REVIEW OF SOME IDEAS...

SPECIFIC HEATS $\quad Q = cm\Delta T$

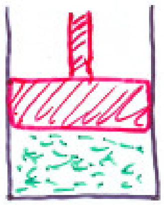
LATENT HEAT
(heat of transformation)

$Q = mL$

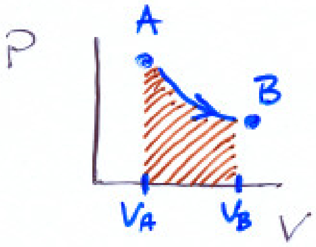
L_V & L_F

changes of phase

SYSTEM of interest...



W by gas
P
V



$$W_{gas} = \int_A^B P\,dV$$

1st LAW OF THERMODYNAMICS

$$\Delta Q = \Delta U + \Delta W$$

internal energy characterized by temperature

STATE FUNCTIONS

U, T, P, V

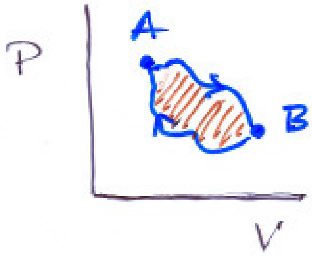
PARTICULAR FOCUS...

1) isothermal processes , $\Delta T = 0 \Rightarrow \Delta U = 0$

$$\Delta Q = \Delta W$$

2) adiabatic processes, $\Delta Q = 0 \Rightarrow \Delta U = -\Delta W$

3) cycles



IDEAL GAS

- identical, point masses
- numerous

$\longrightarrow$ FROM SIMPLE NEWTONIAN IDEAS:

$$PV = n\,\tfrac{2}{3}\langle K \rangle$$

$$\left.\begin{array}{l} PV = nRT \\ PV = NkT \end{array}\right\}$$

T is measure of $\langle K \rangle$

WORK done by ideal gas

$$\Delta W = \int_A^B \frac{nRT}{V}\, dV = nRT \ln V_B/V_A$$

MOLAR SPECIFIC HEATS

$$\Delta Q = nC_V \Delta T \Big|_V = \frac{3}{2} nRT \quad \text{ideal}$$

$$\Delta Q = nC_P \Delta T \Big|_P = \underbrace{\frac{5}{2} nRT}_{C_P = C_V + R} \quad \text{ideal}$$

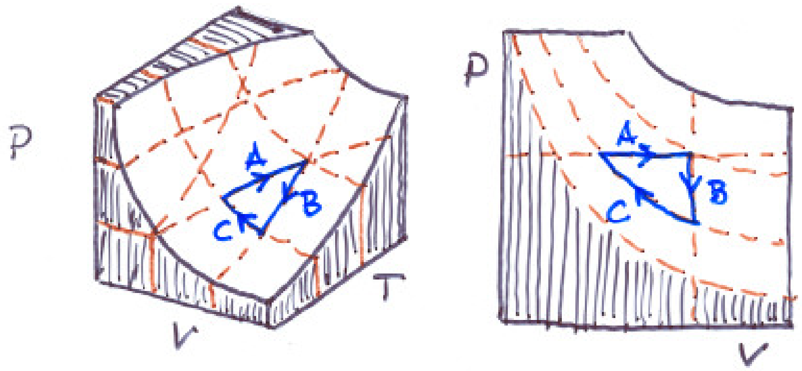
ADIABATIC processes

$$PV^\gamma = \text{constant} \qquad \gamma \equiv \frac{C_P}{C_V}$$

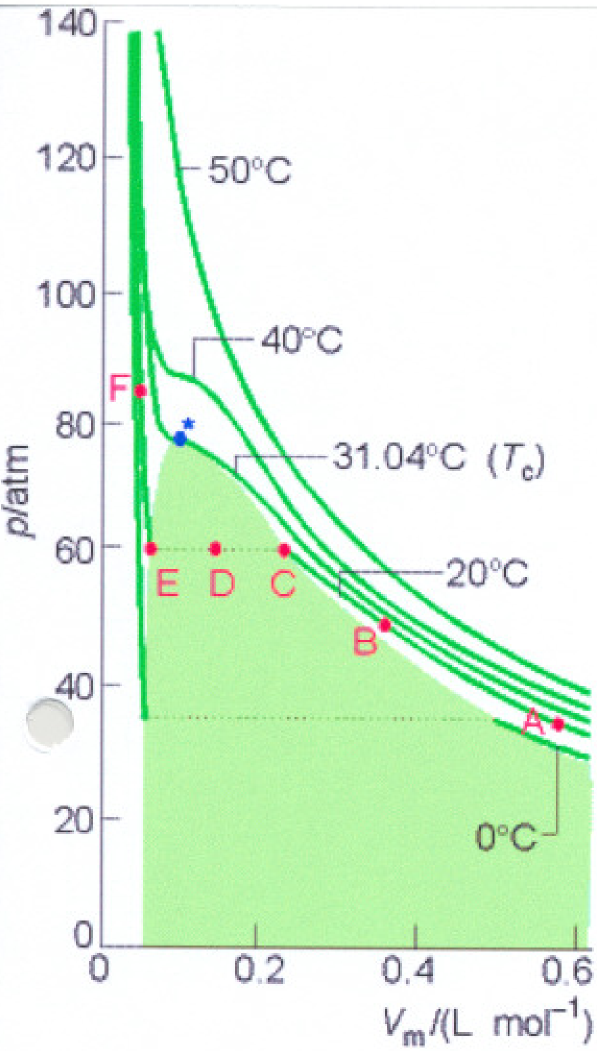
$$W = \frac{P_B V_B - P_A V_A}{1-\gamma}$$

P–V–T Diagrams

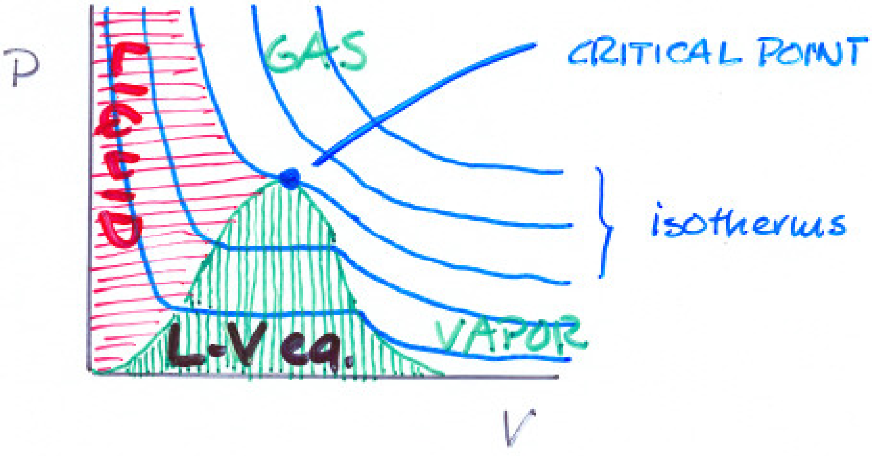
IDEAL GAS:



For non-ideal substances, phase transitions begin to be an issue...



CO_2



MAKING IT REAL...

- finite-sized molecules:

  V – overall volume

  b – volume occupied by molecules

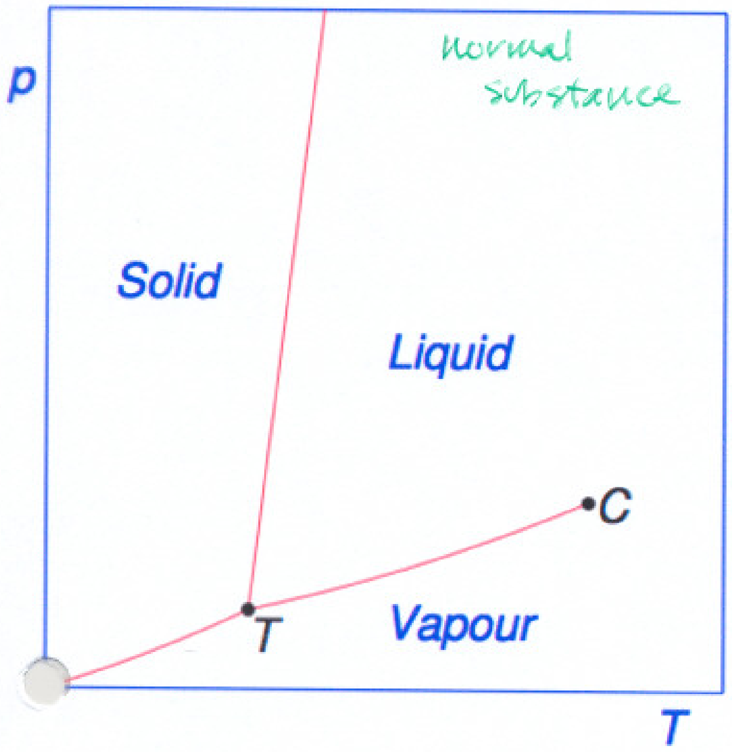
  $V \rightarrow V-b$

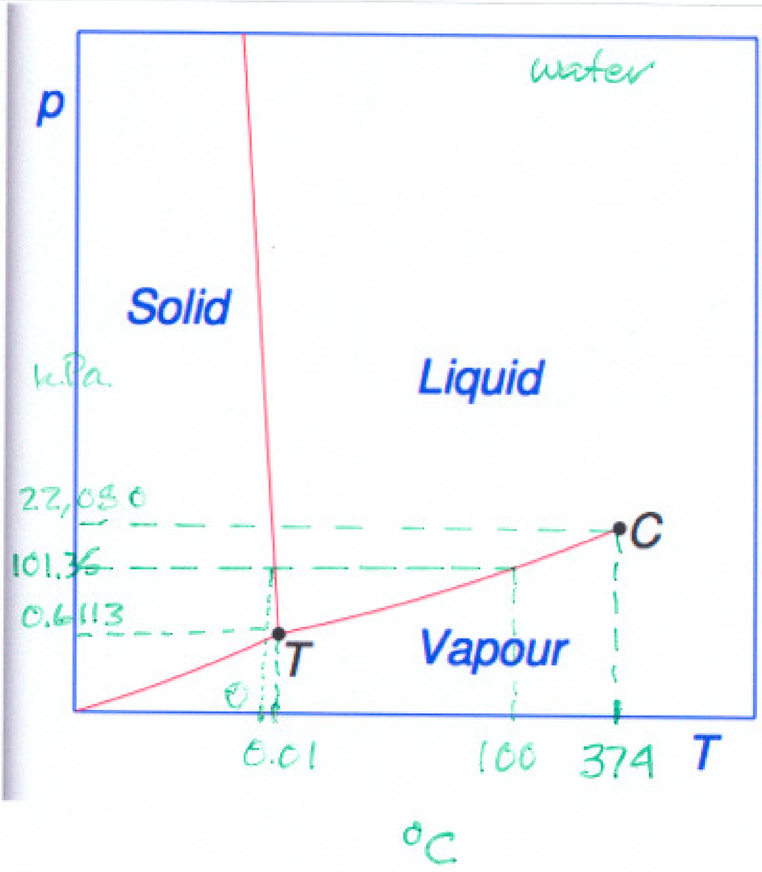
- short-distance attraction

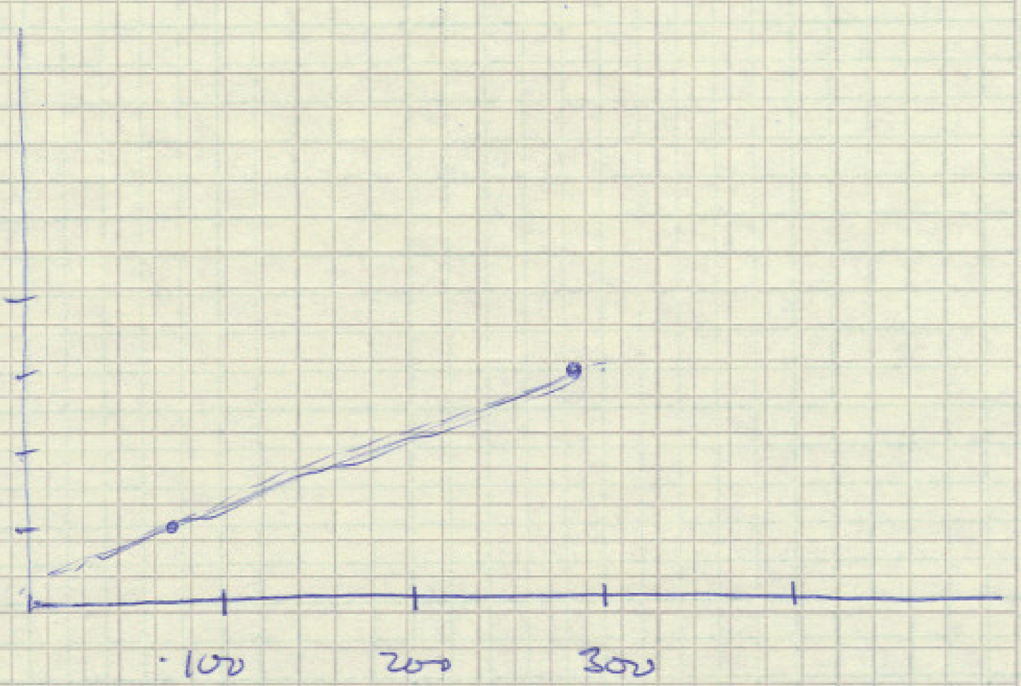
  $P \rightarrow P + a/V^2$

$$\left(P + \frac{a}{V^2}\right)(V-b) = nRT$$

a & b are measurable constants


normal substance
p
Solid
Liquid
C
T
Vapour
T


water
p
Solid
Liquid
kPa
22,090
101.36
0.6113
C
T
Vapour
0
0.01
100
374
T
°C



$$\begin{array}{r} 273 \\ 20 \\ \hline 293 \end{array}$$

$$P_1V_1 = P$$

$$\frac{P_1}{V_1} = \frac{P_2}{V_2} = n$$

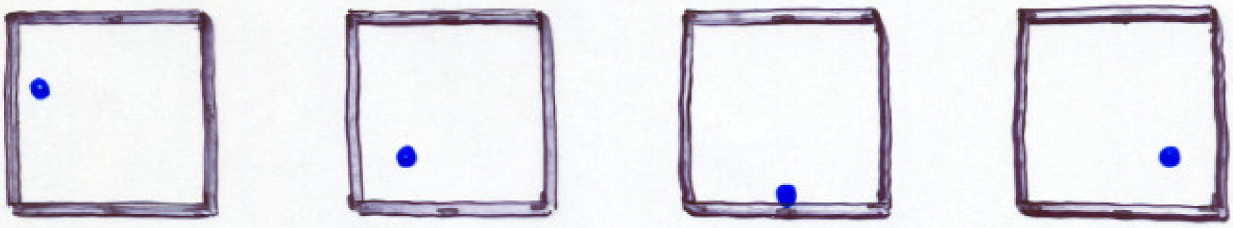
$$\frac{P_1}{T_1} = \frac{P_2}{T_2} = \frac{nR}{V}$$

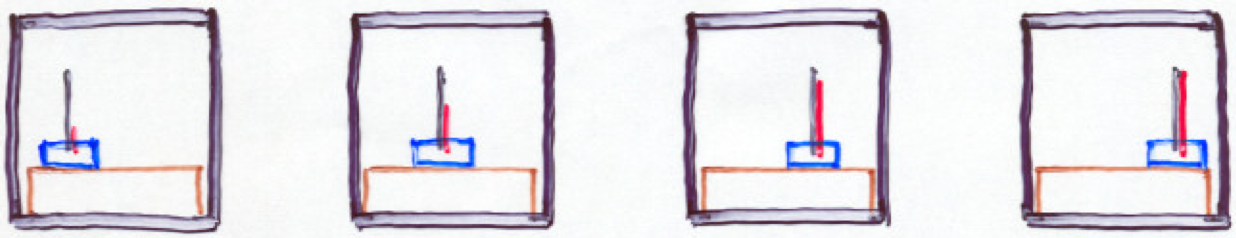
$$P_2 = P_1\left(\frac{T_2}{T_1}\right) \sim 4$$

2nd "LAW" OF THERMODYNAMICS

much subtly here... start gently!

TWO MOVIES:





- KINEMATICS MOVIE (bouncing ball) WORKS
  forward & backward -- equations time-invariant
- FRICTION MOVIE (block slowing down) DOESN'T
  the sliding block always gets hotter, forward or backwards in time → an "arrow of time"

IRREVERSIBILITY..

- a feature of any process that generates heat
- things run down!
- THE FIRST LAW OF THERMODYNAMICS DOES NOT INCLUDE THIS

  cuddling up to a snow drift to warm yourself is consistent with the 1st LAW ... but nature doesn't work this way...!

THERMODYNAMICS IS ONE-WAY

ESTABLISHES A DIRECTION FOR TIME!

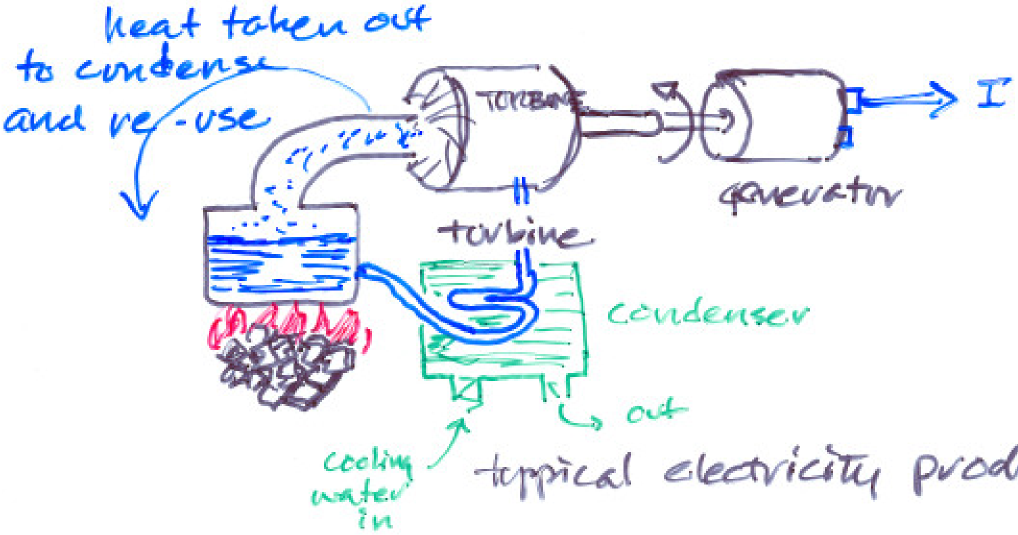
file this thought for a bit...

HEAT ENGINES

- Any device which converts thermal energy into mechanical energy.

- ALL ARE THE SAME:

    1. heat is absorbed from a source at high T
    2. work is done by the engine
    3. waste heat is expelled to a cooler source.



typical electricity production

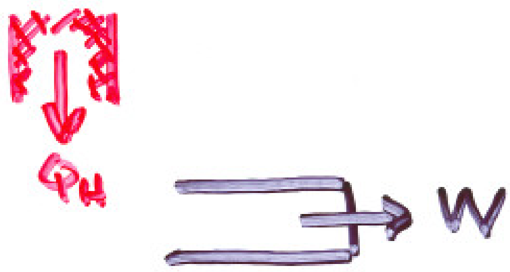
LOTS OF DEVICES TAKE HEAT → WORK

cannon

"ENGINE" MEANS A CYCLICAL PROCESS

OVER & OVER AGAIN...

PERECT



all heat absorbed from T_H source is used for work.

HERE.. the engine is attached to the heat source ⇒ engine's <u>working</u> <u>substance</u> is always at T_H

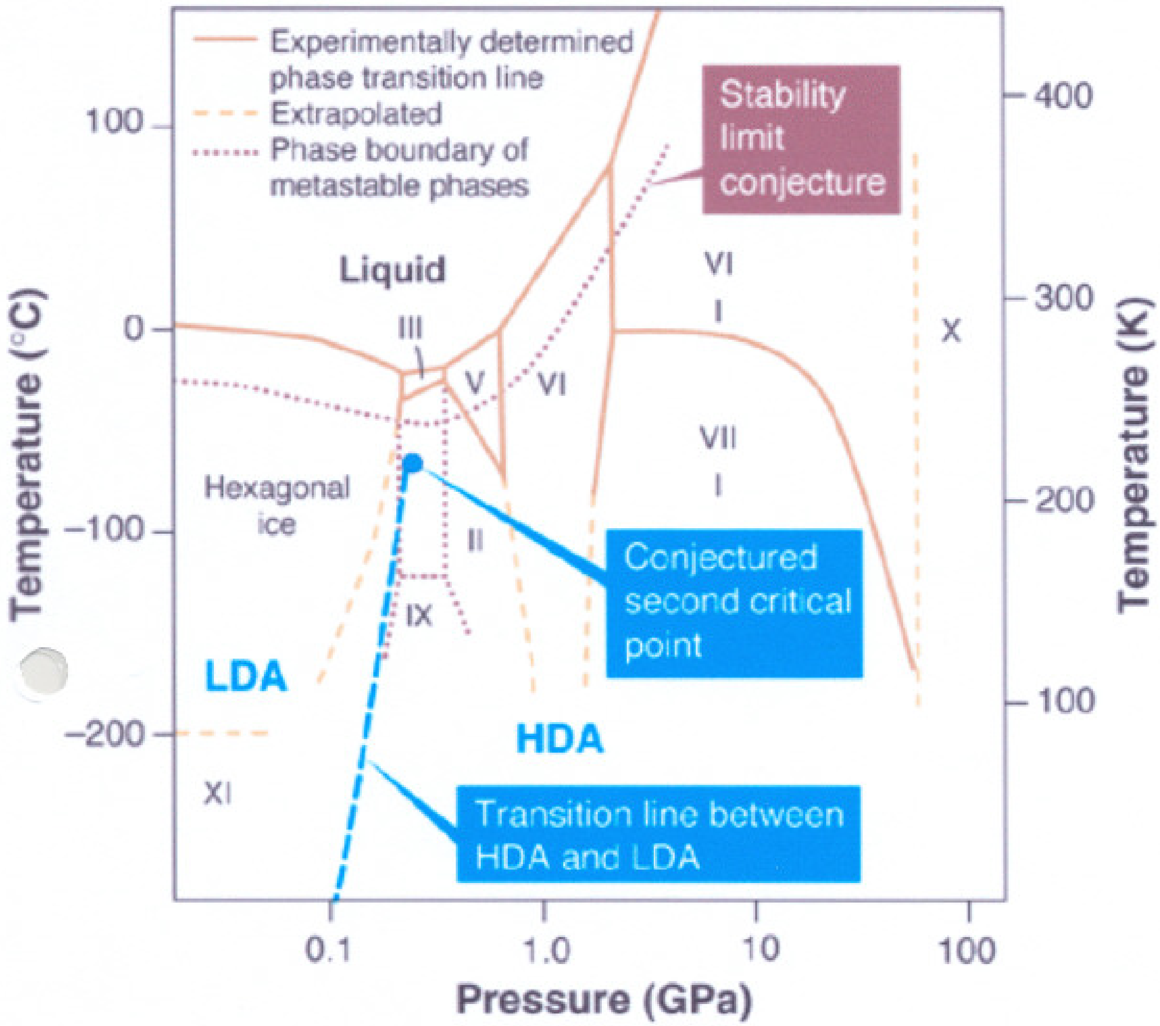
From 1st Law:

$$\Delta U = \Delta Q - \Delta W \quad \Rightarrow \quad \Delta Q_H = \Delta W$$

since $\Delta T = 0$

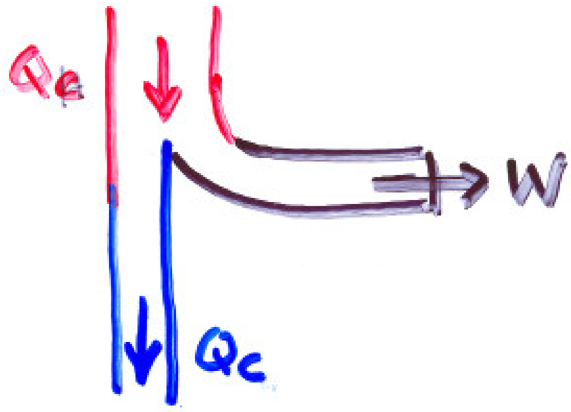
so

$$\Delta U = 0$$



Experimentally determined phase transition line
Extrapolated
Phase boundary of metastable phases
Stability limit conjecture
Liquid
III
V
VI
VI
I
VII
I
X
Hexagonal ice
II
IX
LDA
HDA
XI
Conjectured second critical point
Transition line between HDA and LDA
Temperature (°C)
100
0
−100
−200
Temperature (K)
400
300
200
100
0.1
1.0
10
100
Pressure (GPa)

REALASTIC

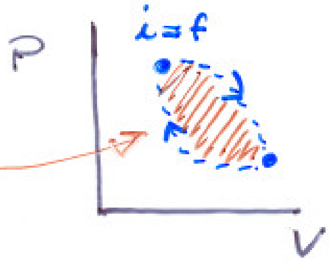


BECAUSE THE ENGINE IS CYCLICAL... IT GOES BACK TO ITS ORIGINAL STATE... $T_i = T_f$

SO $U_i = U_f \Rightarrow \Delta U_{net} = 0$

$$\Delta Q = \Delta U + \Delta W$$

$$Q_H - Q_c = W_{net}$$



THERMAL EFFICIENCY

$$\epsilon = \frac{\text{what you get}}{\text{what you paid}}$$

$$\epsilon = \frac{W}{Q_H}$$

$$\epsilon = \frac{Q_H - Q_c}{Q_H} = 1 - \frac{Q_c}{Q_H}$$

(note: here Q_c is a positive number -- in fact since heat leaves -- Q_c is negative

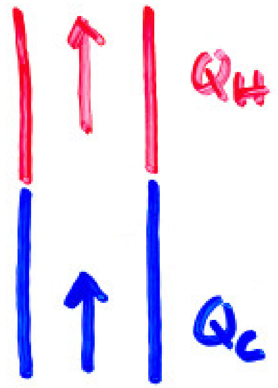
$$Q_{net} = Q_H + Q_c$$
$$= Q_H - |Q_c| \quad)$$

thermal efficiencies are not huge --

$$\epsilon_{automobile} \sim 20\% - 30\%$$

$$\epsilon_{Diesel} \sim 30-40\%$$

PERFECT REFRIGERATOR



Such a perfect machine is impossible...

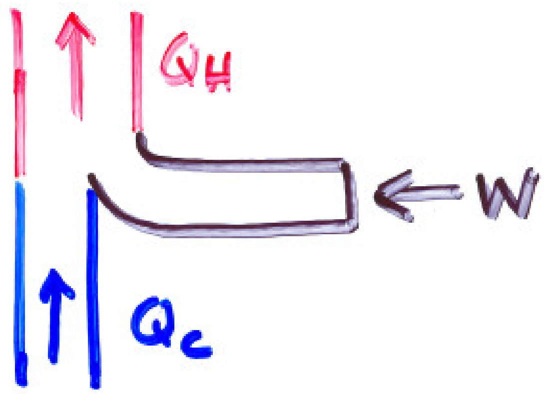
one of the many equivalent statements of the Second Law of Thermodynamics.

2^{nd}_{1}: It is impossible to construct a heat engine that, operating in a cycle, produces no other effect than the absorption of thermal energy from a reservoir and the performance of an equal amount of work.

("Kelvin-Planck Statement")

NEED TO "WASTE" SOME HEAT

REFRIGERATOR



A HEAT ENGINE IN "REVERSE"

Work must be done ON the engine

$Q_H + Q_c = W$

$-Q_H = Q_c - W$ $\quad$ Q_H & W are negative for the system (engine)

$|Q_H| = Q_c + W$

heat leaving hot

more than heat leaving cold

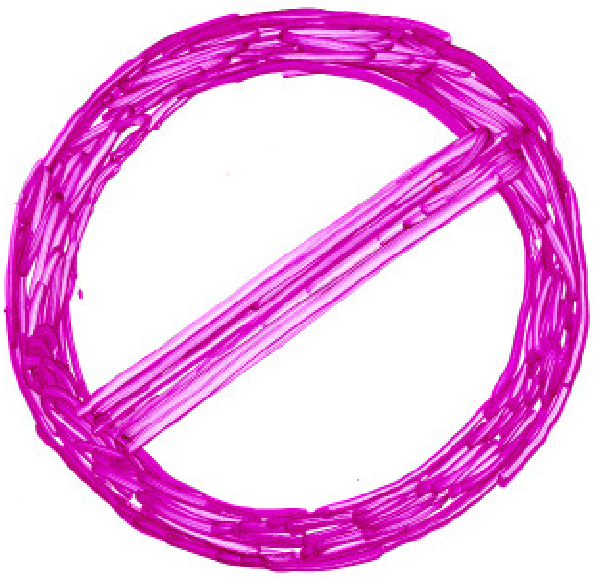
PERFORMANCE COEFFICIENT

$$K \equiv -\frac{Q_c}{W} = -\frac{Q_c}{Q_H + Q_c} = COP$$

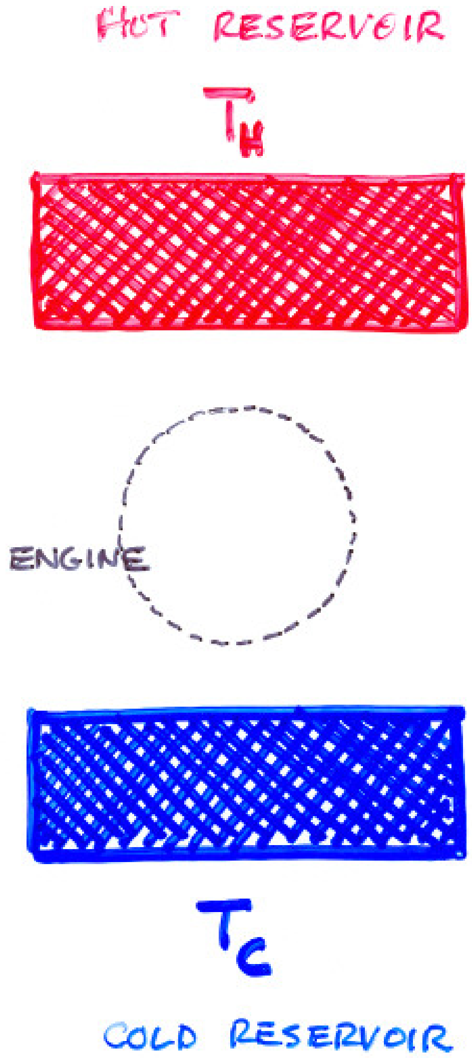
2^{nd}_{2} It is impossible to make a refrigerator, in a cycle, to produce no other effect than to transfer thermal energy from a cold object to a hot object.

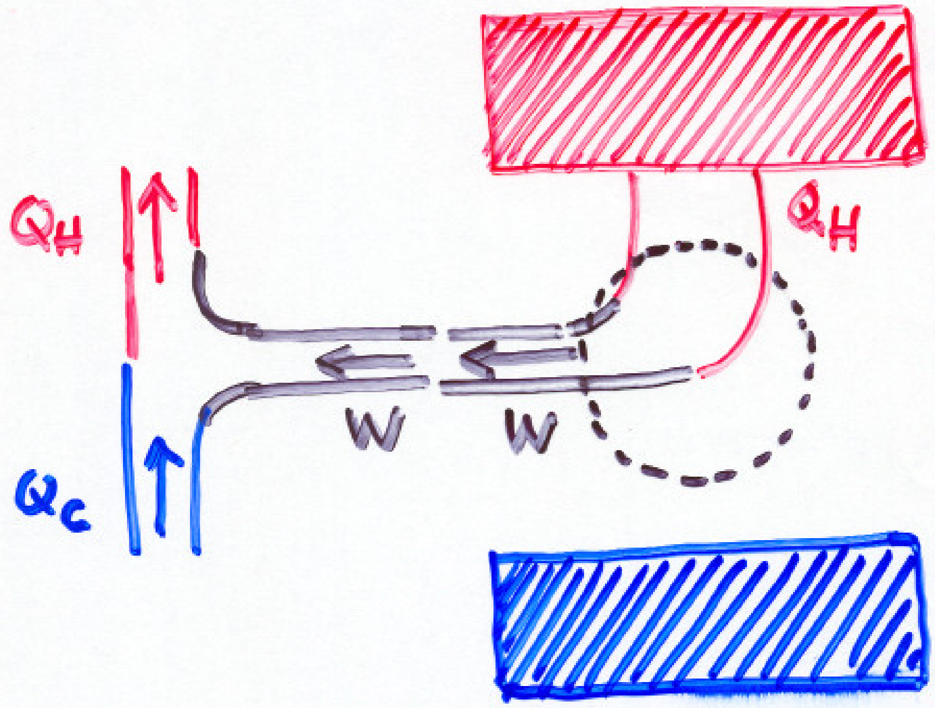
$$COP \neq \infty$$

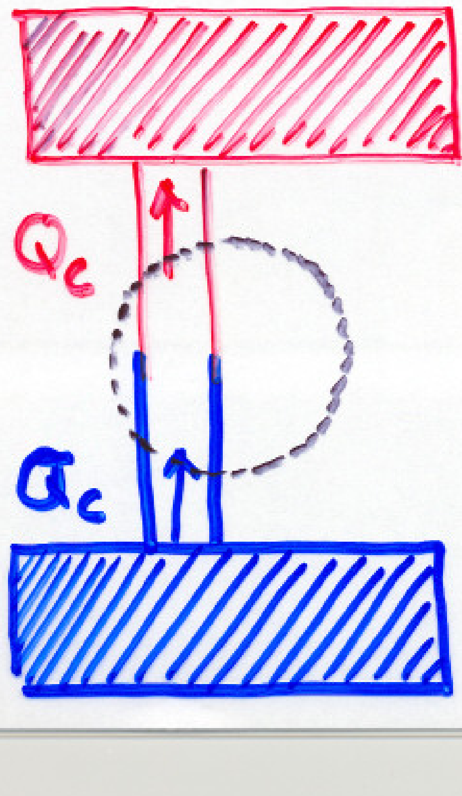
notsomuch



ENGINE

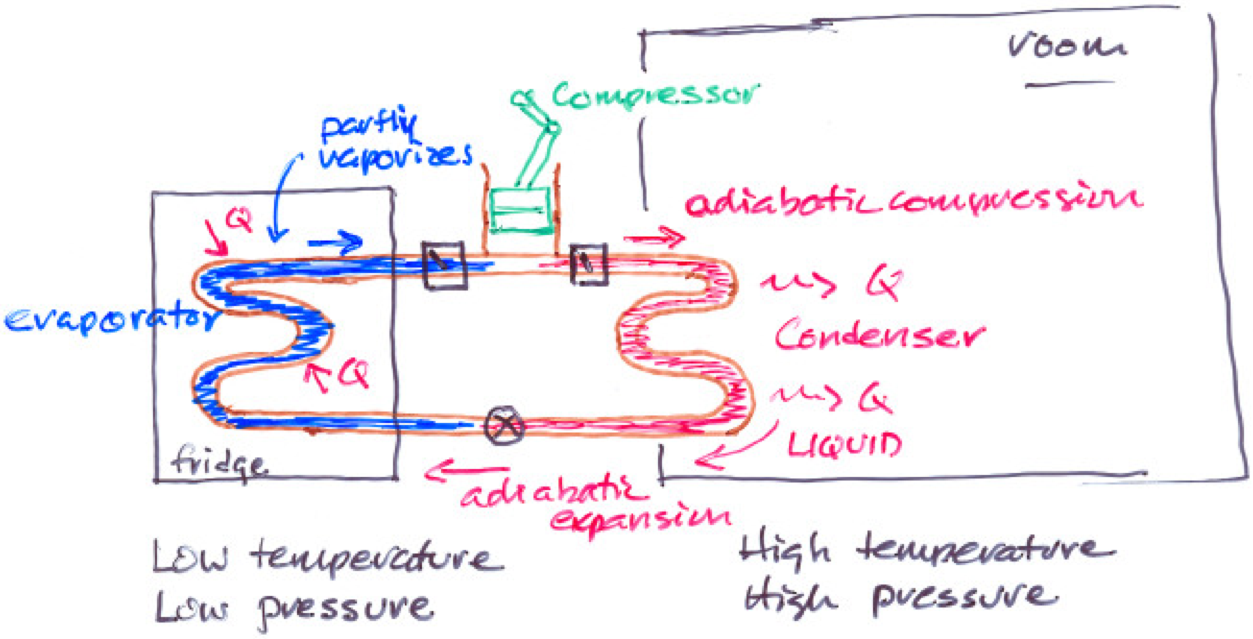






$2^{nd}_{1} \equiv 2^{nd}_{2}$

Refrigerator ~ some Freon family* "refrigerant" fluid



Heat Pump → refrigerator, inside-out.

* not any more !