

Chapter 1 : Fundamentals

1.1 Introduction

The objective of mathematical modeling is the development of sets of quantitative (mathematical) expressions that capture the essential aspects of an existing system. A mathematical model can assist in understanding the complex physical interactions in the system and the causes and effects between the system variables. Mathematical models are valuable tools since they are abstract equations that can be solved and analyzed using computer calculations. It is therefore safer and cheaper to perform tests on the model using computer simulations rather than to carry out repetitive experimentations and observations on the real system. This becomes vital if the real system is new, hazardous, or expensive to operate. Modeling, thus prevails the field of science, engineering and business. It is used to assist in the design of equipment, to predict behavior, to interpret data, to optimize resources and to communicate information.

1.2 Incentives for process modeling

In the chemical engineering field, models can be useful in all the phases, from research and development to plant operation. Models and their simulation are tools utilized by the chemical engineer to help him analyze the process in the following ways:

- *Better understanding of the process*

Models can be used to study and investigate the effects of various process parameters and operating conditions on the process behavior. It can also be used to evaluate the interactions of different parts of the process. This analysis can be carried out easily on a computer simulation without interrupting the actual process, thus avoiding any delay or upsets for the process.

- *Process synthesis and design*

Model simulation can be utilized in the evaluation of equipment's size and arrangements and in the study of alternative process flow-sheeting and strategies.

Furthermore, to verify the reliability and safety of the process design tests can be carried out even prior to plant commissioning.

- *Plant operators training*

Models can be used to train plant personnel to simulate startup and shutdown procedures, to operate complex processes and to handle emergency situations and procedures .

- *Controller design and tuning*

Models help in developing and evaluating better controller structure and configuration. Dynamic simulation of models is usually employed for testing and assessing the effectiveness of various controller algorithms. It is worthwhile to mention that models play a vital part in designing advanced model-based control algorithms such as model predictive and internal model controllers .Moreover it is a common practice of many control engineers to determine the optimum values of the controller settings through dynamic simulation .

- *Process optimization*

It is desirable from economic standpoint to conduct process optimization before plant operation to determine the optimum values of the process key parameters or/and operating conditions that maximizes profit and reduces cost. Process optimization is also performed during process operation to account for variations in the feed-stock and utilities market and for changing environmental regulations.

It is worth mentioning that despite all their usefulness, models at their best are no more than approximation of the real process since they do not necessarily incorporate all the features of the real system . Therefore modeling can not eliminate completely the need for some plant tests, especially to validate developed models or when some poorly known parameters in the process need to be experimentally evaluated.

Models can be classified in a number of ways. But since mathematical models are developed from applying the fundamental physical and chemical laws on a specific system,

we review first the classification of systems since their nature affect the modeling approach and the resulting model.

1.3 Systems

A system is a whole consisting of elements or subsystems. The system has boundaries that distinguish it from the surrounding environment (external world) as shown in Figure 1.1. The system may exchange matter and/or energy with the surrounding through its boundary. Consequently, the state of a system can be defined or understood via the interactions of its elements with the external world. A system may be classified in different ways, some of which are as follows:

1.3.1 Classification based on thermodynamic principles

- Isolated system

This type of system does not exchange matter nor energy with the surrounding. Adiabatic batch reactor is an example of such systems.

- Closed system

This type of system does not exchange matter with the surrounding but it does exchange energy. Non-adiabatic batch reactor is an example of such systems.

- Open system

This system exchanges both matter and energy with the external environment. An example of this system is the continuous stirred tank reactor (CSTR).

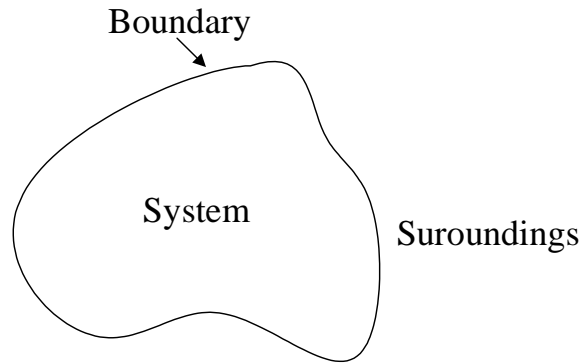


Figure 1.1: system and its boundary

1.3.2 Classification based on number of phases

- Homogeneous system

This is a system that involves only one phase such as gas-phase or liquid-phase chemical reaction processes.

- Heterogeneous system

This is a system that involves more than one phase. This kind of systems exists in multi-phase reaction processes and in phase-based separation processes.

1.4 Classification of Models

Models can be classified according to how they are derived:

- Theoretical models.

These are models that are obtained from fundamental principles, such as the laws of conservation of mass, energy, and momentum along with other chemical principles such as chemical reaction kinetics and thermodynamic equilibrium, etc. This first-principle model is capable of explaining the underlying physics of the process and is often called 'phenomenological model'. For this reason it is particularly suitable for process design and optimization. Theoretical models are, however, generally difficult to obtain and sometimes hard to solve.

- Empirical models

These models are based on experimental plant data. These models are developed using data fitting techniques such as linear and non-linear regression. Models obtained exclusively from experimental plant data are also known as *black-box* models. Such models do not provide detailed description of the underlying physics of the process. However, they do provide a description of the dynamic relationship between inputs and outputs. Thus they are sometimes more adequate for control design and implementation.

- Semi-empirical models

These models are somehow between the two previous models where uncertain or poorly known process parameters are determined from plant data.

This book focuses only on developing theoretical models. The interested reader in empirical modeling is referred to books listed in the references.

1.5 State variables and state equations

Once the system has been classified, developing a theoretical model for it amounts to characterizing its behavior at any time and at any spatial position. For most processing systems a number of fundamental quantities are used to describe the natural state of the system. These quantities are the mass, energy and momentum. Most often these fundamental quantities can not be measured directly thus they are usually represented by other variables that can be measured directly and conveniently. The most common variables are density, concentration, temperature, pressure and flow rate. They are conveniently called '*state variables*' since they characterize the state of the processing system.

In order to describe the behavior of the system with time and position, the state (dependent) variables should be linked to the independent variables (time, spatial position) through sets of equations that are derived from writing mass, energy and momentum balances. The set of equations describing these variables are called '*state equations*'.

1.6 Classification of theoretical models

With this in mind, theoretical models may be further classified in more practical ways as discussed in the following.

1.6.1 Steady state Vs. unsteady state

When the physical state of the processing system remains constant with the time, the system is said to be at steady state. Models that describe steady state situations are also called static, time-invariant or stationary models. Basically, almost all chemical process unit designs are carried out on static models. On the other hand unsteady state processes represent the situation when the process state (dependent variables) changes with time. Models that describe unsteady-state situations are also called dynamic and transient models. Such models are useful for process control design and development. Process dynamics are encountered in practice during startup, shutdown, and upsets (disturbances)

1.6.2 Lumped Vs. distributed parameters

Lumped parameters models are those in which the state variables and other parameters have/or assumed to have no spatial dependence, i.e. they are considered to be uniform over the entire system. In this case the *time* (for unsteady state models) is the only independent variable. The chemical engineering examples for this case include the perfectly mixed CSTR, distillation columns. etc. Conceptually, these models are obtained through carrying out a macroscopic balance for the process as it will be discussed in chapter 2 . On the other hand, distributed parameters models are those in which states and other variables are function of both time and spatial position. In this case, modeling takes into account the variation of these variables with time and from point to point throughout the entire system. Some examples of such systems include plug flow reactor, heat exchangers, and packed columns. These models are essentially obtained through writing microscopic balances equations for the process as it will be discussed later in chapter 2.

1.6.3 Linear Vs non-linear

Linear models have the important property of superposition whereas nonlinear models do not. Superposition means that the response of the system to a sum of inputs is the same as the sum of responses to the individual inputs. In linear models all the dependant variables or their derivatives appear in the model equations only to the first power. These properties do not hold for nonlinear models. In this respect, it is important to recognize the fact that most physical and chemical systems are nonlinear. Linear models are commonly obtained through linearization of the nonlinear model around a certain steady state. Linear models obtained this way are valid approximation of the original non linear model only in the neighborhood of the selected state.

1.6.4 Continuous Vs discrete

When the dependant variables can assume any values within an interval the model is called continuous. When on the other hand one or several variables are assumed to take only discrete values, the model is called discrete. In chemical engineering discrete models arise for example when some variables are required to take only integer values, for example the number of stages in a distillation column, the number of heat exchanger in a plant, etc.

1.6.5 Deterministic Vs probabilistic

Deterministic models are those in which each variable can be assigned a definite fixed number, for a given set of conditions. On the other hand in probabilistic or stochastic models some or all the variables used to describe the system are not precisely known. They are considered as random variables. Probabilistic models are often encountered when modeling systems that are subject to noise.

1.7 Building steps for a mathematical model

Building a theoretical mathematical model of a processing system requires the knowledge of the physical and chemical interactions taking place within the boundaries of the system. With a given degree of fundamental knowledge of the system at a certain stage one can build different models with different degree of complexity depending on the purpose of the model building and the level of rigor and accuracy required. The choice of the level of rigor and degree of sophistication is in itself an art that requires much experience. Theoretical modeling of chemical processes may encounter difficulties that can be classified as follows:

- Problems arising from processes that exhibit complicated physical and chemical phenomena. Such problems appear for instance in multi-component interactive processes.
- Problems arising from imprecisely known process parameters. This situation can be handled by periodically estimating the unknown parameters from plant data.
- Problems arising from the size and complexity of the ensuing model. These can be overcome by proper use of simplifying assumptions.

Consequently a modeler should practice careful utilization of the simplifying assumptions based on engineering sense and experience. Failure to do so, the modeler may fall into one of the two extremes, i.e. creating rigorous but over complicated model or creating oversimplified model that does not capture all the critical features of the true process.

The general procedure for building up a mathematical model includes the following steps:

- Identification of the system configuration, its surrounding environment and the modes of interaction between them, the identification of the relevant state variables that describe the system and identification of the process taking place within the boundaries of the system

- Introduction of the necessary simplifying assumptions.
- Formulation of the model equations based on principles of mass, energy and momentum balances appropriate to the type of the system. This also requires the determination of the fundamental quantitative laws (chemical kinetics, thermodynamic relations...) that govern the rates of the process in terms of the state variables .
- Determination of the solvability of the model using degree of freedom analysis.
- Development of the necessary numerical algorithms for the solution of the model equations.
- Validation of the model against experimental results to ensure its reliability and to re-evaluate the simplifying assumptions which may result in imposing new simplifying assumptions or relaxing others.

1.8 Conservation Laws

As mentioned in previous section, the state equation forming the mathematical model defines a relationship between the state variables (dependent variables) and the independent variables, i.e., time and spatial variables of the system. These equations are derived, from applying the conservation law for a specific fundamental quantity say S , on a specific system with defined boundaries (see Figure 1.2) as follows:

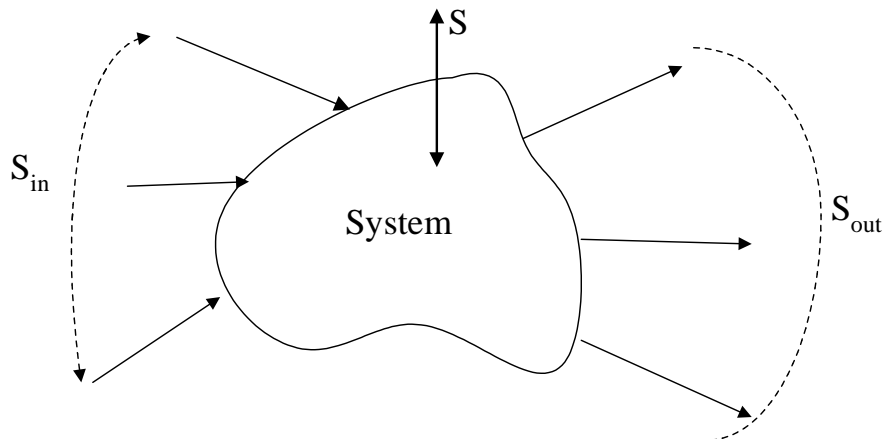


Figure 1.2

Total flow rate of (S) into the system	+	Generation rate of (S) within system	=	Total flow rate of (S) out of the system	+	Accumulation rate of (S) within system	±	amount of (S) exchanged with the surrounding
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(1.1)

The quantity S can be any one of the following quantities:

- Total Mass
- Component Mass (Mole)
- Total Energy
- Momentum

1.8.1 Total mass balance

Since mass is always conserved, the balance equation for the total mass (m) of a given system is:

$$\text{Rate of mass in} = \text{rate of mass out} + \text{rate of mass accumulation} \quad (1.2)$$

The mass balance equation has the SI unit of kg/s .

1.8.2 Component balance

The mass balance for a component A is generally written in terms of number of moles of A . Thus the component balance is

$$\begin{array}{ccccccc} \text{flow of moles} & & \text{Rate of Generation} & & \text{Flow of moles} & & \text{Rate of Accumulation} \\ \text{(A) in} & + & \text{of moles of (A)} & = & \text{of (A) out} & + & \text{of moles of (A)} \end{array} \quad (1.3)$$

The component balance has the unit of *moles A/s*. It should be noted that unlike the total mass, the number of moles of species A is not conserved. The species A can be generated or consumed by chemical reaction.

1.8.3 Momentum balance

The linear momentum (π) of a mass (m) moving with velocity (v) is defined as:

$$\pi = mv \quad (1.4)$$

Since the velocity v is a vector, the momentum, unlike the mass is also a vector. The momentum balance equation using (Eq 1.1) is:

$$\begin{array}{ccccccc} \text{Rate} & & \text{Rate of Generation} & & \text{Rate} & & \text{Rate of Accumulation} \\ \text{momentum in} & + & \text{of momentum} & = & \text{momentum out} & + & \text{of momentum} \end{array} \quad (1.5)$$

The momentum balance has the unit of $kg.m/s^2$. The momentum balance equation is usually written using the Newton's second law. The law states that the time rate of change of momentum of a system is equal to the sum of all forces F acting on the system,

$$\frac{d(mv)}{dt} = \sum F \quad (1.6)$$

1.8.4 Energy balance

The energy balance for a given system is:

$$\begin{array}{ccccccc}
 \text{Rate of} & & \text{Rate of} & & \text{Rate of} & & \text{Rate of} \\
 \text{energy} & + & \text{Generation of} & = & \text{energy} & + & \text{accumulation} \\
 \text{in} & & \text{energy} & & \text{out} & & \text{of energy} \\
 & & & & & & \pm \text{ amount of} \\
 & & & & & & \text{energy} \\
 & & & & & & \text{exchanged} \\
 & & & & & & \text{with the} \\
 & & & & & & \text{surrounding}
 \end{array} \quad (1.7)$$

The energy generated within a system includes the rate of heat and the rate of work. The rate of heat includes the heat of reaction (if a reaction occurs in the system), and the heat exchanged with the surroundings. For the rate of work we will distinguish between the work done against pressure forces (flow work) and the other work such as the work done against the gravity force, against viscous forces and shaft work. The reason for this distinction will appear clearly in the next chapter.

For a given system the general conservation law (Eq. 1.1) can be carried out either on microscopic scale or macroscopic scale.

1.9 Microscopic balance

In the microscopic case, the balance equation is written over a differential element within the system to account for the variation of the state variables from point to point in the system, besides its variation with time. If we choose for example cartesian coordinates, the differential element is a cube as shown in Figure 1.3. Each state variable V of the system is assumed to depend on the three coordinates x, y and z plus the time. i.e. $V = V(x, y, z, t)$. The microscopic balance can be also written in cylindrical coordinates (Figure 1.4) and in spherical coordinates (Figure 1.5). The selection of the appropriate coordinates depends on the geometry of the system under study. It is possible to convert from one coordinate system to an other as it will be discussed in chapter 3.

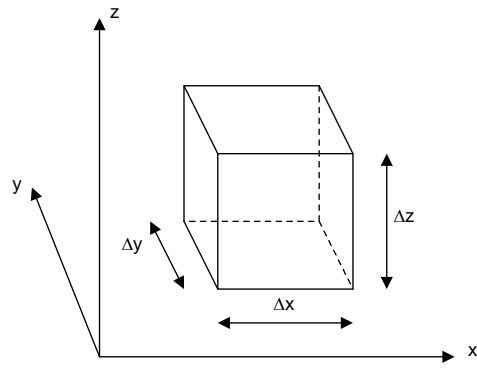


Figure 1.3: Cartesian coordinates

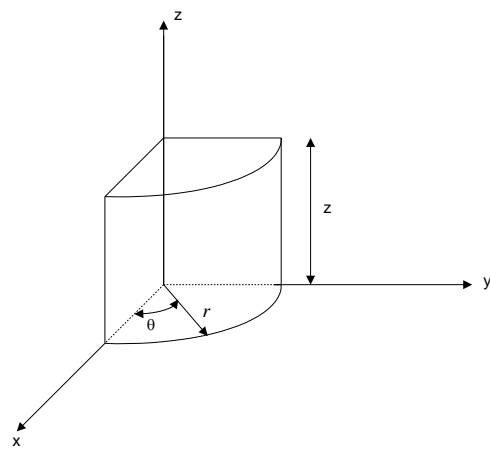


Figure 1.4: Cylindrical coordinates

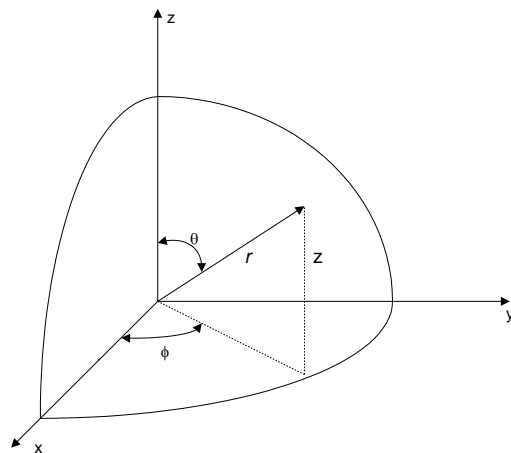


Figure 1.5: Spherical coordinates

1.10 Macroscopic balance

In some cases the process state variables are uniform over the entire system, that is each state variable does not depend on the spatial variables, i.e. x, y and z in cartesian coordinates but only on time t . In this case the balance equation is written over the whole system using macroscopic modeling. When modeling the process on microscopic scale the resulting models consists usually of partial differential equation (PDE) where time and one or more spatial position are the independent variables. At steady state, the PDE becomes independent of t and the spatial positions are the only independent variables. When, on the other hand, the modeling is based on macroscopic scale the resulting model consists of sets of ordinary differential equations (ODE). In the next chapter we present examples of applying macroscopic and microscopic balances to model various chemical processes.

The fundamental balance equations of mass, momentum and energy already discussed are usually supplemented with a number of equations associated with transport rates and thermodynamic relationships. In the following we present an overview of some of these relations.

1.11 Transport rates

Transport of the fundamental quantities, mass, energy and momentum occur by two mechanisms

- Transport due to convection or bulk flow
- Transport due to molecular diffusion or potential difference.

In many cases the two transport mechanism occur together. Therefore, the flux due to the transport of any fundamental quantity is the sum of a flux due to convection and a flux due to diffusion.

1.11.1 Mass Transport

The total flux n_{Au} (kg/m^2s) of species A of density ρ_A (kg/m^3) flowing with velocity v_u (m/s) in the u -direction is the sum of the two terms:

$$n_{Au} = j_{Au} + \rho_A v_u \quad (1.8)$$

$$\text{total flux} = \text{diffusive flux} + \text{bulk flux} \quad (1.9)$$

The diffusive flux j_{Au} (kg/m^2s) for a binary mixture A - B is given by Fick's law:

$$j_{Au} = -\rho D_{AB} \frac{dw_A}{du} \quad (1.10)$$

where $w_A = \rho_A/\rho$ is the mass fraction of species A , ρ (kg/m^3) the density of the mixture and D_{AB} (m^2/s) is the diffusivity coefficient of A in the mixture. In molar unit the flux J_{Au} ($mol A/m^2s$) is given by:

$$J_{Au} = -CD_{AB} \frac{dx_A}{du} \quad (1.11)$$

where C is the total concentration of A and B ($Kg(A+B)/m^3$) and $x_A = C_A/C$ is the mole fraction of A in the mixture. For constant density the flux Eqs.(1.10 and Eq. 1.11) become:

$$j_{Au} = -D_{AB} \frac{d\rho_A}{du} \quad (1.12)$$

$$J_{Au} = -D_{AB} \frac{dC_A}{du} \quad (1.13)$$

1.11.2 Momentum transport

Momentum is also transported by convection and diffusion. But unlike the mass, the linear momentum $\pi = mv$ is a vector. We have to consider then its transport in all directions (x,y,z) of a given system. Let consider for instant the transport of the x -component of the momentum. Similar analysis can be carried out for the transport of the y and z component.

The flux due to convection of the x -component of the momentum in the y -direction, for instant, is

$$(\rho v_x)v_y \quad (kg.m/s^2) \quad (1.14)$$

To determine the diffusion flux denoted by τ_{yx} of the x -component of the momentum in the y -direction, consider a fluid flowing between two infinite parallel plates as shown in Figure 1.6. At a certain time the lower plate is moved by applying a constant force F_x while the upper plate is maintained constant. The force F_x is called a shear force since it is tangential to the area A_y on which it is applied (Fig. 1.6).

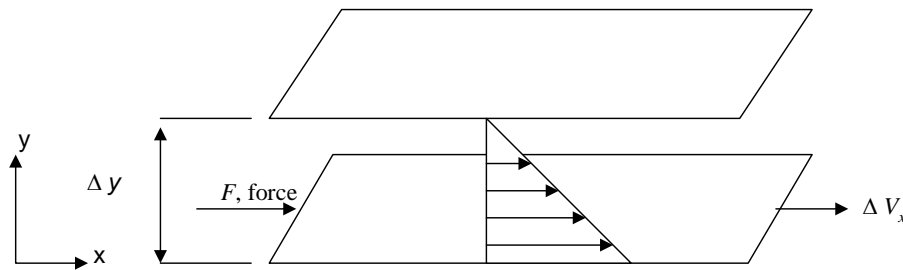


Figure 1.6: Momentum transfer between two parallel plates

The force per unit area

$$\frac{F_x}{A_y} \quad (kg.m/s^2) \quad (1.15)$$

is called a stress and denoted τ_{yx} ($kg.m/s$). It is also a shear stress since it is tangential. The force F_x imparts a constant velocity $V = v_x$ ($y = 0$) to the layer adjacent to the plate. Because of molecular transport, the layer above it has a slightly slower velocity $v_x(y)$ and so on as shown in Figure 1.6. Therefore, there is a transport by diffusion of the x -component of the momentum in the y -direction. The flux of this diffusive transport is in fact the shear stress τ_{yx} .

Therefore, the total flux π_{yx} of the x -component in the y -direction is the sum of the convection term (Eq. 1.14) and diffusive term τ_{yx}

$$\pi_{yx} = \tau_{yx} + (\rho v_x)v_y \quad (1.16)$$

$$\text{momentum flux} = \text{diffusive flux} + \text{bulk flux} \quad (1.17)$$

For a Newtonian fluid the shear stress τ_{yx} is proportional to the velocity gradient:

$$\tau_{yx} = -\mu \frac{\partial v_x}{\partial y} \quad (1.18)$$

where μ ($kg/m.s$) is the viscosity of the fluid.

1.11.3 Energy transport

The total energy flux e_u ($J/s.m^2$) of a fluid at constant pressure flowing with a velocity v_u in the u -direction can be expressed as:

$$e_u = q_u + (\rho C_p T)v_u \quad (1.19)$$

$$\text{energy flux} = \text{diffusive flux} + \text{bulk flux} \quad (1.20)$$

The heat flux by molecular diffusion, i.e. conduction in the u -direction is given by Fourier's law:

$$q_u = -k \frac{\partial T}{\partial u} \quad (1.21)$$

where k ($J/s.m.K$) is the thermal conductivity.

The three relations (Eq. 1.10, 1.18, 1.21) show the analogy that exists between mass, momentum and energy transport. The diffusive flux in each case is given by the following form:

$$\text{Flux} = - \text{transport property} \times \text{potential difference (gradient)} \quad (1.22)$$

The flux represents the rate of transfer per area, the potential difference indicates the driving force and the transport property is the proportionality constant . Table 1.1 summarizes the transport laws for molecular diffusion.

Table 1.1: One-dimensional Transport laws for molecular diffusion

Transport Type	Law	Flux	Transport property	gradient
Mass	Fick's	J_{Au}	D	$\frac{dC_A}{du}$
Heat	Fourrier	q_u	k	$\frac{dT}{du}$
Momentum	Newton	τ_{ux}	μ	$\frac{dv_x}{du}$

When modeling a process on macroscopic level we can also express the flux by a relation equivalent to (Eq. 1.22). In this case the gradient is the difference between the bulk properties, i.e. concentration or temperature in two medium in contact, while the transport property represents an overall transfer coefficient. For example for mass transfer problems, the molar flux can be expressed as follows:

$$J_A = K \times \Delta C_A \quad (1.23)$$

where K an overall mass transfer coefficient.

The heat flux on the other hand is expressed as

$$q = U \times \Delta T \quad (1.24)$$

where U is an overall heat transfer coefficient.

As for the momentum balance, the macroscopic description generally uses the pressure drop as the gradient while the friction coefficient is used instead of the flux. The following relation is for instance commonly used to describe the momentum laminar transport in a pipe

$$f = \frac{D}{2v^2 L \rho} \Delta P \quad (1.25)$$

f is the Fanning friction factor, ΔP is the pressure drop due to friction, D is the diameter of the pipe, L the length and v is the velocity of the fluid.

1.12 Thermodynamic relations

An equation that relates the volume (V) of a fluid to its temperature (T) and pressure (P) is called an *equation of state*. Such equations are used to determine fluid densities and enthalpies .

- Densities :

The simplest equation of state is the ideal gas law:

$$PV = nRT \quad (1.26)$$

which can be used to determine the vapor (gas) density

$$\rho = M_w P / RT \quad (1.27)$$

where M_w is the molecular weight . As for liquids, tabulated values of density can be used and can be considered invariant unless large changes in composition or temperature occur.

- Enthalpies :

Liquid and vapor enthalpies for pure component can be computed from simple formulas, based on neglecting the pressure effect as follows:

$$\tilde{h} = \bar{C}_p (T - T_{ref}) \quad (1.28)$$

$$\tilde{H} = \bar{C}_p (T - T_{ref}) + \lambda \quad (1.29)$$

Where \tilde{h} is the liquid specific enthalpy, \tilde{H} is its vapor specific enthalpy, \bar{C}_p the average liquid heat capacity and λ is the latent heat of vaporization

Note that the reference condition is taken to be liquid at temperature T_{ref} . If heat of mixing is negligible, the enthalpy of a mixture can be taken as the sum of the specific enthalpies of the pure components multiplied by their corresponding mole fractions

Note that the above enthalpy functions are valid for small temperature variation and/or when the heat capacities of fluids are weak function of temperature. In general cases the heat capacity C_p can be taken as function of temperature such as:

$$C_p = a + bT + cT^2 + dT^3 \quad (1.30)$$

The specific enthalpies for vapors and liquids are computed as integrals as follows:

$$\tilde{h} = \int_{T_{ref}}^T C_p dT \quad (1.31)$$

$$\tilde{H} = \int_{T_{ref}}^T C_p dT + \lambda \quad (1.32)$$

- Internal energy :

The internal energy U is a fundamental quantity that appears in energy balance equation. For liquids and solids the internal energy can be approximated by enthalpy .

This can be also a good approximation for gases if the pressure change is small.

1.13 Phase Equilibrium

A large number of chemical processes involve more than one phase. In many cases the phases are brought in direct contact with each other such as in packed or tray towers. When the transfer of either mass or energy occurs from a fluid phase to another phase the interface between fluid phases is usually at equilibrium. In the case of heat transfer between phase I and Phase II, the equilibrium dictates that the temperature is the same at the interface. This is not the case for mass transfer. Figure 1.7 shows for instant the mass transfer of species A from a liquid to a gas phase. The concentration of the bulk gas phase y_{AG} decreases at the interface. The liquid concentration increases, on the other hand, from x_{AL} to x_{Ai} . At the interface, an equilibrium exists and y_{Ai} and x_{Ai} are related by a relation of the form of

$$y_{Ai} = F(x_{Ai}) \quad (1.33)$$

The equilibrium relations are in general nonlinear. However, quite satisfactory results can be obtained through the use of simpler relations that are derived from assumptions of ideal behavior of the two phases:

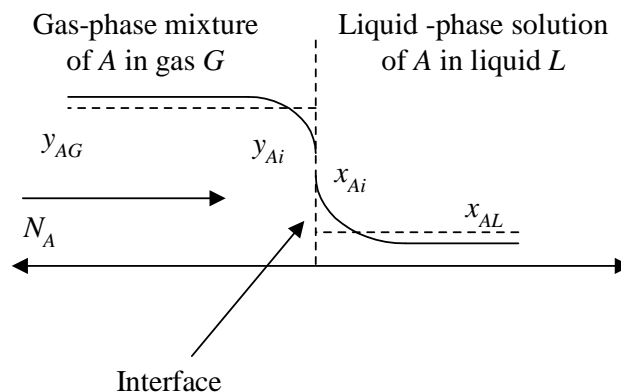


Figure 1.7: Equilibrium at the interface

- For vapor phases at low concentration, Henry's law provides the following simple equilibrium relation:

$$p_A = Hx_A \quad (1.34)$$

Where p_A (atm) is the partial pressure of species A in the vapor, x_A is the mole fraction of A in the liquid and H is the Henry's constant (atm/mol fraction)

Dividing by the total Pressure (P) we get another form of Henry's law:

$$y_A = \tilde{H} x_A \quad (1.35)$$

The constant (\tilde{H}) depends on temperature and pressure.

- Raoult's law provides a suitable equilibrium law for ideal vapor-liquid mixtures

$$y_A P = x_A P_A^s \quad (1.36)$$

Where x_A is the liquid-phase mole fraction, y_A is the vapor-phase mole fraction, P_A^s is the vapor pressure of pure A at the temperature of the system, and P is the total pressure on gas-phase side.

The dependence of vapor pressure P_A^s on temperature can be approximated by the Antoine equation

$$\ln(P_A^s) = A - \frac{B}{C + T} \quad (1.37)$$

where A , B and C are characteristic parameters of the fluid.

- Raoult's law can be modified to account for non-ideal liquid and vapor behavior using the activity coefficients γ_i and ϕ_i of component (i) for liquid and vapor phase respectively. The following equilibrium relation, also known as the Gamma/Phi formulation, can be used:

$$y_i \phi_i P = x_i \gamma_i P_i^S \quad (1.38)$$

The activity coefficients can be determined using correlations found in standard thermodynamics text books. Equation (1.38) is reduced to Raoult law for ideal mixture i.e. ($\phi_i = \gamma_i = 1$).

- In some cases the transfer occurs in liquid-liquid phases (such as liquid extraction) or liquid-solid (such as ion exchange). In such cases an equilibrium relation similar to Henry's law can be defined:

$$y_A = K x_A \quad (1.39)$$

where K is the equilibrium distribution coefficient that depends on pressure, temperature and concentration.

Phase equilibrium relations are commonly used in the following calculations:

- Bubble point calculations :
For a given molar liquid compositions (x_i) and either T or P , the bubble point calculations consist in finding the molar vapor composition (y_i) and either P or T .
- Dew point calculations :

For a given molar vapor compositions (y_i) and either T or P , the dew point calculations consist in finding the molar liquid compositions (x_i) and either P or T .

- Flash calculation :

For known mixture compositions (z_i) and known (T) and (P), the flash calculations consist in finding the liquid and vapor compositions via simultaneous solution of component balance and energy balance equations.

1.14 Chemical kinetics

The overall rate R in *moles/m³s* of a chemical reaction is defined by:

$$R = \frac{1}{v_i V} \frac{dn_i}{dt} \quad (1.40)$$

where

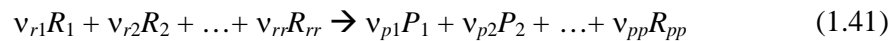
n_i the number of moles

v_i the stoichiometric coefficient of component i

V is the volume due to the chemical reaction.

The rate expression R is generally a complex relation of the concentrations (or partial pressures) of the reactants and products in addition to pressure and temperature.

For a general irreversible reaction



The law of mass action stipulates that the reaction rate is a power law function of temperature and concentration of reactants, i.e.

$$R = k C_{R_1}^{\zeta_1} C_{R_2}^{\zeta_2} \dots C_{R_r}^{\zeta_r} \quad (1.42)$$

The powers ζ_i are determined experimentally and their values are not necessarily integers. The temperature dependence comes from the reaction rate constant k given by Arrhenius law

$$k = k_o e^{\frac{-E}{RT}} \quad (1.43)$$

where k_o is the pre-exponential factor, E the activation energy, T the absolute temperature and R is the ideal gas constant

1.15 Control Laws

Although the discussion of feedback control systems is beyond the scope of this book, the existence of control loops in any processing system provides extra relations for the process. Specifically in many cases some key process variables are required to be controlled, i.e. maintained within desired range. This control objective can be achieved by closing the control loop, i.e., relating the controlled variables to inputs (manipulated variables). This introduces additional independent equations.

1.16 Degrees of Freedom

A key step in the model development and solution is checking its consistency or solvability, i.e. the existence of exact solution. This is done by checking the degrees of freedom of the model after the equations have written and before attempting to solve them . For a processing system described by a set of N_e independent equations and N_v variables, the degree of freedom f is

$$F = N_v - N_e \quad (1.44)$$

Depending on the value of f three cases can be distinguished:

- $f = 0$. The system is exactly determined (specified) system .Thus, the set of balance equation has a finite number of solutions (one solution for linear systems)
- $f < 0$. The system is over-determined (over-specified) by f equations. f equations have to be removed for the system to have a solution.

- $f > 0$. The system is under-determined (under-specified) by f equations. The set of equation, hence, has infinite number of solution .

To avoid the situations of over-specified or under-specified systems it is advised to follow the following steps while checking the consistency of the model.

1. Determine known quantities of the model that can be fixed such as equipment dimensions, constant physical properties, etc.
2. Determine other variables that can specified by the external world, for example, variables that are the outcome of an upstream processing units, and/or variables that can be used as forcing function or manipulated variables.

1.17 Model solution

After the solvability of the model has been checked, the next step is to solve the model. The purpose of the solution of the model is be able to obtain the variations of the state variables with the model independent variables (time, spatial positions..). The solution of the model permits also a parametric investigation of the model, that is a study of the effects of the changing the value of some parameters. It would be ideal to be able to solve the model analytically, that is to get closed forms of the state variables in term of the independent variables. Unfortunately this seldom occurs for chemical processes. The reason is that the vast majority of chemical processes are nonlinear. They may be a sets of nonlinear partial differential equations (PDE) as it is the case for distributed parameter models, or sets of nonlinear ordinary differential equations (ODE) or nonlinear algebraic equations as it is the case for lumped parameter models. However most non linear problems can not be solved analytically. In fact the only class of differential equations for which there is a well-developed framework are linear ODE . However linearizing the original nonlinear model and solving it is not always recommended (except for control purposes) since the behavior of the linearized model matches the original nonlinear model only around the state chosen for linearization . For these reasons the solution of process models is usually carried out numerically, most often through a computer programs.

1.18 Model validation

Model verification (validation) is the last and the most important step of model building. Reliability of the obtained model depends heavily on faithfully passing this test. Implementation of the model without validation may lead to erroneous and misleading results. So, it is essential, as it saves a lot of effort, time and frustration, to verify the model against plant operating data, experimental data, or at least published correlations. If the model failed in the test, then it might be necessary to adjust some of the model parameters, which is believed to be poorly known, in order to minimize the mismatch between the model and the true plant. In worst cases, a modeler may need to reconsider some of the simplifying assumptions used or the neglected modeling parts. However, it should be kept in mind that the model is no more than approximation of the real world, thus some degree of mismatch will remain and could be overlooked.