

$$\frac{E_s}{E_T} = \left(\frac{\partial p}{\partial T} \right)_s \left(\frac{\partial T}{\partial V} \right)_s \frac{1}{\left(\frac{\partial p}{\partial T} \right)_T \left(\frac{\partial V}{\partial T} \right)_T} \quad (7)$$

Thermodynamical relation

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

$$\left(\frac{\partial T}{\partial p} \right)_s = \left(\frac{\partial V}{\partial S} \right)_p \Rightarrow \left(\frac{\partial p}{\partial T} \right)_s = \left(\frac{\partial S}{\partial V} \right)_p$$

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

Using these relations

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

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

$$\boxed{\frac{E_s}{E_T} = \frac{C_p}{C_V} = \gamma}$$

Ratio of isothermal and adiabatic elasticity

The coeff of volume elasticity

$$E = \frac{\text{Stress}}{\text{Volume strain}} = - \frac{dp}{dV/V}$$

isothermal elasticity Temp const

$$= -V \frac{dp}{dV}$$

The adiabatic elasticity E_s

$$E_s = \text{entropy const}$$

$$E_s = -V \left(\frac{dp}{dV} \right)_s$$

$$E_T = -V \left(\frac{dp}{dV} \right)_T$$

$$\text{So } E_s = -V \left(\frac{dp}{dV} \right)_s \quad \text{--- (1)}$$

$$E_T = -V \left(\frac{dp}{dV} \right)_T \quad \text{--- (2)}$$

$$\frac{E_s}{E_T} = \frac{\left(\frac{dp}{dV} \right)_s}{\left(\frac{dp}{dV} \right)_T} \quad \text{--- (3)}$$

$$\frac{E_s}{E_T} = \frac{\left(\frac{\partial p}{\partial T} \frac{\partial T}{\partial V} \right)_s \left(\frac{\partial p}{\partial T} \right)_s \left(\frac{\partial T}{\partial V} \right)_s}{\left(\frac{\partial p}{\partial s} \frac{\partial s}{\partial V} \right)_T \left(\frac{\partial p}{\partial s} \right)_T \left(\frac{\partial s}{\partial V} \right)_T}$$

When $\frac{2a}{RT} > b$ or $T < \frac{2a}{Rb}$ then $\left(\frac{\partial T}{\partial p}\right)_H = -$
cooling effect

$\frac{2a}{RT} < b$ $\left(\frac{\partial T}{\partial p}\right)_H = \text{is negative}$ ∂T is positive

gas will be heated

$$\frac{2a}{RT} = b \quad T = \frac{2a}{Rb} \quad \text{inversion}$$

$$\frac{RT(V-b)}{RT - \frac{2a}{V^3}(V^2 + b^2 - 2Vb)}$$

$b \ll V$ and $2Vb$

is very small

So we can write

$$\frac{2a}{V^3}(V^2 + b^2 - 2Vb) \approx \frac{2a}{V^3} V^2$$

$$= \frac{V-b}{RT - \frac{2a}{V}} = \frac{V-b}{1 - \frac{2a}{VRT}}$$

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

$$= (V-b) \left(1 + \frac{2a}{VRT} \right)$$

$$= V-b + \frac{2a}{RT} + \dots \text{neglecting higher}$$

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

$$\text{So } \mu = \left(\frac{\partial T}{\partial p} \right)_H = \frac{1}{c_p} \left[\frac{2a}{RT} - b \right]$$

$$\mu = +ve$$

$$\mu = -ve$$

$$= 0$$

$$\frac{\partial V}{\partial T} = \frac{R}{P}$$

$$\text{So } T \left(\frac{\partial V}{\partial T} \right) P = \frac{RT}{P} = V$$

$$V - V = 0$$

$$u = 0$$

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

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

at const pressure we apply product rule

~~$$= \frac{\partial a}{\partial V} \left(\frac{dV}{dT} \right)$$~~

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

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

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

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

Multiply by T

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

if we take entropy function of T, P

$$\text{So } ds = \left(\frac{ds}{dT}\right)_P dT + \left(\frac{ds}{dP}\right)_T dP \quad \text{--- ②}$$

Substituting the value ds in equation ①

$$T \left(\frac{ds}{dT}\right)_P dT + T \left(\frac{ds}{dP}\right)_T dP + V dP = 0$$

$$T \left(\frac{ds}{dT}\right)_P \rightarrow C_P \text{ and } \left(\frac{ds}{dP}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P \text{ Maxwell relation}$$

$$C_P dT - T \left(\frac{\partial V}{\partial T}\right)_T dP + V dP = 0$$

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

$$dT = \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T}\right)_P - V \right] dP$$

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

External work done on the gas by piston 1

$$= P_1 A x_1$$

$$= P_1 V_1$$

external work done by the ~~exactly~~ gas on piston 2

$$= P_2 A x_2$$

$$= P_2 V_2$$

Net ~~pressure~~ work done $= P_2 V_2 - P_1 V_1$ cylinder is
freely undisturbed

then $dQ = 0$, Change in internal energy

$$\Delta Q = \Delta U + \Delta W$$

$$0 = U_2 - U_1 + P_2 V_2 - P_1 V_1$$

$$\text{then } U_1 + P_1 V_1 = U_2 + P_2 V_2$$

$U + PV$ is conserved ~~the~~ so

$H_1 = H_2$ It is obvious

when $P_2 V_2 > P_1 V_1$ $U_2 < U_1$ I.E decrease

$P_2 V_2 < P_1 V_1$ $U_2 > U_1$ cooling effect
heating effect will be there

Expression for Change in Temp in Joule Thomson
expansion.

$$H = U + PV = \text{const}$$

$$dH = dU + d(PV) = dU + PdV + VdP$$

we know that $dU = TdS - PdV$

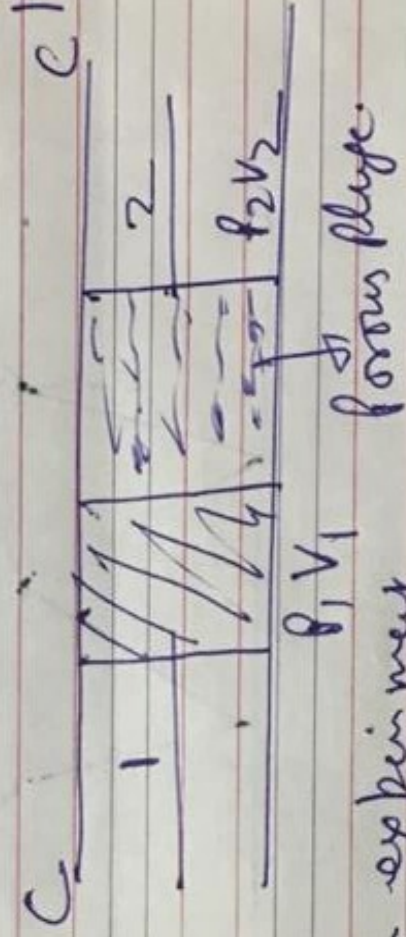
$$\text{So } dH = TdS - PdV + PdV + VdP$$

$$dH = TdS + VdP = 0 \quad \text{--- (1)}$$

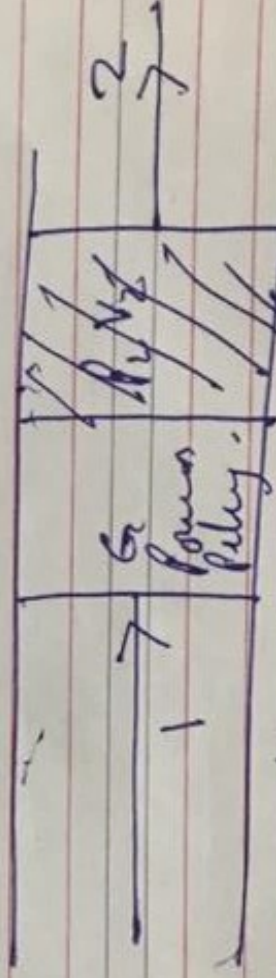
Joule Helmholtz expansion

Const P High Porous Plug exp.
thermally isolated. when gas from constant
high pressure passes through porous plug. to
low pressure side suffer change in pressure
create temp change. this is called
Joule Thomson or Joule Helmholtz effect.

Theory of Joule Thomson Expansion



CC' $\rightarrow$ cylinder experiment
even conductively wall



When gas expands, the pressure difference
created