

Maxwell's four thermodynamic relation

Maxwell's relations can be deduced by making use of the first and second law of thermodynamics.

First Law:— If a substance absorbs a very small amount of heat dQ at a constant pressure, then part of this heat is used up to raise the temperature which results in the increase of internal energy dU . The rest of the heat is used in doing work in allowing the substance to increase in volume by an amount dv against the external pressure P . Thus, according to the first law,

$$dQ = dU + PdV$$

$$\text{or, } dU = dQ - PdV \quad \text{--- (1)}$$

Second Law:— If a substance absorbs a very small amount of heat dQ at a temperature T and if all the changes that it undergoes are perfectly reversible, then the change in entropy ds is equal to $\frac{dQ}{T}$.

$$\therefore ds = \frac{dQ}{T} \quad \text{or, } dQ = T \cdot ds$$

substituting dQ in equation (1), we have

$$dU = T \cdot ds - PdV \quad \text{--- (2)}$$

The thermodynamical state of any system is defined by the variables T, S, P and V . All these variables are not independent. If any two of them are known the others can be found out.

The change in internal energy dU brought about by changing V and T is the same whether we first make the change dV in V and then the change dT in T or in reverse order. Mathematically this is expressed by saying that dU is a perfect differential.

If a function of two independent variables x and y , where x and y may be any two of the quantities T, S, P and V , then dU is a perfect differential if,

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

Similarly dS and dV are also completely defined if any two of the variables are known and thus are perfectly differentials.

$$\therefore \left[\frac{\partial}{\partial x} \left(\frac{\partial S}{\partial y} \right)_x \right]_y = \left[\frac{\partial}{\partial y} \left(\frac{\partial S}{\partial x} \right)_y \right]_x$$

$$\text{and } \left[\frac{\partial}{\partial x} \left(\frac{\partial V}{\partial y} \right)_x \right]_y = \left[\frac{\partial}{\partial y} \left(\frac{\partial V}{\partial x} \right)_y \right]_x$$

Since U is a function of two independent variables x and y differentiating equation (2) first with respect to x and then with respect to y , we have

$$\frac{\partial U}{\partial x} = T \frac{\partial S}{\partial x} - P \frac{\partial V}{\partial x} \quad \text{--- (3)}$$

$$\text{and } \frac{\partial U}{\partial y} = T \frac{\partial S}{\partial y} - P \frac{\partial V}{\partial y} \quad \text{--- (4)}$$

Again differentiating (3) with respect to y keeping x constant and (4) with respect to x , keeping y constant, we have.

$$\left[\frac{\partial}{\partial y} \left(\frac{\partial u}{\partial x} \right)_y \right]_x = \frac{\partial T}{\partial y} \cdot \frac{\partial s}{\partial x} + T \left[\frac{\partial}{\partial y} \left(\frac{\partial s}{\partial x} \right)_y \right]_x - \frac{\partial P}{\partial y} \cdot \frac{\partial v}{\partial x} - P \left[\frac{\partial}{\partial y} \left(\frac{\partial v}{\partial x} \right)_y \right]_x \quad (5)$$

and

$$\left[\frac{\partial}{\partial x} \left(\frac{\partial u}{\partial y} \right)_x \right]_y = \frac{\partial T}{\partial x} \cdot \frac{\partial s}{\partial y} + T \left[\frac{\partial}{\partial x} \left(\frac{\partial s}{\partial y} \right)_x \right]_y - \frac{\partial P}{\partial x} \cdot \frac{\partial v}{\partial y} - P \left[\frac{\partial}{\partial x} \left(\frac{\partial v}{\partial y} \right)_x \right]_y \quad (6)$$

Equating equation (5) and (6) and cancelling equal terms, we have

$$\frac{\partial T}{\partial y} \cdot \frac{\partial s}{\partial x} - \frac{\partial P}{\partial y} \cdot \frac{\partial v}{\partial x} = \frac{\partial T}{\partial x} \cdot \frac{\partial s}{\partial y} - \frac{\partial P}{\partial x} \cdot \frac{\partial v}{\partial y} \quad (7)$$

(i) Let us take the temperature and volume as the independent variables.

then

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

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

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

From equation (7), we have

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

$$\frac{\partial s}{\partial y} - \frac{\partial P}{\partial x} = 0, \text{ or, } \frac{\partial s}{\partial y} = \frac{\partial P}{\partial x}$$

Now replacing x by T and y by v , we have

$$\boxed{\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v} \quad \text{--- (8)}$$

This is known as Maxwell's first thermodynamic relation.

This shows that increase in entropy per unit increase in volume at constant temperature is equal to the increase per unit increase of temperature at constant volume.

Multiplying both sides equation (8) by T ,

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

But $T ds = dQ$

$$\therefore \left(\frac{\partial Q}{\partial v}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_v$$

(ii) Now let us take the temperature T and the pressure p as independent variables then

$$T = x \quad \text{and} \quad p = y$$

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

Also

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

From equation (1), we have

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

$$-\frac{\partial v}{\partial x} = \frac{\partial s}{\partial y}$$

Replacing x by T and y by p , we have

$$\boxed{\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T} \quad \text{--- (9)}$$

This is Maxwell's second thermodynamic relation.

This shows that the decrease in entropy per unit increase of pressure during an isothermal change is equal to the increase in volume per unit increase of temperature during an isobaric process.

Multiplying both sides of equation (9) by T , we have

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

But $T ds = dQ$, $\therefore T \left(\frac{\partial v}{\partial T} \right)_p = \left(\frac{\partial Q}{\partial p} \right)_T$

(iii) Now let us take the volume v and entropy s as independent variables,

then $s = x$ and $v = y$

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

Also

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

Substituting these values in equation (7), we have.

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

Replacing y by s and x by v , we have

$$\boxed{\left(\frac{\partial T}{\partial s} \right)_v = - \left(\frac{\partial p}{\partial v} \right)_s} \quad \text{--- (10)}$$

This is Maxwell's third thermodynamic relation.

(iv) Let us take entropy s and the pressure p as independent variables then

$$S = x \quad \text{and} \quad P = y$$

$$\therefore \frac{\partial S}{\partial x} = 1, \quad \text{and} \quad \frac{\partial P}{\partial y} = 1$$

Also

$$\frac{\partial S}{\partial y} = 0 \quad \text{and} \quad \frac{\partial P}{\partial x} = 0$$

\therefore from equation (7), we have

$$\left(\frac{\partial T}{\partial y} \right) = - \left(\frac{\partial V}{\partial x} \right)$$

Replacing $x = S$ and y by P , we have

$$\boxed{\left(\frac{\partial T}{\partial P} \right)_S = - \left(\frac{\partial V}{\partial S} \right)_P} \quad (11)$$

This is Maxwell's fourth thermodynamic relation.

$$\left(\frac{\partial T}{\partial P} \right)_S = - \left(\frac{\partial V}{\partial S} \right)_P$$

$$\left[\left(\frac{\partial T}{\partial P} \right)_S = - \left(\frac{\partial V}{\partial S} \right)_P \right]$$