Chemistry 163B, Winter 2014
Lecture 1- Introductory Lecture

Chemistry 163B
Thermodynamics
Winter 2014

1

Thermodynamics is a

really beautiful scientific

story !!

2

"rules" of science

• observations

↓

• guiding principles

↓

• predictions and applications based on principles

3

Observations (QM vs Thermo)

Thermodynamics is very 'working class' in its origins:

quantum mechanics

thermodynamics

$H\,\Psi = E\,\Psi$

$\Delta S_{universe} > 0$

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observations: thermo ≡ heat

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

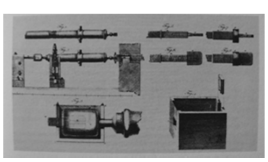
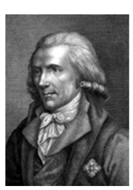


FIGURE 11. An illustration from Rumford's paper, "An Inquiry Concerning the Source of the Heat Which is Excited by Friction," showing the apparatus used by him in the cannon boring experiment. Figure 1, upper left, shows the cannon as received from the foundry, and Figure 2, below, shows it mounted in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



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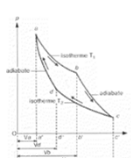
observations: mechanical efficiency of steam engine

• Sadi Carnot, 1824
• efficiency of engines


RÉFLEXIONS
PUISSANCE MOTRICE
DU FEU
SUR LES MACHINES
Par S. CARNOT,
A PARIS,



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Chemistry 163B, Winter 2014
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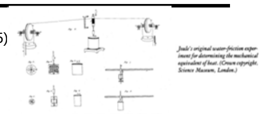
guiding principles

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



• 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)

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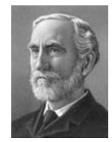
"Applications" U,H,S,G

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 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

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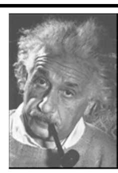
from: Einstein's "Autobiographical Notes"



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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types of problems that thermodynamics addresses (reactions)

1. Under what conditions ~~will~~ **might** 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

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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 • 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]

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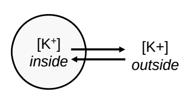
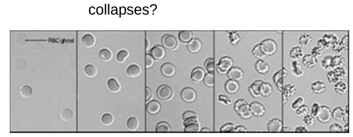
types of problems that thermodynamics addresses (biology)

3. Chemical and physical changes in biological systems



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

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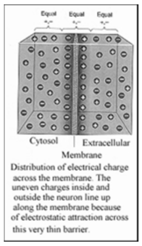
types of problems that thermodynamics addresses (biology)

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



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.

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types of problems that thermodynamics addresses (ecology)

6. Thermodynamic feasibility of SO_2 removal

SO_2 (g) ⇆ S(s) + O_2 (g)

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:

   chem 163A ⇔ 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*.

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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

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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: 31^{st} January
  26^{th} February
- final: 20^{th} March, 12:00-3:00 PM
  (*last class 17^{th} March*)

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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**

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Winter 2014 Chemistry 163B

Homework Problems (#1-#4)

Sections week of 6th January

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

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

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

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

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

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

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

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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:

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

$$P = RT\left[\frac{C_1(T)}{\bar{V}} + \frac{C_2(T)}{\bar{V}^2} + \frac{C_3(T)}{\bar{V}^3} \ldots + \frac{C_n(T)}{\bar{V}^n} \ldots\right] \quad \textit{virial}$$

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 $z^k = \left(\frac{1}{\bar{V}}\right)^k$

$$\frac{P}{RT} = \sum_{k=0}^{\infty} C_k(T)\left(\frac{1}{\bar{V}}\right)^k = \sum_{k=0}^{\infty} C_k(T) z^k = f(z;T)$$

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 $C_2(T)$?

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

- **VOLUME:** MEASURED WITH A RULER

- **TEMPERATURE:** <u>SEE IDEAL GAS THERMOMETER HANDOUT</u>
- **PRESSURE:** FORCE/AREA
- **EQUATION of STATE:** RELATES P, V, T *(more later)*

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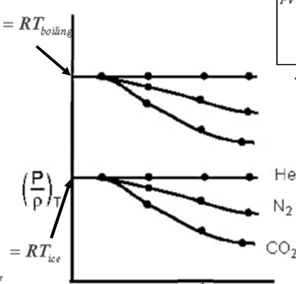
empirical TEMPERATURE: universal behavior of gas $\left(\frac{P}{\rho}\right)_T$ vs ρ

handout *and pp. 4-5*

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

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

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



T_{eq}=boiling water at 1atm

T_{eq}=ice at 1atm

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

$\rho = n/V = \frac{1}{\bar{V}}$ **Choose R so that $T_{boiling}$-T_{ice}=100**

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

Pressure, Kinetic Energy, and Temperature <u>**SEE HANDOUT**</u>

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

$PV=n^*kT$ $\quad$ *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)*

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

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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 $E=\frac{3}{2}n^*kT$ (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)*]

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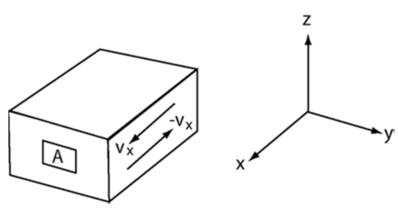
heuristic *derivation of E=E(T) for ideal gas [U=U(T)]*



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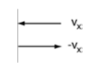
heuristic derivation

1. molecules all with same $|v_x|$ (all same v_x is 'heuristic')
2. elastic collision with wall mass velocity goes $v_x \longrightarrow -v_x$
3. from physics $P=\frac{F}{A}$ *P=pressure*
4. from physics $F=\frac{dp}{dt}$ *p=mv, momentum; t=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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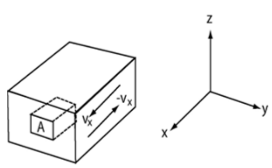
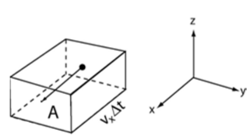
heuristic derivation

7.





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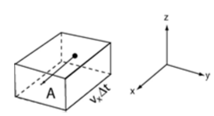
heuristic derivation



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

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

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

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heuristic derivation

11. after some algebra and equating

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

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

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

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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)

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

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

T constant $\Longrightarrow$ E constant

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Some comments on the

Van der Waals equation of state

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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	$PV_m = RT$	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	$P = RT\left[V_m^{-1} + \sum_{n=2}^{\infty} C_n(T)V_m^{-n}\right]$	HW#1 *4	∞
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	$P = \frac{RT}{(V_m - b)} - \frac{a}{T^{1/2}V_m(V_m + b)}$		2
Reichsanstalt	$PV = RT + AP + BP^2 + CP^3 + \cdots$.		∞

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van der Waals equation

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

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

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

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van der Waals equation

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

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

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

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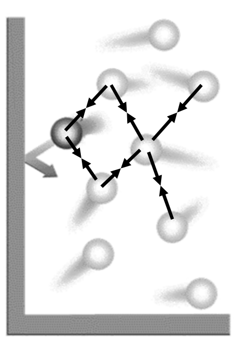
heuristic justification for attractive constant a

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



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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 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_20	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

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

Table 1.1 repulsive | attractive

Gas	b (L mol^{-1})	a (L^2 bar mol^{-2})
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CO_2	0.04286	3.658

? size (He–Kr) — polarizability (He–Kr) — polarity (Acetylene–CO_2)

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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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
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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 $\gamma = c_o/T^3V_m$, $\beta = b_o[1 - b/V_m]$, and $\alpha = a_o[1 + a/V_m]$	5
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Reichsanstalt	$PV = RT + AP + BP^2 + CP^3 + \cdots$.	∞

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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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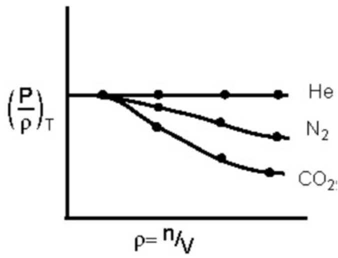
universal behavior of gas $\left(\frac{P}{\rho}\right)_T$ vs ρ



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