

Velammal Institute of Technology, Panchetti
Department of Mechanical Engineering

ME8351- ENGINEERING THERMODYNAMICS
Focused question

UNIT – IV

IDEAL AND REAL GASES AND THERMODYNAMIC RELATION

PART –A (2 marks)

1. State Charle's law.

Charle's law states "The volume of a given mass of a gas varies directly as its absolute temperature, when the pressure remains constant.

$$V \propto T$$

2. State Joules's law.

Joules's law states "The internal energy of a given quantity of a gas depends only on the temperature".

3. State Regnault's law.

Regnault's law states that C_p and C_v of a gas always remains constant.

4. State Avogadro's law.

Avogadro's law states."Equal volumes of different perfect gases at the same temperature and pressure, contain equal number of molecules".

5. State Dalton's law of partial pressure.

Dalton's law of partial pressure states "The total pressure of a mixture of gases is equal to the sum of the partial pressure exerted by individual gases if each one of them occupied separately in the total volume of the mixture at mixture temperature".

$$P = p_1 + p_2 + p_3 + \dots P_k$$

6. How does the Vander waals equation differ from the ideal gas equation of states?

1. Intermolecular attractive study is made.

2. Shape factor is considered.

These assumptions are not made in ideal gas equation of state.

8. Distinguish between ideal and real gas.

An ideal gas is one which strictly follows the gas laws under all conditions of temperature and pressure.

In actual practice, there is no real gas which strictly follows the gas laws over the entire range of temperature and pressure. However hydrogen, oxygen, nitrogen and air

behave as a gas under certain temperature and pressure limits.

9. What are Maxwell relations?

$$(\partial T / \partial v)_s = - (\partial p / \partial s)_v$$

$$(\partial T / \partial p)_s = (\partial v / \partial s)_p$$

$$(\partial p / \partial T)_v = (\partial s / \partial v)_t$$

$$(\partial v / \partial T)_p = - (\partial s / \partial p)_t$$

10. Define Joule – Thomson Co-efficient.

Joule – Thomson Co-efficient is defined as the change in temperature with change in Pressure, keeping the enthalpy remains constant. It is denoted by the

$$\mu = (\partial T / \partial p)_h$$

11. Define Co – efficiency of volume expansion and isothermal compressibility. Co – efficiency of volume expansion:

Co – efficiency of volume expansion is defined as the change in volume with change in temperature per unit volume keeping the pressure constant. It is denoted by β

$$\beta = 1/v (\partial v / \partial T)_p$$

Isothermal compressibility:

It is defined as the change in volume with change in pressure per unit volume by keeping the temperature constant. It is denoted by K

$$K = 1/v (\partial v / \partial p)_T$$

12. What is compressibility factor?

We know that , the perfect gas equation is $pV = RT$.But for real gas , a correction factor has to be introduced in the perfect gas equation to take into account the deviation of real gas from the perfect gas equation .This factor is known as compressibility factor (Z) and is denoted by

13. $Z = pV/RT$ What is compressibility factor value for an ideal gas at critical point?

1. Intermolecular attractive study is made.
2. Shape factor is considered.

14. What is Joule's Thomson coefficient? Why is it zero for an ideal gas?

Joule's Thomson coefficient is defined as the change in temperature with change in pressure, keeping the enthalpy remains constant. It is denoted by

$$\mu = (\partial T / \partial p)_h = 1/C_p [T(\partial v / \partial T)_p - v]$$

We know that the equation of state as

Differentiate the above equation of state with respect to T by keeping pressure, p constant

15. What is ClasiusClapeyron Equation?

ClasiusClapeyron Equation which involves relationship between the saturation pressure, saturation temperature, the enthalpy of evaporation and the specific volume of the two phases involved

$$dp/dT = h_{fg}/T v_{fg}$$

17. State the assumption made in kinetic theory of gases?

1. There is no intermolecular force between particles.
2. The volume of the molecules is negligible in comparison with the gases.

18. State Helmholtz function

Helmholtz function is property of a system and is given by subtracting the product of absolute temperature (T) and entropy (s) from the internal energy u.

$$\text{ie Helmholtz function} = u - Ts$$

.19. State Gibbs function.

Gibbs function is property of a system and is given by $G = u - Ts + Pv = h - Ts$

Where

h – Enthalpy

T – Temperature

s - Entropy

PART –B

1. Over a certain range of pressures and temperatures the equation of a certain substance is given by the relation.

$$V = \frac{RT}{P} - \frac{C}{T^3} \quad \text{Where } C \text{ is constant, let us derive an expression for}$$

1. The change of enthalpy
2. The change of entropy of this substance in an isothermal process.

$$dh = C_p dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dp$$

$$(h_2 - h_1)_T = \int_1^2 \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dp$$

$$V = \frac{RT}{P} - \frac{C}{T^3}$$

$$\left[\frac{\partial V}{\partial T} \right]_P = \frac{R}{P} + \frac{3C}{T^4}$$

$$T \left(\frac{\partial V}{\partial T} \right)_P = \frac{RT}{P} + \frac{3C}{T^3}$$

$$V - T \left[\frac{\partial V}{\partial T} \right]_P = \frac{RT}{P} - \frac{C}{T^3} - \frac{RT}{P} - \frac{3C}{T^3}$$

$$= -\frac{4C}{T^3}$$

On substitution

$$(h_2 - h_1)_T = \int_{p_1}^{p_2} \frac{4C}{T^3} dp$$

$$= \frac{4C}{T^3} (p_1 - p_2) T$$

(b) Using second Tds equation

$$Tds = C_p dT - T \left[\frac{\partial V}{\partial T} \right]_P dp$$

$$dS_T = - \left[\frac{\partial V}{\partial T} \right]_P dp_T$$

$$= - \left[\frac{R}{P} + \frac{3C}{T^4} \right] dp_T$$

$$(S_2 - S_1)_T = R \ln \frac{p_1}{p_2} + \frac{3C}{T^4} [p_1 - p_2] T$$

2. Derive van der Waal's equation in terms of reduce parameters.

The scientist van der Waal's considered these two corrections to analyse the behaviour of real gases during 1879.

\therefore the equation of state for real gases is given by

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

For ideal gases, the constants a and b are zero, the values of a and b are dependent upon the type of fluid or gases used.

If we consider molar volume in analysis, the equation of state becomes

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

where, V = Molar Volume

R = Universal gas constant = 8.314 Nm/kg mol k.

The value of a and b is theoretically determined of

$$a = \frac{27R^2 (T_c)^2}{64P_c}$$

$$b = \frac{RT_c}{8P_c}$$

Where, T_c = Critical temperature, P_c = Critical pressure.

Van der Waal's equation has same limitations as follows:

1. The study has not been made closely under actual conditions and its validity bias failed.
2. The values of a and b are assumed as constant, but they will vary with temperature which is found experimentally,

$$\frac{P_c V_c}{RT_c} = \frac{3}{8} \text{ for real gases}$$

$$\frac{P_c V_c}{RT_c} = 1 \text{ for ideal gases.}$$

But, experimentally, $\frac{P_c V_c}{RT_c}$ changes from 0.2 to 0.3 for more of the gases.

3. What do you mean by "Compressibility factor"? Write a short note on Generalized Compressibility chart.

Compressibility Factor:

WKT, the perfect gas equation is $PV = RT$.

But for real gas, a correction factor has to be introduced in the perfect gas equation to take into account the deviation of the real gas from the perfect gas equation. This factor is known as compressibility factor (Z).

W.K.T., the perfect gas equation is $PV = RT$. But for real gas, a correction factor has to be introduced in the perfect gas equation to taken into account the deviation of real gas from the perfect gas equation. This factor is from as compressing factor (z) and B defined by

$$Z = \frac{Pv}{RT}$$

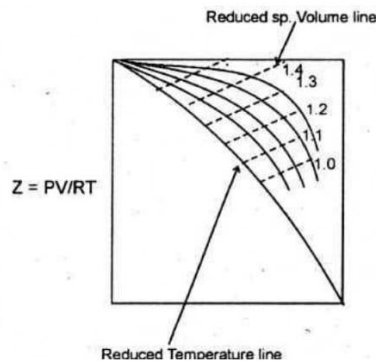


Fig.: Reduced Pressure

1. Inter molecular attractive study is made.
2. Shape factor is considered,

At critical point, the van der Waal's equation

$$\frac{P_2 V_2}{RT_2} = 1 \text{ for ideal gas.}$$

4. Derive the Maxwell's equations.

The Maxwell's equations relate entropy to the three directly measurable properties P , V and T for pure simple compressible substances.

From first law of thermodynamics $Q = W + \Delta U$

Rearranging the parameters $Q = \Delta + W$

$$TdS = du + PdV$$

[$\therefore dS = Q/T$ by second law of thermodynamics]

$W = PdV$ by first law of thermodynamics]

$$du = TdS - PdV \quad \dots (1)$$

We know that

$$h = u + PV$$

$$dh = du + d(PV) = du + VdP + PdV \quad \dots (2)$$

Substituting the value du in equation (2),

$$dh = TdS - PdV + VdP + PdV = TdS + VdP \quad \dots (3)$$

Example: Hurwitz's function,

[\therefore By differentiation rule, $d(UV) = u dv + V du$]

$$a = u - TS$$

$$\therefore da = du - d(TS) = du - TdS - SdT \quad \dots (4)$$

Substituting the value of du is equation (4),

$$da = TdS - PdV - TdS - SdT = -PdV - SdT \quad \dots (5)$$

By Gibbs functions

$$G = h - TS$$

$$dg = dh - d(TS) = dh - TdS - SdT \quad \dots (6)$$

Substituting the value of dh is equation (6)

$$dg = TdS + VdP - TdS - SdT = VdP - SdT \quad \dots (7)$$

By inverse exact differential we can write equation (1) as

$$du = TdS - PdV \quad (\partial T / \partial V)_S = - (\partial P / \partial S)_V \quad \dots (8)$$

Similarly, equation (3) as

$$(\partial T / \partial P)_S = (\partial V / \partial S)_P \quad \dots (9)$$

Similarly, equation (5) as

$$(\partial P / \partial T)_V = (\partial S / \partial V)_T \quad \dots (10)$$

Similarly, equation (7) as

$$(\partial V / \partial T)_P = - (\partial S / \partial P)_T \quad \dots (11)$$

These equations (8), (9), (10) and (11) are Maxwell's equations.

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

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

$$\left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T \quad \text{and} \quad \left(\frac{\partial V}{\partial T} \right)_P = - \left(\frac{\partial S}{\partial P} \right)_T$$

5. Derive Tds equation when (i) T and V independent (ii) T and P independent (iii) P and V independent.

(i) T and V independent:

By considering the entropy of pure substance as a function of temperature and specific volume (i.e.) $S = f(T, V)$

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

We know that

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V \Rightarrow \left(\frac{\partial S}{\partial T} \right)_V = \frac{C_V}{T}$$

From Maxwell equations,

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

Substituting in dS equation

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T} \right)_V dV$$

Multiply by T , T ,

$$Tds = C_V dT + T \left(\frac{\partial P}{\partial T} \right)_V dV.$$

(ii) T and P independent: The entropy (S) of a pure substance can be expressed as a function of temperature (T) and Pressure (P).

$S = f(T, P)$

We know that,

$$dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP \text{ and}$$

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_P \Rightarrow \left(\frac{\partial S}{\partial T} \right)_P = \frac{C_P}{T}$$

From Maxwell equation,

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

Substituting in ds equation,

$$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T} \right)_P dP$$

Multiplying by T on both sides of the equation,

$$Tds = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_P dP$$

(iii) **P and V independent:** The entropy (S) of a pure substance can be expressed as a function of temperature (V) and pressure (P). From mathematical rule

$$dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP$$

Multiplying the equation by T on both sides,

$$Tds = T \left(\frac{\partial S}{\partial T} \right)_P dT + T \left(\frac{\partial S}{\partial P} \right)_T dP \quad \dots (1)$$

From Maxwell's equation,

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P \quad \dots (2)$$

$$\left(\frac{\partial S}{\partial T} \right)_P = C_p \quad \dots (3)$$

Substitute (2) & (3) in (1)

$$Tds = C_p dT + C_v dT$$

6. Show that the internal energy of an ideal gas and an in-compressible substance is a function of temperature only, $u = u(T)$.

Internal Energy

$u = u(T)$ for ideal gases and in compressible substances.

Analysis:

The differential change in internal energy of a general simple compressible

$$du = e_v dT + \left[T \left(\frac{\partial e}{\partial T} \right)_v - P \right] dv.$$

a) For an ideal gas $Pv = RT$

$$T \left[\frac{\partial P}{\partial T} \right]_v - P = T \left(\frac{R}{v} \right) - P = P - P = 0$$

$$du = C_v dT$$

Complete proof need to show that C_v is not a junction of V either. This is done with help of

$$\left(\frac{\partial C_v}{\partial v} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_v$$

For an ideal gas,

$$P = \frac{RT}{V}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \text{ and } \left(\frac{\partial^2 P}{\partial T^2}\right)_V = \left[\frac{\partial(R/V)}{\partial T}\right]_V = 0$$

$$\left(\frac{\partial C_V}{\partial V}\right) = 0$$

Which states that C_V does not change specification C_V is not a function of specific volume. Internal energy of an ideal gas equation is a function of temperature only.

b_{in} compressible substance $V = C$ $d = 0$.

$C_p = C_V = C$ $\alpha = \beta = 0$ in compressible substance

$du = C dT$

Again we need to show the specific heat C depends on temperature only and not a pressure an specific volume.

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T \left[\frac{\partial^2 V}{\partial T^2}\right]_P = 0$$

Since $V=C$

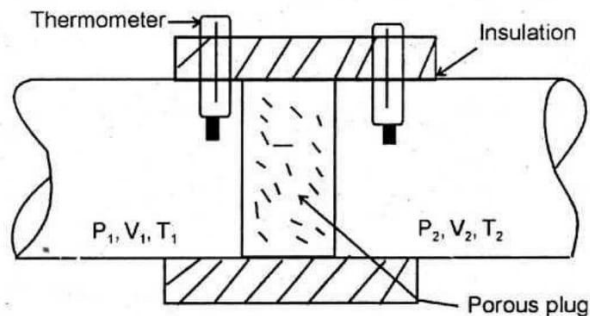
Internal energy of fluid is truly in compressible substance depends on temperature only.

7. Explain the flow process of a real gas through a throttle value. Derive the expression for Joule Thomson coefficient and deduce its value for an ideal gas.

Throttling Process: Throttling process is defined as the fluid expansion through a minute orifice or slightly opened value. During the throttling process, pressure and velocity are reduced. But there is no heat transfer and no work done by the system. In this process, enthalpy remains constant.

Joule-Thomson Experiment:

Figure shows the arrangement of Porous plug experiment. In this experiment, a stream of gas at a pressure P_1 and Temperature T_1 is allowed to flow continuously through a Porous Plug. The gas comes out from the other side of the Porous plug at a pressure P_2 and temperature T_2 .



The whole apparatus is completely insulated. Therefore, no heat transfer takes place.
i.e., $Q = 0$.

The system does not exchange work with the surrounding. So, $w = 0$ from steady flow energy equation,

We know that,

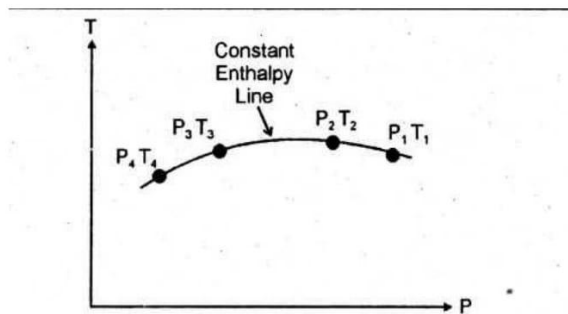
$$gZ_1 + V_1^2/2 + h_1 + Q = gZ_2 + V_2^2/2 + h_2 + W \quad \dots (1)$$

Since there is no considerable change velocity, $V_1 = V_2$ and $Z_1 = Z_2$. $Q = 0$, $W = 0$, $V_1 = V_2$ and $Z_1 = Z_2$ are applied in steady flow energy equation. So the equation (1) becomes
 $h_1 = h_2$

Enthalpy at inlet, h_1 = Enthalpy at Outlet, h_2 .

It indicates that the enthalpy is constant for throttling process.

It is assumed that a series of experiments performed on a real gas keeping the initial pressure P_1 and temperature T_1 constant with various reduced down steam pressures (P_2 , P_3 , P_4 ...). It is found that the down steam temperature also changes. The results from these experiments can be plotted as a constant enthalpy curve on T-P (Temperature-Pressure) plane.



The slope of a constant enthalpy is known as Joule-Thomson co-efficient, it is denote dby μ ,

$$\mu = \left[\frac{\partial T}{\partial P} \right]_h$$

For real gas, μ may be either positive or negative depending upon the thermodynamic state of the gas.

Case (i): There is always pressure drop in throttling process. So ΔP and temperature change are negative therefore μ is positive,

$$\mu = \left(\frac{\partial T}{\partial P} \right)$$

This throttling process produces cooling effect ... [Temperature reduces].

Case (ii): There is always pressure drop in throttle process. So, ΔP is negative. When the temperature

change is positive, μ is negative. $\mu = \left(\frac{\partial T}{\partial P} \right)$

This throttling process produces heating effect. [\because Temperature Increases].

Case (iii): When μ is zero, the temperature of the gas remains constant with throttling. The temperature at which 0 is called inversion temperature for a given pressure.

Inversion Curve: The maximum point on each curve is called inversion point and the locus of the inversion point is called inversion as shown in Figure.

A generalized equation of the Joule-Thomson Co-efficient can be derived by using change of enthalpy equation.

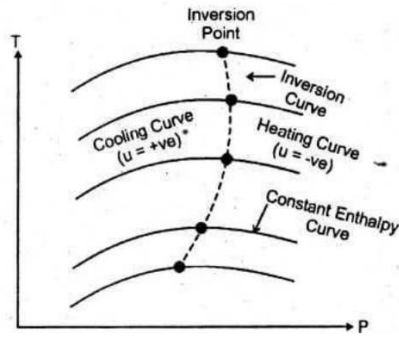
We know that

$$\text{Change in Enthalpy, } dh = \left[C_p dT - T \left(\frac{\partial V}{\partial T} \right)_P dP \right] + v dP.$$

$$\Rightarrow dh - V dP = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_P dP = C_p dT$$

Dividing by C_p on both sides,

$$\begin{aligned} \frac{dh}{C_p} - \frac{V dP}{C_p} + \frac{T}{C_p} \left(\frac{\partial V}{\partial T} \right)_P dP &= dT \\ dT &= \frac{dh}{C_p} + \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] dP \quad \dots (2) \end{aligned}$$



Differentiate this equation with respect to pressure at constant enthalpy

$$\begin{aligned} \left(\frac{\partial T}{\partial P} \right)_h &= 0 + \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] \\ \mu = \left(\frac{\partial T}{\partial P} \right)_h &= \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] \quad \dots (4) \end{aligned}$$

Joule-Thomson Coefficient for Ideal Gas:

The Joule Thomson Coefficient is defined as the change in temperature with change in pressure, keeping the enthalpy remains constant.

$$\mu = \left(\frac{\partial T}{\partial P} \right)_h = \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right]$$

We know the equation of state as $PV = RT$

Different with respect to T by keeping pressure, P constant

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P} = \frac{V}{T}$$

$$\mu = \frac{1}{C_P} \left[T - \frac{V}{T} - V \right]$$

$\therefore \mu = 0$ implies that the Joule-Thomson coefficient is zero for

8. Derive the Clapeyron equation.

Clapeyron Equation:

It involves the relationship between the saturation pressure, saturation temperature, the enthalpy of evaporation and the specific volume of the two phases involved. It gives a slope of a curve separating the two phases in the P – T diagram.

Entropy is a function of Temperature (T) and Volume (V).

$S = f(T, V)$

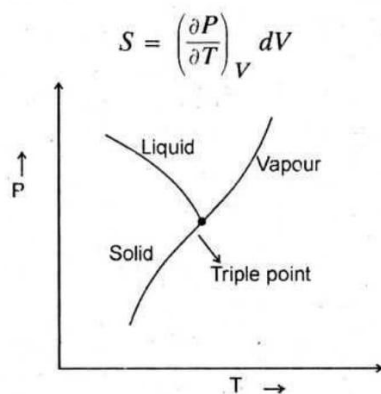
$$ds = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV.$$

When the phase is changing from saturated liquid to saturated vapour temperature remains constant. So ds equation reduces to

$$ds = \left(\frac{\partial S}{\partial T} \right)_T dV \quad (\because dT = 0)$$

From Maxwell equation,

$$WKT, \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$



The term $\left(\frac{\partial P}{\partial T}\right)$ is the slope of saturation curve

$$\int_{S_f}^{S_g} ds = \frac{dP}{dT} \int_{V_f}^{V_g} dv \Rightarrow S_g - S_f = \frac{dP}{dT} [V_g - V_f]$$

$$\frac{dP}{dT} = \frac{S_g - S_f}{V_g - V_f} = \frac{S_{fg}}{V_{fg}}$$

From second law of thermodynamics

WKT, $dS = \frac{dQ}{T}$

For constant pressure process,

$$dQ = dh$$

$$\therefore dS = \frac{dh}{T}$$

$$S_{fg} = \frac{h_{fg}}{T}$$

$$\therefore \frac{dP}{dT} = \frac{S_g - S_f}{V_g - V_f} = \frac{S_{fg}}{V_{fg}} = \frac{h_{fg}}{TV_{fg}}$$

This equation is known as Clapeyron Equation.