Lecture 13 Chemistry 163B Winter 2020
Third Law and Entropy of Mixing
(ideal gas, distinguishable molecules)

Lecture 13
Chemistry 163B
Winter 2020

Absolute Entropies and Entropy of Mixing

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APPENDIX A: ***ΔH_f, ΔG_f, BUT S (no Δ, no "sub f")***

Substance	ΔH^o_f ΔH_f° (kJ mol^{-1})	ΔG^o_f ΔG_f° (kJ mol^{-1})	S^o S° (J mol^{-1} K^{-1})	$C_{P,m}^\circ$ (J mol^{-1} K^{-1})	Atomic or Molecular Weight (amu)
Carbon					
Graphite(*s*)	0	0	5.74	8.52	12.011
Diamond(*s*)	1.89	2.90	2.38	6.12	12.011
C(*g*)	716.7	671.2	158.1	20.8	12.011
CO(*g*)	−110.5	−137.2	197.7	29.1	28.011
Hydrogen					
H_2(*g*)	0	0	130.7	28.8	2.016
H_2O(*g*)	−241.8	−228.6	188.8	33.6	18.015
H_2O(*l*)	−285.8	−237.1	70.0	75.3	18.015
H_2O(*s*)			48.0	36.2 (273 K)	18.015
H_2O_2(*g*)	−136.3	−105.6	232.7	43.1	34.015
H^+(*aq*)	0	0	0		1.008
OH^-(*aq*)	−230.0	−157.24	−10.9		17.01
Oxygen					
O_2(*g*)	0	0	205.2	29.4	31.999
O(*g*)	249.2	231.7	161.1	21.9	15.999
O_3(*g*)	142.7	163.2	238.9	39.2	47.998
OH(*g*)	39.0	34.22	183.7	29.9	17.01
OH^-(*aq*)	−230.0	−157.2	−10.9		17.01

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Third Law of Thermodynamics

The entropy of any perfect crystalline substance

approaches 0 as T→ 0K

S=k ln W

for perfectly ordered crystalline substance
W → 1 as T→ 0K ⇒ S → 0

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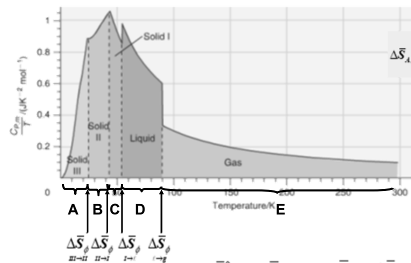
to calculate absolute entropy from measurements
(E&R$_{4th}$ pp. 119-122 [101-103]$_{3rd}$, Figs 5.8-5.10)



$$\Delta \bar{S}_{A,B,C,D,E} = \int_{T_1}^{T_2} \frac{(\bar{C}_P)_{A,B,C,D,E}}{T} dT$$

$$\Delta \bar{S}_\phi = \frac{\Delta \bar{H}_\phi}{T_\phi}$$

$$\bar{S}^0_{298.15} = \bar{S}(0K) + \Delta\bar{S}_{A\,(0\to 23.66)} + \Delta\bar{S}_{\phi\,(III\to II \text{ at } 23.66K)} + \Delta\bar{S}_{B\,(23.66\to 43.76)} + \Delta\bar{S}_{\phi\,(II\to I \text{ at } 43.76K)}$$
$$+ \Delta\bar{S}_{C\,(43.76\to 54.39)} + \Delta\bar{S}_{\phi\,(I\to\ell \text{ at } 54.39K)} + \Delta\bar{S}_{D\,(54.39\to 90.20)} + \Delta\bar{S}_{\phi\,(\ell\to g \text{ at } 90.20K)} + \Delta\bar{S}_{E\,(90.20\to 298.15)}$$

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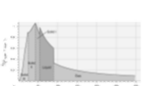
full calculation of S^o_{298} for O_2 (g) (Example Problem 5.7,p123$_{4th}$ [5.9, E&R pp103-104]$_{3rd}$)



	$\Delta\bar{S}$ J K^{-1} mol^{-1}
$\bar{S}(0K)$	0
$\Delta\bar{S}_A(0\to 23.66)$	8.182 (1.534+6.649)
$\Delta\bar{S}_\phi(\text{III}\to\text{II at } 23.66\text{K})$	3.964
$\Delta\bar{S}_B(23.66\to 43.76)$	19.61
$\Delta\bar{S}_\phi(\text{II}\to\text{I at } 43.76\text{K})$	16.98
$\Delta\bar{S}_C(43.76\to 54.39)$	10.13
$\Delta\bar{S}_\phi(\text{I}\to\ell \text{ at } 54.39\text{K})$	8.181
$\Delta\bar{S}_D(54.39\to 90.20)$	27.06
$\Delta\bar{S}_\phi(\ell\to g \text{ at } 90.20\text{K})$	75.59
$\Delta\bar{S}_E(90.20\to 298.15)$	35.27
total	**204.9 J K^{-1} mol^{-1}**

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$\Delta S_{reaction}$ from absolute entropies

n_AA + n_BB → n_CC + n_DD at 298K

$$\Delta S_{reaction} = n_C\left(\bar{S}^0_{298}\right)_C + n_D\left(\bar{S}^0_{298}\right)_D - n_A\left(\bar{S}^0_{298}\right)_A - n_B\left(\bar{S}^0_{298}\right)_B$$

$$\Delta S^0_{reaction}(298K) = \sum_i \nu_i\left(\bar{S}^0_{298}\right)_i$$

$\left(\bar{S}^0_{298}\right)_i$ are 3rd Law entropies (e.g. Appendix A)

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Third Law and Entropy of Mixing
(ideal gas, distinguishable molecules)

qualitative factors affecting molecular entropy

- **Higher T ⇒ ______** $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} > 0$
- **Higher P ⇒ ______** $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P < 0$
- **Phase S(g) ___ S(ℓ) ___ S(s)** (usually)

(in a reaction the side (reactants vs products) with the greater number of moles of gas generally has higher S
$\Delta n_{gas}>0$ ➔ $\Delta S_{reaction}$ ___ ; $\Delta n_{gas}<0$ ➔ $\Delta S_{reaction}$ ___)

- **Mixing or dissolving of components**
  (ℓ+ℓ), (s+s), (ℓ+s), (g+g) solutions
  ⇒ ______
- **(g + ℓ) or (g + s) solution ⇒ ______**

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qualitative factors affecting molecular entropy

- **Higher T ⇒ Higher S** $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} > 0$
- **Higher P ⇒ Lower S** $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P < 0$
- **Phase S(g) > S(ℓ) > S(s)**

(in a reaction the side (reactants vs products) with the greater number of moles of gas generally has higher S
$\Delta n_{gas}>0$ ➔ $\Delta S_{reaction} > 0$; $\Delta n_{gas}<0$ ➔ $\Delta S_{reaction} < 0$)

- **Mixing or dissolving of components**
  (ℓ+ℓ), (s+s), (ℓ+s), (g+g) solutions
  ⇒ Higher S
- **(g + ℓ) or (g + s) solution ⇒ Lower S**

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more qualitative factors affecting molecular entropy

- **substances with higher mass have ______**

	F_2 (g)	<	Cl_2(g)	<	Br_2(g)	<	I_2(g)	
S^o_{298}	202.78		223.07		245.46		260.69	$J\,K^{-1}mol^{-1}$

(more closely spaced rotational and vibrational levels)

- **more rigid substances have ______**

	C(gr)	C(dia)	
S^o_{298}	5.74	2.377	$J\,K^{-1}mol^{-1}$

- **more complex substances have ______**

	HF (g)	H_2O (g)	D_2O(g)	
MW	20	18	20	amu
S^o_{298}	173.78	188.83	198.34	$J\,K^{-1}mol^{-1}$

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more qualitative factors affecting molecular entropy

- **substances with higher mass have higher S**

	F_2 (g)	<	Cl_2(g)	<	Br_2(g)	<	I_2(g)	
S^o_{298}	202.78		223.07		245.46		260.69	$J\,K^{-1}mol^{-1}$

(more closely spaced rotational and vibrational levels)

- **more rigid substances have lower S**

	C(gr)	C(dia)	
S^o_{298}	5.74	2.377	$J\,K^{-1}mol^{-1}$

- **more complex substances have higher S**

	HF (g)	H_2O (g)	D_2O(g)	
MW	20	18	20	amu
S^o_{298}	173.78	188.83	198.34	$J\,K^{-1}mol^{-1}$

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calculating entropy <u>(see summary on review handout)</u> ➡

- Thermal properties of entropy and entropy calculations
  - ✓ $dS = \frac{đq_{rev}}{T}$; $\Delta S = \int \frac{đq_{rev}}{T}$; $\oint \frac{đq_{rev}}{T} = 0$
  - ✓ $\Delta S \geq \int \frac{đq}{T}$; $0 \geq \oint \frac{đq}{T}$; (= *for reversible process*; > *for spontaneous ['real'] process*)
  - ✓ $\Delta S_{total\,universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$
  - ✓ S is a state function; dS is an exact differential
  - Dependence of S on
    - ✓ T: $\left(\frac{\partial \bar{S}}{\partial T}\right)_V = \frac{\bar{C}_V}{T}$; $\left(\frac{\partial \bar{S}}{\partial T}\right)_P = \frac{\bar{C}_P}{T}$
    - ✓ P: $\left(\frac{\partial \bar{S}}{\partial P}\right)_T = -\left(\frac{\partial \bar{V}}{\partial T}\right)_P$
    - ✓ V: $\left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
    - ✓ Phase: $\Delta S = \frac{\Delta H_{equilibrium\ phase\ change}}{T_{equilibrium\ phase\ change}}$
  - ✓ Calculation of entropy changes for changes in P, V, T, phase
  - ✓ Third Law and calculations using Third Law Entropies: $\bar{S}^o(T)$
  - $\Delta S^o_{reaction}(T) = \sum_i \nu_i \bar{S}^o_i(T)$
  - Entropy of mixing: $\Delta S = -n_{total} R \sum_i X_i \ln X_i$ *where* $X_i = \frac{n_i}{n_{total}}$

> *from lecture on 2nd Law and probability (disorder)*
>
> (*something special about* $\frac{đq_{rev}}{T}$)
> - Disorder, **W**, did not change during an adiabatic reversible expansion (q_{rev} =0)
> - Disorder, **W**, increased in isothermal reversible expansion (q_{rev} >0)
> - Disorder, **W**, increased with T increase (q>0)
> - Disorder, **W**, decreased with T decrease (q<0)
> - As T → 0, **W** → 1
>
> **Lecture 8, slide 32** 3

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HW#5 Prob 31

31.
a. Prove, in general (but $đw_{other} = 0$; $dn = 0$), the relationship in equation 3.15 E&R4th)

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

Lecture 5 slide 19 *"derive ~~later~~" now*

b. Evaluate $\left(\frac{\partial U}{\partial V}\right)_T$ for an ideal gas.
c. Evaluate $\left(\frac{\partial \bar{U}}{\partial \bar{V}}\right)_T$ for a Van der Waals gas $\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT$
d. Interpret your (correct!) results for parts (b) and (c).
e. Prove, in general (but $đw_{other} = 0$; $dn = 0$), the relationship in equation 3.40 E&R4th:

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

analogous to 31a

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the relationships

definitions:

- U ≡ internal energy
- H ≡ U + PV
- A ≡ U –TS
- G ≡ H –TS

differentials of state functions:

- dU= TdS–PdV
- dH= TdS+VdP
- dA= –SdT–PdV
- dG= –SdT+VdP

heat and temperature:

$$đq_V = n\bar{C}_V\, dT \qquad đq_P = n\bar{C}_P\, dT$$

$$dU = đq + đw = đq - PdV$$

$$dS = \frac{đq_{rev}}{T} \qquad dq = Tds$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{n\bar{C}_V}{T} \qquad \left(\frac{\partial S}{\partial T}\right)_P = \frac{n\bar{C}_P}{T}$$

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do some examples:

HW#5 Prob 31a: (and Mid1 2b)
derive E&R$_{4th}$ equation 3.15 'LATER is NOW'

$$\left(\frac{\partial U}{\partial V}\right)_T = ???$$

in terms of P, V, T and their derivatives

technique applies to HW#5 Prob: 31e as well

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do another example:

One mole of CO_2(g) is expanded isothermally and reversibly from V_1 to V_2 .Using the van der Waals equation of state

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

to describe CO_2(g) calculate w, ΔU, q, and ΔS in terms of V_1 and V_2 and the van der Waals constants a and b.

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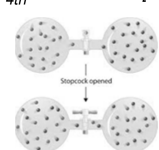
Entropy of Mixing of Distinguishable Ideal Gasses

(EXTRA *but not OPTIONAL*)

E&R$_{4th}$ ≈ Sec 6.5 *[6.6]$_{3rd}$*



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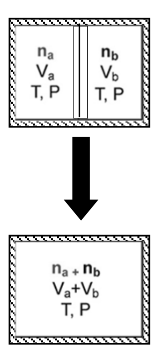
Entropy of mixing for ideal gas (distinguishable particles)

- **isolated from surroundings**
  q_{sys}= q_{surr} =0
  w=0
- **ΔS_{surr}=0**
- **$\Delta S_{universe}$>0**
- **ΔS_{sys}>0 = ???**



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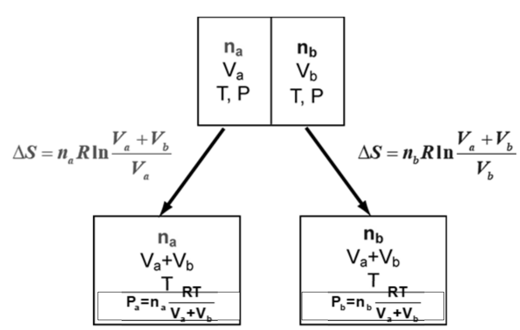
***reversible** isothermal expansion to total volume* $\Delta S = nR\ln\frac{V_{final}}{V_{initial}}$



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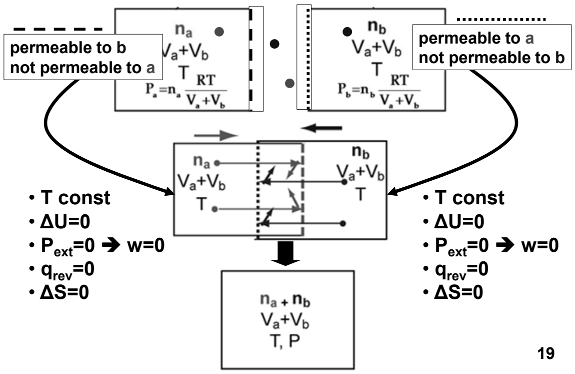
reversible *recombining of volumes*



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some arithmetic

note 'flip' leads to *−ln*

$$\Delta S_{total} = n_a R \ln \frac{V_a+V_b}{V_a} + n_b R \ln \frac{V_a+V_b}{V_b}$$

(only isothermal expansion steps contribute)

note 'flip' leads to *−ln*

$$\textit{partial pressure}: \; P_i = \frac{n_i}{n_{total}} P_{total} \qquad \textit{mole fraction}: \; X_i = \frac{n_i}{n_{total}}$$

$$\textit{ideal gas: at start} \; PV_a = n_a RT \; ; \; PV_b = n_b RT$$ ← divide

$$\textit{at end} \; P(V_a+V_b) = (n_a+n_b)RT$$ ← by

$$\frac{V_a}{V_a+V_b} = \frac{n_a}{n_a+n_b} = X_a \qquad \frac{V_b}{V_a+V_b} = \frac{n_b}{n_a+n_b} = X_b$$

$$\Delta S = -n_a R \ln X_a - n_b R \ln X_b$$

and per mole

$$\frac{\Delta S}{n_{total}} = \Delta \bar{S} = -X_a R \ln X_a - X_b R \ln X_b$$

$$\Delta \bar{S}_{mixing} = -R \sum_i X_i \ln X_i$$

$$\Delta S_{mixing} = -n_{total} R \sum_i X_i \ln X_i$$

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calculating entropy ***(see summary on review handout)*** ➡

- Thermal properties of entropy and entropy calculations
  - ✓ $dS = \frac{đq_{rev}}{T}$; $\Delta S = \int \frac{đq_{rev}}{T}$; $\oint \frac{đq_{rev}}{T} = 0$
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  - ✓ Dependence of S on
    - ✓ T: $\left(\frac{\partial \bar{S}}{\partial T}\right)_V = \frac{\bar{C}_V}{T}$; $\left(\frac{\partial \bar{S}}{\partial T}\right)_P = \frac{\bar{C}_P}{T}$
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  - ✓ Entropy of mixing: $\Delta S = -n_{total} R \sum_i X_i \ln X_i \quad \textit{where } X_i = \frac{n_i}{n_{total}}$

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What formulas I have to memorize for midterm and final ?


Relationships FOR MIDTERM #2 CHEMISTRY 163B

definitions for U, H, A, and G (student fills in at exam time):

total differentials for: dU, dH, dA, and dG (student fills in at exam time):

For reversible adiabatic path, ideal gas:
- (adiabatic reversible path)
- (adiabatic reversible path, PV^γ = constant)
- (adiabatic reversible path)

Energy and enthalpy:

For ideal gas:
- $\bar{C}_V = \frac{3}{2}R$ (monatomic ideal gas)

For ideal, reversible, Carnot Engine:

Some entropy relationships:
- (where X_i is mole fraction component i)

[see reverse side for more relationships]

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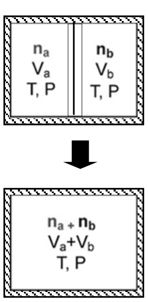
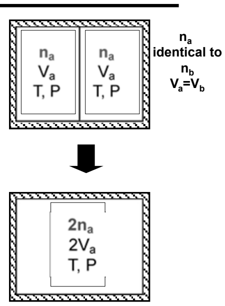
Gibb's Paradox: distinguishable vs identical (don't fret)



$n_a = n_b$
$V_a = V_b$

$$\Delta S_{total} = 2 n_a R \ln 2$$



$$\Delta S_{total} = n_a R \ln \frac{V_a+V_b}{V_a} + n_b R \ln \frac{V_a+V_b}{V_b}$$

CORRECT

$$\Delta S_{total} = 0$$

CORRECT TOO

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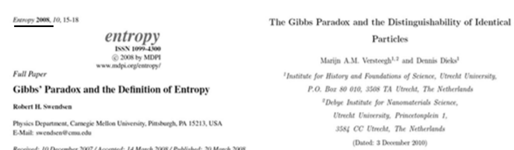
Gibb's Paradox: distinguishable vs identical (don't fret)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Full Paper

Gibbs' Paradox and the Definition of Entropy

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The Gibbs Paradox and the Distinguishability of Identical Particles

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(Dated: 3 December 2010)

statistics, Chemistry 163C

Some references:

www.mdpi.org/lin/entropy/Chua-Thermodynamics.ppt
http://bayes.wustl.edu/etj/articles/gibbs.paradox.pdf
http://www.nyu.edu/classes/tuckerman/stat.mech/lectures/lecture_6/node5.html
http://www.jstor.org/stable/186086

24

where we have been

and

what's next

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observations: thermo ≡ heat

- Count Rumford, 1799
- observed water turning into steam when canon barrel was bored
- *work ⇔ heat*

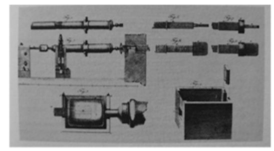
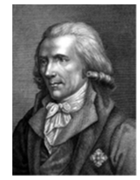


FIGURE 11. An illustration from Rumford's paper, "An Inquiry Concerning the Source of the Heat Which is Excited by Friction," showing the apparatus used by him in the cannon boring experiment. Figure 1, upper left, shows the cannon as received from the foundry, and Figure 2, below, shows it mounted in the machine used for boring. (Reproduced with the permission of Harvard University Press.)



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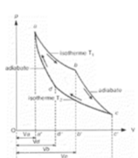
observations: mechanical efficiency of steam engine

- Sadi Carnot, 1824
- efficiency of engines

REFLEXIONS
SUR LA
PUISSANCE MOTRICE
DU FEU
ET
SUR LES MACHINES
PAR S. CARNOT,
A PARIS,



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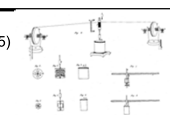
guiding principles

- Conservation of heat and work (Joule, 1845)
  1st LAW OF THERMODYNAMICS



Joule's original water-friction apparatus for determining the mechanical equivalent of heat. (Crown copyright, Science Museum, London.)

- Clausius, 1860 Entropy
  2nd LAW OF THERMODYNAMICS
- Boltzmann, late 19th century,
  molecular picture of entropy

Clausius

Boltzmann

the thermodynamic functions U, H, and S
(1st and 2nd laws)

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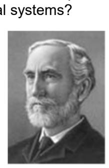
"Applications"

How does knowledge about efficiencies of steam engines, mechanical systems, etc, relate to processes in chemical, biological, and geological systems?

ANSWERED BY:



J. W. Gibbs- arguably the frist great American scientist who combined the concepts of heat and entropy and proposed "[Gibbs] Free Energy", **G**, a thermodynamic state function that leads to a whole spectrum of applications

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End of Lecture

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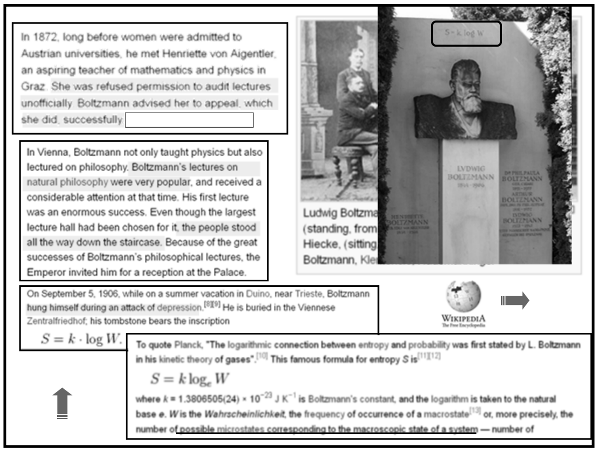
In 1872, long before women were admitted to Austrian universities, he met Henriette von Aigentler, an aspiring teacher of mathematics and physics in Graz. She was refused permission to audit lectures unofficially. Boltzmann advised her to appeal, which she did, successfully.
In Vienna, Boltzmann not only taught physics but also lectured on philosophy. Boltzmann's lectures on natural philosophy were very popular, and received a considerable attention at that time. His first lecture was an enormous success. Even though the largest lecture hall had been chosen for it, the people stood all the way down the staircase. Because of the great successes of Boltzmann's philosophical lectures, the Emperor invited him for a reception at the Palace.
Ludwig Boltzma
(standing, from
Hiecke, (sitting
Boltzmann, Kle
LVDWIG
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On September 5, 1906, while on a summer vacation in Duino, near Trieste, Boltzmann hung himself during an attack of depression.[8][9] He is buried in the Viennese Zentralfriedhof; his tombstone bears the inscription
$S = k \cdot \log W.$
To quote Planck, "The logarithmic connection between entropy and probability was first stated by L. Boltzmann in his kinetic theory of gases".[10] This famous formula for entropy S is[11][12]
$S = k \log_e W$
where $k = 1.3806505(24) \times 10^{-23}$ J K^{-1} is Boltzmann's constant, and the logarithm is taken to the natural base e. W is the *Wahrscheinlichkeit*, the frequency of occurrence of a macrostate[13] or, more precisely, the number of possible microstates corresponding to the macroscopic state of a system — number of