

CH 4 MEAS T, Q

SO FAR T IS ABSTRACT, FROM $\frac{\partial \ln \Omega}{\partial E}$ } HOW TO GET CHG IN # MICROST. BY MEAS 1 SYS?

THERMOMETER: SYS M

(1) SMALL → TO NOT AFFECT MEAS'D SYS

(2) HAS MACRO "THERMOMETRIC PARAM" $\Theta(E)$ THAT CHGS AS M ABS. Q

ex (a) Hg THERM

$\Theta = V$ (EXPANDS w/ Q)

(b) RESISTANCE THERM

$\Theta = R$ (IN OHMS) (INCR w/ Q)

(c) CONST. VOL GAS THERM

$\Theta = \bar{p}$ (INCR. w/ Q)

[NOTE: USEFUL IN DIFF REGIONS
(ex (c) GOOD AT LOW T,
(a) FREEZES)
HARD TO CP
⇒ DIFF UNITS
⇒ RELN NOT LINEAR

TO USE:

(a) PUT IN CONTACT w/ SYS A
KNOW: ABS. Q UNTIL EQUIL: $T_M = T_A$ ⇒ RECORD $\Theta(A)$

(b) REPEAT FOR B: IF $\Theta(A) = \Theta(B)$
A & B IN THERM EQUIL ⇒ $T_B = T_A$

PROBLEM: KNOW EQUAL, BUT DON'T KNOW VALUE

TO GET T (ie ABS TEMP)

- FOR EACH THERM. WANT FN $T(\theta)$ (ie fn relating $\theta \rightarrow T$)

- CAN DO THIS IF KNOW $T(\theta)$ FOR JUST 1 SYS

\Rightarrow SERVES AS REFERENCE

\Rightarrow USE TO CALIBRATE ALL OTHERS

WE DO: IDEAL GAS IN FIXED-V THERM

$$\left. \begin{array}{l} \bar{p} V = NKT \\ \left. \begin{array}{l} \uparrow \\ \text{HOLD CONST} \\ \uparrow \\ \equiv \theta \end{array} \right\} \end{array} \right\} \text{HAVE } T(\theta) \equiv T(\bar{p}) \\ = \bar{p} \frac{V}{nK}$$

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

TO CALIBRATE:

MEAS $\bar{p} \rightarrow$ GIVES T (ABS. TEMP)

USE NEW THERM (ex Hg)

MEAS $\theta \rightarrow$ GIVES $T(\theta)$

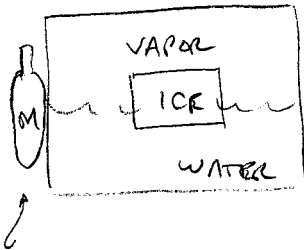
RELATES (ABSTRACT) ABS. T TO MEASBLE QTY θ

[could simplify]

DEFN. FOR °K (KELVIN): (INTL CONVENTION) (AS OF 1960's)

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- (1) MAKE IG. FIXED-V THERM
- (2) CHOOSE REF. TEMP $T_{\epsilon} \equiv$ TRIPLE PT. OF H_2O



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

MEAS. \bar{p}_{ϵ} AT T_{ϵ} FOR M } no gives \bar{p}_{ϵ} for my therm in my lab

(3) TO MEAS. T FOR NEW SYS:

$$\frac{\bar{p} V}{\bar{p}_{\epsilon} V} = \frac{N k T}{N k T_{\epsilon}} \Rightarrow \frac{T}{T_{\epsilon}} = \frac{\bar{p}}{\bar{p}_{\epsilon}}$$

GIVES RATIO OF T TO T_{ϵ}
can now meas T directly w/ IG therm

CONVENTION:

$$T_{\epsilon} \equiv 273.16 \text{ } ^{\circ}\text{K} \text{ (EXACT)}$$

{ DEFINES $^{\circ}$ KELVIN

$$\Rightarrow T = (273.16 \text{ } ^{\circ}\text{K}) \frac{\bar{p}}{\bar{p}_{\epsilon}}$$

(dimensionless \Rightarrow it's a ratio of pressures)

$$(4) \bar{p}_{\epsilon} V = N k T_{\epsilon}$$

measure once FIXES $k = 1.38 \times 10^{-16} \text{ ergs/}^{\circ}\text{K}$

"BOLTZMANN CONST"

(COULD HAVE ALSO FIXED k AS EXACT, MEAS T_{ϵ} , TO DEF UNIT)

TORTURED DEFN?

DESIGNED TO MATCH CELSIUS (w/ OFFSET) (OLDER, IN WIDE USE)
 i.e. $\Delta^\circ\text{K} = \Delta^\circ\text{C}$
 $0^\circ\text{C} = (T - 273.15)^\circ\text{K}$
 ↑ SO ZERO AT PROPER PLACE

DEFN. BASED ON H₂O:

FREEZES AT 0°C ($p = 1 \text{ ATM}$)

BOILS AT 100°C

⇒ TRIPLE PT: 0.01°C

(NOTE: p IS DIFFERENT)

LOWEST TEMP: (ABS ZERO): -273.15°C

MORE RATIONAL:

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

⇒ UNITS OF E (OK UNLESS)

THEN

$$pV = NT \quad \Rightarrow \text{DON'T NEED REF. TEMP, NEW UNIT}$$

HEAT CAPACITY

- USEFUL MACRO PARAM TO RELATE Q TO T
- WILL HELP TRACK ΔS AS T CHGS
- BEHAVIOR AT T ~ 0 GAVE EARLY CLUE OF NEED FOR QM
 - CLASSICAL PHYS. PREDICTION FOR HEAT CAP GIVES ΔS ~ ∞
 - ⇒ LIKE BLACKBODY SPECT; NOT JUST A LITTLE OFF

HEAT CAP $C_y \equiv \left(\frac{\delta Q}{dT} \right)_y$ } NOT DERIV; JUST EXPTL DEFN
 ABS. SMALL δQ & DIV BY dT
 (USE SMALL AMTS SINCE NOT CONST)

↑ (OTHERS) HELD FIXED (ex \bar{p} OR V)

IN GEN'L $C_y = C_y(\bar{E}, y_\alpha)$ OR $C_y(T, y_\alpha)$

(DEP. ON WHETHER CHOOSE TO SPECIFY SYS W/ \bar{E} OR T;
 KNOWING $\bar{E} \rightarrow T$ & V.V.)

SPECIFIC HEAT: DIV. OUT AMT → GIVES INTRINSIC PROPERTY OF MATERIAL

PER MOLE:

$C_y \equiv \frac{1}{R} C_y$
 # MOLES

PER GRAM:

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

Reif's notation; don't know how you'd

ASIDE:

EXTENSIVE VS INTENSIVE PARAMS:

- WAY TO CHARACTERIZE MACRO VARS (~ LIKE DIMS.)

EXTENSIVE: ∝ SYSTEM SIZE (if double sys, then double)

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

S: $S_{TOT} = S_A + S_{A'}$

INTENSIVE: INDEP. OF SIZE (INTRINSIC)

ex \bar{p} , T, ρ, C_y

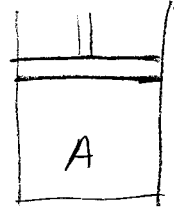
NOTE: $\frac{EXT}{EXT} = INT$
 (ρ, C_y -)

EQNS: MUST MATCH

C_y DEP. ON WHICH PARAM FIXED

ex SPS MACRO SYSTEM SPECIFIED BY \bar{E}, V (or T, V):

(a) V FIXED: $dQ = d\bar{E}$
(CLAMPED PISTON) (no work)



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

$$dQ = d\bar{E} + \bar{p} dV$$

$\Rightarrow T$ dep. ^{strongly} in gen. on \bar{E} (ideal gas \Rightarrow only on T , not V)

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

(b) SOME dQ to $d\bar{E}$
SOME TO WORK

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

EXPECT

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

greater dQ to get same rise in T

CAN RELATE TO ENTROPY:

$$dS = \frac{dQ}{T} \quad (Q-S)$$

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

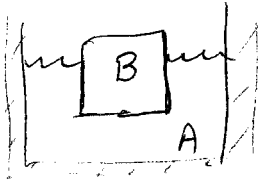
this is a deriv; partial since y held fixed

THINKING OF $S(T, y)$
RATHER THAN $S(\bar{E}, y)$; GEN'L BUT ASSUMES Q-S.

ALSO, FOR C_v , $dQ = d\bar{E}$

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



USING C:(1) FIND T_f JK PUT BLOCK OF CU IN H_2O \Rightarrow LET V. CHG, BUT DO IN ROOM $\Rightarrow \bar{p} = 1 \text{ ATM}$ 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)(easier for Eq, solids to keep \bar{p} fixed, not V)

$$Q_A + Q_B = 0$$

$$Q = \int \dot{Q} dt = \int \dot{Q}(T) dt = \int m c'(T) dT$$

$$\Rightarrow 0 = \int_{T_A}^{T_f} m_A c'_A(T) dT + \int_{T_B}^{T_f} m_B c'_B(T) dT$$

(stop writing p)

 \Rightarrow CAN SOLVE FOR T_f (NEED MEASMT OR MODEL FOR $c'(T)$ TO FINISH)SPECIAL CASE: $c' \sim \text{CONST}$ (FOR BOTH) (over this range)

$$m_A c'_A \cdot (T_f - T_A) + m_B c'_B (T_f - T_B) = 0$$

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

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

(2) COMPUTE ΔS :

Q-S PROCESS

not a well-def'd integral; more a meanit prescription

now it's def'd

$$S(T_f) - S(T_i) = \int_{T_i}^{T_f} \frac{dQ}{T} = \int_{T_i}^{T_f} \frac{C_y(T) dT}{T} \quad (\text{can see that } C \rightarrow 0 \text{ for } T \rightarrow 0)$$

SPECIAL CASE:

IF $C_y(T) \sim \text{CONST}$ OVER THIS RANGE (not generally true; consider $\uparrow \sim 0$)

$$\Delta S \sim C_y \ln(T_f / T_i)$$

PREVIOUS EXAMPLE:

$$\Delta S_A = S_A(T_f) - S_A(T_A) = \int_{T_A}^{T_f} \frac{m_A C_A' dT}{T} \approx m_A C_A' \ln \frac{T_f}{T_A}$$

$$\Delta S = \Delta S_A + \Delta S_B \approx m_A C_A' \ln \frac{T_f}{T_A} + m_B C_B' \ln \frac{T_f}{T_B}$$

w/ T_f ABOVE

THIS IS CORRECT, BUT SOMETHING FISHY IN THIS EX: NOT Q-S

- ONLY IN EQUIL AT BEG & END
- FLOW OF \bar{E} DEP. ON MICRO DETAILS; NOT PREDICTABLE
- NO WELL-DEF'D $T, C(T)$ DURING Q
(well-def'd T means all sys. in ens. are at same \bar{E} (w/ small deviations) at every instance, so have single $\frac{1}{kT} = \frac{\partial \ln R}{\partial \bar{E}}$)

- $ds \neq \frac{dQ}{T}$

BUT USE YOUR IMAGINATION

- $S(T_{i,f})$ PROP. OF EQUIL. MACRO SYS AT ENDS - DOESN'T MATTER HOW GOT THERE

- ΔS SAME IF FOLLOW Q-S ROUTE (FOR EACH SEPARATELY) VIA SEQUENCE OF HT RES.

\Rightarrow R.P.I.F. SHOWS $\Delta S = \Delta S_A + \Delta S_B > 0$ FOR ANY T_A, T_B (AS EXPECTED FOR NON-QS PROCESS IN ISOLATION)

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#3

ship in 1A

USUALLY ONLY AS MATTER; HERE'S AN EXAMPLE WHERE ABS. VAL. OF S IS IMPORTANT (use at $T=0$) C.B

EV WHITE / GRAY TIN (S_H)

$T > T_0 = 292^{\circ}K$ ($\approx 13^{\circ}C$)

WHITE \Rightarrow METAL

$T < T_0$

GRAY \Rightarrow SEMICONDUCTOR

AT $T \gtrsim T_0$ GRAY \rightarrow WHITE, REQUIRING $Q_0 \equiv$ "HEAT OF TRANSFORMATION" (PHASE TRANS) (like melting ice) (DAYS/WEEKS)

BUT: VERY SLOW

- CAN TREAT BOTH AS \approx EQUIL TO LOW T

- CAN MEASURE $C_p^{(w)}(T)$ & $C_p^{(g)}(T)$ BOTH DOWN TO $T \sim 0$

(note: statistical reasoning works (either if system reacts very quickly to changes, a part of it very slowly; either case, stay close to equil)
2 very diff T scales:
(1) usual transfer of E \rightarrow fast \Rightarrow reorders liquid structure
(2) chg of basic structure \Rightarrow slow (can use our guide $kT \lesssim E_A$ to know when ok)
can think of freezing structure \sim no diff

$T \sim 0$ (BUT NOT LOW ENOUGH TO AFFECT NUCL SPINS)

$S \rightarrow S_0 = k \ln \Omega_s$

Ω_s # NUCL. SPIN STATES

\Rightarrow SAME NUCLEI $\therefore \Omega_s$ SAME FOR BOTH

$\Rightarrow S^{(w)}(T \rightarrow 0) = S^{(g)}(T \rightarrow 0)$

3RD LAW } MAIN PT

CAN PREDICT Q_0 :

1 MOLE, \bar{p} FIXED: $C_p = \sqrt{C_p} = C_p$

(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 $\therefore \Delta S = \frac{Q_0}{T_0}$

PREDICT
MEAS

↓
↓
↘

$$\Rightarrow \frac{Q_0}{T_0} = \int_0^{T_0} \frac{[C_p^{(w)}(T) - C_p^{(g)}(T)]}{T} dT$$

\Rightarrow WORKS : $Q_0 = 2130 \text{ J}$ (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 $T \sim 0$)

Could mention 2nd ex in Ref:

using S_0 same for 2 elements at 0 + $C_p(T)$'s
 to C_p S (separate) to S (combined in molecules) at T_{room}

\Rightarrow see if chem. reaction can occur w/out looking at details of bonds, etc