

Chap. 3. The 2nd law of Thermo.

3.1 Intro.

① Work & heat determine the Δ in U

② (reversible process) \leftarrow ② Is there a way to do max. work during its change and introduction of S.
(irreversible process) answer.

a state function, entropy, S.
 ① for quantification of the degree of irreversibility of a process
 ② a quantity which has all the prop. of a state fn.

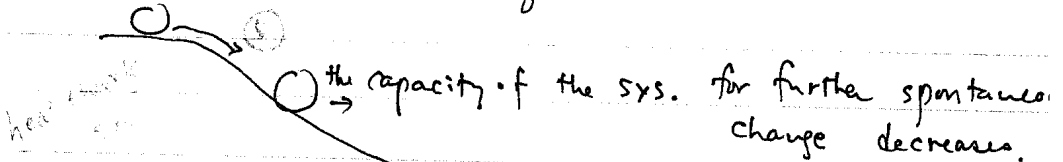
3.2 Spontaneous or Natural Process.

① a sys - remain in the state
 tend to move toward the equil^m

② Spontaneous = natural = irreversible process - need the appli. of an external agency to go
 movement from low & non-equil^m state to an equil^m state

③ 1) the mixing of two gases
 2) the equalization of temp. \rightarrow sys. being brought near the equil^m
 \rightarrow can't be unaided again

④ Determination of the equil^m state - ~~the~~ direction
 reaction proceed in a certain direction until it reaches equil^m.



⑤ As a result of the spontaneous process, the sys. becomes degraded (useful work)

3.3 Entropy and the quantification of irreversibility.

① $\Delta S = \frac{q}{T}$ = the extent of degradation = the increase in entropy.
 = the degree of irreversibility

a spontaneous process, which cause the absorption of heat q at T .

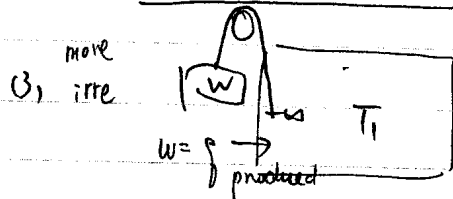
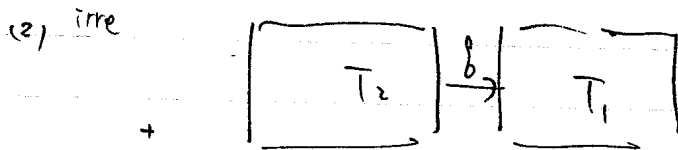
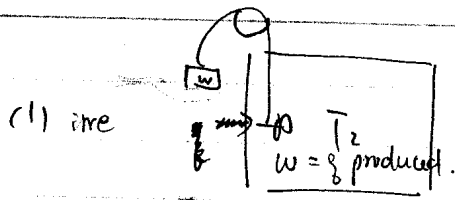
$$\Delta S = \frac{q}{T}$$

3/13/15

(2)

Two distinct types of spontaneous process

- (1) the conversion of work into heat (mech. E to thermal)
- (2) the flow of heat down a temp.



process (3) = process (1) + (2)

∴ process (3) is more irreversible than (1) (∵ sum of two steps).

$$\int p/T_2 < \int p/T_1 = \Delta S_i$$

∴ $\int p/T$ is thus taken as a measure of the extent of irreversibility, coincide w/ magnitude of irreversibility for a process. Irreversibility can be expressed well by

3.4. Reversible process.

- The degree of irreversibility of a process depends on a process.
- then, there should be a way for the process to be conducted w/ min. irreversibility.

- If irreversibility = 0, no degradation. → The limit is ^{the} reversible

Spontaneity occurred as a result of the system moving, of its own accord, from a non-equil^m state to an equil^m state.

∴ If no spontaneity, the sys is at equil^m.

∴ A reversible process is one during which the sys. is never away from equil^m.

All a man's ways seem innocent to him
 but motives are weighed by the Lord (Prov 16:2) ④
 4월 15일 수요일 139 쪽 44쪽
 4월 15일 수요일 139 쪽 44쪽

3.6. Entropy and Reversible Heat.

($P_{ext} = 0$)

$W_{max} = P_{ext} V$ (reversible during the evap. of 1 mole H₂O)

$w = (P_{ext} - \Delta P) V$ (irreversible)

$\Rightarrow \Delta U$ is indep. of whether the process is carried out
 $V_1 \rightarrow V_2$ reversibly or not as long as
 isothermal $T = const.$
 $\Delta U_{irr} = \Delta U_{rev} = f(\text{process}) = f(T)$

\therefore from the 1st law.

① if it is reversible, max. amount of heat, $q_{rev} \rightarrow$ enter the cylinder from the heat reservoir $q_{rev} = \Delta U + W$

② if it is irreversible, $q = \Delta U + W$ less heat $q < q_{rev}$

The difference betn the works obtained in the reversible & irr. process, $(W_{max} - W)$, is the mech. E. degraded to thermal E (heat) in the cylinder as a result of irr. process.

disturbance in water molecules etc.

① $q_{rev} - q = W_{max} - W$ explains (= the heat produced by degradation)

less heat is absorbed the cylinder from the heat reservoir during the irr. p than is absorbed during the rev. evaporation

the rev. evaporation $\Delta S_{reservoir} = -\frac{q_{rev}}{T}$

$\Delta S_{water + water vapor} = \frac{q_{rev}}{T}$

$\therefore \Delta S_{total} = 0 \therefore$ no degradation.

A(2) If the evap. process is irreversible.

$$\Delta S_{\text{reservoir}} = -\frac{q}{T} \quad (q < q_{\text{rev}}) \quad W_{\text{max}} = PV$$

total heat appearing in the cylinder = q from the reservoir
 + heat produced by de of work due to the irr.
 $(W_{\text{max}} - W) = V\Delta P$
 abrupt motion of piston

$$\Delta S_{\text{water+water vap}} = \frac{q}{T} + \frac{q_{\text{rev}} - q}{T}$$

$$\therefore \Delta S_{\text{total}} = \frac{q_{\text{rev}} - q}{T} > 0 \quad \text{since } q_{\text{rev}} > q.$$

$$(3.2) \quad \therefore \Delta S_{\text{water+vap}} = \frac{q}{T} + \Delta S_{\text{irr.}}$$

B(1) Condensation Process

$$(P_{\text{ext}} = \Delta P) V$$

$$(= P_{\text{ext}} V.)$$

if Reversible condensation - W_{min} (work done on the sys. has a min)

$$\Delta S_{\text{total}} = -\frac{q_{\text{rev}}}{T_{\text{cylinder}}} + \frac{q_{\text{rev}}}{T_{\text{res}}} = 0.$$

B(2) irreversible condensation - $W (= (P_{\text{ext}} + \Delta P) V)$

he and $V\Delta P$ (excess work) is degraded

(work) path in irreversible process

this extra heat is the diff. bet'n

const heat leaving the cylinder (q) and

the min. heat (q_{rev})

$$(3.3) \quad \Delta S_{\text{water+vap}} = -\frac{q}{T} + \frac{q - q_{\text{rev}}}{T}$$

heat leaving the cylinder - heat produced in cylinder by degradat.

$$(3.4) (3.3) \quad q > 0$$

$$\Delta S_{\text{irr.}} = \frac{q}{T}$$

→ All other ways seen in previous problems are weighted by the Legend (가장의 독립성)

- the left-hand sides of (3.2), (3.3) are constants. ($= \pm \frac{q_{rev}}{T}$)

|| ΔS_{system} bet'n the initial and final states - indep. of whether the process is conducted reversibly or irreversibly. $\therefore \Delta S_{system}$ - indep. of the path.

$$\Delta S_{system} = S_B - S_A = \frac{q}{T} + \Delta S_{irr}$$

$$= \frac{q_{rev}}{T}$$

\therefore the entropy changes can only be measured for reversible where $\Delta S_{irr} = 0$

3.7. Reversible Isothermal Compression of an ideal Gas.

$\Delta U = 0$
 $DU = 0$

reversible isothermal ($T = \text{const}$) compression. $(V_A, T) \rightarrow (V_B, T)$

$$P_{inst} = RT / V_{inst}$$

$T = \text{const.}$
ideal gas } $\rightarrow \Delta U = 0$

Work done on the gas = heat drawn from

$$W_{max} = \int_{rev} q_{heat}$$

$$W_{max} = \int_{V_A}^{V_B} P dV = \int_{V_A}^{V_B} \frac{RT dV}{V} = RT \ln \frac{V_B}{V_A}$$

$$\Delta S_{heat, Res} = \frac{\text{the heat entering the Res.}}{T} = \frac{-q_{rev}}{T} = \frac{-W_{max}}{T} = -R \ln \left(\frac{V}{V} \right)$$

Reversible? then $\Delta S_{gas} = -\Delta S_{heat, Res} = R \ln \left(\frac{V_B}{V_A} \right) < 0$ (\therefore)

3.8. Reversible adiabatic Expansion of an ideal gas.

no dissipative

$\Delta S_{system} = 0$

$\Delta S_{sur} = 0$

$(P_A, T_A) \rightarrow (P_B, T_B)$

$q = 0$ adiabatic & $PV^\gamma = \text{const.}$

$(\gamma = C_p / C_v)$

consider 1 mole of ideal gas

of inorganic Materials Engineering

when not $\Delta U_{irr} = \Delta U_{rev}$ or is-hatic case

adiabatic process

$q=0, \Delta U = 0 - W_{max}$

no degradation $\Delta S=0$
no heat flowing $q=0$

①

Since $\Delta S=0$, all states of a gas lying on a $PV^\gamma = \text{const}$ line are states of equal entropy. (isentropic process)

(all states of an ideal gas lying on a $PV = RT$ line are states of equal internal Energy (~~$\Delta U=0$~~) ($\Delta U=0$))

$\Delta S = \frac{P_2}{T_2} - \frac{P_1}{T_1}$
creation of entropy

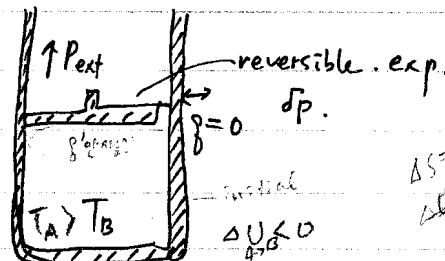
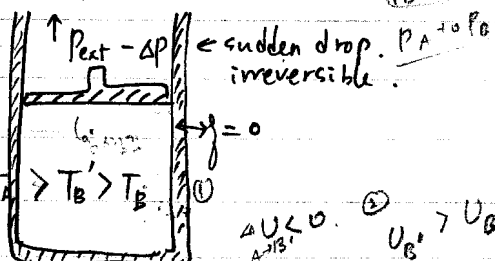
irreversible adiabatic expansion

$PV^\gamma \neq \text{const}$

reversible adiabatic

$PV^\gamma = \text{const}$

$(S_f - S_i) = \Delta S = \Delta S_{irr}$



∴ heat produced by the degradation of the work enters into the cylinder.

$(P_{ext} - \Delta P) V$

↑ corresponding heat.

for a given pressure change ($P_A \rightarrow P_B$)

- ∴ the more irreversible the process is, the greater the heat produced in the gas due to the degradation.
- ② the higher the final temp. & ③ internal energy
- ④ the greater the entropy increases.

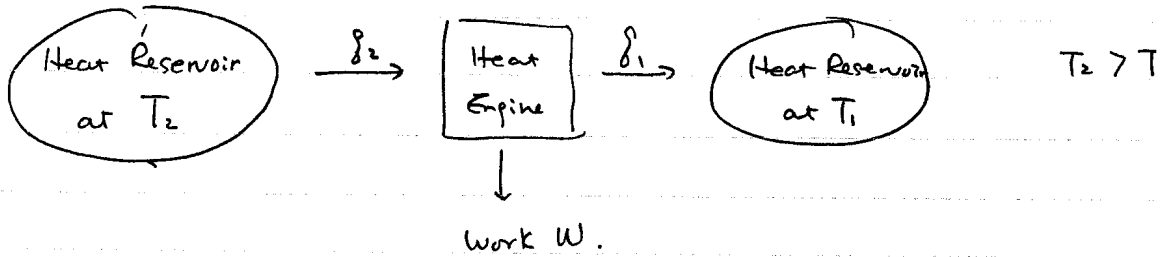
∴ $W_{irreversible exp. by gas} = -\Delta U < W_{rev. exp.}$

due to the heat appearing in the gas as a result of degradation.

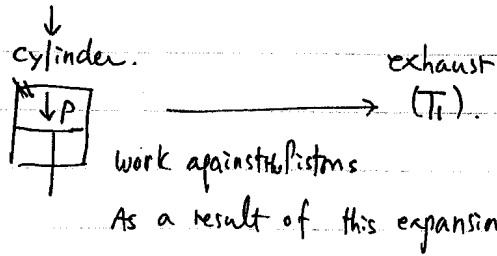
isothermal	$\Delta U_{rev} = \Delta U_{irr} = 0$
adiabatic	$W_{rev} \neq \Delta U_{irr}$
	$U_B \neq U_A$

$PV^\gamma \rightarrow P_2 V_2^\gamma$

3.10. Heat Engine.



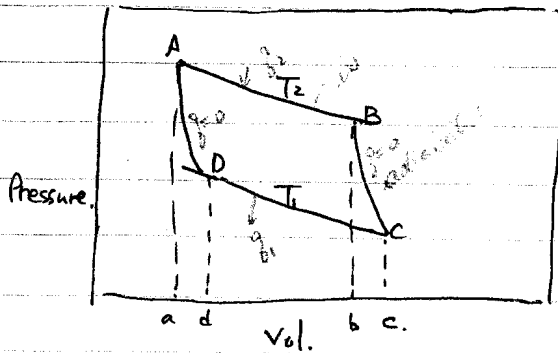
例: Steam Engine superheated steam from the boiler (T_2)



$T_2 \rightarrow T_1$

$$\text{Efficiency} = \frac{\text{work obtained}}{\text{heat input}} = \frac{W}{Q_2}$$

The Carnot Cycle (Reversible Process)!!



i) step $A \rightarrow B$. reversible heat transfer (Q_2) from heat res. to the cylinders (isothermal, reversible expansion)
 $W_1 = ABba$.

ii) step $B \rightarrow C$. reversible (adiabatic) expansion
 $T_2 \rightarrow T_1$ $W_2 = BCcb$.

iii) step $C \rightarrow D$. heat (Q_1) is isothermally, reversibly transferred from the cylinders to a heat reservoir at T_1 . $W_3 = DCcd$.

iv) step $D \rightarrow A$ reversibly (adiabatically) compressed.
 $T_1 \rightarrow T_2$ $W_4 = ADda$.

During the cyclic process. ($A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$)

Work performed $W = W_1 + W_2 - W_3 - W_4$

heat absorbed $Q = Q_2 - Q_1$

For a cyclic process $\Delta U = 0$. From the 1st law.

$$Q = W \quad Q_2 - Q_1 = W \quad \therefore \text{efficiency} = \frac{W}{Q_2} = \frac{Q_2 - Q_1}{Q_2}$$

Methods for better efficiency.

1. If more W' is obtained ($W' > W$) when Q_2 is ^{with} drawn from a heat reservoir (at T_2)

then $Q = W' > W \quad \therefore W' = Q_2 - Q_1'$ which

then efficiency = $\frac{W'}{Q_2} = \frac{Q_2 - Q_1'}{Q_2} \leftarrow \text{improved!!}$ $Q_1' < Q_1$

2. Or. the same work W , is obtained by withdrawing less heat Q_2' at T_2 $Q_2' < Q_2$. Thus less heat Q_1' is rejected

then efficiency = $\frac{W}{Q_2'} = \frac{Q_2' - Q_1'}{Q_2'}$ $(Q_2' - Q_1' = Q_2 - Q_1)$
 \therefore $\leftarrow \text{improved.}$

step reading assigned

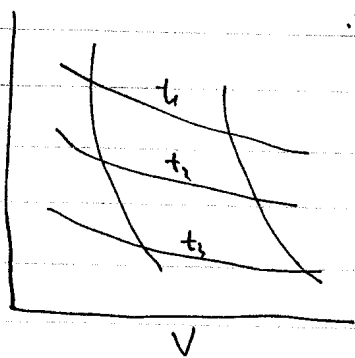
3.11. Thermodynamic Temp. Scale.

Previous discussion \rightarrow all reversible Carnot cycles operating bet'n the same upper & lower temp. should have the same efficiency (max. eff.)

// which is indep. of the working substance.
only function of the working temp (t_1, t_2).

$$\therefore \text{Efficiency} = \frac{Q_2 - Q_1}{Q_2} = f'(t_1, t_2) = 1 - \frac{Q_1}{Q_2}$$

$$\therefore \frac{Q_1}{Q_2} = f(t_1, t_2)$$



Carnot cycles

For two cycles operating bet'n t_1 & t_2 , t_2 & t_3 .
= equivalent to a cycle operating bet'n t_1 & t_3

Thus $\frac{Q_1}{Q_2} = f(t_1, t_2)$, $\frac{Q_2}{Q_3} = f(t_2, t_3)$

$$\frac{Q_1}{Q_3} = f(t_1, t_3)$$

$$\therefore \left(\frac{Q_1}{Q_2}\right) \times \left(\frac{Q_2}{Q_3}\right) = \frac{Q_1}{Q_3} = f(t_1, t_3)$$

indep. of t_3 .

indep. of t_2

$\frac{q_1}{T_1} = \frac{q_2}{T_2}$

$$\therefore f(t_1, t_2) = \frac{F(t_1)}{F(t_2)} \quad \text{if } \frac{q_1}{T_1} = \frac{q_2}{T_2} \quad \left(\frac{F(t_1)}{F(t_2)} \right)$$

$\times \theta$

$$\therefore f(t_1, t_2) = \frac{F(t_1)}{F(t_2)} \quad \text{if } \frac{q_1}{T_1} = \frac{q_2}{T_2} \quad \left(\frac{F(t_1)}{F(t_2)} \right)$$

$\times \theta$

$$\text{Thus } \frac{q_1}{T_1} = \frac{q_2}{T_2} \quad \text{if } \frac{F(t_1)}{F(t_2)} = \frac{F(t_1)}{F(t_2)}$$

Kelvin used the simplest form T_1 & T_2

$$\therefore \frac{q_1}{T_1} = \frac{q_2}{T_2} \quad \therefore \text{efficiency} = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

The absolute thermo. temp. scale is identical w/ the ideal gas temp. see
In a Carnot cycle of 1 mole of an ideal gas.

State A to state B. Reversible isothermal exp. at T_2 .

$$\Delta U = 0 \quad \text{from eq. (2.10)}$$

$$q_2 = w_1 = RT_2 \ln \left(\frac{V_B}{V_A} \right)$$

State B to state C. Reversible adiabatic exp.

$$q = 0 \quad w_2 = -\Delta U = - \int_{T_2}^{T_1} C_v dT$$

State C to state D. Reversible isothermal compression at T_1 .

$$\Delta U = 0 \quad q_1 = w_3 = RT_1 \ln \left(\frac{V_D}{V_C} \right)$$

State D to state A. Reversible adiabatic compression

$$q = 0 \quad w_4 = -\Delta U = - \int_{T_1}^{T_2} C_v dT$$

All a more ways seem innocent to him
but motives are weighed by the Lord

모든 것이 보기에 무죄에 보였지만
주님은 그 동기를 저울질하신다. (Prov. 16:2)

(12)

3/17 ⑦

Total work done by the gas $w = \sum_1^4 w_i$

$$= RT_2 \ln \left(\frac{V_B}{V_A} \right) - \int_{T_2}^{T_1} C_V dT + RT_1 \ln \left(\frac{V_D}{V_C} \right) -$$

Heat absorbed from the heat reservoir $= \oint_2 = w_1 = RT_2 \ln \left(\frac{V_B}{V_A} \right)$

From $PV = nRT$ for isothermal
 $PV^\gamma = \text{const}$ for adiabatic

$$\frac{V_B}{V_A} = \frac{V_C}{V_D} \quad (\text{derivation in the book})$$

$$\therefore w = R(T_2 - T_1) \ln \left(\frac{V_B}{V_A} \right)$$

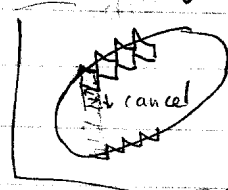
$$\therefore \text{efficiency} = \frac{w}{\oint_2} = \frac{R(T_2 - T_1) \ln \left(\frac{V_B}{V_A} \right)}{RT_2 \ln \left(\frac{V_B}{V_A} \right)} = \frac{T_2 - T_1}{T_2}$$

\therefore thermo temp scale is identical w/ the ideal gas temp. scale

3.12 The 2nd law of Thermo.

$$\text{efficiency} = \frac{\oint_2 - \oint_1}{\oint_2} = 1 - \frac{\oint_1}{\oint_2} = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2} \quad \therefore \frac{\oint_1}{\oint_2} = \frac{T_1}{T_2}$$

$$(3.6) \quad \therefore \frac{\oint_2}{T_2} - \frac{\oint_1}{T_1} = 0$$



- Any cyclic process can be represented by a number of Carnot cycles. \rightarrow Fig. 3.6.

- for the zigzag path of these cycles $\left| \sum \frac{\oint}{T} = 0 \rightarrow \oint \frac{d\oint}{T} = 0 \right.$

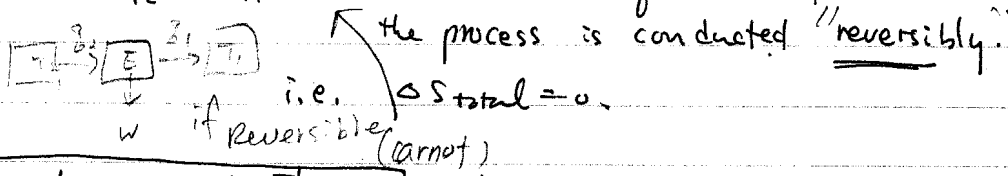
$\oint \left(\frac{\delta Q}{T} \right) = 0$ The vanishing of the cyclic integral indicates that the integral is a perfect diff. of some func. of the state of the system. \rightarrow called the entropy.

(3.7) $dS = \frac{\delta Q}{T}$ \leftarrow reversible heat increment. (path of Q in Q . $\frac{\delta Q}{T}$ rev equilth state. $PV = nRT$)

\therefore for the loop ABA $\oint dS = 0 = \int_A^B dS + \int_B^A dS = (S_B - S_A) + (S_A - S_B)$

(3.8) $dS = \frac{\delta Q_{rev}}{T}$ - from the consideration of Carnot cycles (reversible operation).

(3.6) $\frac{Q_2}{T_2} - \frac{Q_1}{T_1} = 0$ is a consequence of the fact that



The 2nd law of Thermo.

- The entropy, S , defined by the eq. $dS = \frac{\delta Q_{rev}}{T}$, is a state function.
- (a) S of a system \uparrow in an irreversible process
 (b) remains const in a reversible pr
 (c) In no cases (even in an adiabatic) $S \downarrow$ always S

\therefore for an infinitesimal change of state of an adiabatically contained system

(3.9)

$\sum dS_i \geq 0$

(3.10)

$\sum dS_i = dS_{irr}$ only irreversible portion in a pro

3.13 maximum work.

The 1st law gives no indication (from $U_B - U_A = q - w$) about the mag. of q and w in the given process
 but the 2nd law sets a limit on the "max" amount of w

For an infinitesimal change of state.

$$dS_{sys} = \frac{\delta q}{T} + dS_{irr.} \quad (= \frac{\delta q_{rev}}{T})$$

substitute.

1st law $\delta q = dU_{sys} + \delta w$

$$dS_{sys} = \frac{dU_{sys} + \delta w}{T} + dS_{irr.} \quad \text{General}$$

$$\Rightarrow \delta w = T dS_{sys} - dU_{sys} - T dS_{irr.}$$

by 2nd law. ($dS_{irr} \geq 0$)

$$(3.11) \quad \boxed{\therefore \delta w \leq T dS_{sys} - dU_{sys.}} \quad \text{General}$$

① $\boxed{\text{if } T = \text{const.}}$ $\rightarrow w \leq T(S_B - S_A) - (U_B - U_A)$
 = when $w = w_{max}$. \leftarrow ②
 when the process is carried out reversible
 $w_{max} = T(S_B - S_A) - (U_B - U_A)$
 = q_{rev}
 $\leq T = \text{const.}$
 reversible

\Rightarrow means // as entropy is a state fn., the entropy change is the
 whether the process is carried out reversibly or irreversibly
 \therefore The above discussion (3.11) indicates that
 if is the heat effect that is different !!

reversible the heat (= q_{rev}) > the heat (= q_{irr})

XQ

① 1 mole ideal gas isothermal reversible exp. from state A to state B.

$$\text{heat } q_{rev} = W_{max} = \int_{V_A}^{V_B} p dV = RT \ln \left(\frac{V_B}{V_A} \right)$$

$$\therefore \Delta S_{sys} = S_B - S_A = \frac{q_{rev}}{T} = R \ln \left(\frac{V_B}{V_A} \right)$$

$$\Delta S_{heat res} = -R \ln \left(\frac{V_B}{V_A} \right) \Rightarrow \left(= -\frac{q_{rev}}{T} \right)$$

$\therefore \Delta S_{total} = 0$ no entropy created.

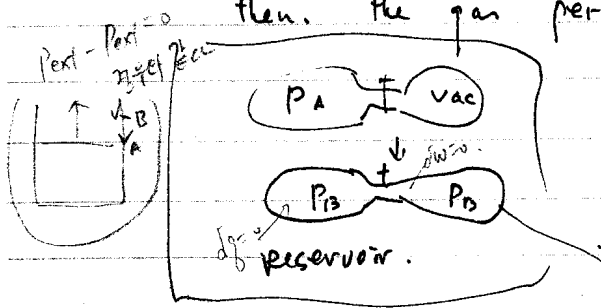
② 1 mole ideal gas is allowed to expand freely from P_A to P_B (as in Joule's exp.)

then, the gas performs no work ($\because p dV = dW$)

\uparrow against

$$\therefore \Delta U = 0 \because dW = dQ = 0$$

\rightarrow heat from reservoir.



irreversible process

As entropy is a state fn: $S_B - S_A$ is indep. of the path

$$\therefore S_B - S_A = R \ln \left(\frac{V_B}{V_A} \right) = \int_{V_A}^{V_B} \frac{dq_{rev}}{T} + \Delta S_{irr} = \frac{q_{rev}}{T}$$

$$\therefore \Delta S_{total} = \Delta S_{irr} = R \ln \left(\frac{V_B}{V_A} \right)$$

\downarrow created as a result of degraded

work. which would have

been performed by the gas if the expansion had not been carried out against a zero external pressure

$$\begin{aligned} \text{The degraded work} &= W_{max} - W \\ &= W_{max} - 0 = W_{max} = q_{rev} \end{aligned}$$

$$\therefore 0 \leq \Delta S_{irr} \leq$$

3/20/95

16

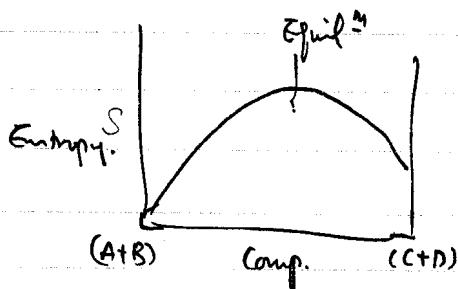
3.14. Entropy and the Criterion of Equil^m.

if a sys at equil^m, no movement, if nonequil^m, spontaneously ^{move to it}
 the attainment of the equil^m state coincides w/ the entropy reaching a max. value. ∴ the entropy can be used as a criterion for determination of the attainment of equil^m
 (with eqn $\int ds = 0$)

For a system of const. U and const V.

equil^m state is attained when the entropy of the sys. is a max.

$ds_{irr} \uparrow$ as i revers \uparrow from 0 \leftrightarrow revers.



$ds = 0$ means S at max.

in chemical rxn $A+B = C+D$

3.15 Combined Statement of the 1st & 2nd laws.

For a small change of state of a closed sys.

$$dU = d\bar{q} - d\bar{w}$$

if the process occurs reversibly, from the 2nd law

$dS_{rev} = \frac{d\bar{q}_{rev}}{T}$
 $d\bar{q}_{rev} = T ds$
 $d\bar{w} = PdV$ (consider only PV work)



(3.12) ∴ Combination of the two laws. $dU = Tds - PdV$ (no exchange of matter with surround)

Restriction ① closed system (adiabatic enclosure!!)

② The work is only due to vol. change

(3.12) \Rightarrow the dependent variable $\bullet U$, related to indep U
 $\therefore S$ and V

$$U = U(S, V)$$

total differential.

3.13
$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

(3.12)
$$dU = T dS - P dV$$

$$\therefore T \equiv \left(\frac{\partial U}{\partial S}\right)_V, \quad P \equiv -\left(\frac{\partial U}{\partial V}\right)_S$$

If consider S as dep. variable, and U and V indep.

$$S = S(U, V)$$

$$dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$$

from (3.12) $\rightarrow ds = \frac{dU}{T} + \frac{P}{T} dV$

$$\left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}$$

\therefore Equil^m ^{이완}, if $U, V = \text{const}$, occurs when $ds = 0$ $S(U, V)$
" " if $S, V = \text{const}$, " " $du = 0$ $U(S, V)$

$\frac{\partial S}{\partial U} = \frac{1}{T}$

$\frac{\partial U}{\partial V} = -P$