LECTURE 2 [WEEK 3]

- THERMODYNAMICS OF SURFACES
  - REFERENCES
    - PHYS. & CHEM. OF I.F. (BUTT ET AL.)
      - CH. 3 : THERMO.
      - CH. 11, SEC. 2 : MICELLES

PT. 1: THERMODYNAMICS REFRESHER*

- STATE VARIABLES
  - A THERMODYNAMIC SYSTEM IS CHARACTERISED BY A COLLECTION OF "STATE VARIABLES" WHICH ARE MEASURABLE AND TO SOME EXTENT CONTROLLABLE PROPERTIES OF THE SYSTEM IN EQUILIBRIUM

* FOR FULL TREATMENT, SEE "THERMODYNAMICS" BY H. CALLEN

- FOR SIMPLE SYSTEMS LIKE PURE GASES & LIQUIDS THESE STATE VARIABLES WILL INCLUDE:
  - VOLUME (V)
  - MOLE NUMBER (N)
- STATE VARIABLES ARE "EXTENSIVE" IN THE SENSE THAT DOUBLING THE SYSTEM REQUIRES DOUBLING THE VALUES OF THE STATE VARIABLES.

- ENTROPY
  - AMONG THE STATE VARS IS ALWAYS INCLUDED A VAR S CALLED THE ENTROPY WHOSE PROPERTIES WILL BE EXPLAINED

BELOW.

- ENERGY
  - FOR ANY T.D. SYSTEM W/ STATE VARIABLES $X_1, X_2, \ldots, X_N$ THERE IS A FUNCTION CALLED THE "ENERGY":

$$U(X_1, \ldots, X_N)$$

WHICH IS ALSO EXTENSIVE IN THAT: $U(2X_1, \ldots, 2X_N)$

$$= 2U(X_1, \ldots, X_N)$$

- 1^{ST} LAW OF T.D.
  - THE CHANGE IN THE ENERGY OF A SYSTEM ΔU AFTER UNDERGOING SOME CHANGE

IS EQUAL TO THE SUM OF:

- THE WORK ΔW DONE BY THE SURROUNDINGS ON THE SYSTEM, AND
- THE HEAT ΔQ ABSORBED BY THE SYSTEM FROM THE SURROUNDINGS:

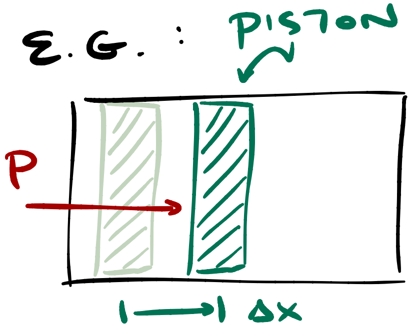
$$\left[\ \Delta U = \Delta W + \Delta Q \qquad [1^{ST}\ LAW]\ \right]$$

- HEAT & WORK
  - IT IS IN GENERAL POSSIBLE TO INSULATE A SYSTEM FROM ITS SURROUNDINGS SO THAT $\Delta Q = 0$ DURING SOME PROCESS.

    SUCH PROCESSES ARE CALLED "ADIABATIC".

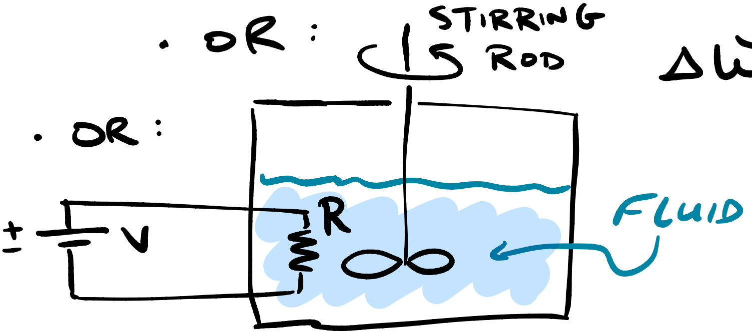
- GIVEN TWO T.D. STATES A & B, IT IS TRUE THAT *EITHER*:
  - AN ADIABATIC PROCESS EXISTS WHICH TRANSFORMS $A \rightarrow B$
  - " " " "

    " " $B \rightarrow A$.
- SINCE WORK [E.G. $F \Delta x$] CAN BE MEASURED, THIS MEANS ENERGY DIFFERENCES $\Delta U = U_A - U_B$ CAN BE MEASURED.
- E.G.:



$$\Delta W = F \Delta x$$
$$= P A \Delta x$$
$$= P \Delta V$$

- OR :
- OR :



$$\Delta W = T_{DRAG} \times \Delta\theta$$

$$\left[\underset{\substack{\uparrow \\ \text{TORQUE}}}{T_{DRAG}} \propto \frac{\Delta\theta}{\Delta t}\right]$$

$$\Delta W = \frac{V^2}{R}\Delta t$$

- NOTE HERE THAT WE CAN "HEAT UP" A SYSTEM W/ OUT ABSORBING HEAT $[\Delta Q = 0]$!

- THIS ALSO THEN PERMITS THE MEASUREMENT OF HEAT TRANSFER ΔQ DURING SOME NON-ADIABATIC PROCESS $A \rightarrow B$:

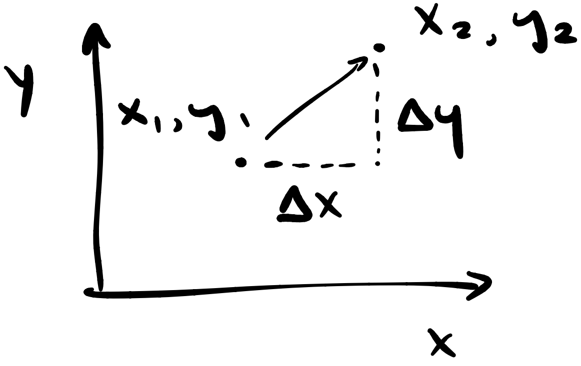
$$\Delta Q = \Delta U - \Delta W$$

$$= \Delta W_{ADIABATIC} - \Delta W$$

- E.G. WE CAN INCREASE THE ENERGY OF A LIQUID EITHER

BY STIRRING ADIABATICALLY OR HEATING W/ A FLAME.

- DIFFERENTIALS
  - differentials DESCRIBE HOW TO compare THE VALUES OF A FUNCTION EVALUATED @ TWO NEARBY points:



"$dz = z_x dx + z_y dy$" MEANS:

$$\Delta z = z(x_2, y_2) - z(x_1, y_1)$$

$$= + z_x \Delta x + z_y \Delta y$$

WHERE: $$z_x = \frac{\partial z}{\partial x}\bigg|_y (x_0, y_0)$$

$$z_y = \frac{\partial z}{\partial y}\bigg|_x (x_0, y_0)$$

WITH :

$$(x_1, y_1) \simeq (x_0, y_0) \simeq (x_2, y_2)$$

- SIMILARY WE CAN WRITE FOR THE T.D. ENERGY $U(S, V, N)$:

$$dU = T dS - P dV + \mu dN,$$

WHERE: $$T = \frac{\partial U}{\partial S}\bigg|_{V,N},$$ "TEMPERATURE"

$$P = -\frac{\partial U}{\partial V}\bigg|_{S,N},$$ "PRESSURE"

$$\mu = \frac{\partial U}{\partial N}\bigg|_{S,V}$$ "CHEMICAL POTENTIAL"

- 2^{ND} LAW OF T.D.
  - THE 2^{ND} LAW RELATES THE ABSTRACT NOTIONS OF ENTROPY & HEAT. IT STATES:

[
- FOR ANY PROCESS WE HAVE:

$$T\Delta S \geq \Delta Q \quad [2^{ND} \text{ LAW}]$$
]

- ASSERTING $T > 0$ THEN GIVES $\Delta S \geq 0$ FOR ADIABATIC PROCESSES.

- WHEN WE HAVE EQUALITY, i.e. $T\Delta S = \Delta Q$, WE TALK ABOUT A "QUASI-STATIC"

PROCESS.

- FOR QUASI-STATIC PROCESSES WE HAVE:

$$\Delta W = \Delta U - \Delta Q = \Delta U - T\Delta S$$

$$= \cancel{T\Delta S} - P\Delta V + \mu\Delta N - \cancel{T\Delta S}$$

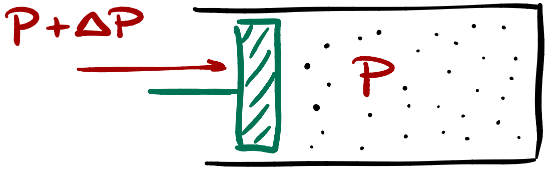
$$= -P\Delta V + \mu\Delta N$$

  - OR, FOR "CLOSED" SYSTEMS W/ $\Delta N = 0$:

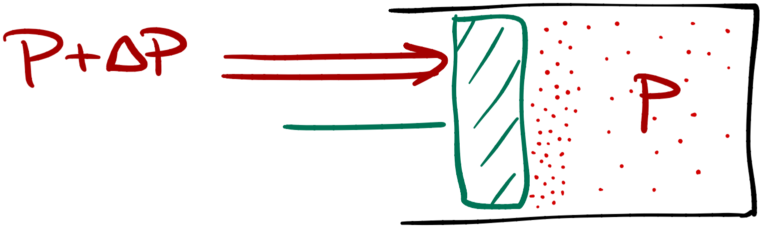
$$\Delta W = -P\Delta V$$

- QUASI-STATIC PROCESSES
- ARE THOSE WHICH ARE SUFFICIENTLY SLOW THAT THE SYSTEM REMAINS FOR ALL TIMES ARBITRARILY CLOSE TO EQUILIBRIUM.

- EXAMPLES:
  - ADIABATIC COMPRESSION OF GAS:



  - $\Delta P \rightarrow 0$:
    - QUASI-STATIC
    - GAS DENSITY REMAINS UNIFORM THROUGHOUT COMPRESSION.
    - $$\Delta U = \Delta W + \cancelto{0 \text{ (ADIABATIC)}}{\Delta Q}$$
      $$= -[P+\Delta P]\Delta V \rightarrow -P\Delta V$$
  - $\Delta P \not\rightarrow 0$:
    - VIOLENT COMPRESSION SETS UP PRESSURE GRADIENTS:



- "EXTRA" ENERGY $\Delta P \Delta V$ PUT INTO SYSTEM IN FORM OF PRESSURE GRADIENT
    - THIS GRADIENT CREATES WAVES INSIDE GAS WHICH DISSIPATE AND LEAD TO INCREASE IN ENTROPY

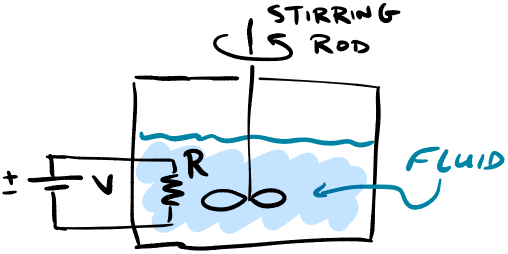
$$\Delta S = \Delta P \Delta V / T$$

@ EQUILIBRIUM

- ADIABATIC STIRRING OR JOULE $[V^2/R]$ HEATING:
    - $\Delta U = \Delta W > 0$

BUT:

- $\Delta N = 0$
- $\Delta V = 0$



- SO:

$$T\Delta S = \Delta U + P\cancelto{0}{\Delta V} - \mu \cancelto{0}{\Delta N}$$

$$= \Delta U = \Delta W > 0 \implies \text{NON QUASI STATIC.}$$

TEST FOR COMPREHENSION: WHAT IS THE CHANGE IN ENTROPY OF AN IDEAL GAS DURING ISOTHERMAL COMPRESSION?

- SURFACE TENSION, REVISITED
  - FOR SINGLE-COMPONENT [i.e. $\emptyset$ SOLUTES] GAS-LIQUID INTERFACE WE HAVE AS STATE VARIABLES JUST THE SURFACE ENTROPY S AND THE SURFACE AREA A:

$$dU = T\,dS + \sigma\,dA$$

$$T = \frac{\partial U}{\partial S}\bigg|_{A} \qquad \sigma = \frac{\partial U}{\partial A}\bigg|_{S}$$

FOR SOME PROCESS PRODUCING A CHANGE ΔA IN THE INTERFACIAL AREA WE HAVE:

$$\Delta W = \Delta U - \Delta Q = T\Delta S + \sigma\,\Delta A - \Delta Q$$

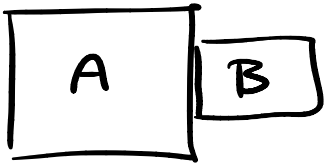
$$\underset{\text{VIA 2ND LAW}}{\geq} \sigma\,\Delta A$$

- BUT!
  - WE ALREADY AGREED THAT THE COEFFICIENT RELATING A CHANGE IN SURFACE AREA ΔA TO SOME MINIMUM NECESSARY WORK ΔW WAS WHAT WE CALLED THE SURFACE TENSION γ:

$$\boxed{\gamma = \sigma = \left.\frac{\partial U}{\partial A}\right|_S}$$

- TEMPERATURE
  - TO FINISH OUR RECAP OF GENERAL T.D., LET'S JUSTIFY OUR USE OF THE WORD "TEMPERATURE" AS A NAME FOR $\left.\frac{\partial U}{\partial S}\right|_{V,N}$.

- CONSIDER TWO RIGID CONTAINERS THAT ARE THERMALLY ISOLATED FROM THE OUTSIDE WORLD BUT CAN EXCHANGE ENERGY BETWEEN EACH OTHER:



$$\Delta U = \Delta \cancelto{0}{W} + \Delta \cancelto{0}{Q} = 0$$

(∅ WORK) (ADIABATIC)

$$= \Delta U_A + \Delta U_B \implies \Delta U_B = -\Delta U_A$$

$$\Delta U_A = T_A \Delta S_A - P_A \Delta \cancelto{0}{V_A} + \mu_A \Delta \cancelto{0}{N_A}$$

(RIGID) (CLOSED)

$$= T_A \Delta S_A$$

$$\Delta U_B = T_B \Delta S_B = -T_A \Delta S_A$$

$(\Delta U_B = -\Delta U_A)$

$$\Delta S = \Delta S_A + \Delta S_B = \Delta S_A \left[1 - \frac{T_A}{T_B} \right] \geq 0$$

(2ND LAW)

- SO:

$$\Delta U_A = T_A \Delta S_A \geq 0$$

IF $T_A < T_B \implies$ HEAT FLOWS FROM HOT TO COLD!

- WHILE THE 2ND LAW AS WE STATED IT ONLY PLACED A CONSTRAINT ON ADIABATIC PROCESSES [$\Delta S \geq 0$], WE CAN IN FACT MAKE A STRONGER STATEMENT:

ANY ADIABATICALLY ISOLATED SYSTEM WILL SPONTANEOUSLY EVOLVE OVER ITS UNCONSTRAINED STATE VARIABLES IN ORDER TO MAXIMIZE ITS ENTROPY.

- W/ THE EXAMPLE WE JUST WORKED THROUGH WE SAW

HOW A COMPOSITE SYSTEM WILL EXCHANGE ENERGY (THE DIFFERENCE $U_B - U_A$ WAS UNCONSTRAINED WHILE THE SUM $U_A + U_B$ WAS FIXED) UNTIL $T_A = T_B$.

- Similarly:
  - TWO SYSTEMS THAT CAN EXCHANGE VOLUME (VIA, E.G., A MOVABLE WALL OR PISTON) CAN INCREASE THEIR COLLECTIVE ENTROPY BY EXPANDING THE HIGHER PRESSURE $\left(P = -\frac{\partial U}{\partial V}\Big|_{S,N}\right)$ SUBSYSTEM AND VICE VERSA.

- TWO SYSTEMS THAT CAN EXCHANGE PARTICLES WILL DO SO UNTIL THEIR CHEMICAL POTENTIALS $\mu = \left.\frac{\partial U}{\partial N}\right|_{S,V}$ BECOME EQUAL.

SEE PART II FOR REST OF LECTURE.