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# THE KINETIC THREORY OF GASES

**OBJECT**: To study the gas laws and the kinetic theory of gases using a system consisting of "plastic molecules" visible to the naked eye.

**METHOD**: A cylinder with a movable piston has small plastic balls placed in it. The lower end of the cylinder is closed with a circular impeller disk, which can be rotated at various speeds by an electric motor. Slots cut into the impeller disk cause the rotating disk to throw the plastic balls with random motion into the cylinder. The plastic balls strike the upper movable piston and exert a force on it. This force and the resulting pressure are measured by placing weights on the movable piston. The corresponding volume is proportional to the height of the piston above the impeller disk. The speed of rotation of the impeller disk determines the kinetic energy of the plastic balls. This kinetic energy can be considered proportional to the temperature of the "plastic molecule gas". Thus, one can assign numerical values to the volume, pressure, and temperature of the "plastic molecule gas" in the cylinder.

**THEORY**: In the kinetic theory of gases it is assumed that a gas is composed of molecules in random motion, and that the molecules have elastic collisions with one another and with the walls of the container. If there are *n* molecules per unit volume, each of mass *m* and having a root mean square speed $v_{rms}\left(\sqrt{\overline{v^2}}\right)$, the pressure *p* exerted by the gas composed of these molecules is given by

$$p = \frac{1}{3} n m \overline{v^2} \tag{1}$$

If a volume *V* of gas contains *N* molecules, the number of molecules per unit volume is *n* = *N/V*, and Eq. (1) can be written as

$$p = \frac{1}{3}\frac{N}{V} m \overline{v^2} \tag{2}$$

Hence

$$pV = \frac{1}{3Nm\overline{v^2}} = \frac{2N}{3}\left(\frac{1}{2} m \overline{v^2}\right) \tag{3}$$

where $1/2m\overline{v^2}$ is the average kinetic energy of the molecules. For an ideal gas the pressure, volume, and temperature in degrees Kelvin are related by the ideal gas law

$$pV = R'T \tag{4}$$

where *R'* is a constant having different values for different gases. Thus, according to the kinetic theory of gases, the Kelvin, or absolute, temperature of an ideal gas is proportional to the average kinetic energy of its molecules.
For a real gas Eq. (4) does not hold, and a better approximation to the experimental data was given by van der Waals in 1873, as indicated by the expression

$$\left(p + \frac{a}{V^2}\right)(V - b) = R'T \tag{5}$$

where again *R'* is a constant for any given gas. The quantities a and b are different for different gases and must be determined experimentally. The term $a/V^2$ is added to the pressure to take into account the forces between the molecules, while the term *b* is a correction for the effective volume of the molecules.
In order to calculate an approximate value for the volume correction *b*, the gas molecules are considered to be spheres of diameter $\sigma$ and volume $V_s$ where

$$V_s = \frac{4}{3}\pi(\sigma/2)^3 \tag{6}$$

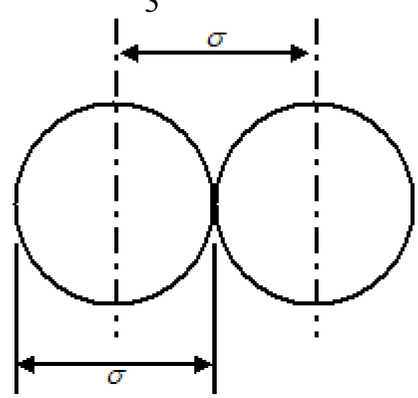


Fig. 1. Centers of two molecules can approach only to a distance equal to the diameter of one molecule.

As may be seen in Fig. 1, the centers of two molecules can approach only to a distance equal to the diameter $\sigma$ of one molecule. Thus each molecule can be considered to have an effective radius of $\sigma$ and an effective volume of

$$\frac{4}{3}\pi\sigma^3 = 8V_s$$

 

The probability of finding a molecule in a volume $V$ is proportional to the volume $V$. For a second molecule, the volume available is $V$- $8V_s$; for a third, the volume available is $V - 2 \times 8V_s$, and for $N$ molecules the volume available is $V - (N - 1)\, 8V_s$. Thus the probability of finding $N$ molecules in a volume $V$ is proportional to the product

$$P = V(V - 8V_s)(V - 2 \times 8V_s)\ldots[V - (N-1)8V_s]$$

In practice $8NV_s$ is small compared to the volume $V$ so that the product $p$ in the above equation can be written approximately as

$$\begin{aligned} P &\approx V^N - 8V^{N-1}V_s[1 + 2 + \ldots + (N-1)] \\ &\approx V^N\left(1 - \frac{8N^2V_s}{2V}\right) \end{aligned} \qquad (7)$$

The volume $V$ is obtained by taking the Nth root of Eq. (7). Taking the Nth root shows that if the volume of the molecules is to be taken into account, the volume $V$ is replaced by

$$V\left(1 - \frac{4NV_s}{V}\right) = V - b_1 \qquad (8)$$

so that the effective excluded volume $b_1$ is four times the actual volume of the molecules, or

$$b_1 = 4NV_s \qquad (9)$$

There is an additional correction term $b_2$ due to the fact that the molecules can only approach to a distance of $\sigma/2$ of the walls of the vessel, Fig. 2, so that

$$b_2 = \frac{\sigma S}{2} \qquad (10)$$

where $S$ is the total internal surface area of the vessel containing the molecules. Thus the total volume excluded to the molecules is

$$b = b_1 + b_2 \qquad (11)$$

and substituting for $V_s$ gives

$$b = \frac{2}{3}\pi N\sigma^3 + \frac{\sigma S}{2} \qquad (12)$$

or

$$\sigma^3 + \frac{3\sigma S}{4\pi N} - \frac{3b}{2\pi N} = 0 \qquad (13)$$

It should be pointed out that when van der Waals' equation is fitted to experimental data, the values of $a$ and $b$ are not constant but vary with the temperature. As the temperature is increased, the speed of the molecules increases, their effective diameter is reduced, and the value of $b$ decreases with increasing temperature. Despite this variation of b with

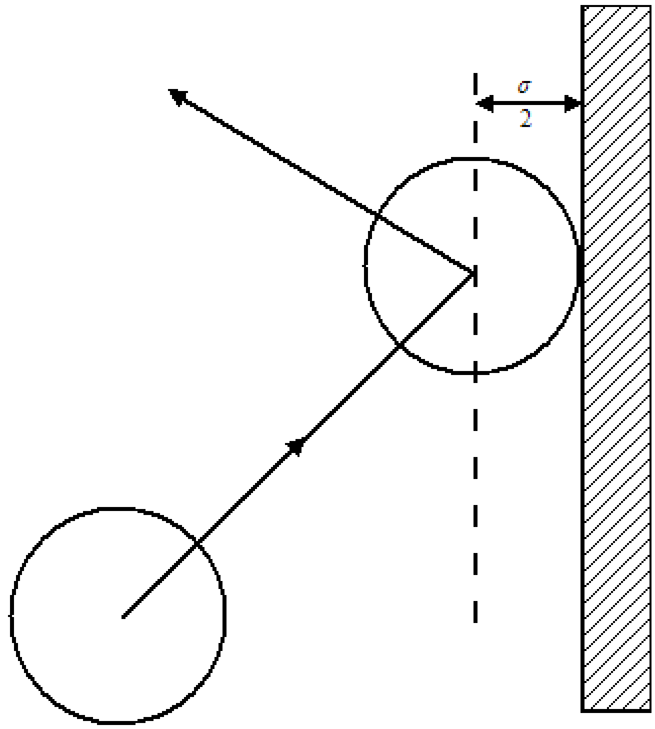


Fig. 2. Molecules can approach only to a distance from the wall equal to one half of their diameter.

temperature, approximate values of molecular diameters can be obtained from van der Waals' equation applied to real gases. In a similar manner, the diameter of the plastic balls will be determined in this experiment.

It is fairly obvious that the "plastic molecule gas" can never reproduce all the properties of a real gas. The plastic balls do not undergo elastic collisions, and energy has to be continuously supplied by the rotating impeller to keep them in motion. Nevertheless, the plastic balls do illustrate quantitatively some of the properties of a real gas, as will be shown by the experiments. It will be assumed that van der Waals' equation is valid for the "plastic molecule gas", or that the pressure and volume are given by

$$\left(p + \frac{a}{V_2}\right)(V - b) = K \qquad (14)$$

where $K$ is the random energy of all the molecules. From Eq. (3) the value of $K$ is taken to be equal to two-thirds of the total average kinetic energy of the plastic balls, or

$$K = \frac{2}{3}N\left(\frac{1}{2}m\overline{v^2}\right) \qquad (15)$$

The plastic balls obtain their energy from the rotating impeller. It will be assumed that the average kinetic energy of the plastic balls is proportional to the square of the angular speed $\omega$ of the impeller, or

$$\frac{1}{2}m\overline{v^2} = C\omega^2 \qquad (16)$$

where $C$ is a constant.

As is seen in the operation of the apparatus, the concentration of the plastic balls decreases with the height $h$ above the impeller disk. This is because the potential energy $mgh$ per plastic ball is comparable with its kinetic energy $C\omega^2$. If $n$ is the number of plastic balls per unit volume at height h, the decrease in number - $dn$ with increase of height $dh$ is

$$-dn = \frac{nmg}{C\omega^2}dh \tag{17}$$

By integration

$$\ln n = \frac{-mgh}{C\omega^2} + \text{constant}$$

At $h = 0$, $n = n_o$ so that the constant is $\ln n_o$ and

$$\ln\frac{n}{n_o} = \frac{-mgh}{C\omega^2}$$

Hence

$$n = n_o e^{-mgh/C\omega^2} \tag{18}$$

In the case of a real gas the ratio of $mgh$ to $\frac{1}{2}mv^2$ for the molecules is very small, and the concentration of molecules is very nearly constant in any relatively small volume.

**APPARATUS**: The kinetic theory apparatus, Fig. 3, with 1000 plastic balls, a set of masses, a stroboscope and an adjustable platform, Fig. 4.

**PROCEDURE**: Setting up the apparatus. Remove the impeller cylinder and place the piston assembly on the impeller disk. Adjust the scale, attached to the piston support rod, Fig. 3, so that the pointer near the top of the piston assembly reads zero. When the scale is so adjusted, the pointer reading is proportional to the volume occupied by the plastic balls. Next, remove the piston assembly, put the impeller cylinder in position and secure it with the four screws. Replace the piston assembly. Observe the electrode located just above the impeller; this is the high voltage electrode, about which more will be said a little later. Using a steel ruler with a spirit level attached or a plumb line, level the apparatus so that the cylinder walls are vertical. Using the cord provided, attach the piston to the counter weight and place the cord over the two pulleys. Adjust the pulley assembly to the position shown in Fig. 3. The pulley supports are fastened to the horizontal rod of the pulley assembly by means of a set screw and can be moved along this rod to a position which allows the cord to run freely between the fork of the mounts without touching the rod. Adjust the pulleys for minimum friction. Lubricate the bearings with a drop or so of very *light oil*, such as Nye watch oil. If very light oil is not available, use no lubrication. When the pulleys are correctly adjusted, the piston can move freely in the impeller cylinder. This is important, for the piston must not touch the wall of the cylinder in any part of its travel. Check this adjustment by looking into the impeller cylinder from above. The magnet, which is used to damp the vibrations of the copper vane attached to the piston should be mounted so that its lower edge is resting just far enough

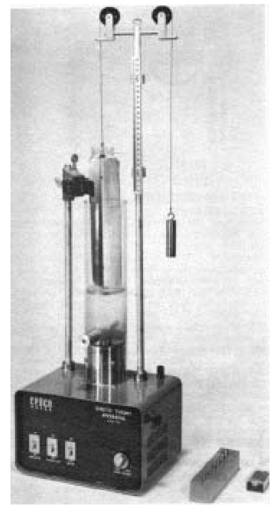

Fig. 3. The kinetic theory apparatus.

above the top of the cylinder to permit easy withdrawal of the piston. After these adjustments have been made, check again to see that the piston moves freely within the cylinder. Actually, the piston assembly is made about 5gm heavier than the counter weight to compensate for friction during downward motion. Connect the three-way plug to the 120volt ac line and be sure that the apparatus is well grounded; if necessary, ground the apparatus by means of the grounding post. Check to see that the drain-valve plug is turned all the way in; otherwise the plastic balls can leave the cylinder. The short plastic rod on the drain valve plug is a diffuser. It interferes with the rotary motion of the plastic balls, produced by the impeller, and imparts a random motion.

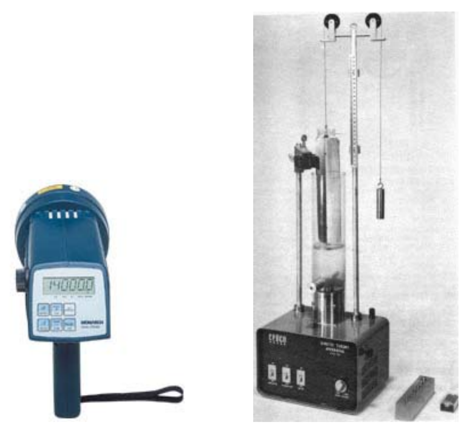

Fig. 4. The kinetic theory apparatus with the stroboscope.

Remove the piston assembly from the cylinder and drop 100 plastic balls into the cylinder. Be sure to do this when the impeller disk is at rest; otherwise some of the plastic balls may be thrown out. Replace the piston and see that it still moves freely within the cylinder. Mount the stroboscope on the adjustable platform as shown in Fig. 4. Start the motor, which is connected to the impeller disk, and adjust its speed with the speed control resistor. If a rotational speed of 3000rpm is desired, set the stroboscope at this speed and adjust the speed control on the apparatus until the black line on the impeller shaft appears to be at rest. At this time check the induction coil deionizer circuit. Turn on the IONIZATION switch and notice the sparks within the apparatus coming from the high-voltage electrode. The intensity of the sparks can be changed by turning the knob on the right hand side of the apparatus. These sparks produce ionization within the cylinder and neutralize the charges on the plastic balls and on the inside of the cylinder.

***Caution:*** the IONIZATION switch should be turned on for short intervals during the course of the experiments but should not be left on indefinitely. Be sure not to touch the high-voltage connection.

**Experiments: 1. Effect of the number of plastic balls on pressure and on volume**

(A) Place 4gm on the weight holder at the top of the piston assembly. This represents the pressure of the plastic ball "gas". Having 100 plastic balls in the cylinder, adjust the impeller speed to 3000rpm. After a short time read the height of the piston as indicated by the pointer reading on the scale. Move the piston and pointer about 1cm from the scale reading and allow time for the piston to come to equilibrium. Repeat until consistent readings are obtained making sure the piston moves freely. Record the value $h_1$ of the pointer reading.

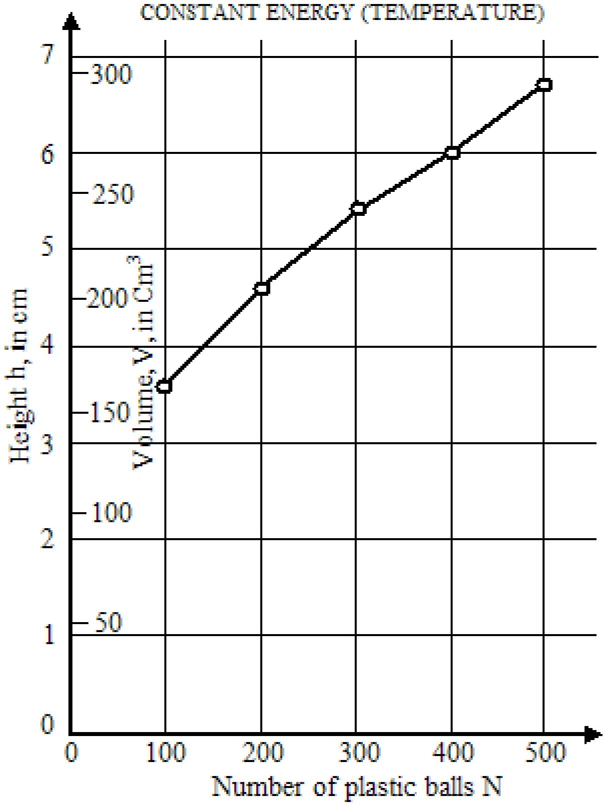


Fig. 5. Volume plotted against concentration, with pressure and rotational speed constant.

(B) Stop the impeller-disk motor, remove the piston and place another 100 plastic balls within the cylinder so that $N$ = 200. Replace the piston assembly within the cylinder using 4gm on the weight holder. Adjust the motor speed to 3000 rpm and carefully determine the new pointer reading $h_2$. Place additional masses on the weight holder until the piston and pointer are returned to the value of $h$, in part (A). Record the total mass $M_2$ on the weight holder. Check the motor speed and the state of ionization within the cylinder, i.e., run the induction coil for a short time. These two checks should be done regularly during the experiments.

(C) Place an additional 100 plastic balls in the cylinder so that $N$ = 300. Adjust the speed to 3000rpm. Find the height $h_3$ of the pointer and the total mass $M_3$ which must be placed on the weight holder to bring the pointer back to $h_1$. (D), (E) Repeat these steps for $N$ = 400 and for $N$ = 500 plastic balls using the rotational speed of 3000rpm. Determine $h_4$ and $M_4$ and $h_5$ and $M_5$. Plot the results in the manner shown in Figs. 5 and 6.

**2. Effect of change of speed of plastic balls on pressure and volume**

With 500 balls in the cylinder, place 4gm on the weight holder and adjust the speed to 2000rpm.

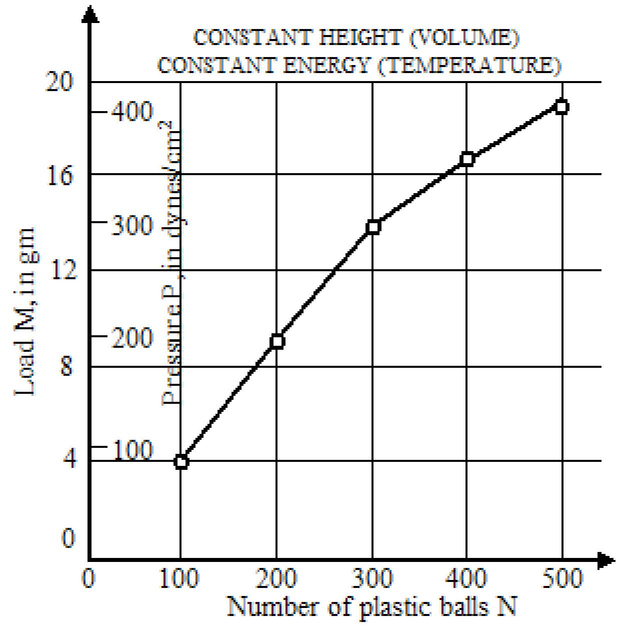


Fig. 6. Pressure plotted against concentration, with volume and rotational speed constant.

Record the pointer height $h_1$. Increase the speed to 2500rpm and find the pointer height with 4gm on the weight holder. Bring the piston and pointer height back to $h_1$ by increasing the load from 4gm to $M_3$ gm on the weight holder. Record $h_3$ and $M_2$. Repeat the above for speeds of 3000, 3500, and 4000rpm, recording the heights $h_3$, $h_4$, and $h_5$ and the corresponding loads on the weight holder $M_3$, $M_4$, and $M_5$. Plot these data in the manner illustrated in Figs, 7 and 8.

When the increased speed of the impeller disk requires for its measurement a change in scales of the stroboscope, check the relative accuracy of the two scales by running the disk at such a speed that it can be measured on both scales.

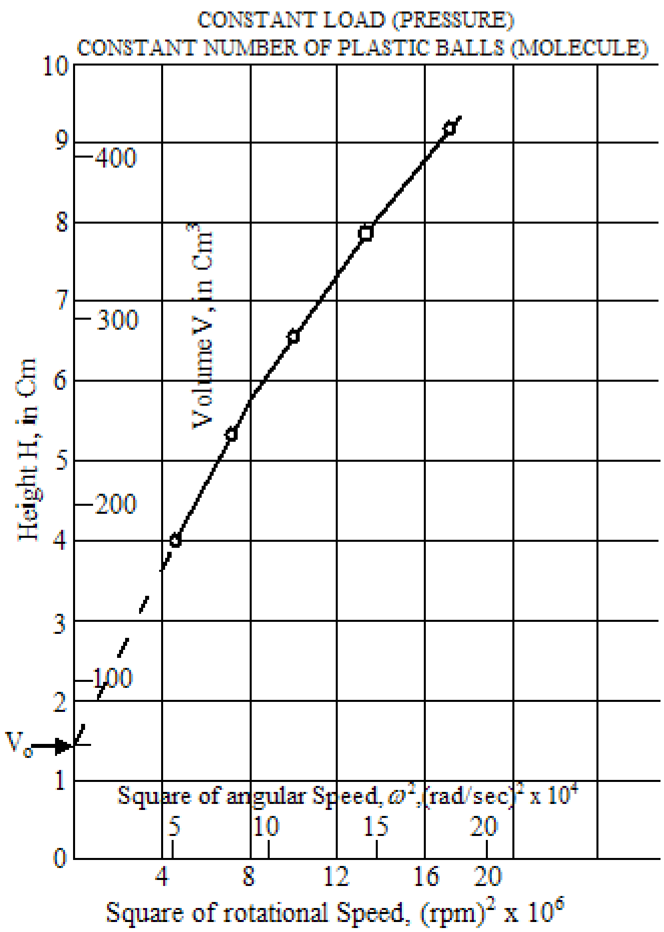


Fig. 7. Volume plotted against the square of the rotational speed. with pressure and concentration constant.

### 3. Effect of change of volume with pressure at constant rotational speed of the impeller disk

Use $N$ = 500 and a rotational speed of 5000rpm throughout this experiment. Start with a mass of 4gm on the weight holder and record the pointer height h. Increase the load on the weight holder in 4gm steps until a weight of 20gm is reached and then increase the load in 5gm steps until 90gm is reached. Record the pointer height $h$ for each load $M$. See that the load does not force the piston on to the high-voltage electrode. Plot the load $M$ against the height $h$, or the pressure $p$ against the volume $V$, as is shown in Fig. 9. (The pressure $p = Mg/A$ and volume $V = hA$ where $A$ is the cross-sectional area of the cylinder.)

**Analysis of Data**:

**Experiment 1**: Qualitatively compare the results of this experiment as shown in Figs. 5 and 6 with the results which would be expected for an ideal gas. Assuming that the plastic ball "gas" behaves as an ideal gas, find $v_{rms}$ for 100 balls, using Eq. (2). Compare this result with the maximum peripheral speed of the impeller disk and comment on the difference.

**Experiment 2**: From the graph of the data in which the volume $V$ is plotted against $\omega^2$, find by extrapolation the volume $V_o$ at which $\omega^2$ = 0. This volume $V_o$ is the effective volume $b$ of the plastic ball "molecules" as may be seen from Eqs. (14), (15) and (16), since $\omega^2$ = 0 is equivalent to $K$ = 0. From the value of $b$ the diameter of the plastic balls $\sigma$ can be obtained.

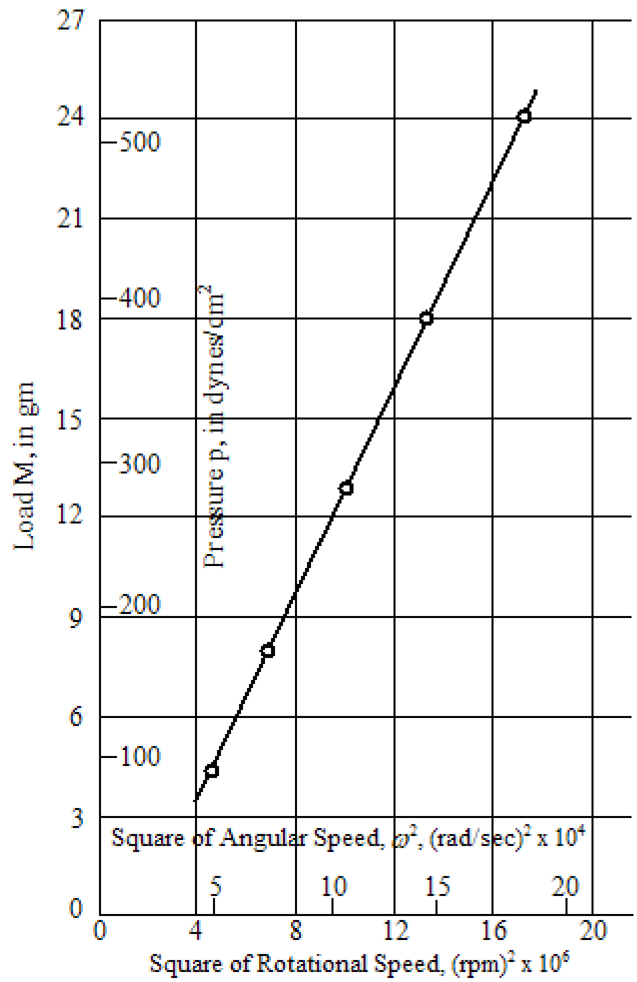


Fig. 8. Pressure plotted against the square of the rotational speed, with volume and concentration constant.

The following sample calculations are made on the data shown in Fig. 7 for an intercept at $\omega^2$ = 0 of 1.3cm. Thus $b = V_o = Ah_o$, where $A$ is the area of the impeller disk, which has a radius of 3.8cm. Hence $A = \pi(3.8\text{cm})^2 = 45.3\text{cm}^2$ and $b = V_o = 45.3cm^2 \times 1.3cm = 58.9cm^3$. As a first approximation for $\sigma$, neglect $b_2$ and let $b = b_1$. From Eqs. (6) and (9)

$$\sigma^3 = \frac{3b_1}{2\pi n} = \frac{3 \times 58.9cm^3}{2 \times 500 \times 3.14} = 0.0563cm^3$$

Hence

$$\sigma = 0.380cm$$

By direct measurement the average diameter of the plastic balls was found to be 0.302cm. (A simple direct measurement of $\sigma$ can be made by cutting a saw slot in a piece of wood into which the plastic balls just fit. Then a known number, 20 or more, can be put into the slot and their length measured with a vernier caliper.)

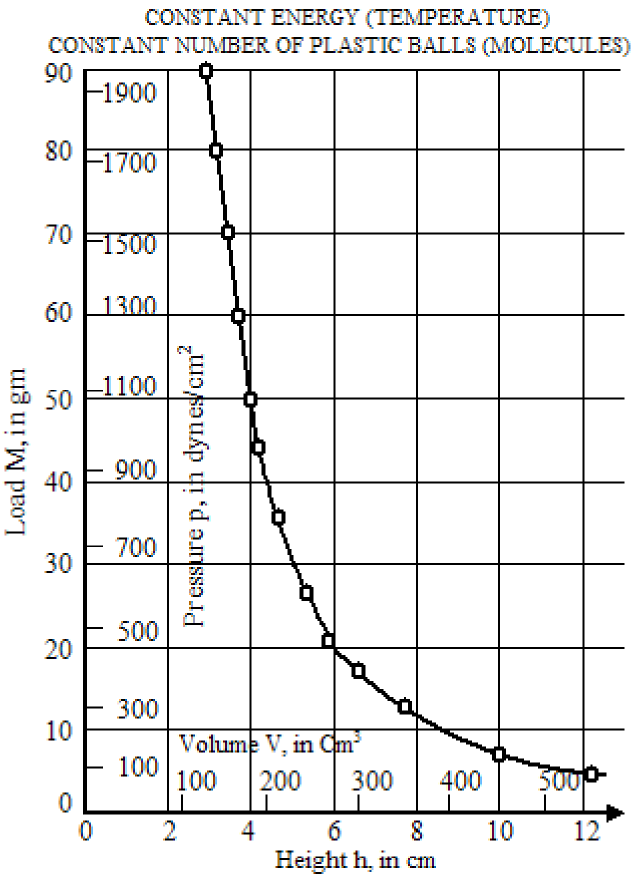

Fig. 9. Pressure plotted against the volume, with concentration and rotational speed constant.

**Optional Analysis**: A more correct value for $\sigma$ can be obtained by using Eq. (11), namely $b = b_1 + b_2$. This necessitates solving Eq. (13)

$$\sigma^3 + \frac{3S\sigma}{4\pi N} - \frac{3b}{2\pi N} = 0$$

For a height of 1.3cm the internal surface area $S$ is
$S = \pi D^2/2 + \pi D h_o = 121.7 cm^2$
Also, $N = 500$, $b = 58.9 cm^3$, $3S/4\pi N = 0.0582 cm^2$ and $3b/2\pi N = 0.0562 cm^3$.
Hence the equation to be solved is:

$$f(\sigma) = \sigma^3 + 0.0582 cm^2 \sigma - 0.0562 cm^3 = 0$$

For solving such an equation by Newton's method, consider as a first approximation that $\sigma = 0.380$cm, the value obtained above.

$$f(\sigma_1) = (0.380cm)^3 + 0.0582cm^2 \times 0.380cm$$
$$- 0.0562cm^3 = 0.0208cm^3$$

Now,

$$f'(\sigma_1) = df/d\sigma = 3\sigma^2 + 0.0582cm^2 = 0.491cm^2$$

$$\sigma_2 = \sigma_1 - \frac{f(\sigma_1)}{f'(\sigma_1)} = 0.380cm - \frac{0.0208cm^3}{0.491cm^2} = 0.338cm$$

Continuing this procedure gives $\sigma_3$ = 0.333cm where $f(\sigma_3)$ is 0.0001. This number is nearly zero and may be so taken, so that the diameter of the plastic balls as obtained from a calculation involving van der Waals' equation gives 0.333cm as compared with the directly measured value of 0.302cm. Repeat this calculation using your own data.

**Experiment 3**: Calculate the product *pV* for the data obtained in experiment 3. Suggest any reasons for the change of these values with change in pressure.

**Optional Analysis**: in this analysis van der Waals' equation is applied to the data in experiment 3. From the high-pressure region select three sets of values of *p* and *V* such that $(p + a/V^2)(V - b)$ may be assumed to be constant. The three values of pressure and volume selected from Fig. 9 are:

| Mass M gm | Pressure P dynes/cm$^2$ | Piston Height h cm | Volume V cm$^3$ |
|---|---|---|---|
| 90 | 1947.0 | 2.90 | 131.4 |
| 70 | 1514.3 | 3.30 | 149.5 |
| 50 | 1981.5 | 4.00 | 181.3 |

Substitution of these values in van der Waals' equation, Eq. (14), gives for *a, b*, and *K* the following:

$a = 1.19 \times 10^7$ dynes cm$^4$, $b = 70.7$cm$^3$
$K = 1.60 \times 10^5$ ergs.

In making these calculations use either a calculating machine or five-place logarithm tables since a slide rule does not give sufficient accuracy. The high-pressure values were selected for this calculation to minimize frictional effects, which are more noticeable at low pressures and high volumes.
From the value of b obtained in this experiment, namely 70.7cm$^3$, it is possible to calculate $\sigma$, the diameter of the plastic balls, using Eq. (14). In this equation *N*, the number of balls, is strictly the number striking the piston and producing the pressure. The variation of concentration with height is given by Eq. (18), namely;

$$n = n_o e^{-mgh/C\omega^2}$$

The following data are used in this calculation:

$K = 1.60 \times 10^5$ergs,
$H = 3.30$cm (the mean height).

The average mass *m* of the plastic balls = 0.0165gm, and *mgh* = 53.4 ergs. From Eqs. (15) and (16) $C\omega^2 = 3K/2N$ = 480 ergs where *N* is taken as 500, the total number of plastic balls. The number at the height of 3.3cm is

$$N = 500e^{-53.4/480} = 448$$

Also,

$$3S/4\pi N = 0.0649cm^2, 3b/2\pi N = 0.0754cm^3$$

The equation to be solved for *a* is

$$\sigma^3 + 0.0649cm^2\sigma - 0.0754cm^3 = 0$$

Using Newton's method of approximations, we find the value of $\sigma$ to be 0.37 cm. Although this is not equal to the directly measured value for $\sigma$, namely 0.30cm, it does show, nevertheless, that the plastic ball "gas" behaves approximately according to van der Waals' equation.

The value of *K* as calculated from van der Waal's equation, using the values of a and b given above, are given for the range in pressures and volumes shown in Fig. 9.

From your own data find the values of *a, b* and *K* in van der Waals' equation, the change in concentration with height and value of $\sigma$. Also, compare the average speed $v_{rms}$ of the plastic balls with the maximum tangential speed of the impeller disk.

| p dynes/cm$^2$ | V cm$^3$ | K ergs |
|---|---|---|
| 346 | 297 | $1.09 \times 10^5$ |
| 540 | 245 | 1.29 |
| 865 | 213 | 1.60 |
| 1082 | 181 | 1.60 |
| 1513 | 150 | 1.61 |
| 1947 | 131 | 1.60 |

**QUESTIONS**: 1. The molecules in a real gas are said to make elastic collisions, whereas the plastic balls do not make elastic collisions. Give evidence which supports these statements.

2. Give reasons why $\omega^2$ for the impeller disk can be considered as being proportional to the temperature of the plastic ball "gas".

3. The following data are given for oxygen at S.T.P: $v_{rms}$ = $4.6 \times 10^4$cm/sec; $\sigma$ = $10^{-8}$cm; n = $3 \times 10^{19}$ molecules/cm$^3$. If the collision frequency or the number of collisions per unit time of the molecules in a gas is $c = \pi\sigma^2 n v_{rms}$, find c for oxygen molecules and for 500 plastic balls in a volume corresponding to a piston height of 5cm and a rotational impeller speed of 5000rpm.

4. Calculate the mean free path $\lambda$ for the oxygen molecules and the plastic balls in Question 2, where $\lambda = 1/\sigma n$.

5. Show that for a real gas the value of $b_2$, given by Eq. (10), is negligible compared to $b_1$, given by Eq. (9). Use the data for oxygen given in question 3.