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Title of Study: AVAGADRO'S HYPOTHESIS AND ITS DEVELOPMENT
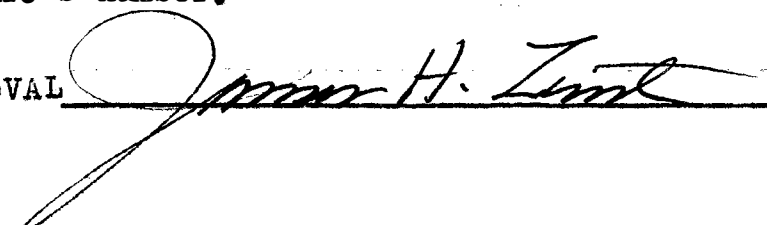
Pages in Study: 26

Candidate for Degree of Master of Science

Major Field: Natural Science

Scope of Study: The development of Avagadro's hypothesis
    from the time of its introduction has several impor-
    tant aspects. The first deals with its introduction
    and the events that led to its acceptance. The second
    deals with its applications that resolved some of the
    important controversies in chemistry when it was ac-
    cepted. Next, is the importance of Avagadro's number.
    The determinations of this constant are important
    because of the constant itself and also because of the
    principles that they illustrate. The last aspect deals
    with the way that Avagadro's hypothesis fits into the
    different areas of science. These aspects are devel-
    oped with materials taken from books dealing with
    general chemistry, physical chemistry, general physics,
    atomic and nuclear physics and history of chemistry.

Findings and Conclusions: Avagadro's hypothesis was among
    the first empirical laws introduced into science and
    accepted. This fact was at least partially responsible
    for the fact that it was not accepted when it was first
    advanced. Its acceptance led to a solution of several
    important problems in chemistry. The solutions of
    these problems provided a basis that was badly needed
    at that time. Much of the modern work concerning
    Avagadro's hypothesis deals with Avagadro's number.
    The methods of determining Avagadro's number vary wide-
    ly in principle. The five discussed best illustrate
    these methods, have the most historical significance
    or illustrate important scientific principles. The
    disagreement of the electrolytic and x-ray values
    are used to show the importance of these determinations
    to science as a whole. This example deals with the
    final adjustment of the value of the electronic charge
    and Avagadro's number.

ADVISER'S APPROVAL _____

AVAGADRO'S HYPOTHESIS AND

ITS DEVELOPMENT

By

REX DAVID GLOVER
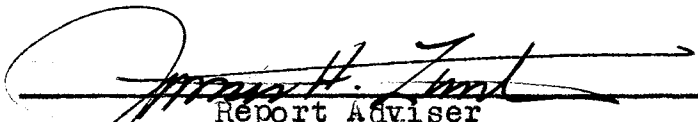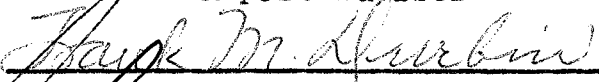
Bachelor of Science

Nebraska State Teachers College

Kearney, Nebraska

1955

AVAGADRO'S HYPOTHESIS AND

ITS DEVELOPMENT

Report Approved:

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Report Adviser

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Dean of the Graduate School

ACKNOWLEDGMENTS

I wish to express my appreciation to Dr. Frank M. Durbin and Dr. James H. Zant for their encouragement and advice while preparing this report. Acknowledgment is also due my colleagues in the seminar for their helpful suggestions and encouragement. I also wish to acknowledge the support of the National Science Foundation which made this study possible.

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PART I. INTRODUCTION

The scope of this report is to trace the development of Avagadro's hypothesis from the time of its introduction to the time that the value of Avagadro's number was definitely established. To do this, this report will be divided into four parts including the Introduction. The first part after the Introduction will deal with the introduction of Avagadro's hypothesis and the condition of science, especially chemistry, at that time. The next part will show how Avagadro's hypothesis was first applied. It is interesting to note that these applications were principally in the field of chemistry and were separate from any quantitative determinations of Avagadro's number. The last part will include discussions of several of the more important determinations of Avagadro's number. Several of these methods will be derived mathematically and the method used by the particular investigator will be discussed. The last part will deal principally with the field of physics.

This topic is important for several reasons. Four that are most important will be cited here. First is the fact that Avagadro's hypothesis has applications in

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the fields of both chemistry and physics. This, along with the mathematical treatment necessary, demonstrates remarkably well the continuity and interrelationships of science and mathematics. Second, Avagadro's hypothesis was among the first of the empirical laws of science to be introduced and finally accepted. Third, Avagadro's hypothesis is the basis for the determination of atomic weights and much of the present atomic theory. Fourth, the importance of the quantitative determinations is indicated by the statement, "Avagadro's number is the most important physical constant known".[1]

There are three apparent ways that the material in this report can be used by or will benefit a high school science teacher. First is the fact that it should add to one's background in science and mathematics. Second, parts of the content of this report can be used in most science classes, especially chemistry and physics. Third, it should be possible to use the content of this report as enrichment material for the more able students.

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[1]Alexandar Findlay, A Hundred Years of Chemistry (New York, 1937), p. 85

PART II. STATEMENT AND ACCEPTANCE

"The devil may write chemical textbooks", Berzelius had remarked, "because every few years the whole thing changes."[1] This was once again true in 1811. Chemistry was about to undergo far reaching changes. These changes, however, were to be much more basic and permanent than many previous changes had been. They also were going to resolve many of the conflicts and controversies that had hindered the progress of chemistry for many years. This was all due to the work of Amedreo Avagadro, a professor of physics at the University of Turin in Italy.

Avagadro's hypothesis is simply stated as "equal volumes of gases under same conditions contain the same number of molecules".[2] His hypothesis along with an explanation was published in the scientific magazine, Journal de Physique, in 1811.[3] This hypothesis introduced two new concepts into science. The first was a new meaning

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[1] Bernard Jaffe, Crucibles: The Story of Chemistry (New York, 1948), p. 157

[2] Ibid., p. 169

[3] Ibid., p. 157

of the word, "molecule". Until Avagadro's hypothesis was accepted, the word, "atom", was used to represent both atoms and molecules. It was also common for the words "atom" and "molecule" to be used interchangeably. The second was the simple idea that the number of these "molecules" in equal volumes of gases measured under the same conditions was the same.

Strangely, Avagadro's hypothesis was not immediately accepted by his contemporaries. This was true in spite of the fact that Ampere advanced a similar theory in 1814.[4] Several reasons have been given for this lack of immediate acceptance. The first was the fact that Avagadro was not a crusader. He was content to continue his teaching at Turin without being concerned with the lack of acceptance of his hypothesis. Second, Avagadro's hypothesis was not based on experiment. This was something new at that time and kept many from considering his hypothesis. Third, at about this same time the element iodine was discovered and isolated. This discovery was sensational and probably diverted the attention of many away from Avagadro's work.

Avagadro's hypothesis did not gain full acceptance until 1860, four years after Avagadro's death. Leading up to this was a period of turmoil in the world of chemistry. There were serious conflicts between the work of Gay-Lussac and that of Dalton. Equally serious was the lack of any

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[4]J. R. Partington, A Short History of Chemistry (London, 1951), p. 208

definite basis for the determination of atomic weights.
To resolve these and other conflicts so that chemistry
could once more advance, a meeting known as the Congress
of Karlsruhe was called at Karlsruhe, Germany in 1860.
At the Congress Cannizarro, a former student of Avagadro's,
presented a paper explaining how Avagadro's hypothesis
could be used to resolve many of the difficulties of chem-
istry. After three days the congress broke up without
any progress except the acceptance of Berzelius' atomic
symbols and the general realization that matters concerning
chemistry could not be decided by debate and vote.

All was not lost, however, as Cannizarro had taken
to the Congress copies of a letter published as "Outline
of a Course in the Philosophy of Chemistry".[5] The course
explained in this letter was based on Avagadro's hypothesis.
Cannizarro distributed copies to the members of the Congress.
They did not receive immediate attention but, as Cannizarro
had hoped, many later read his letter. It has been said
that Lothar Meyer put a copy in his pocket and later after
reading and rereading it he wrote, "It was as though the
scales fell from my eyes, doubt vanished, and was replaced
by a feeling of peaceful clarity".[6] Later, Meyer incorporated
Avagadro's ideas into his Modern Theories of Chemistry.

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[5]Jaffe, p. 163

[6]Ibid., p. 164

He, along with Cannizarro, caught the missionary spirit that Avagadro had lacked and soon Avagadro's hypothesis was accepted some fifty years after it was first advanced.

PART III. EARLY APPLICATIONS

It has been previously stated that Avagadro's hypothesis was first used in a non-quantitative way in the field of chemistry. To illustrate this use, two examples will be cited. The first is the use of Avagadro's hypothesis to explain the apparent conflicts between Dalton's atomic theory and Gay-Lussac's law of combining volumes. The second is the way that Avagadro's hypothesis provided a basis for the determination of atomic weights.

Dalton's atomic theory was much like the modern atomic theory except that he always spoke of atoms without mentioning molecules and he stated that the correct formula of a compound was always its simplest formula. This lead to errors such as speaking of "atoms" of water with the formula of HO.

Gay-Lussac had performed many experiments with gaseous reactions. He had carefully measured the volumes of reacting gases and their products. After analyzing his data, he stated his law. Gay-Lussac's law states that gases measured under the same conditions take part in chemical changes in simple volume ratios.

To illustrate the conflict between the work of Gay-Lussac and Dalton, consider the reaction of nitrogen and oxygen to form nitric oxide. According to Gay-Lussac's data, one volume of nitrogen reacts with one volume of oxygen to form two volumes of nitric oxide. Dalton, using his symbols, represented the reaction in this way:[1]

$$O + ⦶ \longrightarrow ⦶⦶$$

It can be seen that there is no possible way to make Dalton's representation agree with Gay-Lussac's experimental results. The controversy continued and Dalton finally chose to reject Gay-Lussac's law since it apparently disagreed with his atomic theory.

Others tried to resolve this difficulty in at least two different ways. The first was to "split" Dalton's atoms thus:[2]

$$⊖ + ⊕⊖ \longrightarrow ⊖⊕ + ⊖⊕$$
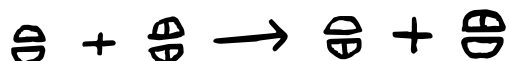
Another explanation introduced the word "molecule". These "molecules" then were divided into "integral molecules" represented in this way:[3]

$$∞ + ∞∞ \longrightarrow ∞∞ + ∞∞$$

The basis of these explanations was arbitrary. Therefore, neither could be considered valid. It is interesting to

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[1] Jaffe, p. 170

[2] Ibid.

[3] Edward Farber, The Evolution of Chemistry (New York, 1952), p. 132

note the similarity of these explanations to an explanation based on Avagadro's hypothesis.

An explanation, based on Avagadro's hypothesis, started with the concept of diatomic molecules in most elementary gases. If it is assumed that one started with N molecules of nitrogen and N molecules of oxygen, 2N atoms of each element could have been formed by dissociation. Since these atoms combined in a 1:1 ratio, 2N molecules of nitric oxide would have been formed. Since Avagadro's hypothesis also stated that there were equal numbers of molecules in equal volumes of gases, Dalton's atoms could be made to fit very well into Gay-Lussac's law. In fact, Gay-Lussac's law lends considerable support to Dalton's atomic theory. Another result of such reasoning was to change the concept of gaseous chemical reactions from a simple combination of atoms to the dissociation of molecules and then the combination of the resulting atoms.

Dalton, Dumas and Berzelius spent a great deal of time determining atomic weights. This was necessary in order to put chemistry on a quantitative basis. Each made separate basic assumptions and therefore none of their results agreed completely.

Dalton based his atomic weight determinations on his formulas. He considered the formula of the most common compound of two elements to be the simplest formula. For example, he considered that the formula of water was HO, of ammonia NH, of ethylene CH and his formula for methane

was CH_2. Since hydrogen was the lightest known element, he chose it as his standard and set its atomic weight at one. After running his analyses, he stated that the atomic weight of oxygen was 8, nitrogen was 4.5 and carbon was 6.[4]

Dumas, using Avagadro's hypothesis, assumed that the atomic weights of gases were in ratios of their density. This led to errors for two reasons. The first was that gases do not conform strictly to Boyle's law. The second was that all gases are not diatomic. Some examples of his values are mercury(monatomic) 100.8, sulfur(hexatomic) 94.4 and phosphorus(tetratomic) 68.5.[5]

The methods of Berzelius were more refined than those of Dalton and Dumas. His results were considerably more accurate. In fact, his results compare favorably with present values. His method was to take as many compounds of an element as he could obtain or synthesize, purify and then analyze them. By carefully studying his data and applying his own criteria, which was constantly changing, he obtained his values. He chose oxygen as his standard at 16 for two reasons. The first was his belief that oxygen was the center of all chemistry and the second was the fact that oxygen combines freely with almost all other elements.

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[4]F. J. Moore, A History of Chemistry (New York, 1939) p. 132

[5]Findlay, p. 48

To understand Berzelius' method better, consider his method for determining the atomic weight of sulfur. He prepared lead sulfate by oxidizing lead sulfide with nitric acid. After showing that no excess of lead or sulfur remained, he assumed that the ratio of lead to sulfur was the same in the sulfate as in the sulfide. At that time lead sulfate was considered to be a binary compound of lead oxide and the anhydride of sulfuric acid. Since he knew the amount of oxygen in the oxide of lead, he considered that the balance or three times that quantity, as his analysis showed, must be combined with the sulfur. Therefore, the number of atoms of oxygen combined with the sulfur must be three or some multiple of three. Since there was no evidence to indicate a multiple of three, Berzelius assumed it be be exactly three. Using his oxygen standard, the formula SO_3, and the results of his analysis, he set the atomic weight of sulfur at 32.[6] It is apparent that the methods of Berzelius were superior to those of Dalton and Dumas. Since he was never able to free himself from arbitrary assumptions, it was necessary for him to be continually modifying his figures as long as he lived.

To understand how Avagadro's hypothesis has been used to determine atomic weights, consider how the atomic

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[6]Moore, p. 105

weight of nitrogen could have been found. First, the
approximate molecular weight of free nitrogen was found
by determining the weight of 22.4 liters of the gas under
standard conditions. This step was based directly on
Avagadro's hypothesis. The result, 28, was the approximate
molecular weight of nitrogen gas. Since this may or may
not have been the atomic weight because the number of
atoms in a molecule was not known, it was necessary to
analyze several compounds of nitrogen after finding their
molecular weights. Again, Avagadro's hypothesis was ap-
plied when finding the molecular weights of gases. After
analyzing several compounds, a table such as follows could
have been set up.[7]

TABLE I

AMOUNT OF NITROGEN IN NITROGEN COMPOUNDS

substance	molecular weight	nitrogen per cent	amount of N in 1 mol. wt.
nitrogen	28	100.00	28 grams
nitrous oxide	44	63.64	28 grams
nitric oxide	30	46.68	14 grams
ammonia	17	77.68	14 grams

Since the smallest weight of an element found in a mol-
ecular weight of any of its compounds is considered to
be its atomic weight, the approximate atomic weight of
nitrogen was determined at 14.

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[7]John Arrend Timm, _An Introduction to Chemistry_
(New York, 1932), p. 80

To obtain an accurate atomic weight of nitrogen, one
of its oxides was analyzed. For example, nitrous oxide
is 63.64 per cent nitrogen and 36.36 per cent oxygen.
To determine the amount of nitrogen combined with 16
grams or one gram atomic weight of oxygen, the following
calculations can be used.

$$\frac{63.64}{36.36} = \frac{x}{16}$$

$$x = 28.016$$

Since this weight is a multiple or a factor of the true
atomic weight and the approximate value is 14, the atomic
weight of nitrogen is fixed at one-half of 28.016 or 14.008.

PART IV.   DETERMINATIONS OF AVAGADRO'S NUMBER

There have been many determinations of Avagadro's
number. The five that are probably most important will
be discussed here.

The first determination of Avagadro's number was by
Joseph Loschmidt, a Viennese schoolmaster.[1] Loschmidt
did his work in 1865. His method made use of two expres-
sions for the mean free path of a gaseous molecule. The
expressions are

$$L = 1/\sqrt{2\pi Na^2} \text{ and}$$

$$L = k/0.499 \text{ cd,}$$

where N represents Avagadro's number, a the diameter of
a molecule, k the viscosity constant, c the mean velocity
of a molecule and d represents the density of the par-
ticular gas. By setting the right members of the equations
equal to each other, Loschmidt obtained

$$1/\sqrt{\pi 2Na^2} = k/0.499cd.$$

This equation has only the quantities N and a undetermined.
Loschmidt's problem was to express a in terms of N. To
do this he assumed that the molecules were spherical and

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[1]Neil Adam, Physical Chemistry (London, 1956), p. 636

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therefore the volume, V, of N molecules was expressed by

$$V = N\pi a^3/6.$$

When this equation was solved for a, it gave

$$a = \sqrt[3]{6V/\pi N}.$$

In order to determine the volume, V, Loschmidt liquefied one cubic centimeter of the gas and used that volume as V. When he substituted the value obtained into his equation, he found that there was 2.705×10^{19} molecules in one cubic centimeter of a gas. This set Avagadro's number at 6.062×10^{23}. Since Loschmidt first determined this constant, it is sometimes known as Loschmidt's number instead of Avagadro's number. This is especially true in Germany.

Another method of determining Avagadro's number was done by Perrin in 1908. Perrin's method involved Brownian motion and was probably the first quantitative demonstration of the actual presence of molecules. Brownian motion is the phenomenon involving the motion of extremely small particles in a medium of some sort. Examples of Brownian motion are the motion of smoke particles in still air and the motion of colloidal particles. Since these particles follow a path such as the kinetic theory postulates for gas molecules, it was thought that their motion was due to their collisions with molecules of the medium in which they were suspended.

Perrin's method of determining Avagadro's number was based on the fact that in certain colloidal suspensions

the energy of translation of the colloidal particles is the same as that of the volecules in the suspending medium. Thus, the kinetic energy, $\frac{1}{2}MU^2$, of the colloidal particle is equal to $\frac{1}{2}mu^2$, the kinetic energy of the suspending molecules.[2] M and m represent the masses and U and u represent the mean velocities of the colloidal particles and molecules respectively.

For gas molecules, it can be shown that the pressure, p, is represented by

$$p = nmu^2/3$$

where n represents the concentration of molecules. If V represents the gram molecular volume,

$$pV = nmVu^2/3 = RT,$$

where R is the universal gas constant and T represents the temperature on the Kelvin scale. The quantity, nV, becomes N, the total number of molecules in a molecular volume or Avagadro's number. Since

$$Nmu^2/3 = RT$$

and RT is known, any method of determining $mu^2/3$ makes N determinable. Since the kinetic energy relationships stated above make

$$MU^2/3 = mu^2/3,$$

a determination of either quantity makes Avagadro's number determinable.

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[2] C. N. Hinshelwood, _The Structure of Physical Chemistry_ (New York, 1951) p. 16

Perrin's method of evaluating $MU^2/3$ depends upon a study of the sedimentation equilibrium in colloidal suspensions.[3] Colloidal particles tend to settle to the bottom until they come into equilibrium on account of their motion. This sedimentation equilibrium is analagous to the equilibrium of a column of gas under gravitational force and may be treated similarly. Since this is true, the concentration, n, of colloidal particles in a dispersion decreases as the height, h, increases. Suppose that in a column of unit cross-section at a height, h, the concentration is n and at the height $h + dh$ the concentration is $n + dn$. (The expressions dh and dn are used to represent small changes or increments in the value of h and n respectively) Between the two respective planes there are n dh particles. These particles are urged downward with a force of wn dh where w is the effective weight of each particle. Since the suspension is in equilibrium, the downward momentum must be balanced by an upward momentum which is due to the motion of the particles. This is analagous to gas pressure. Since

$$p = nMU^2/3 \text{ and}$$
$$dp = MU^2 dn/3,$$

this expression for dp must balance the expression, wn dh. Thus

$$wn \ dh = -MU^2/3.$$

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[3] Henshelwood, p. 17

The significance of the minus sign is that the forces are
equal but oppositely directed. This differential equa-
tion is solved with the following steps.

$$\frac{dn}{n} = -\frac{w}{MU^2/3}dh$$

$$\ln\frac{n}{n_0} = \frac{w(h-h_0)}{-MU^2/3}$$

Thus $MU^2/3$ can be determined if n, n_0, h, h_0 and w are
determined.

Perrin's first step was to prepare uniform colloidal
suspensions of gum mastic and gum gamboge. He first pre-
pared colloidal particles by grinding and then prepared
uniform suspensions by fractional centrifugation. His
next step was to determine w, the effective weight of each
particle. To do this, he first determined the density of
the particles by placing them in solutions of varying
densities until they did not settle when violently cen-
trifuged. He took the density of the final solution as
the density of the particles. To find the volume of the
particles, he evaporated dilute suspensions on a slide.
By taking advantage of the fact that the particles lined
up in rows during evaporation, he measured the length
of a row and then counted the number in such a row to
determine the diameter of a particle. He could not make
direct measurements because of diffraction. He used
particles whose radius was about 2.12×10^{-5} centimeters.[4]

[4]A. J. Rutgers, Physical Chemistry (New York, 1954)
p. 35

Perrin's evaluation of h and n was done with a microscope with a sharp focus and a micrometer arrangement for measuring the distance between settings. He found, for example, that the concentration of particles decreased by one-half in a height of 0.03 millimeters.

It can be seen that Perrin's work must have been very difficult and exacting. His values of Avagadro's number ranged from 6.5×10^{23} to 7.2×10^{23} with an average of 6.85×10^{23}.[5]

Rutherford, Geiger and Boltwood used the phenomenon of radioactivity to determine Avagadro's number. It was known that many of the heavier elements spontaneously undergo nuclear changes. Some of these changes involve the emission of alpha particles. Experiments had shown that alpha particles were helium ions and soon after emission take up two electrons to become helium atoms. Since alpha particles were emitted at a constant rate, all that was necessary to determine Avagadro's number was to determine the rate that radium (in this case) emitted alpha particles and then measure the volume of helium formed in a given interval of time.

Rutherford and Geiger used two different methods to determine the rate at which radium emits alpha particles. The first method was based on the fact that a zinc sulfide screen gives off flashes of light when subjected to alpha

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[5] Rutgers, p. 35

particles. It was possible to set up an apparatus so that the operator could count the number of scintillations occuring in a given period of time. The second method made use of electronic circuits to run the count. They found that one gram of radium emits 3.4×10^{10} alpha particles per second.

Rutherford and Boltwood set up an apparatus to collect the helium gas given off from a given amount of radium. they found that one gram of radium emits helium at the rate of 1.07×10^{-4} milliliters per day at standard conditions. These figures can be used to calculate Avagadro's number as follows:

$$\frac{22,400}{1.07 \times 10^{-4}} \times 3.4 \times 10^{10} \times 24 \times 60 \times 60$$

This calculation sets the value of Avagadro's number at 6.15×10^{23}.[6]

The earliest accurate method of determining Avagadro's number was the electrolytic method. The basis of this method was given by Faraday when he stated that a given current through solutions of different univalent elements deposits weights of these elements proportional to their atomic weights. This statement lead to the determination of E/M, the ratio of the charge of an ion to its mass.

As an example of E/M consider silver. One emu of charge deposits 0.01118 grams of silver. This makes E/M

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[6]Farrington Daniels, Outlines of Physical Chemistry (New York, 1958) p. 626

for silver 1/0.01118 or 89.44 emu. Consider hydrogen as another example. Since the ratio of the atomic weights of hydrogen and silver is 107.88/1.008, E/M for hydrogen is expressed by

$$\frac{107.88}{1.008} \times 89.44 = 9,573 \text{ emu.}$$

One should note that E/M is not constant for all elements.

Next, consider the product, Ne, where N is Avagadro's number and e is the electronic charge. Let m refer to an imaginary univalent atom of weight equal to 1/16 of oxygen or 1/107.88 of silver. For this case, E/M becomes e/m which is calculated by

$$\frac{107.88}{0.01118} = 9,649.4 \text{ emu or}$$

$$\frac{e}{m} = 9,649.4 \text{ emu.}$$

Now multiply by N/N. The equation becomes

$$\frac{Ne}{Nm} = 9,649.4 \text{ emu.}$$

Since the original conditions set Nm at one, the equation becomes

$$Ne = 9,649.4 \text{ emu.}$$

This product is constant for all elements having a valence of one. This can be shown true for hydrogen by using the previous figures. With Ne known, any determination of e makes N determinable.

The first accurate determination of e was done by Robert Millikan with his famous oil drop experiment in 1913. Millikan's value for e was 4.774×10^{-10} esu. Since Ne is 9,649.4 emu or $28,948 \times 10^{10}$ esu, N was

determinable. Millikan's value of N was 6.062 x 10^{23}.[7]

Probably the most accurate single determination of Avagadro's number was done through a study of x-ray diffraction by Compton, Duan, Bearden and others.

To understand the principle of diffraction, consider the "reflection" of x-rays from the atomic planes such as exist in rocksalt or any other crystal. This arrangement is shown in figure 1. Consider the incident rays I and
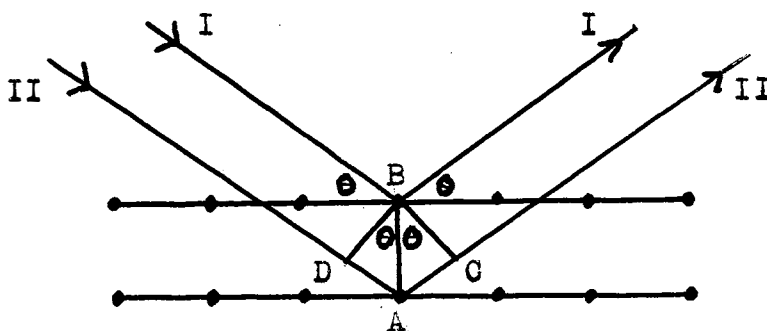
Fig. 1 Reflection of X-rays by
Atomic Planes

II along with their reflections. In order for reflections I and II to reinforce each other and thus produce a bright spot on a photographic plate, they must be in phase.

[7] Robert Andrews Millikan, Electrons (+and -), Protons, Photons, Neutrons and Cosmic Rays (Chicago, 1939) p. 27

Since ray II travels the distance AD   AC farther than
ray I, this distance must be the wave length or some
whole-number multiple, nW, of the wave length. The con-
dition for reinforcement is

$$AD + AC = nW.$$

But from the figure

$$AC = AB \sin \theta, \text{ and}$$

$$AC = AB \sin \theta.$$

If AB, the distance between atomic planes, is represented
by d, these equations added together become

$$AC + AD = 2d \sin \theta.$$

By substitution

$$nW = 2d \sin \theta.$$

This equation is known as the Bragg equation and gives
the condition for the reinforcement of reflected x-rays
from a series of atomic planes. Since n can take any
integral value, there can be a series of reinforcements
corresponding to $n = 1, 2, 3,$ etc. and $\theta = \theta_1, \theta_2, \theta_3,$ etc.

To understand the application of the Bragg equation
to a determination of Avagadro's number, consider the
arrangement of ions in a crystal of rocksalt. Rocksalt
has a cubical arrangement of ions with sodium and chloride
ions arranged alternately at the corners of the cube as
shown in figure 2. To find d, the distance between ions,
consider a crystal weighing M grams, M being the molecular
weight, with a density, D grams per cubic centimeter and
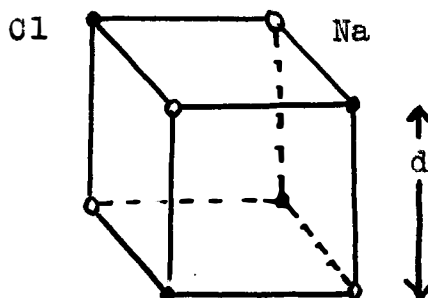volume, V cubic centimeters. Then V is expressed by

Fig. 2. Arrangement of Sodium and Chloride Ions
in a Rocksalt Crystal

$$V = M/D.$$

Since there are $2N$ ions in Avagadro's number or N molecules,
the volume, V, of each ion is expressed by

$$V = M/2DN.$$

Since

$$V = d^3,$$

the distance, d, between ions becomes

$$d = \sqrt[3]{M/2DN}.$$

Since M and D are known, N becomes determinable when d
is found by the Bragg equation.

To determine d by the Bragg equation, x-rays of known
wave length must be used. At first this was impossible.
In fact, the wave length of x-rays was first determined
by using this same method and previous values of Avagadro's
number. In 1925, Compton and Doan showed that it was
possible to measure accurately the wave lengths of x-rays
of the order of 10^{-8} centimeters with a ruled grating of
a few hundred lines per millimeter. This technique gave

values of the wave length of better than 0.01 per cent.

Since it was difficult to obtain rocksalt crystals of sufficient size and purity, calcite was frequently used. Since calcite does not have a regular cubic arrangement, the expression,

$$V = \phi d^3,$$

was used to determine d. In the case of calcite, $\phi =$ 1.09594. Bearden, using calcite, found Avagadro's number to be 6.0221×19^{23}.[8]

Since Millikan's value of Avagadro's number was known before ruled grating values of x-ray wave lengths were determinable, his value was used to determine x-ray wave lengths with crystals. When ruled grating values of wave lengths were determined, it was found that the x-ray wave lengths determined by grating disagreed with those found by the crystal method. Several investigated this difference and first suggested that the ruled grating method of determining x-ray wave lengths was inaccurate. The work of several investigators showed that the ruled grating values were accurate and the suggestion was made that Millikan's value of e, the electronic charge, and Avagadro's number were in error. After many careful investigations, it was found that the value of e needed to be raised and Millikan's value of Avagadro's number needed to be lowered. It was also found that Millikan's value

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[8]Adam, p. 640

for the viscocity of air used in his oil drop experiment was in error. When the corrected value was used, the new oil drop value of e and Avagadro's number agreed very closely with the values obtained by the x-ray method.

The present accepted value of e is

$$(4.8025 \pm 0.0010) \times 10^{-10} \text{ esu}$$

and the present value of Avagadro's number is

$$(6.0228 \pm 0.0011) \times 10^{23}.[9]$$

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[9]Adam, p. 637

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