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Maxwell's thermodynamic relation →

As we know that the entropy function ( $ds$ ) is a perfect differential, we deduce a few general thermodynamical theorems applicable to a simple homogeneous system consisting of a single chemical substance.

Now,  $\delta Q = du + pdv$  from 1st law of thermodynamics

$\delta Q = Tds$  from 2nd law of thermodynamics

' $\delta Q$ ' being the heat taken in a reversible process.

Combining these two relations

$$Tds = du + pdv \quad \text{--- (1)}$$

$$\text{or, } du = Tds - pdv \quad \text{--- (2)}$$

Where 'p' is the equilibrium pressure.

Since 'du' is a perfect differential, for 'x' & 'y' any two independent variable, we have

$$\frac{\delta^2 u}{\delta x \delta y} = \frac{\delta^2 u}{\delta y \delta x}$$

Using this relation aided substitution from eqn (2) it can be shown that:

$$\frac{\delta(T \cdot s)}{\delta(x \cdot y)} = \frac{\delta(p \cdot v)}{\delta(x \cdot y)} \quad \text{--- (3)}$$

Since  $ds$  and  $dv$  are also perfect differentials.

where  $\frac{\delta(T \cdot s)}{\delta(x \cdot y)}$  stands for the Jacobian  $\begin{vmatrix} \frac{\delta T}{\delta x} & \frac{\delta T}{\delta y} \\ \frac{\delta s}{\delta x} & \frac{\delta s}{\delta y} \end{vmatrix}$

Any two of the four quantities  $T, s, p, v$  can be chosen as the independent variables  $x, y$ . This can be done in six different ways resulting in six thermodynamical relationships. Though all of them are not independent.

First relation →

Let us consider the temp and the volume as independent variables.

$$x = T, \quad y = V$$

$$\frac{\delta T}{\delta x} = 1, \quad \frac{\delta V}{\delta y} = 1$$

$$\frac{\delta T}{\delta y} = \frac{\delta T}{\delta V} = 0; \quad \frac{\delta V}{\delta x} = \frac{\delta V}{\delta T} = 0$$

from eqn. (3) we have

$$\left( \frac{\delta S}{\delta V} \right)_T = \left( \frac{\delta p}{\delta T} \right)_V \quad \text{--- (4)}$$

Which implies that the increase of entropy per unit increase of volume at constant temperature is equal to the increase of pressure per unit increase of temp. when the volume is kept constant. Eqn (4) can be applied to the equilibrium between two states of the same substance. multiplying both sides by  $T$ ,

$$T \left( \frac{\delta S}{\delta V} \right)_T = T \left( \frac{\delta p}{\delta T} \right)_V$$

$$\left( \frac{\delta Q}{\delta V} \right)_T = T \left( \frac{\delta p}{\delta T} \right)_V \quad \text{--- (5)}$$

Which means that the latent heat of isothermal expansion is equal to the product of the absolute temp. and the rate of increase of pressure with temp. at constant volume. Thus if, a body changes its phase at  $T$  and absorbs the latent heat  $L$ , and the specific volumes in the first and the second phases are  $v_1$  and  $v_2$ , then eqn (5), becomes

$$\frac{L}{v_2 - v_1} = T \left( \frac{\delta p}{\delta T} \right)_V$$

When we apply this equation to change of phase such as the vaporisation of liquid, the various thermodynamic quantities refer to a mixture of the liquid and vapour in equilibrium. For such a case

$$\left(\frac{\delta p}{\delta T}\right)_v = \left(\frac{\delta p}{\delta T}\right)_{sat}$$

$$\left(\frac{\delta p}{\delta T}\right)_{sat} = \frac{L}{T(v_2 - v_1)} \quad \text{--- (6)}$$

This is Clapeyron's equation and is one of the most important formulae in thermodynamics.

Second relation  $\rightarrow$  let  $x = T$ ,  $y = p$

$$\frac{\delta T}{\delta x} = 1, \quad \frac{\delta p}{\delta y} = 1$$

Eqn (4) then reduces to:

$$\left(\frac{\delta s}{\delta p}\right)_T = -\left(\frac{\delta v}{\delta T}\right)_p \quad \text{--- (7)}$$

Which means that the decrease of entropy per unit increase of pressure during an isothermal transformation is equal to the increase of volume per unit increase of temp. when the pressure is kept constant multiplying both sides by T

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

$$\text{or, } \left(\frac{\delta a}{\delta p}\right)_T = -T \cdot \alpha \quad \text{--- (8)}$$

Where  $\alpha$  is the coefficient of volume expansion at const. pressure.

From this relation it follows that if  $\alpha$  is positive

$\left(\frac{\delta v}{\delta T}\right)_p$  i.e. the substance expands on heating

$\frac{\delta Q}{\delta p}$  is negative, and hence in this case an amount

of heat must be taken away from the substance when the pressure is increased, in order that the temp. may remain constant. That is heat is perusted when a substance which expands on heating is compressed. For substances which contract on heating, a cooling should take place. These results have been verified by Joule in the case of water below and above  $4^\circ\text{C}$ . Thus the thermodynamical theory explains the remarkable fact that water below  $4^\circ\text{C}$  cools by adiabatic compression in spite of its internal energy increasing.

Thus, the second thermodynamical relation is applied to certain adiabatic changes, such as the sudden compression of a liquid or sudden stretching of a rod.

If  $x = S$ ,  $y = V$ , eqn (8) reduces to,

$$\frac{\delta S}{\delta x} = 1, \quad \frac{\delta v}{\delta y} = 1$$

$$\left(\frac{\delta T}{\delta v}\right)_S = - \left(\frac{\delta p}{\delta S}\right)_V \quad \text{--- (9)}$$

And for,  $x = S$ ,  $y = p$

$$\frac{\delta S}{\delta x} = 1, \quad \frac{\delta p}{\delta y} = 1, \quad \therefore \left(\frac{\delta T}{\delta p}\right)_S = \left(\frac{\delta v}{\delta p}\right)_p \quad \text{--- (10)}$$

Eqn (9) implies that the rate of increase of temp. with volume at constant entropy is equal to rate of decrease of pressure with entropy at constant volume.

while eqn. (10) explains that the rate of change of temp. with pressure at constant entropy is equal to the rate of change of volume with entropy at constant pressure.

Now, we derive two more relations of mathematical interest only.

for  $x = p$ ,  $y = V$

$$\frac{\delta p}{\delta x} = 1, \quad \frac{\delta v}{\delta y} = 1$$

Eqn (9) becomes: 
$$\left(\frac{\delta T}{\delta p}\right)_v \left(\frac{\delta s}{\delta v}\right)_p - \left(\frac{\delta T}{\delta v}\right)_p \left(\frac{\delta s}{\delta p}\right)_v = 1$$
 (11)

for,  $x = T$ ,  $y = S$

$$\frac{\delta T}{\delta x} = 1, \quad \frac{\delta s}{\delta y} = 1$$

$$\left(\frac{\delta p}{\delta T}\right)_s \left(\frac{\delta v}{\delta s}\right)_T - \left(\frac{\delta p}{\delta s}\right)_T \left(\frac{\delta v}{\delta T}\right)_s = 1 \quad (12)$$

The above relations are known as Maxwell's six thermodynamic relations.

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