Chemistry 163B Winter 2014
notes for $\Delta S_{UNIVERSE}$ and Thermodynamic Tools

Chemistry 163B

ΔS of the UNIVERSE

and

Deriving Thermodynamic Relationships

Challenged Penmanship

Notes

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1. **$\Delta S_{universe} > 0$**

2. **Maxwell-Euler Relationships**

3. **$\Delta S_{\Phi} = \Delta H_{\Phi} / T_{\Phi}$ (Φ is phase transition)**

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2nd Law of Thermodynamics in terms of entropy

- **S is a STATE FUNCTION**

- $\Delta S = \int_{rev} \frac{đq_{rev}}{T} > \int_{irrev} \frac{đq_{irrev}}{T}$

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$\Delta S_{universe} \geq 0$

today

~~soon :~~

$\Delta S_{system} + \Delta S_{surroundings} = \Delta S_{universe} \geq 0$

disorder increases

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the entropy of the UNIVERSE increases

$dS \geq \dfrac{đq}{T}$

$\Delta S_{system} \geq \int \dfrac{đq_{sys}}{T}$ $\Delta S_{surr} \geq \int \dfrac{đq_{surr}}{T}$

$\Delta S_{system} + \Delta S_{surr} \geq \left[\int \dfrac{đq_{sys}}{T} + \int \dfrac{đq_{surr}}{T} \right]$

$đq_{surr} = ?\ đq_{sys}$

$\Delta S_{system} + \Delta S_{surr} \geq \left[\int \dfrac{đq_{sys}}{T} - \int \dfrac{đq_{sys}}{T} \right] =$

$\Delta S_{system} + \Delta S_{surroundings} = \Delta S_{??} = \Delta S_{UNIVERSE} \geq 0$

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towards a universal PEA SOUP

Plotkin's Entropy   *Clark's Entropy # 2 Acrylic 30 x 24*

http://www.donnabellas.com/abstract/science/plotkinentropy.htm   http://www.williamgclark.com/entropy.jpg

UNIVERSE $\Delta S > 0$ PEA SOUP

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BUT ALAS: $\Delta S_{system} < 0$ (order) if $\Delta S_{surroundigns} > 0$ (disorder)

$\Delta S_{surroundings} > 0$ $\Delta S_{system} < 0$

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Raff's Sammy

$P_{ex} = 0$
$P_{int} = \frac{nR(300K)}{20L}$ → $P_{int} = \frac{nR(300K)}{40L}$

w=0
q=0
ΔU=0
ΔT=0

4.16 Sam is still having great difficulty with physical chem-
istry. However, he has found a problem he can solve:
"An ideal gas is expanded isothermally and adiabati-
cally into a vacuum to double its volume from 20 L to
40 L at 300 K. Compute ΔS for the process." Noting
that q for the adiabatic process is zero and that the
process is isothermal, Sam computes

$$\Delta S = \int \frac{\delta q}{T} = T^{-1} \int \delta q = \frac{q}{T} = 0. \quad ?$$

Has Sam finally gotten a problem correct? Explain.
Leigh, who is making an A in physical chemistry,
obtains a different answer for this problem. What
answer does she obtain?

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trepanation, the mind and the brain

P. Treveris, 1525, England

H. Bosch, 1480, Dutch   Peru, ~ 1000AD, pre-Incan

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trepanation and the second

$$\Delta S = \int \frac{\bar{d}q_{REVERSIBLE}}{T} \geq \int \frac{\bar{d}q}{T} \text{ hould}$$

a music major !!

I'll fix that !

...m163B ...nt thought

$$\Delta S = \int \frac{\bar{d}q_{REVERSIBLE}}{T}$$

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remember

same initial and final states of system:

- $\Delta S = \Delta S_{reversible} = \Delta S_{irreversible}$

- $\displaystyle \Delta S = \int_{initial}^{final} \frac{\bar{d}q_{reversible}}{T} \geq \int_{initial}^{final} \frac{\bar{d}q}{T}$

**so how will reversible and irreversible processes between
same initial and final states of system differ???**

- $\Delta S_{system} + \Delta S_{surroundings} \equiv \Delta S_{universe} \geq 0$

  (= for reversible, > for irreversible)

- $\Delta S_{surroundings}$ will differ

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tools for evaluating thermodynamic relationships: **starting relationships**

definitions:
U ≡ internal energy
H ≡ U + PV
A ≡ U –TS
G ≡ H –TS

relationships from 1st and 2nd Laws:
[no change of material (dn_i=0) and, only PV work (dw_{other}=0)]

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

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

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

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differential relationships

$U \equiv$ internal energy
$H \equiv U + PV$
$A \equiv U - TS$
$G \equiv H - TS$

$$dU = đq + đw = đq - PdV$$
$$dS = \frac{đq_{rev}}{T} \quad dq = TdS$$

$$dU = TdS - PdV \qquad U(S,V)$$
$$\overset{TdS-PdV}{dH = dU + PdV + VdP}$$
$$dH = TdS + VdP \qquad H(S,P)$$
$$\overset{TdS-PdV}{dA = dU - TdS - SdT}$$
$$dA = -SdT - PdV \qquad A(T,V)$$
$$\overset{TdS+VdP}{dG = dH - TdS - SdT}$$
$$dG = -SdT + VdP \qquad G(T,P)$$

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example of Maxwell-Euler (dG=-S dT +V dP)

$$dG = -S \ dT + V \ dP \qquad \textbf{1}^{st} \text{ and } \textbf{2}^{nd} \text{ Laws}$$

$$G(T,P):$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \qquad \textbf{math, total differential}$$

so: $\left(\frac{\partial G}{\partial T}\right)_P = -S \ \text{ and } \ \left(\frac{\partial G}{\partial P}\right)_T = V$

what about: $\left(\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right)_P$

thus: $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$ $\qquad$ **Maxwell-Euler Relationship from dG**

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Euler-Maxwell relationships **(handout #4 Math Comments)** ➡

5. Suppose we know that a differential is of the form and is an **exact differential**:
$d\psi(x,y) = M\,dx + N\,dy$ (where M and N are some functions or variables)

example (1st and 2nd Laws of Thermodynamics give dG as exact differential)
$dG(T,P) = -S\,dT + V\,dP$ (G and S are free energy and entropy)

THEN WE HAVE THE FOLLOWING USEFUL RELATIONSHIPS:

a. $\left(\frac{\partial \psi}{\partial x}\right)_y = M \ \text{ and } \ \left(\frac{\partial \psi}{\partial y}\right)_x = N$ $\qquad$ $d\psi(x,y) = \left(\frac{\partial \psi}{\partial x}\right)_y dx + \left(\frac{\partial \psi}{\partial y}\right)_x dy$
or $\qquad\qquad\qquad\qquad\qquad\qquad \| \qquad\qquad\qquad \|$
$\left(\frac{\partial G}{\partial T}\right)_P = -S \ \text{ and } \ \left(\frac{\partial G}{\partial P}\right)_T = V$ $\qquad$ $d\psi(x,y) = M \ dx + N \ dy$

b. and since, for well behaved functions, "mixed" second partial derivatives are equal (i.e. the order of differentiation does not matter)

$\left(\frac{\partial^2 \psi}{\partial y\partial x}\right)_{x,y} = \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial^2 \psi}{\partial x\partial y}\right)_{y,x}$ $\qquad$ $\left(\frac{\partial}{\partial y}\left(\frac{\partial \psi}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial \psi}{\partial y}\right)_x\right)_y$
or
$\left(\frac{\partial(-S)}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$ which is same as $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ $\qquad$ $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

this is an example of the Maxwell-Euler relationships that we will use often

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Euler-Maxwell relationships

$$dU = TdS - PdV \longrightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$dH = TdS + VdP \longrightarrow \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$dA = -SdT - PdV \longrightarrow -\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$$

$$dG = -SdT + VdP \longrightarrow \begin{array}{c} \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \\[4pt] -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \end{array}$$

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

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entropy variations with T and P

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

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

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

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

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finite changes from derivatives: isothermal volume change

$$dS(T,V) = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

isothermal $dT = 0$

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV = \left(\frac{\partial P}{\partial T}\right)_V dV$$

general for no work other; no change of composition

$$\Delta S_{V_1 \to V_2, Tconst} = \int_{V_1}^{V_2} dS = \int_{V_1}^{V_2}\left(\frac{\partial S}{\partial V}\right)_T dV = \int_{V_1}^{V_2}\left(\frac{\partial P}{\partial T}\right)_V dV$$

$$\Delta S_{V_1 \to V_2} = \int_{V_1}^{V_2} dS = \int_{V_1}^{V_2}\left(\frac{\partial P}{\partial T}\right)_V dV$$

$$\Delta S_{V_1 \to V_2} = \int_{V_1}^{V_2} \frac{nR}{V} dV = nR\ln\frac{V_2}{V_1}$$

for ideal gas:
$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$$

[note: same as $\Delta S_{V_1 \to V_2} = \frac{q_{rev}}{T}$, q_{rev} for isothermal volume change]

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calculating entropy (see summary on review handout) ➡

- Thermal properties of entropy and entropy calculations
  - ✓ $dS = \dfrac{d\,q_{rev}}{T}$; $\Delta S = \int \dfrac{d\,q_{rev}}{T}$; $\oint \dfrac{d\,q_{rev}}{T} = 0$
  - ✓ $\Delta S \geq \int \dfrac{d\,q}{T}$; $0 \geq \oint \dfrac{d\,q}{T}$; ($=$ for reversible process; $>$ for spontaneous ['real'] process)
  - ✓ $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$
  - 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: $\left(\dfrac{\partial \bar{S}}{\partial V}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_V$
    - 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: $\bar{S}^\circ(T)$
  - $\Delta S^\circ_{rxn}(T) = \sum_i \nu_i \bar{S}^\circ_i(T)$
  - Entropy of mixing: $\Delta S = -n_{total} R \sum_i X_i \ln X_i$, where $X_i = \dfrac{n_i}{n_{total}}$

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ΔS for equilibrium phase transition

for phase transition ϕ **at equilibrium conditions**

(e.g.) $H_2O(\ell) \rightleftharpoons H_2O$ (g, 1atm, 373K)

or $H_2O(\ell) \rightleftharpoons H_2O$ (s, 1atm, 273K)

$$\left(\Delta H_\phi\right)_P = q_{reversible}$$

$$\left(\Delta S_\phi\right)_P = \frac{\left(\Delta H_\phi\right)_P}{T_\phi}$$

HW6 #35 ΔS for $H_2O(\ell) \longrightarrow H_2O$ (s, 1atm, 263K)

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End of Lecture

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Slide 22

Thermodynamics and Black Holes (and other cosmology?)

Black Hole Thermodynamics

Entropy of a black hole

http://nrumiano.free.fr/Estars/bh_thermo.html

Black Holes and Beyond:
Harvard's Andrew Strominger on String Theory

http://archive.sciencewatch.com/may-june99/sw_may-june99_page3.htm

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Thermodynamics and Black Holes (and other cosmology?)

McMaster University

Thermodynamics of Black Holes
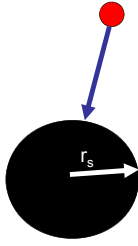
Eric Monkman, Matthew J. Farrar
Department of Physics and Astronomy
McMaster University, Hamilton, ON L8S 4M1
2007 03 29

http://physwww.physics.mcmaster.ca/phys3a03/Thermodynamics_and_Black_Holes.ppt

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Slide 24

$\Delta S_{universe} < 0????$

- system with entropy S falls into black hole ($r < r_s$)

- whole system gets sucked into black hole → includes entropy

- what happens to the entropy of the universe?

- What happened to the 2nd law of thermodynamics???

Striking Similarity

- 2nd Law of Thermodynamics: $dS \geq 0$
  - vs.
- Hawking Area Theorem: $dA \geq 0$

- a coincidence? Bekenstein, 1973, says "no"

- Hawking, Bekenstein derived entropy of black hole:

$$S_{BH} = A/4$$

Generalized Second Law (GSL)

- In words:

- "*The common entropy in the black-hole exterior plus the black-hole entropy never decreases.*"
- Bekenstein, J. Black Holes and Entropy, *Phys. Rev. D.*, 7, 2333, (1973).

- In math:

- $\Delta S_{BH} + \Delta S_c \geq 0$ (S_c is common entropy to the exterior)