1. BASIC CONCEPTS OF THERMODYNAMICS

1.1 Definition of Thermodynamics

Thermodynamics is the study of the effects of work, heat, and energy on a system. It deals only with the large-scale response of a system, which can be observed and measured in an experiment, of heat and work. Small-scale gas interactions are described by the kinetic theory of gases.

1.2 Idea of a System and its Surrounding

System is a restricted region of space or a finite portion of matter one has chosen to study. Or the part of the universe, with well-defined boundaries, one has chosen to study.

Surrounding is the rest of the universe outside the region of interest (i.e. the rest of space outside the system).

Boundary or Wall is the surface that divides the system from the surroundings.

This wall or boundary may or may not allow interaction between the system and the surroundings.

1.3 Thermodynamic Properties/Coordinates

These are macroscopic coordinates or properties used to describe or characterize a system. Because they are macroscopic properties or coordinates, they can be observed and measured. Some examples are Temperature (**T**), Pressure (**P**), Volume **(V)**, density (**ρ**), mass (**m**), specific heat capacity at constant volume ($\mathbf{C_V}$), specific heat capacity at constant pressure **(**$\mathbf{C_P}$**),** thermal conductivity (**k**), thermal diffusivity (**α**), and chemical potential (**μ**).

1.4 Thermodynamic System

This is a system that could be described in terms of thermodynamic coordinates or properties. Thermodynamic Systems can be categorised into the followings depending on the type of boundary:

Open System: This is a system that its boundary allows transfer of **mass and energy** into or out of the system. In other words, the boundary allows exchange of mass and energy between the system and the surrounding.

Closed System: This is a system that its boundary allows exchange of **energy alone** (inform of heat) between the system and its surrounding (i.e. the boundary allows exchange of **energy alone**). This type of boundary that allows exchange of heat is called diathermal boundary.

Isolated System: This is a system that its boundary allows **neither mass nor energy** between it and the surrounding. In other words, the boundary does not allow exchange of mass nor energy.

1.5 Thermodynamic Processes

A system undergoes a thermodynamic process when there is some sort of energetic change within the system, generally associated with changes in pressure, volume, internal energy, temperature, or any sort of heat transfer.

There are several specific types of thermodynamic processes that happen frequently enough (and in practical situations) that they are commonly treated in the study of thermodynamics. Each has a unique trait that identifies it, and which is useful in analyzing the energy and work change related to the process.

Adiabatic process: This is a thermodynamic process in which there is no heat transfer into or out of the system. For this process, change in quantity of heat is zero (i.e. $\Delta Q = 0$ during this process)

Isochoric process: This is a thermodynamic process that occurs at constant volume (i.e. $\Delta V = 0$ during this process). This implies that during this process no work is done on or by the system.

Isobaric process: This is a thermodynamic process that occurs at constant pressure (i.e. $\Delta p = 0$ during this process).

Isothermal process: This is a thermodynamic process that takes place at constant temperature (i.e. $\Delta T = 0$ during this process)

Cyclic Processes: These are series of processes in which after certain interchanges of heat and work, the system is restored to its initial state. For a cyclic process $\Delta U = 0$, and if this is put into the first law (unit 3) $Q = W$

This implies that the net work done during this process must be exactly equal to the net amount of energy transferred as heat; the store of internal energy of the system remains unchanged.

Reversible Process: A reversible process can be defined as one which direction can be reversed by an infinitesimal change in some properties of the system.

Irreversible Process: An irreversible process can be defined as one which direction cannot be reversed by an infinitesimal change in some properties of the system

Quasi-static Process: This is a process that is carried out in such a way that at every instant, the system departs only infinitesimal from an equilibrium state (i.e. almost static). Thus a quasi-static process closely approximates a succession of equilibrium states.

Non-quasi-static Process: This is a process that is carried out in such a way that at every instant, there is finite departure of the system from an equilibrium state.

1.6 Thermodynamic Equilibrium

Generally, a system is said to be in equilibrium when its properties do not change appreciably with time over the interval of interest (i.e. observation time).

A system is said to be in thermodynamic equilibrium with its surrounding or with another system if and only if the system is in thermal equilibrium, in chemical equilibrium and in mechanical equilibrium with the surrounding or with another system. If any one of the above conditions is not fulfilled, the system is not in thermodynamic equilibrium.

1.6.1 Mechanical Equilibrium

A system attains mechanical equilibrium with its surrounding or with another system when there is no unbalance or net force in the interior of the system and also none between the system and its surroundings or another system. Suppose two systems are separated by a movable boundary that does not allow exchange of mass or heat as shown in figure 1.1. If P1 is greater than P2 , the partition will continue to move toward system 2 until P1 is equal to P2 . When this occurs, the two systems are said to be in mechanical equilibrium.

1.6.2 Chemical Equilibrium

A system attains chemical equilibrium when there are no chemical reactions going on within the system or there is no transfer of matter from one part of the system to other due to diffusion. Two systems are said to be in chemical equilibrium with each other when their chemical potentials are same.

1.6.3 Thermal Equilibrium

This occurs when two systems in thermal contact or a system that is in thermal contact with the surrounding attains the same temperature. For example if system 1 with temperature T_1 and system 2 with temperature T_2 are in thermal contact, there will be exchange of heat between the two systems if there is a temperature gradient (i.e. when $T_1 \neq T_2$). This process of heat exchange will continue until thermal equilibrium is attained (i.e. $T_1 = T_2$).

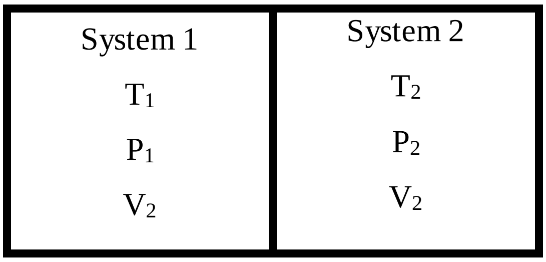

Fig. 1.1: Two Systems Separated by a Movable Partition

1.7 State of a System

This is a specific situation in which macroscopic properties (thermodynamic properties) of a system have certain values (e.g. P=10 Pa, V=100 cm^3, and T=300 K would be a state of a gas). It is important to note that the state of a pure substance or a system can be defined or specified by any two of its properties.

Change of state occurs when there is change in one, two or all the properties of the system. Using figure 1.1 above as example, suppose P1 is greater than P2 the partition will continue to move towards system 2 until P1 is equal to P2. When this happens, the system 1 and 2 have a new set of coordinates in which Temperature remain constant for the two systems but pressure and volume changed. Then we say that the state of system 1 and system 2 has changed.

1.8 Equation of State

This is the known relationship between the thermodynamic variables or properties. It is an equation which provides a mathematical relationship between two or more state functions associated with matter such as its temperature, pressure, volume, or internal energy.

From the above descriptions, Boyle's law, Charles' law, Dalton's law of partial pressures are examples of equation of state. Some other examples of equation of state are:

1.8.1 The Ideal Gas

The equation of state for ideal gas is

$$\mathbf{PV = nRT}$$

where P is the pressure, V is the volume, R is the molar gas constant ($R=8.314\ JK^{-1}\ mol^{-1}$), T is temperature in Kelvin, and n is the number of mole of gas.

1.8.2 Van der Waals Equation of State

The equation of state for real gas also known as Van der Waals Equation is

$$\left(P + \frac{a}{V_m}\right)(V_m - b) = RT$$

where quantities a and b are constants for a particular gas but differ for different gases.

There are many more equations of state besides these two given above.

1.9 Extensive and Intensive Properties

Thermodynamic properties of a system can be categorised into two namely:

Extensive properties: These are properties of system that depend on the mass of the system (e.g. n, V and total energy U)

Intensive properties: These are properties of system that are independent of the mass of the system (e.g. T, P and ρ).

Specific Value of an extensive property (for example Volume, V) is defined as the ratio of the volume of the property to the mass of the system, or as volume per unit mass.

Specific volume Vs is

$$\mathbf{Vs = V/m}$$

Note that the specific volume is evidently the reciprocal of the density ρ, defined as the mass per unit volume:

$$\boldsymbol{\rho} = \mathbf{m/V = 1/Vs}$$

Molar Value of an extensive property (for example Volume, V) is defined as the ratio of the volume of the property to the number of moles of the system, or as volume per unit mole. Molar volume Vm is

$$\mathbf{Vm = V/n}$$

1.2. Differential Calculus

1.2.1 Partial Derivatives

A partial derivative of a function of several variables is its derivative with respect to one of those variable with the others held constant.

$$\mathbf{X = x(y,z) \qquad 1.1}$$

From equation1, x a dependent variable is a function of two independent variables z and y . Partial derivative of x with respect to y with z held constant is $(\partial x/\partial y)z$

For example, if

$$\mathbf{X = zy^2 \qquad 1.2}$$

then, the partial derivative of x with respect to y with z held constant is

$$\mathbf{(\partial x/\partial y)z = 2zy \qquad 1.\ 3}$$

Similarly, the partial derivative of x with respect to z with y held constant is

$$\mathbf{(\partial x/\partial z)y = y^2 \qquad 1.4}$$

1.2.2 Exact Differential

Suppose that there exists a relation among the three coordinates x , y , and z in such a way that x is a function of y and z (i.e x (y ,z)); thus

$$\mathbf{f(x,y,z) = 0 \qquad 1.\ 5}$$

The exact differential of x (dx) is

$$\mathbf{dx = (\partial x/\partial y)z\, dy + (\partial x/\partial z)y\, dz \qquad 1.\ 6}$$

Generally for any three variables x, y, and z we have relation of the form

$$dx = M(y,z)\,dy + N(y,z)\,dz \qquad 1.7$$

If the differential dx is exact, then

$$(\partial M/\partial z)_y = (\partial N/\partial y)_z \qquad 1.8$$

1.2.3 Implicit Differential

Consider an equation of the form

$$xy = x^2 y^2 \qquad 1.9$$

One can differentiate the two sides of the equation 1.9 using equation 6 (i.e differentiating both the left and right hands side with respect to x while y is held constant and with respect to y while x is held constant).

$$\left(\frac{\partial(xy)}{\partial x}\right)_y dx + \left(\frac{\partial(xy)}{\partial y}\right)_x dy = \left(\frac{\partial(x^2y^2)}{\partial x}\right)_y dx + \left(\frac{\partial(x^2y^2)}{\partial y}\right)_x dy \qquad 1.10$$

Equation 1.10 gives

$$ydx + xdy = 2xy^2dx + 2x^2ydy \qquad 1.11$$

Collecting like term and then factorize to have

$$\frac{dy}{dx} = \frac{2xy^2 - y}{x - 2x^2y} \qquad 1.12$$

Another way to obtain expression for (dy/dx) is to consider equation 1.9 as

$f = xy - x^2 .y^2$ (i.e. moving the expression in the right side of equation 1.9 to the left side and then equate the result to f). Then

$$\frac{dy}{dx} = -\frac{\partial f}{\partial x}\Big/\frac{\partial f}{\partial y} \qquad 1.13$$

1.2.4 Product of Three Partial Derivatives

Suppose that there exists a relation among the three coordinates x, y, and z; thus

$$f(x,y,z)=0 \qquad 1.14$$

Then x can be imagined as a function of y and z

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \qquad 1.15$$

Also, y can be imagined as a function of x and z , and

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \qquad 1.16$$

Insert equation 1.16 in 1.15

$$dx=(\frac{\partial x}{\partial y})_z[(\frac{\partial y}{\partial x})_z dx+(\frac{\partial y}{\partial z})_x dz]+(\frac{\partial x}{\partial z})_y dz$$

Rearrange to get

$$dx=(\frac{\partial x}{\partial y})_z(\frac{\partial y}{\partial x})_z dx+[(\frac{\partial x}{\partial y})_z(\frac{\partial y}{\partial z})_x+(\frac{\partial x}{\partial z})_y]dz$$

1.17

If dz = 0 and dx ≠ 0 , it follows that

$$(\frac{\partial x}{\partial y})_z(\frac{\partial y}{\partial x})_z=1$$

$$(\frac{\partial x}{\partial y})_z=\frac{1}{(\partial y/\partial x)_z}$$

1.18

Take note of the z in the expression on both sides of the equation 1.18, indicating that the derivatives in equation 18 are at constant z .

Also from equation 1.17, if dx = 0 and dz ≠ 0, it follows that

$$(\frac{\partial x}{\partial y})_z(\frac{\partial y}{\partial z})_x+(\frac{\partial x}{\partial z})_y=0$$

Move $(\partial x/\partial z)y$ to the other side of equation to get

$$(\frac{\partial x}{\partial y})_z(\frac{\partial y}{\partial z})_x=-(\frac{\partial x}{\partial z})_y$$

1.19

Then divide both sides of the equation 1.19 by $(\partial z/\partial x)y$

$$(\frac{\partial x}{\partial y})_z(\frac{\partial y}{\partial z})_x(\frac{\partial z}{\partial x})_y=-1$$

1.20

This is called minus-one product rule.

1.2.5 Chain Rule of Partial Derivatives

Another useful relation is called chain rule of partial derivatives. Suppose T is a function of V and P, and that each of V and P is a function of Z, then

$$(\frac{\partial T}{\partial V})_P=(\frac{\partial T}{\partial Z})_P(\frac{\partial Z}{\partial V})_P$$

1.21

Equation 1.21 is the chain rule of partial derivative. Going by 1.21, the following can as well be written:

$$\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T$$

1.22a

$$\left(\frac{\partial U}{\partial V}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P$$

1.22b

Equations 1.21 and 1.22 are called chain rule of partial derivatives.

1.2.6 Second Derivatives or Second Order Derivatives

Let f(x,y)) be a function with continuous order derivatives, then we can calculate first derivatives to be $(\partial f/\partial x)z$ and $(\partial f/\partial z)x$. One can further calculate the second derivatives $\partial^2 f/\partial x^2$, $\partial^2 f/\partial z^2$, $\partial^2 f/\partial x.\partial y$ and $\partial^2 f/\partial y.\partial x$. Take note of these two second order derivates i.e. $\partial^2 f/\partial x.\partial y$ and $\partial^2 f/\partial y.\partial x$, they are called mixed second derivatives. It can be shown that the mixed second derivatives are equal, i.e. it does not matter the order will perform the differentiation.

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$$

1.23

1.2.7 Functions of More than Two Variables

Suppose that f (x ,y,z) the derivative of f with respect to one of the variables with the other two constant (e.g. derivative of f x with y and z constant) can be written as

$$\left(\frac{\partial f}{\partial x}\right)_{yz},\ \left(\frac{\partial f}{\partial y}\right)_{xz},\ \text{and}\ \left(\frac{\partial f}{\partial z}\right)_{xy}$$