Slide 1

Chemistry 163B
Thermodynamics
Winter 2014

1

Slide 2

Thermodynamics is a

really beautiful scientific

story !!

2

Slide 3

"rules" of science

- observations

- guiding principles

- predictions and applications
  based on principles

3

Slide 4

Observations (QM vs Thermo)

Thermodynamics is very 'working class' in its origins:

quantum mechanics   thermodynamics

$H \Psi = E \Psi$ $\Delta S_{universe} > 0$

4

Slide 5

observations: thermo ≡ heat

- Count Rumford, 1799
- observed water turning into steam when canon barrel was bored
- *work ⇔ heat*

FIGURE 11. An illustration from Rumford's paper, "An Inquiry Concerning the Source of the Heat Which is Excited 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.)

5

Slide 6

observations: mechanical efficiency of steam engine
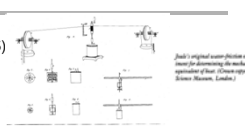
- Sadi Carnot, 1824
- efficiency of engines

6

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guiding principles

• Conservation of heat and work (Joule, 1845)
1st LAW OF THERMODYNAMICS

Joule's original water-friction experiment for determining the mechanical equivalent of heat. (Crown copyright, Science Museum, London.)

• Clausius, 1860 Entropy
2nd LAW OF THERMODYNAMICS

Clausius

• Boltzmann, late 19th century,
molecular picture of entropy

Boltzmann

the thermodynamic functions U, H, and S
(1st and 2nd laws)

7

"Applications" **U,H,S,G**

How does knowledge about efficiencies of steam engines, mechanical systems, etc, relate to processes in chemical, biological, and geological systems?
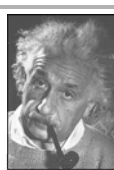
ANSWERED BY:

J. W. Gibbs- arguably the frist great American scientist who combined the concepts of heat and entropy and proposed "[Gibbs] Free Energy", **G**, a thermodynamic state function that leads to a whole spectrum of applications

8

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from: Einstein's "Autobiographical Notes"

A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Hence the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown (for the special attention of those who are skeptics on principle).

9

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types of problems that thermodynamics addresses (reactions)

might

1. Under what conditions will a reaction occur ?

C (graphite) $\rightarrow$ C (diamond) 30,000 -100,000 atm
1000 K – 3000 K
1st artificially produced diamonds, 1954 at General Electric Labs

10

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types of problems that thermodynamics addresses (equilibria)

2. How far will a reaction proceed (given enough time)?
How do the thermal and entropic properties determine EQUILIBRIUM ?
How do the EQUILIBRIUM conditions depend on T,P ?

N_2 (g) + $3H_2$ (g) $\leftrightarrows$ $2NH_3$ (g)

what are best T,P for NH_3 products?

The Haber Process

SiO_2 + $CaCO_3$ $\leftrightarrows$ $CaO \cdot SiO_2$ + CO_2 (g)
quartz   calcite   wollastonite
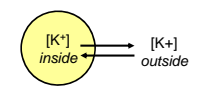
geologic thermometer:
The fraction of wollastonite in a rock sample can be used to estimate the temperature at which the rock metamorphosis occurred [the T at which the equilibrium was rapidly frozen]

11

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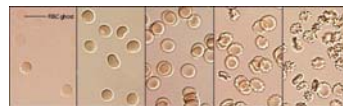
types of problems that thermodynamics addresses (biology)

3. Chemical and physical changes in biological systems

$[K^+]$ *inside* $\rightarrow$ $[K+]$ *outside*

cell

what difference in $[K^+]_{out}$ vs $[K^+]_{in}$ can be tolerated before cell wall bursts or collapses?

low hypotonic (rupture) extracellular salt **normal isotonic** extracellular salt *high hypertonic (collapse)*

http://www.vivo.colostate.edu/hbooks/cmb/cells/pmemb/osmosis.html

12

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types of problems that thermodynamics addresses (biology)

4. Why does an egg hard boil? (protein conformation)

5. Membrane potentials and ion concentrations in neurons. (electrochemistry and thermodynamics)

13

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types of problems that thermodynamics addresses (ecology)

6. Thermodynamic feasibility of SO_2 removal

$$SO_2 (g) \leftrightharpoons S(s) + O_2 (g)$$

http://healthandenergy.com/images/magnitka%20smoke%20stacks.jpg

14

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what thermodynamics can't answer

1. How fast a reaction proceeds (kinetics, catalysts, enzymes; in chem 103, BMB 100, chem 163C)

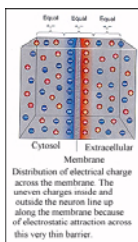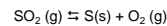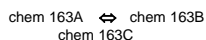2. Macroscopic thermodynamics does not prove or require hypotheses about molecular structure; however we will use our knowledge of molecular structure to get an atomic "picture" of thermodynamic processes. The quantitative connection is made by statistical thermodynamics:

chem 163A $\Leftrightarrow$ chem 163B
chem 163C

3. 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*.

15

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aims of class

1. Clear conceptual picture of thermodynamics

2. Ability to relate and apply thermodynamics to chemical and biological systems

3. **PROBLEM SOLVING: Chemistry + Logic + Mathematics**

4. How to do independent and advanced reading/research in areas that utilize thermodynamics.

5. THE GRAND PICTURE of how thermodynamics and quantum mechanics fit into our picture of 'nature'.

6. Advanced mathematical techniques

16

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class administration

www.chemistry.ucsc.edu $\Rightarrow$ course pages $\Rightarrow$ 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: 31st January
                        26th February
• final: 20th March, 12:00-3:00 PM
                    (*last class 17th March*)

17

Learn Thermodynamics

• **Lectures**
• **Sections** *(start TOMORROW Tues, Jan 7; HW#1 Probs 1-4)*
• **Tutorial Event** *(starts THIS Thurs, Jan 9)*
• **Office hours** *(start TODAY Mon, Jan 6)*
• **LSS Tutor**

18

Slide 19

Winter 2014 — *Chemistry 163B*

Homework Problems
(#1-#4)

Sections week of 6th January

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

a. $\left(\dfrac{\partial P}{\partial \overline{V}}\right)_T$

b. $\left(\dfrac{\partial \overline{V}}{\partial T}\right)_P$

c. $\left(\dfrac{\partial T}{\partial P}\right)_V$

d. $\left(\dfrac{\partial P}{\partial \overline{V}}\right)_T \left(\dfrac{\partial \overline{V}}{\partial T}\right)_P \left(\dfrac{\partial T}{\partial P}\right)_V$

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

a. $\left(\dfrac{\partial P}{\partial \overline{V}}\right)_T$

b. $\left(\dfrac{\partial^2 P}{\partial \overline{V}^2}\right)_T$

c. $\left(\dfrac{\partial P}{\partial T}\right)_{\overline{V}}$

d. $\left[\dfrac{\partial}{\partial T}\left(\dfrac{\partial P}{\partial \overline{V}}\right)_T\right]_{\overline{V}}$

19

Slide 20

Winter 2014 — *Chemistry 163B*

3. Engel & Reid problem P1.3 | *Van der Waals gas* |

★**4.** *(optional)* The Van der Waals and virial expressions are two commonly used equations of state as approximations to real gas behavior:

$$P = \frac{RT}{(\overline{V} - b)} - \frac{a}{\overline{V}^2} \quad \text{Van der Waals}$$

$$P = RT\left[\frac{C_1(T)}{\overline{V}} + \frac{C_2(T)}{\overline{V}^2} + \frac{C_3(T)}{\overline{V}^3} + \ldots + \frac{C_k(T)}{\overline{V}^k}\right] \quad \text{virial}$$

a. Show that the first three virial coefficients are related top the Van der Waals parameters a and b in the following way:

$C_1(T)=1$

$C_2(T)=b-a/RT$

$C_3(T)=b^2$

HINT:

note that the virial expansion is just a Taylor (Maclaurin) series in $z^k = \left(\frac{1}{\overline{V}}\right)^k$

$$\frac{P}{RT} = \sum_{k=1}^{\infty} C_k(T)\left(\frac{1}{\overline{V}}\right)^k = \sum_{k=1}^{\infty} C_k(T)z^k = f(z;T)$$

$$\text{with coefficient } C_k(T) = \frac{1}{k!}\left(\frac{d^k f}{dz^k}\right)_{z=0}$$

b. Why does the Van der Waals "a" only appear in $C_2(T)$?

20

Slide 21

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)

21

Slide 22

empirical TEMPERATURE: universal behavior of gas $\left(\dfrac{P}{\rho}\right)_T$ **vs** ρ

handout → *and pp. 4-5*

$PV = nRT \qquad P\dfrac{V}{n} = P\overline{V} = RT$

$\dfrac{P}{\frac{1}{\overline{V}}} = \dfrac{P}{\rho} = RT$

$\lim\limits_{\rho \to 0}\left(\dfrac{P}{\rho}\right)_{T_{boiling}} = RT_{boiling}$

T_{eq}=boiling water at 1atm

$\left(\dfrac{P}{\rho}\right)_T$

He
N$_2$
CO$_2$

T_{eq}=ice at 1atm

$\lim\limits_{\rho \to 0}\left(\dfrac{P}{\rho}\right)_{T_{ice}} = RT_{ice}$

$\rho = \dfrac{n}{V} = \dfrac{1}{\overline{V}}$ **Choose R so that $T_{boiling}$-T_{ice}=100**

[n.b. curves for various gasses are 'cartoons' but actual data would converge to limit]

22

Slide 23

Pressure, Kinetic Energy, and Temperature SEE HANDOUT →

$PV=nRT$ $n=moles$, $R= gas\ constant$

$PV=n^*kT$ $n^*=molecules$, $k=Boltzmann's\ constant$

$k=\dfrac{R}{N}$, $N=Avogadro's\ number$

Fundamental and Defined Constants

Engel & Reid [front cover, Table 1.1 (p8[7]$_{2nd}$), Table 1.2 (p9[8]$_{2nd}$)]

$R= 8.3145\ J\ mol^{-1}\ K^{-1}$

$= .083145\ L\ bar\ mol^{-1}\ K^{-1}$

$= .082058\ L\ atm\ mol^{-1}\ K^{-1}$

$0.986923\ atm = 1\ bar = 10^5\ kg\ m^{-1}s^{-2} = 10^5\ Pa$ *(pascal)*

$1L=1\ dm^3=10^{-3}m^3$

23

Slide 24

Ideal Gas Energy: Game Plan Handout #6 → *[E&R pp 2-4]*

for monatomic ideal gas

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

⇩

use physics to relate pressure ⇔ energy of gas

⇩

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

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

24

Slide 25

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

25

Slide 26

heuristic derivation

1. molecules all with same $|v_x|$ (all same v_x is 'heuristic')

2. elastic collision with wall mass velocity goes $v_x \longrightarrow -v_x$

3. from physics $P=\dfrac{F}{A}$ P=pressure

4. from physics $F=\dfrac{dp}{dt}$ p=mv, momentum; t=time

5. $dp \approx \Delta p = 2m\, v_x$ per collision (m is mass of particle)

$\leftarrow v_x$
$\rightarrow -v_x$

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

would depend on number of collisions in that interval

26

Slide 27

heuristic derivation

7.

27

Slide 28

heuristic derivation

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

$\dfrac{n^*}{V} A v_x \Delta t$ is number of molecules colliding with area A

9. total $\Delta p = (2mv_x)\left(\dfrac{1}{2}\right)\left(\dfrac{n^*}{V}\right)(Av_x \Delta t) = (mv_x^2)\left(\dfrac{n^*}{V}\right)(A\Delta t)$

28

Slide 29

heuristic derivation

11. after some algebra and equating

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

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

$$(mv_x^2) = kT$$

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

$$KE = \left(\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2\right) = \frac{3}{2}n^* kT = \frac{3}{2}nRT$$

29

Slide 30

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 $\Longrightarrow$ E constant

30

5

Slide 31

Some comments on the

Van der Waals equation of state

31

Slide 32

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	$PV_m = RT$ — HW#1 1	0
van der Waals	$(V_m - b)(P + a/V_m^2) = RT$ — HW#1 2-3	2
Dieterici	$P(V_m - b)\exp[a/RTV_m] = RT$	2
Berthelot	$(V_m - b)(P + a/TV_m^2) = RT$	2
Virial	$P = RT\left[V_m^{-1} + \sum_{n=2} C_n(T)V_m^{-n}\right]$ — HW#1 *4	∞
Beattie–Bridgman	$PV_m^2 = (1 - \gamma)RT(V_m + \beta) - \alpha$,	5
	with $\gamma = c_o/T^3V_m$	
	$\beta = b_o[1 - b/V_m]$, and	
	$\alpha = a_o[1 + a/V_m]$	
Redlich–Kwong	$P = \dfrac{RT}{(V_m - b)} - \dfrac{a}{T^{1/2}V_m(V_m + b)}$	2
Reichsanstalt	$PV = RT + AP + BP^2 + CP^3 + \cdots$	∞

32

Slide 33

van der Waals equation

$$\underbrace{P_{ideal}}\ \underbrace{\bar{V}_{ideal}} = RT$$

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

interpretation of parameters:

b is correction for actual volume of atoms/molecules

- volume available to molecules $\left(\bar{V} - b\right)$ smaller than $\bar{V}$
- b is associated with repulsive forces

33

Slide 34

van der Waals equation

$$\underbrace{P_{ideal}}\ \underbrace{\bar{V}_{ideal}} = RT$$

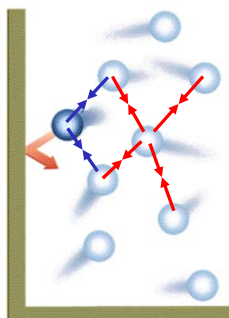$$\left(P + \frac{a}{\bar{V}^2}\right)\left(\bar{V} - b\right) = RT$$

interpretation of parameters:

a is correction for attractive forces of atoms/molecules

- a is associated with attractive forces
- $P_{bulk} \equiv P_{ideal}$ is greater than $P \equiv P_{meas}$ measured at surface
- $P_{bulk} = \left(P_{meas} + \frac{a}{\bar{V}^2}\right)$ $P_{meas} \to P_{bulk}$ $\bar{V} \to \infty$

34

Slide 35

heuristic justification for attractive constant a

- asymmetric attractive forces for molecule at surface
- molecule at surface has less momentum less than molecule in bulk
- $P \equiv P_{meas} < P_{bulk}$
- $P_{bulk} = \left(P + \frac{a}{\bar{V}^2}\right)$

35

Slide 36

van der Waals equation

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

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$0	0.03049	5.537
CO$_2$	0.04286	3.658

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

36

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van der Waals equation

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

Table 1.1	repulsive	its pa	attractive
Gas	b (L mol^{-1})		a (L^2 bar mol^{-2})
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polarizability

polarity

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

37

Validity
However, the Van der Waals model is not appropriate for rigorous quantitative calculations, remaining useful only for **teaching** and qualitative purposes.[1]

Nowadays, Eq. 2.9 belongs to **"pedagogical physics:"** it is the simplest equation that illustrates several important concepts, but its accuracy is not satisfactory.

38

End of Lecture 1

39

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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
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Virial	$P = RT\left[V_m^{-1} + \sum_{n=2}^{\infty} C_n(T)V_m^{-n}\right]$	∞
Beattie–Bridgman	$PV_m^2 = (1 - \gamma)RT(V_m + \beta) - \alpha$, with $\gamma = c_a/T^3V_m$, $\beta = b_a[1 - b/V_m]$, and $\alpha = a_a[1 + a/V_m]$	5
Redlich–Kwong	$P = \frac{RT}{(V_m - b)} - \frac{a}{T^{1/2}V_m(V_m + b)}$	2
Reichsanstalt	$PV = RT + AP + BP^2 + CP^3 + \cdots$	∞

40

The Haber Process (thermodynamics and kinetics)

Previously the problem had been that N$_2$ is a very stable molecule, and so most attempts to convert it to less stable molecules, such as NH$_3$, 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.

41

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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.

42