SECOND YEAR COLLEGE CHEMISTRY

BY

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LABORATORY MANUAL.

Intended to accompany ‘Second Year College Chemistry” or to be used in connection with a course in Quantitative Analysis. 121 pages. 6 by 9. 28 figures. Cloth, $1.50 net.

" When you can measure what you are speaking about and express it in numbers, you know something about it, and when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind. It may be the beginning of knowledge, but you have scarcely in your thought advanced to the stage of a science."

Lord Kelvin.

PREFACE

THE trend of our present-day research in both pure and applied Chemistry implies that principles are more important than facts and methods; and this trend, it would seem, should be reflected in our teaching. It is conceded, however, that general principles cannot be profitably taught without first building a background of facts, and for this reason the first year course must be largely given over to descriptive matter. It is true that the student has many principles and laws thrust upon him during the first year; but, due to his lack of perspective and his crudeness as a manipulator, he gets these only in a vague, qualitative form. They do not become a part of his stock-in-trade; and so, after a summer's vacation, they have for the most part passed into oblivion.

Now, if we grant that these general principles are the framework of our science we should not allow them to be thus forgotten; we should revive them, and expand them, and work them over, until they become familiar, usable tools. With this in mind, therefore, the selection of courses immediately following General Chemistry is seen to be a matter of great importance. The traditional course in Qualitative Analysis, with its endless round of reactions and "unknowns," offers very little in the development and fixing of principles, although it has a distinct value in the first-year course as a means of systematizing a multitude of facts. Even the modernized course based on the Ionic Theory and the Laws of Chemical Equilibrium makes too small a contribution in proportion to the time consumed. The fact is that too little impression is made on a student by a multiplication of qualitative statements or the use of qualitative problems and laboratory exercises. What a student needs is an accurate restatement of principles and the opportunity to verify and use these in a quantitative way.

The course covered by this text and the accompanying manual is an attempt to put into operation the plan implied in the above discussion. It, therefore, assumes that the student knows very little about general principles but that he has a fair knowledge of facts. With this slight assumption, the text takes up the principles touched upon during the first year, and restates them without apology. After this

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it extends the development beyond the possibilities of the first year, and, wherever possible, puts matters into strictly quantitative form, emphasizing this principle by the use of quantitative problems and exercises. The laboratory course follows the same method; it requires the student to verify the principles and to use them in a quantitative way, and thus make them his own.

Neither the student nor the teacher is asked to accept very much on faith. Wherever possible, statements are supported by experimental data, and these are covered by references to books and original papers. This tends to disarm much of the skepticism which the beginner carries over from the first year, and allows those who are interested, whether students or teacher, to extend the treatment of any topic beyond the narrow limits of this course. More than this, it develops the indispensable habit of consulting the literature.

With many of the most important topics, the historical method of treatment has been used. This consumes a little more time, but it serves to introduce the student to the pioneers of our science, and attracts those who are interested in the personal side. The same end is furthered by the use of footnotes introducing the persons mentioned in the text, and referring to books and papers where further information may be found.

The treatment throughout the course is intended to lead the student to feel that Chemistry is a growing science. To this end, the author often discusses questions which are still unsolved and upon which work is now being done; and in many cases also, the values presented are frankly acknowledged to have only a temporary standing.

Neither the choice of topics nor the treatment of those which have been chosen will suit every reader. The aim has been to emphasize those principles which are of fundamental importance to every chemist who aspires to be something more than an " analyst," and to treat them in such a way that the second-year student, with his poor perspective, may constantly feel that he is master of the situation. Moreover, the course is not intended to usurp the place held by formal Physical Chemistry. It is intended only to place in the student's hands, at the earliest possible moment, some of the indispensable tools of the science. It does serve, however, as an introduction to Physical Chemistry, and it causes the student to feel the need of such a course and to look upon it as a logical and necessary step in advance.

The author wishes to acknowledge his great indebtedness to Professor H. N. Holmes of Oberlin College, who has taken the keenest interest in the devolpment of this course from its beginning. Special mention should also be made of Dr. W. V. Metcalf of Oberlin, Ohio, who as been kind enough to read the manuscript and make most valuable suggestions; also of Dr. A. P. Lothrop of Queens College, Ont., who has read the page proof.

William H. Chapin.

SUGGESTED COURSE OF STUDY

As taught by the author, the text is made to cover a year's work (thirty-two weeks, two recitations per week). The ground is actually covered in twenty-eight weeks, and the last four weeks are used in reviews. The laboratory manual can be made to cover thirty-two weeks, working at the rate of five hours per week; but the author has preferred to use it in connection with a course in Quantitative Analysis, alternating the two kinds of work to suit the work in the classroom. For example, the chapters in the text on the Periodic System, Atomic Structure, etc., cannot be illustrated in the laboratory, and are best accompanied by gravimetric analysis, which consists quite largely of technique. This also gives a fine opportunity to apply the principles relating to calculations, etc., previously studied. Volumetric analysis is introduced in the second semester, while the matter of equilibrium is being studied, and as a fine illustration of such matters as concentration, valence, oxidation, reduction, and indicators, previously treated. This combined analytical and theoretical work occupies about nine or ten hours per week for a year of thirty-two weeks.

The actual division of the time for class and laboratory has been about as follows:

First Semester

TEXT	LABORATORY
7 weeks, through " Valence."	7 weeks, through " Valence."
9 weeks, through " Osmotic Pressure."	7 weeks, through "Gravimetric Analysis."
	2 weeks, through " Freezing Points."

Second Semester

TEXT	LABORATORY
12 weeks, through " Electro-chemistry."	3 weeks, through " Indicators."
4 weeks, reviews or study of analytical problems and principles.	7 weeks, Volumetric analysis.
	6 weeks, through " Electro-chemistry."

The course as above outlined has given the best satisfaction, but there would be no difficulty in substituting a course in advanced Qualitative for the Quantitative, if it were so desired.

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SECOND YEAR CHEMISTRY

CHAPTER I

OUTLINE OF THE KINETIC THEORY

Much of the material before us deals with simple applications of the Kinetic Theory—the theory of moving molecules. We shall, therefore, begin by outlining the postulates of this theory, at the same time presenting some of the experimental evidence upon which they are based.

The Molecular Structure of Matter.—That matter is not continuous, but is made up of minute particles more or less widely separated, is now accepted by every one whose judgment is worth considering. Originally the idea of molecules rested on mere philosophical speculation, but in modern times quantitative evidence has accumulated, until scientists the world over now feel that the theory is not even open to question: it is accepted as a demonstrated fact.

This does not mean that we can see molecules, or ever hope to do so, for the limitations of our organs of vision make this forever impossible. " But," as Professor Millikan * says, " after all, the evidence of our eyes is about the least reliable kind of evidence which we have. We are continually seeing things which do not exist, even though our habits are unimpeachable. It is the relations which are seen by the mind's eye to be the logical consequences of exact measurement which are for the most part dependable." If we cannot see molecules we can, nevertheless, make all sorts of exact and reliable measurements relating to them, and can successfully predict their deportment under any given conditions. This is better than seeing.

As to the matter of evidence upon which the conception of molecules rests we shall say very little here. The volume of this evidence is enormous, for practically all the physical deportment of matter in all its states can be explained on no other basis. We therefore prefer to let the evidence appear and accumulate as we proceed. We might, however, mention one or two striking cases in passing. We note, for example, the enormous compressibility of gases. We cannot conceive how matter can be made to occupy a smaller space if it already occupies it all. There must be free space; and admitting this is equivalent to admitting that gases have a discontinuous structure. The manner in which one substance dissolves in another and diffuses about in it is another convincing piece of evidence. But perhaps the best evidence is the fact that certain properties of matter change suddenly in a very striking way when the dimensions pass a certain limit of smallness. It is known, for example, that a particle of camphor gum placed upon the surface of pure water, is made to skip or whirl about by changes of surface tension. Now, Lord Rayleigh * found that this action was stopped when a film of oil 10×10^{-8} cm. in thickness was formed upon the water, while a film of 8×10^{-8} cm. had no effect. This difference was due, he said, to the fact that in the first case the water was covered over with a film of liquid oil, while in the second case only individual molecules were dotted about, leaving exposed surfaces of water between.

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* Robert Andrews Millikan (1868–), Chairman of the Executive Committee and Director of Physical Research, California Institute of Technology. Noted for his magnificent work on the determination of the electronic charge.

We may note in passing that the methods employed in molecular measurement are largely statistical in nature. We predict the happenings and conditions in a world of molecules just as we predict matters having to do with human society. An insurance company, for example, can predict with considerable accuracy the number of people who will be killed in automobile accidents during a year, or can give the exact weight of the average American man or woman of a given age. Concerning a single individual they can tell very little, but the larger the number of individuals the more accurate the prediction will be. In the molecular world, where the number of individuals is extremely large, the predictions and averages are very exact. To quote Professor Millikan again: "We can estimate the number of molecules in a cubic centimeter of gas with greater precision than we can attain in determining the number of people living in New York." In the same way we can probably determine the mass of a molecule of oxygen much more accurately than we can determine the average weight of an American Indian.

We shall now proceed to describe certain molecular properties and

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* Phil. Mag. (5) **30**, 474 (1890). [Lord Rayleigh (1842–). One of the world's most brilliant physicists. Co-discoverer of the rare gases in the atmosphere.]

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dimensions and to show in a very elementary way how some of these matters have been found out.

Motion and Kinetic Energy of Molecules.—Molecules are in rapid motion and their kinetic energy is proportional to the absolute temperature.

Pressure, in the case of gases, we believe to be due to the impacts of vibrating molecules; and the fact that gases do not settle down like dust can be accounted for only on the supposition that the molecules are constantly moving and stirring each other up.

What we call *heat* we also believe to be due to the energy of motion (the kinetic energy *) of moving molecules.† When we touch a body whose molecules are in very rapid motion the motion is imparted to the molecules of the hand, and we sense the effect as what we call "heat." An object expands as heat is applied because the moving molecules, as their rate of vibration increases, jostle each other apart.

But the motion and kinetic energy of molecules are shown most convincingly by what is called *Brownian movement.* If a very fine powder suspended in water is examined under a good microscope the particles are seen to be in rapid vibration—the smaller the particles the more rapid the vibration. This motion has been named Brownian movement after its discoverer, Robert Brown, a botanist. It has been very carefully studied by Perrin ‡ and others, and these investigators have come to the very important conclusion that what we see is only an example of what is going on all the way down from the largest particles through all grades of smallness to the molecules themselves. They believe that all the particles of every size, whether visible or invisible, have by their mutual impacts imparted their kinetic energy to each other until, on the average, they all have the same amount.§ The difference in the rate of movement is due to the fact that to have the same kinetic energy the large particles need only move slowly, while the smaller particles must move more rapidly, and the smallest particles most rapidly. That this supposition is correct has been proved experimentally for the visible particles, and the smallest of these is not far removed in size from the largest molecules. It is, therefore, not a serious stretch of the imagination to believe that the slightly smaller particles—the molecules—act in the same way and have the same amount of kinetic energy.

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* The kinetic energy of any moving object is related to the mass and speed, as shown in the common kinetic expression: $K.E. = MS^2/2$. The derivation of this expression may be found in any text-book of physics, e.g., Millikan and Gale, p. 151. Note that kinetic energy varies as the square of the speed. This means that the kinetic energy of an object will be quadrupled when the speed is doubled.

† Or of the smaller particles constituting the molecules.

‡ "Brownian Movement and Molecular Reality," and "Atoms." [Jean Perrin (1870–), Professor of Physical Chemistry at the Sorbonne, Paris.]

§ This is called the Law of Equipartition of Energy.

That the kinetic energy is proportional to the absolute temperatures has been demonstrated in the case of the visible particles, and that the same thing is true for the molecules, is evidenced by the fact that gaseous pressure is proportional to the absolute temperature. Pressure is, of course, a measure of kinetic energy, and if pressure is proportional to the temperature, the kinetic energy must also be proportional to the temperature.

It may be interesting to include here some of the actual speeds which molecules possess.* The average speed of the hydrogen molecule between impacts with other molecules is, under standard conditions, 183,000 cm. (1.15 miles) per second. That of the oxygen molecule is 46,000 cm. per second. It is to be carefully noted that we say "average speed." † It is not to be expected that all the molecules, or any one individual, will necessarily be moving at this speed; but the average speed for many millions of molecules will certainly come very near these values. Particular individuals will be moving at every conceivable speed, some above, some below this average. The method by which these average speeds are calculated will be described later.

Elasticity of Molecules.—Molecules must be perfectly elastic. By this we mean that if two molecules collide and rebound no kinetic energy is lost.

When a given quantity of a gas is allowed to stand under constant conditions the pressure remains perfectly constant. As before stated, pressure is undoubtedly due to molecular impact. If the pressure remains constant it must be that the average speed of the molecules also remains constant, and this could not be so if the molecules were not perfectly elastic. If the molecules were like balls of putty, or even balls of lead, they would rebound after impact with constantly lessened speed until they finally came to rest. The pressure would, therefore, decrease correspondingly until it became zero.

Number and Spacing of the Molecules of a Gas.—The number of molecules of gas per liter under standard conditions is known with considerable accuracy. As determined by several reliable methods the number is about 2.7×10^{22}. The remarkable thing is that, although the methods of measurement are very different, the results are so nearly the same. This is a good argument in favor of their accuracy. One of the methods of determining this number involves an actual count of the number of particles seen in Brownian movement. Perrin * made the determination in this way. He prepared suspensions of mastic or gamboge particles of uniform size and examined them under the microscope in a tiny cell 0.1 mm. deep. Pressure due to their kinetic energy tends to make the particles scatter and become equally distributed through the cell. Gravity pulls them towards the bottom, bringing them closer together there. When equilibrium is established these two tendencies balance. Perrin counted the number present at different levels (*a*, *b*, *c*) equal distances apart, as seen in the fields *a*′, *b*′, and *c*′, and from the rate of increase in the concentration was able to calculate the number required in unit volume to give a pressure of one atmosphere (760 mm.) at 0° C. He varied the size of the particles fifty-fold, and always found nearly the same number (as above). He therefore inferred that the number would be the same even for gaseous molecules. This means that a liter of any gas under given conditions of temperature and pressure will contain the same number of molecules, no matter what their size may be. This fact

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* First calculated by Joule, the English Physicist, in 1851. See Phil. Mag., XIV, 211.

† Nernst, Theoretical Chemistry, pp. 434–437, (1911). Other references are given.

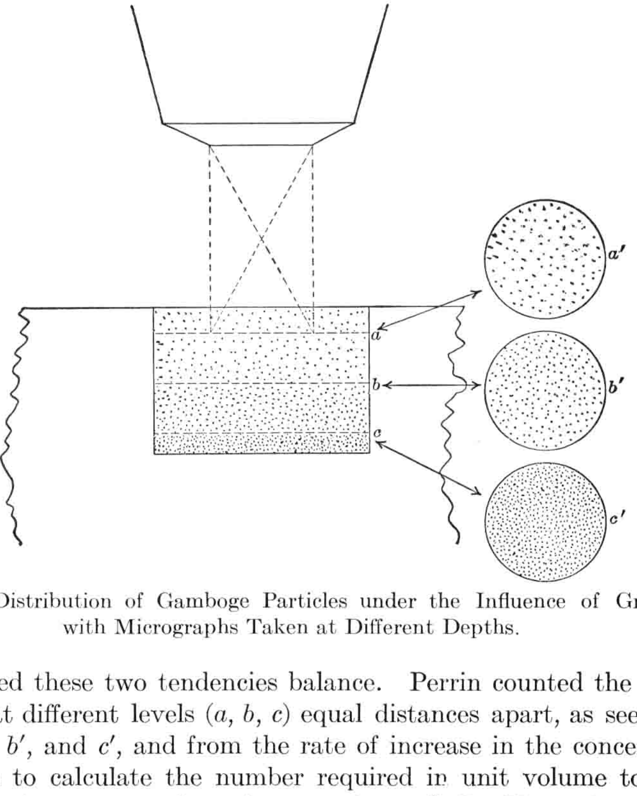

FIG. 1.—Distribution of Gamboge Particles under the Influence of Gravitation with Micrographs Taken at Different Depths.

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* "Atoms," pp. 83–108.

was suspected by the Italian physicist, Avogadro,* long before the kinetic theory was developed, and is known as Avogadro's Law.

Considering the number of molecules per liter, we can see that the spacing of the molecules of a gas under standard conditions must be very close if measured in the relatively coarse units of centimeters or inches. But relative to their own size the molecules of a gas are really quite far apart. That this is true is shown by the wonderful compressibility of gases. Thus one liter of carbon dioxide gas at 0° C. and one atmosphere pressure can be compressed until it changes into a liquid which occupies only 2 cc. If we assume that the volume of the liquid represents the total volume of the molecules, the free space between the molecules of one liter of the gas is 998 cc., or 449 times the volume occupied by the molecules themselves. One liter of steam at 100° C. and one atmosphere pressure can be compressed to water which occupies 0.6 cc. In this case, therefore, the free space in one liter of gaseous water must have been at least 999.4 cc.

The actual spacing of the molecules may be calculated with fair accuracy from the number per cubic centimeter. Thus 1 cc. contains 2.7×10^{19} molecules. Taking the cube root of this we have the number in one linear centimeter. This number is 3×10^6. The distance apart from center to center averages, therefore, 3.3×10^{-7} cm. ($=0.00000033$ cm.). It must be noted that this is the *average* spacing. The actual distance apart of contiguous individuals will, of course, vary widely, and will be constantly changing.

Size of Molecules.—Molecules vary considerably in size, depending on the substance from which they come. This we should, of course, expect. And yet the variation is not so great as one might expect it to be. The fact is that molecules must be regarded as complex systems, and not at all like smooth balls, as we sometimes erroneously imagine. To speak about the size of a molecule is somewhat like speaking about the size of our solar system. We might consider it as extending to the orbit of Neptune, for example, but the sphere of influence of our sun certainly extends farther than this. So the size of molecules is probably not a very definite thing, and is probably a question of how far the sphere of influence extends in each case. Hence we are not very much surprised to find that, so far as we can measure, the hydrogen molecule does not differ very largely in size from the water molecule or even from others which we might expect to be much larger. We may include here one method of calculating at least the approximate size of molecules. In speaking about the spacing of molecules we showed that one liter of carbon dioxide gas under standard conditions could be condensed to a liquid occupying 2 cc. If we call 2 cc. the total volume of all the molecules in one liter and divide this by the number of molecules in one liter (2.7×10^{22}) we shall have the volume occupied by one molecule of CO_2. We find this to be 7×10^{-23} cc. The volume of one water molecule, calculated in the same way, is 3.03×10^{-23} cc. One liter of hydrogen gas under standard conditions gives, when condensed, 1.3 cc. of liquid hydrogen. Dividing this by the number of molecules per liter, as above, we obtain for the volume of one hydrogen molecule 4.8×10^{-23} cc. All these calculations are based on the assumption that the space occupied by the liquid is equivalent to the combined volume of all the molecules, and this may not be quite true; but the values obtained in this way are not far from those calculated in other ways, and so are probably not greatly in error. They show conclusively that molecules of different substances do not necessarily vary widely in size even when they do vary in mass.

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* Amadeo Avogadro (1776–1856), Professor of Physics at the University of Turin. No physical law ever discovered is more fundamental and far-reaching than Avogadro's Law.

We should note here that all calculations lead inevitably to the conclusion that the molecules of any one kind are of the same size and mass. Thus, if some of the molecules of a gas were larger and heavier than the rest they would move at a slower speed. If such a gas were made to pass through a porous partition the small, speedy molecules would get through first, and we should thus be able to separate the gas into varieties having different physical properties. This has never been done, and we therefore conclude that the molecules of any one kind are exactly alike.*

Mean Free Path in Gases.—One of the most important points connected with the theory of gases is the matter of the average distance over which the molecules travel between collisions. This is called the " mean free path." It is not to be confused with the average spacing mentioned above, for a molecule may travel several times the average spacing distance before colliding with another molecule. As calculated by several reliable methods, the mean free path for any gas under standard conditions is not far from 0.00001 cm.† If the average spacing is 0.00000033 cm., it follows that a molecule passes about thirty of its neighbors before it finally collides with one; that is, the mean free path is about thirty times the average spacing.

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* Some very recent work by W. D. Harkins seems to indicate that ordinary chlorine gas may possibly be separated by diffusion into two isotopic forms having the same chemical properties but different molecular weights. This fact does not, however, refute the statement made above, for the two forms of chlorine cannot be regarded as quite the same substance. Harkins' paper appears in Science, Mar. 19, 1920, page 289.

† This value was first calculated by Clerk-Maxwell, the noted English physicist, 1860. See Phil. Mag. (1860; 4th series), **28**. See also, O. E. Meyer, Kinetic Theory of Gases.

The matter of mean free path carries with it some important consequences. In the case of a gas at ordinary pressure where the mean free path is only 0.00001 cm., it is evident that the molecules, in diffusing over a distance of a few centimeters, would have to travel over a very intricate zigzag path. Such diffusion would then be, in general, a rather slow process. If, however, the pressure of the gas were lowered to say 1 mm. the mean free path would be several hundred times as great, and, other things being equal, the rate of diffusion should be very much increased. This is nicely shown by the great increase in the speed with which a liquid evaporates in a vacuum desiccator. The molecules must diffuse between the molecules of the air to get away from the surface of the liquid, and since the number of these air molecules is made small the rate of diffusion is greatly increased.

Another matter which is dependent on the mean free path is the passage of electricity through gases. The only way gases can conduct electricity is by the process of convection. Certain molecules touch one of the electrodes and become charged. This charge they then carry by the process of diffusion to the opposite electrode. With gases at atmospheric pressure, the process, due to the short free path, is almost infinitely slow. They practically do not conduct at all. But in the so-called vacuum tubes where the mean free path is very much greater, conduction takes place with considerable readiness.

The Mutual Attraction of Molecules.—What we have said thus far might lead to the supposition that molecules always act as perfectly independent individuals. It is well known, however, that this is not the case. When a gas is dilute, that is, when the pressure is low, the molecules are so widely separated that they are for the most part outside each other's spheres of influence; but at high pressures when the molecules are brought close together, the attraction at once makes itself felt. This is seen in the fact that gases under high pressure depart widely from the ordinary gas laws—those of Boyle and Charles. In the liquid and solid states also, we can see at once that the molecules really exert an enormous pull upon each other. We know, for example, how much heat energy is required to vaporize a liquid, a process which acts against the molecular attraction. We shall often have occasion to consider this matter of attraction—a matter which was not taken into account in the early work on gases.

Structure and Kinetic Properties of Liquids.—Our discussion thus far has referred mainly to gases, and most of this applies equally well

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