

Ideal & Non-Ideal Gases

PreLab submission with a pass grade is required to begin the lab.
Must be submitted no later than a day before the lab.

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Section:H5

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Readings

The Ideal Gas, A short review

The ideal gas law states that $PV = nRT$ where T is the absolute temperature measured in Kelvins. This equation is also called the equation of state of an ideal gas. It is a good description of most gases in the low-density regime where, on average, the gas molecules are far apart. The purpose of the experiment is to determine experimentally how the pressure P of a gas varies with temperature when no change is made in either the volume V or the number of moles of gas n . Using this information, you will determine T_0 , the absolute zero temperature measured in degrees Centigrade, by linear extrapolation of the ideal gas equation to where the pressure P of the gas is zero (no molecular bombardment of the walls of the gas container).

In this experiment you will measure T_C , the temperature in degrees Centigrade, which you will recall is related to T (in Kelvins) by $T = T_C - T_0$ (T_0 is a negative number). The graphical technique you will use is to plot T_C (vertical axis) vs. P (horizontal axis). The equation for the straight line fitted to the data points will have the form of a linear equation,

$$(1) \quad T_C = a + bP = T_0 + \left(\frac{V}{nR}\right)P,$$

where V is the volume of the gas, n is the number of moles, and $R = k_B N_A$ is the universal gas constant.

For $P = 0$ the vertical axis intercept, T_0 , in degrees Centigrade, can be read directly from the equation.

A Non-Ideal Gas, A short review of van der Waals gas

We noted above that the ideal gas law holds for low-density gases. Theoretically, for deriving the ideal gas law, it is necessary to make two assumptions

- the gas molecules are very small (they have no volume) and
- the molecules are non-interacting (there is no force between them).

In 1873 the Dutch physicist van der Waals derived an equation of state without these assumptions. It is known as the van der Waals equation of state:

$$(2) \quad \left(P + \frac{a}{v^2}\right)(v - b) = RT,$$

where a and b are constants chosen to agree with experiment, and v is the molar specific volume, i.e. the volume of the container divided by the number of moles of gas inside. b is also a molar specific volume and represents the total volume per mole of gas that is inaccessible to other molecules because it is already occupied by a molecule, considering you can't have two molecules at the same place at the same time. If the

molecules in the gas have a radius r , then when two collide the centers can only come with a distance $2r$ of each other. Thus if we want to consider the molecules to have no volume, we must subtract from the volume of the container the volume of a “sphere of exclusion” of radius $2r$ around each molecule,

$$(3) \quad b = \frac{1}{2} N_A \frac{4}{3} \pi (2r)^3,$$

where N_A is the Avogadro’s number, the number of molecules in a mole. The $1/2$ occurs because only the hemisphere facing the colliding molecule is effective in excluding it. The term a/v^2 that is added to the pressure of the gas in the container arises from a very short range attractive force between molecules known as the van der Waals force. When a molecule is not near the wall of the container, it is surrounded by molecules and, on average, this force cancels out. But near the wall the molecule experiences a net force pulling it away from the wall, which reduces the force (pressure) it exerts on the wall when it collides. This is the force that makes some gases liquefy at low enough temperatures.

The values for a and b are determined experimentally for each gas. For oxygen $a = 1.38 \times 10^5 \text{ Pa} \cdot \text{m}^6 / (\text{kmol})^2$ and $b = 0.0319 \text{ m}^3 / (\text{kmol})$.

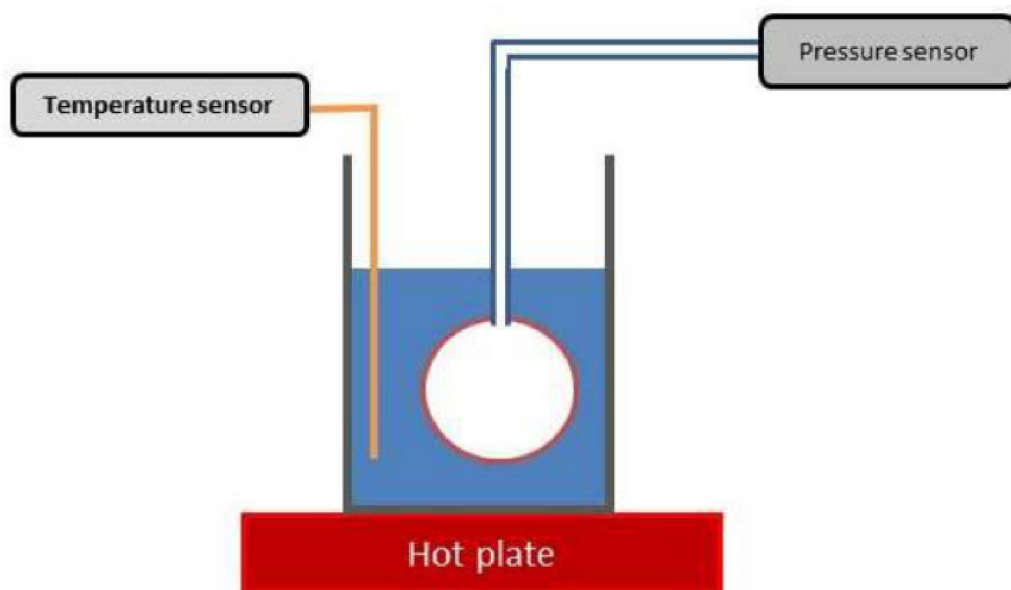
[Pa = Pascal = N / m^2 , where N is Newton.]

For the purposes of your calculations remember that $R = 8314 \text{ J} / (\text{kmol K})$. Avogadro’s number is $N_A = 6.02 \times 10^{23}$ molecules per mole, and the volume occupied by one kmol of a gas at standard temperature and pressure (0°C and $760 \text{ torr} = 1 \text{ atm} = 1.01 \times 10^5 \text{ Pa}$) is 22.4 m^3 .

[Note: the mole is defined to be the quantity of material whose mass in grams is equal to the molecular weight of the material. The proper SI unit is not the mole, but rather the kmol = 1000 moles. The mass of a kmol in kilograms equals the molecular weight of the material, the number of molecules in the kmol is 6.02×10^{26} and the standard volume is 22.4 m^3 .]

Equation (2) gives a fairly good description of a real gas. Other equations of state such as the Beattie-Bridgman equation (which uses five adjustable parameters instead of two) gives even better agreement with experiment.

Figure 1. The setup of the experiment.



Dialog:

Question 1.

- Use equation (3) and $b = 0.0319 \text{ m}^3/\text{kmol}$ to estimate the size of an oxygen molecule. Express your answer in Angstroms ($= 10^{-10}\text{m}$) and in nm. Show your work.

Answer 1.

$$b = \frac{1}{2} N_A \frac{4}{3} \pi (2r)^3$$

\Rightarrow solving for r , $r = \text{cbrt}(6 b / 32 \pi N_A)$

Hence, $r = \mathbf{1.46768 \text{ Angstroms or } 0.146768 \text{ nm}}$

```
In[*]:= (* This is an Input cell in case you need *)
b = 0.0319 / 1000 ; (*m³/mol*)
N_A = 6.02214076 × 10^23; (*mol⁻¹*)

r = CubeRoot [6 b / (32 * Pi * N_A) ]
```

```
Out[*]= 1.46768 × 10⁻¹⁰
```

Question 2.

- The metal bulb on the ideal gas apparatus, shown in the fig. 1, has a diameter of 10.4 cm. The bulb is filled with oxygen at standard temperature and pressure. Calculate the number of kilomoles of oxygen in the bulb and the molar specific volume v , assuming oxygen is an ideal gas.

Answer 2.

As stated in the reading, the volume occupied by 1 kmol of gas is about 22.4 m^3
 For a spherical (assume spherical shape) bulb of diameter 10.4 cm, $r = 0.052 \text{ m}$
 Volume of the sphere is hence 0.000588977 m^3

Therefore, number of kmol of oxygen is $\text{vol}/22.4 = \mathbf{0.0000262414 \text{ kmol}}$ or $\mathbf{2.62414 \times 10^{-5} \text{ kmol}}$

```
In[*]:= (* This is an Input cell in case you need *)

(*Constants*)
P0 = 101.325; (*Pressure in kPa*)
T0 = 273.15; (*Temperature in K*)
R0 = 8.314; (*kJ/(kmol.K)*)
a0 = 1.382 * 10^-5; (*kPa.m^6/kmol^2*)
b0 = 0.03186; (*m^3/kmol*)

(*Volume of the bulb (sphere)*)
d0 = 0.104; (*Diameter in m*)
V0 = (4 / 3) * Pi * (d0 / 2) ^3; (*Volume in m^3*)

(*Solve Van der Waals equation for v*)
vMolar = Solve[R0 * T0 / (volume - b0) - a0 / volume^2 - P0 == 0, volume, Reals]

rbulb = 10.4 / 100 / 2; (*m*)
volbulb = 4 / 3 * Pi * r^3;
noxy = vol / 22.44458242176299
```

```
Out[*]=
{{volume -> 22.4446}}
```

```
Out[*]=
0.0000262414
```

Question 3.

- a and b for nitrogen are $1.37 \times 10^5 \text{ Pa.m}^6 / (\text{kmol})^2$ and $0.0387 \text{ m}^3 / (\text{kmol})$. How much does the pressure differ for pure nitrogen from pure oxygen at $T = 273 \text{ K}$ and $v = 22.4 \text{ m}^3/\text{kmol}$. Take both oxygen and nitrogen to be van der Waals gases.

Answer 3.

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

$$\Rightarrow P = RT/(v-b) - a/v^2$$

Given in the reading:

For oxygen $a = 1.38 \times 10^5 \text{ Pa}\cdot\text{m}^6 / (\text{kmol})^2$ and $b = 0.0319 \text{ m}^3 / (\text{kmol})$

$$\Rightarrow P_{\text{oxygen}} = 101229.20 \text{ Pa}$$

$$\Rightarrow P_{\text{nitrogen}} = 101196.35 \text{ Pa}$$

They seem to be really close, hence we can assume they have practically the same behaviour in standard conditions.

$$P_{\text{Nitro}} - P_{\text{Oxy}} = 32.8501 \text{ Pa}$$

In[154]:=

```
(* This is an Input cell in case you need *)
R = 8.314; (*J/K.mol*)
T = 273; (*K*)
v = 22.4 / 1000; (*m^3/kmol*)
aOxy = 1.38 * 10^5 / 10^6; (*Pa.m^6/(mol)^2*)
bOxy = 0.0319 / 1000; (*m^3/mol*)
aNitro = 1.37 * 10^5 / 10^6; (*Pa.m^6/(mol)^2*)
bNitro = 0.0387 / 1000; (*m^3/mol*)

PNitro = NumberForm[(R * T / (v - bNitro)) - (aNitro / (v^2)), 15]
POxy = NumberForm[(R * T / (v - bOxy)) - (aOxy / (v^2)), 15]
NumberForm[((R * T / (v - bNitro)) - (aNitro / (v^2))) - ((R * T / (v - bOxy)) - (aOxy / (v^2)))]
(*Difference Between the Two*)
```

Out[161]//NumberForm=
101229.199338901

Out[162]//NumberForm=
101196.349230892

Out[163]//NumberForm=
32.8501

Table X. Copy All Your Final Results.

In[164]:=

```
Grid[{{Text["Table X. Final Answers, Lab 3 Prerequisite"], SpanFromLeft},
  {"Q1. size of an oxygen molecule (nm)",
    "Q2. n (kmol)", "Q2. v (m3/kmol)", "Q3. PN2-PO2 (Pa)"},
  {"0.146768", "0.0000262414 or 2.62414 * 10-5", "22.44458", "32.8501"}
}, Frame → All]
```

Out[164]=

Table X. Final Answers, Lab 3 Prerequisite			
Q1. size of an oxygen molecule (nm)	Q2. n (kmol)	Q2. v (m ³ /kmol)	Q3. P _{N₂} -P _{O₂} (Pa)
0.146768	0.0000262414 or 2.62414 * 10 ⁻⁵	22.44458	32.8501

Rutgers 276 Classical Physics Lab

“Ideal & Non-Ideal Gasses”

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