

THERMODYNAMIC RELATIONS MOD - 6

The application of thermodynamic principles to engineering systems requires data for specific internal energy, enthalpy, entropy and other properties. The thermodynamic relations allow u, h, s and other thermodynamic properties of simple compressible systems to be evaluated from data that are more readily measured.

Properties used for defining single phase substance

8 properties : P, v, T, s, u, h, g, f .

measurable properties are pressure (P), volume (v) and Temperature (T).

The non measurable properties can be expressed in terms of measurable properties.

Thermodynamic Potential — ability to do work.

1. Internal Energy, u
2. Enthalpy, h
3. Helmholtz potential, f
4. Gibbs potential, g

These are the potential (properties) of the system which cannot be measured directly. For a pure substance in single phase, a thermodynamic potential can be expressed as a function of 2 other properties.

★ Thermodynamic Potentials

★ Internal Energy: Suppose a system undergoes a change of state during an adiabatic process.

Applying 1st law of Thermodynamics,

$$du = -dw \quad (dq = 0)$$

As a decrease in 'u' represents the potential to do work, 'u' is called thermodynamic potential



As per 1st law of TD, we know $du = dq - dw$ - (1)

As per 2nd law of TD, $\frac{dq}{T} = ds \rightarrow dq = Tds$ - (2)

Hence by combining eqns (1) + (2) for a reversible process, we can have -

$$du = Tds - PdV \rightarrow \text{Gibb's First equation}$$

★ Enthalpy

Let us consider a steady flow device (turbine)

Applying 1st law of TD for control volume of turbine,

we have,

$$\frac{dE}{dt} + m(e)(h_e + \frac{V_e^2}{2} + gZ_e) - m_i(h_i + \frac{V_i^2}{2} + gZ_i) = \dot{Q} - \dot{W}_{shaft}$$

considering steady flow, KE & potential energy terms are negligible, device is insulated.

$$\text{We have, } \dot{W}_{shaft} = -(h_e - h_i)$$

(2)

We know, $h = u + pv$.

$$dh = du + p dv + v dp$$

$$dh = T ds - p dv + p dv + v dp$$

$$dh = T ds + v dp \rightarrow \text{Gibbs 2nd equation}$$

★ Helmholtz Potential

Let us consider a system interacting with surrounding.

As per 1st law of TD, work done by the system during a given process.

$$dw = dq - du$$

Let the surrounding be maintained at constant temperature T_0 .

By 2nd law of TD, $dS_{\text{system}} + dS_{\text{surrounding}} \geq 0$

$$dS - \frac{dq}{T_0} \geq 0 \rightarrow dq \leq T_0 dS \quad \text{--- (2)}$$

Work done by the system is given by

$$dw = dq - du$$

$$dw \leq T_0 dS - du$$

$$W_{12} \leq (u_1 - u_2) - T_0 (S_1 - S_2)$$

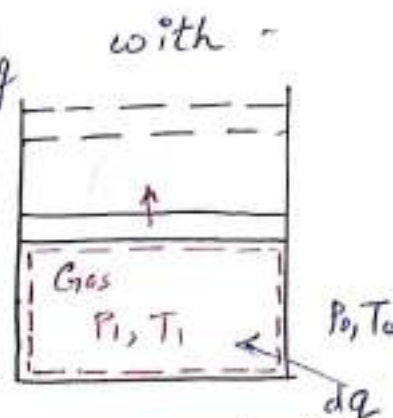
$$W_{12} \leq (u_1 - T_1 S_1) - (u_2 - T_2 S_2)$$

$$W_{12} \leq f_1 - f_2$$

$f_1 = u_1 - T_1 S_1 \rightarrow$ Helmholtz function / potential

$f_2 = u_2 - T_2 S_2 \rightarrow$ Helmholtz function / potential

$f_1 - f_2 \rightarrow$ Helmholtz free energy.



$f = u - Ts$ — Helmholtz potential / function.

$$df = du - Tds - sdT \quad \text{--- (1)}$$

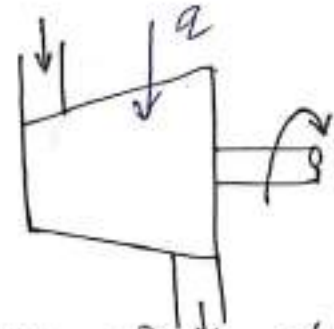
But $du = Tds - PdV$

$$df = Tds - PdV - Tds - sdT$$

$$df = -sdT - PdV \rightarrow \text{Helmholtz free energy equation}$$

★ Gibb's Free Energy

Let us consider a system which is operating under steady state flow through a control volume.



$$\frac{dE}{dt} + m_e \left(h_e + \frac{V_e^2}{2} + g z_e \right) - m_i \left(h_i + \frac{V_i^2}{2} + g z_i \right) = \dot{Q} - \dot{W}_{\text{shaft}}$$

$$W_{\text{sh}} = q - (h_e - h_i) \quad \text{--- (1)}$$

If the CV receives heat energy from surrounding at T_0 ,

$$\text{Then } \Delta S_{\text{surrounding}} = \frac{-q}{T_0}$$

By 2nd law of TD, $\Delta S_{\text{sys}} + \Delta S_{\text{sur}} \geq 0$

$$\Delta S - \frac{q}{T_0} \geq 0$$

$$q \leq T_0 (s_e - s_i) \quad \text{--- (2)}$$

Combining (1) & (2).

$$W_{\text{shaft}} \leq T_0 (s_e - s_i) - (h_e - h_i)$$

If the process takes place isothermally, $T_i = T_e = T_0$

③

$$W_{sh} \leq (h_i - T_i s_i) - (h_e - T_e s_e)$$

$$W_{sh} \leq g_i - g_e$$

$$g = h - Ts \rightarrow \text{Gibbs function} / \text{Potential}$$

$$g_i - g_e \rightarrow \text{Gibbs free energy}$$

$$dg = dh - Tds - sdT \quad \text{--- ③}$$

$$dh = Tds + vdp \quad \text{--- ④}$$

$$dg = Tds + vdp - Tds - sdT$$

$$dg = vdp - sdT \quad \text{--- Gibbs free energy eqn.}$$

Thermodynamic Potential	Differential Expression (Specific property)	Differential Expression (Total property)	Natural Variables
u	$du = Tds - pdu$	$dU = TdS - PdV$	s, v
h	$dh = Tds + vdp$	$dH = TdS + VdP$	s, p
f	$df = -pdu - sdT$	$dF = -PdV - SdT$	v, T
g	$dg = vdp - sdT$	$dG = VdP - SdT$	p, T

$$U = \phi(s, v)$$

$$F = \phi(v, T)$$

$$H = \phi(s, p)$$

$$G = \phi(p, T)$$

★ MAXWELL RELATIONS

The equations that relate the partial derivatives of properties P, V, T and S of a simple compressible system to each other are called Maxwell relations. They are obtained by the four Gibbs equations by exploiting the exactness of the differentials of thermodynamic properties.

Note: If $Z = Z(x, y) \rightarrow$ continuous function of x & y .

$$dZ = \left(\frac{\partial Z}{\partial x} \right)_y dx + \left(\frac{\partial Z}{\partial y} \right)_x dy$$
$$dZ = M dx + N dy \quad \text{--- (1)}$$
$$\therefore \left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y$$

$$\left(\frac{\partial M}{\partial y} \right)_x = \frac{\partial}{\partial y} \left(\frac{\partial Z}{\partial x} \right) = \frac{\partial^2 Z}{\partial x \partial y}$$
$$\left(\frac{\partial N}{\partial x} \right)_y = \frac{\partial^2 Z}{\partial x \partial y}$$

we have Gibbs's first eqn, $dU = Tds - PdV$ --- (2)

By analogy, of eqns (1) & (2)

we have $\boxed{\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_U} \quad \text{--- (I)}$

we have, Gibbs second eqn, $dH = Tds + Vdp$

$$\boxed{\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_H} \quad \text{--- (II)}$$

(4)

We have Gibbs 3rd eqn, $dF = -PdV - SdT$

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

We have Gibbs 4th eqn, $dG = VdP - SdT$

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

Thermodynamic Potential	Natural Variables	Differential Expression	Maxwell Relations
U	S, V	$dU = Tds - PdV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$
H	S, P	$dH = Tds + VdP$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
F	V, T	$-PdV - SdT$	$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$
G	P, T	$VdP - SdT$	$\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial S}{\partial P}\right)_T$

The above 4 relations ^(I, II, III & IV) are called Maxwell Relations.

- These Relations are extremely valuable in thermodynamics because they provide means of determining the changes in properties (non measurable) by simply measuring the changes in properties P, V & T.
- Maxwell Relations are limited to simple compressible systems.

Note

$$\text{If } f(x, y, z) = 0 \quad \text{or } z = z(x, y)$$

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy$$

Rules for Partial Derivative Method

1. Reciprocal Relation $\rightarrow \left(\frac{\partial x}{\partial y} \right)_z = \frac{1}{\left(\frac{\partial y}{\partial x} \right)_z}$

2. cyclic Relation $\rightarrow \left(\frac{\partial x}{\partial y} \right)_z \cdot \left(\frac{\partial y}{\partial z} \right)_x \cdot \left(\frac{\partial z}{\partial x} \right)_y = -1$

3. Chain Rule $\rightarrow \left(\frac{\partial z}{\partial x} \right)_y = \left(\frac{\partial z}{\partial P} \right)_y \cdot \left(\frac{\partial P}{\partial x} \right)_y$
if $z = z(P, y)$, $P = P(x)$ and $y = y$

$$\text{If } U = \phi(s, v)$$

$$dU = \left(\frac{\partial U}{\partial s} \right)_v ds + \left(\frac{\partial U}{\partial v} \right)_s dv \quad \text{--- (1)}$$

we have,

$$dU = T ds - P dv \quad \text{--- (2)}$$

Comparing 2 eqns, $T = \left(\frac{\partial U}{\partial s} \right)_v$; $P = - \left(\frac{\partial U}{\partial v} \right)_s$

IIIth $H = \phi(s, P)$

$$dH = \left(\frac{\partial H}{\partial s} \right)_P ds + \left(\frac{\partial H}{\partial P} \right)_s dP$$

we have, $dH = T ds + V dP$

$$T = \left(\frac{\partial H}{\partial s} \right)_P ; \quad V = \left(\frac{\partial H}{\partial P} \right)_s$$

(5)

$$F = \phi(V, T)$$

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

$$dF = -P dV - S dT$$

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

$$G = \phi(P, T)$$

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

$$\text{we have } dG = V dP - S dT$$

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

★ T-dS Equations

★ First T-dS Equation

$S = S(T, V)$ for single component single phase substance.

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

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

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

↓
First Tds Equation

$$C_V = \left(\frac{dQ}{dT}\right)_V \rightarrow 0$$

$$dU = T dS - P dV \rightarrow 0$$

$$dQ = dU + P dV \rightarrow 0$$

$$dQ = dU = T dS$$

$$C_V = \frac{dQ}{dT} = T \left(\frac{dS}{dT}\right)_V$$

Also from Maxwell Relation

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

★ The second T-ds Equation

$$S = S(T, P)$$

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

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

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

↓
2nd T-ds Equation

$$C_P = \left(\frac{dQ}{dT}\right)_P$$

$$(dQ)_P = (dH)_P$$

$$dQ = dU + PdV$$

$$dQ = d(U + PV)$$

$$dQ = dH$$

$$dH = TdS + VdP$$

$$dH = TdS$$

$$C_P = \left(\frac{dQ}{dT}\right)_P = \left(\frac{dH}{dT}\right)_P = T\left(\frac{dS}{dT}\right)_P$$

Also from Maxwell Relation

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

★ Third T-ds Equation

$$S = S(P, V)$$

$$dS = \left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P dV$$

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V dP + T\left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P dV$$

$$TdS = C_V \left(\frac{\partial T}{\partial P}\right)_V dP + C_P \left(\frac{\partial T}{\partial V}\right)_P dV \quad \text{--- (1)}$$

Note

Volume Expansivity, $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$

Isothermal compressibility, $k_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$

Isentropic compressibility, $k_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_S$

(6)

we have, $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \rightarrow \left(\frac{\partial T}{\partial V} \right)_P = \frac{1}{\beta V} \quad \text{--- (2)}$

Also we have, $k_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$

$$\frac{k_T}{\beta} = - \left(\frac{\partial V}{\partial P} \right)_T \cdot \left(\frac{\partial T}{\partial V} \right)_P \quad \text{--- (3)}$$

From cyclic relation, If $\mathcal{P}(P, V, T) = 0$

$$\left(\frac{\partial P}{\partial V} \right)_T \cdot \left(\frac{\partial V}{\partial T} \right)_P \cdot \left(\frac{\partial T}{\partial P} \right)_V = -1$$

$$\left(\frac{\partial T}{\partial P} \right)_V = - \left(\frac{\partial V}{\partial P} \right)_T \cdot \left(\frac{\partial T}{\partial V} \right)_P \quad \text{--- (4)}$$

$$\therefore T ds = C_v \cdot \frac{k_T}{\beta} + C_p \cdot \frac{1}{\beta V} dV$$

★ Difference in Specific Heat Capacities.

we have, $T ds = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_P dP \leftarrow 2^{nd} T ds eqn \rightarrow (1)$

$$T ds = C_v dT + T \left(\frac{\partial P}{\partial T} \right)_V dV \leftarrow 1^{st} T ds eqn \rightarrow (2)$$

$$(1) - (2) \Rightarrow (C_p - C_v) dT - T \left(\frac{\partial V}{\partial T} \right)_P dP - T \left(\frac{\partial P}{\partial T} \right)_V dV = 0$$

$$(C_p - C_v) dT = T \left(\frac{\partial V}{\partial T} \right)_P dP + T \left(\frac{\partial P}{\partial T} \right)_V dV$$

$$dT = \frac{T}{C_p - C_v} \left(\frac{\partial V}{\partial T} \right)_P dP + \frac{T}{C_p - C_v} \left(\frac{\partial P}{\partial T} \right)_V dV \quad \text{--- (3)}$$

$$dT = \left(\frac{\partial T}{\partial P} \right)_V dP + \left(\frac{\partial T}{\partial V} \right)_P dV \quad \text{--- (4)} \quad T = T(P, V)$$

By analogy,

$$\frac{T}{C_p - C_v} \left(\frac{\partial v}{\partial T} \right)_p = \left(\frac{\partial T}{\partial p} \right)_v \Rightarrow C_p - C_v = T \left(\frac{\partial v}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_v$$

$$\frac{T}{C_p - C_v} \left(\frac{\partial p}{\partial T} \right)_v = \left(\frac{\partial T}{\partial v} \right)_p \Rightarrow C_p - C_v = T \left(\frac{\partial v}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_v$$

$$C_p - C_v = T \left(\frac{\partial v}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_v \quad \text{--- (4)}$$

From cyclic relations, we have

$$f(p, v, T) = 0$$

$$\left(\frac{\partial p}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p \left(\frac{\partial T}{\partial p} \right)_v = -1$$

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

$$\therefore C_p - C_v = -T \left(\frac{\partial v}{\partial T} \right)_p^2 \left(\frac{\partial p}{\partial v} \right)_T \quad \text{--- (5)}$$

Note:

$\left(\frac{\partial v}{\partial T} \right)_p^2$ is always positive quantity

$\left(\frac{\partial p}{\partial v} \right)_T$ is always negative for all substance

$$C_p - C_v > 0$$

$$C_p > C_v$$

The above relation (eqn 5) can be expressed in terms of two other thermodynamic properties called volume expansivity (β) and the isothermal compressibility (κ_T).

(7)

we have, $\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p$

$$k_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T$$

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

$$C_p - C_v = \frac{T v \left[\frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p \right]^2}{-\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T} = \frac{T v \beta^2}{k_T}$$

$C_p - C_v = \frac{T v \beta^2}{k_T}$

← Mayer Relation

For an ideal gas, we know $C_p - C_v = R$
 where C_p & C_v are specific heat capacities

Proof:

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

$$C_p - C_v = -T \cdot \frac{v^2}{T^2} \cdot -\frac{RT}{v^2}$$

$C_p - C_v = R$

Conclusions of Mayer Relation

- The isothermal compressibility k_T is a positive quantity for all substance in all phases. Volume expansivity β is negative for some substance. But its square is always +ve
 $\therefore C_p \geq C_v$

$$pv = RT$$

$$v = \frac{RT}{p}$$

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

$$pv = RT$$

$$p = \frac{RT}{v}$$

$$\frac{\partial p}{\partial v} = -\frac{RT}{v^2}$$

2. The difference between C_p & C_v approaches zero as the absolute temperature approaches zero.
3. The two specific heats are identical for truly incompressible substance since $v = \text{constant}$.
The difference between two specific heats is very small and is usually disregarded for substances that are nearly incompressible such as liquids and solids.

★ Ratio of specific heat capacity

$$Tds = C_p dT - T \left(\frac{\partial v}{\partial T} \right)_p dp \leftarrow 2^{\text{nd}} Tds \text{ eqn} - (1)$$

$$Tds = C_v dT + T \left(\frac{\partial p}{\partial T} \right)_v dv \leftarrow 1^{\text{st}} Tds \text{ eqn} - (2)$$

Assuming Isentropic process, $ds = 0$

$$C_p = T \left(\frac{\partial v}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_s \quad - (3)$$

$$C_v = -T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_s \quad - (4)$$

We have cyclic relation $f(p, v, T) = 0$

$$\left(\frac{\partial p}{\partial v} \right)_T \cdot \left(\frac{\partial v}{\partial T} \right)_p \cdot \left(\frac{\partial T}{\partial p} \right)_v = -1$$

$$\frac{C_p}{C_v} = - \left(\frac{\partial v}{\partial T} \right)_p \cdot \left(\frac{\partial p}{\partial T} \right)_s \cdot \left(\frac{\partial T}{\partial p} \right)_v \cdot \left(\frac{\partial T}{\partial v} \right)_s$$

(8)

Using cyclic relations & suitable Rearrangements

$$\frac{C_p}{C_v} = \frac{k_T}{k_S} = \gamma$$

☆ Internal Energy Change

For a system undergoes reversible process between two equilibrium states, change of internal energy, $du = Tds - PdV$

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

$$\text{i.e. } du = C_v dT + \left(T \left(\frac{\partial P}{\partial T} \right)_V - P \right) dV$$

we have $du = \left(\frac{\partial u}{\partial T} \right)_V dT + \left(\frac{\partial u}{\partial V} \right)_T dV$ if $u = u(T, V)$

From the above eqn, we have.

$$C_v = \left(\frac{\partial u}{\partial T} \right)_V = \frac{du}{dT}$$

$$\text{Also, } \left(\frac{\partial u}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P \quad \leftarrow \text{Energy eqn.}$$

Proof : Internal energy is a function of temperature only for ideal gas.

$$\text{we have } du = C_v dT + \left(T \left(\frac{\partial P}{\partial T} \right)_V - P \right) dV$$

$$\text{For ideal gas, } PV = RT \rightarrow P = \frac{RT}{V}$$

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

$$\therefore T \left(\frac{\partial p}{\partial T} \right)_v - p = 0$$

$$\therefore \boxed{du = c_v dT}$$

Internal Energy is a function of temperature only.

★ - Change in Enthalpy -

$$dh = T ds + v dp$$

From 2nd Tds equation.

$$T ds = c_p dT - T \left(\frac{\partial v}{\partial T} \right)_p dp$$

$$dh = c_p dT + \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp$$

we have.

$$dh = \left(\frac{\partial h}{\partial T} \right)_p dT + \left(\frac{\partial h}{\partial p} \right)_T dp \quad \text{if } h = h(T, p)$$

By analogy, we have.

$$c_p = \left(\frac{\partial h}{\partial T} \right)_p ; \quad v - T \left(\frac{\partial v}{\partial T} \right)_p = \left(\frac{\partial h}{\partial p} \right)_T$$

★ Enthalpy of an ideal gas is a function of temperature only.

Proof -

$$\text{we have } dh = c_p dT + \left(v - T \left(\frac{\partial v}{\partial T} \right)_p \right) dp$$

(4)
For ideal gas, $Pv = RT \rightarrow v = \frac{RT}{P}$

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

$$dh = C_p dT + \left[v - T \cdot \frac{v}{T}\right] dp$$

$$\therefore \boxed{dh = C_p dT}$$

Therefore enthalpy is a function of temperature only for an ideal gas

★ Proof: For isentropic process, $Pv^\gamma = C$ for ideal gas

$$\text{We have, } du = Tds - Pd v \rightarrow Tds = C_v dT + Pd v \quad \text{--- (1)}$$

$$dh = Tds + v dp \rightarrow Tds = C_p dT - v dp \quad \text{--- (2)}$$

For isentropic process, $ds = 0$

$$C_v dT + Pd v = 0 \rightarrow Pd v = -C_v dT \quad \text{--- (3)}$$

$$C_p dT - v dp = 0 \rightarrow v dp = C_p dT \quad \text{--- (4)}$$

$$\frac{(4)}{(3)} \Rightarrow \frac{dp}{p} + \frac{C_p}{C_v} \frac{dv}{v} = 0$$

$$\text{Integrating, } \ln p + \ln v^\gamma = \ln C$$

$$Pv^\gamma = C$$

★ Entropy change of an ideal gas.

We have, $Tds = C_v dT + Pd v$

$$dS = \frac{C_v}{T} dT + \frac{P}{T} dv$$

$$dS = \frac{C_v}{T} dT + R \frac{dv}{v}$$

$$Pv = RT$$

$$\frac{P}{T} = \frac{R}{v}$$

Integrating -

$$S_2 - S_1 = C_v \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{V_2}{V_1} \right) \quad \text{--- (I)}$$

III^{ly} $Tds = C_p dT - v dp$

$$ds = C_p \frac{dT}{T} - \frac{v}{T} dp$$

$$pv = RT$$

$$ds = C_p \frac{dT}{T} - R \frac{dp}{p}$$

$$\frac{v}{T} = \frac{R}{p}$$

Integrating, $S_2 - S_1 = C_p \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{p_2}{p_1} \right) \quad \text{--- (II)}$

Since $R = C_p - C_v$

$$S_2 - S_1 = C_p \ln \left(\frac{T_2}{T_1} \right) - (C_p - C_v) \ln \left(\frac{p_2}{p_1} \right)$$

$$S_2 - S_1 = C_p \ln \frac{T_2}{T_1} - C_p \ln \frac{p_2}{p_1} + C_v \ln \frac{p_2}{p_1}$$

$$S_2 - S_1 = C_p \left[\ln \left(\frac{T_2}{T_1} \right) - \ln \left(\frac{p_2}{p_1} \right) \right] + C_v \ln \left(\frac{p_2}{p_1} \right)$$

$$S_2 - S_1 = C_p \ln \left(\frac{V_2}{V_1} \right) + C_v \ln \left(\frac{p_2}{p_1} \right) \quad \text{--- (III)}$$

Any one of the above 3 equations can be used for computing the entropy change between any two states of an ideal gas -

Entropy change in Polytropic process

In a reversible adiabatic (isentropic) process entropy remains constant. But in a reversible polytropic process, the entropy changes

we have, $S_2 - S_1 = C_v \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{V_2}{V_1} \right)$

$$S_2 - S_1 = \frac{R}{\gamma - 1} \ln \left(\frac{T_2}{T_1} \right) + \frac{R}{n - 1} \ln \left(\frac{T_1}{T_2} \right)$$

$$S_2 - S_1 = \frac{n - \gamma}{(\gamma - 1)(n - 1)} R \ln \left(\frac{T_2}{T_1} \right) \quad \text{--- (1)}$$

$$\text{|||}^{\text{ly}} \quad S_2 - S_1 = \frac{n - \gamma}{n(\gamma - 1)} R \ln \left(\frac{p_2}{p_1} \right) \quad \text{--- (2)}$$

$$S_2 - S_1 = -\frac{(n - \gamma)}{\gamma - 1} R \ln \left(\frac{V_2}{V_1} \right) \quad \text{--- (3)}$$

★ JOULE KELVIN EFFECT

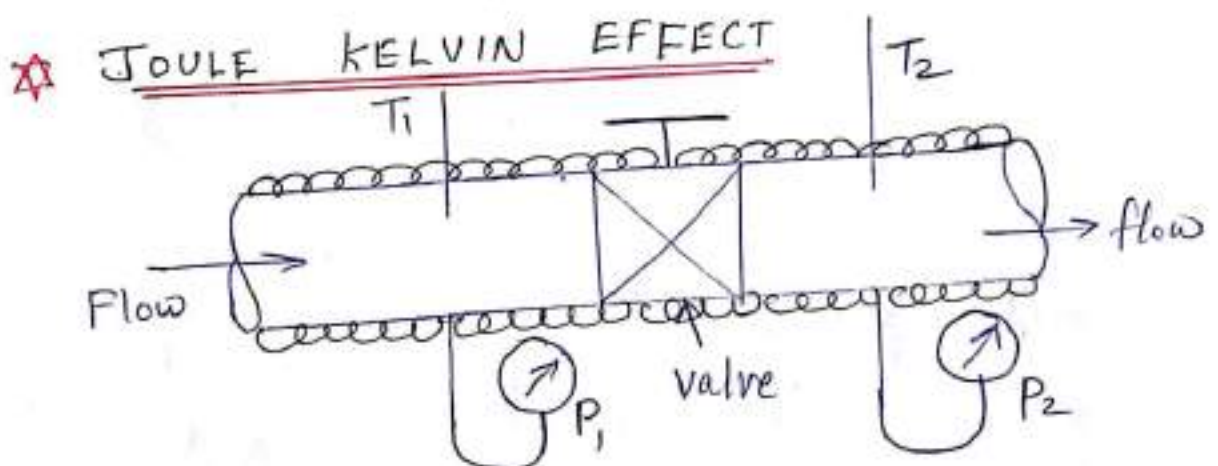
Note: When a fluid passes through a restriction such as porous plug, a capillary tube or an ordinary valve, its pressure drops. The enthalpy of the fluid remains approximately constant during the process called throttling.

The fluid may experience large drop in its temperature as a result of throttling which forms the basis of operation of refrigerators and air conditioners. Some times during throttling process

the temperature may remain same or even increase.

Two counterweighing effects which decide whether temperature increase or decrease during throttling process

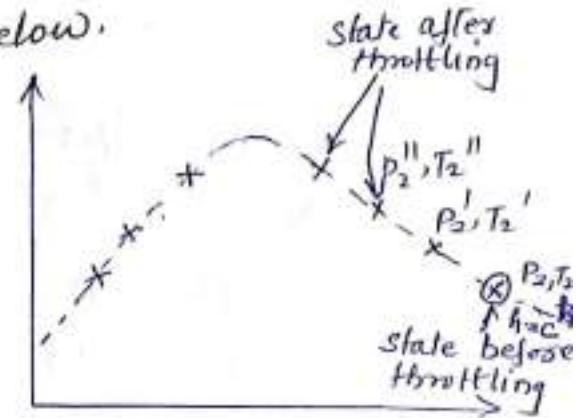
1. Temperature will decrease because of its decrease in pressure following equation of state.
2. During throttling, because of friction, part of the mechanical energy is converted to intermolecular energy, thereby temperature increase.



A gas is made to undergo continuous throttling process. The pressure and temperature of the gas in the insulated pipe upstream and downstream of the valve are measured with suitable manometres and thermometers.

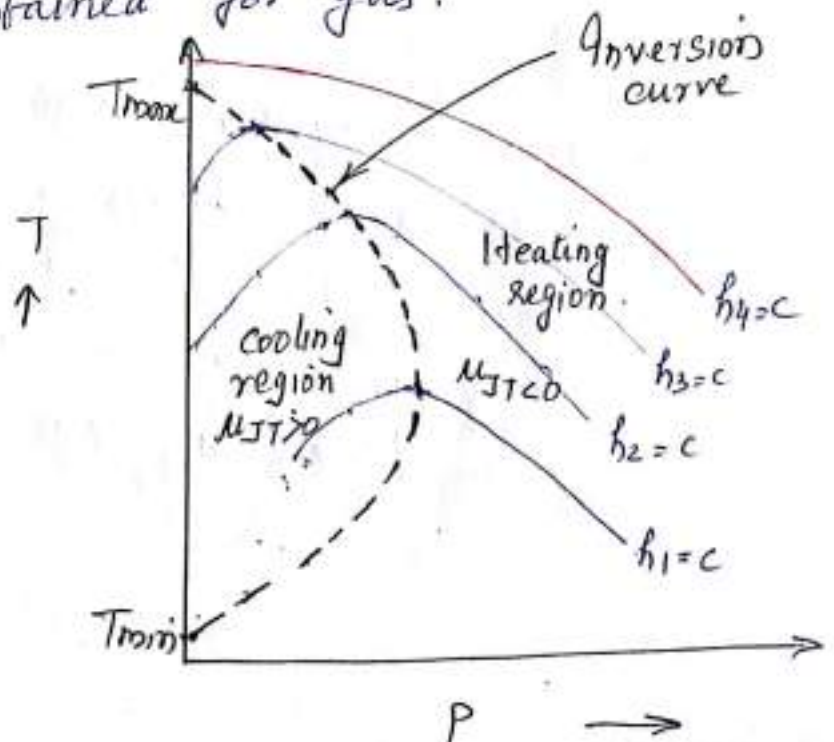
Let P_1, T_1 be arbitrarily chosen pressure and temperature before throttling and is kept constant. By operating the valve manually, the gas is throttled successively to different pressure and temperature (P_2', T_2') ; (P_2'', T_2'') These are then plotted on T - P co-ordinates as shown in figure below.

All the points represent equilibrium states of some constant mass of gas at which gas has same enthalpy.



The curve passing through all these points is an isenthalpic curve or an isenthalpe.

The initial and temperature and pressure of the gas are then set to new values and by throttling to different states, a family of isenthalps are obtained for gas.



★ Joule Thomson Coefficient (μ_{JT})

The temperature behaviour of a fluid during a throttling ($h = \text{constant}$) process is described by Joule Thomson coefficient (μ_{JT})

The numerical value of slope of the isenthalpe on a T-P diagram at any point is called Joule Thomson or Joule kelvin coefficient. i.e. It is a measure of the change in temperature with pressure during a constant enthalpy process.

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_h$$

$\mu_{JT} < 0 \rightarrow$ Temperature increases.

$\mu_{JT} = 0 \rightarrow$ Temperature remains constant.

$\mu_{JT} > 0 \rightarrow$ Temperature decreases.

Some constant enthalpy lines on the T-P diagram pass through a point of zero Joule Thomson coefficient or zero slope. The locus of all these points at which μ_{JT} is zero is called Inversion curve or Inversion line.

★ The region inside the inversion curve where μ_{JT} is +ve is called cooling region. The region outside the inversion curve where μ_{JT} is -ve is called heating region.

★ Inversion Temperature: The temperature at a point where constant enthalpy line intersects the inversion curve/line is called Inversion temperature.

★ Expression of Joules Thomson coefficient

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_h$$

We know, $dh = Tds + vdp$

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

If $h = h(T, P)$

$$dh = \left(\frac{\partial h}{\partial T} \right)_p dT + \left(\frac{\partial h}{\partial P} \right)_T dP$$

$$Tds = dh - vdp$$

$$Tds = C_p dT - T \left(\frac{\partial v}{\partial T} \right)_p dp$$

For constant enthalpy process (throttling)

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

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

$$dT = \frac{1}{C_p} \left[T \left(\frac{\partial v}{\partial T} \right)_p - v \right] dp$$

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_h = \frac{1}{C_p} \left[T \left(\frac{\partial v}{\partial T} \right)_p - v \right]$$

For an ideal gas, $\mu_{JT} = 0$

Additional Information

For achieving the effect of cooling by Joule Kelvin expansion, the initial temperature of the gas must be below the point where the inversion curve intersects the temperature axis, i.e. below the maximum inversion temperature.

For nearly all substances, the maximum inversion temperature is above the normal ambient temperature and hence cooling can be obtained by the Joule Kelvin effect.

In the case of H_2 and He , the gas is first precooled in a heat exchanger below the maximum inversion temperature.

CLAPEYRON EQUATION

Note: Maxwell Relations have far reaching implications in thermodynamics and are frequently used to derive useful thermodynamic relations.

Clapeyron Equation or relation derived from Maxwell relations enables us to determine the enthalpy change associated with a phase change (such as enthalpy of vapourisation, h_{fg}) from a knowledge of



Clapeyron Equation

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CLAPEYRON - CLAUSIUS EQU

The Clapeyron relation enables us to determine enthalpy change associated with a phase change (such as enthalpy of vapourisation h_{fg}) from a knowledge of P , v and T alone.

Let us consider a single component system containing 2 phases (L & V) in a state of equilibrium. For a reversible process at constant T & P , the Gibbs function remains constant.

For phase transition from liquid state to vapour state,

$$g_{f1} = g_{g1}$$

$$\text{Similarly } g_{f2} = g_{g2}$$

In liquid phase,

$$g_{f2} - g_{f1} = v_f dp - s_f dT \quad \text{--- (1)}$$

In gaseous phase:

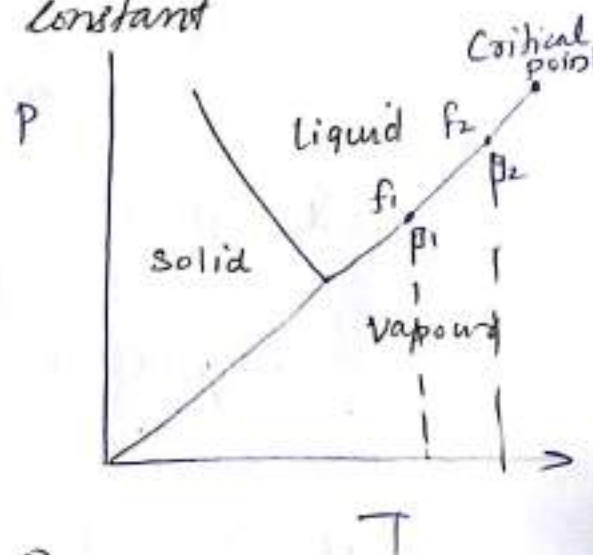
$$g_{g2} - g_{g1} = v_g dp - s_g dT \quad \text{--- (2)}$$

$$\text{(1) - (2)} \Rightarrow v_f dp - s_f dT = v_g dp - s_g dT$$

$$dp(v_f - v_g) = dT(s_f - s_g)$$

$$\frac{dp}{dT} = \frac{s_g - s_f}{v_g - v_f} = \frac{s_{fg}}{v_{fg}}$$

$$\text{i.e. } \left(\frac{dp}{dT} \right)_{\text{sat}} = \frac{s_{fg}}{v_{fg}}$$



we have $s_{fg} = \frac{h_{fg}}{T}$, where h_{fg} - enthalpy of vapourisation

$$\left(\frac{\partial P}{\partial T} \right)_{\text{sat}} = \frac{h_{fg}}{T \cdot v_{fg}}$$

★ This Clapeyron^{Clapeyron} equation enables us to determine the enthalpy of vapourisation h_{fg} at a given temperature by simply measuring the slope of the saturation curve on a P-T diagram and the specific volume of saturated liquid and saturated vapour at the given temperature.

★ Clapeyron equation is applicable to any phase change process that occurs at constant temperature and pressure.

★ Clapeyron equation can be simplified for liquid - vapour and solid - vapour phase changes by utilising some approximation.

At low pressures, $v_g \gg v_f$ and thus $v_{fg} \approx v_g$.

By treating the vapour as an ideal gas, we have $v_g = RT/p$.

Substituting these approximations into Clapeyron equation, we get

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$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{h_{fg} \cdot P}{RT^2}$$

$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{h_{fg}}{R} \frac{P}{T^2}$$

$$\left(\frac{dP}{P}\right)_{\text{sat}} = \frac{h_{fg}}{R} \left(\frac{dT}{T^2}\right)_{\text{sat}}$$

For small temperature intervals, h_{fg} can be treated as constant.

Integrating, we get -

$$\ln \left(\frac{P_2}{P_1}\right)_{\text{sat}} = \frac{h_{fg}}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]_{\text{sat}}$$

This equation is called Clapeyron - Clausius equation and it can be used to determine the variation of saturation pressure with temperature.

★ Clapeyron equation can be derived from 3rd Maxwell Relations also.

Real Gas Equation of state other
than Vander Waals equation (Mod 5)

1. Berthelot , $P = \frac{RT}{v-b} - \frac{a}{Tv^2}$ — (1)

2. Dieterici eqns of state , $P = \frac{RT}{v-b} e^{-a/RTv}$

3. Redlich - kwong eqns of state ,

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2} \cdot v(v+b)}$$

The constants a and b are evaluated from critical data.

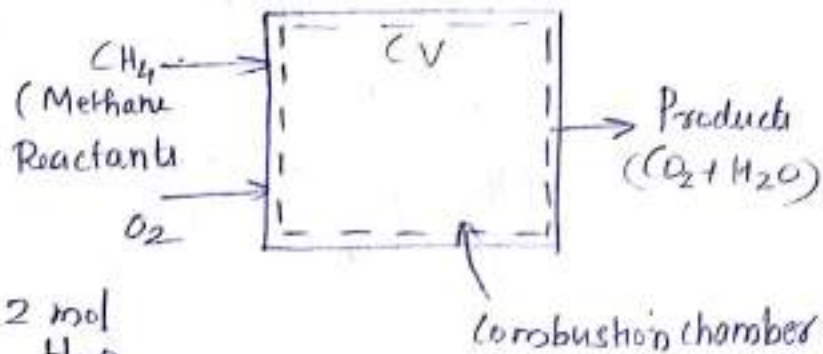
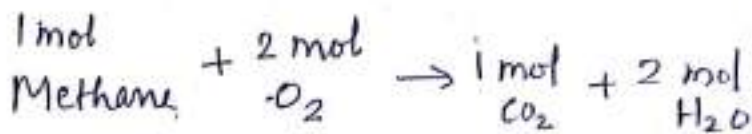
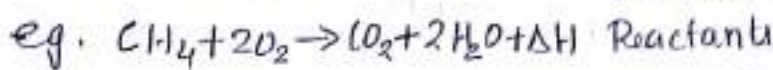
Berthelot and Dieterici equations of state, like the Vanderwaals equation of state has limited accuracy.

But the Redlich - kwong equation gives good results at high pressure and is fairly accurate for temperature above critical value

INTRODUCTION TO THERMODYNAMICS OF CHEMICALLY REACTING SYSTEM

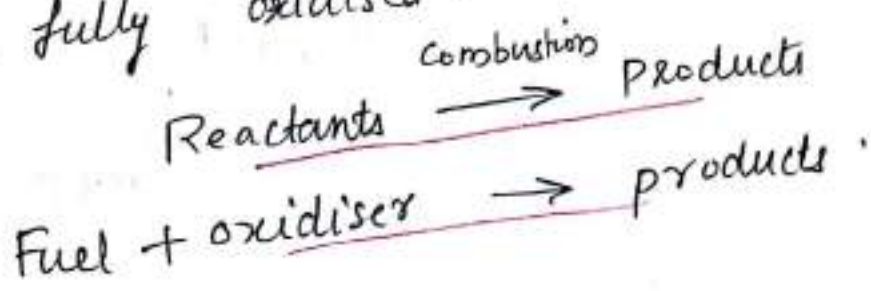
Combustion : A chemical process in which fuel is reacted with oxidiser while releasing large quantity of energy (heat & light).

Note: When a chemical reaction occurs, the bonds within the molecules of the reactants are broken and atoms and electrons rearrange to form products.



Note: The three major combustible chemical elements in most common fuels are C, H₂ and sulphur.

Combustion is complete when all the carbon present in fuel is burned to CO_2 , all the hydrogen is burnt to water, all the sulphur is burnt to sulphur dioxide and all other combustible elements are fully oxidised.



Fuel : A combustible substance.

Hydro carbon fuel

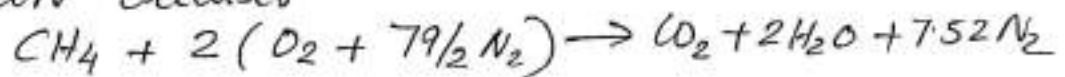
- Liquid form → gasoline, diesel fuel, kerosene
- Gaseous form → CH_4 (Methane)
- Solid form → coal.

MODELLING COMBUSTION AIR

Oxygen is required in every combustion reactions.

Pure oxygen is used only in special applications such as cutting and welding.

Mostly in combustion applications, air is used as an oxidiser.



AIR FUEL RATIO & FUEL-AIR RATIO

These parameters used to quantify the amount of fuel and air in a particular combustion process.

Air-fuel ratio = $\frac{\text{mass of air}}{\text{mass of fuel}}$, based on mass basis

Air-fuel ratio = $\frac{\text{mole of air} \cdot M_{\text{air}}}{\text{mole of fuel} \cdot M_{\text{fuel}}}$

$$\boxed{\begin{array}{l} n = \frac{m}{M} \\ m = nM \end{array}}$$

↓
mole Basis.

$$\underline{\text{Fuel-Air Ratio}} = \frac{1}{\text{Air-fuel Ratio}}$$

Stoichiometric Air or Theoretical Air

The minimum amount of air that supplies sufficient oxygen for the complete combustion of all the carbon, hydrogen and sulphur present in the fuel.

But normally, the amount of air supplied is either greater or less than the theoretical amount.

The amount of air actually supplied is - commonly expressed in terms of the percent of theoretical air.

eg. 150% theoretical air implies the actual air supplied is 1.5 times the theoretical amount of air.

The amount of air supplied can be - expressed alternatively as a percent excess or percent deficiency of air.

150% theoretical air \rightarrow 50% excess air

90% theoretical air \rightarrow 10% deficiency of air.

Equivalence Ratio (ϕ)

It is the ratio of the actual fuel air ratio to the stoichiometric fuel air ratio for complete combustion.

$$\phi = \frac{(F/A)_{\text{actual}}}{(F/A)_{\text{stoichiometric}}}$$

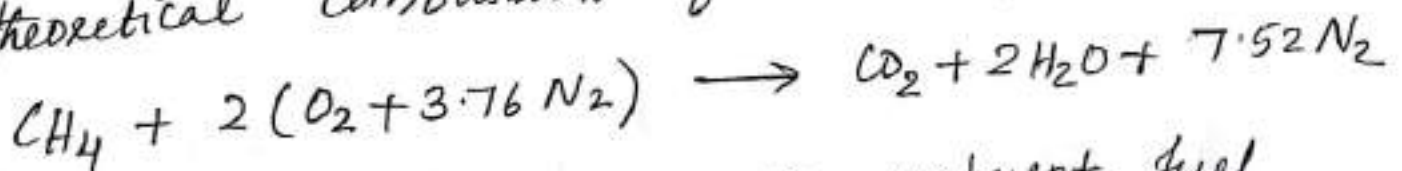
$\phi = 1 \rightarrow$ operating at stoichiometric conditions

$\phi < 1 \rightarrow$ Fuel lean \rightarrow less fuel.

$\phi > 1 \rightarrow$ fuel rich \rightarrow more fuel.

Theoretical Combustion Process

The ideal combustion process is during which a fuel is burnt completely with theoretical air is called stoichiometric or theoretical combustion of that fuel.



Theoretical combustion process \rightarrow no unburnt fuel
no free O_2 in products

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Actual Combustion process

In actual combustion process it is common practice to use more air than the stoichiometric amount to increase the chances of complete combustion or to control the temperature of combustion chamber.

Note: Orsat Gas Analyser: It is used to analyse the composition of combustion gases.

Enthalpy of Formation (compound)

It is the amount of energy released or absorbed when 1 mole of a compound is formed from its respective stable elements, the compound and elements all being at T_{ref} and P_{ref} (standard state).



$$\Delta \bar{h}_f = \Delta H_R = \bar{h}_{CO_2} - (\bar{h}_C + \bar{h}_{O_2})$$

(product)

$$\Delta \bar{h}_f = \Delta H_R = \bar{h}_{\text{compound}}$$

$\Delta \bar{h}_f$ - molar enthalpy
 ΔH_R - Enthalpy of



This reaction is exothermic, so for the CO_2 to exit at the same temperature as entering elements, there should be heat transfer from reactor to surroundings.

of formation
 Reaction

Note: An enthalpy datum for the study of reacting systems can be established by assigning arbitrarily a value of zero to the enthalpy of the stable elements at a state called the standard reference state ($T_{ref} = 25^{\circ}\text{C}$ & $P_{ref} = 1 \text{ atm}$).

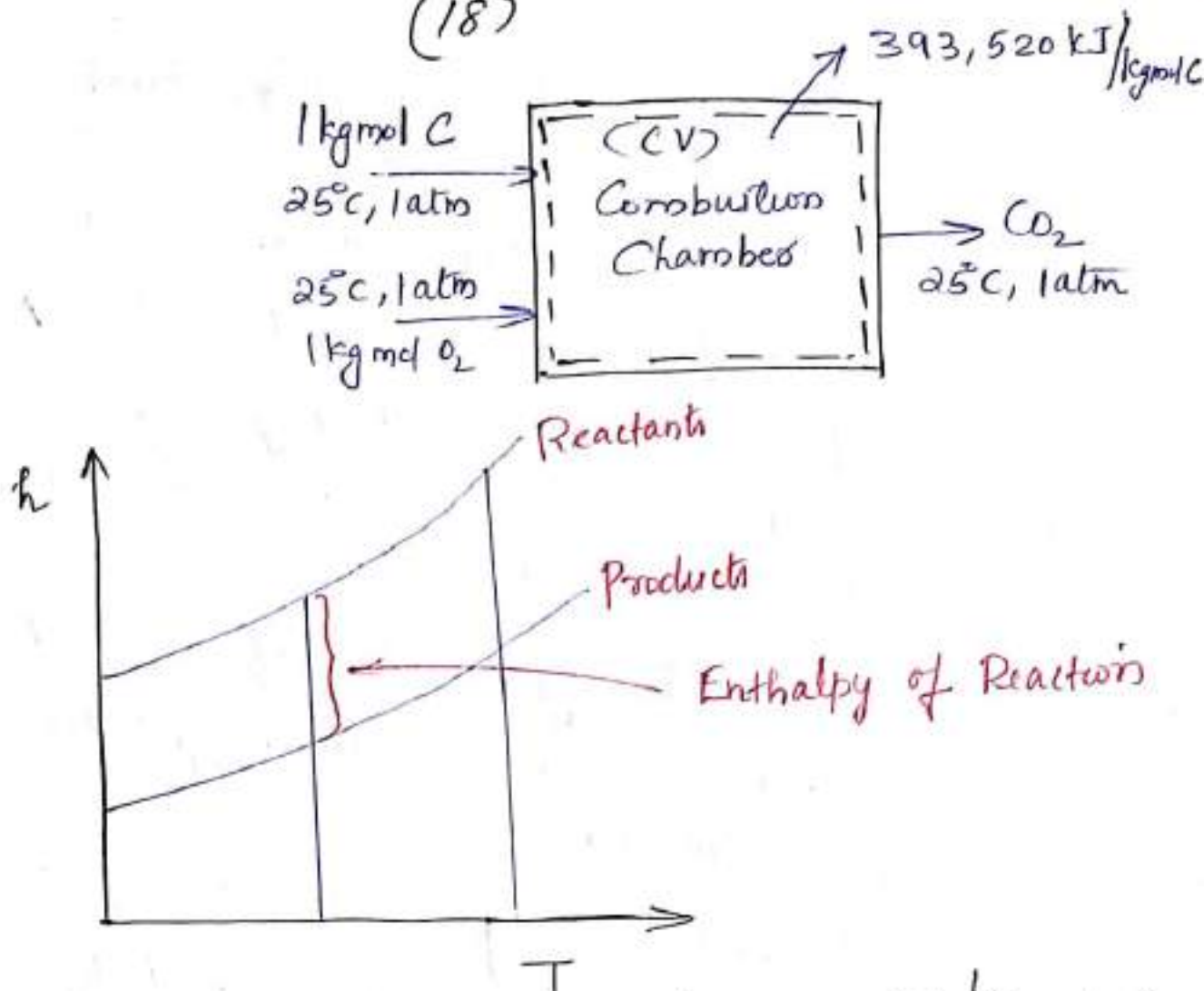
Evaluating Enthalpy: The specific enthalpy of a compound at a state other than the standard state is found by adding the specific enthalpy change Δh between the standard state and state of interest to the enthalpy of formation.

$$\bar{h}_{\text{Compound}} = \bar{h}_f + \Delta h$$

Enthalpy of Reaction (Δh_R)

It is defined as the difference between the enthalpy of product at a specified state and enthalpy of reactant at the same state for a complete reaction.

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Enthalpy of Reaction, $\Delta h_R = h_{\text{products}} - h_{\text{Reactants}}$

Enthalpy of Combustion: It represents the amount of heat (energy) released during a steady flow combustion process when 1 kgmol of fuel is burnt completely at a specified temperature and pressure.

$$\Delta h_R = h_c = h_{\text{product}} - h_{\text{Reactants}}$$

Heating Value of the Fuel.

Heating value is defined as the amount of heat released when 1 kg mol of fuel is burnt completely in a steady flow process while products and reactants are at a specified state.

The heating value of a fuel is a positive number equal to the magnitude of enthalpy of combustion.

Higher Heating value: It is obtained when all the water formed by combustion is a liquid.

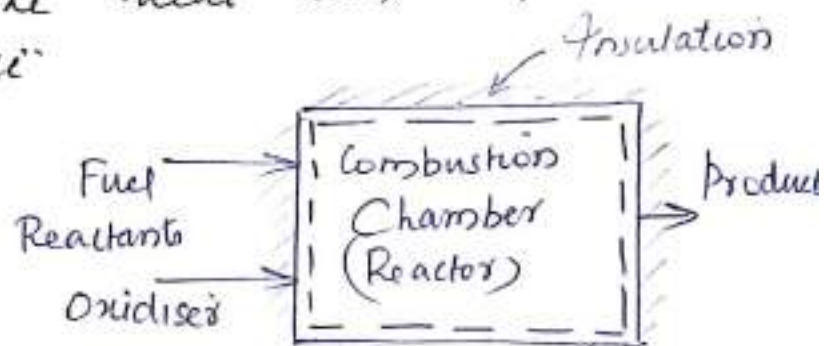
Lower Heating value: It is obtained when all the water formed by combustion is a vapour.

$$HHV = LHV + \text{Energy reqd to vaporise the liquid}$$

$$HHV = LHV + (m \cdot h_{fg})_{H_2O}$$

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Adiabatic Flame Temperature /
Adiabatic Combustion Temperature

In the absence of any work interactions and any change in kinetic and potential energy, the chemical energy released during a combustion process is either lost as heat to surroundings or is used internally to raise the temperature of combustion products. The smaller the heat loss, larger the temperature rise.



The temperature of a combustion chamber becomes maximum when combustion is complete and no heat is lost to the surroundings ($Q=0$). This maximum temperature achieved in the limit of adiabatic operation of the reactor is called adiabatic flame or adiabatic combustion temperature.

Adiabatic flame temperature can be determined by setting, $W=0$, $Q=0$

$$Q - W = H_{\text{product}} - H_{\text{Reactants}}$$

$$H_{\text{products}} = H_{\text{Reactants}}$$