MODELING

The flow information of a process is divided into two stages. In the first stage, the model is compared with the real process and considered adequate if the discrepancy is negligible. In the second stage, the expectations are compared with the indications of the model. This procedure is called modelling. Modelling is subdivided into two groups

- Physical modelling
- Matthematical modelling

Deterministic versus Stochastic Processes

Deterministic Process:- In this process the observables take on a continuous set of values in a well defined manner, while the output variable representative of the process is uniquely determined by the input variable. These processes can be adequately described by classical analysis and numerical methods. An example is the process that takes place in a simple continuous stirred tank reactor (CSTR)

Stochastic Process: This is a process in which observeables change in a random manner and often discontinuously. The output variable is not directly related to the input variable. These processes are described in terms of statistics and probabilistic theory. Examples are the contact-catalytic process (packed beds) in which the yield of the product diminishes with decrease in the activity in the catalyst as it ages with time and the pulse properties in trickle bed reactor.

A deterministic process is one whose behavior (with respect to time, since it is of interest) can be predicted exactly. However, for stochastic processes, we can predicts its response only approximately. Simple CSTR and hydrocracking in trickle bed reactors are quoted as examples for deterministic and stochastic processes, respectively.

Physical Modelling

In physical modelling, the experiment is carried out directly on the real process. The process of interest is reproduced on different scales, and the effect of physical features and linear dimension is analysed. The experimental data are reduced to relationships involving dimensionless groups made up of various combinations of physical quantities and linear dimensions. The relationships determined with this dimensionless presentation can be generalized to classes of events having these dimensionless groups or similarity criteria. The resulting models are also known as 'empirical models.'

Let us consider the example of designing an industrial heat exchanger. For computing the heat transfer co-efficient that are required for designing a heat exchanger, the empirical correlations (of the form $Nu = c\,Re^{m}\,Pr^{n}$, where Nu is the Nusselt number, Re is the Reynolds number and Pr is the Prandtl number; c, m and n are constant and the exponents are determined experimentally) developed at laboratory scale could be scaled up to industrial scale using geometric and dynamic similarities.

Mathematical Modelling

A mathematical model of real chemical process is a mathematical description which combines experimental facts and establishes relationship among the process variable. Mathematical Modelling is an activity in which qualitative and quantative representations or abstractions of the real process is reduced to its bare essentials, and the resultant scheme is described by a mathematical formalism selected according to the complexity of the process. The resulting models could be either analytical or numerical in nature depending upon the method used for obtaining the solution.

Mathematical Modelling involves three steps:-

- Formalization- the mathematical description of the process under investigaton (Mathematical formulation)
- Development of an algorithm for the process
- Testing of the model and the solution derived from it.

Process Simulation requires the following skills

- A sound understanding of engineering fundamentals
- Modelling skills
- Computational skills.

Energy or momentum transport

Newton's law of viscosity

$$\tau = -\mu\left(\frac{dv}{dx}\right)$$

Can be rearranged to

$$\tau = -\nu\left(\frac{d(v\rho)}{dx}\right)$$

where $v\rho$ is the momentum per unit volume. In addition, in term of driving force it becomes

$$2f\rho v^2 = \frac{g_c D\Delta P}{L}$$

Heat transport (heat flux)

Fourier's law of heat conduction

$$\frac{Q}{A} = -k\left(\frac{dT}{dx}\right)$$

Can be rearranged to

$$\frac{Q}{A} = -\alpha\left[\frac{d(\rho C_p T)}{dx}\right]$$

where $\rho C_p T$ is the heat per unit volume. Similarly heat flux Q/A in terms of driving force ΔT

$$\frac{Q}{A} = -h_T \Delta T$$

Mass Transport (mass flux)

Fick's first law of diffusion

$$q_m = J = -D\left(\frac{dc}{dx}\right)$$

Can be rearranged to

$$q_m = J = -D\left[\frac{d(c)}{dx}\right]$$

where c is the mass per unit volume. Similarly, mass flux N_A in terms of driving force Δc is

$$N_A = -k_c \Delta c$$

Electricity transport:- Ohm's law $i = -\frac{1}{\rho}\left(\frac{dv}{dx}\right)$

Chemical System Modelling

Performing experiments and, analysis and interpreting the results are general practice in all applied sciences research. This may be done quantitavely by taking accurate measurements of the system variables, which are subsequently analysed and correlated, or quanlilavety by investigating the general behaviour of the system in terms of one variable influencing another.

- Introduction of the mathematical principles at the earliest possible stage, done by looking for an idealized mathematical model of the system.
- The collection of all relevant physical information in the form of conservation laws and rate equation. The conservation laws of chemical engineering are material balances, heat balances, and other energy balances, whilst the rate equation express the relationship between flow rate and driving force in the field of fluid flow, heat transfer, and diffusion of matter.

- Steady State Simulation
- Dynamic Simulation

Model Formulation Principles

Basis- The bases for mathematical models are the fundamental physical and chemical laws such as the laws of conservation of mass, energy and momentum.

Assumption:- Valid assumptions play key role in the mathematical modeling. Engineering judgement is important for selection of valid assumption.

Mathematical consistency of model:- once all the equation of the mathematical model have been written, to make sure that the number of variables equals the number of equation. The so-called degree of freedom of the system much be zero in order to obtain a solution. If this is not true, the system is underspecified or overspecified and something is wrong with the formulation of the problem.

Solution of the model equation:- The available solution techniques and tools must be kept in mind as a mathematical model is developed. An equation without any way to solve it is not worth much.

Verification:- Comparison of the simulation results with real situation or experimental results is very important in modelling aspect. If results are well agreement with experimental ones, model equation and simulation process are elegant, if not then further modification or improvement of model equation and simulation process are required.

Fundmental laws used in Modelleng : Some fundamental laws of Physics and chemistry are required for modelling a chemical engineering system. These laws are reviewed in their general time dependent form.

Continuity equations :-

Total continuity equation (mass balance) : The principle of Conservation of mass applied to a dynamic system is

[Mass flow into system] − [mass flow out of system] = [time rate of change of mass inside system]

ODE/ PDE sometimes require for mass balance equation.

Component continuty equations (component balances) : Unlike mass, chemical components are not consered. Again, to be precise, the total mass for a reacting/non reacting system is conserved.

The component continuity equation of the ith chemical species of the system is

[Flow of moles of ith component into system] − [Flow of moles of ith component out of system] + [rate of formation of moles of ith component from chemical reactions] = [time rate of change of moles of ith component inside system]

Energy equation :- The first law of thermodynamics puts forwards the principle of conservation of energy. writen for a general open system (where flow of material in and out of the system can occur) it is

Flow of interal, kintetic and potential energy into system by convection of diffusion] − [flow of internal, kinetic and potential energy out of system by convection or diffusion] + [heat added to system by conduction radiation, and reaction] − [work done by system on surroundings (shaft work and PV work] = [time rate of change of internal, kinetic, and potential energy inside system]

Equation of motion

According to Newton's second law of motion, force F is equal to mass M time acceleration a for a system with constant mass M ie.

$F = \frac{Ma}{g_c}$ where g_c is the conversion constant needed FPS and MKS units are used.

This is the basic relationship used in writing the equation of motion for a system. In a slightly more general form, where mass can vary with time $\frac{1}{g_c} \cdot \frac{d(Mv_i)}{dt} = \sum_{j=1}^{N} F_{ji}$

Transport equations:-

The equations discussed so far are the laws governing the transfer of momentum, energy and mass. These transport laws all have the form of a flux (rate of transfer per unit area) being proportional to a driving force (a gradient in velocity, temperature, or concentration).

Equation of state

In mathematical modelling we need equations for physical properties primarily density and enthalpy, as a function of temperature, pressure and composition.

Liquid density $\rho_L = f(P, T, x_i)$

vapor density $\rho_v = f(P, T, y_i)$

Liquid enthalpy $h = f(P, T, x_i)$

vapor enthalpy $H = f(P, T, y_i)$

Occasionally, these relationship have to be fairly complex to describe the system accurately. But in many cases simplification can be made without sacrificing much overall accuracy. Some of the simple enthalpy equations that can be used in energy balances are

$$h = c_p T$$

$$H = c_p T + \lambda$$

The next level complexity would be made the c_p's functions of temperature $h = \int_{T_0}^{T} c_p(T)\,dt$

A polynomial in T is often used for c_p

$$c_p(T) = A_1 + A_2 T$$

Then

$$h = \left[A_1 T + A_2 \frac{T^2}{2}\right]_{T_0}^{T} = A_1(T - T_0) + \frac{A_2}{2}(T^2 + T_0^2)$$

If heat of mixing effects are negligible, the pure-component enthalpies can be averaged

$$h = \frac{\sum_{j=1}^{NC} x_j h_j M_j}{\sum_{j=1}^{NC} x_j M_j}$$

where x_j is the mole fraction of the jth component, M_j is the molecular weight of jth component, and h_j is the pure component enthalpy of the jth component (energy per unit mass). The denominator is the average molecular weight of the mixture.

The simplest and most often used is the perfect gas law

$$PV = nRT$$

Rearranging to get an equation for the density ρ_v (kg/m³) of a perfect gas with molecular weight M, we get $\rho_v = \frac{nM}{} = MP/RT$

Equilibrium relations

The basis for the equations that give the conditions of a system when equilibrium conditions prevail is the second law of thermodynamics.

chemical equilibrium: Equilibrium occurs in a reacting system when

$$\sum_{j=1}^{NC} v_i \mu_j = 0$$

where v_j is the stoichiometric co-efficient of the jth component with reactant having a negative sign and product a positive sign and μ_j is the chemical potential of the jth component.

$$v_a A \overset{k_1}{\leftrightarrow} v_b B$$ (rate constant for reverse reaction k_2)

equilibrium whill occur when

$$v_b \mu_b - v_a \mu_a = 0$$

The chemical potential for a perfect gas mixture can be written as

$$\mu_j = \mu_j^0 + RT \ln P_j$$

where μ_j^0 is the standard chemical potential (or Gibbs free energy per mole), P_j is the partial pressure of the jth component, R is the perfect gas law constant and T is the absolute temperature

Further simplification can be dine

$$\ln\left(\frac{P_B^{v_b}}{P_A^{v_a}}\right) = \frac{v_a \mu_A^0 - v_b \mu_B^0}{RT}$$

The term in the parentheses on the left hand side is defined as the equilibrium constant K_p, which gives us the equilibrium ratios of products and reactants

$$K_p = \frac{P_B^{v_b}}{P_A^{v_a}}$$

Phase equilibrium: Equilibrium between two phases occur when The chemical potential of each component is the same in the two phases

$$\mu_j^{I} = \mu_j^{II}$$

where μ_j^{I} is the chemical potential of the jth component in phase I and μ_j^{II} is the chemical potential of the jth component in phase II.

Raoult's law:- Mixture that obey Raoult's law are called ideal mixture

$$P = \sum_{J=1}^{NC} x_j P_j^s$$ P_j^s = vapor pressure of pure component j

$$y_j = \frac{x_j P_j^s}{P}$$

$$\ln P_j^s = \frac{A_j}{T} + B_j$$

Relative volatility :- The relative volatility α_{ij} of component i to component j is defined as

$$\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j}$$

In a binary system the relative volatility α of the more volatile component compared with the less volatile component is

$$\alpha = \frac{y/x}{(1-y)/(1-x)}$$

$$y = \frac{\alpha x}{1+(\alpha-1)x}$$

K values: Equilibrium vaporization ratios of K values are widely used, particularly in the petroleum industry

$$K_j = \frac{y_j}{x_j}$$

The K's are function of temperature and composition and to a lesser extent pressure.

Activity co-efficients:- For non-ideal liquids, Raoult's law must be modified account for non-ideality in the liquid phase. The fudge factor use are called activity coefficient

$$P = \sum_{j=1}^{NC} x_j P_j^s \gamma_j$$

where γ_j is the activity co-efficient for the jth component. The activity co-efficient is equal to 1 if the component is ideal. The γ's are functions of composition and temperature.

chemical kinetics:- In modelling of chemical reactors, we must familiar with the basic relationship and terminology used in describing the kinetics (rate of reaction) of chemical reaction

Arrhenius temperature dependence: The effect of temperature on the specific reaction rate K is usually found to be exponential

$$K = \alpha e^{-E/RT}$$

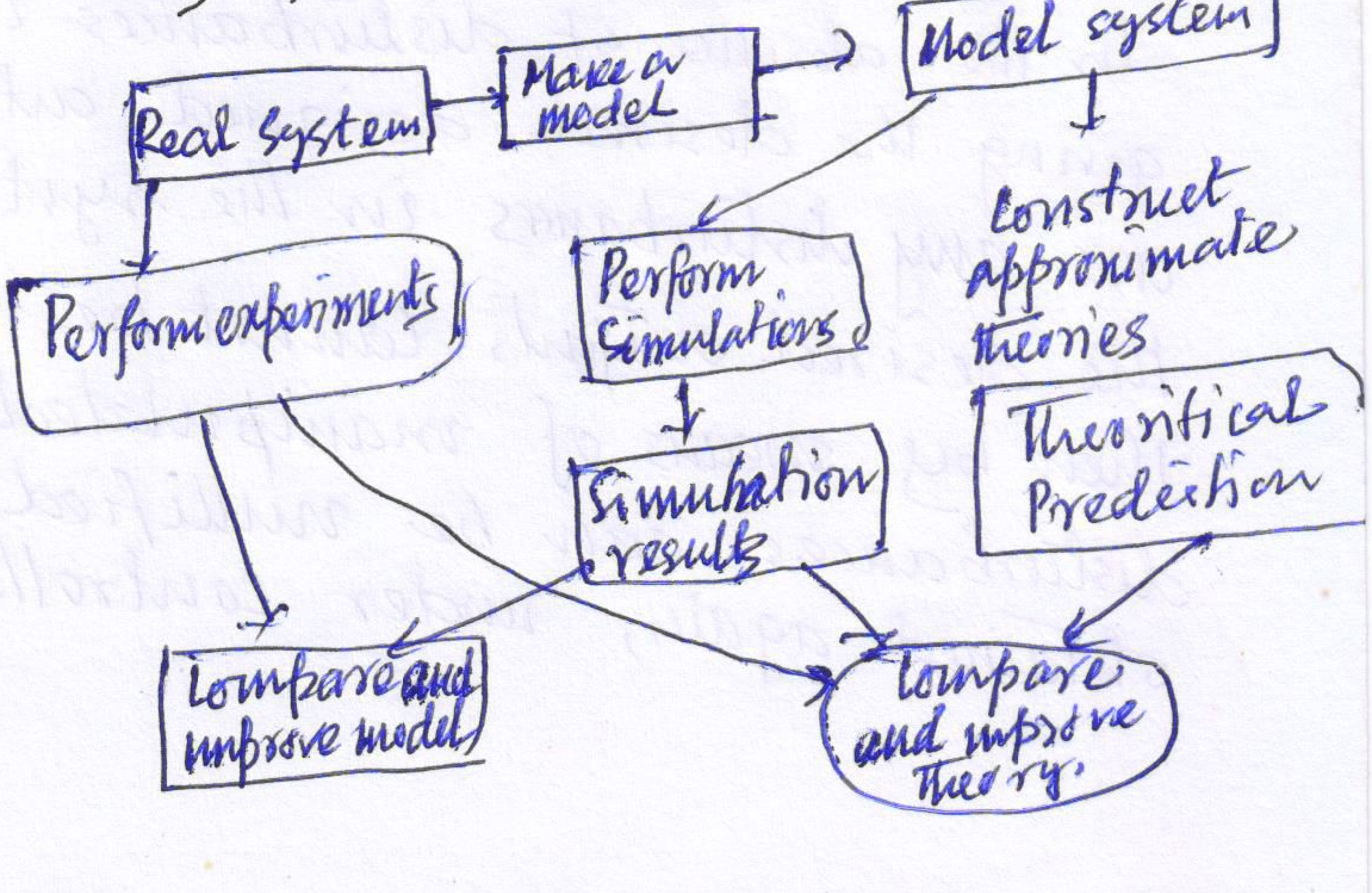
K = specific reaction rate

α = preexponential factor

E = activation energy

T = absolute temperature

R = perfect gas constant



Law of mass action :- Let us define an overall reaction rate R with the conventional notation

$$R = \frac{1}{\nu_j V}\left(\frac{dn_j}{dt}\right)_R$$

The stoichiometric co-efficient ν_j are positive for products of the reaction and negative for reactants.

A irreversible reaction in which components A and B react to form components C and D

$$\nu_a A + \nu_b B \xrightarrow{K} \nu_c C + \nu_d D$$

Then

$$R = \frac{1}{-\nu_a V}\left(\frac{dn_A}{dt}\right) = \frac{1}{-\nu_b V}\left(\frac{dn_B}{dt}\right)$$

$$= \frac{1}{-\nu_c V}\left(\frac{dn_c}{dt}\right) = \frac{1}{-\nu_d V}\left(\frac{dn_D}{dt}\right)$$

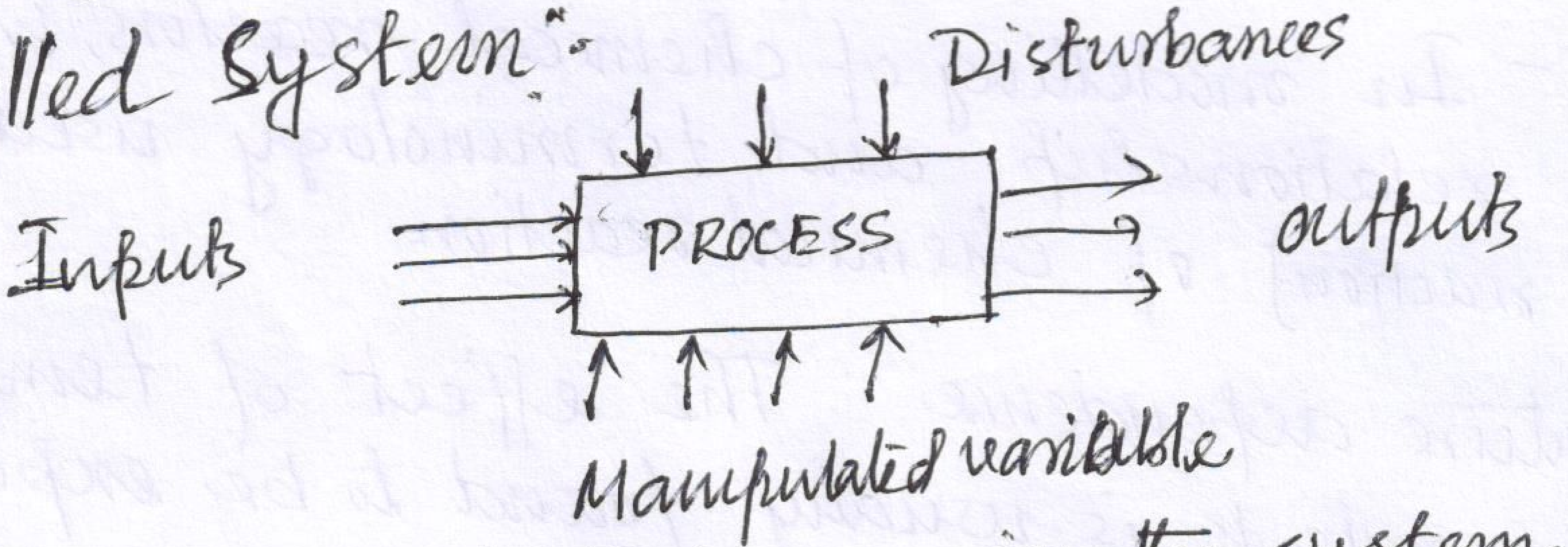
$$R = K_{(T)}(C_A)^a (C_B)^b$$

where C_A is the concentration of component A and C_B is the concentration of component B. The constant a, b are not, in general equal to stoichiometric co-efficients ν_a and ν_b. The reaction is said to be first order in A if $a = 1$. It is second order in A if $a = 2$. The constant a and b can be fractional numbers.

Cybernetics: Cybernetics is a science dealing with any system capable of perceiving, storing, and processing information for the purposes of optimum control.

Mathematical modelling, Computers, and cybernetics are interrelated. Computers are tools of cybernetics and mathematical modelling is the basic method of cybernetics

Controlled System:-

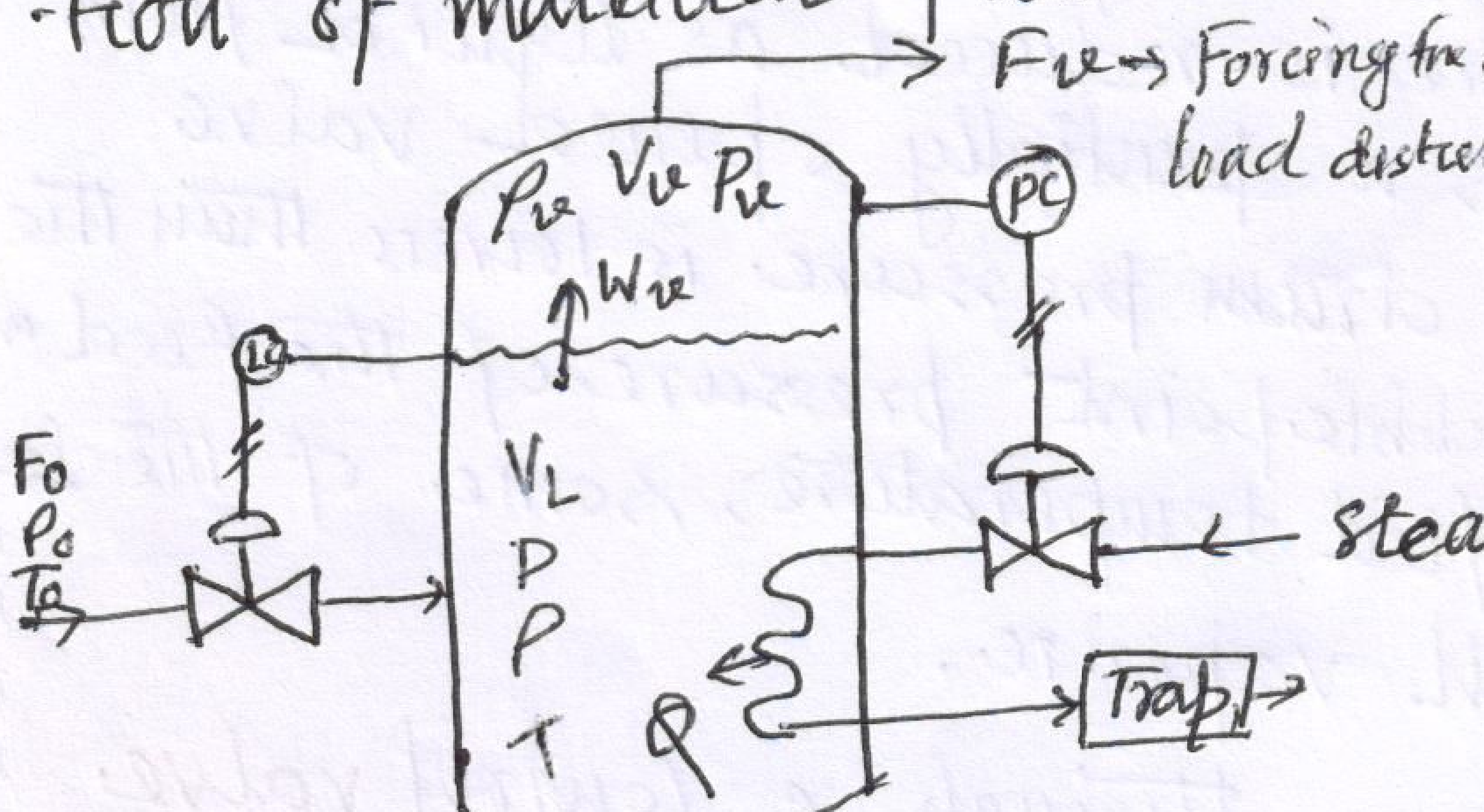


A Simple Controlled Chemical system

In the absence of disturbances in the system, the process runs smoothly, giving the desired designed outputs for given inputs. But if there are any disturbances in the system, the outputs will change and the desired outputs cannot be obtained for the given inputs. Then by means of manipulated variables, the effect of these disturbances can be nullified and the desired outputs can be obtained again, under controlled condition.

Single component vaporizer

Boiling system represent some of the most interesting and important operation in chemical process engineering. Conservation equation must be written for both the vapor and liquid phases. The basic problem is finding the rate of vaporization of material from the liquid phase into the vapor phase.



- A Steady state model (Neglect dynamics of both liquid and vapor phases

$$F_v \rho_v (H_v - h_0) = Q$$

H_v = Enthalpy of vapor leaving tank

h_0 = Enthalpy liquid feed

Heat losses and the mass of the tank walls are assumed negligible.

- Liquid phase dynamic model

We assume that volume of the vapor phase is small enough to make its dynamics negligible. (few moles of liquid vaporized) $P = P_v$, $W_v = \rho_v F_v$ vapor pressure relationship gives the pressure in the vaporizon at that temp.

Q, F_0, P, V_L, ρ_0 and T

$$Q = f_1(P) \quad \text{and} \quad F_0 = f_2(V_L)$$

liquid is assumed incompressible so that $C_v = C_p$

Total continuity $\rho \dfrac{dV_L}{dt} = F_0 \rho_0 - \rho_v F_v$

Energy $C_p \rho \dfrac{d(V_L T)}{dt} = \rho_0 C_p F_0 T_0 - \rho_v F_v (C_p T + \lambda_v) + Q$

State $\rho_v = \dfrac{MP}{RT}$

vapor pressure $\ln p = \dfrac{A}{T} + B$

* An energy equation for the liquid phase gives the temperature (as a function of time)

* The vapor-pressure relationship gives the pressure in the vaporizer at that temperature.

- Liquid and vapor dynamics model

$P = P_v$

$W_v = K_{MT}(P - P_v)$ Pheudo Mass transfer co-efficient (K_{MT})

The equation describing the system are

$PV = nRT$

equation of state

$W = nM$ → molecular weight

$\rho_v = \dfrac{W}{V} = \dfrac{nMP}{nRT}$

liquid phase

Total continuity $\rho \dfrac{dV_L}{dt} = \rho_0 F_0 - W_v$

Energy $\rho \dfrac{d(V_L U_L)}{dt} = \rho_0 F_0 h_0 - W_v H_L + Q$

vapor Pressure $P = e^{A/T} + B$

vapor phase

Total continuity $\dfrac{d(V_v \rho_v)}{dt} = W_v - F_v \rho_v$

Energy $\dfrac{d(V_v \rho_v U_v)}{dt} = W_v H_L - \rho_v F_v H_v$

$\rho_v = \dfrac{M P_v}{RT}$

U_L = internal energy of liquid at temp T

H_L = Enthalpy of vapor boiling off liquid

U_v = internal energy of vapor at temp T_v

H_v = enthalpy of vapor phase

$Q, F_0, V_L, W_v, T, V_v, \rho_v, T_v, P$ & P_v

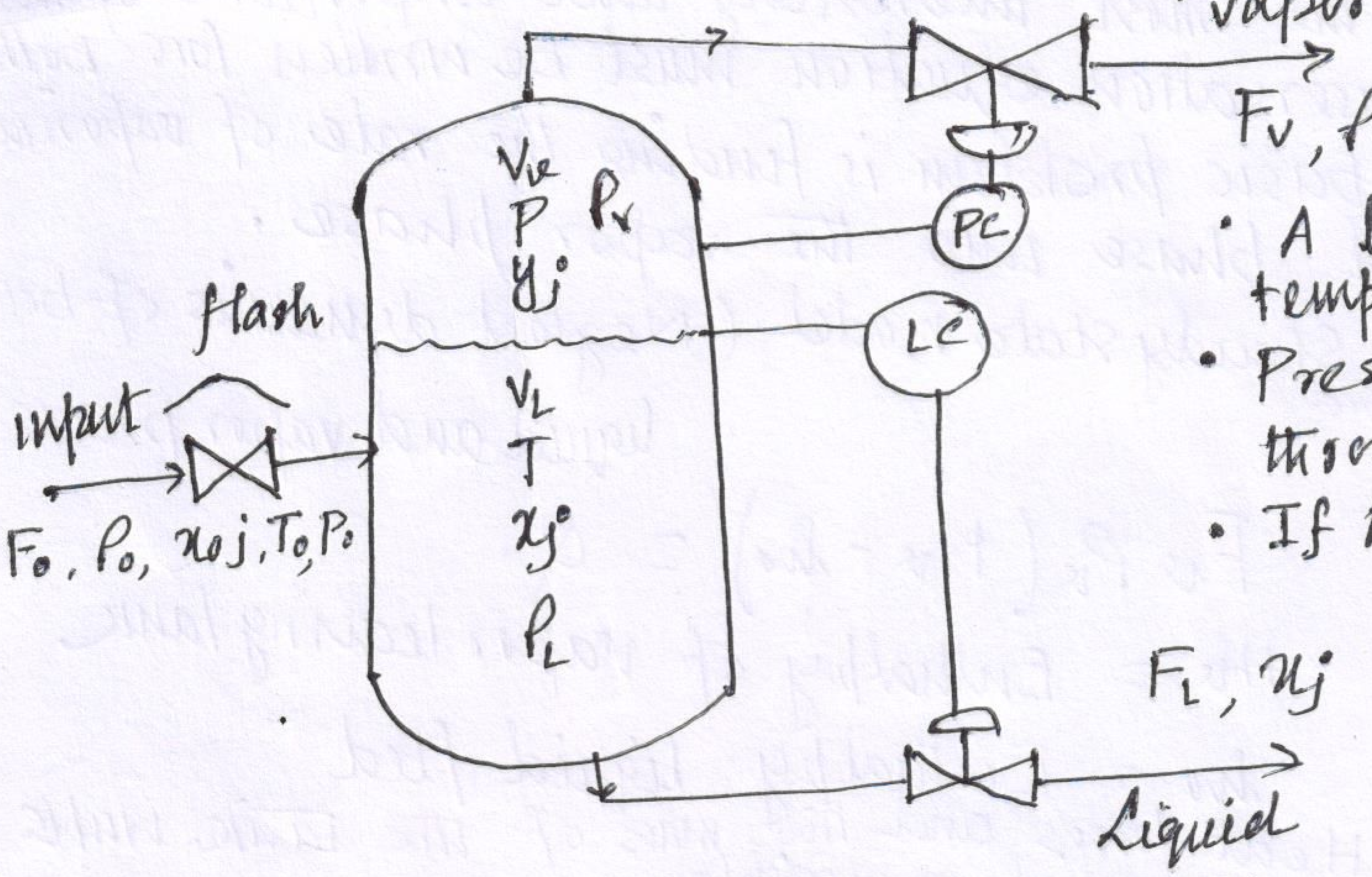
A physical constraint $V_L + V_v$ = total volume of tank

- Thermal equilibrium model

$T = T_v$

$$\rho C_p \frac{d(V_L T)}{dt} = \rho F_0 C_p T_0 - W_v (C_p T + \lambda_v) + Q$$

Multicomponent flash drum



- liquid - vapor system
- More than one compenent
- A liquid stream at high pressure and temperature is flash into a drum
- Pressure is reduced as liquid flows through a partially opened valve
- If the drum pressure is lower than the bubblepoint pressure of the feed at a feed temperature, some of the liquid will vaporize.

- Gas is drawn off the top of the drum through a control valve whose stem position is set by a pressure controller
- Liquid comes off the bottom of the tank on level control

Assumptions

No heat losses; adiabatic conditions

$\rho_L = f(x_j, T)$ known (density of water)

$\rho_v = \frac{M_v^{av} P}{RT}$ gas. density in the tank

$M_v^{av} = \sum_{j=1}^{N} M_j y_i$ The average molecular weight M_j = Molecular weight of the j^{th} component

P_0 should be high enough to prevent any vaporization of feed at its temperature T_0 and composition x_{0j}.

Elimmate dynamics

- P constant, steady state equations: vapor and liquid are assumed to be in equilibrium.

Continuity equation : $\rho_0 F_0 = \rho_v F_v + \rho_L F_L$

Component continuity equation: $\frac{\rho_0 F_0}{M_0^{AV}} x_{0j} = \frac{\rho_v F}{M_v^{AV}} y_j + \frac{\rho_L F_L}{M_L^{AV}} x_j$

vapor liquid equilibrium

$y_j = f(x_j, T, P)$

energy continuity equation $h_0 \rho_0 F_0 = H_v \rho_v F_v + h_L \rho_L F_L$

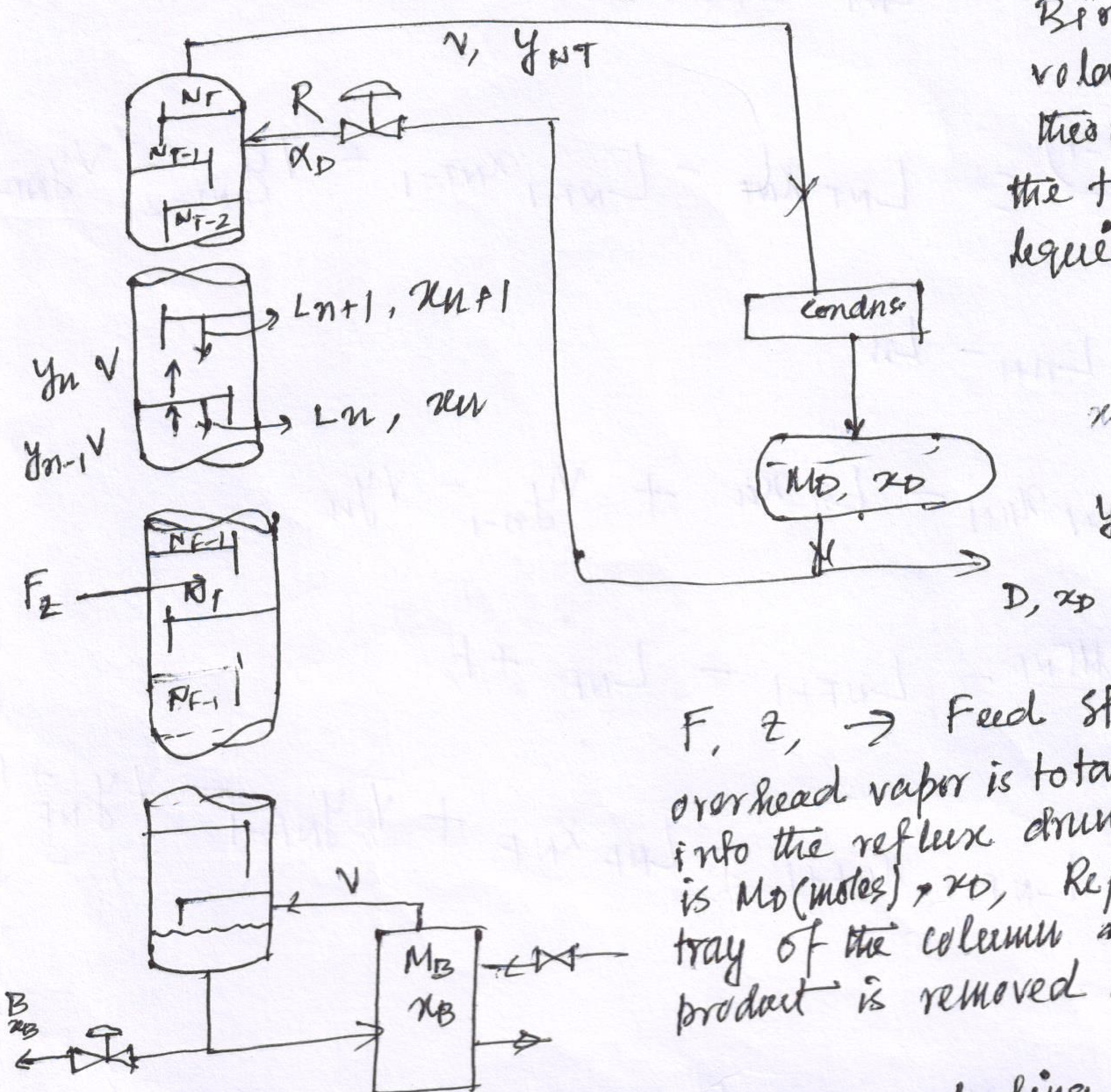
Thermal properties $h_0 = f(x_{0j}, T_0)$, $h_L = f(x_j, T)$, $H_v = f(y_j, T, P)$

Total continuity equation	1
Energy equation	1
Component continuity equation	NC-1
vapor. liquid equilibrium	NC
Densities of liquid and vapor	2
Thermal properties	2
The average molecular weights	2
Total	2NC+7

The number of variable is
$\rho_v, F_v, M_v^{av}, y_1 \cdots y_{NC-1}, \rho_L, \rho_v$
$M_L^{av}, x_1 \cdots x_{NC-1}, T, h_L, H = 9 + 2(NC-1)$

Initial values
P and all input properties.

Ideal Binary Distillation column.



Binary system with constant relative volatility throughout the column and theoritical trays, the vapor leaving the tray is in equilibrium with the liquid on the tray.

$$y_n = \frac{\alpha x_n}{1+(\alpha-1)x_n}$$

x_n = liquid composition on the n^{th} tray (mole fraction of more volatile component)

y_n = vapor composition on the n^{th} tray (mole fraction of more volatile comp)

α = relative volatility

F, z, → Feed stream, at saturated liquid. overhead vapor is totally condensed in a condenser and flows into the reflux drum, whose holdup ~~is totally~~ of liquid is M_D(moles), x_D, Reflux is pumped back to the top tray of the column at a rate R. overhead distillate product is removed at a rate D.

The liquid hold up on each tray including the downcomer is M_n.

Assumption: equimolal overflow

Heat losses up the column and temperature changes from tray to tray are assumed negligible.

the vapor and liquid rates through the stripping and rectifying sections will be constant under steadystate conditions.

Negligible vapor holdup, mean that the vapor rate through all trays of the column is the same $V = V_1 = V_2 = V_3 = \ldots = V_{NT}$

Francis weir formula relationship → $F_L = 3.33\, L_W (h_{ow})^{1.5}$

Where F_L = liquid flowrate over weir (ft^3/s) $M_n = f(L_n)$.

L_W = length of weir (ft)

h_{ow} = height of liquid over weir (ft)

Condenser and Reflux drum

Total continuity: $\frac{dM_D}{dt} = V - R - D$

Component continuity (more volatile component)

$$\frac{d(M_D x_D)}{dt} = V y_{NT} - (R+R)\, x_D$$

Top tray ($n = NT$)

Total continuity $\frac{dM_{NT}}{dt} = R - L_{NT}$

Component continuity

$$\frac{d(M_{NT} \cdot x_{NT})}{dt} = R x_D - L_{NT} x_{NT} + V y_{NT-1} - V y_{NT}$$

Next to Top Tray ($n = N_T - 1$)

Total continuity: $\frac{dM_{NT-1}}{dt} = L_{NT} - L_{NT-1}$

Component continuity:

$$\frac{d(M_{NT-1}\, x_{NT-1})}{dt} = L_{NT}\, x_{NT} - L_{NT-1}\, x_{NT-1} + V y_{NT-2} - V y_{NT-1}$$

n^{th} tray $\frac{dM_n}{dt} = L_{n+1} - L_n$

Component continuity

$$\frac{d(M_n x_n)}{dt} = L_{n+1}\, x_{n+1} - L_n x_n + V y_{n-1} - V y_n$$

Feed tray $(n = N_F)$

total continuity $\frac{dM_{NF}}{dt} = L_{NF+1} - L_{NF} + F$

Component continuity

$$\frac{d(M_{NF} \cdot z_{NF})}{dt} = L_{NF+1}\, x_{NF+1} - L_{NF}\, x_{NF} + V y_{NF-1} - V y_{NF} + FZ$$

First tray $(n=1)$

Total continuity: $\frac{dM_1}{dt} = L_2 - L_1$

Component continuity $\frac{d(M_1 x_1)}{dt} = L_2 x_2 - L_1 x_1 + V y_B - V y_1$

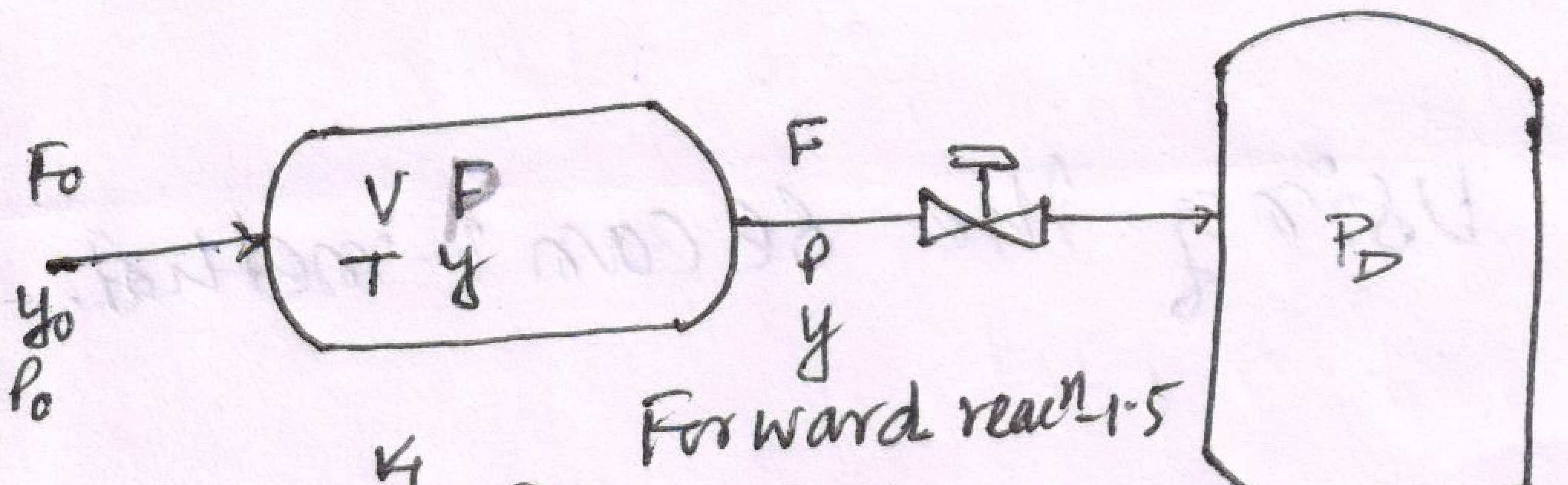
Reboiler and column base

Total continuity $\frac{dM_B}{dt} = L_1 - V - B$

Component continuity $\frac{d(M_B x_B)}{dt} = L_1 x_1 - V y_B - B x_B$

Two equation representing the level controllers on the controller base and reflux drum $D = f_1(M_D)$ $B = f_2(M_B)$

Gas phase, Pressurized CSTR



Forward reacⁿ 1.5

$$2A \underset{K_2}{\overset{K_1}{\rightleftarrows}} B$$ Backward → 1

Mole fraction of reactant A in the reactor y

The pressure inside the reactor is P (absolute)

Both P and y can vary with time

The volume of the reactor V is constant

Isothermal, Perfect gases

$$F = C_V \sqrt{\frac{P - P_D}{\rho}}$$

C_V is the valve sizing coefficient

Density varies with pressure and composition

$$\rho = \frac{MP}{RT} = \left[y M_A + (1-y) M_B\right] \frac{P}{RT}$$

where M = average molecular weight

M_A = molecular weight of reactant A

M_B = molecular weight of Product B

The concentration of reactant in the reactor is

$$C_A = \frac{Py}{RT}$$

Isothermal
Perfect gases

$$r_F = K_1 C_A^{1.5} = -\frac{1}{2V}\left(\frac{dn_A}{dt}\right) = \frac{1}{V}\left(\frac{dn_B}{dt}\right)$$

The overall reaction rate for the reverse reaction is

$$r_R = K_2 C_B = \frac{1}{2V}\left(\frac{dn_A}{dt}\right) = -\frac{1}{V}\left(\frac{dn_B}{dt}\right)$$

total and component continuity equation

$$V \frac{d\rho}{dt} = \rho_0 F_0 - \rho F$$

Component A continuity

$$V \frac{dC_A}{dt} = F_0 C_{A0} - F C_A - 2VK_1 C_A^{1.5} + 2VK_2 C_B$$

the 2 in the reaction term comes into from the stoichiometric coefficient of A

A fluid of constant density ρ is pumped into a cone-shaped tank of total volume $H\pi R^3/3$. The flow out of the bottom of the tank is proportional to the square root of the height of liquid in the tank. Derive the equation describe the system