Chapter 1. Chemical Processes

1.1 Introduction

Chemical processes usually have three interrelated steps:

1. Transfer of reactants to the reaction zone.
2. Chemical reactions involving various unit processes.
3. Separation of the products from the reaction zone using various unit operations.

Processes may involve homogeneous system or heterogeneous systems. In homogeneous system, reactants are in same phase liquid, gases or solids while heterogeneous system include two or more phases; gas-liquid, gas-solid, liquid-solid. Various type reactions involve may be reversible or irreversible, endothermic or exothermic, catalytic or non-catalytic.

Various variables affecting chemical reactions are temperature, pressure, reactants composition, catalyst activity, and the rate of heat and mass transfer.

The reaction may be carried out in batch, semi batch or continuous reactor. Reactors may be batch, plug flow (PFR), CSTR. It may be isothermal or adiabatic. Catalytic reactors may be packed bed, moving bed or fluidized bed.

The most important factors for chemical processes are: basic data, yield, conversion, and kinetics.

Basic data: are the physical and chemical properties of reactants and products.

Yield is that fraction of raw material recovered as the main product.

Conversion is that fraction of material changed to another desired product.

The yield is frequently above 90 percent, whereas the conversion is limited by equilibrium, changing the operating conditions, the equilibrium can be shifted and the conversion enhanced.

Kinetics: is the study of reaction rates. Such information is essential for plant design, since reaction rate determines equipment size. Catalysts are materials that increase reaction speed.

Along with knowledge of various unit processes and unit operation, the following information and requirements are very important for the development of a commercial process:

1. Material and Energy Balances, and Process Flow and Piping and Instruments Diagrams (PFD and P& ID).
2. Raw Material and Energy Consumption per Ton of Product.
3. Batch vs. Continuous.
4. Chemical Process Selection: design and operation, pilot plant data, equipment required, material of construction.
5. Chemical Process Control and Instrumentation.
6. Chemical Process Economics: Material and Energy Cost, Labor, Overall Cost of Production.
7. Market Evaluation: Purity and Uniformity of Products for Further Processing.
8. Plant Location.
9. Environment Protection, Health, Safety and Hazardous Material.
10. Construction, Building and Commissioning.
11. Management for Productivity and Creativity, Training of Plant Personals.
12. Research and Development (R&D).

The chemical process is a combination of unit process and unit operation:

1.2 Unit Processes

Unit process involves principle chemical conversions leading to synthesis of various useful products and provide basic information regarding;

1. the reaction temperature and pressure, 2. the extent of chemical conversions, 3. the yield of product of reaction, 4. the nature of reaction whether endothermic or exothermic, 5. and the type of catalyst.

Various unit processes in chemical industries are given in Table 1.1

Nitration

Nitration involves the insertion of one or more nitro groups into reacting molecules using various nitrating agents such as nitric acid or mixture of nitric acid and sulphuric acid in batch or continuous process. Nitration products find wide application in chemical industry as solvent, dyestuff, pharmaceuticals, explosive, chemical intermediates. Typical products: TNT, Nitrobenzene, m-dinitrobenzene, Nitroacetanilide, Alpha Nitronaphthalene, Nitroparaffins.

Table 1.1: Unit Processes in Chemical Industries

Alkylation and Hydro delkylation	Decomposition
Acylation	Fermentation
Ammonoxidation	Halogenation
Amination by reduction	Hydsogenation
Amination	Hydrohenatlysis
Aromatisation	Hydroformylation
Amination by ammonalysis	Hydro lysis
Calcination	Hydration
Carbonation	Hydroammonalysis
Causticisation	Isomerisation
Chlorination and Oxy chlorination	Neutralistion
Condensation	Nitration
Biomethhanation	Methanation
Carbinisation	
Disproportination	Oxidation and partial oxidation
Cracking; Thermal, steam cracking, catalytic cracking	Pyrolysis
Dehydration	Polymeristion: Addition and condensation Chain growth and step growth,Bulk, Emulsion, suspension, solution, Radical and coordination polymeristion
Dehydrogenation	Reduction
Ditozitation and coupling	Reforming: Steam reforming Catalytic reforming
Gasification of coal and biomass	Sulphidation
Desulphurisation and hydro desulphurisation	Sulphonatiomn
Electrolysis	Sulphation
Etherification	Xanthation
Estertification and Trans Estrerificartion	

Halogenation

Halogenation is the replacement of one or more hydrogen atoms in an organic or inorganic compound by a halogen (fluorine, chlorine, bromine or iodine) for making various halogen derivatives. Although chlorine derivatives find larger application, however some of the bromine and fluorine derivatives are also important. Various chlorinating agents are; Cl_2, HCl, phosgene ($COCl_2$), hypochlorite (NaOCl). For bromination; bromine Br_2, hydrobromic acid HBr, bromide Br^-, bromated ($NaBrO_3$), alkaline hypobromites BrO^-. In iodination; iodine I_2, hydroiodic acid HI and alkali hypoiodites NaIO. In fluorination: fluorine F_2, hydrofluoric acid HF, and silver tetrafluoroborate $AgBF_4$.

Sulfonation and Sulfation

Sulfonation involves the replacement of H atom of an organic compound with a sulfonic acid group $-SO_3H$ or corresponding salt like sulfonyl halide.

Sulfation involves the replacement of H atom of an organic compound with a sulfate $-OSO_2OH$ or $-SO_4-$. Various sulfonating agents are SO_3 and its compounds, SO_2, sulfoalkylating agents. Sulfonation and sulfation are major industrial chemical processes used to make a diverse range of products, including dyes and color intensifiers, pigments, medicines, pesticides and organic intermediates. Typical application of sulfonation and sulfation are production of lingo sulfonates, linear alkyl benzene sulfonate, Toluene sulfonates, phenolic sulfonates, chlorosulfonic acid, sulfamates for production of herbicide.

Oxidation

Oxidation used extensively in the organic and inorganic chemical industry for the manufacture of a large number of chemicals. Oxidation using O_2 are combinations of various reactions like oxidation via dehydrogenation using O_2, dehydrogenation and the introduction of O_2 and destruction of carbon, partial oxidation, peroxidation, oxidation in presence of strong oxidizing agent like potassium permanganate $KMnO_4$, sodium chlorate $NaClO_3$, potassium dichromate $K_2Cr_2O_7$, hydrogen peroxide H_2O_2, lead dioxide PbO_2, MnO_2, nitric acid, oleum, and O_3. Oxidation maybe carried out either in liquid phase or vapor phase. Some of the important products of organic oxidation are aldehyde, ketone, benzyl alcohol, phthalic anhydride, ethylene oxide, vanillin, benzaldehyde, acetic acid, cumene, synthesis gas from hydrocarbon, propylene oxide, benzoic acid, maleic acid, etc.

Hydrogenation

Hydrogenation is a chemical reaction between hydrogen gas (H_2) and another compound or element, usually in the presence of a catalyst such as nickel, palladium or platinum. Some reactions with H_2 gas are: hydrodesulfurization, hydrocracking, hydroformylation (is an industrial process for the production of aldehydes from alkenes), hydroammonolysis (is a process in which NH_3-H_2 mixture is made in the presence of a hydrogenation catalyst), synthesis of ammonia NH_3, hydrogenation of vegetable oils.

Hydration

Hydration is the process of combining a substance chemically with water molecules. Hydrate, a term used to indicate that a substance contains water, many minerals and crystalline substances are hydrates. In organic chemistry, water is added to an unsaturated substrate, which is usually an alkene or an alkyne. This type of reaction is employed industrially to produce ethanol, isopropanol, and 2-butanol.

Hydrolysis

Hydrolysis is the chemical breakdown of a compound due to reaction with water. The reaction mainly occurs between an ion and water molecule and often changes the pH of a solution. Hydrolysis is used both in inorganic and organic chemical industry. Typical application is in oil and fats industry during soap manufacture where hydrolysis of fats are carried out to obtain fatty acid and glycerol followed by addition of NaOH to form soap. Various types of hydrolysis reaction may be pure hydrolysis, hydrolysis with aqueous acid or alkali, dilute or concentrated.

Electrolysis

Electrolysis is a chemical decomposition produced by passing an electric current through a liquid or solution containing ions. Electrolysis is a technique that uses a direct electric current (DC) to drive non-spontaneous chemical reaction. Electrolysis is commercially important as a stage in the separation of elements from naturally occurring sources such as ores using an electrolytic cell.

Esterification

Esterification is the conversion of carboxylic acid into an ester by combination with an alcohol and removal of a molecule of H_2O. It is an important process in the manufacture of polyethylene terephthalate, methyl meta acrylate, cellulose ester in viscose rayon manufacture, nitroglycerine.

Alkylation

Alkylation is the transfer of an alkyl group from one molecule to another compound by substitution or reduction. Products from alkylation find application in detergent, lubricants, high octane gasoline, photographic chemicals, plasticizers, synthetic rubber, chemicals etc. Some of the alkylating agents are olefins, alcohols, alkyl halides. Although sulfuric acid and phosphoric acid were commonly used as catalyst in alkylation process.

Polymerization

Polymerization is a process of reacting monomer molecules together in a chemical reaction to form polymer chains or three-dimensional networks. Polymerization is one of the very important unit processes which find application in manufacture of polymer, synthetic fiber, synthetic rubber, polyurethane, paint and petroleum industry for high octane gasoline. Polymerization may be carried out either with single monomer or with co-monomer. Polymerization reaction can be addition or condensation reaction. Various Polymerization methods may be bulk, emulsion, solution, suspension. Typical important product from polymerization are, polyethylene, PVC, polystyrene, nylon, polyester, acrylic fiber, polybutadiene, polystyrene, vinyl compounds, urea, melamine and epoxy resin, etc.

Pyrolysis

Pyrolysis is a thermochemical decomposition of hydrocarbon at elevated temperatures in the absence of oxygen (or any halogen). It involves the simultaneous change of chemical composition and physical phase, and is irreversible. Application involves plastic and tire pyrolysis at temperature of 400-450 °C, in absence of oxygen to break down into smaller molecules of oil and gas. The pyrolysis of coal is the first step of gasification. Biomass pyrolysis include biochar, bio-oil and gases of CH_4, H_2, CO, and CO_2 production.

Carbonization is the term for the conversion of an organic substance into carbon or a carbon-containing residue through pyrolysis or destructive distillation.

Carbonation

Carbonation is created by adding dissolved CO_2 and carbonic acid into the liquid. Carbonation is added to soft drinks to give the soft drinks a "bite" to them.

Methanation

Methanation is the reaction by which carbon oxides CO_x and hydrogen H_2 are converted to methane CH_4 and water. The reaction is catalyzed by nickel catalysts.

1.3 Unit Operations

Unit operations are very important in chemical industries for separation of various products formed during the reaction. Table 1.2 give some details of unit operation in chemical process industries.

Table 1.2 Unit Operations in Chemical Process Industries

Absorption and stripping	Membrane Process: Reverse osmosis, Ultrafiltration, Dialysis, Electrodialysis, Perevaporation
Adsorption and desorption Pressure Swing adsorption Chromatography	Crushing Grinding, Pulverizing and Screening
Distillation: Batch distillation Flash distillation, Azeotropic distillation, Extractive distillation Reactive distillation	Solid liquid extraction
Evaporation	Striping
Fluidisation	Sublimation
Crystallisation	Solvent extraction
Liquid- Liquid extraction	

Distillation

Distillation is the process of separating the components or substances from a liquid mixture by successive evaporation and condensation steps and most widely used separation technology. Distillation is used in petroleum refining and petrochemical manufacture. Distillation is the heart of petroleum refining and all processes require distillation at various stages of operations.

Membrane Technology

Membrane technology is a generic term for a number of different, very characteristic separation processes. These processes are of the same kind, because in each of them a membrane is used. Membranes are used more and more often for the creation of process water treatment. Membrane technology has finding increasing application in desalination, wastewater treatment and gas separation and product purification. Membrane separation processes operate without heating and therefore use less energy than conventional thermal separation processes such as distillation, sublimation or crystallization. The separation process is purely physical and both fractions (permeate and retentate) can be used.

Absorption

Absorption is a physical or chemical a process in which molecules or ions of gaseous stream enter another absorbing bulk phase of gas or liquid. Absorption is the most commonly used separation technique for the gas cleaning purpose to remove pollutants such as H_2S, CO_2, SO_2 and NH_3. Cleaning of solute gases is achieved by transferring to a liquid solvent with good contact of the gas stream and liquid stream which offers specific or selectivity for the gases to be recovered. The absorption is mass transfer phenomena where the solute of a gas is removed from being fed in contact with a nonvolatile liquid solvent that absorbs the components from the gas.

Solvent: Liquid applied to remove the solute from a gas stream.

Solute: Components to be removed from entering streams.

Adsorption

Adsorption is the adhesion of molecules of gas, liquid, or dissolved solids to a surface based adsorbent. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. Adsorption is present in many natural, physical, biological, and chemical systems, and is widely used in industrial applications such as heterogeneous catalysts, activated charcoal, air conditioning and other process requirements (adsorption chillers), synthetic resins, and water purification. Adsorption process is often a much cheaper and easier option than distillation, absorption or extraction. One of the most effective method for recovering and controlling emissions of volatile organic compounds is adsorption. Some of the commercial adsorbents are silica gel, activated carbon, carbon molecular sieve, charcoal, zeolites molecular sieves, polymer and resins, clays, biosorbents. Some of the key properties of adsorbents are capacity, selectivity, regenerability, kinetics, compatibility and cost.

Crystallization

Crystallization is a chemical solid–liquid separation technique, in which mass transfer of a solute from the liquid solution to a pure solid crystalline phase occurs. Crystallization occurs in two major steps. The first is nucleation; the appearance of a crystalline phase from either a supercooled liquid or a supersaturated solvent. The second step is known as crystal growth, which is the increase in the size of particles and leads to a crystal state. The most important application in the petroleum industry for separation of wax. The process involves nucleation, growth, and agglomeration and gelling. Some of the applications of crystallization is in the separation of wax, separation of p-xylene from xylenes stream. Typical process of separation of p-xylene involves cooling the mixed xylene feed stock to a slightly higher than that of eutectic followed by separation of crystal by centrifugation or filtration.

Solvent Extraction

Solvent extraction is a method to separate compounds based on their relative solubilities in two different immiscible liquids, usually water and an organic solvent. It consists of transferring one (or more) solute(s) contained in a feed solution to another immiscible liquid (solvent). The solvent that is enriched in solute(s) is called extract. The feed solution that is depleted in solute(s) is called the raffinate. Liquid-liquid extraction has been commonly used in petroleum and petrochemical industry for separation of close boiling hydrocarbons. Some of the major applications are: removal of sulfur compound from liquid hydrocarbons, recovery of aromatics from liquid hydrocarbon, separation of butadiene from C4 hydrocarbons, extraction of acetic acid, removal of phenolic compounds from wastewater, recovery of copper from leach liquor, and extraction of glycerides from vegetable oil. Some of the important property of a good solvent are:

high solvent power/capacity, high selectivity for desired component, sufficient difference in boiling points of the solvent and the feed for effective separation, low latent heat of evaporation an specific heat to reduce utility requirement, high thermal an chemical stability, low melting point, relatively inexpensive, non-toxic and non-corrosive.

1.4 Engineering Flowsheets

For a chemical process in general, equipment, operating details, and all reactions as that occurred, which should include data covering not only materials, but labor and utilities as well.

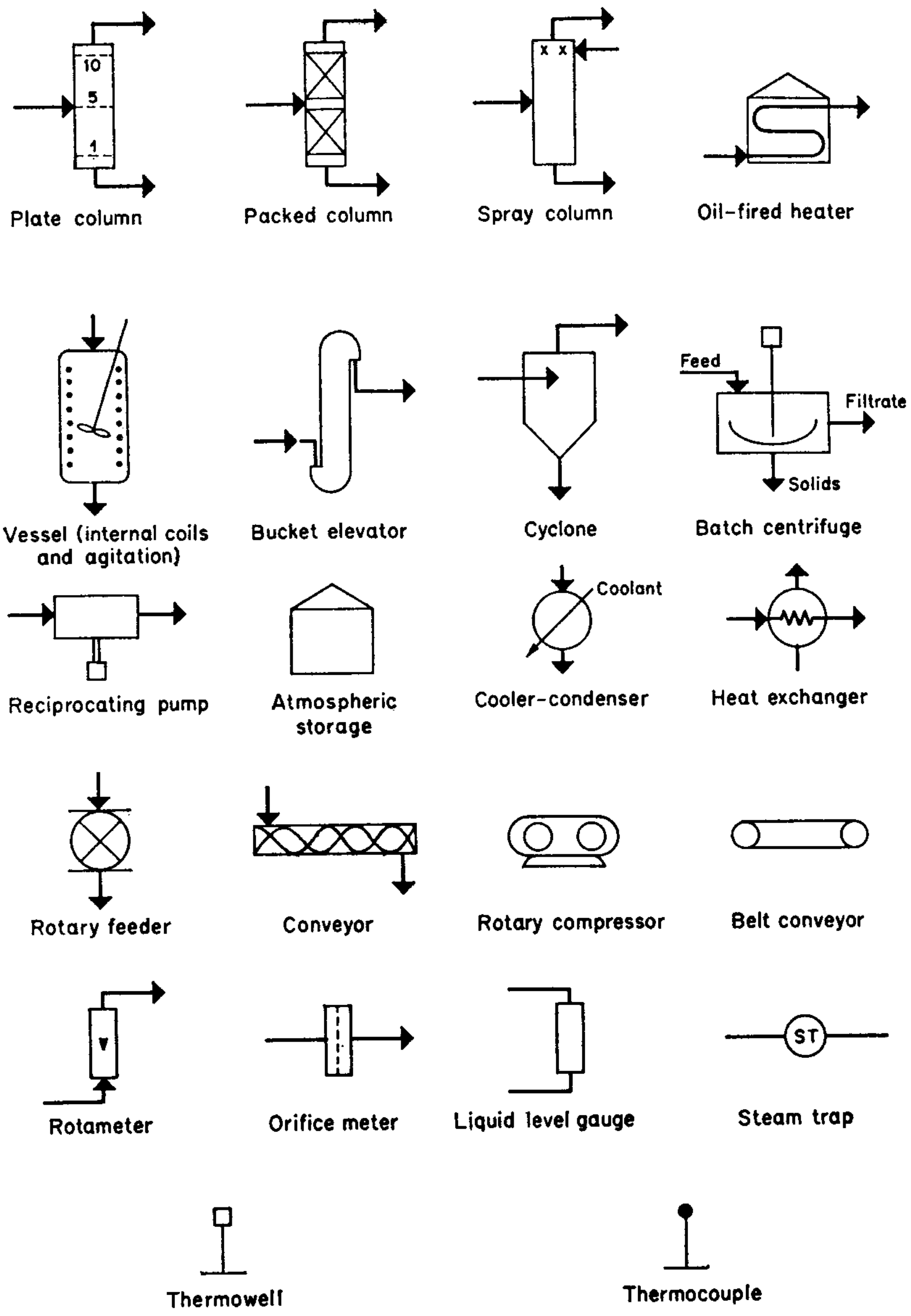

Fig. 1.1 Typical flowsheet symbols

Process Flow Diagrams (PFD) are usually prepared when the design is completed and are used to coordinate all the data from the drawings of individual plant items, which must be prepared separately. It is conventional to show pipes with flanges, heat exchangers with supports, flanges and nozzles and so on, each item being given a code number, various companies have their own ideas on this, but E for exchangers, C for columns, V for vessel and so on seems to be generally accepted. Some useful and generally accepted symbols are shown in Figure 1.1.

Piping and Instrument Diagrams (P&ID) are mechanical flow diagrams allied to the engineering flowsheets. These include all pipe sizes, size and type of valves, pipe fittings, etc., and are necessary where this information, which is required by mechanical, electrical and instrument engineers, is too complicated to be included in the process flowsheet. A portion of a typical piping flow diagram is shown in Fig.1.2. In such diagrams it is conventional to number the various pipelines and branches as an aid to clarity and also in locating lines once the plant is completed. There are a multitude of systems, though the following coding is fairly widespread: nominal pipe size/material code/sequence number.

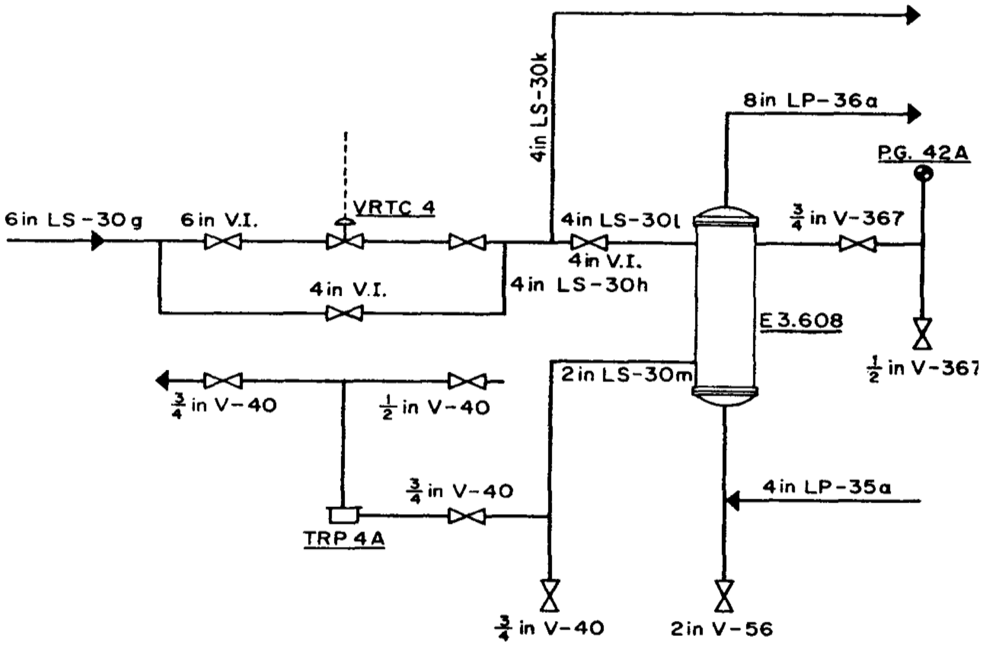

Fig. 1.2 Part of a typical piping flowsheets

For example, `2-Cl-6a'-represents a 2 in. diameter, number 6a carrying chlorine, whilst `4-S150-21' refers to pipe 21, which is 4 in. diameter carrying steam at 1501b/in^2 g. Other material codes are fairly obvious and a matter of personal reference. In numbering pipes, letters are often used to indicate branches. Useful symbols for incorporation in such diagrams are as in Figure 1.3.

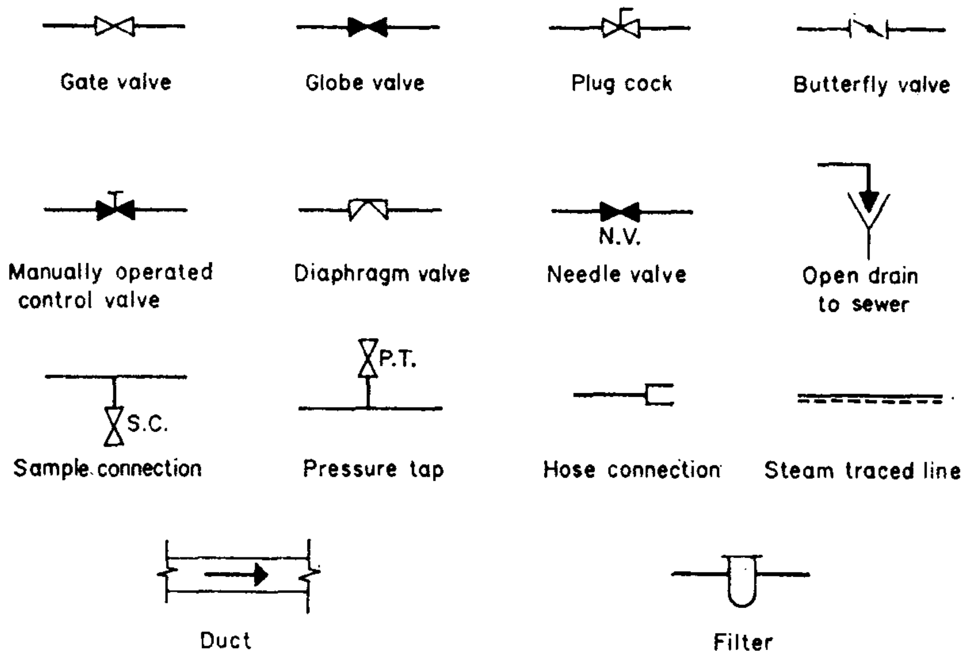

Fig. 1.3 Symbols used in piping flowsheets

1.5 Chemical Process Design

The process engineer is a specialist in current aspects of chemical process design. Practical experience is a necessity if the senior design engineer is to be able to foresee and solve plant problems of a less obvious nature, such as maintenance, safety, and conformation to government environmental controls. Experienced consultants, either individuals or professional consulting firms, are available to advise, design, and/or erect chemical process plants.

1.5.1 Pilot Plants

Pilot plants are small-scale units designed to allow experiments that obtain design data for larger plants and sometimes to produce significant quantities of a new product to permit user evaluation of it. Pilot plant development experiments are expensive but frequently essential. Where possible, current practice is to calculate more and use pilot plants less. The design engineer should plan pilot plant runs carefully by using statistical analysis of the procedures necessary to determine the data required for design. Particularly in completely new operations, the pilot plant should be constructed with equipment identical in material with that to be used by the commercial plant in order to ascertain the effects of corrosion and "to commit blunders on a small scale and make profits on a large scale."

Corrosion data from the pilot plant are much more reliable than small-scale tests with pure chemicals, and the other aspect of corrosion, the effect of corrosion products on the chemical reaction and final products, generally appears here first.

1.5.2 Equipment

Equipment is emphasized in conjunction with descriptions of the various processes and with flowcharts representing these processes. Any chemical engineer should start early to become familiar with industrial equipment such as pumps, filter presses, distillation towers, nitrators, evaporators, sulfonators, electrolyzers, and fuel cells. The Chemical Engineering Catalog includes convenient information concerning the actual equipment that can be supplied by various manufacturers.

1.5.3 Corrosion, Materials of Construction

Successful operation of chemical plants depends not only on the original strength of the materials of construction but also upon proper selection to resist corrosion. Mechanical failures are seldom experienced unless there has been previous corrosion or weakening by chemical attack. Erosion is occasionally a factor in the deterioration of equipment; it can be reduced by avoiding sudden changes in flow direction.

Corrosion cannot be prevented; it can only be minimized. Advances in materials science have provided many corrosion-resistant materials: rubber-covered steel, resin-bonded carbon, and tantalum to resist hydrochloric acid; stainless steel to resist the action of aqueous nitric acid and organic acids even under pressure; and nickel or nickel-clad steel to resist caustic solutions, hot or cold. Polymeric organic materials have become important in the fight against corrosion. Among the construction materials used by chemical engineers are many of the commonest substances and some of the rarest-brick, cast iron, steel, wood, cement, platinum, tantalum, and silver. Corrosion testing must be done with commercial chemicals rather than pure laboratory chemicals since it frequently happens that a small amount of a contaminant in a commercial raw material affects corrosion appreciably.

1.6 Instrumentation and Process Control

1.6.1 Instruments are the essential tool for modern processing. Automatic and instrument controlled chemical processes are common and essential. Data processing and computing instruments actually take over the running of complex chemical processing systems. Some instruments can even optimize plant conditions to meet changing feed conditions. Instruments should be chosen simply to record process variables and to assure:

(1) Quality, usually by sensing.

(2) Controlling.

(3) Recording.

(4) Maintaining desired operating conditions.

In large-scale continuous operations, the function of the workers and the supervisory chemical engineer is to maintain the plant in proper running order. Batch sequences require few instruments, hence more supervision on the part of the workers and the process engineer because conditions or procedures usually differ from start to finish. Even these problems can be solved by programmed instruments if the expense can be justified.

Instrumentation has been forced into this position of importance by the increase in continuous procedures, by the increased cost of labor and supervision, by the relative unreliability of human actions, and by the availability of many types of instruments and monitors at decreasing price and increasing reliability. Instrument types include:

1. Indicating instruments-presenting current data, value, or deviation from a norm
2. Recording instruments-permit study and analysis
3. Indicating/ recording and controlling instruments.

Two types of instruments are currently used, analog and digital:

Analog instruments such pressure spring, thermometers and Bourdon pressure gages, that show results by mechanical movement of some type of device which is proportional to the quantity being measured.

Digital devices generally utilize a "transducer" a device to convert the quantity being measured into some type of signal (usually electrical or pneumatic) and electronic circuitry to this signal to readable numerical figures (digits) which are displayed and/or recorded.

Instruments are indicated by appropriate symbols with the following typical abbreviations:

RTC recording temperature controller

RFM recording flowmeter

ILC indicating level controller

ORFM orifice for recording flowmeter

PG pressure gauge

HPA high pressure alarm

In most designs, diagrams of instrumentation lines, power supplies, and so on, have to be prepared. Instruments and control lines should be presented on the piping flow diagram and on the drawings of the plant items together with full mechanical.

1.6.2 Chemical analytical control has been used in factory procedures for analysis of incoming material and outgoing product, but generally conventional procedures are too slow, expensive, and dependent on frequently questionable sampling procedures. With the advent of fast, reliable, and sensitive procedures capable of automation, control based on analysis within the process has become economically feasible. Quality devices are produced far more reliably than when human analyses are used. Chromatographic systems, pH sensors, conductivity meters, even mass spectroscopy have been automated and used industrially.