

Chemistry 163B Thermodynamics Winter 2020

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Menu: for TODAY



- **Introduction and Class Resources, etc.**
- **Careful definition of thermodynamic variables (P , V , T , etc)**
- **Ideal gas ENERGY DEPENDS ONLY ON TEMPERATURE (*derivation*)**
- **Van der Waals equation (*example of equation of state for 'real' gas*)**

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Thermodynamics is a
really beautiful scientific
story !!

3

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"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>photoelectrons spectra</p> <p>reaction</p> <p>Effete</p> <p>$H \Psi = E \Psi$</p>	<p>thermodynamics</p> <p>Blue Collar</p> <p>disorder</p> <p>$\Delta S_{\text{universe}} > 0$</p>
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observations: thermo \equiv heat

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

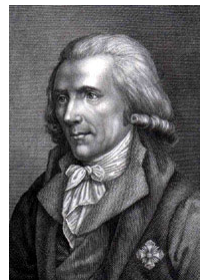
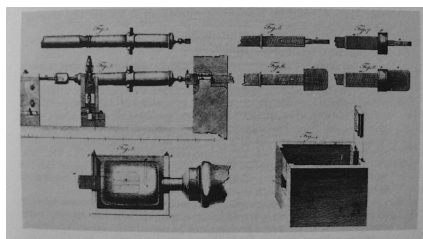


FIGURE 11. An illustration from Rumford's paper, "An Inquiry Concerning the Source of the Heat Which is Excited by Friction," showing the apparatus used by him in the cannon boring experiment. Figure 1, upper left, shows the cannon as received from the foundry, and Figure 2, below, shows it mounted in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

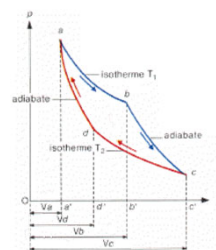
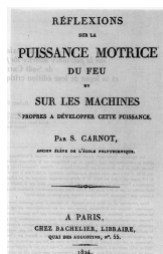
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Lecture 1- Introductory Lecture

observations: mechanical efficiency of steam engine

- Sadi Carnot, 1824
- efficiency of engines

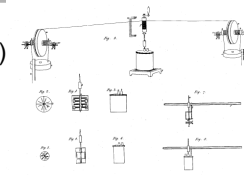


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guiding principles

- 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

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

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

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“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:

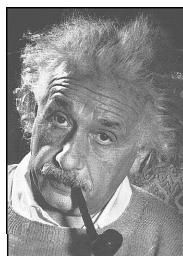


J. W. Gibbs- arguably the first great American scientist who combined the concepts of heat and entropy and proposed “[Gibbs] Free Energy”, **G**, a thermodynamic state function that leads to a whole spectrum of applications

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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).

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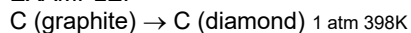
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types of problems that thermodynamics addresses (reactions)

might

1. Under what conditions ~~will~~ a reaction occur ?

EXAMPLE:



nada

30,000 -100,000 atm

¡Hurra!

1000 K – 3000 K

1st artificially produced diamonds, 1954 at General Electric Labs



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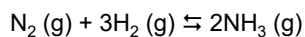
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types of problems that thermodynamics addresses (equilibria)

2. How far will a reaction proceed (given enough time)?

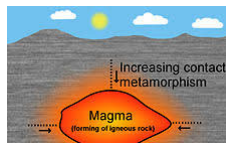
How do the thermal and entropic properties determine EQUILIBRIUM ?

How do the EQUILIBRIUM conditions depend on T,P ?



what are best T,P for NH₃ products?

The Haber Process



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]

Geologic Thermometer

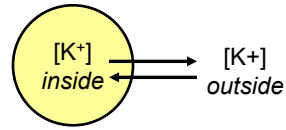
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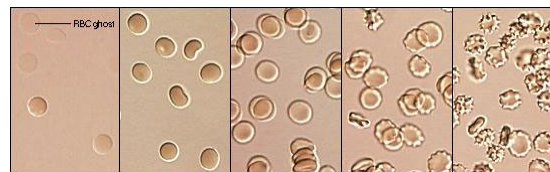
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types of problems that thermodynamics addresses (biology)

3. Chemical and physical changes in biological systems



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)

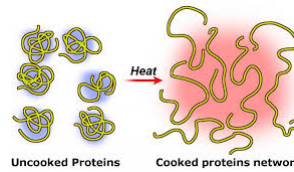
<http://www.vivo.colostate.edu/hbooks/cmb/cells/pmemb/osmosis.html>

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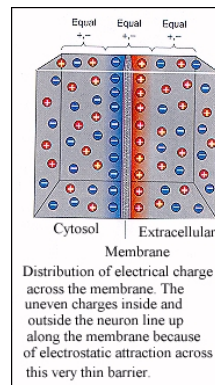
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types of problems that thermodynamics addresses (biology)

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



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



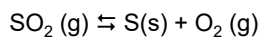
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types of problems that thermodynamics addresses (ecology)

6. Thermodynamic feasibility of SO₂ removal



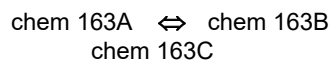
<http://healthandenergy.com/images/magnitka%20smoke%20stacks.jpg>

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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:



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*.

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Lecture 1- Introductory Lecture

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

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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: 31st January
28th February
- final: 19th March, 4:00-7:00 PM
(last class 13th March)



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Learn Thermodynamics

- **Lectures**
- **Sections** (start Monday, Jan 13; HW#1 Probs 1-8)
- **Tutorial Event** (starts TOMORROW Tues, Jan 7, HW#1 Probs1-2)
- **Office hours** (start TODAY Mon, Jan 6)
- **LSS Tutor**



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first Tutorial Tuesday 7th January, NS Annex 102, 5:25PM-6:30PM

Chemistry 163B
Winter 2020
Chemistry 16

Comments on Mathematical Techniques for Chemistry 163B

Our text (E&R: ME2, pp 17-26; ME3, pp 63-68) [superscripts 1, 2, 1, 2, 3] contains detailed information on the aspects of differential and integral calculus relevant to our study of thermodynamics. We will review these techniques in the context of class derivations and homework problems, rather than just as abstract mathematical exercises. However it is useful to categorize them below. In your first discussion section the TAs will also comment on the techniques.

1. Partial derivatives:
 - a. Know physical meaning of partial derivatives
 - b. Know how to evaluate them mechanically
 - c. Know chain rule
2. You should have "at hand" the derivatives and integrals of functions like: x^n , x^a , $\ln(x)$, e^{ax} , $\sin ax$, $\cos ax$ ["at hand" = in your accessible neurons]
3. Differential expressions (E&R 2.8, pp 39-41, 63) [pp 28, 45-49]
 - a. dV is inexact differential if $\int_{initial}^{final} dV$ depends on the path from initial \rightarrow final
This implies there is no "underlying" well behaved, function v that changes like dV
 - b. dV is exact differential if $\int_{initial}^{final} dV$ does not depend on the path from initial \rightarrow final
4. Implications that arise from dV being an exact differential:
 - a. There is a well behaved function v whose change is described by dV
 - b. $dV(T, T) = \left(\frac{\partial v}{\partial T}\right)_T dT + \left(\frac{\partial v}{\partial T}\right)_T dT$
or in more general notation
 $dV(x, y, z) = \left(\frac{\partial v}{\partial x}\right)_x dx + \left(\frac{\partial v}{\partial y}\right)_y dy + \left(\frac{\partial v}{\partial z}\right)_z dz$
 - c. $\oint dV = 0$ (integral for any cyclic path; i.e. the initial and final states are identical)
 - d. $\int_{initial}^{final} dV = v(final) - v(initial)$

Homework Problems

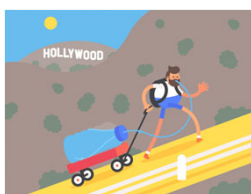
1. For an ideal gas: $P\bar{V} = RT$ ($\bar{V} = V_m = \frac{V}{n}$ molar volume) evaluate:
 - a. $\left(\frac{\partial P}{\partial T}\right)_T$
 - b. $\left(\frac{\partial \bar{V}}{\partial T}\right)_P$
 - c. $\left(\frac{\partial T}{\partial P}\right)_P$
 - d. $\left(\frac{\partial P}{\partial \bar{V}}\right)_T \left(\frac{\partial \bar{V}}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_P$
- e. One can often get, via the chain rule for differentiation, rigorous results by "canceling d 's". However the correct result for part d is **NOT** what one would obtain by just "canceling d 's" in the numerators and denominators in each of the three terms. Why for part d can one NOT apply the chain rule to get $\left(\frac{\partial P}{\partial P}\right) = 1$? [NOTE: you may evaluate part d and e using the specific results from a, b, c for an ideal gas. However the correct result is a more general relationship for any well behaved function $z(x, y)$.]
2. For a Van der Waals gas: $\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT$ evaluate:
 - a. $\left(\frac{\partial P}{\partial \bar{V}}\right)_T$
 - b. $\left(\frac{\partial^2 P}{\partial \bar{V}^2}\right)_T$
 - c. $\left(\frac{\partial P}{\partial T}\right)_T$
 - d. $\left[\frac{\partial}{\partial T} \left(\frac{\partial P}{\partial \bar{V}}\right)_T\right]$
 - e. $\left[\frac{\partial}{\partial \bar{V}} \left(\frac{\partial P}{\partial T}\right)_T\right]$
- f. How do the results of parts d and e compare? Why is this?

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enough hellos

and NOW TO BEGIN !!

our thermodynamics trek



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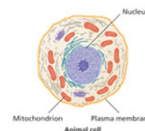
system and surroundings (careful definitions)  *E&R_{4th} sec 1.3*

A thermodynamic **system** consists of all the materials involved in the process under study. This material could be the contents of an open beaker containing reagents, the electrolyte solution within an electrochemical cell, or the contents of a cylinder and movable piston assembly in an engine.

In thermodynamics, the rest of the universe is referred to as the **surroundings**.

system + surroundings = the **UNIVERSE**

If a system can exchange matter with the surroundings, it is called an **open system**; if not, it is a **closed system**.



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Lecture 1- Introductory Lecture

Variables of state: V, T, P (careful definitions)  E&R_{4th} sec 1.2

STATE VARIABLES:


properties whose values are required to specify the **STATE** of a system

• **VOLUME:** MEASURED WITH A RULER



• **PRESSURE:** FORCE/AREA (*physics 5-6A*)

• **TEMPERATURE:** [SEE IDEAL GAS THERMOMETER HANDOUT](#) 

• **EQUATION of STATE:** RELATES P, V, T
(*more later*) 

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

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

$PV=(nN)\frac{R}{N}T$ N =Avogadro's number $\left[\frac{\text{molecules}}{\text{mol}}\right]$

$PV=n^*kT$ $nN=n^*$ = number of molecules

$k=\frac{R}{N}$ Boltzmann's constant

Fundamental and Defined Constants

Engel & Reid [front cover, Table 1.1 (p13_{4th} [8]_{rd}), Table 1.2 (p13_{4th} [9]_{rd})]

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

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

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

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

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

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Ideal Gas Energy: Game Plan Handout #6

[E&R pp 7-8]_{4th}

for monatomic ideal gas

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



use physics to relate pressure \leftrightarrow energy of gas



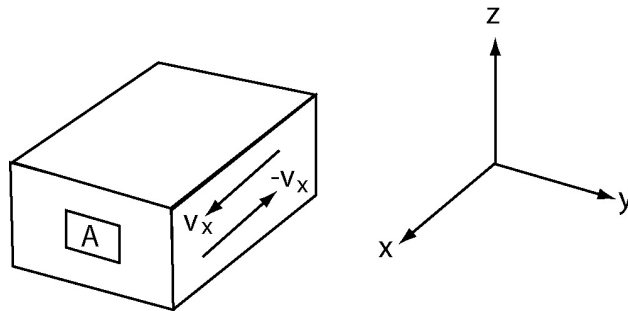
show $E=\frac{3}{2}n*kT$ ($n*$ atoms gas) or $E=\frac{3}{2}nRT$ (n moles gas)

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 [$U=U(T)$] E&R pp.7-8_{4th}



RESULT: for ('monatomic') ideal gas
(how) **energy depends only on temperature**

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Lecture 1- Introductory Lecture

heuristic derivation

1. molecules all with same $|v_x|$ (all same v_x is 'heuristic')
2. elastic collision with wall velocity of mass 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 , $\left(\frac{\Delta p}{\Delta t}\right) \approx \left(\frac{dp}{dt}\right)$

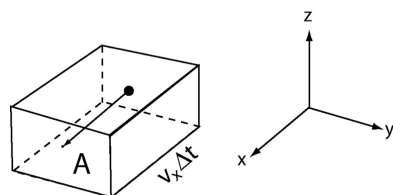
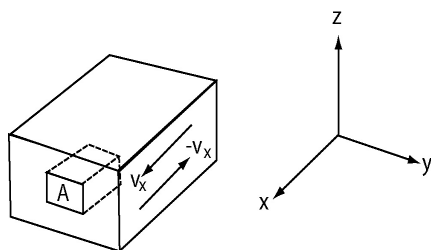
would depend on number of collisions in that interval

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heuristic derivation

7.

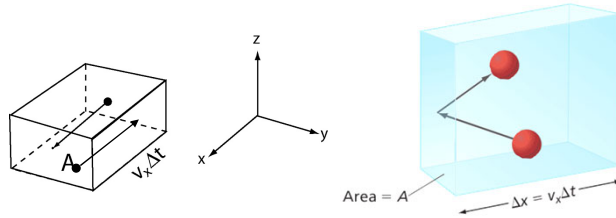


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Lecture 1- Introductory Lecture

heuristic derivation



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

9. $\frac{1}{2} \frac{n^*}{V} A v_x \Delta t$ is total number of molecules colliding with area A in Δt

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

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ES2

heuristic derivation

11. after some algebra and equating

$$P = \frac{F}{A} = \frac{\Delta p}{A \Delta t} = (m v_x^2) \left(\frac{n^*}{V} \right) = \frac{n^* k T}{V}$$

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

$$\left(\frac{m v_x^2}{2} \right) = \frac{k T}{2} \quad \text{for each molecule of 1-D ideal gas}$$

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

$$\text{total KE} = \left(\frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 \right) n^* = \frac{3}{2} n^* k T = \frac{3}{2} n R T$$

$\frac{1}{2} RT$ for each degree (x, y, z) of 'classical freedom'

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Slide 32

ES2

Eugene Switkes, 1/6/2020

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)

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

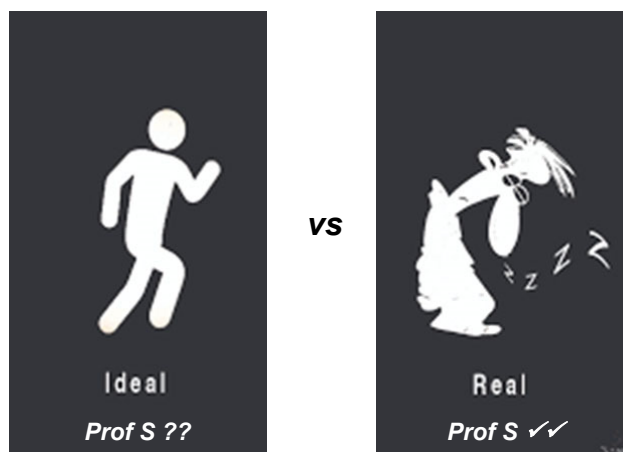
- For monatomic ideal gas, E is function of **only T**;

$$T \text{ constant} \Leftrightarrow E \text{ constant}$$

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beyond PV=nRT: 'real' gases and equations of state (E&R sec 1.5)



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Lecture 1- Introductory Lecture

various equations of state (Raff Table 1.2) $\frac{V}{n} \equiv \bar{V} \equiv V_m$ molar volume
gene E&R

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	$P = RT \left[V_m^{-1} + \sum_{n=2}^{\infty} C_n(T) V_m^{-n} \right]$	∞
Beattie-Bridgman	$PV_m^2 = (1 - \gamma)RT(V_m + \beta) - \alpha,$ with $\gamma = c_0/T^3V_m,$ $\beta = b_0[1 - b/V_m],$ and $\alpha = a_0[1 + a/V_m]$	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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Some comments on the
Van der Waals equation of state

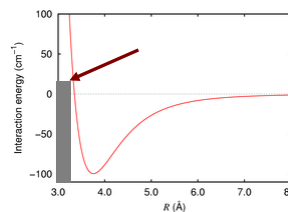
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van der Waals equation the parameter b

ideal gas law $P_{ideal} \bar{V}_{ideal} = RT$

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



interpretation of parameters:

b is correction for actual volume of atoms/molecules

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

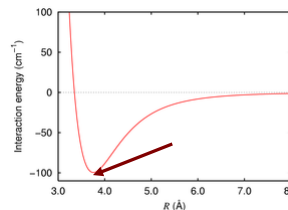
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van der Waals equation the parameter a

ideal gas law $P_{ideal} \bar{V}_{ideal} = RT$

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



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
- $P_{bulk} = \left(P_{meas} + \frac{a}{\bar{V}^2}\right)$ $P_{meas} \rightarrow P_{bulk}$ $\bar{V} \rightarrow \infty$

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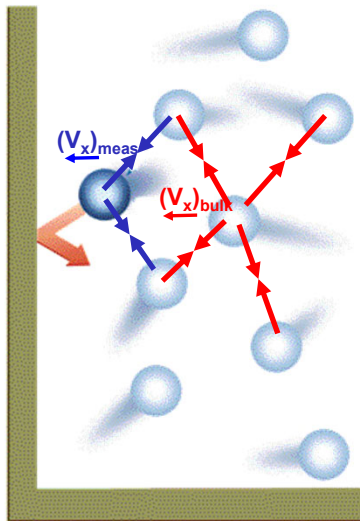
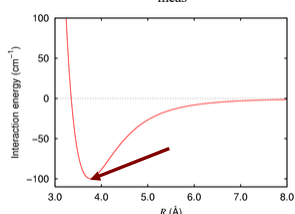
heuristic justification for attractive constant a

- asymmetric attractive forces for molecule at surface
- molecule at surface has less momentum than molecule in bulk

$$P \equiv P_{\text{meas}} < P_{\text{bulk}}$$

$$P_{\text{bulk}} = \left(P + \frac{a}{\bar{V}^2} \right)$$

\uparrow
 P_{meas}



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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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van der Waals equation

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

Table 1.1 **repulsive** vs **attractive**

Gas	b (L mol ⁻¹)	a (L ² bar mol ⁻²)
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H ₂ O	0.03049	5.537
CO ₂	0.04286	3.658

Annotations: A red arrow labeled "size" points down from He to Ar. A red arrow labeled "polarizability" points down from He to CO₂. A red bracket labeled "polarity" spans from N₂ to CO₂.

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

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some trash talk on VDW eqn: **inaccurate but instructive !!!** (from other texts)

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.

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Menu: for TODAY



- ✓ Introduction and Class Resources, etc.
- ✓ Careful definition of thermodynamic variables (P , V , T , etc)
- ✓ Ideal gas ENERGY DEPENDS ONLY ON TEMPERATURE (T)
- ✓ Van der Waals equation (example of equation of state for 'real' gas)

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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	$P = RT \left[V_m^{-1} + \sum_{n=2}^{\infty} C_n(T) V_m^{-n} \right]$	∞
Beattie-Bridgman	$PV_m^2 = (1 - \gamma)RT(V_m + \beta) - \alpha,$ with $\gamma = c_0/T^3V_m,$ $\beta = b_0[1 - b/V_m],$ and $\alpha = a_0[1 + a/V_m]$	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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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.

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heuristic

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

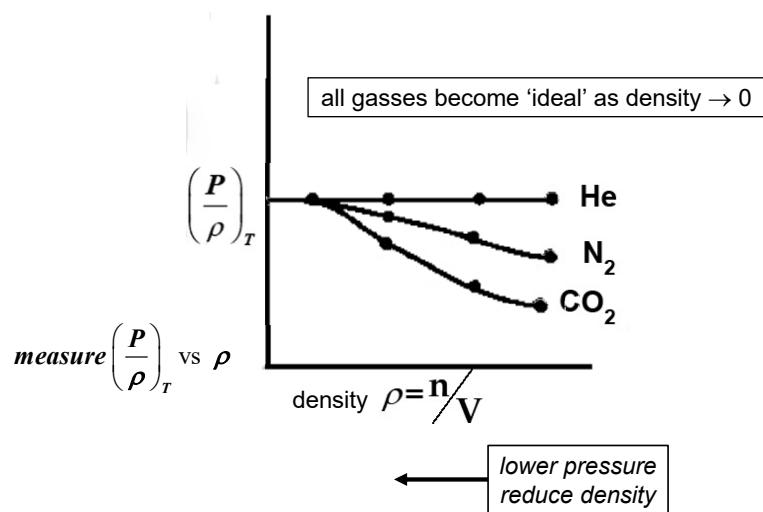
1. serving to indicate or point out; stimulating interest as a means of furthering investigation.



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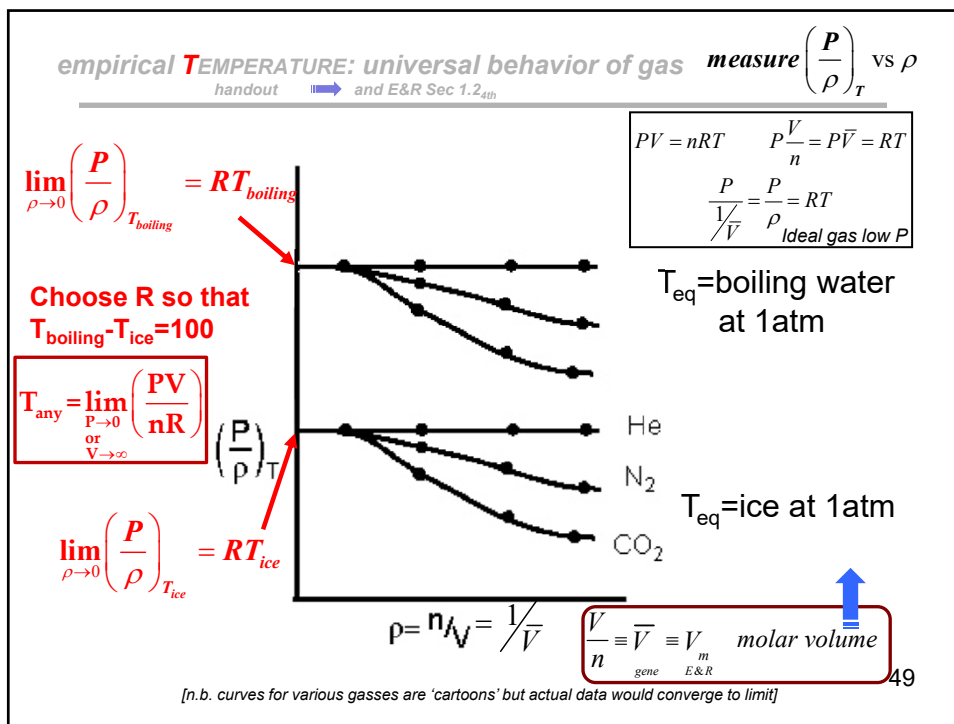
universal behavior of gas



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