

Basic concepts of Thermodynamics.

→ Systems $\left\{ \begin{array}{l} \text{Isolated} - \text{no exchange of energy \& matter} \\ \text{Closed} - \text{exchange of energy but not matter} \\ \text{Open} - \text{" " " " \& matter both.} \end{array} \right.$

→ Boundary $\left\{ \begin{array}{l} \text{adiabatic} \rightarrow \text{No exchange of heat / thermal interaction} \\ \text{diathermic} \rightarrow \text{exchange of heat through a boundary} \end{array} \right.$

→ Thermodynamic variable $\left\{ \begin{array}{l} \text{Intensive} \rightarrow P (P_1 = P_2) ; y = y_1 = y_2 \\ \text{extensive} - V (V_1 + V_2 = V) ; y = y_1 + y_2 \end{array} \right.$

f and g intensive $\Rightarrow f+g, fg, f/g, \partial f/\partial g \rightarrow$ all intensive

f and g extensive $\Rightarrow f+g \rightarrow$ ext; $f/g, \partial f/\partial g \rightarrow$ intensive

f - I, F - E $\Rightarrow fF, F/f, \partial F/\partial f \rightarrow$ extensive.

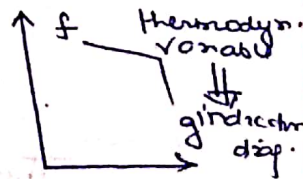
→ Equilibrium state $\left\{ \begin{array}{l} \text{Mechanical} \rightarrow \text{no stress or pressure felt} \\ \text{Thermal equilibrium} \rightarrow \text{no change in temp.} \\ \text{chemical} \rightarrow \text{no change in chemical composition} \end{array} \right.$

→ Processes:

• Thermodynamic process: values of thermodynamic variables change from one equilibrium state to another.

Reversible \rightarrow if every possible state of a ~~thermodynamic~~ process is retracable \Rightarrow process should be very slow

Irreversible \rightarrow if not retracable \rightarrow



• Quasi-static process: when a process is carried out extremely slowly so that every state through which the system passes departs only infinitesimally from equilibrium.

→ Zeroth Law of Thermodynamics: - If two systems are in thermal equilibrium with a third system, then they will also be in thermal equilibrium with each other. *The state of such systems can be determined by assigning a parameter called temp. Thus, temp. of a system is a parameter that determines whether a system is in thermal eqm or not with other sys.*

Proof: Consider three systems 1, 2, and 3 in equilibrium separately. Each system can be described by two independent variables P and V. We choose system P₃, V₃ to be in equilibrium with 1 (P₁, V₁) and 2 (P₂, V₂) individually. Then, the condition ~~between~~ of equilibrium between systems 1 and 3 can be written as

$$f_{13}(P_1, V_1, P_3, V_3) = 0 \quad \rightarrow \textcircled{1} \Rightarrow \text{for 2 systems in equilibrium, there is a definite relationship b/w 4 variables \& for fixed } P_1, V_1 \& P_3, V_3 \text{ will be uniquely determined i.e. only 2 of 4 is independent.}$$

Summary, the eqm b/w 2 and 3. $\rightarrow \textcircled{2}$

$$f_{23}(P_2, V_2, P_3, V_3) = 0$$

From both equations (1) and (2), p_3 can be uniquely determined as

$$p_3 = F_{13}(p_1, v_1, v_3) \quad \text{--- (3)}$$

$$\Rightarrow p_3 = F_{23}(p_2, v_2, v_3) \quad \text{--- (4)}$$

Elimination p_3 b/w (3) and (4):

$$F_{13}(p_1, v_1, v_3) = F_{23}(p_2, v_2, v_3) \quad \text{--- (A)}$$

This may be solved for p_1 and we get,

$$p_1 = G(p_2, v_1, v_2, v_3)$$

From zeroth law, if 1 and 3 and 2 and 3 are in eqm, then 1 and 2 also must be in eqm i.e. we must have,

$$f_{12}(p_1, v_1, p_2, v_2) = 0 \quad \text{--- (5)}$$

we may again solve for p_1 and get,

$$p_1 = F_{12}(v_1, p_2, v_2) \quad \text{--- (6)}$$

$\therefore p_1$ must be uniquely determined by v_1, p_2, v_2 and hence v_3 must cancel out in (A). Therefore, we may write:

$$F_{13} = \phi_1(p_1, v_1) \eta(v_3) + \xi(v_3)$$

$$F_{23} = \phi_2(p_2, v_2) \eta(v_3) + \xi(v_3)$$

$$\Rightarrow \phi_1(p_1, v_1) = \phi_2(p_2, v_2) \rightarrow \text{Thermal eqm b/w 1 and 2.}$$

In general, we can write,

$$\boxed{\phi_1(p_1, v_1) = \phi_2(p_2, v_2) = \phi_3(p_3, v_3)}$$

$$\Leftrightarrow \boxed{\phi(p, v) = \text{constant} = \theta}$$

\Rightarrow If two macro states are in thermal eqm, then there exists a single valued function of p and v for each system having common numerical value.

This constant is called Temp.

i.e. in thermal equilibrium temp remains constant.

We can write in general,

$$\boxed{\phi(p, v, \theta) = \text{constant}} \quad \text{Equation of state.}$$

Application

From eqn of state, we know that,

$$\phi(p, v, T) = 0$$

We can determine p as:

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

An infinitesimal change in p would be:

$$dp = \left(\frac{\partial p}{\partial v}\right)_T dv + \left(\frac{\partial p}{\partial T}\right)_v dT$$

For an isobaric process,

$$dP = 0$$

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

We know that,

coefficient of volume expansivity: $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$

isothermal elasticity = $\frac{1}{\text{isothermal compression}} = \frac{1}{\beta} = -V \left(\frac{\partial P}{\partial V}\right)_T$

{ As $\partial T = 0$, $\partial V \propto -\partial V$ }

\therefore we get,

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_V = +\alpha E_T} \rightarrow \text{change in pressure with change in temp.}$$

\therefore we can write:

$$\boxed{dP = -\frac{E_T}{V} dV + \alpha E_T dT}$$

$$\frac{1}{P} \left(\frac{\partial P}{\partial T}\right)_V = \text{pressure coefficient}$$

\therefore For an isochoric process:

$$dP = \alpha E_T dT$$

$$\Rightarrow \boxed{P_2 - P_1 = \alpha E_T (T_2 - T_1)}$$

* Pressure coefficient = $\alpha / \beta_T = \boxed{\alpha E_T}$

(A) α for van der Waals gas.

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

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)$$

$$PV + \frac{a}{V} - Pb - \frac{ab}{V^2} = RT$$

$$\alpha \left(P - \frac{a}{V^2} + \frac{2ab}{V^3}\right) dV = R dT$$

$$\alpha \frac{dV}{dT} = \frac{R}{P - \frac{a}{V^2} + \frac{2ab}{V^3}}$$

$$\alpha = \frac{R}{PV - \frac{a}{V} + \frac{2ab}{V^2}}$$

$$= \frac{RV^2}{RV^3 - aV + 2ab}$$

$$= \frac{RV^2}{V^3 \left(P - \frac{a}{V^2}\right) + 2ab}$$

$$= \frac{RV^2(V-b)}{RTV^3 - 2ab(V-b)}$$

$$\alpha V \left(-\frac{2a}{V^3}(V-b) + \left(P + \frac{a}{V^2}\right)\right) = R dT$$

$$\alpha \frac{dV}{dT} = \frac{R}{-\frac{2a}{V^3}(V-b) + \left(P + \frac{a}{V^2}\right)}$$
$$= \frac{R}{-\frac{2a}{V^3}(V-b) + \frac{RT}{V-b}}$$

$$\alpha = \frac{RV^2(V-b)}{RTV^3 - 2a(V-b)^2}$$

$$\textcircled{B} \beta_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad \beta_T = +\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

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

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

$$\Rightarrow dP = \left(-\frac{RT}{(V-b)^2} + \frac{2a}{V^3} \right) dV$$

$$\begin{aligned} \Rightarrow \frac{dV}{dP} &= \frac{1}{\frac{RT}{(V-b)^2} - \frac{2a}{V^3}} \\ &= \frac{(V-b)^2 V^3}{RTV^3 - 2a(V-b)^2} \end{aligned}$$

$$\Rightarrow \boxed{\beta = \frac{V^2 (V-b)^2}{RTV^3 - 2a(V-b)^2}}$$

Taking pressure and temp. as independent variables:

$$V = V(P, T).$$

$$\Rightarrow dV = \left(\frac{\partial V}{\partial P} \right)_T dP + \left(\frac{\partial V}{\partial T} \right)_P dT. \quad dV = \left(\frac{\partial V}{\partial P} \right)_T dP + \left(\frac{\partial V}{\partial T} \right)_P dT.$$

In terms of α and β_T ,

$$\frac{dV}{V} = -\beta_T dP + \alpha dT.$$

$$\Rightarrow \boxed{\frac{dV}{V} = -\beta_T dP + \alpha dT.}$$

For an isobaric process,

$$dP = 0$$

$$\Rightarrow \frac{dV}{V} = \alpha dT.$$

$$\Rightarrow \ln V = \alpha T$$

$$\text{ex: } \beta_T = \frac{aT^3}{P^2} \Rightarrow \alpha = \frac{bT^2}{P}$$

$$\Rightarrow \frac{dV}{V} = -\frac{aT^3}{P^2} dP + \frac{bT^2}{P} dT.$$

$$\Rightarrow \boxed{\ln \left(\frac{V_2}{V_1} \right) = \frac{aT^3}{P_2} - \frac{aT^3}{P_1} + \frac{b}{P} (T_2^3 - T_1^3).}$$