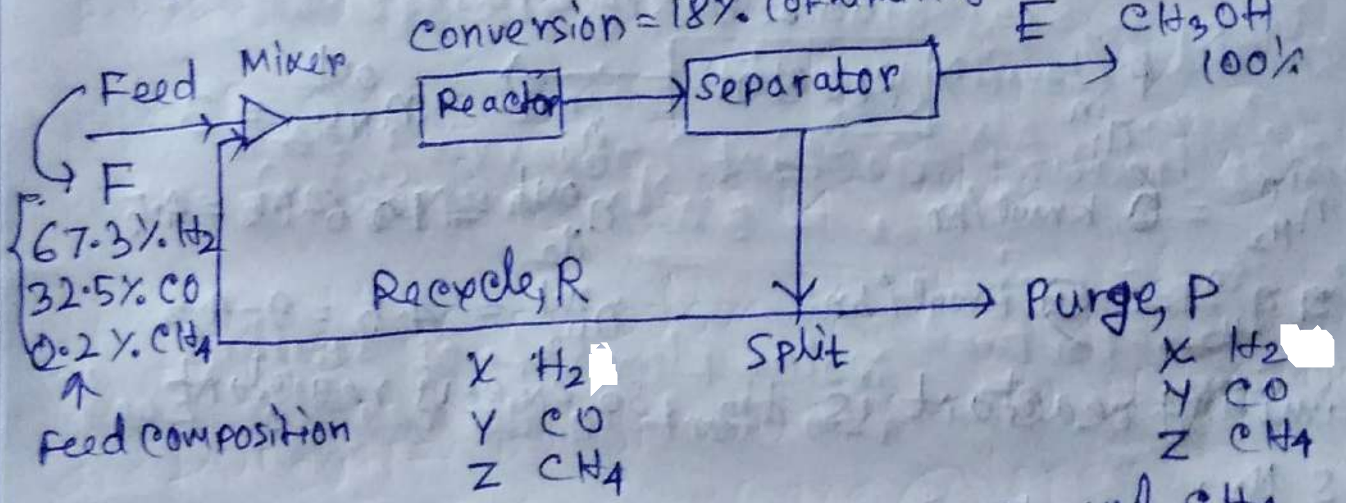
2nd case study

Material balance equation with chemical reaction Recycle and purging streams calculation

Consider a steady state open process where the following reaction takes place.

$$CO + 2H_2 \rightarrow CH_3OH$$

The preliminary flowsheet of the process is given by.



X, Y, Z are mole fractions of H_2O, CO and CH_4 respectively in the recycle/purge stream.

The purge stream is used to maintain the CH_4 concentration in the exit stream from the separator (R+P+E).

where, Z = 0.032

Now $\underset{-1}{CO} + \underset{-2}{2H_2} \rightarrow \underset{+1}{CH_3OH}$

Stoichiometric co-efficient ν_i of species, i: $\nu_{CO} = -1$; $\nu_{H_2} = -2$; $\nu_{CH_3OH} = 1$

-ve for reactant; +ve for Product

Material balance of stoichiometric reactor is given by $\boxed{n_i^{out} = n_i^{in} + \nu_i \xi}$

n_i^{out} and n_i^{in} are molar flow rates of ~~inlet~~ outlet stream and inlet stream respectively

ξ = extent of reaction.

$$\therefore \xi = \frac{n_i^{out} - n_i^{in}}{\nu_i}$$

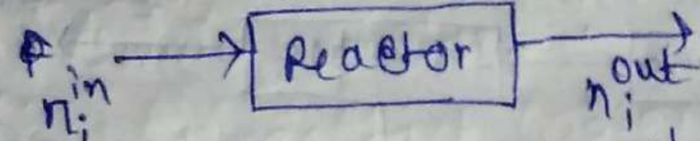
consider another reaction

$$3H_2 + N_2 \rightleftharpoons 2NH_3$$

$\nu_i = -3 \quad -1 \quad +2$

Now 6 Kmol/hr N_2, 9 kmol/hr H_2 are in the feed stream

50% conversion



$n_{NH_3}^{out} = 3$

$n_{N_2}^{in} = 6$ kmol/hr $\quad \therefore n_{N_2}^{out} = 6 - 1.5 = 4.5$

$n_{H_2}^{in} = 9$ kmol/hr $\quad n_{H_2}^{out} = 4.5 = 9 - 4.5$

Limiting reactant is H_2, so excess reactant is N_2.

$$\xi = \frac{n_{N_2}^{out} - n_{N_2}^{in}}{-1} = \frac{4.5 - 6}{-1} = 1.5$$

$$\xi = \frac{n_{H_2}^{out} - n_{H_2}^{in}}{-3} = \frac{4.5 - 9}{-3} = 1.5$$

$$\xi = \frac{n_{NH_3}^{out} - n_{NH_3}^{in}}{2} = \frac{3 - 0}{2} = 1.5$$

So, extent of reaction is 1.5 in all species. consideration, and is constant for a specific single reaction.

Now, come to the main reaction or problem component balance for different species in the mixer, reactor and separator system are written in form of $\eta_i^{out} = \eta_i^{in} + \upsilon_i \xi$.

$$\boxed{CO:}\ [E+R+P]_{CO} = [R+F]_{CO} + \upsilon_{CO}\xi$$

⇓ CO molar flow rate in reactor outlet.

⇓ CO molar flowrate in reactor inlet.

↘ volume change contribution

$$\therefore\ Y\cancel{R} + YP = Y\cancel{R} + 0.325F - 1\xi$$

$$\Rightarrow\ YP - 0.325F + \xi = 0 \quad - \text{(i)}$$

$$\boxed{H_2:}\ X\cancel{R} + XP = X\cancel{R} + 0.673F - 2\xi$$

~~$\Rightarrow XP + 0.673F$~~

$$XP - 0.673F + 2\xi = 0 \quad - \text{(ii)}$$

~~N_2: ZP~~

$$\boxed{CH_4:}\ Z\cancel{R} + ZP = \cancel{R}Z + 0.02F$$

As CH_4 is not reacting (inert)

$\xi\upsilon_i = 0$ volume change contribution is zero.

$$Z = 0.032$$

$$0.032P = 0.02F$$

$$\Rightarrow\ 0.032P - 0.02F = 0 \quad - \text{(iii)}$$

$$\boxed{CH_3OH:}\ E \times 1 = 0 + \xi \times 1 \quad - \text{(iv)}$$

$$E = \xi \quad - \text{(iv)}$$

composition equation is:

$$x + y + z = 1 - ⑤$$

$$x + y + z - 1 = 0 - (V)$$ $z = 0.032$

Fractional conversion in the reactor is 18 %.

$$\frac{-\upsilon_{LR}\xi}{n_{LR}^{reactor\ feed}} = 0.18$$

υ_{LR} = Stoichiometric coefficient of limiting reactant.

CO is limiting reactant (observing feed composition).

$\therefore \upsilon_{LR} = -1$

$n_{LR}^{reactor\ feed}$ = Molar flow rate of limiting reactant in the reactor feed

$$= RY + 0.325F$$

$$\therefore \frac{-(-1)\xi}{RY + 0.325F} = 0.18$$

$$\Rightarrow 0.18RY + 0.18 \times 0.325F - \xi = 0 - (VI)$$

So six independent equation. (6).

no. of variables are F, E, R, P, X, Y, ξ ⑦

DOF (degree of freedom) = no. of variables − no. of equation

$$= 7 - 6 = ①$$

Take ① basis. F = 100 kmol/hr

Equation 3 will be ruled out

as $0.032P - 0.02F = 0$

$\Rightarrow P = \frac{0.02 \times 100}{0.032} = 6.25$ kmol/hr.

as there is only one variable P, in the equation.

$\therefore$ no. of equation will be $= 6 - 1 =$ ⑤.

no. of variables will be $= 7 - 2 =$ ⑤

$\underline{\underline{DOF = 0}}$

$6.25y + \xi - 32.5 = 0$ – (i) ①

$6.25y + 2\xi - 67.3 = 0$ – (ii) ②

$E - \xi = 0$ – (iv) ③

$x + y + 0.032 - 1 = 0$ – (v) – ④

$0.18Ry - \xi + 32.5 \times 0.18 = 0$ – (vi) – ⑤

Take initial guess $E = 50$; $R = 50$;

$x = 0.9$, $y = 0.1$; $\xi = 100$.

Solve by Newton Method. after $\underline{19}$ iterations

Solution is converged upto $f < 10^{-10}$ order accuracy.

$E = 31.25$. kmol/hr

$R = 705.55$ kmol/hr

$x = 0.768$ (unit less)

$y = 0.2$ (unitless)

$\xi = 31.25$ kmol/hr

only nonlinear term in the set is in eq ⑤

$$\overset{\text{that is} \rightarrow \text{nonlinear term}}{\underline{0.18 R \dot{y}}} - \rho + 32.5 \times 0.18 = 0 .$$

If R is known the set of equation becomes a linear algebraic equation set.

then ~~0.18~~ say $R = 100$ kmol/hr

and 5 set of linear equations are solved by Matrix (algebraic linear) solver.

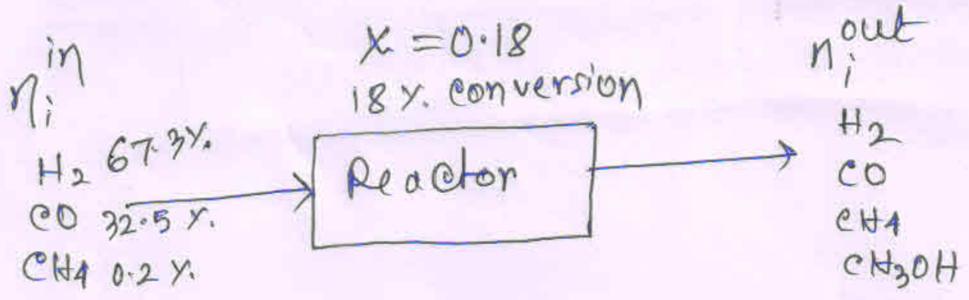
~~$[A] X_{sol} = B$~~ .

~~$X_{sol} = B A^{-1}$~~ .

$$A X = B$$

$$\underline{\underline{X = A^{-1} B}}$$

Solved by Gauss elimination, Gauss seidel, cholesky decomposition. etc.



i = species.

$$CO + 2H_2 \rightarrow CH_3OH$$
$$\upsilon_i \quad -1 \quad -2 \quad +1$$

υ = stoichiometric coefficient

CO is Limiting reactant
H_2 " excess reactant } → 32.5% CO will be reacted with 65% H_2.

H_2 composition is 67.3%

∴ % Excess H_2 = $(67.3 - 65)/65 \times 100\%$

$$\therefore \boxed{n_i^{out} = n_i^{in} + \xi \upsilon_i} \quad \text{—(i)}$$

so, 4 composition balance will be there.

Material valance of reactor

Molar chang term due to chemical reaction [ξ = Extent of reaction]

$$\therefore \xi = \frac{n_i^{out} - n_i^{in}}{\upsilon_i} \quad \text{—(ii)}$$ from equation (i)

if i = CO. that is limiting reactant

$$\Rightarrow \xi = \frac{n_{CO}^{out} - n_{CO}^{in}}{\upsilon_{CO}} = \frac{n_{CO}^{out} - n_{CO}^{in}}{n_{CO}^{in}} \quad \frac{n_{CO}^{in}}{\upsilon_{CO}}$$

or $\xi = -\frac{x\, n_{CO}^{in}}{\upsilon_{CO}}$ where x = conversion (fractional)

$$x = \frac{-n_{CO}^{out} + n_{CO}^{in}}{n_{CO}^{in}} = \frac{n_{CO}^{in} - n_{CO}^{out}}{n_{CO}^{in}}$$

if we replace CO with LR.
where LR = Limiting reactant

$$\boxed{x = \frac{-\upsilon_{LR}\,\xi}{n_{LR}^{in}} = \frac{-\upsilon_{LR}\,\xi}{n_{LR}^{Reactor\ feed}}} \quad \text{—(iii)}$$

①

$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$ — ① Reaction

ϑ_i : -1 $\quad -1 \quad +1 \quad +1$ (stoichiometric coefficient.)

$C_6H_6 + 2Cl_2 \rightarrow C_6H_4Cl_2 + 2HCl$ — ②

$-1 \quad -2 \quad +1 \quad +2$

1st reaction having extent of reaction, ξ_1

2nd " " " " " , ξ_2

Take 100 kmol/hr of benzene in the reactor inlet ∴ (Fresh feed + Recycle) of benzene = 100 kmol/hr

∴ Flowrate of chlorine in the reactor inlet $= \frac{100}{0.9} = 111.11$ kmol/hr

Benzene is excess reactant, Cl_2 is excess reactant.

∴ If 100% conversion of Cl_2

then 111.11 kmol/hr Cl_2 will be reacted.

with $= 111.11 \times \frac{2}{3}$ kmol/hr Benzene,

$= 74.07$ kmol/hr Benzene

But over all Benzene conversion is = 55.3%.

So, converted benzene molar flowrate

$= 0.553 \times 100$

$= 55.3$ kmol/hr.

So product stream having Benene flowrate

unreacted benzene $= 100 - 55.3 =$

$= 44.7$ kmol/hr (Reactor outlet)

② 4P.–
~~so, overall Cl_2 converted of flowrate~~

② so, overall Cl_2 conversion flowrate $= 44.7 \times \frac{3}{2}$

$= 67.05$. kmol/hr

so, product stream having Cl_2 flowrate

$\boxed{\text{reactor outlet}}$ $\underline{\text{Unreacted } Cl_2}$ $= 111.11 - 67.05$

$= \underline{44.06}$. kmol/hr.
(Reactor outlet)

∴ Monochlorobenze flowrate in

$\boxed{\text{reactor outlet}}$ = converted benzene flowrate $\times \frac{1}{2}$

$= 55.3 \times \frac{1}{2} = \underline{27.65}$ kmol/hr

di chrolrobenzene flowrate in

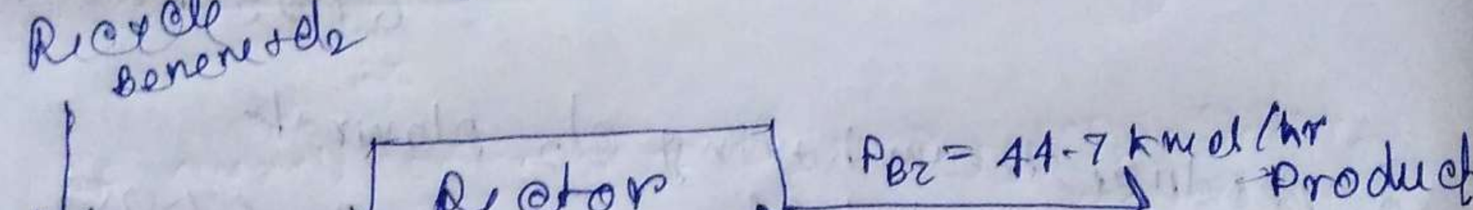
$\boxed{\text{reactor outlet}}$ = converted benzene $\times \frac{1}{2}$ kmol/hr

$= 55.3 \times \frac{1}{2} = \underline{27.65}$.

③ HCl Molar flowrate in reactor outlet

$= 27.65 + 2 \times 27.65$ kmol/hr

$= 82.95$ kmol/hr



$F_{Cl_2} = 111.11$ kmol/hr

$F_{Bz} = 100$ kmol/hr

$P_{Cl_2} = 44.06$ kmol/hr

$P_{MCLB} = 27.65$ kmol/hr

$P_{DCLB} = 27.65$ kmol/hr

$P_{HCl} = 82.95$ kmol/hr

F = Feed flow rate
P = Product flowrate
Bz = Benzene (suffix)
DCLB = Dichlorobenzene ("
MCLB = Mono chlorobenzene.

Mole fraction of Benzene in Feed $x_{Bz}^F = \frac{100}{100 + 111.11}$

" " " Chlorine " " $x_{Cl_2}^F = \frac{111.11}{100 + 111.11}$

Mole fraction of Benzene in product Stream $x_{Bz}^P = \frac{44.7}{227.01}$

" " " chlorine " " " $x_{Cl_2}^P = \frac{44.06}{227.01}$

" " " MCLB " " " $x_{MCLB}^P = \frac{27.65}{227.01}$

" " " DCLB " " " $x_{DCLB}^P = \frac{27.65}{227.01}$

" " " HCl " " " $x_{HCl}^P = \frac{82.95}{227.01}$

④ Generalized material balance for Multiple reactions

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl \quad — ①$$

$$-1 \qquad -1 \qquad +1 \qquad +1$$

$$C_6H_6 + 2Cl_2 \rightarrow C_6H_4Cl_2 + 2HCl \quad — ②$$

$$-1 \qquad -2 \qquad +1 \qquad +2$$

ξ_1 = extent of 1st reaction

ξ_2 = extent of 2nd reaction.

Flowrates of inlet and outlet streams are related to each others by foollowing balance equations.(material balance).

$\boxed{\text{Bz:}}$ $n^{out}_{BZ} = n^{in}_{BZ} + \xi_1 \upsilon^1_{BZ} + \xi_2 \upsilon^2_{BZ}$ — (i)

$\upsilon^1_{BZ} = -1$ and $\upsilon^2_{BZ} = -1$ are stoichiometric coeffs. of reaction ① & ② respectively.

$\boxed{\text{Cl}_2\text{:}}$ $n^{out}_{Cl_2} = n^{in}_{Cl_2} + \xi_1 \upsilon^1_{Cl_2} + \xi_2 \upsilon^2_{Cl_2}$ — (ii)

$\upsilon^1_{Cl_2} = -1 ; \upsilon^2_{Cl_2} = -2$

$\boxed{\text{MCBL:}}$ $n^{out}_{MCBL} = n^{in}_{MCBL} + \xi_1 \upsilon^1_{MCBL}$ — (iii)

$\upsilon^1_{MCBL} = +1 ; \upsilon^2_{MCBL} = 0 ;$

$\boxed{\text{DCBL:}}$ $n^{out}_{DCBL} = n^{in}_{DCBL} + \xi_2 \upsilon^2_{DBCL}$ — (iv)

$\upsilon^2_{DBCL} = 1 ; \upsilon^1_{DCBL} = 0 ;$

$\boxed{\text{HCl:}}$ $n^{out}_{HCl} = n^{in}_{HCl} + \xi_1 \upsilon^1_{HCl} + \xi_2 \upsilon^2_{HCl}$ — (v)

$\upsilon^1_{HCl} = +1 ; \upsilon^2_{HCl} = 2 ;$ - -

⑤ Now f(conversion) = $f(\xi_1, \xi_2)$.

If overall conversion of Bz is x_{Bz} (Bz is Limitting reactant here)

$$\frac{-\upsilon^1_{Bz}\xi_1 - \upsilon^2_{Bz}\xi_2}{n^{in}_{Bz}} = x_{Bz} \quad - \text{(vi)}$$

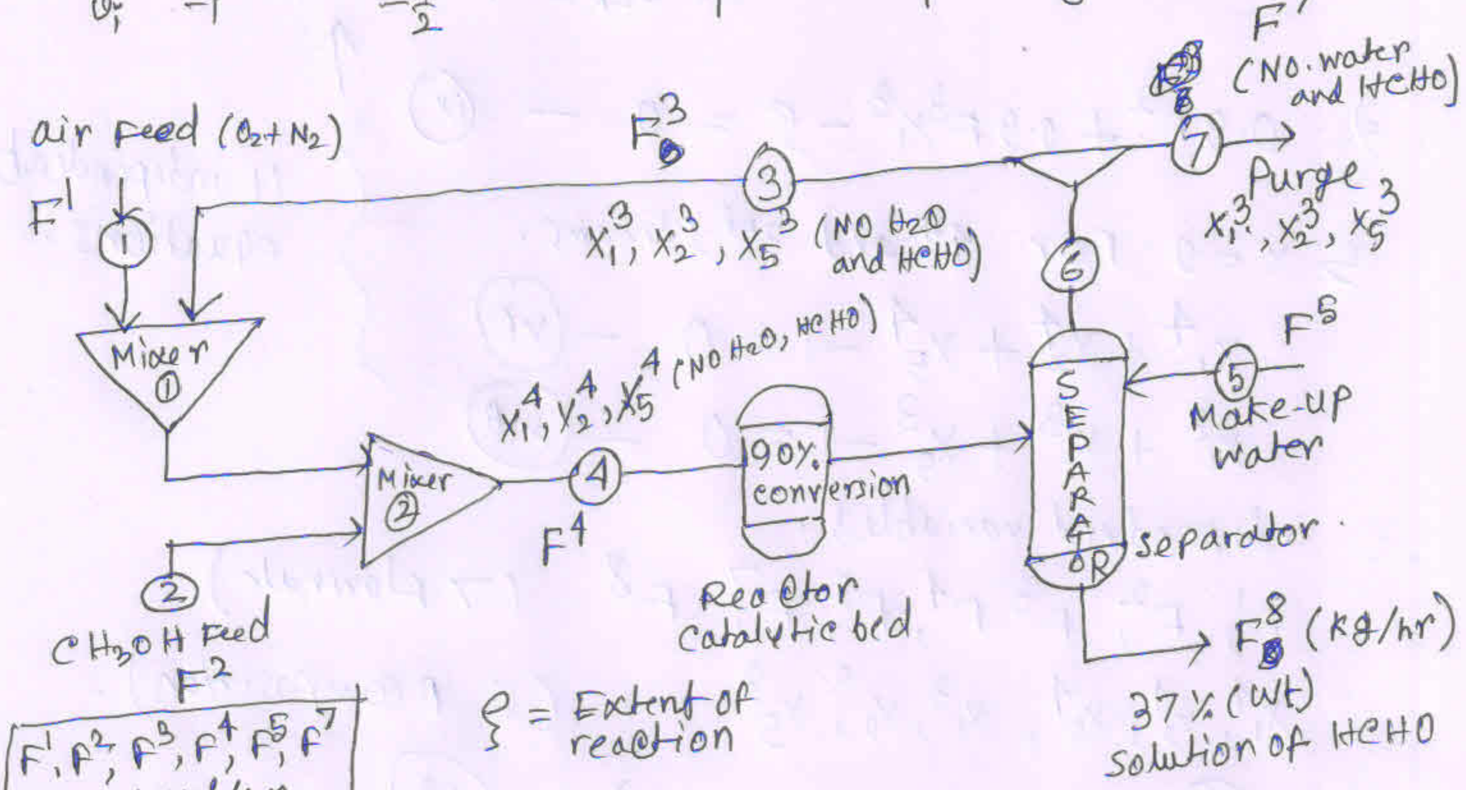
If overall conversion of Cl_2 is x_{Cl_2} (Cl_2 is Limiting reactant here)

$$\frac{-\upsilon^1_{Cl_2}\xi_1 - \upsilon^2_{Cl_2}\xi_2}{n^{in}_{Cl_2}} = x_{Cl_2} \quad - \text{(vii)}$$

Methanol oxidation

$$(N_2)\ CH_3OH + \tfrac{1}{2}O_2 \xrightarrow{catalyst} HCHO + H_2O\ \ (N_2)$$

$i =$	1	2	3	4	5
υ_i	-1	$-\frac{1}{2}$	1	1	0



$F^1, F^2, F^3, F^4, F^5, F^7$ are in kmol/hr and F^8 is in kg/hr.

ξ = Extent of reaction

Mixer before reactor (Mixer 2)

CH_3OH: $F^2 + F^3x_1^3 = F^4x_1^4$ — (i)

O_2: $0.21F^1 + F^3x_2^3 = F^4x_2^4$ — (ii)

~~HCHO: $F^3x_3^3 = F^4x_3^4$ — (iii)~~

N_2: $0.79F^1 + F^3x_5^3 = F^4x_5^4$ — (iii)

{input F^1, F^2, F^3}
{output F^4}

Reactor separator

CH_3OH: $(F^3+F^7)x_1^3 = F^4x_1^4 + \xi(-1)$. — (iv)

O_2: $(F^3+F^7)x_2^3 = F^4x_2^4 - \frac{1}{2}\xi$ — (v)

HCHO: $\cancel{(F^3+F^7)x_3^3}$ $F^8\frac{0.37}{30} = \cancel{F^4x_3^4}^{\,0} + \xi$ — (vi)

H_2O: $F^8\frac{0.63}{18} = F^5 + \xi$ — (vii)

N_2: $(F^3+F^7)x_5^3 = F^4x_5^4$ — (viii)

{input F^5, F^4}
{output F^3, F^7, F^8}

Conversion = F(ξ)

∴ $-\frac{\upsilon_{LR}\xi}{F^2+F^3x_1^3} = 0.9$ [CH_3OH is limiting reactant]

∴ $\upsilon_{LR} = -1$

⇒ $0.9F^2 + 0.9F^3x_1^3 - \xi = 0$ — (ix)

Σx = 0 for 4th and 3rd streams.

$x_1^4 + x_2^4 + x_5^4 - 1 = 0$ — (x)

$x_1^3 + x_2^3 + x_5^3 - 1 = 0$ — (xi)

11 independent equations.

∴ independent variables.

$F^1, F^2, F^3, F^4, F^5, F^7, F^8$ (7 flowrate).

$x_1^4, x_2^4, x_5^4, x_1^3, x_2^3, x_5^3$ → (6 composition).

∴ (13) → (13)

∴ DOF = No. of variable − no. of equation

$= 13 - 11 = \cancel{1}\ (2)$

Take F^1 and F^2 as basis (or specify F^1 and F^2).

Take $F^1 = 100$ kmol/hr

$F^2 > \frac{100}{21} \times 50 \Rightarrow F^2 > 238.09$ kmol/hr] Note *

Take $F^2 = 250$ or $F^2 = 300$ kmol/hr.

For each trial of F^2, simulate the flowsheet and evaluate maximum or optimum F_8 (product).

*Note → [100 kmol/hr of CH_3OH in F^1 is reacting with $\frac{100}{2} = 50$ kmol/hr of O_2 for 100% conversion.

∴ 50 kmol of O_2 = $\frac{100}{21} \times 50$ kmol/hr = 238.09 kmol/hr of air ($O_2 + N_2$). Air must be in excess, so $F^2 > 238.09$ kmol/hr

Energy Balance of Unit Operations

Module-1

Arnab Karmakar

BIT Mesra, Ranchi

Macroscopic energy balance

It requires evaluation of changes in the thermodynamic enthalpy function over the range of process conditions.

Case I Real gases (Ethylene, propylene, refinery gases)

Enthalpy departure function → $H'(T,V) = PV - RT + \int_V^{\infty}\left[\left(P - T\frac{\partial P}{\partial T}\right)_V\right] dV$

RKS (Redlich-Kwong-Soave) equation of state

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} - \frac{da}{dT}\frac{1}{V(V+b)}$$

$$\frac{da}{dT} = -0.653812 R\sqrt{\frac{T_c}{P_c}}\,\alpha(\omega)\sqrt{\frac{a(T)}{T}}$$

$$H'(T,V) = PV - RT + \frac{(a - T\,da/dT)}{b}\ln\left[1+\frac{b}{V}\right]$$

$$\Delta H = \Delta H^0 + H_2' - H_1' \quad \text{[1, 2 are process conditions]}$$

$$\Delta H^0 = \int_{T_1}^{T_2} C_p\, dT \quad \text{[standard state enthalpy changes → Ideal gas]}$$

Case II Liquids and solids.

Equation of state

$$H = H(T_0, P_0) + \int_{T_0}^{T}\left[\frac{\partial H}{\partial T}\right]_P dT + \int_{P_0}^{P}\left[\frac{\partial H}{\partial P}\right]_T dP$$

$$H = \underbrace{\int_{T_0}^{T} C_p\, dT}_{\text{constant } P} + \underbrace{\int_{P_0}^{P}\left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP}_{\text{constant } T} \quad [H(T_0, P_0) = 0]$$

$$H = \int_{T_0}^{T} C_p\, dT + \int_{P_0}^{P} V[1 - \alpha_T T]\, dP$$

$$\alpha_T = \frac{1}{V_T}\left(\frac{\partial V}{\partial T}\right)_P = \text{coefficient of thermal Expansion.}$$

substituting pvT relation

$$H = \int_{T_0}^{T} C_p\,dT + \frac{V_0}{k} e^{\alpha_T (T-T_0)} \left[1-\alpha_T T\right]\left[1-e^{-k(P-P_0)}\right]$$

$$k = \frac{1}{-V_T}\left(\frac{\partial V}{\partial P}\right)_T$$ = isothermal compressibility.

Case III Ideal gas mixture

$$N H^0 = \sum_{i=1}^{N} N_i H_i^0(T).$$ N = number of gas molecules.

↓ standard state enthalpy of gas mixture.

↑ pure standard state enthalpy.

~~H^{ideal}~~ $$\sum_{i=1}^{N} x_i H_i^0(T) = H^0$$

Case IV Non-ideal gas mixtures.

Departure functions can be used for mixture. Equation of state (cubic). is adopted for the mixture.

Case-V Non ideal liquid solutions

~~It results~~ Mixing of liquids into a non-ideal solution results ~~ke~~. significant heat effect. Enthalpy of mixing results heat of solution. and is defined as

$$\Delta H_{mix} = H - \sum_{i=1}^{N} x_i \tilde{H}_i^{+}(T, P).$$

HCL-H_2O system, the energy balance equation is

$$N_a Q_{soln} = (N_a + N_w)\,\Delta H_{mixing}$$
$$= (N_a + N_w)H - N_a H_a^{+} - N_w H_w^{+}$$

w = water, a = acid ~~kcal~~
(solvent) (solute) Q = kcal/mol HCl

H = Enthalpy of the mixture

N_a = mole of acid, N_w = Mole of water.

$$r = \frac{N_w}{N_a}, \quad \tilde{H}_a = \tilde{\Delta} H_{mixing,a} + H_a^+$$

$$\tilde{H}_w = \tilde{\Delta} H_{mixing,w} + H_w^+$$

Now $H = x_a \tilde{H}_a + x_w \tilde{H}_w$

$$H = x_a \tilde{\Delta} H_{mixing,a} + x_w \tilde{\Delta} H_{mixing,w} + H_a^+ x_a + H_w^+ x_w .$$

For HCl-water system.

$$Q_{sol} = -\frac{1}{0.0821 (N_a/N_w)^2 + 0.0208 (N_a/N_w) + 0.0563} .$$

$$\tilde{\Delta} H_{mixing,a} = \tilde{H}_1 - H_1^+ = \frac{-0.0821x^2(1-x)^2 + 0.0563(1-x)^4}{(0.0821x^2 + 0.0208\,x(1-x) + 0.0563(1-x)^2)^2}$$

$$\Delta H_{mixing,w} = \tilde{H}_2 - H_2^+ = \frac{2(0.0821)x^3(1-x) + 0.0208x^2(1-x)^2}{(0.0821x^2 + 0.0208x(1-x) + 0.0563(1-x)^2)^2}$$

For $x = 0.5$, $X = 1$ $Q_{sol} = -6.28141$ kcal/mol

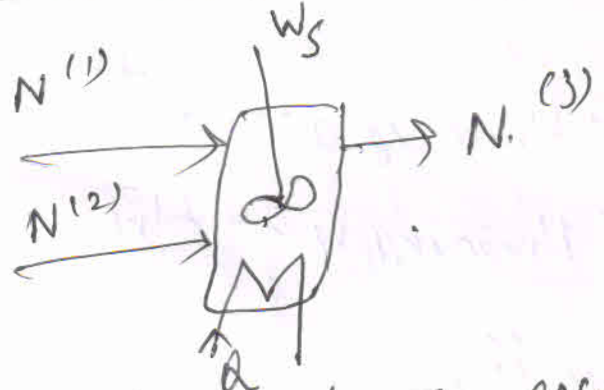
$\tilde{\Delta} H_{mix,a} = -1.01797$ kcal/mol ~~delmix~~

$\tilde{\Delta} H_{mix,w} = 7.299347$ 〃

$\Delta H_{mix} = 3.140704$ kcal/mol HCl

Energy flow and First Law

Mixing of Two liquids streams at different temperatures and concentration.



nonideal-mixture. ($HCl + H_2O$, $H_2SO_4 + H_2O$) etc.

$$Q = \sum_{i=1}^{N} \left(N_i^{(3)} \tilde{H}_i^{(3)} - N_i^{(1)} \tilde{H}_i^{(1)} - N_i^{(2)} \tilde{H}_i^{(2)} \right)$$

$$Q = \sum_{i=1}^{N} \left[N_i^{(3)} \left(\tilde{H}_i^{(3)} - H_i^{\dagger} \right) - N_i^{(1)} \left(\tilde{H}_i^{(1)} - H_i^{\dagger} \right) - N_i^{(2)} \left(\tilde{H}_i^{(2)} - H_i^{\dagger} \right) \right]$$

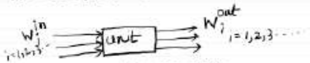
$H_i^{\dagger}$ = Enthalpy of species i in its pure reference state. Here reference state is same, when reference state is different

$$Q = \sum_{i=1}^{N} \left[N_i^{(3)} \left(\tilde{H}_i^{(3)} - H_i^{\dagger} \right) - N_i^{(1)} \left(\tilde{H}_i^{(1)} - H_i^{\dagger} \right) - N_i^{(2)} \left(\tilde{H}_i^{(2)} - H_i^{\dagger} \right) \right] + N^{(3)} \int_{T^*}^{T_3} C_p^{(3)} dT - N^{(1)} \int_{T^*}^{T_1} C_p^{(1)} dT - N^{(2)} \int_{T^*}^{T_2} C_p^{(2)} dT$$

Referance: DELANCEY, G., Principles of Chemical Engineering Practice, Wiley, 2013.

Energy balance

Macroscopic view.



Conservation of Energy

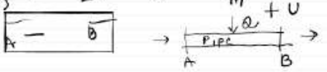
Rate of Accumulation of Energy = rate of Energy in − rate of Energy + Potential Source

at Steady State

rate of energy in − rate of energy out + Source = 0

Total energy = kinetic energy + Potential Energy + mechanical Energy + internal Energy.

Energy/unit mass } $\rightarrow E = \frac{1}{2}v^2 + gh + \frac{PV}{m} + U$



at Steady State $\Sigma\, \text{energy}_A - \Sigma\, \text{energy}_B + Q = 0$

$u + \frac{PV}{m}$ = Enthalpy / unit mass

$u + \frac{P}{\rho} = H_i$ (enthalpy/unit mass)

(internal + mechanical) energy = Enthalpy

ρ = density (kg/m³)

E = KJ / kg

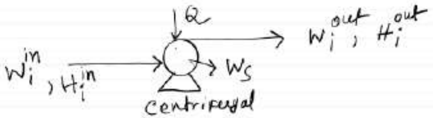
$W\left(\frac{kg}{hr}\right)$

$$E_i = \frac{1}{2}v_i^2 + gh_i + H_i$$

$$\Sigma W_i^{in} E_i - \Sigma W_i^{out} E_i + Q = 0$$

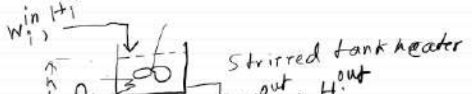
$\frac{KJ}{hr}$ KJ/hr $\frac{KJ}{hr} \simeq$ Watt

$\frac{KJ \times 1000}{3600} \simeq$ Kwatt



$$Q + \Sigma W_i^{in}\left[H_i^{in} + \frac{1}{2}v_i^{in} + gh^{in}\right] =$$

$$= \Sigma W_i^{out}\left[H_i^{out} + \frac{1}{2}v_i^{out} + gh^{out}\right] + W_S$$



$h \leq$

$$Q + \Sigma W_i^{in} H_i^{in} = \Sigma W_i^{out} H_i^{out}$$

in case of negligible change of mechanical Energy. $\left(\frac{PV}{m}\right) \rightsquigarrow \frac{P}{\rho}$

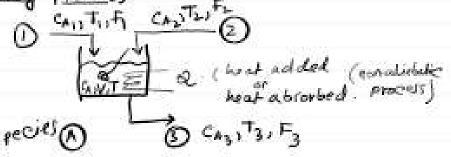
$$Q + \Sigma u_i^{in} W_i^{in} = \Sigma u_i^{out} W_i^{out}$$

internal Energy } $\rightarrow u = f(T)$

$= f(mc_p T)$

$$Q + \Sigma T_i^{in} c_{p_i}^{in} W_i^{in} = \Sigma T_i^{out} c_{p_i}^{out} W_i^{out}$$

Mixing process



one species Ⓐ

overall mass balance

$$\frac{d(\rho V)}{dt} = \rho_1 F_1 + \rho_2 F_2 - \rho_3 F_3 \quad \text{— (i)}$$

$\rho_1 = \rho_2 = \rho_3 = \rho$ (density) kg/m³

F = volumetric flowrate (m³/s)

V = volume of Liquid in the vessel.

$$\frac{dV}{dt} = F_1 + F_2 - F_3 \quad \text{— (ii)}$$

$V = Ah$

A = cross sectional area of the vessel

$$\frac{dV}{dt} = A\frac{dh}{dt}$$

h = height of Liquid.

Component balance

$$\frac{d(C_A V)}{dt} = C_{A1}F_1 + C_{A2}F_2 - C_{A3}F_3 \quad \text{— (iii)}$$

C_A = concentration of species A in the reactor

For well stirred system.

$C_A = C_{A3}$ (no distribution)

$$\frac{d(C_{A3}V)}{dt} = C_{A1}F_1 + C_{A2}F_2 - C_{A3}F_3 \quad \text{— (iv)}$$

$$\Rightarrow C_{A3}\frac{dV}{dt} + V\frac{dC_{A3}}{dt} = C_{A1}F_1 + C_{A2}F_2 - C_{A2}F_3$$

replace $\frac{dV}{dt} = F_1 + F_2 - F_3$

$$\Rightarrow C_{A3}(F_1 + F_2 - F_3) + V\frac{dC_{A3}}{dt} = C_{A1}F_1 + C_{A2}F_2 - C_{A3}F_3$$

$$\Rightarrow V\frac{dC_{A3}}{dt} = F_1(C_{A1} - C_{A3}) + F_2(C_{A2} - C_{A3}) \quad \text{— (v)}$$

If no. of component = n.
so, n number of component material balance will be needed.

Energy balance equation

$$E = U + K + P + \overset{O}{M}$$

$$dE = dU + \cancel{dK}^{0} + \cancel{dP}^{0} + \cancel{dM}^{0}$$

Total energy

U = internal
K = kinetic
P = potential
M = mechanical

} → Energy

$dU = f(T)$.

$dE = dH$ → H = enthalpy

$H = U + PV$

$dH = dU + \cancel{d(PV)}^{0}$

J/s (watt)

$$\frac{d(\rho V H_3)}{dt} = \rho(F_1H_1 - F_2H_2) - \rho_3F_3H_3 + Q \quad \text{— (vi)}$$

H = Enthalpy (J/kg).

$\rho V H$ in (J) | Q = heat addition or absorption in watt.

$$\frac{dV}{dt} = F_1 + F_2 - F_3 \quad \text{— (ii)}$$

$$\frac{d(VC_{A3})}{dt} = F_1(C_{A1} - C_{A3}) + F_2(C_{A2} - C_{A3}) \quad \text{— (v)}$$

$$\frac{d(VH_3)}{dt} = F_1H_1 + F_2H_2 - F_3H_3 \pm Q \quad \text{— (vi)}$$

} independent equations

State variables are

V, C_{A3}, H_3

if density is not constant

$$\frac{d(V\rho)}{dt} = F_1\rho_1 + F_2\rho_2 - F_3\rho_3 \quad \text{— (ii)}$$

$$\frac{d(V\rho H_3)}{dt} = \rho_1F_1H_1 + \rho_2F_2H_2 - \rho_3F_3H_3 \pm Q \quad \text{— (v)}$$

If V = constant (is not changing with time)
↗ Flow is steady

$0 = F_1 + F_2 - F_3$

$$F_3 = F_1 + F_2 \quad \text{— (vii)}$$

in this case
eqn. (v), (vi) & (vii)
are independent equation.
or one can replace $F_3 = F_1 + F_2$ and make
it 2 independent equation

If equations $\underbrace{\text{(ii) (v), (vi)}}_{3\ \text{equations.}}$ are considered

For single comonent.

∴ For n components.
independent material balance
will be n component balance
+
2 (overall balance & Energy balance)

no. of. independent equations $\underline{n+2}$ →

1) Energy balance of mixing

$$\Delta H_{mixing,total} = \sum x_i \, \Delta H_{mixing,i}$$

i = water (2), HCl (1).

$$\Delta H_{mixing} = x_1 \, \Delta H_{mixing,1} + x_2 \Delta H_{mixing,2}$$

$$= H - H_1^{+} x_1 - H_2^{+} x_2$$

H_1^{+}, H_2^{+} are enthalpies of species for pure components.
H is enthalpy of mixture after mixing.

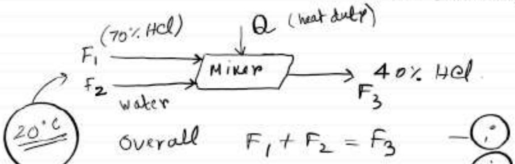
$$\Delta H_{mixing} = \underbrace{(\tilde{H}_1 - H_1^{+})}_{\Delta H_{mixing,1}} x_1 + \underbrace{(\tilde{H}_2 - H_2^{+})}_{\Delta H_{mixing,2}} x_2$$

$$\Delta H_{mixing,1} = f_1(x)$$

$$\Delta H_{mixing,2} = f_2(x).$$

$\tilde{H}_i$: enthalpy of species i after mixing.

$Q = \Delta H_{mixing,total}$
→ heat of solution



Overall $F_1 + F_2 = F_3$ — (i)

HCl : $0.7 F_1 = F_3 \, 0.4$ — (ii)

3 variables, 2 equations

DOF = 3 − 2 = ①

Specify $F_1 = 100$ kg.

$$F_3 = \frac{0.7}{0.4} \times F_1 = 175 \text{ kg}$$

$$F_2 = 75 \text{ kg}.$$

2) Energy balance (isothermal, non-adiabatic operation).

(heat duty)
$$Q = F_3 \times 0.4 \times \Delta H_{mixing,a}(\overset{=0.4}{x}) + F_3 \times 0.6 \times \Delta H_{mixing,w}(\overset{=0.4}{x})$$
$$- F_1 \times 0.7 \times \Delta H_{mixing,a}(\overset{=0.7}{x}) - F_1 \times 0.3 \times H_{mixing,w}(\overset{=0.7}{x})$$
$$- F_2 \times 1 \times [\Delta H_{mixing,a}(\overset{=0}{x})]$$
$$+ \int_{298.16}^{293.16} [F_3 \, 0.4 \, C_p(a,T) \, dT + F_3 \, 0.6 \, C_p(w,T) \, dT]$$
$$- \int_{298.16}^{293.16} [F_1 0.7 \, C_p(a,T) + F_1 0.3 \, C_p(w,T)] \, dT$$
$$- \int_{298.16}^{293.16} F_2 \, C_p(w,T) \, dT$$

$T^{*} = 298.16$ K = 25°C is reference Temperature

w = water
a = acid

C_p = specific heat capacities
$= a + bT + cT^2 + dT^3$
a, b, c, d are constants

Q = Heat duty (kJ/hr) or (kcal/hr)

F (kg/hr)

ΔH_{mix} (kJ/kg) or (kcal/kJ)

Q (kJ/hr) or (kcal/hr)

C_p kJ kg^{-1} hr^{-1}

heat of Solution kcal/kg
↓
kJ/kg

1 J = 0.000239 cal

1 cal = 4.184 J.

Energy Balance of Chemical Reactions

Module-1

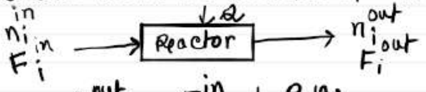
Arnab Karmakar

BIT Mesra, Ranchi

Energy balance in unit process (Chemical reactor)

$\hookrightarrow$ Macroscopic view.

First come to material balance of reactor



Q = heat duty.

$$F_i^{out} = F_i^{in} + \xi \vartheta_i \quad - (i)$$

$$F_i^{out} = F_i^{in} + \frac{x_A F_A^{in}}{(-\vartheta_A)} \vartheta_i \quad - (ii)$$

A = Limiting reactant

$$\xi = \frac{x_A F_A^{in}}{(-\vartheta_A)} = f(x_A)$$

F_A^{in} = molor flow rate of limiting reactant in the reactor inlet.

x_A = conversion of Limiting reactant

ϑ_A = Stoichiometric coefficient of Limiting reactant.

Energy balance.

$$Q + \sum F_i^{in} H_i^{in}(T^F, P^F) = \sum F_i^{out} H_i^{out}(T^{out}, P^{out}) \quad - (iii)$$

Q + total rate of heat in = total rate of heat out.

T^F, P^F = Feed Temperature & Pressure

T^{out}, P^{out} = outlet temperature & pressure.

H = enthalpy.

replace equation ( ) (F_i^{out}) in equation (iii)

$$Q + \sum F_i^{in} H_i^{in} = \sum \left[F_i^{in} + \frac{x_A F_A^{in}}{(-\vartheta_A)} \vartheta_i \right] H_i^{out}$$

$$Q - \sum \frac{x_A F_A^{in}}{(-\vartheta_A)} \vartheta_i H_i^{out} = \sum F_i^{in} (H_i^{out} - H_i^{in})$$

$$Q + \frac{x_A F_A^{in}}{(-\vartheta_A)} \left[\sum \vartheta_i H_i^{out} \right] = \sum F_i^{in} (H_i^{out} - H_i^{in}) \quad (iv)$$

In case of ideal Solution $\longrightarrow$ $\Delta H = \int_{T_1}^{T_2} C_p \, dT$

$$H_i^{out} - H_i^{in} = \int_{T_F}^{T_{out}} C_p \, dT$$

$$Q + \frac{x_A F_A^{in}}{(-\vartheta_A)} \left[-\sum \vartheta_i H_i^{out} \right] = \sum \int_{in}^{out} F_i^{in} c_p \, dT$$

$$Q + \frac{x_A F_A^{in}}{(-\vartheta_A)} \left[-\sum \vartheta_i H_i^{out} \right] = \sum F_i^{in} \int_{T_F}^{T^{out}} c_p \, dT \quad - (v)$$

in case of adiabatic operation

$$Q = 0$$

$$i = \text{①}\quad \text{②}\quad \text{⑤}\quad \text{③}\quad \text{④}$$

$$\underset{1}{CH_3OH} + \tfrac{1}{2}O_2 \xrightarrow[\text{catalyst (Fe+Mo)}]{(N_2)} HCHO + H_2O \;(N_2)$$

gas phase catalytic reaction.

Feed: 8 mol% CH_3OH
10 mol% O_2
82 mol% N_2

		ϑ_i
1	CH_3OH	-1
2	O_2	$-\frac{1}{2}$
3	$HCHO$	1
4	H_2O	1
5	N_2	0

$y_1 = 0.08$
$y_2 = 0.1$
$y_3 = 0$
$y_4 = 0$
$y_5 = 0.82$

$T^{out} = 425°C$
Adiabatic operation
$Q = 0$
unkown is $\boxed{T^{in}}$?
> From energy balance

at standard state at (kJ/mol)

$$H_f = \begin{bmatrix} -200.6 \\ 0 \\ -108.0 \\ -241.8 \\ 0 \end{bmatrix} \begin{array}{l} \cdots CH_3OH \\ \cdots O_2 \\ \cdots HCHO \\ \cdots H_2O \\ \cdots N_2 \end{array} \Bigg\} \; 0 \text{ heat of reaction with respect to standard state.}$$

$$C_p(k,T) = \sum_{j=1}^{5} a_k T^{j-1} = a_1 + a_2 T + a_3 T^2 + a_4 T^3$$

$\to$ (J/(mol·K))

$$a = \begin{array}{c} CH_3OH \\ O_2 \\ HCHO \\ H_2O \\ N_2 \end{array} \begin{bmatrix} 19.038 & 9.146\times10^{-2} & -1.218\times10^{-5} & -8.034\times10^{-9} \\ 25.460 & 1.519\times10^{-2} & -0.715\times10^{-5} & 1.311\times10^{-9} \\ 22.791 & 4.075\times10^{-2} & -0.713\times10^{-5} & -8.695\times10^{-9} \\ 28.883 & -0.157\times10^{-2} & 0.808\times10^{-5} & -2.872\times10^{-9} \\ 32.218 & 0.192\times10^{-2} & 1.055\times10^{-5} & -3.593\times10^{-9} \end{bmatrix}$$

Energy balance

$$Q + \frac{\boxed{X_A}\, y_A^F}{(-\vartheta_A)}\left[-\sum \vartheta_i H_i(T^{out}, P^{out})\right] = \sum y_i^F \left[H_i(T^{out}, P^{out}) - H_i(T^F, P^F)\right]$$

X_A → fractional conversion of limiting reactant

$$= \sum y_i^F \int_{T^{in}}^{T^{out}} C_p\, dT$$

$Q = 0$ For adiabatic operation

$T^{in} = ?$
$T^{out} = 425°C = 425 + 273.15\ K$

Limiting reactant is CH_3OH

$X_A = 100\% = \text{①}$ fractional conversion

$-\vartheta_A = -(-1) = 1$
$y_A^F = 0.08$

$$0.08\left[-\sum_{i=1}^{5} \vartheta_i H_{f_i} - 0.001 \sum_{i=1}^{5} \vartheta_i \int_{298}^{425+273.15} C_p(i,T)\, dT\right]$$

H_{f_i} → standard state (25°C = 298 K)

0.001 → conversion factor for J/(mol-K) to kJ/(mol-K).

$$= +\boxed{0.001} \sum_{i=1}^{5} \vartheta_i \int_{T^{in}}^{425+273.15} C_p(i,T)\, dT$$

0.001 → conversion factor for J/(mol-K) to kJ/(mol K)

T^{in} unknown, polynomid of T^{in}

Energy balance equation $= F(T^{in})$

= polynomial of order ④

There is ② real solution.

$T^{in} = \{103.95\ °C,\ 4834.8\ °C\}$

4834.8 °C unrealistic

$T^{in} = \underline{103.95°C}$

2nd case consider

non-adiabatic operation

$T^{in} = 150°C$
$T^{out} = 425°C$

Calculate Q (kJ/mol-K)