~~(next time: do for arbitrary v)~~
no, this notation is used in HW

ex

VAN DER WAAL'S GAS:

- ACCTS FOR INTERACTIONS
- MORE GEN. THAN IG
- WORKS IF NOT DILUTE (GOOD DN. TO LIQUID)

FOLLOW REIF: ALL QTY'S PER MOLE (so everything is intensive)

$$v \equiv V/\nu \qquad \epsilon \equiv E/\nu \qquad s \equiv S/\nu \qquad c_V \equiv C_V/\nu$$

EMPIRICAL:

$$\boxed{\left(p + \frac{a}{v^2}\right)(v - b) = RT}$$

VdW, 1 MOLE

a, b: CONSTS FIT TO DATA; DEP. ON GA[S]

b: FROM SHORT-RANGE REPULSION

(MOLECULES TAKE UP SPACE; NOT INFINITELY COMPRESSIBLE

$\Rightarrow$ $p \to \infty$ IF $v \to b$ (FIXED T)

$\Rightarrow$ $b \sim$ MOLAR VOL. OF MOLECULES

(FIT: GIVES ~SIZE OF ")

$\dfrac{a}{v^2}$: FROM LONG-RANGE ATTRACTION (assume $a > 0$) else → repulsion

$\Rightarrow$ p LESS FOR SAME v (FIXED T)

$\Rightarrow$ MORE DRAMATIC FOR SMALLER v

$a, b \to 0$ $\Rightarrow$ IG. LAW (EQUIV. TO v LARGE)

skip {COULD DERIVE APPROX FROM $\Omega \propto (V - V_{\text{MOLECULES}})^N$; cf REIF
CAN IMPROVE w/ EVEN MORE PARAMS

USE GEN. RELNS TO GET $s(T, v)$, $\epsilon(T, v)$:

EOS $\quad p(T, v) = \dfrac{RT}{v - b} - \dfrac{a}{v^2} \quad \Rightarrow \quad \left(\dfrac{\partial p}{\partial T}\right)_v = \dfrac{R}{v - b}$

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0$$

$$T\left(\frac{\partial p}{\partial T}\right)_v - p = \frac{a}{v^2}$$

$$\left(\frac{\partial C_V}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0 \Rightarrow \boxed{C_V = C_V(T)}$$

(NOT v)

$$ds = \frac{C_V(T)}{T}\,dT + \underbrace{\left(\frac{\partial p}{\partial T}\right)_v}_{\frac{R}{v-b}} dv$$

$$de = C_V(T)\,dT + \underbrace{\left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right]}_{\frac{a}{v^2}} dv$$

INTEGRATE :

$$\boxed{\begin{aligned} s(T,v) &= \int_{T_0}^{T} \frac{C_V(T')}{T'}\,dT' + R\ln(v-b) + \text{CONST} \\ \epsilon(T,v) &= \int_{T_0}^{T} C_V(T')\,dT' - \frac{a}{v} + \text{CONST} \end{aligned}}$$

VdW

NOTE : ϵ DEP. ON v NOW

$a>0$: ATTRACTIVE $\Rightarrow$ ϵ DECR. AS v DECR.

<u>IG</u>: $a, b \to 0$

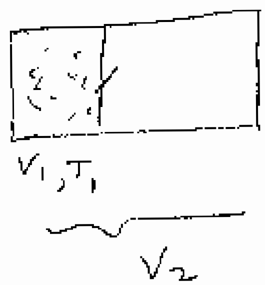
IF USE MICRO RESULT (OR MEAS) : $C_V = \frac{3}{2}R$

$$S(T,v) = \frac{3}{2}R\ln T + R\ln v + \text{CONST}$$

$$\epsilon(T,v) = \frac{3}{2}RT + \text{CONST}$$

(could use these to reconstruct $\Omega_{IG}(\epsilon, V)$ up to const)

FREE EXPANSION (AGAIN) (VdW GAS)



INSULATED

OPEN VALVE; WHAT IS T_2?

$Q = 0 \quad W = 0 \Rightarrow \Delta E = 0$

IG: $E = E(T) \quad \therefore \quad T_2 = T_1$

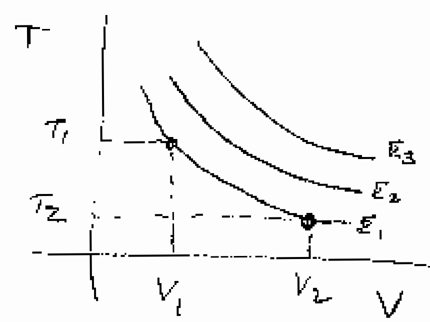
↓ skip

IN GENERAL: $E(T_2, V_2) = E(T_1, V_1)$

(NOTE – NOT Q-S; IRREV. BUT
- IN EQUIL IN INIT & FINAL STATES
- E ONLY DEP. ON " " ", NOT PROCESS

GET SAME RESULT IF USE Q-S PROCESS)

TO GET T_2:
- FIND CURVES OF CONST. E
- LOCATE " W/ (T_1, V_1)
- FOLLOW OUT TO $V_2 \rightarrow T_2$



↑

V.D.W. GAS:

$$\epsilon(T_2, v_2) = \epsilon(T_1, v_1)$$

$$\int_{T_0}^{T_2} c_V(T')\,dT' - \frac{a}{v_2} = \int_{T_0}^{T_1} c_V(T')\,dT' - \frac{a}{v_1}$$

$$\Rightarrow \quad \int_{T_1}^{T_2} c_V(T')\,dT' = a\left(\frac{1}{v_2} - \frac{1}{v_1}\right)$$

IF $c_V \sim$ CONST FROM T_1 TO T_2 LHS $\rightarrow c_V(T_2 - T_1)$

$$T_2 - T_1 = \frac{a}{c_V}\underbrace{\left(\frac{1}{v_2} - \frac{1}{v_1}\right)}_{<0} \quad \Bigg\} \quad v_2 > v_1 \Rightarrow T_2 < T_1 \Rightarrow \text{COOL}$$

can verify

(could also see from * that $T_2 < T_1$ since rhs <

HEAT ENGINES

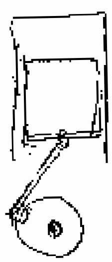
WANT :

(a) TURN Q TO USEFUL W VIA MACHINE M

(b) SYS IS CYCLICAL : RETURNS TO ORIG CONFIG
(so, for ex, rule out getting useful W by setting M on fire)

$\Rightarrow$ STUDY 1 CYCLE

ex AUTO ENGINE :



STEPS (rough)

(1) COMBUST $\Rightarrow$ HEAT CHAMBER QUICKLY (E, T INCR)

(2) CHAMBER EXPANDS :

$W > 0$ (WORK BY SYS) (ON CRANKSHAFT)

T DROPS A LITTLE

(3) VENT TO ATMOS.

T DROPS A LOT

(4) RECOMPRESS

$W < 0$ (WORK ON SYS)

$|W|$ LESS THAN (2) SINCE T, p LESS

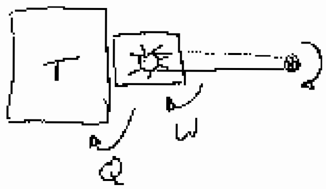
STEP (3) : DUMP LOTS OF E $\Rightarrow$ INEFFICIENT

NECESSARY ? YES

HERE : NEED SO (4) TAKES LESS W THAN (2) GIVES

THERMO : WHAT'S BEST POSSIBLE ?

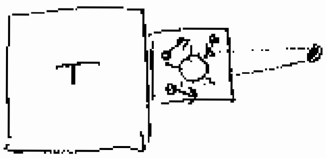
EASY TO TURN W TO Q:



PADDLE WHEEL (OR resistor or whatever)

EFFICIENCY: 1

HARD TO RUN IN REVERSE:



to get macro work: (*)

(1) WAIT FOR LARGE (MACRO) E TO ACCUM IN 1 MOL.

(2) HITS WHEEL, TURNS, DOES W.

(3) TEMP DROPS, ABSORBS FROM RES $Q = W$

(4) PUT Q BACK INTO RES, REPEAT

OR WAIT FOR LARGE # SMALL HITS IN ROW THAT HAPPEN TO ALL BE IN SAME DIRECTION

- E CONS OK - EFFICIENCY: 1
- PROBLEM: (1) IS ASTRONOMICALLY UNLIKELY

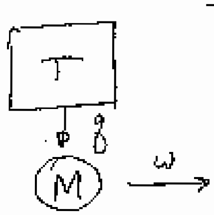
(acquiring large E → limits E avail for others; have seen most random is most likely; wait for many times age of universe for one mol. to have signif (macroscopic) amt of E)

(Or just think of wheel as 1 dof in sys. → needs to spontaneously acquire >>> ave E)

A CLASSICAL THERMO: $\Delta S < 0$ → DOESN'T HAPPEN;

IN GENERAL: PERFECT ENGINE: turn all Q TO W

(NOTATION: $q, w > 0$)



machine

E CONS: $w = q$

S:

(1 CYCLE:)

M: (think of macro machine as system w/ 1 dof → don't include T, etc of particles which make it up; negligible) not necessarily

$\Delta S_M = 0$ (back to start)

⋮

(*) For me: cf Feynman Lectures I-46 for ratchet/pawl discussion

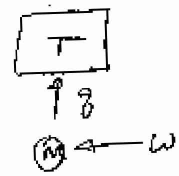
RES: $\Delta S_R = \frac{-q}{T}$

$\Delta S_{TOT} = \frac{-q}{T} = \frac{-w}{T}$

$\therefore$ CAN'T HAVE $w > 0$

REQUIRE $\Delta S_{TOT} \geq 0$ (classical way of saying it's extremely unlikely) / from prob 5-25, can say how unlik

{ NO PROBLEM OTHER WAY: }



CAN I GET ANY USEFUL W FROM Q?

say { TRICK: CONVERT SOME Q → W

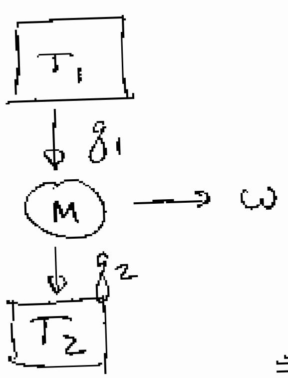
DUMP " Q → ANOTHER SYS

SUCH THAT RESULT IS MORE PROB.

HOW: OTHER SYS. HAS LOWER T / LARGER β

⇒ TAKES LESS Q TO INCR. # AVAIL STATES }

REALISTIC ENGINE:



E CONS: $w = q_1 - q_2$ (each cycle)

NEED $\Delta S_{TOT} = \frac{-q_1}{T_1} + \frac{q_2}{T_2} \geq 0$

$\frac{q_1 - w}{T_2} \Rightarrow w \leq q_1\left(1 - \frac{T_2}{T_1}\right)$ (a)

⇒ WORKS IF $T_2 < T_1$ (the more the better) (SINCE $q_1 > w$)
(then gains more states than res. at T_1 loses even though uses less q to do it)

EFFICIENCY: $\eta \equiv \frac{w}{q_1} = \frac{\text{WORK OUT}}{\text{E IN}}$ { still have to provide q_1 each cycle by heating res. 1

FROM (a) $\eta \leq 1 - \frac{T_2}{T_1} = \frac{T_1 - T_2}{T_1}$

BEST IF

(1) Q-S (THEN: $\eta = \eta_{MAX} = 1 - \frac{T_2}{T_1}$)

(2) $T_1 >> T_2$

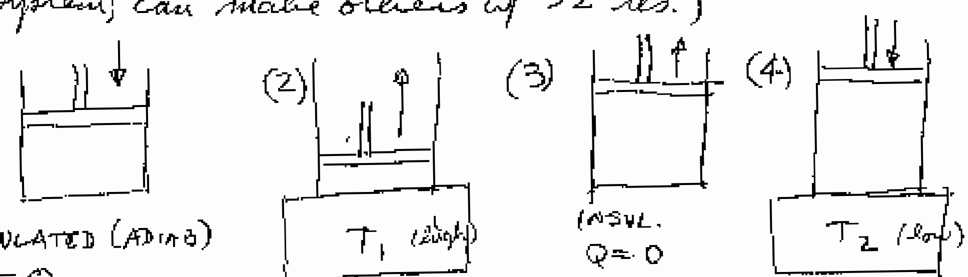
skip { $\eta_{MAX} = 1 - \frac{T_2}{T_1}$ for any engine between 2 res.

CARNOT ENGINE:

skip {
- SIMPLEST Q-S HEAT ENGINE USING 2 RES. AT CONST T
- SIMILAR TO CAR ENGINE
- Carnot's study of heat engines led to 2ND law. ($\Delta S \geq 0$)
  Case of engineer contributing to fund. physics; didn't even have 1ST law (E CONS) ⇒ didn't know Q was transf. of E

- 1 REALIZATION: V AS EXT PARAM (CAN MAKE W/ OTHERS)
- SIMPLE: Q-S BUT W/ ONLY 2 RES. AT DIFF T'S ($T_1 > T_2$)
  (simplest optimal system; can make others w/ >2 res.)

4 STEPS:



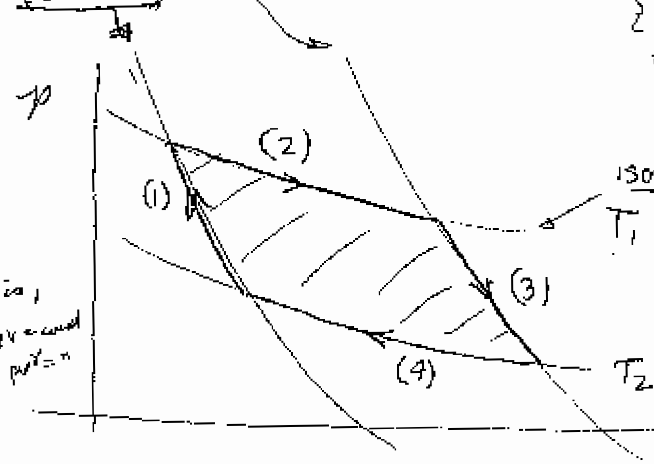
(1) INSULATED (ADIAB)
$Q = 0$
V DECR (Q-S)
$T_C = T_2 \to T_1$ (INCR.)
$W < 0$. (ON SYS)

(2) V INCR
T_1 CONST
ABSORBS Q
$W > 0$ (BY SYS)
{SYS. ALREADY AT T_1, SO Q-S}

(3) INSUL.
$Q = 0$
V INCR
$T_1 \to T_2$ (DECR)
$W > 0$

(4) V DECR
T_2 CONST (Q-S)
DUMP Q
$W < 0$
GET BAC. V_i
{LOWER T, p LESS, LESS W LOST THAN GAINED IN (2)}

ADIABATIC (S CONST)



ISOTHERMAL (note if hold T fixed, can keep p up)

not necess. ideal gas; if is, know ISO: pV = cons; ADIA: pV^γ = n

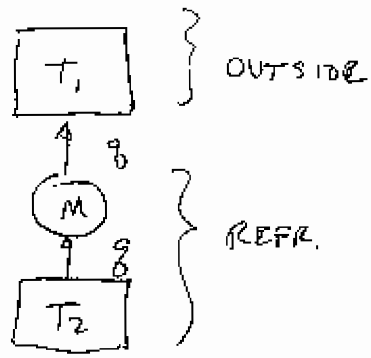
TOTAL W: AREA INSIDE
$= |W_2 + W_3| - |W_4 + W_1|$

EFFICIENCY: $\frac{W}{Q_{ABS}}$ ← IN (2)

REFRIGERATOR

MACHINE TO LOWER T BY $Q \to T_{OUTSIDE}$
($T < T_{OUT}$) {won't amaze anyone if $T > T_{OUT}$}

PERFECT:



E CONS: OK

PROBLEM: $T_2 < T_1$

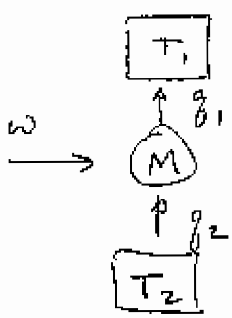
W/ SAME q, (2) LOSES STATES FASTER THAN (1) GAINS

2ND LAW: NEED $\Delta S = \frac{q}{T_1} + \frac{(-q)}{T_2}$

$= q\left(\frac{T_2 - T_1}{T_1 T_2}\right) \geq 0$ FAILS IF $T_2 < T_1$
(OK IF $T_2 > T_1$)

REAL: RUN ENGINE IN REVERSE

IDEA: $T_1 > T_2$ ∴ NEED TO DUMP MORE Q INTO (1) THAN LOST BY (2) SO NET INCR IN STATES



E CONS. $q_1 = q_2 + W$

2ND LAW: $\Delta S = \frac{q_1}{T_1} + \frac{(-q_2)}{T_2} \geq 0$

$\Rightarrow \frac{q_2}{q_1} \leq \frac{T_2}{T_1}$ OR $\boxed{\frac{W}{q_2} \geq \frac{T_1}{T_2} - 1}$

BEST: Q-S → EQUAL

≡ WORK TO REMOVE q_2; HARDER FOR HIGHER T_1, LOW T_2

HEAT PUMP:

- MOVE HEAT FROM OUTSIDE (COLD) TO INSIDE (WARM)

⇒ (1) = HOUSE AT T_1

(2) = OUTSIDE AT T_2

⇒ REFRIGERATE THE OUTSIDE

- EFFICIENT: MOVE E RATHER THAN GENERATE

EFFICIENCY:

$$\eta \equiv \frac{q_1}{\omega} \le \frac{T_1}{T_1 - T_2}$$ { HEAT IN VS WORK

- CAN HAVE $q_1 > \omega$
- $\eta \to 1$ FOR $T_2 \ll T_1$

⇒ LOSE ADVANTAGE (might as well burn something)

⇒ NOT GOOD IN VERY COLD CLIMATES

REALIZATION: (REFR. OR HEAT PUMP)
CARNOT ENGINE RUN BACKWARDS

(refrig. really do look like this)