

CH 5 MACRO (CLASSICAL) THERMO :

- RELNS AMONG PURELY MACRO VARS
- BASED ON (MACRO) LAWS

eqs: (1) $d\bar{E} = \delta Q - \delta W$

(2) Q-S: $dS = \frac{\delta Q}{T}$

- Key
- CAN MAKE USEFUL GEN. STATEMENTS INDEP. OF DETAILS (TYPICAL FOR CONSERV. LAWS \Rightarrow not necessary: all contained in dynamics - ex For but very useful to check results etc)
 - MAKE LOTS OF USE OF $dS =$ DIFFERENTIAL (cf web resources on intro \rightarrow translating)
 - HISTORICALLY: PRECEDED MICRO DESCRIPTION, BASED ON EMPIR. OBSERV.
 - FOR SIMPLICITY, MAINLY CONSIDER SYS w/ ONE EXT. PARAM: V

THEN E, V ^{CAN} SPECIFY MACROSTATE: (ie specify uniquely all macro \rightarrow tips typically covered (can see from micros descr.))

$\Omega(E, V) = \#$ ALLOWED MICROSTATES of E, V $\left\{ \begin{array}{l} \Rightarrow$ ALL MACRO VARS. ARE FNS OF E, V $\left\{ \begin{array}{l} \text{determines everything} \end{array} \right.$

AT EQUIL: E FROM PEAK OF Ω

$S(E, V) \equiv k \ln \Omega(E, V)$

$\frac{1}{kT(E, V)} = \beta(E, V) = \frac{\partial \ln \Omega(E, V)}{\partial E}$

$\bar{p}(E, V) = \frac{1}{\beta} \frac{\partial \ln \Omega(E, V)}{\partial V}$

(but here, won't have access to Ω)

THEN: $\delta W = p dV$

(1) & (2): $T dS = dE + p dV$

CLASS. THERMO:
 - DIDN'T THINK IN TERMS OF MICRO-
 - SOME DIDN'T BE IN ATOMS
 - TREATED MACRO VAR AS COMPLETE OF
 - IT WORKS BECAUSE SHARPNESS OF DIST LAY $E \approx \bar{E}$; $S \approx S$ AT ETC

KEEP IN MIND - COULD ALSO HAVE \vec{B} , etc. THEN $\delta W_B = \vec{M} \cdot d\vec{B}$

etc
 LET V STAND IN FOR ALL EXT PARAM

- RELATION DESCRIBING ^{STRAIGHTFORWARD} EASILY ~~MEASURABLE~~ MACRO
~~PROPERTIES~~ VARIABLES (HAVE ELIMINATED TRANSFERS OF Q, W)

- TELLS ~~WHAT IS~~ HOW SYS. MOVES FROM ONE EQUIL
 STATE TO ANOTHER w/OUT MICRO DETAILS

- RELATES 3 CHNGING QTY'S, BUT ONLY 2 INDEP
 VARS \Rightarrow PHYS. CONSEQUENCES

- BASED ON Q-S. CHG BUT:

~~IF IT~~ RELATES POSSIBLE ^{EQUIL} MICRO STATES
 OF SYS \Rightarrow DOESN'T MATTER HOW
 GET THERE

\Rightarrow TRUE FOR EQUIL. SYS. IN GENERAL

OFTEN E, V NOT MOST CONVENIENT:

CHG VARIABLES:

IF FIXED $E, V \rightarrow$ UNIQUE p

\therefore COULD SPECIFY $E, p \rightarrow$ KNOW V

TYPICAL SWITCHES: RELATED QTYs

$$\begin{array}{l}
 E \leftrightarrow T \leftrightarrow S \\
 p \leftrightarrow V
 \end{array}
 \left. \vphantom{\begin{array}{l} E \leftrightarrow T \leftrightarrow S \\ p \leftrightarrow V \end{array}} \right\} \begin{array}{l} \text{PAIRS:} \\ (E, V) \quad (E, p) \\ (T, V) \quad (T, p) \text{ etc} \\ (S, V) \end{array}$$

(not all changes possible. ex. for IG

$E = E(T)$ only; couldn't choose $(V, p) \rightarrow$ any E, T possible)
or (E, T)

TECHNICAL REQMT:

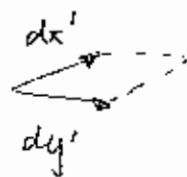
$$(x, y) \rightarrow (x', y')$$

(ie $x'(x, y), y'(x, y)$)

$$\text{JACOBIAN} \equiv \begin{vmatrix} \frac{\partial x'}{\partial x} & \frac{\partial y'}{\partial x} \\ \frac{\partial x'}{\partial y} & \frac{\partial y'}{\partial y} \end{vmatrix} \neq 0 \text{ ANYWHERE}$$

WHY?

MEASURES AREAS / VOLUMES



$$\begin{aligned}
 A &= |d\vec{x}' \times d\vec{y}'| \\
 &= |J| d\vec{x} \times d\vec{y}
 \end{aligned}$$

(cf MULTI-DIM INTEGRALS)

$$\text{ex } dx dy \rightarrow \int_{|J|} r dr d\theta$$

{note: if had 2 ext params: $V, B \Rightarrow$ 3 indep vars }
etc

- so main tools:
- $T ds = dE + p dV$
 - ds IS DIFFERENTIAL
 - 2 INDEP. VARS.

can get lost in sea of partial derivs.

(d) EQN OF STATE:



slip

EQNS OF STATE:

(EASILY MEASURABLE)

- ~~MORE SPECIFIC~~ RELNS AMONG VARS FOR SPECIFIC SYSTEM
 - IN-PRINCIPLE DERIVABLE FROM MICRO SYSTEM
 - HISTORICALLY: EMPIRICAL
- (EX IDEAL GAS)
- ⇒ GEN RELNS APPLY
 ⇒ CAN SAY MUCH MORE

EX: START WITH IDEAL GAS (GEN. RELNS LATER)MICRO:

(a) EQN OF STATE:

(R = gas const)

$$pV = nRT \quad (\text{FROM } \Omega \propto V^N)$$

(b) AND

$$E = E(T) \quad (\text{FROM } \Omega = V^N \chi(E))$$

(is result of stat. mech)

(WE ALSO KNOW $\chi \propto E(T)$)

↑ FN OF E

CLASSICAL:

IF HAVE (a) EMPIRICALLY, COULD DEDUCE (b)

CHOOSE

IND. VARS:

(easy to meas, included in eqn of state)

$$(V, T) \Rightarrow$$

$$E(V, T),$$

$$p(V, T),$$

$$S(V, T).$$

MATH

$$(i) \quad dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV$$

$$\left(\text{math: } \left(\frac{\partial E}{\partial T}\right)_V = \frac{\partial E(V, T)}{\partial T}\right)$$

$$(ii) \quad dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

PHYSICS:

$$T dS = dE + p dV$$

$$p(V, T) = \frac{nRT}{V}$$

ID. GAS

$$\text{COMBINE: } dS = \frac{1}{T} dE + \frac{nR}{V} dV$$

REPLACE dE FROM (i): GIVES IN TERMS OF dT, dV (ind vars.)

$$dS = \frac{1}{T} \left(\frac{\partial E}{\partial T} \right)_V dT + \left[\frac{1}{T} \left(\frac{\partial E}{\partial V} \right)_T + \frac{pR}{V} \right] dV$$

OP TO (ii)

$$\underbrace{\hspace{10em}}_{= \left(\frac{\partial S}{\partial T} \right)_V} = \underbrace{\hspace{10em}}_{= \left(\frac{\partial S}{\partial V} \right)_T}$$

MERE MATH: $\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial^2 S}{\partial T \partial V}$

$$\Rightarrow \left(\frac{\partial}{\partial V} \right)_T \frac{1}{T} \left(\frac{\partial E}{\partial T} \right)_V = \left(\frac{\partial}{\partial T} \right)_V \left[\frac{1}{T} \left(\frac{\partial E}{\partial V} \right)_T + \frac{pR}{V} \right]$$

$$\frac{1}{T} \left(\frac{\partial^2 E}{\partial V \partial T} \right) = \left[-\frac{1}{T^2} \left(\frac{\partial E}{\partial V} \right)_T + \frac{1}{T} \left(\frac{\partial^2 E}{\partial T \partial V} \right) \right]$$

$$\Rightarrow \left(\frac{\partial E}{\partial V} \right)_T = 0 \quad \therefore E = E(T), \text{ NOT } E(T, V) \quad (\text{IG})$$

CONTENT: ~~E const.~~ $Tds = dE + p dV$

ID, GAS LAW

MACRO. VARS FNS OF 2 VARS

(rest is gymnastics of partial derivs)

EXPT: FREE EXPANSION (JOULE) (def. not @-s)

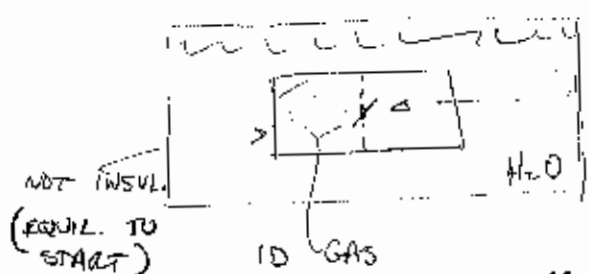
VALVE OPENED, GAS EXPANDS
WAIT FOR EQUIL

ΔT FOR H₂O? $\frac{\text{FINDS}}{\Delta T = 0}$

MEANS: $Q = 0$

$$E_f(T, V_f) - E_i(T, V_i) = 0 \Rightarrow E(T)$$

(presumably for non-ideal gas - attractive part \rightarrow E higher: absorbs Q from H₂O)



{ FOR ME:

$$E_{IG}(T_f, V_f) - E_{IG}(T_i, V_i) = Q = - \int_{T_i}^{T_f} C_{H_2O}(T) dT$$

IF $E_{IG}(T)$ ONLY, AND $T_f = T_i + dT$ (but we have done 8-5)

$$\left(\frac{\partial E_{IG}}{\partial T} \right) (T_f - T_i) = - C_{H_2O}(T_i) (T_f - T_i) = dQ$$

EITHER $\left(\frac{\partial E}{\partial T} \right)_{IG} = - C_{H_2O}(T)$ (UNLIKELY?)

OR $T_f - T_i = 0$ }

SPECIFIC HEATS (I.G.)

macro steps;
(can get specific expressions)

V CONST: $dW = 0$
 $dQ = dE$

could compute from S & Ω from micro description
but try to say something via macro laws.

MOLAR $C_V \equiv \frac{1}{V} \left(\frac{dQ}{dT} \right)_V = \frac{1}{V} \left(\frac{\partial E}{\partial T} \right)_V$

\Rightarrow (IG): $C_V = C_V(T)$ (not V)

ALSO $dE = \left(\frac{\partial E}{\partial T} \right)_V dT + \left(\frac{\partial E}{\partial V} \right)_T dV \Rightarrow \boxed{dE = V C_V dT}$ IG
(USED $E(T)$ ONLY)

p CONST:

NATURAL VARS: T (which changes), while p fixed

IG: $pV = \nu RT$

IN GEN: T, V INDEP \rightarrow CAN VARY SEP.
BUT p WILL CHG. SINCE $p(V, T)$

$\Rightarrow d(pV) = dp V + p dV = \nu R dT$

HOLD p FIXED: $p dV = \nu R dT$

$\Rightarrow \left(\frac{\partial V}{\partial T} \right)_p = \frac{\nu R}{p}$

{ REQNT. p FIXED
TIES dV & dT
TOGETHER THIS WAY

p CONST.NATURAL VARS WOULD BE T (CHG) } p (FIXED) } ONLY MOVES IN 1 DIMBUT IF USE T, V , CHG'S IN EACH MUST BE CONNECTED SO $p(T, V)$ STAYS CONST

IG: $pV = \nu RT$

$$d(pV) = dp \bar{V} + p dV = \nu R dT$$

$$\boxed{p dV = \nu R dT} \quad \text{IG, } p \text{ FIXED}$$

} SHOWS HOW V, T TIED TOGETHERCAN E DEP. ON p ?CHG VARS: $(T, V) \rightarrow (T, p)$ i.e. NOW THINK OF $V = V(T, p)$ $E(T, V) \rightarrow E(T, V(T, p))$ GIVES p DEP. (COMES IN VIA V)

BUT FOR IG:

NO V DEP. \Rightarrow NO p DEP. $E = E(T)$ AGAIN ~~\neq~~

$$\Rightarrow dE(T, p) = \left(\frac{\partial E}{\partial T}\right)_p dT + \left(\frac{\partial E}{\partial p}\right)_T dp$$

ALSO

$$\left(\frac{\partial E}{\partial T}\right)_p = \left(\frac{\partial E}{\partial T}\right)_V = \nu C_V$$

(DOESN'T MATTER IF HOLD p OR V FIXED)

STILL HAVE

$$\boxed{dE = \nu C_V dT} \quad \text{IG (} p \text{ OR } V \text{ FIXED)}$$

 \uparrow
 $C_V(T)$

COMBINE:

$$dQ = dE + p dV$$

$$= \nu C_V dT + \nu R dT = \nu (C_V + R) dT$$

$$C_p = \frac{1}{\nu} \left(\frac{\partial Q}{\partial T}\right)_p$$

 \hookrightarrow all results under condition p const

$$\Rightarrow \boxed{C_p = C_V + R} \quad \text{IG}$$

WANT

$$C_p \equiv \frac{1}{V} \left(\frac{\partial Q}{\partial T} \right)_p = \frac{1}{V} T \left(\frac{\partial S}{\partial T} \right)_p$$

from
T dS = dE + p dV

For me:
more carefully:
E(T, p), (Cp, p)
dE = (∂E/∂T)_p dT + (∂E/∂p)_T dp
dV = (∂V/∂T)_p dT + (∂V/∂p)_T dp
same for S

$$= \frac{1}{V} \left[\left(\frac{\partial E}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p \right]$$

BUT FOR I.G. E = E(T) ∴ (∂E/∂T)_p = (∂E/∂T)_V } doesn't matter which hold
= γ C_V } fixed

COMBINING:

$$C_p = C_v + R$$

as claimed: C_p > C_v

NOTE FOR ME:
IG laws as well
as this reln
work for all gases
not just MONATOM.

USEFUL RATIO:

$$\gamma \equiv \frac{C_p}{C_v} = 1 + \frac{R}{C_v}$$

> 1 ALWAYS

typical: mono
gives lot of
relns among
steps even if
don't allow
calc?

CP TABLE PG 157 C_v VS GAS @ 15°C (w/ C_v as input)

(column on right uses reln; next to it, measured)

~~ASIDE~~

MICRO CALC: CAN SAY EVERYTHING → GET C_p, C_v EXPLICITLY

FROM $\mu = \beta V^N E^{3N/2}$

(MONATOMIC I.G.)

$$\Rightarrow E = \frac{3}{2} NKT = \frac{3}{2} \nu RT$$

$$\beta = \frac{1}{KT} = \frac{\partial \ln \mu}{\partial E} = \frac{3N}{2} \frac{1}{E}$$

$$\Rightarrow C_v = \frac{1}{V} \left(\frac{\partial E}{\partial T} \right)_V = \frac{3}{2} R$$

$$C_p = C_v + R = \frac{5}{2} R$$

$$\gamma = \frac{5}{3} = 1.667$$

MONATOMIC I.G.

note: const in T
... (must fail for T → 0)

(CLASSICAL THERMODYNAMICISTS → DIDN'T KNOW THIS; WON'T USE THIS INFO IN CH 5)

⇒ VERY SIMPLE RELN.

⇒ WORKS BEAUTIFULLY (of He & Ar)

FOR MONATOMIC I.G.'S (WILL DERIVE EQUIV. RELN FOR DIATOMICS IN HW)

But, by definition,

$$c_p = \frac{1}{\nu} \left(\frac{dQ}{dT} \right)_p$$

Using (5.2.7), this becomes

$$\blacktriangleright \quad c_p = c_v + R \quad (5.2.8)$$

Thus $c_p > c_v$, in general agreement with (4.4.7), and these molar specific heats of an ideal gas differ precisely by the gas constant R .

The ratio γ of the specific heats is then given by

$$\gamma \equiv \frac{c_p}{c_v} = 1 + \frac{R}{c_v} \quad (5.2.9)$$

The quantity γ can be determined from the velocity of sound in the gas and can also be measured directly by other methods. Table 5.2.1 lists some representative experimental values of c_v for a few gases. It also illustrates the extent of agreement between the values of γ computed by (5.2.9) and the experimentally measured values of this quantity.

Table 5.2.1 Specific heats of some gases (at 15°C and 1 atm)*

Gas	Symbol	c_v (experimental) (joules mole ⁻¹ deg ⁻¹)	γ (experimental)	γ (computed by (5.2.9))
Helium	He	12.5	1.666	1.666
Argon	Ar	12.5	1.666	1.666
Nitrogen	N ₂	20.6	1.405	1.407
Oxygen	O ₂	21.1	1.396	1.397
Carbon dioxide	CO ₂	28.2	1.302	1.298
Ethane	C ₂ H ₆	39.3	1.220	1.214

* Experimental values taken from J. R. Partington and W. G. Shilling, "The Specific Heats of Gases," p. 201, Bena, London, 1924.

Microscopic calculation of specific heats If one is willing to make use of microscopic information, one can, of course, make many more interesting statements. The situation of a *monatomic* ideal gas is particularly simple. In (2.5.19) we found for the number of states of such a gas in some small energy range δE the expression

$$\Omega(E, V) = BV^N E^{3N/2}$$

where N is the number of molecules in the gas and B is some constant independent of E and V . Hence

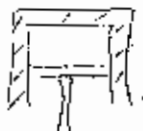
$$\ln \Omega = \ln B + N \ln V + \frac{3N}{2} \ln E$$

ISOTHERMAL VS ADIABATIC EXPANSION: (IG)

(1) ISOTH: T CONST

$$pV = \nu RT = \text{CONST}$$

$$\Rightarrow p \propto \frac{1}{V}$$

(2) ADIABATIC:

p incr. faster
as V decr?
yes

AS USUAL, START w/

$$dQ = 0 = dE + dW$$

$$= \nu c_v dT + p dV \quad (a)$$

Want to relate p to $V \Rightarrow$ get rid of dT : (p, V)

$$d(pV) = p dV + V dp = \nu R dT \quad \text{from IG law (as before)}$$

REPLACE dT IN (a): (little algebra)

$$(c_v + R) p dV + c_v V dp = 0$$

DIV. BY $c_v pV$:

$$\left(\frac{c_v + R}{c_v} \right) \frac{dV}{V} + \frac{dp}{p} = 0$$

$$= \gamma / c_v \equiv \gamma$$

IF $\gamma \sim \text{CONST}$ (MICRO: PROVED CLASSICAL: MEASURED)INTEG: $\gamma \ln V = - \ln p + \text{CONST}$

can fix const
if know p & V
at some pt.

$$p V^\gamma = \text{CONST}$$

ADIAB. IG
 γ CONST

$$\text{OR } V^{\gamma-1} T = \text{CONST} \quad (T, V)$$

(via IG LAW)

$\gamma > 1$
so p decs quav
faster

surprising
that it depends
on c_v & c_p , since
no heat being exch.
by defn

leave for it in gen'l discussion

GEN. EXPRESSION FOR $S(T, V; \nu)$ FOR IG: { will discuss gen'l case later

DEF. REFERENCE ENTROPY (std state)

$$S_0 \equiv S(T_0, V_0; \nu_0)$$

CHG 1 PARAM AT A TIME

1. V_0 TO V MOLES

PUT $n \equiv V/V_0$ COPIES TOGETHER

{ IG: can neglect edge effects }

{ T, p INTENSIVE ; ν, V, S EXTENSIVE }

STAY SAME

INCR. BY $n \times$

{ no. increasing + but leaving V fixed \rightarrow would chg p, T ; would chg S in complex way }

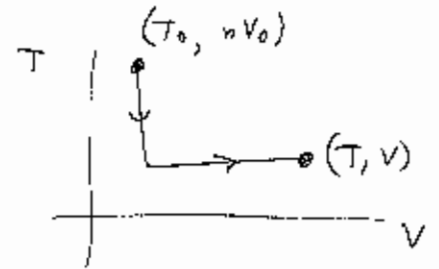
$$S(T_0, nV_0, n\nu_0) = n S_0$$

{ the additivity of S is an approx for large sys; it neglects small contribs $\sim R \ln \nu$ for ex $[nV_0]$ $\nu_1 \neq \nu_2$ }

2. FROM (T_0, nV_0) TO (T, V)

(a) V FIXED, $T_0 \rightarrow T$

(b) T " , $nV_0 \rightarrow V$



USE $TdS = dE + pdV$

$$\nu C_V dT + \frac{\nu RT}{V} dV$$

$$\Rightarrow dS = \nu C_V(T) \frac{dT}{T} + \nu R \frac{dV}{V}$$

{ use what's know from classical thermo }

THEN

$$\Delta S = S(T, V; \nu) - n S_0$$

$$= \nu \int_{T_0}^T \frac{C_V(T') dT'}{T'} + \nu R \int_{nV_0}^V \frac{dV'}{V'}$$

line integrals

OR

$$S(T, V; \nu) = \nu \left[\int_{T_0}^T \frac{C_V(T') dT'}{T'} + R \ln \left(\frac{V}{nV_0} \right) + \frac{1}{\nu_0} S_0 \right]$$

$$S(T, V; \nu) = \nu \left[\int_{T_0}^T \frac{C_V(T') dT'}{T'} + R \ln V - R \ln \nu + \text{CONST} \right]$$



USED: GEN'L LAWS, EOS, $C_V(T)$

GENERAL RELNS (ALL SYSTEMS)

- NOT JUST FG.
- STILL ONLY V

IDRA:

2 VARS. DETERMINE SYS: E, V

CHG $E, V \Rightarrow p, T$ CHG. IN RELATED WAY

EXTRACT RELNS (MAXWELL RELNS) BY CHOOSING
DIFF. INDEP. VARS & CR. DERIVS

CONSIDER 1 PAIR AT TIME!

(0) (E, V) $dQ - dW$

$$dE = T dS - p dV \Rightarrow dS = \frac{1}{T} dE + \frac{p}{T} dV \quad (a)$$

$$\Rightarrow \boxed{\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T}}$$

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_E = \frac{p}{T}}$$

\Updownarrow

SAME AS $\frac{1}{kT} = \beta = \frac{\partial \ln \Omega}{\partial E}$

\Updownarrow

$$p = \frac{1}{\beta} \frac{\partial \ln \Omega}{\partial V}$$

(THESE LED TO (a); GOING BACKWARDS HERE
MACRO \rightarrow MICRO)

GENERAL RELNS (ANY SYSTEM; NOT JUST I.G.)

- USE (1) E CONS. SINGLE FN OF
 (2) SYS DET. BY E, V (extension to $E, V, B \dots$ simple)
 (3) $\frac{\partial f(x,y)}{\partial x \partial y} = \frac{\partial f}{\partial y \partial x}$

HAVE $S(E, V), T(E, V), p(E, V) \dots$

- IF CHG S VIA E, V THEN p, T MUST CHG IN RELATED WAY, etc

- CAN EXTRACT RELNS (MAXWELL RELNS) BY CHOOSING DIFF IND. VARS AND COMPARING DERIVS

Maxwell's 1st eqn

(1) (S, V)

$$dE = T dS - p dV$$

$$dE(S, V) = T(S, V) dS - p(S, V) dV$$

$$\Rightarrow \left[\left(\frac{\partial E}{\partial S} \right)_V = T \right] \quad \left[\left(\frac{\partial E}{\partial V} \right)_S = -p \right]$$

ships (have seen $T = \left(\frac{\partial E}{\partial S} \right)_V$ before)
 $\frac{1}{kT} = \beta = \frac{\partial \ln R}{\partial E} \quad (V \text{ fixed})$
 $T = \left(\frac{\partial S}{\partial E} \right)_V^{-1}$ ships

$$\frac{\partial^2 E}{\partial V \partial S} = \frac{\partial^2 E}{\partial S \partial V}$$

$$\Rightarrow \left(\frac{\partial}{\partial V} \right)_S \underbrace{\left(\frac{\partial E}{\partial S} \right)_V}_T = \left(\frac{\partial}{\partial S} \right)_V \underbrace{\left(\frac{\partial E}{\partial V} \right)_S}_{-p}$$

$$\Rightarrow \left[\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V \right]$$

↑ NO dE, dS

↑ NEGATIVE Q.W. V FIXED

TRIVIAL, BUT AT SAME TIME NOT OBVIOUS: HOLD \neq STATES FIXED, CHG V, WATCH $\Delta T \Rightarrow$ GIVES Δp IF CHG S AT const V (via dQ)



(2) (S, p)

$$dE = TdS - pdV \quad (-Vdp + Vdp)$$

$$= TdS - d(pV) + Vdp$$

$$\Rightarrow d(E + pV) = TdS + Vdp$$

{ *std trick - (move to end of Legendre trans, change dV to dp by add. pV to LHS)*

NOW IN FORM WHERE CAN ISOLATE EFFECT OF CHG. IN S & p SEPARATELY ON RHS

LHS:

ENTHALPY: $H \equiv E + pV$

- H DEPENDS ON STATE (LIKE E)

- dH (EXACT DIFF) = $TdS + Vdp$

- IF THINK OF $H = H(S, p)$ (also $T(S, p)$, $V(S, p)$)

$$\Rightarrow \left(\frac{\partial H}{\partial S}\right)_p = T$$

$$\left(\frac{\partial H}{\partial p}\right)_S = V$$

{ This is main pt; it's a qty whose deriv are simply related to fun ^{above} don't really need it to derive max relns

SAME TRICK:

$$\left(\frac{\partial}{\partial p}\right)_S \left(\frac{\partial H}{\partial S}\right)_p = \left(\frac{\partial}{\partial S}\right)_p \left(\frac{\partial H}{\partial p}\right)_S$$

$$\Rightarrow \boxed{\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p}$$

H DISAPPEARS \rightarrow TRICK FOR GETTING THIS RELN (ELEGANT; NOT REALLY NECESSARY)

FOR ME:

{ DON'T REALLY NEED Legm. trans to get this }

$$dE = T ds - p dV(s, p)$$

$$= T ds - p \left[\left(\frac{\partial V}{\partial s} \right)_p ds + \left(\frac{\partial V}{\partial p} \right)_s dp \right]$$

$$dE = \left[T - p \left(\frac{\partial V}{\partial s} \right)_p \right] ds - \left[p \left(\frac{\partial V}{\partial p} \right)_s \right] dp$$

$$\left(\frac{\partial E}{\partial s} \right)_p = T - p \left(\frac{\partial V}{\partial s} \right)_p$$

$$\left(\frac{\partial E}{\partial p} \right)_s = - p \left(\frac{\partial V}{\partial p} \right)_s$$

$$\left(\frac{\partial}{\partial p} \right)_s \left(T - p \left(\frac{\partial V}{\partial s} \right)_p \right) = \left(\frac{\partial}{\partial s} \right)_p \left(- p \left(\frac{\partial V}{\partial p} \right)_s \right)$$

$$\left(\frac{\partial T}{\partial p} \right)_s - \left(\frac{\partial V}{\partial s} \right)_p - p \left(\frac{\partial^2 V}{\partial p \partial s} \right)$$

$$= - p \left(\frac{\partial^2 V}{\partial p \partial s} \right)$$

$$\left(\frac{\partial T}{\partial p} \right)_s = \left(\frac{\partial V}{\partial s} \right)_p$$

}

(3) (T, V)

SAME PROCEDURE

$$dE = Tds - pdv$$

$$= d(Ts) - s dT - pdv$$

$$d(E - Ts) = -s dT - pdv$$

HELMHOLTZ FREE ENERGY:

$$F \equiv E - Ts$$

$$\left(\frac{\partial F}{\partial T}\right)_V = -s$$

$$\left(\frac{\partial F}{\partial v}\right)_T = -p$$

2ND DER. EQUAL:

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$$

(4) (T, p)

This is perhaps most useful set -
easiest to control in labGIBBS FREE ENERGY:

$$G \equiv E - Ts + pv$$

(chg. both s & v
→ T & p)

$$\Rightarrow dG = -s dT + v dp$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -s \quad \left(\frac{\partial G}{\partial p}\right)_T = v$$

$$-\left(\frac{\partial s}{\partial p}\right)_T = \left(\frac{\partial v}{\partial T}\right)_p$$

SUMMARY

THERMO FNS: ({ ^{NATURAL} MOST CONVENIENT VARS }) (of which partials are related to useful steps)

$E(S, V) \quad dE = TdS - pdV$

enthalpy $H(S, p) \equiv E + pV \quad dH = TdS + Vdp$

helm. free en. $F(T, V) \equiv E - TS \quad dF = -SdT - pdV$

gibbs free en. $G(T, p) \equiv E - TS + pV \quad dG = -SdT + Vdp$

(1) TRICK TO RELATE THERMO QTY'S:
 point: classically, only have incomplete info; squeeze out as many relns as possible

MAXWELL RELNS:

$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$

$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$

$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$

relate easily measured PHS to chgs in nice qty S

STRUCTURE: $\left(\frac{\partial}{\partial a}\right)_b = \left(\frac{\partial}{\partial b}\right)_a$
 MNEMONIC:
 (remember 2 pairs) $(T, S) \quad (p, V)$

- (1) CIRCLE (of arrows)
- (2) OTHER IN PAIR IS FIXED
- (3) (+) IF 1 → 1 2 → 2
 (-) IF 1 → 2 2 → 1

← incr in pressure as incr. T (fixed V)

← " " vol w/ T (fixed p, thermal expansion)

note both related to how S changes w/ V or p could get pHS via eqn. of state (more detail later)

[just do ΔF, next pg]

THERMO FNS

(2) ALSO HAVE PHYSICAL MEANING: (of CH 8)

chg in E:

ex $\Delta E = Q$ GAINED AT CONST V
 $= -W$ DONE IF INSULATED

chg in H:

$\Delta H = Q$ GAINED AT CONST p

$\Delta F = -W$ DONE AT CONST T

slip $\Delta G = 0$ IF T, p CONST

ie for volume chg gives Q gained when p can keep track of work done at const T (Q-S) from ΔS ≥ 0 can show this is max work done at fixed T

EX HELM. FREE ENERGY

$$\Delta F = -W \text{ DONE AT CONST } T \quad (Q-S)$$

CAN SHOW (CA 8) FROM $\Delta S \geq 0$

$$\Delta F = \text{MAX WORK CAN DO AT FIXED } T$$

~~RE~~ Q-S OR NOT (ie Q-S IS BEST)

amp
↓
b

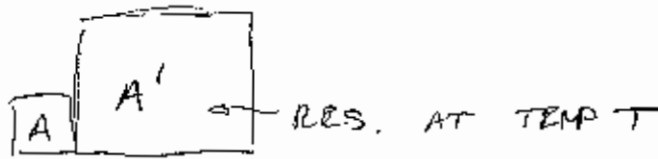
(cf CHB for more details)

IB.T.
5.12

HELM. FREE ENERGY: $F = E - TS$

SPS HAVE T CONST FOR SYS A:

save these
for later



A DOES WORK, ALSO EXCHANGES Q W/ A' (T FIXED)

$$\Delta S' = \frac{Q'}{T} = -\frac{Q}{T}$$

SPS NOT NECESS. $Q-S$:

$$\Delta S_{TOT} = \Delta S + \Delta S' \geq 0 \quad (\text{LAW II})$$

$$\Delta S \geq \frac{Q}{T} \quad (\text{AFTER BACK IN EQUIL})$$

E CONS (ALWAYS HOLDS)

FOR A: $\Delta E + W = Q \leq T \Delta S$

$$W \leq -\Delta E + T \Delta S = -\Delta(E - TS) - \cancel{S \Delta T}$$

$$= -\Delta F$$

QS: $W = -\Delta F$ (QS WK BY SYS AT CONST -
LOWERS F)

GENERAL: $W \leq -\Delta F$ "FREE ENERGY"

\Rightarrow MAX WORK SYS CAN DO FROM ^{STATE}(1) TO (2)
IS $F(1) - F(2)$ (ANY PROCESS)

\rightarrow USEFUL FOR MACHINES AT FIXED T $\left\{ \begin{array}{l} \text{if } W = -\Delta E \\ \text{FOR ADIABATI} \\ (Q=0) \end{array} \right.$

MECHANICALLY ISOLATED (\bar{w} V FIXED) & T CONST:
FROM ^{STATE} (1) TO (2) $w = 0$

$$\Delta F \leq 0$$

- F EITHER SAME (QS) OR DECREASING (NOT QS, IRREV.)

- AT EQUIL, F IS AT MIN.

(CONSISTENT w/ FIXED V, T)

(Like a kind of potential, but at fixed T:

system wants to min.)



GIBBS;

SAME WAY

$$G = E - TS + pV$$

IF T, p FIXED

$$\Delta G \leq 0$$

ie sps of another parameter that can chg leaves V, T fixed; doesn't do work \rightarrow sys sits at value of that param for which F is min

- EQUIL (FIXED p, T): G AT MIN

SYS. IS IN EQUIL, THEN

\Rightarrow IF ONLY PARAMS CHARACTERIZING SYS. IS p, T

VACUOUS STATEMENT: $G(p, T)$ CAN'T CHANGE

\Rightarrow BUT SPS of ANOTHER PARAM

ex MIX TWO CHEMICALS AT CONST T, p

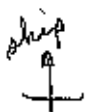
REACT? • NOT QS, REVERS.

• SYS CAN CHG EVEN IF FINAL T, p SAME \rightarrow FORMS NEW COMPOUND

• $\Delta G < 0$

REACTION GOES IF $G(T, p, \text{NEW COMP.}) < G(T, p, \text{OLD})$

(so param is how much of new vs old compound)



APPX A.9 RELNS AMONG PARTIALS (3 VARS)SPS x, y IND. VARIABLES, $z = z(x, y)$

(A) $dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$

GIVEN $x, y \rightarrow z$; IF UNIQUE, $y, z \rightarrow x$ (a valid chg of vars)

$x = x(y, z)$

(B) $dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$

RELATE PARTIALS FROM 2 CASES:① z FIXED:

(A) $= 0 \Rightarrow \left(\frac{\partial z}{\partial x}\right)_y dx = -\left(\frac{\partial z}{\partial y}\right)_x dy$

reg. z const puts
restrict on dx \rightarrow dy

$\Rightarrow \frac{dx}{dy} \Big|_{z \text{ FIXED}}$

$$= \left(\frac{\partial x}{\partial y}\right)_z = -\frac{\left(\frac{\partial z}{\partial y}\right)_x}{\left(\frac{\partial z}{\partial x}\right)_y}$$

units work

② y FIXED:

(A): $dz \Big|_{y \text{ FIXED}} = \left(\frac{\partial z}{\partial x}\right)_y dx$

can relate something
w/ z fixed to "
with x, y fixed

$\frac{dx}{dz} \Big|_{y \text{ FIXED}}$

$$= \left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}$$

These relns ok as long as denom $\neq 0$
(can't invert eqns then)hard to
imagine
not true

APPLICATION OF MAXWELL RELNS:

(I) HEAT CAPACITIES

IDEA: (T, V) CONVENIENT FOR CALCS (E, V even better)

(T, p) " " MEAS, ESP. SOLIDS

OFTEN WANT TO HOLD ONE VAR FIXED WHILE CHG OTHER;
 VERY HARD TO KEEP V FIXED, ESP FOR SOLIDS \rightarrow
 REQUIRES ENORMOUS p : EASIER TO CHG T, p INDEP,

\Rightarrow MEASURE C_p BUT CALC. C_v

$$C_v \equiv \left(\frac{dQ}{dT} \right)_v = T \left(\frac{\partial S}{\partial T} \right)_v \quad (a)$$

$$C_p \equiv \left(\cdot \right)_p = T \left(\cdot \right)_p \quad (b)$$

IN (T, p) :

$$dS(T, p) = \left[\left(\frac{\partial S}{\partial T} \right)_p dT + \left(\frac{\partial S}{\partial p} \right)_T dp \right]$$

FROM (b) $\frac{1}{T} C_p dT + \left(\frac{\partial S}{\partial p} \right)_T dp \quad (c)$

BUT C_v USES (T, V) :

$$\text{CONVERT: } dp(T, V) = \left(\frac{\partial p}{\partial T} \right)_v dT + \left(\frac{\partial p}{\partial V} \right)_T dV \quad (d)$$

COMBINE (c) & (d)

$$dS(T, V) = \frac{1}{T} \left[C_p + T \left(\frac{\partial S}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_v \right] dT + \left(\frac{\partial S}{\partial p} \right)_T \left(\frac{\partial p}{\partial V} \right)_T dV$$

$$\left(\frac{\partial S}{\partial T} \right)_v$$

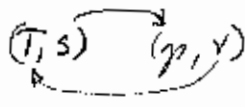
from (1)

$$C_V = C_p + T \left(\frac{\partial S}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_V \quad (1)$$

5.15

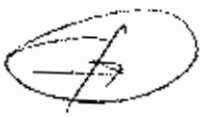
QTY'S W/ S HARD TO MEASURE; KNOW $\left(\frac{\partial S}{\partial p} \right)_T$ RELATED TO $\left(\frac{\partial ?}{\partial T} \right)_p$ BY MAX RELNS:

$$\Rightarrow \left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p \quad (2)$$



INTENSIVE QTY: $\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$

"VOLUME COEFFICIENT OF EXPANSION"



\Rightarrow VERY EASY TO MEASURE

$\left(\frac{\partial p}{\partial T} \right)_V$ HARD (V CONST); CAN USE MAX RELN. } $\left(\frac{\partial S}{\partial V} \right)_T$ WORSE

CONVERT TO (T, p);
 $dV = \left(\frac{\partial V}{\partial T} \right)_p dT + \left(\frac{\partial V}{\partial p} \right)_T dp$
IF $dV = 0$ DIVIDE

$$\left(\frac{\partial p}{\partial T} \right)_V = - \frac{\left(\frac{\partial V}{\partial T} \right)_p}{\left(\frac{\partial V}{\partial p} \right)_T}$$

INT. QTY: $\kappa \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$

"ISOTHERMAL COMPRESSIBILITY"

\Rightarrow EASY

(- sign since V dec. w/ p; so $\kappa > 0$)

$$\Rightarrow \left(\frac{\partial p}{\partial T} \right)_V = \frac{\alpha}{\kappa} \quad (3)$$

COMBINE (1) - (3)

$$C_V = C_p - VT \frac{\alpha^2}{\kappa}$$

hard

all easy to meas.

again - surprising! rate at which T chgs w/ Q related to expansion rate w/ T & p; true for sys.

SPECIAL CASES:

S.16

SOLIDS: LAST TERM SMALL (cf TEXT) (α is small)

$C_p \sim C_v$ (ex C_u ROOM TEMP)
 $\gamma = \frac{C_p}{C_v} = 1.05$

ID. GAS: $V(p, T) = \frac{VRT}{p}$

$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \frac{1}{T}$ *cold: expand quickly*

$K = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = \frac{1}{p}$ *note: T, p are intensive*

$\Rightarrow C_p = C_v + VR$

$C_p = C_v + R$ AS BEFORE

p. sleep

LOW T: Can use max relns to S to understand $T \rightarrow 0$ limit

$T \rightarrow 0 \quad E \rightarrow E_0 \quad S \rightarrow 0$ (OR CONST S_0)

CAN'T LOWER E (OR S) BY LOWERING T FURTHER

$\Rightarrow C(T) \rightarrow 0$ (both p, V) *{ note: correct for ideal gas, but no good in this limit would you? }*

$\left\{ \begin{array}{l} \text{KNOW } S(T) - S(0) = \int_0^T \frac{C(T') dT'}{T'} \\ \text{FINITE} \\ \text{becomes const} \end{array} \right. \Rightarrow C(T) \rightarrow 0 \text{ w/ } T$ *mentioned before*

ALSO $\left(\frac{\partial S}{\partial p} \right)_T \rightarrow 0 \Rightarrow \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \rightarrow 0$ *max reln*

$K = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \neq 0$ *(no reln to $\left(\frac{\partial S}{\partial p} \right)_T$)*

$\Rightarrow \frac{C_p - C_v}{C_v} \rightarrow 0$ *(diff goes to zero faster than C)*

↑

(MORE APPLICATIONS:)

(II) AS & ΔE FROM EQN OF STATE & C_V:

CAN I GET FROM MACRO INFO TO MICRO?

ex IG:

$$\Omega \propto V^N \chi(E)$$

ONLY USE \int TO GET $pV = NkT$ (EOS)

⇒ CAN'T GET $\chi(E)$ FROM EOS.

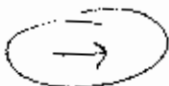
NEED INFO CONNECTING E & T

WILL SHOW:

$$C_V(T, V_1) + \text{EOS} \Rightarrow S(T, V) - S(T_0, V_0)$$

ONE REFERENCE V , BUT FOR ALL T
(V_1, V_0 CAN BE DIFF.)

ALSO INPUT
(USUALLY CARE ABOUT ΔS; THO UNLIKE IT'S ACTUAL VALUE HAS MEANING. (CAN'T GET FROM CLASSIC THERMO))



HOW:

(a) $dS(T, V) = \underbrace{\left(\frac{\partial S}{\partial T}\right)_V}_{\frac{1}{T} C_V} dT + \underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{\left(\frac{\partial p}{\partial T}\right)_V} dV$

MAX RELN; CAN GET FROM EOS

CAN SAY SOMETHING ABOUT C_V FROM EOS:

$$\begin{aligned} \left(\frac{\partial}{\partial V}\right)_T C_V &= \left(\frac{\partial}{\partial V}\right)_T + \left(\frac{\partial S}{\partial T}\right)_V \\ &= + \left(\frac{\partial}{\partial T}\right)_V \left(\frac{\partial S}{\partial V}\right)_T \\ &= T \left(\frac{\partial^2 p}{\partial T^2}\right)_V \end{aligned}$$

into deriv so can use max reln (no good reln for $\left(\frac{\partial S}{\partial T}\right)_V$)

USE (SAME RELN) FROM EOS

so can't get C_V from EOS, but can get $\left(\frac{\partial C_V}{\partial V}\right)_T$

INTEGRATE :

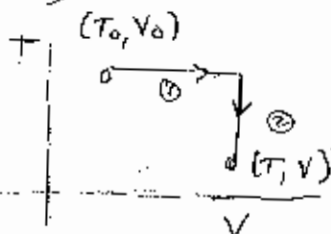
(b) $C_V(T, V) = C_V(T, V_1) + \int_{V_1}^V \left(\frac{\partial C_V(T, V')}{\partial V} \right)_T dV'$

(defn of def. integral)

MEAS FOR ALL T

EOS

any V_1 I like

NOW HAVE $C_V(T, V)$ (all V)INTEGRATE (a) ALONG
(for ds).

$$S(T, V) - S(T_0, V_0) = \int_{T_0}^T \frac{C_V(T', V)}{T'} dT' + \int_{V_0}^V \left(\frac{\partial p(T_0, V')}{\partial T} \right)_V dV'$$

FROM (b)

EOS

CAN DO SAME FOR E : (SHOULD BE ABLE TO IF HAVE S)

$$dE = T ds - p dV =$$

USE (a)

$$= \underbrace{C_V(T, V)}_{\left(\frac{\partial E}{\partial T} \right)_V} dT + \left[\underbrace{T \left(\frac{\partial p}{\partial T} \right)_V}_{\left(\frac{\partial E}{\partial V} \right)_T} - p \right] dV$$

HAVE ABOVE

EOS

INT. IN SAME WAY :

$$\text{FIG: } \left(\frac{\partial p}{\partial T} \right)_V = \frac{pR}{V}$$

$$T(\cdot) = \frac{VIRT}{V} = p \Rightarrow \left(\frac{\partial E}{\partial V} \right)_T$$

$$E(T, V) - E(T_0, V_0)$$

$$= \int_{T_0}^T C_V(T', V) dT' + \int_{V_0}^V \left[T_0 \left(\frac{\partial p(T_0, V')}{\partial T} \right)_V - p(T_0, V') \right] dV'$$