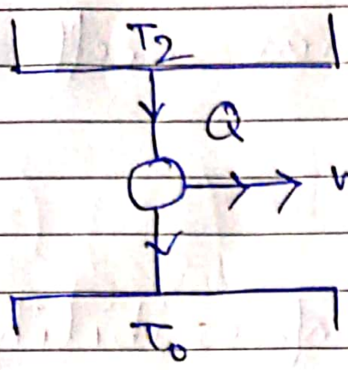
Entropy and available energy:

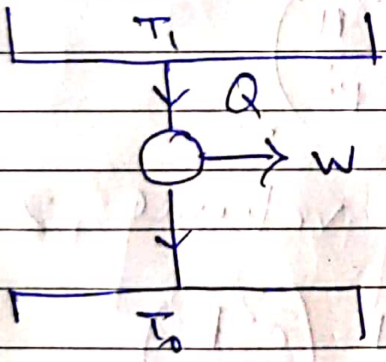


$$\eta = \left(1 - T_0/T_2\right)$$

$$\Rightarrow W_{max} = Q\eta$$

$$\Rightarrow W_2 = Q\left(1 - T_0/T_2\right)$$

Only part of the heat energy from reservoir is available for work.



$$W_1 = Q\left(1 - \frac{T_0}{T_1}\right)$$

Q/T_1 = entropy gain of res T_1

$-\frac{Q}{T_2}$ = entropy decrease of res T_2

$$E' = W_2 - W_1 = Q\left[\frac{T_0}{T_1} - \frac{T_0}{T_2}\right) = T_0\left[\frac{Q}{T_1} - \frac{Q}{T_2}\right]$$

$$= T_0\left[\Delta S^{u}_{irr}\right]$$

= Lost work / energy not available for work

Response Function: 2nd Order Quantities.

Isobaric thermal expansion coefficient.

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\left(\frac{\partial^2 G}{\partial T \partial P}\right)$$

Isothermal & Adiabatic Compressibility.

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_T$$

$$K_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S = -\frac{1}{V}\left(\frac{\partial^2 H}{\partial P^2}\right)_S$$

Specific heat at constant volume & pressure

$$C_V = \left(\frac{dQ}{dT}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V$$

$$C_P = \left(\frac{dQ}{dT}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P$$

$$C_P \geq 0 \; ; \; C_V \geq 0 \; ; \; K_T \geq 0 \; ; \; K_S \geq 0$$

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

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

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

$$= -\left(\frac{\partial V}{\partial T}\right)_P \Big/ \left(\frac{\partial V}{\partial P}\right)_T = \frac{\alpha_P}{K_T}$$

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

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

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

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

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

$$= TV\left(\frac{\alpha_P^2}{K_T}\right)$$

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M	T	W	T	F	S	S	M	T	W	T	F	S	S
		1	2	3	4	5	6	7	8	9	10	11	12
13	14	15	16	17	18	19	20	21	22	23	24	25	26
27	28	29	30	31									

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

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

$$\Rightarrow -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S - \frac{1}{V}\left(\frac{\partial V}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_T$$

$$\Rightarrow K_T - K_S = -\frac{1}{V}\left(\frac{\partial V}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_T$$

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

$$= \frac{V\left[\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right]^2 T}{T\left(\frac{\partial S}{\partial T}\right)_P}$$

$$= TV\left(\frac{\alpha_P^2}{C_P}\right)$$

$$\Rightarrow \frac{C_P - C_V}{K_T - K_S} = \frac{TV\left(\alpha_P^2/K_T\right)}{TV(\alpha_P)^2/C_P} = \frac{C_P}{K_T} \Rightarrow \boxed{\frac{C_P}{C_V} = \frac{K_T}{K_S}}$$

$$\Rightarrow \boxed{K_T(C_P - C_V) = C_P(K_T - K_S) = TV\alpha_P^2}$$

2021

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

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

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

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

$$= C_v\, dT - T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P dV$$

$$TdS = C_v\, dT + \frac{\alpha T}{K_T} dV$$

$$\boxed{\begin{aligned} TdS &= C_p\, dT - T\left(\frac{\partial V}{\partial T}\right)_P dP \\ TdS &= C_p\, dT - \alpha T V\, dP \end{aligned}}$$

Internal Energy Eq^n:

$$dU = TdS - PdV$$

$$U = U(T,V)$$

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

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

$$\Rightarrow \boxed{dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV}$$

$$U = U(T,P)$$

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

Define $\left(\frac{\partial E}{\partial S}\right)_{V,N} = T$ = Temperature.

$-\left(\frac{\partial E}{\partial V}\right)_{S,N} = -P$ = Pressure.

$\left(\frac{\partial E}{\partial N}\right)_{V,S} = \mu$ = Chemical Potential.

$\Rightarrow dE = TdS - pdV + \mu dN$

T, p, μ are intensive parameter since they are derivative ~~of~~ wrt extensive parameter.

$dN = 0 \Rightarrow dE = TdS - pdV$

$TdS = đQ$ = heat absorbed by system

$-pdV = đW$ = mechanical work done by the system.

Heat ~~absorb~~ absorbed $\Rightarrow$ Entropy increase

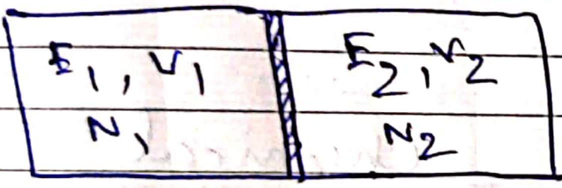
Alternatively. $S = S(E, V, N)$

$$TdS = dE + pdN - \mu dN$$

$$\Rightarrow dS = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN$$

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T} ; \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{p}{T} ; \left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T}$$

Thermal Equilibrium:



$$E = E_1 + E_2$$

$$S = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2)$$

1. Wall is imoveable, impermiable, insulating
$\Rightarrow$ Nothing will happen.

2. Wall is now only allowing energy exchange.

Q: What is final E_1 & E_2 after equilibrium is reached.

$$E = E_1 + E_2 \Rightarrow dE = dE_1 + dE_2 = 0$$

Change in entropy

$$dS = \left(\frac{\partial S_1}{\partial E_1}\right)_{V_1, N_1} dE_1 + \left(\frac{\partial S_2}{\partial E_2}\right)_{V_2, N_2} dE_2$$

$$\Rightarrow dS = \frac{dE_1}{T_1} + \frac{dE_2}{T_2}$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1$$

At equilibrium $dS = 0$ (since S is maximized by Postulate - II)

$\Rightarrow T_1 = T_2$ since $dE_1 \neq 0$

3. Wall is now <u>also</u> allowed to move.

$E = E_1 + E_2$ $\quad\quad V = V_1 + V_2$

$\Rightarrow dE_1 = -dE_2$ $\quad\quad dV_1 = -dV_2$

$$dS = \left(\frac{\partial S_1}{\partial E_1}\right)_{V_1 N_1} dE_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_{E_1 N_1} dV_1 + \ldots$$

$$= dE_1\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) dV_2$$

$dS = 0$ At equilibrium $\Rightarrow$

$$\boxed{\begin{aligned} T_1 &= T_2 \\ p_1 &= p_2 \end{aligned}}$$

4.) Similarly for chemical eq $\boxed{\mu_1 = \mu_2}$

Grand Thermodynamic Potential.

$$\Phi = E - TS - \mu N = F - \mu N =$$

$$d\phi = dE - TdS - SdT - \mu dN - Nd\mu$$

$$= -SdT - PdV - Nd\mu$$

$$\left(\frac{\partial \phi}{\partial T}\right)_{V,\mu} = -S \, ; \left(\frac{\partial \phi}{\partial V}\right)_{T,\mu} = -P \, ; \left(\frac{\partial \phi}{\partial \mu}\right)_{T,V} = -N$$

If $\underbrace{dT = 0, \; dV = 0,}$ $d\mu = 0$

$d\phi = 0$.