Some Important topics related to Thermodynamics

Topics covered here:

- Intensive and extensive properties
- State function and path function
- exact and inexact differentials,
- partial derivatives,
- Euler's reciprocity,
- Cyclic rules.

Intensive and extensive properties

Intensive properties: According to International Union of Pure and Applied Chemistry (IUPAC), an intensive property or intensive quantity is one whose magnitude is independent of the size of the system. That is, an intensive property is a physical quantity whose value does not depend on the amount of substance which was measured. An intensive property is not necessarily homogeneously distributed in space; it can vary from place to place in a body of matter and radiation. Examples of intensive properties include temperature, T; refractive index, n; density, ρ; and hardness, η.

Extensive property

An extensive property is a physical quantity whose value is proportional to the size of the system it describes, or to the quantity of matter in the system. For example, the mass of a sample is an extensive quantity; it depends on the amount of substance. Thus, **extensive property** or **extensive quantity** is the one whose magnitude is additive for subsystems. Examples include mass, volume and entropy.

The most obvious intensive quantities are ratios of extensive quantities. Thus, dividing one extensive property by another extensive property, generally gives an intensive value—for example: mass (extensive) divided by volume (extensive) gives density (intensive). The density of water is approximately 1g/mL whether you consider a drop of water or a swimming pool, but the mass is different in the two cases.

- In a homogeneous system divided into two halves, all its extensive properties, in particular its volume and its mass, are divided into two halves.

- All its intensive properties, such as the mass per volume (mass density) or volume per mass (specific volume), must remain the same in each half.
- The temperature of a system in thermal equilibrium is the same as the temperature of any part of it, so temperature is an intensive quantity. If the system is divided by a wall that is permeable to heat or to matter, the temperature of each sub-system is identical. Additionally, the boiling temperature of a substance is an intensive property. For example, the boiling temperature of water is 100 °C at a pressure of one atmosphere, regardless of the quantity of water remaining as liquid.
- Not all properties of matter fall into these two categories. For example, the square root of the volume is neither intensive nor extensive. If a system is doubled in size by juxtaposing a second identical system, the value of an intensive property equals the value for each subsystem and the value of an extensive property is twice the value for each subsystem. However the property $\sqrt{V}$ is instead multiplied by $\sqrt{2}$.

State functions and Path Functions:

State functions: The different thermodynamic variables such as the internal energy (U), volume, pressure, and temperature, entropy (S), free energy (G), etc., can be used to specify the state of a system. They are properties of the current state of the system, and they do not depend on the way the system got to that state.

For example, if you have a system consisting of 1 mol of He at 298 K and 1 atm, the system will have a given pressure, internal energy, entropy and free energy regardless of its history. You may have compressed the system from 2 atm, or heated the gas from 273 K. All this is irrelevant to specify the pressure, entropy, etc, because all these variables are what we call **state functions**. State functions depend only on the state of the system.

Path functions: Other quantities such as work (w) and heat (q), on the other hand, are not state functions. There is no such a thing as an amount of work or heat in a system. The amounts of heat and work that "flow" during a process connecting specified initial and final states depend on how the process is carried out. Quantities that depend on the path followed between states are called **path functions**.

Differentials in Thermodynamics

Exact differentials: ***Quantities whose values are independent of path are called state functions, and their differentials considered as exact differentials. (dp, dV, dG, dT,...).***

Inexact differentials: Quantities that depend on the path followed between states are called path functions, and their differentials considered as inexact differentials (dw, dq).

Distinguishing between exact and inexact differentials has very important consequences in thermodynamics. As we will discuss in a moment, when we integrate an exact differential the result depends only on the final and initial points, but not on the path chosen. However, when we integrate an inexact differential, the path will have a huge influence in the result, even if we start and end at the same points.

Importance:

Knowing that a differential is exact will help you derive equations and prove relationships when you study thermodynamics. For example, all the state functions, like internal energy (U), volume, pressure, and temperature, entropy (S), enthalpy (H), free energy (G), Helmholtz free energy (A), are related through these equations:

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

Here, T, P, V and S are not constants.

Partial Derivative:

The partial derivative is used in vector calculus and differential geometry. In Mathematics, sometimes the function depends on two or more variables. Here, the derivative converts into the partial derivative since the function depends on several variables.

Definition: Suppose, we have a function f(x, y), which depends on two variables x and y, where x and y are independent of each other. Then we say that the function f partially depends on x and y. Now, if we calculate the derivative of f, then that derivative is known as the partial derivative of f. If we differentiate the function f with respect to x, then we take y as a constant and if we differentiate f with respect to y, then we take x as a constant.

***Example**:* Suppose f is a function in x and y then it will be expressed by f(x, y). So, the partial derivative of f with respect to x will be ∂f/∂x keeping y as constant. It should be noted that it is ∂x, not dx. ∂f/∂x is also known as f_x.

We can extend the concept of differentiation of a function of one variable to that of a function of two or more variables. Let z = *f*(x, y) be a function of two independent variables (x, y). The partial derivatives of *f*(x, y) with respect to x and y are defined by

$$\frac{\partial z}{\partial x} = \frac{\partial f}{\partial x} = \lim_{\Delta x \to 0} \frac{f(x+\Delta x, y) - f(x,y)}{\Delta x} \quad \text{……………..} (1)$$

$$\frac{\partial z}{\partial y} = \frac{\partial f}{\partial y} = \lim_{\Delta y \to 0} \frac{f(x, y+\Delta y) - f(x,y)}{\Delta y} \quad \text{……………….} (2)$$

Provided the limits exist. For the partial derivative ∂f/∂x, y is held constant and x is considered as a variable. Similarly, for the partial derivative ∂f/∂y,, x is held constant and y is considered as a variable.

The differentiation of ∂f/∂x, w.r.t. x or y yields second-order derivatives:

$$\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial^2 f}{\partial x^2} \text{ and } \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial^2 f}{\partial y \partial x} \quad \text{…………………} (3)$$

Similarly, $$\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial^2 f}{\partial y \partial x}, \quad \text{and} \quad \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial^2 f}{\partial y^2} \quad \text{…………….. ….}(4)$$

If *f(*x, y) and its partial derivatives (also called partial differential coefficients) are continous, then the order of differentiation is immaterial, i.e.

$$\partial^2 f/\partial x \partial y = \partial^2 f/\partial y \partial x \quad i.e., \; f_{xy} = f_{yx} \quad \text{………..} (5)$$

The total differential **df** of the function *f(*x, y) is defined as

$$df = \left(\frac{\partial f}{\partial x}\right)dx + \left(\frac{\partial f}{\partial y}\right)dy \quad \text{………..}(6)$$

Euler's Theorem or Euler's reciprocity:

Let z = f (, y) be the state function of the two independent variables x and y. A State function depends upon the initial and the final states of a System and is independent of the path via which the state is reached. The differential of z, called an exact or total differential, is given by:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \quad \text{............ (7)}$$

$$= M(x, y)\, dx + N(x, y)\, dy \quad \text{............ (8)}$$

Where, $M(x, y) = (\partial z/x)_y$ and $N(x, y) = (\partial z/\partial y)_x$ .... (9)

Since, M(x, y) and N(x, y) are assumed to have continuous partial derivatives:

$$\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x} \quad \text{............ (10)}$$

Taking mixed second derivatives of equation 9, we have,

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial y\, \partial x}; \quad \text{and} \quad \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial x\, \partial y} \quad \text{................ (11)}$$

From eq, 10 and 11 we have,

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \quad \text{.............. (12)}$$

Eq 12 is called the **Euler reciprocity relation. This is only applicable to state functions.**

Since z is a state function, the finite change, △z, as the system passes from initial state A to final state B, is given by:

$$\Delta z = z_B - z_A.$$

Also, $\oint dz = 0$, where cyclic integral means $\oint$. that the means that the system is in the same state at the end of its path as it was at the beginning, i.e., it has traversed a closed path. Thus, dz is an exact differential. If,

$$\left(\frac{\partial M}{\partial y}\right)_x \neq \left(\frac{\partial N}{\partial x}\right)_y$$

I.e., Euler reciprocity relation is not obey, then the differential of z, called an inexact differential

The Cyclic Rule or Euler Chain Relation:

From eq. 7, we see that if the change occurs at see that, if the change occurs at constant z, then dz = 0 so that,

$$0 = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \qquad \text{.............................. (13)}$$

Hence, $$\left(\frac{\partial x}{\partial y}\right)_z = -\frac{(\partial z/\partial y)_x}{(\partial z/\partial x)_y} \qquad \text{............................ (14)}$$

or, $$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1 \qquad \text{.................. (15)}$$

Eq 15 is called the **Euler chain relation (or the cyclic rule), applicable only for state functions.**