

## Applications of Maxwell's Relations

### 1. Thermodynamic Relations Involving Heat Capacities

Let  $T$  and  $V$  be taken as independent variables. Since entropy can be function of them, hence

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

so that

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

Multiplying both sides of this relation by  $T$  and dividing throughout by  $dT$  keeping  $p$  constant,

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

or,

$$C_p = C_v + T \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

Using the Maxwell's first relation,

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

and rearranging the terms, we get

$$C_p - C_v = T \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p \quad (12)$$

For  $pVT$  system undergoing infinitesimal reversible change between two equilibrium states, the change in internal energy is given by,  $dU = TdS - pdV$

Differentiating this equation with respect to volume at constant temperature, we get

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

Using the Maxwell's first relation eq. (6.06), we get

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

rearranging the terms

$$T \left(\frac{\partial p}{\partial T}\right)_V = \left[ p + \left(\frac{\partial U}{\partial V}\right)_T \right]$$

Substituting in eq. (12),

$$C_p - C_v = \left[ p + \left(\frac{\partial U}{\partial V}\right)_T \right] \left(\frac{\partial V}{\partial T}\right)_p \quad (13)$$

#### (a) For a Perfect Gas

The equation of state for a perfect gas is,  $pV = RT$

On differentiating it with respect to temperature at constant volume, we get

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

and differentiating it with respect to temperature at constant pressure, we get

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

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Hence, eq. (12) becomes

$$C_p - C_v = T \left( \frac{R}{V} \right) \left( \frac{R}{p} \right) = \frac{R^2 T}{pV} = \frac{R^2 T}{RT}$$

$$C_p - C_v = R \quad (14)$$

#### (b) For a Vander-Waal's Gas

The equation of state for Vander-Waal's gas is,

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT, \text{ or } \left( P + \frac{a}{V^2} \right) = \frac{RT}{(V - b)}$$

On differentiating it with respect to temperature at constant volume, we get

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

and differentiating it with respect to temperature at constant pressure, we get

$$0 - \frac{2a}{V^3} \left( \frac{\partial V}{\partial T} \right)_p = - \frac{RT}{(V - b)^2} \left( \frac{\partial V}{\partial T} \right)_p + \frac{R}{(V - b)}$$

or,

$$\left[ \frac{RT}{(V - b)^2} - \frac{2a}{V^3} \right] \left( \frac{\partial V}{\partial T} \right)_p = \frac{R}{(V - b)}$$

or,

$$\left( \frac{\partial V}{\partial T} \right)_p = \frac{\frac{R}{(V - b)}}{\left[ \frac{RT}{(V - b)^2} - \frac{2a}{V^3} \right]}$$

Putting these values of  $(\partial p / \partial T)_V$  and  $(\partial V / \partial T)_p$  in eq. (12), we get

$$C_p - C_v = T \frac{\frac{R}{(V - b)} \frac{R}{(V - b)}}{\frac{RT}{(V - b)^2} - \frac{2a}{V^3}} = \frac{R}{1 - \frac{2a}{V^3} \frac{(V - b)^2}{RT}}$$

As  $b \ll V$ , therefore  $(V - b)$  may be replaced by  $V$  in square term. Then we get

$$C_p - C_v = \frac{R}{1 - \frac{2a}{V^3} \frac{V^2}{RT}} = \frac{R}{1 - \frac{2a}{VRT}} = R \left( 1 - \frac{2a}{VRT} \right)^{-1}$$

Using binomial theorem to expand and neglecting the higher order terms, we get

$$C_p - C_v = R \left( 1 + \frac{2a}{VRT} \right) \quad (15)$$

#### (c) In Terms of Bulk Modulus of Elasticity and Compressibility

To simplify the eq. (12) we note that we can also write,  $p = p(T, V)$

so that 
$$dp = \left( \frac{\partial p}{\partial T} \right)_V dT + \left( \frac{\partial p}{\partial V} \right)_T dV$$

For an isobaric process, i.e., if  $dp = 0$ . Then we can write it as

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

Using this result in eq. (12), we get

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$$C_p - C_v = -T \left( \frac{\partial p}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p^2 \quad (16)$$

The volume expansion coefficient of a substance is defined as

$$\alpha = \left( \frac{\partial V/V}{\partial T} \right)_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \quad \text{so that} \quad \left( \frac{\partial V}{\partial T} \right)_p^2 = \alpha^2 V^2$$

and by definition of the bulk modulus of elasticity at constant temperature

$$E = - \left( \frac{\partial p}{\partial V/V} \right)_T = -V \left( \frac{\partial p}{\partial V} \right)_T \quad \text{so that} \quad \left( \frac{\partial p}{\partial V} \right)_T = -\frac{E}{V}$$

Putting these relations into eq. (16), we get

$$C_p - C_v = TE \alpha^2 V \quad (17)$$

Similarly by the definition, isothermal compressibility is

$$\beta = - \left( \frac{\partial V/V}{\partial p} \right)_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \quad \text{so that} \quad \left( \frac{\partial p}{\partial V} \right)_T = \frac{1}{\beta V}$$

Using this relation into eq. (6.16), we get

$$C_p - C_v = \frac{T \alpha^2 V}{\beta} \quad (18)$$

## 2. Clausius Clapeyron Equation

As we know from the Maxwell's first relation

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

We can apply this equation to the equilibrium between two states of the same substance, say phase change such as vaporization of liquid or melting of a solid. Multiplying both sides by  $T$ , because  $\delta Q = T dS$  we have

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

which means that the heat absorbed per unit volume of isothermal expansion is equal to the product of the absolute temperature and the rate of increase of pressure with temperature at constant volume.

Now imagine a cylinder which contains a liquid with some of its vapour in equilibrium. If we allow the system to expand at constant temperature, the vapour pressure will stay constant but liquid will evaporate to fill the extra space with vapour. Then  $\delta Q = L dm$ , where  $L$  is the specific latent heat of evaporation. The change in volume will be equal to  $(v_{vap} - v_{liq}) dm$  where  $v_{vap}$  and  $v_{liq}$  are the specific volumes for the vapour and the liquid, respectively. So we may write

$$\left( \frac{\partial Q}{\partial V} \right)_T = \frac{L}{v_{vap} - v_{liq}} = T \left( \frac{\partial p}{\partial T} \right)_V$$

If we hold the volume constant and increase the temperature somewhat, liquid will evaporate till the mixture attains a new equilibrium and hence a new saturated vapour pressure. Then, we write

$$\left( \frac{\partial p}{\partial T} \right)_V = \left( \frac{\partial p}{\partial T} \right)_{sat}$$

since the pressure is saturation pressure and is consequently independent of  $v$ , being only a function of  $T$ . Hence on combining these results, we find that

$$\left(\frac{\partial p}{\partial T}\right)_{sat} = \frac{L}{T(v_{vap} - v_{liq})} \quad (19)$$

This is **Clausius Clapeyron equation** and is one of the most important formulae in thermodynamics. It gives the rate at which vapour pressure must change with temperature for two phases to coexist in equilibrium.

### 3. Joule Thomson Effect

When a gas under a constant pressure is made to pass through an insulated porous plug to a region of low constant pressure, it suffers a change in temperature. This is called the **Joule Thomson effect**. This process is called **adiabatic throttling process**. In such a process, although there is a pressure difference across the two sides of porous plug, however, the enthalpy  $H$  remains constant. Therefore,

$$dH = d(U + pV) = 0, \text{ or } dU + p dV + V dp = 0$$

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

$$T dS + V dp = 0 \quad (20)$$

Let  $p$  and  $T$  be taken as independent variables. Since entropy can be function of them, hence

$$S = S(T, p)$$

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

Substituting the value of  $dS$  in eq. (20), we get

$$T \left(\frac{\partial S}{\partial T}\right)_p dT + T \left(\frac{\partial S}{\partial p}\right)_T dp + V dp = 0 \quad (21)$$

Now we will make two substitution, first substitution is

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = T \left(\frac{\partial S}{\partial T}\right)_p$$

where,  $C_p$  is the heat capacity at constant pressure. The next substitution is

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

which is the Maxwell's second relation. Therefore eq. (21) becomes

$$C_p dT - T \left(\frac{\partial V}{\partial T}\right)_p dp + V dp = 0$$

or, 
$$C_p dT = \left[ T \left(\frac{\partial V}{\partial T}\right)_p - V \right] dp$$

Therefore, the **Joule Thomson coefficient** is

or, 
$$\mu = \left(\frac{dT}{dp}\right)_H = \frac{1}{C_p} \left[ T \left(\frac{\partial V}{\partial T}\right)_p - V \right] \quad (22)$$

#### (a) For Perfect Gas

The equation of state for a perfect gas is,  $pV = RT$

On differentiating it with respect to temperature at constant pressure, we get

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

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Then, 
$$\left[ T \left( \frac{\partial V}{\partial T} \right)_p - V \right] = \left[ \frac{RT}{P} - V \right] = \left[ \frac{pV}{P} - V \right] = 0$$

Therefore, we get 
$$\mu = \left( \frac{\partial T}{\partial p} \right)_H = 0 \quad (23)$$

The Joule Thomson coefficient is zero means there is no change in temperature of a perfect gas, if it is expand adiabatically across the porous plug.

#### (b) For Vander Waal's Gas

The equation of state for Vander-Waal's gas is,

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT, \text{ or } \left( P + \frac{a}{V^2} \right) = \frac{RT}{(V - b)}$$

On differentiating it with respect to temperature at constant pressure, we get

$$0 - \frac{2a}{V^3} \left( \frac{\partial V}{\partial T} \right)_p = - \frac{RT}{(V - b)^2} \left( \frac{\partial V}{\partial T} \right)_p + \frac{R}{(V - b)}$$

or, 
$$\left[ \frac{RT}{(V - b)^2} - \frac{2a}{V^3} \right] \left( \frac{\partial V}{\partial T} \right)_p = \frac{R}{(V - b)}$$

or, 
$$\left( \frac{\partial V}{\partial T} \right)_p = \frac{\frac{R}{(V - b)}}{\left[ \frac{RT}{(V - b)^2} - \frac{2a}{V^3} \right]}$$

Multiplying both sides by  $T$ , we get

$$T \left( \frac{\partial V}{\partial T} \right)_p = \frac{\frac{RT}{(V - b)}}{\left[ \frac{RT}{(V - b)^2} - \frac{2a}{V^3} \right]} = \frac{RT(V - b)}{\left[ RT - \frac{2a}{V^3}(V - b)^2 \right]}$$

As  $b \ll V$ , we may neglect  $b$  in the square term  $(V - b)^2$ . Then equation reduces to

$$T \left( \frac{\partial V}{\partial T} \right)_p = \frac{RT(V - b)}{RT - \frac{2a}{V}} = \frac{(V - b)}{1 - \frac{2a}{VRT}} = (V - b) \left( 1 - \frac{2a}{VRT} \right)^{-1}$$

Using binomial theorem to expand and neglecting the higher order terms, we get

$$T \left( \frac{\partial V}{\partial T} \right)_p = (V - b) \left( 1 + \frac{2a}{VRT} \right) = V - b + \frac{2a}{RT} - \frac{2ab}{VRT}$$

neglecting last term because product of  $a$  and  $b$  is negligibly small. Thus

$$\left[ T \left( \frac{\partial V}{\partial T} \right)_p - V \right] = \frac{2a}{RT} - b$$

Putting this result in eq. (6.22) we get

$$\mu = \left( \frac{dT}{dp} \right)_H = \frac{1}{C_p} \left[ \frac{2a}{RT} - b \right] \quad (24)$$

This is the *Joule Thomson coefficient* for a Vander Waal's gas. As the pressure is lower on the emergent side of the porous plug therefore, the  $dp$  is necessarily a negative quantity. It is clear that;

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1. If  $\frac{2a}{RT} > b$  or  $T < \frac{2a}{Rb}$  then right side term would be positive, hence  $dT$  will be negative or the gas will be *cooled down* on passing through porous plug.
2. If  $\frac{2a}{RT} < b$  or  $T > \frac{2a}{Rb}$  then right side term would be negative, hence  $dT$  will be positive or the gas will be *heated up* on passing through porous plug.
3. If  $\frac{2a}{RT} = b$  or  $T = \frac{2a}{Rb}$  then right side term would be zero, hence  $dT$  will be zero or the gas will be neither cooled nor warmed on passing through porous plug, i.e., *no change in temperature*. The temperature below which the gases shows cooling effect and above which shows heating effect is known as the *temperature of inversion*, and is written as

$$T_i = \frac{2a}{Rb} \quad (25)$$

#### 4. Cooling or Heating in Adiabatic Processes

As we know from Maxwell's third relation

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

Multiplying by  $T$  to the right side term both in numerator and denominator and using second law by which,  $\delta Q = TdS$ , we get

$$\left(\frac{\partial T}{\partial V}\right)_S = -T\left(\frac{\partial p}{\partial Q}\right)_V \quad (26)$$

Consider a cylinder filled with gas, to which we are supplying heat. Any increase in supply of heat keeping volume constant, will definitely cause an increase in pressure. Therefore right side term of eq. (26)  $(\partial p/\partial Q)_V$  is obviously a positive quantity. Hence the left side term  $(\partial T/\partial V)_S$  should be negative.

It means, at constant entropy there should be decrease in temperature on account of increase in volume.

In other words, ***an adiabatic expansion must cause a cooling effect.***

As we know from Maxwell's fourth relation

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

Multiplying by  $T$  to the right side term both in numerator and denominator and using second law by which,  $\delta Q = TdS$ , we get

$$\left(\frac{\partial T}{\partial p}\right)_S = T\left(\frac{\partial V}{\partial Q}\right)_p \quad (27)$$

Consider a cylinder filled with gas, to which we are supplying heat. Any increase in supply of heat keeping pressure constant, will definitely cause an increase in volume. Therefore right side term of eq. (27)  $(\partial V/\partial Q)_p$  is obviously a positive quantity. Hence the left side term  $(\partial T/\partial p)_S$  should be positive.

It means, at constant entropy there should be increase in temperature on account of increase in pressure.

In other words, ***an adiabatic compression must cause a heating effect.***