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:

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

a, b : CONSTS FIT TO DATA; DEP. ON GAS (unlike IG ⇒ general) (a, b also intensive by choice above)

11/20/02

b: FROM SHORT-RANGE REPULSION
(MOLECULES TAKE UP SPACE; NOT INFINITELY COMPRESSIBLE)

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

⇒ b ~ MOLAR VOL. OF MOLECULES
(FIT: GIVES ~SIZE OF ")

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

⇒ p LESS FOR SAME v (FIXED T)

⇒ MORE DRAMATIC FOR SMALLER v

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

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

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

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

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

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

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

(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.

STILL NEED TO MEAS $C_v(T)$

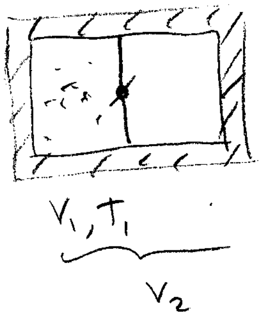
MON. IG: $a, b \to 0$

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

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

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

(could use these to reconstruct $\Omega_{IG}(\epsilon, V) \equiv e^{S/k}$ up to const) ex **FREE EXPANSION w/ VdW GAS:**



INSULATED

OPEN VALVE, FIND T_2 AFTER EQUIL

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

IN GEN'L:

$$E(T_2, V_2) = E(T_1, V_1)$$

(RECALL: IG: NO V DEP $\therefore$ $E(T_2) = E(T_1) \Rightarrow T_2 = T_1$)

VdW (PER MOLE): $\epsilon(T_2, v_2) = \epsilon(T_1, v_1)$

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

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

IF MEAS (OR KNOW) c_V, CAN SOLVE FOR T_2

CAN SEE: RHS $v_2 > v_1$ (USUALLY $a > 0$) $\Rightarrow$ RHS < 0

$c_V > 0$ $\Rightarrow$ $T_2 < T_1$ $\Rightarrow$ CAN USE FOR COOLING

IF $c_V \sim$ CONST FROM $T_1 \to T_2$

$$\boxed{T_2 - T_1 = \frac{a}{c_V}\left(\frac{1}{v_2} - \frac{1}{v_1}\right)}$$

$v_2 > v_1$ $\Rightarrow T_2 < T_1$

($a \to 0 \Rightarrow$ IG)

ex **THROTTLING** (JOULE - THOMPSON) PROCESS:

cf TEXT

cf DISCUSSION IN VAN NESS

APPLICATION OF $\Delta S \geq 0$:

HEAT ENGINES

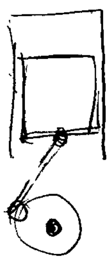
WANT:

(a) TURN Q TO USEFUL (MACRO) 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

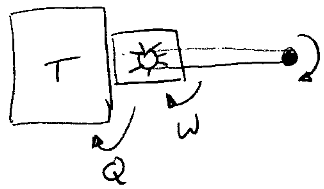
(4) RECOMPRESS
$W < 0$ (WORK ON SYS)
$|W|$ LESS THAN (2) SINCE T, p LESS

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)

NO S ASSOC w/ MACHINE
S is assoc. w/ microscopic ignorance;
the thing being driven (the wheel) has 1 dof ⇒ contribs 0 to S because macro vars track everything it's doing

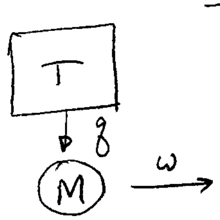
CLASSICAL THERMO: $\Delta S < 0$ in step (1) → DOESN'T HAPPEN:

IN GENERAL: PERFECT ENGINE: Turn all Q TO W

(NOTATION: q, $w > 0$)

model for internal combustion

entire system is therm. insulated



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 necess; skip

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

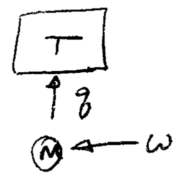
⋮

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

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

$\Delta S_{TOT} = \dfrac{-q}{T} = -\dfrac{w}{T}$ ← REQUIRE $\Delta S_{TOT} \geq 0$ (classical way of saying it's extremely unlikely) (from prob 5-25, can say how unlikely more & more w/ greater w)

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

{ NO PROBLEM OTHER WAY:  }

4/20/04

TAKING ALL $Q \to W$ CAN'T SUCCEED: Q OUT LOWERS S BUT W HAS NO ΔS

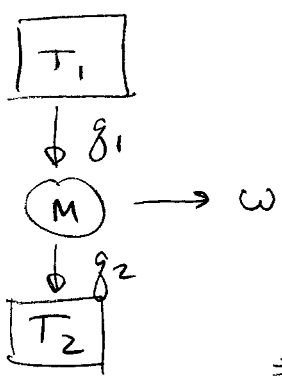
CAN I GET __ANY__ USEFUL W FROM Q? take hint from auto eng.

say { __TRICK:__ CONVERT SOME $Q \to W$
DUMP " $Q \to$ ANOTHER SYS
SUCH THAT RESULT IS __MORE__ PROB.

__HOW:__ OTHER SYS. HAS LOWER T / LARGER β
$\Rightarrow$ TAKES LESS Q TO INCR. # AVAIL STATES }

4/26 → 1xA

__REALISTIC ENGINE:__ 1 CYCLE



__E CONS:__ $w = q_1 - q_2$

__NEED__ $\Delta S_{TOT} = \dfrac{-q_1}{T_1} + \underbrace{\dfrac{q_2}{T_2}}_{\dfrac{q_1 - w}{T_2}} \geq 0$

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

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

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

BEST IF

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

(2) $T_1 \gg T_2$

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

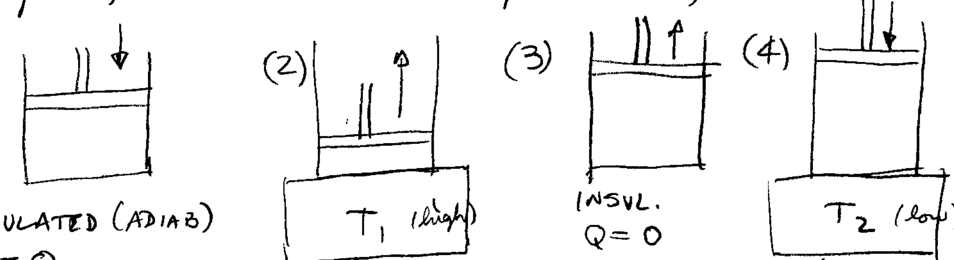
CARNOT ENGINE: can I imagine a machine that was at max efficiency?

say {
- SIMPLEST Q-S HEAT ENGINE USING 2 RES. AT CONST T
- SIMILAR TO CAR ENGINE
- Carnot's study of heat engines led to 2^{ND} law. ($\Delta S \geq 0$)
  Case of engineer contributing to fund. physics; didn't even have 1^{ST} law (E CONS) $\Rightarrow$ 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) (2) (3) (4)



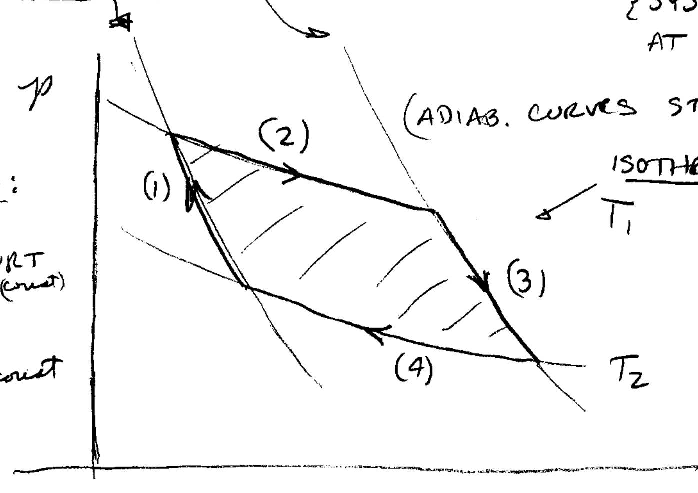
(1) INSULATED (ADIAB)
$Q = 0$
V DECR (Q-S)
$T_i = T_2 \to T_1$ (INCR.)
$W < 0$ (ON SYS)

(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 BACK TO V_i
{LOWER T, p LESS, LESS W LOST THAN GAINED IN (2)}

ADIABATIC (S CONST)



(ADIAB. CURVES STEEPER THAN ISOTH.)

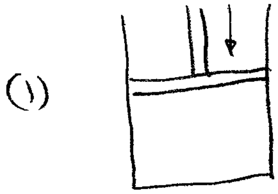
ISOTHERMAL (note if hold T fixed, can keep p up)

IF IG:
ISO: $pV = \nu RT$ (const)
ADIAB: pV^γ = const

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

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

CARNOT ENGINE



INSULATED (ADIAB)
$Q = 0$
V DECR (Q-S)
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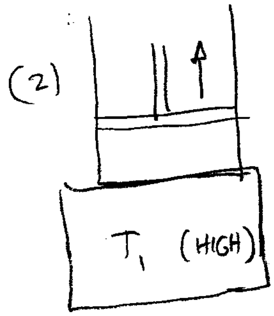
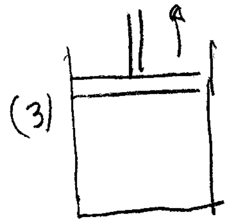
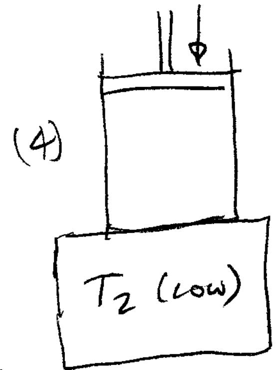


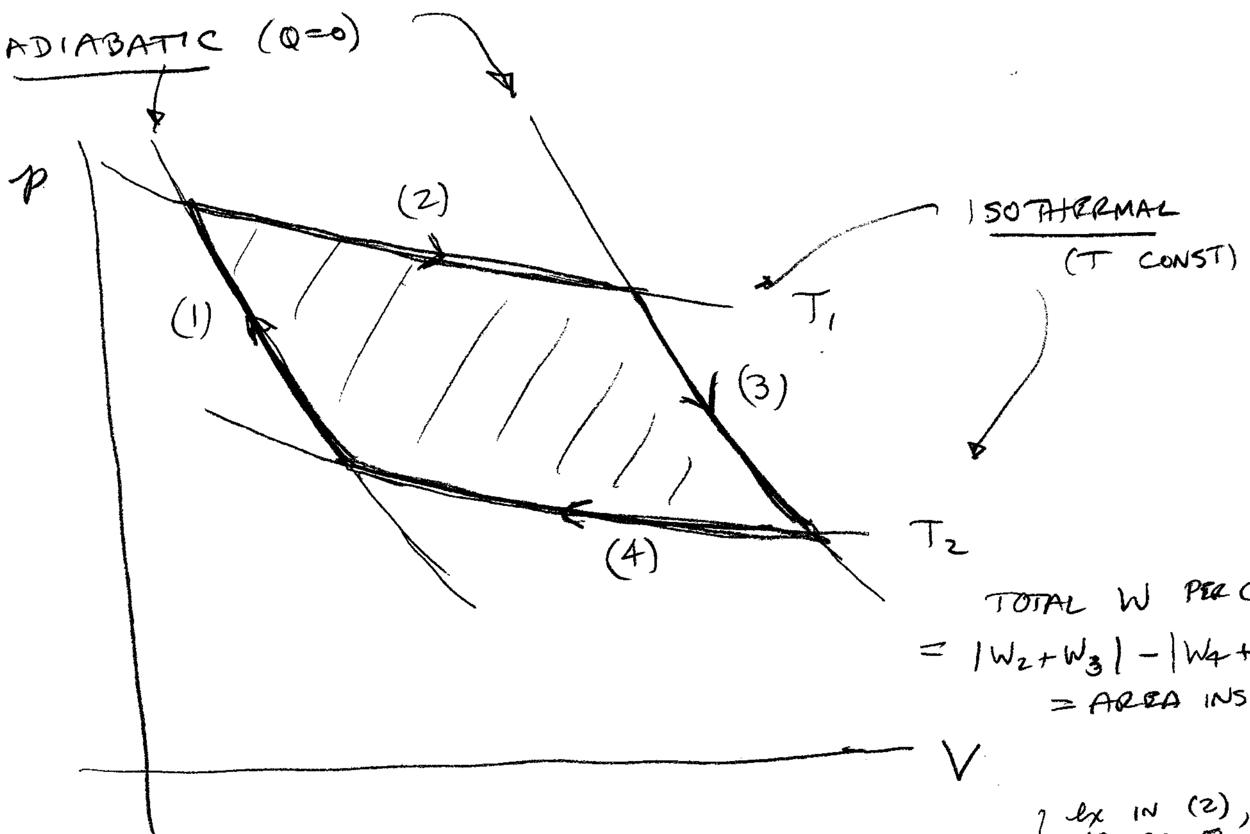
V INCR
T_1 CONST
ABSORBS Q
$W > 0$ (BY SYS)
(ALREADY AT T_1, SO Q-S)



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



V DECR
T_2 CONST (Q-S)
DUMP Q
$W < 0$
RETURN TO V_i
(LOWER T, LESS W LOST THAN GAINED IN (2))



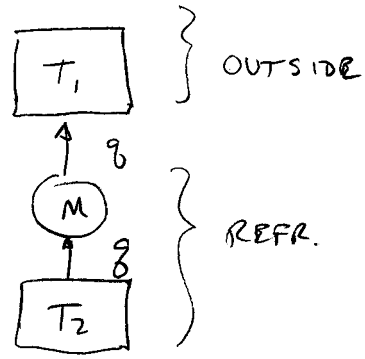
TOTAL W PER CYCLE:
$= |W_2 + W_3| - |W_4 + W_1|$
= AREA INSIDE

ADIAB. CURVES ALWAYS STEEPER THAN ISOTHERM. } ex IN (2), SYS ABS. Q → LARGER p
(cf IG: ADIAB: $pV^\gamma = \text{CONST}$ ISOTH: $pV = \text{CONST}$)

REFRIGERATOR

MACHINE TO LOWER T BY $Q \to T_{OUTSIDE}$
$(T < T_{OUT})$

PERFECT:



E CONS: OK

PROBLEM: $T_2 < T_1$

w/ SAME q, ② LOSES STATES FASTER THAN ① GAINS

2ND LAW: NEED

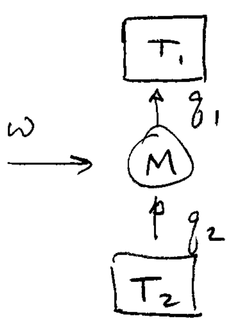
$$\Delta S = \frac{q}{T_1} + \frac{(-q)}{T_2}$$

$$= q\left(\frac{T_2 - T_1}{T_1 T_2}\right) \geq 0$$

FAILS IF $T_2 < T_1$
(OK IF $T_2 > T_1$)
(won't sell many of these)

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

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

$\equiv$ WORK TO REMOVE q_2; HARDER FOR HIGHER T_1, LOW T_2

BEST: Q-S → EQUAL

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:

$$\eta \equiv \frac{q_1}{w} \leq \frac{T_1}{T_1 - T_2} \quad \Big\{ \text{HEAT IN VS WORK}$$

- CAN HAVE $q_1 > w$, $\underline{\eta > 1}$

- $\eta \to 1$ 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; my heat pump and air cond. are same machine.)