

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

1

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


Substance	ΔH_f° ΔH_f° (kJ mol ⁻¹)	ΔG_f° ΔG_f° (kJ mol ⁻¹)	S° S° (J mol ⁻¹ K ⁻¹)	$C_{p,m}$ $C_{p,m}$ (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 ₂ O(g)	-241.8	-228.6	188.8	33.6	18.015
H ₂ O(l)	-285.8	-237.1	70.0	75.3	18.015
H ₂ O(s)	-285.8	-237.1	48.0	36.2 (273 K)	18.015
H ₂ O ₂ (g)	-136.3	-105.6	232.7	43.1	34.015
H ⁺ (aq)	0	0	0	1.008	1.008
OH ⁻ (aq)	-230.0	-157.24	-10.9	17.01	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	17.01

2

Third Law of Thermodynamics

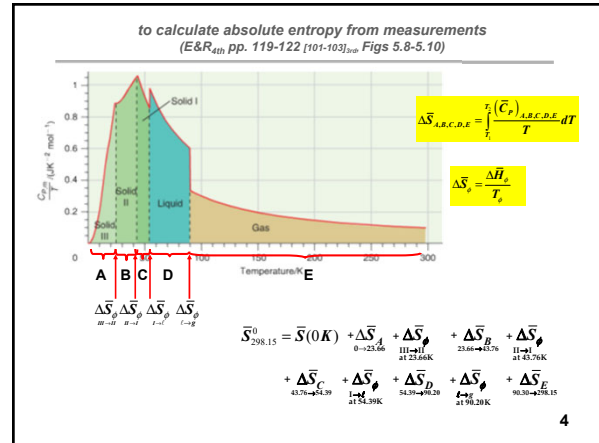
The entropy of any perfect crystalline substance
approaches 0 as T → 0K

S = k ln W

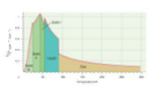


for perfectly ordered crystalline substance
W → 1 as T → 0K ⇒ S → 0

3



full calculation of S°_{298} for O₂(g) (Example Problem 5.7, p123_{4th} (5.9, E&R pp103-104), rd)



	$\Delta\bar{S}^\circ$ J K ⁻¹ mol ⁻¹
$\bar{S}^\circ(0K)$	0
$\Delta\bar{S}^\circ_i(0 \rightarrow 23.66)$	8.182 (1.534+6.649)
$\Delta\bar{S}^\circ_p(\text{III} \rightarrow \text{II} \text{ at } 23.66K)$	3.964
$\Delta\bar{S}^\circ_p(23.66 \rightarrow 43.76)$	19.61
$\Delta\bar{S}^\circ_p(\text{II} \rightarrow \text{I} \text{ at } 43.76K)$	16.98
$\Delta\bar{S}^\circ_c(43.76 \rightarrow 54.39)$	10.13
$\Delta\bar{S}^\circ_p(\text{I} \rightarrow \ell \text{ at } 54.39K)$	8.181
$\Delta\bar{S}^\circ_p(54.39 \rightarrow 90.20)$	27.06
$\Delta\bar{S}^\circ_p(\ell \rightarrow g \text{ at } 90.20K)$	75.59
$\Delta\bar{S}^\circ_g(90.20 \rightarrow 298.15)$	35.27
total	204.9 J K⁻¹ mol⁻¹

5

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

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

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

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

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

6

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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+l), (s+s), (l+s), (g+g) solutions \Rightarrow
- (g + l) or (g + s) solution \Rightarrow

7

qualitative factors affecting molecular entropy

- Higher T \Rightarrow Higher S $\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} > 0$
- Higher P \Rightarrow 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
 $\Delta n_{\text{gas}} > 0 \Rightarrow \Delta S_{\text{reaction}} > 0$; $\Delta n_{\text{gas}} < 0 \Rightarrow \Delta S_{\text{reaction}} < 0$)
- Mixing or dissolving of components (l+l), (s+s), (l+s), (g+g) solutions \Rightarrow Higher S
- (g + l) or (g + s) solution \Rightarrow Lower S

8

more qualitative factors affecting molecular entropy

- substances with higher mass
 $F_2(g) < Cl_2(g) < Br_2(g) < I_2(g)$
 S_{298}° 202.78 223.07 245.46 260.69 J K⁻¹mol⁻¹
(more closely spaced rotational and vibrational levels)
- more rigid substances have
C(gr) C(dia)
 S_{298}° 5.74 2.377 J K⁻¹mol⁻¹
- more complex substances have
HF(g) H₂O(g) D₂O(g)
MW 20 18 20 amu
 S_{298}° 173.78 188.83 198.34 J K⁻¹mol⁻¹

9

more qualitative factors affecting molecular entropy

- substances with higher mass have higher S
 $F_2(g) < Cl_2(g) < Br_2(g) < I_2(g)$
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MW 20 18 20 amu
 S_{298}° 173.78 188.83 198.34 J K⁻¹mol⁻¹

10

calculating entropy (see summary on review handout)

- Thermal properties of entropy and entropy calculations
- $ds = \frac{\delta q_{\text{rev}}}{T}$; $\Delta S = \int \frac{\delta q_{\text{rev}}}{T}$; $\oint \frac{\delta q_{\text{rev}}}{T} = 0$
- $\Delta S \geq \int \frac{\delta q}{T}$; $0 \geq \int \frac{\delta q}{T}$; (= 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: $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_p$
- Phase: $\Delta S = \frac{\Delta H_{\text{transition}}}{T_{\text{equilibrium phase change}}}$
- Calculation of entropy changes for changes in P, V, T, phase
- Third Law and calculations using Third Law Entropies: $S^\circ(T)$
- $\Delta S_{\text{mix}}^\circ(T) = -R \sum_i X_i \ln X_i$ where $X_i = \frac{n_i}{n_{\text{total}}}$
- 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 2nd Law and probability (disorder)

- Disorder, W, did not change during an adiabatic reversible expansion ($\Delta S_{\text{rev}} = 0$)
- Disorder, W, increased in isothermal reversible expansion ($\Delta S_{\text{rev}} > 0$)
- Disorder, W, increased with T increase ($\Delta S > 0$)
- Disorder, W, decreased with T decrease ($\Delta S < 0$)
- As T \rightarrow 0, W \rightarrow 1

Lecture 8, slide 32

11

HW#5 Prob 31

31.

- Prove, in general (but $\delta w_{\text{other}} = 0$; $dn = 0$), the relationship in equation 3.15 E&R_{th}:
 $\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_p - P$
- Evaluate $\left(\frac{\partial U}{\partial V}\right)_T$ for an ideal gas.
- Evaluate $\left(\frac{\partial U}{\partial V}\right)_T$ for a Van der Waals gas $\left(P + \frac{a}{V^2}\right)(V-b) = RT$
- Interpret your (correct) results for parts (b) and (c).
- Prove, in general (but $\delta w_{\text{other}} = 0$; $dn = 0$), the relationship in equation 3.40 E&R_{th}:
 $\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_p$ **analogous to 31a**

Lecture 5 slide 19 "derive later" now

12

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

the relationships

definitions:	differentials of state functions:
$U \equiv$ internal energy	$dU = TdS - PdV$
$H \equiv U + PV$	$dH = TdS + VdP$
$A \equiv U - TS$	$dA = -SdT - PdV$
$G \equiv H - TS$	$dG = -SdT + VdP$

heat and temperature:

$$\bar{dq}_v = n\bar{C}_v dT \quad \bar{dq}_p = n\bar{C}_p dT$$

$$dU = \bar{dq} + \bar{dw} = \bar{dq} - PdV$$

$$dS = \frac{\bar{dq}_{rev}}{T} \quad dq = Tds$$

$$\left(\frac{\partial S}{\partial T}\right)_v = \frac{n\bar{C}_v}{T} \quad \left(\frac{\partial S}{\partial T}\right)_p = \frac{n\bar{C}_p}{T}$$

13

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

14

do another example:

One mole of CO₂(g) is expanded isothermally and reversibly from V₁ to V₂. Using the van der Waals equation of state

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

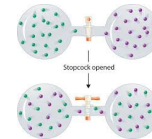
to describe CO₂(g) calculate w, ΔU, q, and ΔS in terms of V₁ and V₂ and the van der Waals constants a and b.

15

Entropy of Mixing of Distinguishable Ideal Gasses

(EXTRA but not OPTIONAL)

$$E\&R_{4th} \approx \text{Sec 6.5 [6.6]}_{3rd}$$

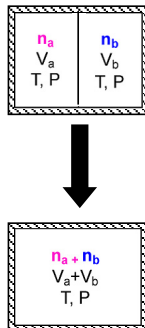


16

Entropy of mixing for ideal gas (distinguishable particles)

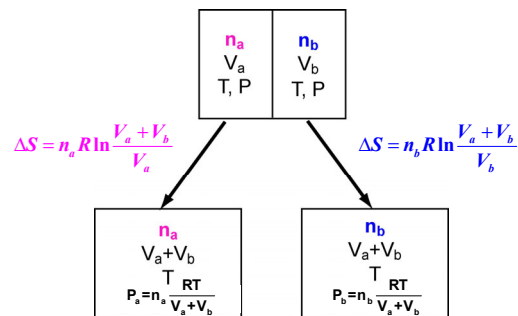
- isolated from surroundings
- $q_{sys} = q_{surr} = 0$
- $w = 0$

- $\Delta S_{surr} = 0$
- $\Delta S_{universe} > 0$
- $\Delta S_{sys} > 0 = ???$



17

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



18

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

reversible recombining of volumes

permeable to b
not permeable to a

permeable to a
not permeable to b

• T const
• ΔU=0
• P_{ext}=0 → w=0
• q_{rev}=0
• ΔS=0

• T const
• ΔU=0
• P_{ext}=0 → w=0
• q_{rev}=0
• ΔS=0

19

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)

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

ideal gas: at start $P V_a = n_a R T$; $P V_b = n_b R T$ → divide by
at end $P(V_a + V_b) = (n_a + n_b) R T$

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

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

and per mole

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

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

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

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

note 'flip' leads to -ln

20

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- 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 $X_i = \frac{n_i}{n_{total}}$

21

What formulas I have to memorize for midterm and final?

22

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

permeable to b
not permeable to a

permeable to a
not permeable to b

identical to n_b
 $V_b = V_b$

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

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

$\Delta S_{total} = 0$ **CORRECT TOO**

23

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

Entropy 2008, 10, 15-16

entropY
ISSN 1099-4300
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www.mdpi.com/entropy/

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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(Date: 3 December 2008)

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



statistics, Chemistry 163C

Some references:
www.mdpi.org/lin/entropy/Chua-Thermodynamics.pdf
http://bayes.wustl.edu/eti/articles/gibbs_paradox.pdf
http://www.nyu.edu/classes/tuckerman/stat.mech/lectures/lecture_6/node5.html
<http://www.istor.org/stable/186086>

24

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


where we have been
and
what's next


25

observations: thermo = heat

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

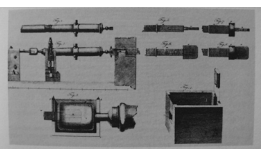
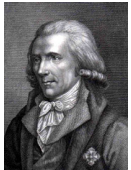

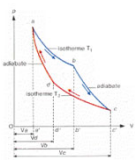




FIGURE 11. An illustration from Rumford's paper, "An Inquiry Concerning the Source of the Heat Which is Excited by Friction," showing the apparatus used by him in the cannon boring experiment. Figure 1, upper left, shows the apparatus as received from the foundry, and Figure 2, below, shows it mounted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

26

observations: mechanical efficiency of steam engine

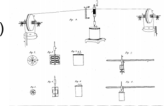


- Sadi Carnot, 1824
- efficiency of engines

27

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


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

28

"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

29

End of Lecture

30

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

<p>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.</p>	 <p>Ludwig Boltzmann (standing, from Hiecke, (sitting Boltzmann, Kie</p>
<p>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.</p>	
<p>On September 5, 1906, while on a summer vacation in Duino, near Trieste, Boltzmann hung himself during an attack of depression.^[19] He is buried in the Viennese Zentralfriedhof; his tombstone bears the inscription</p>	<p>To quote Planck, "The logarithmic connection between entropy and probability was first stated by L. Boltzmann in his kinetic theory of gases"^[19] This famous formula for entropy S is^{[11][17]}</p> $S = k \log_e W$ <p>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 <i>Wahrscheinlichkeit</i>, the frequency of occurrence of a macrostate^[19] or, more precisely, the number of possible microstates corresponding to the macroscopic state of a system — number of</p>