Welcome to lecture 3. This is more of a continuation from the second lecture which is really broad. Today we will be talking of

Chemical changes and reaction rates

Chemical change is guided and driven by energetics, but the actual route it takes and the speed with which it occurs is the subject of "dynamics". Dynamics is itself divided into two general areas: kinetics, which deals with the rate of change and is the subject of this lesson. Mechanistic, introduced in a later lesson, is an exploration of the "road map" that links reactants to products.

The energetic aspects of change are governed by the laws of thermodynamics (the "dynamics" part of this word is related to the historical origins of the field and is not a part of dynamics in the sense of these lessons.)

Energetics + dynamics = chemical change

Chemical change is driven by the tendency of atoms and molecules to rearrange themselves in a way that results in the maximum possible dispersion of thermal energy into the world. The observable quantity that measures this spreading and sharing of energy is the *free energy* of the system. As a chemical change takes place, the quantities of reactants and products change in a way that leads to a more negative free energy. When the free energy reaches its minimum possible value, there is no more net change and the system is said to be in *equilibrium*.

The beauty of thermodynamics is that it enables us to unfailingly predict the net direction of a reaction and the composition of the equilibrium state even without conducting the experiment; the standard free energies of the reactants and products, which can be independently measured or obtained from tables, are all we need.

Half the Story

Thermodynamics points the way and makes it possible...but it says nothing about how long it will take to get there!

It is worth noting that the concept of "time" plays no role whatsoever in thermodynamics. But kinetics is all about time. The "speed" of a reaction — how long it takes to reach equilibrium — bears no relation at all to how spontaneous it is (as given by the sign and value of $\Delta G°$) or whether it is exothermic or endothermic (given by the sign of $\Delta H°$). Moreover, there is no way that reaction rates can be predicted in advance; each reaction must be studied individually. One reason for this is that

The stoichiometric equation for the reaction says nothing about its mechanism. By mechanism, we mean, basically, "who does what to whom". Think of a reaction mechanism as something that goes on in a "black box" that joins reactants to products:

What is particularly noteworthy is that these striking differences cannot be reliably predicted from theory; they were revealed only by experimentation.

The rates of chemical reactions

Chemical reactions vary greatly in the speed at which they occur. Some are essentially instantaneous, while others may take years to reach equilibrium. The speed of a chemical reaction may be defined as the change in concentration of a substance divided by the time interval during which this change is observed:

Let me read the simplified version for the rate calculation

Rate = change in concentration level divide by change in time

For a reaction of the form A + B to have C, the rate can be expressed in terms of the change in concentration of any of its components:

Reactors and Fundamentals of Reactors Design for Chemical Reaction

Introduction

A *Chemical reaction* is a process that results in the conversion of chemical substances. The substance or substances initially involved in a chemical reaction are called *reactants*. These reactants are characterized by a chemical change and they yield one or more products. These products are generally different from the original reactants. Chemical reactions may be of different nature depending on the type of reactants, type of product desired, conditions and time of the reaction, for example, *synthesis, decomposition, displacement, precipitation, isomerization, acid-base, redox* or o*rganic reactions.*

Chemical reactors are vessels designed to contain chemical reactions[2]. It is the site of conversion of raw materials into products and is also called the heart of a chemical process. The design of a chemical reactor where bulk drugs would be synthesized on a commercial scale would depend on multiple aspects of chemical engineering. Since it is a very vital step in the overall design of a process, designers ensure that the reaction proceeds with the highest efficiency towards the desired output, producing the highest yield of product in the most cost effective way.

Reactors are designed based on features like *mode of operation* or *types of phases present* or the *geometry of reactors*.

Chemical Energetics: Chemical reactions are always associated with energy changes. Quite often, the energy change accompanying a chemical reaction is more significant than the reaction itself. The branch of science which deals with the energy changes associated with chemical reactions is called *chemical energetics*. The energy changes occurring during the chemical reactions may not always appear as heat energy, but also as *electrical* energy, *work energy* and *radiant energy* as well. Thus, it is evident that chemical reactions are accompanied by energy changes appearing in different forms. These energy changes take place because during chemical reactions certain bonds are cleaved and certain new bonds are formed. Energy is consumed during cleavage of bonds while energy is released during the formation of bonds.

Thermodynamics: Since the bond energy varies from one bond to another, the chemical reactions are always accompanied by absorption or release of energy. Most of the time the energy is in the form of heat. Therefore, it becomes imperative that some concepts of thermodynamics may be understood. *Thermodynamics* literally means conversion of heat into work and vice-versa because *thermo* refers to heat and *dynamics* refers to movement. *Thermodynamics* may, therefore, be defined as *the branch of science which deals with the quantitative relationship between heat and other forms of energies*. When thermodynamics of chemical processes is studied, it is often referred to as *chemical thermodynamics*.

Thermodynamics is primarily based upon *three* fundamental generalizations, popular as *Laws of Thermodynamics*. They are :

1) First Law of Thermodynamics, which deals with the equivalence of different forms of energies.
2) Second Law of thermodynamics, which deals with the direction of chemical change.
3) Third Law of thermodynamics, which helps to evaluate the thermodynamic parameter like entropy.

Therefore, the design of an industrial chemical reactor must satisfy the following requirements:

1. **The chemical factors:** *The kinetics of the reaction.* The design must provide sufficient residence time for the desired reaction to proceed to the required degree of conversion.
2. **The mass transfer factors:** With heterogeneous reactions, the reaction rate may be controlled by the rates of diffusion of the reacting species, rather than the chemical kinetics.
3. **The heat transfer factors:** The removal or addition of the heat of reaction.
4. **The safety factors:** - The confinement of hazardous reactants and products and the control of the reaction and the process conditions.
5. **Economic factors:** Minimum amount of money should be required to purchase and operate. Normal operating expenses include energy input, energy removal, raw material costs, labour, etc. Energy changes can come in the form of heating or cooling, pumping, agitation, etc. The need to satisfy these are interrelated and often contradictory factors makes reactor design a complex and difficult task. However, in

many instances one of the factors will predominate and will determine the choice of reactor type and the design method.

Design Procedure and Reactor Designing

An industrial chemical reactor is a complex device in which heat transfer, mass transfer, diffusion and friction must be considered and it must be safe and controllable. In large vessels, problem of mixing of reactants, flow distribution, residence time distribution and efficient utilization of the surface of porous catalysts also arise. A successful commercial unit is an economic balance of all these factors.

A general procedure for reactor design is outlined below:

1. The kinetic and thermodynamic data on the desired reaction is initially collected. Values will be needed for the rate of reaction over a range of operating conditions, for example, pressure, temperature, flow rate and catalyst concentration. This data may be normally obtained from either laboratory or pilot plant studies.
2. Data on physical properties is required for the design of the reactor. This may be either estimated, or collected from the literature or obtained by taking laboratory measurements.
3. The rate controlling mechanism which has a predominant role is then identified, for example, *kinetic*, *mass* or *heat* transfer.
4. A suitable reactor type is then chosen, based on experience with similar studies or from the laboratory and pilot plant work.
5. Selection of optimal reaction conditions is initially made in order to obtain the desired yield
6. The size of the reactor is decided and its performance estimated. Since exact analytical solutions of the design relationship are rarely possible, semi-empirical methods based on the analysis of idealized reactors are used.
7. Materials for the construction of the reactor is/are selected.
8. A preliminary mechanical design for the reactor including the vessel design, heat transfer surfaces etc., is made.
9. The design is optimized and validated
10. An approximate cost of the proposed and validated design is then calculated.

In choosing the reactor conditions, and optimizing the design, the interaction of the reactor design with the other process operations must not be overlooked. The degree of conversion of raw materials in the reactor will determine the size and the cost of any equipment needed to separate and recycle unreacted materials. In these circumstances the reactor and associated equipment must be optimized as a unit.

Reactor Designing – Mathematical Models

Chemical reactors are vessels designed to contain chemical reactions. The design of a chemical reactor deals with multiple aspects of chemical engineering including mathematical modeling. *A model of a reaction process is a set of data and equation that is believed to represent the performance of a specific vessel configuration* (mixed, plug flow, laminar, dispersed, etc.). Chemical engineers, design reactors to maximize net present value for the given reaction. Designers ensure that the reaction proceeds with the highest efficiency towards the desired output product, producing the highest yield of product. The equations used in mathematical modeling include the stoichiometric relations, rate equations, heat and material balances and auxiliary relations such as those of mass transfer, pressure variation, residence time distribution, etc. The data not only describe physical and thermodynamic properties but also the economic factors. Correlations of heat and mass – transfer rates are fairly well developed and can be incorporated in models of a reaction process, but the chemical rate data must be determined individually. Since equipment are now widely available to obtain such data, hence an initial exploratory work can be carried out.

Once fundamental data is obtained, the goal is to develop a mathematical model of the process, which may be further utilized to explore possibilities such as *product selectivity, start-up and shut down behavior, vessel configuration, temperature, pressure and conversion profiles,* etc.

Any mathematical model has two components, the *symbols* in which it is expressed and their relationship to the quantities in the real world and the *equations* that link the symbols and through which the values of certain variables are computed. These two elements normally coevolve, but they are often separated for the sake of presentation into the parameter and variable definitions and their equations.

Principle: First a mechanism is assumed and then a model is designed accordingly, for example, whether the reaction is steady or unsteady, completely mixed, or plug flow or laminar or with dispersion or with bypass or recycle or dead space, etc.

Then, for a differential element of space and/or time, the elements of conservation are formulated and put together.

Inputs + Sources = Outputs + Sinks + Accumulations

Any transport properties are introduced through known correlations together with the parameters of specified rate equations. *The model can be used to find the performance under various conditions, or its parameters can be evaluated from experimental data.*