

LI SP9 13,

I) Macroscopic system $\Rightarrow$

A) Macro thermovls $T, P, V, \rho,$
 e, s, h, g, α

B) Important ^{useful} questions:

- 1) What's the eqn of state?
Empirical relationship
telling us how P, T and
 V or $\tilde{V} \equiv \frac{V}{\rho}$ behave in
relation to one another
(at least for gas systems)
- 2) How does h, u, s change
as the system undergoes
a process?
- 3) What are the linear
response coefficients
for the system, e.g.,
 $C_p = \text{const } P$ ^{specific} heat
 $C_v = \text{'' } V$ ^{''} ^{''} ^{''}
 $\chi_m =$ magnetic suscept. ^{or} ^{1/4g}
 $\mu =$ viscosity

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- 4) How can we use ^{macro} thermodynamics to determine work, heat transfer etc. associated with applied/ ~~applied~~ technical problems, e.g., engines, refrigerators, air conditioning, power plants.

II) Microscopic thermodynamics

A) (SOME) IMPORTANT IDEAS/QUESTIONS.

- 1) WHAT ARE THE ESSENTIAL physical processes ~~happening~~ occurring on small scale?
- 2) CAN (AND HOW DO) WE ^{FIND} USE MODELS OF MICROSCOPIC physics that lead to experimentally verifiable/predictive

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MACROSCOPIC thermodynamics)

3) THE BRIDGE Between

Microstate physics

AND Macroscopic Thermo

is Boltzmann's (EPIC)

Relationship:

$$\boxed{S = k \ln \Omega} \quad (3.1)$$

S = macroscopic entropy

k = Boltzmann constant

Ω = The ^{MAXIMUM} ~~number~~ number
of microstates, each
having a given total
internal energy E , and

EACH SATISFYING GIVEN

CONSTRAINTS, SUCH AS OCCUPANCY
OF A GIVEN VOLUME, V , AND
CONSISTING OF A GIVEN

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Number of ptcls, N .

4) THE WAY THE GAME ~~IS~~
(= STATISTICAL MECHANICS) IS
PLAYED:

A) GUESS / PROPOSE AN

ENERGY-BASED Model
of microscale physics

i) usually involves
construction of a
Hamiltonian, H , that
gives the total
energy of either
an individual ptcl -

use this approach
when the ptcls in
the system are
non-interacting.

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or energy of multiple
particles when interactions
are important.

ii) Use the proposed

H in ~~the~~ Schrödinger's
eqn to determine
the energy (eigen) states
of the individual
or collection of particles

iii) Given the energy
states, ~~for the microscale system~~
find the

find / identify the
 $\Omega(E, V, N)$
largest number of microstates,
each of which satisfy

given volume, (V) particle
number, (N) and energy constraints
 (E)

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iv) ^{use} THIS NUMBER in (3.1) ^{to}
to get the macroscopic
entropy (of the system
under study)

$$\boxed{S(E, V, N) = k \ln \Omega(E, V, N)}$$

B) Given $S(E, V, N)$, ~~or~~
or equivalently, $\Omega(E, V, N)$,
use macroscopic thermo
relations to back
out $h, u, P, T, g, a,$
 C_p, C_v , etc. etc.
for the given system

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III) EXERCISE / REVIEW OF
MACROSCOPIC THERMO
RELATIONSHIPS.

(1A)

I) $du = Tds - Pd\tilde{v}$ no chemical rxn
only work is expansion

2) Objective get a general eqn for
 du, dh, ds ^{medium only} $P, T, \tilde{v}, C_p, C_v$
plug in eqn of state

3) ~~Then~~ First get Maxwell relns
AND introduce Helmholtz and
Gibbs free energy

A) GIBBS 4: ~~then~~ $du = Tds - Pd\tilde{v}$

Heuristic = 1st LAW w/ $dq = dgrw = Tds$

Quick thermo review

Aside: i) ALL THERMO fns

u, h, s, g, G are point fns, =
path independent

ii) For non-reacting substance,
equilibrium state det'd by
any two of h, u etc, P, T, ρ

iii) pt fns have property
given $f = f(x, y)$
 $df = Mdx + Ndy$

$$\left[M_{iy} = N_{ix} \right] \quad (A.1)$$

(13)

END ASIDE

B) Given "Gibbs 1" get
"Maxwell 1" using (A.1)

$$du = T ds - P d\tilde{v}$$

$M \times \qquad N \times$

$$\Rightarrow M_{iy} = N_{ix}$$

$$\Rightarrow \boxed{T_{,i} \tilde{v}_{,x} = -P_{,s} \tilde{v}} \quad \text{"Maxwell 1"}$$

C) Gibbs plus: eliminate/re-express
 all differentials of s
 (ds), and partials with
 respect to s , e.g.,
 $\frac{\partial P}{\partial s}$, in terms of $P, T, \tilde{v}$,
 C_p, C_v . ~~Then~~

D) Since Gibbs 4 involves
 dT and $d\tilde{v}$, express
 s as $s = s(T, \tilde{v})$; then take
 d . P.K.L.:

(10)

$$\Rightarrow ds = S_{i,T}/_T d\tilde{P} + S_{i,T}/_T dT \quad (C.1)$$

$\Rightarrow$ use (C.1) in Gibbs L to eliminate ds ;

$$du = T[S_{i,T}/_T d\tilde{V} + S_{i,T}/_T dT] - P d\tilde{V}$$

$$(C.2) \left[du = [T S_{i,T}/_T - P] d\tilde{V} + T S_{i,T}/_T dT \right]$$

E) use (recognize) the defn of C_V :

$$C_V \equiv \frac{\partial u}{\partial T} |_V \quad \text{USE LAW}$$

Aside

$$\left[\begin{array}{l} \text{i.e., i) } \boxed{du = dq} - P d\tilde{V} \\ \text{ii) add } \text{known heat } \int dq = Q \text{ to fixed vol.; this gives } u = \int du \\ \text{iii) measure } T \\ \text{iv) ii) and iii) give } u(T) \Rightarrow \frac{\partial u}{\partial T} |_V = C_V \end{array} \right]$$

(10)

E1) Since (C.2) is of the generic form

$$du(T, \tilde{V}) = \left. \frac{\partial u}{\partial \tilde{V}} \right|_T d\tilde{V} + \left. \frac{\partial u}{\partial T} \right|_{\tilde{V}} dT$$

AND since now, G must correspond to $\left. \frac{\partial u}{\partial T} \right|_{\tilde{V}}$

$$\therefore \boxed{-T \left. \frac{\partial S}{\partial \tilde{V}} \right|_T = C_V} \quad (D.1)$$

⊕ This is used when we derive gen'l relationship for ds .

E2) ALMOST THERE -- we use (D.1) to eliminate $\left. \frac{\partial S}{\partial \tilde{V}} \right|_T$ term in (C.1) -- JUST NEED TO (somehow) re-express $\left. \frac{\partial S}{\partial \tilde{V}} \right|_T$ in terms of $P, \tilde{V}, T, C_V, C_P$ -- THIS will come out of one of the MAXWELL relns (to be derived).

(15)

II) "GIBBS 2": = diff'l expr
for dh involving ds and
(it turns out) dp

1) $h \equiv u + p\tilde{v}$

2) $\Rightarrow dh = du + \tilde{v}dp + p d\tilde{v}$

Use GIBBS 1

3) $dh = Tds - p d\tilde{v} + \tilde{v}dp + p d\tilde{v}$

$$\boxed{dh = Tds + \tilde{v}dp} \quad (\text{E.1}) \quad \boxed{\text{GIBBS 2}}$$

$m \times \quad N \times$

4) GIBBS ASS'D MAXWELL reln using

$$\begin{aligned} M_{ix}|_x &= N_{ix}|_y \\ \Rightarrow \boxed{T_{ip}|_s = \tilde{v}_{is}|_p} & \quad (\text{Eq. 1}) \quad \boxed{\text{MAXWELL 2}} \end{aligned}$$

5) ~~One~~ we'll come back to
this to derive gen'l'd
expr for dh (in terms
of $p, \tilde{v}, T, C_p$, and/or α_v).

⊕ 1st quickly work out
MAXWELL 3 and 4

(IF)

III) GET GIBBS $\bar{z}$ AND MAXWELL
USING HELMHOLTZ FREE ENERGY
 $\bar{z}$ (USING GIBBS $\bar{z}$ AND
AND
 $M_{ix}/x = N_{ix}/y$)

1) $A \equiv a \equiv u - Ts \equiv$ Helmholtz
free energy

⊕ Note, since u, T, s are
all point fns,
so is a .

2) $\therefore da = du - Tds - sdt$

3) use GIBBS $\bar{z} \Rightarrow da = Tds - Pd\bar{v}$
 $-Tds - sdt$

$$\therefore \boxed{da = -Pd\bar{v} - sdt} \quad \begin{matrix} \text{(f.1)} \\ \text{GIBBS} \\ \bar{z} \end{matrix}$$

$M \times N \times Y$

4) $\therefore \boxed{P_{i,T}/x = S_{i,\bar{v}}/T}$ (MAXWELL
 $\bar{z}$)

⊕ here's the term
 $S_{i,\bar{v}}/T$ we need in (1.2)

(16)

IV) GET GIBBS & AND
MAXWELL & USING THE
GIBBS FREE ENERGY

(⊕ GIBBS 1 and $M_{ix}|_x = N_{ix}(y)$)

1) $g \equiv h - TS$

2) $dg = dh - Tds - sdt$
USE GIBBS

3) $dg = Tds + \bar{v}dp - sdt - Tds$

$\therefore \boxed{dg = \bar{v}dp - sdt}$ (6.1) GIBBS &

4) $\therefore \boxed{\bar{v}_{iT}|_P = -s_{iT}|_T}$ (MAXWELL &)

NOW CAN FINISH OFF (C.2):
(Using & MAXWELL 3)

* $\boxed{du = [T P_{iT}|_{\bar{v}} - P] d\bar{v} + C_v dT}$ *

⊕ General expr for any substance ^{ADAPTING}
undergoing complex expansion motion.