MEAS. T :
THERMOMETERS :

{ 1ST question —
(1) are temps round   3.4
(2) what are they   t.1

skip { - WANT TO KNOW HOW Q FLOWS FROM SYS A TO B
         WITHOUT PUTTING IN CONTACT.

say { - NOT DIRECT $\rightarrow$ T DEF'D IN TERMS OF MICRO SYS. ; HOW TO GET AT IT VIA MEAS?

THERMOMETER: SYS M WHICH

(1) HAS SOME MICRO "THERMOMETRIC PARAM" $\Theta(\bar{\varepsilon})$
    WHICH CHANGES AS M ABSORBS Q. { will detect diff in T by Q

ex
(a)   MERCURY THERM :

   say { ABS Q, AVE ε OF MOLS INCR $\rightarrow$ EXPANDS

   $\Rightarrow$ $\underline{\Theta = V}$ (meas. temp in units of vol.)

(b) RESISTANCE THERM :

   RES. INCR, AS ABSORBS ε $\Rightarrow$ $\underline{\Theta}$ IN OHMS

(c) CONST VOL GAS THERM $\Rightarrow$ $\Theta = \bar{p}$

(2) SMALL $\rightarrow$ DOESN'T AFFECT MEAS'D SYS

TO USE :
(a) PUT IN THERM. CONTACT w/ SYS A

   ABSORBS Q UNTIL EQUIL ; THEN $\beta_M = \beta_A$
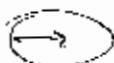
   $\rightarrow$ RECORD $\Theta(A)$

(b) REPEAT FOR SYS B

IF $\Theta(A) = \Theta(B)$, THEN $\beta_M = \beta_A$, $\beta_M = \beta_B$ { Therm. equil depends on single param

$\Rightarrow$ $\beta_A = \beta_B$ $\rightarrow$ EQUIL IF PUT IN CONTACT

$\longrightarrow$ (but doesn't tell me what β is)

DIFF THERMS USEFUL IN DIFF CASES:

ex LOWER T : CONST V GAS BETTER THAN Hg (FREEZES)

— HARD TO COMPARE:

DIFF UNITS

NOT PROPORTIONAL $\left\{\begin{array}{l}\text{ex Hg MIGHT DOUBLE WHILE}\\ \text{RESIST. INCR. A LITTLE}\end{array}\right.$

NOTE:

IF PARAM Θ WORKS, SO DOES ANY $f(\Theta)$ $\left(\text{IF } \frac{\partial f}{\partial \Theta} \neq 0\right)$

VERY USEFUL $f(\Theta)$:
$$\beta_M(\Theta) \equiv \frac{1}{kT}$$

$\Rightarrow$ IF HAVE $\beta_M(\Theta)$ $\{$ $\beta_{M'}(\Theta')$, CAN CP. M, M' DIRECTLY.
NOW MEAS. SAME FUND. QTY

TO DO THIS:

NEED $\underline{1}$ SYS. WHERE KNOW $\beta_M(\Theta)$ (OR $T_M(\Theta)$)

THEN:

USE TO CALIBRATE EVERY OTHER $M' \Rightarrow \beta_{M'}(\Theta')$

<u>ex</u>

IDEAL GAS

$$\overset{\text{‖}}{\underset{\Theta}{p}} V = N k T = (\nu N_a) kT \qquad \left.\begin{array}{l}\text{GIVES } T(\Theta)\\ \equiv T(p)\end{array}\right.$$
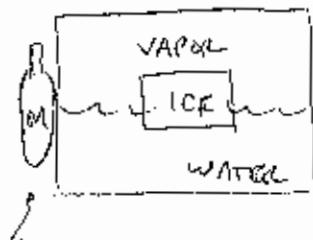
$\underset{\text{HELD CONST}}{}$

USEFUL: ALL GASES OBEY FOR LOW DENSITY
SOME TO VERY LOW T

DEFN. FOR °K (KELVIN).   (INTL CONVENTION)

(1)   MAKE I.G. FIXED-V THERM

(2)   CHOOSE REF. TEMP $T_t \equiv$ TRIPLE PT. OF H_2O

MEAS. $\bar{P}_t$ AT T_t FOR M

TEMP. AT WHICH ICE, WATER, VAPOR
IN EQUIL $\Rightarrow$ UNIQUE, AVAIL., EASY TO
PREP. (JUST PUT TOGETHER AND WAIT
FOR EQUIL)

(3) TO MEAS. T FOR NEW SYS:

$$\frac{\bar{P} V}{\bar{P}_t V} = \frac{\nu N_q k T}{\nu N_a k T_t} \qquad \Rightarrow \qquad \frac{T}{T_t} = \frac{\bar{P}}{\bar{P}_t} \qquad \left\{ \begin{array}{l} \text{GIVES RATIO} \\ \text{OF } T \text{ TO } T_t \end{array} \right.$$

CONVENTION:

$$T_t \equiv 273.16 \ °K \quad (\text{EXACT}) \qquad \left\{ \begin{array}{l} \text{DEFINES} \\ °\text{KELVIN} \end{array} \right.$$

$$\Rightarrow \boxed{ T = (273.16°K) \frac{\bar{P}}{\bar{P}_t} }$$

(4) $\bar{P}_t V = \nu N_a k T_t$

FIXES $\boxed{ k = 1.38 \times 10^{-16} \ ergs/°K }$

'BOLTZMANN CONST"

(COULD HAVE ALSO FIXED k AS EXACT, MEAS T_t,
TO DEF UNIT)

TORTURED DEFN?

DESIGNED TO MATCH CELSIUS (w/ OFFSET) (OLDER)
ie $\Delta°K = \Delta°C$

IN WIDE USE)

$$0°C = (T - 273.15)°K$$

DEFN. BASED ON H_2O:

FREEZES AT $0°C$ $\boxed{p} = 1$ ATM)

BOILS AT $100°C$

$\Rightarrow$ TRIPLE PT: $.01°C$ (NOTE: $\boxed{p}$ DIFF)

LOWEST TEMP: (ABS ZERO): $-273.15°C$

MORE RATIONAL:

$$T \equiv \frac{1}{\beta} = \left(\frac{\partial \ln \Omega}{\partial E}\right)^{-1} \qquad (\text{i}e \quad k=1)$$

$\Rightarrow$ UNITS OF E (°K UNNECESS)

THEN
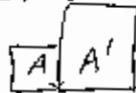
$$\boxed{p}V = \nu N_a T \qquad \Rightarrow \text{DON'T NEED REF.}$$

just say
WILL SEE: PROVIDES CONVENIENT, MEAS'BLE
MACRO VAR. WHICH GIVES INFO ON.
S, WHICH COUNTS MICRO INFO
⇒ BEHAVIOR AT LOW T GAVE FIRST
CLUE THAT CLASS. PHYS WRONG →NEED QM

HEAT CAPACITY:

ANOTHER USEFUL MACRO PARAM RELATING Q, T:

ex problem

$T_A < T_A'$ IF $T_A < T_A'$

$$đQ_A > 0$$

T_A INCR T_A' DECR UNTIL $T_A = T_A'$

(smaller system will usually have
T chg more)

FIND
FINAL T ? (from properties of materials)

HEAT CAPACITY:

not a deriv, just small amt of
đQ dev. by small chg in T

$$C_y \equiv \left(\frac{đQ}{dT} \right)_y$$

{ how much heat abs.
for given chg in T

use small amts because it's not const

—— PARAM ⓨ HELD FIXED (ex $\bar{p}$ or V)

⇒ IN GENERAL $C_y =$ $C_y(T, y_a)$ { or $C_y(\bar{E}, y_a)$ }

(mention once give $\bar{E}, y_a$ for sys., completely
specifies; can compute T. Could chg vars then $\bar{E}$ →T ; easier to measure)

SPECIFIC HEAT : DIV. OUT AMT OF MATERIAL
SO GIVES PROPERTY OF " , NOT AMT

PER MOLE :

$$c_y \equiv \frac{1}{\nu} C_y$$

↳ # MOLES

PER GRAM:

$$c_y' \equiv \frac{1}{m} C_y$$

↳ MASS

(usually obvious
which one by units)

ASIDE:

EXTENSIVE vs INTENSIVE PARAMS.

say { USEFUL TO CATEGORIZE MACRO PARAMS BY
DEPEND. ON SYSTEM SIZE :

EXTENSIVE :

- INCR $\propto$ SYS. SIZE

ex $V, \bar{E}, S, C_y,$ m (MASS), ν (# MOLES)

~ IF DOUBLE SIZE OF SYS, THESE DOUBLE

{ how to know S is extensive ?

[I] $\Omega_{TOT} = \Omega_A \cdot \Omega_{A'}$ $S_{TOT} = S_A + S_{A'}$ }

INTENSIVE:

- INTRINSIC PROPERTIES OF SYS $\rightarrow$ IND. OF SIZE

ex $\bar{p}, T, \rho, c_y$

NOTE, $\dfrac{EXT.}{EXT.} \rightarrow$ INT. (ex $\rho = \dfrac{M}{V}$

$c_y = \dfrac{C_y}{\nu}$)

etc

(like units, eqns must balance)

$\underline{C_y \quad DEP. \; ON \; WHICH \; PARAM \; FIXED}$

<u>ex</u> SPS MACRO SYSTEM SPECIFIED BY $\bar{E}, V$ (or T, V):

(a) V FIXED : $đQ = d\bar{E}$

(CLAMPED PISTON) (no work)

(b) $\bar{p}$ FIXED : PISTON (w/ FIXED WT) FREE

$$đQ = d\bar{E} + \bar{p} \, dV$$

$\Rightarrow$ T dep.^{strongly} in gen. on $\bar{E}$ (ideal gas $\nRightarrow$ only on T)

(a) ~~GIVEN~~ $đQ$ ALL GOES TO $d\bar{E}$ $\Rightarrow$ RAISES T

(b) SOME $đQ$ TO $d\bar{E}$

SOME TO WORK

$d\bar{E}$ LESS $\Rightarrow$ RAISES T LESS

EXPECT

$\Rightarrow$ $\boxed{C_p > C_V}$

CAN <u>RELATE TO ENTROPY</u>:

$$dS = \frac{đQ}{T} \qquad (q \to s)$$

$$\Rightarrow \boxed{C_y = \left(\frac{đQ}{dT}\right)_y = T\left(\frac{\partial S}{\partial T}\right)_y}$$

is a deriv; partial since y held fixed

THINKING OF $S(T, y)$
RATHER THAN $S(\bar{E}, y)$
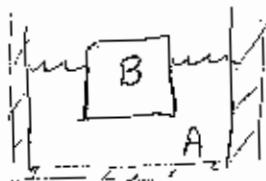
ALSO, FOR C_V, $đQ = d\bar{E}$

$$\Rightarrow \boxed{C_V = T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V}$$

USING C:

(1) FIND T_f

∗ PUT BLOCK OF Cu IN H_2O

⇒ LET V CHG, BUT DO IN ROOM ⇒ $\bar{p} = 1$ ATM

(easier for exp, solids to high p fixed, not V)

INIT TEMPS: T_A, T_B

AMT: m_A, m_B

(GRAM) SP. HT: $c'_{p,A}$, $c'_{p,B}$

(properties of H_2O, Cu)

$$Q_A + Q_B = 0$$

$Q = \int dQ = \int C(T)\, dT = \int m\, c'(T)\, dT$

$$0 = \int_{T_A}^{T_f} m_A\, c'_{p,A}(T)\, dT + \int_{T_B}^{T_f} m_B\, c'_{p,B}(T)\, dT$$

(stop writing p)

⇒ CAN SOLVE FOR T_f

SPECIAL CASE: $c' \sim$ CONST (FOR BOTH) (over this range)

$$m_A\, c'_{p,A}(T_f - T_A) + m_B\, c'_{p,B}(T_f - T_B) = 0$$

⇒
$$\boxed{T_f = \frac{m_A\, c'_A\, T_A + m_B\, c'_B\, T_B}{m_A\, c'_A + m_B\, c'_B}}$$

(note if m_B or c'_B large
$T_f \sim T_B$)

(2)   COMPUTE ΔS:

Q-S PROCESS

$$S(T_b) - S(T_a) = \int_a^b \frac{d\!\!\!/ Q}{T} = \sum_{T_a}^{T_b} \frac{C_y(T)\, dT}{T}$$

SPECIAL CASE:

IF $C_y(T) \sim$ CONST OVER THIS RANGE   (NOT GENERALLY TRUE)

$$\sim C_y \, \ln(T_b/T_a)$$ (why not? consider $T \sim 0$)

something fishy here:

THIS EX: NOT Q-S

 — ONLY IN EQUIL AT BEG & END

 — FLOW OF E DEPENDS ON MICRO DETAILS

 — NO WELL-DEFINED T, $C(T)$ DURING HEAT TRANS.

{ well-defined T means all sys. in ensemble at same $\bar{E}$ at every instance, so all have same $T = \frac{\partial \bar{E}}{\partial \bar{S}}$ }

BUT   USE YOUR IMAGINATION:

 — $S(T_{a,b})$ PROPERTY OF EQUIL MACRO SYS. AT ENDS —
   DOESN'T MATTER HOW GET THERE

 — ΔS SAME IF FOLLOW Q-S ROUTE (VIA FOR EACH SEPARATELY
   SEQUENCE OF HT. RESERVOIRS) $\Rightarrow$ pretend each A, B got there via Q-S process

PREVIOUS EXAMPLE:

$$\Delta S_A = S_A(T_f) - S_A(T_A) = \int_{T_A}^{T_f} \frac{m_A C_A'\, dT}{T} = m_A C_A' \, \ln\frac{T_f}{T_A}$$
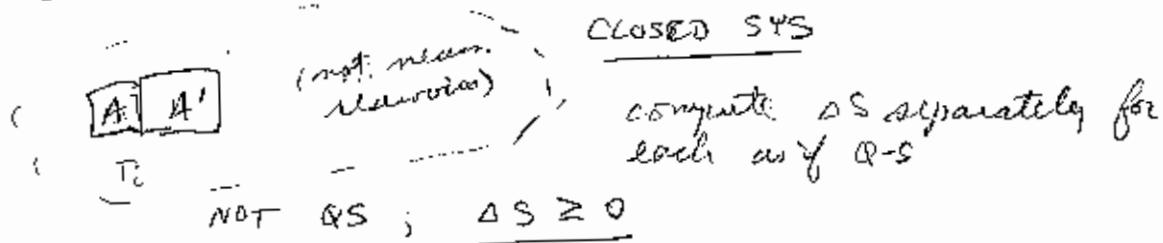
$$\boxed{\Delta S_A + \Delta S_B = m_A C_A' \, \ln\frac{T_f}{T_A} + m_B C_B' \, \ln\frac{T_f}{T_B}}$$

 = REIF SHOWS $\Delta S_A + \Delta S_B > 0$ FOR ANY T_A, T_B (AS IT MUST BE FOR NON Q-S PROCESS ON ISOLATED SYS)
   (have T_f above)

⊘ 9

↓ only if necessary

NOTE

(not. necs. new. various)

CLOSED SYS

compute ∆S separately for each as if Q-S

NOT QS ; $\Delta S \geq 0$
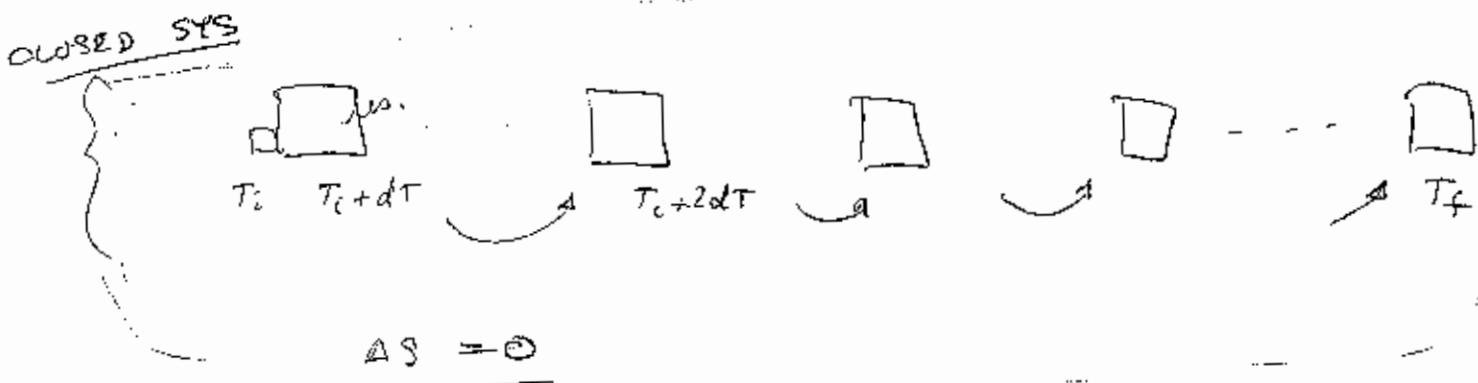
BUT FOR A, IF FINAL STATE GIVEN BY SAME E, V (OR T, V) DOESN'T MATTER HOW GOT THERE →

SAME S

FOCUS ON A alone:

CLOSED SYS

T_i $T_i + dT$ $T_i + 2dT$ T_f

$\Delta S = 0$

Then do same for A'

(3) FIND HEAT OF TRANSFORMATION:

eN   WHITE / GRAY   TIN   (Sn)

$T > T_0 = 292°K$ (~ RM TEMP)

WHITE ⟹ METAL

$T < T_0$

GRAY ⟹ SEMICONDUCTOR

AT $T \gtrsim T_0$ GRAY → WHITE , REQUIRING $Q_0 \equiv$ "HEAT OF
(PHASE TRANS)   (like melting ice)   TRANSFORMATIO

(note: statistical reasoning works
either if system reacts very quickly to changes
a part of it very slowly; either case, stay close to
equil
BUT: VERY SLOW   2 very diff

— CAN TREAT BOTH AS $\propto$ EQUIL TO LOW T   T scales:
                                                            (1) usual Transp
— CAN MEASURE $C^{(w)}(T)$ & $C^{(g)}(T)$ BOTH   of E → fa
        DOWN TO $T \sim 0$ → reaches
                                                            equil
                                                    (2) chg of phase
                                                        structure →
$T \sim 0$ (BUT NOT LOW ENOUGH TO AFFECT NUCL SPINS) (slow
                    (can use our guide $kT \lesssim R/$
                    to know when ok)

$S \to S_0 = k \ln \mathcal{N}_s$

    ↑
    # NUCL. SPIN STATES

⟹ SAME NUCLEI ∴ $\mathcal{N}_s$ SAME FOR BOTH   } MAIN PT

⟹ $\boxed{S^{(w)}(T \to 0) = S^{(g)}(T \to 0)}$

CAN PREDICT Q_0:
1 MOLE ; $\bar{p}$ FIXED ! $C_p = \mathcal{N}\bar{c}_p = c_p$
(a) TAKE WHT. FROM 0 TO T_0
    $S^{(w)}(T_0) = S^{(w)}(0) + \int_0^{T_0} \frac{C_p^{(w)}(T)}{T} dT$ ← MEAS

(b) TAKE GR. FROM 0 TO T_0, THEN QS TRANS TO WHT. AT T_0
    $S^{(w)}(T_0) = S^{(g)}(0) + \int_0^{T_0} \frac{C_p^{(g)}(T)}{T} dT + \frac{Q_0}{T_0}$

DURING TRANS. , T FIXED AT T_0 ∴ $\Delta S = \frac{Q_0}{T_0}$

PREDICT MEAS

$$\Rightarrow \quad \frac{Q_0}{T_0} = \int_0^{T_0} \frac{\left[c_p^{(w)}(T) - c_p^{(g)}(T) \right] \, dT}{T}$$

$\Rightarrow$ WORKS: $Q_0 = 2130$ J (1 MOLE)

(VS 2240 J MEAS DIRECTLY)

$\Rightarrow$ RELATED Q_0, WHICH DEPENDS ON DIFF IN STRUCTURE OF 2 STATES, TO c_p FOR INDIV. STATES VIA ENTROPY CONSIDERATIONS (ESP: SAME AT $T \sim 0$)