Chemistry 163B
Thermodynamics
Winter 2013

Thermodynamics is a

really beautiful scientific

story !!

- observations

$$\downarrow$$

- guiding principles

$$\downarrow$$

- predictions and applications based on principles

Thermodynamics is very 'working class' in its origins:

quantum mechanics   thermodynamics

Effete

photoelectrons

spectra

Blue Collar

disorder

$$H \Psi = E \Psi$$

$$\Delta S_{universe} > 0$$

4

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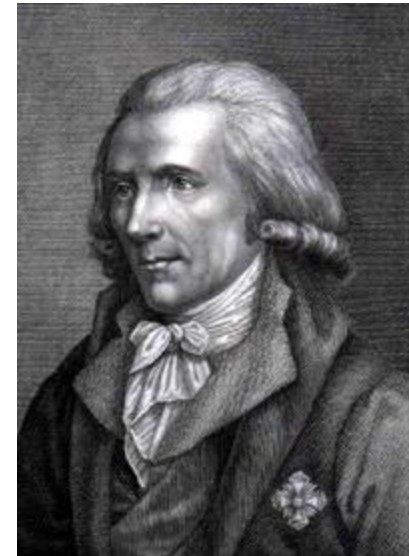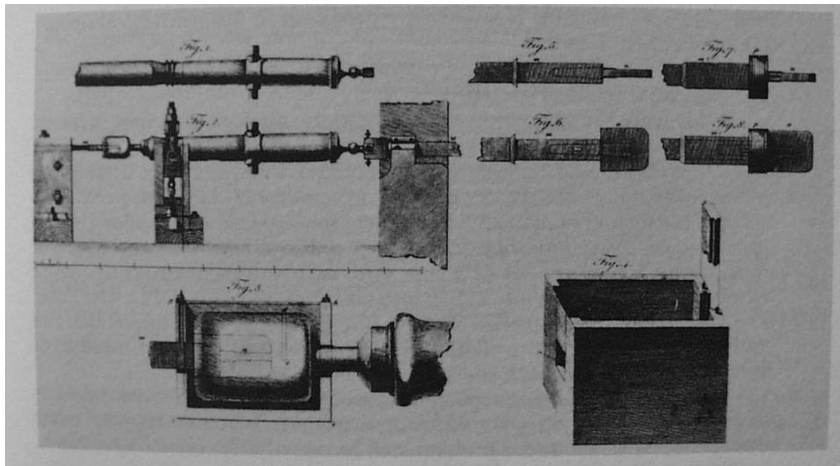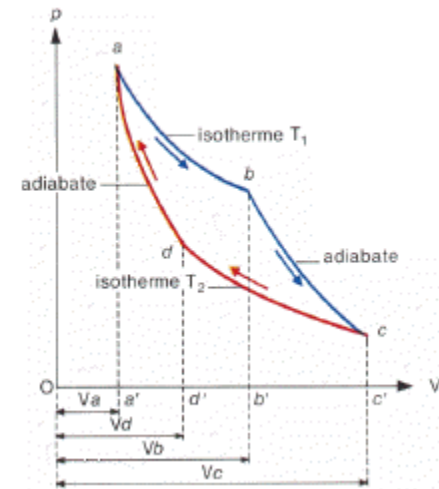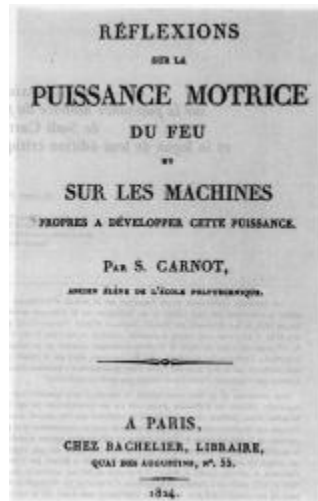- observed water turning into steam when canon barrel was bored
- *work ⇔ heat*

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.)
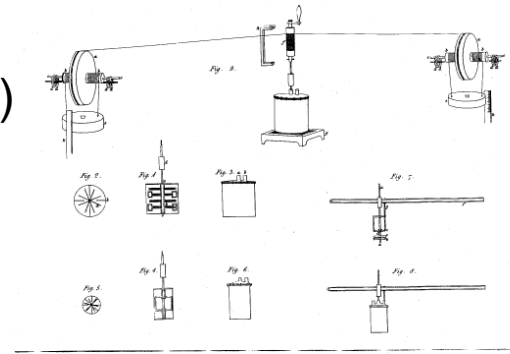
- Sadi Carnot, 1824
- efficiency of engines

- 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

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

Clausius

Boltzmann

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

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
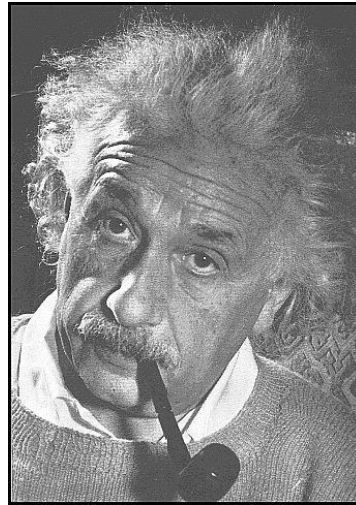
A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Hence the deep impression that ==classical thermodynamics== made upon me. It is the only physical theory of universal content concerning 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).

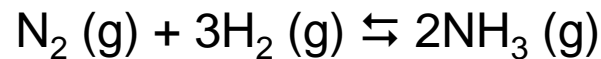**might**

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

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 ?

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

what are best T,P for NH_3 products?

The Haber Process

$$SiO_2 + CaCO_3 \leftrightarrows CaO \cdot SiO_2 + CO_2 \text{ (g)}$$
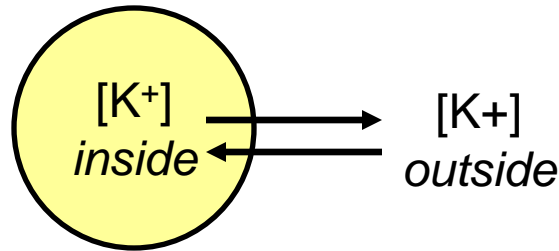*quartz   calcite   wollastonite*

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
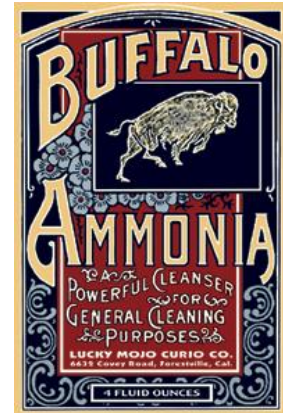
3. Chemical and physical changes in biological systems

$[K^+]$ *inside* → $[K+]$ *outside*

cell

what difference in $[K^+]_{out}$ vs $[K^+]_{in}$ can be tolerated before cell wall bursts or collapses?
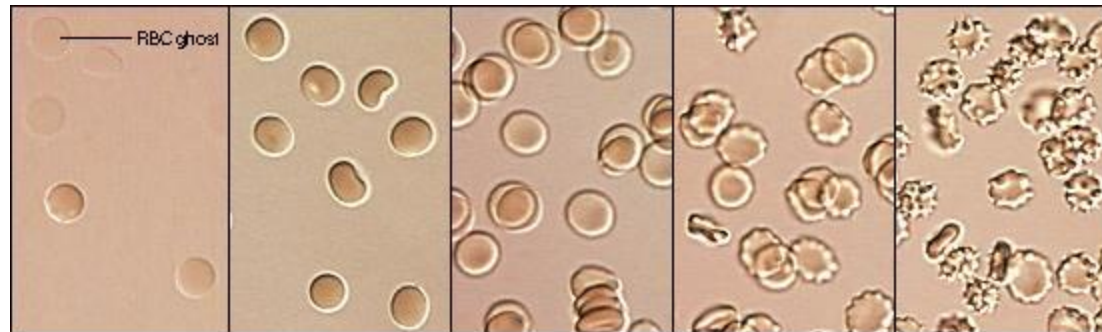
| *low* *hypotonic* *(rupture)* | ← *extracellular salt* | **normal** **isotonic** | → *extracellular salt* | *high* *hypertonic* *(collapse)* |

12

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

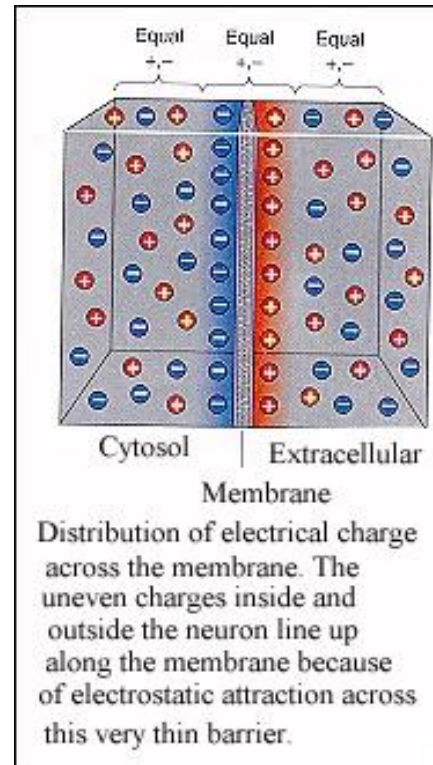5. Membrane potentials and ion concentrations in neurons. (electrochemistry and thermodynamics)

Equal +,−   Equal +,−   Equal +,−

Cytosol | Extracellular
Membrane

Distribution of electrical charge across the membrane. The uneven charges inside and outside the neuron line up along the membrane because of electrostatic attraction across this very thin barrier.

13

6. Thermodynamic feasibility of SO_2 removal

$$SO_2 \text{ (g)} \leftrightarrows S\text{(s)} + O_2 \text{ (g)}$$

http://healthandenergy.com/images/magnitka%20smoke%20stacks.jpg
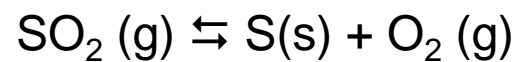
1. How fast a reaction proceeds (kinetics, catalysts, enzymes; in chem 103, BMB 100, chem 163C)

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:

$$\text{chem 163A} \quad \Leftrightarrow \quad \text{chem 163B}$$
$$\text{chem 163C}$$
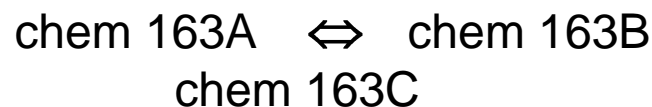
3. Although in chemistry 163B we will study how thermodynamics put limits on processes at equilibrium, there exists a whole other field of *non-equilibrium thermodynamics*.

15

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

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: 1st February
                1st March
- final: 20th March, 4:00-7:00 PM
                (*last class 18th March*)

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**

EXCUSES

Homework Problems
(#1-#8)

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

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

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

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

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

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

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

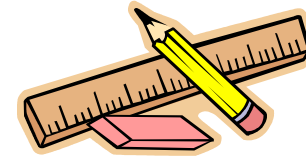   b. $\left(\dfrac{\partial^2 P}{\partial \bar{V}^2}\right)_T$

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

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

19

- **VOLUME:**   **MEASURED WITH A RULER**

- **TEMPERATURE:** **SEE IDEAL GAS THERMOMETER HANDOUT** ⇨

- **PRESSURE:**   **FORCE/AREA**

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

$$PV = nRT \qquad P\frac{V}{n} = P\bar{V} = RT$$

$$\frac{P}{1/\bar{V}} = \frac{P}{\rho} = RT$$

$$\lim_{\rho \to 0}\left(\frac{P}{\rho}\right)_{T_{boiling}} = RT_{boiling}$$

T_{eq}=boiling water at 1atm

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

He

N$_2$

T_{eq}=ice at 1atm

$$\lim_{\rho \to 0}\left(\frac{P}{\rho}\right)_{T_{ice}} = RT_{ice}$$

CO$_2$

$\rho = \dfrac{n}{V} = \dfrac{1}{\bar{V}}$ **Choose R so that T$_{boiling}$-T$_{ice}$=100**

21

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

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

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

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

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)*

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

for monatomic ideal gas

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

⇩
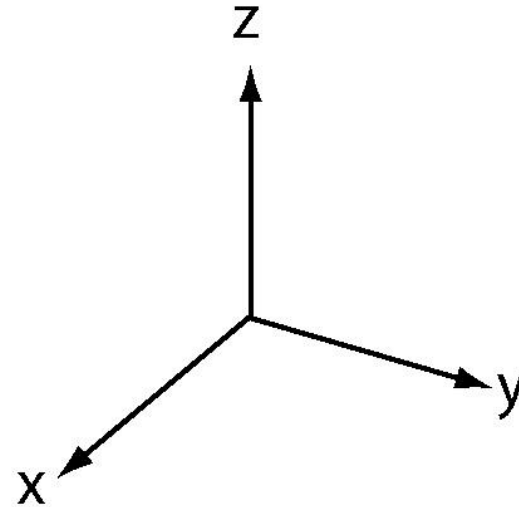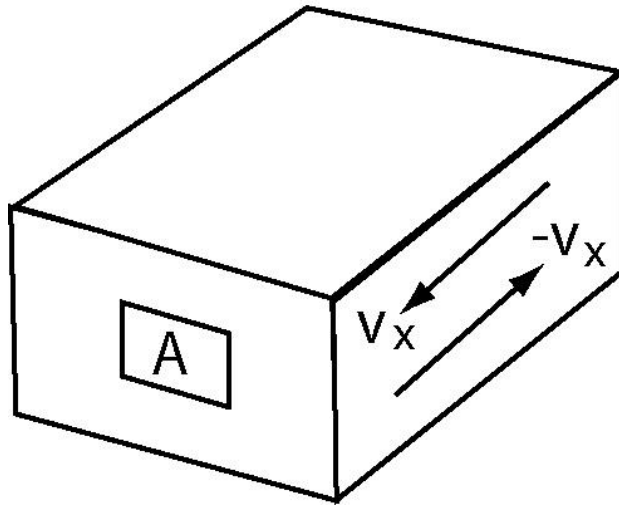
use physics to relate pressure ⇔ energy of gas

⇩

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≡U (internal energy)*]

23

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

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)

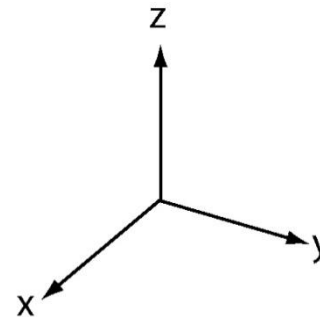$$\xleftarrow{\hspace{2cm}} \quad v_x$$
$$\xrightarrow{\hspace{2cm}} \quad -v_x$$
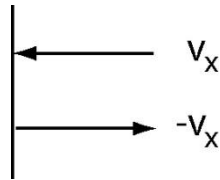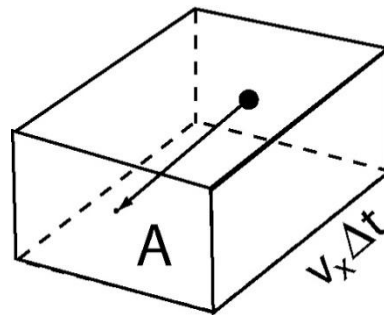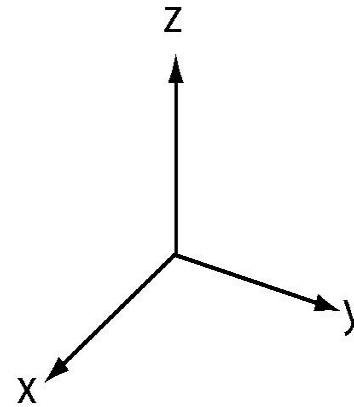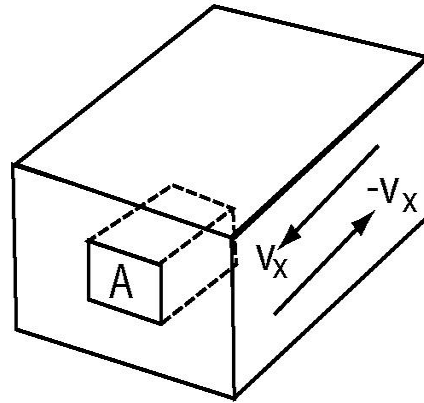
6. total Δp in given time Δt, $\left(\dfrac{\Delta p}{\Delta t} \right) \approx \left(\dfrac{dp}{dt} \right)$

     would depend on number of collisions in that interval

25

7.
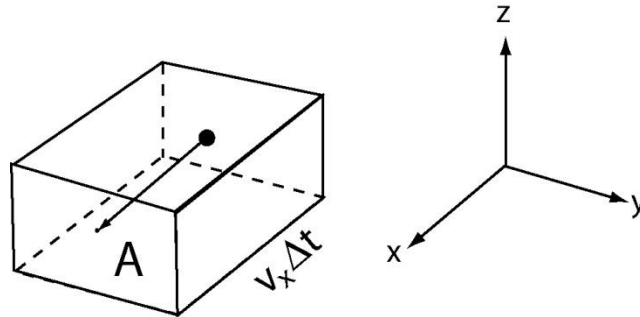
8. $\dfrac{n^*}{V}$ is density of molecules, $Av_x\,\Delta t$ is volume of rectangular box,

$$\dfrac{1}{2}\dfrac{n^*}{V}\,Av_x\Delta t$$ is number of molecules colliding with area A

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

27

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 $|v_x| = |v_y| = |v_z|$

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

- 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)

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

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

T constant $\Longrightarrow$ E constant

29

End of Lecture 1

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 $\gamma = c_o/T^3V_m,$ $\beta = b_o[1 - b/V_m],$ and $\alpha = a_o[1 + a/V_m]$	5
Redlich–Kwong	$P = \dfrac{RT}{(V_m - b)} - \dfrac{a}{T^{1/2}V_m(V_m + b)}$	2
Reichsanstalt	$PV = RT + AP + BP^2 + CP^3 + \cdots.$	∞

31

van der Waals equation

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

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

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

Table 1.1 van der Waals parameters

?

size

polarizability

polarity

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

33

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 <u>catalyst of iron</u> with a small amount of <u>aluminium</u> 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.

heu·ris·tic [hy*oo*-**ris**-tik *or, often*, y*oo*-] ***adjective***

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