# Chemistry 163B
# Absolute Entropies
# and
# Entropy of Mixing

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

| Substance | $\Delta H^o_f$ $\Delta H_f^\circ$ (kJ mol$^{-1}$) | $\Delta G^o_f$ $\Delta G_f^\circ$ (kJ mol$^{-1}$) | $S^o$ $S^\circ$ (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

*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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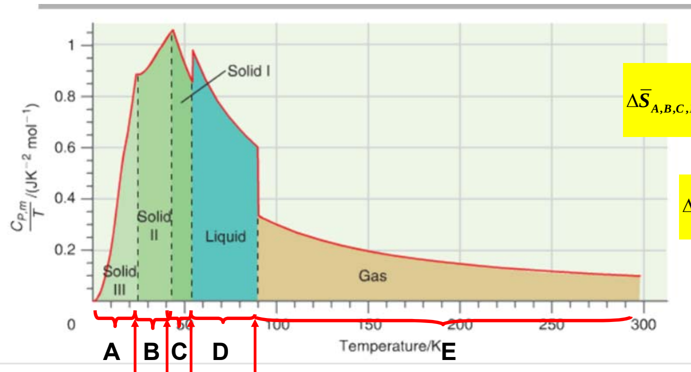
*to calculate absolute entropy from measurements* *(E&R pp. 101-103, Figs 5.8-5.10)*




$$\Delta\bar{S}_{A,B,C,D,E} = \int_{T_1}^{T_2} \frac{(\bar{C}_P)_{A,B,C,D,E}}{T}\, dT$$

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

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

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

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

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

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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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## 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
  - ✓ $dS = \frac{đq_{rev}}{T}$; $\Delta S = \int \frac{đq_{rev}}{T}$; $\oint \frac{đq_{rev}}{T} = 0$
  - ✓ $\Delta S \geq \int \frac{đq}{T}$; $0 \geq \oint \frac{đq}{T}$; $(= \textit{for reversible process}; > \textit{for spontaneous ['real'] process})$
  - ✓ $\Delta S_{total \equiv universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$
  - ✓ S is a state function; $dS$ is an exact differential
  - Dependence of S on
    - ✓ T: $\left(\frac{\partial \bar{S}}{\partial T}\right)_V = \frac{\bar{C}_V}{T}$; $\left(\frac{\partial \bar{S}}{\partial T}\right)_P = \frac{\bar{C}_P}{T}$
    - ✓ P: $\left(\frac{\partial \bar{S}}{\partial P}\right)_T = -\left(\frac{\partial \bar{V}}{\partial T}\right)_P$
    - ✓ V: $\left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)_T = \left(\frac{\partial P}{\partial T}\right)_{\bar{V}}$
    - ✓ 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: $\bar{S}^o(T)$
  - $\Delta S^0_{reaction}(T) = \sum_i \nu_i \bar{S}^0_i(T)$
  - Entropy of mixing: $\Delta S = -n_{total} R \sum_i X_i \ln X_i \quad where\ X_i = \frac{n_i}{n_{total}}$

*from lecture on 2nd Law and probability (disorder)*

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

- 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 → 0, **W** → 1

**Lecture 9, slide 3**

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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)

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

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

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

**Sample midterm 3a**

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:**

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:**

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

$$dU = đq + đw = đq - PdV$$

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

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

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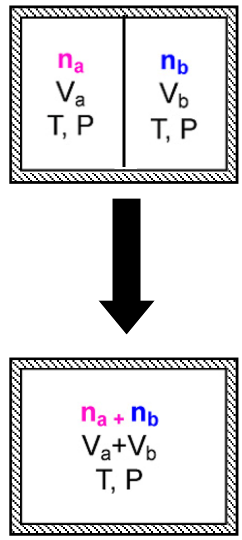
## *Entropy of mixing for ideal gas (distinguishable particles)*

- **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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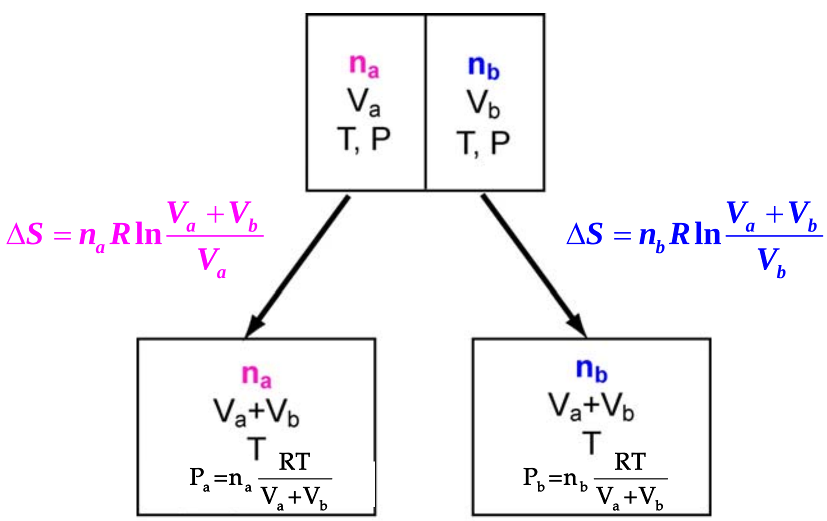
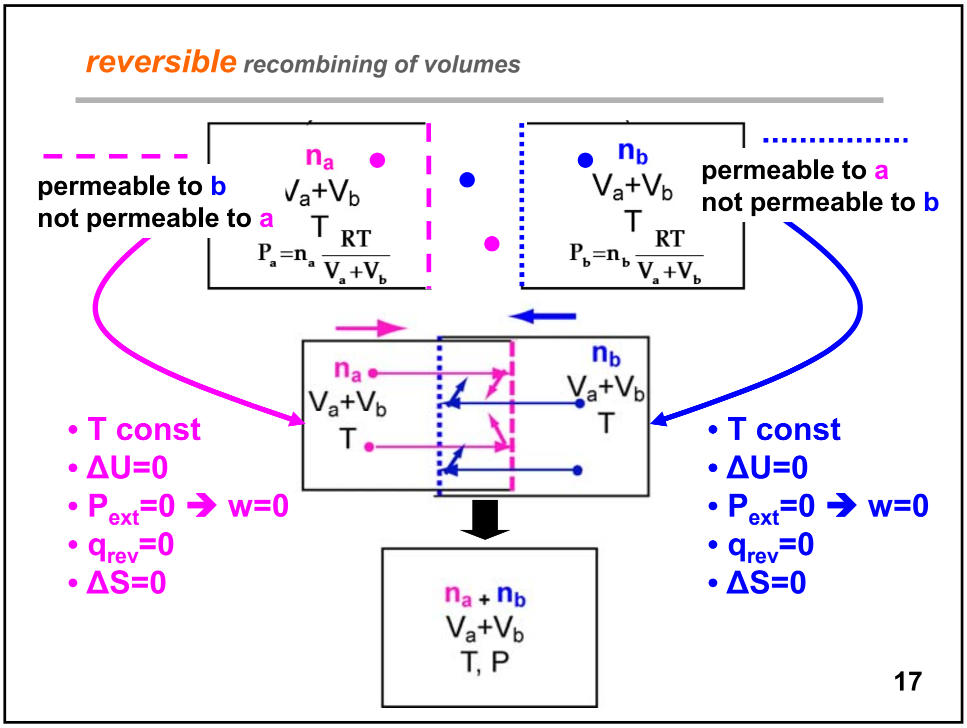
## ***reversible** isothermal expansion to total volume*

$$\Delta S = nR\ln\frac{V_{final}}{V_{initial}}$$




**16**




*some arithmetic*

note 'flip' leads to *–ln*

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

note 'flip' leads to *–ln*

(only isothermal expansion steps contribute)

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

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

← 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*

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

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

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

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## *calculating entropy* [*see summary on review handout*]

- Thermal properties of entropy and entropy calculations
  - $dS = \frac{đq_{rev}}{T}$; $\Delta S = \int \frac{đq_{rev}}{T}$; $\oint \frac{đq_{rev}}{T} = 0$
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    - P: $\left(\frac{\partial \bar{S}}{\partial P}\right)_T = -\left(\frac{\partial \bar{V}}{\partial T}\right)_P$
    - V: $\left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)_T = \left(\frac{\partial P}{\partial T}\right)_{\bar{V}}$
    - 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: $\bar{S}^\circ(T)$
  - $\Delta S^0_{reaction}(T) = \sum_i \nu_i \bar{S}_i^\circ(T)$
  - Entropy of mixing: $\Delta S = -n_{total} R \sum_i X_i \ln X_i$ $\quad \textit{where } X_i = \frac{n_i}{n_{total}}$

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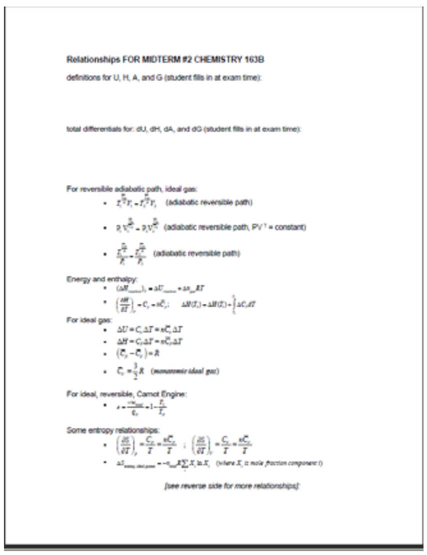
## *What formulas I have to memorize for midterm and final ?*


**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:
- $T_1^{\bar{C}_V/R} V_1 = T_2^{\bar{C}_V/R} V_2$ (adiabatic reversible path)
- $P_1 V_1^{\bar{C}_P/\bar{C}_V} = P_2 V_2^{\bar{C}_P/\bar{C}_V}$ (adiabatic reversible path, $PV^\gamma$ = constant)
- $\frac{T_1^{\bar{C}_P/R}}{P_1} = \frac{T_2^{\bar{C}_P/R}}{P_2}$ (adiabatic reversible path)

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

For ideal gas:
- $\Delta U = C_V \Delta T = n\bar{C}_V \Delta T$
- $\Delta H = C_P \Delta T = n\bar{C}_P \Delta T$
- $(\bar{C}_P - \bar{C}_V) = R$
- $\bar{C}_V = \frac{3}{2} R$ (*monatomic ideal gas*)

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

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

*[see reverse side for more relationships]*

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

| $n_a$ | $n_b$ |
|---|---|
| $V_a$ | $V_b$ |
| T, P | 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**


$n_a$=$n_b$
$V_a$=$V_b$

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

| $n_a$ | $n_a$ |
|---|---|
| $V_a$ | $V_a$ |
| T, P | 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)

*Entropy* **2008**, *10*, 15-18

*entropy*
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www.mdpi.org/entropy/

*Full Paper*

**Gibbs' 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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(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**

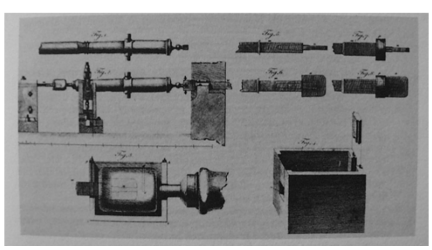
**and**

**what's next**

**23**

***observations: thermo ≡ heat***

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



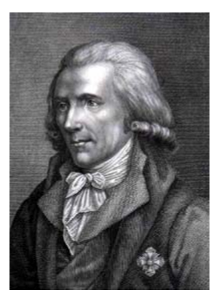


FIGURE 11. An illustration from Rumford's paper, "An Inquiry Concerning the Source of the Heat Which is Excited by Friction," showing the apparatus used by him in the cannon boring experiment. Figure 1, upper left, shows the cannon as received from the foundry, and Figure 2, below, shows it mounted in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

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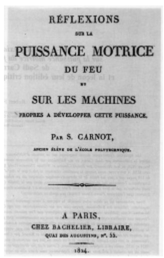
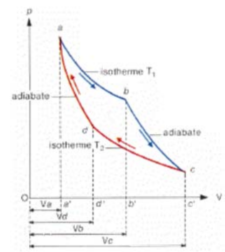
***observations: mechanical efficiency of steam engine***

• Sadi Carnot, 1824
• efficiency of engines

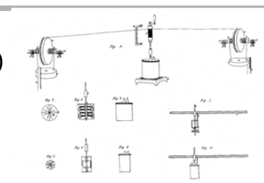

RÉFLEXIONS
SUR LA
PUISSANCE MOTRICE
DU FEU
ET
SUR LES MACHINES
PROPRES A DÉVELOPPER CETTE PUISSANCE.
PAR S. CARNOT,
ANCIEN ÉLÈVE DE L'ÉCOLE POLYTECHNIQUE.
A PARIS,
CHEZ BACHELIER, LIBRAIRE,
QUAI DES AUGUSTINS, nº. 55.
1824.




**25**

***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)***

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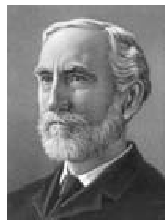
## *"Applications"*

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

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

$$S = k \cdot \log W.$$

WIKIPEDIA
The Free Encyclopedia

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