

Chemistry 163B Winter 2020

Lecture 12: $\Delta S_{\text{UNIVERSE}}$ 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. $\Delta S_{\text{universe}} > 0$
2. Maxwell-Euler Relationships
3. $\Delta S_{\phi} = \Delta H_{\phi} / T_{\phi}$ (ϕ is phase transtion)

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2nd Law of Thermodynamics in terms of entropy

• S is a STATE FUNCTION

• $\Delta S = \int_{\text{rev}} \frac{dq_{\text{rev}}}{T} > \int_{\text{irrev}} \frac{dq_{\text{irrev}}}{T}$

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$\Delta S_{\text{universe}} \geq 0$

today
~~soon :~~

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

disorder increases

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the entropy of the UNIVERSE increases

$$dS \geq \frac{\bar{dq}}{T}$$

$$\Delta S_{\text{system}} \geq \int \frac{\bar{dq}_{\text{sys}}}{T} \quad \Delta S_{\text{sur}} \geq \int \frac{\bar{dq}_{\text{sur}}}{T}$$

$$\Delta S_{\text{system}} + \Delta S_{\text{sur}} \geq \left[\int \frac{\bar{dq}_{\text{sys}}}{T} + \int \frac{\bar{dq}_{\text{sur}}}{T} \right]$$

$$\bar{dq}_{\text{sur}} = \boxed{?} \bar{dq}_{\text{sys}}$$

$$\Delta S_{\text{system}} + \Delta S_{\text{sur}} \geq \left[\int \frac{\bar{dq}_{\text{sys}}}{T} - \int \frac{\bar{dq}_{\text{sys}}}{T} \right] = \boxed{\quad}$$

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

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the entropy of the UNIVERSE increases

$$dS \geq \frac{\bar{dq}}{T}$$

$$\Delta S_{\text{system}} \geq \int \frac{\bar{dq}_{\text{sys}}}{T} \quad \Delta S_{\text{sur}} \geq \int \frac{\bar{dq}_{\text{sur}}}{T}$$

$$\Delta S_{\text{system}} + \Delta S_{\text{sur}} \geq \left[\int \frac{\bar{dq}_{\text{sys}}}{T} + \int \frac{\bar{dq}_{\text{sur}}}{T} \right]$$

$$\bar{dq}_{\text{sur}} = - \bar{dq}_{\text{sys}}$$

$$\Delta S_{\text{system}} + \Delta S_{\text{sur}} \geq \left[\int \frac{\bar{dq}_{\text{sys}}}{T} - \int \frac{\bar{dq}_{\text{sys}}}{T} \right] = 0$$

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

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a thoughtful domestic discussion

POPS, GET REAL !!!
Better review your
Chemistry 163 !!

Honey, what beautiful
and ordered children we
have begot. Surely you
must have violated the 2nd
Law of Thermodynamics

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towards the disorder of a universal PEA SOUP

Plotkin's Entropy

<http://www.donnabellas.com/abstract/science/plotkinentropy.htm>

Clark's Entropy # 2 Acrylic 30 x 24

<http://www.williamclark.com/entropy.jpg>

UNIVERSE $\xrightarrow{\Delta S > 0}$ PEA SOUP

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

$\Delta S_{\text{surroundings}} > 0$

➔

$\Delta S_{\text{system}} < 0$

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Raff's Sammy

$P_{\text{ext}} = 0$
 $P_{\text{ext}} = \frac{nR(300\text{K})}{20\text{L}}$

$P_{\text{ext}} = \frac{nR(300\text{K})}{40\text{L}}$

$w=0$
 $q=0$
 $\Delta U=0$
 $\Delta T=0$
 $\Delta S=?$

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 law

$$\Delta S = \int \frac{dq_{\text{REVERSIBLE}}}{T} \geq \int \frac{dq}{T} \text{ should}$$

I'll fix that!

a music major !!

in 163B
at thought

REVERSIBLE

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remember

same initial and final states of system:


- $\Delta S = \Delta S_{\text{reversible}} = \Delta S_{\text{irreversible}}$
- $\Delta S = \int_{\text{initial}}^{\text{final}} \frac{dq_{\text{reversible}}}{T} \geq \int_{\text{initial}}^{\text{final}} \frac{dq}{T}$

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


- $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \equiv \Delta S_{\text{universe}} \geq 0$
(= for reversible, > for irreversible)
- $\Delta S_{\text{surroundings}}$ will differ

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tools for evaluating thermodynamic relationships: starting relationships



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



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

$dq_v = n \bar{C}_V dT \quad dq_p = n \bar{C}_p dT$

$dU = dq + dw = dq - PdV$

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

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differential relationships

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

$dU = dq + dw = dq - PdV$
 $dS = \frac{dq_{\text{rev}}}{T} \quad dq = Tds$

$dU = Tds - PdV \quad U(S, V)$
 $dH = Tds + PdV + VdP \quad H(S, P)$
 $dA = Tds - PdV - SdT \quad A(T, V)$
 $dG = Tds + VdP - SdT \quad G(T, P)$

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example of Maxwell-Euler ($dG = -SdT + VdP$)

$dG = -SdT + VdP \quad \text{1st and 2nd Laws}$

$G(T, P):$

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

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

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Euler-Maxwell relationships (handout #5 Math Comments) \implies

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)
 $dG(T, P) = -SdT + VdP$ (G and S are free energy and entropy)

THEN WE HAVE THE FOLLOWING USEFUL RELATIONSHIPS:

$\left(\frac{\partial \psi}{\partial x}\right)_y = M$ and $\left(\frac{\partial \psi}{\partial y}\right)_x = N \quad d\psi(x, y) = \left(\frac{\partial \psi}{\partial x}\right)_y dx + \left(\frac{\partial \psi}{\partial y}\right)_x dy$

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

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

$\left(\frac{\partial^2 \psi}{\partial y \partial x}\right)_x = \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial^2 \psi}{\partial x \partial y}\right)_y$ $\left(\frac{\partial}{\partial y} \left(\frac{\partial \psi}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x} \left(\frac{\partial \psi}{\partial y}\right)_x\right)_y$

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

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Euler-Maxwell relationships

$dU = Tds - PdV \quad \rightarrow \quad \left(\frac{\partial T}{\partial V}\right)_s = -\left(\frac{\partial P}{\partial S}\right)_v$

$dH = Tds + VdP \quad \rightarrow \quad \left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial V}{\partial S}\right)_p$

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

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

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entropy variations with T and P

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

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

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

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

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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

$dS = \left(\frac{\partial S}{\partial V}\right)_T dV = \left(\frac{\partial P}{\partial T}\right)_T dV$
 $\Delta S_{T_1 \rightarrow T_2, \text{isotherm}} = \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V}\right)_T dV = \int_{V_1}^{V_2} \left(\frac{\partial P}{\partial T}\right)_T dV$

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

$\Delta S_{T_1 \rightarrow T_2} = \int_{V_1}^{V_2} dS = \int_{V_1}^{V_2} \left(\frac{\partial P}{\partial T}\right)_T dV$
 $\Delta S_{T_1 \rightarrow T_2} = \int_{V_1}^{V_2} \frac{nR}{V} dV = nR \ln \frac{V_2}{V_1}$

[note: same as $\Delta S_{T_1 \rightarrow T_2} = \frac{q_{\text{rev}}}{T}$, q_{rev} for isothermal volume change]

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calculating entropy (see summary on review handout) \implies

- Thermal properties of entropy and entropy calculations
- ✓ $dS = \frac{dq_{\text{rev}}}{T}$; $\Delta S = \int \frac{dq_{\text{rev}}}{T}$; $\oint \frac{dq_{\text{rev}}}{T} = 0$
- ✓ $\Delta S \geq \int \frac{dq}{T}$; $0 \geq \oint \frac{dq}{T}$; (= for reversible process; > for spontaneous [real] process)
- ✓ $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$
- S is a state function; dS is an exact differential
- Dependence of S on
 - T: $\left(\frac{\partial S}{\partial T}\right)_P = \frac{\bar{C}_P}{T}$; $\left(\frac{\partial S}{\partial T}\right)_V = \frac{\bar{C}_V}{T}$
 - P: $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial \bar{V}}{\partial T}\right)_P$
 - V: $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_T$
- Phase: $\Delta S = \frac{\Delta H_{\text{transition phase change}}}{T_{\text{equilibrium phase change}}}$
 - Calculation of entropy changes for changes in P, V, T, phase
 - Third Law and calculations using Third Law Entropies: $S^\circ(T)$
 - $\Delta S_{\text{mix}}(T) = -R \sum_i X_i \ln X_i$
 - Entropy of mixing: $\Delta S = -n_{\text{total}} R \sum_i X_i \ln X_i$ where $X_i = \frac{n_i}{n_{\text{total}}}$

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ΔS for equilibrium phase transition


for phase transition ϕ at equilibrium conditions
 (e.g.) $\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{O}(\text{g}, 1\text{atm}, 373\text{K})$
 or $\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{O}(\text{s}, 1\text{atm}, 273\text{K})$

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

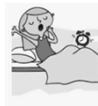
$$(\Delta S_\phi)_P = \frac{(\Delta H_\phi)_P}{T_\phi}$$

HW5 #35 ΔS for $\text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{O}(\text{s}, 1\text{atm}, 263\text{K})$

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End of Lecture 12



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Thermodynamics and Black Holes (and other cosmology?)

Black Hole Thermodynamics


Entropy of a black hole

Black holes confront us with a fundamental problem: what happens to the information when a particle falls into a black hole? General relativity and quantum mechanics are required to fully describe a black hole. In relativity, the electrical charge and the angular momentum. But in order to describe a physical system, we need other information, especially entropy, which is a measurement of its disorder.

Linking entropy to black holes is a violation of the second principle of thermodynamics. The law states that entropy is an always increasing function in a closed system, and the creation of a closed system, all matter can escape it.

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

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



When superstring theory arrived in physics in 1984 as a potential theory of the universe, it was considered by mathematicians and physicists as being far more elegant than the messy, messy world of classical physics. In string theory, the fundamental particles were strings, rather than point particles, the universe had 10 or 11 dimensions, rather than three, and the theory itself consisted of an energy on the face looking straight ahead & took a shape of extended paths to imagine the day when an agreement could ever last. Quite simply, string theory seemed an accessible modern physics, which is still in. But the fact the year has seen the theory undergo a series of changes...

http://archive.sciencemag.com/may-june99/99_may-june99_page3.htm

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Thermodynamics and Black Holes (and other cosmology?)



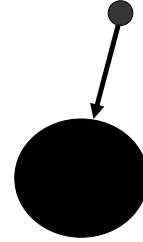
Thermodynamics of Black Holes

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

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

- system with entropy S falls into black hole ($r < r_s$)
- whole system gets sucked into black hole \rightarrow 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:

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

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:

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