1- $w = \int P \cdot dv$ (- closed system; - Reversible process; - for any gas; - work crossing boundary)

(i) Isothermal $w = MRT \ln \frac{V_2}{V_1}$

(ii) Adiabatic $w = \frac{P_1V_1 - P_2V_2}{\gamma - 1}$ (- closed sys; - Reversible; - for ideal gas)

2- $\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$ (Adiabatic)

$T \cdot V^{\gamma-1}$ = constant

open system PV^{γ} or PV^{n}; $w = \frac{\gamma}{\gamma-1}(P_1V_1 - P_2V_2)$, $w = \frac{n}{n-1}(P_1V_1 - P_2V_2)$ } $w = \int v \cdot dP$

E.g. 3.4: $w_{stirrer} = (T\omega) \times$ Time; Fluid w on atm $= P \cdot dV$ → net work equate = $Pdv - (T\omega) \cdot t$

E.g. 3.5: $P_{mep} = \frac{ad}{ld} \times$ spring const → (bar/mm)

3- 1st law for closed system undergoing cycle $\Sigma Q = \Sigma W$ (For both Rev, Irrev)

Consequences (i) Q is path funcn (ii) Energy is property (iii) Energy of isolated system constant (iv) PMM1 not possible. There can be no m/c which produces work continuously w/o absorbing some other form of energy. ($Q = 0$ → W, PMM1 not possible)

4- 1st law for closed system process $dQ = du + dw$ (both Rev, Irrev)

$dQ = du + Pdv$ (for Rev)

5- prove $C_p - C_v = R$; $H = U + PV$; $dH = du + d(PV)$; $dH = du + d(mRT)$

$m \cdot C_p \cdot dT = mC_v dT + mR \cdot dT$; $C_p = C_v + R$

$(dQ)_p = dh$, $(dQ)_v = du$ (For any fluid but R. Process); $dh = C_p \cdot dT$, $du = C_v \cdot dT$ (only for I. gas)

6- Heat transfer in polytropic process $dQ = \frac{\gamma - n}{\gamma - 1} dw_{poly} = \frac{n - \gamma}{n-1} \cdot m \cdot C_v \, dT$

$C_{poly} = \frac{n-\gamma}{n-1} \cdot C_v$ [Thus -ve] - supply of heat ↓es Temp. - Thus work done ↑es < by heat supplied; by ↓ in int. Energy

7- prove $PV^{\gamma} = C$ For adiabatic i.e. $dQ = du + Pdv = 0$

$du = -Pdv$ and $dH = vdP$; $m \cdot C_p \cdot dT = vdP$; $mC_v dT = -Pdv$

Divide & Integrate $PV^{\gamma} = C$. For Adiabatic Rev Ideal

8- Free expansion work = 0 but volume ↑ $Pdv \neq 0$ irreversal ∴ $W \neq Pdv$

if insulated then $dQ = dw = 0$; $du = 0$ (for any gas); T, H = const. (for ideal gas)

Though $dT = 0$ but not isothermal b/c 1st T ↓ then ↑

9- Throttling irreversible $h_1 = h_2$ (for any gas) T, U = const. for ideal gas.

10- γ = 5/3 (mono) 7/5 (di) 4/3 (poly)

11- $Pv = mRT = n\bar{R}T$; $\bar{R} = 8.314 \frac{KJ}{Kg\text{-mol}}$

$mR = n\bar{R}$, $mR = \frac{m}{M}\bar{R}$

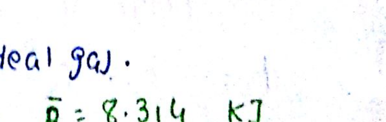
12- vander wall Eqn:

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

$R = \frac{\bar{R}}{M}$; $\bar{R} = 8.314 \frac{KJ}{Kg\text{-}K}$; $R_{air} = .287 \frac{KJ}{Kg\text{-}K}$

For ideal < no attraction b/w molecules; volume occupied by molecules << Total volume

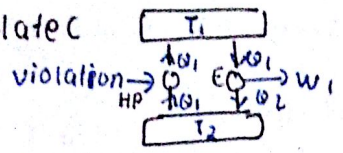
or P↓, V↑



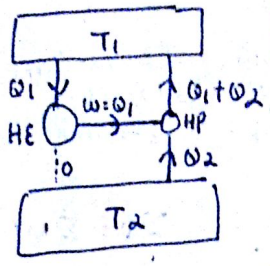
13- II law (i) K-P: PMM2 impossible i.e. impossible to develop a device working continuously in a cycle and producing work by exchanging heat with a single reservoir → b/c conversion of low G.E. to High G.E. is not possible completely. Hence need a sink for Rejech.

(ii) C: impossible to transfer heat from low T to high T w/o any ext. i/p

Equivalence (i) violate C

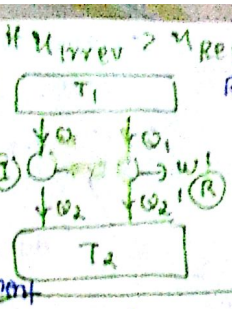


(ii) violate K-P

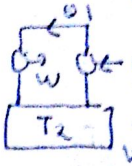


$\eta_I = \eta_R$ Then $w = w'$

Then violates C-Statement



If $\eta_{Irrev} > \eta_{Rev}$ ∴ $w > w'$ Reverse the (R)

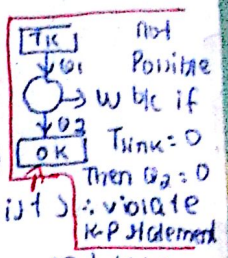


∴ $w > w'$ ∴ $w_{net} > 0$ violate K-P

$\eta = 1 - \frac{Q_R}{Q_S}$ (Both Rev, Irrev)

$\eta_{Rev} = 1 - \frac{Q_R}{Q_S} = 1 - \frac{T_R}{T_S}$ b/c for Rev. by clausius $Q_R/T_R = Q_S/T_S$

14- prove that $\eta_{max} = Rev.$ ⟷ if $\eta_{Irrev} > \eta_{rev}$ (violates K-P) ⟷ if $\eta_{Irrev} = \eta_{rev}$ (i clausius)



15- Fowler-Guggenheim statement of 3rd law ⟶ Definite 0 pt. exist on absolute Temp. scale but it can't be reached w/o violating 2nd law.

16- Clausius Inequality $\oint \frac{dQ}{T} \leq 0$ for (Reversible =) (Irreversible < 0) (Impossible > 0)

show wrt heat engine.

17- Entropy: ∵ for Reversible $\oint \frac{dQ}{T} = 0$ ∴ $\left(\frac{dQ}{T}\right)_{rev}$ is a property

$ds = \left(\frac{dQ}{T}\right)_{Rev}$ (Eqn. for 2nd law)

* Irreversible: $ds = \left(\frac{dQ}{T}\right)_{Irrev} + \delta S_{gen}$

* Hence, $ds \geq \frac{dQ}{T}$ [> for Irrev, = for Rev]

∵ for universe $dQ = 0$

$ds_{univ} \geq 0$ [= for Rev, > for Irrev]

$ds_{sys} + ds_{surr} \geq 0$.

18- Combined 1st, 2nd law $Tds = du + Pdv = dh - vdP$ for both Rev. and Irrev.

as all are properties.

19- Reasons for Entropy change ⟷ External Interaction dQ/T b/c of heat exchange

Internal Irreversibility δS_{gen} b/c of fric, etc.

Causes of Irreversibility 1- lack of Eq. during Proc. - HT thru finite ΔT, lack of Pr. Eq., free Expn

2- Dissipative effects - Fric, paddle-wheel work Transfer, Transfer of Elec. thru Resistor

20- For ideal gas both R.I process

$$ds = C_v \cdot \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1} = C_p \cdot \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} = C_p \cdot \ln \frac{v_2}{v_1} + C_v \ln \frac{P_2}{P_1}$$

Eg. 7.3 (MAG) work to convert back. create a Ref. cycle with heat Removed = Q (Earlier in Q.) and $w = w$ Then supplied to surrounding = Q + w

ds for sys: -ve of Earlier flow $(s_1 - s_4)$

and $(s_1 - s_4) + \frac{Q+w}{T} \geq 0$ find w.

Flow work ⟷ entry $-P_1 v_1$, exit $P_2 v_2$

1st law Flow process: I steady: $(dm/dt)_{cv} = (dE/dt)_{cv} = 0$

$h_1 + \frac{v_1^2}{2} + gz_1 + Q = h_2 + \frac{v_2^2}{2} + gz_2 + W_{cv}$

II unsteady: mass ⟷ initially m_1, After m_2 mass ⟷ Entry Rate $\dot{m}_i$ kg/s, Exit " $\dot{m}_e$ kg/s

$m_2 = m_1 + (\dot{m}_i - \dot{m}_e) \cdot dt$ $\left(\frac{dm}{dt}\right)_{cv} = \dot{m}_i - \dot{m}_e$ kg/s

$(dE/dt)_{cv} = dE_i/dt - dE_e/dt = d/dt\{m_i(h_i + \frac{v_i^2}{2} + gz_i + q)\}$

$m_2u_2 - m_1u_1 = \{\dot{m}_i h_i + \dot{Q} - \dot{m}_e h_e - \dot{W}\} \cdot dt - d/dt\{m_e(h_e + \frac{v_e^2}{2} + gz_e + w)\}$

If $\Delta KE = \Delta PE = 0$

$(dQ/dt)_{cv} = \dot{m}_i h_i + \dot{Q} - \dot{m}_e h_e - \dot{W}$

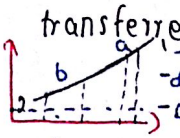
21- Available Energy = max. work o/p obtainable from a certain heat i/p in a cyclic heat Engine is called AE. (EXERGY).

UAE = min. energy that has to be rejected to sink b/c of 2nd law (Anergy)

$$W_{max} = Q_1\left(1-\frac{T_0}{T}\right)$$ As min. sink temp. could be T_0 (ambient temp.)

* when same amt. of Energy (Q_1) is transferred from a lower temp (T_1) then AE ↓es by $\frac{Q_1 \cdot T_0 \cdot (T_1-T_2)}{T_1 \cdot T_2}$

Reason: For same Q, $(A.E.)_a < (AE)_b$ To



-constant pressure heat loss - Area ☐ : []

$-ds_b > ds_a$ ∴ $(UAE)_b = (UAE)_a$ i.e. Q_{loss} = same

* In NWM: Available Energy of a system of mass m at temp. T and Cp with ambient T_0 = $m \cdot cp \int_{T_0}^{T}\left(1-\frac{T_0}{T}\right)dT = m \cdot cp\left[(T-T_0) - T_0 \ln\frac{T}{T_0}\right]$

↳ can also Prove from Entropy

$(\Delta S)_{un} = ds_{sys} + \frac{Q-W}{T_0}$ * Body at T losing heat only to surr at T_0.

$Q = m \cdot cp (T-T_0)$

$ds_{sys} = dQ/T = m \cdot cp \cdot dT/T$

$ds_{sys} = m \cdot cp \ln\frac{T_0}{T}$

22- Availability = max. useful work that can be obtained in a process when the system comes in Equilibrium with surroundings.

open system	$\phi = h - T_0 s$	$W_{max} = \phi_1 - \phi_2$
closed system	$\phi = U - T_0 S + P_0 V$	$W_{max} = \phi_1 - \phi_2$

These eqn. valid if heat exchange taking place only with surroundings

* if heat exchange with surr (T_0) and TER (T_R)

Then add $Q_R\left(1-\frac{T_0}{T_R}\right)$ to $\phi_1 - \phi_2 = W_{max}$

Q_R = heat Received

Steady flow open process:

$A = (H_1 + \frac{mv_1^2}{2} + mgz_1) - (H_2 + \frac{mv_2^2}{2} + gz_2) - T_0(s_1 - s_2)$

* $h - T_0 s = B$ = Keenan funct.

23- Irreversibility $I = W_{max} - W_{act} = T_0 \cdot \Delta S_{univ} = T_{se}$ in UAE

- $I = T_0 \cdot \Delta S_{univ}$ (for both closed, open process)

closed: $dQ = du + dW$ $W_{max} = (U_1 - U_2) - T_0(S_1 - S_2)$ $I = T_0(S_2 - S_1) - Q$

$W_{ac} = T_0(S_2 - S_1)$ $Q - du = (U_1 - U_2) + W$

open: $W_{max} = (h_1 + \frac{v_1^2}{2} + gz_1) - (h_2 + \frac{v_2^2}{2} + gz_2) - T_0(s_1 - s_2)$

$W = T_0(s_2 - s_1) - Q$

24- $dz = M\,dx + N\,dy$ $f = \phi(x, y, z)$ $z = \phi(x, y)$

$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$ - max well TDS - 3, 4 for TDS

$\left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f \left(\frac{\partial z}{\partial x}\right)_f = 1$ - Prove independence of v from p

$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$ - To Prove $cp - cv > 0$

use $du = Tds - Pdv$, $dh = Tds + v\,dP$, $F = U - TS$ (used for Tds), $G = H - TS$ (used for Td)

(i) Tds eqn: $s = f(T, v)$ or $s = f(T, P)$ → use slopes of T-S

$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP$ → use from 4 eqn.

$Tds = cv \cdot dT + T\left(\frac{\partial P}{\partial T}\right)_v dv = cp \cdot dT - T\left(\frac{\partial v}{\partial T}\right)_P dP$

From Energy eqn. manipulate: $\left(\frac{\partial u}{\partial T}\right)_v = cv$, $\left(\frac{\partial h}{\partial T}\right)_P = cp$

(ii) To prove $cp - cv > 0$ equate both Tds eqn. and write in terms of T

$T = f(P, v)$ ↔ differential eqn. and equate with $T = \phi(P, v)$ $dT = \left(\frac{\partial T}{\partial P}\right)_v dP + \left(\frac{\partial T}{\partial v}\right)_P dv$

↔ use Theorem (3) for $T = \phi(P, v)$

$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$ $K_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$

$cp - cv = -T\left\{\left(\frac{\partial v}{\partial T}\right)_P\right\}^2 \left(\frac{\partial P}{\partial v}\right)_T$

Q1- $cp - cv > 0$ Q- For ideal $cp - cv = R$.

2- At $T_{abs} = 0$ $cp = cv$ $= T \cdot v \cdot \frac{\beta^2}{K_T}$

3- water 4°c $\left(\frac{\partial v}{\partial T}\right)_P = 0$ ∴ $cp = cv$

For further manipulations from Energy eqn. use $u = f(T, v)$ $du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$ & compare with E. eqns.: $h = f(T, P)$ $dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP$

(iii) Energy Eqn. $du = Tds - Pdv$ and $dh = Tds + v\,dP$ (put Tds from Tds eqn.)

$du = cv \cdot dT + \left\{T\left(\frac{\partial P}{\partial T}\right)_v - P\right\} dv$ $dh = cp \cdot dT - \left\{T\left(\frac{\partial v}{\partial T}\right)_P - v\right\} dP$

→ Use ideal gas eqn. to Prove $du = cv \cdot dT$ $dh = cp \cdot dT$

(iv) J-T coeff $\mu = \left(\frac{dT}{dP}\right)_h = \frac{1}{cp}\left[T\left(\frac{\partial v}{\partial T}\right)_P - v\right]$ * $\mu = 0$ for ideal gas

T, H, P - Process where pressure ↓es ∴ left side cooling, Rt. side heating

24- C-C Eqn: use $\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$ For ϕ change use P,T constr. $\frac{dP}{dT} = s_g - s_f / v_g - v_f$

$\frac{dP}{dT} = \frac{h_g - h_f}{T \cdot v_g}$ ($\because v_f$ ↓↓) use $v_g = \frac{RT}{P}$

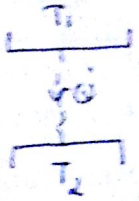
$$\boxed{\frac{dP}{dT} = \frac{P \cdot (h_g - h_f)}{RT^2}}$$

* From $F = U - TS$

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

$R = \frac{P \cdot v_g}{T}$

25- Application of Guy-Stodola Eqn: I HT thru finite Temp. diff:



$S_{gen} = \frac{\dot{Q}}{T_2} - \frac{\dot{Q}}{T_1} = \dot{Q}\left(\frac{T_1 - T_2}{T_1 \cdot T_2}\right)$ $\dot{W}_{lost} = T_2 \cdot \dot{S}_{gen} = \frac{\dot{Q}(T_1 - T_2)}{T_1}$

II flow with frict: Pressure drop from P to P-ΔP

∵ Throttling : T=const. $ds = ds_{rev} + ds_{irr}^{0} = -R \cdot \ln \frac{P_2}{P_1} = -R \ln\left(1 - \frac{\Delta P}{P}\right) \simeq R \cdot \ln \frac{\Delta P}{P_1}$

$\dot{W}_{lost} = T_0 \cdot \dot{S}_{gen} = \dot{m} \cdot R \cdot T_0 \frac{\Delta P}{P}$ assumption $\Delta P/P$.

III mixing of 2 fluids: $m_3 = m_1 + m_2$ $m_3 T_3 = m_1 T_1 + m_2 T_2$ ~~$m_3 s_3$~~ =

$S_{gen} = m_3 s_3 - m_1 s_1 - m_2 s_2 =$ ~~$m_1(s_3 - s_1) + m_2(s_3 - s_2)$~~

$\frac{S_{gen}}{m} =$ ~~$x(s_3 - s_1) + (1-x)(s_3 - s_2)$~~ $s_3 - x \cdot s_1 - (1-x)s_2 = (s_3 - s_2) + x(s_2 - s_1)$

if $\tau = \frac{T_2}{T_1}$ $\dot{W}_{lost} = T_0 \cdot \dot{m} \cdot c_p \ln \frac{x + \tau(1-x)}{\tau^{1-x}}$ $x = \frac{m_1}{m_1 + m_2}$

$N_S = \ln \frac{x + \tau(1-x)}{\tau^{1-x}} = S_{gen}$ number (dimensionless) τ^{1-x}

26- Availability balance: generally not conserved $\dot{E}_{x_{in}} - \dot{E}_{x_{out}} = \dot{E}_{x_{destroyed}}$

E_x destruction could be due to Q, W or I.

-use 1st law -2nd law (multiply by T_0) -substract (1) - (2)

closed- $A_2 - A_1 = \int_1^2 \left(1 - \frac{T_0}{T}\right) \cdot dQ - \left\{W_{1-2} - P_0(v_2 - v_1)\right\} - T_0 \cdot S_{gen}$

steady open- $A_2 - A_1 = \int_1^2 \left(1 - \frac{T_0}{T}\right) dQ - W_{1-2} - T_0 \cdot S_{gen}$

Both Q, W +ve i.e. Q↑P W↓P

27- II law of η: $\eta_I = \frac{\text{energy o/p}}{\text{energy i/p}}$ $\eta_{II} = \frac{\text{min. A.E. needed to do a task}}{\text{Actual " " " "}} = \frac{A_{min}}{A_{act}}$

$= \frac{W_{act}}{W_{max}} = \frac{W_{act}}{Q_{ip}} \frac{Q_{ip}}{W_{max}} = \frac{\eta_I}{\eta_{carnot}}$

E.g. if Solar Energy Q_R available at TER temp. T_R & it qty. Q_a is transferred by solar collector at temp. T_a. $T_{surr} = T_0$

$\eta_I = \frac{Q_a}{Q_R}$ $\eta_{II} = \frac{Q_a(1 - T_0/T_a)}{Q_R(1 - T_0/T_R)} = \eta_I \frac{(1 - T_0/T_a)}{(1 - T_0/T_R)}$.

28- Ratio of heat capacities: For Rev. adiabatic $ds = 0$ ∴ use in Tds eqns. & divide

$\frac{c_p}{c_v} = -\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial T}{\partial P}\right)_v \left(\frac{\partial P}{\partial v}\right)_s = \frac{(\partial P/\partial v)_s}{(\partial P/\partial v)_T} = \gamma$ ∵ $c_p > c_v$ ∴ $\gamma > 1$ ∴ $(\partial P/\partial v)_s > (\partial P/\partial v)_T$

∴ $(\text{slope})_{Ad} > (\text{slope})_{iso}$ → ∴ W comp. min for iso.

H.O- differentiates c_p or c_v

use $c_p = \left(\frac{\partial h}{\partial T}\right)_p \cdot \eta$ $c_v = \left(\frac{\partial s}{\partial T}\right)_v \cdot T$ & then differentiate