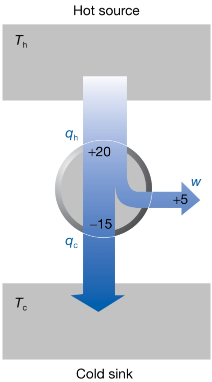
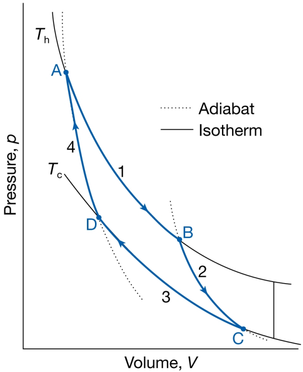
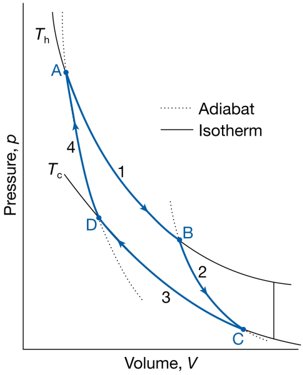
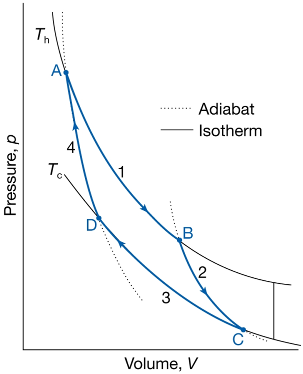
Example of a Carnot engine




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

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





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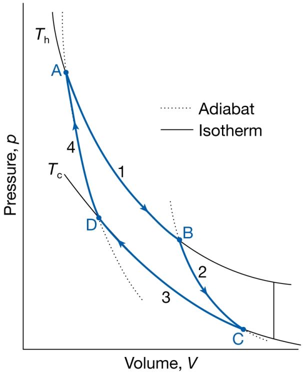
adiabats: $V_A T_h^c = V_D T_c^c$ (exponent $c = \frac{C_V}{nR}$)

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



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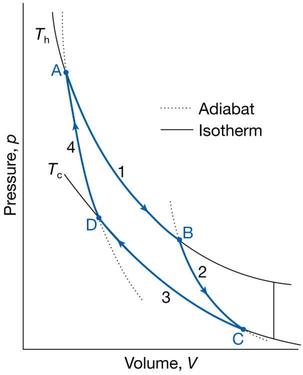
$$\therefore \frac{q_h}{q_c} = -\frac{T_h}{T_c}$$



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

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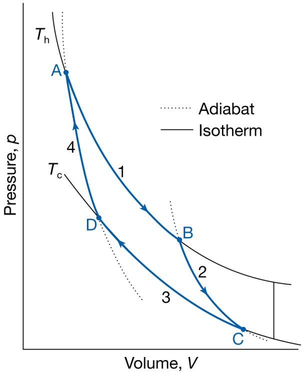

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2nd Law : all reversible engines have same efficiency regardless of their construction

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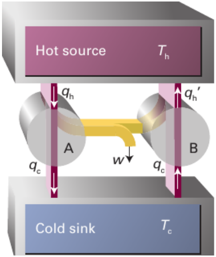
- Equivalent to Kelvin-Planck statement : Proof by contradiction



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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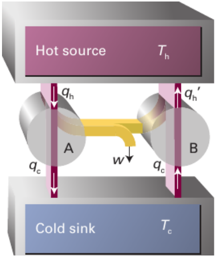

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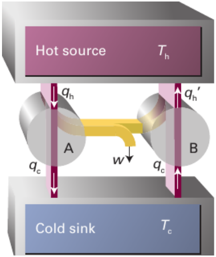

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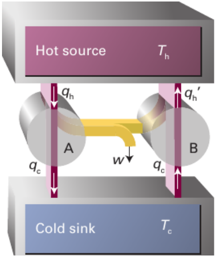

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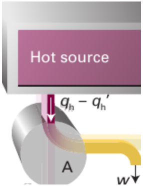

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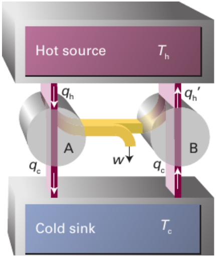

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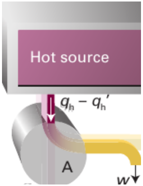

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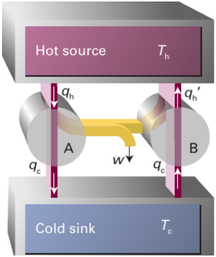

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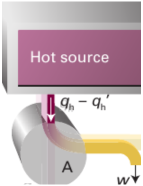

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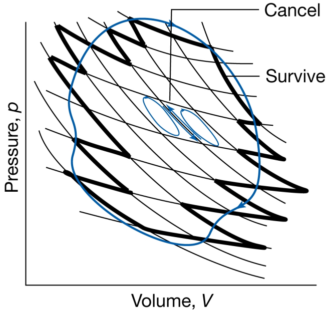
$\implies$ violation of Kelvin-Planck statement of second law

universality of 2nd law :

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



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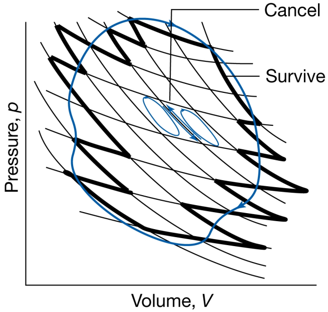

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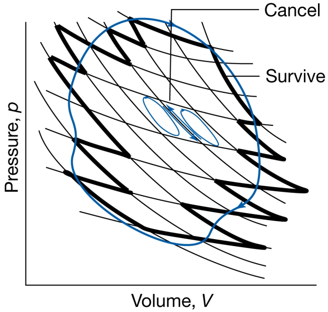

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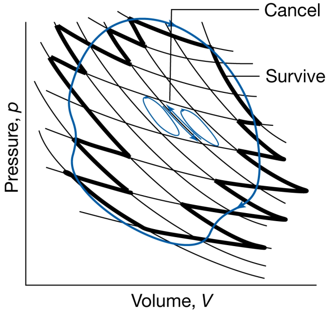

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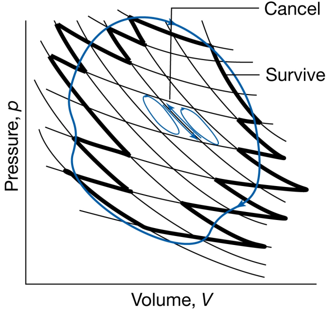

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In the limit of infinitesimal cycles, the non-cancelling edges of Camot cycles match the overall cycle exactly, and the sum becomes an integral

$\implies$ 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 the reverse of an engine :
transfer of energy as heat from
one system - hot source-at T_h
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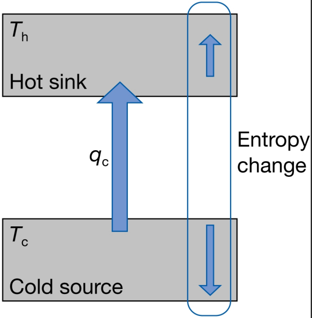
thermodynamic refrigerator
?



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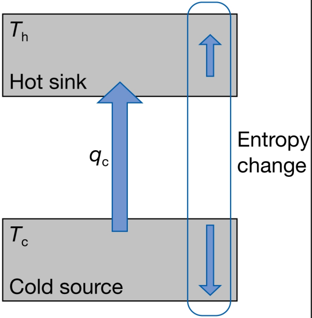

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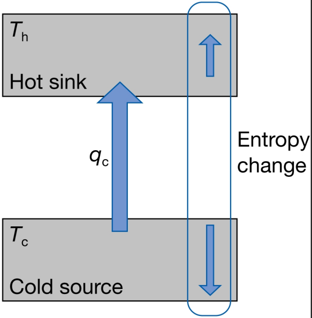

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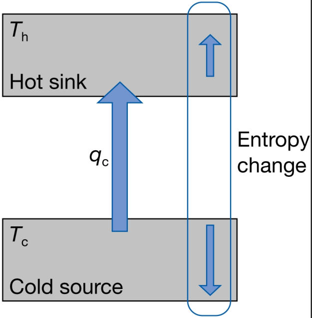

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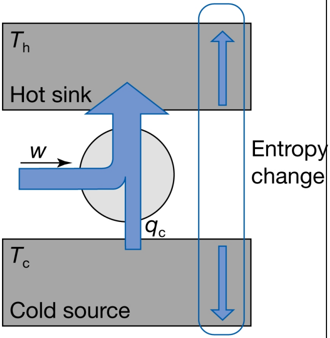
to generate more entropy, energy must be added to the stream that enters the warm sink.

task: find minimum energy to be supplied

Thermodynamic refrigerator



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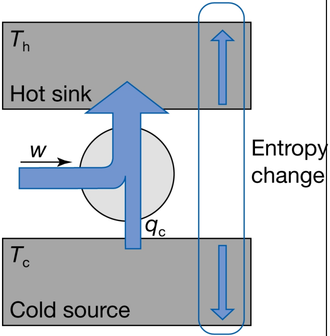

coefficient of peformance,

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

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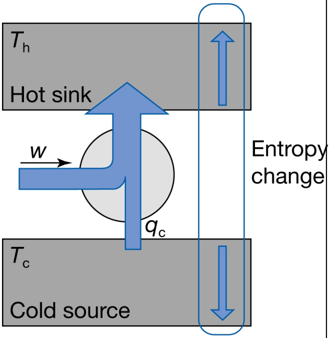

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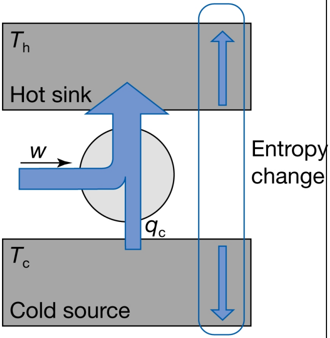

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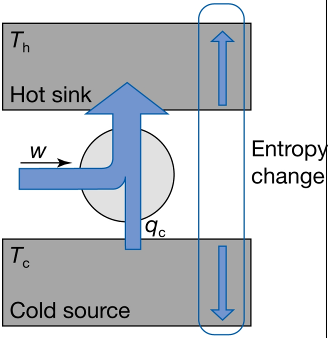

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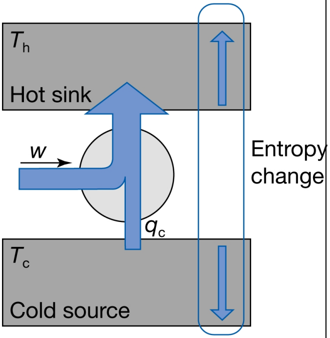

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using $\frac{q_h}{q_c} = -\frac{T_h}{T_c}$, we get, $c = \frac{T_c}{T_h - T_c}$

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then minimum power, P, required to maintain original ΔT by pumping out energy by heating surroundings

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

Equivalence of Kelvin-Planck (K) and Clausius statements (C)

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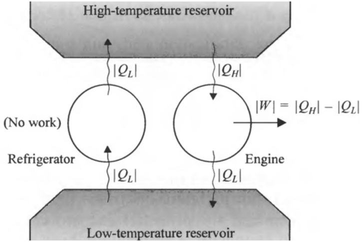

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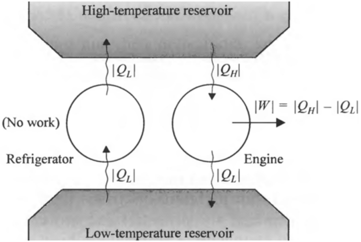

$$-\mathsf{C} \subset -\mathsf{K}$$

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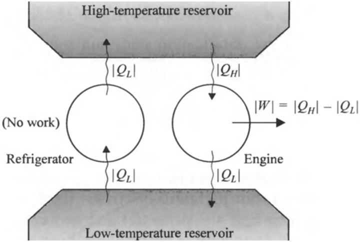

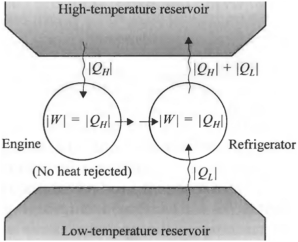

$-C \subset -K$

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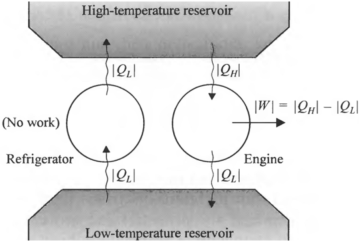

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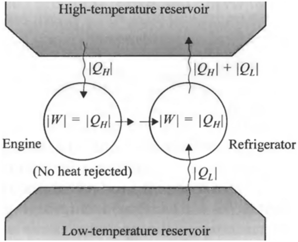

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entropy change in isothermal expansion :

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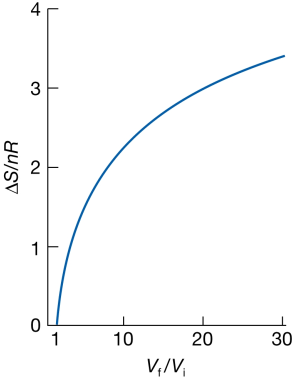
consider a perfect gas



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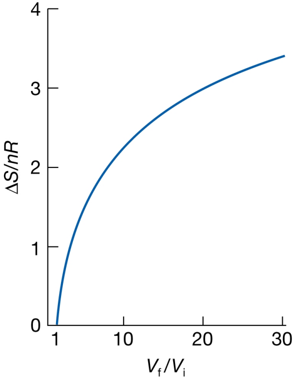

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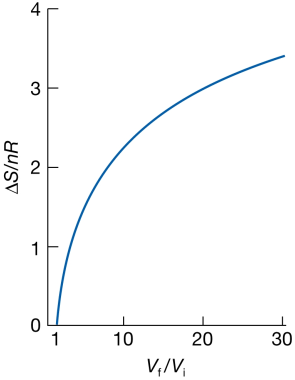

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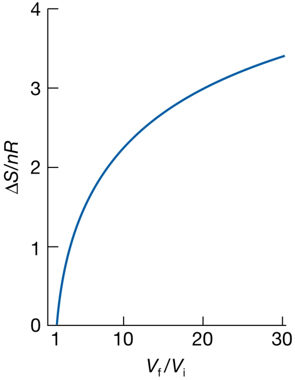

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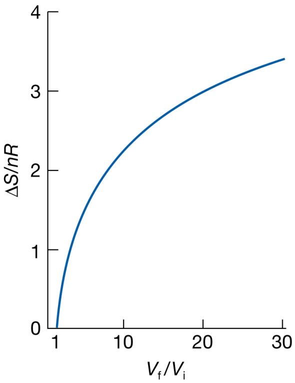

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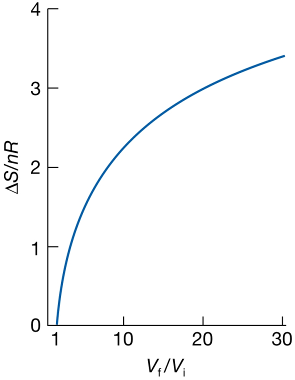

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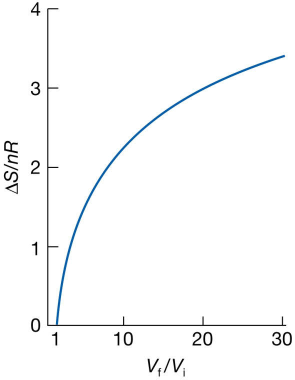

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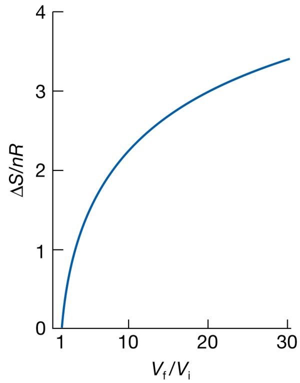

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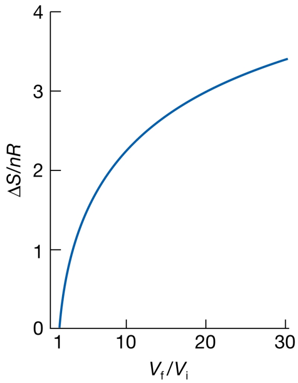

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$$\Delta S_{\text{total(rev)}} \begin{array}{l} = 0 \text{ rev} \\ > 0 \text{ irrev} \end{array}$$

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experimental value : 29.45 kJ mol^{-1}

entropy change as a function of temperature (varying heat capacity) :

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{dq_{rev}}{T}$$

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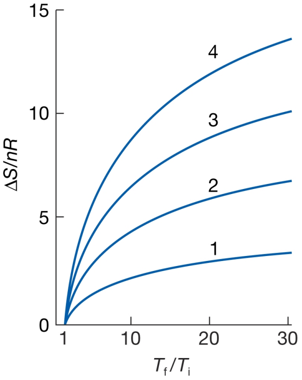
$$= S(T_i) + C_{p(V)} \ln \frac{T_f}{T_i}$$



label : heat capacity

solved problem : Calculate ΔS when 0.500 dm^3 of Ar at 25°C and 1.00 bar expands to 1.000 dm^3 and is simultaneously heated to 100°C

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$$\Delta S = \Delta S_{\mathrm{I}} + \Delta S_{\mathrm{II}} = nR\left(\ln\frac{V_f}{V_i} + \frac{3}{2}\ln\frac{T_f}{T_i}\right) = \frac{p_i V_i}{T_i}\ln\left(\frac{V_f}{V_i}\left[\frac{T_f}{T_i}\right]^{\frac{3}{2}}\right)$$

$$= \frac{10^5\mathrm{Pa}\times 0.5\times 10^{-3}\mathrm{m}^3}{298}\ln\left(\frac{1}{0.5}\left[\frac{373}{298}\right]^{\frac{3}{2}}\right)$$

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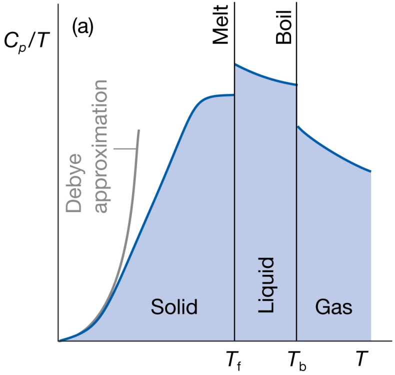
$$= \frac{10^5\mathrm{Pa} \times 0.5 \times 10^{-3}\mathrm{m^3}}{298} \ln\left(\frac{0.05}{0.5}\left[\frac{248}{298}\right]^{\frac{3}{2}}\right) =$$

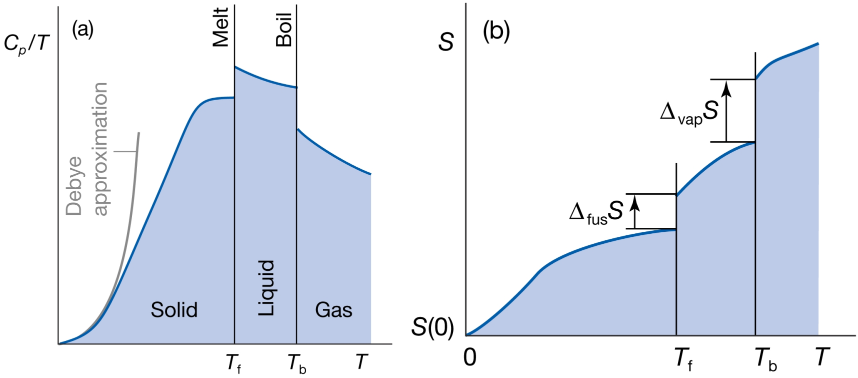
$$= -0.44 = -0.44\ \mathrm{JK^{-1}}$$

Heat capacity vs. temp.



entropy vs. T

Heat capacity vs. temp. entropy vs. T



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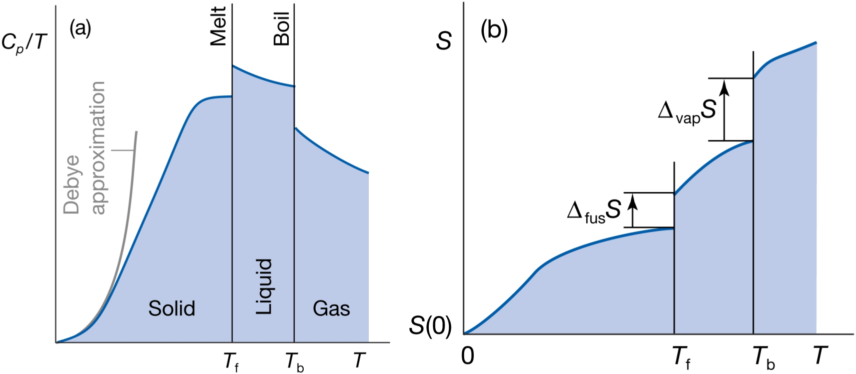

$$S(T) = S(0) + \int_0^{T_f} \frac{C_p(s)dT}{T} + \frac{\Delta_{fus}H}{T_{fus}} + \int_{T_1}^{T_b} \frac{C_p(l)dT}{T} + \frac{\Delta_{vap}H}{T_{vap}} + \int_{T_b}^{T} \frac{C_p(g)dT}{T}$$

All terms except $S(0)$ can be measured calorimetrically

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

Ex. $S_m^{\ominus}$ for N_2(g) at 25°C calculated from following data :

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	$S_m^\ominus / \mathrm{J\ K^{-1} mol^{-1}}$
Debye extrapolation	1.92
$\int_{10}^{35.61}$	25.25
Phase transition : 35.61K	6.43

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Phase transition : 35.61K	6.43
$\int_{35.61}^{63.14}$	23.38
Fusion : 63.14K	11.42

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$\int_{63.14}^{77.32}$	11.41

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Debye extrapolation	1.92
$\int_{10}^{35.61}$	25.25
Phase transition : 35.61K	6.43
$\int_{35.61}^{63.14}$	23.38
Fusion : 63.14K	11.42
$\int_{63.14}^{77.32}$	11.41
Vaporization : 77.32K	72.13

Ex. $S_m^{\ominus}$ for N_2(g) at 25^{o}C calculated from following data :

	$S_m^{\ominus}$/J K^{-1}mol^{-1}
Debye extrapolation	1.92
$\int_{10}^{35.61}$	25.25
Phase transition : 35.61K	6.43
$\int_{35.61}^{63.14}$	23.38
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$\int_{63.14}^{77.32}$	11.41
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$\int_{77.32}^{298.15}$	39.20

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Debye extrapolation	1.92
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$\int_{77.32}^{298.15}$	39.20
Correction for gas imperfection	0.92

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$\int_{77.32}^{298.15}$	39.20
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Total	192.06

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Debye extrapolation	1.92
$\int_{10}^{35.61}$	25.25
Phase transition : 35.61K	6.43
$\int_{35.61}^{63.14}$	23.38
Fusion : 63.14K	11.42
$\int_{63.14}^{77.32}$	11.41
Vaporization : 77.32K	72.13
$\int_{77.32}^{298.15}$	39.20
Correction for gas imperfection	0.92
Total	192.06

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

Nernst heat theorem : $\mathop{\mathcal{L}t}\limits_{T \to 0} \Delta S \longrightarrow 0$ for any transformation provided all substances involved are perfectly crystalline

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3rd law (?) :
The entropy of all perfect crystalline substances is zero at $T = 0$

Boltzmann formula : $S = k_B \ln \Omega$

$\Omega = \#$ways the molecules can be arranged in a crystalline form

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$\Omega = \#$ways the molecules can be arranged in a crystalline form

In most cases, $\underset{T \to 0}{\mathcal{L}t}\, \Omega = 1, \qquad \therefore \underset{T \to 0}{\mathcal{L}t}\, S = 0$

when $\Omega \neq 0$, then $S = S(0)$, residual entropy

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 $= 2^{2N}$

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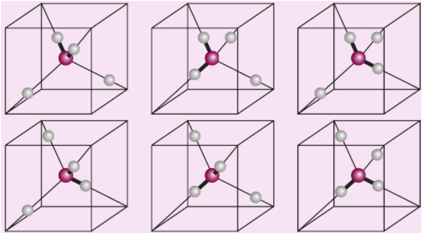
consider a single central O atom.

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



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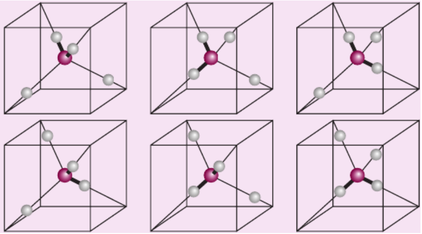

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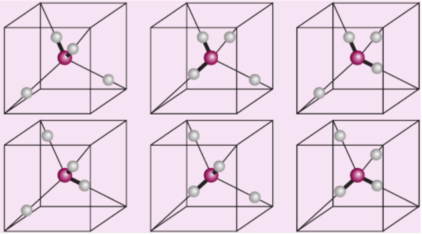

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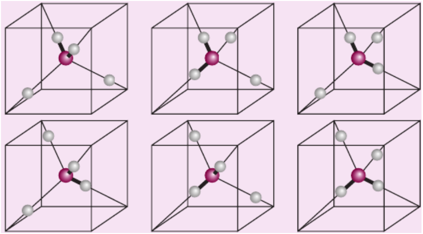

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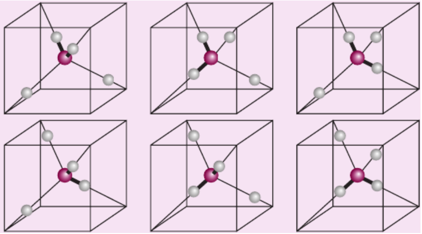

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$$S(0) = Nk_B \ln\left(\frac{3}{2}\right) = 3.37 \text{ J mol}^{-1}\text{K}^{-1}$$

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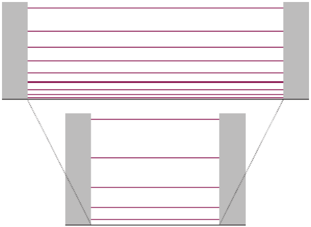

ways of achieving same energy (Ω) increases

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A gas initially in one chamber, connected via a closed tap to a second chamber containing only vacuum
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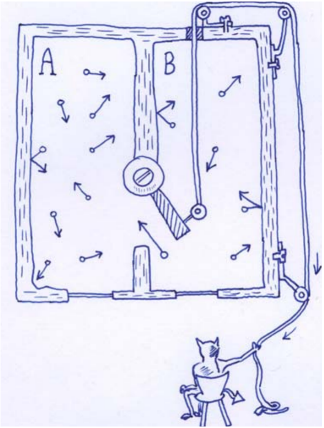

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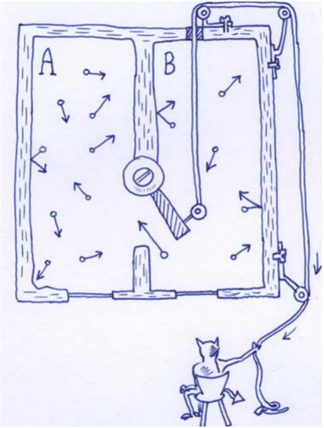

Demon does no work and yet it makes molecules in second chamber all go back into the first chamber

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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 operation

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- generally, $S = k_B H$, where $H =$information entropy

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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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- $\therefore$ it must obey the laws of physics and, first and foremost, the laws of thermodynamics.

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(2) any logically reversible process can be implemented thermodynamically reversibly.
• 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 hν > kT