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Action and entropy in heat engines: A modern revision of the Carnot cycle

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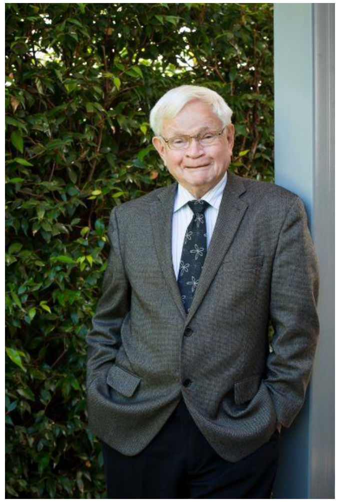


Kennedy et al 2019, *Entropy 21,454*
A simple method to estimate entropy and free energy
of atmospheric gases from their action

Making thermodynamics easier using the least action principle

Kennedy IR Action in Ecosystems Wiley 2001

Least action is nature's statistical means for economy of energy resources $S = \int (T - V)dt$ - integrating the Lagrangian w/r time

Partition functions of statistical mechanics can be interpreted as ratios of action compared to Planck's quantum of action ħ

In revising the Carnot cycle, can we discover anything new from the idea of action to apply to the greatest issue of our time – climate change

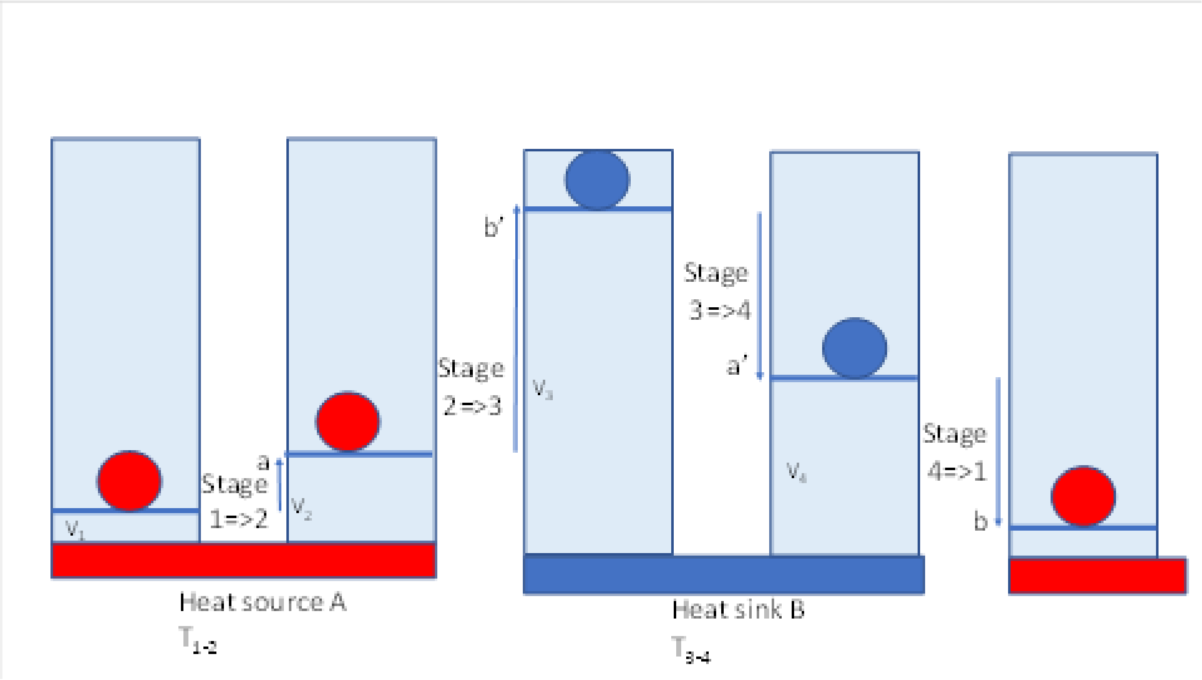
Sadi Carnot’s legacy

- Carnot’s legacy is often still misunderstood, given Lord Kelvin was misled by Clapeyron’s paper that the cycle assumed conservation of caloric between the extremes of temperature. Clausius was deceived too, but generously corrected Carnot’s “error” in 1850
- In fact, as we will show here, there was no such error. Richard Feynman in his lectures also concluded there was no error and that the Clausius-Clapeyron equation should really be called the Carnot equation, since it was already described in Carnot’s 1824 memoire
- Using an action revision can we obtain a better understanding of Carnot’s cycle?

Carnot’s postulates

- *“The motive power of heat is independent of the agents employed to realize it; its quantity is fixed solely by the temperatures between which is effected, finally, the transfer of caloric”*
- *“When a gas varies in volume without change in temperature the quantity of heat absorbed or liberated are in arithmetical progression if the increments or decrements of volume are in geometrical progression”*
- *“The temperature is higher during the movements of dilatation than during the movements of compression. During the former the elastic force of air is found to be greater and consequently the quantity of motive power during dilatation is more considerable than that consumed to produce movements of compression”*
- *“The quantities of heat absorbed or set free in these different transformations are exactly compensated”*

Four stages of Carnot cycle

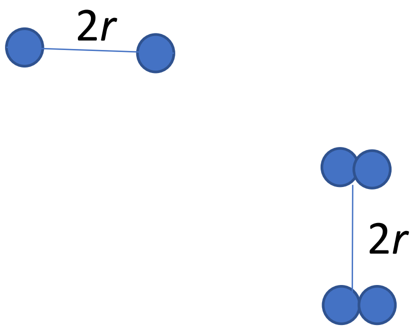


Stage 1=2: Isothermal	Carnot's caloric	a
Stage 2=3: Adiabatic		b'
Stage 3=4: Isothermal		a'
Stage 4=1: Adiabatic		b

$$
\begin{aligned}
Q_{1-2} = W_{1-2} &= RT_{1,2}\ln(V_2/V_1) \\
W_{2-3} &= Cv(T_2-T_1) \\
-Q_{3-4} = W_{3-4} &= RT_{3,4}\ln(V_4/V_3) \\
W_{4-1} &= Cv(T_1-T_2) \\
W &= R(T_1-T_2)\ln(V_2/V_1)
\end{aligned}
$$

$$
\begin{aligned}
\Upsilon &= (Q_2 - Q_1)/Q_2 \\
&= (T_2 - T_1)/T_2
\end{aligned}
$$

Action @ = $\int mvds$ = $mvr\delta\phi$ - a scalar property similar to angular momentum



$p = kT/a^3 = NkT; \; a = 2r$

$pa^3 = kT = mv^2/3 = mr^2\omega^2/3$

@ = $mr^2\omega$

- *@ relative action (per radian)*

Action space = Phase space *dp.dq*
Gibbs' extension in phase

Translational relative action

- $@_t^3 = [(3kTI_t)^{1.5}/z_t) = mrv$
  $I = mr^2$
- $z_t = (2)^3(1.0854)^3 = 10.2297$

Mean velocity/RMS velocity

$= v/\bar{u} = 1/1.0854$

2^3 symmetry factor

Rotational relative action

- Diatomic
  $@_r^2 = (2kTI)/\sigma = (I\omega)^2$
- Polyatomic
  $@_{ra}@_{rb}@_{rc} = [(2kTI_a)^{0.5}(2kTI_b)^{0.5}(2kTI_c)^{0.5}/\sigma]$

σ symmetry factor

Entropy from relative action

$$s = (h-g)/T$$

- Translational

$$-g_t = k\ln[(@_t)/\hbar)^3 = k\ln[n_t)^3$$

- Rotational

$-g_r = k\ln[(@_r)/\hbar)^2 = k\ln[j_r)^2$ - diatomic

$-g_r = k\ln[(@_{ra})/\hbar)\ (@_{rb})/\hbar)(@_{rc})/\hbar) = k\ln[j_{ra} x\ j_{rb} x\ j_{rc})$

- polyatomic

$$s = 3.5k + k\ln[\mathrm{n_t})^3 + k\ln[\mathrm{j_r})^2$$

Entropy of N_2

Entropic energy = sT

$$sT = 3.5kT + kT\ln[\mathrm{n_t}]^3 + kT\ln[\mathrm{j_r}]^2$$

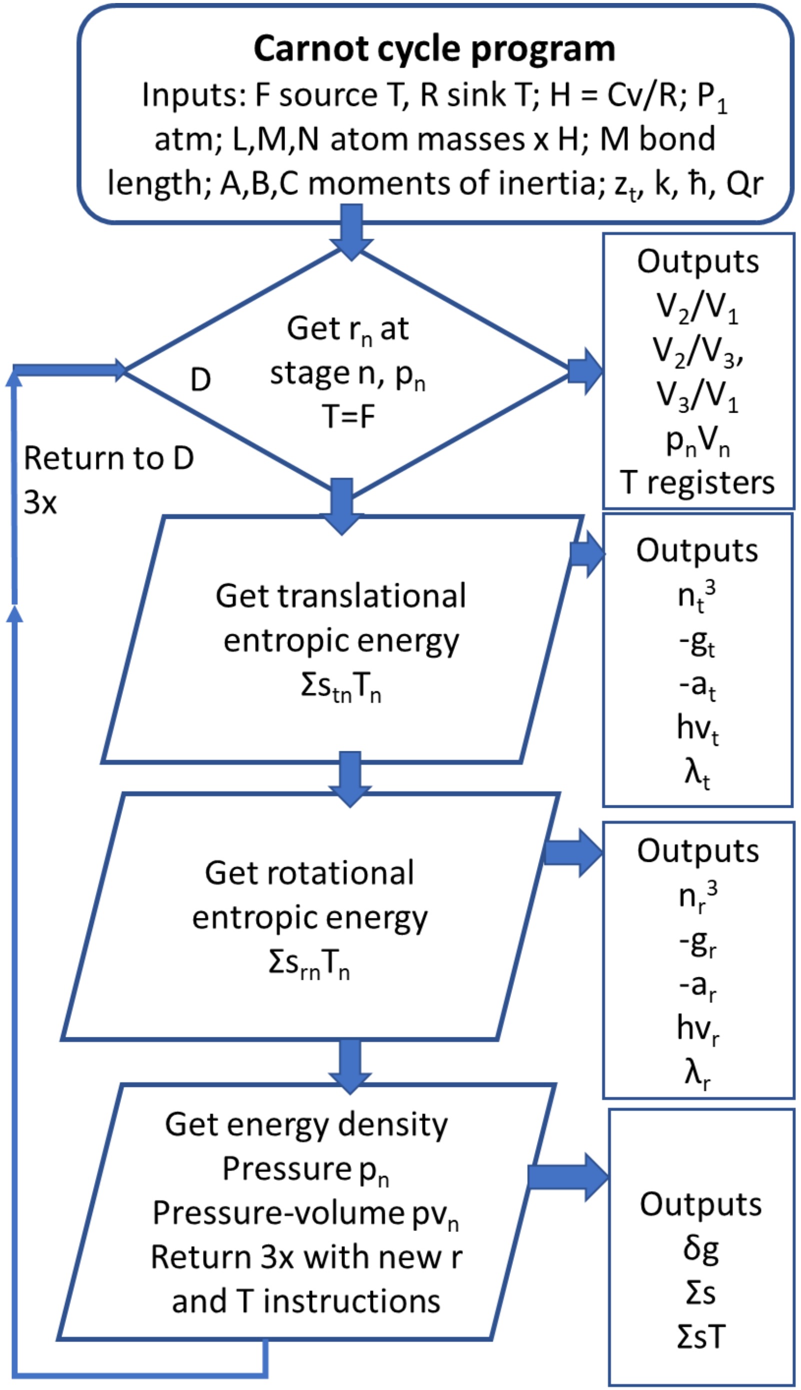
$$sT = kT\ln \mathrm{e}^{3.5}\{[\mathrm{n_t}]^3\,[\mathrm{j_r}]^2\}$$

$$= h - g$$

$$g = h - sT$$

Flow sheet for computation

Program code available from ivan.kennedy@sydney.edu.au



Carnot cycle program

Inputs: F source T, R sink T; H = Cv/R; P_1 atm; L,M,N atom masses x H; M bond length; A,B,C moments of inertia; z_t, k, ħ, Qr

D

Get r_n at stage n, p_n T=F

Return to D 3x

Outputs
V_2/V_1
V_2/V_3,
V_3/V_1
p_nV_n
T registers

Get translational entropic energy $\Sigma s_{tn}T_n$

Outputs
n_t^3
$-g_t$
$-a_t$
hv_t
λ_t

Get rotational entropic energy $\Sigma s_{rn}T_n$

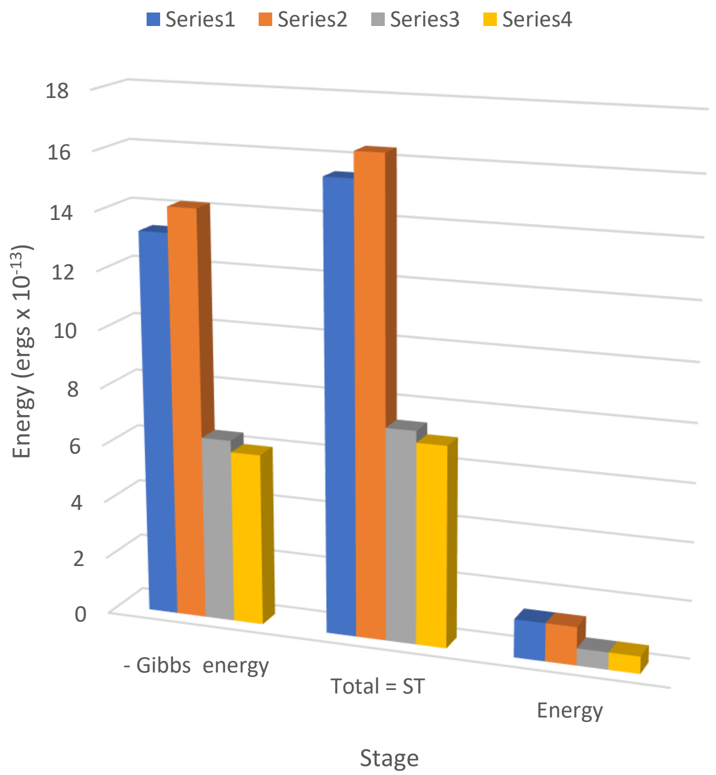
Outputs
n_r^3
$-g_r$
$-a_r$
hv_r
λ_r

Get energy density
Pressure p_n
Pressure-volume pv_n
Return 3x with new r and T instructions

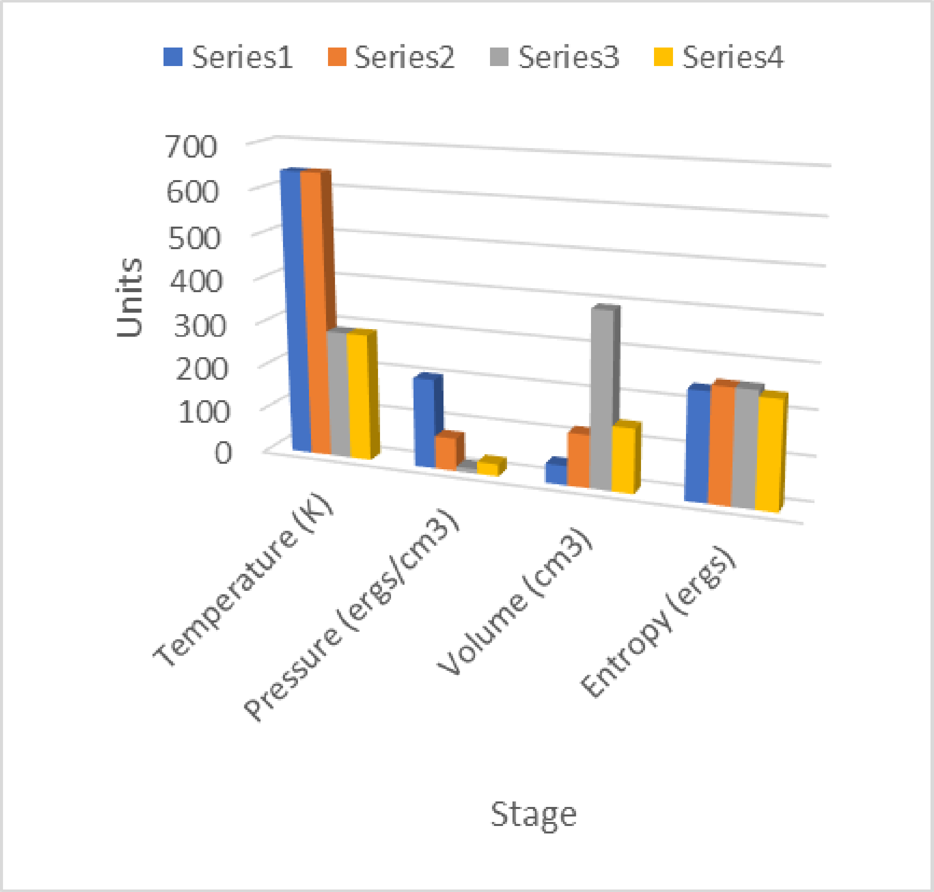
Outputs
δg
Σs
ΣsT

Carnot cycle stages

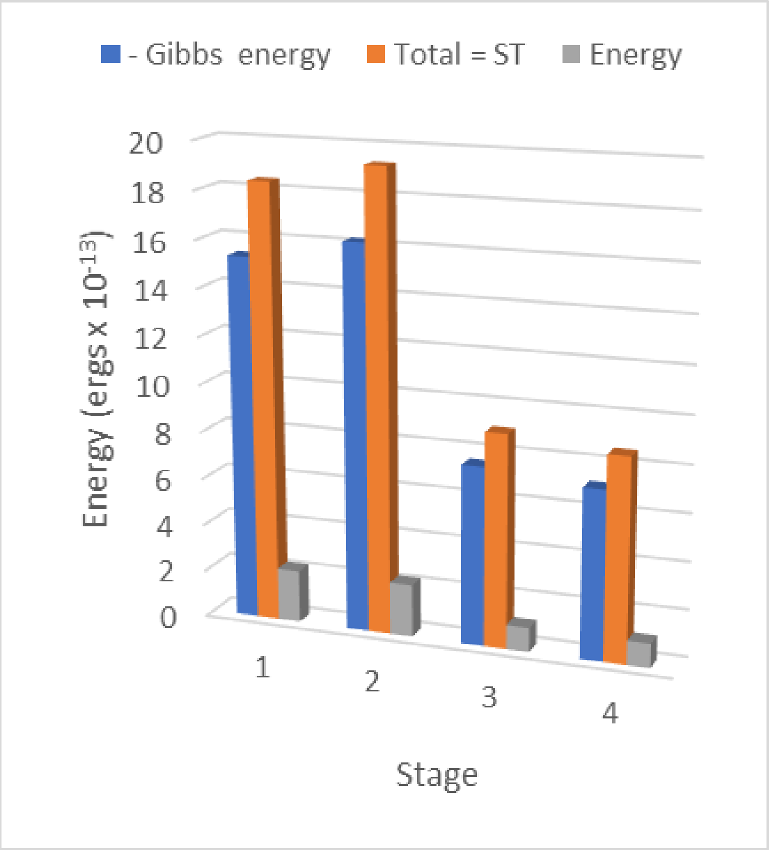
ARGON -*G*, *ST* and *E*

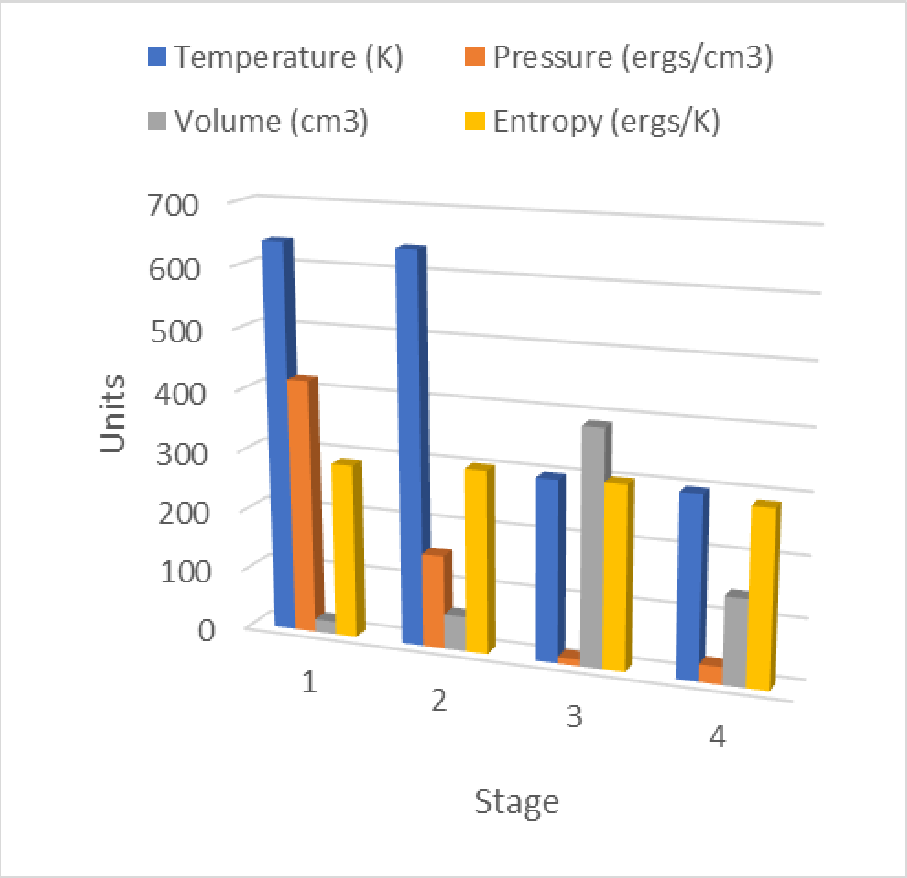


T, p, V, S



N_2 as working fluid





-Gibbs energies or configurational entropic energy

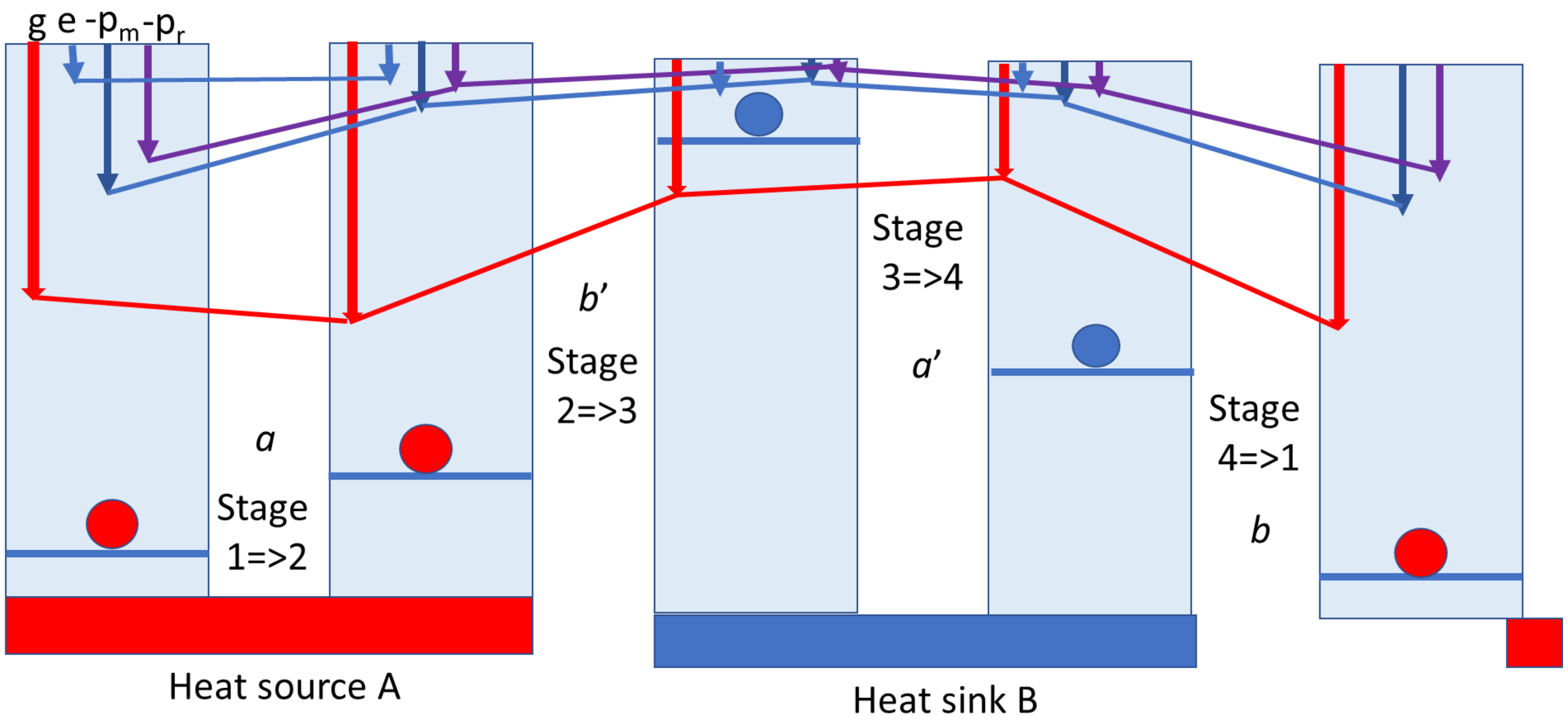
ARGON	Stage 1=2	Stage 2=3	Stage 3=4	Stage 4=1
Action $@_t$ ($I\omega$ erg.sec)	8.441202×10^{-26}	1.178065×10^{-25}	1.178065×10^{-25}	8.441202×10^{-25}
Quantum number	n = 80.042	n = 111.708	n = 111.708	n =80.042
hv	1.4154×10^{-14}	1.1191×10^{-14}	5.036×10^{-15}	6.531×10^{-15}
-Gibbs energy ($-g$)	$11.617287 \times 10^{-13}$	$12.500888 \times 10^{-13}$	5.625399×10^{-13}	5.227779×10^{-13}
δGibbs energy (δg)	-0.8837×10^{-13} a	$+6.875489 \times 10^{-13}$ b’	$+0.39762 \times 10^{-13}$ a’	$-6.389508 \times 10^{-13}$ b

NITROGEN	Stage 1=2	Stage 2=3	Stage 3=4	Stage 4=1
Translational action $@_t$ (Iω erg.sec)	7.062416×10^{-26}	9.856396×10^{-26}	1.118839×10^{-25}	9.216142×10^{-26}
Virtual quantum no.	n_t = 66.968	n_t = 93.462	n_t = 121.963	n_t = 87.391
$-g_t$ (ergs)	1.114455×10^{-12}	1.202815×10^{-12}	5.730170×10^{-13}	5.332550×10^{-13}
hv_t	1.664154×10^{-14}	1.286960×10^{-14}	4.698270×10^{-15}	$6.1019722 \times 10^{-15}$
Rotational action $@_r$	1.118839×10^{-26}	1.118839×10^{-26}	7.505400×10^{-27}	7.50540×10^{-27}
Rotational free energy	4.173639×10^{-13}	4.173639×10^{-13}	1.560635×10^{-13}	1.560635×10^{-13}
–Gibbs energy ergs/molecule ($-g_t - g_r$)	1.531819×10^{-12}	1.620179×10^{-12}	7.290805×10^{-13}	6.893185×10^{-13}
δGibbs energy	-0.88360×10^{-13} **a**	$+8.910985 \times 10^{-13}$ **b’**	$+0.39762 \times 10^{-13}$ **a’**	$-8.425005 \times 10^{-13}$ **b**
hv_r	3.933976×10^{-14}	3.933976×10^{-14}	2.192865×10^{-14}	2.192865×10^{-14}

- Relative action = @
- Quantum number = $@/\hbar$ = n_t
- Gibbs energy = $-kT(n_t)^3$
- Virtual quanta = hv = $-g_t/n_t$

Work = a - a’ for both positive

Carnot caloric cycle



$$|a + b| = |b' + a'|$$

$$|a - a'| = |b' - b| = \text{maximum work possible}$$

$$\text{Efficiency} = (a - a')/a = (Q_f - Q_r)/Q_f = (T_f - T_r)/T_f$$

Carnot’s legacy is confirmed by this action based analysis

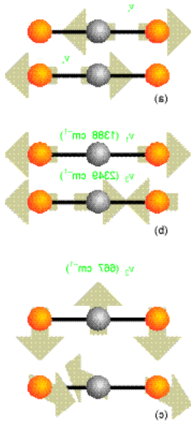
Carnot’s postulates of the independence of working fluid, the importance of temperature gradient and the logarithmic effect of volume on specific heat are all logically modelled as action thermodynamics.

Carnot’s (Clausius-Clapeyron) equation regarding the heat of vaporization even predicted the difference in vapour pressure of water at different temperatures, an important feature of climate science

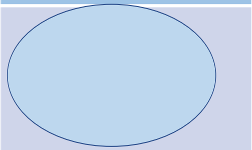
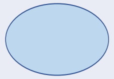
Consistency of his analysis with action thermodynamics suggests that all ensembles of molecules in relative action should infer sustaining negative Gibbs energy or entropic energy

Can we recognise the heat-work-heat processes of a Carnot cycles in climate

CALCULATING ENTROPY AS A FUNCTION OF ACTION (*MRVδφ*)



Vibrational

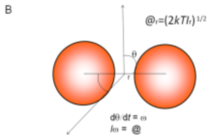
ε_{vib}	N_n/N_o	r_n/r_o	Action phase space	$@_n/@_o$	$3kT\ln(@_n/@_o)$
$7hv/2$	$e^{-3hv/kT}$	24.996		24.996	$=3hv$
$5hv/2$	$e^{-2hv/kT}$	8.549		8.549	$=2hv$
$3hv/2$	$e^{-hv/kT}$	2.924		2.924	$= hv$
$hv/2$	e^{0}	1.000		1.000	0

$N_r/N_s = e^{-Er/kT}/e^{-Es/kT} = e^{-\delta E/kT}$
$-\delta E = -kT\ln(N_r/N_s) = -kT\ln(r_s/r_r)^3 =$
$-kT\ln(@_s/@_r)^3$

$S_{vib} = (E-G)/T = Rxe^{-x}/(1-e^{-x}) - R\ln(1-e^{-x})$
$S_v = \Sigma S\nu_i$

$S_vT = \Sigma S\nu_iT$ = Vibrational entropic energy

Rotational



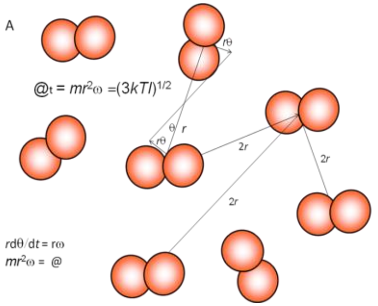
$@_r = mr_rv_r$

$S_r = R\ln[e(8\pi^2kTI_r/\sigma_rh^2)]$

$S_r = R\ln[e(@_r/\hbar)^2/\sigma_r]$
$\quad = R + R\ln[(@_r/\hbar)^2/\sigma_r]$

$S_r = R\ln[\pi^{1/2}e^{3/2}(@_A@_B@_C/\hbar^3)/\sigma_r]$

Translational



$@_t = mr_tv_t$

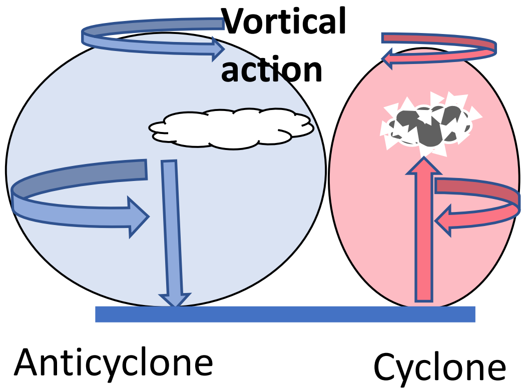
$S_t = R\ln[8e^{5/2}(2\pi mr_t^2kT)^{3/2}/h^3]$
$S_t = R\ln[8e^{5/2}(2\pi mr_t^2kT)^{3/2}/h^3]$

$S_t = R\ln[e^{5/2}(@'_t/\hbar)^3/z_t]$
$\quad = R\ln[e^{5/2}(@_t/\hbar)^3] = R\ln[e^{5/2}(n_t)^3]$

$S_tT = RT\ln[e^{5/2}(@_t/\hbar)^3]$

Translational entropic energy

Vortical



$@_{vor} = mR^2\Omega$

$S_{vor} = Nk\ln(mR^2\Omega/\hbar)$

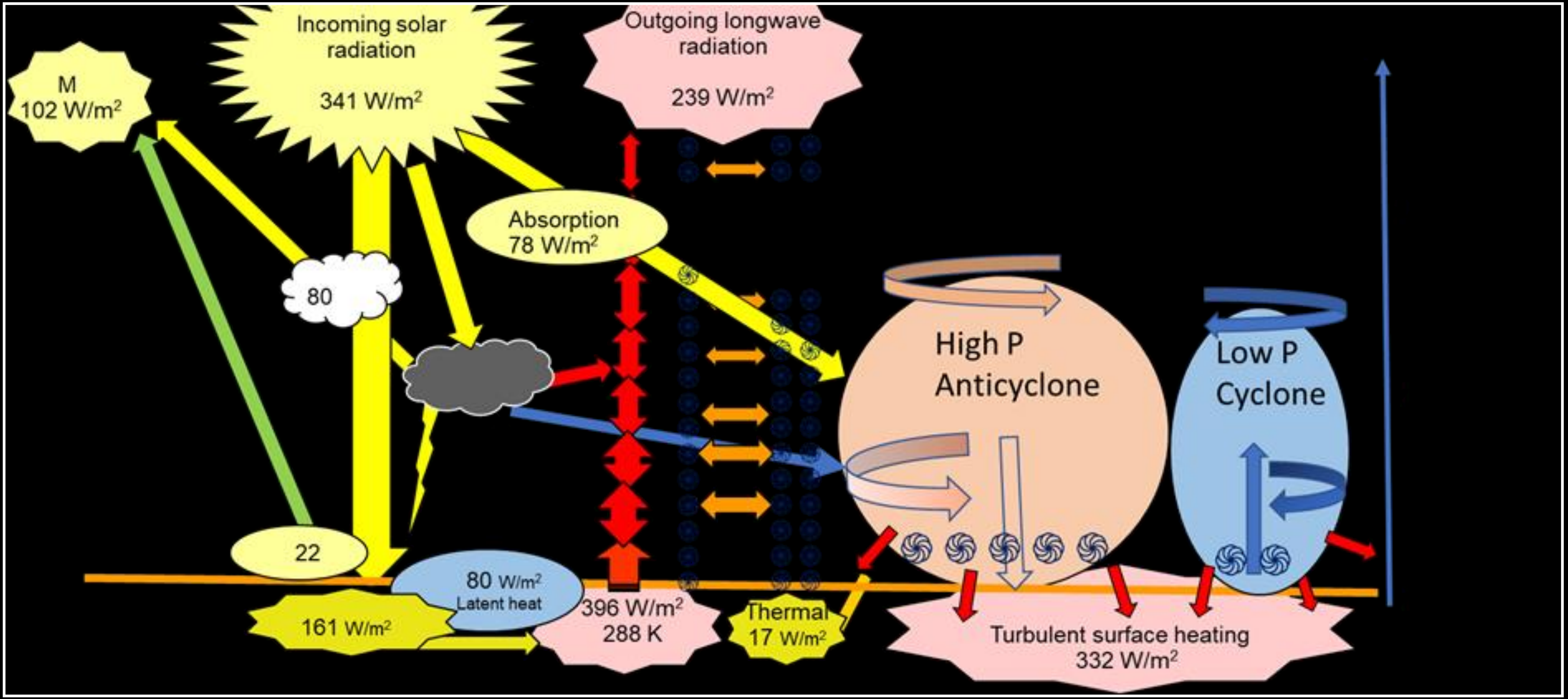
$S_{vor}T$ = *Vortical potential energy*

$\Sigma S = \Sigma S_{vi} + S_{rot} + S_{trans} + S_{vor}$ – increases heat capacity of air several times

Heat capacity or specific heat in air of cyclonic and anticyclonic motion

288.2 K	Vibrational	Rotational	Translational	Vortical (ω=5.10^{-5}; r = 10^{8} cm)	Vortical (ω=5.10^{-5}; r = 10^{5} cm)	Vortical (ω=5.10^{-5}; r = 10^{2} cm)
Action (@/ħ)	<0.1	8.1	152.2	2.28259×10^{15}	2.28259×10^{9}	2.28259×10^{3}
Entropy *ln*(@/ħ)^{n}	<0.01	4.18k	15.07k	35.364k	21.549k	7.733k
Energy	kJ per mol	10.017	36.115	84.749	51.642	18.532

Thus, with vortical configurational entropy, heat capacity is ca. three times greater, effectively a capacitor providing a major source for heat-work-heat cycling



Vortical entropic energy coupled to Trenberth energy budget
This is a testable hypothesis

Conclusions

- Not only is his establishment of the second law of thermodynamics clear, but the first conservation law of reversible heat and work is established in his equation for caloric establishing the *pussiance motrice* = (a – a’)
- Carnot’s temperature-sensitive caloric can be taken as a primitive view of the work of Clausius, Boltzmann, Gibbs, Planck and Einstein’s quantum or action field
- The second law of increasing entropy and energy dissipation is also recognised in the proposing cyclonic vortical entropy as a heat-work-heat cycle, as proposed in this presentation