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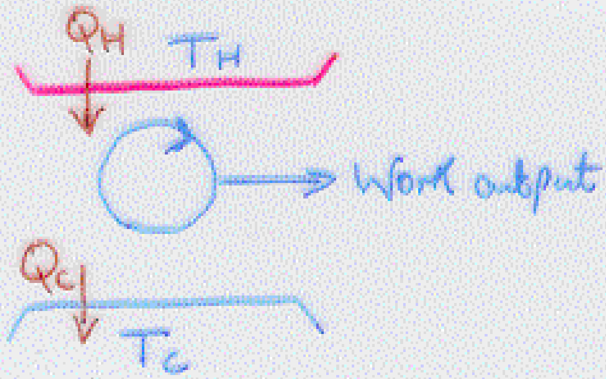
Review of Engines:

Basic cycle:




- Heat absorbed $Q_H$ from hot reservoir, $\Delta S_H = -\frac{Q_H}{T_H}$
- Some heat converted to work $W$. In "ideal" engine $\Delta S_{gas} = 0$
- Some heat $Q_C$ <u>must</u> be dumped into cold res, $\Delta S_C = \frac{+Q_C}{T_C}$

– For <u>ideal</u> engine, all processes reversible so

$$\Delta S_{system} = \Delta S_H + \Delta S_{gas} + \Delta S_C = 0$$

i.e. $$\Delta S_{system} = \frac{Q_C}{T_C} - \frac{Q_H}{T_H} = 0$$

Conclude: • $Q_C$ must be $\neq 0$ otherwise 2nd law violated

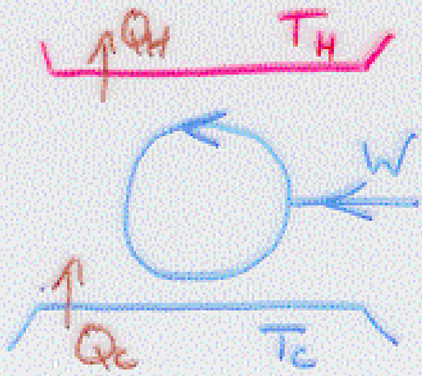
- Since work $W = Q_H - Q_C$, no engine can be 100% efficient

Efficiency $$\varepsilon = \frac{W}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

For ideal engine: $$\varepsilon = 1 - \frac{T_C}{T_H}$$

# Refrigerators, AC and Heat Pumps

Basic cycle = engine in reverse :




Work input required (anti-clockwise P-V cycle)

- e.g. compressor + motor

Heat $Q_c$ absorbed from "cold" reservoir ( freezer, room, outside)

$Q_H$ ejected into "hot" " ( room, outside, room )

Coeff. of performance (Define: ) $\boxed{K = \frac{Q_c}{W} = \frac{\text{heat extracted}}{\text{work required}}.}$

$\simeq 5.0$ ( fridge)

$\simeq 2.5$ ( household AC )

For "ideal" refrigerator: Work $W = Q_H - Q_c$

$$\Rightarrow K = \frac{Q_c}{Q_H - Q_c}$$

As for engine, 2nd. law $\Rightarrow$ $\Delta S = \frac{Q_H}{T_H} - \frac{Q_c}{T_c} = 0$

$$\Rightarrow K = \frac{T_c}{T_H - T_c} \quad \text{(ideal case).}$$

Note: K increases as temp. difference ("uphill" rise) decreases
$\rightarrow$ less work required.

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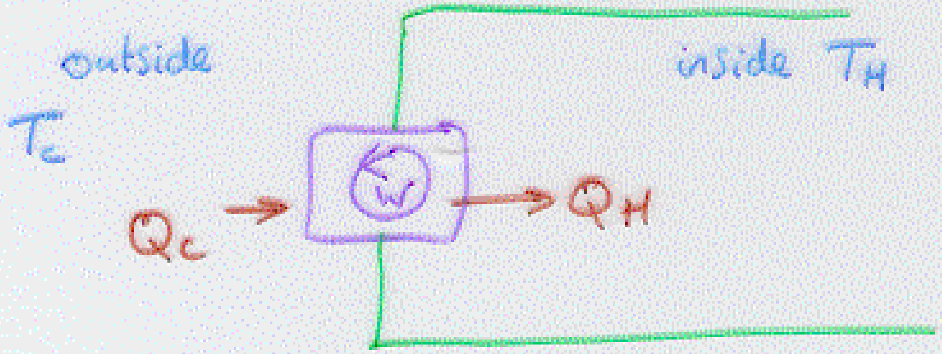
# Heat Pumps : "backwards" air conditioners




Efficient way to heat building : heat pump compresses large volume of outside air, "squeezing" out heat ($\sim$150 kJ/mol – quiz 3) $Q_c$ to dump into (smaller) volume of building

– even friction in compressor → adds heat to interior!

e.g. Ch 21 Prob 58 : $T_c = -5\,°C$ , $T_H = 17°C$

For ideal heat pump, how many joules $Q_H$ delivered into room for work input $W = 1$ J?

Ideal case: $K = \dfrac{Q_c}{W} = \dfrac{T_c}{T_H - T_c} = \dfrac{268\,K}{[17-(-5)]} = 12.2$   Kelvin!

$$\Rightarrow Q_H = W + Q_c = 13.2\,J$$

∴ 1 J of work delivers 12.2 J of heat from outside

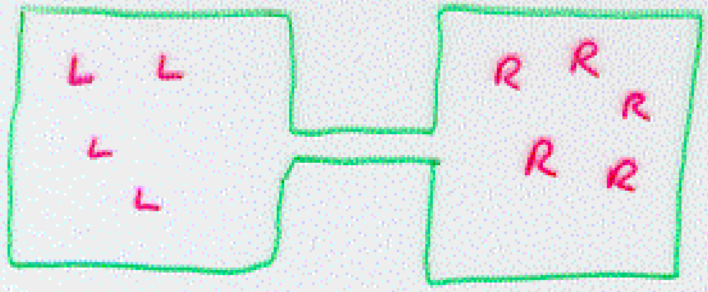
– much better than using a heater element (1 J work → 1 J heat). 100% efficient

Note: Work always required to push heat from cold → hot ("uphill")

– an alternative statement of 2nd law.

# Entropy and Order : Statistical Mechanics (21.6)

Consider $N$ molecules in 2-sided box




Take "snapshot"

Label each molecule (1 through $N$) with "L" or "R"

$\Rightarrow$ Microstate configuration: e.g.

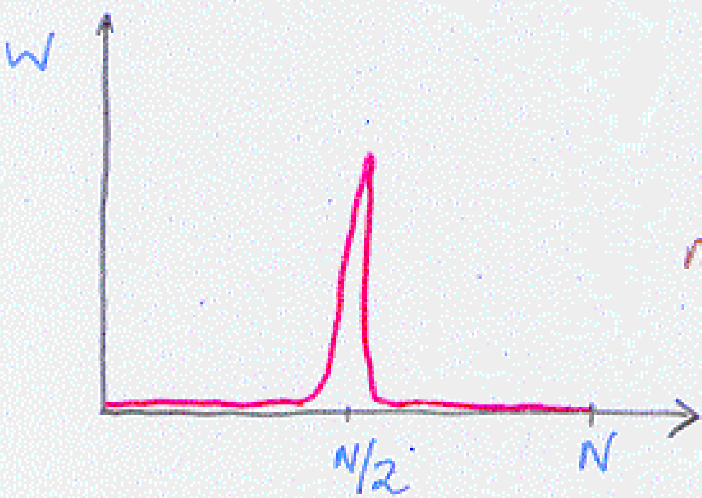
$$\begin{array}{ccccccc} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ L & L & R & L & R & R & L \end{array} \ldots\ldots$$

Count $n_L$ = # on left, $n_R$ = # on right $= N - n_L$

For each macrostate $n_L$, # of microstates

given by Multiplicity $W = \dfrac{N!}{n_L!\,\underbrace{(N-n_L)!}}$ (e.g. Table 21.1, $N=4$)

Plot $W$ as a function of $n_L$: e.g. $W=1$ for $n_L = N$ or $n_L = 0$




$n! = 1 \times 2 \times 3 \ldots . n.$

# Order / Disorder Quantified

Each microstate equally likely:

i.e. LLLLL.... likely as LRRLRLR....

( Lottery #s 123456 likely as 22 18 3 14 6 1 ..... )

BUT many more microstates have $n_L \approx n_R = N/2$

than "one-sided" $n_L >> N/2$

or $n_L << N/2$

$\Rightarrow$ "Disordered" arrangement (state) much more likely

Boltzmann (1877) : $\boxed{\text{Entropy } S = k_B \ln W}$

( Proof: gives same $\Delta S$ for free expansion, Sample prob. 21·6 )

What does this mean?

2nd law $\Delta S \geq 0 \Rightarrow$ Universe tends to most probable macrostate (disorder)

Note: Can create order locally ( cool gas, tidy room )

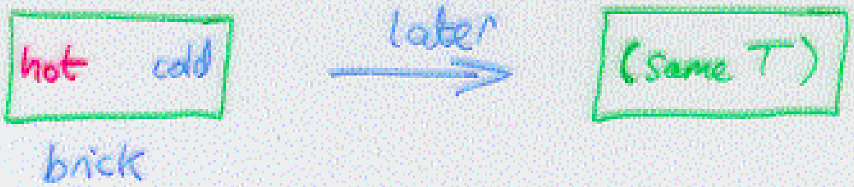
BUT work required $\rightarrow$ heat generated $\rightarrow$ disorder produced somewhere else !

– "Can't win, can't get even, can't get out of the game"

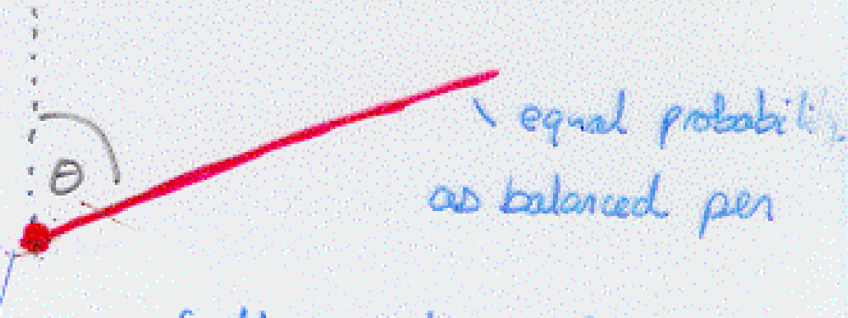
# Entropy of General Systems

2nd law applies not just to gases

e.g. solids




Breaking eggs, falling pencils ......

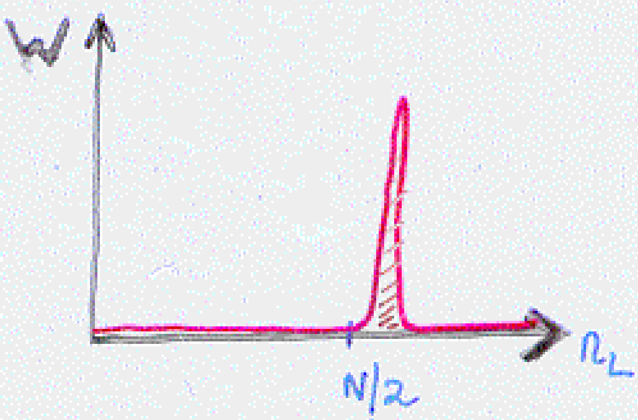



Casinos rely on 2nd. law of thermodynamics

e.g. Roulette wheel c.f. gas in 2-sided box :


1 spin : 1 molecule ~ 48% probability of win

N spins : N molecules




⇒ many more ways to lose than win!