

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

Lecture 12 Chemistry 163B  
Winter 2020

$\Delta S$  of the **UNIVERSE**

and

Deriving Thermodynamic Relationships

Challenged Penmanship

Notes

1

*goals*

---

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

2

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

*2<sup>nd</sup> Law of Thermodynamics in terms of entropy*

---

• **S is a STATE FUNCTION**

$$\bullet \Delta S = \int_{\text{rev}} \frac{\bar{d}q_{\text{rev}}}{T} > \int_{\text{irrev}} \frac{\bar{d}q_{\text{irrev}}}{T}$$

3

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

---

*today*

~~soon :~~

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

***disorder increases***

4

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

*the entropy of the UNIVERSE increases*

---

$$dS \geq \frac{\bar{d}q}{T}$$

$$\Delta S_{\text{system}} \geq \int \frac{\bar{d}q_{\text{sys}}}{T} \quad \Delta S_{\text{surr}} \geq \int \frac{\bar{d}q_{\text{surr}}}{T}$$

$$\Delta S_{\text{system}} + \Delta S_{\text{surr}} \geq \left[ \int \frac{\bar{d}q_{\text{sys}}}{T} + \int \frac{\bar{d}q_{\text{surr}}}{T} \right]$$

$$\bar{d}q_{\text{surr}} = ? \bar{d}q_{\text{sys}}$$

$$\Delta S_{\text{system}} + \Delta S_{\text{surr}} \geq \left[ \int \frac{\bar{d}q_{\text{sys}}}{T} - \int \frac{\bar{d}q_{\text{sys}}}{T} \right] =$$

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

5

*the entropy of the UNIVERSE increases*

---

$$dS \geq \frac{\bar{d}q}{T}$$

$$\Delta S_{\text{system}} \geq \int \frac{\bar{d}q_{\text{sys}}}{T} \quad \Delta S_{\text{surr}} \geq \int \frac{\bar{d}q_{\text{surr}}}{T}$$

$$\Delta S_{\text{system}} + \Delta S_{\text{surr}} \geq \left[ \int \frac{\bar{d}q_{\text{sys}}}{T} + \int \frac{\bar{d}q_{\text{surr}}}{T} \right]$$

$$\bar{d}q_{\text{surr}} = - \bar{d}q_{\text{sys}}$$

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

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

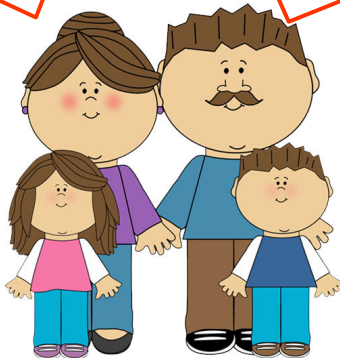
6

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

*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 2<sup>nd</sup>  
Law of Thermodynamics



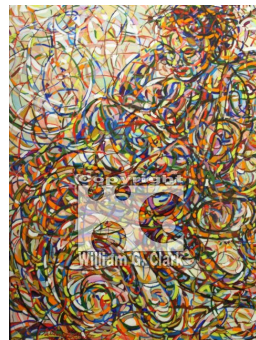
7

*towards the disorder of a universal PEA SOUP*



Plotkin's Entropy

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



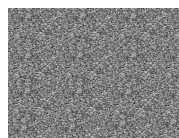
Clark's Entropy # 2 Acrylic 30 x 24

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

UNIVERSE



$\Delta S > 0$

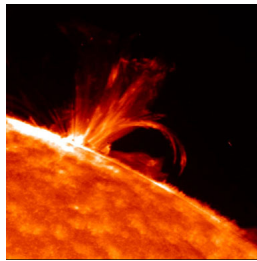


PEA  
SOUP

8

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

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



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

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

9

**Raff's Sammy**

$$P_{\text{ext}} = 0$$

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



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

$$w=0$$

$$q=0$$

$$\Delta U=0$$

$$\Delta T=0$$

$$\Delta S=?$$

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  $\Delta S$  for the process." Noting that  $q$  for the adiabatic process is zero and that the process is isothermal, Sam computes

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

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?

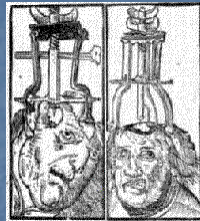
10

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

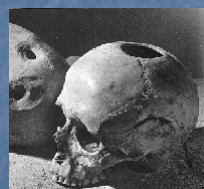
*trepanation, the mind and the brain*



H. Bosch, 1480, Dutch



P. Treveris, 1525, England



Peru, ~ 1000AD, pre-Incan

*trepanation and the second law*

$$\Delta S = \int \frac{\delta q_{\text{REVERSIBLE}}}{T} \geq \int \frac{\delta q}{T} \text{ should}$$

I'll fix that!

a music major !!

Chem 163B  
 don't thought  
 ~~$\Delta S = \int \frac{\delta q}{T}$~~



$$\Delta S = \int \frac{\delta q_{\text{REVERSIBLE}}}{T}$$

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

*remember*

**same initial and final states of system:**

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

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

**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

13

*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 1<sup>st</sup> and 2<sup>nd</sup> Laws:**

[no change of material ( $dn_i=0$ ) and, only PV work ( $dw_{\text{other}}=0$ )]

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

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

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

14

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

*differential relationships*

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

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

$$dS = \frac{\delta q_{\text{rev}}}{T} \quad \delta q = TdS$$

$$dU = TdS - PdV \quad U(S, V)$$

$$dH = dU + PdV + VdP$$

$$dH = TdS + VdP \quad H(S, P)$$

$$dA = dU - TdS - SdT$$

$$dA = -SdT - PdV \quad A(T, V)$$

$$dG = dH - TdS - SdT$$

$$dG = -SdT + VdP \quad G(T, P)$$

15

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

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

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:

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

Maxwell-Euler Relationship  
from dG

16



# Chemistry 163B Winter 2020

## Lecture 12: $\Delta S_{\text{UNIVERSE}}$ and Thermodynamic Tools

### Euler-Maxwell relationships (handout #5 Math Comments) ➡

5. Suppose we know that a differential is of the form and is an **exact** differential:

$$d\psi(x, y) = M dx + N dy \quad (\text{where } M \text{ and } N \text{ are some functions or variables})$$

example (1<sup>st</sup> and 2<sup>nd</sup> Laws of Thermodynamics give dG as exact differential)

$$dG(T, P) = -S dT + V dP \quad (G \text{ and } S \text{ are free energy and entropy})$$

**THEN WE HAVE THE FOLLOWING USEFUL RELATIONSHIPS:**

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

a. or || ||

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

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

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

or

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

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

17

### Euler-Maxwell relationships

$dU = TdS - PdV$	→	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$
$dH = TdS + VdP$	→	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
$dA = -SdT - PdV$	→	$-\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$
$dG = -SdT + VdP$	→	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$ $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

18

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

*entropy variations with T and P*

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

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

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

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

19

*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*  $dT = 0$

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

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

general for no work other;  
no change of composition

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

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

*for ideal gas:*

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

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

20

# Chemistry 163B Winter 2020

## Lecture 12: $\Delta S_{\text{UNIVERSE}}$ and Thermodynamic Tools

### calculating entropy (see summary on review handout) ➡

- 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)
- ✓ ◦  $\Delta S_{\text{total=universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$
- ✓ ◦ S is a state function; dS is an exact differential
- Dependence of S on
  - ✓ ◦ T:  $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$ ;  $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_V}{T}$
  - ✓ ◦ P:  $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$
  - ✓ ◦ V:  $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
  - Phase:  $\Delta S = \frac{\Delta H_{\text{equilibrium phase change}}}{T_{\text{equilibrium phase change}}}$
- Calculation of entropy changes for changes in P, V, T, phase
- Third Law and calculations using Third Law Entropies:  $S^\circ(T)$
- $\Delta S^\circ_{\text{reaction}}(T) = \sum_i \nu_i S_i^\circ(T)$
- Entropy of mixing:  $\Delta S = -n_{\text{total}} R \sum_i X_i \ln X_i$  where  $X_i = \frac{n_i}{n_{\text{total}}}$

21

### $\Delta S$ for equilibrium phase transition

for phase transition  $\phi$  **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  $\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{O}(\text{s}, 1\text{atm}, 273\text{K})$

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

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

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

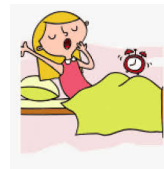
22

# Chemistry 163B Winter 2020

## Lecture 12: $\Delta S_{\text{UNIVERSE}}$ and Thermodynamic Tools



# End of Lecture 12



23

## 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 inside a black hole? Remember that only three parameters are required to fully describe a black hole: its mass, its electrical charge, and its angular momentum. But, in order to describe a physical system, we need other information, especially entropy, which is a measurement of its disorder.

Losing entropy by falling into a black hole is a violation of the second principle of thermodynamics. This law states that entropy is an always increasing function in a closed system - and the universe is a closed system, as nothing can escape it.

[http://numiano.free.fr/Estars/bh\\_thermo.html](http://numiano.free.fr/Estars/bh_thermo.html)

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

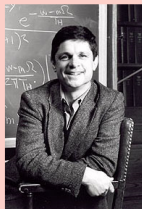


Photo by Cassidy Libell Orsco



When superstring theory arrived in physics in 1984 as a potential theory of the universe, it was considered by mainstream physicists as little better than religion in terms of constituting a viable, testable theory. In string theory, the fundamental particles were string-like, rather than point particles, the universe had 10 or 11 dimensions, rather than four, and the theory itself existed at an energy so far from earthly energies that it took a leap of enormous faith to imagine the day when an experiment could ever test it. Quite simply, string theory seemed an excessively esoteric pursuit, which it still is. But the last five years have seen the theory undergo a series of major

**Q** Since when do black holes have quantum microstates?

Strominger: Well, that was suggested by the entropy formula. We know that, in general, entropy counts the number of quantum microstates for everything besides black holes. It would be a deep and awesome symmetry if the relation between entropy and the number of microstates was valid for every system in nature except a black hole.

**Q** So what are these quantum microstates?

Strominger: That was the problem we had to solve. In 1997 to count microstates, you need a microscopic theory. Outman had an idea: We needed a microscopic theory for black holes that had to have three characteristics. One, it had to include quantum mechanics. Two, it obviously had to include gravity, because black holes are the quintessential gravitational objects. And three, it had to be a theory in which we would be able to do the hard comparisons of string interactions. I say string interactions because the faces inside a black hole are large, and whenever you have a system in which faces are large it becomes hard to do a calculation. The old version of string theory, pre-1995, had these three features. It includes quantum mechanics and gravity, but the kinds of things we could calculate were pretty limited. All of a sudden in 1995, we learned how to calculate things when the interactions are strong. Suddenly we understood a lot about the theory. And so figuring out how to compute the entropy of black holes became a really obvious challenge. For one, let it be incumbent upon the theory to give us a solution to the problem of computing the entropy, or it wasn't the right theory. Of course we were all grateful that it did. **P** continued

[http://archive.sciencewatch.com/may-june99/sw\\_may-june99\\_page3.htm](http://archive.sciencewatch.com/may-june99/sw_may-june99_page3.htm)

24

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

*Thermodynamics and Black Holes (and other cosmology?)*



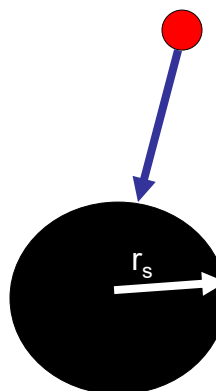
*Thermodynamics of Black Holes*

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

25

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

- 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 2<sup>nd</sup> law of thermodynamics???



## Striking Similarity

- 2<sup>nd</sup> 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)