Gases and Kinetic Theory

Chemistry 35

Fall 2000

Gases

- One of the four states of matter
- Simplest to understand both *physically* and *chemically*
- **Gas Properties**
  - Low density
  - *Fluid*
  - Can be defined by their:
    1. Pressure (P)
    2. Volume (V)
    3. Temperature (T)

Pressure

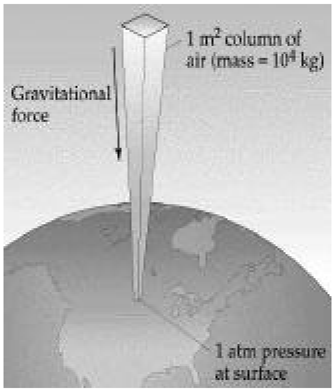
- How do we measure/quantify pressure?

Define: P = force/area
= N/m^2
= *Pascals* (Pa)

Atmospheric Pressure:

- force exerted by the atmosphere on the surface of the Earth

P = *1 atm = 101,325 Pa*



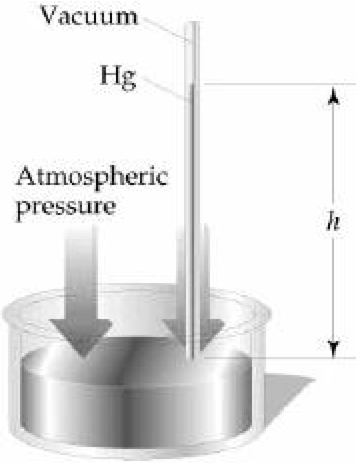
Measuring Pressure

- Torricelli (1600's):

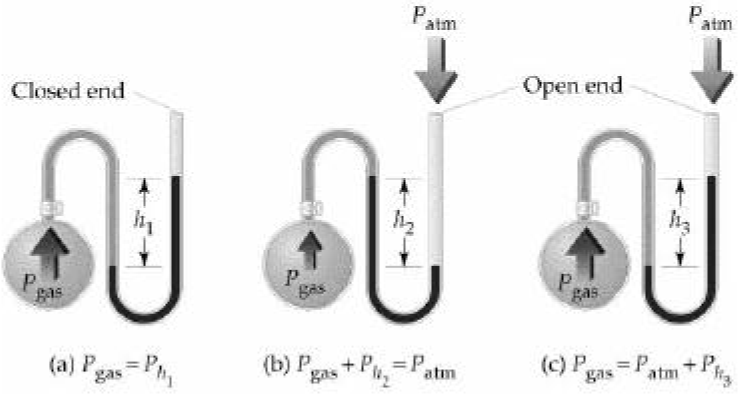
- atmospheric pressure raises a column of *mercury* 760 mm

- *Barometer*

1 atm = 760 mm Hg
= 760 *torr*
= 101,325 Pa
= 101.325 kPa



Manometer

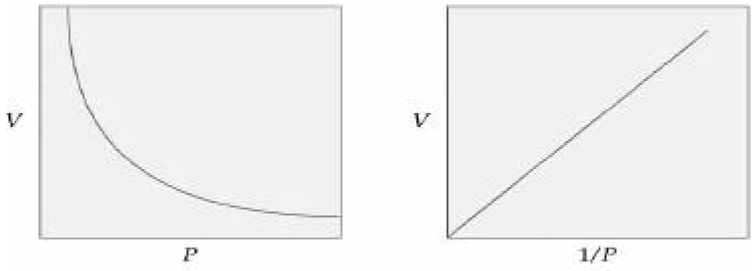


(a) $P_{gas} = P_{h_1}$ (b) $P_{gas} + P_{h_2} = P_{atm}$ (c) $P_{gas} = P_{atm} + P_{h_3}$

$P_{atm} > P_{gas}$ $P_{atm} < P_{gas}$

Boyle's Law: Pressure-Volume

- Changing *pressure* on a <u>fixed amount of gas</u> resulted in a corresponding change in **volume:**



Boyle found that: **P x V = constant**

movie

Boyle's Law Example

- If a gas occupies **1.00 L** at a pressure of **0.50 atm**, what *volume* would it occupy if the pressure were decreased to *0.10 atm*?

<u>Since P x V = constant:</u> $P_1V_1 = P_2V_2$

$$V_2 = P_1V_1/P_2 = (0.50\ \text{atm})(1.00\ \text{L})/(0.10\ \text{atm})$$

$$\mathbf{V_2 = 5.0\ L}$$

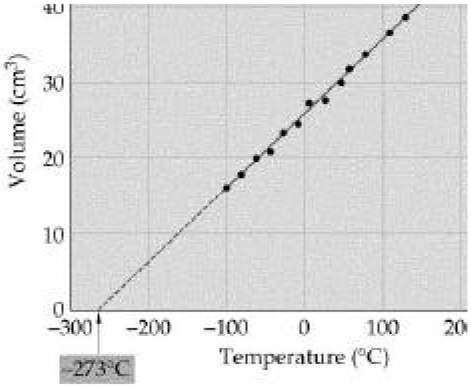
Charles' Law: Temperature

- Changing *temperature* of a <u>fixed amount of gas</u> resulted in a corresponding change in **volume:**

At a fixed pressure, it was found that:

Volume $\propto$ Temp

-**<u>implication</u>**: at some temp, volume would decrease to ***ZERO***



Charles' Law Example

- If a gas occupies **1.00 L** at **25.0 ºC** and, after heating, expands to a volume of *2.00 L*, to what *temperature* was the gas heated?

$$\frac{V_1}{V_2} = \frac{T_1}{T_2} \Rightarrow \mathbf{T_2 = \frac{T_1 V_2}{V_1}}$$

$$T_2 = \frac{(25.0 + 273.15)(2.00\ \text{L})}{(1.00\ \text{L})} = \mathbf{596.3\ K}$$

$$T_2 = 596.3\ \text{K} - 273.15 = 323.15\ {}^{o}\text{C}$$

$$= \underline{\mathbf{323.\ {}^{o}C}}$$

Avogadro's Law

- Recall: *Equal volumes of gases (at the same temperature and pressure) contain equal number of molecules.*

So, it follows that:

Volume $\propto$ # mol gas

(at constant temperature and pressure)

Ideal Gas Law

- Puts together all of the three previous laws:

Boyle:	P-V @ constant T and n
Charles:	V-T @ constant P and n
Avogadro:	V-n @ constant P and T

So: **PV = nRT** Ideal Gas Law

R = *universal gas constant* = **0.082058 L-atm-mol^{-1}-K^{-1}**

(In S.I. Units: R **= 8.3145 J-mol^{-1}-K^{-1}**)

Standard Temp and Pressure

- **One implication of IGL**: *at a particular T and P, a fixed amount of ANY GAS will occupy the same volume*

-Define a ***reference condition:***

T= 0°C (=273.15 K)
P = 1 atm

Standard Temp and Pressure:
STP

Solving IGL for VOLUME: **V = nRT/P**

$$= \frac{(1\ \text{mol})(0.08206)(273.15\ \text{K})}{1\ \text{atm}}$$

= ***22.41 L***

(volume occupied by 1 mol of ANY GAS at STP)

Tips for using the IGL

- There are FOUR variables!
  -you've gotta know THREE to find the 4th one
- **UNITS! UNITS! UNITS!**
  -convert all quantities to appropriate units

  V = *L*, **P** = *atm*, **T** = *K*, **n** = *mol*

  -use dimensional analysis to check your units
  -HINT: look at the units of **R** as a final check:
  (0.08206 *L-atm/mol-K*)

Example: P, V and T changes

- For a *fixed amount* (n mol) of gas:

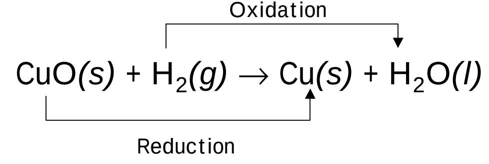
$P_1V_1 = nRT_1$ - *initial condition*
$P_2V_2 = nRT_2$ - *final condition*

So: $$\frac{P_1V_1}{T_1} = \boldsymbol{nR} = \frac{P_2V_2}{T_2}$$

Leaving: $$\boxed{\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}}$$

How does this relate to Chemistry?

- What *mass* of Cu will be produced by the reduction of excess CuO by **250. mL H_2** at **1.025 atm** and **15.0ºC**?



$CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(l)$

Excess

250. mL

1.025 atm

15.0 ºC

? grams

The Solution: Gas Stoichiometry

<u>Strategy:</u>

vol/press/temp ® mol H_2 ® *mol Cu* ® *g Cu*

PV = nRT: *solve for n*

$$n = \frac{PV}{RT} = \frac{(1.025\ \text{atm})(0.250\ \text{L})}{(0.08206\ \text{L-atm/mol-K})(288.15\text{K})} = 0.010837\ mol\ H_2$$

$$0.010837\ \text{mol } H_2 \times \frac{1\ \text{mol Cu}}{1\ \text{mol } H_2} \times \frac{63.546\ \text{g Cu}}{1\ \text{mol Cu}} = 0.68855\ g\ Cu$$

= ***0.689 g Cu***

Gas Density

- Density (d) = mass/volume
- Rearranging IGL:

$$\frac{n}{V} = \frac{P}{RT}$$

- Convert mol → grams (mass):

$$\frac{MW \times n}{V} = \frac{P \times MW}{RT}$$

- Now we have density:

$$d = \frac{P(MW)}{RT} = g/L$$

Gas Density:

-varies with PRESSURE

-varies with TEMPERATURE

-varies with MOLAR MASS

Molar Mass Determination

- If a sample of an unknown gas weighs *0.893 grams* and occupies a volume of *250. mL at STP*, what is its **molar mass** (MW)?

MW (molar mass) = g/mol

-solve IGL for mol (n): $n = \frac{PV}{RT} = \frac{(1\ \text{atm})(0.250\ \text{L})}{(0.08206)(273.15\ \text{K})}$

$n = 0.0111534\ \text{mol}$

So: MW = 0.893 g/0.0111534 mol = *80.065 g/mol*

= ***80.1 g/mol***

Gas Mixtures

- Dalton's Law of Partial Pressures:

*The **TOTAL PRESSURE** of a gas mixture is the **SUM of the pressures** exerted by each of the gases in the mixture.*

$$P_{total} = P_1 + P_2 + P_3 + \ldots\ldots$$

At constant Temp and Volume:

$$P_1 = n_1\,(RT/V) \rightarrow P_1 \propto n_1$$

- partial pressure of a gas in a mixture is proportional to the number of mol of that gas in the mixture

Partial Pressures: Example

- If dry air is 21.0% O_2, 78.0% N_2 and 1.0% Ar (wt%), what is the *partial pressure* of O_2 in a dry air sample at **1.00 atm** total pressure?

$$P_{O2} = X_{O2}P_{Total}$$

We need X_{O_2}:

$$X_{O2} = \frac{n_{O2}}{n_{O2} + n_{N2} + n_{Ar}} = \textit{mol fraction of } O_2$$

We need mol of each:

$$n_{O2} = 21.0 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{31.998 \text{ g } O_2} = 0.6563 \text{ mol } O_2 \text{ (in 100 g Air)}$$

Partial Press Example: Cont'd

- Putting it all together:

$$X_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{N_2} + n_{Ar}} = \frac{0.6563 \text{ mol}}{0.6563 + 2.784 + 0.02503 \text{ mol}}$$

$$= \mathbf{0.18939}$$

Finally: $P_{O_2} = X_{O_2}P_{Total}$

$$= (0.18939)(1.00 \text{ atm}) = \mathbf{0.18939 \text{ atm}}$$

In *torr*: $0.18939 \text{ atm} \times \frac{760 \text{ torr}}{1 \text{ atm}} = 143.9 \text{ torr} = \underline{\mathbf{144. Torr}}$

Kinetic Theory of Gases

- Developed in the 1800's by physicists Clausius, Maxwell and Boltzmann
- **Model of Gas Behavior:**
  - Pure gas is ***dilute***
    - atoms/molecules separated by distances >> size
  - Molecular motion is:
    - continuous, random
    - in straight lines between *collisions*
    - defined by a *distribution* of velocities
  - Collisions:
    - are elastic (no energy loss)
    - are the ***only*** interactions
    - change the *direction* of motion

More Gas Kinetic Theory

- **Implications:**

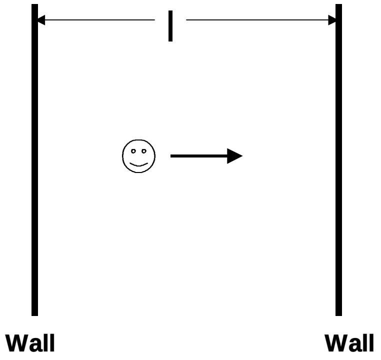
1. **Temperature**
    - The *average kinetic energy* of the molecules does not change over time (at constant temperature)
    - The *average kinetic energy* of the molecules is proportional to the **absolute temperature**
2. **Pressure**
    - The pressure exerted by a gas is caused by collisions of the gas molecules with the walls of the container
    - The *magnitude* of the pressure depends on collision frequency and force

Gas Kinetic Theory: Qualitatively

- Can explain empirical observations:
    - Boyle's Law (PV = constant)
        - *Increase volume*: fewer molecules per unit volume, so there are fewer collisions with the container walls (*decreased pressure).*
    - Charles' Law (P/T = constant)
        - *Increase Temp*: molecules move faster, so there are more collisions with the container walls (*increased pressure*).

Gas Kinetic Theory: Quantitatively

- Consider a molecule in a cube moving in one direction:



l = *distance between walls*

v = l/t = velocity of molecule

l/v = time to travel across cube

$\Delta t = 2l/v$ = *time to travel from wall to wall round trip*

Momentum of the molecule:

$$p = mv_x$$

Due to collision:

$$\underline{\mathbf{\Delta p = 2mv_x}}$$

Quantitative Gas Kinetic Theory: Cont'd

- What is the *force* exerted by the molecule on the wall due to the collision?

Force (F) = $\Delta p/\Delta t = 2mv/(2l/v)$

$$\mathbf{F = mv^2/l}$$

- Relating this to *pressure:*

Pressure = force/unit area

$$P = F/l^2 = (mv^2/l)/l^2 = mv^2/l^3$$

So: $\boxed{\mathbf{P = \frac{mv^2}{V}}}$ ***Boyle's Law!***

Now, apply to an *aggregate* of gas particles

- For N_0 molecules moving in 3-dimensional space, it can be shown that:

$$\mathbf{PV = 1/3\ N_0 m\langle v^2\rangle}$$

where $\langle v^2\rangle$ is the *mean squared speed* of the aggregate of molecules

-Again, we've got **Boyle's Law** (PV = constant) at constant temperature and for a fixed number of gas molecules

But, what about ***temperature***?

Kinetic Energy

- Recall that kinetic energy is: $1/2\ mv^2$
- *Rearranging* the previous equation *and substituting* in the kinetic energy:

$$\mathbf{PV = 2/3\ N_0\langle \varepsilon_k\rangle}$$

Where $\langle \varepsilon_k\rangle$ is the ***average*** *kinetic energy* ***per particle***

- We also know that $N_0\langle e_k\rangle$ is the *total kinetic energy* (E_k) for a mole of gas molecules, so:

$$\mathbf{E_k = 3/2\ PV}$$

Kinetic Energy and Temperature

- Recalling the IGL, we can substitute *nRT* for *PV:*

$$\boxed{E_k = 3/2\ nRT}$$

-for a fixed amount of gas, *temperature* is determined ***solely*** by the total kinetic energy of the gas molecules

  -Temp is independent of the *mass* or *density* or of the ***composition*** of the gas

  -the *velocities* of gas molecules must then be dependent upon their masses

Temperature and Velocity

- Bringing back our initial result:

$$PV = 1/3\ N_0m\langle v^2\rangle$$

- And recognizing that: $N_0m = M$ (molar mass)
- And that for a mole of gas: $PV = RT$
- We obtain: $1/3\ M\langle v^2\rangle = RT$
- Rearranging:

$$\langle v^2\rangle = 3RT/M$$

- And taking the square root of both sides:

$$\boxed{v_{rms} = (3RT/M)^{1/2}}$$

rms Velocity and Molar Mass

- Knowing that:

$$v_{rms} = (3RT/M)^{1/2}$$

Thus, the rms velocity of a gas at a constant temperature must vary with gas composition.

For example: N_2 at 25.0 °C

$v_{rms} = (3(8.3145\ J/mol\text{-}K)(298.15\ K)/28.014 \times 10^{-3}\ kg/mol)^{1/2}$

$= \underline{\mathbf{\mathit{515\ m/s}}}$

Other examples: **Helium** (4.003 g/mol) @ *1360 m/s*

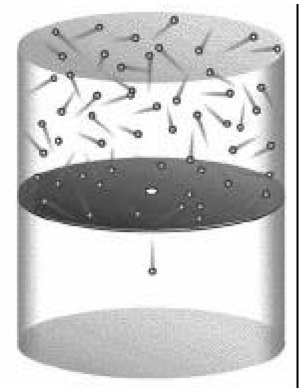
Sulfur Hexafluoride (146 g/mol) @ *226 m/s*

Graham's Law of Effusion

If gas molecules are allowed to enter a vacuum only through a small opening:

The rate at which they *effuse* through the opening will vary with the *square root* of their molar masses:

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$



So that's why those cheap helium-filled balloons don't last very long!

▪

substance)

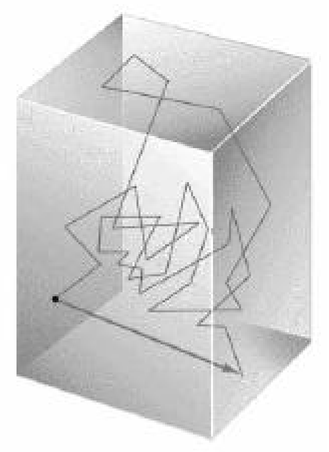
- gas molecules travel in a

with something, after which,
change direction

- that they travel before they collide is called the **mean free path** *(mfp)*

  -

  nm @ atm pressure



---

particles?

We can also express the *average kinetic energy*

$\langle\varepsilon$ = *Total Kinetic Energy* $\underline{E_k}$ = $\underline{3/2\ RT}$

N   0

$$\boxed{\langle\varepsilon_k\rangle = 3/2\ k_B T}$$

Boltzmann'

(= 1.38066 x 10^{-23} J/K)

Maxwell-Boltzmann Statistics

- Allows us to characterize the behavior of *individual particles* by statistical analysis of the *aggregate*
- The speed distribution for a gas at thermal equilibrium:

$$\boxed{F(v) = Kv^2 e^{-mv^2/2k_bT}}$$

where: $K = 4\pi(m/2\pi k_bT)^{3/2}$ - constant at fixed temp

There are two opposing trends:

$F(v) \propto v^2$ (incr) AND $F(v) \propto e^{-v^2}$ (decr)

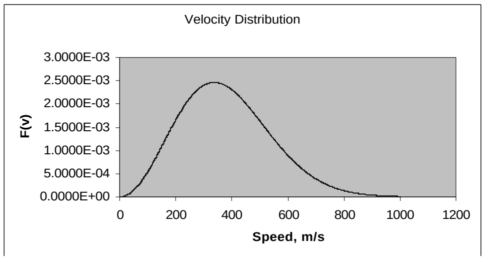
Maxwell-Boltzmann Speed Distribution

Example: **Argon**

T_1 = 273.15 K

v_{rms}= 413.0 m/s

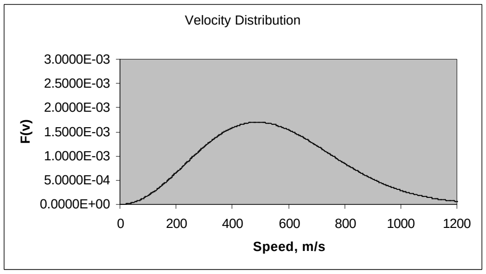
v_{mp} = 337.2 m/s



T_2 = 573.15 K

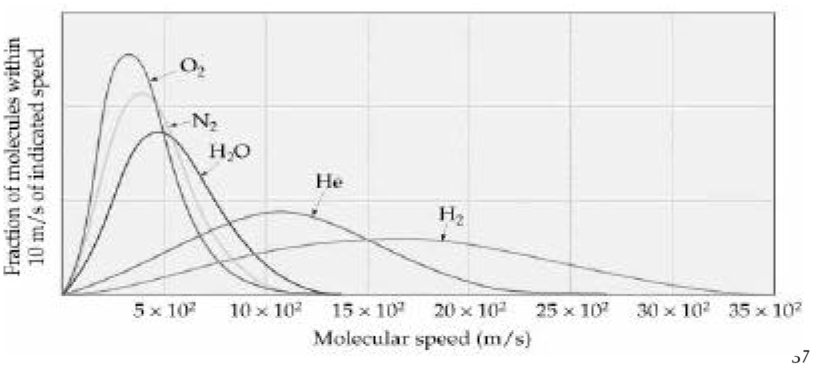
v_{rms}= 598.2 m/s

v_{mp} = 488.4 m/s



Maxwell-Boltzmann: Effect of Gas Composition

- Avg Kinetic Energy is *independent of gas composition* ® depends **only** on <u>temperature</u>
  - ***mass*** of the gas molecules varies with composition, the **<u>velocities of the molecules</u>** must vary with composition:



NON-Ideal Gases: The *Real* Thing

- If a gas acts *ideally*:

$$\frac{PV}{RT} = 1 \quad \textbf{for 1 mol gas}$$

- A plot of $\frac{PV}{RT}$ versus P should yield a straight line at a constant value of 1.00

Let's take a look, shall we?

Real Gas Behavior

No deviations until P>20 atm

➢*Negative Deviations* at

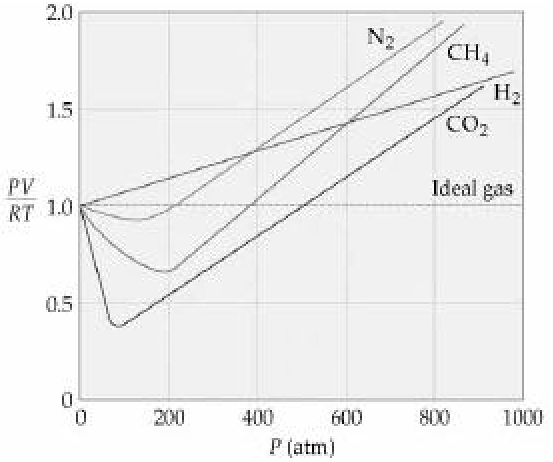
Due to lower than *ideal*

Molecular ***attractions***

Positive Deviations at

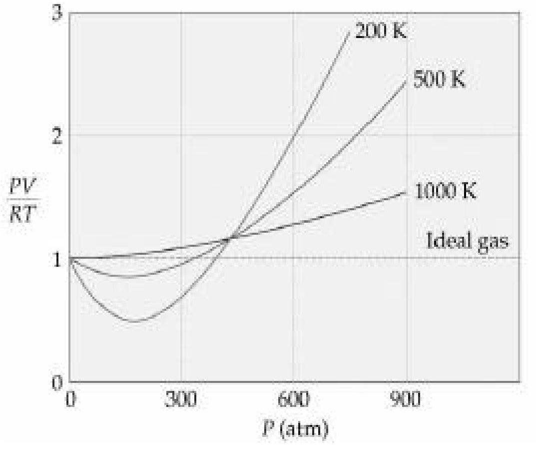
➢Due to higher than *ideal* volumes

➢*Molecular* ***repulsions***



At constant temperature (300 K)

Effect of Temperature



at lower temps

-due to decreased molecular motion, allowing more significant intermolecular interactions

van der Waals Equation

- *Corrects* the IGL using *empirically-corrected*

Volume: $\mathbf{V - nb}$

\# mol *actual volume* of

Pressure: $\mathbf{P + \frac{n^2 a}{V^2}}$

attractions between pairs of molecules

“strength” of molecular attractions

van der Waals Equation

Putting it all together:

$$\mathbf{(P + n^2a/V^2)(V - nb) = nRT}$$

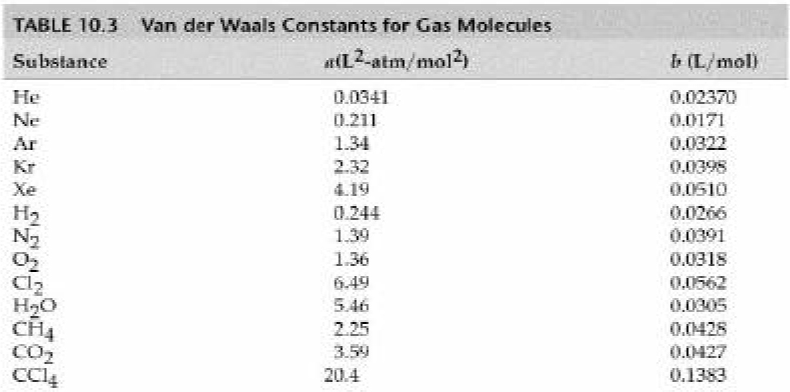


TABLE 10.3 Van der Waals Constants for Gas Molecules

Substance	a (L^2-atm/mol^2)	b (L/mol)
He	0.0341	0.02370
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0510
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
Cl_2	6.49	0.0562
H_2O	5.46	0.0305
CH_4	2.25	0.0428
CO_2	3.59	0.0427
CCl_4	20.4	0.1383