Chemistry 163B
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})	$C_{P,m}$ (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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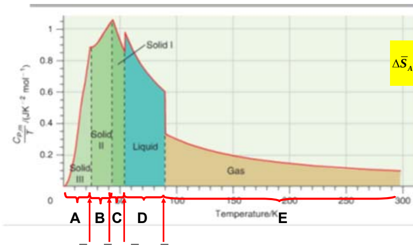
to calculate absolute entropy from measurements (E&R pp. 101-103, Figs 5.8-5.10)



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

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

$\Delta\bar{S}_{\phi}$ (III→II) $\Delta\bar{S}_{\phi}$ (II→I) $\Delta\bar{S}_{\phi}$ (I→ℓ) $\Delta\bar{S}_{\phi}$ (ℓ→g)

$$\bar{S}^0_{298.15} = \bar{S}(0K) + \Delta\bar{S}_{A\,(0\to 23.66)} + \Delta\bar{S}_{\phi\,(III\to II \text{ at } 23.66K)} + \Delta\bar{S}_{B\,(23.66\to 43.76)} + \Delta\bar{S}_{\phi\,(II\to I \text{ at } 43.76K)}$$
$$+ \Delta\bar{S}_{C\,(43.76\to 54.39)} + \Delta\bar{S}_{\phi\,(I\to \ell \text{ at } 54.39K)} + \Delta\bar{S}_{D\,(54.39\to 90.20)} + \Delta\bar{S}_{\phi\,(\ell\to g \text{ at } 90.20K)} + \Delta\bar{S}_{E\,(90.30\to 298.15)}$$

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full calculation of S^o_{298} for O_2 (g) (Example Problem 5.9, E&R pp103-104 [96-97]$_{2nd}$)

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

$n_A A + n_B B \longrightarrow n_C C + n_D D$ 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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Chemistry 163B Winter 2012
Handouts for 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 ⇒** $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P < 0$ *usually*
- **Phase S(g) vs S(ℓ) vs S(s)**
  (in a reaction the side with the greater number of moles of gas generally has higher S)
- **Mixing or dissolving of components**
  (ℓ+ℓ), (s+s), (ℓ+s), (g+g) solutions
  ⇒
- **(g + ℓ) or (g + s) solution ⇒**

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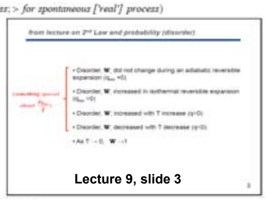
calculating entropy ***(see summary on review handout)***

- Thermal properties of entropy and entropy calculations
  - ✓ $dS = \frac{đq_{rev}}{T}$; $\Delta S = \int \frac{đq_{rev}}{T}$; $\oint \frac{đq_{rev}}{T} = 0$
  - ✓ $\Delta S \ge \int \frac{đq}{T}$; $0 \ge \oint \frac{đq}{T}$; (= for reversible process; > for spontaneous ['real'] process)
  - ✓ $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} \ge 0$
  - ✓ 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: $\bar{S}^o(T)$
  - $\Delta S^o_{rxn}(T) = \sum_i \nu_i \bar{S}^o_i(T)$
  - Entropy of mixing: $\Delta S = -n_{total} R \sum_i X_i \ln X_i$ where $X_i = \frac{n_i}{n_{total}}$



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HW#5 Prob 31

31.
a. Prove, in general (but $đw_{other} = 0$; $dn = 0$), the relationship in equation 3.19 E&R)

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

Sample midterm 3a

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

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

e. Prove, in general (but $đw_{other} = 0$; $dn = 0$), the relationship in equation 3.44 E&R:

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

analogous to 31a

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the relationships

definitions:	**differentials of state functions:**
U ≡ internal energy	dU= TdS–PdV
H ≡ U + PV	dH= TdS+VdP
A ≡ U –TS	dA= –SdT–PdV
G ≡ H –TS	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:
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:

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 Ideal Gasses

(EXTRA)

E&R ≈ Sec 6.6

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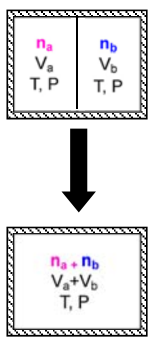
Entropy of mixing for ideal gas (distinguishable particles)

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



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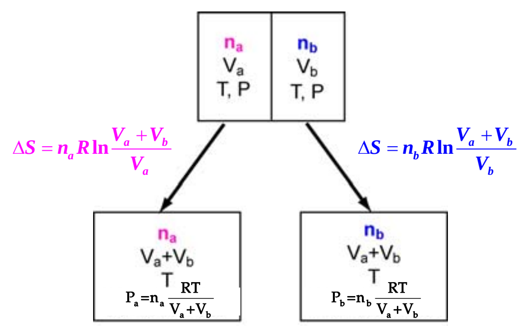
reversible *isothermal expansion to total volume* $\Delta S = nR\ln\frac{V_{final}}{V_{initial}}$



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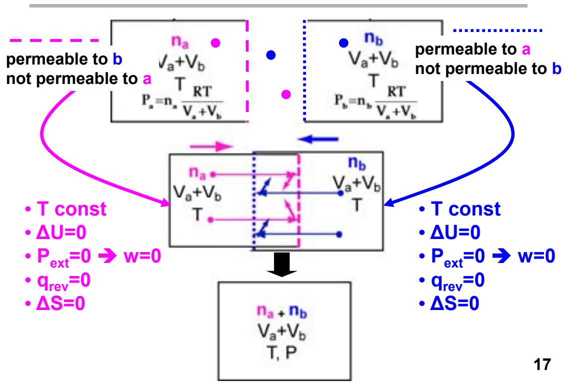
reversible *recombining of volumes*



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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*

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

$$ideal\ gas:\ at\ \ start\ PV_a=n_aRT\ ;\ \ PV_b=n_bRT$$
$$at\ \ end\ \ P(V_a+V_b)=(n_a+n_b)RT$$

← divide
← 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

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

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

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Chemistry 163B Winter 2012
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calculating entropy *[(see summary on review handout)]*

- Thermal properties of entropy and entropy calculations
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What formulas I have to memorize for midterm and final ?

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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

⬇

$n_a + n_b$, $V_a + V_b$, T, P

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

CORRECT

$n_a = n_b$, $V_a = V_b$

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

n_a, V_a, T, P | n_a, V_a, T, P

n_a identical to n_b, $V_a = V_b$

⬇

$2n_a$, $2V_a$, T, P

$\Delta S_{total} = 0$

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]

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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* ⇔ *heat*

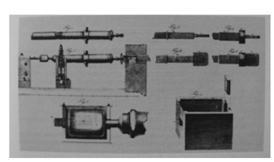

FIGURE 11. An illustration from Rumford's paper, "An Inquiry Concerning the Source of the Heat Which is Excited by Friction," showing the apparatus used by him in the cannon boring experiment. Figure 1, upper left, shows the cannon as received from the foundry, and Figure 2, below, shows it mounted in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

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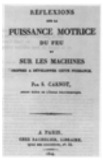
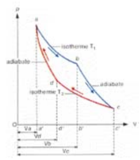
Chemistry 163B Winter 2012
Handouts for Third Law and Entropy of Mixing
(ideal gas, distinguishable molecules)

observations: mechanical efficiency of steam engine

- Sadi Carnot, 1824
- efficiency of engines





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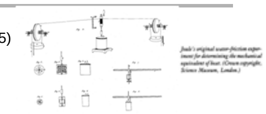
guiding principles

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



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

Clausius

Boltzmann

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

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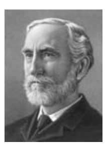
"Applications"

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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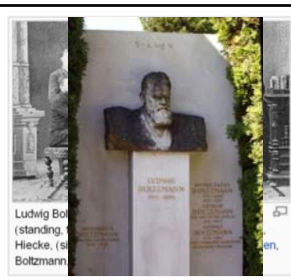
In 1872, long before women were admitted to Austrian universities, he met Henriette von Aigentler, an aspiring teacher of mathematics and physics in Graz. She was refused permission to audit lectures unofficially. Boltzmann advised her to appeal, which she did, successfully.

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.



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