

Chemistry 163B

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

and

Deriving Thermodynamic Relationships

Challenged Penmanship

Notes

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

2. Maxwell-Euler Relationships

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

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

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- **S is a STATE FUNCTION**

- $$\Delta S = \int_{rev} \frac{\vec{dq}_{rev}}{T} > \int_{irrev} \frac{\vec{dq}_{irrev}}{T}$$

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

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*today*

~~soon :~~

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

***disorder increases***

*the entropy of the UNIVERSE increases*

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

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

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

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

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

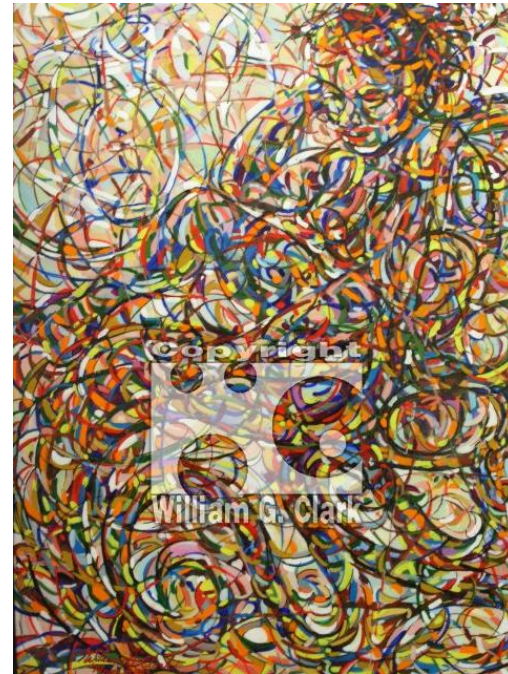
$$\Delta S_{system} + \Delta S_{surroundings} = \Delta S_{??} = \Delta S_{UNIVERSE} \geq 0$$

# towards a universal PEA SOUP



**Plotkin's Entropy**

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



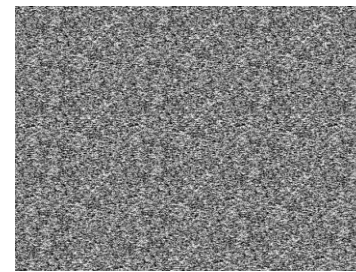
**Clark's Entropy # 2 Acrylic 30 x 24**

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

UNIVERSE



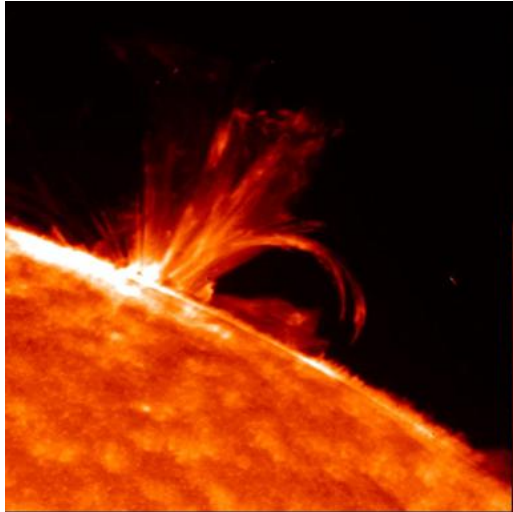
$$\Delta S > 0$$



PEA  
SOUP

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

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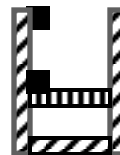
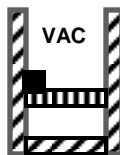
**$\Delta S_{\text{surroundings}} > 0$**



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

## Raff's Sammy

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



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

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

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

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

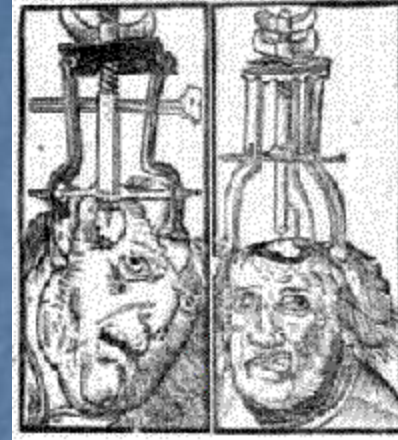
Has Sam finally gotten a problem correct? Explain. Leigh, who is making an A in physical chemistry, obtains a different answer for this problem. What answer does she obtain?



# *trepanation, the mind and the brain*



H. Bosch, 1480, Dutch



P. Treveris, 1525, England



Peru, ~ 1000AD, pre-Incan

trepanation and the second

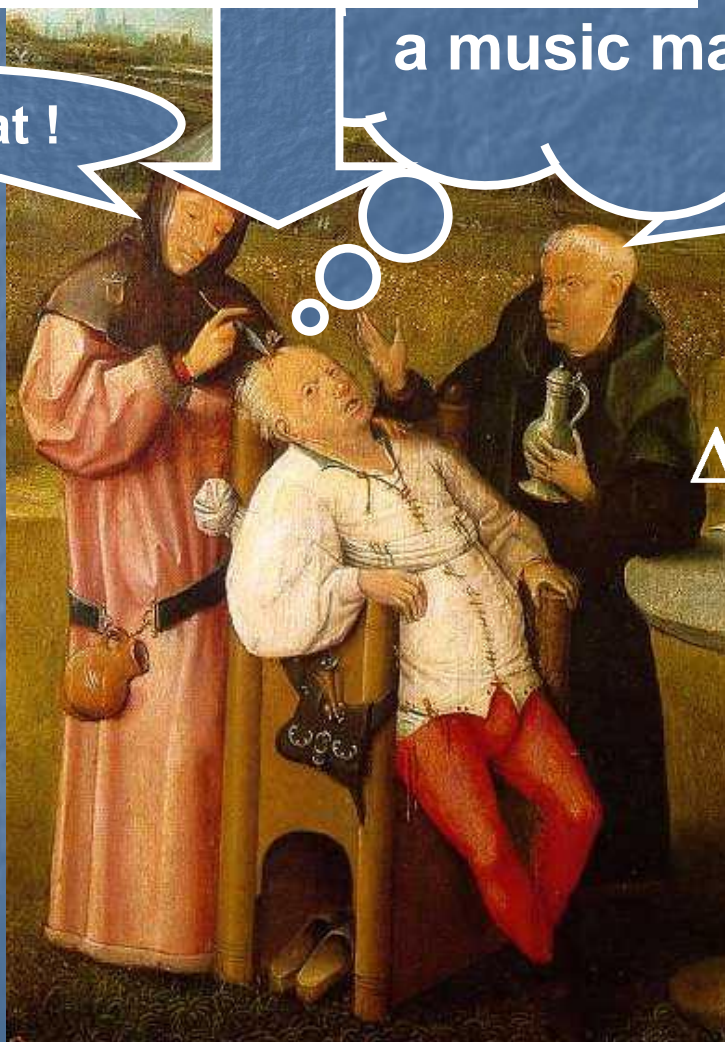
$$\Delta S = \int \frac{\vec{d}q}{T} \text{REVERSIBLE} \geq \int \frac{\vec{d}q}{T} \text{ should}$$

I'll fix that !

a music major !!

m163B  
nt thought

$$\Delta S = \int \frac{dq}{T}$$



$$\Delta S = \int \frac{\vec{d}q \text{REVERSIBLE}}{T}$$

*remember*

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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

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



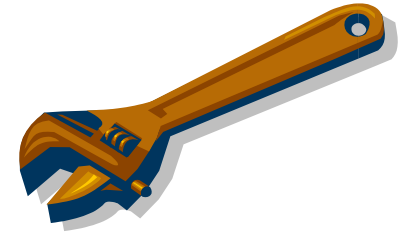
**definitions:**

$U \equiv$  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 ( $dw_{\text{other}}=0$ )]

$$\bar{dq}_V = n \bar{C}_V dT \quad \bar{dq}_P = n \bar{C}_P dT$$

$$dU = \bar{dq} + \bar{dw} = \bar{dq} - PdV$$

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

## *differential relationships*

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$U \equiv$  internal energy

$H \equiv U + PV$

$A \equiv U - TS$

$G \equiv H - TS$

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

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

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

*TdS - PdV*

$$dH = dU + PdV + VdP$$

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

*TdS - PdV*

$$dA = dU - TdS - SdT$$

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

*TdS + VdP*

$$dG = dH - TdS - SdT$$

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

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

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$$dG = -S dT + V dP$$

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

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

**Maxwell-Euler Relationship  
from dG**

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

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

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

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:**

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

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

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

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

## Euler-Maxwell relationships

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$$dU = TdS - PdV$$

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

$$dH = TdS + VdP$$

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

$$dA = -SdT - PdV$$

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

$$dG = -SdT + VdP$$

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

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

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



## entropy variations with $T$ and $P$

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

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

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

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

## 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*  $dT = 0$

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

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

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  $\Delta S_{V_1 \rightarrow V_2} = \frac{q_{rev}}{T}$ ,  $q_{rev}$  for isothermal volume change]

# calculating entropy (see summary on review handout)

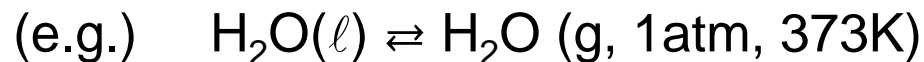


- Thermal properties of entropy and entropy calculations
  - ✓ ○  $dS = \frac{\delta q_{rev}}{T}$ ;  $\Delta S = \int \frac{\delta q_{rev}}{T}$ ;  $\oint \frac{\delta q_{rev}}{T} = 0$
  - ✓ ○  $\Delta S \geq \int \frac{\delta q}{T}$ ;  $0 \geq \oint \frac{\delta q}{T}$ ; (= for reversible process; > 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:  $\left(\frac{\partial \bar{S}}{\partial T}\right)_V = \frac{\bar{C}_V}{T}$ ;  $\left(\frac{\partial \bar{S}}{\partial T}\right)_P = \frac{\bar{C}_P}{T}$
    - ✓ ■ P:  $\left(\frac{\partial \bar{S}}{\partial P}\right)_T = -\left(\frac{\partial \bar{V}}{\partial T}\right)_P$
    - ✓ ■ V:  $\left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)_T = \left(\frac{\partial P}{\partial T}\right)_{\bar{V}}$
    - 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:  $\bar{S}^0(T)$
  - $\Delta S_{reaction}^0(T) = \sum_i \nu_i \bar{S}_i^0(T)$
  - Entropy of mixing:  $\Delta S = -n_{total} R \sum_i X_i \ln X_i$  where  $X_i = \frac{n_i}{n_{total}}$

## $\Delta S$ for equilibrium phase transition

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for phase transition  $\phi$  **at equilibrium conditions**



$$\Delta H_{\phi, P} = q_{\text{reversible}}$$

$$\Delta S_{\phi, P} = \frac{\Delta H_{\phi, P}}{T_{\phi}}$$

HW6 #35  $\Delta S$  for  $\text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{O}(\text{s}, 1\text{atm}, 263\text{K})$

*End of Lecture*