Qu.: Derive Maxwell's four thermodynamics relations .

Ans. Originally four thermodynamic relations connecting P,V,T and D were deduce by Maxwell. Two more relations have since been added. All the six are often then referred to as the thermodynamic relations. They do not constitute new low but are more deduction from the 1st law and 2nd law of thermodynamics in the equilibrium conditions. According to 1st law of thermodynamics

$$dQ = dU + PdV \quad (1)$$

and 2nd law of thermodynamics

$$dQ = TdS \quad (2)$$

From Eq.(1) and Eq. (2), we get

$$TdS = dU + PdV \quad (3)$$

The internal energy dU is a perfect differential depending upon any two of the thermodynamic function P, V. T and S. for this we obtain the perfect differential .

Perfect differential

Taken two independent variables x and y, since internal energy dU is a function of x and y then.

$$\left[\frac{\partial}{\partial y}\left\{\left(\frac{\partial U}{\partial x}\right)_y\right\}\right]_x = \left[\frac{\partial}{\partial x}\left\{\left(\frac{\partial U}{\partial y}\right)_x\right\}\right]_y \quad (4)$$

The Eq. (3) differentiated with respect to independent variable x and y, we get

$$\left(\frac{\partial U}{\partial x}\right)_y = T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y$$

And with respect to y as

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial U}{\partial x}\right)_y\right)_x = \left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y + T\left(\frac{\partial^2 S}{\partial y \partial x}\right) - \left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y - P\left(\frac{\partial^2 V}{\partial y \partial x}\right) \quad (5)$$

Similarly,

$$\left(\frac{\partial U}{\partial y}\right)_x = T\left(\frac{\partial S}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x$$

And with respect to x as

$$\left(\frac{\partial}{\partial x}\left(\frac{\partial U}{\partial y}\right)_x\right)_y = \left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x + T\left(\frac{\partial^2 S}{\partial x \partial y}\right) - \left(\frac{\partial P}{\partial x}\right)_y\left(\frac{\partial V}{\partial y}\right)_x - P\left(\frac{\partial^2 V}{\partial x \partial y}\right) \qquad (6)$$

The internal energy dU is a perfect differential as mention in Eq. (4). Equating Eq. (5) and Eq. (6), we get

$$\left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y + T\left(\frac{\partial^2 S}{\partial y \partial x}\right) - \left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y - P\left(\frac{\partial^2 V}{\partial y \partial x}\right)$$

$$= \left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x + T\left(\frac{\partial^2 S}{\partial x \partial y}\right) - \left(\frac{\partial P}{\partial x}\right)_y\left(\frac{\partial V}{\partial y}\right)_x - P\left(\frac{\partial^2 V}{\partial x \partial y}\right) \qquad (7)$$

I

n Eq. (7) 2nd and 3rd terms both sides cancelled and rest terms written as

$$\left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y\left(\frac{\partial V}{\partial y}\right)_x \qquad (8)$$

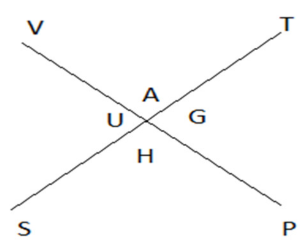

Fig.1 figure calculate the Maxwell's relations as trick

The Eq.(8) is known as perfect differential equation for thermodynamic function P,V,T and S with respect to variable x and y.

Maxwell' 1st thermodynamic relations.

Let us take the volume v and temperature T as independent variables, Let the parameter v = x and T = y

$$\frac{\partial v}{\partial x} = 1, \text{ and } \frac{\partial T}{\partial y} = 1$$

$$\frac{\partial v}{\partial y} = 0, \text{ and } \frac{\partial T}{\partial x} = 0$$

Putting this value in Eq.(8), we get

$$\left(\frac{\partial s}{\partial x}\right)_y = \left(\frac{\partial p}{\partial y}\right)_x$$

changing the value of parameter x =V and y=T, we get

$$\left(\frac{\partial s}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

(9)

The Eq. (1) is the equation of thermodynamics relations.

Maxwell 2nd thermodynamic relations

Let us take the entropy s and volume v as independent variables, Let the parameter v = x and s = y

$$\frac{\partial v}{\partial x} = 1, \quad \text{and} \quad \frac{\partial s}{\partial y} = 1$$

$$\frac{\partial v}{\partial y} = 0, \quad \text{and} \quad \frac{\partial s}{\partial x} = 0$$

Putting this value in Eq.(8), we get

$$\left(\frac{\partial T}{\partial x}\right)_y = -\left(\frac{\partial p}{\partial y}\right)_x$$

changing the value of parameter x = v and y = s, weget

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v$$

(10)

The Eq. (2) is the equation of thermodynamics relations

Maxwell 3rd thermodynamic relations

Let us take the entropy s and pressure p as independent variables, Let the parameter s = x and p = y

$$\frac{\partial s}{\partial x} = 1, \quad \text{and} \quad \frac{\partial p}{\partial y} = 1$$

$$\frac{\partial s}{\partial y} = 0, \quad \text{and} \quad \frac{\partial p}{\partial x} = 0$$

Putting this value in Eq.(8), we get

$$\left(\frac{\partial T}{\partial y}\right)_x = \left(\frac{\partial v}{\partial x}\right)_y$$

changing the value of parameter x = s and y = p, we get

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial V}{\partial S}\right)_p \tag{11}$$

The Eq. (3) is the equation of thermodynamics relations

Maxwell 4th thermodynamic relations

Let us take the pressure p and temperature T as independent variables, Let the parameter p = x and T = y

$$\frac{\partial p}{\partial x} = 1, \quad \text{and} \quad \frac{\partial T}{\partial y} = 1$$

$$\frac{\partial p}{\partial y} = 0, \quad \text{and} \quad \frac{\partial T}{\partial x} = 0$$

Putting this value in Eq.(8), we get

$$\left(\frac{\partial s}{\partial x}\right)_y = -\left(\frac{\partial v}{\partial y}\right)_x$$

changing the value of parameter x = p and y = T, we get

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \tag{12}$$

The Eq. (4) is the equation of thermodynamics relations

***

In addition to these four equations two more equations are added.

5th Maxwell's equation

Let us take the pressure p and temperature T with independent variables x and y, we get v = x and p = y

$$\frac{\partial v}{\partial x} = 1, \quad \text{and} \quad \frac{\partial p}{\partial y} = 1$$

$$\frac{\partial v}{\partial y} = 0, \quad \text{and} \quad \frac{\partial p}{\partial x} = 0$$

Putting this value in Eq.(8), we get

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial s}{\partial x}\right)_y - \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial s}{\partial y}\right)_x = 1$$

changing the value of parameter x = v and y = p, we get

$$\left(\frac{\partial T}{\partial p}\right)_v \left(\frac{\partial s}{\partial v}\right)_p - \left(\frac{\partial T}{\partial v}\right)_p \left(\frac{\partial s}{\partial p}\right)_v = 1$$

(13)

The Eq. (5) is the equation of the thermodynamics relations

6th Maxwell's equation

Let us take the entropy s and temperature T with independent variables x and y, we get

s = x and T = y

$$\frac{\partial s}{\partial x} = 1, \quad \text{and} \quad \frac{\partial T}{\partial y} = 1$$

$$\frac{\partial s}{\partial y} = 0, \quad \text{and} \quad \frac{\partial T}{\partial x} = 0$$

Putting this value in Eq.(8), we get

$$\left(\frac{\partial p}{\partial y}\right)_x \left(\frac{\partial v}{\partial x}\right)_y - \left(\frac{\partial p}{\partial x}\right)_y \left(\frac{\partial v}{\partial y}\right)_x = 1$$

changing the value of parameter x = s and y = T, we get

$$\left(\frac{\partial p}{\partial T}\right)_s \left(\frac{\partial v}{\partial s}\right)_T - \left(\frac{\partial p}{\partial s}\right)_T \left(\frac{\partial v}{\partial T}\right)_s = 1$$

(14)

The Eq. (6) is the equation of the thermodynamics relations

***

Maxwell's Relations

Thermodynamic Function	Derivative	Thermodynamic Relations
Internal Energy U	dU = TdS – PdV	$\left(\frac{\partial T}{\partial V}\right)_s = -\left(\frac{\partial p}{\partial S}\right)_v$
Enthalpy H	dH = TdS + vdP	$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial V}{\partial S}\right)_p$
Free Energy A	A = - PdV - SdT	$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial s}{\partial V}\right)_T$
Gibb's Function G	dG = VdP- SdT	$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$
