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CHAPTER 2

MODELLING ASPECTS

Most of the engineering processes that demand accurate product quality, and proceed at high rates, high temperatures, and high pressures, are distinct for their utmost complexity. A simple change in one of the variables may bring about complex and non-linear changes in other variables.

The external potential of information about any engineering process is extremely high. This complex situation can be handled diligently with very narrow channels of perception by gaining an insight into a particular process using models. A *model* is a simplified representation of those aspects of an actual process that are being investigated (Kafarov & Kuznetsov 1976).

The flow of information is broken down 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
- Mathematical modelling

We will also focus on specific applications of mathematical modelling in chemical engineering, which is generally referred to as *chemical systems modelling.*

Before actually going into the details of and differences among physical, mathematical, and chemical systems modelling, we need to have a good grasp of different types of processes, such as deterministic and stochastic processes, and their differences.

2.1 Deterministic Versus Stochastic Processes

2.1.1 Deterministic Process

In this process the observables take on a continuous set of values in a well-defined (or definable) manner, while the output variable most 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).

2.1.2 Stochastic Process

This is a process in which observables 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 (such as pulse frequency, pulse velocity, pulse height, base hold-up, and pulse hold-up) in trickle bed reactors (Babu 1993).

A deterministic process is one whose behaviour (with respect to time, since it is of interest) can be predicted exactly. However, for stochastic processes, we can predict its response only approximately (generally invoking probabilistic notions). Simple CSTR and hydrocracking in trickle bed reactors are quoted as examples for deterministic and stochastic processes, respectively. However, it may be noted that any process, whether it is a process in CSTR or hydrocracking or fluid catalytic cracking (FCC), can be modelled as a deterministic or stochastic process, depending on how much trust we repose in the model we have constructed and how well we can describe all the inputs that affect the process behaviour. While a CSTR is a simpler process to describe than an FCC, this does not in any way imply that we can model CSTR behaviour exactly or that we know all the inputs that affect the response of a CSTR. It is more a matter of our faith than of the process itself.

2.2 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 dimensions 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'.

Physical modelling consists in seeking the same or nearly the same similarity criteria for the model and the real process. The real process is modelled on a progressively increasing scale, with the principal linear dimensions scaled up in proportion (the similarity principle). Thus, a physical model is restrained directly *within the system* where the real process of interest takes place. This approach requires that the process be modelled up to the commercial scale, along with the

complex systems that one has to deal with in chemical engineering. For relatively simple systems (such as single-phase fluid-flow or heat-transfer systems) the similarity principle and physical modelling are justified because the number of criteria involved is limited. However, with complex systems and processes described by a complex system of equations, one has to deal with a large set of similarity criteria that are not simultaneously compatible and, as a consequence, cannot be realized.

Let us consider the example of designing an industrial heat exchanger. For computing the heat-transfer coefficients 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. Section 2.7 contains a detailed discussion on similarity principles.

The similarity principle has proved its worth in the analysis of deterministic processes that obey the laws of classical mechanics and proceed in bounded single-phase systems (within solid walls as a rule). It is, however, difficult to apply physical similarity to an analysis of probabilistic processes involving multivalued stochastic relationships between the events, an analysis of two-phase unbounded systems, and to processes complicated by chemical reactions.

2.3 Mathematical Modelling

A *mathematical model* of a real chemical process is a mathematical description which combines experimental facts and establishes relationships among the process variables. Mathematical modelling is an activity in which qualitative and quantitative representations or abstractions of the real process are carried out using mathematical symbols. In building a mathematical model, a real process is reduced to its bare essentials, and the resultant scheme is described by a mathematical formalism (formulation) 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.

The objective of a mathematical model is to predict the behaviour of a process and to work out ways to control its course. The choice of a model and whether or not it represents the typical features of the process in question may well decide the success or failure of an investigation.

A good model should reflect the important factors affecting a process, but must not be crowded with minor, secondary factors that will complicate the mathematical analysis and might render the investigation difficult to evaluate. Depending on the process under investigation, a mathematical model may be a system of algebraic or differential equations or a mixture of both. It is important that the model should also represent with sufficient accuracy both quantitative and qualitative properties

of the prototype process and should adequately fit the real process. For a check on this requirement, the observations made on the process should be compared with the predictions derived from the model under identical conditions. Thus, a mathematical model of a real chemical process is a mathematical description combining experimental facts and establishing relationships between the process variables. For this purpose, it uses both theory and experimentation (Babu & Ramakrishna 2002a). When one is lacking information about a process or a system, one begins with the simplest model, taking care not to distort the basic (qualitative) aspects of the prototype process.

Mathematical modelling involves three steps:

- formalization—the mathematical description of the process under investigation (mathematical formulation)
- development of an algorithm for the process
- testing of the model and the solution derived from it

In this method of analysis, the *model itself is restrained* through simulation on a computer, rather than with the real process or plant, as is the case with physical modelling. For this purpose, the variables that affect the course of a process are changed from the computer control console to a predetermined program (algorithm) and the computer represents the resultant outputs. With a conservative capital outlay, mathematical modelling coupled with present-day computers makes it possible to investigate various plant configurations in order to trace process behaviour under different conditions, and to find ways and means for improvement. Furthermore, this approach always guarantees an optimum solution within the framework of the model being used. However, it should be stressed that mathematical modelling is in no way set to oppose physical modelling. Rather, the former supplements the latter with its wealth of mathematical formulation and numerical analysis. The importance of lateral mixing from experimental evidence in thermal resistance models (Babu 1993; Shah et al. 1995) is a very good example of this combination.

Mathematical modelling involves the simulation of a process on a computer by changing in the interlinked variables. Using this technique, all promising alternatives can be simulated in order to arrive at an optimum model and, as a consequence, to optimize the process itself within a relatively short time. Mathematical modelling is economic and less time consuming than physical modelling. Mathematical modelling also uses the principles of analogies, or correspondence between different physical phenomena, described by analogous mathematical equations. An example is the analogy among energy, heat, mass and electricity transport as is demonstrated below.

Energy or momentum transport (force of friction)

Newton's law of viscosity

$$\tau = -\mu\left(\frac{dv}{dx}\right) \tag{2.1}$$

can be rearranged to

$$\tau = -v\left(\frac{d(v\rho)}{dx}\right) \tag{2.2}$$

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

$$2f\rho v^2 = \frac{g_c D\Delta P}{L} \tag{2.3}$$

Heat transport (heat flux)

Fourier's law of heat conduction

$$\frac{Q}{A} = -k\left(\frac{dT}{dx}\right) \tag{2.4}$$

can be rearranged to

$$\frac{Q}{A} = -\alpha\left[\frac{d(\rho C_p T)}{dx}\right] \tag{2.5}$$

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

$$\frac{Q}{A} = -h_T \Delta T \tag{2.6}$$

Mass transport (mass flux)

Fick's first law of diffusion

$$q_m = J = -D\left(\frac{dc}{dx}\right) \tag{2.7}$$

can be rearranged to

$$q_m = J = -D\left[\frac{d(c)}{dx}\right] \tag{2.8}$$

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

$$N_A = -k_L \Delta c \tag{2.9}$$

Electricity transport (current)

Ohm's law

$$i = -\frac{1}{\rho}\left(\frac{dv}{dx}\right) \tag{2.10}$$

2.4 Chemical Systems Modelling

Performing experiments and interpreting the results is routine in all applied sciences research. This may be done quantitatively by taking accurate measurements of the system variables, which are subsequently analysed and correlated, or qualitatively by investigating the general behaviour of the system in terms of one variable influencing another. The first method is always desirable, and if a quantitative investigation is to be attempted, it is better to introduce the mathematical principles at the earliest possible stage, since they may influence the course of investigation. This is done by looking for an idealized mathematical model of the system. The second step is the collection of all relevant physical information in the form of conservation laws and rate equations. The conservation laws of chemical engineering are material balances, heat balances, and other energy balances; whilst the rate equations express the relationships between flow rate and driving force in the fields of fluid flow, heat transfer, and diffusion of matter. These are then applied to the model, and the result should be a mathematical equation which describes the system. The type of equation (algebraic, differential, finite difference, etc.) will depend upon both the system under investigation and its model. For a particular system, if the model is simple, the equation may be elementary; whereas if the model is more refined, the equation will be more complex. Appropriate mathematical techniques are then applied to this equation and a result is obtained. This mathematical result must then be interpreted using the original model in order to give it physical significance.

Most chemical engineering processes that proceed at high rates, high temperatures, and high pressures in multiphase systems are distinct in their utmost complexity. A change in one system variable may bring about non-linear changes in other variables. This complexity becomes still more formidable in the case of multiple feedback loops. In addition, random disturbances are superimposed on the process. The external potential of information about chemical engineering process is very high. An analysis of the system and system variables may therefore be carried out with very narrow channels of perception by gaining insight into a particular process through modelling. The development of new processes in the chemical industry is becoming more complex and increasingly expensive. If the research and development of a process can be carried out with confidence, the ultimate design will be more exact and the plant will operate more economically.

Mathematics, which is the language of quantitative analysis, plays a vital role in all facets of such a project. Therefore, training in mathematical methods is of utmost importance to chemical engineers.

The most important result of developing a mathematical model of a chemical engineering system is the understanding that is gained of what really makes the process work. This insight enables one to strip away from the problem many extraneous confusing factors and get to the core of the system. It is basically trying to find cause-and-effect relationships between the variables. Mathematical models can be useful in all phases of chemical engineering, from research and development to plant operations, and even in business and economic studies (Luyben 1990). In research and development: determining chemical kinetic mechanisms and parameters from laboratory or pilot-plant reaction data; exploring the effects of different operating conditions for optimization and control studies; aiding in scale-up calculations. In design: exploring the sizing and arrangement of processing equipment for dynamic performance; studying the interactions of various parts of the process, particularly when material recycling or heat integration is used; evaluating alternative process and control structures and strategies; simulating startup, shutdown, and emergency situations and procedures. In plant operations: troubleshooting control and processing problems; aiding in startup and operator training; studying the effects of and requirements for expansion (bottleneck-removal) projects; optimizing plant operation. It is usually much cheaper, safer, and faster to conduct the kinds of studies listed above on mathematical model simulations than experimentally on an operating unit. This is not to say that plant tests are not needed. As we will discuss later, they are vital for confirming the validity of a model and for verifying important ideas and recommendations that evolve from model studies.

2.4.1 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. To study dynamics we will use them in their general form with time derivatives included.

Assumptions   Probably the most vital role an engineer plays in modelling is in exercising his engineering judgement as to what assumptions can be validly made. Obviously an extremely rigorous model that includes every phenomenon down to microscopic detail would be so complex that it would take a long time to develop and might be impractical to solve, even on the latest supercomputers. An engineering compromise between a rigorous description and getting an answer that is good enough is always required. This has been called 'optimum sloppiness'. It involves making as many simplifying assumptions as are reasonable. In practice, this

optimum usually corresponds to a model, which is as complex as the available computing facilities will permit. The development of a model that incorporates the basic phenomena occurring in a process requires a lot of skill, ingenuity, and practice. It is an area where the creativity and innovativeness of the engineer is a key element for the success of the process. The assumptions that are made should be carefully considered and listed. They impose limitations on the model that should always be kept in mind when evaluating its predicted results.

Mathematical consistency of model   Once all the equations of the mathematical model have been written, it is usually a good idea, particularly with big, complex systems of equations, to make sure that the number of variables equals the number of equations. The so-called degrees of freedom of the system must 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. This kind of consistency check may seem trivial, but experience shows that it can save many hours of frustration, confusion, and wasted computer time. This is required for a simulation exercise. For an optimization exercise, there should be some degrees of freedom available for optimizing, that is, an optimization problem is an underspecified problem. Checking to see that the units of all terms in all equations are consistent is perhaps another trivial and obvious step, but one that is often forgotten. It is essential to be particularly careful of the time units of parameters in dynamic models. Any unit can be used (seconds, minutes, hours, etc.), but these cannot be mixed. Dynamic simulation results are frequently in error because the engineer has forgotten a factor of '60' somewhere in the equations.

Solution of the model equations   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   An important but often neglected part of developing a mathematical model is proving that the model describes the real-world situation. At the design stage, this sometimes cannot be done because the plant has not yet been built. However, even in this situation there are usually either similar existing plants or a pilot plant from which some experimental dynamic data can be obtained. The design of experiments to test the validity of a dynamic model can sometimes be a real challenge and should be carefully thought out.

2.4.2 Fundamental Laws used in Modelling

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 in this section.

2.4.2.1 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]   (2.11)

The units of Eq. (2.11) are mass per time. Only one total continuity equation can be written for one system. According to the normal steady-state design equation we use, we say that 'what goes in, comes out'. The dynamic version of this says the same thing with the addition of the word 'eventually'. For any property in a system, if we assume that the property does not vary with respect to spatial location, we obtain an ordinary differential equation (ODE). Otherwise we obtain a partial differential equation (PDE). If we assume that the property does not change with time (steady-state assumption), we get an algebraic equation. The right-hand side of the above equation will be either a partial derivative or an ordinary derivative of the mass inside the system with respect to the independent variable t.

Component continuity equations (component balances)   Unlike mass, chemical components are not conserved. Again, to be precise, the total mass for a reacting/non-reacting system is conserved. However, in general, for a reacting system, the total number of moles is not a conserved quantity. For a reacting system, while the masses of individual elements are conserved, masses/moles of individual components are not conserved due to molecular rearrangement during a reaction. If a reaction occurs inside a system, the number of moles of an individual component will increase if it is a product of the reaction or decrease if it is a reactant. Therefore the component continuity equation of the jth chemical species of the system is

> [Flow of moles of jth component into system] – [flow of moles of jth component out of system] + [rate of formation of moles of jth component from chemical reactions] = [time rate of change of moles of jth component inside system]   (2.12)

The units of Eq. (2.12) are moles of component j per unit time. The flows in and out can be both convective (due to bulk flow) and molecular (due to diffusion). We can write one component continuity equation for each component in the system. If there are NC components in a system, there are NC component equations. However, the total mass balance and these NC component balances are not all independent, since the sum of all the moles times their respective molecular weights equals the total mass. Therefore a given system has only NC independent continuity equations. We usually use the total mass balance and NC – 1 component balances. For example, in a binary (two-component) system, there would be one total mass balance and one component balance.

There are some exceptions to the above rule. Consider a non-reacting system first. If we consider a flow balance involving *S* streams connected to a process unit (either in terms of moles or mass), NC component balances and *S* 'normalization' relations (one for each stream), which describe how the total mass of a stream is related to the composition of the stream, then together these constitute NC + *S* + 1 equations, out of which one equation is redundant. Generally, it is not possible to work with NC – 1 components (and implicitly use the normalization equation for computing it) because the specified compositions may be distributed arbitrarily.

The same holds for a reacting system, but we should note that the equations involve *r* parameters corresponding to the extents of reaction (with known stoichiometry) assumed to occur in the reactor. A further complication is that element balances are not equivalent to component balances unless some conditions are satisfied (Reklaitis 1983; Felder & Rousseau 1999).

2.4.2.2 Energy equation

The first law of thermodynamics puts forward the principle of conservation of energy. Written for a general *open* system (where flow of material in and out of the system can occur) it is

> [Flow of internal, kinetic, and potential energy into system by convection or 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]   (2.13)

2.4.2.3 Equation of motion

According to Newton's second law of motion, force *F* is equal to mass *M* times acceleration *a* for a system with constant mass *M*, i.e.,

$$F = \frac{Ma}{g_c}$$ (2.14)

where g_c is the conversion constant needed when FPS or MKS units are used

$= 32.2 \ (\text{lb}_\text{m}\,\text{ft})/\text{lb}_\text{f}\,\text{s}^2$ in FPS (English engineering) units
$= 9.81 \ \text{kg}_\text{m}\,\text{m}/\text{kg}_\text{f}\,\text{s}^2$ in MKS units
$= 1 \ \text{kg}_\text{m}\,\text{m}/\text{N}\,\text{s}^2$ in SI units
$= 1 \ \text{g}_\text{m}\,\text{cm}/\text{dyn}\,\text{s}^2$ in CGS units

This is the basic relationship used in writing the equations of motion for a system. In a slightly more general form, where mass can vary with time,

$$\frac{1}{g_c}\frac{d(Mv_i)}{dt} = \sum_{j=1}^{N} F_{ji}$$ (2.15)

where v_i is the velocity in the i direction and F_{ji} is the jth force acting in the i direction. From Eq. (2.15), we can say that the time rate of change of momentum in the i direction (mass times velocity in the i direction) is equal to the net sum of the forces pushing in the i direction. It can be thought of as a dynamic force balance, or more eloquently it is called the *conservation of momentum.*

In the real world there are three directions: *x, y, z.* Thus, three force balances can be written for any system. Therefore, each system has three equations of motion (plus one total mass balance, one energy equation, and NC – 1 component balances). Instead of writing three equations of motion, it is often more convenient (and always more elegant) to write the three equations as one vector equation. The field of fluid mechanics makes extensive use of the conservation of momentum.

2.4.2.4 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). The proportionality constant is a physical property of the system (such as viscosity, thermal conductivity, or diffusivity). However, for transport on a molecular level, the laws bear the familiar names of Newton, Fourier, and Fick [Eqs (2.1), (2.4), and (2.7), respectively].

Transfer relationships of a more macroscopic overall form are also used; for example, film coefficients and overall coefficients in heat transfer. Here the difference in the bulk properties between two locations is the driving force [Eqs (2.3), (2.6), and (2.9), respectively]. The proportionality constant is an overall transfer coefficient.

2.4.2.5 Equations 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,

$$\rho_L = f(P, T, x_i) \tag{2.16}$$

Vapor density,

$$\rho_V = f(P, T, y_i) \tag{2.17}$$

Liquid enthalpy,

$$h = f(P, T, x_i) \tag{2.18}$$

Vapour enthalpy,

$$H = f(P, T, y_i) \tag{2.19}$$

Occasionally, these relationships 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

$$h = C_p T \tag{2.20}$$

$$H = C_p T + \lambda_v \tag{2.21}$$

The next level of complexity would be to make the C_p's functions of temperature:

$$h = \int_{T_0}^{T} C_p(T) dt \tag{2.22}$$

A polynomial in T is often used for C_p:

$$C_p(T) = A_1 + A_2 T \tag{2.23}$$

Then Eq. (2.22) becomes

$$h = \left[A_1 T + A_2 \frac{T^2}{2} \right]_{T_0}^{T} = A_1(T - T_0) + \frac{A_2}{2}(T^2 - T_0^2) \tag{2.24}$$

Of course, with mixtures of components, total enthalpy is needed. If heat-of-mixing effects are negligible, the pure-component enthalpies can be averaged:

$$h = \frac{\displaystyle\sum_{j=1}^{NC} x_j h_j M_j}{\displaystyle\sum_{j=1}^{NC} x_j M_j} \tag{2.25}$$

where x_j is the mole fraction of the jth component, M_j is the molecular weight of the jth component, and h_j is the pure-component enthalpy of the jth component (energy per unit mass). The denominator of Eq. (2.25) is the average molecular weight of the mixture.

Liquid densities can be assumed constant in many systems unless large changes in composition and temperature occur. Vapor densities usually cannot be considered invariant and some sort of *PVT* relationship is almost always required. The simplest and most often used is the perfect-gas law:

$$PV = nRT \tag{2.26}$$

where P is the absolute pressure (kPa), V is the volume (m³), n is the number of moles (kmol), R is a constant $= 8.314$ kPa m³/kmol K, and T is the absolute temperature (K). Rearranging to get an equation for the density ρ_v (kg/m³) of a perfect gas with molecular weight M, we get

$$\rho_v = \frac{nM}{V} = \frac{MP}{RT} \tag{2.27}$$

2.4.2.6 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

$$\sum_{j=1}^{NC} v_j \mu_j = 0 \tag{2.28}$$

where v_j is the stoichiometric coefficient of the jth component with reactants having a negative sign and products a positive sign, and μ_j is the chemical potential of the jth component.

The usual way to work with this equation is in terms of the equilibrium constant for a reaction. For example, consider a reversible gas-phase reaction of A to form B at a specific rate k_1 and B reaching back to A at a specific reaction rate k_2. The stoichiometry of the reaction is such that v_a moles of A react to form v_b moles of B.

$$v_a A \xleftrightarrow{k_1} v_b B \text{ (rate constant for reverse reaction is } k_2) \tag{2.29}$$

From Eq. (2.28), equilibrium will occur when

$$v_b \mu_b - v_a \mu_a = 0 \tag{2.30}$$

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

$$\mu_j = \mu_j^0 + RT \ln P_j \tag{2.31}$$

where μ_j^0 is the standard chemical potential (or Gibbs free energy per mole) of the jth component, which is a function of temperature only, P_j is the partial pressure of the jth component, R is the perfect-gas law constant, and T is the absolute temperature. Substituting into Eq. (2.30) and simplifying, we get

$$\ln\left(\frac{P_B^{v_b}}{P_A^{v_a}}\right) = \frac{v_a \mu_A^0 - v_b \mu_B^0}{RT} \tag{2.32}$$

The right-hand side of this equation is a function of temperature only. The term in parentheses on the left-hand side is defined as the equilibrium constant K_p, which gives us the equilibrium ratios of products and reactants.

$$K_p \equiv \frac{P_B^{v_b}}{P_A^{v_a}} \tag{2.33}$$

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

$$\mu_j^{\mathrm{I}} = \mu_j^{\mathrm{II}} \tag{2.34}$$

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

Since a vast majority of chemical engineering systems involve liquid and vapour phases, many vapour–liquid equilibrium relationships are used. They range from very simple to the very complex. Some of the most commonly used relationships are listed below. More detailed treatments are presented in many thermodynamics texts. Basically, we need a relationship that permits us to calculate the vapor composition if we know the liquid composition, or vice versa.

The most common problem is a *bubble point* calculation: calculate the temperature *T* and vapour composition y_j, given the pressure *P* and the liquid composition x_j. This usually involves a trial-and-error, iterative solution because the equations can be solved explicitly only in the simplest cases. Sometimes we have bubble point calculations that start from known values of x_j and *T* and we want to find *P* and y_j. This is frequently easier than when pressure is known, because the bubble point calculation is usually non-iterative. *Dew point* calculations must be made when we know the composition of the vapour y_j and *P* (or *T*) and want to find the liquid composition x_j and *T* (or *P*). *Flash* calculations must be made when we know neither x_j nor y_j and must combine phase equilibrium relationships, component balance equations, and an energy balance to solve for all the unknowns.

Let us assume ideal vapour-phase behaviour in our examples, i.e., the partial pressure of the *j*th component in the vapour is equal to the total pressure *P* times the mole fraction of the *j*th component in the vapour y_j (Dalton's law):

$$P_j = Py_j \tag{2.35}$$

Corrections may be required at high pressures. As far as the liquid phase is concerned, several approaches are being used, which are shown below.

Raoult's law   Mixtures that obey Raoult's law are called *ideal* mixtures.

$$P = \sum_{j=1}^{\mathrm{NC}} x_j P_j^S \tag{2.36}$$

$$y_j = \frac{x_j P_j^S}{P} \tag{2.37}$$

where P_j^S is the vapour pressure of pure component *j*. Vapour pressures are functions of temperature only. This dependence is often described by

$$\ln P_j^S = \frac{A_j}{T} + B_j \tag{2.38}$$

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

$$\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j} \tag{2.39}$$

Relative volatilities are fairly constant in a number of systems. They are convenient and hence are frequently used. In a binary system the relative volatility α of the more volatile component compared with the less volatile component is

$$\alpha = \frac{y/x}{(1-y)/(1-x)} \tag{2.40}$$

Rearranging,

$$y = \frac{\alpha x}{1 + (\alpha - 1)x} \tag{2.41}$$

K values   Equilibrium vapourization ratios of K values are widely used, particularly in the petroleum industry.

$$K_j = \frac{y_j}{x_j} \tag{2.42}$$

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

Activity coefficients   For non-ideal liquids, Raoult's law must be modified to account for the non-ideality in the liquid phase. The *fudge factors* used are called *activity coefficients.*

$$P = \sum_{j=1}^{NC} x_j P_j^S \gamma_j \tag{2.43}$$

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

2.4.2.7 Chemical kinetics

In modelling of chemical reactors, we must be familiar with the basic relationships and terminology used in describing the kinetics (rate of reaction) of chemical reactions.

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

$$k = \alpha e^{-E/RT} \tag{2.44}$$

where k is the specific reaction rate, α is the preexponential factor, E is the activation energy [shows the temperature dependence of the reaction rate, i.e., the bigger E is, the faster the increase in k with increasing temperature (cal/gmol) is], T is the absolute temperature, and R is the perfect-gas constant = 1.99 cal/gmol K.

This experimental temperature dependence represents one of the most severe non-linearities in a chemical engineering system. It may be noted that the *apparent* temperature dependence of a reaction may not be exponential if the reaction is mass-transfer limited and not chemical-rate limited. If both zones are encountered in the operation of the reactor, the mathematical model must obviously include both reaction-rate and mass-transfer effects.

Law of mass action Let us define an overall reaction rate $\Re$, with the conventional notation, as the rate of change of moles of any component per volume due to the chemical reaction divided by that component's stoichiometric coefficient:

$$\Re = \frac{1}{v_j V}\left(\frac{dn_j}{dt}\right)_R \tag{2.45}$$

The stoichiometric coefficients v_j are positive for products of the reaction and negative for reactants. It may be noted that $\Re$ is an intensive property and can be applied to systems of any size. For example, assume we are dealing with an irreversible reaction in which components A and B react to form components C and D.

$$v_a A + v_b B \xrightarrow{\ k\ } v_c C + v_d D \tag{2.46}$$

Then

$$\Re = \frac{1}{-v_a V}\left(\frac{dn_A}{dt}\right)_R = \frac{1}{-v_b V}\left(\frac{dn_B}{dt}\right)_R$$

$$= \frac{1}{-v_c V}\left(\frac{dn_C}{dt}\right)_R = \frac{1}{-v_d V}\left(\frac{dn_D}{dt}\right)_R \tag{2.47}$$

From the law of mass action, the overall reaction rate $\Re$ will vary with temperature (since k is temperature-dependent) and with the concentrations of reactants raised to some powers:

$$\Re = k_{(T)}(c_A)^a (c_B)^b \tag{2.48}$$

where c_A is the concentration of component A and c_B is the concentration of component B. The constants a and b are not, in general, equal to the stoichiometric coefficients v_a and v_b. The reaction is said to be first-order in A if $a = 1$. It is second-order in A if $a = 2$. The constants a and b can be fractional numbers.

As indicated earlier, the units of the specific reaction rate k depend on the order of the reaction. This is because the overall reaction rate $\Re$ always has the same units (moles per unit time per unit volume). For a first-order reaction of A reacting to form B, the overall reaction rate $\Re$, written for component A, would have units of moles of A/min ft^3.

$$\Re = kc_A \tag{2.49}$$

If c_A has units of moles of A/ft^3, k must have units of min^{-1}. If the overall reaction rate for the above system is second-order in A,

$$\Re = kc_A^2 \tag{2.50}$$

$\Re$ still has units of mol$A$/min ft^3 (mol$A$ denotes moles of A). Therefore k must have units of ft^3/min mol$A$. Considering the reaction $A + B \rightarrow C$, if the overall reaction rate is first-order in both A and B,

$$\Re = kc_A c_B \tag{2.51}$$

$\Re$ still has units of mol$A$/min ft^3. Therefore k must have units of ft^3/min mol$B$.

2.5 Cybernetics

Cybernetics is a science dealing with any system capable of perceiving, storing, and processing information for the purposes of optimum control. Thus, cybernetics encompasses the concepts of a system, information, data storage and processing, system control, and system optimization.

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

2.6 Controlled System

After having discussed the details of modelling, let us see how a simple controlled chemical system is represented schematically (Fig. 2.1). In the absence of disturbances in the system, the process runs smoothly, giving the desired designed outputs for the given inputs. But if there are any disturbances in the system, the outputs will change and the desired designed 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 conditions.
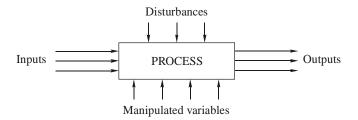
Fig. 2.1 A simple controlled chemical system

2.7 Principles of Similarity

These are useful in scaling up operations in physical modelling. Similarity is used when models are either true or distorted ones. True models reproduce features of the prototype but at a scale—that is they are similar as per either any or all of the three similarity criteria, namely, *geometric similarity, kinematic similarity,* and *dynamic similarity*.

2.7.1 Geometric Similarity

The solid boundaries of any flow system may be adequately described by a number of length dimensions such as $L_1, L_2, L_3, ..., L_n$. If these lengths are divided by L_1, the system may be defined by 1, $\lambda_2, \lambda_3, ..., \lambda_n$, where $\lambda_2 = \lambda_2 / L_1$, $\lambda_3 = L_3 / L_1$, ..., and $\lambda_n = L_n / L_1$. Geometric similarity exists between a model and a prototype if the ratios of all corresponding dimensions in the model and the prototype are equal.

$$\frac{L_{\text{model}}}{L_{\text{prototype}}} = \frac{L_m}{L_p} = \lambda_L \tag{2.52}$$

where λ_L is the scale factor for length. For area,

$$\frac{A_{\text{model}}}{A_{\text{prototype}}} = \frac{L_m^2}{L_p^2} = \lambda_L^2 \tag{2.53}$$

All corresponding angles are the same.

2.7.2 Kinematic Similarity

Kinematic similarity refers to the motion occurring in the system and considers the existing components of velocities. Kinematic similarity is the similarity of time as well as geometry. For kinematic similarity to exist in two geometrically similar systems, the velocities at the same relative point in each system must be related. It exists between the model and the prototype if (i) the paths of moving particles are geometrically similar and (ii) the ratios of the velocities of particles are similar. Some useful ratios are the following.

For velocity,

$$\frac{V_m}{V_p} = \frac{L_m/T_m}{L_p/T_p} = \frac{\lambda_L}{\lambda_T} = \lambda_u \tag{2.54}$$

For acceleration,

$$\frac{a_m}{a_p} = \frac{L_m/T_m^2}{L_p/T_p^2} = \frac{\lambda_L}{\lambda_T^2} = \lambda_a \tag{2.55}$$

and for discharge,

$$\frac{Q_m}{Q_p} = \frac{L_m^3/T_m}{L_p^3/T_p} = \frac{\lambda_L^3}{\lambda_T} = \lambda_Q \tag{2.56}$$

Similarly, the velocity gradients in each system will bear a similar relationship to each other. As a consequence, streamline patterns are the same.

2.7.3 Dynamic Similarity

Dynamic similarity exists between geometrically and kinematically similar systems if the ratios of all the forces in the model and the prototype are the same. The force ratio is

$$\frac{F_m}{F_p} = \frac{M_m a_m}{M_p a_p} = \frac{\rho_m L_m^3}{\rho_p L_p^3} \frac{\lambda_L}{\lambda_T^2} = \lambda_p \lambda_L^2 \left(\frac{\lambda_L}{\lambda_T}\right)^2 = \lambda_p \lambda_L^2 \lambda_u^2 \tag{2.57}$$

This occurs when the controlling dimensionless group on the right-hand side of the defining equation is the same for the model and the prototype.

Illustration 2.1

When a hydraulic structure is built it undergoes some analysis in the design stage. Often the structures are too complex for simple mathematical analysis and a hydraulic model is built. Usually the model is smaller than the full size, but it can be larger. The real structure is known as the prototype. The model is usually built to an exact geometric scale of the prototype, but in some cases—notably the river model—this is not possible. Measurements can be taken from the model and a suitable scaling law applied to predict the values in the prototype.

To illustrate how these scaling laws can be obtained, we will use the relationship for the resistance of a body moving through a fluid. The resistance R depends on the following physical properties:

$$r \ (ML^{-3}), \quad u \ (LT^{-1}), \quad l \ (L), \quad m \ (ML^{-1}T^{-1})$$

So the defining equation is $f(R, r, u, l, m) = 0$. Thus, $m = 5$, $n = 3$, so there are $5 - 3 = 2$ p groups:

$$\pi_1 = \rho^{a_1} u^{b_1} l^{c_1} R$$

$$\pi_2 = \rho^{a_2} u^{b_2} l^{c_2} \mu \tag{2.58}$$

For the p_1 group,

$$M^0 L^0 T^0 = (ML^{-3})^{a_1} (LT^{-1})^{b_1} (L)^{c_1} MLT^{-2} \tag{2.59}$$

leading to p_1 as

$$\pi_1 = \frac{R}{\rho u^2 l^2} \tag{2.60}$$

For the p_2 group,

$$M^0 L^0 T^0 = (ML^{-3})^{a_3} (LT^{-1})^{b_3} (L)^{c_3} ML^{-1} T^{-1} \tag{2.61}$$

leading to p_2 as

$$\pi_2 = \frac{\mu}{\rho u l} \tag{2.62}$$

Notice how $1/p_2$ is the Reynolds number. We can call this p_{2a}. So the defining equation for resistance to motion is

$$f(p_1, p_{2a}) = 0 \tag{2.63}$$

We can write

$$\frac{R}{\rho u^2 l^2} = \phi\left(\frac{\rho u l}{\mu}\right)$$

$$R = \rho u^2 l^2 \phi\left(\frac{\rho u l}{\mu}\right) \tag{2.64}$$

This equation applies irrespective of the size of the body, i.e., it is applicable to the prototype and the geometrically similar model. Thus, for the model,

$$\frac{R_m}{\rho_m u_m^2 l_m^2} = \phi\left(\frac{\rho_m u_m l_m}{\mu_m}\right) \tag{2.65}$$

and for the prototype,

$$\frac{R_p}{\rho_p u_p^2 l_p^2} = \phi\left(\frac{\rho_p u_p l_p}{\mu_p}\right) \tag{2.66}$$

Dividing these two equations gives

$$\frac{\dfrac{R_m}{\rho_m u_m^2 l_m^2}}{\dfrac{R_p}{\rho_p u_p^2 l_p^2}} = \frac{\phi\left(\dfrac{\rho_m u_m l_m}{\mu_m}\right)}{\phi\left(\dfrac{\rho_p u_p l_p}{\mu_p}\right)} \tag{2.67}$$

At this point we can go no further unless we make some assumptions. One common assumption is to assume that the Reynolds number is the same for both the model and the prototype, i.e.,

$$\frac{\rho_m u_m l_m}{\mu_m} = \frac{\rho_p u_p l_p}{\mu_p} \tag{2.68}$$

This assumption then allows the following equation to be written:

$$\frac{R_m}{R_p} = \frac{\rho_m u_m^2 l_m^2}{\rho_p u_p^2 l_p^2} \tag{2.69}$$

which gives this scaling law for resistance force,

$$\lambda_R = \lambda_\rho \lambda_u^2 \lambda_L^2 \tag{2.70}$$

That the Reynolds numbers were the same was an essential assumption for this analysis. The consequence of this should be explained.

$$Re_m = Re_p$$

$$\frac{\rho_m u_m l_m}{\mu_m} = \frac{\rho_p u_p l_p}{\mu_p} \tag{2.71}$$

$$\frac{u_m}{u_p} = \frac{\rho_p}{\rho_m} \frac{\mu_m}{\mu_p} \frac{l_p}{l_m}$$

$$\lambda_u = \frac{\lambda_\mu}{\lambda_\rho \lambda_L} \tag{2.72}$$

Substituting this into the scaling law for resistance gives

$$\lambda_R = \lambda_\rho \left(\frac{\lambda_\mu}{\lambda_\rho}\right)^2 \tag{2.73}$$

So the force on the prototype can be predicted from the measurement of the force on the model, but only if the fluid in the model is moving with the same Reynolds number as it would in the prototype. That is to say, R_p can be predicted by

$$R_p = \frac{\rho_p u_p^2 l_p^2}{\rho_m u_m^2 l_m^2} R_m \tag{2.74}$$

provided that

$$u_p = \frac{\rho_m \mu_p l_m}{\rho_p \mu_m l_p} u_m \tag{2.75}$$

In this case the model and prototype are *dynamically similar*.

Formally, this occurs when the controlling dimensionless group on the right-hand side of the defining equation is the same for the model and the prototype. In this case, the controlling dimensionless group is the Reynolds number.

Example 2.1   An underwater missile, diameter 2 m and length 10 m is tested in a water tunnel to determine the forces acting on the real prototype. A 1/20th scale model is to be used. If the maximum allowable speed of the prototype missile is 10 m/s, what should be the speed of the water in the tunnel to achieve dynamic similarity?

Solution

For dynamic similarity, the Reynolds number of the model and the prototype must be equal:

$$Re_m = Re_p$$

$$\left(\frac{\rho u d}{\mu} \right)_m = \left(\frac{\rho u d}{\mu} \right)_p$$

So the model velocity should be

$$u_m = u_p \frac{\rho_p d_p \mu_m}{\rho_m d_m \mu_p}$$

As both the model and the prototype are in water, $m_m = m_p$ and $r_m = r_p$, so

$$u_m = u_p \frac{d_p}{d_m} = 10 \frac{1}{1/20} = 200 \, \text{m/s}$$

Note that this is a *very high* velocity. This is one reason why model tests are not always done at exactly equal Reynolds numbers. Some relaxation of the equivalence requirement is often acceptable when the Reynolds number is high. Using a wind tunnel could have been possible in this example. If this were the case, then the appropriate values of the *r* and *m* ratios need to be used in the above equation.

Example 2.2 A model aeroplane is built at 1/10th scale and is to be tested in a wind tunnel operating at a pressure of 20 times atmospheric pressure. The aeroplane will fly at 500 km/h. At what speed should the wind tunnel operate to give dynamic similarity between the model and the prototype? If the drag measure on the model is 337.5 N, what will be the drag on the plane?

Solution

Earlier, we derived the equation for resistance on a body moving through air:

$$R = \rho u^2 l^2 \phi \left(\frac{\rho u l}{\mu} \right) = \rho u^2 l^2 \phi(Re)$$

For dynamic similarity $Re_m = Re_p$, so

$$u_m = u_p \frac{\rho_p \, d_p \, \mu_m}{\rho_p \, d_m \, \mu_p}$$

The value of *m* does not change much with pressure, so $m_m = m_p$. The equation of state for an ideal gas is $p = rRT$. As the temperature is same, the density of the air in the model can be obtained from as follows:

$$\frac{p_m}{p_p} = \frac{\rho_m RT}{\rho_p RT} = \frac{\rho_m}{\rho_p}$$

$$\frac{20 p_p}{p_p} = \frac{\rho_m}{\rho_p}$$

$$\rho_m = 20 \rho_p$$

So the model velocity is found to be

$$u_m = u_p \frac{1}{20} \frac{1}{1/10} = 0.5 u_p$$

$$u_m = 250 \, \text{km/h}$$

The ratio of forces is found from

$$\frac{R_m}{R_p} = \frac{(\rho u^2 l^2)_m}{(\rho u^2 l^2)_p}$$

$$\frac{R_m}{R_p} = \frac{20}{1} \frac{(0.5)^2}{1} \frac{(0.1)^2}{1} = 0.05$$

So the drag force on the prototype will be

$$R_p = \frac{1}{0.05} R_m = 20 \times 337.5 = 6750 \, \text{N}$$

EXERCISES

2.1 Classify modelling emphasizing on details of mathematical modelling.

2.2 Discuss the principles of similarity.

2.3 Describe deterministic and stochastic processes.

2.4 Discuss the various aspects involved in physical modelling.

2.5 What are the various model formulation principles?

2.6 Give a detailed account of the fundamental laws used in modelling.

2.7 Define cybernetics and discuss the controlled system by means of a neat schematic diagram.

2.8 What are the various similarity criteria?

2.9 Discuss physical modelling versus mathematical modelling.