Lecture Notes Dated: Oct 20, 2012

The Maxwell's General Relationship

We have from the first law $\delta Q = dU + p\,dV$, and from the second law $\delta Q = TdS$ where δQ is the heat taken in a reversible process. Combining these we get

$$dU = T\,dS - p\,dV \tag{1}$$

This equation involves five functions of state: *p, V, T, S* and *U*. We may choose any two of these variables, such as pressure and temperature as independent variables. Then internal energy *U*, volume *V* and entropy *S* will be functions of pressure *p* and temperature *T*.

However, if *x* and *y* are any two independent variables, then we have $U = U(x, y)$, $S = S(x, y)$ and $V = V(x, y)$. Since *U, S* and *V* are a perfect differential,we can write

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial U}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial U}{\partial y}\right)_x\right]_y \tag{2a}$$

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial S}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial S}{\partial y}\right)_x\right]_y \tag{2b}$$

and

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial V}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial V}{\partial y}\right)_x\right]_y \tag{2c}$$

i.e., for a state function the order of differentiation doesn't change the value of the double differential.

Simultaneously, their differential can be written as,

$$dU = \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy \tag{3a}$$

$$dS = \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy \tag{3b}$$

and

$$dV = \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy \tag{3c}$$

On substituting eq. (3abc) in eq. (1) and comparing the coefficients of *dx* and *dy*, we get

$$\left(\frac{\partial U}{\partial x}\right)_y = T\left(\frac{\partial S}{\partial x}\right)_y - p\left(\frac{\partial V}{\partial x}\right)_y \tag{4a}$$

and

$$\left(\frac{\partial U}{\partial y}\right)_x = T\left(\frac{\partial S}{\partial y}\right)_x - p\left(\frac{\partial V}{\partial y}\right)_x \tag{4b}$$

Now differentiate eq. (4a) with respect to *y* at constant *x* and eq. (4b) with respect to *x* at constant *y*.

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial U}{\partial x}\right)_y\right]_x = \left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y + T\left[\frac{\partial}{\partial y}\left(\frac{\partial S}{\partial x}\right)_y\right]_x - \left(\frac{\partial p}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y - p\left[\frac{\partial}{\partial y}\left(\frac{\partial V}{\partial x}\right)_y\right]_x$$

and,

$$\left[\frac{\partial}{\partial x}\left(\frac{\partial U}{\partial y}\right)_x\right]_y = \left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x + T\left[\frac{\partial}{\partial x}\left(\frac{\partial S}{\partial y}\right)_x\right]_y - \left(\frac{\partial p}{\partial x}\right)_y\left(\frac{\partial V}{\partial y}\right)_x - p\left[\frac{\partial}{\partial x}\left(\frac{\partial V}{\partial y}\right)_x\right]_y$$

We now subtract these two equations and use the eq. (2abc), we get

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

or, $$\left(\frac{\partial p}{\partial x}\right)_y\left(\frac{\partial V}{\partial y}\right)_x-\left(\frac{\partial p}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y=\left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x-\left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y \qquad (5)$$

This equation is the ***Maxwell's general relationship***. Any two of the four quantities *p, V, T* and *S* can be chosen as the independent variables *x, y*. This can be done in six different ways and correspondingly, we have six thermodynamical relations but only four give useful results known as ***Maxwell's relations***.

 # First Relation

Let us take the temperature and the volume as independent variables and put $x = T$ and $y = V$ in eq. (5).

$$\left(\frac{\partial T}{\partial x}\right)_y=1 \quad , \quad \left(\frac{\partial V}{\partial y}\right)_x=1 \quad , \quad \left(\frac{\partial T}{\partial y}\right)_x=0 \quad \text{and} \quad \left(\frac{\partial V}{\partial x}\right)_y=0$$

since *T* and *V* are independent, therefore we have

$$\left(\frac{\partial S}{\partial V}\right)_T=\left(\frac{\partial p}{\partial T}\right)_V \qquad (6)$$

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 temperature when the volume is kept constant*. This is known as ***Maxwell's first thermodynamical relation***.

 # Second Relation

Let us take the temperature and the volume as independent variables and put $x = T$ and $y = p$ in eq. (5).

$$\left(\frac{\partial T}{\partial x}\right)_y=1 \quad , \quad \left(\frac{\partial p}{\partial y}\right)_x=1 \quad , \quad \left(\frac{\partial T}{\partial y}\right)_x=0 \quad \text{and} \quad \left(\frac{\partial p}{\partial x}\right)_y=0$$

since *T* and *p* are independent, therefore we have

$$\left(\frac{\partial S}{\partial p}\right)_T=-\left(\frac{\partial V}{\partial T}\right)_p \qquad (7)$$

which implies that *the increase of entropy per unit increase of pressure at constant temperature is equal to the decrease of volume per unit increase of temperature when the pressure is kept constant*. This is known as ***Maxwell's second thermodynamical relation***.

 # Third Relation

Let us take the temperature and the volume as independent variables and put $x = S$ and $y = V$ in eq. (5).

$$\left(\frac{\partial S}{\partial x}\right)_y=1 \quad , \quad \left(\frac{\partial V}{\partial y}\right)_x=1 \quad , \quad \left(\frac{\partial S}{\partial y}\right)_x=0 \quad \text{and} \quad \left(\frac{\partial V}{\partial x}\right)_y=0$$

since *S* and *V* are independent, therefore we have

$$\left(\frac{\partial T}{\partial V}\right)_S=-\left(\frac{\partial p}{\partial S}\right)_V \qquad (8)$$

which implies that *the increase of temperature per unit increase of volume at constant entropy is equal to the decrease of pressure per unit increase of entropy when the volume is kept constant*. This is known as ***Maxwell's third thermodynamical relation***.

 # Forth Relation

Let us take the temperature and the volume as independent variables and put $x = S$ and $y = p$ in eq. (5).

$$\left(\frac{\partial S}{\partial x}\right)_y=1 \quad , \quad \left(\frac{\partial p}{\partial y}\right)_x=1 \quad , \quad \left(\frac{\partial S}{\partial y}\right)_x=0 \quad \text{and} \quad \left(\frac{\partial p}{\partial x}\right)_y=0$$

since S and p are independent, therefore we have

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \qquad (9)$$

which implies that *the increase of temperature per unit increase of pressure at constant entropy is equal to the increase of volume per unit increase of entropy when the pressure is kept constant*. This is known as ***Maxwell's fourth thermodynamical relation***.

The above relations are known as ***Maxwell's four thermodynamical relations***. Besides these, there are two more relations of mathematical interest only which may be obtained by taking $x = p$ and $y = V$ or $x = T$ and $y = S$ as the pair of independent variables. They are

$$\left(\frac{\partial T}{\partial p}\right)_V \left(\frac{\partial S}{\partial V}\right)_p - \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial S}{\partial p}\right)_V = 1 \qquad (10)$$

or,

$$\left(\frac{\partial p}{\partial T}\right)_S \left(\frac{\partial V}{\partial S}\right)_T - \left(\frac{\partial p}{\partial S}\right)_T \left(\frac{\partial V}{\partial T}\right)_S = 1 \qquad (11)$$