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 (kJ mol^{-1})	ΔG°_f (kJ mol^{-1})	S° (J mol^{-1} K^{-1})	$C^\circ_{p,m}$ (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

2

Third Law of Thermodynamics

The entropy of any perfect crystalline substance

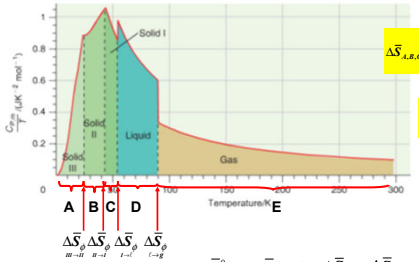
approaches 0 as T→ 0K

S=k ln W

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

3

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



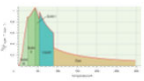
$$\Delta\bar{S}_{A,B,C,D,E} = \int_{T_i}^{T_f} \frac{(\bar{C}_P)_{A,B,C,D,E}}{T} dT$$

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

$$\bar{S}^0_{298.15} = \bar{S}(0K) + \Delta\bar{S}_A + \Delta\bar{S}_\phi + \Delta\bar{S}_B + \Delta\bar{S}_\phi + \Delta\bar{S}_C + \Delta\bar{S}_\phi + \Delta\bar{S}_D + \Delta\bar{S}_\phi + \Delta\bar{S}_E$$

4

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

5

$\Delta S_{reaction}$ from absolute entropies

$n_A A + n_B B \rightarrow n_C C + n_D D$ 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)

6

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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 ⇒** $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P < 0$ *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
$\Delta n_{gas} > 0$ ➔ $\Delta S_{reaction}$ $\Delta n_{gas} < 0$ ➔ $\Delta S_{reaction}$)

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

7

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**

8

more qualitative factors affecting molecular entropy

- **substances with higher mass have**

	F_2 (g)	< Cl_2(g)	< Br_2(g)	< I_2(g)	
$S°_{298}$	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)	
$S°_{298}$	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
$S°_{298}$	173.78	188.83	198.34	J K^{-1}mol^{-1}

9

more qualitative factors affecting molecular entropy

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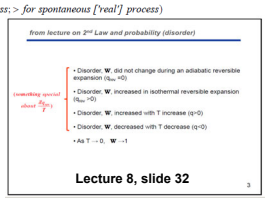
10

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

- Thermal properties of entropy and entropy calculations
  - ✓ $dS = \frac{d\bar{q}_{rev}}{T}$; $\Delta S = \int \frac{d\bar{q}_{rev}}{T}$; $\oint \frac{d\bar{q}_{rev}}{T} = 0$
  - ✓ $\Delta S \geq \int \frac{d\bar{q}}{T}$; $0 \geq \oint \frac{d\bar{q}}{T}$; (= 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: $\left(\frac{\partial S}{\partial T}\right)_V = \frac{\bar{C}_V}{T}$; $\left(\frac{\partial S}{\partial T}\right)_P = \frac{\bar{C}_P}{T}$
    - 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: $\bar{S}°(T)$
  - ✓ $\Delta S°_{reaction}(T) = \sum_i \nu_i \bar{S}°_i(T)$
  - Entropy of mixing: $\Delta S = -n_{total} R \sum_i X_i \ln X_i$ *where* $X_i = \frac{n_i}{n_{total}}$



11

HW#5 Prob 31

31.
a. Prove, in general (but $d w_{other} = 0$; $dn = 0$), the relationship in equation 3.15 E&R$_{4th}$)

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

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

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

e. Prove, in general (but $d w_{other} = 0$; $dn = 0$), the relationship in equation 3.40 E&R$_{4th}$:

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

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

analogous to 31a

12

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

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:

$\bar{d}q_V = n\bar{C}_V\,dT \qquad \bar{d}q_P = n\bar{C}_P\,dT$

$dU = \bar{d}q + \bar{d}w = \bar{d}q - PdV$

$dS = \frac{\bar{d}q_{rev}}{T} \qquad dq = Tds$

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

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

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

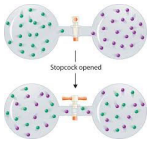
to describe CO_2(g) calculate w, ΔU, q, and ΔS in terms of V_1 and V_2 and the van der Waals constants a and b.

15

Entropy of Mixing of Distinguishable Ideal Gasses

(EXTRA *but not OPTIONAL*)

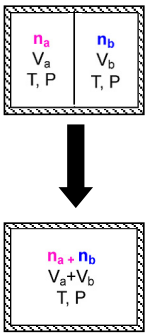
E&R$_{4th}$ ≈ Sec 6.5 [6.6]$_{3rd}$



16

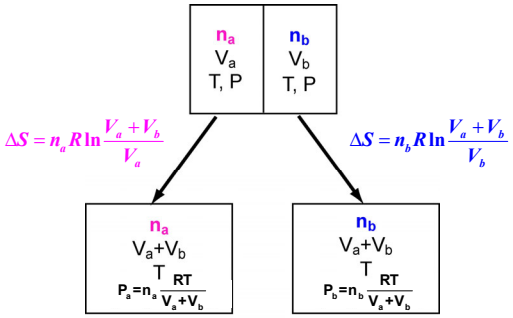
Entropy of mixing for ideal gas (distinguishable particles)

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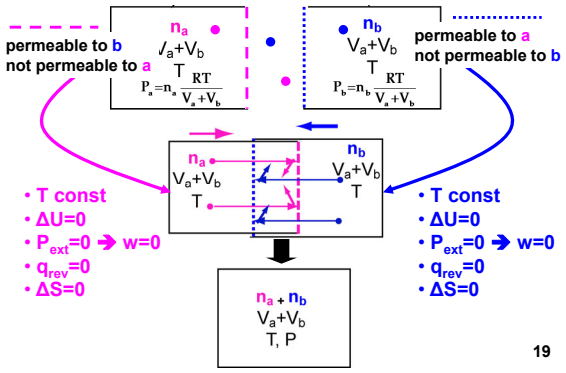
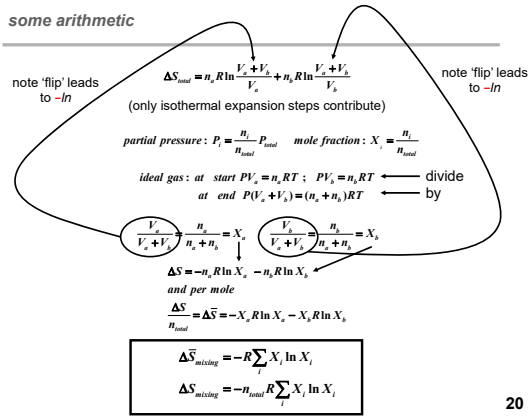
Third Law and Entropy of Mixing
(ideal gas, distinguishable molecules)

reversible recombining of volumes



19

some arithmetic



20

calculating entropy (see summary on review handout)

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  - T: $\left(\frac{\partial \bar{S}}{\partial T}\right)_P = \frac{\bar{C}_P}{T}$; $\left(\frac{\partial \bar{S}}{\partial T}\right)_P = \frac{\bar{C}_P}{T}$
  - P: $\left(\frac{\partial \bar{S}}{\partial P}\right)_T = -\left(\frac{\partial \bar{V}}{\partial T}\right)_P$
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- Calculation of entropy changes for changes in P, V, T, phase
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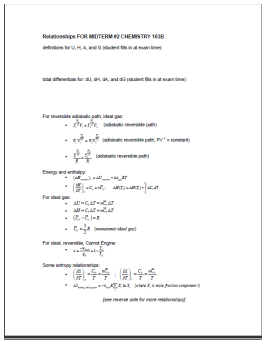
- Entropy of mixing: $\Delta S = -n_{total} R \sum_i X_i \ln X_i$ $\quad where\ X_i = \frac{n_i}{n_{total}}$

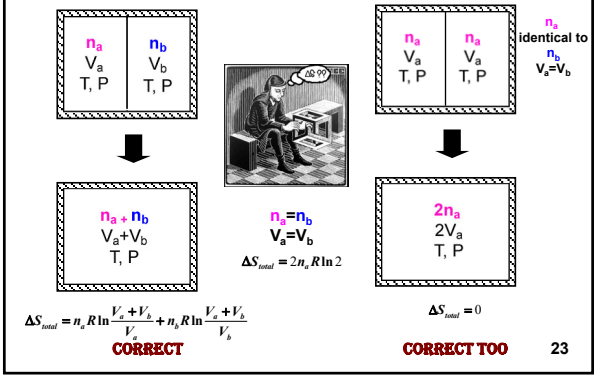
21

What formulas I have to memorize for midterm and final ?



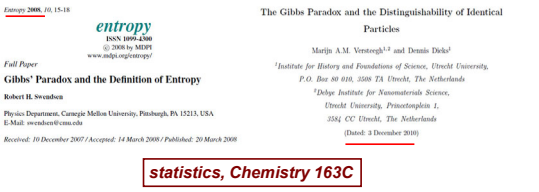
22

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



23

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



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

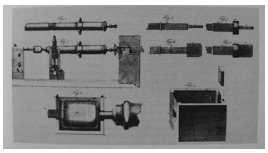
and

what's next

25

observations: thermo ≡ heat

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



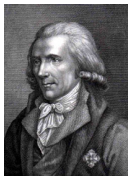


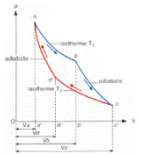
FIGURE 11. An illustration from Rumford's paper, "An Inquiry Concerning the Source of the Heat Which is Excited by Friction," showing the apparatus used by him in the cannon boring experiment. Figure 1, upper left, shows the cannon as received from the foundry, and Figure 2, below, shows it mounted in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

26

observations: mechanical efficiency of steam engine

- Sadi Carnot, 1824
- efficiency of engines

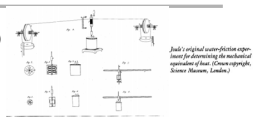

REFLEXIONS
PUISSANCE MOTRICE
DU FEU
SUR LES MACHINES
A PARIS.



27

guiding principles

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


Joule's original water-friction experiment 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

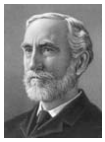
the thermodynamic functions U, H, and S
(1st and 2nd laws)

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 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

29

End of Lecture

30

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