

# THERMODYNAMICS : DETAILS

FOUNDATIONS ARE BASED ON EMPIRICAL OBSERVATIONS  
⇒ LAWS

## I 1ST LAW

CONSERVATION OF ENERGY

1ST IN ANY PROCESS ENERGY IS CONSERVED

$$dE = \delta W + \delta Q$$

$E \Rightarrow$  total energy  $\Rightarrow dE$  variation of energy due by some process

$W \Rightarrow$  MECHANICAL WORK  $\Rightarrow \delta W$  mechanical work made on the system

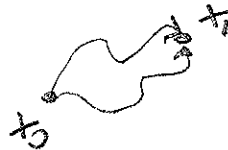
$Q \Rightarrow$  HEAT  $\Rightarrow \delta Q$  heat given to the system.

Why  $dE$  &  $\delta W$ ? What is the difference between  $d(\cdot)$  &  $\delta(\cdot)$ ? FUNDAMENTAL!

$E$  is a function of state of the system ( $\bar{x}$ )

$\Rightarrow$  going from  $x_0$  to  $x_1$  (states)  
is function only on FINAL & INITIAL position, not path!!!

$$\Delta E = \int_{x_0}^{x_1} dE$$



DOES NOT  
DEPEND ON  
PATH

$$\Rightarrow \Delta E(\text{closed loop}) = \int_{x_0}^{x_0} dE = 0$$



CHANGE OF A STATE FUNCTION ON A REVERSIBLE PROCESS IS ZERO

IN MATHEMATICAL TERMS

$d =$  DIFFERENTIAL

EXAMPLE  $f(x, y) =$  STATE FUNCTION  
 $(x, y)$  STATE

DIFFERENTIAL  $df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy$

$\partial^2?$   $\frac{\partial^2 f}{\partial x \partial y}$  &  $\frac{\partial^2 f}{\partial y \partial x}$ , are they identical?

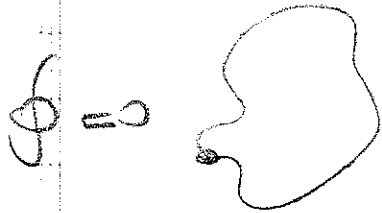
IF  $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \Rightarrow f$  is CALLED CLOSE FORM.

$\Updownarrow$  IF & ONLY IF

$\oint_{\text{loop}} df = 0$  integral on a loop = 0

$\Updownarrow$

$\int_{(x_0, y_0)}^{(x_1, y_1)} df =$  does NOT depend on path



$\Rightarrow$   $df$  is differential of  $E$   
 &  $E$  is a function of state (for the 1st law)

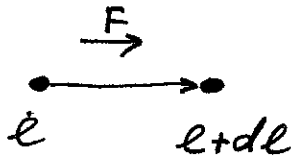
What about  $\delta$ ?

$\delta$  represents a tiny <sup>variation</sup> amount of something but it is not a differential!!!!

$\delta \neq d$   
NO DIFF      DIFF

EXAMPLE

$\delta W$  = tiny amount of work to go from close states

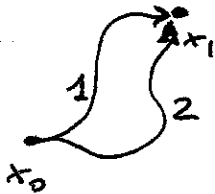


$\delta W = F dl$

$\delta W$  is not differential of  $W$ !!

$W = FL$        $\delta W$   
 $dW = d(FL) = Fdl + LdF$        $\parallel$   
 $\delta W = Fdl$        $\Downarrow$   
 NOTHING

$\delta$  (SOMETHING) <sup>symbol</sup> is applied when the variation depends on the path



$\delta Q_1 \neq \delta Q_2$  depends on the path, the way you go from 1 to 2

so  $dF = \frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy \Rightarrow$  if  $\frac{\partial^2 F}{\partial x \partial y} \neq \frac{\partial^2 F}{\partial y \partial x} \Rightarrow$

PATH DEPENDENCE  $\Rightarrow$  need  $\delta$  & not  $d$

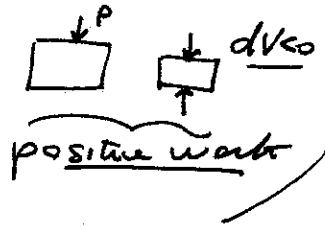
USUALLY CALLED

$d$  = PERFECT DIFFERENTIAL, DIFFERENTIAL ... FOR STATE FUNCTIONS  
 $\delta$  = DELTA, VARIATION OF, ... FOR NO-STATE FUNCTIONS!

we know  $\delta W = -pdV$

V is a state function!!  $\Rightarrow dV$   
of course, V is a state by itself.  
variable

(- because  
if V decreases  
with positive  
pressure, we  
make work



$$\Rightarrow dE = \underbrace{-pdV}_{\text{comes from } -PV} + \delta Q$$

$$H \equiv E - (-PV) = E + PV$$

ENTHALPY

(Legendre  
transformation

$$\Rightarrow dH = VdP + \delta Q$$

= subtract conjugate  
variables

ENTHALPY, at constant pressure, contains HEAT VARIATION!!

$$dH|_P = \delta Q \Rightarrow$$

EXPERIMENT:

IN OPEN AIR (CONSTANT 1 ATM)

RAISE TEMPERATURE OF  
ONE SOLID  $\Rightarrow$  MAKE  $\Delta H$   
NOT  $\Delta E$ !!

$$\delta Q = dH|_P = dE|_V$$

$$C \equiv \frac{\delta Q}{\delta T}$$

specific heat:

HOW MUCH  
HEAT TO GIVE  
TO RAISE TEMPER  
OF 1 DEGREE

$$C_p = \frac{\delta Q}{\delta T}|_P = \frac{dH}{dT}|_P$$

$$C_v = \frac{\delta Q}{\delta T}|_V = \frac{dE}{dT}|_V$$

T4

USE H to describe systems @ P=const  
NOTE

# III)

$\delta Q$  is NOT A FUNCTION OF STATE BUT

THERE IS A STATE FUNCTION, S. ENTROPY, FOR WHICH  
 FOR ALL REVERSIBLE PROCESSES  $dS = \frac{\delta Q_{rev}}{T}$   
 AND ALL IRREVERSIBLE PROCESSES  $dS > \frac{\delta Q}{T}$

EQUILIBRA ARE NOT ALWAYS REVERSIBLE

REV OF EQ: SMALL VARIATION TAKEN & GIVEN BACK BRINGS TO THE SAME POINT

⇒ IF in a close loop 

I get some extra ENTROPY ⇒ THIS MEASURES DEGRADATION

(MORE HEAT EXCHANGE ⇒ MORE ENTROPY)

- ⇒  $dE = -pdV + Tds$  ENERGY
- $dH = Vdp + Tds$   $H = E + PV$  ENTHALPY
- $dA = -pdV - SdT$   $A = E - ST$  (HELMHOLTZ)
- good @ V, T constant
- $dG = Vdp - SdT$   $G = E + PV - ST$  (GIBBS)
- good @ P, T constant
- Like normal Life

(TOTAL ENTROPY OF UNIVERSE ↑)

# TS

# III)

STABILITY? WHAT TO MINIMIZE?

SECOND LAW IRREV. REV  $Tds \geq \delta Q$  IF IRR  
 $\delta Q \leq Tds$  IF REV

A VARIATION  $\delta$  (NOT A DIFFERENTIAL)

$$dE = \delta W + \delta Q \leq \delta W + Tds$$

$$\Rightarrow dE - \delta W - Tds \leq 0 \quad \text{suppose } \delta W = -pdv \text{ for mech work}$$

$$dE + pdv - Tds < 0 \quad \text{FOR ALL IRREVERSIBLE PROCESSES}$$

PROCESS = SOMETHING MOVING  $\delta Q \leq Tds$ , IRR  $\delta Q < Tds$

IF EQUILIBRIUM, NO PROCESS  $\Rightarrow \delta Q \geq Tds$

$\Rightarrow$  od equilibrium (variation back/forth does not change state) Virtual Variation  
 if you vary  $S \rightarrow \delta S$ , you need to violate THE irreversible process (because you need to come back)



$$\Rightarrow \delta S \leq \delta Q/T$$

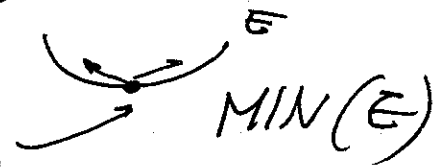
$\downarrow$   
 VIRTUAL VARIATION  
 APPLIES TO STATE FUNCTIONS TOO

$$\Rightarrow \delta E - T\delta S + P\delta V \geq 0 \Rightarrow$$

$$\delta Z = \delta E - T\delta S + P\delta V \geq 0 \quad \text{EQUILIBRIUM}$$

→ at  $T=0$ , constant volume →  
 equilibrium is  $\delta E \geq 0$  →

(the point)  
 where every variation  
 of  $E$  is  $\geq 0$



What about  $H$ ? ENTHALPY (IF NO EXTRA HEAT MOVES  $\delta Q=0$ )  
 $dH = \cancel{dE} + VdP + Tds$   
 $Tds=0$

$$\frac{dH|_s}{d} = VdP \Rightarrow \frac{dH|_{s,P}}{d} = 0$$

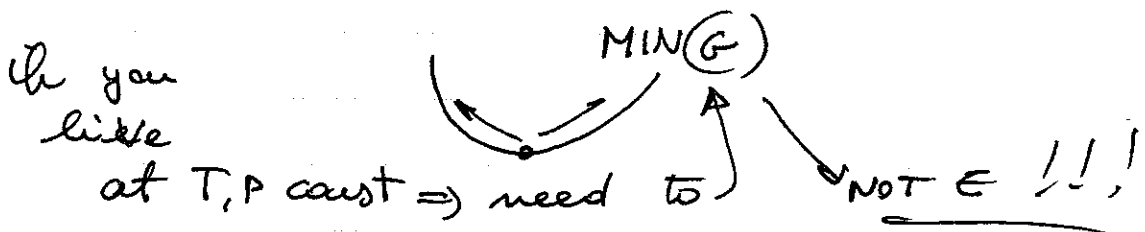
$$\delta Z|_{s,P} = \underbrace{(\delta E - T\delta S + P\delta V)}_{\geq 0 \text{ always}} \Big|_{s,P} = (\delta E + P\delta V)_{s,P} = \delta H_{s,P}$$

at constant P  ~~$\delta E$~~   ~~$\delta S$~~  →  $V\delta P = 0 \Rightarrow$   
 $\delta Z = (\delta E + P\delta V + \underbrace{V\delta P}_{=0})_{s,P} = \delta(E + PV)_{s,P} = \delta H_{s,P}$

$$\Rightarrow \delta Z \geq 0 \Rightarrow \delta H_{s,P} \geq 0$$

FOR  $G$ ?

$$dG = VdP - SdT \Rightarrow \delta Z \geq 0 \Rightarrow \delta G_{P,T} \geq 0$$



IIII)

MELTING  $\Rightarrow$  where the HEAT OF MELTING GOES?

$T=0$  SOLID CONST PRESSURE!

~~Q~~  $Q \Rightarrow$  SOLID  $T \uparrow$

$Q \Rightarrow$  SOLID  $T \text{ const}$   
liq

$Q \Rightarrow$  LIQUID  $T \text{ const}$   
sol

$Q \Rightarrow$  LIQUID  $T \uparrow$

$\Delta Q$  to MELT?

Melt happens at const  $T$

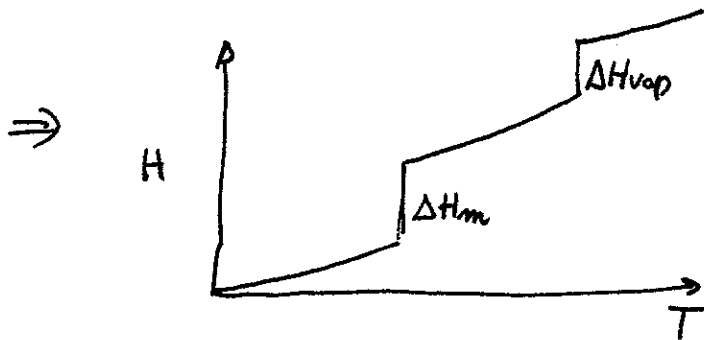
$$dE = -pdV + Tds = \delta Q$$

$$dH = VdP + \delta Q$$

at  $P = \text{const}$   $dH_p = \delta Q$

$$\Rightarrow \Delta Q_{\text{MELTING}} = \Delta H_p \text{ measurable}$$

$$\Rightarrow T_m \Delta S_m = \Delta H_m \Rightarrow \Delta S_m = \frac{\Delta H_m}{T_m}$$





# WHERE S COMES FROM?

F, L, P, V, T, W, are all easy to measure!

where S comes from?

What is ~~the~~ its functional slope?

2nd law tells that

$$S \text{ is function of state}$$
$$\text{and } \frac{\delta Q}{T} \leq dS !!$$

## INTENSIVE PROPERTIES:

T, P, F ... properties and quantities that do not depend on the size of the system

## EXTENSIVE PROPERTIES

E, Q, S, V ... depend on the size!

EXAMPLE: 1kg of ~~water~~ WATER @ 100° CONTAINS  $E^{100}$  JOULES  $\Rightarrow$

3kg of WATER @ 100° CONTAINS  $3 * E^{100}$  JOULES!

$\Rightarrow$  Energy is Extensive, Volume too (obvious)  
Heat too ( $\Rightarrow$  therefore S)

IN THERMODYNAMICS INTENSIVE & EXTENSIVE ARE ASSOCIATED

$$\begin{array}{ccc} -PdV & TdS & \text{and so on} \\ \downarrow \quad \downarrow & \downarrow \quad \downarrow & \\ \text{INT} \quad \text{EXT} & \text{INT} \quad \text{EXT} & \end{array}$$

$Q$  is extensive  $\Rightarrow S$  is extensive

### BOLTZMANN IDEA

# of states

1) at constant Energy the system can be in  $\Omega(E)$  number of states (DEFINITION)

2) all states are equiprobable (ASSUMPTION)  
(why a state should be more probable?)

3) ①+②  $\Rightarrow P_E(\bar{x}) = \frac{1}{\Omega(E)}$  (for every state,

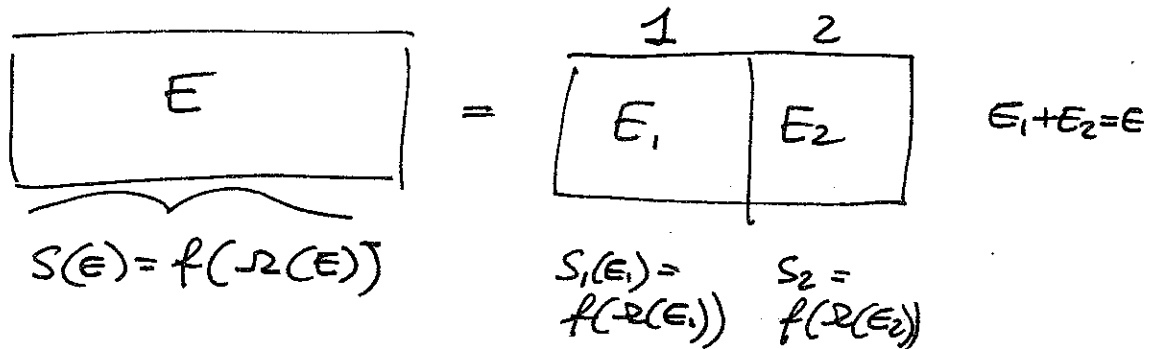
all states are  $\Omega(E)$   
 $\Rightarrow \sum_{\Omega(E)} P_E(\bar{x}) = 1$

0) BOLTZMAN SAYS

ENTROPY MEASURES THE MAX PROBABILITY DISTRIBUTION

~~$S(E) = k_B \ln \Omega(E)$~~   $S(E) = f_{\max}(P_E(\bar{x})) = f(\Omega(E))$

BUT  $S$  is EXTENSIVE  $\Rightarrow$  TAKE SYSTEM OF ENERGY  $E$  & CUT IN TWO  $\Rightarrow E_1, E_2$



but if ① has  $\Omega(E_1)$  states & ② has  $\Omega(E_2)$  states, then ①+② has a total of  $\Omega(E_1) * \Omega(E_2)$  possible configurations

**TIP** (for every one of one, pick  $\Omega$  of the other)

$$\Rightarrow \Omega(E_1 + E_2) = \Omega(E_1) * \Omega(E_2) \quad \text{obvious.}$$

$$\Rightarrow f(\Omega(E_1) * \Omega(E_2)) = f(\Omega(E_1)) + f(\Omega(E_2))$$

which function has this property?

$$f(a * b) = f(a) + f(b) ? \quad \underline{\underline{\underline{\log}}}$$

$$\Rightarrow S(E) \propto \log \Omega(E) \Rightarrow$$

$$S(E) = k_B \log \Omega(E)$$

↑  
to get Joules  
after multiplying  
for T

### ⇒ DEFECTS (FRENKEL)

$$N_I = N_A \exp\left(-\frac{Q_I}{RT}\right)$$

⇒  $N_A$  sites

$N_I$  possible defects ⇒

choose  $N_I$  on a set of  $N_A$  places

$$\Omega = \# \text{ choose } N_I \text{ identical defects}$$

| on a set of  $N_A$  identical places

$$\binom{N_A}{N_I} = \frac{N_A!}{N_I! (N_A - N_I)!}$$

identical places ~~has~~ contains  
 $N_I$  identical defects  
&  $(N_A - N_I)$  identical  
good places

TII

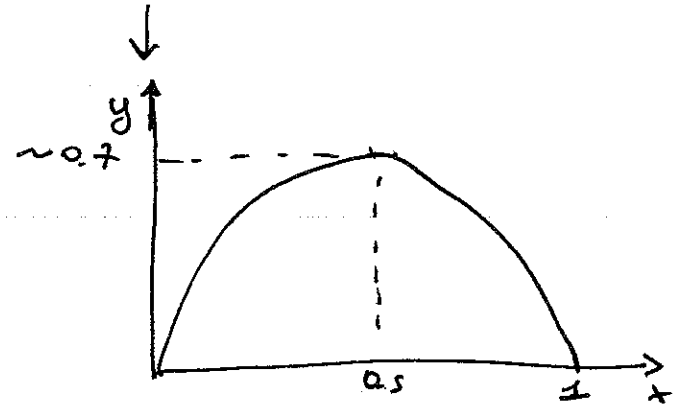
and remember Sterling  $\log n! \sim n \log n - n$

and  $x \equiv \frac{N_I}{N_A}$

$$\Rightarrow S = -kN_A [x \log x + (1-x) \log(1-x)]$$

No defect: how many choices?  $1 \Rightarrow \Omega = 1 \Rightarrow S = 0$   
All defects: how many choices?  $1 \Rightarrow \Omega = 1 \Rightarrow S = 0$

$$y \equiv - [x \log x + (1-x) \log(1-x)]$$



To form FRENKEL. (low double vacancy)

I TOLD THIS !!

$$N_I = N_A e^{-Q/2kT}$$
$$\Rightarrow \frac{Q}{2kT} = -\log x$$

IS THIS TRUE??

$$Q = -2kT \log x$$

MUST PROVE!

T12

$T, P, \text{const} \Rightarrow \text{min } G!$

$$G = E - TS + PV$$

$$\Delta G = \Delta E - T\Delta S + P\Delta V$$

$$dT, dP = 0$$

defects do not change volume !!

$\Rightarrow$

$\frac{Q}{2}$  because every  $Q$  gets 2 defects  $\Rightarrow \frac{Q}{2}$  per defects

$$\Delta G = \Delta E - T\Delta S =$$

$$N_A x \Rightarrow \Delta G = N_A * \left[ x \frac{Q}{2} - T \Delta S(x) \right]$$

$$\downarrow S(x) - S(0) = S(x)$$

$$\Rightarrow N_A * \left[ x \frac{Q}{2} + kT [x \log x + (1-x) \log(1-x)] \right]$$

suppose here  $\Rightarrow x \approx 0 \Rightarrow (1-x) \log(1-x) \approx 0$

$\Rightarrow \text{min } \Delta G \Rightarrow \text{min } \Delta G \text{ over all possible configurations } \{x\}$

$$\Rightarrow \frac{\partial \Delta G}{\partial x} = 0$$

$$\Rightarrow 0 = \frac{\partial}{\partial x} \left[ x \frac{Q}{2} + kT [x \log x + kT (1-x) \log(1-x)] \right]$$

$$\Rightarrow \frac{Q}{2} + kT \log x + kT \frac{x}{x} - kT \log(1-x) + \frac{(1-x)}{(1-x)} (-1) kT$$

$$0 = \frac{Q}{2} + kT \log x - kT \log(1-x) = 0$$

$$\Rightarrow \frac{-Q}{2kT} \log x \Rightarrow \Rightarrow \boxed{N_0 = N_A e^{-\frac{Q}{2kT}}}$$

EQ CONCENTRATION