# PROCESS THERMODYNAMICS

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**Summary**

This Appendix is meant for those who lack a background in process thermodynamics. In a nutshell, it covers the essential features of the subject. Thermodynamics, as suggested by its name, involves heat in motion. It has two major applications that are as follows.

(a) To calculate the heat and work effects associated with a process, as well as to calculate the maximum work that can be obtained from a process or the minimum work needed to drive a process.
(b) To establish relationships between the different variables describing a system at equilibrium.

## 1. Terminology

*System*: a system is any part of the process that is chosen for study or analysis. It may have real or imaginary boundaries, and these boundaries may be rigid or movable. Great care has to be exercised in defining a system and its boundaries, since the analysis of a given problem is much simplified by their proper choice.

*State*: state refers to the condition in which a particular system exists. It should be both reproducible and time invariant.

*Surroundings*: once the system and its boundaries are selected, whatever is outside the boundaries becomes surroundings for the system. More practically, surroundings are the immediate environment beyond the boundaries, which is affected by the processes occurring within the system.

*Closed system*: a closed system is one which does not exchange any mass with the surroundings. Hence, the mass of a closed system remains constant. Only heat and work are exchanged between the system and its surroundings. Therefore, changes in energy, volume, or other properties are experienced within the system.

*Isolated system*: if neither mass nor heat nor work are exchanged between the system and its surroundings, it becomes an isolated system. In this case, the surroundings are unaffected by the processes occurring within the system.

*Open system*: in an open system, mass is exchanged between the system and its surroundings. To further distinguish between an open and a closed system, consider the mixture of liquid and vapor phases of a pure substance contained in a cylinder that is fitted with a piston. When the piston moves, it causes changes in the masses of each phase accompanied by heat exchange with the surroundings. If individual phases are selected that increase or decrease in mass, it constitutes an open system. However, the two phases taken together would make a closed system.

*Isothermal system*: if any process occurs in a system at constant temperature, the process as well as the system are said to be isothermal. This applies both to the open and closed systems and to maintain isothermal conditions there has to be an exchange of heat with the surroundings.

*Adiabatic system*: in an open or closed system, when there is no exchange of heat with the surroundings, the process and the system are called adiabatic. To be adiabatic, a system must be perfectly insulated against the flow of heat. This being an ideal condition, it is closely approached in many situations.

## 2. Variables and Properties

The commonly encountered variables and properties in thermodynamics are as defined below.

*State variables*: the value of a state variable depends upon the state in which the system

exists. The change in a state variable between the two states of a system is always the same irrespective of the path by which the system moves from one state to the other. Temperature, pressure, and volume are examples of state variables.

*Path variables*: changes in the path variables depend on the path by which the system moves. Therefore, they have meaning only when the path between the initial and final states is specified. Heat and work are path variables and exist only when a system undergoes a change in state.

*Extensive properties*: the extensive properties depend upon the size of the system and they are additive. Volume is an extensive property. The volume of a system is the sum of the volumes of its several identifiable parts.

*Intensive properties*: intensive properties do not depend on the size of the system. Temperature, pressure, and density are examples of intensive properties. If a system is homogeneous, an extensive property can be converted into an intensive one by dividing the former by the total quantity of the system. For instance, the volume of a system is divided by its mass to obtain an intensive property, i.e. the specific volume.

*Work*: work is defined as the product of a force $F$ and the displacement $dl$ it produces, i.e.

Work $dw = Fdl$

or, for a finite displacement,

$$W = \int F dl \tag{1}$$

In engineering thermodynamics, the predominant type of work is that of either expansion or contraction of a fluid, such as a gas confined in a cylinder fitted with a piston. In such a case, the force required to produce a volume change $dv$ will be the product of pressure $P$ and the piston area $A$. In turn, $dv = Adl$ where $dl$ is the linear movement of the piston. Therefore,

$$dw = Fdl = PA\left(\frac{dv}{A}\right) = Pdv$$

or

$$w = \int P dv. \tag{2}$$

*Heat*: generally expressed by the symbol $Q$, it is a path quantity and has meaning only when exchanged between two bodies in contact due to a difference in their temperatures.

## 2.1. Equilibrium

A system is said to be in equilibrium when its measurable properties do not change with

time. In this definition, it is implied that the system is not interacting with the surroundings. All spontaneous changes cause a system to reach an equilibrium state; hence, all closed systems eventually reach equilibrium. An equilibrium state should also be reproducible. The number of variables that should be specified to ensure an equilibrium state is given by the phase rule, which is expressed as follows:

$$F = C + 2 - \Pi \tag{3a}$$

where $F$ is the degrees of freedom or the number of intensive variables to be fixed, $C$ is the number of components in the system, and $\Pi$ is the number of phases.

For example, to have a vapor-liquid mixture ($\Pi = 2$) at equilibrium in a system containing two components ($C = 2$), the degrees of freedom available are $F = 2$. Suppose one degree of freedom is utilized by fixing the pressure $P$ in the system, then the remaining degree of freedom can be either temperature or composition of one of the phases.

## 2.2. Reversible Process

A process moving a system from state 1 to state 2 is said to be reversible, provided that the heat and work effects thus realized are just sufficient to restore the system to its original state 1. No real process can be truly reversible, because of the presence of friction and other effects, energy would be dissipated. However, the reversible process represents a limiting case to which an actual process should approach. A reversible process produces maximum work or requires a minimum amount of work and is the only type for which work can be calculated. Hence, to determine the actual work, one first has to calculate the reversible work and multiply it by an efficiency factor.

The necessary conditions for reversibility are as follows.

The absence of dissipative process such as friction.

The system needs to exist in an equilibrium state at all times.

The maintenance of only an infinitesimal difference in the thermodynamic potential between the system and its surroundings. For instance, when heat is exchanged the uniform system temperature should only differ infinitesimally from that of the surroundings.

## 3. First Law of Thermodynamics

Energy manifests itself in its various forms, which are convertible from one to the other. For example, electrical energy flowing into an oven is converted into heat or into light in an electric lamp. Heat and work, denoted by the symbols $Q$ and $W$, respectively, are the forms of energy that are exchanged between a system and its surroundings. Because of this change, a system undergoes a change of state that could be manifested by a change in its temperature or a phase change. Therefore, it suggests that any system

possesses a form of energy associated with the state of the system which is called its "internal energy" and expressed by the symbol $U$.

Moreover, a system can possess kinetic energy by virtue of its velocity and potential energy due to its elevation. Changes in these forms of energy can be calculated as follows.

Change in kinetic energy

$$\Delta E_k = (m\Delta u^2)/2 \tag{3b}$$

Change in potential energy

$$\Delta E_p = mg\Delta z \tag{4}$$

where $u$ and $z$ are the velocity and elevation, respectively, $m$ is the mass of the system, and $g$ is the gravitational acceleration. Thus, the total energy change of the system will be

$$\Delta E = \Delta U + \Delta E_k + \Delta E_p \tag{5}$$

In Eq. (5), the various types of energy changes are extensive property changes of the system. In addition, there can be other changes such as surface energy and energy due to external fields, e.g. electric or magnetic. For a closed system, it can be written

$$\Delta E = Q + W$$

where, by convention, $Q$ and $W$ are taken as positive when the exchange occurs from the surroundings to the system. In many processes, the system remains stationary and does not experience any changes in the kinetic and potential energies. In such cases, the change in internal energy predominates; therefore, the above equation is written

$$\Delta U = Q + W \tag{6}$$

or, for infinitesimal changes,

$$\mathrm{d}u = \mathrm{d}Q + \mathrm{d}W \tag{7}$$

Equations (6) and (7) represent the conservation of energy known as the first law of thermodynamics and define internal energy as a state property. The absolute value of this property is never known; only its changes between states can be evaluated.

### 3.1. Enthalpy

In the application of the first law, often the internal energy $U$ and the product $PV$ (of pressure $P$ and volume $V$) are added. It is therefore convenient to define a new

thermodynamic variable, enthalpy $H$ as $H = U + PV$. Since $U$, $P$, and $V$ are all state variables, $H$ is also a state variable.

For a constant pressure process, it is seen from the definition of enthalpy that

$$\Delta H = \Delta U + P\Delta V.$$

Now, from the first law Eq. (6)

$$Q_p = \Delta U - W_p.$$

If the system can perform only $PV$ work reversibly at constant pressure, then

$$W_p = -\int P\mathrm{d}v = -P\Delta V$$

or

$$Q_p = \Delta U + P\Delta V = \Delta H \tag{8}$$

Thus, from Eq. (8), at constant pressure the enthalpy change equals the heat effect of a reversible process when the system is capable of performing only $PV$ work. In applications, the constraint of reversibility is relaxed with certain justification.

For an ideal gas, the internal energy and enthalpy depend only on temperature. For real gases, the effect of pressure may be small.

## 3.2. Heat Capacity

The heat capacity $C$ is defined in terms of heat required to bring a temperature change in the system by a specified path. Paths of constant volume and constant pressure are of practical interest. When the volume is constant, $\mathrm{d}W = 0$, hence $\mathrm{d}U = \mathrm{d}Q_v$. Therefore, a constant volume heat capacity is given by

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v, \tag{9}$$

where $T$ is temperature.

Similarly, for a constant pressure heating from Eq. (8), $dH = dQ_P$, and the constant pressure heat capacity becomes

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{10}$$

Because $U$ and $H$ are state properties, so are $C_v$ and $C_P$.

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