

Thermodynamics

- For conservative forces $\nabla \times F = 0$

1 First Law of Thermodynamics

- $dU + dE_k + dE_p = dQ + dW$
 - dU is generally in per unit mass.
 - $dE_k + dE_p$ is generally **negligible**.
 - dQ is the heat **given** to the system.
 - dW is the work done **on** the system.
 - $dW = -P\Delta V$

- Energy Balance

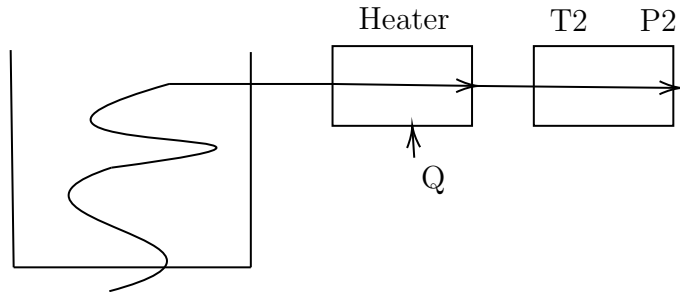
$$\frac{d(mU)_{cv}}{dt} + \Delta \cdot \left[\{ (U + PV) + \frac{1}{2}v^2 + gz \} \dot{m} \right] = \dot{Q} + \dot{W}$$

- $\frac{d(mU)_{cv}}{dt}$ here, **cv** means **control volume** which becomes *zero* in *steady state & slow process*.
- $U + PV = H$
- \dot{W} is the **shaft work**

- Flow Calorimeter

Used to find enthalpy of a system

$$H = Q$$



- Thermal Equilibrium

- Mechanical (Sum of all forces is 0)
- Thermal (No gradient of temp) ($\nabla T = 0$)
- Chemical (No gradient of chemical potential)

- Quasi-Static Process

- PdV & TdS like terms can be applied only in a quasi-static process
- τ_r or the *relaxation time* is the time required to achieve equilibrium when disturbed

- Reversible Processes

- Frictionless
- we can write $-PdV$ for only reversible processes

- Specific heat (C) $\equiv \frac{\partial Q}{\partial T} \Rightarrow$ So, $mC\partial T = Q$

$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_V \quad \& \quad C_P \equiv \left(\frac{\partial H}{\partial T} \right)_P$$

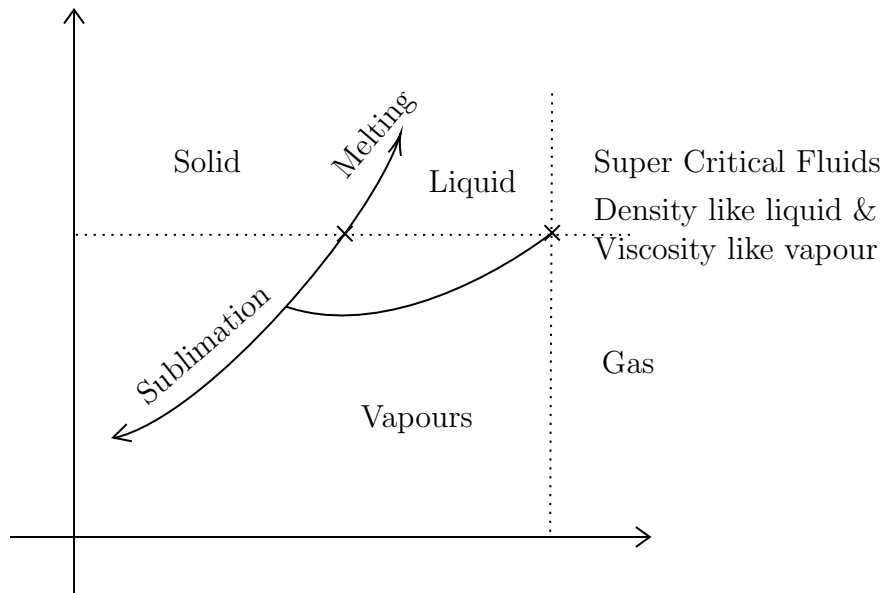
$$C_P - C_V = R$$

- Gibbs Phase Rule

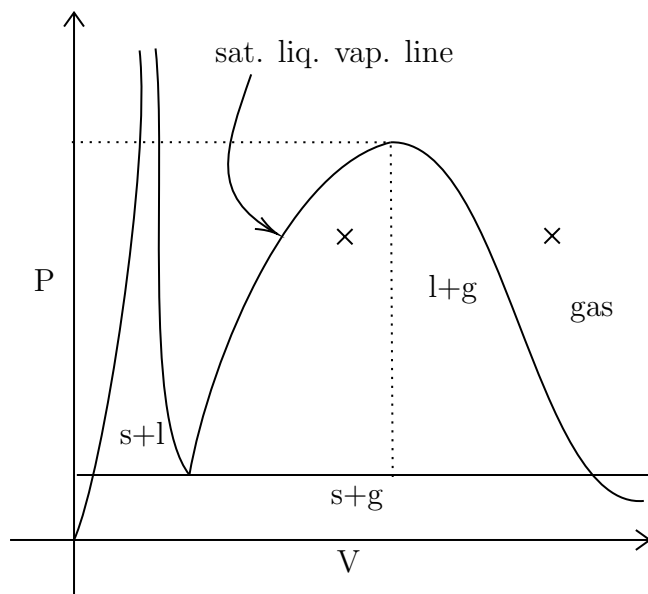
$$F = 2 - \pi + N$$

- F is the no. of *intensive* degree of freedom
- π is the no. of phases
- N is the no. of chemical species

- Vol. properties of pure substance



This curve is a slice of constant V .



Super cooled liquid exists at temp lower than the boiling point at that pressure.

- Volume Expansivity

Think of it as fractional increase in volume per unit rise in temperature (division by V because *fractional*).

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

- Isothermal Compressibility

$$\kappa \equiv \frac{-1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

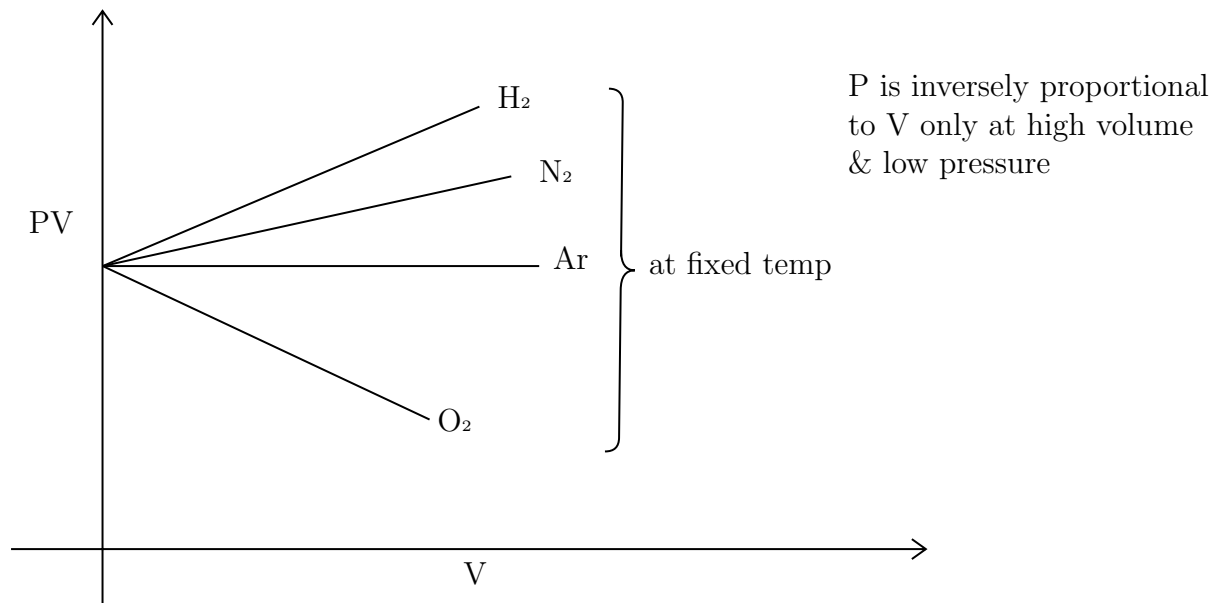
$$\frac{\partial V}{V} = \beta \partial T - \kappa \partial P$$

$$\Rightarrow \ln \left(\frac{V_2}{V_1} \right) = \beta(T_2 - T_1) - \kappa(P_2 - P_1)$$

Fractional decrease in volume per unit change in pressure. Here, negative sign $-$ is to maintain sign convention.

For incompressible fluids $\beta = \kappa = 0$

- Equation of State



—

$$T(\text{Kelvin scale}) = \frac{273.16(PV)^*}{227118.8 \text{ cm}^3 \text{ bar mol}^{-1}}$$

- $PV = a(T) + b(T)P + c(T)P^2$
 a, b, c are temperature dependent constants.
- $Z = \frac{PV}{RT}$
 $Z = 1 + B'P + C'P^2 + \dots$

- Virial Equation of State

$$\begin{aligned} PV &= a + bP + cP^2 + \dots \\ &= a[1 + B'P + C'P^2 + \dots] \\ Z &= 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots \\ B' &= \frac{B}{RT} \quad , \quad C' = \frac{C - B^2}{(RT)^2} \end{aligned}$$

if we take first two terms,

$$Z = 1 + \frac{BP}{RT} = \frac{PV}{RT}$$

$$\implies P = \frac{RT}{V - B} \quad (1)$$

$$Z = 1 + \frac{B}{V} = \frac{PV}{RT}$$

$$P = \frac{RT}{V} \left(1 + \frac{B}{V} \right) \quad \dots \quad (2)$$

(2) is a special case of (1) when $B \ll V$.

During Ideality (low P)

$$PV^{ig} = a = RT$$

- Vanderwaal Eqn. of State

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

where,

$\frac{a}{V^2} = \text{interaction force}$

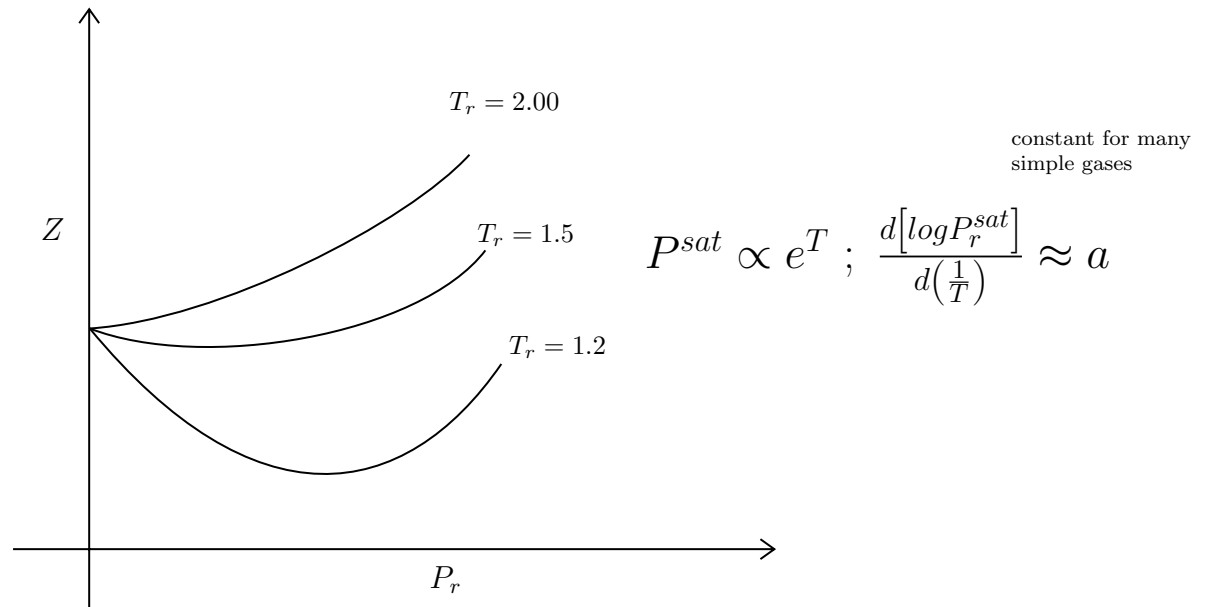
$b = \text{finite size of molecules}$

$$a = \frac{27 R^2 T_c^2}{64 P_c}, \quad b = \frac{1 R T_c}{8 P_c}, \quad P_c = \frac{a}{27 b^2}, \quad T_c = \frac{8 a}{27 R b}, \quad V_c = 3 b$$

$$Z_c = \frac{P_c V_c}{R T_c} = \frac{3}{8}$$

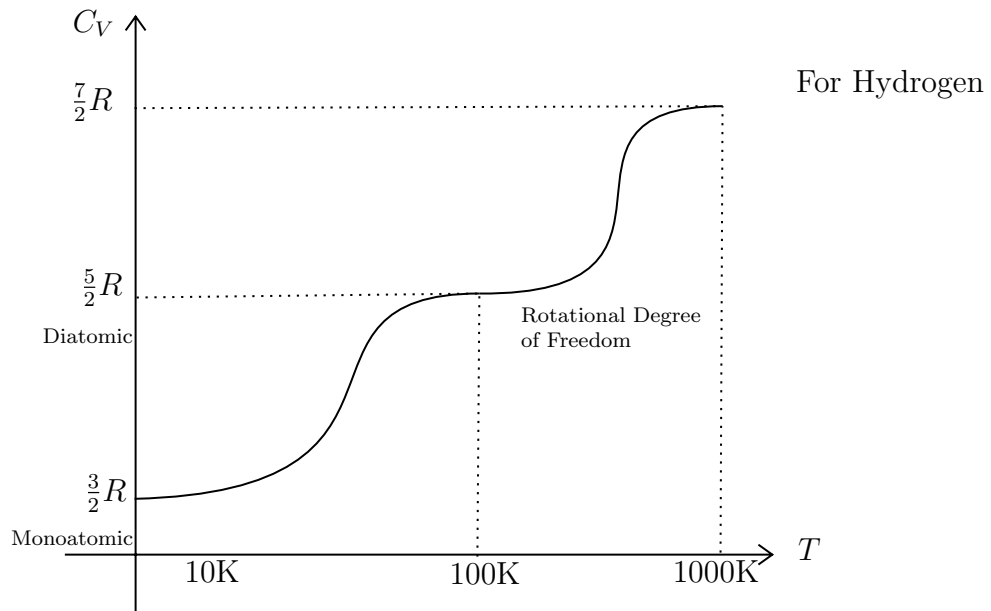
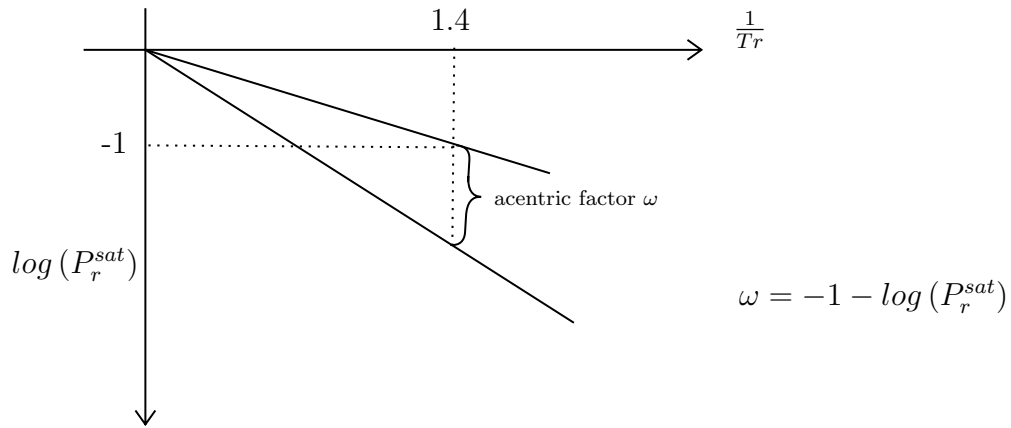
$$P_r = \frac{P}{P_c}, \quad V_r = \frac{V}{V_c}, \quad T_r = \frac{T}{T_c}$$

Fluids with any of the above 2 same have same compressibility factor & deviate from ideal gas behaviours by same factor.



- **Acentric Flow** : non sphericity of molecules

According to law of corresponding state for 3 parameters, if P^r , T^r , & ω of the species is same, then the other reduced quantities will be the same.



- **Sensible Heat Effects**

$$\partial U = \left(\frac{\partial U}{\partial T} \right)_V \partial T + \left(\frac{\partial U}{\partial V} \right)_T \partial V \text{ [Pure Substances in Single Phase]}$$

$$\text{Here : } \partial U = \left(\frac{\partial U}{\partial T} \right)_V \partial T = C_V dT$$

$$\partial H = \left(\frac{\partial H}{\partial T} \right)_P \partial T + \left(\frac{\partial H}{\partial P} \right)_T \partial P$$

Here: $\partial H = \left(\frac{\partial H}{\partial T} \right)_P \partial T = C_P dT$

For incompressible substance: $Q = \Delta V = \int C_V dT$

For ideal gas/ low pressure gas: $Q = \Delta H = \int C_P dT$

– Empirical Relation

$$\frac{C_P^{ig}}{R} = A + BT + CT^2 + DT^{-2}$$

$$\frac{C_V^{ig}}{R} = \frac{C_P^{ig}}{R} - 1$$

$$\int_{T_0}^T C_P dT = R \left[A(T_0 - 1)T_0 + \frac{B}{2}T_0^2(\tau^2 - 1) + \frac{C}{3}T_0^3(\tau^3 - 1) + \frac{D}{T_0} \left(\frac{\tau - 1}{\tau} \right) \right]$$

$$\tau = \frac{T}{T_0} \quad \left\langle \frac{C_P}{R} \right\rangle (T - T_0) = \int_{T_0}^T \frac{C_P}{R} dT$$

$$\left\langle \frac{C_P}{R} \right\rangle = A + \frac{B_0 T_0}{2}(Z + 1) + \frac{C}{3}T_0^3(Z^2 + Z + 1) + \frac{D}{T_0} \left(\frac{1}{Z} \right) \quad (1)$$

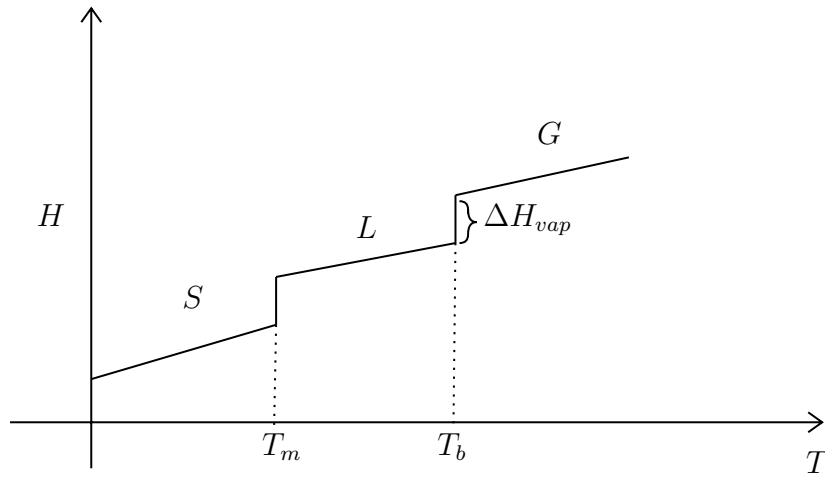
To find τ for a given ΔH use this

- Guess a τ & substitute in (??)
- Substitute $\langle C_P \rangle$ in below equation to find next τ

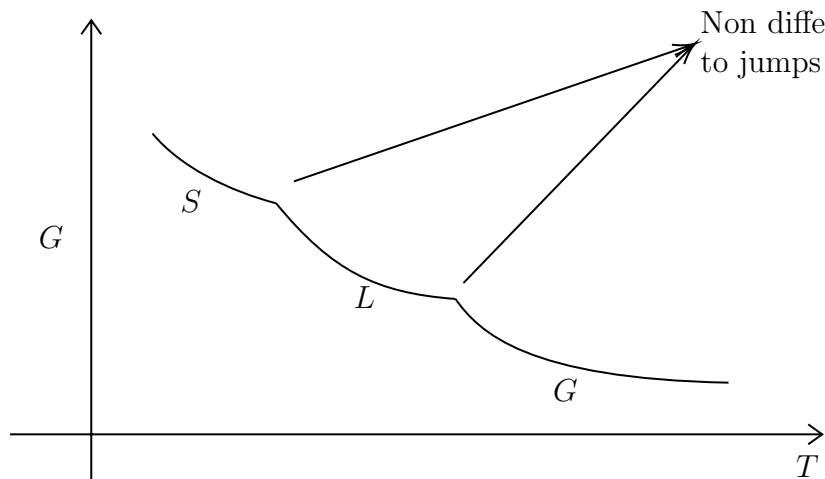
$$\tau = 1 + \frac{\Delta H}{T_0 \langle C_P \rangle}$$

- Repeat the process till $[\tau^{(N)} - \tau^{(N-1)}] < 10^{-5}$

• Latent Heat of Pure Substance

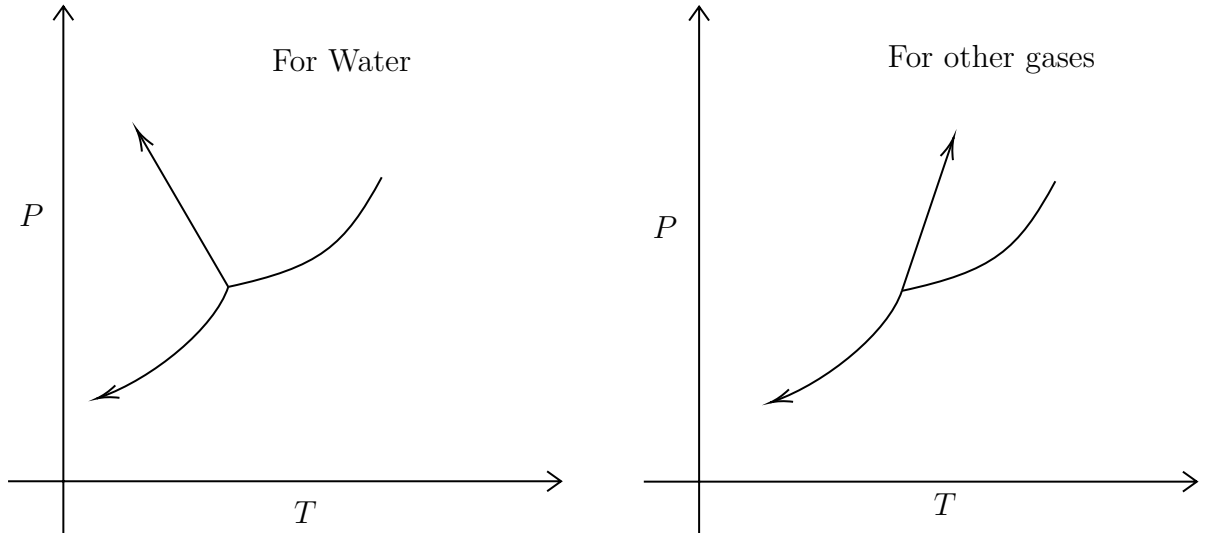


Almost same for all substances



- Clayperon Equation

$$\left(\frac{\partial P}{\partial T}\right)_{\text{Coexistence Curve}} = \frac{\Delta H_{\text{Transition}}}{T \Delta V_{\text{Transition}}}$$



For water
 $\left(\frac{\partial P}{\partial T}\right)_{S \rightarrow L} < 0$ as $\Delta H_{S \rightarrow L} > 0$ and $V_L - V_S < 0$

If we are given T_0 we can find $\left(\frac{\partial P}{\partial T}\right)$ by above curve, $\Delta H_{Transition}$ by ΔH vs T curve and $\Delta V_{Transition}$ by P vs V graph.

- **Trouton Rule**

- Normal BP : In this, the temperature of boiling point at a pressure of 1 atm
- $\frac{\Delta H_{vap}}{RT_n} \simeq 10$ for almost every substance
- $\frac{\Delta H_n}{RT_n} = \frac{1.092(\ln P_C - 1.013)}{0.93 - T_n}$; It is basically $\ln \left(\frac{P_C}{P}\right)$ where P is 1 atm.

- **Watson's Equation** $\frac{\Delta H_2}{\Delta H_1} = \left(\frac{1 - T_{r2}}{1 - T_{r1}}\right)^{0.38}$

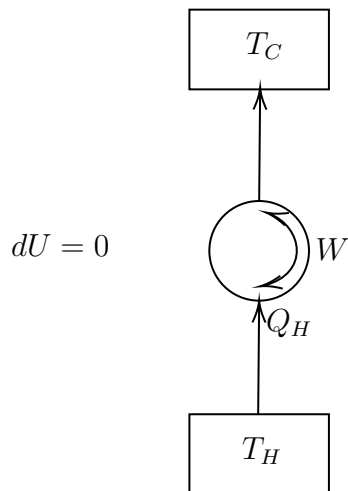
2 Second Law of Thermodynamics

- No apparatus can operate in such a way that it's only effect is to convert heat observed by the system completely to work done by a system.
- No process is possible which consists solely in the transfer of heat from one temperature level to a higher temperature level.
- Heat Engines: Cycles which involve absorption of heat at a higher temperature and rejection of heat at lower temperature.

$$Q_H - Q_C = W$$

- Q_H is heat absorbed
- Q_C is the heat rejected, it can never be zero

- Reversible Engine

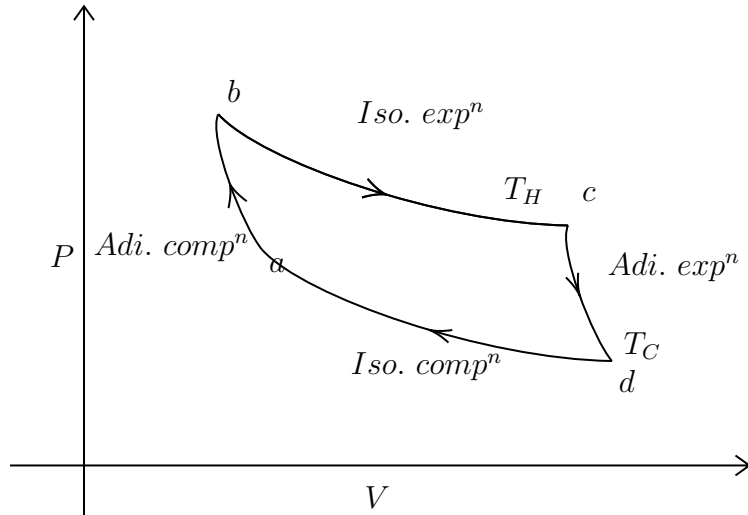


$$dU = Q_H - Q_C - W$$

$$\boxed{\eta = \frac{W}{|Q_H|} = 1 - \left| \frac{Q_C}{Q_H} \right|}$$

- Carnot Engine

- Carnot's Theorem: For two given heat reservoirs, no heat engine can have a thermal efficiency higher than a Carnot engine.
- Corollary: All Carnot engines operating between the same temperature have the same η



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- Thermodynamic Temperature Scaling

$$\eta = 1 - \frac{Q_C}{Q_H}$$

For carnot engine $\eta = 1 - \frac{T_C}{T_H}$

$$|Q_H| = RT_H \ln \left(\frac{V_c}{V_b} \right)$$

$$|Q_C| = RT_C \ln \left(\frac{V_d}{V_a} \right)$$

- Entropy

- $\frac{\partial Q}{\partial T}$ is a state function.

$$- \partial S^t = \frac{\partial Q_{rev}}{T} \quad \partial S \geq \frac{\partial Q}{T}$$

Equality holds when process is reversible.

- Entropy change for an ideal gas

$$\partial U = \partial Q_{rev} - P dV$$

$$\partial H = \partial Q_{rev} + V \partial P$$

$$\text{For Ideal gas, } \partial H = C_p^{ig} dT, V = \frac{RT}{P}$$

$$\text{So, } \frac{\partial Q_{rev}}{T} = \frac{\partial H}{T} - \frac{R \partial P}{P}$$

$$\Rightarrow \partial S = C_p^{ig} \frac{\partial T}{T} - \frac{R \partial P}{P} \text{ So, } \frac{\Delta S}{R} = \int_{T_0}^T \frac{C_p}{RT} dT - \ln \left(\frac{P}{P_0} \right)$$

By this we can prove for adiabatic equation with constant C_p

$$TP^{\frac{1-\gamma}{\gamma}} = \text{constant} \quad \gamma = \frac{C_p}{C_v}$$

- Entropy balance for open system

$$\frac{\partial}{\partial t} [mS]_{\text{controlled vol.}} = -\Delta(\dot{m}S) + \sum_j \frac{\dot{Q}_j}{T_j} + \dot{S}_G$$

- Calculation of ideal work

$$\Delta(\dot{m}S)_{\text{flow surface}} - \sum_j \frac{Q_j}{T_{\sigma,j}} = \dot{S}_G \geq 0$$

- SS flow process req, work

$W_{ideal} \rightarrow$ minimum amount of work required to obtain a change of state

- SS flow producing work

$W_{ideal} \rightarrow$ maximum amount of work produced for a given change

- SS rev process

$$(\Delta(\dot{m}S))_{fs} = \frac{\dot{Q}}{T_\sigma} \Rightarrow \dot{Q} = T_\sigma \Delta(\dot{m}S)_{fs}$$

$$\text{So, } \Delta \left[\dot{m} \left(H + \frac{1}{2} u^2 + gz \right) \right] = T_\sigma \Delta(\dot{m}S)_{fs} + \dot{W}_S \text{ (rev)}$$

$$W_{ideal} \Rightarrow \Delta(\dot{m}H) - T_\sigma \Delta(\dot{m}S)_{fs} \quad (\text{mostly})$$

For single inlet, outlet $\dot{m}_1 = \dot{m}_2 = \dot{m}_3$

$$\therefore W_{ideal} = m(\Delta H - T \Delta S)$$

$$\dot{W}_{ideal} = \Delta \left[\dot{m} \left(H + \frac{1}{2} u^2 + gz \right) \right] - \dot{Q}$$

$$\dot{W}_{lost} = \dot{W}_S - \dot{W}_{ideal} = T_\sigma \dot{S}_G \geq 0 \text{ By putting original } Q \text{ in } \dot{W}_S$$

- Closed System of 'n' moles

- $U \equiv Q + W$
- $H \equiv U + PV$
- Free energy
- $G \equiv H - TS$
- $A \equiv U - TS$ (Helmholtz free energy)

These lead to,

$$\begin{aligned}
 - d(nH) &= Td(nS) + (nV)dP \\
 \implies \left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P \\
 - d(nU) &= Td(nS) - Pd(nV) \\
 \implies \left(\frac{\partial T}{\partial V}\right)_S &= - \left(\frac{\partial P}{\partial S}\right)_V \\
 - dG &= (nV)dP - (nS)dT \\
 \implies \left(\frac{\partial V}{\partial T}\right)_P &= \left(\frac{\partial S}{\partial P}\right)_T \\
 - dA &= -Pd(nV) - (nS)dT \\
 \implies \left(\frac{\partial P}{\partial T}\right)_V &= \left(\frac{\partial S}{\partial V}\right)_T
 \end{aligned}$$

- Enthalpy & Entropy as function of T & P

- $\partial H(T, P) = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$
 1. Writing ∂H at const. T & P
 2. Using Maxwell's equations
$$\partial H(T, P) = C_P dT + \left[V - T \left(\frac{\partial V}{\partial T}\right)_P \right] dP$$
- $\partial S(T, P) = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$

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

Alternative form for liquid

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

$$\left(\frac{\partial H}{\partial P}\right)_T = (1 - \beta T)V$$

So,

$$\partial H = C_P dT + (1 - \beta T)V dP$$

$$\partial S = \frac{C_P}{T} dT - \beta V dP$$

For liquids, β & V are weak functions of P

- Internal Energy & Entropy as a function of T , V

$$\partial U = C_V dT + \left(\frac{\beta T}{\kappa} - P\right) dV$$

$$\partial S = \frac{C_V}{T} dT + \frac{\beta}{\kappa} dV$$

- Gibbs' Free Energy as a generating function

$$\partial G = V dP - S dT$$

$$\partial \left(\frac{G}{RT}\right) = \frac{V}{RT} dP - \frac{H}{RT^2} dT$$

G and T are both variables so partial differentiation. So,

$$\frac{V}{RT} = \left(\frac{\partial \left(\frac{G}{RT}\right)}{\partial P}\right)_T \quad \text{and} \quad \frac{H}{RT} = - \left[T \frac{\partial \left(\frac{G}{RT}\right)}{\partial T}\right]_P$$

- Residual Properties

$M^R = M - M^{ig}$ where M & M^{ig} are at the same temperature and pressure

$$V^R = V - V^{ig} = V - \frac{RT}{P} \quad R = \text{Residual}$$

So, $G^R = G - G^{ig}$

$$\left[\frac{\partial \left(\frac{G}{RT}\right)}{\partial P}\right]_T = \frac{V^R}{RT} \quad ; \quad \left[\frac{\partial \left(\frac{G^R}{RT}\right)}{\partial T}\right]_P = -\frac{H^R}{RT^2}$$

$$\partial \left(\frac{G^R}{RT}\right) = \frac{V^R}{RT} dP - \frac{H^R}{RT^2} dT$$

At constant Temperature

$$\partial \left(\frac{G^R}{RT}\right) = \frac{V^R}{RT} dP \frac{G^R}{RT} = \int_0^P \frac{V^R}{RT} dP + \left(\frac{G^R}{RT}\right)_P \quad ; \quad \left(\frac{G^R}{RT}\right)_P = 0$$

Using $V^R = V - \frac{RT}{P} = \frac{RT}{P}(Z - 1) \quad \therefore \frac{G^R}{RT} = \int_0^P \frac{\partial P}{P}(Z - 1)$

$G = G^{ig} + G^R$

So, $\frac{H^R}{RT} = -T \int_0^P \left[\left(\frac{\partial Z}{\partial T} \right)_P \frac{\partial P}{P} \right] \quad \& \quad \frac{S^R}{R} = \frac{H^R}{RT} - \frac{G^R}{RT}$
 $\implies \frac{S^R}{R} = -T \int_0^P \left(\frac{\partial Z}{\partial T} \right)_P \frac{\partial P}{P} - \int_0^P \frac{(Z - 1)\partial P}{P}$

By equation of state $Z = 1 + B'P = 1 + \frac{BP}{RT}$

$\frac{G^R}{RT} = \frac{BP}{RT} \quad , \quad \frac{H^R}{RT} = \frac{P}{R} \left[\frac{B}{T} - \frac{\partial B}{\partial T} \right]$

$\frac{S^R}{R} = -\frac{R}{R} \frac{\partial B}{\partial T}$

Pressure Explicit Form

$P = \rho ZRT$

$\partial P = RT[Z\partial\rho + \rho\partial Z]$

$\frac{\partial P}{P} = \frac{\partial\rho}{\rho} + \frac{\partial Z}{Z}$ Now, we know that $\frac{H^R}{RT} = -T \int_0^P \frac{\partial Z}{\partial T}$

and $\partial \left(\frac{G}{RT} \right) = \frac{V}{RT} \partial P - \frac{H}{RT} \partial T$

Substituting $\frac{\partial P}{P}$ with these

$\frac{G^R}{RT} = \int_0^P \frac{(Z - 1)\partial\rho}{\rho} + Z - 1 - \ln Z$

$\frac{H^R}{RT} = -T \int_0^P \left(\frac{\partial Z}{\partial T} \right)_\rho \frac{\partial\rho}{\rho} + Z - 1$

$\frac{S^R}{R} = \ln Z - T \int_0^P \left(\frac{\partial Z}{\partial T} \right)_P \frac{\partial\rho}{\rho} - \int_0^P (Z - 1) \frac{\partial\rho}{\rho}$

- Clayperon Equation

$$\left. \frac{\partial P}{\partial T} \right|_{\text{along a coexistence curve}} = \frac{\Delta H_{\text{trans}}}{T \Delta V_{\text{trans}}}$$

Proof

Taking Gibbs' Free energy as a function of Temperature and Pressure (as it is the only one which has a continuous graph at transition against temperature

$$G(T, P)$$

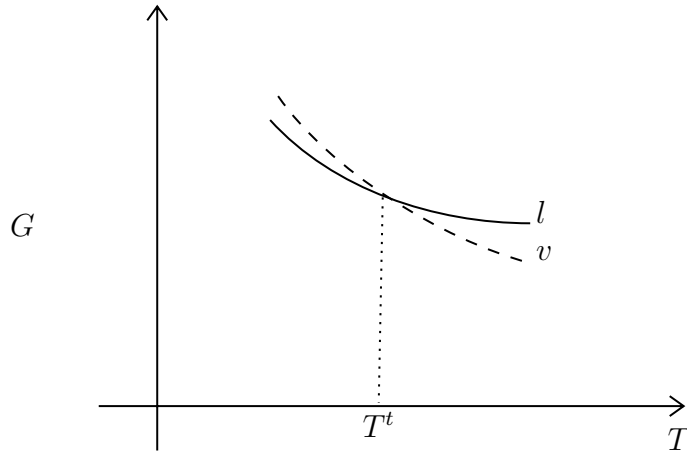
$$G^t = m_l G_l + m_v G_v$$

$$\partial G^t = \partial m_l G_l + \partial m_v G_v$$

$$0 = \partial m_l G_l - \partial m_v G_v$$

as $\partial G = V\partial P - S\partial T$ as ∂P & ∂T are zero at transition

$$\therefore G^l = G^v$$



For a pure species co-existing in 2 phases (α, β) in equation

$$G^\alpha = G^\beta$$

[molar/specific Gibbs' free energy]

And we can also say

$$\partial G^\alpha = \partial G^\beta$$

$$V^\alpha \partial p^{sat} - S^\alpha \partial T^{sat} = V^\beta \partial p^{sat} - S^\beta \partial T^{sat}$$

$$\implies \frac{\partial p^{sat}}{\partial T^{sat}} = \frac{(S^\beta - S^\alpha)}{\Delta V_{transition}}$$

$$dH = TdS + VdP \quad [dP = 0]$$

$$\Delta H^{\alpha\beta} = T\Delta S^{\alpha\beta}$$

$$\implies \frac{\partial p^{sat}}{\partial T^{sat}} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}}$$