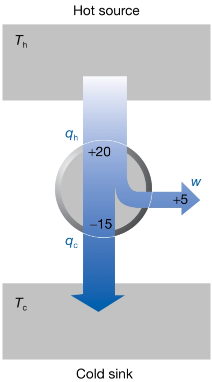
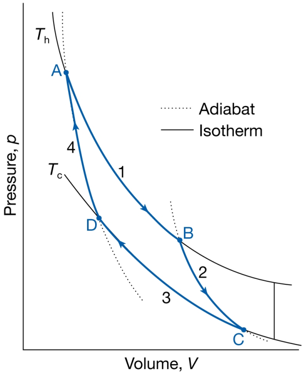
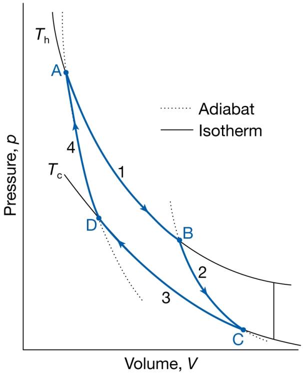
# Example of a Carnot engine

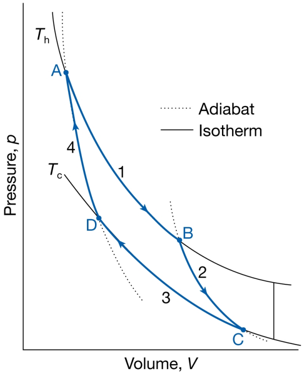




$T_h$
A
Adiabat
Isotherm
4
1
$T_c$
D
B
2
3
C
Pressure, $p$
Volume, $V$

$$q_h = nRT_h \ln \frac{V_B}{V_A}; \quad q_c = nRT_c \ln \frac{V_D}{V_C}$$



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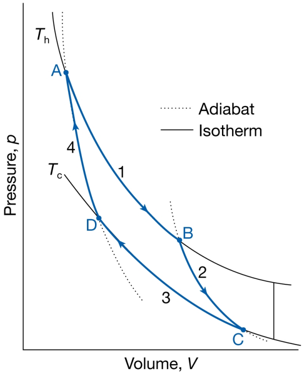
adiabats: $V_A T_h^c = V_D T_c^c$ (exponent $c = \frac{C_V}{nR}$)

and $V_C T_c^c = V_B T_h^c$

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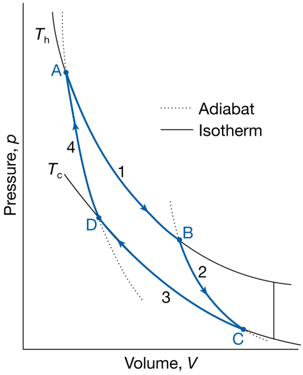


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efficiency, $\eta = \frac{\text{work performed}}{\text{heat absorbed}} = \frac{|w|}{q_h}$

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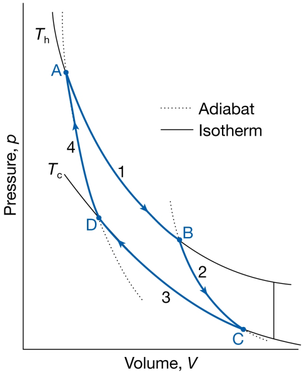


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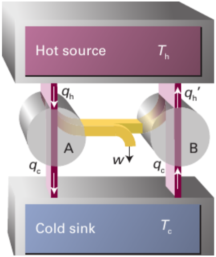
- Equivalent to Kelvin-Planck statement : Proof by contradiction

Let $\eta_A > \eta_B$
engine A takes heat $q_h$ from hot source and dumps $q_c$ in cold reservoir



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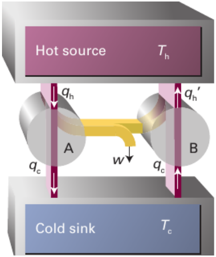

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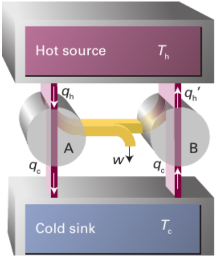


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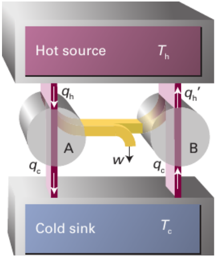

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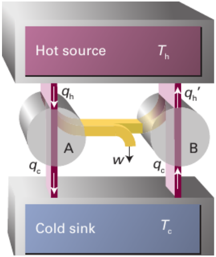


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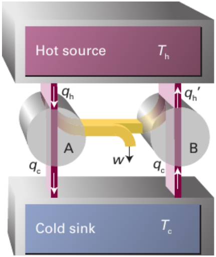


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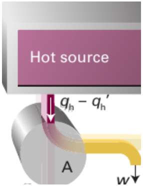
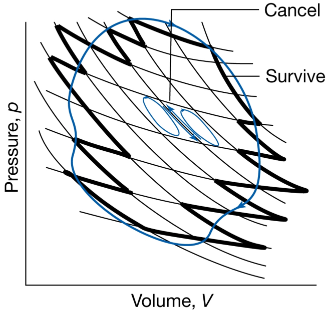
$\Longrightarrow$ violation of Kelvin-Planck statement of second law



universality of 2nd law :

any reversible cycle $\approx$
collection of Carnot cycles
$\oint$(arbitrary path)
$$= \sum \oint \text{ (each cycle)}$$



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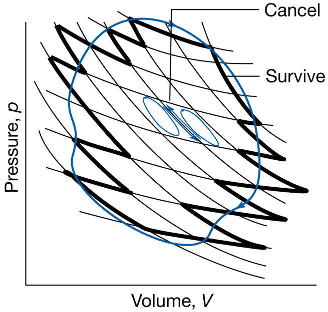


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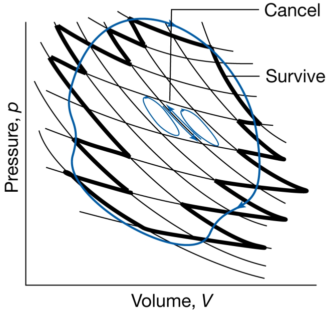


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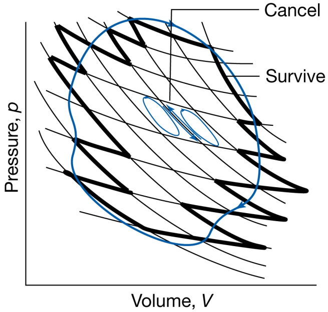


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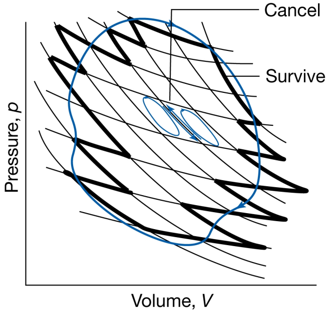


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In the limit of infinitesimal cycles, the non-cancelling edges of Camot cycles match the overall cycle exactly, and the sum becomes an integral

$\Longrightarrow$ $dS$ is exact differential and $S$ is state function

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$dq_{\text{rev}} \geq dq$, $\therefore \Delta S = \int \frac{dq_{\text{rev}}}{T} \geq \int \frac{dq}{T}$

Consider transfer of energy as heat from
one system - hot source-at $T_h$
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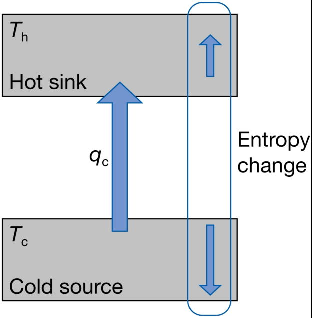
thermodynamic refrigerator




energy removed from cool source at temp. $T_c$

$$= \frac{|q_c|}{T_c}$$

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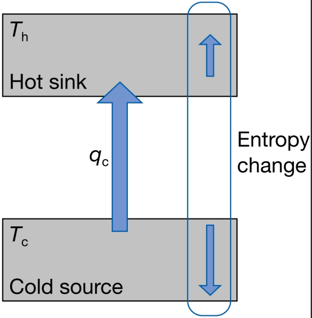


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and deposited in warmer sink at temp. $T_h$

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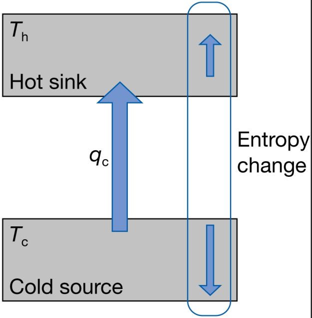


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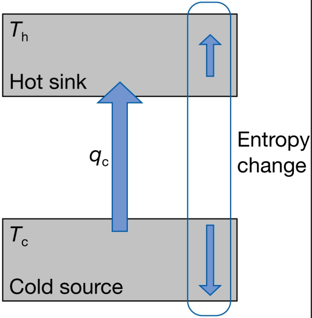


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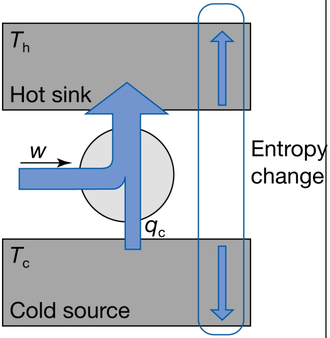
to generate more entropy, energy must be
added to the stream that enters the warm sink.
task: find minimum energy to be supplied

## Thermodynamic refrigerator



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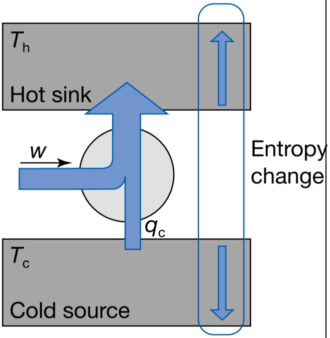


coefficient of peformance,

$$c = \frac{\text{energy transferred as heat}}{\text{energy transferred as work}} = \frac{|q_c|}{|w|}$$

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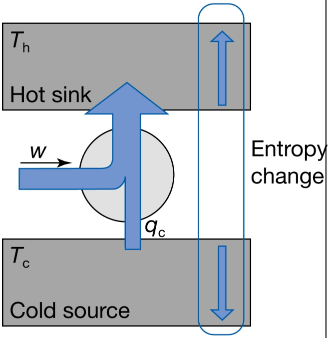


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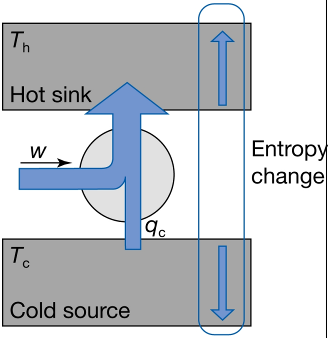


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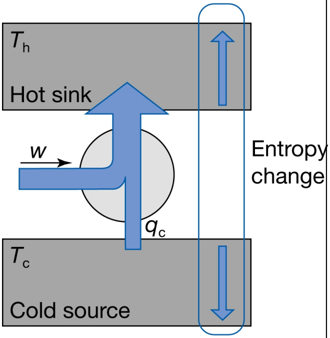


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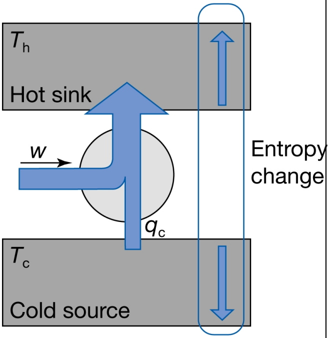


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using $\frac{q_h}{q_c} = -\frac{T_h}{T_c}$, we get, $c = \frac{T_c}{T_h - T_c}$

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where A depends on sample size and insulation
then minimum power, $P$, required to maintain original $\Delta T$ by pumping out energy by heating surroundings

$$P = \frac{1}{c}.A\,(T_h - T_c) = \frac{A(T_h - T_c)^2}{T_c} \propto (\Delta T)^2$$

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$\therefore$ air-conditioners more expensive to run on hot days than on mild days

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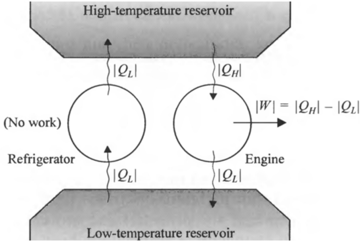

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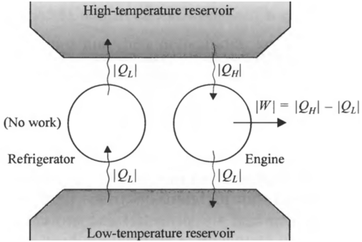


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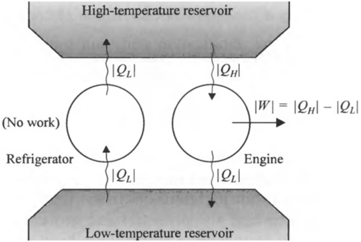


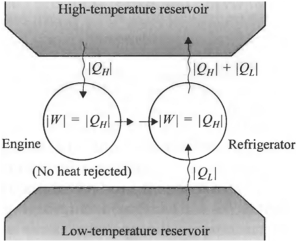


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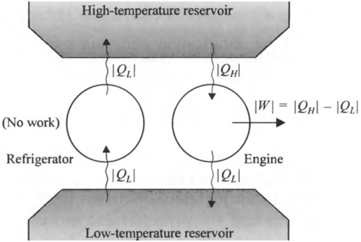


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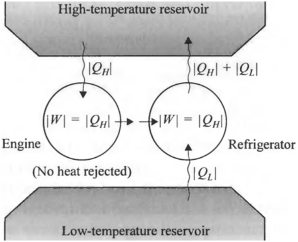


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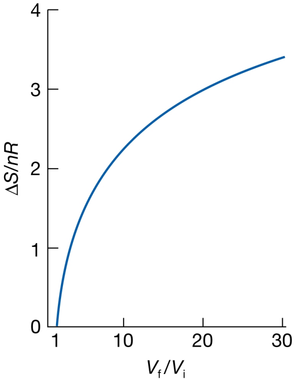
entropy change in isothermal expansion :



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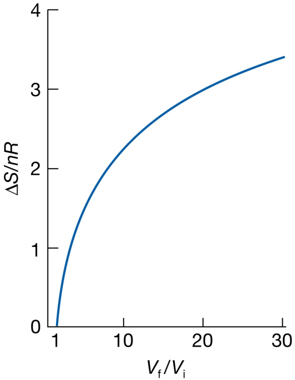


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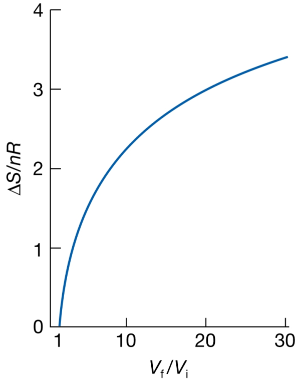


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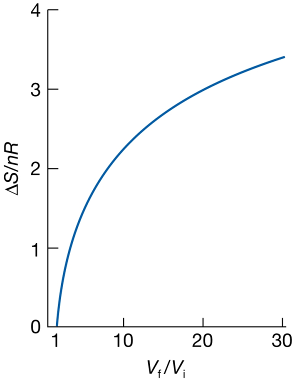


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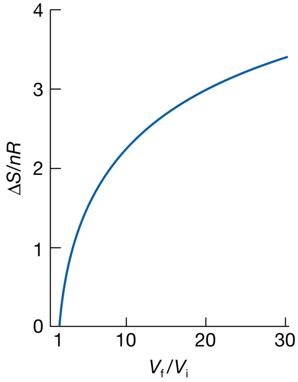


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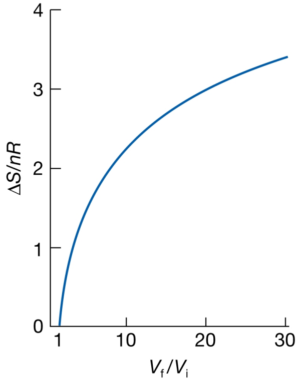


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experimental value : 29.45 kJ mol$^{-1}$

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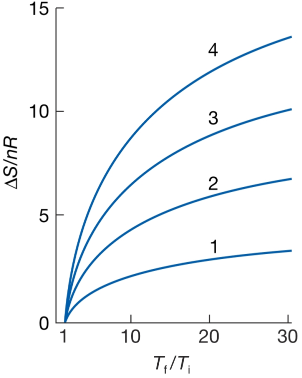
$$= S(T_i) + C_{p(V)} \ln \frac{T_f}{T_i}$$




label : heat capacity

solved problem : Calculate $\Delta S$ when 0.500 $dm^3$ of Ar at 25$^o$C and 1.00 bar expands to 1.000 $dm^3$ and is simultaneously heated to 100$^o$C

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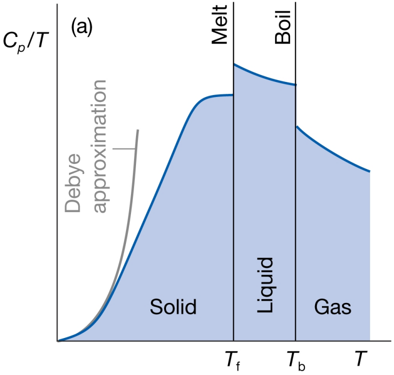
$$= \frac{10^5 \mathrm{Pa} \times 0.5 \times 10^{-3} \mathrm{m}^3}{298} \ln \left( \frac{0.05}{0.5} \left[ \frac{248}{298} \right]^{\frac{3}{2}} \right) =$$

$$= -0.44 = -0.44\ \mathrm{JK}^{-1}$$

Heat capacity vs. temp.




entropy vs. T

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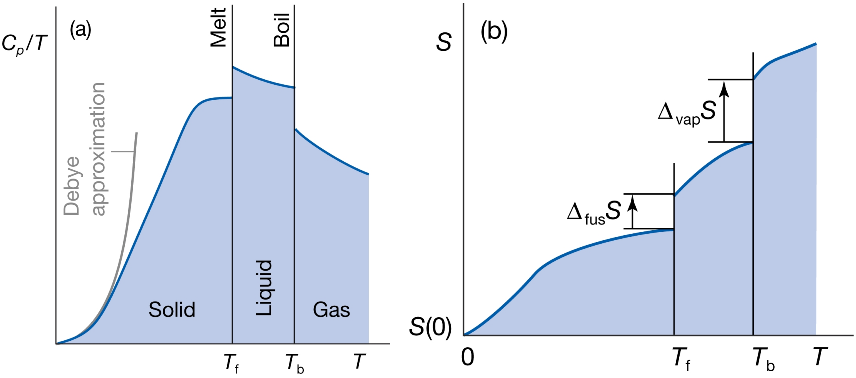

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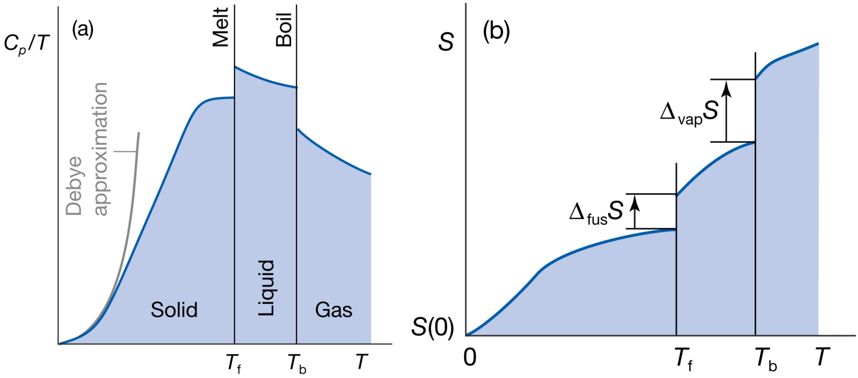


$$S(T) = S(0) + \int_0^{T_f} \frac{C_p(s)dT}{T} + \frac{\Delta_{fus}H}{T_{fus}} + \int_{T_1}^{T_b} \frac{C_p(l)dT}{T} + \frac{\Delta_{vap}H}{T_{vap}} + \int_{T_b}^{T} \frac{C_p(g)dT}{T}$$

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Debye extrapolation : $\underset{T \to 0}{\mathcal{L}t}\, C_p \longrightarrow aT^3$

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$S_m\,(298.15\text{K}) = S_m(0) + 192.06 \text{ J K}^{-1}\text{mol}^{-1}$

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3rd law (?) :
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when $\Omega \neq 0$, then $S = S(0)$, residual entropy

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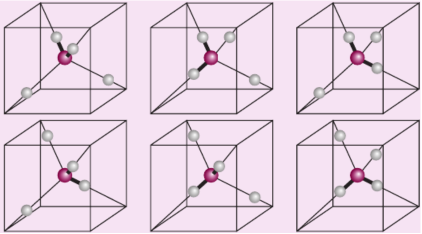

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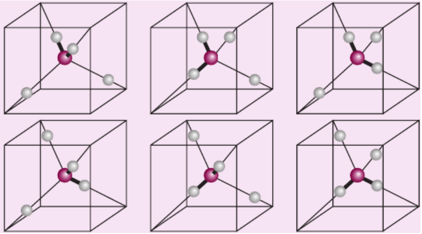


$\therefore$ for $N$ water molecules

# of possible configurations

$= 2^{2N}(3/8)^N = \left(\frac{3}{2}\right)^N$

Ice-$I_h$ :

each H atom can lie either close to or far from its ‘parent’ O atom

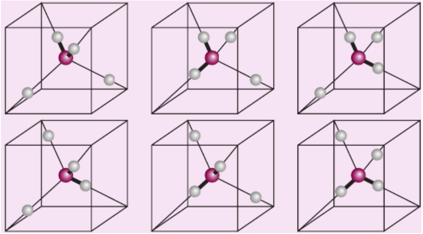
total # of arrangements in sample of $N$ $H_2O$ molecules with $2N$ H atoms $= 2^{2N}$

consider a single central O atom.

total number of arrangements of locations of H atoms around central O atom of one $H_2O$ molecule is $2^4 = 16$

Of these , only 6 correspond to two short and two long bonds

only $\frac{6}{16} = \frac{3}{8}$ of all arrangements are possible, and for $N$ molecules only $(3/8)^N$ of all arrangements are possible



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$$S(0) = Nk_B \ln\left(\frac{3}{2}\right) = 3.37 \text{ J mol}^{-1}\text{K}^{-1}$$

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As the system size increases
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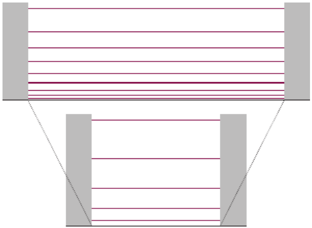

# ways of achieving same energy ($\Omega$) increases

**Maxwell's demon** : a thought experiment
A gas initially in one chamber, connected via a closed tap to a second chamber containing only vacuum
Open the tab and gas in first chamber expands to fill both chambers

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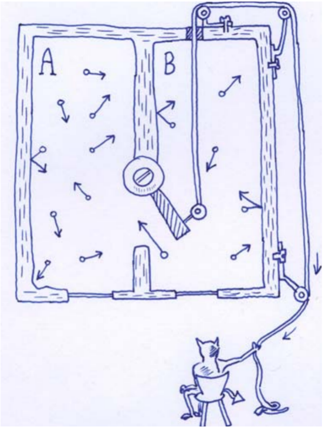
- Maxwell imagined that the tap was operated by a microscopic intelligent creature. If it sees a molecule heading from the second chamber back into the first, it opens the tap and then shuts it, just letting the molecule through. If it sees a molecule heading from the first chamber back into the second chamber, it keeps the tap closed



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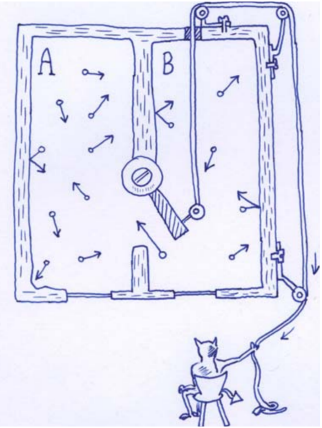


Demon does no work and yet it makes molecules in second chamber all go back into the first chamber

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as if the demon could therefore cause entropy to decrease in a system with no consequent increase in entropy anywhere else

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- Maxwell's demon can operate reversibly therefore, but only if it has a large enough hard disc that it doesn't ever need to clear space to continue operating.

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- Erasure of one bit of information requires a minimum energy cost equal to $k_B T \ln 2 \approx$0.018 eV, where $T$ is the temperature of a thermal reservoir used in the process.

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- Landauer argued that information is physical and it has an energy equivalent. It may be stored in physical systems such as books and memory chips and it is transmitted by physical devices exploiting electrical or optical signals.
- $\therefore$ it must obey the laws of physics and, first and foremost, the laws of thermodynamics.

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• an amount of energy equal to $k_B T \ln 2$ ($k_B T$ = thermal noise per unit bandwidth) is needed to transmit a bit of information, and more if quantized channels are used with photon energies $h\nu > kT$