

**Department of Chemical Engineering, Faculty of Engineering and
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Fundamental of Engineering Thermodynamics (CHE 242)

CHAPTER ONE

1. INTRODUCTION

The word thermodynamics is a combination of two words, thermo which means heat and dynamics which means force. Thermodynamics is a subject that deals with the transformation of energy of all kinds from one form to another in processes involving either physical or chemical changes. It cannot however handle the issue of rates of transformation. As a subject, it is concerned with quantification of *inter-relation* between energy and the *change of state* of any real world system. It is restricted to the definition of the direction through which transformation of energy can take place and the amount of transformation possible. The extent of such change of state due to transfer of energy *to* or *from* the system is captured through the basic equations of thermodynamics which are derived starting from a set of fundamental observations known as “Laws of Thermodynamics”. These laws of thermodynamics have applications ranging from the microscopic to the macroscopic order, and indeed to cosmological processes. It can therefore be said that all processes taking place in the universe, whether in non-living or living systems, are subject to the laws of thermodynamics.

1.2 Thermodynamic System: Basic Definitions

There are some terms that will be repeatedly used in this course. This section gives the definition of these basic terms.

1.2.1 A **system**, in general, is any part of the universe which may be defined by a boundary which distinguishes it from the rest of the universe. Such a thermodynamic system is usually referred to as **control volume** as it would possess a volume and would also contain a definite quantity of matter. The system boundary may be real or imaginary, and may change in shape as well as in size over time, i.e., increase or decrease.

1.2.2 Any part of the universe that is external to the system constitutes the **surroundings**. The combination of the system and surroundings is called the **universe**. That is

system + surrounding = universe

1.1

1.2.3 A system can either be *closed* or *open*. An open system is one which involves exchange of mass or matter between it and its surrounding. A closed system does not allow any transfer of mass (material) across its boundary. In either case energy transfer can occur across the system boundary in any of its various forms; for example, heat, work, electrical / magnetic energy, etc. However, for most real-world systems of interest to chemical engineers the primary forms of energy that may transfer across boundaries are heat and work. In contrast to closed or open systems, a system which is enclosed by a boundary that allows neither mass nor energy transfer is an *isolated* system.

1.2.4 A **Thermodynamic state** of a system is a condition of the system to which can be ascribed clearly defined attributes or properties.

1.2.5 Thermodynamic properties are typically classified as *intensive* and *extensive*. An intensive property is independent of the extent (size) of the system for which it is defined. Examples are temperature, pressure and mass density. An extensive property is one with a magnitude that is dependent on the extent of mass involved in the system or medium. Examples are volume, internal energy, enthalpy, kinetic energy and potential energy. If the extensive properties are defined per unit mass, they yield the equivalent intensive properties. Thus, we have specific volume (v), specific internal energy (u), specific enthalpy (h), specific kinetic energy $e_k = \frac{1}{2}v^2$, and specific potential energy $e_p = gz$. Note that the quantifier “specific” implies “per unit mass” while “molar” denotes “per unit mole”. The ratio of an extensive property to the mass or the property *per unit mass* is called *specific* property. The ratio of an extensive property to the number of moles of the substance in the system, or the property per mole of the substance, is called the molar property.

$$\text{Specific volume } v = V^t/m$$

1.2

$$\text{molar volume } V = V^t/n$$

1.3

1.2.6 A **thermodynamic process** is a transformation which takes a system from one equilibrium state to another equilibrium state through a succession of states. The aggregates of states traversed by the process defines the *process path*

1.2.7 A cyclic process is a process whose final state is coincidental with its initial state

1.2.8 State and Path Dependent Thermodynamic Variables

A state function is a function which is independent of the process path and depends only on the terminal states. Examples of state functions are temperature, pressure, mass density, internal energy, volume and enthalpy. Consider a gas at a certain temperature and a pressure within a piston-cylinder assembly which we may assume to be isolated. If the piston position is held fixed at this point the gas state is said to be characterized by the temperature and the pressure and its corresponding volume. If the gas is compressed, the gas will also attain a new equilibrium state wherein the pressure and temperature would attain a new set of values. If, on the other hand the extra applied pressure is removed and the gas reverts to the earlier state the original temperature and pressure (and, of course volume) is restored. Extending this argument, in general, if the gas is heated or cooled, compressed or expanded, and then returned to its initial temperature and pressure, its intensive properties are restored to their initial values. It is evident, therefore, that such properties do not depend on the past history of the fluid or on the path by which it reaches a given state. They depend only on present state, irrespective of how they are attained. Such quantities are thus defined as *state variables*. Mathematically, this idea may be expressed as follows:

$$\int_{T_1}^{T_2} dT = T_2 - T_1 = \Delta T; \int_{V_1}^{V_2} dV = V_2 - V_1 = \Delta V; \int_{P_1}^{P_2} dP = P_2 - P_1 = \Delta P \quad 1.4$$

The changes in the above intensive properties depend only on the initial and final states of the system. They constitute point functions and their differentials are exact.

A path function however, depends on the process. Consider the case of thermodynamic work depicted as the area under the curve on a P-V graph. This is illustrated in fig. 1.1.

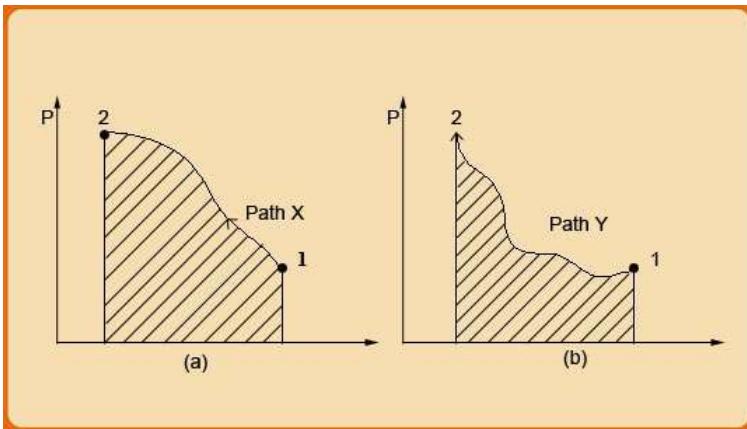


Figure 1.1: Illustration of thermodynamic work on P-V plot

As shown in the figure, the work associated with a thermodynamic process clearly is dependent on the path followed in terms of P and V. It follows that if one were to go from state '1' to '2' by path X and then return to '1' by path Y the work in the two processes would differ and so one would not be giving and taking work out of the system in equal measure. An entity such as P-V work is, therefore, described as a *path variable*, and therefore is not directly dependent on the state of the system. Heat is another example of path function.

1.2.9 Energies associated with Thermodynamic Processes:

These are forms that energy assumes when it is resident in a system. **The internal energy** on **intrinsic energy u** is energy possessed by a body/ medium by virtue of its configuration. It is the energy possessed by matter due to the microscopic modes of motion. The microscopic variety of energy forms the principal consideration in case of transformations that occur in a thermodynamic system. The **potential energy E_p** is the energy which exist in a medium due to its relative elevation in the gravitational field. For body with mass m , acceleration due to gravity g and elevation relative to reference level z , potential energy has the mathematical definition

$$E_p = mgz \quad 1.5$$

The **kinetic energy** is a measure of the state of motion of a body on a macroscopic level. It is defined mathematically by the relationship

$$E_k = \frac{1}{2} mv^2 \quad 1.6$$

where m is the mass of the body and v is the velocity.

1.2.10 Thermodynamic Work and heat

Work and heat are two forms of energy but they are forms of *energy in transit*, forms assumed by energy when it flows from one medium to another. Work is said to be accomplished when a force experiences a displacement. Heat is that form of energy which when transmitted to or from a medium causes a change either in its degree of hotness or its phase. In general work refers to a form of energy transfer which results due to changes in the external *macroscopic* physical constraints on a thermodynamic system. For example, electrical work results when a charge moves against an externally applied electrical field. It is mechanical work that is most commonly encountered in real thermodynamic systems, for example a typical chemical plant.

1.2.11 Enthalpy

This is a thermodynamic function which features in the analysis of flow processes. It is defined by

$$H = U + PV$$

where P is pressure and V is total volume.

1.2.12 Thermodynamic Equilibrium

In general change of state of a thermodynamic system results from existence of gradients of various types *within* or *across* its boundary. Thus a gradient of pressure results in momentum or convective transport of mass. Temperature gradients result in heat transfer, while a gradient of concentration (more exactly, of *chemical potential*) promotes diffusive mass transfer. Thus, as long as *internal* or *cross-boundary* gradients of any form as above exist with respect to a thermodynamic system it will undergo change of state in time. The result of all such changes is to annul the gradient that in the first place causes the changes. This process will continue till all types of gradients are nullified. In the ultimate limit one may then conceive of a state where all gradients (external or internal) are non-existent and the system exhibits no further changes. Under such a limiting condition, the system is said to be in a state of thermodynamic *equilibrium*. For a system to be thermodynamic equilibrium, it thus needs to also satisfy the criteria for mechanical, thermal and

chemical equilibrium.

Types of Thermodynamic Equilibrium

A thermodynamic system may exist in various forms of equilibrium: *stable*, *unstable* and *metastable*. These diverse types of equilibrium states may be understood through analogy with a simple mechanical system as depicted in fig. 1.2 – a spherical body in a variety of gradients on a surface.

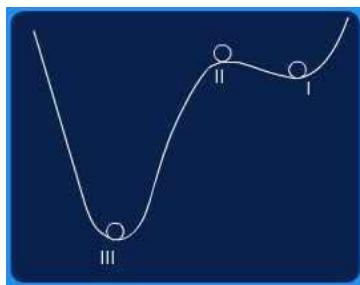


Fig. 1.2 Types of Mechanical Equilibrium

Consider the body to be initially in state ‘I’. If disturbed by a mechanical force of a very small magnitude the body will return to its initial state. However, if the disturbance is of a large magnitude, the body is unlikely to return to its initial state. In this type of situation the body is said to be in *unstable* equilibrium. Consider next the state ‘II’; even a very small disturbance will move the body to either positions ‘I’ or ‘III’. This type of original equilibrium state is termed *metastable*. Lastly, if the body is initially in state ‘III’, it will tend to return to this state even under the influence of relatively larger disturbances. The body is then said to be in a *stable* equilibrium state.

1.3 Some Types of Processes

1.3.1 Reversible and Irreversible Thermodynamic Processes

In the absence of any gradients (or motive forces) a thermodynamic system continues to remain in a state of equilibrium. Obviously, if a disturbance (i.e., mechanical, thermal or chemical potential gradient) is impressed upon such a system it will transit from its initial state of equilibrium. However, as it moves away from its initial state the originally applied gradients will diminish progressively in time, and ultimately when they are reduced to infinitesimal levels the system will attain a new equilibrium state. A question arises here as to the nature of the process of change: if the initially impressed disturbances are reversed in direction (not magnitude) can the system return

to its first equilibrium state back through the same intermediate states as it went through during the first phase of change? If that happens we depict the process as *reversible*, if not, then the process is termed *irreversible*. A reversible process must satisfy the following two conditions

- a. It should experience negligible differences in mechanical potential and any other potential.
It should therefore be quasi-static, that is occurring extremely slowly
- b. It must be devoid of any form of friction both internal and external.

Because real processes violate at least one of these constraints, every real process is irreversible to some degree.

1.3.2 An **isothermal process** is a process which occurs such that the temperature of the system is constant at every point along the process path. An **isobaric process** is a process occurs such that the system does not experience any change in pressure through out the process. An **isochoric or isometric process** is a process which occurs at a constant system volume. An **isenthalpic process** is a process which charts a constant-enthalpy path. An **adiabatic process** is a process which does not involve any heat interaction between the system and its surrounding.

1.4 The Phase Rule

Originally formulated by the American scientist Josiah Willard Gibbs in the 1870's, the phase rule determines the number of independent variables that must be specified to establish the *intensive* state of *any* system at equilibrium and hence fix all other properties of the system

$$F = C + 2 - P - r \quad 1.8$$

where F is the degree of freedom, C is the number of components or chemical species in the system, P is the number of phases present in the system and r is the number of independent reactions that may occur between the system components. For a non-reactive system, the phase rule simplifies to:

$$F = C + 2 - P \quad 1.9$$

In the most general sense a thermodynamic system may be multiphase and multi- component in nature. A phase is a form of matter that is homogeneous in chemical composition and physical

state. Typical phases are solids, liquids and gases. For a multiphase system, interfaces typically demarcate the various phases, properties changing abruptly across such interfaces. Various phases can coexist, but they *must be in equilibrium* for the phase rule to apply. An example of a three-phase system at equilibrium is water at its triple point ($\sim 0^{\circ}\text{C}$, and 0.0061 bar), with ice, water and steam co-existing. A system involving one pure substance is an example of a single-component system. On the other hand mixtures of water and acetone have two chemically independent components.

The degrees of freedom derivable from the phase rule gives the number of variables which must be specified to fix all other remaining phase-rule variables. For example, superheated steam (water vapour at its saturation temperature) has $C = 1$, and $P = 1$. Hence $F = 1 + 2 - 1 = 2$. Specifying the temperature and pressure fixes the state and all other properties (specific volume, enthalpy, internal energy, e.t.c). On the other hand, wet steam (a mixture of liquid water and water vapour) has $C = 1$, and $P = 2$; hence $F = 1 + 2 - 2 = 1$ and it is sufficient to fix either the temperature or the pressure in order to fix the state and all other properties.

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CHAPTER TWO

The Laws of Thermodynamics

2.1 The zeroth law of thermodynamics

The law states that if two media are in thermal equilibrium with a third medium, then they are in thermal equilibrium with each other. Thermal equilibrium implies equality of temperature

2.2 The First Law of Thermodynamics

The law of conservation and conversion of energy is the fundamental general law of nature. It is also referred to as the first law of thermodynamics. It states that energy cannot be created or destroyed but can only be changed from one form to the other.

If stated mathematically, this would imply

$$\Delta E = \text{Energy input} - \text{Energy output}$$

where E denotes the energy of the system and is generally given by

$$E = U + \frac{1}{2}mv^2 + mgz$$

Energy input refers to the energy into the system in whatever form, transmitted from the surrounding to the system while energy output is the summation of energy transferred from the system to the surrounding.

2.2.1 The Closed System

For a closed system, energy interchange between the system and its surroundings is generally only in form of work and heat. The convention is to define heat input to the system as positive and to regard work as positive when it is done by the system. Then equation 2.1 becomes

$$\Delta E = Q - W \quad 2.3$$

or in differential form as

$$dE = \delta Q - \delta W \quad 2.4$$

Note that dE denotes a differential change in E but δQ and δW imply infinitesimal quantities of Q and W respectively since Q and W are not properties. Most closed systems do not experience changes in their kinetic and potential forms of energy and the first law becomes

$$dU = \delta Q - \delta W \quad 2.5$$

$$\text{or } \Delta U = Q - W \quad 2.6$$

For a cyclic process, $dE = 0$ and equation 2.4 yields

$$\oint \delta Q = \oint \delta W \quad 2.7$$

equation 2.7 is the basis of the popular statement of the first law –“ when a system executes a cyclic process, the total heat input to the system is proportional to (equal to – where the same unit are used for work and heat) the total work output.

As is often the case for a closed system, W is due only to expansion or contraction of the system (electric and magnetic fields are absent and there is no chemical work), then it is given by

$$W = \int P dV \quad 2.8$$

where P is the pressure of the system. A relationship to define P as a function of V is required for the evaluation of equation 2.8.

For an isochoric process, equation 2.8 gives $W = 0$. so that equation 2.6 becomes

$$Q = \Delta U \quad 2.9$$

For an isobaric process, equation 2.8 gives $W = P\Delta V = \Delta(PV)$...since P is constant.

Thus equation 2.6 yields

$$Q = \Delta U + \Delta(PV) = \Delta(U + PV) = \Delta H \quad 2.10$$

The heat capacity (the heat a body can retain in the form of energy) is mathematically defined as:

$$C = \frac{\delta Q}{dT} \quad 2.11$$

Using Equations 2.9 and 2.10 , two types of heat capacity may be defined

- Constant pressure heat capacity C_P

$$C_P = \frac{\delta Q}{dT} = \left(\frac{\partial H}{\partial T} \right)_P \quad 2.12$$

- Constant volume capacity C_V

$$C_V = \frac{\delta Q}{dT} = \left(\frac{\partial U}{\partial T} \right)_V \quad 2.13$$

Equations 2.12 and 2.13 can then be re-written as

$$Q = \Delta H = \int_{T_1}^{T_2} C_P dT \quad (\text{at const. pressure}) \quad 2.14$$

$$Q = \Delta U = \int_{T_1}^{T_2} C_V dT \quad (\text{at const. volume}) \quad 2.15$$

Applications to Ideal Gases

The other two types of thermodynamic processes – *isothermal and adiabatic* – in closed systems are conveniently understood by applying the first law to a system comprised of an ideal gas. For such a case the relationship between U and H may be rewritten using the EOS

$$H = U + PV = U + RT \quad 2.16$$

or $H - U = RT$

Since both H and U are only temperature dependent for ideal gases we write:

$$\frac{dH}{dT} - \frac{dU}{dT} = R$$

Using equations 2.12 and 2.13

$$C_P - C_V = R$$

For an isothermal process

$$dU = 0 \quad (\text{equation 2.5})$$

$$\delta Q = -\delta W, Q = -W$$

If we consider only P-V work, the work term is calculable if the process is carried out reversibly, as the ideal gas EOS relate the P and V at all points of change, hence:

$$W = - \int_{V_1}^{V_2} P dV = - \int_{V_1}^{V_2} \frac{RT}{V} dV = RT \ln \frac{V_1}{V_2} = RT \ln \frac{P_2}{P_1} \quad 2.18$$

$$\text{thus } Q = RT \ln \frac{V_2}{V_1} = RT \ln \frac{P_1}{P_2} \quad 2.19$$

For isobaric process:

$$Q = \Delta H = \int C_P dT \quad 2.20$$

$$W = - \int_{V_1}^{V_2} P dV = -P(V_2 - V_1) = -R(T_2 - T_1) \quad 2.21$$

The steady state steady flow SSSF Process

This is a process which involves constant and equal flow of mass into and out of an open system (no accumulation) and is such that no point in the system experiences a change in state with time. Such processes are very common in the industry.

Figure 2.1

If the control surface is defined as the embodiments of the cross sections at points 1 and points 2 and the fluid-solid interface within the equipment. The work (actually power) device could be a pump (for a liquid) or a compressor (for a gas) supplying power (negative W_s) to the system (the fluid) or a turbine drawing power (positive W_s) from the fluid. If a heat device would be a heat exchanger supplying heat to (positive Q) or removing heat from (negative Q) the system. Given that mass flow rate is m , then applying the concept of the first law to the control volume gives

$$\Delta(mu) + \Delta\left(\frac{1}{2}mv^2\right) + \Delta(mgz) = Q - (W_s + W_f) \quad 2.22$$

Where W_f denotes flow work and $\Delta(mu) = m_2u_2 - m_1u_1$, Q and W represent *rates* of heat input and work output respectively.

For open system, the first law should be considered along with the *continuity equation* which results from the application of the concept of conservation of mass. For the SSSF process, continuity gives

$$m_1 = \rho_1 u_1 A_1 = m_2 = \rho_2 u_2 A_2 = m \quad 2.23$$

where ρ = fluid density, u = fluid velocity and A = aperture cross sectional area

In order to define W_f , consider the work interactions between the control volume and the flowing fluid at points 1 and 2. At point 1, the influent liquid does work on the system and we have

$$W_{f1} = -P_1 u_1 A_1 = -P_1 A_1 \left(\frac{m_1}{\rho_1 A_1} \right) = -m P_1 v_1$$

where v is the specific volume

At point 2, the system does work on the effluent fluid and we have

$$W_{f2} = P_2 u_2 A_2 = P_2 A_2 \left(\frac{m_2}{\rho_2 A_2} \right) = m P_2 v_2$$

$$\text{Hence, } W_f = W_{f1} + W_{f2} = m P_2 v_2 - m P_1 v_1 = m \Delta(Pv) \quad 2.24$$

Employing 2.23 and 2.24 in 2.22 and introducing the definition of enthalpy, we have

$$m \left(\Delta h + \frac{1}{2} \Delta v^2 + g \Delta z \right) = Q - W_s \quad 2.25$$

Equation 25 is the practical form of the first law for an SSSF system. Note that Δv^2 means $v_2^2 - v_1^2$ not $(v_2 - v_1)^2$.

If we define $q = \frac{Q}{m}$ and $w_s = \frac{W_s}{m}$, then equation 2.25 becomes

$$\Delta h + \frac{1}{2} \Delta v^2 + g \Delta z = q - w_s \quad 2.26$$

Note that Q and W_s have the units of power (W) while q and w_s have the units of specific energy J/kg. Equation 2.26 indicates that the specific energy for a flowing fluid is given by

$$e = h + \frac{1}{2} v^2 + gz \quad 2.27$$

The general open system

Consider an open system with N_I inflow channels and N_E effluent channels. The rate at which energy is borne into the control volume by the influent mass is

$$\sum_{j=1}^{N_I} m_{ij} \left(h_{ij} + \frac{1}{2} v_{ij}^2 + gz_{ij} \right)$$

where m denotes mass flow rate, and z corresponds to elevation at the point of measurement of h and v . It should be noted that equation 2.27 was directly used to obtain the above result. Similarly, the stream energy effluent rate is

$$\sum_{j=1}^{N_E} m_{ej} \left(h_{ej} + \frac{1}{2} v_{ej}^2 + gz_{ej} \right)$$

the rate of accumulation of energy in the control volume is

$$\frac{d}{dt} \left\{ m \left(u + \frac{1}{2} v^2 + gz \right) \right\}$$

The unsubscripted quantities refer to the contents of the control volume. Taking Q and W to define the rates of energy flow, then the first law is

$$\frac{d}{dt} \left\{ m \left(u + \frac{1}{2} v^2 + gz \right) \right\} = \left[\sum_{j=1}^{N_I} m_{ij} \left(h_{ij} + \frac{1}{2} v_{ij}^2 + gz_{ij} \right) + Q \right] - \left[\sum_{j=1}^{N_E} m_{ej} \left(h_{ej} + \frac{1}{2} v_{ej}^2 + gz_{ej} \right) + W \right] \quad 2.28$$

The continuity equation for this process is derived in a similar manner to equation 2.28 as

Rate of increase in the mass content of the control volume = Mass inflow rate – Mass outflow rate

$$\frac{dm}{dt} = \sum_{j=1}^{N_I} m_{ij} - \sum_{j=1}^{N_E} m_{ej} \quad 2.29$$

Equations 2.28 and 2.29 can be integrated over the time duration for any given process, accounting appropriately for any variations in mass and energy flow rates with time.

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CHAPTER THREE

3.0 SECOND LAW OF THERMODYNAMICS

The first law addresses the issue of the amount of energy in its various forms involved in a process. It suffers the limitation of failing to provide any clue as to the direction of change and the transformation that can occur spontaneously. Thus, going by the first law alone, it should be possible to convert a given quantity of heat completely into work energy and a kettle of water placed on a hot stove should be able to lose energy in form of heat to the stove and in the process bring about the freezing of the water. Experience is however contrary to this. The second law addresses the issue, imposing restrictions on the direction of energy transformations and providing the criterion for the spontaneity of a process.

It need be mentioned that the second law is a product of experiential observations involving *heat engines* that powered the Industrial Revolution of the 19th century. A heat engine is a machine that produces work from heat through a cyclic process. An example is a steam power plant in which the working fluid (steam) periodically goes through a series of steps in a cyclic manner as follows:

- *Step 1:* Liquid water at ambient temperature is pumped into a boiler operating at high pressure
- *Step 2:* Heat released by burning a fossil fuel is transferred in the boiler to the water, converting it to steam at high-temperature and pressure
- *Step 3:* The energy contained in the steam is then transferred as shaft work to a turbine; during this process steam temperature and pressure are reduced.
- *Step 4:* Steam exiting the turbine is converted to water by cooling it and transferring the heat released to the surroundings. The water is then returned to step 1.
- The schematic of a heat engine (for example: steam / gas power plant, automotive engines, etc) is shown in fig. 3.1

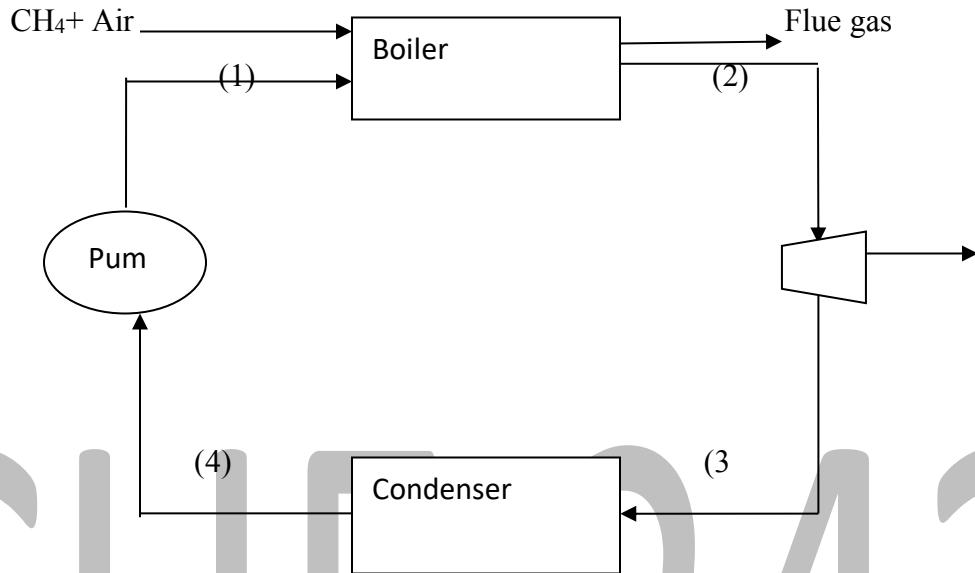


Figure 3.1 Schematic of steam power plant (heat Engine)

3.2 Statements of the second law

Two useful statements of the second law are presented

Clausius Statement: It is impossible to design a cyclic process that produces no effect (on the universe) other than the transfer of heat from a low temperature body to a high temperature body.

Kelvin-Planck Statement: It is impossible to devise a cyclic process that produces no effect (on the universe) other than to absorb energy in the form of heat from a single thermal reservoir and to deliver an equivalent amount of work.

3.3 Carnot Heat Engine Cycle and the Second Law

In theory, we may say that a heat engine absorbs a quantity of heat $|Q_H|$ from a high temperature reservoir at T_H and rejects $|Q_C|$ amount of heat to a colder reservoir at T_C . It follows that the net work W delivered by the engine is given by:

$$W = |Q_H| - |Q_C| \quad 3.1$$

Hence the efficiency of the engine is:

$$\eta = \frac{W}{|Q_H|} = \frac{|Q_H| - |Q_C|}{|Q_H|}$$

$$\eta = 1 - \frac{|Q_C|}{|Q_H|} \quad 3.2$$

The *Carnot engine* proposed in 1824 by the French engineer Nicholas Leonard Sadi Carnot (1796-1832), provides a fundamental reference concept in the development of the second law. The so-called Carnot cycle (depicted in fig. 3.2) is a series of *reversible* steps executed as follows:

- **Step 1:** A system at the temperature of a cold reservoir T_C undergoes a *reversible* adiabatic compression which raises its temperature to that of a hot reservoir at T_H .
- **Step 2:** While in contact with the hot reservoir the system absorbs $|Q_H|$ amount of heat through an isothermal process during which its temperature remains at T_H .
- **Step 3:** The system next undergoes a *reversible* adiabatic process in a direction reverse of step 1 during which its temperature drops back to T_C .
- **Step 4:** A *reversible* isothermal process of expansion at T_C transfers $|Q_C|$ amount of heat to the cold reservoir and the system state returns to that at the commencement of step 1.

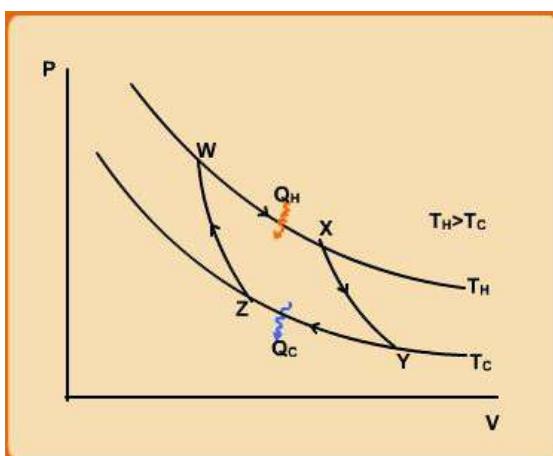


Figure 3.2: The Carnot cycle

The Carnot engine, therefore, operates between two heat reservoirs in such a way that all heat exchanges with heat reservoirs occur under isothermal conditions for the system and at the temperatures corresponding to those of the reservoirs. This implies that the heat transfer occurs under *infinitesimal* temperature gradients across the system boundary, and hence these processes are reversible (see last paragraph of section 1.3.1). If in addition the isothermal and adiabatic processes are also carried out under mechanically reversible (quasi-static) conditions the cycle operates in a fully reversible manner.

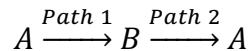
3.4 The inequality of Clausius and the concept of entropy

The inequality of Clausius states that for any cyclic process

$$\oint \frac{\delta Q}{T} \leq 0$$

Where the equality applies only to a reversible process.

Consider the cyclic process



If the process is reversible, then the inequality of Clausius assumes the form

$$\oint \frac{\delta Q}{T} = 0$$

which gives

$$\int_A^B \frac{\delta Q}{T} (1) + \int_B^A \frac{\delta Q}{T} (2) = 0 \quad \text{OR}$$

$$\int_A^B \frac{\delta Q}{T} (1) - \int_A^B \frac{\delta Q}{T} (2) = 0 \quad \text{OR}$$

$$\int_A^B \frac{\delta Q}{T} (1) = \int_A^B \frac{\delta Q}{T} (2)$$

3.3

3.4

3.5

The implication of equation 3.5 is that the integral $\int_A^B \frac{\delta Q}{T} (1)$ has a value which is independent of the process path adopted in going from A to B, provided it is a reversible process path. When this fact is considered along with equation 3.4, it follows that the quantity $\frac{\delta Q_{rev}}{T}$ defines a differential

change in a property of the system. This property is called entropy S. Thus by definition

$$dS = \frac{\delta Q_{rev}}{T} \quad 3.6$$

Entropy is an extensive property which has the unit J/K. Thus, specific entropy s an intensive property has the units of J/(kgK). It should be noted that T in equation 3.6 is defined in absolute units (kelvin for SI units) and not any other scale of unit.

To evaluate $\Delta S = S_B - S_A$ for an irreversible process $A \rightarrow B$, construct any convenient reversible process or combination of reversible processes originating from A and terminating at B and evaluate $S_B - S_A$ by integrating equation 3.6 along this path. This gives ΔS for the irreversible path, since S is a state function. For a reversible process, equation 3.6 gives

$$\delta Q = TdS$$

$$\text{implying, } Q = \int TdS$$

Note that for an irreversible process,

$$\delta Q \neq TdS$$

3.5 Irreversibility and entropy Change.

$A \xrightarrow{P} B$ depicts a process which could be reversible or irreversible. Applying the inequality of Clausius, we have

$$\int_A^B \frac{\delta Q_P}{T} + \int_B^A \frac{\delta Q_{rev}}{T} \leq 0$$

$$\int_A^B \frac{\delta Q_P}{T} - \int_A^B \frac{\delta Q_{rev}}{T} \leq 0 \quad 3.9$$

$$\int_A^B \frac{\delta Q_P}{T} - \int_A^B dS \leq 0 \quad 3.10$$

$$\text{Hence, } ds \geq \frac{\delta Q_P}{T}$$

$$\text{Or } S_B - S_A \geq \int_A^B \frac{\delta Q_P}{T} \quad 3.11$$

Where the equality sign applies only when P defines a reversible process.

The implication of equation 3.11 is that for an irreversible process, there is a contribution to entropy change which is not the result of the heat energy transmitted between the system and its surroundings. Then, this component must derive from the irreversibilities in the system. In fact, it is due to that part of the work effect in the process which is irretrievably lost due to frictional effects converted as it were to friction heat. If we denote the useful work by W and the lost (friction) work by W_i , then,

$$PdV = \delta W + \delta W_i \quad 3.12$$

The first law for a closed system gives

$$\delta Q = dE + \delta W \quad 3.13$$

Let equation 3.13 define a differential irreversible process. If the process were reversible, we would have

$$dQ = TdS \text{ and } dW = PdV$$

so that equation 3.13 yields

$$TdS = dE + PdV \quad 3.14$$

Eliminating dE between equations 3.13 and 3.14, we have

$$TdS = \delta Q + PdV - \delta W \quad 3.15$$

From equation 3.12

$PdV - \delta W = \delta W_i$ so that equation 3.15 becomes

$$TdS = \delta Q + \delta W_i \quad 3.16$$

from which we have

$$dS = \frac{\delta Q}{T} + \frac{\delta W_i}{T} \quad 3.17$$

Thus, an irreversible adiabatic process experiences a change in entropy (always positive) irrespective of whether work is done on or by the system which is due solely to frictional effects and is equal to $\int \frac{\delta W_i}{T}$. On the other hand, a reversible process occurs at constant entropy and is said to be an isentropic process

3.6 Entropy statement of the second law

The second law in terms of entropy change requires every thermodynamic process to satisfy the relationship

$$\Delta S_{system} + \Delta S_{surrounding} \geq 0 \quad 3.18$$

where the equality applies only to reversible process. Thus, a thermodynamic process cannot bring about a decrease in the total entropy content of the universe and a process involving a decrease in the entropy of a given system must entail at least as much increase in the entropy of its surroundings. It should be noted that the various statements of the second law are consistent and a violation of one amounts to a violation of all of them.

3.7 Entropy and Disorder

Entropy has the significance of being a measure of disorder. Any system that undergoes transformation from a given state to a less ordered state (such as temperature elevation without phase change, mixing of two or more fluids of different compositions and phase transformation from solid to liquid (fusion), liquid to vapour (vapourisation) or solid to vapour (sublimation) experiences an increase in entropy. Equation 3.18 implies that any irreversible process has the effects of increasing the degree of disorder in the universe.

Entropy balance for an open system

Consider figure 2.2, let q denote heat flux (heat flow rate per unit area) through the control surface area $=A$ and let w_i define rate of lost work per unit volume in the control volume V . Then the rate of entropy input to the control volume is $\sum_{j=1}^{N_I} m_{ij} s_{ij} + \int_A \left(\frac{q}{T}\right) dA$. The rate of entropy output is

$\sum_{j=1}^{N_E} m_{ej} s_{ej}$, while the rate of entropy generation is $\int_V \left(\frac{w_i}{T}\right) dV$. The rate of entropy accumulation is $\frac{d}{dt}(ms)$. A balance gives

$$\text{Input} + \text{Generation} = \text{Output} + \text{Accumulation}$$

Hence, we have

$$\sum_{j=1}^{N_I} m_{ij} s_{ij} + \int_A \left(\frac{q}{T}\right) dA + \int_V \left(\frac{w_i}{T}\right) dV = \sum_{j=1}^{N_E} m_{ej} s_{ej} + \frac{d}{dt}(ms)$$

or

$$\frac{d}{dt}(ms) = \int_A \left(\frac{q}{T}\right) dA + \int_V \left(\frac{w_i}{T}\right) dV + \sum_{j=1}^{N_I} m_{ij} s_{ij} - \sum_{j=1}^{N_E} m_{ej} s_{ej} \quad 3.19$$

Equation 3.19 applies to all systems [including closed systems]. Because of the difficulty of evaluating $\int_V \left(\frac{w_i}{T}\right) dV$ a non-negative term in equation 3.19, the equation is often utilized in the form

$$\frac{d}{dt}(ms) \geq \int_A \left(\frac{q}{T}\right) dA + \sum_{j=1}^{N_I} m_{ij} s_{ij} - \sum_{j=1}^{N_E} m_{ej} s_{ej} \quad 3.20$$

where the equality holds true for a reversible process. Given sufficient data, equation 3.20 could for example be used to ascertain the feasibility or otherwise of a new process being developed.

The third Law of Thermodynamics

The third Law of Thermodynamics also known as Nernst's theorem states that the entropy of a system in equilibrium approaches zero as the system's absolute temperature approaches zero.

Mathematically, it implies that

$$\lim_{T \rightarrow 0} S = 0 \quad 3.21$$

Where T is absolute temperature (Kelvin in SI unit). The third law enables the knowledge of absolute value of entropy. Note that this is not the case for enthalpy and internal energy and other

energy functions (there is no known state of matter at which the energy content assumes zero value) any reference defined for them for the purpose of analysis or representation of data are purely arbitrary.

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CHAPTER FOUR

4. EVALUATION OF THERMODYNAMIC PROPERTIES

4.1 Thermodynamic Work Tools

In thermodynamic analysis, the laws of thermodynamics serve as basic working tools. But these laws are defined in terms of properties of the system. It follows therefore, that there should be adequate data on the properties of the system for any given process. In generating such data, experimentation is often resorted to. However, not all the thermodynamic properties can be measured experimentally. While mass, pressure, temperature, specific heat capacity, specific volume (mass density) can be measured experimentally, properties such as internal energy, enthalpy and entropy do not yield to experimental measurement. To generate data for properties in the latter class, use is made of thermodynamic relationships that define these properties as functions of the measurable properties. In obtaining such relationships, the following two thermodynamic functions play useful roles

- **Gibbs Free Energy, G:** This is an extensive property defined by

$$G = H - TS \quad 4.1$$

The specific Gibbs free energy is

$$g = h - Ts \quad 4.2$$

- **Helmholtz Free Energy, A:** The Helmholtz free energy also called the *work function* is an extensive property defined by

$$A = U - TS \quad 4.3$$

The specific Helmholtz free energy a is given by

$$a = u - Ts$$

4.4

By their definition, G and A has the units of joules in SI units.

4.2 Relationships Among the State Functions

Since changes in state functions are independent of process path, relationships between state functions can be derived based on any convenient system and process path. If we choose a reversible non-flow process (a closed system) and take the system to be a unit mass of a homogenous material, then we have

$\delta w = pdv$ and $\delta q = Tds$ (from the second law) and the first law yields

$$du = Tds - Pdv$$

4.5

From the definition of enthalpy, we have

$$dh = du + d(Pv) = Tds - Pdv + Pdv + vdp$$

$$dh = Tds + vdp$$

4.6

The definition of the specific work function equation 4.4 results in

$$da = du - d(Ts) = Tds - Pdv - Tds - sdT$$

$$da = -sdT - Pdv$$

4.7

Employing the definition of the specific Gibbs free energy (eqn. 4.2), we obtain

$$dg = dh - d(Ts) = Tds + vdp - Tds - sdT$$

$$dg = -sdT + vdp$$

4.8

It can be clearly seen that equations 4.5 through 4.8 involve only properties and they are very useful in thermodynamic property data generation.

4.3 Specific Heat Capacities

Heat capacity information is generally required in the process of generating data for thermodynamic properties which cannot be measured experimentally. An incompressible medium (a liquid or a solid with a mass density or specific volume which is insensitive to pressure changes) has a unique specific heat capacity, simply given by

$$c = \frac{1}{m} \frac{\delta Q}{dT}$$

4.9

where a differential quantity of heat δQ elevates the temperature of a mass m of the medium by dT . On the other hand, compressible fluids (gases and vapours) have specific heat capacities that depend on the nature of the process. For those fluids, there are two specific heat capacities in common use. One of these is the *isochoric specific heat capacity* c_V given by

$$c_V = \frac{1}{m} \frac{\delta Q}{dT} \Big|_{constant V} = \frac{1}{m} \left(\frac{\partial U}{\partial T} \right)_V = \left(\frac{\partial u}{\partial T} \right)_V \quad 4.10$$

The other one is the *isobaric specific heat capacity* c_P given by

$$c_P = \frac{1}{m} \frac{\delta Q}{dT} \Big|_{constant P} = \frac{1}{m} \left(\frac{\partial H}{\partial T} \right)_P = \left(\frac{\partial h}{\partial T} \right)_P \quad 4.11$$

It should be noted that the specific heat capacities are intensive state variables.

4.4 Maxwell's Relations

Consider equation 4.5 which gives u as a function of s and v . If we write $u = u(s, v)$, then

$$du = \left(\frac{\partial u}{\partial s} \right)_V ds + \left(\frac{\partial u}{\partial v} \right)_S dv \quad 4.12$$

A comparison of equation 4.5 and 4.12 leads to the identities

$$\left(\frac{\partial u}{\partial s} \right)_V = T, \text{ and } \left(\frac{\partial u}{\partial v} \right)_S = -P$$

Cross differentiating these first partial derivatives, we have

$$\frac{\partial^2 u}{\partial v \partial s} = \left(\frac{\partial T}{\partial v} \right)_S \quad 4.13$$

$$\frac{\partial^2 u}{\partial s \partial v} = - \left(\frac{\partial P}{\partial s} \right)_v \quad 4.14$$

Since u is a continuous point function with continuous derivatives, $\frac{\partial^2 u}{\partial v \partial s} = \frac{\partial^2 u}{\partial s \partial v}$.

Hence combining equations 4.13 and 4.14, we have

$$\left(\frac{\partial T}{\partial v} \right)_S = - \left(\frac{\partial P}{\partial s} \right)_v \quad 4.15$$

By applying a similar analysis to equations 4.6, 4.7 and 4.8, we obtain the following respective relationships

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial v}{\partial s} \right)_P \quad 4.16$$

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial S}{\partial v}\right)_T \quad 4.17$$

$$\left(\frac{\partial v}{\partial T}\right)_P = - \left(\frac{\partial S}{\partial P}\right)_T \quad 4.18$$

Equations 4.15 through 4.18 constitutes the Maxwell relations (for a system without magnetic, electric and chemical work effects) and they are most useful in the formulation of a practical thermodynamic working relationship between any unmeasurable properties and the measurable properties (see section 4.1) for direct data generation. The following guidelines will be useful:

1. All the four Maxwell relations involve four properties: T, v, P and S. Of these, only S cannot be measured experimentally. Thus, in setting up thermodynamic working relationships for data generation, any derivative involving S is eliminated by means of Maxwell's relations leaving derivatives involving the measurable properties T, v and P.
2. The development of the working relationships would generally involve either equation 4.5 or equation 4.6 at the early stage. If, in the process, an S derivative having (T, v) as independent variables is generated, the Maxwell relation deriving from the Helmholtz function (that is equation 4.17 deriving from equation 4.7), is used to eliminate the S derivative. If on the other hand an S derivative having (T, P) as independent variables is generated, the Maxwell relation deriving from the Gibbs function (that is equation 4.18 deriving from equation 4.8), is used to eliminate it.
3. The Maxwell relations can easily be generated from the thermodynamic mnemonic diagram shown in figure 4.1 which is constructed from equations 4.5 through 4.8. the sides of the square are labelled with the four functions (a, g, h, u) in alphabetical order clockwise with a at the top. The variables (v, T, P, S) are then placed at the vertices of the square such that each function is flanked by its two independent variables. The diagonals are constructed with arrows pointing upwards. To determine the Maxwell relation based on a given energy function, the side containing it is made the base, the adjacent side conceptually becoming the vertical sides. Then, the two equal derivatives are obtained by differentiating each variable at the top of a 'vertical' side with respect to the one at its bottom holding that at the bottom of the other vertical side constant. Where the arrow points to the top of the vertical sides, the derivative takes a positive sign, otherwise, it is negative.

Figure 4.1: Mnemonic diagram for Maxwell's relations

4. The Maxwell relation can also be very easily generated through a simple process of cross-differentiation of variables applied to equations 4.5 through 4.8. For example, equation 4.8 gives

$$-sdT + vdP \Rightarrow \begin{bmatrix} -S & dT \\ +v & dP \end{bmatrix} \Rightarrow \left(\frac{-\partial S}{\partial P}\right)_T = \left(\frac{-\partial v}{\partial T}\right)_P$$

4.5 Thermodynamic working relationships for data generation

The formulation of thermodynamic working relationships for data generation will be done here for some properties for single-phase, single-component systems. For systems with more than one component, the mass (mole fraction) will normally constitute additional independent state variables.

4.5.1 Internal energy: Generally, internal energy is a function of temperature and volume. Hence, we may write

$$\partial u = \left(\frac{\partial u}{\partial T}\right)_V dT + \left(\frac{\partial u}{\partial V}\right)_T dv \quad 4.19$$

By definition, (see equation 4.10), $\left(\frac{\partial u}{\partial T}\right)_V = C_V$

Therefore,

$$du = C_V dT + \left(\frac{\partial u}{\partial V}\right)_T dv \quad 4.20$$

Differentiating equation 4.5 partially with respect to v , holding T constant, we have

$$\left(\frac{\partial u}{\partial v}\right)_T = T \left(\frac{\partial s}{\partial v}\right)_T - P \quad 4.21$$

From Maxwell's relations, equation 4.17, we have

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v \quad 4.21a$$

Substituting equation 4.21a into 4.21 and using this in equation 4.20, we have the final result as

$$du = C_V dT + \left[T \left(\frac{\partial P}{\partial T}\right)_v - P\right] dv \quad 4.22$$

Equation 4.22 shows that $P - v - T$ data and experimental data relating C_V to T and v are all that is needed to generate necessary data on u as a function of T and v .

4.5.2 Enthalpy: Enthalpy is generally taken to be a function of temperature and pressure. In view of this, let us define $h = h(T, P)$. Then,

$$dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP \quad 4.23$$

By definition, (see equation 4.11), $\left(\frac{\partial h}{\partial T}\right)_P = C_P$

$$dh = C_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP \quad 4.24$$

Differentiating equation 4.6 partially with respect to P and holding T constant we have

$$\left(\frac{\partial h}{\partial P}\right)_T = T \left(\frac{\partial s}{\partial P}\right)_T + v \quad 4.25$$

From Maxwell's relations, equation 4.18, we have

$$\left(\frac{\partial s}{\partial P}\right)_T = - \left(\frac{\partial v}{\partial T}\right)_P \quad 4.26$$

Substituting equation 4.26 into equation 4.25 and employing this in equation 4.24, we obtain

$$dh = C_P dT + \left[v - T \left(\frac{\partial v}{\partial T}\right)_P\right] dP \quad 4.27$$

Enthalpy data can be generated by means of equation 4.27 using $P - v - T$ data and experimental data relating C_P to T and P .

4.5.3 Entropy: We may use $s = s(T, v)$ or $s = s(T, P)$. If we use the latter, then

$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP \quad 4.28$$

Differentiating equation 4.6 partially with respect to T and holding P , we have

$$\left(\frac{\partial h}{\partial T}\right)_P = T \left(\frac{\partial s}{\partial T}\right)_P \quad \text{which yields}$$

$$\left(\frac{\partial s}{\partial T}\right)_P = \frac{C_P}{T} \quad 4.29$$

From Maxwell's relations, equation 4.18, we have

$$\left(\frac{\partial s}{\partial P}\right)_T = - \left(\frac{\partial v}{\partial T}\right)_P \quad 4.30$$

Substituting equation 4.29 into equation 4.30 and employing this in sequation 4.28, we obtain

$$ds = C_P \frac{dT}{T} - \left(\frac{\partial v}{\partial T}\right)_P dP \quad 4.31$$

Alternatively, employing $s = s(T, v)$ and using equation 4.5 instead of equation 4.6 and equation 4.17 instead of equation 4.18 yield

$$ds = C_V \frac{dT}{T} + \left(\frac{\partial P}{\partial T} \right)_v dv \quad 4.32$$

4.5.4 Relationship between C_P and C_V

From equation 4.6, $C_P = \left(\frac{\partial h}{\partial T} \right)_P = T \left(\frac{\partial s}{\partial T} \right)_P$

From equation 4.5, $C_V = \left(\frac{\partial u}{\partial T} \right)_v = T \left(\frac{\partial s}{\partial T} \right)_v$

$$\text{Hence, } C_P - C_V = T \left[\left(\frac{\partial s}{\partial T} \right)_P - \left(\frac{\partial s}{\partial T} \right)_v \right] \quad 4.33$$

Using $s = s(T, v)$, we have

$$ds = \left(\frac{\partial s}{\partial T} \right)_V dT + \left(\frac{\partial s}{\partial v} \right)_T dv \quad 4.34$$

Differentiating equation 4.34 with respect to T holding P constant, we have

$$\left(\frac{\partial s}{\partial T} \right)_P = \left(\frac{\partial s}{\partial T} \right)_V + \left(\frac{\partial s}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_P \quad 4.35$$

Substituting equation 4.35 into 4.33 and using the Maxwell relation (equation 3.17) $\left(\frac{\partial s}{\partial v} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$,

we have

$$C_P - C_V = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial v}{\partial T} \right)_P \quad 4.36$$

4.6 How to use existing data

Existing thermodynamic data are in three general forms

1. Mathematical correlations: This form of data finds convenient use in computer analysis
2. Data charts: These include compressibility factor diagrams (compressibility factor versus reduced pressure with reduced temperature as parameter), temperature – entropy diagrams (T versus s with h and P as parameters), Mollier diagrams [h versus s with parameters such as P, T , degree of superheat (in a super heated vapour region), and moisture content (in a two phase vapour-liquid region)], temperature-enthalpy diagrams (P versus h with T, v and s as parameters). Examples of these charts are presented in Smith, Van Ness and Abbot.

3. Data Tables: Thermodynamic data tables exist for some common fluids. Such Tables generally include data on T, P, v, h and s presented on a one dimensional $T -$ or P – coordinate system for a single-phase medium. Some table also include u data.

On the use of the steam tables, the following point should prove useful

- For data on a two-phase vapour-liquid mixture (wet vapour) or on saturated vapour or liquid, the Pressure Table if it is available should be used for problem where P rather than
- T is specified.
- If a property w (denoting v, h, u or s) is desired for wet vapour having a *vapour quality or dryness x* ($x = \text{mass of vapour} \div \text{total mass}$), it should be computed from either

$$w = xw_g + (1 - x)w_f \quad 4.37$$

$$\text{or } w = w_f + xw_{fg} \quad 4.38$$

where according to the tables, subscripts f, g and fg denote liquid, vapour and liquid to vapour transition (that is , the change in going from saturated liquid to saturated vapour) Equations 4.37 and 4.38 could also be used to determine x if it is the only unknown in the equation.

- If both P and T are specified, and it is not certain what phase is involved, it may be ascertained as follows: read from column 2 of the Temperature table the saturation pressure P_s corresponding to the given T ; if $P_s < P$, it is subcooled liquid; if $P_s > P$, it is superheated vapour.
- Where u is required but it is not tabulated, it should be computed from

$$u = h - pv$$

- If data are not tabulated at the operating point, they should be estimated by linear interpolation as follows:

Saturated liquid: denote the coordinate variable (T or P) by y . If the operating value y_0 is straddled by y_1 and y_2 such that $y_1 < y_0 < y_2$, define $\alpha = (y_0 - y_1)/(y_2 - y_1)$. Then any desired property w is given by

$$w_0 = w_1 + \alpha(w_2 - w_1)$$

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Fundamentals of Engineering Thermodynamics (CHE242)

5.0 P – V – T RELATIONS OF GASES AND LIQUIDS

5.1 P – V – T BEHAVIOUR OF PURE GASES

The data generation working relationships presented in chapter 4 reveal that information relating pressure, volume and temperature is required in the process of generating data on the unmeasurable properties. The pressure-volume-temperature ($P - V - T$) behavior of gases has enjoyed much of the attention in view of the high compressibility of gases which makes their volumes to be highly sensitive to pressure changes.

Information of the $P - V - T$ behavior of a pure gas is often presented in the form of an equation of state which is a semi-empirical mathematical correlation relating P, v (or V and m) and T through a few empirical parameters. The simplest known equation of state (EOS) is the ideal gas law. Where the ideal gas law is not suitable, some other complex equations of state (the van der Waals EOS, Redlich-Kwong EOS, and popular modifications of it by Wilson and by Soave, the Benedict-Webb-Rubin(BWR) EOS, etc) could be used. Apart from these, charts defining gas-phase $P - V - T$ behavior have been developed based on the principle of corresponding states.

5.1.1 The Ideal Gas: The ideal gas model is founded on the assumption of zero force of interaction among molecules. *Real gases behave essentially like the ideal gas at sufficiently low pressure and sufficiently high temperature.* An ideal gas is governed by the ideal gas law which is given by the relation

$$PV = n\bar{R}T \quad 5.1$$

where in SI units, n is in kmole, V is total volume in m^3 , and \bar{R} is in $\text{J}/(\text{kmole.K})$. \bar{R} is the universal gas constant and is $8.314\text{J}/(\text{kmole.K})$.

Equation 5.1 may be written on the basis of 1kmole as

$$Pv = \bar{R}T \quad 5.2$$

where v is molar volume (m^3/kmole).

The ideal gas law can also be stated on a mass (rather than molar) basis. Then it becomes

$$PV = mRT \quad 5.3$$

where m is in kg and R is a specific gas constant in $\text{J}/(\text{kg/K})$ and is related to \bar{R} by

$$R = \bar{R}/M \quad 5.4$$

M being the molecular mass of the gas.

Equation 5.3 expressed on the basis of 1kg becomes

$$Pv = RT \quad 5.5$$

where v is specific volume (m^3/kg).

Some useful relationships are presented next

Internal energy: Using equation 5.5, we have

$$T \left(\frac{\partial P}{\partial T} \right)_v = \frac{RT}{v} = P, \text{ so that equation 4.22 becomes}$$

$$du = c_v dT \quad 5.6$$

While c_v is generally a function of T and v , it depends only on T for an ideal gas. It follows from equation 5.6 that u is a function of T only for an ideal gas.

Enthalpy: Equation 5.5, gives $T \left(\frac{\partial v}{\partial T} \right)_P = \frac{RT}{P} = v$, so that equation 4.27 reduces to

$$dh = c_p dT \quad 5.7$$

For an ideal gas, c_p depends only on T (for real gases, it also depends on P) and equation 5.7 leads to the conclusion that h is a function of T only for an ideal gas.

Note that equations 5.6 and 5.7 are applicable to any process involving an ideal gas, irrespective of the process path.

Entropy: Substituting $\left(\frac{\partial v}{\partial T} \right)_P$ from equation 5.5 into equation 4.31 gives

$$ds = c_p \frac{dT}{T} - R \frac{dP}{P} \quad 5.8$$

While the use of $\left(\frac{\partial P}{\partial T} \right)_v$ obtained from equation 5.5 results in

$$ds = c_v \frac{dT}{T} + R \frac{dv}{v} \quad 5.9$$

Either Equation 5.8 or 5.9 can be used to evaluate Δs for a process involving an ideal gas.

Relationship between c_p and c_v

From equation 5.5, $\left(\frac{\partial P}{\partial T} \right)_v = R/v$ and $\left(\frac{\partial v}{\partial T} \right)_P = R/P$. Substituting these into equation 4.36, we have

$$c_p - c_v = T \frac{R}{v} \frac{R}{P} = R \left(\frac{RT}{v} \right) \frac{1}{P} = R \frac{P}{P} \quad \text{OR}$$

$$c_P - c_V = R$$

5.10

Some Processes Involving Ideal Gas

- For an isothermal process in a closed system, substituting equation 5.3 for P in equation 2.8 and integrating gives $W = mRT \ln\left(\frac{V_2}{V_1}\right)$. Since T is constant and m and R are constants, Equation 5.3 gives $PV = \text{constant}$ or $P_1V_1 = P_2V_2$. Hence we also have $W = mRT \ln\left(\frac{P_1}{P_2}\right)$. Equation 5.6 yields $du = 0$ or $\Delta u = 0$. So that the first law gives $Q = W$.
- For an ideal gas with constant c_V and c_P . Integrating equation 5.9 from state 1 to state 2 gives

$$\Delta s = c_V \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{v_2}{v_1}\right) \quad 5.11$$

if the process is isentropic, $\Delta s = 0$ and equation 5.11 yields

$$\ln\left(\frac{T_2}{T_1}\right) = \frac{R}{c_V} \ln\left(\frac{v_1}{v_2}\right) \text{ OR } \left(\frac{T_2}{T_1}\right)^{\frac{R}{c_V}} = \left(\frac{v_1}{v_2}\right)^{\frac{R}{c_V}} \text{ OR } T v^{\frac{R}{c_V}} = \text{constant.}$$

Defining the specific heat ratio (preferably the specific heat capacity ratio), $\alpha = \frac{c_P}{c_V}$, then equation 5.10 yields

$$\frac{R}{c_V} = \alpha - 1.$$

Hence an isentropic process requires

$$T v^{(\alpha-1)} = \text{constant} \quad 5.12$$

Using equation 5.5 to eliminate v and T from equation 5.12 gives the respective equivalent relationships

$$T P^{\left(\frac{1}{\alpha}-1\right)} = \text{constant} \quad 5.13$$

$$\text{and } P v^\alpha = \text{constant} \quad 5.14$$

Note that v can be replaced with V in equation 5.11 through 5.14. If we substitute equation 5.14 for P in equation 2.8, evaluate the integral and simplify the result, we would obtain

$$W = (P_2V_2 - P_1V_1)/(1-\alpha) \quad 5.15$$

which in view of equation 5.3 can also be written as

$$W = -mR\Delta T/(\alpha - 1) \quad 5.16$$

from equation 5.6, $\Delta u = c_V \Delta T$ OR $\Delta U = mc_V \Delta T$. But $c_V = \frac{R}{\alpha-1}$. Thus

$$\Delta U = \frac{mR\Delta T}{\alpha-1} = -W \text{ and the first law for closed system gives}$$

$Q = \Delta U + W = 0$ as expected.

3. A polytropic process is one which is governed by the general relationship

$$PV^n = \text{constant} \quad 5.17$$

where the exponent n can be determined experimentally and is equal to ∞ only for an isentropic process. Employing equation 5.17 in evaluating W from equation 2.8 gives the equivalents of equations 5.15 and 5.16 with ∞ replaced by n . Since ΔU is given by

$\Delta U = \frac{mR\Delta T}{\infty - 1}$, the first law for a closed system gives

$$Q = \left[\frac{1}{\infty - 1} - \frac{1}{n - 1} \right] mR\Delta T = \left[c_V - \frac{R}{n - 1} \right] m\Delta T$$

OR $Q = mc_n\Delta T \quad 5.18$

Where $c_n = \frac{(n-\infty)c_V}{n-1}$ and it may be regarded as a polytropic specific heat capacity.

For an isobaric process, $n = 0$ and $c_n = c_P$. For an isochoric process $n \rightarrow \infty$ and $c_n = c_V$. For an isentropic process, $n = \infty$ and $c_n = 0$.

If we substitute from equation 5.17 in the form $TV^{(n-1)} = \text{constant}$ into equation 5.11, we would obtain

$$\Delta s = c_n \ln \left(\frac{T_2}{T_1} \right)$$

5.19a

which may also be represented as

$$\Delta s = c_n \Delta(\ln T) \quad 5.19b$$

This applies generally to processes including isochoric, isobaric and isentropic processes ($c_n = c_V$, $c_n = c_P$, and $c_n = 0$ respectively), but excluding isothermal processes.

5.1.2 The generalized compressibility factor chart

The compressibility factor and z is defined by the relationship

$$z = \frac{\text{Actual volume of a gas}}{\text{its volume according to ideal gas model}} = \frac{Pv}{RT} \quad 5.20$$

A rearrangement of equation 5.20 gives

$$Pv = zRT \quad 5.21$$

Compare equations 5.5 and 5.21. Considering from the definition of z , we find that $z = 1$ for an ideal gas. Equation 5.21 therefore, represents a modification of the ideal gas law which is applicable to gases that do not obey the ideal-gas law. The departure of the behavior of a gas from ideal gas behavior is measured by the deviation of its compressibility factor from one.

In order to employ equation 5.21 in analysis, compressibility factor data are required. Such data have been generated for various substances. A comparison of these data reveals that all substances have essentially the same value of z for a given set of (P_r, T_r) , where

$$P_r = \frac{P}{P_c} \quad 5.22$$

$$\text{and } T_r = \frac{T}{T_c} \quad 5.23$$

P_c and T_c represent P and T at the critical point. The critical point is denoted by point C in the $P - v$ plot in figure 5.1 where the area under the dome ACB defines the two-phase (liquid-vapour) region, curve AC defines saturated liquid, curve BC represents saturated vapour and L, L-V, V, and G denote the liquid, liquid-vapor, vapour and gas regions respectively. The critical point has the attribute that for $T > T_c$, a vapour strictly becomes a gas and cannot be condensed to form a liquid through isothermal compression. At the critical point, the distinction between liquid and vapour vanishes as the two phases then have identical properties.

Figure 5.1 P-v diagram

P_r is called reduced pressure while T_r is called reduced temperature. The fact that all gases at the same (T_r, P_r) have essentially the same z is referred to as the principle of corresponding states. Taking advantage of this fact, generalized compressibility factor charts have been developed giving z as a function of P_r for various values of T_r .

To refine the results obtainable by means of this generalized compressibility factor charts, a third parameter Z_c (the critical compressibility factor) has been introduced in addition to P_c and T_c . Z_c is defined by $Z_c = P_c v_c / (RT_c)$. Based on available data, all materials have been classified into four groups: Group 1 with $0.24 \leq Z_c \leq 0.26$; Group 2 with $0.26 \leq Z_c \leq 0.28$; Group 3 with $0.28 \leq Z_c \leq 0.30$; and Group 4 with $Z_c = 0.23$ (the value for water). Each group yields one chart. Group 2 includes more than 60% of the substances considered and is normally regarded as adequate for all substances for most Engineering purposes. [Note: in using the chart, if either P or T is the unknown, it can be determined only iteratively.]

5.1.3 Other Equations of State: For applications where the ideal gas law is not valid and the compressibility factor method is either not suitable or not convenient, one of the many existing more complex equations of state may need to be employed. As a general rule, the most accurate equations of state are also the most complex and difficult to apply. A few of these equations of state will be presented here.

The Van der Waals EOS: This is the oldest practical equation of state and it is given by

$$(P + a/v^2)(v - b) = RT \quad 5.24$$

where a and b are positive parameters that correct for the two limiting assumptions of the ideal gas model. Setting $a = b = 0$ converts equation 5.24 to the ideal gas equation of state. Note that R may be replaced by \bar{R} in equation 5.24 or in any other equation of state depending on the unit of v and volume associated parameters. Based on the total volume, the Van der Waals equation assumes the form

$$(P + am^2/v^2)(v - mb) = mRT \quad 5.25$$

A rearrangement of equation 5.24 gives the pressure explicit form

$$P = \frac{RT}{(v-b)} - a/v^2 \quad 5.26$$

The parameters a and b may be defined in terms of critical properties by using the fact that the isotherm $T = T_c$ has a point of inflection at the critical point on the $P - v$ diagram (see figure 5.1). The implication of this is that

$\left(\frac{\partial P}{\partial v}\right)_{T_c} = 0$ and $\left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} = 0$ which yield $v_c = 3b$ and $T_c = \frac{3a}{27Rb}$. Substituting for v_c and T_c in equation 5.26 gives $P_c = a/(27b^2)$. By manipulating the above relationships for T_c and P_c , we have $a = 27R^2T_c^2/(64P_c)$ and $b = RT_c/(8P_c)$. Where experimental $P - v - T$ data exist, a and

b should be determined more accurately by fitting equation 5.24 to such data in preference to values based on only the critical point.

The Redlich-Kwong EOS: This is a better equation of state than the Van der waals equation. It involves only two parameters and it is of the form

$$P = \frac{RT}{(v-b)} - \frac{a}{T^{1/2}v(v+b)} \quad 5.27$$

Modifications of the Redlich-Kwong equation such as those by Wilson and by Soave replace $T^{1/2}$ in equation 5.27 by more complex function of reduced temperature and acentric factor ω (a structural parameter). These upgraded versions of equation 5.27 are relatively accurate and are popular in industrial analysis.

The Benedict-Webb-Rubin EOS: The original form of the relationship is given by the relationship

$$P = \frac{RT}{v} + \frac{B_0 RT - A_0 - C_0/T^2}{v^2} + \frac{bRT - a}{v^3} + \frac{aa}{v^6} + \frac{c}{v^3 T^2} \left(1 + \frac{\alpha}{v^2}\right) e^{-\alpha/v^2} \quad 5.28$$

There are eight empirical parameters involved in the equation (some extensions of the equation which have up to 20 parameters have been proposed). Extensive experimental data are required in order to evaluate these parameters. The BWR equation gives very accurate results but it is quite cumbersome to use. For example to determine v for a given set of P and T would require finding the desired root of a highly non linear function of the form

$$f(v) = \frac{c_1}{v} + \frac{c_2}{v^2} + \frac{c_3}{v^3} + \frac{c_4}{v^6} + \frac{c_5}{v^3} \left(1 + \frac{c_6}{v^2}\right) e^{-c_6/v^2} - P \quad 5.29$$

A computer is generally required for any serious application of the BWR equation of state.

Applying a Cubic EOS: To illustrate how the equation of state of non-ideal gases can be applied in a data generation, we will make use of a cubic equation of state. The Van der Waals equation and the Redlich-Kwong equation or modifications of it fall into this class because a rearrangement of any of them would yield a cubic polynomial in v . Defining v and b in m^3/kg , the equation takes the form

$$P = \frac{RT}{(v-b)} - \frac{a}{T^{1/2}v(v+b)} \quad 5.30$$

A rearrangement of equation 5.30 yields

$$v^3 - c_2 v^2 - c_1 v - c_0 = 0 \quad 5.31$$

where $c_0 = ab/(PT^{1/2})$, $c_2 = RT/(PT^{1/2})$, $c_1 = c_2 b + b^2 - c_0/b$.

For any thermodynamic state corresponding to a specified set of P and T , the values of v which satisfy equation 5.31 may be determined directly or iteratively. If we differentiate equation 5.30 with respect to T , holding v constant, we obtain

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-b} + \frac{a}{2T^2v(v+b)} \quad 5.32$$

if on the other hand, it is differentiated with respect to T , holding P constant, we would have

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{\frac{R}{v-b} + \frac{a}{2T^2v(v+b)}}{\frac{RT}{(v-b)^2} - \frac{a(2v+b)}{T^2v^2(v+b)^2}} \quad 5.33$$

substituting 5.32 into equation 4.22 gives the internal energy function as

$$du = c_V dT + \left\{ \frac{3a}{2T^2v(v+b)} \right\} dv \quad 5.34$$

substituting 5.33 into equation 4.27, we have the enthalpy function defined by

$$dh = c_P dT + \left\{ v - \frac{\frac{RT}{v-b} + \frac{a}{2T^2v(v+b)}}{\frac{RT}{(v-b)^2} - \frac{a(2v+b)}{T^2v^2(v+b)^2}} \right\} dP \quad 5.35$$

substituting 5.32 into equation 4.32 results in the entropy function

$$ds = \frac{c_V dT}{T} + \left\{ \frac{R}{v-b} + \frac{a}{2T^2v(v+b)} \right\} dv \quad 5.36$$

substituting both equations 5.32 and 5.33 into equations 4.36, we find that c_P and c_V are related by the equation

$$c_P - c_V = \frac{T \left\{ \frac{R}{v-b} + \frac{a}{2T^2v(v+b)} \right\}^2}{\frac{RT}{(v-b)^2} - \frac{a(2v+b)}{T^2v^2(v+b)^2}} \quad 5.37$$

With suitable specific heat capacity data, equations 4.34, 4.35 and 4.36 can be integrated along convenient process paths to give desired data on u , h , and s respectively.

5.2. $P - v - T$ BEHAVIOUR OF GAS MIXTURES

Various methods exist for predicting the $P - v - T$ behavior of gas mixtures in the absence of experimental data. Such methods utilize information on the $P - v - T$ behavior of each constituent gas as well as its mole fraction in the mixture. The mole fraction of constituent i (y_i) in a mixture containing n_i moles of i and a total of n moles is given by

$$y_i = n_i/n \quad 5.38$$

and n is defined by

$$n = \sum_{i=1}^c n_i \quad 5.39$$

where c is the number of constituents (components) in the mixture. The quality of results obtained by any method for a given gas mixture depends on the thermodynamic state of the mixture, in accordance with Gibb's phase rule. Some models for predicting the $P - v - T$ behaviour of gas mixtures are now considered.

5.2.1 Mixtures of Ideal Gases

At *sufficiently high temperatures or sufficiently low pressures*, each component of a gas mixtures will behave like an ideal gas such that what we have is a mixture of ideal gases. The question of what is quantitatively a sufficiently high temperature or a sufficiently low pressure may be answered in terms of the reduced properties T_r and P_r . If (P_r, T_r) gives z to be approximately 1 for each component, then the criterion is satisfied.

Let us consider a c -component gas mixture with volume V at temperature T and pressure P . Define P_i as the *pure component pressure* for component i (this is the pressure component i will exert at temperature T if the n_i moles of it which the mixture contains should occupy the entire volume V all alone), and let V_i be the pure component volume (the volume which pure component i would occupy if n_i moles of it existed alone at T and P). Then for an ideal gas mixture, we have

$$P_i = n_i \bar{R}T/V \quad 5.40$$

$$V_i = n_i \bar{R}T/P \quad 5.41$$

$$P = n \bar{R}T/V \quad 5.42$$

$$V = n \bar{R}T/P \quad 5.43$$

Dividing equation 5.40 by 5.42 and rearranging the result, we have

$$P_i = n_i P / n = y_i P \quad 5.44$$

A similar combination of equation 5.41 and 5.43 yields

$$V_i = n_i V / n = y_i V \quad 5.46$$

By definition, $y_i P$ is the partial pressure of component i in the mixture (that is the fraction of the mixture pressure that is due to component i) and $y_i V$ is the partial volume of component i in the mixture. Thus, for an ideal gas, the pure component volume and the pure component pressure are respectively equal to the partial volume and partial pressure for each constituent.