

Chemistry 163B Winter 2014  
Handouts for Third Law and Entropy of Mixing  
(ideal gas, distinguishable molecules)

Chemistry 163B  
Absolute Entropies  
and  
Entropy of Mixing

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**APPENDIX A:  $\Delta H_f^\circ$ ,  $\Delta G_f^\circ$ , BUT  $S^\circ$  (no  $\Delta$ , no "sub f")**


Substance	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G_f^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$C_{p,m}$ (J mol <sup>-1</sup> K <sup>-1</sup> )	Atom or Molecular Weight (amu)
<b>Carbon</b>					
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
<b>Hydrogen</b>					
H <sub>2</sub> (g)	0	0	130.7	28.8	2.016
H <sub>2</sub> O(g)	-241.8	-228.6	188.8	33.6	18.015
H <sub>2</sub> O(l)	-285.8	-237.1	70.0	75.3	18.015
H <sub>2</sub> O(s)	-329.1	-235.1	35.7	36.2 (273 K)	18.015
H <sub>2</sub> O <sub>2</sub> (g)	-136.3	-105.6	232.7	43.1	34.015
H <sub>2</sub> O <sub>2</sub> (l)	-187.8	-120.4	109.9	75.3	34.015
<b>Oxygen</b>					
O <sub>2</sub> (g)	0	0	205.2	29.4	31.999
O <sub>3</sub> (g)	142.7	163.2	238.9	39.2	47.998
OH <sup>-</sup> (aq)	-230.0	-157.2	-10.9	29.9	17.01

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**Third Law of Thermodynamics**

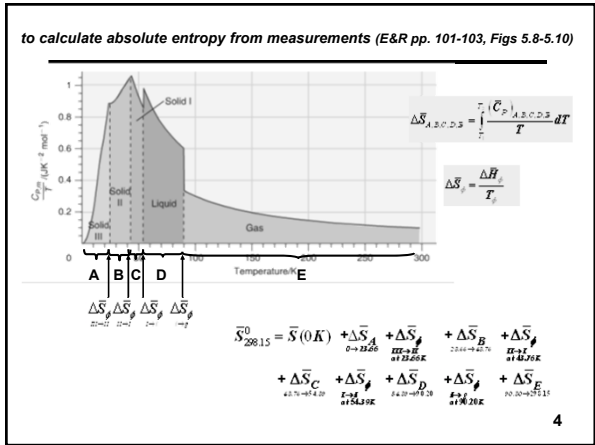
The entropy of any perfect crystalline substance  
approaches 0 as T → 0K

$S = k \ln W$



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

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full calculation of  $S_{298}^\circ$  for O<sub>2</sub>(g) (Example Problem 5.9, E&R pp103-104)

	$\Delta \bar{S}^\circ$ J K <sup>-1</sup> mol <sup>-1</sup>
$\bar{S}^\circ(0K)$	0
$\Delta \bar{S}_A^\circ(0 \rightarrow 23.66)$	8.182
$\Delta \bar{S}_B^\circ(III \rightarrow II \text{ at } 23.66K)$	3.964
$\Delta \bar{S}_C^\circ(23.66 \rightarrow 43.76)$	19.61
$\Delta \bar{S}_D^\circ(II \rightarrow I \text{ at } 43.76K)$	16.98
$\Delta \bar{S}_E^\circ(43.76 \rightarrow 54.39)$	10.13
$\Delta \bar{S}_F^\circ(I \rightarrow \ell \text{ at } 54.39K)$	8.181
$\Delta \bar{S}_G^\circ(54.39 \rightarrow 90.20)$	27.06
$\Delta \bar{S}_H^\circ(\ell \rightarrow g \text{ at } 90.20K)$	75.59
$\Delta \bar{S}_I^\circ(90.20 \rightarrow 298.15)$	35.27
<b>total</b>	<b>204.9 J K<sup>-1</sup> mol<sup>-1</sup></b>

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$\Delta S_{\text{reaction}}$  from absolute entropies

$n_A A + n_B B \rightarrow n_C C + n_D D$  at 298K

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

$\Delta S_{\text{reaction}}^\circ(298K) = \sum_i \nu_i (\bar{S}_{298}^\circ)_i$

$(\bar{S}_{298}^\circ)_i$  are 3<sup>rd</sup> Law entropies (e.g. Appendix A)

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# Chemistry 163B Winter 2014

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

**qualitative factors affecting molecular entropy**

- Higher  $T \Rightarrow \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} > 0$
- Higher  $P \Rightarrow \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P < 0$   
usually
- Phase **S(g) vs S(l) vs S(s)**  
*(in a reaction the side (reactants vs products) with the greater number of moles of gas generally has higher S)*  
 $\Delta n_{\text{gas}} > 0 \Rightarrow \Delta S_{\text{reaction}} > 0$     $\Delta n_{\text{gas}} < 0 \Rightarrow \Delta S_{\text{reaction}} < 0$
- Mixing or dissolving of components  
(l+s), (s+s), (l+s), (g+g) solutions  
 $\Rightarrow$
- (g + l) or (g + s) solution  $\Rightarrow$

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**more qualitative factors affecting molecular entropy**

- substances with higher mass have  $S^\circ_{298}$   

$F_2(g)$	$Cl_2(g)$	$Br_2(g)$	$I_2(g)$
202.78	223.07	245.46	260.69

*(more closely spaced rotational and vibrational levels)*
- more rigid substances have  $S^\circ_{298}$   

C(gr)	C(dia)
5.74	2.377

*J K<sup>-1</sup> mol<sup>-1</sup>*
- more complex substances have  $S^\circ_{298}$   

HF (g)	H <sub>2</sub> O (g)	D <sub>2</sub> O (g)
20	18	20
MW		amu
S <sup>o</sup> <sub>298</sub>	173.78	188.83
		198.34

*J K<sup>-1</sup> mol<sup>-1</sup>*

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

- Thermal properties of entropy and entropy calculations
- $dS = \frac{\delta q_{\text{rev}}}{T}$ ;  $\Delta S = \int \frac{\delta q_{\text{rev}}}{T}$ ;  $\oint \frac{\delta q_{\text{rev}}}{T} = 0$
- $\Delta S \geq \int \frac{\delta q}{T}$ ;  $0 \geq \oint \frac{\delta q}{T}$ ; (= for reversible process; > for spontaneous [“real”] process)
- $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$
- S is a state function; dS is an exact differential
- Dependence of S on
  - T:  $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$ ;  $\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$
  - P:  $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$
  - V:  $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
- Phase:  $\Delta S = \frac{\Delta H_{\text{transition phase change}}}{T_{\text{transition phase change}}}$
- Calculation of entropy changes for changes in P, V, T, phase
- Third Law and calculations using Third Law Entropies:  $S^\circ(T)$
- $\Delta S^\circ_{\text{reaction}}(T) = \sum \nu_i S^\circ_i(T)$
- Entropy of mixing:  $\Delta S = -n_{\text{total}} R \sum_i X_i \ln X_i$  where  $X_i = \frac{n_i}{n_{\text{total}}}$

from lecture on 2<sup>nd</sup> Law and probability (disorder)

- Disorder, W, did not change during an adiabatic reversible expansion (iso-T)
- Disorder, W, increased in isothermal reversible expansion (iso-T)
- Disorder, W, increased with T increase (iso-P)
- Disorder, W, decreased with T decrease (iso-P)
- At T → 0, W → 1

**Lecture 9, slide 3**

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**HW#6 Prob 31**

31. a. Prove, in general (but if  $w_{\text{ext}} = 0$ ;  $dw = 0$ ), the relationship in equation 3.19 E&R:

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

b. Evaluate  $\left(\frac{\partial U}{\partial V}\right)_T$  for an ideal gas.

c. Evaluate  $\left(\frac{\partial U}{\partial V}\right)_T$  for a Van der Waals gas  $\left(P + \frac{a}{V^2}\right)(V-b) = RT$ .

d. Interpret your (correct) results for parts (b) and (c).

e. Prove, in general (but if  $w_{\text{ext}} = 0$ ;  $dw = 0$ ), the relationship in equation 3.44 E&R:

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

**analogous to 31a**

**Lecture 5 slide 17 “derive later” now**

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**the relationships**

<p><b>definitions:</b></p> <p>U ≡ internal energy</p> <p>H ≡ U + PV</p> <p>A ≡ U - TS</p> <p>G ≡ H - TS</p>	<p><b>differentials of state functions:</b></p> <p>dU = TdS - PdV</p> <p>dH = TdS + VdP</p> <p>dA = -SdT - PdV</p> <p>dG = -SdT + VdP</p>
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**heat and temperature:**

$\delta q_V = n \bar{C}_V dT$     $\delta q_P = n \bar{C}_P dT$

$dU = \delta q + \delta w = \delta q - PdV$

$dS = \frac{\delta q_{\text{rev}}}{T}$     $\delta q = T dS$

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

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**do some examples:**

**HW#6 Prob 31a:**  
**derive E&R equation 3.19 ‘LATER is NOW’**

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

in terms of P, V, T and their derivatives

technique applies to HW#6 Prob: 31e

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*do another example:*

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One mole of  $\text{CO}_2(\text{g})$  is expanded isothermally and reversibly from  $V_1$  to  $V_2$ . Using the van der Waals equation of state

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

to describe  $\text{CO}_2(\text{g})$  calculate  $w$ ,  $\Delta U$ ,  $q$ , and  $\Delta S$  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 Ideal Gasses

(EXTRA *but not* OPTIONAL)

*E&R*  $\approx$  Sec 6.6

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### Entropy of mixing for ideal gas (distinguishable particles)

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

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

---

$\Delta S = n_a R \ln \frac{V_a + V_b}{V_a}$

$\Delta S = n_b R \ln \frac{V_a + V_b}{V_b}$

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### reversible recombining of volumes

---

permeable to b  
not permeable to a

permeable to a  
not permeable to b

- T const
- $\Delta U = 0$
- $P_{\text{ext}} = 0 \Rightarrow w = 0$
- $q_{\text{rev}} = 0$
- $\Delta S = 0$

- T const
- $\Delta U = 0$
- $P_{\text{ext}} = 0 \Rightarrow w = 0$
- $q_{\text{rev}} = 0$
- $\Delta S = 0$

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### some arithmetic

---

note 'flip' leads to  $-\ln$  note 'flip' leads to  $-\ln$

(only isothermal expansion steps contribute)

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

ideal gas: at start  $P V_i = n_i R T$ ;  $P V_f = n_i R T$  divide by

at end  $P V_i + V_f = (n_i + n_j) R T$  ←

$$\frac{V_i}{V_i + V_f} \frac{n_i}{n_i + n_j} = X_i \quad \frac{V_j}{V_i + V_f} \frac{n_j}{n_i + n_j} = X_j$$

and per mole

$$\frac{\Delta S}{n_{\text{total}}} = \Delta S = -X_i R \ln X_i - X_j R \ln X_j$$

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

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

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# Chemistry 163B Winter 2014

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

**calculating entropy (see summary on review handout)**  $\implies$

- Thermal properties of entropy and entropy calculations
- ✓  $dS = \frac{\delta q_{rev}}{T}$ ;  $\Delta S = \int \frac{\delta q_{rev}}{T}$ ;  $\oint \frac{\delta q_{rev}}{T} = 0$
- ✓  $\Delta S \geq \int \frac{\delta q}{T}$ ;  $0 \geq \oint \frac{\delta q}{T}$  (= for reversible process; > for spontaneous [real] process)
- ✓  $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$
- ✓ S is a state function; dS is an exact differential
- ✓ Dependence of S on
  - T:  $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T}$ ;  $\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T}$
  - P:  $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$
  - V:  $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
- ✓ 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:  $S^\circ(T)$
- ✓  $\Delta S^\circ_{mix}(T) = -R \sum_i X_i \ln X_i$
- ✓ Entropy of mixing:  $\Delta S = -n_{total} R \sum_i X_i \ln X_i$  where  $X_i = \frac{n_i}{n_{total}}$

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**What formulas I have to memorize for midterm and final ?**

Relationships FOR MECHANICAL CHEMISTRY 163B  
Definitions for C, H, N, and O (values in kJ or eV as given here)

State differentials for dU, dH, dA, and dG (values in kJ or eV as given here)

For reversible adiabatic path, ideal gas

- $P V^\gamma = \text{const}$  (adiabatic reversible path,  $P V^\gamma = \text{const}$ )
- $T V^{C_p} = \text{const}$  (adiabatic reversible path,  $P V^\gamma = \text{const}$ )
- $\frac{P}{T} = \text{const}$  (adiabatic reversible path)

Energy and entropy

- $dU = C_v dT + P dV$
- $dH = C_p dT + V dP$
- $dA = -S dT - P dV + \mu dN$
- $dG = -S dT + V dP + \mu dN$

For ideal gas, internal energy

- $U = C_v n T$
- $H = C_p n T$
- $A = -k_B T \ln \Omega$
- $G = \mu N$

Some useful relationships

- $\left(\frac{\partial U}{\partial T}\right)_V = C_v$
- $\left(\frac{\partial H}{\partial T}\right)_P = C_p$
- $\left(\frac{\partial A}{\partial T}\right)_V = -S$
- $\left(\frac{\partial G}{\partial T}\right)_P = -S$


(See lecture notes for more relationships!)

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

$n_a$   
 $V_a$   
 $T, P$

$n_b$   
 $V_b$   
 $T, P$



$n_a$   
 $V_a$   
 $T, P$

$n_b$   
 $V_b$   
 $T, P$

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

$n_a$   
 $V_a$   
 $T, P$

$n_b$   
 $V_b$   
 $T, P$

$n_a = n_b$   
 $V_a = V_b$   
 $\Delta S_{total} = 0$

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

**CORRECT**

$\Delta S_{total} = 0$

**CORRECT TOO**

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

Entropy 2008, 10, 15-18

*entropy*

MDPI

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Full Paper

**Gibb's Paradox and the Definition of Entropy**

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Received: 10 December 2007 / Accepted: 14 March 2008 / Published: 20 March 2008

The Gibbs Paradox and the Distinguishability of Identical Particles

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(Email: 3 December 2008)

**statistics, Chemistry 163C**

**Some references:**


[www.mdpi.org/lin/entropy/Chua-Thermodynamics.ppt](http://www.mdpi.org/lin/entropy/Chua-Thermodynamics.ppt)

[http://haves.wustl.edu/eti/articles/gibbs\\_paradox.pdf](http://haves.wustl.edu/eti/articles/gibbs_paradox.pdf)

[http://www.nyu.edu/classes/tuckerman/stat\\_mech/lectures/lecture\\_6/node5.html](http://www.nyu.edu/classes/tuckerman/stat_mech/lectures/lecture_6/node5.html)

<http://www.istor.org/stable/186086>


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where we have been

and

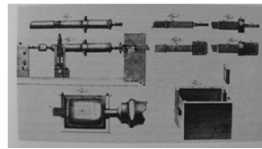
what's next



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**observations: thermo = heat**

- Count Rumford, 1799
- observed water turning into steam when canon barrel was bored
- work  $\leftrightarrow$  heat



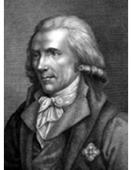


FIGURE 11. An illustration from Rumford's paper, "An Inquiry Concerning the Source of the Heat Which is Evolved by Friction," showing the apparatus used by him in the cannon boring experiment. Figure 1, upper left, shows the apparatus as received from the foundry, and Figure 2, below, shows it mounted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


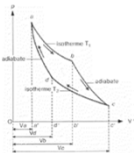

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# Chemistry 163B Winter 2014

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

**observations: mechanical efficiency of steam engine**

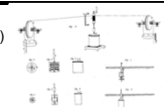


- Sadi Carnot, 1824
- efficiency of engines

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**guiding principles**

- Conservation of heat and work (Joule, 1845)  
**1st LAW OF THERMODYNAMICS**
- Clausius, 1860 Entropy  
**2nd LAW OF THERMODYNAMICS**
- Boltzmann, late 19<sup>th</sup> century,  
**molecular picture of entropy**

*Clausius*                      *Boltzmann*


**the thermodynamic functions U, H, and S  
(1<sup>st</sup> and 2<sup>nd</sup> 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 first 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 Aigentier, 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.



On September 5, 1906, while on a summer vacation in Duino, near Trieste, Boltzmann hung himself during an attack of depression.<sup>[13]</sup> 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"<sup>[14]</sup> This famous formula for entropy S is<sup>[15]</sup>[17]

$S = k \log_e W$

where  $k = 1.3806505(24) \times 10^{-23} \text{ J K}^{-1}$  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<sup>[18]</sup> or, more precisely, the number of possible microstates corresponding to the microscopic state of a system — number of

↑