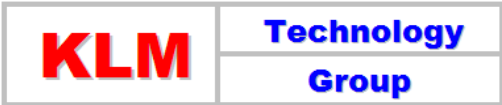


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## INTRODUCTION

### Scope

Chemical engineering is a branch of science that applies physical sciences (physics and chemistry) and life sciences (microbiology and biochemistry) together with applied mathematics and economics to produce, transform, transport, and properly use chemicals, materials and energy. Essentially, chemical engineers design large-scale processes that convert chemicals, raw materials, living cells, microorganisms and energy into useful forms and products.

This guideline provides an overview to basic concepts of the chemical engineering, there are: thermodynamics; material and heat balance; energy and mass transfer; kinetics of chemical reactions; and separation processes.

### General Considerations

#### A. Chemical Engineering

Engineering is the application of mathematics, empirical evidence and scientific, economic, social, and practical knowledge in order to invent, innovate, design, build, maintain, research, and improve structures, machines, tools, systems, components, materials, and processes.

The discipline of engineering is extremely broad, and encompasses a range of more specialized fields of engineering, each with a more specific emphasis on particular areas of applied science, technology and types of application.

Engineering is the creative application of scientific principles to design or develop structures, machines, apparatus, or manufacturing processes, or works utilizing them singly or in combination; or to construct or operate the same with full cognizance of their design; or to forecast their behavior under specific operating conditions; all as respects an intended function, economics of operation or safety to life and property.

Chemical engineering is a branch of science that applies physical sciences (physics and chemistry) and life sciences (microbiology and biochemistry) together with applied mathematics and economics to produce, transform, transport, and properly use chemicals, materials and energy. Essentially, chemical engineers design large-scale

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processes that convert chemicals, raw materials, living cells, microorganisms and energy into useful forms and products.<sup>[13]</sup>

In 1805, John Dalton published Atomic Weights, allowing chemical equations to be balanced and the basis for chemical engineering mass balances. Sadi Carnot in 1824 was the first to study the thermodynamics of combustion reactions. In 1850, Rudolf Calusius applied the principles developed by Carnot to chemical systems at the atomic to molecular scale. Josiah Willard Gibbs developed a mathematical-based, graphical methodology, for the study of chemical systems using the thermodynamics of Clausius in 1873 to 1876.

Hermann von Helmholtz in 1882 showed that measure of chemical affinity is determined by the measure of the free energy of the reaction process. And in 1883, Osborne Reynolds defined the dimensionless group for fluid flow, leading to practical scale-up and understanding of flow, heat and mass transfer.

## B. Unit Operations

An economical method of organizing much of the subject matter of chemical engineering is based on two facts: (1) although the number of individual processes is great, each one can be broken down into a series of steps, called operations, each of which in turn appears in process; (2) the individual operations have common techniques and are based on the same scientific principles.

For example, in most processes solids and fluids must be moved; heat or other forms of energy must be transferred from one subtsbce to another; and tasks like drying, size reduction, distillation, and evaporation must be performed. The unit-operation concept is this: by studying systematically these operations themselves—operations that clearly cross industry and process lines—the treatment of all processes is unified and simplified.

The strictly chemical aspects of processing are studied in a companion area of chemical engineering called reaction kinetics. The unit operation are largely used to conduct the primarily physical steps of preparing the reactants, separating and purifying the products, recycling unconverted reactants, and controlling the energy transfer into or out of the chemical reactor.

The unit operations are as applicable to many physical processes as to chemical ones. For example, the process used to manufacture common salt consists of the following sequence of the unit operations: transportation of solids and liquids, transfer of heat,

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evaporation, crystallization, drying, and screening. No chemical reaction appears in these steps. On the other hand, the cracking of petroleum, with or without the aid of a catalyst, is a typical chemical reaction conducted on an enormous scale. Here the unit operations—transportation of fluids and solids, distillation, and various mechanical separations—are vital, and cracking reaction could not be utilized without them. The chemical steps themselves are conducted by controlling the flow of material and energy to and from the reaction zone. [7]

Chemical engineering unit operations consist of five classes:

- Fluid flow processes, including fluids transportation, filtration, and solids fluidization.
- Heat transfer processes, including evaporation and heat exchange.
- Mass transfer processes, including gas absorption, distillation, extraction, adsorption, and drying.
- Thermodynamic processes, including gas liquefaction, and refrigeration.
- Mechanical processes, including solids transportation, crushing and pulverization, and screening and sieving.

Chemical engineering unit operations also fall in the following categories which involve elements from more than one class:

- Combination (mixing)
- Separation (distillation, crystallization, chromatography)
- Reaction (chemical reaction)

Furthermore, there are some unit operations which combine even these categories, such as reactive distillation and stirred tank reactors. A "pure" unit operation is a physical transport process, while a mixed chemical/physical process requires modeling both the physical transport, such as diffusion, and the chemical reaction. This is usually necessary for designing catalytic reactions, and is considered a separate discipline, termed chemical reaction engineering.

Chemical engineering unit operations and chemical engineering unit processing form the main principles of all kinds of chemical industries and are the foundation of designs of chemical plants, factories, and equipment used.

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In general, unit operations are designed by writing down the balances for the transported quantity for each elementary component (which may be infinitesimal) in the form of equations, and solving the equations for the design parameters, then selecting an optimal solution out of the several possible and then designing the physical equipment. For instance, distillation in a plate column is analyzed by writing down the mass balances for each plate, wherein the known vapor-liquid equilibrium and efficiency, drip out and drip in comprise the total mass flows, with a sub-flow for each component.

Combining a stack of these gives the system of equations for the whole column. There is a range of solutions, because a higher reflux ratio enables fewer plates, and vice versa. The engineer must then find the optimal solution with respect to acceptable volume holdup, column height and cost of construction. <sup>[14]</sup>

### C. Application

Chemical engineers "develop economic ways of using materials and energy". Chemical engineers use chemistry and engineering to turn raw materials into usable products, such as medicine, petrochemicals and plastics on a large-scale, industrial setting. They are also involved in waste management and research. Both applied and research facets could make extensive use of computers.

A chemical engineer may be involved in industry or university research where they are tasked in designing and performing experiments to create new and better ways of production, controlling pollution, conserving resources and making these processes safer. They may be involved in designing and constructing plants as a project engineer. In this field, the chemical engineer uses their knowledge in selecting plant equipment and the optimum method of production to minimize costs and increase profitability.

After its construction, they may help in upgrading its equipment. They may also be involved in its daily operations. Chemical engineers may be permanently employed at chemical plants to manage operations. Alternatively, they may serve in a consultant role to troubleshoot problems, manage process changes and otherwise assist plant operators. <sup>[13]</sup>

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### Chemical engineering contribution to society

- **Fueling the world's economies**  
The world's economy needs energy to keep it moving. Chemical engineers stretch fossil fuels into various energy supplies.
- **Creating cleaner energy**  
Chemical engineering created a new generation of clean energy technologies. Such as nuclear power plant, NiMH battery, and alternative energies (air, wind, water, solar, etc)
- **Products for growing populations**  
Water purification, water desalination, and green productions.
- **Removing harmful sulfur from fuels**
- **Better living through chemistry**
- **Stretching natural resources**  
Chemical engineering made innovative materials like synthetic rubbers, bio-plastic, kevlar, etc.
- **Convenient and abundant food**  
Processed food, canned food, powder coffee, powder milk, and sterilized food.
- **Healing diseases and extending life**  
Advance medical science, improving the quality of life. Such as dialysis (artificial kidneys).
- **Powering the personal computer**  
Germanium-based silicon chips that help laptop perform faster. From thin-film liquid crystal displays to software that simulates complex industrial processes.

### Biomedical Therapies and Materials

Although many chemical engineers do not take courses in college biology, their knowledge of reactions and separations make them uniquely suited to working on problems on a cellular level. A cell is a membrane separator, only allowing certain chemicals and materials to pass through into its interior; additionally, there are a plethora of chemicals processes occurring in the cell, such as respiration and photosynthesis.

Chemical engineering is often intertwined with biology and biomedical engineering, particularly with regard to harnessing the chemical machinery inside a cell, and developing and manufacturing "markers" for detecting cancer cells. Chemical engineering learn to design biodegradable scaffolds for culturing cells for medical implants and to provide key technology to study the human genome.



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## Development of Alternative Energy Systems

Fossil fuels are non-renewable resources that have environmental implications as they are used to power our industrialized society. Chemical engineering learn to develop alternative fuels and energy systems that allow our dependance on fossil fuels to be reduced.

The polymer electrolyte fuel cell is one promising technology that has already been shown capable of powering automobiles. Fuel cells are subject to the same general operating principles as a typical battery used in our household devices, the difference being that fuel is continually provided in the form of hydrogen and oxygen, so fuel cells do not run out of power.

Electrochemistry is the fundamental science behind these devices. One of the key issues in unlocking the full potential alternative energy systems is energy storage—needed when the sun goes down, the wind does not blow, or excess energy from alternative sources is received and needs to be captured for later use. Efficient batteries are essential to the development of energy systems needed to meet the needs of society. Chemical engineering not only about improve processes for the electrochemical conversion of energy, but also create novel materials essential for the improvement of these storage devices.

## Reducing the Environmental Impact of Technology

Chemical engineering provide study of chemical purification to make sure that the output streams from processes are safe for the environment. If water is polluted, chemical engineer designs processes to purify that water, and we can do until virtually all of the pollutant is removed. When a smokestack emits carbon dioxide and sulfur dioxide which may form acid rain later on, process units to remove these undesirable gases can be designed. Many government and ethical constrains that require fractions of contaminants to be reduced to mass fractions in the parts per million and parts per billion range.

## Transformation of Raw Materials into Essential Chemicals

Chemical engineering develops processes for transforming raw materials into the vast array of high-value chemicals required by modern society that enhances human's quality of life. Examples include nano scale composites, pharmaceuticals, plastics, fibers, metals, and ceramics. <sup>[12]</sup>

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## DEFINITIONS

**Absorption** – A physical or chemical phenomenon or a process in which atoms, molecules or ions enter some bulk phase – gas, liquid or solid material.

**Adsorbent** – A substance that attracts other materials or particles to its surface.

**Adsorption** – The phenomenon of accumulation of large number of molecular species at the surface of liquid or solid phase in comparison to the bulk.

**Biodegradable** – Capable of being broken down (decomposed) rapidly by the action of microorganisms.

**Catalyst** – A substance that speeds up a chemical reaction, but is not consumed by the reaction

**Composite** – A material made from two or more constituent materials with significantly different physical or chemical properties that, when combined, produce a material with characteristics different from the individual components.

**Conduction** – The transfer of internal energy by microscopic diffusion and collisions of particles or quasi-particles within a body due to a temperature gradient.

**Convection** – The concerted, collective movement of groups of aggregates of molecules within fluids and solids.

**Countercurrent exchange** – A mechanism occurring in nature and mimicked in industry and engineering, in which there is a crossover of some property, usually heat or some component, between two flowing bodies flowing in opposite directions to each other.

**Electrochemistry** – The branch of physical chemistry that studies chemical reactions which take place at the interface of an electrode, usually a solid metal or a semiconductor, and an ionic conductor, the electrolyte.

**Enthalpy** – A measure of energy in a thermodynamic system.

**Entropy** – A quantity of the number of specific ways in which a thermodynamic system may be arranged, commonly understood as a measure of disorder.

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**Fossil fuel** – A general term for buried combustible geologic deposits of organic materials, formed from decayed plants and animals that have been converted to crude oil, coal, natural gas, or heavy oils by exposure to heat and pressure in the earth's crust over hundreds of millions of years.

**Heat Balance** – Often called an 'energy balance', a version of law of conservation of energy adapted thermodynamic systems.

**Heat Transfer** – Exchange of thermal energy between physical systems depending on the temperature and pressure of substance.

**Material balance** – An application of conservation of mass to the analysis of physical systems.

**Ore** – A type of rock that contains sufficient minerals with important elements including metals that can be economically extracted from the rock.

**Petrochemicals** – Chemicals made from petroleum (crude oil) and natural gas.

**Purification** – The process of rendering something pure, i.e. clean of foreign elements and/or pollution.

**Radiation** – A process in which electromagnetic waves (EMR) travel through a vacuum or through matter-containing media.

**Solute** – A substance dissolved in another substance, known as a solvent.

**Thermodynamic** – A branch of physics that concerned with heat and temperature and relation to energy and work.

**Van der Waals force** – The residual attractive or repulsive forces between molecules or atomic groups that do not arise from a covalent bond, or electrostatic interaction

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## NOMENCLATURE

A	: Area perpendicular of the x direction ( $m^2$ )
B	: Coefficient of volume expansion ( $1/K$ )
$C_f$	: Friction coefficient
$C_p$	: Specific heat of constant pressure
$C_v$	: Specific heat of constant volume
c	: the speed of light (m/s)
D	: Diameter (m)
$F_D$	: Drag force (N)
G	: Gravitational acceleration ( $m/s^2$ )
Gr	: Grashof number
H	: Convective heat transfer coefficient ( $W/m^2 \cdot ^\circ C$ )
$H_P$	: Energy of product
$H_R$	: Energy of reactant
J	: The flux of a constituent relative to the average molar velocity of all constituents ( $mol/m^2 \cdot s$ )
K	: Thermal conductivity ( $W/m \cdot K$ )
$L_c$	: The characteristic length (m)
$p_A$	: partial pressure of component A (kPa)
Nu	: Nusselt number
$p_i$	: total pressure (kPa)
Pr	: Prandtl number
Q	: The rate of heat transfer (W)
$Q_{cond,wall}$	: The rate of conduction (W)
$Q_L$	: The amount of heat absorbed from the low-temperature medium (W)
$Q_H$	: The amount of heat rejected to the high-temperature medium (W)
q	: Heat-flux density through concentric surface radius r
R	: Thermal resistance ( $K/W$ )
$R_A$	: Rate of reaction
Re	: Reynolds number
$r_A$	: Intensive rate of reaction
$r_1$	: Inner radius (m)
$r_2$	: Outer radius (m)
S	: Conduction shape factor
$S'$	: The total entropy of the system (J/K)
T	: Absolute temperature of the system ( $^\circ C$ )
$T_s$	: Temperature of the surface ( $^\circ C$ )
$T_\infty$	: Temperature of the fluid sufficiently far from the surface ( $^\circ C$ )

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- $V$  : Upstream velocity (m/s)  
 $\nu$  : Kinematic viscosity of fluid ( $m^2/s$ )  
 $W$  : Work (Joule)  
 $x$  : The thickness of the plane (m)  
 $y_A$  : Mole fraction concentration

### Greek Letter

- $\lambda$  : Wavelength (m)  
 $\beta$  : Coefficient of volume expansion (1/K)  
 $\eta$  : Wavenumber ( $m^{-1}$ )  
 $\eta_{th}$  : Thermal efficiency (%)  
 $\sigma$  : Stefan – Boltzmann constant ( $5.67 \times 10^{-8} W/m^2.K^4$ )  
 $\gamma$  : Specific heat ratio

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## THEORY

### A. Thermodynamics

Thermodynamics is the branch of science that lends substance to the principles of energy transformation in macroscopic systems. The general restrictions shown by experience to apply to all such transformations are known as the laws of thermodynamics. These laws are primitive; they cannot be derived from anything more basic.

The first law of thermodynamics states that energy is conserved, that although it can be altered in form and transferred from one place to another, the total quantity remains constant. Thus the first law of thermodynamics depends on the concept of energy, but conversely energy is an essential thermodynamic function because it allows the first law to be formulated. This coupling is characteristic of the primitive concepts of thermodynamics.

The words system and surroundings are similarly coupled. A system can be an object, a quantity of matter, or a region of space, selected for study and set apart (mentally) from everything else, which is called the surroundings. An envelope, imagined to enclose the system and to separate it from its surroundings, is called the boundary of the system.

Attributed to this boundary are special properties which may serve either to isolate the system from its surroundings or to provide for interaction in specific ways between the system and surroundings.

When a system is isolated, it cannot be affected by its surroundings. Nevertheless, changes may occur within the system that are detectable with measuring instruments such as thermometers and pressure gauges. However, such changes cannot continue indefinitely, and the system must eventually reach a final static condition of internal equilibrium. For a closed system which interacts with its surroundings, a final static condition may likewise be reached such that the system is not only internally at equilibrium but also in external equilibrium with its surroundings.

The concept of equilibrium is central in thermodynamics, for associated with the condition of internal equilibrium is the concept of state.

When a system is displaced from an equilibrium state, it undergoes a process, a change of state, which continues until its properties attain new equilibrium values. During such a process, the system may be caused to interact with its surroundings so as to interchange

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energy in the forms of heat and work and so to produce in the system changes considered desirable for one reason or another. A process that proceeds so that the system is never displaced more than differentially from an equilibrium state is said to be reversible, because such a process can be reversed at any point by an infinitesimal change in external conditions, causing it to retrace the initial path in the opposite direction.

Thermodynamics finds its origin in experience and experiment, from which are formulated a few postulates that form the foundation of the subject. The first two deal with energy.

### Postulate 1

There exists a form of energy, known as internal energy, which for systems at internal equilibrium is an intrinsic property of the system, functionally related to the measurable coordinates that characterize the system.<sup>[9]</sup>

### Postulate 2 (First Law Of Thermodynamics)

The recognition of heat and internal energy as forms of energy makes possible a generalization of the law of conservation of mechanical energy. The first law of thermodynamics could be stated as one formal sentences as sounds :

**“Although energy assumes many forms, the total quantity of energy is constant, and when energy dissapears in one form it appears simultaneously in other forms.”**

As cited before, the sphere of influence of the process is divided into two parts, the system and its surroundings. In its basic form, the first law requires :

$$\Delta(\text{Energy of the system}) + \Delta(\text{Energy of surroundings}) = 0 \quad (1)$$

The region of space identified for analysis of open systems is called a control volume, it is separated from its surroundings by a control surface. The fluid within the control volume is the thermodyanmic system for which mass and energy balance are written. Figure 14 schematically represents the control volume that is separated from its surroundings by an extensible control surface.

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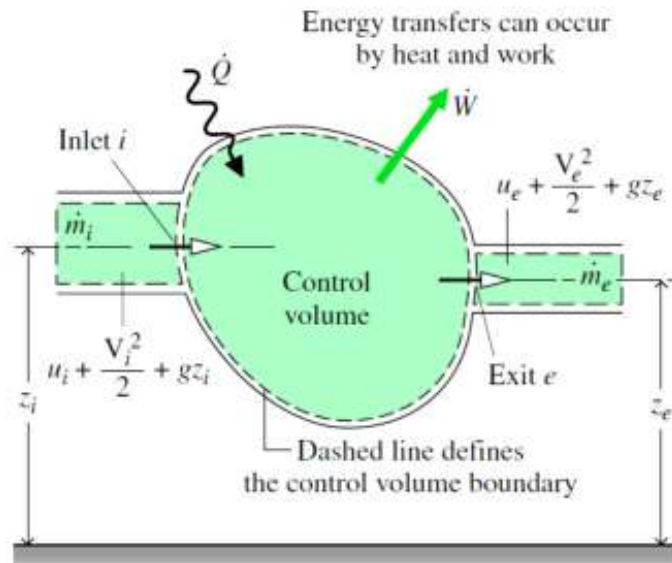


Figure 1 : Control Volume

Accordingly, the conservation of energy principle applied to a control volume states :

$$\frac{dE_{cv}}{dt} = Q - \dot{W} + \dot{m}_i \left( u_i + \frac{V_i^2}{2} + gz_i \right) - \dot{m}_e \left( u_e + \frac{V_e^2}{2} + gz_e \right) \quad (2)$$

Where  $E_{cv}$  denotes the energy of the control volume at time  $t$ . Flow processes for which the accumulation is zero are generally said to occur at steady state. This means that the mass of the system within the control volume is constant, it also consider that no changes occur with time in the properties of the fluid within the control volume nor at its entrances and exits. No expansion of the control volume is possible under these circumstances. The only work of the process is shaft work, and the general energy balance becomes

$$\Delta H + \frac{\Delta u^2}{2} + g \Delta z = Q + W_s \quad (3)$$

In many applications, kinetic and potential energy terms are negligible compared with other terms. Therefore, the equation could rearrange as

$$\Delta H = Q + W_s \quad (4)$$



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The expression of the first law for a steady state, steady flow process is analogous for a nonflow process. Nonetheless, enthalpy rather than internal energy is the thermodynamic property of importance.

If the boundary of a system does not permit the transfer of matter between the system and its surroundings, the system is said to be closed, and its mass is constant. Since no stream enter or leave a closed system, no internal energy is transported across the boundary of the system. Thus, all energy exchange between a closed system and its surroundings then appears as heat and work. Closed systems often undergo processes that cause no change in the systems other than in its internal energy, which described as

$$\Delta U' = Q + W \quad (5)$$

In differetial form, the equation becomes

$$dU' = dQ + dW \quad (6)$$

The term of  $dW$  represents any form of work transfer to or from the system. In many situations of practical interest the thermodynamic work for closed systems is typically the  $p.dV$  work.

Hence, the equation could be reframed as

$$dU' = dQ - \int_{V_1}^{V_2} p dV \quad (7)$$

Where,

$W > 0$  : Work is done on system.

$W < 0$  : Work is done by system.

$Q > 0$  : Heat addition to system.

$Q < 0$  : Heat removal from system.

The process of change in a thermodynamic system may occur under various type of constrains which are enlisted below :

- Isobaric (constant pressure).
- Isochoric (constant volume).
- Isothermal (constant temperature).

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- Adiabatic (without heat transfer).

For other thermodynamic processes such as Isothermal and Adiabatic in closed systems are conveniently understood by applying the first law to a system comprised of an ideal gas. Since  $dU = 0$ , the relationship for an isothermal process becomes

$$dQ = -dW \quad (8)$$

Or, it could be written as

$$Q = -W \quad (9)$$

If P-V work is considered, the work term is calculable if the carried reversibly, as the ideal gas Equation of State relate the P and V at all points of change, thus :

$$W = - \int_{V_1}^{V_2} p \, dV \quad (10)$$

$$W = - \int_{V_1}^{V_2} \left( \frac{RT}{V} \right) dV \quad (11)$$

$$W = RT \ln \frac{V_1}{V_2} \quad (12)$$

$$W = RT \ln \frac{P_2}{P_1} \quad (13)$$

And the final equation will be

$$Q = RT \ln \frac{P_2}{P_1} \quad (14)$$

Or

$$Q = RT \ln \frac{V_1}{V_2} \quad (15)$$

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Meanwhile, for isobaric process the equation will be:

$$Q = \Delta H \quad (16)$$

Where,

$$\Delta H = \int C_p dT \quad (17)$$

Then,

$$W = - \int_{V_1}^{V_2} p dV \quad (18)$$

$$W = -P(V_2 - V_1) \quad (19)$$

For adiabatic process where dQ equals to zero value, the equation yields

$$dU = dW = C_p dT \quad (20)$$

Since,

$$W = - \int p dV \text{ and } \gamma = 1 + \frac{R}{C_v} \quad (21)$$

The equation becomes

$$W = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1} \quad (22)$$

Or

$$W = \frac{P_1 V_1}{\gamma - 1} \left[ \left( \frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} - 1 \right] \quad (23)$$

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$$W = \frac{RT_1}{\gamma - 1} \left[ \left( \frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} - 1 \right] \quad (24)$$

For Polytropic Process where  $PV^\delta$ ,  $TV^{\delta-1}$ , and  $TP^{(1-\delta)/\delta}$  remaining a constant value, the equation could written as

$$W = \frac{(\delta - \gamma)RT_1}{(\delta - \gamma)(\gamma - 1)} \left[ \left( \frac{P_2}{P_1} \right)^{(\delta-1)/\delta} - 1 \right] \quad (25)$$

### Postulate 3

There exists a property called 'entropy', which for systems at internal equilibrium is an intrinsic property of the system, functionally related to the measurable coordinates that characterize the system. For reversible processes, changes in this property may be calculated by the equation<sup>[9]</sup>

$$ds' = \frac{dQ_{rev}}{T} \quad (26)$$

Where :

S' = The total entropy of the system

T = Absolute temperature of the system

### Postulate 4 (Second Law of Thermodynamics)

The first law of thermodynamic places no restriction on the direction of a process, but satisfying the first law does not ensure that the process can actually obtain. The use of the second law thermodynamics is not limited to identifying the direction of processes. Hence, the second law also asserts that energy has quality as well as quantity.

The observation suggests a general restriction on processes beyond that imposed by the first law. The second law is equally well expressed in the two statements that defined the restriction as follows :

- There's no apparatus can operate in such a way that its only effect (in system and surroundings) is to convert heat absorbed by a system completely into work done by the system.

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- No process is possible which consists solely in the transfer of heat from one temperature level to a higher one.
- It is impossible by a cyclic process to convert the heat absorbed by a system completely into work done by the system.

The third statement is the alternative way of the first statement. If the original state of the system is restored in order to comply with the requirements of statement 1, energy from the surroundings in the form of work is needed to compress the gas back to its original pressure. At the same time energy as heat is transferred to the surroundings to maintain constant temperature. This reverse process requires at least the amount of work gained from the expansion. Thus, no net work is achieved or produced.

The term of cyclic requires that the system be restored periodically to its original state. By the case of gas in piston cylinder assembly, its initial expansion and recompression to the original state constitute a complete cycle. The restriction to a *cyclic* process in the third statement amounts to the same limitation as that introduced by the words *only effect* in the first statement. The preceding discussions could be summarized by noting that the second law and deductions from it are useful because they provide means for :

- The prediction of the direction of processes.
- Determine the best possible theoretical performances of cycles, engines, and other devices.
- Establish a condition for the equilibrium state.
- Calculate a temperature scale independent of the properties of any thermometric substance.
- Evaluate quantitatively the factors that preclude the attainment of the best theoretical performance level.
- Develop means for evaluating properties like internal energy ( $u$ ) and enthalpy ( $h$ ).

The Clausius statement has been selected as a point of departure for the study of the second law and its consequences because it is in accord with experience and therefore easier to accept. On the other hand, the Kelvin – Planck statement has the advantage that it provides an effective means for bringing out important second law deductions related to systems undergoing thermodynamic cycles.

One of the approachment (the Clausius inequality) leads directly to the property entropy and formulation of the second law convenient for the analysis of closed systems and control volumes as they undergo processes that are not necessarily cycles. The Clausius statement of the second law asserts that

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**“It is impossible for any system to operate in such a way that the sole result would be an energy transfer by heat from a cooler to a hotter body.”**

This statement does not rule out the possibility of transferring energy by heat from a cooler body to a hotter body, for this is exactly what refrigerators and heat pumps accomplish. The Clausius statement implies that it is impossible to construct a refrigeration cycle that operates without an input of work.

The concept of thermal reservoir at the begin inspires the Kelvin-Planck statement of the second law. A thermal reservoir is a hypothetical body with a relatively large thermal capacity that can supply or absorb finite amounts of heat without undergoing any change in temperature. Having introduced the thermal reservoir concept, The Kelvin – Planck statement of the second law sounds as :

**“It is impossible for any system to operate in a thermodynamic cycle and deliver a net amount of energy by work to its surroundings while receiving energy by heat transfer thermal reservoir.”**

The Kelvin – Planck statement could described analytically. For this case, a system undergoing a cycle while exchanging energy by heat transfer with a single reservoir. The first and second laws each impose constraints :

- The net work done by the system undergoing a cycle equals to the heat transfer to the system. Although the cycle energy balance allows the net work  $W_{\text{cycle}}$  to be positive or negative, the second law imposes a constraint on its direction.
- A system undergoing cycle while communicating thermally with a single reservoir cannot deliver a net amount of work to its surroundings. Thus, the net work of the cycle cannot be positive and the analytical form of the Kelvin-Planck statement becomes

$$W_{\text{cycle}} \leq 0 \qquad (27)$$