

Chemistry 163B, Winter 2013

Introductory Lecture

Chemistry 163B Thermodynamics Winter 2013

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Thermodynamics is a
really beautiful scientific
story !!

2

"rules" of science

- observations
- ↓
- guiding principles
- ↓
- predictions and applications based on principles

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Observations (QM vs Thermo)

Thermodynamics is very 'working class' in its origins:

<p>quantum mechanics</p> <p>$H \Psi = E \Psi$</p>	<p>thermodynamics</p> <p>$\Delta S_{\text{universe}} > 0$</p>
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observations: thermo = heat

- Count Rumford, 1799
- observed water turning into steam when canon barrel was bored
- $\text{work} \leftrightarrow \text{heat}$

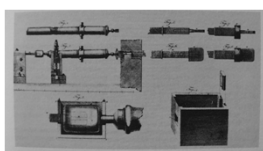
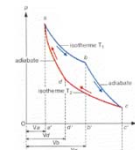


FIGURE 11. An illustration from Rumford's paper, "An Inquiry Concerning the Source of the Heat Which is Evolved by Friction," showing the apparatus used by him in the cannon boring experiment. Figure 1, upper left, shows the cannon as received from the foundry, and Figure 2, below, shows it mounted in the machine used for boring. (Reproduced with the permission of Harvard University Press.)

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observations: mechanical efficiency of steam engine

- Sadi Carnot, 1824
- efficiency of engines



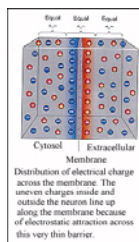
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types of problems that thermodynamics addresses (biology)

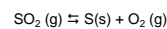
- Why does an egg hard boil? (protein conformation)
- Membrane potentials and ion concentrations in neurons. (electrochemistry and thermodynamics)



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types of problems that thermodynamics addresses (ecology)

- Thermodynamic feasibility of SO₂ removal

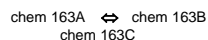


<http://healthandenergy.com/images/magnikka%20smoke%20stacks.jpg>

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what thermodynamics can't answer

- How fast a reaction proceeds (kinetics, catalysts, enzymes; in chem 103, BMB 100, chem 163C)
- Macroscopic thermodynamics does not prove or require hypotheses about molecular structure; however we will use our knowledge of molecular structure to get an atomic "picture" of thermodynamic processes. The quantitative connection is made by statistical thermodynamics.



- Although in chemistry 163B we will study how thermodynamics put limits on processes at equilibrium, there exists a whole other field of *non-equilibrium thermodynamics*.

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aims of class

- Clear conceptual picture of thermodynamics
- Ability to relate and apply thermodynamics to chemical and biological systems
- PROBLEM SOLVING: Chemistry + Logic + Mathematics**
- How to do independent and advanced reading/research in areas that utilize thermodynamics.
- THE GRAND PICTURE of how thermodynamics and quantum mechanics fit into our picture of 'nature'.
- Advanced mathematical techniques

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class administration

www.chemistry.ucsc.edu ⇒ course pages ⇒ Chemistry 163B

<http://switkes.chemistry.ucsc.edu/teaching/CHEM163B/>

- lectures: **A MUST**
- homework: **A MUST**
- sections: required (**A MUST**)
- tutorial EVENT & Office Hours & LSS (for YOU!)
- midterms: 1st February
1st March
- final: 20th March, 4:00-7:00 PM
(last class 18th March)

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Learn Thermodynamics

- Lectures**
- Sections** (start TODAY Mon, Jan 7; HW#1 Probs 1-2)
- Tutorial Event** (starts NEXT Tues, Jan 15)
- Office hours** (start TODAY Mon, Jan 7)
- LSS Tutor**



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Sections week of 7th January

Homework Problems (#1-#8)

1. For an ideal gas $P\bar{V} = RT$ ($\bar{V} \equiv V_m \equiv \frac{V}{n}$ molar volume) evaluate:




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

2. For a Van der Waals gas: $\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT$ evaluate:

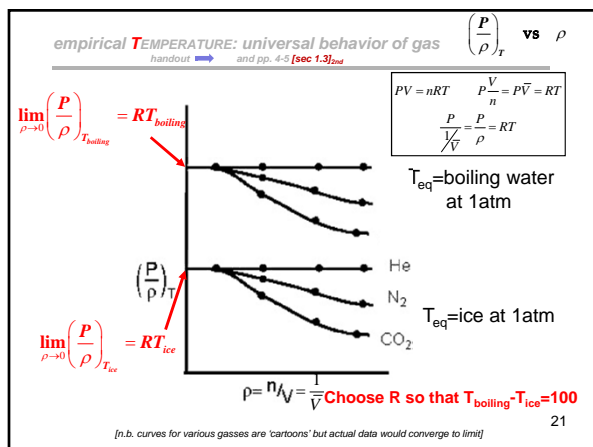
- $\left(\frac{\partial P}{\partial \bar{V}}\right)_T$
- $\left(\frac{\partial^2 P}{\partial \bar{V}^2}\right)_T$
- $\left(\frac{\partial P}{\partial T}\right)_P$
- $\left[\frac{\partial}{\partial T} \left(\frac{\partial P}{\partial \bar{V}}\right)_T\right]_P$

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Variables of state: V, T, P (careful definitions)

- **VOLUME:** MEASURED WITH A RULER 
- **TEMPERATURE:** [SEE IDEAL GAS THERMOMETER HANDOUT](#) 
- **PRESSURE:** FORCE/AREA
- **EQUATION of STATE:** RELATES P, V, T (more later) 

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Pressure, Kinetic Energy, and Temperature [SEE HANDOUT](#)

$PV = nRT$
 $PV = n^*kT$

$n = \text{moles}, R = \text{gas constant}$
 $n^* = \text{molecules}, k = \text{Boltzmann's constant}$
 $k = \frac{R}{N}, N = \text{Avogadro's number}$

Fundamental and Defined Constants
Engel & Reid [front cover, Table 1.1 (p8[7]), Table 1.2 (p9[8])]

$R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$
 $= .083145 \text{ L bar mol}^{-1} \text{ K}^{-1}$
 $= .082058 \text{ L atm mol}^{-1} \text{ K}^{-1}$
 $0.986923 \text{ atm} = 1 \text{ bar} = 10^5 \text{ kg m}^{-1} \text{ s}^{-2} = 10^5 \text{ Pa (pascal)}$
 $1 \text{ L} = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3$

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Game Plan Handout #6 [E&R pp 2-4] 3rd only

for monatomic ideal gas

from $PV = n^*kT$ and $P = F/A$

↓

use physics to relate pressure ↔ energy of gas

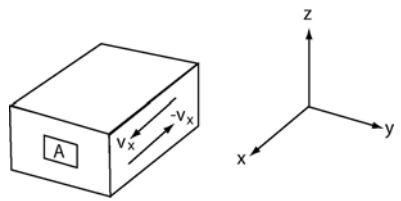
↓

show $E = \frac{3}{2} n^* kT$ (n^* atoms gas) or $E = \frac{3}{2} nRT$ (n moles gas)

and thus for monatomic ideal gas E depends only on T !!!
[in thermodynamic notation $E \equiv U$ (internal energy)]

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heuristic derivation of $E = E(T)$ for ideal gas [$U = U(T)$]



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heuristic derivation

1. molecules all with same $|v_x|$ (all same v_x is 'heuristic')
2. elastic collision with wall mass velocity goes $v_x \rightarrow -v_x$
3. from physics $P = \frac{F}{A}$ $P = \text{pressure}$
4. from physics $F = \frac{dp}{dt}$ $p = mv$, momentum; $t = \text{time}$
5. $dp \approx \Delta p = 2m v_x$ per collision (m is mass of particle)



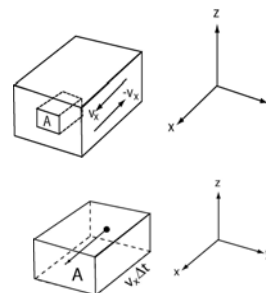
6. total Δp in given time Δt , $\left(\frac{\Delta p}{\Delta t}\right) \approx \left(\frac{dp}{dt}\right)$

would depend on number of collisions in that interval

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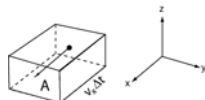
heuristic derivation

7.



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heuristic derivation



8. $\frac{n^*}{V}$ is density of molecules, $A v_x \Delta t$ is volume of rectangular box,

$\left(\frac{1}{2} \frac{n^*}{V} A v_x \Delta t\right)$ is number of molecules colliding with area A

9. total $\Delta p = (2m v_x) \left(\frac{1}{2} \left(\frac{n^*}{V}\right) (A v_x \Delta t)\right) = (m v_x^2) \left(\frac{n^*}{V}\right) (A \Delta t)$

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heuristic derivation

11. after some algebra and equating

$$P = \frac{F}{A} = \frac{n^* kT}{V}$$

$$P = (m v_x^2) \left(\frac{n^*}{V}\right) = \left(\frac{n^*}{V}\right) kT$$

$$(m v_x^2) = kT$$

12. in 3D with $|v_x| = |v_y| = |v_z|$

$$KE = \left(\frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2\right) = \frac{3}{2} n^* kT = \frac{3}{2} nRT$$

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TAKE HOME MESSAGES

- Good warm up of physics and equation derivation
- For a molecule with only kinetic energy (e.g. monatomic species), and ideal gas (no intermolecular forces)

$$E = \frac{3}{2} kT \text{ per molecule or } E = \frac{3}{2} RT \text{ per mole}$$

- For monatomic ideal gas, E is function of only T;

T constant \Rightarrow E constant

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End of Lecture 1

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various equations of state (Raff Table 1.2)

Table 1.2 Some commonly used equations of state

Equation of State	Functional Form	Number of Parameters
→ Ideal gas	$PV_m = RT$	0
van der Waals	$(V_m - b)(P + a/V_m^2) = RT$	2
Dieterici	$P(V_m - b) \exp(a/RTV_m) = RT$	2
Berthelot	$(V_m - b)(P + a/TV_m^2) = RT$	2
Virial	$P = RT \left[V_m^{-1} + \sum_{i=2}^{\infty} C_i(T) V_m^{-i} \right]$	∞
Beattie-Bridgman	$PV_m^2 = (1 - \gamma)RT(V_m + \beta) - \alpha$ with $\gamma = c_v/TV_m$ $\beta = b_1[1 - b/V_m]$, and $\alpha = a_1[1 + a/V_m]$	5
Redlich-Kwong	$P = \frac{RT}{(V_m - b)} - \frac{a}{T^{1/2}V_m(V_m + b)}$	2
Reichsanstalt	$PV = RT + AP + BP^2 + CP^3 + \dots$	∞

↑

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van der Waals equation

$$\left(P + \frac{a}{\bar{V}^2} \right) (\bar{V} - b) = RT$$

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van der Waals equation

$$\left(P + \frac{a}{\bar{V}^2} \right) (\bar{V} - b) = RT$$

Table 1.1 van der Waals parameters

Gas	b (L mol ⁻¹)	a (L ² bar mol ⁻²)
He	0.0238	0.0346
Ne	0.01672	0.208
Ar	0.03201	1.355
Kr	0.0396	2.325
Acetylene	0.0522	4.516
N ₂	0.0387	1.37
H ₂ O	0.03049	5.537
CO ₂	0.04286	3.658

↑

Source: Handbook of Chemistry and Physics, 78th edition, CRC Press, Boca Raton, FL, 1997-98

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The Haber Process (thermodynamics and kinetics)

Previously the problem had been that N₂ is a very stable molecule, and so most attempts to convert it to less stable molecules, such as NH₃, failed because of **thermodynamic or entropy problems**. The secret to the Haber-Bosch process proved to be a **catalyst of iron** with a small amount of **aluminium** added (aluminium was at the time an exotic and expensive metal that probably attracted Haber's attention as a novelty). The Haber-Bosch process operates at high pressure so as to shift the equilibrium to the right, and high temperature to **increase the rates of the reaction**. Of course, operating at high temperature actually shifted the reaction to the left, but the trade-off for faster rates was accepted. By removing the ammonia as liquid ammonia, the equilibrium is continuously shifted to the right.


↑

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heuristic

heu-ris-tic [hyoo-ris-tik or, often, yoo-] **adjective**

1. serving to indicate or point out; stimulating interest as a means of furthering **investigation**.



↑

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