Chemistry 163B Winter 2020
Lecture 12: $\Delta S_{UNIVERSE}$ and Thermodynamic Tools

Lecture 12 Chemistry 163B
Winter 2020

ΔS of the UNIVERSE

and

Deriving Thermodynamic Relationships

Challenged Penmanship

Notes

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goals

1. **$\Delta S_{universe} > 0$**
2. **Maxwell-Euler Relationships**
3. **$\Delta S_{\Phi} = \Delta H_{\Phi} / T_{\Phi}$ (Φ is phase transtion)**

2

2nd Law of Thermodynamics in terms of entropy

- **S is a STATE FUNCTION**
- $\Delta S = \int_{rev} \frac{đq_{rev}}{T} > \int_{irrev} \frac{đq_{irrev}}{T}$

3

$\Delta S_{universe} \geq 0$

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

$$dS \geq \frac{đq}{T}$$

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

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

$$đq_{surr} = ? \; đq_{sys}$$

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

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

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the entropy of the UNIVERSE increases

$$dS \geq \frac{đq}{T}$$

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

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

$$đq_{surr} = - đq_{sys}$$

$$\Delta S_{system} + \Delta S_{surr} \geq \left[\int \frac{đq_{sys}}{T} - \int \frac{đq_{sys}}{T} \right] = 0$$

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

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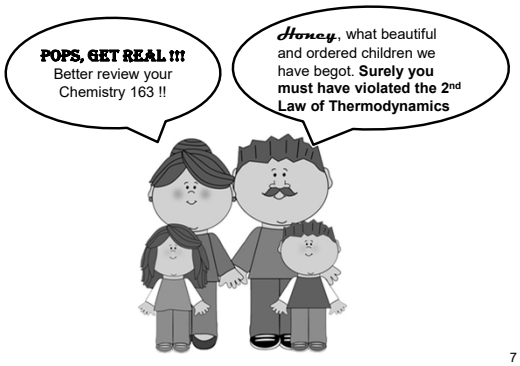
a thoughtful domestic discussion



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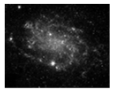
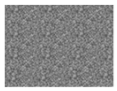
towards the disorder of a universal PEA SOUP

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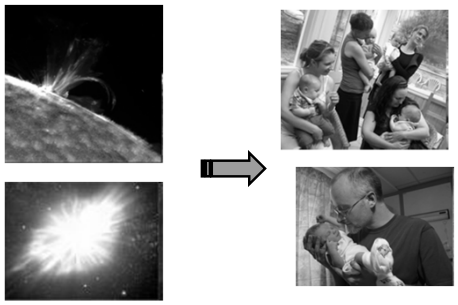
BUT ALAS: if $\Delta S_{surroundings} > 0$ (disorder) then $\Delta S_{system} < 0$ (order)



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

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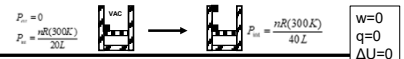
Raff's Sammy



w=0
q=0
ΔU=0
ΔT=0
ΔS=?

4.16 Sam is still having great difficulty with physical chemistry. However, he has found a problem he can solve:

"An ideal gas is expanded isothermally and adiabatically 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

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

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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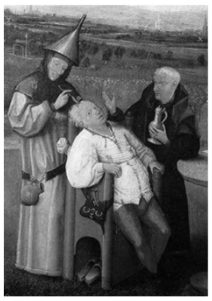
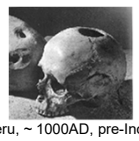
trepanation, the mind and the brain



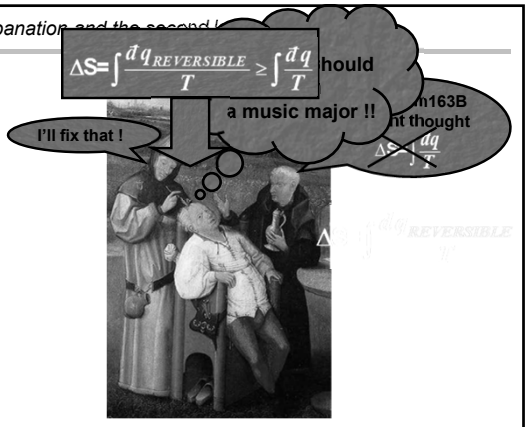
H. Bosch, 1480, Dutch

P. Treveris, 1525, England



Peru, ~ 1000AD, pre-Incan

trepanation and the second l



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remember

same initial and final states of system:

- $\Delta \mathbf{S} = \Delta \mathbf{S}_{reversible} = \Delta \mathbf{S}_{irreversible}$
- $\Delta \mathbf{S} = \int_{initial}^{final} \frac{đq_{reversible}}{T} \geq \int_{initial}^{final} \frac{đq}{T}$

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)]

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

$$dU = đq + đw = đq - PdV$$

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

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differential relationships

U ≡ internal energy	$dU = đq + đw = đq - PdV$
H ≡ U + PV	
A ≡ U –TS	$dS = \frac{đq_{rev}}{T} \qquad đq = TdS$
G ≡ H –TS	

$$dU = T\underline{dS} - P\underline{dV} \qquad U(\underline{S},\underline{V})$$

$$dH = dU + PdV + VdP \quad (TdS - PdV)$$

$$dH = T\underline{dS} + V\underline{dP} \qquad H(\underline{S},\underline{P})$$

$$dA = dU - TdS - SdT \quad (TdS - PdV)$$

$$dA = -S\underline{dT} - P\underline{dV} \qquad A(\underline{T},\underline{V})$$

$$dG = dH - TdS - SdT \quad (TdS + VdP)$$

$$dG = -S\underline{dT} + V\underline{dP} \qquad G(\underline{T},\underline{P})$$

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

$dG = -S\ dT + V\ dP$ **1st and 2nd Laws**

$G(T,P)$:

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

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

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Euler-Maxwell relationships (handout #5 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. $\left(\frac{\partial \psi}{\partial x}\right)_y = M$ 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

$\left(\frac{\partial G}{\partial T}\right)_P = -S$ 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

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

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

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Euler-Maxwell relationships

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

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

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

$dG = -SdT + VdP \rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

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

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

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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 $dT = 0$

general for no work other; no change of composition

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

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

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

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

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
- ✓ $dS = \frac{\partial q_{rev}}{T}$; $\Delta S = \int \frac{\partial q_{rev}}{T}$; $\oint \frac{\partial q_{rev}}{T} = 0$
- ✓ $\Delta S \geq \int \frac{\partial q}{T}$; $0 \geq \oint \frac{\partial q}{T}$; (= *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: $\left(\frac{\partial \bar{S}}{\partial T}\right)_V = \frac{\bar{C}_V}{T}$; $\left(\frac{\partial \bar{S}}{\partial T}\right)_P = \frac{\bar{C}_P}{T}$
  - P: $\left(\frac{\partial \bar{S}}{\partial P}\right)_T = -\left(\frac{\partial \bar{V}}{\partial T}\right)_P$
  - V: $\left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
  - 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: $\bar{S}^o(T)$
- $\Delta S^o_{reaction}(T) = \sum_i \nu_i \bar{S}^o_i(T)$
- Entropy of mixing: $\Delta S = -n_{total} R \sum_i X_i \ln X_i$ *where* $X_i = \frac{n_i}{n_{total}}$

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ΔS for equilibrium phase transition

for phase transition ϕ **at equilibrium conditions**

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

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

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

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

HW5 #35 ΔS for $H_2O(\ell) \rightarrow H_2O$ (s, 1atm, 263K)

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End of Lecture 12

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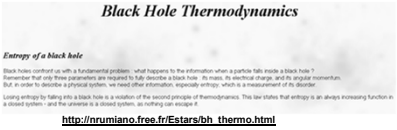
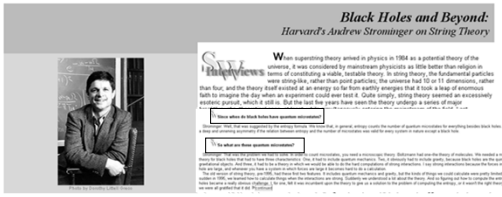
Thermodynamics and Black Holes (and other cosmology?)



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



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

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

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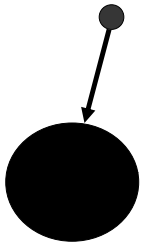
$\Delta S_{universe} < 0????$

- 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)