Lecture 13
Chemistry 163B
Winter 2020

Absolute Entropies
and
Entropy of Mixing

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})	$C^\circ_{P,m}$ (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$_2$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)			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
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

The entropy of any perfect crystalline substance

approaches 0 as T$\rightarrow$ 0K

S=k ln W

for perfectly ordered crystalline substance
W $\rightarrow$ 1 as T$\rightarrow$ 0K $\Rightarrow$ S $\rightarrow$ 0
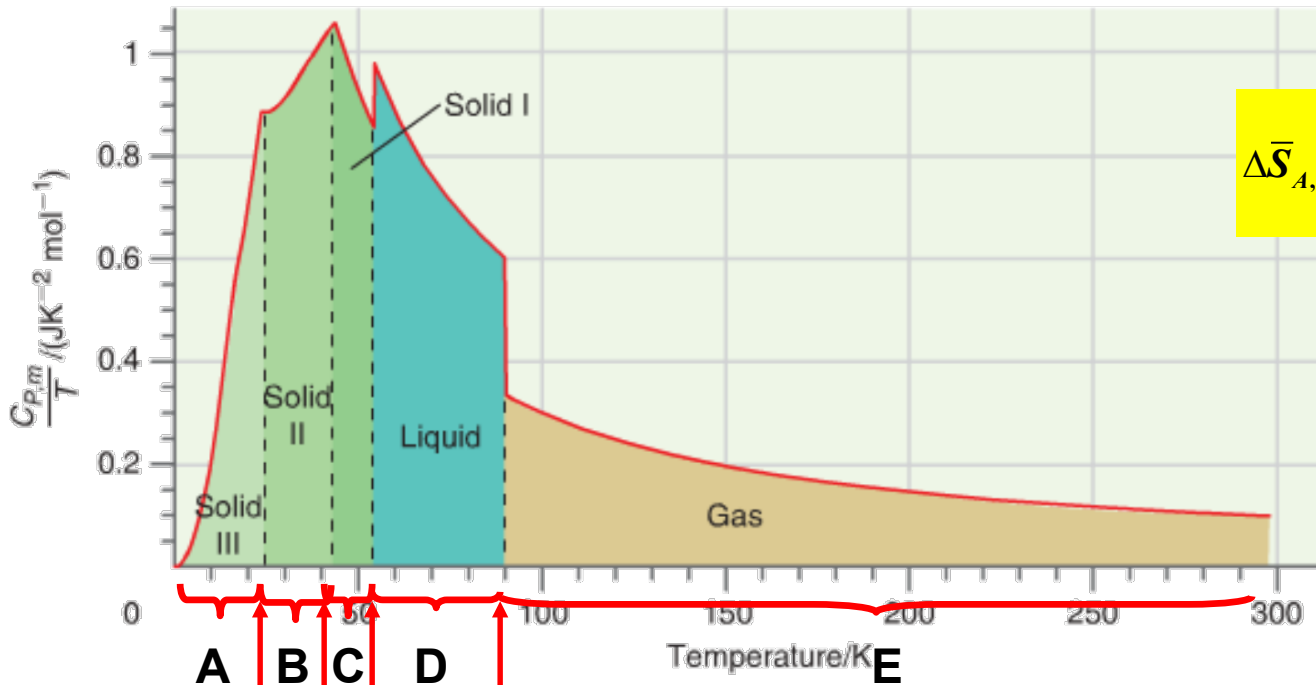
$$\Delta\overline{S}_{A,B,C,D,E} = \int_{T_1}^{T_2} \frac{\left(\overline{C}_P\right)_{A,B,C,D,E}}{T} dT$$

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

$$\overline{S}^0_{298.15} = \overline{S}(0K) + \underset{0\to23.66}{\Delta\overline{S}_A} + \underset{\substack{III\to II\\ \text{at } 23.66K}}{\Delta\overline{S}_\phi} + \underset{23.66\to43.76}{\Delta\overline{S}_B} + \underset{\substack{II\to I\\ \text{at } 43.76K}}{\Delta\overline{S}_\phi}$$

$$+ \underset{43.76\to54.39}{\Delta\overline{S}_C} + \underset{\substack{I\to\ell\\ \text{at } 54.39K}}{\Delta\overline{S}_\phi} + \underset{54.39\to90.20}{\Delta\overline{S}_D} + \underset{\substack{\ell\to g\\ \text{at } 90.20K}}{\Delta\overline{S}_\phi} + \underset{90.30\to298.15}{\Delta\overline{S}_E}$$

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full calculation of S°₂₉₈ for O₂ (g) (Example Problem 5.7,p123₄th [5.9, E&R pp103-104]₃rd)
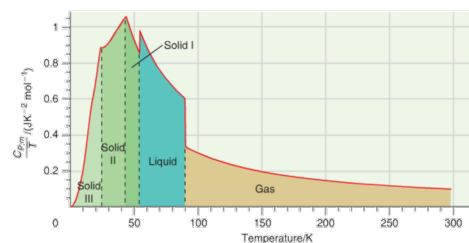
	$\Delta \bar{S}$ $\mathbf{J}$ $\mathbf{K}^{-1}$ $\mathbf{mol}^{-1}$
$\bar{S}(0K)$	0
$\Delta \bar{S}_A (0 \to 23.66)$	8.182 (1.534+6.649)
$\Delta \bar{S}_\phi (\text{III} \to \text{II at } 23.66K)$	3.964
$\Delta \bar{S}_B (23.66 \to 43.76)$	19.61
$\Delta \bar{S}_\phi (\text{II} \to \text{I at } 43.76K)$	16.98
$\Delta \bar{S}_C (43.76 \to 54.39)$	10.13
$\Delta \bar{S}_\phi (\text{I} \to \ell \text{ at } 54.39K)$	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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$n_A A + n_B B \rightarrow n_C C + n_D D$ at 298K

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

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

$\left(\overline{S}^0_{298} \right)_i$ 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
$\Delta n_{gas} > 0$ ➜ $\Delta S_{reaction}$ $\Delta n_{gas} < 0$ ➜ $\Delta S_{reaction}$ *)*

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

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

- **Higher T $\Rightarrow$ Higher S** $\qquad \left(\dfrac{\partial S}{\partial T}\right)_P = \dfrac{C_P}{T} > 0$

- **Higher P $\Rightarrow$ Lower S** $\qquad \left(\dfrac{\partial S}{\partial P}\right)_T = -\left(\dfrac{\partial V}{\partial T}\right)_P < 0$
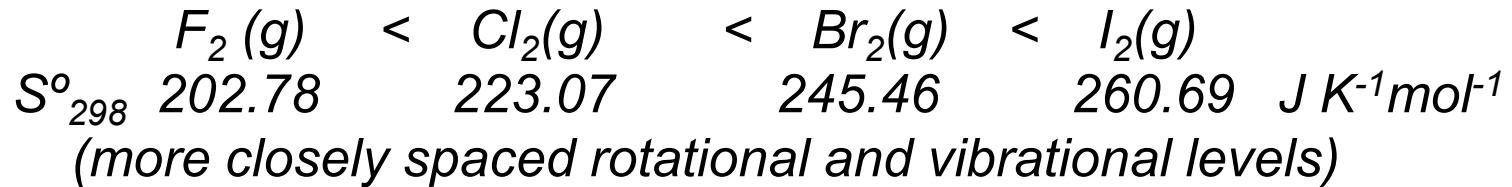
- **Phase $\qquad$ S(g) $>$ S(ℓ) $>$ S(s)**

(in a reaction the side (reactants vs products) with the greater number of moles of gas generally has higher S
$\Delta n_{gas} > 0 \Rightarrow \Delta S_{reaction} > 0$; $\Delta n_{gas} < 0 \Rightarrow \Delta S_{reaction} < 0$)

- **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**

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

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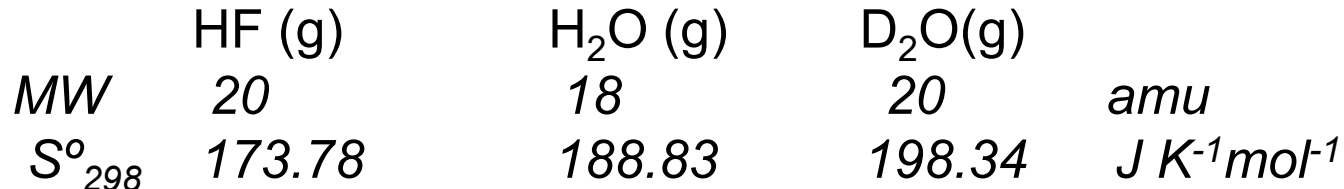
- **substances with higher mass have higher S**

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

S^o_{298} 202.78   223.07   245.46   260.69   *J K^{-1}mol^{-1}*

(more closely spaced rotational and vibrational levels)
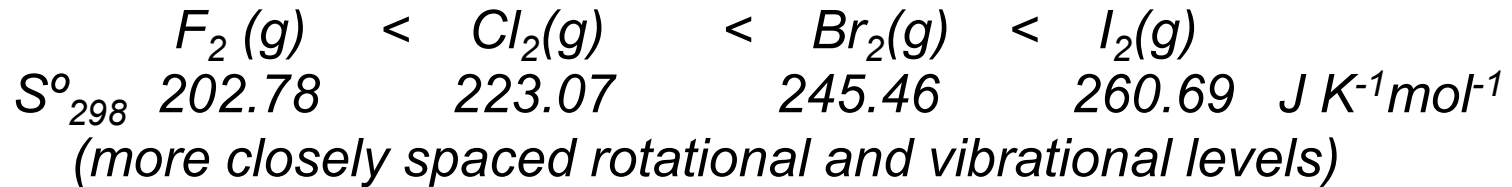
- **more rigid substances have lower S**

C(gr)   C(dia)

S^o_{298} 5.74   2.377   *J K^{-1}mol^{-1}*

- **more complex substances have higher S**

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

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

✓ ○ $\Delta S \geq \int \dfrac{đq}{T}$; $0 \geq \oint \dfrac{đq}{T}$; (= 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: $\left(\dfrac{\partial \overline{S}}{\partial T}\right)_V = \dfrac{\overline{C}_V}{T}$; $\left(\dfrac{\partial \overline{S}}{\partial T}\right)_P = \dfrac{\overline{C}_P}{T}$

✓ ▪ 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: $\overline{S}^{\circ}(T)$

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

○ Entropy of mixing: $\Delta S = -n_{total} R \sum_i X_i \ln X_i$ 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 → 0, **w** →1

Lecture 8, slide 32

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31.

    a. Prove, in general (but $\not{d}\,w_{other} = 0;\quad dn = 0$), the relationship in equation 3.15 E&R$_{4th}$)

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

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

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

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

    e. Prove, in general (but $\not{d}\,w_{other} = 0;\quad dn = 0$), the relationship in equation 3.40 E&R$_{4th}$:

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

analogous to 31a

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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:

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

$$dU = \dbar q + \dbar w = \dbar q - PdV$$

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

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

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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

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

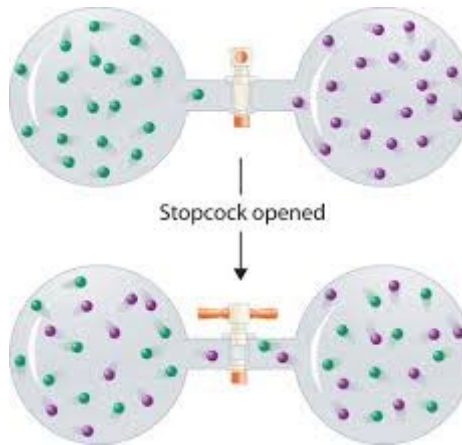$$\left(P + \frac{a}{\overline{V}^2} \right) \left(\overline{V} - b \right) = RT$$

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 Distinguishable Ideal
Gasses

(EXTRA *but not OPTIONAL*)

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

Stopcock opened

Entropy of mixing for ideal gas (distinguishable particles)

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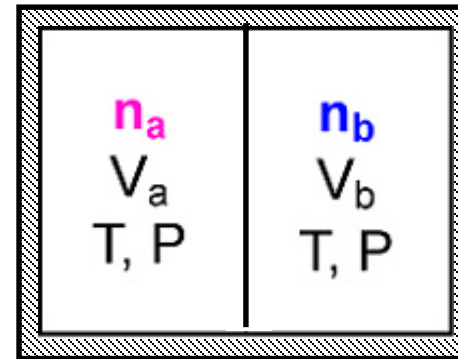
  $q_{sys} = q_{surr} = 0$
  $w = 0$

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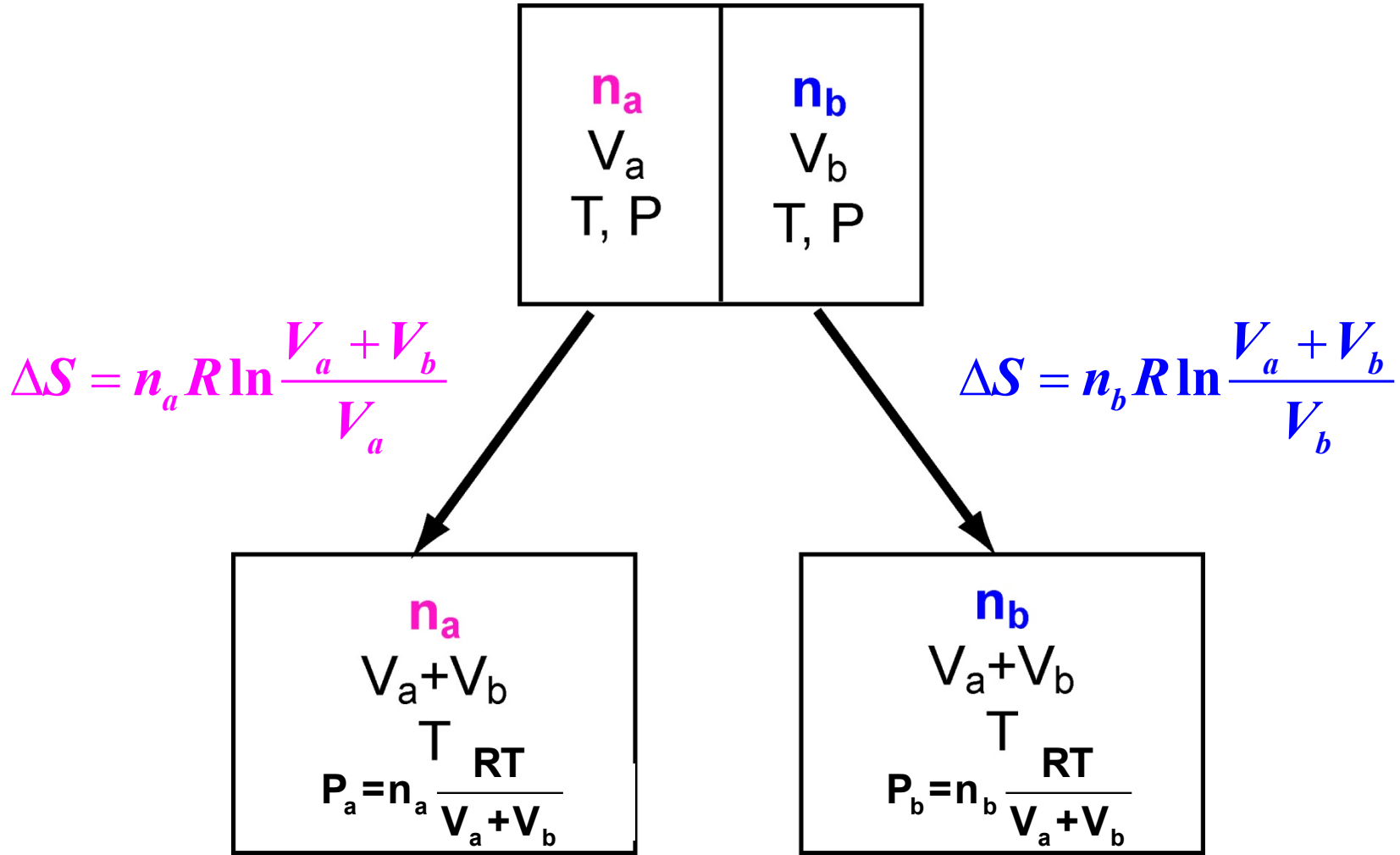
- $\Delta S_{universe} > 0$

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

n_a
V_a
T, P

n_b
V_b
T, P

$n_{a} + n_{b}$
$V_a + V_b$
T, P
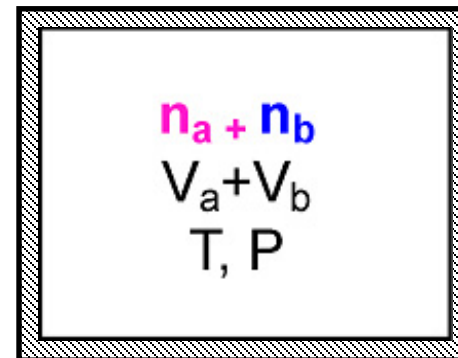
reversible *isothermal expansion to total volume*

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

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

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

n_a

V_a

T, P

n_b

V_b

T, P

n_a

$V_a + V_b$

T

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

n_b

$V_a + V_b$

T

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

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reversible *recombining of volumes*

permeable to b
not permeable to a

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

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

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**

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

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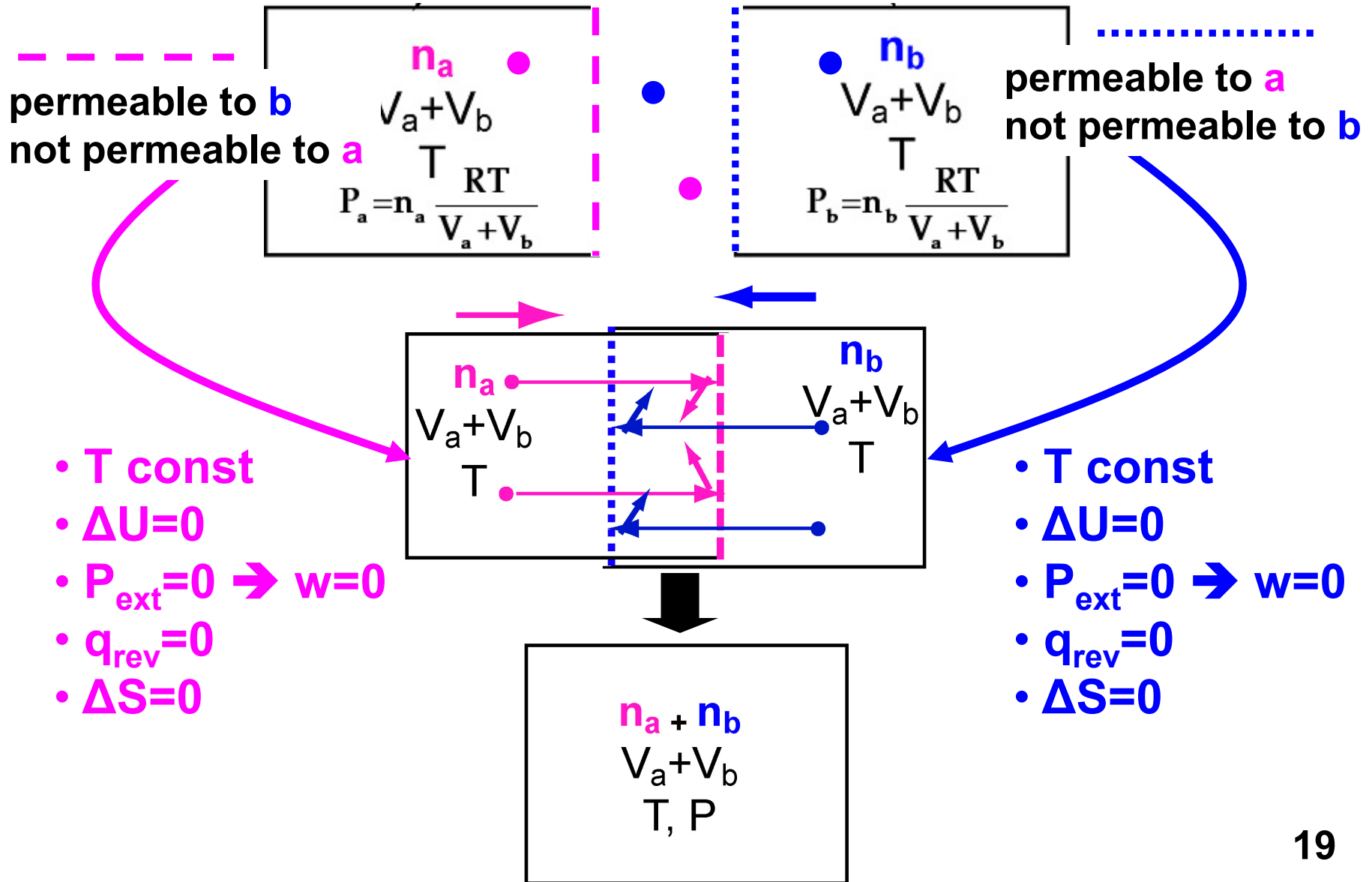
some arithmetic

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)

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

$$ideal\ gas: at \quad start\ PV_a = n_a RT\ ; \quad PV_b = n_b RT$$ ⟵ divide

$$at \quad end\ P(V_a + V_b) = (n_a + n_b)RT$$ ⟵ 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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- Thermal properties of entropy and entropy calculations
    - $dS = \dfrac{đ q_{rev}}{T}$; $\Delta S = \displaystyle\int \dfrac{đ q_{rev}}{T}$; $\displaystyle\oint \dfrac{đ q_{rev}}{T} = 0$

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

    - $\Delta S_{total \equiv universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$
    - S is a state function; dS is an exact differential
    - Dependence of S on
        - T: $\left(\dfrac{\partial \bar{S}}{\partial T}\right)_V = \dfrac{\bar{C}_V}{T}$; $\left(\dfrac{\partial \bar{S}}{\partial T}\right)_P = \dfrac{\bar{C}_P}{T}$

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

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

        - 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: $\bar{S}^\circ(T)$
    - $\Delta S^0_{reaction}(T) = \displaystyle\sum_i v_i \bar{S}^0_i(T)$
    - 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)

- $P_1 V_1^{\frac{C_P}{C_V}} = P_2 V_2^{\frac{C_P}{C_V}}$ (adiabatic reversible path, PV^{γ} = constant)

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

Energy and enthalpy:

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

For ideal gas:

- $\Delta U = C_V \Delta T = n\overline{C}_V \Delta T$
- $\Delta H = C_P \Delta T = n\overline{C}_P \Delta T$
- $(\overline{C}_P - \overline{C}_V) = R$
- $\overline{C}_V = \dfrac{3}{2} R$ (*monatomic ideal gas*)
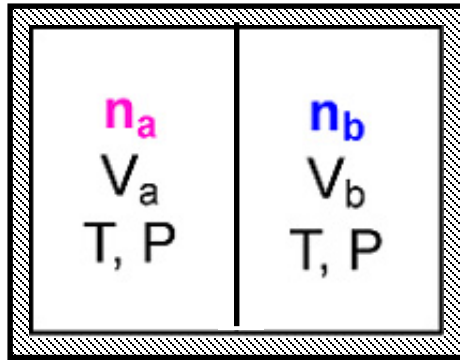
For ideal, reversible, Carnot Engine:

- $\varepsilon = \dfrac{-w_{total}}{q_H} = 1 - \dfrac{T_L}{T_H}$

Some entropy relationships:

- $\left(\dfrac{\partial S}{\partial T}\right)_P = \dfrac{C_P}{T} = \dfrac{n\overline{C}_P}{T} \quad ; \quad \left(\dfrac{\partial S}{\partial T}\right)_V = \dfrac{C_V}{T} = \dfrac{n\overline{C}_V}{T}$
- $\Delta S_{mixing\_ideal\_gases} = -n_{total} R \sum_i X_i \ln X_i$ (*where X_i is mole fraction component i*)
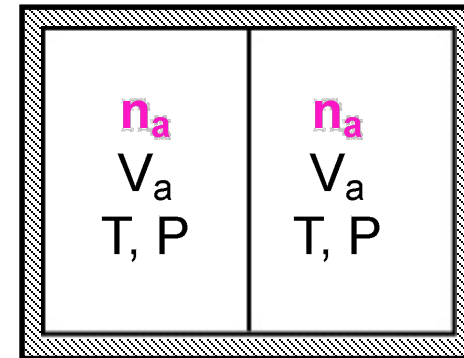
[see reverse side for more relationships]:

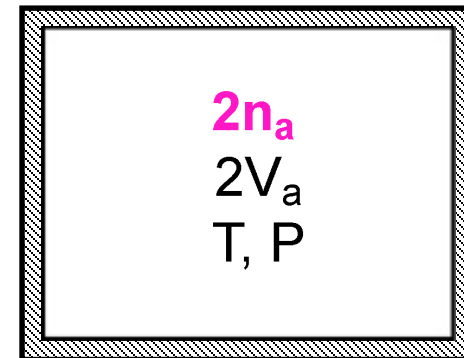# Gibb's Paradox: distinguishable vs identical (don't fret)

Left panel:

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

Middle:

$n_a = n_b$
$V_a = V_b$

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

Right panel:

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)

entropy

Full Paper

Gibbs' Paradox and the Definition of Entropy

Robert H. Swendsen

Physics Department, Carnegie Mellon University, Pittsburgh, PA 15213, USA
E-Mail: swendsen@cmu.edu

The Gibbs Paradox and the Distinguishability of Identical Particles

Marijn A.M. Versteegh[1,2] and Dennis Dieks[1]

[1]*Institute for History and Foundations of Science, Utrecht University,
P.O. Box 80 010, 3508 TA Utrecht, The Netherlands*

[2]*Debye Institute for Nanomaterials Science,
Utrecht University, Princetonplein 1,
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

observations: thermo ≡ heat

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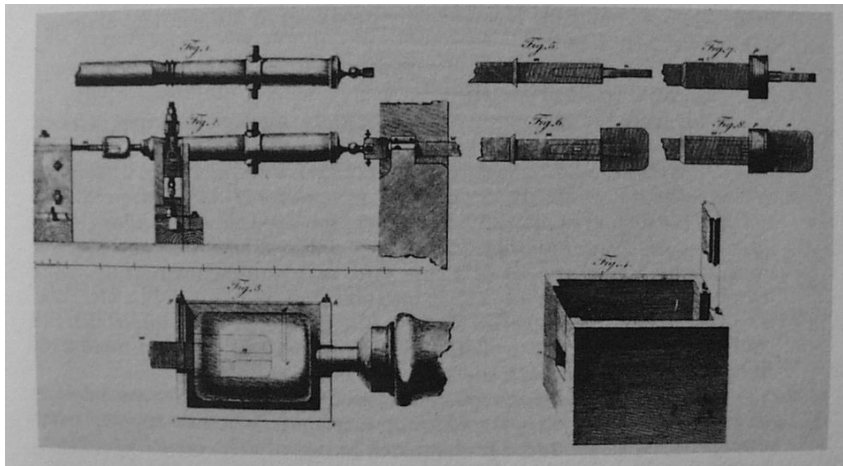- observed water turning into steam when canon barrel was bored
- *work ⇔ heat*

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.)
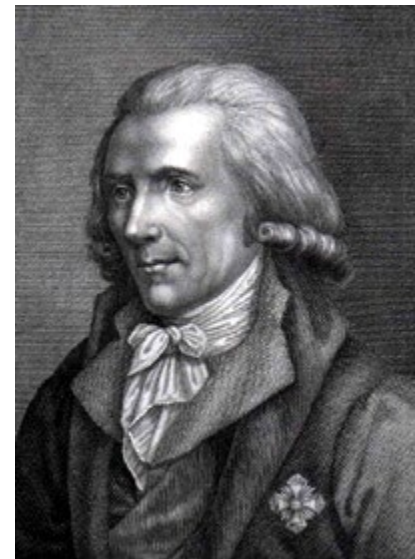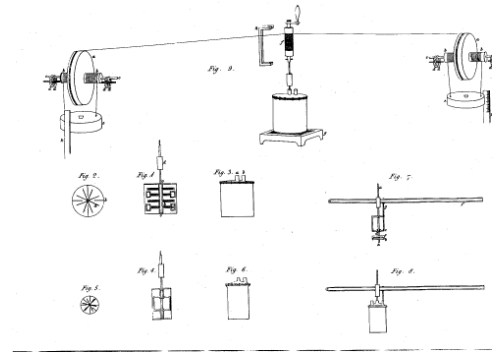
observations: mechanical efficiency of steam engine

- Sadi Carnot, 1824
- efficiency of engines
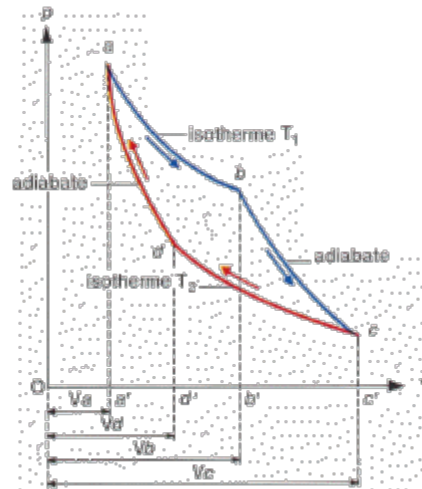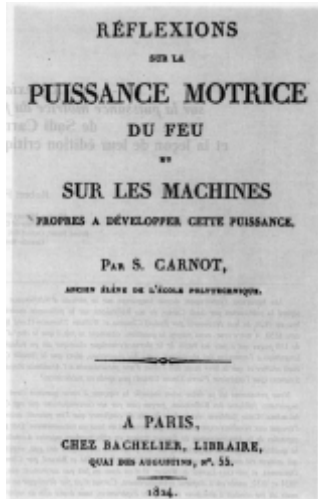
guiding principles

- 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

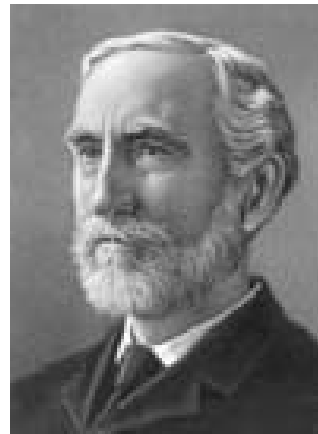- Boltzmann, late 19th century,
  molecular picture of entropy

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.

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

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

Ludwig Boltzma...
(standing, from...
Hiecke, (sitting...
Boltzmann, Kle...

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) × 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

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