

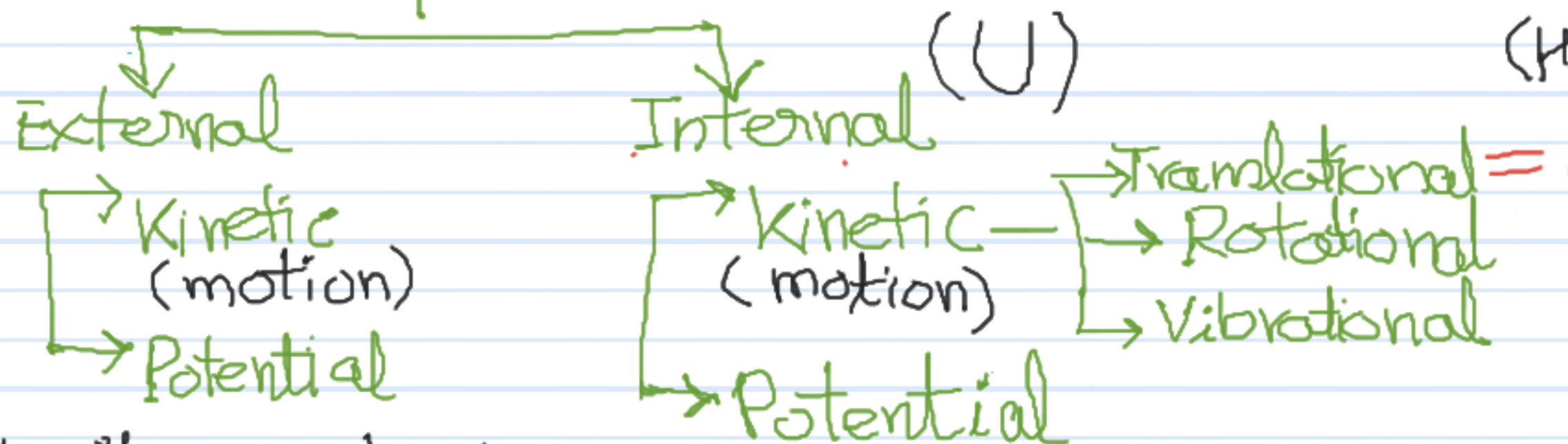
Date: 25/10/23

Lecture - 28

Energy Balance Topics

Thermophysics

Energy



(position, compression, elongation, surface energy, flow (PV) energy)

Enthalpy, $H = U + PV$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + P\Delta V + V\Delta P$$

Flow work $\Delta(PV)$

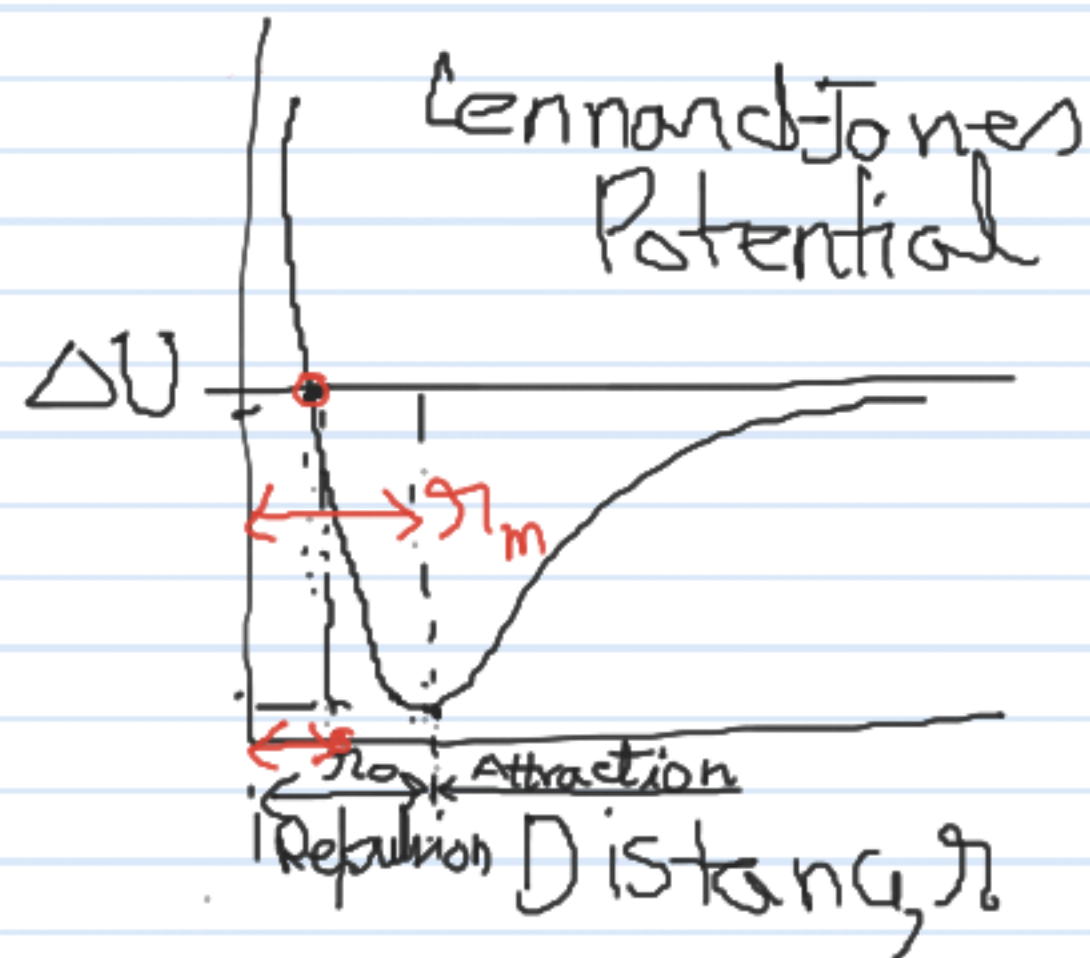
(proximity and structure, attractive/repulsive forces)

Thermochemistry

Heat of reactions

(Heat of formation, combustion, ...)

= 0 at absolute zero T



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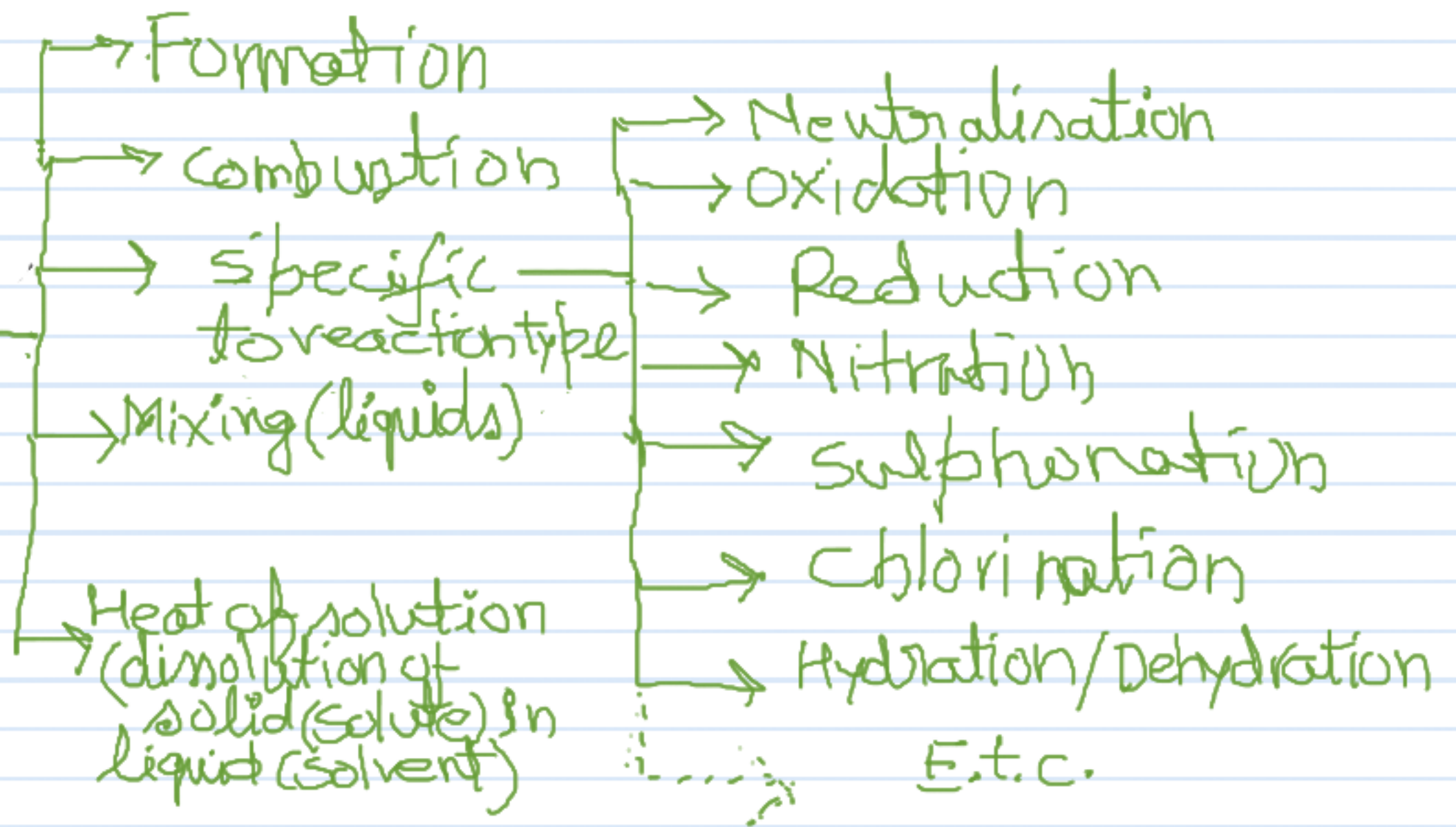
Topics of Study

Thermophysics — sensible heat and heat capacity, heat of phase change —
heat of unit operations — absorption, adsorption, crystallisation etc.

- evaporation/condensation
- melting/freezing
- sublimation

Thermochemistry —

Enthalpy change / Heat of
(Heat of unit process)
 ΔH_{rxn}

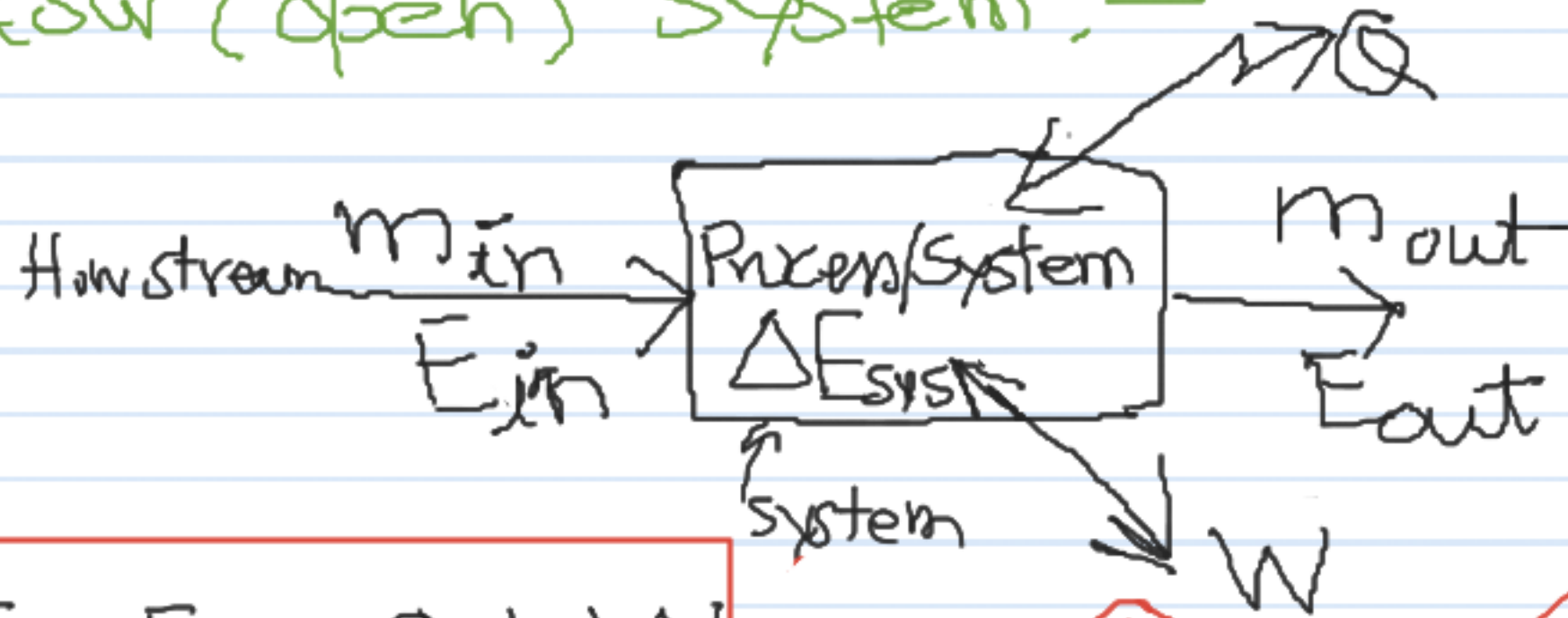


Date: 26/10/23

Thermodynamics Lecture - 29

Law of Energy Conservation / I Law of Thermodynamics

⇒ General Energy Balance for close (non-flow) and flow (open) system: -



Q, W are forms of transport of energies

$$\Delta E_{sys} = E_{in, f.s.} - E_{out, f.s.} \pm Q_b \pm W_{mech., electr.}$$

expansion contraction

$$E_{KE} = \frac{1}{2} m u^2$$

$$E_{PE} = \underbrace{PV}_{\text{pressure energy}} + mgz$$

$$\text{pressure energy} = \frac{P \cdot m}{\rho}$$

Flow stream: $E_{f.s.} = E_{int} + E_{ext} = U^{total} + E_{KE} + E_{PE} + E_{flow}$

(E_{in} and E_{out}) $= U + \frac{1}{2} m u^2 + mgz + P m V$

System: $E_{sys} = \left[U + \frac{1}{2} m u^2 + mgz \right]_{sys}$

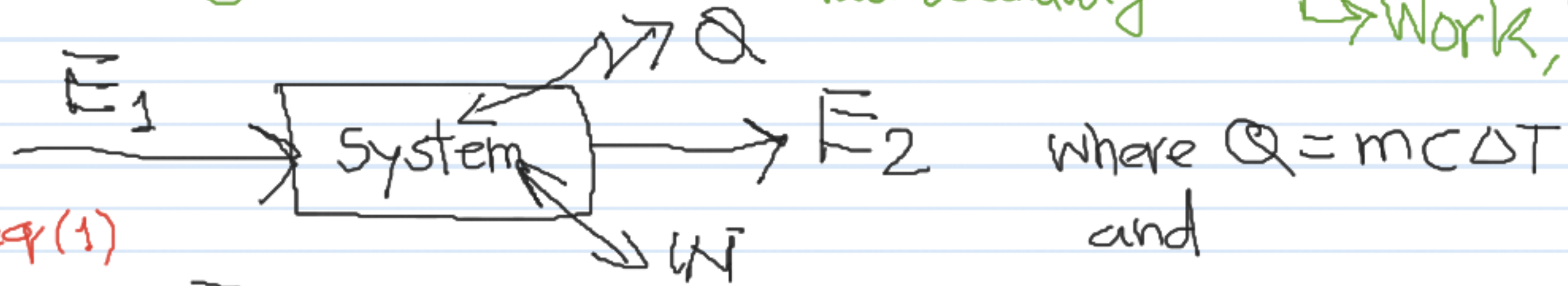
Steady Process: $\Delta E_{sys} = 0$ (energy of system) $= U + \frac{1}{2} u^2 + gz + PV$ (for unit mass, $m=1$)

energy of flow stream $\frac{P}{\rho}$

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L-29 contd....

Energies transferred to/from the system via boundary Heat Q
Work, W



Steady flow process

from eq (1)

$$E_1 \pm Q \pm W = E_2$$

$$E_2 - E_1 = \Delta E_{f.s.} = \pm Q \pm W \quad \text{usually } \Delta E_{f.s.} = \Delta H_{f.s.} \text{ (since kinetic \& potential energy changes are negligible)}$$

Unsteady nonflow/closed system

Usually $\Delta H_{f.s.} = \pm Q \pm W$ --- (2)

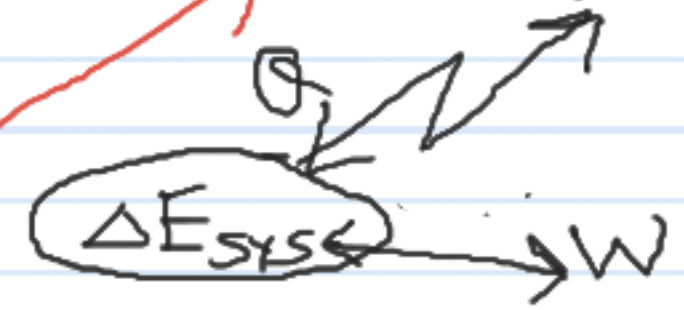
$$E_{f.s.} = 0 \text{ and}$$

From eq. (1)

$$\Delta E_{sys} = \pm Q \pm W \quad \text{usually } \Delta E_{sys} = \Delta U_{sys} \quad \Delta KE = \Delta gZ = 0$$

Or $\Delta U_{sys} = \pm Q \pm W$ --- (3)

→ (Subscript 1 and 2 represent states of system) + into system
→ Sign of Q & W - out from system



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Lecture-30

I Law of Thermodynamics:

Steady flow: $\Delta H_{f.s.} = \pm Q \pm W$

Unsteady non-flow: $\Delta E_{sys} = \Delta U_{sys}$
 $\Delta U_{sys} = \pm Q \pm W$

Usually for chemical processes $W = 0$

therefore $\Delta H_{f.s.} = \pm Q$ (for steady flow system)

and $\Delta U_{sys} = \pm Q$ (for batch/non flow
unsteady state system)

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Definitions:-

Heat capacity: $C = \frac{Q}{\Delta T}$, Specific heat $S = \frac{Q}{m\Delta T}$

For solids & liquids (incompressible materials) only one C is defined whereas gases have heat capacity at constant pressure, C_p and constant volume, C_v

For ideal gas $C_p - C_v = R$ $C_p > C_v$

Sensible Heat (change in temperature is observed)

$$Q_{\text{sensible}} = m C \Delta T$$

Latent heat (Phase change/state of aggregation changes)

$$Q_{\text{latent}} = m \lambda$$

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Lecture-31

Heat capacity of gases:

$$C = \frac{\partial Q}{dT} \Rightarrow C_p = \frac{\partial Q_p}{dT} \text{ and } C_v = \frac{\partial Q_v}{dT}$$

I Law: $dU = \partial Q + \partial W$

$$dU = \partial Q - PdV$$

$$dU = \partial Q_p - PdV \Rightarrow \partial Q_p = \underline{dU + PdV}$$

We know, $H = U + PV$

$$\therefore dH = dU + PdV + VdP$$

at constant P, $dH_p = dU + PdV$ ($dP=0$)

$$dH_p = \partial Q_p$$

$$C_p = \frac{\partial Q_p}{dT} = \left(\frac{dH}{dT} \right)_p$$

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Lecture-31 contd.

Heat capacities of gas.

$$Q = m c \Delta T$$

I Law: $dU = \delta Q - PdV$

at constant volume: $dU_v = \delta Q_v$ (since $dV=0$)

$$c_v = \frac{\delta Q_v}{dT} = \left(\frac{dU}{dT}\right)_v$$

It can be shown that for ideal (monatomic) gases

$$c_p - c_v = R \rightarrow \text{Universal gas constant}$$

For ideal gas U is function of only T . Also $c_p = a + bT + cT^2$

Mean heat capacity $c_{p, \text{mean}} = \frac{\int_{T_1}^{T_2} c_p dT}{T_2 - T_1}$

$$c_{p, \text{mean}} = a + \frac{b}{2}(T_2 + T_1) + \frac{c}{3}(T_2^2 + 2T_1 T_2 + T_1^2)$$

$$c_p = 2.5 + 4 \times 10^{-3} T - 1.4 \times 10^{-4} T^2$$

$c_{p, \text{mean}} = ?$
50-100°C
323K-373K

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Lecture-32

Heat capacities of monatomic gases (He, Ar, Kr, Xe, Ne, Rn)

Internal energy is only composed of kinetic energy of translation of molecules:

$$U = \frac{3}{2} RT$$

$$C_v = \frac{dU}{dT} = \frac{3}{2} R = 3 \text{ gcal/gmolK}$$

$$R \approx 2 \text{ g-cal/g-mol K}$$

$$C_p = R + C_v = 2 + 3 = 5 \text{ gcal/gmolK}$$

$$\frac{C_p}{C_v} = \gamma = \frac{5}{3} = 1.67$$

Data on heat capacity is given in texts (eg. Table 18, Fig 60, page 253)

Thumb rule: C_p of water $\approx 2 C_p$ of steam $\approx 4 C_p$ of air

$$C_{p \text{ mean}} = \frac{\int_{T_1}^{T_2} C_p dT}{T_2 - T_1}$$

(Refer Table 19, Hougan. Watson Text)

Fig 62 and 63

Properties of Water and Air

	Water	Air
Density	1000 kg/m^3	1.23 g/L
Heat capacity	1 cal/g K	0.24 cal/g K
Viscosity	1 cP	$1 \times 10^{-3} \text{ cP}$
Mol. wt.	18	29