

MEAS. T:

THERMOMETERS:

- 1<sup>st</sup> question -
- (1) are temps same
  - (2) what are they

3.9  
t.1

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

prob { - NOT DIRECT  $\Rightarrow$  T DEFD IN TERMS OF MICRO SYS.; HOW TO GET AT IT VIA MEAS?

THERMOMETER: SYS M

- (1) w/ SOME MACRO "THERMOMETRIC PARAM"  $\Theta(\bar{E})$   
WHICH CHANGES AS M ABSORBS Q. } will detect diff in T by Q

ex

(a) MERCURY THERM:

prob { ABS Q, AVE  $\bar{E}$  OF MOLS INCR  $\rightarrow$  EXPANDS

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

(b) RESISTANCE THERM:

RES. INCR. AS ABSORBS  $\bar{E} \Rightarrow \underline{\Theta}$  IN OHMS

(c) CONST VOL GAS THERM  $\Rightarrow \underline{\Theta} = \bar{p}$ (2) SMALL  $\rightarrow$  DOESN'T AFFECT MEAS'D SYS

TO USE:

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

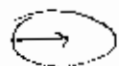
ABSORBS Q UNTIL EQUIL; THEN  $\beta_M = \beta_A$

$\rightarrow$  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



(did not tell me what  $\beta$  is)

DIFF THERMS USEFUL IN DIFF CASES:

EX LOWER T: CONST V GAS BETTER THAN  $H_g$  (FREEZES)

- HARD TO COMPARE:

DIFF UNITS

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

- DON'T GIVE ASS T (YET)

NOTE:

IF PARAM  $\theta$  WORKS, SO DOES ANY  $f(\theta)$  (IF  $\frac{df}{d\theta} \neq 0$ )

VERY USEFUL  $f(\theta)$ :

$$\beta_M(\theta)$$

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

TO DO THIS:

NEED 1 SYS. WHERE KNOW  $\beta_M(\theta)$  (OR  $T_M(\theta)$ )

THEN:

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

EX

IDEAL GAS

$$\bar{p} V = NKT$$

$\theta$   $\swarrow$  HELD CONST

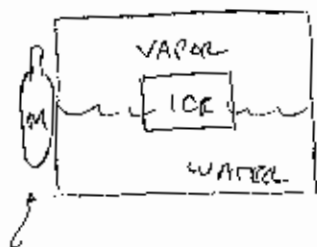
$\left. \begin{array}{l} \text{GIVES } T(\theta) \\ \equiv T(\bar{p}) \end{array} \right\}$

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

DEFN. FOR  $^{\circ}\text{K}$  (KELVIN): (INTL CONVENTION)

(1) MAKE IG. FIXED-V THERM

(2) CHOOSE REF. TEMP  $T_E \equiv$  TRIPLE PT. OF  $\text{H}_2\text{O}$



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

MEAS.  $\bar{p}_E$  AT  $T_E$  FOR M

(3) TO MEAS.  $T$  FOR NEW SYS:

$$\frac{\bar{p} V}{\bar{p}_E V} = \frac{N k T}{N k T_E} \quad \Rightarrow \quad \frac{T}{T_E} = \frac{\bar{p}}{\bar{p}_E} \quad \left. \vphantom{\frac{T}{T_E}} \right\} \text{GIVES RATIO OF } T \text{ TO } T_E$$

CONVENTION:

$$T_E \equiv 273.16^{\circ}\text{K} \quad (\text{EXACT}) \quad \left. \vphantom{T_E} \right\} \text{DEFINES } ^{\circ}\text{KELVIN}$$

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

$$(4) \quad \bar{p}_E V = N k T_E$$

$$\text{FIXES } \left[ k = 1.38 \times 10^{-16} \text{ ergs}/^{\circ}\text{K} \right]$$

"BOLTZMANN CONST"

(COULD HAVE ALSO FIXED  $k$  AS EXACT, MEAS  $T_E$ ,  
TO DEF. UNIT)

TORTURED DEFN?

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

DEFN. BASED ON  $H_2O$ :

FREEZES AT  $0^{\circ}C$  ( $p = 1 \text{ ATM}$ )

BOILS AT  $100^{\circ}C$

⇒ TRIPLE PT:  $0.01^{\circ}C$  (NOTE:  $p \neq 1 \text{ ATM}$ )

LOWEST TEMP. (ABS ZERO):  $-273.15^{\circ}C$

MORE RATIONAL:

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

⇒ UNITS OF  $E$  (OK UNLESS)

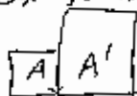
THEN

$$pV = N T \quad \Rightarrow \text{DON'T NEED REF.}$$

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



IF  $T_A < T_{A'}$

$dQ_A > 0$

$T_A$  INCR

$T_{A'}$  DECR

UNTIL  $T_A = T_{A'}$

(smaller system will usually have  
 T chg more)

FIND  
 FINAL T? (from properties of materials)

step

HEAT CAPACITY:

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

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

{ how much heat abs.  
 for given chg in T

use small amts because it's not const

PARAMETER HELD FIXED (ex  $p$  or  $V$ )

⇒ IN GENERAL  $C_y = C_y(T, y)$  {OR  $C_y(\bar{E}, y)$ }

(mention once give  $\bar{E}, y$  for sys, completely  
 specifies; can compute T. Could chg var than  $\bar{E} \rightarrow T$ ; 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.

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

EXTENSIVE:

- INCR  $\propto$  SYS. SIZE

ex  $V, \bar{E}, S, C_y, M(\text{MASS}), \nu$  (# MOLES)

~ IF DOUBLE SIZE OF SYS, THESE DOUBLE

{ how to know S is extensive?

INTENSIVE:

[I]  $S_{\text{tot}} = S_A + S_{A'}$   $S_{\text{tot}} = S_A + S_{A'}$  }

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

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

NOTE:

$\frac{\text{EXT.}}{\text{EXT.}} \rightarrow \text{INT.}$

(ex  $\rho = \frac{M}{V}$ )

$c_y = \frac{G_A}{\nu}$  )

etc

(like units, eqns must balance)

$C_y$  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. <sup>strongly</sup> in gen. on  $\bar{E}$  (ideal gas  $\Rightarrow$  only on  $T$ )

(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

$\Rightarrow$

$$C_p > C_v$$

CAN RELATE TO ENTROPY:

$$dS = \frac{dQ}{T} \quad (9-5)$$

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

is a deriv;  
partial since  $y$   
held fixed

THINKING OF  $S(T, y)$   
RATHER THAN  $S(\bar{E}, y)$

ALSO,  
FOR

$$C_v, \quad dQ = d\bar{E}$$

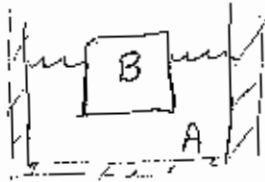
$$\Rightarrow C_v = T \left( \frac{\partial S}{\partial T} \right)_v = \left( \frac{\partial \bar{E}}{\partial T} \right)_v$$

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.)

$$Q_A + Q_B = 0$$

$$Q = \int \delta Q = \int C(T) dt = \int m C'(T) dt$$

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

$\Rightarrow$  CAN SOLVE FOR  $T_f$

(stop writing !!)

SPECIAL CASE:  $C_{p,A}' \sim \text{CONST}$  (FOR BOTH) (over this range)

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

$$\Rightarrow T_f = \frac{m_A C_{p,A}' T_A + m_B C_{p,B}' T_B}{m_A C_{p,A}' + m_B C_{p,B}'}$$

(note if  $m_B$  or  $C_{p,B}'$  large  
 $T_f \sim T_B$ )



(2) COMPUTE  $\Delta S$  :

not a well-defined integral; more a meas. prescription  
 now it's well-def'd

Q-S PROCESS

$$S(T_b) - S(T_a) = \int_a^b \frac{dQ}{T} = \int_{T_a}^{T_b} \frac{C_y(T) dT}{T}$$

SPECIAL CASE:

IF  $C_y(T) \sim \text{CONST}$  OVER THIS RANGE (NOT GENERALLY TRUE)  
 $\sim C_y \ln(T_b/T_a)$  (why not? consider  $T \rightarrow 0$ )

something fishy here:

THIS EX: NOT Q-S

- ONLY IN EQUIL AT BEG & END
- FLOW OF E DEPENDS ON <sup>MICRO</sup> DETAILS
- NO WELL-DEFINED T, C(T) DURING HEAT TRANS.

BUT USE YOUR IMAGINATION: EQUIL

-  $S(T_a, b)$  PROPERTY OF MACRO SYS. AT ENDS —  $T = \frac{\partial S}{\partial E}$  (well-defined T means all exp. in ensemble at same E at every instance, so all have same  $\frac{\partial S}{\partial E}$ )

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

PREVIOUS EXAMPLE:

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

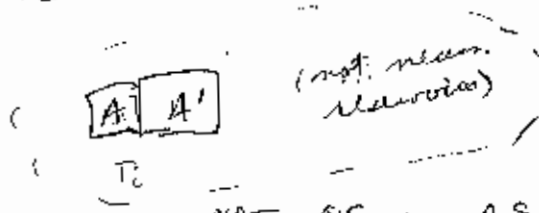
$$\Delta S_A + \Delta S_B = m_A C_A' \ln \frac{T_f}{T_A} + m_B C_B' \ln \frac{T_f}{T_B}$$

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



only if necessary

NOTE



CLOSED SYS

compute  $\Delta S$  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  $\rightarrow$  SAME S

FOCUS ON A alone:

CLOSED SYS



$\Delta S = 0$

Then do same for A'



(3) FIND HEAT OF TRANSFORMATION:

OR WHITE / GRAY TIN (Sn)

$T > T_0 = 292^{\circ}K$  (~ RM TEMP)

WHITE  $\Rightarrow$  METAL

$T < T_0$

GRAY  $\Rightarrow$  SEMICONDUCTOR

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

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 trans of E  $\rightarrow$  fast  $\rightarrow$  reaches equil  
 (2) change of phase structures  $\rightarrow$  slow

$T \sim 0$  (BUT NOT LOW ENOUGH TO AFFECT NUCL SPINS) (can use our guide  $kT \lesssim E_A$  to know when ok)

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

$\Omega_s \neq$  NUCL. SPIN STATES

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

} MAIN PT

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

CAN PREDICT  $Q_D$ :

1 MOLE;  $\bar{p}$  FIXED:  $C_p = \nu C_p^* = C_p$

(a) TAKE WHT. FROM 0 TO  $T_0$

$S^{(w)}(T_0) = S^{(w)}(0) + \int_0^{T_0} \frac{C_p^{(w)}(T)}{T} dT$  (HEATS)

(b) TAKE GR. FROM 0 TO  $T_0$ , THEN QS TRANS TO WHT. AT  $T_0$

$S^{(w)}(T_0) = S^{(g)}(0) + \int_0^{T_0} \frac{C_p^{(g)}(T)}{T} dT + \frac{Q_D}{T_0}$

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

$$\begin{array}{c} \text{PREDICT} \\ \downarrow \\ \Rightarrow \frac{Q_0}{T_0} = \int_0^{T_0} \frac{[C_p^{(w)}(T) - C_p^{(g)}(T)]}{T} dT \end{array}$$

$\Rightarrow$  WORKS :  $Q_0 = 2130 \text{ J}$  (1 MOLE)  
(VS  $2240 \text{ J}$  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  $T \sim 0$ )