

Udai Pratap (Autonomous) College, Varanasi**E-learning Material**

Module/ Lecture	07
Topic	Applications of Maxwell's Thermodynamic Relations
Developed by	<i>Dr. Devendra Kumar Singh</i> <i>Assistant Professor,</i> <i>Physics Department,</i> <i>Udai Pratap (Autonomous) College, Varanasi</i>

Applications of Maxwell's Thermodynamic Relations

1. TdS Equations

(i). Let $S=S(T, V)$

$$\text{Then } dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\text{or } TdS = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV \quad (1)$$

Since $TdS = \delta Q$

$$\text{Thus } T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\delta S}{\delta T}\right)_V = C_V, \quad (2)$$

Where C_V is the molar specific heat at constant volume.

Also from Maxwell's relation,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad (3)$$

Using Eqs. (2 & 3) Eqn. (1) becomes

$$TdS = C_V dT + T\left(\frac{\partial p}{\partial T}\right)_V dV \quad (4)$$

Eq. (4) is known as first TdS equation. This equation has the peculiarity that the coefficients of dT and dV on the RHS of the equation are at constant Volume.

(ii). Let $S=S(T, p)$

$$\text{Then } dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$$

$$\text{or } TdS = T\left(\frac{\partial S}{\partial T}\right)_p dT + T\left(\frac{\partial S}{\partial p}\right)_T dp \quad (5)$$

Since $TdS = \delta Q$

$$\text{Thus } T \left(\frac{\partial S}{\partial T} \right)_p = \left(\frac{\delta S}{\delta T} \right)_p = C_p, \quad (6)$$

Where C_p is the molar specific heat at constant pressure.

Also from Maxwell's relation,

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

Using Eqs. (6 & 7) Eqn. (5) becomes

$$TdS = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_p dp \quad (8)$$

Eq. (8) is known as second TdS equation.

2. Energy Equations

(i) According to Maxwell's relation

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V \quad (1)$$

But, according to 1st and 2nd law of thermodynamics

$$\delta S = \frac{\partial U + p\delta V}{T} \quad (2)$$

From Eq. (1) and (2)

$$\begin{aligned} \frac{1}{T} \left(\frac{\partial U + p\delta V}{\partial V} \right)_T &= \left(\frac{\partial p}{\partial T} \right)_V \\ \left(\frac{\partial U}{\partial V} \right)_T + p &= T \left(\frac{\partial p}{\partial T} \right)_V \\ \left(\frac{\partial U}{\partial V} \right)_T &= T \left(\frac{\partial p}{\partial T} \right)_V - p \end{aligned} \quad (3)$$

This is first energy equation. It gives the change in internal energy of a gas with respect to change in volume at constant temperature.

(ii) According to Maxwell's relation

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad (4)$$

Using Eq. (2), Eq. (4) becomes,

$$\begin{aligned} \frac{1}{T}\left(\frac{\partial U + p\partial V}{\partial p}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_p \\ \left(\frac{\partial U}{\partial p}\right)_T &= -T\left(\frac{\partial V}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial p}\right)_T \end{aligned} \quad (5)$$

This is second energy equation. It gives the change in internal energy of a gas with respect to change in pressure at constant temperature.

Note: 1. For 1 mole of an ideal gas

$$pV=RT$$

thus $\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V}$

hence from 1st energy equation

$$\begin{aligned} \left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial p}{\partial T}\right)_V - p \\ &= \frac{TR}{V} - p \\ &= 0 \end{aligned}$$

Thus if temperature remains constant, the internal energy of an ideal gas is independent of volume.

2. For 1 mole of an real gas

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

or $p = \frac{RT}{V - b} - \frac{a}{V^2}$

and $\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V - b}$

hence from 1st energy equation

$$\begin{aligned}\left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial p}{\partial T}\right)_V - p \\ &= \frac{TR}{V-b} - \frac{RT}{V-b} + \frac{a}{V^2} \\ &= \frac{a}{V^2}\end{aligned}$$

Which is a positive quantity, thus the internal energy of a real gas at constant temperature depends on the volume. As $\left(\frac{\partial U}{\partial V}\right)_T = +ve$, the internal energy increases with the increase in volume.

3. Clausius-Clapeyron Equation

A substance can exist in three states solid, liquid and gas. Out of these three only two can co-exist. Whenever there is a change of state, the temperature remains constant as far as the change takes place.

The melting or boiling points of a substance vary with pressure. The relation showing how the melting and boiling points vary with pressure is known as Clausius-Clapeyron Equation or First latent heat equation.

From Maxwell's relation,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad (1)$$

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

$$\left(\frac{T\partial S}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V \quad (\text{from 2nd law, } T\partial S = \partial Q)$$

$$\left(\frac{\partial Q}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V \quad (2)$$

In Eq. (2)

$\left(\frac{\partial Q}{\partial V}\right)_T$ represent the quantity of heat absorbed or released per unit change

in volume at constant temperature, therefore this heat absorbed or released is the latent heat L and change in volume must be due to change in the state. Considering a unit mass of substance and let volume changes from V_1 to V_2

$$\text{Thus } \partial Q = L \text{ and } \partial V = V_2 - V_1$$

Hence Eq. (2) becomes

$$\frac{L}{V_2 - V_1} = T \left(\frac{\partial p}{\partial T}\right)_V$$

Since $\left(\frac{\partial p}{\partial T}\right)_V$ is same throughout the liquid and vapor mixture span, we can write

$$\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)} \quad (3)$$

Eq. (3) is known as Clausius-Clapeyron Equation or first latent heat equation.

Application:

1. Effect of pressure on melting points of solids:

When solid melts

- (i) If $V_2 > V_1$, e.g. wax, sulphur etc.

From Eq. (3),

$$\frac{dp}{dT} = +ve$$

Thus melting point increases with increase in pressure and vice-versa.

- (ii) If $V_2 < V_1$, e.g. gallium, bismuth, ice etc

From Eq. (3),

$$\frac{dp}{dT} = -ve$$

Thus melting point increases with decrease in pressure and vice-versa. E.g. ice melts at low temperature when pressure is increases.

2. Effect of pressure on boiling points of liquids:

Since $V_2 > V_1$ always.

From Eq. (3),

$$\frac{dp}{dT} = +ve$$

Thus boiling point increases with increase in pressure and vice-versa. As in case of Water boiling in pressure cooker the pressure increases to 2 times the atmospheric pressure and the boiling point of water increases to 125° C.

4. Specific Heat Relations

Let entropy $S = S(T, V)$

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV \quad (1)$$

Multiplying both sides with T and dividing throughout by dT while holding p-constant, we find

$$T \left(\frac{\partial S}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_V + T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p \quad (2)$$

For one mole of gas

$$T \left(\frac{\partial S}{\partial T} \right)_p = \left(\frac{\partial Q}{\partial T} \right)_p = C_p = \text{Molar specific heat at constant pressure}$$

$$T \left(\frac{\partial S}{\partial T} \right)_V = \left(\frac{\partial Q}{\partial T} \right)_V = C_v = \text{Molar specific heat at constant Volume}$$

And from maxwell's relation $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$

Using these, Eq. (2) gives

$$C_P - C_V = T \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P \quad (3)$$

Equation (3) is known as specific heat equation.

Note: 1. For 1 mole of an ideal gas

$$pV = RT$$

$$\text{thus} \quad \left(\frac{\partial p}{\partial T} \right)_V = \frac{R}{V} \quad \text{and} \quad \left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{p}$$

hence from Specific heat equation (3)

$$\begin{aligned} C_P - C_V &= T \frac{R}{V} \frac{R}{p} \\ &= R \end{aligned} \quad (4)$$

Equation (4) is known as Mayer's relation.

2. For 1 mole of an ideal gas

$$\left(p + \frac{a}{V^2} \right) (V - b) = RT$$

$$\left(p + \frac{a}{V^2} \right) = \frac{RT}{V - b}$$

$$\text{thus} \quad \left(\frac{\partial p}{\partial T} \right)_V = \frac{R}{(V - b)}$$

$$\text{and} \quad \left(\frac{\partial V}{\partial T} \right)_P = \frac{\left(\frac{R}{V - b} \right)}{\left(\frac{RT}{(V - b)^2} - \frac{2a}{V^3} \right)} \quad (5)$$

hence from Specific heat equation (3)

$$C_P - C_V = T \frac{R}{(V - b)} \frac{\left(\frac{R}{V - b} \right)}{\left(\frac{RT}{(V - b)^2} - \frac{2a}{V^3} \right)}$$

$$= \frac{R}{1 - \frac{2a(V-b)^2}{RTV^3}} \quad (6)$$

Neglecting b in comparison to $(V-b)^2 \approx V^2$, hence from Eq. (6)

$$C_P - C_V = \frac{R}{1 - \frac{2a}{RTV}}$$

$$C_P - C_V \approx R\left(1 + \frac{2a}{RTV}\right) \quad (7)$$