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 $E, \bar{P}$) 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 $\bar{E}, \bar{p}, \cdots$ 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) $d\bar{E} = đQ - đW$

(2) $dS = \frac{đQ}{T}$ (Q-S)

FOR SIMPLICITY : ASSUME 1 EXT PARAM V

E, V CAN SPECIFY MACRO STATE

$\Rightarrow$ OFTEN WHAT'S KNOWN
$\Rightarrow$ HAVE FREEDOM TO CHOOSE INDEPENDENTLY } couldn't use $E, V, \bar{p}$
$\Rightarrow$ 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

$$đW = p\,dV$$

(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 $\vec{B} \Rightarrow đW_B = \vec{M} \cdot d\vec{B}$ 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 :

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)

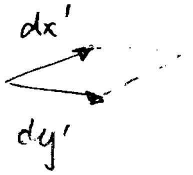
TECHNICAL REQMT :

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

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

WHY?

MEASURES AREAS / VOLUMES
(cf integration)



DON'T WANT
$dx' \parallel dy'$
$\Rightarrow$ dA collapses

4/8/04
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)

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

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

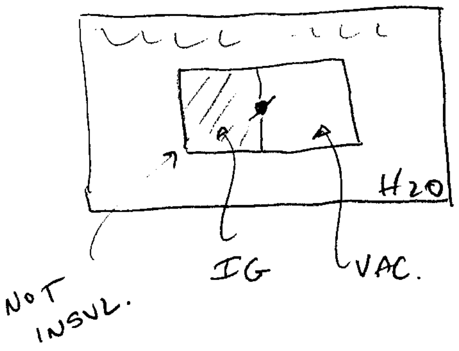
$$\frac{1}{T}\left(\frac{\partial^2 E}{\partial V \partial T}\right) = \left[\frac{-1}{T^2}\left(\frac{\partial E}{\partial V}\right)_T + \frac{1}{T}\left(\frac{\partial^2 E}{\partial T \partial V}\right)\right]$$

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

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 NON-IG: EXPECT E_{GAS} HIGHER IF U ATTRACTIVE

⇒ T DROPS }

RELN BETW SPECIFIC HEATS: (IG) C_V vs C_p

V CONST $$đW = 0$$
$$đQ = dE$$

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

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

thinking of $E = E(T,V)$

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

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

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

p CONST

NATURAL VARS: (T, p)

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

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

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

COMBINE W (A):

look at $đQ$ since want $c_{p,v}$'s

$$đQ = dE + p\, dV \quad (E \text{ cons.})$$
$$= \nu C_V\, dT + \nu R\, dT = \nu(C_V + R)\, dT \quad \Big\}\ p \text{ FIXED}$$

$$C_p \equiv \frac{1}{\nu}\left(\frac{đQ}{dT}\right)_p \Rightarrow \boxed{C_p = C_V + R}_{IG}$$

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 $R \equiv N_A k$

USEFUL RATIO:

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

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)

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

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

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

▶ $$c_p = c_V + R \qquad (5\cdot2\cdot8)$$

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

$$\gamma \equiv \frac{c_p}{c_V} = 1 + \frac{R}{c_V} \qquad (5\cdot2\cdot9)$$

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

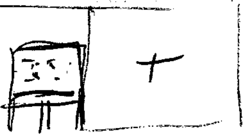
$$\Omega(E,V) = BV^N E^{3N/2}$$

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

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

p VS V IN

ISOTHERMAL VS ADIABATIC EXPANSION: (IG)

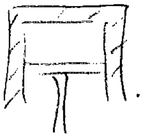


(1) ISOTH: T CONST

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

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

(2) ADIABATIC:



p incr. faster as V decr? yes

AS USUAL, START w/

$$đQ = 0 = dE + đW$$

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

Want to relate p to $V \Rightarrow$ 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 if 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

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

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

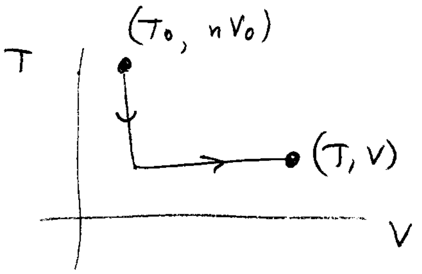
$$S(T_0, nV_0, n\nu_0) = n S_0$$

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

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

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

(b) T ″, $nV_0 \to V$



USE
$$T dS = \underbrace{dE}_{\nu c_V dT} + \underbrace{p}_{\frac{\nu RT}{V}} dV$$

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

{ use what's known from classical thermo

THEN

$$\Delta S = S(T, V; \nu) - n S_0$$
$$= \underset{(a)}{\nu \int_{T_0}^{T} \frac{c_V(T')\,dT'}{T'}} + \underset{(b)}{\nu R \int_{nV_0}^{V} \frac{dV'}{V'}}$$

line integrals

OR

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

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

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

GENERAL RELNS (ALL SYSTEMS)

- NOT JUST IG. (won't use specific EOS)
- STILL ONLY V   - USE $TdS = dE + p\,dV$

IDEA:

2 VARS. DETERMINE SYS: E, V

CHG E, V ⇒ p, T, S CHG IN RELATED WAY } GOVERNED BY THERMO LAWS

35 ~~30~~

MAXWELL RELNS: EXTRACT BY CHOOSING DIFF. INDEP. VARS & CP. DERIVS

⇒ USE BASIC THERMO RELN TO EXTRACT MAX INFO ABOUT MACRO PARAMS E, S, T, p, V

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CONSIDER 1 PAIR AT TIME:

(0) (E, V) (most natural for micro descr.)

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

(from fund. laws)

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

$$\Updownarrow \qquad\qquad \Updownarrow$$

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

(THESE LED TO (a); GOING BACKWARDS HERE; MACRO → MICRO)
recover same relns from Top down

14 (p3) 10

(1) (S, V) $dE = TdS - p\,dV$

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

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

⇐ DEFN OF AVE GENLD FORCE (NOTE $đQ = 0$)

The higher the T, the more E w/ V fixed (so Q) you need to get same chg in S; really just defn for T again

2ND DERIVS: $$\left(\frac{\partial}{\partial V}\right)_S \underbrace{\left(\frac{\partial E}{\partial S}\right)_V}_{T} = \left(\frac{\partial}{\partial S}\right)_V \underbrace{\left(\frac{\partial E}{\partial V}\right)_S}_{-p}$$

1ST Max Reln

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

} TRIVIAL, BUT NOT OBVIOUS:
* STATES FIXED (NO Q), CHG V, WATCH ΔT ⇒ GIVES Δp IF CHG S VIA Q AT CONST V ⇒ TRUE ALL

(2) (s, p)

$$dE = TdS - pdV$$ ← not convenient; involves chgs in S & p

{add $(-Vdp + Vdp)$

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

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

{ std Trick — (save to end of eq) 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: $\boxed{H \equiv E + pV}$

- H DEPENDS ON STATE (LIKE E)
- dH (EXACT DIFF) = $TdS + Vdp$
- IF THINK OF $H = H(S, p)$ (also $T(S,p)$, $V(S,p)$)

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

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

{ This is main pt; it's a qty whose derivs are simply related to ind. vars. 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 → TRICK FOR GETTING THIS RELN
(ELEGANT; NOT REALLY NECESSARY)

ASIDE:

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

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

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

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

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

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

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

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

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

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

}

(3) (T, V)

SAME PROCEDURE

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

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

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

HELMHOLTZ FREE ENERGY:

$$\boxed{F \equiv E - TS}$$

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

2ND DER. EQUAL:

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

(4) (T, p) This is perhaps most useful set - easiest to control in lab

GIBBS FREE ENERGY:

$$\boxed{G \equiv E - TS + pV}$$

(chg. both $S \to T$
$V \to p$)

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

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

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

(put on overhead)

SUMMARY

THERMO FNS: ($\{$ NATURAL VARIABLES)

(ie in terms of which partials are related to useful qtys)

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

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

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

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

(1) THESE ARE TRICK TO RELATE THERMO QTYS:

$\{$ point: classically, only have incomplete info; squeeze out as many relns. as possible

STRUCTURE: $\left(\frac{\partial}{\partial a}\right)_b = \left(\frac{\partial}{\partial b}\right)_a$

MAXWELL RELNS:

MNEMONIC:

(remember 2 pairs)

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

(1) CIRCLE (cf ARROWS)

(2) OTHER IN PAIR IS FIXED

(3) (+) IF 1↔1 2↔2

(−) IF 1↔2 2↔1

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

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

relate easily measured RHS to chgs in abstract qty S $\Big\{$

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

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

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

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

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

(just do ΔF, next pg)

(2) THERMO FNS ALSO HAVE PHYSICAL MEANING: (cf CH 8)

ex chg in E:
ΔE = Q GAINED AT CONST V

= −W DONE IF INSULATED

chg in H:
ΔH = Q GAINED AT CONST p $\Big\{$ ie fn whose chg gives Q gained when p const

ΔF = −W DONE AT CONST T $\Big\{$ keeps track of wk done at const T (Q−S)

skip $\{$ ΔG = 0 IF T, p CONST

↑ $\{$ from ΔS ≥ 0 can show this is

[illegible] at fixed T

ever if not — hence the name]

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)

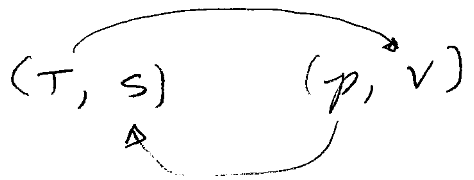
3 VARS x, y, z

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

<u>ex</u> HELM. FREE ENERGY

ΔF = $-W$ DONE AT CONST T (Q-S)

} drop in F means
$\Delta F < 0$ means
sys. does $W > 0$

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

$-\Delta F$ = <u>MAX</u> WORK CAN DO AT FIXED T

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

(hence the name)

AS SYS. MOVES FROM INIT TO FINAL STATE

(F_i TO F_f)

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~~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: $dz = 0$

{reg. z const puts reqmt on dx ↔ 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 ≠ 0 (can't invert eqns then)

hard to imagine not true

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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)

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

$$C_p \equiv \left(\;"\; \right)_p = T\left(\;"\; \right)_p \qquad (b)$$

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

IN (T, V) FOR C_V:

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

COMBINE (c) & (d)

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

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

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:

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

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

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

⇒ EASY TO MEAS

⇒ CAN GET FROM EOS (IF AVAIL)

$\left(\frac{\partial p}{\partial T}\right)_V$ CAN BE HARD (V CONST): CAN USE MAX RELN: ⇒ $\left(\frac{\partial S}{\partial V}\right)_T$ 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) $$\boxed{K \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T}$$ "ISOTHERMAL COMPRESSIBILITY"

⇒ EASY TO MEAS;

⇒ CAN USE EOS.

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

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

COMBINE ① - ③

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

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; T... [illegible]

SPECIAL CASES:

SOLIDS: α SMALL (cf TEXT) → 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

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}

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

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

← becomes const

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

(no any reln to $\left(\frac{\partial S}{\cdots}\right)$)

$\Rightarrow \frac{C_p - C_V}{C_V} \to 0$ (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 (ie TO KNOW EVERYTHING)?

ex IG: $\Omega \propto \overset{\uparrow}{V^N} \chi(E)$

ONLY USE ↑ TO GET $pV = NkT$ (EOS)

⇒ 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, 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:

(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

save

CAN SAY SOMETHING ABOUT C_V FROM EOS:

$$\underbrace{\left(\frac{\partial}{\partial V}\right)_T C_V}_{\text{inter. deriv so can use max reln (no good reln for } \left(\frac{\partial S}{\partial T}\right)_V\text{)}} = \left(\frac{\partial}{\partial V}\right)_T T \left(\frac{\partial S}{\partial T}\right)_V$$

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

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 $\left(\frac{\partial C_V}{\partial V}\right)_T$

INTEGRATE :

any V_1 I like

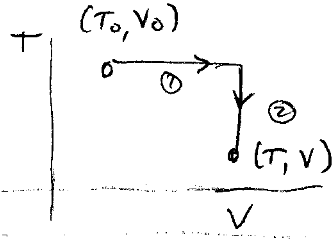
(b) $$C_V(T,V) = \underbrace{C_V(T,V_1)}_{\text{MEAS FOR ALL } T} + \int_{V_1}^{V} \underbrace{\left(\frac{\partial C_V(T,V')}{\partial V}\right)_T}_{T\underbrace{\left(\frac{\partial^2 p}{\partial T^2}\right)_V}_{\text{EOS}}} dV'$$

(defn of def. integral)

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

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)

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

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

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

INT. IN SAME WAY :

$\Big\{$ IG : $\left(\frac{\partial p}{\partial T}\right)_V = \frac{\nu R}{V}$

$T(\,''\,) = \frac{\nu R T}{V} = p \Rightarrow \left(\frac{\partial E}{\partial V}\right)_T = 0 \Big\}$

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