Thermodynamics

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* Mathematical Interlude :-

Some simple calculus are often used in thermodynam-al treatments. It may be worth to get familiar with those mathematical ingradients which provide us with some elementary comfort during our study of thermodyna

1. Partial Derivatives :-

Let a quantity 'Z' is a function of two independent variables of 'x' and 'y' i.e. $Z = f(x, y)$. If the coordinates of x and y charge by a small amounts dx & dy then the change in the value of 'Z' is given by

$$dZ = \left(\frac{\partial Z}{\partial x}\right)_y dx + \left(\frac{\partial Z}{\partial y}\right)_x dy$$

where $\left(\frac{\partial Z}{\partial x}\right)_y$ is the change of 'Z' for unit change of 'x' at constant y; Similarly, $\left(\frac{\partial Z}{\partial y}\right)_x$ is the change of 'Z' for unit change of 'y' at constant 'x'.

Let us suppose the three quantities x, y, z are related as $f(x, y, z) = 0$; So, we have $x = \psi(y, z)$ & $y = \phi(z, x)$

Therefore, we can write, $dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$ ...(1) and

$$dy = \left(\frac{\partial y}{\partial z}\right)_x dz + \left(\frac{\partial y}{\partial x}\right) dx \quad \text{....(2)}$$

Substituting (2) in (1), we have,

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left[\left(\frac{\partial y}{\partial z}\right)_x dz + \left(\frac{\partial y}{\partial x}\right)_z dx\right] + \left(\frac{\partial x}{\partial z}\right)_y dz \quad \text{---(3)}$$

$$= \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] dz \quad \text{.... (3')}$$

Eq 3 and 3' are generally true for all values of x, y, z.

Considering x and z as independent variables in Eq. 3 & 3' :-

a) Let's suppose $dz = 0$, but $dx \neq 0$ then

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx$$

$$\Rightarrow \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1. \quad \Rightarrow \quad \left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} \quad \text{.... (4)}$$

b) Let us take $dz \neq 0$, but $dx = 0$, then

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

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

As we can write, $$\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}$$

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

—— This is called cyclic rule.

A proof of the cyclic relation can be shown in the following on natural variables, P, V, T.

we know $PV = RT$

here, $f(P, V, T) = 0$ and $\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{V^2}$; $\left(\frac{\partial V}{\partial T}\right) = \frac{R}{P}$

& $\left(\frac{\partial T}{\partial P}\right)_V = \frac{V}{R}$.

Thus, $$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -\frac{RT}{V^2} \times \frac{R}{P} \times \frac{V}{R} = -1$$

Thus, $$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1 \quad \text{(Proved)}$$

Perfect differentials:-

Let us consider a quantity 'z' whose value is determined solely by two other variables x and y at any moment, in any given state, that is, if x & y are given a particular value, the value of 'z' is thereby fixed. If x & y vary, then z will also vary. Thus, mathematically, if we consider $z = f(x,y)$, the change of z can be estimated provided the derivative of the function z w.r.t. x and y are known. Formal derivatives are

* $\left(\frac{\partial z}{\partial x}\right)_y$ = rate of change of 'z' (dependent variable) with respt. to x (Independent variable) at const y

* $\left(\frac{\partial z}{\partial y}\right)_x$ = " " " " z " " y at const x

If x & y both change simultaneously, the total change is expressed as,

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

$$\Rightarrow dz = M(x,y)\,dx + N(x,y)\,dy$$

where $M(x,y) = \left(\frac{\partial z}{\partial x}\right)_y$ and $N(x,y) = \left(\frac{\partial z}{\partial y}\right)_x$

* Conditions for Exactness :-

For a differential $M(x,y)dx + N(x,y)\,dy$ to be exact, it must satisfy the following relation (which is mathematically known as Schwarz's theorem; also called the cross partial derivative test):

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x} \Rightarrow \frac{\partial^2 Z}{\partial x\,\partial y} = \frac{\partial^2 Z}{\partial y \cdot \partial x}$$

$\Rightarrow$ this ensures M, N come from a common potential function $Z = f(x,y)$.

Example :- Consider the differential expression:

$$dZ = (2xy)\,dx + (x^2+3y^2)\,dy$$

Here, $M = 2xy$ and $N = x^2+3y^2$

Performing cross partial derivative test :-

$$\frac{\partial M}{\partial y} = \frac{\partial}{\partial y}(2xy) = 2x$$

$$\frac{\partial N}{\partial x} = \frac{\partial}{\partial x}(x^2+3y^2) = 2x$$

Since, $\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$, the differential 'dZ' is exact.

This means there exists a function $Z(x,y)$ such that

$$\frac{\partial Z}{\partial x} = 2xy \quad , \quad \frac{\partial Z}{\partial y} = x^2+3y^2$$

Integrating $\frac{\partial u}{\partial x}$ w.r.t. x:

$$Z(x,y) = \int 2xy\,dx = x^2y + g(y)$$

To determine $g(y)$, differentiate w.r.t. y:

$$\frac{\partial Z}{\partial y} = x^2 + g''(y) = x^2+3y^2$$

Comparing L.H.S & R.H.S. we get

$g''(y) = 3y^2$, Integrating we get $g(y) = y^3$

Therefore $Z(x,y) = x^2y + y^3$

* A differential is perfect (exact) if it derives from a function $Z(x,y)$
* The exactness condition is $\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$
* If exact, we can find $Z(x,y)$ by integration.