Chemistry 163B
Absolute Entropies
and
Entropy of Mixing

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

Substance	ΔH^0_f ΔH_f° (kJ mol^{-1})	ΔG^0_f ΔG_f° (kJ mol^{-1})	S^0 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

2

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

to calculate absolute entropy from measurements (E&R pp. 101-103, Figs 5.8-5.10)
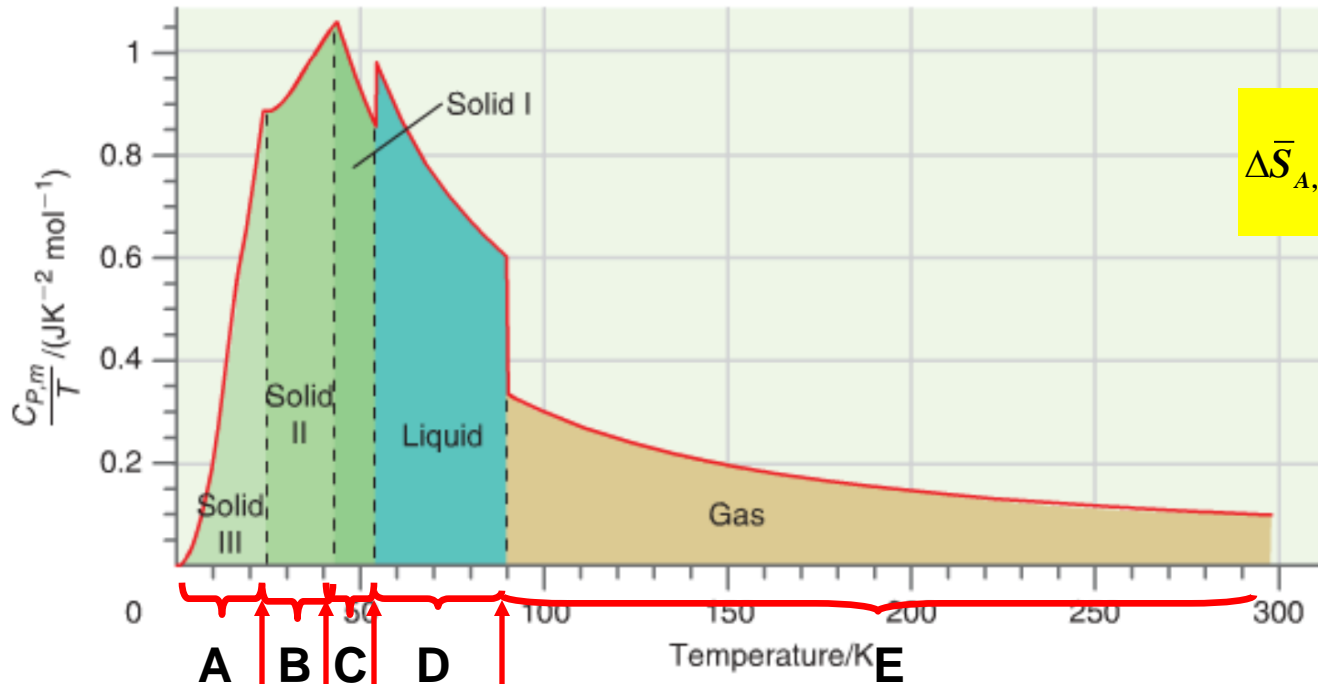
$$\Delta \bar{S}_{A,B,C,D,E} = \int_{T_1}^{T_2} \frac{\left(\bar{C}_P\right)_{A,B,C,D,E}}{T} dT$$

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

$$\Delta \bar{S}_{\phi} \atop {\scriptstyle III \to II} \qquad \Delta \bar{S}_{\phi} \atop {\scriptstyle II \to I} \qquad \Delta \bar{S}_{\phi} \atop {\scriptstyle I \to \ell} \qquad \Delta \bar{S}_{\phi} \atop {\scriptstyle \ell \to g}$$

$$\bar{S}^0_{298.15} = \bar{S}(0K) + \Delta \bar{S}_{A \atop 0 \to 23.66} + \Delta \bar{S}_{\phi \atop {III \to II \atop at\ 23.66K}} + \Delta \bar{S}_{B \atop 23.66 \to 43.76} + \Delta \bar{S}_{\phi \atop {II \to I \atop at\ 43.76K}}$$

$$+ \Delta \bar{S}_{C \atop 43.76 \to 54.39} + \Delta \bar{S}_{\phi \atop {I \to \ell \atop at\ 54.39K}} + \Delta \bar{S}_{D \atop 54.39 \to 90.20} + \Delta \bar{S}_{\phi \atop {\ell \to g \atop at\ 90.20K}} + \Delta \bar{S}_{E \atop 90.30 \to 298.15}$$

4

full calculation of S^0_{298} for O_2 (g) (Example Problem 5.9, E&R pp103-104)

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

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$$n_A A + n_B B \longrightarrow n_C C + n_D D \quad \text{at 298K}$$

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

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

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

• **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
  $\Delta n_{gas} > 0 \rightarrow \Delta S_{reaction}$ $\Delta n_{gas} < 0 \rightarrow \Delta S_{reaction}$ *)*

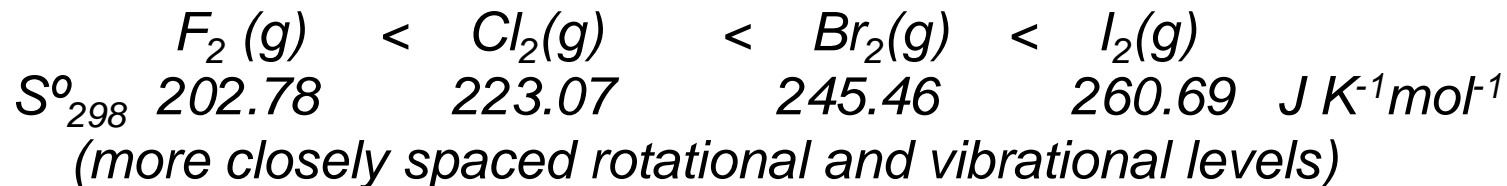• **Mixing or dissolving of components**
  (ℓ+ℓ), (s+s), (ℓ+s), (g+g) solutions
      $\Rightarrow$

• **(g + ℓ) or (g + s) solution** $\Rightarrow$

- **substances with higher mass have**

$$F_2\ (g) \quad < \quad Cl_2(g) \quad < \quad Br_2(g) \quad < \quad I_2(g)$$

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 $J\ K^{-1}mol^{-1}$

- Thermal properties of entropy and entropy calculations

✓ ○ $dS = \dfrac{đq_{rev}}{T}$; $\quad \Delta S = \int \dfrac{đq_{rev}}{T}$; $\quad \oint \dfrac{đq_{rev}}{T} = 0$

✓ ○ $\Delta S \geq \int \dfrac{đq}{T}$; $\quad 0 \geq \oint \dfrac{đq}{T}$; $\quad$ (= *for reversible process*; > *for spontaneous* ['real'] *process*)

✓ ○ $\Delta S_{total \equiv universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$

✓ ○ S is a state function; dS is an exact differential

○ Dependence of S on

✓ - T: $\left(\dfrac{\partial \overline{S}}{\partial T}\right)_V = \dfrac{\overline{C}_V}{T}$; $\quad \left(\dfrac{\partial \overline{S}}{\partial T}\right)_P = \dfrac{\overline{C}_P}{T}$

✓ - P: $\left(\dfrac{\partial \overline{S}}{\partial P}\right)_T = -\left(\dfrac{\partial \overline{V}}{\partial T}\right)_P$

✓ - V: $\left(\dfrac{\partial \overline{S}}{\partial \overline{V}}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_{\overline{V}}$

✓ - Phase: $\Delta S = \dfrac{\Delta H_{equilibrium\ phase\ change}}{T_{equilibrium\ phase\ change}}$

✓ ○ Calculation of entropy changes for changes in P, V, T, phase

○ Third Law and calculations using Third Law Entropies: $\overline{S}^{\circ}(T)$

✓ ○ $\Delta S^0_{reaction}(T) = \sum_i \nu_i \overline{S}^0_i(T)$

○ Entropy of mixing: $\Delta S = -n_{total}R\sum_i X_i \ln X_i \quad$ where $X_i = \dfrac{n_i}{n_{total}}$

---

from lecture on 2nd Law and probability (disorder)

(something special about $\dfrac{đq_{rev}}{T}$)

- 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 $\rightarrow$ 0, **w** $\rightarrow$ 1

Lecture 9, slide 3

3

9

31.

a. Prove, in general (but $d\!\!\!/\, w_{other} = 0;\quad dn = 0$), the relationship in equation 3.19 E&R)

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

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

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

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

e. Prove, in general (but $d\!\!\!/\, w_{other} = 0;\quad dn = 0$), the relationship in equation 3.44 E&R:

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

Lecture 5 slide 17
"derive ~~later~~"
now

analogous to 31a

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definitions:

U $\equiv$ internal energy

H $\equiv$ U + PV

A $\equiv$ U $-$TS

G $\equiv$ H $-$TS

differentials of state functions:

dU= TdS$-$PdV

dH= TdS+VdP

dA= $-$SdT$-$PdV

dG= $-$SdT+VdP

heat and temperature:

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

$$dU = đq + đw = đq - PdV$$

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

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

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do some examples:

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

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

in terms of P, V, T and their derivatives

technique applies to HW#6 Prob: 31e

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

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

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.

Entropy of Mixing
of Ideal Gasses

(EXTRA *but not OPTIONAL*)

E&R≈ Sec 6.6

- **isolated from surroundings**

  $q_{sys} = q_{surr} = 0$
  $w = 0$

- $\Delta S_{surr} = 0$

- $\Delta S_{universe} > 0$

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

n_a
V_a
T, P

n_b
V_b
T, P

n_{a+n_b}
$V_a + V_b$
T, P

15
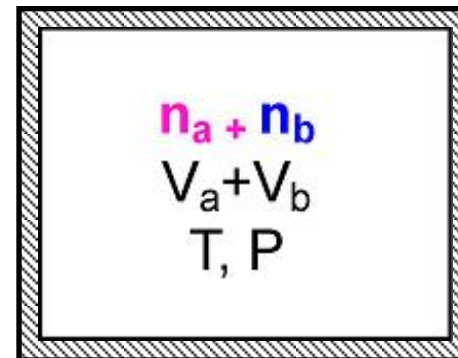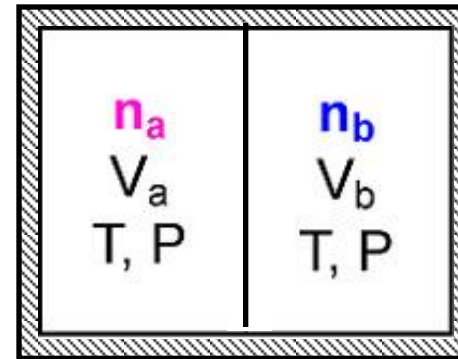
reversible *isothermal expansion to total volume* $\Delta S = nR \ln \dfrac{V_{final}}{V_{initial}}$

na
Va
T, P

nb
Vb
T, P

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

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

na
Va+Vb
T
$P_a = n_a \dfrac{RT}{V_a + V_b}$

nb
Va+Vb
T
$P_b = n_b \dfrac{RT}{V_a + V_b}$

16
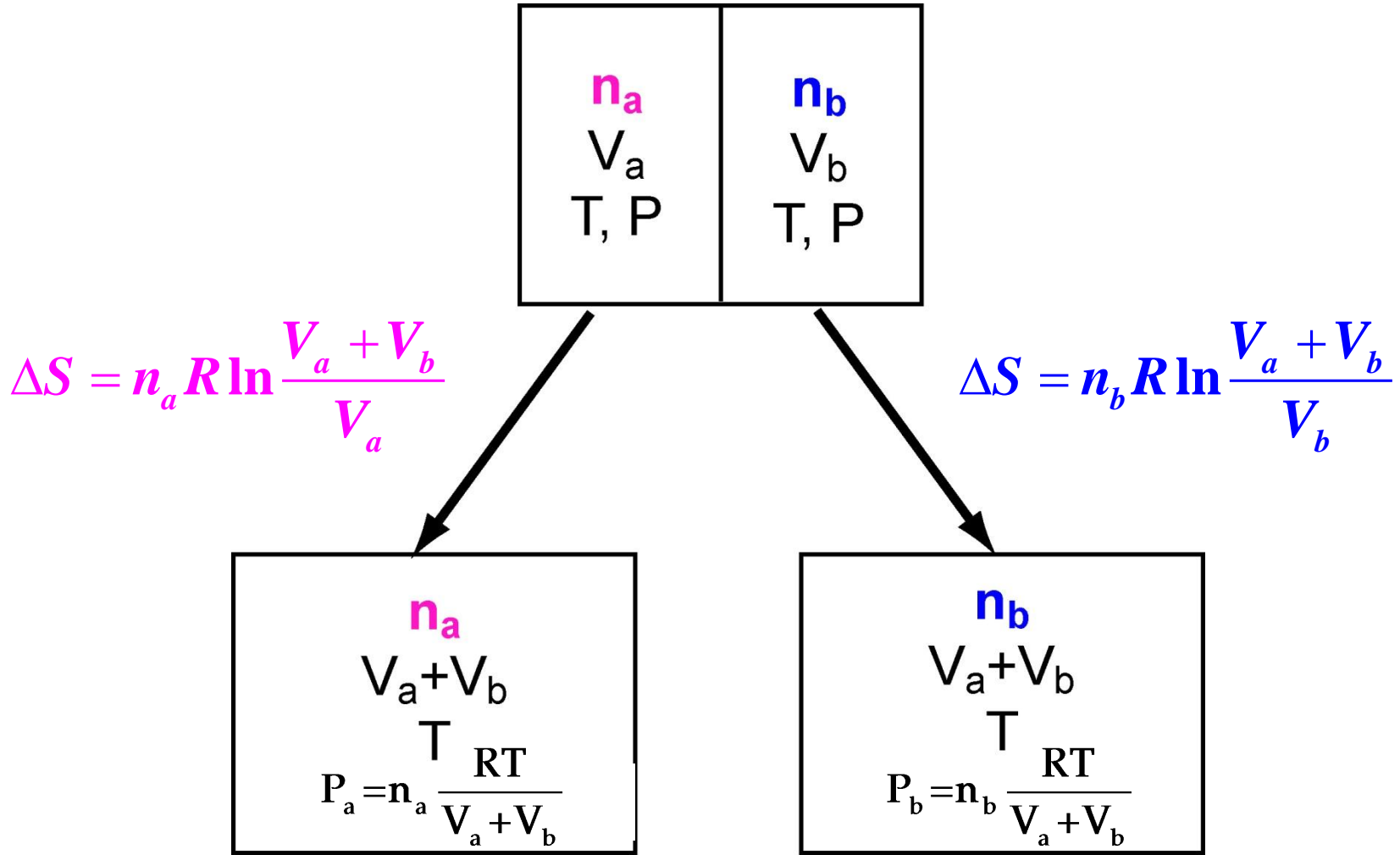
reversible *recombining of volumes*

permeable to b
not permeable to a

n_a
V_a+V_b
T
$P_a = n_a \dfrac{RT}{V_a+V_b}$

n_b
V_a+V_b
T
$P_b = n_b \dfrac{RT}{V_a+V_b}$

permeable to a
not permeable to b

n_a
V_a+V_b
T

n_b
V_a+V_b
T

- **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**

$n_a + n_b$
V_a+V_b
T, P

17
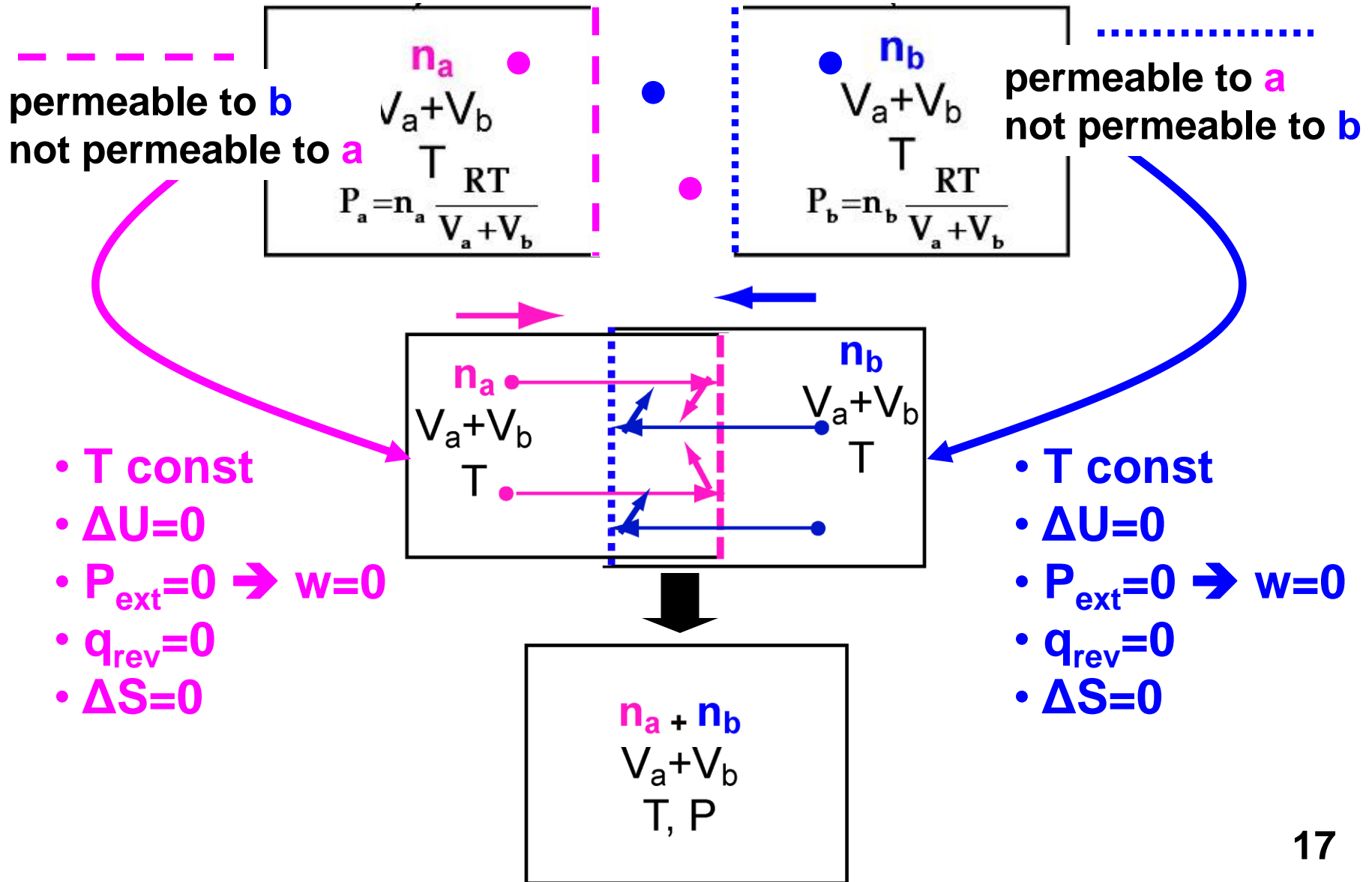
some arithmetic

note 'flip' leads to $-ln$

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)

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

$$ideal\ gas: at\ \ start\ PV_a = n_a RT \ ; \ \ PV_b = n_b RT \quad \leftarrow \text{divide}$$
$$at\ \ end\ \ P(V_a + V_b) = (n_a + n_b)RT \quad \leftarrow \text{by}$$

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

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

$$and\ per\ mole$$

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

$$\boxed{\begin{array}{c} \Delta \bar{S}_{mixing} = -R \sum_i X_i \ln X_i \\[2mm] \Delta S_{mixing} = -n_{total} R \sum_i X_i \ln X_i \end{array}}$$

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calculating entropy (see summary on review handout)

- Thermal properties of entropy and entropy calculations

  ✓ ○ $dS = \dfrac{d\!\!\!^- q_{rev}}{T}$; $\Delta S = \displaystyle\int \dfrac{d\!\!\!^- q_{rev}}{T}$; $\displaystyle\oint \dfrac{d\!\!\!^- q_{rev}}{T} = 0$

  ✓ ○ $\Delta S \geq \displaystyle\int \dfrac{d\!\!\!^- q}{T}$; $0 \geq \displaystyle\oint \dfrac{d\!\!\!^- q}{T}$; $(= \text{for reversible process}; > \text{for spontaneous ['real'] process})$

  ✓ ○ $\Delta S_{total\equiv universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$

  ✓ ○ S is a state function; dS is an exact differential
  ○ Dependence of S on

  ✓ ▪ T: $\left(\dfrac{\partial \overline{S}}{\partial T}\right)_V = \dfrac{\overline{C}_V}{T}$; $\left(\dfrac{\partial \overline{S}}{\partial T}\right)_P = \dfrac{\overline{C}_P}{T}$

  ✓ ▪ P: $\left(\dfrac{\partial \overline{S}}{\partial P}\right)_T = -\left(\dfrac{\partial \overline{V}}{\partial T}\right)_P$

  ✓ ▪ V: $\left(\dfrac{\partial \overline{S}}{\partial \overline{V}}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_{\overline{V}}$

  ✓ ▪ Phase: $\Delta S = \dfrac{\Delta H_{equilibrium\ phase\ change}}{T_{equilibrium\ phase\ change}}$

  ✓ ○ Calculation of entropy changes for changes in P, V, T, phase
  ○ Third Law and calculations using Third Law Entropies: $\overline{S}^{\circ}(T)$
  ✓ ○ $\Delta S^{0}_{reaction}(T) = \displaystyle\sum_i \nu_i \overline{S}^{0}_i(T)$

  ✓ ○ Entropy of mixing: $\Delta S = -n_{total} R \displaystyle\sum_i X_i \ln X_i$ where $X_i = \dfrac{n_i}{n_{total}}$

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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:

- $T_1^{\frac{C_V}{R}}V_1 = T_2^{\frac{C_V}{R}}V_2$ (adiabatic reversible path)

- $P_1V_1^{\frac{C_p}{C_V}} = P_2V_2^{\frac{C_p}{C_V}}$ (adiabatic reversible path, PV^{γ} = constant)

- $\frac{T_1^{\frac{C_p}{R}}}{P_1} = \frac{T_2^{\frac{C_p}{R}}}{P_2}$ (adiabatic reversible path)

Energy and enthalpy:
- $(\Delta H_{reaction})_T = \Delta U_{reaction} + \Delta n_{gas}RT$
- $\left(\frac{\partial H}{\partial T}\right)_P = C_p = n\overline{C}_p;$ $\Delta H(T_2) = \Delta H(T_1) + \int_{T_1}^{T_2}\Delta C_p dT$

For ideal gas:
- $\Delta U = C_V\Delta T = n\overline{C}_V\Delta T$
- $\Delta H = C_p\Delta T = n\overline{C}_p\Delta T$
- $(\overline{C}_p - \overline{C}_V) = R$
- $\overline{C}_V = \frac{3}{2}R$ (monatomic ideal gas)

For ideal, reversible, Carnot Engine:
- $\varepsilon = \frac{-w_{total}}{q_H} = 1 - \frac{T_L}{T_H}$

Some entropy relationships:
- $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T} = \frac{n\overline{C}_p}{T}$; $\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} = \frac{n\overline{C}_V}{T}$
- $\Delta S_{mixing, ideal gases} = -n_{total}R\sum_i X_i \ln X_i$ (where X_i is mole fraction component i)

[see reverse side for more relationships]:

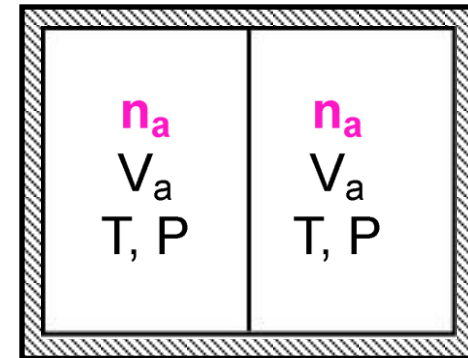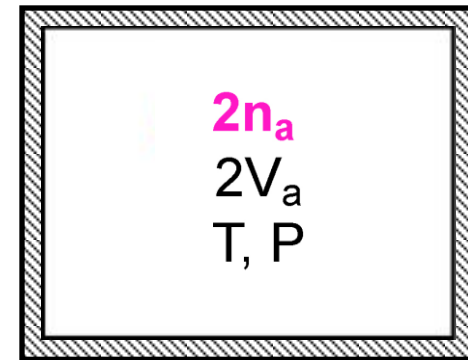# Gibb's Paradox: distinguishable vs identical (don't fret)

n_a
V_a
T, P

n_b
V_b
T, P

n_a
V_a
T, P

n_a
V_a
T, P

n_a
identical to
n_b
$V_a=V_b$

$n_{a + b}$
V_a+V_b
T, P
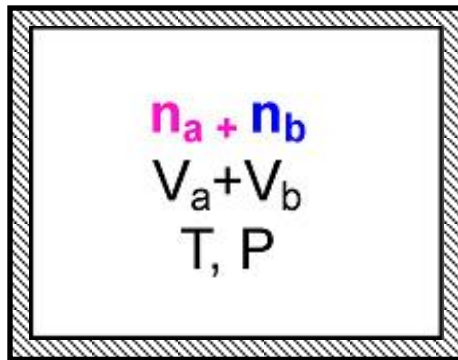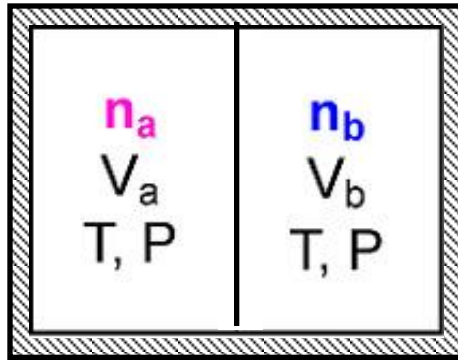
$n_a=n_b$
$V_a=V_b$

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

$2n_a$
$2V_a$
T, P

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

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

CORRECT

CORRECT TOO

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

entropy

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www.mdpi.org/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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3584 CC Utrecht, The Netherlands

(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

where we have been

and

what's next

23

observations: thermo ≡ heat

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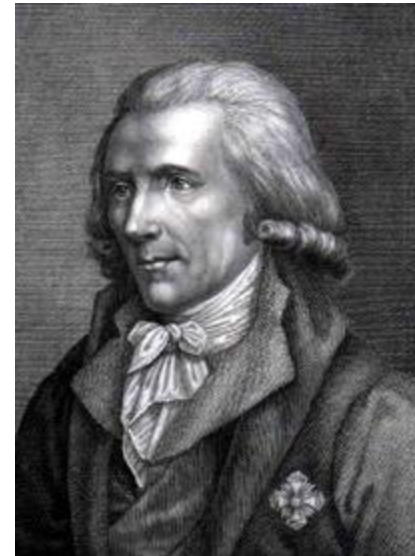- observed water turning into steam when canon barrel was bored
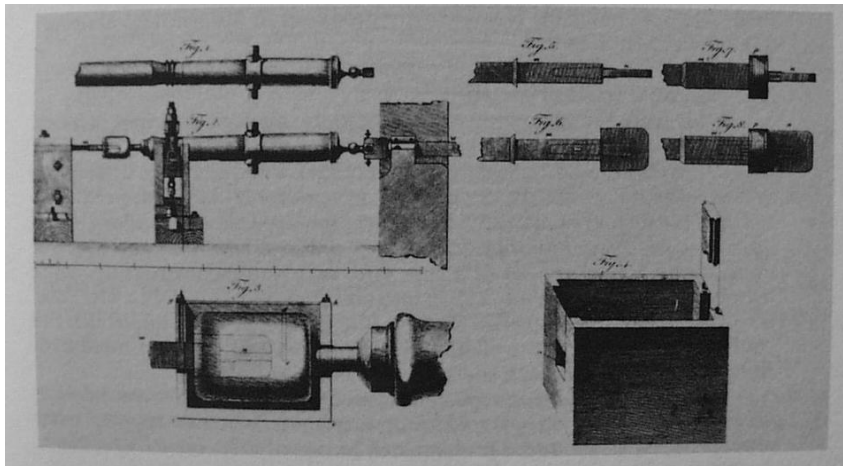- *work* ⟺ *heat*

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.)
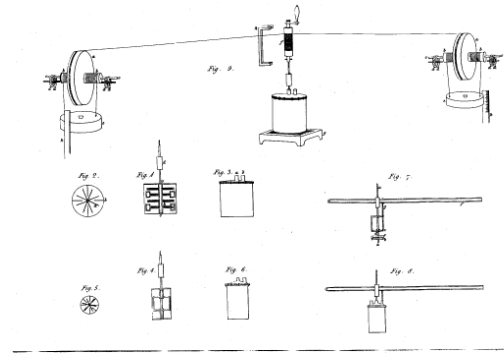
observations: mechanical efficiency of steam engine

• Sadi Carnot, 1824
• efficiency of engines
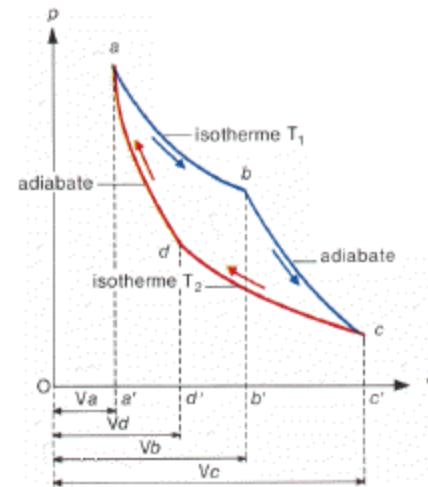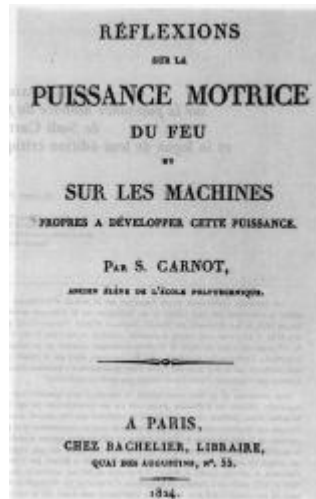
guiding principles

- 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

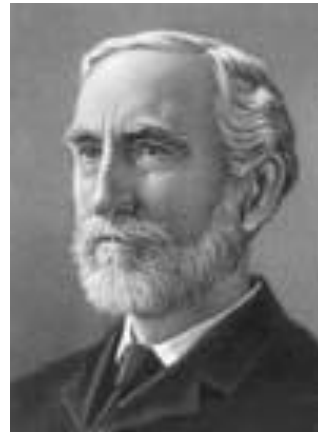- Boltzmann, late 19th century,
  molecular picture of entropy

Clausius

Boltzmann

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

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

End of Lecture

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...

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