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ABSTRACT

This booklet is both a teacher's manual and a student's manual in a series of booklets that make up the core of a Physical Science course designed for the freshman year of college and used by teachers in the 27 colleges participating in the Thirteen College Curriculum Program. This program is a curriculum revision project in support of 13 predominantly Negro colleges and reflects educational research in the area of disadvantaged youth. This unit investigates the behavior of gases using the gas laws as an example of empirical relationships and the kinetic theory as an example of a microscopic model. Experiments are provided to illustrate the major concepts. (MLH)

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THE GAS LAWS
and
THE KINETIC THEORY

CURRICULUM GUIDE

for the
Thirteen-College Curriculum Program

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ABOUT THE INSTITUTE FOR SERVICES TO EDUCATION

The Institute for Services to Education was incorporated as a non-profit organization in 1965 and received a basic grant from the Carnegie Corporation of New York. The organization is founded on the principle that education today requires a fresh examination of what is worth teaching and how to teach it. ISE undertakes a variety of educational tasks, working cooperatively with other educational institutions, under grants from government agencies and private foundations. ISE is a catalyst for change. It does not just produce educational materials or techniques that are innovative; it develops, in cooperations with teachers and administrators, procedures for effective installation of successful materials and techniques in the colleges.

ISE is headed by Dr. Elias Blake, Jr., a former teacher and is staffed by college teachers with experience in working with disadvantaged youth and Black youth in educational settings both in predominantly Black and predominantly white colleges and schools.

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From 1967 to the present, ISE has been working cooperatively with the Thirteen-College Consortium in developing the Thirteen-College Curriculum Program. The Thirteen-College Curriculum Program is an educational experiment that includes developing new curricular materials for the entire freshman year of college in the areas of English, mathematics, social science, physical science, and biology and two sophomore year courses, humanities and philosophy. The program is designed to reduce the attrition rate of entering freshmen through well thought-out, new curricular materials, new teaching styles, and new faculty arrangements for instruction. In addition, the program seeks to alter the educational pattern of the institutions involved by changing blocks of courses rather than by developing single courses. In this sense, the Thirteen-College Curriculum Program is viewed not only as a curriculum program with a consistent set of academic goals for the separate courses, but also as a vehicle to produce new and pertinent educational changes within the consortium institutions. At ISE, the program is directed by Dr. Frederick S. Humphries, Vice-President. The curricular developments for the specific courses and evaluation of the program are provided by the following persons:

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ABOUT THE THIRTEEN-COLLEGE CURRICULUM PROGRAM

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In addition, Miss Patricia Parrish serves as general editor of the curriculum materials as well as an Administrative Assistant to the Director. Mrs. Joan Cooke is Secretary to the Director.

The curriculum staff is assisted in the generation of new educational ideas and teaching strategies by teachers in the participating colleges and outside consultants. Each of the curriculum areas has its own advisory committee, with members drawn from distinguished scholars in the field but outside the program.

The number of colleges participating in the program has grown from the original thirteen of 1967 to neneteen in 1970. The original thirteen colleges are:

Alabama A and M University	Huntsville, Alabama
Bennett College	Greensboro, North Carolina
Bishop College	Dallas, Texas
Clark College	Atlanta, Georgia
Florida A and M University	Tallahassee, Florida
Jackson State College	Jackson, Mississippi
Lincoln University	Lincoln University, Pennsylvania

Norfolk State College	Norfolk, Virginia
North Carolina A and T State University	Greensboro, North Carolina
Southern University	Baton Rouge, Louisiana
Talladega College	Talladega, Alabama
Tennessee State University	Nashville, Tennessee
Voorhees College	Denmark, South Carolina

A fourteenth college joined this consortium in 1968, although it is still called the Thirteen-College Consortium. The fourteenth member is

Mary Holmes Junior College	West Point, Mississippi

In 1971, five more colleges joined the effort although linking up as a separate consortium. The members of the Five-College Consortium are:

Elizabeth City State University	Elizabeth City, North Carolina
Langston University	Langston, Oklahoma
Southern University at Shreveport	Shreveport, Louisiana
Saint Augustine's College	Raleigh, North Carolina
Texas Southern University	Houston, Texas

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The Ford Foundation
The Carnegie Corporation
The ESSO Foundation

Thirteen College Consortium
Physical Science Teachers

	1967 - 1968	1968- 1969	1969 - 1970	1970 - 1971
Alabama A & M:	Army Daniels	Army Daniels	Army Daniels	Army Daniels
Bennett:	Perry Mack	Perry Mack	Dorothy Harris	Dorothy Harris
Bishop:	Burtis Robinson	Burtis Robinson	Burtis Robinson	Burtis Robinson
Clark:	Arthur Hannah	Arthur Hannah	Arthur Hannah	Arthur Hannah
Florida A & M:	Ralph Turner	Lewis Allen	Robert Flakes	Melvin Gadson
Jackson State:	Dennis Holloway	Dennis Holloway	Dennis Holloway	Dennis Holloway
Lincoln:	Sabinus Christensen	Sabinus Christensen	Julian McCreary	Julian McCreary
Mary Holmes:	----------	Thomas Wirth	Thomas Wirth	William Royal
Norfolk State:	Melvin Smith	Melvin Smith	Leon Ragland	Leon Ragland
North Carolina State:	Curtis Higgenbotham	Vallie Guthrie	Vallie Guthrie	Vallie Guthrie
Southern:	Thomas Wirth	Charles Osborne	Charles Osborne	-----------
Talladega:	Harban Singh	Harban Singh	Aleyamma George	Aleyamma George
Tennessee State:	Berry Hempstead	Berry Hempstead	Wil Cumming	Wil Cumming
Voorhees:	Bernie Dingle	Bernie Dingle	Bernie Dingle	Donald Volz

Five College Consortium
Physical Science Teachers

1970-71

Elizabeth City State College	Kumar Chatterjie
Langston University	Jimmie White
Saint Augustine's College	Ramesh Mathur
Southern University at Shreveport	Margaret Knighton
Texas Southern University	Edward Booker

PREFACE TO STUDENT

This booklet is one of a series of seven used in the Thirteen College Curriculum Physical Science Course. The series includes:

"The Nature of Physical Science",
"Chemistry" - Part I - A Macroscopic View",
"Chemistry" - Part II - A Microscopic View",
"Chemistry" - Part III - The Organic Molecule",
"The Conservation Laws - Momentum and Energy",
"Optics", and
"The Gas Laws and Kinetic Theory".

Each unit is designed to be self-contained. It starts with a fundamental concept and develops it in a spiral fashion through a hierarchy of levels. Each level contains the development of at least one fundamental idea from empirical data obtained in the laboratory, the demonstration of the utility of the concept, and a natural termination point. By virtue of their self-containment, a given unit may be interchanged in a course sequence with almost any other; consequently, a teacher constructs his course around the sequence of units that best suits his own interests and the background of his students.

This booklet itself, however, is not self-contained or complete. Its effective use is strongly dependent on students' own input and individual response. Laboratory exercises are designed to place students into working contact with physical principles that naturally lead them to ask questions and discover for themselves the hidden laws. Physical concepts and statements of physical laws are arrived at in the laboratory after careful experimental investigation of physical phenomena and are not given at the outset of experiments. Consequently, statements of the physical laws to be studied do not appear in this workbook. They are derived from laboratory activities. It is essential then that in the use of this workbook supplementary readings from several sources be relied on for a background of the history, development, and application of the concepts encountered in the course of our experimental studies.

Althought it is designed to be used flexibly, this unit has a consistent format, designed to insure a deliberate and disciplined approach to an open ended study of the principles of the physical sciences. Each chapter begins with a brief discussion of the concept to be studied, raises a series of questions about it, and outlines the rationale for an investigation. On occasion, detailed experimental procedures are suggested; though in the main, the details of the experimental design are left to the students and his instructor. Answers to the experiments are not given. Each student must supply his own. During classroom presentation and discussion of these results general patterns will be cited and physical laws identified. At the end of each chapter, questions, problems, and extensions to activities are offered to assist the students in assessing their progress and the value of the concepts they have encountered.

It is our hope that students and teachers alike will find the use these materials a challenging and rewarding experience that leads to a deeper insight into the laws and practices of science and the process of education.

PREFACE TO TEACHER

This booklet is one of a series of seven that make up up the core of a course in Physical Science designed and used by teachers in the twenty-seven colleges participating in the Thirteen-College Curriculum Program.

The course has several unique features. Especially important is its balanced emphasis on effective teaching methodology and basic concepts in the physical sciences. The two are closely woven into the fabric of the course. Consequently, in order that a teacher gain maximum use of these materials which were designed especially for the TCCP course it is essential that he understands the purposes it was designed to serve and the style and techniques chosen to accomplish them.

Course Objectives

The basic goal of the course is to make clear the nature of science as an enterprise and illustrate by numerous examples how science really proceeds. Exercises are chosen according to their potential to bring students into working contact with the essential aspects of the scientific experience. In these experiences the students develop concrete ideas about the operational meaning of, and the association between observation, experiment, measurement, hypothesis, theory, the nature of evidence, test, modification, formulating questions, accuracy of language, the role and value of schematic language in general and mathematics as an appropriate language in particular, the role of the observer, prediction, and the residual mystery of unanswered questions.

Secondly we strive to develop an appreciation for the features of science that distinguishes it from the other major disciplines, namely, the ability to establish a clear and testible criterion for the value of concepts and the role of experimentation as the sole criterion for the scientific truth. "Facts" and theories are never presented without a description; at least, of the experiments which support them.

By the use of a judicious choice of problems in the course we seek to divulge the peculiar nature of physical science that distinguishes it from other sciences. The course stresses the use of mathematics as a major analytical tool and the use of numerical patterns to describe physical phenomena.

Finally we are concerned with developing an appreciation for the value of "rigor" as a quality measure of a scientific study. A natural part of this is an exposure to- the development of the analytical tools and skills to deal with-scientific problems.

Pedagogical Priorities

High on our list of priorities in the course is the requirement that a substantial amount of learning take place in the classroom. Attention is given to creating learning situations where students collect information firsthand, consider its implications, and draw conclusions all within the same class period. The classrooms learning experiences are constructed so that they closely approximate real life situations where one has to search for clues and insights from a variety of sources, from reference materials, the teacher, as well as other students. The student must acquire the habit of weighing carefully the value of the information obtained from each.

Because of the variety of learning styles among the students, a mechanism is established for generating a variety of models of information integration. By encouraging students to actively participate in classroom exercises and develop ideas from the evidence that is presented for class inspection, the students themselves provide a range of models of learners. Students are encouraged to seek information from one another and teach themselves while the teacher supervises. This setting generates a number of dramatic experiences in a process of vital intellectual interaction.

The role of the teacher in the classrooms described above differs from that in a more traditional lecture oriented classroom where he is the central figure in the classroom and the prime source of information. In the settings described above the teacher becomes a coordinator. It is his responsibility to assist the students in seeking information and judging the value of what they find. He asks students the questions he would ask himself when he is in search of answers to crucial questions, displays the criteria he uses to reach conclusions, and thus allows the students themselves to make the crucial steps in the learning process. In order to be effective in this role, a teacher must accept as legitimate a wider base of student experiences, priorities, intellectual styles, and range of abilities.

It has been our experience that if these things are given proper attention, students develop an attitude about learning, where the learner is active, aggressive, and effective.

The Scope and Structure of the Course

The course is based upon five topics:

1. The Nature of Physical Science
2. Light
3. Inorganic and Organic Chemistry
4. Conservation principles
5. Gas Laws and Kinetic Theory

Each unit is self-contained, starting with a fundamental concept and developing in a spiral fashion through a hierarchy of levels. Each level contains the development of at least one fundamental idea from empirical data obtained in the laboratory, the demonstration of the utility of the concept, and a natural termination point that permits a study to end at a variety of levels always with a sense of completion. By virtue of their self-containment, a given unit may be interchanged in a course sequence with almost any other; consequently, a teacher may construct his course around the sequence of units that best suits his own interests and the background of his students.

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I. GENERAL INTRODUCTION

A. BACKGROUND

Gases, liquids, and solids constitute the three principal states of matter. From earliest childhood everyone becomes familiar with these three states. Everyone has handled solid objects, like rods of steel, which retain their shape unless violently twisted or deformed; everyone has poured liquids, like water, which do not retain any one fixed form but adjust their shapes to those of the containers in which they are placed; and nearly everyone has seen a toy balloon inflated, a process which leads to the conclusion that gases tend to fill completely any container which encloses them.

Among these states the gaseous state may be considered fundamental. A knowledge of the behavior of gases is essential for understanding the physiochemical nature of many other more complex forms of matter, both animate and inanimate. Almost all the life processes (metabolism, growth, and even replication) involve the transfer of molecules into and out of solution. Although this process involves fluids, it may be understood in terms of the properties of gases. Thus, a knowledge of the thermodynamic and kinetic nature of gases is an essential foundation for the understanding of these fundamental, vital processes.

Historically, men have always been fascinated by the study of gases. During the seventeenth century man began to look for proofs that the earth was enveloped by a "sea of air." This search led to one of the first breakthroughs, the discovery of a method to measure air pressures. It was Evangelista Torricelli, a student of Galileo, who developed the first barometer in 1643. About twenty years later, Robert Boyle developed a device which could pump air into and out of a confined space. However, although men sought patterns between the parameters of gases, general laws were elusive. The search went on for years until Boyle observed that as he increased the pressure on this space, its volume decreased. Boyle was the first to describe this relationship, known as Boyles" Law. The first quantitative measurements of the effect on the volume of a gas by a change in temperature were made by a French scientist Jacques Charles in 1801. A third relationship, one between the pressure and temperature of a gas, was found by Joseph Louis Gay-Lussac.

The works of these men laid the foundation for a basic macroscopic theory of gases. Their studies resulted in accurate descriptions of the properties of gases that enables one to make useful quantitative predictions about the behavior of gases. Using the laws they discovered, one is able to build many useful instruments such as thermometers, barometers, and pressure gauges. Theirs was the first step in an understanding of this state of matter.

These laws are, however, not connected to the rest of our knowledge of physics. For they deal only with the relation between the pressure, volume, and temperature of gases. They are a set of laws unto themselves. They are useful but limited. It is a basic feature of science that connections between areas of physical laws are always sought. How are these laws related to the other laws of physics? Is there a relation? Why do gases behave as they do? Why is the behavior of gases different from that of the other states of matter? In order to make thses connections, we must seek a more fundamental understanding of the gas laws. That is, we must investigate the possibility that these laws are a natural consequence of other basic laws, such as Newtons laws, and the ultimate molecular structure of gases. This line of investigation leads us to the Kinetic Theory of Gases which was invented to make these connections. These two sets of theories, the Macroscopic and the Kinetic, comprise a complete study of the physics of gases, together they provide us with an indepth understanding of the nature of gases.

B. STRUCTURE OF THIS UNIT

This unit is divided into three sections; each sheds light on a different aspect of the properties of gases. The first section is devoted to an experimental study of the macroscopic properties of gases. In this section, three basic experiments are outlined to provide guidelines for an experimental study of the relationships between the parameters of a gas. The objective of each of these experiments is to provide information from which we can obtain mathematical expressions describing those relationships. In each of these investigations several gases are studied to assure that the relationships discovered are properties of the gaseous state in general and not a feature of a particular gas. In the second section we seek a more fundamental understanding of these laws by studying the Kinetic Theory. In that study the elements of the Kinetic Theory of Gases are introduced and their logical consequences pursued. In the final section, a composite of the three macroscopic laws, called the Ideal Gas Law, is compared to the experimental results of gases and some of the limitations of the gas laws are pointed out.

PART I

THE GAS LAWS

(AN EMPIRICAL STUDY OF THE BEHAVIOR OF GASES)

Chapter II. THE PROPERTIES OF GASES

EXPERIMENT I - RELATIONSHIP BETWEEN VOLUME AND PRESSURE AT CONSTANT TEMPERATURE (BOYLE'S LAW)

PURPOSE: The object of this experiment is to study the variation in the volume of a sample of gas as a result of changes in it's pressure while the system remains at a fixed temperature. Studies are to be made on samples of several different gases to insure that any significant properties found are characteristic of the gaseous state in general and not just those of a particular gas.

EQUIPMENT: A commercial volume - pressure apparatus such as shown in figure 1, a set of weights, and cannisters of several different gases.

PROCEDURE: During this experiment the apparatus and the gas within it will be at room temperature. Thus we maintain a condition of constant temperature.

Starting with air, adjust the initial volume of the air confined in the cylinder by placing a cord or wire along the piston seal when inserting the piston into the cylinder, and withdrawing it when the desired position has been attained. Be sure the inside of the cylinder and the air used are dry; the presence of water vapor will affect the results. Set the volume of the trapped gas initially at the top of the scale. This allows the piston to advance far enough into the cylinder so that it will support a load without binding excessively against

PLASTIC SYRINGE USED IN INVESTIGATING THE PRESSURE-VOLUME RELATIONSHIP

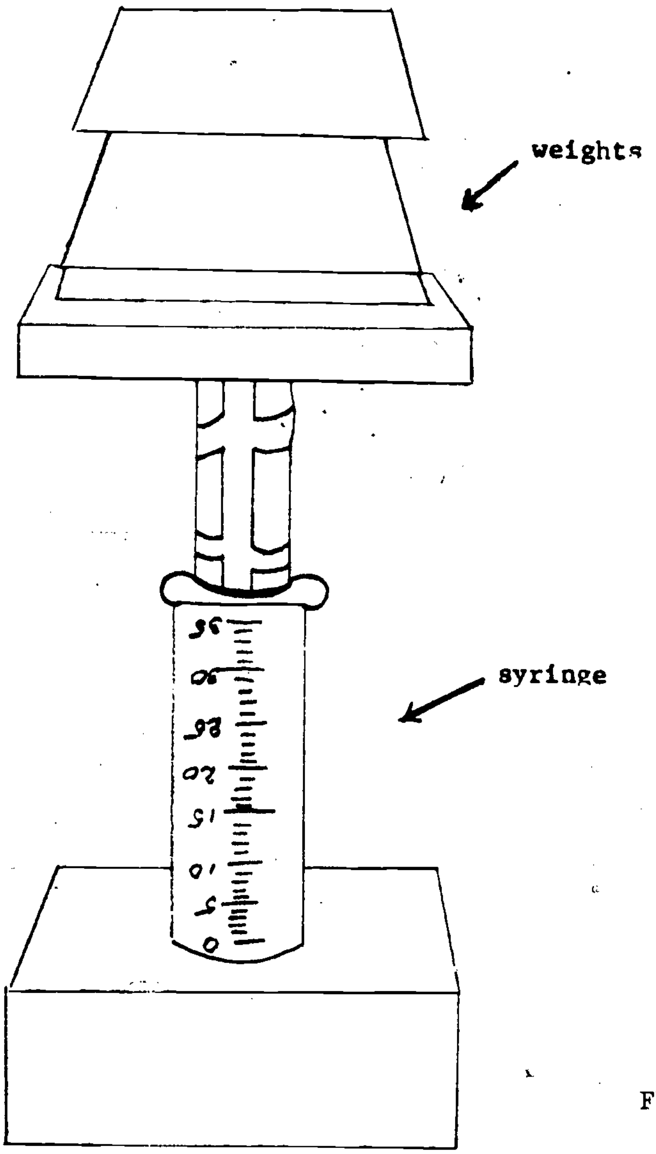


FIG. 1

the side of the cylinder.

It may help, after you have placed a load on the piston, to compress the gas further by pushing down on the piston and then releasing it. The piston is then more likely to come to rest at a position uninfluenced by friction. Then, by twisting the piston laterally without giving it a push either up or down, you can be sure to find the best position for it.

Find the gas volume for five or six different loads from 1/2 kg to several kilograms.

Convert the weights of the loads into pressures, remembering that pressure is defined as a force per unit area. Recalling that $V = r^2h$ and $A = \pi r^2$

Where: A = area of the piston

V = volume taken from the scale

h = distance between the scale marks

r = radius of the inside circular base of the piston

Make plots of the volume of the gas and the corresponding pressure. Also for each set of data, find the value of 1/volume and plot a graph of these values versus the pressure applied to the syringe system.

Repeat the procedure using three different gases in the syringe.

QUESTIONS AND PROBLEMS:

1. Compare your graphs for the three different gases. Discuss the similarities and differences.
2. Using your experimental data express the relation on each of your graphs of 1/volume versus pressure as an algebraic equation. From this obtain an expression for the relationship displayed in your graph of volume versus pressure.
3. Express any relationships that you find to hold for all gases in algebraic form.
4. Test the value of your algebraic equation for the relation between the pressure and volume of gases by:
    a. theoretically predicting the value of the volume of a gas when the pressure applied to the syringe is between two of the values you used and twice as much of the largest value you used. Experimentally check the accuracy of these predictions by applying these pressures to the syringe and measuring the resulting volume in each case.
    b. theoretically predicting the pressure needed to give you "zero" volume and an infinitely "large" volume. Discuss the possibility of checking these results experimentally.

EXPERIMENT II - RELATIONSHIP BETWEEN TEMPERATURE AND VOLUME AT CONSTANT PRESSURE

You will be given a glass tube containing a drop of mercury (or oil) that keeps a given amount of air trapped in the capillary tube. (The teacher must prepare these tubes before the laboratory). The mass of the air trapped in this glass tube will remain constant throughout the course of the measurements you make even though its volume may change. Use care when measuring or manipulating the gas tube.

In making your measurements, you will need to assume that the volume of trapped air is proportional to the length of the trapped air column. That is, if the length of the air column doubles, the volume also doubles. If the length of the air column triples, the volume also triples. One quantity is said "to be proportional" to another when they are related in this way.

Our assumption that the volume of the trapped air column is a reasonable one, since the diameter of the gas tube and thus the cross-sectional area is uniform. You will recall that to find the volume of a cylinder you multiply the cross-sectional area by the height of the cylinder; doubling the height would double the volume. Thus, your measurement of the change in height of the trapped air column in the gas tube is also a measure of the change in volume of the trapped gas.

We will perform this experiment at constant pressure, so we will not be concerned with measuring the pressure. Set up the apparatus as shown below. Use a large test tube, and clamp it on a pegboard or ring stand at a height convenient for heating with a burner.

APPARATUS FOR TEMPERATURE - VOLUME RELATIONSHIP

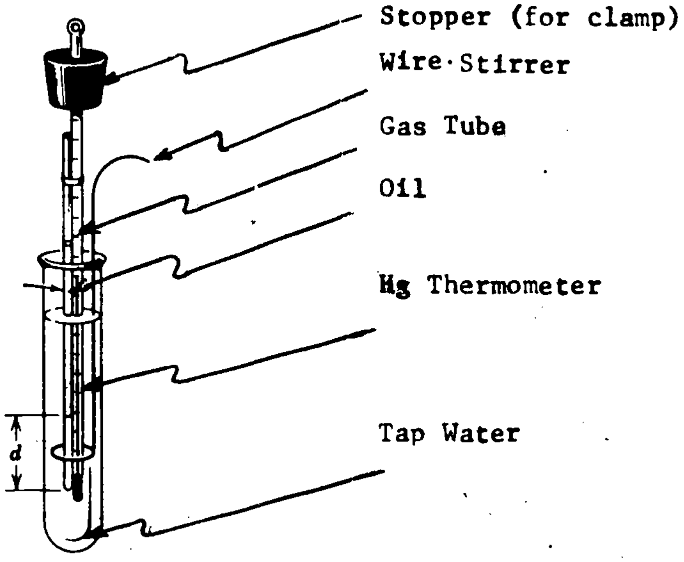


FIG. 2

Secure the thermometer to the glass tube with a rubber band. Support the thermometer and gas tube inside the test tube by means of a split cork around the combination, and attach the thermometer and tube to the pegboard by a clamp. Fill the test tube about two-thirds full of ice water, being sure that the length d can double and still be entirely in the water. (d should be about 6 cm.)

To determine the dependence of the volume of trapped air in the gas tube on temperature, you will need to measure the height of the trapped air column at various temperatures. Can you measure d conveniently when the gas tube is immersed in the water? If not, devise a method to determine d without direct measurement. Desribe your method in your notebook. (Note to the Instructor - be sure, that the student records the position of the bottom of the air column, or have the student position the bottom of the air column (cappillary tube) at zero °C.)

Record the temperature of the water; calculate and record the length d.

Gently heat the test tube until the temperature rises about 5°. Stop heating, wait 10 - 15 seconds, read and record the temperature and determine the length of d of the trapped air column. Repeat the measurement at approximately 5° intervals until the water in the test tube is close to boiling (stop at about 90 °C).

Record all of the temperature-volume data in tabular form. You will need a table with five columns. It will be convenient to head the first two columns: (1) Temperature °C, (2) Length d of trapped air column. The other three will be labeled as the need arises.

A graphical presentation of data will be far more informative than the raw data in your table above. First, plot Celsius Temperature on the x (horizontal) axis and plot the height d (which is proportional to the volume) on the y (vertical) axis. It is convenient to have the two axes meet at a temperature of)°C and a height (volume) of zero. When this is done, any point actually on the y axis represents zero volume. You will need a temperature range from about -350° C to 100° C along the x axis. Plot your experimental points, one value of d for the particular temperature reading at which that d was measured. When all of your points are plotted, draw the best straight line through the experimental points. The best line will usually have as many points on one side of the line as on the other. However, it is not just the number of points on each side of the line, but the sum of the distances of those points from the line. For example, one point at a given distance from a line will balance two points closer to and on the other side of the line.

Extend the straight line so that it intersects the temperature axis. At that temperature, the height of the air column d, and thus the volume of the gas, would presumably be zero. Record that temperature. Note: More precise measurement shows this value to be 273.15°C. On the Kelvin Scale of temperature this is zero degrees. To convert from Celsius to Kelvin one need merely add 273° (273.15° for more precise measurements). Thus 20°C, which is approximately room temperature, is changed to Kelvin degrees as follows:

20°C = (20 + 273)°K = 293°K

With this in mind, you can now complete your five-column table. Column 3, appropriately labeled, should contain all of your temperature readings converted to the Kelvin scale. Column 4 should contain your values of each length d divided by the corresponding temperature in degrees Kelvin. Column 5 should contain each length d divided by the corresponding temperature in degrees Celsius. You will want to compare the numbers in columns 4 and 5. Which has values which are more nearly constant? Which of the two temperature scales appears the more significant?

QUESTIONS:1. What do your results show about the relationship between the volume of a gas and its temperature on the Kelvin scale if the pressure and mass are constant?

2. Does your graph show that the volume of the confined gas doubles if its temperature doubles?

3. From your own graph predict that the volume of the trapped gas should be at -273°C. Why do you suppose you were not asked to measure the volume of the gas at temperatures near this value?

4. Why do you think you were advised to wait 10-15 seconds after you stopped heating before taking the temperature reading?

EXPERIMENT III - RELATIONSHIP BETWEEN THE TEMPERATURE AND PRESSURE AT CONSTANT VOLUME

The apparatus for this experiment is a commercial device illustrated by figure 3 . It consists of a hollow copper ball which is attached to one end of a short length of copper tubing. A pressure gauge is attached to the other end of the tubing.

To start the experiment, the air or gas is removed from the ball and tubing. What does the pressure gauge read?

Introduce air into the apparatus at room pressure and temperature. Record the pressure and the temperature. Close the valve on the ball. Now submerge the ball first in freezing water and then in boiling water. Record the proper gauge reading with its corresponding temperature.

A fourth pressure reading can be obtained if dry ice and alcohol are available. The temperature of a mixture of these two substances will be close to 78° C.

A fifth pressure reading can be obtained above the boiling temperature of water with an oil bath.

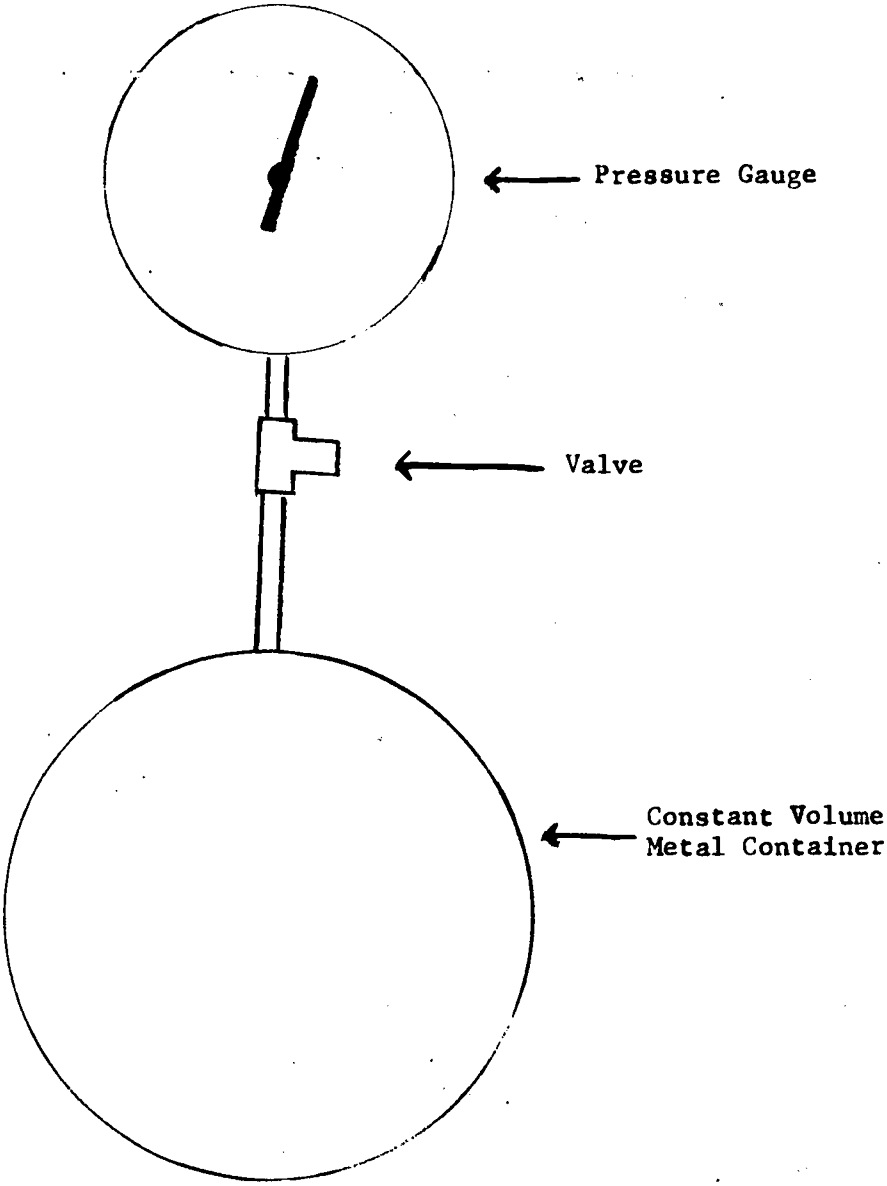
Plot these sets of pressure temperature points and draw the best smooth curve through them.

QUESTIONS: 1. When the apparatus was completely evacuated, we observed a zero pressure reading. After studying your graph, can you suggest a temperature at which a zero pressure reading might be expected when there is gas in the tube?

2. How is the temperature referred to in Question 1 above related to the temperature found in Experiment II?

FIG. 3

APPARATUS FOR TEMPERATURE PRESSURE RELATIONSHIP



III. APPLICATION OF THE GAS LAWS

A. NUMERICAL CALCULATIONS

The mathematical form of the three gas laws obtained in the previous chapter are similar. Thus, mathematical methods of handling these laws are similar. We shall first consider in detail the treatment of one of them and leave it to you as an exercise to develop the method of applying the others.

Boyles' Law:

Our experimental study of the relation between the pressure and volume of a gas shows that the pressure is proportional to the reciprocal of the volume or mathematically, $P \propto \frac{1}{V}$ This means that if the temperature is held constant, and the pressure increases, the volume must decrease so that the product of their values remains the same.

On transposing the volume V to the left-hand side of the equation, we may write the expression as $PV \propto 1$ i.e. a constant. This equation tells us, if we compress a system of trapped gas and thus double its pressure, its volume will decrease by a half.

Sample Problem

Consider a system of trapped gas which has a volume of 786 ml. and a pressure of 760 mm. of Hg. If the pressure of the gas is decreased to 380 mm of Hg what will the new volume be?

Let us represent the initial values of the pressure and volume of the gas by the quantities P_1 and V_1 and the final values of the pressure and volume by P_2 and V_2. The statement that the product of the values of their pressure and volume remain the same may be written mathematically as:

$$P_1V_1 = P_2V_2$$

To find the value of the final volume of the gas we simply solve to the above equation for V_2. Thus we obtain,

$$V_2 = \frac{P_1V_1}{P_2}$$

Using the above numerical values for the quantities on the right-hand side of the equation we obtain.

$$V_2 = \frac{(760 \text{ mm. of Hg})\ (786 \text{ ml.})}{380 \text{ mm. of Hg}} = 1572 \text{ ml.}$$

Exercises:

1. Using Charles' Law, derive a mathematical relationship between the values of the initial volume and temperature, V_1 and T_1, and the final volume and temperature, V_2 and T_2, of a gas that undergoes an expansion at constant pressure.
2. Using Gay-Lussac's Law as stated above, derive a mathematical relationship between the values of the initial pressure and temperature, P_1 and T_1, and the final pressure and temperature, P_2 and T_2, of a gas that is heated or cooled while maintaining a constant volume.

Apply these expressions to solve the following problems:

Hint: Remember there is something special about the Kelvin or Absolute Temperature scale.

3. A gas has a volume of 2.4 liters and a temperature of 27° K.

If it is heated at constant pressure to a temperature of 123°K at a constant volume, what will be the value of its new pressure?

4. A gas which has a temperature of 50°C and a volume of 63 mm, is heated to twice the temperature at a constant pressure. What will be the value of the new volume?

B. CONSTRUCTION OF AN AIR THERMOMETER

One of the values of studying the gas laws is that their results may be put to a practical use such as building a thermometer. For example, once the relationship between the volume and temperature of a gas at constant pressure is established, we may measure the volume of the system and obtain an indirect measure of its temperature. Below we have outlined the directions for building a device called an air thermometer.

Theory

As our apparatus for this experiment we may use the system described in experiment I.

As a first step we must "calibrate" the instrument, thus measuring the precise numerical relationship between the volume and temperature of the air in the cylinder. It must be remembered that at any given pressure the value of the volume of the air at a given temperature depends on the amount of air in the system. But we know that a plot of that relationship yields a straight line. All we need to establish the line is two points. This may be done by determining the volumes of the gas at two easily reproducible temperatures such as the boiling point of water and the freezing point of water. A straight line can then be drawn between these two points to define the rest of the scale.

Procedure

Immerse the cylinder and piston of the apparatus you used in Experiment I in a mixture of ice and water. (Use as much ice as possible). Support the cylinder firmly as shown in figure two, place a load of about two kilograms on the piston, and adjust the volume of air (use the wire between seal and cylinder wall) at a little more than half the measured capacity of the cylinder. Allow some time for the immersed cylinder and the air to come to the temperature of the ice-water bath. What is the volume of the confined air?

Now place the apparatus in hot water and bring to a full, rolling boil. Continue to boil until you are sure the temperature of the confined air is the same as that of the boiling water. Record the volume of the gas.

To plot the temperature of the gas as a function of its volume, draw a pair of perpendicular axes on graph paper. On the horizontal axes mark off a scale for volume that includes zero volume and the values two measured above volumes V_1 and V_2. On the vertical axis arbitrarily mark two points T_1 and T_2 to represent the freezing and boiling points of water. Mark the two points on the paper which represent the volumes and the temperatures at the freezing point and the boiling point, and draw a straight line through them all the way to the intersection with the temperature axis. This line establishes a temperature scale relating the volume and temperature of the gas.

Now you can choose units for your temperature scale. For example, to get the centigrade (Celsius) scale, we choose 0 for the freezing point and 100 for the boiling point, and then divide the vertical axis into units of Celsius degrees. You now have an air thermometer.

Use your air thermometer to measure the temperature of tap water and compare the value you get with that obtained with a mercury or alcohol thermometer.

What is the temperature in degrees centigrade when the volume on the graph is zero?

So far you have constructed an air thermometer. You may repeat the experiment, using a different gas, such as carbon dioxide or methane, and compare these results with those for air.

Test the accuracy of your thermometer by using it to measure the temperature of tap water. Compare this value obtained using a commercial mercury thermometer.

C. A COMPOSITE OF THE GAS LAWS - THE IDEAL GAS LAW

Each of the three gas laws may be put to good use solving practical problems where we need to predict the change in one of the properties (such as pressure or volume) as a result of the change of another. The problems we are able to solve with these laws, however, are limited, because the law only relates two properties if the third remain fixed. For example, if the pressure of a gas increases, the volume can be expected to decrease only if the temperature is kept constant. But what if the temperature is not kept constant? What may we predict about the changes in the values of volume and pressure then? If the temperature and pressure of a gas increased simultaneously, what effect do they have on the change of the volume? Charles' Law demands that an increase of temperature should result in a corresponding increase of the volume, while Boyles' Law requires that the vooume decrease as a result of an increase in pressure. Which effect wins out? In this situation we must combine the two laws and apply them simultaneously. In so dioing we would arrive at a law which contained more information and thus be more powerful than either of the laws separately.

Before we are able to obtain this powerful law, we must add another factor to our considerations of the important parameters of a gas, namely, a measure of the amount of gas under consideration. Clearly at a given temperature and pressure, the volume a gas will assume depends on how much gas is involved. A convenient set of units is the "mole" which is a measure of the number of molecules of a gas. There are $6.0^2 \times 10^{23}$ molecules in a mole of gas. Experimental evidence shows that under conditions of constant pressure and temperature, the volume of a gas is proportional to the number of "moles" of the gas. Mathematically this may be stated as:

$$V \propto n \quad \text{(P and T held constant)}$$

Boyle's law tells us that the volume is inversely proportional to the pressure when the amount of gas and the temperature are held constant, or mathematically

$$V \propto \frac{1}{P} \quad \text{(n and T constant)}$$

Similarly, Charles' Law tells us that the volume is directly proportional to the temperature (measures in degrees Kelvin) when the amount of gas the the pressure are held constant, or mathematically:

$$V \propto T \quad \text{(n and P constant)}$$

Combining the above proportions, we get,

$$V \propto \frac{1}{P} nT$$

In order to go from a proportion to an equality, we insert a constant of proportionality.

$$V = K \frac{1}{P} nT$$

Rearranging the above equation, we get,

$$PV = nKT.$$

This expression tells us that the product of the values of the volume, pressure, and the reciprocal of the temperature is a constant for a given amount of gas. We may use it to solve the problem posed at the outset of this section. Namely, what is the effect on the volume of a simultaneous change in temperature and pressure. Moreover it allows us to do more than predict changes. It tells us that the amount of gas, its temperature, and pressure determine the volume of the gas, or conversely the volume, pressure and temperature of a gas will determine the amount of gas we have.

Before we can use this equation to make predictions of the behavior of a gas, however, we must determine the value of the constant K. This is done by experimentally measuring the volume, pressure, temperature and number of moles of gas in a container and using their values in the above equation to compute the value for the constant K. Once this value is obtained, it is the same for all gases under all conditions. Experimentally we find that 1 mole of gas in a volume, of 22.4 liters and at a pressure of 1 atmosphere has a temperature of 273° K. Thus using the above formula we find that:

$$K = \frac{PV}{nT}$$

$$= \frac{(1\ \text{atm})(22.4)\ell}{(1\ \text{mole})(273°\text{K})}$$

$$K = 0.082\ \frac{\text{atm.}\ \ell.}{\text{mole}\ °\text{K}}$$

Using this value for the constant K, we can predict the volume of a gas if we know its pressure, temperature, and the number of moles it contains. For example, if the temperature of the one mole of gas cited above doubles to become 546° K and its pressure increases to 2 atmospheres, then we can obtain the value of its new volume by applying the ideal gas law as follows:

$$V = \frac{KnT}{P}$$

$$= \frac{0.082\ \frac{\text{atm.}\ell}{\text{mole}^\circ K} \times 1\ \text{mole} \times 546^\circ K}{3\ \text{atm.}}$$

$$= 22.4\ \ell$$

Thus the volume of the gas is unchanged. It should be borne in mind that the numerical value of the constant K depends on the system of units used to measure the volume, pressure, and temperature.

e.g. P could be in dynes cm^2

V could be in cm^3

T could be in °K

then $R = 8.3143 \times 10^7\ \frac{\text{dynes - cm}}{^\circ\text{K mole}}$ or $\frac{\text{erg}}{^\circ\text{K mole}}$

The ideal law afford a much more powerful handle on the behavior of gases than is provided by any of the laws cited above separately.

PART II

KINETIC THEORY

(A MICROSCOPIC MODEL FOR THE BEHAVIOR OF GASES)

IV. INTRODUCTION

In the previous section we discovered the relations among the properties of gases and established them as useful in making predictions about the behavior of gases. In this section we study the causes of this behavior.

In general the structure of any theory constructed to explain a set of empirical laws has certain common features regardless of the problem to which it is applied, whether it is a microscopic theory of gases or a microscopic theory of chemistry.

NAMELY:

1. It sets up laws and postulates that are more basic than those it is constructed to explain.
2. It establishes connections between the basic set of laws and the properties of the system it is constructed to describe.
3. Since the new set of laws are more basic, they must be more general, i.e., have a wider range of applications.
   In addition to explaining the older set of laws, they must lead to new laws and make new connections that the others could not.

In this section we will examine a basic theory of gases, namely, the Kinetic Theory and show that it has the elements of a good theory as outlined above. We will consider the basic postulates of the Kinetic Theory, and its implications as they give rise to explanations of the behavior of gases.

As a first step we must establish connections between the behavior of molecules and the consequence of the Kinetic Theory and the macroscopic properties of gases such as pressure and temperature. For example, we know what the pressure of a gas means when we measure it in the laboratory; if we push against a balloon full of gas it resists. The system of gas creates a force outward on the container that holds it. But how do we interpret this in terms of the behavior of molecules that make up the gas? Any theory of gases must make this type of connection, giving properties such as pressure a new meaning, one that is comprehensible in terms of the behavior of the molecules. This is the subject of chapters V and VI. Finally in chapter VIIwe will use some of the concepts devised in chapter with the postulates of the Kinetic Theory to establish the mathematical connection between macroscopic and microscopic properties of a gas such as the pressure, volume and temperature of a gas and the average velocity of its molecules. After this is done the basis of the theory is complete and we are able to apply it to derive new relationships between properties of gases.

Before we proceed with it's implication let us consider the postulates of the Kinetic Theory. Simply stated, it is the basic premise of the Kinetic Theory that a gas is a collection of molecules and that the properties of a gas as a whole are a consequence of the collective properties of its molecules. Listed point by point, the Kinetic Theory proposes:

a. All gases are made up of molecules that are moving randomly in all directions with a constant average speed.

b. Since most laboratory samples of gases on which we make measurements contain a tremendous number of molecules, it is a good approximation to neglect the size of the molecules in any calculation, thus regarding them as having, for all practical purposes, no size at all.

c. The molecules undergo frequent collisions with one another.

d. The collisions take place without a net loss of energy, consequently, the total energy of the molecules is constantly being redistributed among themselves.

e. The molecules obey the laws of classical physics during their collisions with one another and with the walls of their container.

V. DIFFUSION

A. SYNOPSIS

In order to gain insight into the properties of the gaseous state and their relation to the assumptions of the Kinetic Theory, it is valuable to conduct a detailed study of one of these properties.

One of the important properties of gases is their ability to diffuse or spread out. A gas always expands to fill its container. If a bottle containing a substance with a strong odor is opened on one side of the room, a few minutes later its odor can be detected on the other side of the room. The molecules of the substance have traveled across the room by traveling in straight lines between collisions but they did not travel straight across the room. It took several minutes for them to reach the other side, because they were continually colliding with one another and with air molecules. Some may even have been turned completely around. This random scattering of the gas molecules resulting in a net motion in some direction is called diffusion. As the gas molecules diffuse, they become more and more evenly distributed through-out the room. The gas molecules spread throughout the space in which they are contained by the process called diffusion.

In this chapter we study the phenomenon of diffusion in gases and show it to be a natural consequence of the random collisions of molecules that make up the gas.

B. BROWNIAN MOTION

The first and most fundamental question that arises is, "How may a molecule that is being randomly bombarded by other molecules ever undergo a net displacement in any given direction?" As a rough model of how the effects come about, consider the following activity.

Place a point in the center of a line on a sheet of paper to represent the position of a molecule at some initial time. Assume that it is moving with some velocity to the right. Draw a line one inch long to represent its new position. Assume at the new position it undergoes a collision with another molecule which either forces it ahead at the same speed or makes it move in the opposite direction with the same speed. The direction in which the molecule is to move is to be randomly selected. One way to assure that the direction of motion is randomly selected is to flip a coin. If the coin lands head up move the molecule to the right. On the other hand if the coin lands tails up, move the molecule to the left. Draw another line an inch long to represent the motion of the molecule in an interval of time following the first collision. At the end of that interval assume that the molecule undergoes another collision. By flipping the coin again, decide in which direction the molecule would be forced to move. Draw another inch long line to represent the displacement of the molecule following that collision. Continue this process ten times.

Note the final position of the molecule in relation to its starting point. Repeat this process five more times. That is, collect data for five more sets of ten "collisions" each.

After one of these sets of collisions you should have a diagram similar to that in figure 4 below.

Using your data for the six sets of collisions, note:

a. What is the least distance that you could have moved in one wet of tosses?

b. What is the greatest distance that could be moved in one set?

c. What is the average distance moved in each of your sets of 10 tosses? (e.g. in the example set, the distances were 0, 4L, 6R, 2L, 2L, 4R, and the average of, 0,4,6,2,2 and 4 is 18/6 or 3).

Notice that a "big jump", corresponding to 8 or 10 moves to the left or right, is very rare, but smaller moves of two or four are common. So it is with particles. This motion that results from random collitions is called Brownian Motion. There are clearly some important differences between this kind of imitation "Brownian Motion" by coin-tossing, and real Brownian Motion. Motion in a real gas takes place in three dimensions along all directions. Our example above is all along one line. Particles moving with real Brownian Motion move many different distances between one change of direction and the next because they exchange energy in this process. But in our exchange each "step" or distance equals every other step.

You may simulate the feature of random motion in two dimensions by repeating the above activity This time in addition to flipping a coin, spin some object such as a pencil or bottle that assumes random orientations after each spin and plot the motion of the molecule in the direction of the randomly oriented object. Maintain the rule that the molecule moves forward or backward depending on whether the coin lands heads or tails. The results will be the same, namely, that there is a net displacement of the molecule from its initial position. This time the direction it moved will have been random.

C. AN EXPERIMENTAL STUDY.

As we have seen above, the random motion of the molecule of a gas leads to diffusion. It remains to be seen how this applies to real gases.

Below we outline experiments that will shed some light on the relation between diffusion and the molecular properties of gases.

DISPLACEMENT PATTERNS FOR OBJECTS MOVING RANDOMLY IN ONE DIMENSION

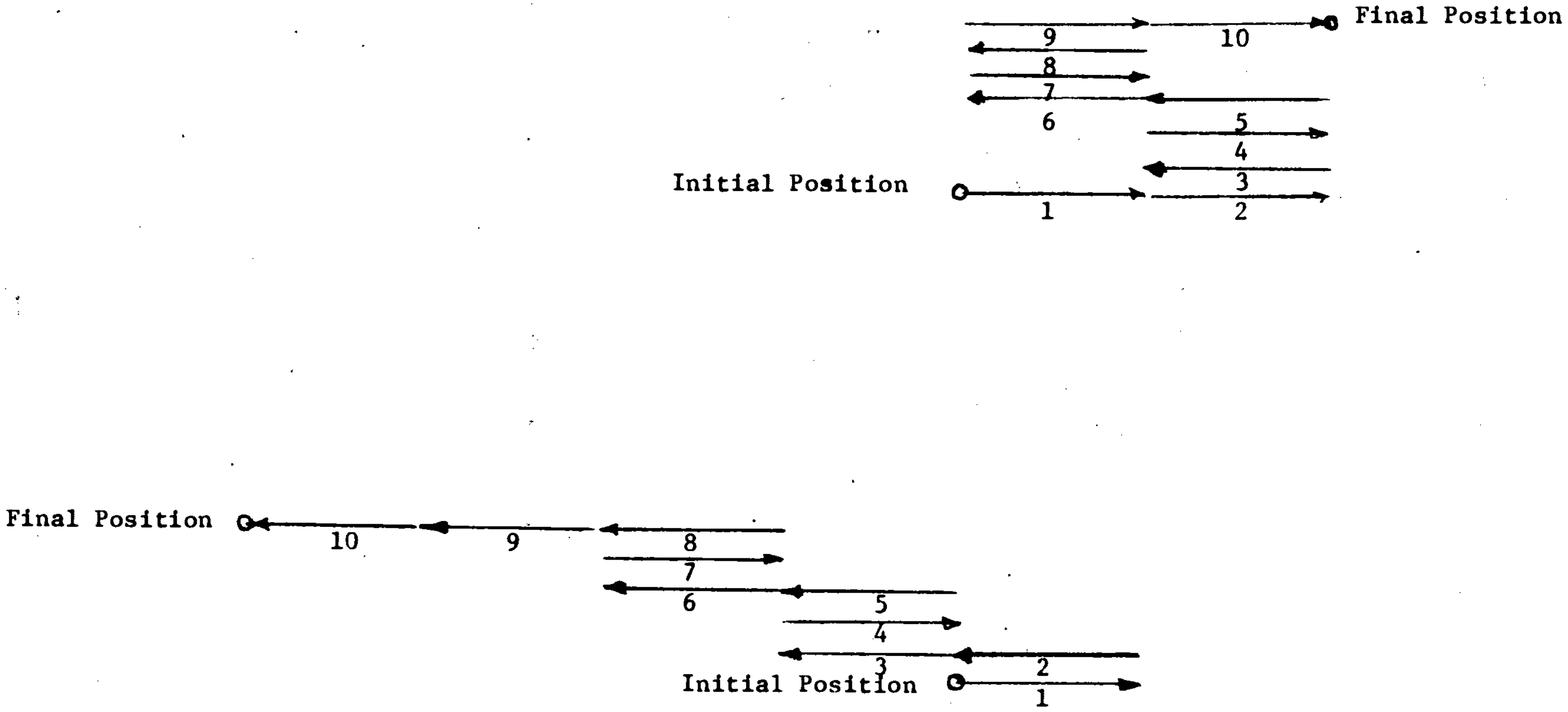


FIG. 4

EXPERIMENT IV - DIFFUSION OF A GAS
A QUALITATIVE STUDY

PURPOSE: A demonstration of gaseous diffusion

MATERIAL:

1. Ring stand and clamps
2. A 24 inch glass tube with approximately one inch diameter open on both ends
3. A solution of NH_4OH
4. A solution of HCl
5. Cotton wads

PROCEDURE: Fasten the glass or plastic tube horizontally to a ring stand as shown below:

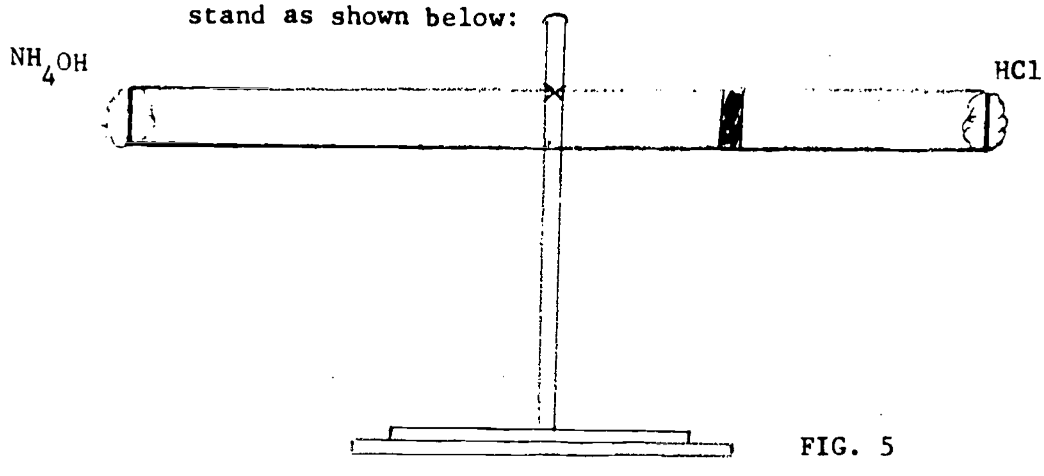


FIG. 5

Moisten two pieces of cotton, one with hydrochloric acid (HCl) and the other with ammonium hydroxide (NH_4OH). Plug one end of the tube with one piece of the moistened cotton and plug the other end of the tube simultaneously with the other. Carefully watch for the appearance of white smoke on the tube. Chemical analysis would show that this is neither NH_4OH or HCl but a new compound NH_4CL. (NOTE: Ammonium hydroxide gives off ammonia gas, NH_3.)

QUESTIONS:

1. Construct an explanation for the appearance of NH_4CL in the tube.
2. How might the property of diffusion of gases enter your explanation?
3. How might you explain the fact that the ring of NH_4CL is closest to the cotton with HCl on it?

Clearly diffusion is involved somehow. Remembering that diffusion is a result of moleculor motion, it would be reasonable to attempt to correlate some property of diffusion, such as the diffusion rate, with some property of molecules, such as moleculor weight. In order to gain more detailed information on this, we must conduct additional experimental studies. For this purpose we recommend the experiment V.

EXPERIMENT V - DIFFUSION OF A LIQUID

PURPOSE: To gather experimental evidence relating the diffusion rate of molecules to their molecular weight.

As we have seen from a study of Brownian Motion of molecules, the property of diffusion is a consequence of the random motion of molecules. Thus, in any medium where the molecules are free to move about we can expect diffusion to occur. The liquid state of matter allows the molecules free motion. Hence we may expect that we may use liquids in this part of our study. If we choose colored liquids we may gain the additional advantage over experiment IV in that we may be able to see the material diffusing.

Ideally we could place a colored liquid soluble in water and watch the diffusion of the colored liquid as it spreads out. But since water is a liquid, its molecules also undergo random motions and the diffusion of water molecules would interfere with that of the colored liquid. To circumvent this we use a gel to arrest the motion of the water molecules. The gel which is used is an agar-water gel in a petri dish. Agar is a protein obtained from certain sea weeds which readily forms a gel when a small amount is added to hot water and the mixture cooled.

MATERIALS NEEDED:

1. Agar suspension (1.5%)

2. Petri plates (dishes).
3. Forceps
4. Potassium dichromate (crystal)
5. Potassium permanganate (crystal)
6. Methylene blue
7. Stop watch or wall clock with second hand
8. Plastic ruler or micrometer caliper
9. Graph paper

WARNING: All chemicals should be handled with normal laboratory decorum, especially potassium dichromate. It is a harmful dust which may cause skin rash or external ulcers. If you get this substance on your skin or eyes, wash thoroughly with water. Handle all the crystals with a pair of forceps.

PROCEDURE: Select crystals of potassium permanganate, methylene blue, and potassium dichromate of equal size . Place each crystal carefully on the surface of the agar. Noting the rate at which they spread over the surface of the agar, in 45 second intervals. Measure the diameter of the spreading colored area several times for each crystal. Begin immediately after adding the crystals to the agar. Record the distance in milimeters and the time in seconds. Record both the time and diameters in tabular form as shown below.

The next important factor that we must consider is organization of the data gathered in the experiment. The data should be ordered in such a way as to clearly test the validity of the hypothesis. The hypothesis is "The rate of diffusion is dependent on the size or molecular weight of the diffusible molecules." The most direct means of evaluating the data is to inspect the recorded data and see if, indeed, the potassium permanganate diffused the greatest distance and methylene blue, the least.

Results of the data collected should be compared and discussed.

TABLE II

SAMPLE TABLE FOR RECORDING DATA

Time	Potassium Permanganate Mol. Wt. 158	Potassium dichromate Mol. Wt. 294	Methylene Blue Mol. Wt. 374
0 min.			

DIFFUSION PATTERNS IN AGAR GEL

Plate No. 1

Methylene Blue
(M.W. 374)

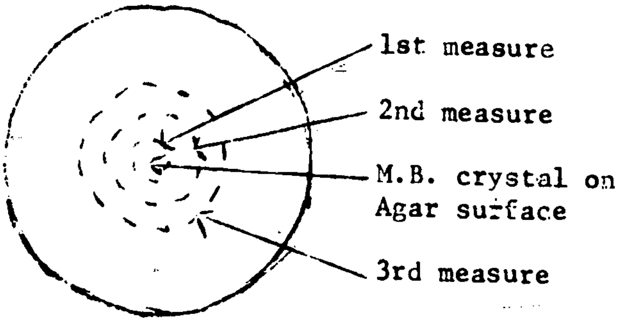


Plate No. 2

Potassium Permanganate
(M.W. 158)

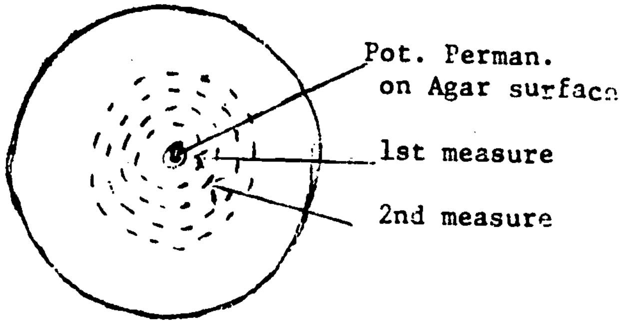


Plate No. 3

Potassium dichromate
(M.W. 294)

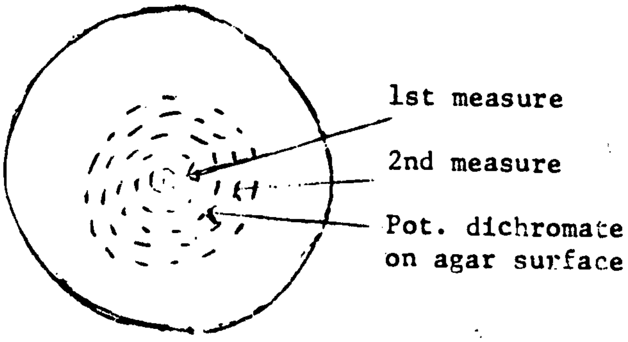


FIG. 6

EXPERIMENT VI - DIFFUSION OF A GAS
A QUANTITATIVE STUDY

PURPOSE: Measurement of diffusion rate of gases.

EQUIPMENT:

1. Same as Experiment IV
2. Stop watch

PROCEDURE: Use the set-up for showing diffusion of HCl and NH_4OH in a glass and perform the experiment again but this time take time to measure the length of the tube, and the distance from one end of the tube to the ring of NH_4CL.

Measure the time from the insertion of the two pieces of cotton into each end of the tube to the appearance of the smoke ring.

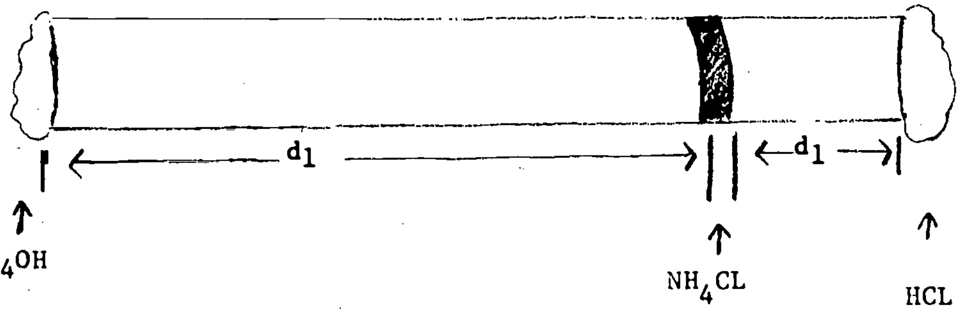


FIG. 7

A clearer relationship frequently emerges when data are graphed. For this experiment it is instructive to plot two relationships. First plot the diameter the colored spot attains after 3 minutes against its molecular weight. Then plot the various diameters against time for each of the crystals tested.

If the rate of diffusion under our experimental conditions are closely related to molecular weight, the graph will indicate a regular trend. A positive result will bear out our hypothesis.

Graph I.

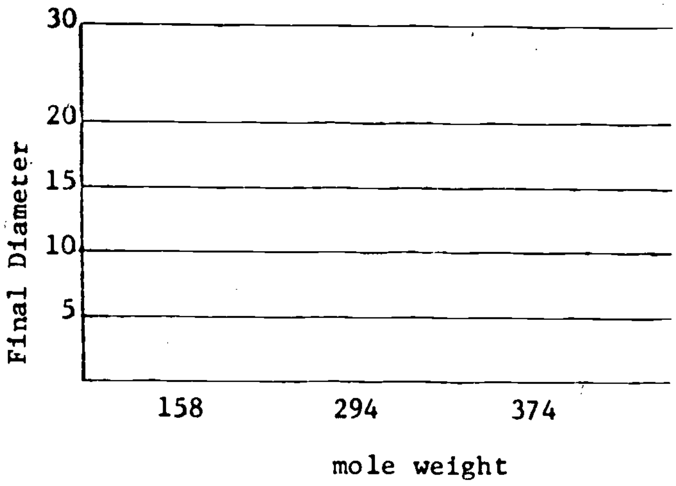


FIG. 8

Graph II (represent for each crystal)

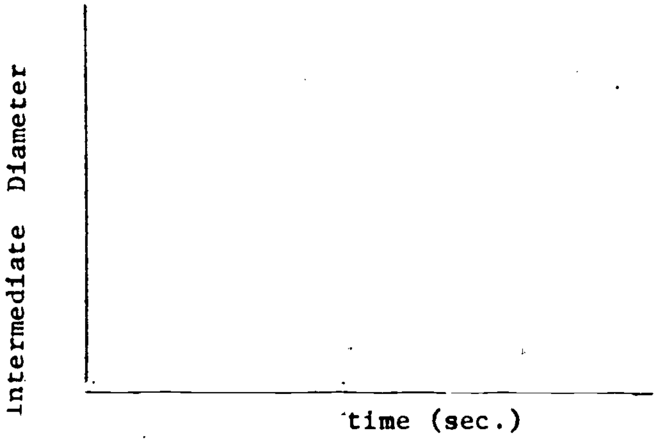


FIG. 9

COMPUTATIONS:

1. Measure the diffusion time of the NH_3 gas as it moves from the NH_4OH pad to the reaction site where NH_4CL is formed. Using the distance from the pad to the reaction site, compute the diffusion rate or speed.
2. Repeat these measurements and computations for the HCl gas.
3. Compare these results with the results of experiment V., i.e.,discuss whether or not the diffusion rates of gases are related to their molecular weight, as they are for liquids.

VI. MECHANICAL ANALOGUE SYSTEM

One way of gaining insight into the consequences of the Kinetic Theory of Gases is to study a system that has much the same properties. In this section we outline experiments with two mechanical systems that simulate the behavior of the moleculor properties of gases. Both systems are made up of a large number of randomly colliding objects which imitate the motion of the molecules of gas. The purpose of studying these mechanical models is to construct a molecular interpretation of the large scale or macroscopic properties of a gas, namely pressure and volume.

The two systems described below have similar features and are studied for the same purpose. The first employs an inexpensive commercial device that uses small steel balls enclosed in a transparent cylinder to represent the molecules of a gas. The balls are kept in constant motion by the use of a motor driven piston. The second requires an air table and employs cylindrical disks to simulate the action of molecules. The air table is the more preferable since it is a low friction device and thus imitates more closely the properties of real gas molecules. Once the disks are set into motion they maintain their speed through several collisions without outside interference.

EXPERIMENT VII - STEEL SPHERE MECHANICAL MODEL

PURPOSE: The purpose of this experiment is to establish qualitative connections between the collective properties of molecules in motion and the pressure and volume of a gas.

APPARATUS: A commercial device known as the "Mechanical Gas Model." A sketch of this apparatus is given in figure 10.

PROCEDURE: Place steel balls in the cylinder of apparatus and set them into motion by turning on the motor. Note that as the balls begin to move, the plastic lid on top the cylinder uses and is maintained at nearly a constant height by the bombardment of the balls. Measure the volume taken up by the moving balls in the cylindrical chamber. Record this volume.

Double the number of balls in the cylinder and repeat the above procedure.

By adding a resistor in series with the motor, decrease the speed of the motor and repeat the procedures above.

QUESTIONS:

1. How is the force on the lid related to:
    a. The number of steel balls in the cylinder?
    b. The speed of the steel balls?
2. Construct an interpretation for what is meant by the "pressure of the steel balls within the container." i.e., how is it related to the speed and number of steel balls?

STEEL SPHERE MECHANICAL GAS MODEL

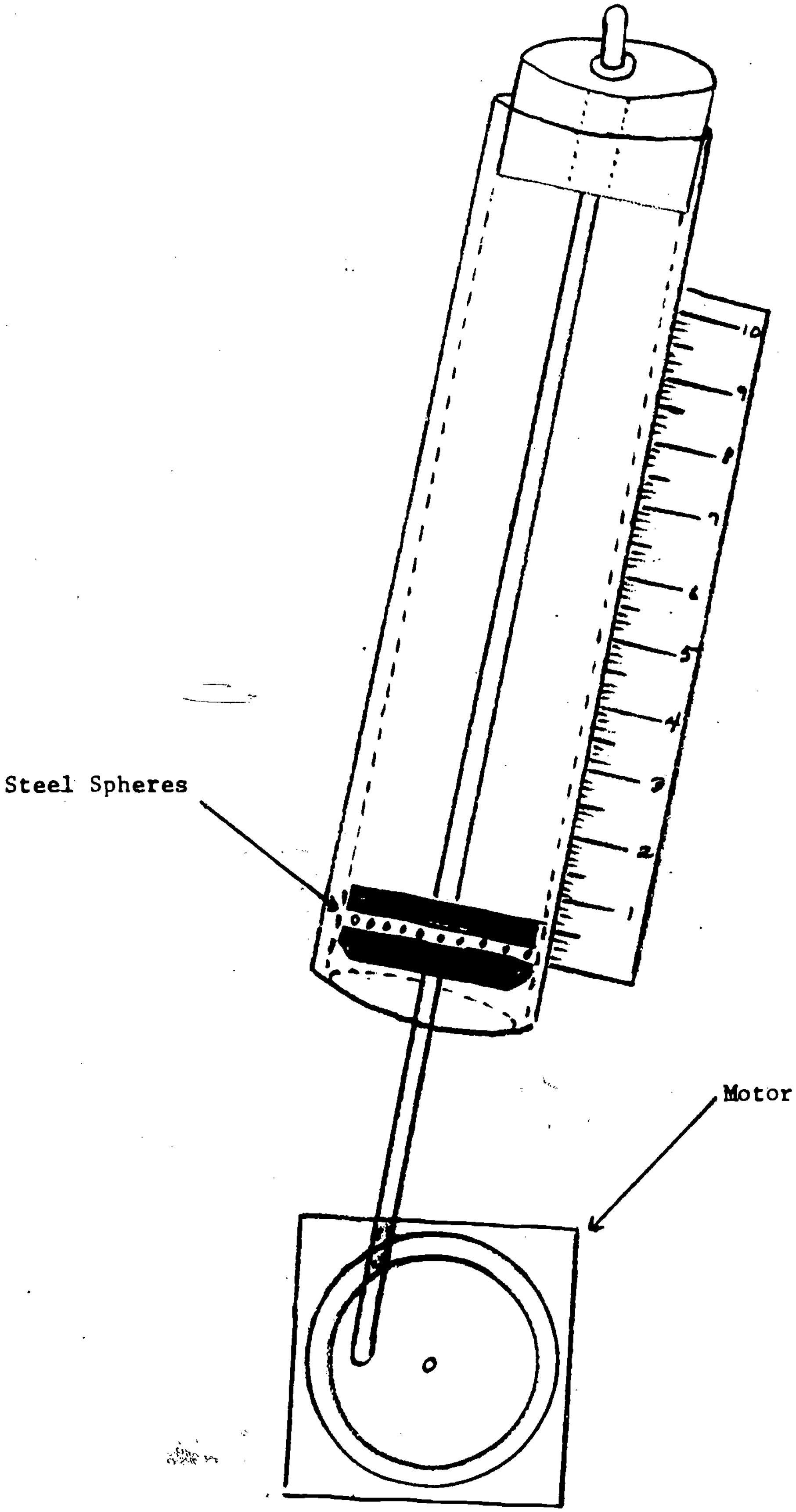


FIG. 10

3. What is the relation between the pressure and volume of the steel balls within the container?
4. How is the volume of the chamber containing the balls related to the actual volume of the balls?
5. By placing small weights atop the movable lid, prove that the balls within do create a pressure.
6. Using the above results, construct a qualitative model of the moleculor behavior of gases.

EXPERIMENT VIII - AIR TABLE MECHANICAL MODEL

PURPOSE: The purpose of this experiment is to establish qualitative connections between the collective properties of molecules in motion and the pressure and volume of a gas.

APPARATUS: A commercial air table, plastic disks or pucks, and a "Shaking wall" apparatus.

Although the air table has less friction than a normal table, it nonetheless has some. After gaining some initial motion, the pucks slow down and stop eventually. Molecules of a gas do not. If possible, it is advisable to construct a closer representation of the continual motion of the molecules of a real gas by using a "shaking wall" apparatus which supplies energy at the boundaries of the wall to keep the pucks in motion.

PROCEDURE: Using one puck on the table, set it into motion and note the details of its motion along the table and it's interaction with the walls, i.e., How does it move between collisions? Does it gain or lose speed after a collision with the wire walls of the table? Record your results.

Set up 6 to 12 pucks in random motion with different speeds on the table. Note the properties of interaction between them and the walls of the table. Do the pucks maintain different speeds or do they begin to share an average speed?

With several pucks in random motion on the table, stretch a moveable tight wire across one end of the table so that the pucks collide with it. Note the frequency of collision of the pucks with the walls. Stop the pucks and move the wire to the center of the table so that the area accessible to the pucks is half of the original area. Set the pucks into motion again with roughly the same speed. Note the frequency of collision of the pucks with the walls in this instance. How is the frequency of collision related to the pressure? Using the relationship between pressure and the motion of the molecules in experimentVII, construct an explanation of why the pressure of a container of gas molecules increases as the volume decreases.

VII. THEORETICAL IMPLICATIONS

A. SYNOPSIS

In the previous chapter we studied two mechanical systems in order to develop a qualitative understanding of pressure and volume of a gas in terms of its molecular properties. We are now in a position to extend these concepts in a more precise quantitative study of the properties of gases on a molecular level. It is the object of our study in this chapter to establish precise quantitative relations between the macroscopic and microscopic properties of a gas and then to pursue the implications of these relations as they lead to new laws.

Our approach will be mathematical. The kind of reasoning that we will employ is typical of that used in the physical sciences. We begin with a detailed study of the motion of molecules in a container to describe their properties mathematically. Then we use the laws of physics, expressed in mathematical form, to derive a relation between the pressure and volume of the gas and its kinetic properties. We then compare this relation with the expression for the gas law in order to obtain kinetic interpretation for the third property of gases, namely temperature.

As a final step we come full cycle to consider the law governing diffusion rates of gases, this time using the mathematical results derived from the Kinetic Theory. How well these results serve us in understanding new phenomenon such as this is a measure of the value and validity of the Kinetic Theory.

B. RELATIONSHIP BETWEEN PRESSURE, VOLUME, AND THE KINETICS OF GASES

1. The Dynamics of a Single Molecule

As we have seen, molecules strike the wall and impart a force to it. Use of the air table analogy suggested that as molecules collide with the wall, they change direction but maintain their speed. If we are to compute the pressure, we must know how much force is produced. To find this out, we analyze the details of a collision of one molecule. In order to extract a measure of the force imparted during this collision, we must use a law of physics that describes that process, namely, Newton's second law. It states that if an object is forced to change speed and/or direction, a force is required. This force is related to the rate of change of the speed and direction of the molecules by the equation:

$$F = \frac{M \Delta v}{\Delta t}$$

Where: M is the mass of the molecule
Δv is the change in velocity
Δt is the time interval in which the change occurs.

On an average the particles that strike the walls of the container may be considered to be moving perpendicular to the wall before and after a collision. Though this is not an exact representation of the collision - for we know that some molecules strike the wall at an angle - for the sake of this calculation, it is a good approximation. Before the collision, a molecule has a speed, v, as it is moving toward the wall. After the collision, it moves with the same speed, v, but in the opposite direction. We represent the velocity after the collision by $-v$ since it is moving in the opposite direction from it's initial velocity. Thus the change in velocity is

$$\Delta v = (v_{\text{initial}} - v_{\text{final}}) = v - (-v) = 2v.$$

The fact that the change in velocity is twice the initial speed may seem a bit mysterious. But this is a result of the directional property of velocity which can be understood by using the following analogy.

Forces have the same property as velocity, namely they have a magnitude as well as a direction. Consider a force that is applied to an object so that the force is acting to the right. In order to change the total force acting on the object to a force of the same magnitude acting to the left, we must add twice the original force to the left. The addition of the same amount of force acting to the left cancels the original force and the addition of another force of equal strength to the first produces a net force acting to the left of the same strength as our original force. In this way we can see that it takes twice the original speed acting in the opposite direction to reverse the velocity of the particle described above.

Thus the value of the force that the wall on the particle is given be the equation:

$$F = \frac{M2v}{\Delta t}$$

In order to obtain the value of the force of the particle on the wall, we apply Newton's Third Law, an often quoted - but often misinterpreted law which says that for every action, there is a reaction equal in magnitude and opposite in direction. This means that if the wall exerts a force on the particle, the particle exerts a force of equal magnitde - but opposite direction - on the wall in return. Hence, the force of the particle on the wall is also given by the expression

$$F = \frac{M2v}{\Delta t}$$

Thus by analyzing the change in motion of the molecule we have deduced the force exerted on it and on the wall by it. To complete this expression we need a value for the time interval.

As we see in the expression above, in order to obtain a number for the value of the force we must identify the value of the time interval in the denominator of the expression. This is difficult because we cannot inspect the details of each collision sufficiently close to detect how much time is required for the collision. We may, however, compute the average force the wall experiences over a longer period of time; for example, the time between collisions. Because the particle is contained in a box, it will return to this wall again after it travels to the other side of the box, collides with the other wall and returns again. If the box has a length, L, across, it takes an amount of time equal to L/v for the particle to traverse the box. Thus in a time interval, $2L/v$, after the first collision, the particle will have tranversed the length of the box twice and returned for its second collision with the same wall. Every $2L/v$ seconds the wall imparts a change in velocity of $2v$ to the particle. hence the average force imparted is given by:

$$F = \frac{2Mv}{2L/v} = \frac{Mv^2}{L}$$

2. The Effects of Many Molecules

To take into account the effects of more than one particle we need only multiply by the number of particles colliding with the wall over this time interval. If we have N randomly moving particles in the box at any given time, 1/3 will be moving to right and left, 1/3 will be moving up and down, and 1/3 will be moving in and out. Over the time interval it takes one molecule to move across the box twice, all of the molecules moving in that direction will have struck the wall. Thus the total force on the wall in the time interval is N/3 times the force of a single molecule or mathematically it is given by the expression:

$$F = \frac{N}{3}\,\frac{Mv^2}{L}$$

We may convert this force into a pressure by dividing the total force on the wall by the area of the wall. Since we have assumed that the particle is in a cubical box of length L on a side, the area of one wall of the box is L^2. Thus the pressure is given by:

$$P = \frac{F}{L^2} = \frac{N}{3}\frac{Mv^2}{L^3}$$

We may further simplify this expression by replacing the quantity L^3 by the volume of the box **V**. But recalling that a gas fills it's container, the volume of the box is also the volume of the gas. Thus, we may rewrite the above expressions:

$$P = \frac{N}{3}\frac{Mv^2}{V}$$

or

$$PV = \frac{N}{3}Mv^2$$

Hence we have arrived at an expression relating the pressure and volume of the gas within the box to the average speed and mass of its molecules.

C. RELATIONSHIP BETWEEN TEMPERATURE AND KINETICS OF GASES

It should be borne in mind that the above relationship has been derived solely on the basis of considerations made regarding the physics of molecular motion. We have made no reference to the Gas Laws in obtaining it. Our study is, however, incomplete as we have not yet included temperature in our considerations. This is more difficult as there is no analogue for temperature in the laws of mechanics. This is not so with the other parameters of a gas. A single molecule has volume and, as we saw in the above derivation, is capable of exerting a pressure. But it is not capable of exhibiting a "temperature." It turns out that temperature is a property of a collection of molecules.

Thus we are unable to "derive" a connection between temperature and the properties of molecules as we did above, using the laws of physics alone. To establish this connection we must resort to another approach. We will assume the Gas Law is true and that our derivation above is correct and combine the two relations to arrive at an interpretation for temperature.

Combining the relation

$$PV = \frac{N}{3} Mv^2$$

and

$$PV = NKT$$

we arrive at the equation

$$KT = \frac{1}{3} Mv^2$$

This tells us that the temperature of an object is directly proportional to the product of the mass and velocity squared (or the kinetic energy) of the molecules of the object. This is a basic relationship that extends beyond the properties of gases; it also applies to other states of matter as well.

Notice that we have not "explained" the Gas Laws for we have had to assume that they were true in order to arrive at an interpretation for temperature, but we have gone a long way in understanding them. Once we have derived the above equations, we may use them to arrive at new relationships. For example, we are now in a position to investigate the properties of diffusion and explain why its rate depends on the molecular weights as it does.

D. APPLICATION OF KINETIC THEORY

1. Derivation of the Law for the Rates of Diffusion of a Gas (Grahm's Law).

In Experiment VI we saw that the diffusion rate of a gas is related to its molecular weight. Let's see why. In the experiment the two gases that diffused in the tube were both at the same temperature, namely room temperature. The temperature of each is related to the velocity and mass of the molecules by:

$$kT_1 = 1/3\ M_1 v_1{}^2$$

$$kT_2 = 1/3\ M_2 v_2{}^2$$

where the subscripts 1 and 2 refer to the two different gases.

As the temperatures are equal we may equal, the right hand sides of the above equations are also equal to one another, giving the result:

$$1/3\ M_1 v_1{}^2 = 1/3\ M_2 v_2{}^2$$

Or rewriting the equation, we obtain the relation:

$$M_1/M_2 = v_2{}^2/\ v_1{}^2$$

Qualitatively, this equation tells us that at equal temperatures, the heavier a gas the more slowly it diffuses.

This equation is an expression of Grahm's Law. Grahm, a Scottish scientist, in a study of the diffusion rates of gases, arrived at this expression empirically before the advent of the Kinetic Theory. It is a valuable law that was used for many things, one of which, as we shall see below, was to indirectly measure the molecular weights of gases.

PROBLEMS

Sample Problems

1. Two gases are at the same temperature. The mass of a molecule of gas 1 is 121 times the mass of a molecule of gas 2. What is the ratio of their speeds?

Using Graham's Law we can relate the ratio of masses of the molecules of the gases to their velocities.

Thus we have

$$M_1/M_2 = \frac{V_2^2}{V_1^2},$$

where the subscripts 1 and 2 refer to the two gases.

Since the mass of the molecule of one gas 121 times that of the other

$$M_1/M_2 = 121$$

Thus $V_2^2/V_1^2 = 121$

or $V_2/V_1 = \sqrt{121} = 11$

The speed of the lighter molecules is eleven times that of the heavier molecules.

2. Suppose we wanted to double the velocity of a gas that is at a temperature of 100°C. How high would we have to raise the temperature of this gas?

This problem involves an application of the relation $KT = \frac{1}{3}(Mv^2/2)$ to one gas at two different temperatures. It is vital to remember that T is the absolute temperature; before any calculations are performed, all temperatures must first be expressed in the Kelvin scale! Initially the temperature is T_1, where $KT_1 = \frac{1}{3}(Mv_1^2/2)$, and the final temperature is T_2 where

$KT_2 = \frac{1}{3}\,(Mv_2^2/2)$

Thus,
$$\frac{KT_1}{KT_2} = \frac{(Mv_1^2/2)}{(Mv_2^2/2)},$$

or
$$\frac{T_1}{T_2} = \frac{v_1^2}{v_2^2}$$

Since $v_2 = 2v_1$ and $T_1 = 100^\circ C + 273^\circ = 373^\circ K$, we may substitute these values in the above equation obtaining,

$$\frac{373^\circ K}{T_2} = \frac{v_1^2}{(2v_1)^2}$$

or

$$\frac{373^\circ K}{T_2} = \frac{1}{4}$$

Hence
$$T_2 = 4\ (373^\circ K)$$
$$T_2 = 1492\ ^\circ K$$

or

$$T_2\ (\text{degrees centigrade}) = 1219\ ^\circ C$$

Practice Problems

3. The ratio of the velocities of two gases at the same temperature is 3 to 1. What is the ratio of their masses?

4. Gases SO_2 and H_2 have a mass ratio 64/2. What is the ratio of the average speeds of their molecules at a given temperature?

5. If a gas is at 6°C, and its average random kinetic energy is doubled, what does its temperature become?

6. A gas has had its temperature raised from 27°C to 327°C. By what factor have the molecules had their average speed increased?

PART III

THE IDEAL GAS LAW REVISITED

VIII. THE IDEAL GAS LAW REVISITED

By experimenting with gases at conditions close to normal laboratory conditions, we have found that the relation between the pressure, volume, and temperature of a gas is given by $PV = nKT$. It turns out that over a fairly wide range of temperatures and pressures that this law is fairly accurate. But are there any limitations to the applications of this law? As we have seen in the experiment? the formula makes a prediction that we know cannot be correct. Namely that if we set the pressure of a gas at some predetermined value and decreased its temperature to "zero" degrees Kelvin it would have no volume! Clearly this is incorrect. For molecules have volume no matter what temperature.

If we gather data on the properties of several gases over ranges of high pressures and temperatures, we may see this deviation in their bevior from the ideal gas law. One way to represent these deviations in one fell swoop is to plot the value of the quantity $\frac{PV}{nKT}$. If the gas obeys the gas laws, this quantity will equal 1. On the other hand if the volume is greater or less than that predicted by the gas laws the quantity will be vary correspondingly. In figure 11 we have plotted the experimental values of this quantity for two real gases at high pressures and temperatures.

The deviation from ideal behavior is due to a combination of two factors. First the volume that is referred to in the equations is a measure of the volume available for motion of the molecules as we saw in the derivation of the gas laws. For real gases, however, the constant temperature, and the molecules become sufficiently close together, the attractive forces of the molecules take over and the gas changes state going from a gas to a liquid or solid. The ideal gas law can make no such prediction as it neglects these forces.

A plot of P versus V for the ideal gas law is compared to the Van der Waal formula in figure 12below. The two "humps" in the plot of the Van der Waal equation is in the region of volume where a phase change occurs and the gas becomes a liquid.

The Van der Waal equation is not the ultimate equation; it too has its faults. But it was a step in the right direction and an improvement over the Ideal Gas Law. There is no simple equation that describes the behavior of a gas perfectly over all ranges of temperature and pressure. Any that we use will have some limitations.

All of these considerations tell us that the Ideal Gas Law is only an approximate description of the behavior of gases. But we should have expected this as the laws were derived empirically. Nonetheless, the law is an accurate description over a wide range of temperatures and pressure and a valuable contribution to our knowledge of the physics of gases.

MEASURE OF DEVIATION OF BEHAVIOR OF REAL GASES FROM IDEAL GAS LAW

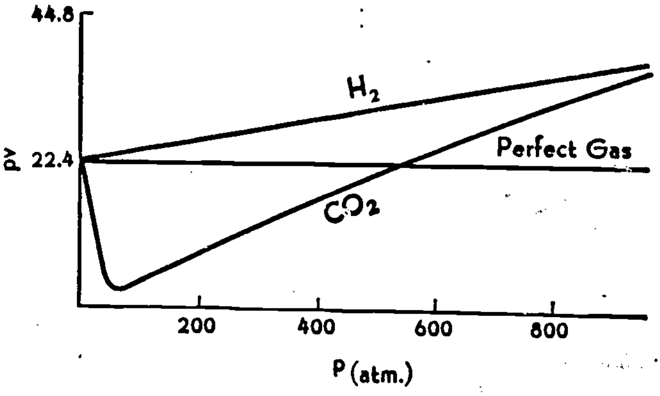


FIG. 11

Explanation for the deviation of the compressibility curve from ideal:

1. At low pressures,below 150 atmospheres,the intermolecular attractive forces cause a decrease in the pressure, which in turn causes the product PV to be lower than expected.
2. At high pressure,above 150 atmospheres,the volume occupied by the molecules is not negligible compared to the total volume. The quantity V should represent only the free available space for motion. Thus the volume measured and plotted is greater than this as it includes the volume of the molecules as well.

VAN DER WALLS EQUATION FOR RELATION BETWEEN PRESSURE AND VOLUME

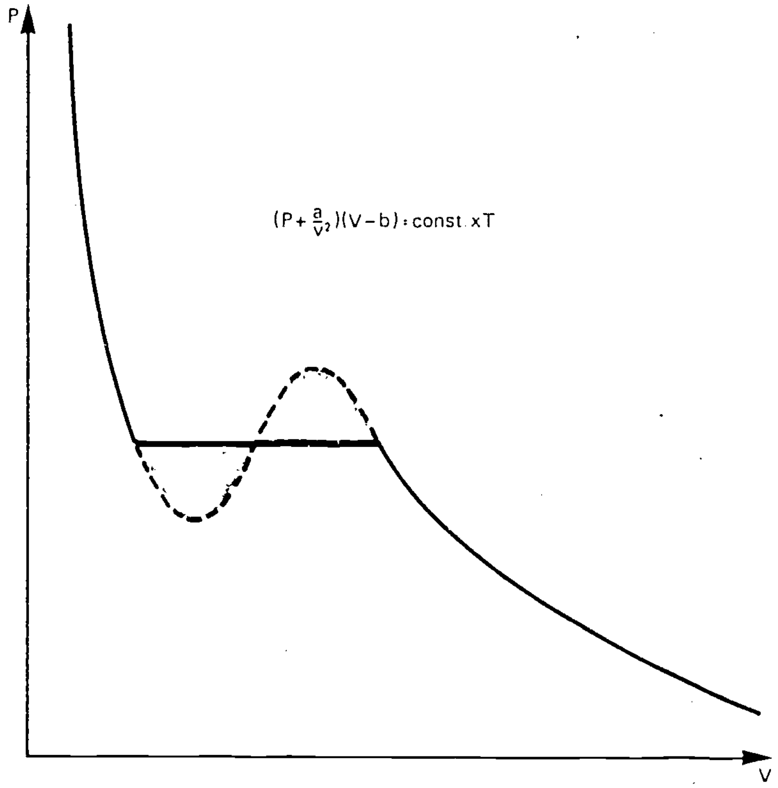


FIG. 12