say

CH 5 CLASSICAL THERMO

NOTE: NOT "CLASS." AS IN CLASS. MECH ⇒
APPLIES TO BOTH " " & QM

BUT "CLASS." AS IN APPROACH FROM ~100 YRS AGO:

- ONLY DISCUSS MACRO VARS $(E, V, p, C, \cdots)$ ⇒ TOP
  ⇒ NOT MICRO, NOT STATISTICAL
- USE MACRO LAWS 0 TO 3 + EQNS OF STATE
- EMPIRICAL (NOT DERIVED FROM MICRO INFO)
- LIKE CONSERVATION LAWS (ex $E, \vec{p}$) IN MECH
  - NOT NECESSARY ⇒ DERIVED FROM NEWT. LAWS
  - PROVIDE BROAD PRINCIPLES FOR ALL SYS.
  - LESS GEN'L, BUT USEFUL WHEN APPLICABLE
- FOCUS ON 1 SYS (NOT ENSEMBLE)
  - NO DISCUSSION OF AVES
  - TREAT $\bar{E}, \bar{p}, \ldots$ AS EXACTLY KNOWABLE FOR 1 SYS
  - CHG VARS $V \leftrightarrow p$
    ⇒ REQUIRES KNOWING SINGLE p FOR GIVEN V

** KEY: LARGE SYS ⇒ NARROW DISTR.
⇒ p, E FOR 1 SYS VERY CLOSE TO $\bar{p}, \bar{E}$

AVE VALS & EXACT VALS FOR 1 SYS
≈ INTERCHANGEABLE

Limitations: can't address flucts, not good for small sys, meaning of S is vague

TOOLS : MACRO RELNS

(1) $d\bar{E} = \text{đ}Q - \text{đ}W$

(2) $dS = \frac{\text{đ}Q}{T}$ (Q-S)

FOR SIMPLICITY: ASSUME 1 EXT PARAM V

E, V CAN SPECIFY MACRO STATE

- ⇒ OFTEN WHAT'S KNOWN
- ⇒ HAVE FREEDOM TO CHOOSE INDEPENDENTLY } couldn't use $E, V, \bar{p}$
- ⇒ UNIQUELY SPECIFIES OTHER MACRO QTYS (ON AVE)

(ie THESE ARE FNS OF (E, V))
KNOW FROM MICRO TREATMENT

$\Omega(E,V)$ = # ALLOWED MICROST. w/ E, V

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

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

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

THEN

$$\text{đ}W = p\, dV$$

(1) & (2): $\boxed{T\,dS = dE + p\, dV}$

(WILL DROP $\bar{E}$, $\bar{p}$ ... IN SPIRIT OF CLASS. THERMO / CH 5)

NOTE: COULD HAVE OTHER EXT. PARAMS

ex $\vec{B}$ ⇒ $\text{đ}W_B = \vec{M} \cdot d\vec{B}$ etc

LET V STAND IN FOR ALL THESE
(extending is simple)

NOTE

- RELATES MACRO VARIABLES (STATE VARS) FOR EQUIL SYS ⇒ HAVE REMOVED Q, W
  ⇒ ALL DIFFERENTIALS

ex CAN SEE HOW S CHGS AS CHG. E, V WHILE STAY IN EQ.

- BASED ON Q-S CHGS
  ⇒ OK SINCE MOVE FROM EQUIL. TO EQUIL
  BUT ⇒ IF INTEGRATE, RESULTS TRUE FOR EQUIL. SYSTEMS IN GEN'L; DOESN'T MATTER HOW GOT THERE

ex ΔS FROM (E_i, V_i) TO (E_f, V_f) CORRECT WHETHER TOOK Q-S PATH OR NOT

23 '14

OFTEN E, V NOT MOST CONVENIENT :

MICRO: E, V most natural indep. vars; all others (T, S, p, ζ) derived after E, V set.

MACRO: these are all macro properties of sys, related, but none are more fund. than others; ex, can meas. both p or V

CHG VARIABLES :

ex FIXED $E, V \longrightarrow$ UNIQUE p

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

TYPICAL SWITCHES : RELATED QTYs

$$E \leftrightarrow T \leftrightarrow S$$

$$p \leftrightarrow V$$

PAIRS :

(E, V) (E, p)

(T, V) (T, p) ETC

(S, V)

(not all changes possible ex, for IG $E = E(T)$ only ; couldn't choose $(E, T) \rightarrow$ any p, V possible)

TECHNICAL REQMT :

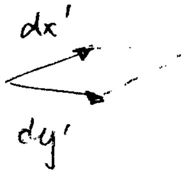
$$(x, y) \rightarrow (x', y') \qquad (\text{ie } x(x', y'),\ y(x', y'))$$

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

WHY?

MEASURES AREAS / VOLUMES

(cf integration)



DON'T WANT $d\vec{x}' \parallel d\vec{y}'$

$\Rightarrow dA$ collapses

7/8/04

11/11/02

~~9~~

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

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*α to main tools: (a) $T\,dS = dE + p\,dV$

(b) dS IS DIFFERENTIAL

(c) 2 INDEP. VARS.

(d) + EQN OF STATE :

can get lost in sea of partial derivs.

skip ✓

2ND TOOL : EQNS OF STATE

- RELATE EASILY MEASBLE QTYS (ex p, V, T, not S, E)
- HISTORICALLY EMPIRICAL BUT CAN DERIVE W/ MICRO INFO

CH5 :

PART I : THERMO LAWS + EOS ← CAN SAY MORE

" II : " " ALONE ← GENERAL; APPLY TO ALL MACRO SYS.

ex : IDEAL GAS

MICRO : WE DERIVED FROM $\Omega(E,V) = V^N \chi(E)$

(a) EOS $pV = \nu R T$

(b) $E = E(T)$ ONLY (NOT V)

CLASSICAL:

GIVEN (a) EMPIRICALLY CAN DERIVE (b) (w/out micro info)

CHOOSE VARS. (T, V) (SO E, p, S ARE FNS OF (T,V))

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

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

PHYS: $T\,dS = dE + p\,dV$ (LAWS 1 & 2)

$p = \frac{\nu R T}{V}$ (EOS)

COMBINE: $dS = \frac{1}{T} dE + \frac{\nu R}{V} dV$

REPLACE dE FROM (i) ⇒ GET IN TERMS OF dT, dV

$$ds = \underbrace{\frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V}_{\left(\frac{\partial S}{\partial T}\right)_V} dT + \underbrace{\left[\frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T + \frac{\nu R}{V}\right]}_{\left(\frac{\partial S}{\partial V}\right)_T} dV$$

cp TO (ii)

<u>MATH</u>: $\dfrac{\partial^2 S}{\partial V\,\partial T} = \dfrac{\partial^2 S}{\partial T\,\partial V}$

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

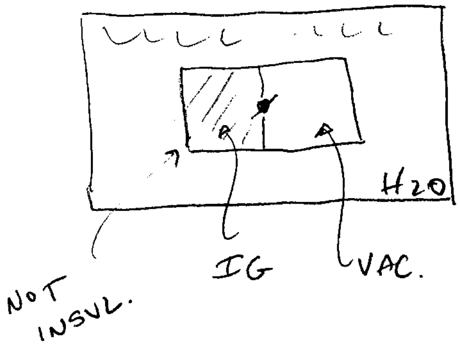
$$\frac{1}{T}\left(\frac{\partial^2 E}{\partial V\,\partial T}\right) = \left[\frac{-1}{T^2}\left(\frac{\partial E}{\partial V}\right)_T + \frac{1}{T}\left(\frac{\partial^2 E}{\partial T\,\partial V}\right)\right]$$

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

CONTENT: $T\,dS = dE + p\,dV$ (LAWS 1 & 2) + EOS

+ EXISTENCE OF $S(T,V)$ } DIDN'T NEED MEANING

EXPT: FREE EXPANSION (JOULE)



- IN EQUIL TO START
- OPEN VALVE, WAIT FOR EQUIL

ΔT FOR H_2O ?

FOUND $\Delta T = 0$

$\Rightarrow Q = 0$

$\Rightarrow E(T, V_f) - E(T, V_i) = 0$ FOR GAS

$\Rightarrow E(T)$ ONLY

{ cp <u>NON-IG</u>: EXPECT E_{GAS} HIGHER IF $\mathcal{U}$ ATTRACTIVE

⇒ T DROPS }

RELN BETW SPECIFIC HEATS: (IG) C_V vs C_p

V CONST $\qquad \text{đ}W = 0$

$$\text{đ}Q = dE$$

NATURAL VARS FOR V CONST: (T, V) (constraint ≡ hold one var. fixed; other gives freedom in system)

MOLAR $\displaystyle C_V \equiv \frac{1}{\nu}\left(\frac{\text{đ}Q}{dT}\right)_V = \frac{1}{\nu}\left(\frac{\partial E}{\partial T}\right)_V$ thinking of $E = E(T, V)$

IG: E IND. OF $V \Rightarrow C_V$ IND. OF $V \Rightarrow C_V = C_V(T)$ ONLY

ALSO: $\displaystyle dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \cancel{\left(\frac{\partial E}{\partial V}\right)_T}^{\,0} dV$

(A) $\boxed{dE = \nu C_V\, dT}_{IG}$ can have $C_V(T)$ here

p CONST

NATURAL VARS: (T, p)

IF USE (T, V), CHGS IN EACH MUST KEEP $p(T, V)$ FIXED
(to relate to above) $\Rightarrow$ TIED TOGETHER

HOW? $\quad pV = \nu RT$

$$d(pV) = \cancel{dp\, V}^{\,0} + p\, dV = \nu R\, dT$$

(B) $\boxed{p\, dV = \nu R\, dT}_{IG,\ p \text{ FIXED}}$ TIES dV, dT

COMBINE w (A):

look at đQ since const $c_{p,V}$'s

$$\text{đ}Q = dE + p\, dV \quad (E \text{ cons.})$$

$$= \nu C_V\, dT + \nu R\, dT = \nu(C_V + R)\, dT \quad \Big\}\ p \text{ FIXED}$$

$\displaystyle C_p \equiv \frac{1}{\nu}\left(\frac{\text{đ}Q}{dT}\right)_p \Rightarrow \boxed{C_p = C_V + R}_{IG}$ $\Big\}$ Typical for classical thermo ⇒ lots of relns between qtys even if can't compute directly

NOTE: C_p ALSO IND. OF V

$C_p > C_V$ as expected $\qquad R \equiv N_A k$

USEFUL RATIO:

$$\boxed{\gamma \equiv \underbrace{\frac{c_p}{c_v}}_{>1} = 1 + \underbrace{\frac{R}{c_v}}_{IG}}$$

cf TABLE pg 157: c_v FOR GAS @ 15°C

FAR RIGHT: USES RELN

NEXT TO ": MEAS c_v, c_p BOTH DIRECTLY

⇒ VERY GOOD

→ WILL COME BACK TO THIS

cf

MICRO CALC: CAN SAY EVERYTHING → GET c_p, c_v EXPLICITLY

RECALL: $\Omega = B V^N E^{3N/2}$ (MON. IG)

$$\beta = \frac{1}{kT} = \frac{\partial \ln \Omega}{\partial E} = \frac{3N}{2}\frac{1}{E}$$

$$\Rightarrow \boxed{\begin{aligned} E &= \frac{3}{2}NkT = \frac{3}{2}\nu RT \\ c_v &= \frac{1}{\nu}\left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2}R \\ c_p &= c_v + R = \frac{5}{2}R \\ \gamma &= \frac{5}{3} = 1.667 \end{aligned}}\ \text{MON IG}$$

NOTE: c_v & c_p CONST IN V & T

↑ needed micro info to get this

SIMPLE, WORKS BEAUTIFULLY (cf He & Ar)

OTHERS: WILL DERIVE DIATOMIC IN HW

CLASSICAL THERMO: CAN GET $c_p = c_v + R$

NOT ACTUAL VALUE $c_v = \frac{3}{2}R$

⇒ WON'T USE IN CH 5

5.5.1

But, by definition,

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

Using (5·2·7), this becomes

▶
$$c_p = c_V + R \tag{5·2·8}$$

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

$$\gamma \equiv \frac{c_p}{c_V} = 1 + \frac{R}{c_V} \tag{5·2·9}$$

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_2H_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, Benn, London, 1924.

Microscopic calculation of specific heats If one is willing to make use of *micro*scopic 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

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

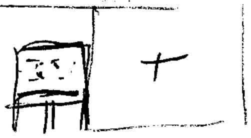
where N is the number of molecules in the gas and B is some constant independent of E and V. Hence

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

5,6

p VS V IN

ISOTHERMAL VS ADIABATIC EXPANSION: (IG)

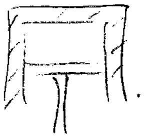


(1) ISOTH: T CONST

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

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

(2) ADIABATIC:



p incr. faster as V decr? yes

AS USUAL, START w/

$$đQ = 0 = dE + đW$$

$$= \nu c_V\, dT + p\,dV \qquad \text{(A)} \qquad \text{(IG)}$$

Want to relate p to V ⇒ get rid of dT: (p, V)

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

from IG law (as before)

REPLACE dT IN (A):

$$(c_V + R)\,p\,dV + c_V\,V\,dp = 0$$

DIV. BY $c_V pV$:

$$\underbrace{\left(\frac{c_V + R}{c_V}\right)}_{= c_p/c_V \,\equiv\, \gamma} \frac{dV}{V} + \frac{dp}{p} = 0$$

IF $\gamma \sim$ CONST (MICRO: PROVED CLASSICAL: MEASURED)

INTEG: $\gamma \ln V = -\ln p + \text{CONST}$

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

(**) surprising that it depends on c_V & c_p, since no heat being exch by defn

$$\boxed{pV^{\gamma} = \text{CONST}}$$

ADIAB. IG γ CONST

$\gamma > 1$ so p does grow faster

$$\text{OR} \quad \underbrace{\boxed{V^{\gamma - 1}\,T = \text{CONST}}}_{\text{(via IG LAW)}} \qquad (T, V)$$

leave for ex in gen'l discussion

GEN. EXPRESSION FOR $S(T, V; \nu)$ FOR IG:

{ will discuss gen'l case later

DEF. REFERENCE ENTROPY (std state)

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

{ can only get S wrt some ref. S; ie, up to const, Micro: get abs. S

CHG 1 PARAM AT A TIME

1. ν_0 TO ν MOLES

PUT $n \equiv \nu/\nu_0$ COPIES TOGETHER

{ IG: can neglect edge effects }

$$\{\underbrace{T, p \text{ INTENSIVE}}_{\text{STAY SAME}} ; \underbrace{\nu, V, S \text{ EXTENSIVE}}_{\text{INCR. BY } n \times}\}$$

{ vs. increasing # but leaving V fixed → would chg p, T; would chg S in complicated way

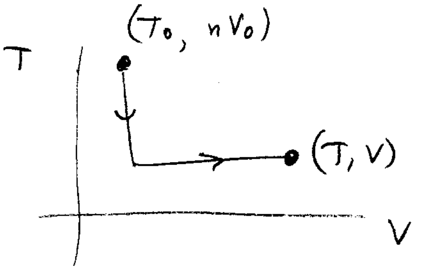
$$S(T_0, nV_0, n\nu_0) = n S_0$$

{ the additivity of S is an approx for large sys; it neglects small contribs to Ω w/ for ex $\boxed{\nu_1 | \nu_2}$ $\nu_1 \neq \nu_2$

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

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

(b) T ″, $nV_0 \to V$



USE

$$T dS = \underbrace{dE}_{\nu c_v dT} + \underbrace{p}_{\frac{\nu R T}{V}} dV$$

$$\Rightarrow \boxed{dS = \nu c_v(T) \frac{dT}{T} + \nu R \frac{dV}{V}}_{IG}$$

{ use what's known from classical thermo

THEN

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

$$= \nu \underbrace{\int_{T_0}^{T} \frac{c_v(T') dT'}{T'}}_{(a)} + \nu R \underbrace{\int_{nV_0}^{V} \frac{dV'}{V'}}_{(b)}$$

line integrals

OR

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

$$\boxed{S(T, V; \nu) = \nu \left[\underset{\text{INDEF}}{\int} \frac{c_v(T') dT'}{T'} + R \ln V - R \ln \nu + \text{CONST} \right]}$$

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

GENERAL RELATIONS (PART II OF CH 5)

- APPLY TO ALL MACRO SYS (NOT JUST IG)
- USES $TdS = dE + p\,dV$ BUT NOT EOS (ie LAWS (1) & (2))
- STILL ASSUME 1 EXT PARAM V (EASY TO REPLACE / EXTEND)

MAIN IDEAS

① - 2 VARS DETERMINE SYS: (E, V) ⇒ INDEP. VARS

⇒ OTHERS (p, T, S, G ---) FNS OF (E,V)

⇒ CHG E,V ⇒ CHG " IN WAY DET. BY THERMO LAWS

MAXWELL RELNS:

② - CAN MAKE DIFF CHOICES FOR 2 IND. VARS ⇒ IMPLIES RELNS BETWEEN PARTIALS

⇒ USES THERMO LAWS TO EXTRACT MAX. INFO ON HOW MACRO PARAMS RELATED

1 PAIR AT TIME:

(0) (E, V) (MOST USEFUL FOR MICRO DESCR.)

$$dS = \frac{1}{T}\,dE + \frac{p}{T}\,dV \qquad (a)$$

INDEP.

DEP. (ie FNS OF (E,V))

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

EQUIV TO

$$\frac{1}{kT} \equiv \beta = \frac{\partial \ln \Omega}{\partial E} \qquad p = \frac{1}{\beta}\frac{\partial \ln \Omega}{\partial V}$$

} THESE LED TO (a); GOING BACKWARDS HERE MACRO → MICRO

(1) (S, V)

$$dE = T\,dS - p\,dV$$

IND.

DEP.

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

} DEFN OF AVE GEN FORCE (NOTE S CONST ⇒ $dQ = 0$)

INVERSE OF RELN ABOVE

GO FURTHER: CONSIST. COND

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

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

1ST MAX RELN

TRIVIAL, BUT NOT OBVIOUS:

HOLD # STATES FIXED (NO Q), CHG V, WATCH ΔT

⇒ GIVES Δp IF CHG S VIA Q AT CONST V (NO W)

<u>(2) (S, p)</u>

$$dE = T\,dS - p\,dV$$ } AWKWARD: dV INVOLVES CHGS IN BOTH S & p

TRICK:

$$= \text{''} \quad \underbrace{\text{''} \quad - V\,dp}_{-d(pV)} + V\,dp$$

$$\Rightarrow \quad d(E + pV) = T\,dS + V\,dp$$ } CAN NOW IDENTIFY CHGS IN S & p ON RHS

LHS: DEFINE $\boxed{H \equiv E + pV}$ ≡ "ENTHALPY" (ONE OF SEVERAL "THERMODYNAMIC FNS")

- A FN OF STATE OF SYS, DEP. ON (S, p) (LIKE E)
- LHS IS DIFF dH

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

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

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

NOTE: H DISAPPEARS

- TRICK TO GET RELN; ELEGANT, NOT NECESSARY
- EX. OF "LEGENDRE TRANSF." ⇒ CHG dV TO dp BY ADD pV TO LHS

  (cf MECHANICS: $L(q, \dot{q}) \rightarrow H(q, p)$; ALSO SEE POSTED REF.)
- NEW FN: (1) HAS SIMPLE PARTIALS (2) OFTEN HAS PHYS MEANING (CF CH 8)

<u>ASIDE</u>: DERIVATION w/OUT LEG. TRANSF.

$$dE = T\,dS - p\,dV(S,p) = T\,dS - p\left[\left(\frac{\partial V}{\partial S}\right)_p dS + \left(\frac{\partial V}{\partial p}\right)_S dp\right]$$

$$= \underbrace{\left[T - p\left(\frac{\partial V}{\partial S}\right)_p\right]}_{\left(\frac{\partial E}{\partial S}\right)_p} dS - \underbrace{\left[p\left(\frac{\partial V}{\partial p}\right)_S\right]}_{-\left(\frac{\partial E}{\partial p}\right)_S} dp$$

CONSIST: $\left(\frac{\partial}{\partial p}\right)_S \left[T - p\left(\frac{\partial V}{\partial S}\right)_p\right] = -\left(\frac{\partial}{\partial S}\right)_p \left[p\left(\frac{\partial V}{\partial p}\right)_S\right]$

$$\text{''} \qquad\qquad \text{''}$$

$$\left(\frac{\partial T}{\partial p}\right)_S - \left(\frac{\partial V}{\partial S}\right)_p - \cancel{p\left(\frac{\partial^2 V}{\partial p\,\partial S}\right)} = \cancel{-p\left(\frac{\partial^2 V}{\partial S\,\partial p}\right)}$$

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

(3) (T, V) $dE = T\,dS - p\,dV$ } USE LEG. TRANS. ON 1ST TERM

$$= d(TS) - S\,dT - p\,dV$$

$$d(E - TS) = -S\,dT - p\,dV$$

$\boxed{F \equiv E - TS}$ ≡ "HELMHOLTZ FREE ENERGY"

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

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

(4) (T, p) ⇒ MOST USEFUL EXPTL PAIR (EASIEST TO CONTROL)

2 TRANSF: $S \to T$ $V \to p$

$\boxed{G \equiv E - TS + pV}$ = "GIBBS FREE ENERGY"

$$dG = -S\,dT + V\,dp$$

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

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

SUMMARY HANDOUT

THERMODYNAMIC FNS:

FN (IN NATURAL VARS)

ENERGY	$E(S, V)$	$dE = T\,dS - p\,dV$
ENTHALPY	$H(S, p) \equiv E + pV$	$dH = T\,dS + V\,dp$
HELMHOLTZ FREE ENERGY	$F(T, V) \equiv E - TS$	$dF = -S\,dT - p\,dV$
GIBBS FREE ENERGY	$G(T, p) \equiv E - TS + pV$	$dG = -S\,dT + V\,dp$

MAXWELL RELATIONS

(FROM EQUAL CROSS DERIVS)

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

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

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

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

CALCULUS (APPX A.9)

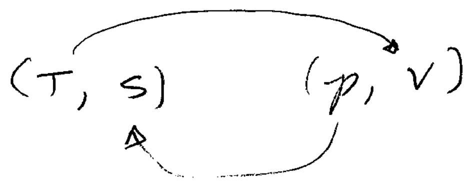
3 VARS x, y, z

2 INDEP.

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

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

MNEMONIC



(1) MAKE CIRCLE (cf ARROWS HERE FOR 1ST RELN)

(2) OTHER VAR. IN PAIR IS FIXED

(3) (+) IF 1 → 1 , 2 → 2

(−) IF 1 → 2 , 2 → 1

COMMENTS

- NATURAL VARS ⇒ PARTIALS ARE RELATED TO SIMPLE, USEFUL FNS

- MAXWELL RELNS:
  - CLASS. LEVEL ⇒ ONLY HAVE INCOMPLETE INFO
    ⇒ SQUEEZE OUT AS MANY USEFUL RELNS AS POSSIBLE (VIA CONSIST. CONDS, ETC)
  - GEN'L STRUCTURE:

  ⇒ RELATE CHGS WRT. S (ABSTRACT BUT FUNDAMENTAL) TO CHGS IN MEASBLE QTYS (p, V, T) ⇒ ACCESS. VIA EOS

ex 3RD RELN: MEAS INCR. IN p w/ T (V FIXED)
= RATE LN(# STATES) INCR. w/ V (FIXED T)

4TH RELN: MEAS INCR. IN V w/ T (THERM. EXP.) (p FIXED)
= RATE LN(# STATES) INCR w/ p (FIXED T)

⇒ RELATE COMPLETELY DIFF PHYS. SITUATIONS

⇒ TRUE ALL MACRO SYS.

ASIDE

- THERM. FNS HAVE PHYS. MEANINGS (CH 8)
  ⇒ NOT JUST TRICK

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

$$dF = -S\,dT - p\,dV$$

⇒ $-\Delta F = (QS)\ W$ AT FIXED T } AS GO FROM INIT TO FINAL ST.

FROM $\Delta S \geq 0$ CAN SHOW

$-\Delta F$ IS MAX W SYS CAN DO AT FIXED T
(ANY PROCESS FROM i TO f ; QS IS MAX)

PRACTICAL IMPORTANCE: T CONST MORE COMMON THAN $Q = 0$

⇒ EXPLAINS NAME (~ USEFUL E AVAIL, FIXED T)

skip
b

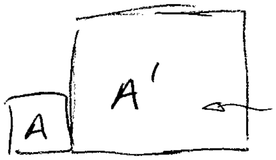
(cf CH8 for more details)

~~IE.T~~
5.12

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

save these for later

SPS HAVE T CONST FOR SYS A:



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

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

SPS NOT NECESS. Q-S:

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

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

E CONS (ALWAYS HOLDS)

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

$$W \leq -\Delta E + T\Delta S = -\Delta(E - TS) - \cancel{S\Delta T}^{\,0}$$

$$= -\Delta F$$

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

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

⇒ MAX WORK SYS CAN DO FROM STATE (1) TO (2) IS $F(1) - F(2)$ (ANY PROCESS)

→ USEFUL FOR MACHINES AT FIXED T

cp $W = -\Delta E$ FOR ADIABATIC ($Q = 0$)

~~FF.2~~
5.13

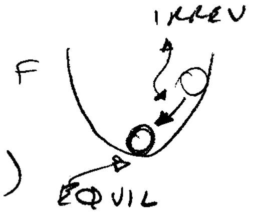
<u>MECHANICALLY ISOLATED</u> (ie V FIXED) & T CONST:
$W = 0$

FROM STATE (1) TO (2)

$$\Delta F \le 0$$

— 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.)



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

<u>GIBBS</u>:

SAME WAY

$$G = E - TS + pV$$

IF T, p FIXED

$$\Delta G \le 0$$

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

⇒ IF SYS. IS IN EQUIL, THEN ONLY PARAMS CHARACTERIZING SYS. IS p, T
VACUOUS STATEMENT: $G(p,T)$ CAN'T CHANGE

⇒ BUT SPS ∃ ANOTHER PARAM

<u>ex</u> MIX TWO CHEMICALS AT CONST T, p

REACT? • NOT Q-S, REVERS.
- SYS CAN CHG EVEN IF FINAL T, p SAME → 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)

skip

24

~~60~~
5.13.1

CAN EXTEND USEFULNESS OF MAX. RELNS:

APPX A.9 RELNS AMONG PARTIALS

3 VARS x, y, z 2 INDEP. (so 3RD is fn of other two)

(x, y) INDEP $\Rightarrow z = z(x,y)$

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

CHG VARS: $x \to z$

(y, z) INDEP $\Rightarrow x = x(y,z)$

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

RELATE PARTIALS FROM 2 CASES:

① z FIXED: $dz = 0$

{req. z const puts reqmt on $dx \leftrightarrow dy$}

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

$$(B) \quad dx = \left(\frac{\partial x}{\partial y}\right)_z dy \Rightarrow \boxed{\left(\frac{\partial x}{\partial y}\right)_z = \frac{-\left(\frac{\partial z}{\partial y}\right)_x}{\left(\frac{\partial z}{\partial x}\right)_y}}$$

(divide top eqn by $\left(\frac{\partial z}{\partial x}\right)_y$)

units work

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

② y FIXED: $dy = 0$

$$(A) \quad dz = \left(\frac{\partial z}{\partial x}\right)_y dx$$

$$(B) \quad dx = \left(\frac{\partial x}{\partial z}\right)_y dz \Rightarrow \boxed{\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}}$$

These relns ok as long as derivs $\neq 0$
(can't invert eqns then)

hard to imagine not true

31 $\rightarrow$

APPLICATION OF MAXWELL RELNS:

(I) HEAT CAPACITIES: C_V vs C_p (IN GEN'L)

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

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

say OFTEN WANT TO HOLD ONE VAR FIXED WHILE CHG OTHER;
VERY HARD TO KEEP V FIXED, ESP FOR SOLIDS, LIQUIDS;
REQUIRES ENORMOUS p. EASIER TO CHG T, p INDEP'LY

$\Rightarrow$ MEASURE C_p BUT CALC. C_V

(have already worked out reln for specific ex of IG)

32 $\rightarrow$

$$C_V \equiv \left(\frac{\text{đ}Q}{dT}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \qquad \text{(a)}$$

$$C_p \equiv \left(\text{"}\right)_p = T\left(\text{"}\right)_p \qquad \text{(b)}$$

IN (T, p) FOR C_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) $$= \frac{1}{T} C_p\, dT + \left(\frac{\partial S}{\partial p}\right)_T dp \qquad \text{(c)}$$

IN (T, V) FOR C_V:

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

COMBINE (c) & (d)

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

5.15

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

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:

$$\begin{tikzcd}(T,S) \arrow[r, bend left] & (p,V) \arrow[l, bend left]\end{tikzcd}$$

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

INTENSIVE QTY: $\boxed{\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p}$ "VOLUME COEFFICIENT OF EXPANSION"

$\Rightarrow$ EASY TO MEAS

$\Rightarrow$ CAN GET FROM EOS (IF AVAIL)

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

drop

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

APPX A.9: (CALC) $$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T}$$

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

$\Rightarrow$ EASY TO MEAS;
$\Rightarrow$ CAN USE EOS.

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

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

COMBINE ① - ③

$$\boxed{\underbrace{C_V}_{\text{hard}} = \underbrace{C_p - VT\frac{\alpha^2}{\kappa}}_{\text{all easy to meas.;}}}$$

2ND term from EOS

again – surprising: rate at which T chgs w/ Q at fixed V related to expansion rates w/ T or p; [illegible]

5.16

SPECIAL CASES:

α SMALL (cf TEXT)

SOLIDS: → LAST TERM SMALL

$$C_p \approx C_V$$ (ex Cu ROOM TEMP $\gamma = \frac{C_p}{C_V} = 1.05$)

IG: $$V(p,T) = \frac{\nu R T}{p}$$

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

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

$$\Rightarrow \quad C_p = C_V + \nu R$$

$$c_p = c_v + R$$ AS BEFORE

p. skip

LOW T: Can use max relns to S to understand T → 0 limit ~~behav~~

$T \to 0 \qquad E \to E_0 \qquad S \to 0$ (OR CONST S_0)

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

$$\Rightarrow \boxed{C(T) \to 0}$$ (both p, V) { note: const for ideal gas, but no good in this lim; need QM

$$\left\{ \text{KNOW} \quad \underbrace{S(T) - S(0)}_{\text{FINITE}} = \int_0^T \frac{C(T')\,dT'}{T'} \quad \Rightarrow \quad C(T) \to 0 \text{ w/ } T \right\}$$

mentioned before

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

← becomes const

$$K = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \not\to 0$$

(no max reln to $\left(\frac{\partial S}{\cdot\cdot}\right)$)

$$\Rightarrow \quad \frac{C_p - C_V}{C_V} \to 0$$ (diff goes to zero faster than C)

(MORE APPLICATIONS:)

(II) ΔS & ΔE FROM EQN OF STATE & C_V:

FUNDAMENTAL QUESTION:

CAN I GET FROM MACRO INFO TO MICRO? WHAT'S THE MIN. I NEED TO MEAS. TO GET Ω OR S (i.e. TO KNOW EVERYTHING)?

ex IG: $\Omega \propto V^N \chi(E)$

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

$\Rightarrow$ CAN'T GET $\chi(E)$ FROM E.O.S.

NEED INFO CONNECTING E & T

so C_V & EOS provide complim. info

WILL SHOW:

RELATES MEASURABLES: p, V, T (not S, E)

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

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

ALSO INPUT (USUALLY CARE ABOUT ΔS; THO UNLIKE E, IT'S ACTUAL VALUE HAS USEFUL MEANING) (CAN'T GET FROM CLASSICAL THERMO)

4/15/04

HOW:

25 14 save

(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:

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

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

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

USE (SAME RELN)

$$= T \left(\frac{\partial^2 p}{\partial T^2}\right)_V$$

} FROM EOS

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

25 + 8 40

INTEGRATE :

any V_1 I like

(b) $$C_V(T,V) = \underbrace{C_V(T,V_1)}_{\text{MEAS FOR ALL } T} + \int_{V_1}^{V} \underbrace{\left(\frac{\partial C_V(T,V')}{\partial V}\right)_T}_{T\left(\frac{\partial^2 p}{\partial T^2}\right)_V} dV'$$

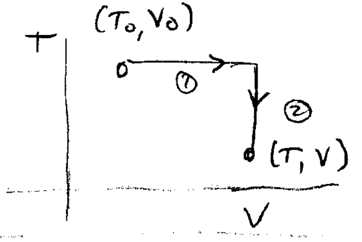
(defn of def. integral)

** (use (I) to get from $C_p(T,V_1)$)

EOS

NOW HAVE $\underline{C_V(T,V)}$ (all V)

INTEGRATE (a) ALONG (for dS)



$$\boxed{S(T,V) - S(T_0,V_0) = \underbrace{\int_{T_0}^{T} \frac{C_V(T',V)}{T'}\, dT'}_{②} + \underbrace{\int_{V_0}^{V} \overbrace{\left(\frac{\partial p(T_0,V')}{\partial T}\right)_V}^{\text{EOS}} dV'}_{①}}$$

FROM (b)

everything on rhs measurable; get C_V from C_p as in (I)

38

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

$$dE = \underbrace{T\, dS}_{\text{USE (a)}} - p\, dV =$$

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

INT. IN SAME WAY :

$$\left\{ \text{IG} : \left(\frac{\partial p}{\partial T}\right)_V = \frac{\nu R}{V} \qquad T(\,''\,) = \frac{\nu R T}{V} = p \Rightarrow \left(\frac{\partial E}{\partial V}\right)_T = 0 \right\}$$

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