ABERRATIONS
FROM THE IDEAL GAS LAWS
AND
A PRECISION METHOD FOR THE DETERMINATION OF
THE DENSITIES OF GASES

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PRECISION METHOD FOR THE DETERMINATION OF THE DENSITIES OF GASES.

Thesis

by

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GENERAL INTRODUCTION.

" Measurement" plays the role of modulator and investigator in many branches of science. In general, it seems to be the avocation of a natural philosopher to enunciate laws, and then by measurement to seek exceptions to them. These usually discovered exceptions and failures of applicability more often than not yield conclusions which may overshadow the fundamental generalization itself. This is very well illustrated in the development of the so called equations of state for gases, and the general applications of the theoretical statements usually referred to on the whole as the Kinetic Theory of Gases.

The combined laws of Boyle and Charles may be expressed in mathematical symbols, and yield what might be called the fundamental equation of state for gases. Gases which obey this law exactly are referred to as ideal gases.

The complete adherance to this equation on the part of a gas must presuppose certain conditions in the gas some of which are true, but all of which may be approached only in certain limiting cases. The expression depends for correctness on the fact that the gas is composed of discrete particles called molecules and the rough approximations that these molecules may be treated as mathematical points, that is they have no real volume, and finally that the molecules have no attraction or repulsion for each other.

Measurements, following the enunciation of the law, showed that at least two of these factors must be in error. Some results of Boyle demonstrated that the equation was not entirely applicable to actual gases, but it remained for the classic researches of Amagat and others to evidence the amount of deviation that could be expected, and to offer sufficient data to make possible a second approximation, and the formulation of a second gas law equation.

Amagat's(1) data discloses that the equation of the ideal gas did not hold. These in the hands of Van der Waals resulted in a second, now famous, equation, the so called Van der Waals equation of state.

Van der Waals postulated a solid spherical molecule which attracted another according to some inverse square law. This leads to two corrections to the gas law equation usually written

$$PV = \frac{w}{M} RT \qquad \text{------------(1)}$$

The first correction was applied to the term V to represent the finite size of the molecules, and the second to the term P to represent the influence of the attraction of the molecules for each other on the pressure at the boundaries of the gas.

The need for the correction to the pressure term may be seen from the rough description that follows.

Consider a molecule at the centre of a gas; this molecule is surrounded by a statistically equal field of force on all its sides granted that the same forces exsist between all the molecules. If however the molecule moves to one of the boundaries of the gas it becomes attracted to the centre more than towards the instrument used for measuring the pressure. This results in the pressure on a manometer being less than the pressure in the centre of the gas. This argument is fully explained by Jeans(13) and others who show the origin of the additive correction term $\frac{a}{V^2}$.

In the same way, if the molecules have a volume the V term must be corrected to allow for this and the ideal gas equation then becomes,

$$\left(P+\frac{a}{V^2}\right)\left(V-b\right)=RT \qquad \text{---------(2)}.$$

where b is a constant and some function of the total volume of the molecules.

Van der Waals' equation follows the experimental results of actual gases more closely that the ideal gas law equation, but does not hold rigidly enough. Subsequent investigation showed that neither a, nor b, were constant over all pressure and temperature ranges. The variation of b may be explained on the results of more recent theory that b does not represent a function of the actual volume of the molecules, but rather of the volume of the sphere of influence which varies at different temperatures, and pressures. Jones puts it,

> " A rigid sphere is merely a repulsive field of infinite magnitude concentrated within a thin spherical shell, so that the attractive and repulsive forces of a Van der Waals' molecule occupy separate compartments of space ".

The variation of b has been measured recently by Maass and Mennie, and Maass and Carpenter.

The recognition of these facts lead to the proposal of many other equations based on Van der Waals' model some of which portrayed the behavoir of actual gases more accurately, but none of which had the applicability of Van der Waals'. Of these only one will be mentioned in detail since a somewhat similar one will be proposed later on in this discussion.

A second general method of development has been used by Jones, Klesson, Core, and others, of which the work of Jones has the greatest applicability since it offers a clear physical picture of the equtaion. This method makes no assumption regarding the nature of a molecule except that it has a spherical field, obeying some inverse square law. From statistical reasoning Jones develops the equation

$$PV = NRT + \frac{B}{V} \qquad \text{-------(3).}$$

where B is some function of the temperature, and the other symbols have their usual significances. The value of B is

$$\frac{\pi N}{j}\int_0^\infty q^2\left(e^{2j\pi(q)}-1\right)dq$$

where a constant attractive force and a varying repulsive force is postulated. Jones points out that a separation of B into Van der Waals' a, and b, is impossible except in a purely mechanical manner.

The molecular models outlined above probably have uses peculiar to themselves, the first in conjunction with gases of high attractive fields the second in consideration of the more permanent gases of relative low molecular constants of attraction.

It has been mentioned above that one equation based on a Van der Waals' molecule will be treated in some detail. This equation is that of Maass and Mennie. It is explained fully in a publication by them.

Maass and Mennie arrived at the expression

$$P = \frac{1}{3} m n x^2\left(1 + \frac{2r}{\ell}\right) \qquad \text{------(4).}$$

which by substitution of the value of ℓ_0 and the use of Sutherlands constant $\ell = \ell_0 \dfrac{1+\frac{C}{273}}{1+\frac{C}{T}}$ reduced to

$$PV^2 - RTV + a - RT\beta\left(1+\frac{C}{T}\right) = 0 \qquad \text{------(5).}$$

where $\beta = \dfrac{8\sqrt{2}\,\pi r^3 N}{1+\frac{C}{273}}$

or $$b = \beta \left(1 + \frac{c}{T}\right)$$

If a first order approximation is made, namely that

$$\left(1 + \frac{2r}{l}\right)^{-1} = 1 - \frac{2r}{l}$$

since l is large compared to r

the equation reduces to the form

$$\left(P + \frac{a}{V^2}\right)\left(V - 8\sqrt{2}\,\pi r^3 N\right) = RT \qquad \text{---------(6).}$$

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

where

$$b = 8\sqrt{2}\,\pi r^3 N$$

an equation identical with that of Van der Waals.

The measurements of Maass and Mennie on carbon dioxide, and those of Carpenter on Sulphur dioxide served to test the validity of this equation. It was found to hold within experimental error at temperatures greater than 0°C but failed at temperatures below, due possibly to the fact that Sutherlands formula is not valid for temperatures below the ice point. It was the first equation that linked up deviations from the ideal gas laws with viscosity measurements.

II.

Equations of state have been used for a second purpose apart from their applicability to the representation of the actual behaviour of gases, namely the determination of theoretical molecular weights from measurements of gas densities.

Guye and Frederich develop the following relationship

$$\frac{M}{L}(1+a)(1-b) = 22.414 \qquad \text{------(7).}$$

where M is the molecular weight of a gas (0 = 32.000) and L is the weight of a normal litre of gas.

This equation holds for actual gases to within the limits of experimental error, but it has been pointed out that both a, and b, which are constants calculated empirically may contain errors that compensate one another.

The use of this equation offers a means of extrapolating the value of the weight of a normal litre of gas, or more truly, Avagadro's molecular weight under standard conditions, to a limiting density by means of Berthelot's equation which is considered to be rigid. Up to the present no data of sufficient accuracy to test these various hypotheses have been available. Data, with sufficient accuracy to do this are presented herein.

III.

The object of the experimental work was to obtain data of sufficient accuracy for several purposes, the first to test Berthelot's hypothesis, the second to determine if the isotherms were straight lines at low densities, and the third to test an equation of state as rigorously as possible over a relatively large temperature range, but at comparatively low densities.

The gases chosen were carbon dioxide, and sulphur dioxide, largely because these have been the subject of many classical investigations, but also on account of the facts that they are relatively easy to purify, and are suitable ones to use with the method of measurement employed.

A greater amount of attention has been paid to carbon dioxide, somewhat on account of its greater historical interest, but mainly on account of the fact that its viscosity has been measured with a great degree of accuracy.(14) The need of accurate viscosity data will be apparent later. Unfortunately the data on the viscosity of sulphur dioxide are neither great in number nor consistent among themselves.

Curves are shown which permit the determination of the theoretical molecular weight to about .02% by direct extrapolation without the use of any equation involving empirical constants. Thus it is demonstrated experimentally for the first time that

Berthelot's assumption, namely that the molecular weight of a gas approaches its theoretical value as its density becomes infinitely small, is true to within the present experimental error in determining atomic weights.

The method of measurement first devised by Maass and Russel, and later used by Maass and Mennie, and Maass and Carpenter, seemed to offer the greatest advantages so a modification of this was used. Experimental technique had to be considerably revised and extended to give results of the desired accuracy. This resulted in several changes in apparatus design, necessitated several extraneous experiments, and required some changes in experimental manipulation.

Improvements were made in all the four measurements contributing to the final result which is expressed as apparent molecular weight. The size of the constant bulb was increased five times and standardized with the same deviation. This in itself offered considerable difficulty. The manometers were enclosed in a constant temperature bath to insure accurate temperature corrections to pressure readings. Temperatures were read to the nearest 0.01°C, with mercury thermometers at the higher temperatures, and with a platinum thermometer used with a Mueller bridge at the lowest temperature. The system of weighing was redesigned entirely. The latter was required not only from the point of view of accuracy, but also from the point of view of the greater danger to person and equipment resulting from the handling of relatively large quantities of gases enclosed in glass tubes at considerable pressure. A knowledge of the bursting point of Pyrex glass tubes was desired; a set of experiments was carried out to determine this. The details of these improvements in apparatus design and experimental technique which enabled the desired accuracy to be obtained are described in detail in the section on experimental procedures.

INTRODUCTION TO MEASUREMENTS

Consider the gas law equation

$$PV = \frac{w}{M} RT \qquad \text{-----------(1).}$$

which may be written in the form

$$M' = \frac{wRT}{PV} \qquad \text{----------(1).}$$

where M' represents the apparent molecular weight at any corresponding set of conditions P', V', and T. In effect M' is equivalent to the molecular weight of the gas under the specified conditions assuming the gas to be ideal. In general the molecular weight of an actual (non ideal) gas is a function of both the temperature and pressure, and a knowledge of the changes in M' admits of an extrapolation along any isothermal to infinitely small densities, and hence affords a means of determining theoretical molecular and atomic weights. Furthermore if the other terms of the equation be known then a solution for $\bar{V}$ is possible, if $\bar{V}$ represents the actual volume occupied by a theoretical molecular weight of the gas under the specified conditions. This is the quantity used in testing the gas law equations. The experiments were designed to enable a calculation of M', and a discussion of the limits of measurement imposed by the necessary accuracy follows.

Reference to equation 8 evidences that

there are five unknowns four of which are capable of direct measurement, and the fifth, M', may be calculated. A maximum experimental error of not greater that 0.02% was indispensable for the reasons mentioned above, therefore each measurement had to be made with an accuracy of something better than 0.005%. This follows immediately from the fact that each term enters the equation directly and to the same power, and the approximate assumption that each unit may be measured to the same degree of accuracy. This is not true but is sufficiently accurate for a preliminary discussion.

Reference to the section on the description of the methods employed to measure each term will show that the following maximum errors can be estimated:- in pressure ± 0.003 cm., in temperature ± 0.01°C., in weight ± 0.0002 gm., and in volume ± 0.0001 l. The lowest measurable quantity of each term is limited by the fact that each must contribute a deviation of not greater than 1/20000 to the final result, thus the lowest possible pressure that can be used with mercury as the manometer liquid is $\frac{1}{4}$ atmosphere or roughly 25 cm. of mercury. At this pressure the corresponding weight was found to be about 3.0 gm. This therefore is the lowest limit of measurement for single readings. In the actual experiments it was found that the volume of 5.5 l. could be determined to ± 0.01 ml. at the point of standardization, and ± 0.05 at other conditions. This justifies the measurement of pressures between 20 and 25 cm. of mercury.

As a result of the above, the apparatus may be described roughly as a unit for measuring simultaneously the four terms, P, V, W, and T. The measurement of each unit will be particularized sufficiently to disclose the possible sources of error.

A typical calculation for M' is shown on page 48. All calculations were based on equation 8 using the necessary corrections described later. For this reason it is well to discuss the units of the equation.

The true value for M' may be defined as that value calculated from the above equation when P is expressed in atmospheres at 45° of latitude, and sea level. All units of the equation must conform to this. For instance if $P = P_{45^\circ \text{lat.}}$ sea level then the value of R must be calculated from the same unit, and not the normal atmosphere. and if R be expressed in $\frac{\text{l. at.}}{\text{moles }^\circ\text{C}}$ V must be expressed in litres and not in cm.^3 T in degrees centigrade + 273.18 and w in gm. at 45° lat. and sea level.

The following units were used in the

standardizations and calculations :-

g	980.616
litre	1000.027 cm .
ice point	273.18 °A
d_{H_2O}	0.996460 $\frac{\text{gm.}}{\text{ml}}$ at 27.29°C.
R	0.082046 $\frac{\text{l. at.}}{\text{moles °C.}}$

THE APPARATUS? AND EXPERIMENTAL MANIPULATION.

I.

Standardization and Calculation of Volume.

The constant volume bulb was constructed from a five litre round bottom Pyrex flask which had been aged for a sufficient length of time to allow for shrinkage. The neck of the flask was drawn down and sealed to a four mm. bore stop-cock.

Standardization of the flask was carried out as follows. The balloon was carefully cleaned with strong cleaning solution, followed by a mixture of zinc and hydrochloric acid, then pure nitric acid, and finally washed with distilled water many times. During this procedure the stop-cock was allowed to remain in position. After complete washing the bulb was thoroughly dried by blowing through it a stream of carbon dioxide free, dry, air. When dry, the bulb contained only pure dry air at a known temperature. The pressure was read on an external barOmeter, and the stop-cock closed immediately after. This procedure permitted a calculation of the weight of air enclosed in the balloon. The bulb was placed on the balance pan and allowed to remain there at least twelve hours before weighing. It was weighed on both scale pans and the mean of the weights, corrected to the resting point of the balance, taken as its true weight in air against brass. The bulb was then filled with pure distilled water.

Filling, and washing the inside of the flask were conveniently carried out by partially evacuating and allowing distilled water to run in. Several repetitions enabled the bulb to be filled almost to the top. At this point the bulb was connected to a good vacuum pump, and the water inside boiled under vacuum for an hour or more to remove any traces of air either in the water or adhering to the walls of the flask. The remainder was then filled with recently boiled water through clean surgical tubing.

In order to secure the required accuracy it was necessary to know the temperature of the water to 0.05°C. This was determined as follows. The bulb was placed in a constant temperature bath controlled to about 0.004°C and running somewhat above room temperature. The overflow rose into a tube of 2 mm. diameter sealed to the stop-cock; readings of the meniscus were taken at intervals. When the position of the meniscus showed no change the water inside the flask was assumed to be at the temperature of that in the constant temperature bath. This required between six and eight hours. The temperature of the bath was read on mercury thermometer # PTR 3191 which was standardized as discussed in the section on temperature measurement.

After the bulb had reached constant temperature the stop-cock was closed, and a quantity of ice thrown into the bath immediately after. One could then assume that the bulb was completely filled with water at the temperature of the constant temperature bath, and that this temperature was known to ± 0.01°C. The extension tube was cleaned with suction, and dried with good alcohol and ether, and finally blown out with dry air. The outside of the bulb was carefully cleaned and the whole weighed in the same manner as before. The barometric height, and temperature of the balance case were read immediately after each weighing.

The standardization was repeated a second time. Again the stop-cock was removed and cleaned and the flask washed out and dried as before. The agreement between the results obtained shows that the absolute value is well within the limits of error.

The balance used was of 10 kilo. capacity, with a sensitivity of .02 gm. per .1 division with 500 gm. on each scale pan. It was tested for the more common structural defects in the usual manner. It was solidly set up, and protected from direct radiation by shades. It was reasonably free from temperature variation, errors from which would in any case be eliminated by the method of double weighing used. The balance arms were fatigued in the usual manner before reading for the balance point in any weighing.

The weights were a tolerance set purchased especially for standardizations. They were made of laquered brass, and were compared against the set used to weigh the small weighing tubes, directly to 50 gm. and then by intercomparison in the usual manner.

The following results were obtained in two complete experiments one of which is given in detail below.

True weight water in vacuo gm.	Temperature
5425.43	27.29°C
5425.40	27.29°C

Mean volume = 5444.70

if the density of water at 27.29°C be 0.996460 gm./ml.

Following are the details of a complete experiment.

Weight full bulb and holder gm.		Corrected weights to R.P. gm.
left pan	6076.820	6076.815
right pan	6076.440	6076.428
Mean		6076.62

Weight empty bulb and holder gm.

left pan	656.880
right pan	656.910
Mean	656.89

Weight water uncorrected = 5419.73

Weight dry air in globe 5419.7 X .001200 < 6.50 gm.
Weight air displaced by weights 5.42/8.39 = .77 gm.

True weight water in vacuo 5425.43 gm.

Volume in ml. 5425.43/0.996460 = 5444.71

Corrections to the Volume used in Calculations.

Two corrections are necessary to obtain the true volume corresponding to the temperature and pressure of any single run. The first is a correction for temperature and corresponding contraction or expansion of the bulb, and the second a small correction for the contraction of the bulb due to differences in pressure between the inside and the outside.

The first correction was calculated from the equation of Keyes, and roughly checked by using the approximate form of the equation involving the linear coefficient of expansion(6) of Pyrex glass. Both methods gave values which agreed sufficiently.

The second correction was measured directly by the method of Raleigh, which was investigated by Moles and Miravalles and adopted by them. Great care was taken to free the water from air. The method which is particularly suitable in this case showed that the function of the decrease in volume of the bulb with differences in pressure was a straight line.

The following results were obtained by direct measurement, and when corrected for the expansion of water were those used in the calculations;

Table I.

Change in volume of the constant volume bulb with differences in pressure between the inside and outside.

ΔP.	ΔV.
75	0.70
50	0.46
25	0.23
10	0.09

II.

Measurement of Pressures.

Reference to numerous tables will show that one of the pit-falls to be avoided in the construction of mercury manometers is the use of narrow bore tubes, since it is nearly impossible to clean a tube of the desired size sufficiently to prevent distortion of the mercury meniscus. At the same time too large a tube will cause loss of accuracy in reading the meniscus with a telescope and cross hair. The optimum size lies possibly between 13 and 20 mm. diameter in consequence of which the manometer arms were constructed of Pyrex tubing 15 mm. in diameter. In the actual manometers used it was proved that readings could be repeated even when the menisci were made to vary considerably in height, that is of the order of 0.1mm..

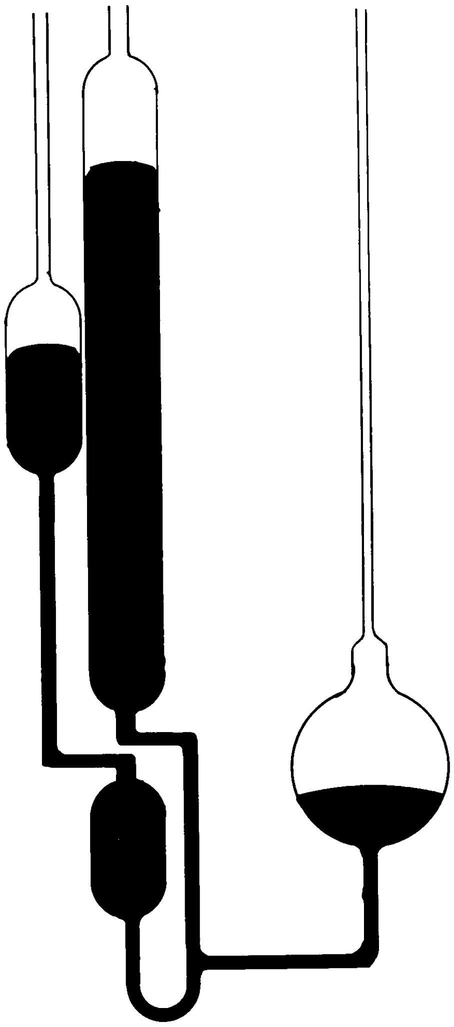

FIGURE 1.

The manometer in its final form.
Not drawn to scale.

The original form of the manometer was that more commonly used, so constructed that the two arms lay side by side. This form was tried, and failure of agreement in many experiments led to the conclusion that the necessary rack motion of a cathetometer bar which was slightly off vertical would cause considerable error in reading large differences in height. Finally the original form of manometer was replaced by one constructed as shown in figure 1 which required no motion of the cathetometer bar in reading original pressures. The small auxilliary arm used in reading residual pressures, placed as shown, required a small turning of the bar, but the difference in height being small, this caused no appreciable error in the difference.

The manometers and control resevoir were enclosed in a well stirred bath, the temperature of which was read immediately after each pressure reading. This was necessary to insure accurate temperature corrections. A variation of greater than 0.1°C causes an appreciable error.

Some interest is attached to the construction of the manometer bath and its lighting system since in a sense this controlls the accuracy of reading.

The bath of galvanized iron, was securely braced to prevent distortion. Five feet in height, with one foot square ends, it accommodated one or two manometers without crowding. The front was pierced and two plate glass windows set in. These were free from distortion. The back of the tank was similarly fitted with a large piece of plate glass Immediately back of this glass was placed a frame of larger size the face of which was covered with a layer of white tissue paper. The back of this frame was grooved to allow a slide of opaque material 4 x 12 inches to travel in a verticle plane parallel to the back of the takk. This slide was controlled from the cathetometer. Before any reading of the meniscus was attempted it was adjusted so that with the telescope (focused and free from parallax), a slight movement of the slide either up or down did not affect the apparent position of the meniscus as seen through the telescope.

The lighting system was fixed back of this slide. This system was so constructed that light from 8, 75 watt clear glass lamps was distributed evenly over the whole surface of the glass wall of the tank after being diffused through the thin tissue paper. A sheet metal reflector which enclosed the lights on three sides prevented undue lighting of the room. It was found that with this arrangement, and proper adjustment of the slide, telescope, and lights, readings of one meniscus could be repeated to 0.002 cm. even when the cathetometer had been thrown completely out of adjustment.

The cathetometer was purchased especially for the determination. The bar, of hard white brass was standardized by the department of Geodesy and Surveying, and showed a maximum correction of 40 u over the whole range, and 1.5 U over the interval used in the pressure readings. The corrections were therefore negligible in all cases.

Table 2.
Corrections to cathetometer bar.

Space cm.	Length at 0°C.	Scale error in microns.
0-5	4.999	-9
0-10	9.998	-17
0-15	14.998	-24
0-20	19.998	-25
0-25	24.999	-15
0-30	30.001	12
0-35	35.001	9
0-40	39.998	-5
0-45	44.998	-23
0-50	49.996	-40
0-55	54.997	-37
0-60	59.998	-21
0-65	64.998	-24
0-70	69.997	-35
0-75	74.996	-42
0-80	79.996	-39
0-85	84.998	-26
0-90	89.999	-14
0-95	95.000	-5
0-100	100.0005	0

The bubble sensitivity of the bubble on the telescope was given as 0.1 div./30" of arc. When received, the telescope had a minimum focal length of one meter which was too long to permit reading to .001 cm. with the bubble sensitivity shown. The lenses of the telescope were substituted by others which gave a minimum focal length of 13 cm.. Assuming that the bubble could be set to 0.1 div. this permitted the desired accuracy.

This was tested by clamping a standard meter bar in a fixed position and repeating readings on a fixed point, throwing the cathetometer completely out of adjustment between each reading. The following typical readings show that the required accuracy could be obtained.

Table 3.

Readings on fixed points.

Bar.	Cathetometer
95.000	84.305
95.000	84.305
97.000	96.836
97.000	96.836

Readings of intervals.

Bar interval	Cathetometer interval
90.000	89.970
90.000	89.968

Corrections to Pressure Readings.

Four corrections must be applied to all pressure readings to give the value used in the calculations

These are, a correction for the density of the mercury at the temperature of the manometer bath, a small correction for the residual pressure, a correction for latitude, and for height above sea level.

The correction for temperature was made by using the equation

$$P_0 = P_T - P_T \left[\frac{\sigma_m t_m - \sigma_c t_c}{1 + \sigma_m t_n - \sigma_c t_c} \right] \quad \text{---------(9).}$$

in which $\delta_m = .0001817$, and $\sigma_c = .0000189$.
Each value was calculated independently using the temperature of the manometer bath, and the temperature of the cathetometer scale.

The two final corrections, which together are very small were combined into one by the use of g as determined in the Observatory. The sizes of the corrections were calculated from the fundamental equation,

$$B_s = B_e \frac{g_e}{g_s} \quad \text{---------------(10).}$$

"g" at the laboratory being taken as 980.652.

III.

Determination of Mass.

The greatest advantage of this method of determining apparent molecular weights lies in the method of the determination of mass. It will be apparent from the detailed description given below that it offers considerable advantage in this particular over any of the classical methods used by Guye, Moles, and others.

The gas was condensed into weighing tubes as described later. These were sealed off and weighed at room temperature. The vapor pressure of carbon dioxide at room temperature is of the order of 60 atm. In view of this considerable pressure, and consequent danger from explosion, it was thought advisable to secure some data on the bursting strength of Pyrex glass tubing made into tubes of sufficient volume to hold the condensed gas. An apparatus was designed and several experiments made.

The tubes were sealed to a hydraulic press by means of the following arrangement. The press was fitted at the pressure end with a threaded nipple to which extraneous apparatus could be fixed. A brass tube of requisite diameter and length, was threaded to fit this outlet. A length of Pyrex capillary just sufficient to extend through this tube was bulged at one end, and covered for about five centimeters of its length with gold china paint.

When the laquer had been burned off a thin layer of gold was left adhering strongly to the outside wall of the capillary. This was heavily copper plated and tinned with ordinary solder. The tube was then centered inside the brass tube, which had been previously tinned on the inside, and the surrounding space filled with molten solder. When the solder had solidified, the tube was firmly held. The capillary was then sealed to one of the tubes to be tested, and the whole filled with water by means of suction, and fixed to the press.

The pressure was raised by means of a hand pump, and the point of rupture noted on a gauge attached to the press. Table 4 shows the results of the experiments.

Table 4.
Pressures required to rupture Pyrex Glass tubes of the nature shown.

Breaking pressure lbs/ in^2	Wall mm.	Diam. mm	Length. cm.
1900	1.0	7.0	30
1750	1.0	7.0	30
1000	1.0	7.0	30
1500	1.0	7.0	15
2000	1.0	7.0	20
2000	1.0	7.0	20
2500	1.0	7.0	20
1100	3.0	30	15
3000	1.2	10.0	15
3000	1.2	10.0	15
2200	1.2	10.0	15
2100	1.2	10.0	15

It is evident that no reliance can be placed on bulbs made from stock Pyrex tubing, although the average allowed a considerable safety factor. Two such tubes were tried, but rupture of one, caused considerable damage, and resulted in their definite abandonment.

It has been shown that complete annealing after shaping increases the strength of glass considerably. The tubes used in the later experiments were blown at the Corning Glass Works, annealed, and strain finder tested after completion. These are described below.

The special tubes were shaped as shown in the diagram, the tube proper of 3mm. glass sealed to a capillary of 3 mm. wall and ½ mm. bore, in turn sealed to a tube of 4 mm. bore which enabled them to be fixed to the apparatus with ease. Each piece was especially annealed, and strain finder tested. On the whole they proved very suitable, some hundred of them from a possible 113 standing the strain without rupture, and offering small glass surface.

The technique of handling was as follows. After the completion of the pressure readings, and during the evacuation of the dead space, the outside of the tube to be used was carefully washed with cleaning solution and distilled water, and finally

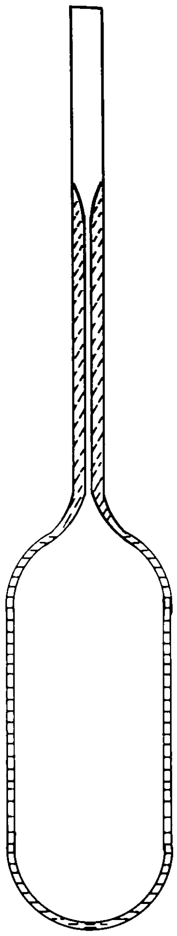

FIGURE 2.

The Weighing Tubes.

wiped dry with a lint free silk cloth. The apparatus being ready, the tube was surrounded with liquid air which came into direct contact with the glass wall of the tube. Experiments showed that the immersion of a weighed tube in liquid air, and reweighing without furthur treatment did not alter its weight within the limit of error of experiment.

After sufficient condensation, the bulbs were sealed off near the top of the capillary, and in the case of carbon dioxide, placed in a well cleaned corked glass tubes for storage in carbon dioxide - ether mixture until they could be weighed. The procedure for sulphur dioxide was somewhat different and will be explained below.

The balance used was a Saritorius, with a sensitivity of .03mg. per 0.01 divisions with a load of 40 gm. on each scale pan. This was enclosed in a glass case one side of which had been removed, and substituted by a window of thin mesh copper gauze loosely covered with tissue paper. In the case of ruptures of the tubes this offered mininum opportunity for damage to the balance. In fact in many cases of rupture, after the scale pan had been replaced, the balance point had not changed. The balance was carefully adjusted, and set up with the usual precautions.

In measurements on carbon dioxide the tubes were not placed directly on the scale pans, but were weighed using the following arrangement. On the left scale pan was soldered a small loop of thin copper wire, and the balance adjusted to zero by a similar piece soldered on the other pan. The pan rest and bearing of the left pan were removed. An air tight copper lined wooden box was placed immediately below the balance so that a hole in its top was aligned with the hole left in the base by the removal of the pan rest bearing. This box was of one inch oak stock 18 inches in length, with square ends on six inch sides. It was bored as described at the top, and coaxially with the whole in the top a three inch opening was bored in the bottom. When in use this hole could be closed by a slide moving between the two sections of the bottom which was double. One side of the box was pierced with three equally spaced holes which admitted tightly fitting glass tubes connected to a pure dry air supply. The box was connected to the balance by a tightly fitting glass tube which fitted the hole at the bottom, and butted the balance base immediately below the pan.

A thin glass rod hung from the loop on the bottom of the balance pan through the glass tube and into the box. This rod was terminated at its lower end by a hook on which hung a small basket made of Pyrex rod, with a suspension of constantin wire. The whole system exclusive of the bulb weighed less than two grams, and did not change weight over long periods of time. A diagram of the arrangement is shown below.

Weighings on carbon dioxide were made as follows. The suspension equipment was carefully cleaned and suspended in such a position that when it held the bulb it came over the centre of the whole in the bottom and about two inches above it. The stored tubes were taken out of their containers using silk or chamois gloves, examined for foreign material, cleaned if necessary in pure, oil free, ether, and placed in the basket while still cold. The dry air was turned on and the whole allowed to warm up to room temperature, and remain in the balance box until it had reached constant weight. This usually required between 7, and 10 hours depending on previous treatment of the bulb room temperature and other variables. The bulb was weighed usually twice to insure that it had reached true equlibrium, fatiguing the balance arms in the usual manner each time. It was then ready to remove from the balance. To do this the slide covering the hole in the bottom was removed and a Dewar of carbon

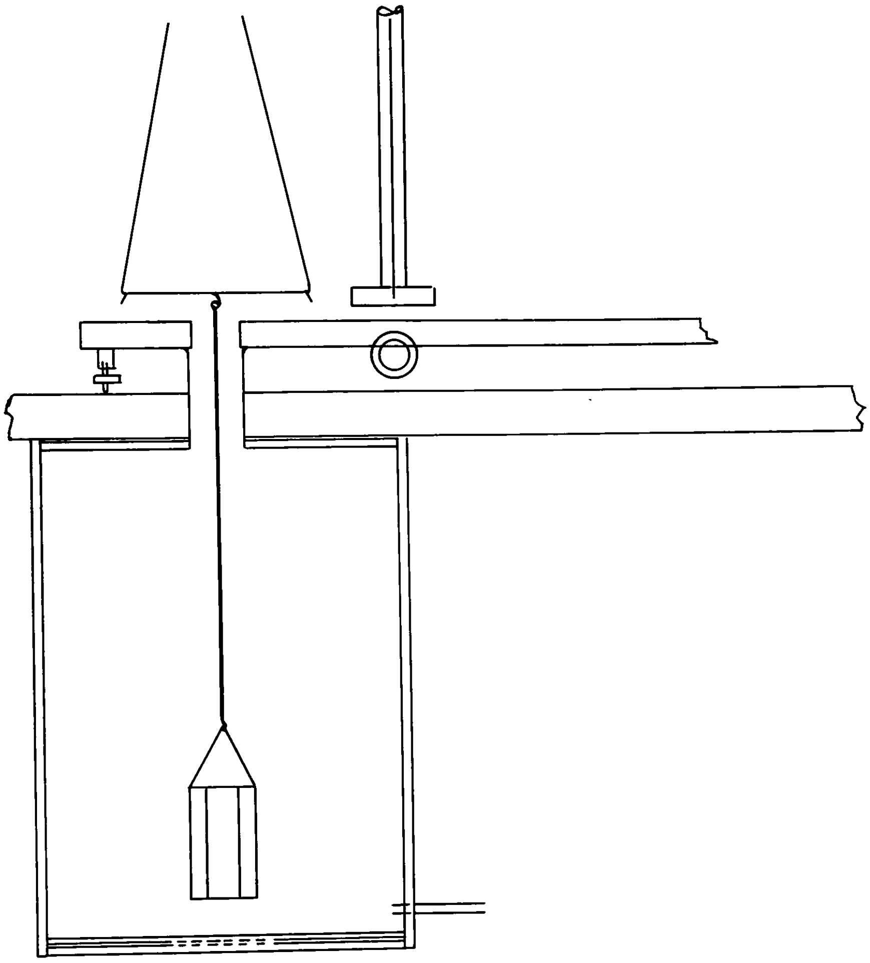

FIGURE 3.

The Weighing System, showing a Basket in place.

dioxide cooled ether inserted until it had surrounded the bulb and cooled it sufficiently to be safe for handling. The bulb was then lifted out, dipped in liquid air and opened.

The method of measurement, finally adopted, was used in both sets of determinations, and was found to be the only suitable one. The tube was placed over a large sheet of glazed paper, and a thin scratch made near the tip of the capillary. The capillary could then be easily snapped off. The difference in weight due to such a scratch was measured and found to be of the order of .0001 gm.. Any small bits of glass were usually sucked into the tube, but in other cases were removed from the glazed paper, and transferred to the balance pan. After some experience it was possible to distinguish a good break very easily, After sublimation of the carbon dioxide, or evaporation of the sulphur dioxide as the case may be, the tubes were blown free from gas with a stream of pure carbon dioxide free air washed through sulphuriceacid, and dried by passing through P_2O_5 . This was continued for at least twenty minutes, the tubes were then carefully cleaned, treated in the same manner as before ommitting the cooling, and allowed to remain in the balance case until they had assumed constant weight. They were then weighed, removed, filled with distilled water, and weighed again for the purpose of correcting to vacuo. Readings of the barometer and temperature were taken at the same time.

A second method of opening was tried but proved unsuccessful. In this case the bulbs were cooled so that the enclosed material had a vapor pressure slightly above atmospheric. A cool, fine, flame was turned on the side of the capillary, and a small hole blown through by the pressure of the gas from the inside. Experiment established that with Pyrex there was no loss in weight due to evaporation of the glass, and it was thought that this method would obviate the always present danger of losing very fine bits of glass which sometimes broke off in the first method. Tubes that were blown open were freed of gas by evacuating several times with the water pump, and refilling with good dry air. The results of many determinations showed that some error was present causing lack of agreement. Agreement with the first method was usually good so it was concluded that it was nearly impossible to free the small tubes from the gas by evacuating. This method of opening was therefore definitely discarded.

Owing possibly to the fact that the surface of the glass tubes was small, and the weighing conditions good, single weights could be repeated with an accuracy beyond the limits of experimental error. Thus in one series on bulbs much larger than those finally used the following sets of weights were recorded.

Table 5.
Repeated weighings on a glass tube showing the accuracy of the determination of mass due to errors in manipulation of the balance.

Time in case hrs.	Weight. gm.
10	118.79216
22	118.79226
27	118.79288
34	118.79285
39	118.79285
59	118.79286

The last four readings were corrected to a definite atmospheric condition.

This particular tube was then placed in a cooling mixture of carbon dioxide and ether, placed cold in the balance case and weighed again at the end of twelve hours. The weight was 118.79293 gm. which remained constant for another twenty-four hours.

The method of weighing tubes containing the sulphur dioxide could be must simpler that that used for carbon dioxide due to the fact that danger from rupture was almost negligible. In this case the tubes were suspended in a constant humidity box while cold, and allowed to remain there until they had reached constant weight. They were then transferred to the balance using chamois gloves and weighed directly on the balance pan. The method of opening, and subsequent procedure was the same as described above.

Corrections to Weights.

The weights used for weighing the small tubes of liquid were carefully standardized against a set of laboratory standards, and the departmental standards at the Department of Weights and Measures in Ottawa. Corrections for these were found to be entirely negligible. The comparison of these weights against those used in the standardization of the constant volume bulb supplied a furthur check.

The only other correction necessary is that needed to correct the weights to vacuum standard. This was done by direct measurement in all cases. After each weighing of the small tubes the tubes were cut open, blown free of gas, and filled with pure dry air. During the weighing of these air filled tubes the barometer and temperature of the balance case were read and the amount of air enclosed in the tube calculated with the use of tables for the density of pure dry air. The volume of each individual bulb was determined immediately after the second weighing by determining its weight when filled with water. Corrections for the density of the brass weights were calculated from the difference in weights in the two cases, the density of brass being 8.39.

The intercomparison of weights in the laboratory avoided the correction for latitude and height above sea level.

IV.

The Measurement of Temperature.

Temperature is the final measurement necessary to discuss, and of the measurements made probably involves the greatest residual error.

It has been shown that it was necessary to measure temperatures to within 0.01°C. This was comparatively easy at the ice point, and at 25°C but more uncertain at the other temperatures.

The Bath, in all cases consisted of a well lagged metal container of some 50 litre capacity, well lagged with insulating material, and stirred with two sets of two stirrers working against each other. The bath liquid was changed to suit the particular temperature desired.

The arrangement at zero was as follows. The bath liquid was a solution of salt in water cooled to the desired temperature, and hand regulated by dropping in finely crushed ice or snow at appropriate times. A Beckmann thermometer used as an indicator showed that the temperature could be held constant to within 0.006°C. Immediately before and after use in any set of experiments the Beckmann was calibrated in a Beckmann freezing point apparatus.using good distilled water. Its ice point was found to remain constant over long periods of time. The motion of the stirrers in the bath sometimes caused a slight movement of the mercury meniscus, so immediately before making a final setting of the cathetometer the stirring was stopped. After the pressure had been recorded, the temperature was read; a variation was usually not noticable.

At 25°C the arrangement was somewhat different. In this case the bath was thermostated to .003°C the absolute point of which was read on mercury thermometer # PTR 3191.

Thermometer PTR3191, a mercury thermometer graduated in 0.1°C. possessed a certificate of calibration from the Reichsanstalt. In the first calculations these certificate corrections were assumed to be correct, but intercomparison showed that some constant error was present so the thermometer was restandardized in the laboratory. The ice point was determined in the usual manner in a Beckmann freezing point apparatus. The 25°C. point was fixed by the absolute method of Richards and Yngve, and also by comparison against a platinum thermometer which had been standardized by the same method. Both the above standardizations yielded the same correction which was -0.10°C. The certificate showed no appreciable correction. The ice point was determined from time to time in order to detect any wandering due to shrinkage of the glass or other causes. After nearly two years of consistent use the ice point had not changed appreciably. At fifty degrees the thermometer was compared with several others which at lower temperatures showed the corrections as noted on the certificates to be true. The 75 ° C. point, read on a different thermometer, was checked by intercomparison in the same manner.

The temperature at -30°C was controlled and measured as follows. The bath liquid in this case was 95% ethyl alcohol, cooled by carbon dioxide snow, and hand regulated in the same manner as the bath at zero . Temperatures were read on a platinum thermometer of 25 ohms resistance at 0°C used with a Mueller bridge. The set-up was sensitive to a change of .002°C. Standardization of the thermometer was made as follows. Resistances at 0° and 25°C were determined. These were used for the calculation of α in the equation

$$R_T = R_0(1 + \alpha t - \beta t^2) \qquad \text{--------}(10)$$

where $\beta = 5.8 \times 10^{-7}$ and $\alpha = .0039275$. Calculation on this basis established the absolute temperature as -30.73°C .

The bath liquid at -8°C was a solution of salt in water cooled by the addition of snow, and hand regulated in the same manner as that at 0°C.. A Beckmann thermometer served as an indicator. The temperature could be held constant to .01°C. The absolute temperature was established by comparing a point at higher temperature on the Beckmann used against another Beckmann, the scale of which had been calibrated, and the ice point determined. The scale of the second Beckmann was also calibrated.

The bath for the higher temperature isothermals consisted of water in all cases. This was usually covered with a layer of wax to prevent evaporation as much as possible. In each case the bath contained several electric heaters with external controls. These were arranged so with the stirrers running the temperature rose very slowly Constant temperature was maintained by adding small portions of cold water from time to time. Again a Beckmann thermometer served as an indicator, and showed that the temperature could be maintained to within 0.02°C. Absolute temperatures were read on standard mercury thermometer, compared as described above.

The errors judged to be present in the absolute temperatures are shown in the section on errors.

V.

Description and Manipulation of the Apparatus Proper.

Subsequent to the various standardiztions the sections of the apparatus were blown to-gether as shown in figure 4. This permitted the determination of the pressure and temperature of a gas in the known volume (D)., and allowed the gas to be condensed out leaving a known dead space to (H), which was closed prior to the condensation of the gas into the weighing tubes (E).

The procedure for an experiment is relatively simple. The gas was purified and condensed into storage bulbs fitted with a pressure tap (B), and held there until ready for use. After condensation each new lot of gas was pumped off several times to remove traces of air. With the storage system closed (F), the apparatus proper was evacuated as completely as possible, usually to about 10 mm. of mercury. The last traces of foreign gases were removed by rinsing several times with the gas to be used. The dead arm of the manometer (K) having been pumped out, the apparatus was then ready for a determination.

Gas was admitted slowly to the constant volume bulb (F? H, I) until its pressure approximated that required, and the dead space closed (H). The mercury in the manometre, was adjusted by the external control acting through (C) until it was in the proper position, that is one meniscus in arm (K), the other in (L). The control was such that the positionnof the mercury menisci could be varied by applying either suction or air pressure to (C). The lights were adjusted, the cathetometer levelled, the manometer bath stirrer started, and the bath (M) adjusted to the temperature required. This bath was held at constant temperature, and pressure readings commenced at the end of fifteen minutes. These were continued at intervals until a constant value had been reached within the limits of reading. At this point the known volume was closed (I) . Temperatures of the cathetometer scale, manometer and constant temperature baths were recorded during the reading of pressures.

The dead space was evacuated and closed to the known volume (H) and the balloon (D) opened to the weighing tubes (E). These tubes were surrounded with liquid air and condensation of the gas continued until the residual pressure became sufficiently low to make the dead space correction negligible. The bulbs were then sealed off while still open to the apparatus, and the residual pressure read, adjusting the mercury so that one meniscus was in the arm (K) and the second in the auxilliary arm (N). The tubes were then stored and weighed as described.

It is well to emphasize the particular feature of this apparatus, namely that the dead space being completely evacuated, corrections for it, with small residual pressures are entirely negligible.

The residual pressure sometimes did not reach a satisfactory value after somewhat lengthy condensation. This usually occurred after the first determination with a new lot of gas. When such happened the run was discarded and the apparatus cleaned again. Apart from this, it was usually possible, especially with sulphur dioxide, to reduce the residual pressure to zero as shown on the cathetometer manometer system.

Determinations were made on two gases carbon dioxide, and sulphur dioxide. The methods of purification differed, and are given below.

Purification of Carbon dioxide.

The method used for the generation and purification of this gas was essentially the same as that used by Maass and Mennie. The same type of condensation apparatus was employed, but the method

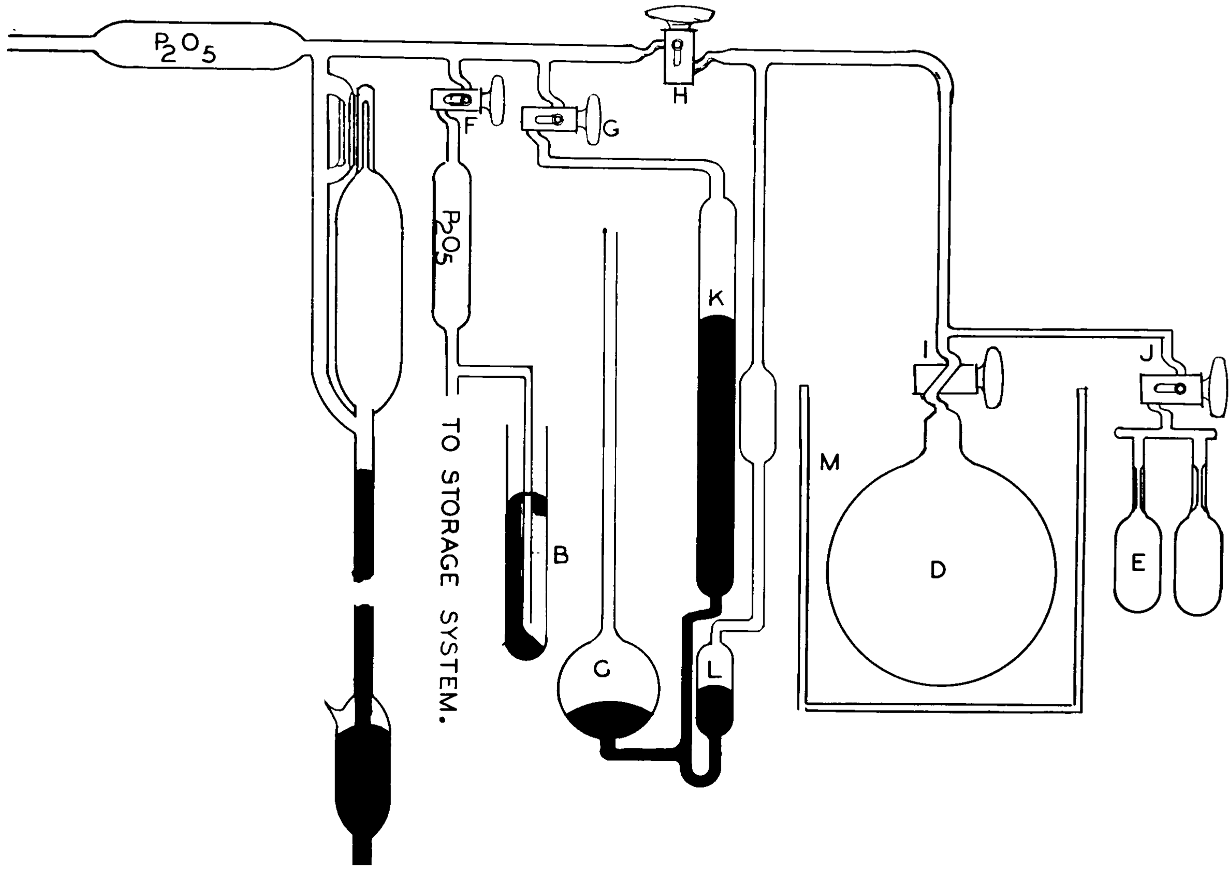

FIGURE 4.
The Apparatus Proper.

of manufacture differed. In this case the gas was generated from pure potassium carbonate, Eimer and Amend TP quality, and pure phosphoric acid. Analysis showed that the gas contained no traces of chlorine or sulphur dioxide. During distillation, and before entering the apparatus the gas passed through several wash waters, and two tubes containing phosphorus pentoxide. The last fraction of the solid was never used for any experiment.

Purification of Sulphur dioxide.

Sulphur dioxide from a tank of the CP material was condensed in the usual manner in a bulb immersed in a carbon dioxide ether bath, and distilled under vacuum in an air free apparatus, until the vapor pressure of two successive fractions were the same. This was indicated on a differential manometer placed between two small condensation bulbs so arranged that they could both be immersed in the same constant temperature bath. The bath was a large Dewar flask of approximately 2 litre capacity, and was filled with 95% ethyl alcohol which was used as the bath liquid. The alcohol was cooled by addition of carbon dioxide snow, and maintained constant by hand regulation in the usual manner. The bath was well stirred, and usually held at -10°C at which temperature the absolute vapor pressure of sulphur dioxide is about one atmosphere. After three or four distillations the vapor pressure of two fractions did not differ by an amount that could be read on the differential manometer. All gas was tested in this manner before distillation into the storage tubes.

EXPERIMENTAL RESULTS.

Results.

The results for both gases are shown numerically in tables 6 to 14, and graphically in figures 5 and 6. The last column of the tables record the mean values of the apparent molecular weights for the temperatures and pressures shown in columns 1, and 2.

The graphs show the mean values of the apparent molecular weights plotted as a function of the pressure, temperature being constant. Two types of isotherms indicate the two applications of the results. Those isotherms, the slope of which was determined definitely, by three sets of determinations at each of three pressures are shown as full lines. These have been used to establish the theoretical molecular weight of the gas in question, along with their use for determining the apparent molecular weight. Those isothermals shown as broken lines were used only to establish the value of the apparent molecular. Their position was fixed by drawing through the mean value of the molecular weight at the highest pressure, a straight line which crosses the y axis at the theoretical molecular weight as determined by the others.

The isothermals are seen to be straight lines within the limits of ex perimental error.

Calculations were based on the equation

$$M' = \frac{wRT}{PV} \qquad \text{---------} \ (1).$$

A typical calculation is given. This shows the results of one complete experiment together with all the corrections necessary to make the calculations.

From recent measurements by Moles(9) and his co-workers it appears that in the case of carbon dioxide any correction for the adsorption of carbon dioxide on the wall of the known volume is negligible. This is confirmed by the nature of the results obtained. The lowest isothermal of sulphur dioxide shows a definite indication of adsorption. This tends to make the molecular weight assume too high a value at the lowest pressures. This curve was not used for the determination of theoretical molecular weights as described later, but was fixed in the same manner as the high temperature isothermals.

An equation of state for gases at low pressures has been developed which permits a calculation of the amount of curvature to be expected in any isothermal due to molecular attraction and other kinetic theory phenomena. Unfortunately sufficiently accurate viscosity data is not available to enable this equation to be applied to sulphur dioxide at the present time. When this is obtained it will be possible to calculate the amount of adsorption on the wall of the known volume bulb with some accuracy.

Example of Typical Calculation.

Temperature of manometer bath	21.92°C.
Temperature of cathetometer scale	23.7°C.

Original pressure	43.573	43.574 cm./Hg.
Residual pressure	0.000	0.000

Temperature of known volume Beckmann #1.	+ 0.100
Ice point of Beckmann	+ 0.100
Temperature of known volume	+ 0.000 C.

Weight tube and gas	37.9854 gm.
Weight tube and air	29.0005 gm.
Weight of gas uncorrected	8.9849 gm.

Weight tube and distilled water	48.265 gm.
Volume of tube	19.243 ml.

Temperature correction to pressure	- .154 cm.
Gravity correction to pressure	+ .002 cm.
True pressure	43.422 cm/Hg.

Weight of air in tube	.0230 gm.
Weight air displaced by weights	.0013 gm.
True weight in vacuo	9.0066 gm.

Apparent molecular weight M' 64.912

TABLE 6.

Pressure	Temperature	Volume	Weight	M'
75.427	297.61	5444.6	9.7851	44.216
72.772	297.63		9.4385	44.209
72.366	297.66		9.3827	44.198
71.168	297.63		9.2274	44.194
69.366	297.60		8.9956	44.199
68.403	297.61		8.8689	44.191
50.683	297.60	5444.3	6.5631	44.138
48.038	297.49	"	6.2233	44.141
48.993	297.49		6.3474	44.144
47.469	297.51		6.1486	44.136
48.477	297.52		6.2801	44.146
24.908	297.61	5444.1	3.2211	44.081
24.610	297.62		3.1824	44.081
24.811	297.64		3.2070	44.064
25.367	297.59		3.2802	44.074
25.294	297.61		3.2706	44.076
25.083	297.61		3.2436	44.080
25.016	297.44	5444.0	3.2354	44.062
25.202	297.44		3.2597	44.066
22.698	297.45		2.9365	44.077
22.325	297.45		2.8882	44.077

TABLE 7.

Pressure	Temperature	Volume	Weight	M'.
70.726	242.45	5441.4	11.3005	44.393
70.986	"	"	11.3430	44.396
44.428	"	5441.2	7.0748	44.246
45.791	"	"	7.2937	44.256
25.299	"	5440.9	4.0087	44.151
26.624	"	"	4.2317	44.166

TABLE 8.

Pressure	Temperature	Volume	Weight	M'.
71.768	273.11	5443.3	10.1569	44.277
70.341	273.18	"	9.9530	44.279
69.693	273.18	"	9.8618	44.281
71.609	273.04	"	10.1370	44.278
70.166	273.18	"	9.9267	44.272
50.065	273.04	" .0	7.0721	44.188
47.962	273.18	"	6.7727	44.192
49.828	273.11	"	7.0379	44.193
50.482	273.01	"	7.1328	44.191
50.051	273.11	"	7.0693	44.192
26.129	273.04	5442.8	3.6851	44.117
24.029	273.11	"	3.3853	44.082
24.333	273.11	"	3.4306	44.113

TABLE 9.

Pressure	Temperature	Volume	Weight	M'.
68.689	322.29	5445.8	8.2187	44.156
67.814	322.30	"	8.1133	44.152
68.885	322.53	"	8.2377	44.163
69.686	322.54	"	8.3333	44.163

TABLE 10.

Pressure	Temperature	Volume	Weight	M'.
69.203	350.57	5447.3	7.6083	44.117
69.256	350.64	"	7.6119	44.115
69.011	350.58	"	7.5881	44.127

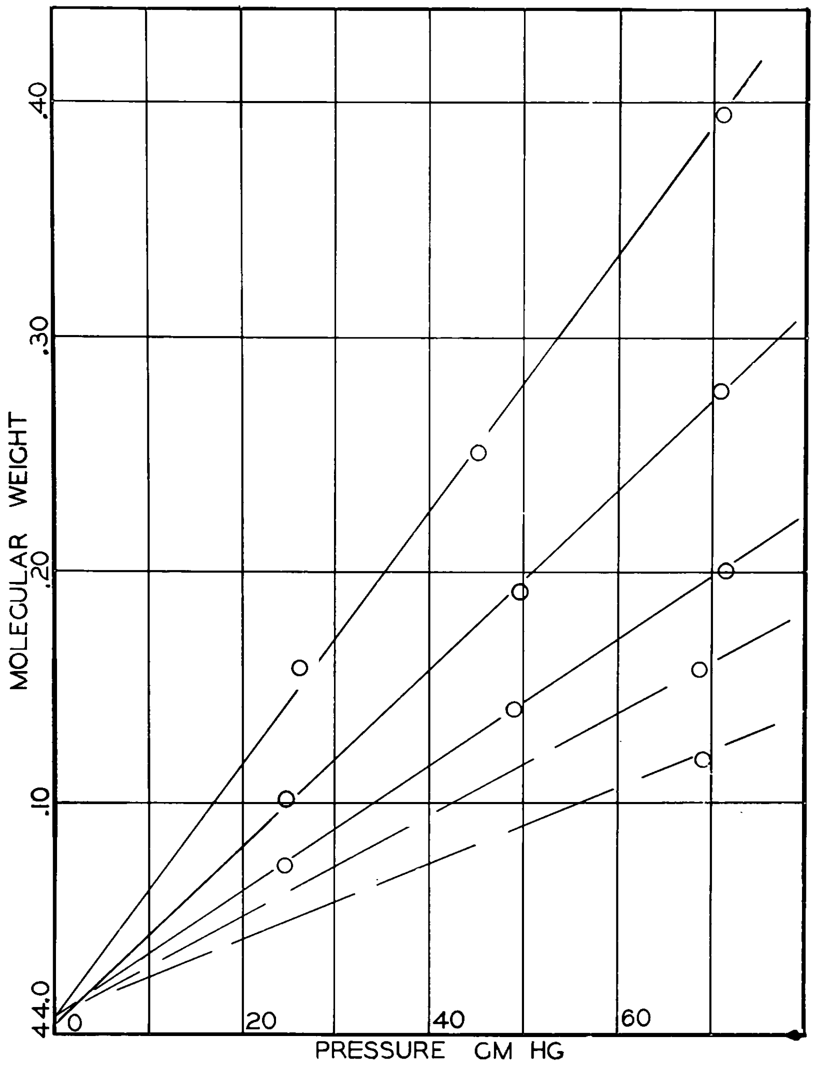

Figure 5.

The Molecular Weight of Carbon Dioxide.

Tables 6-10 record the values of M' for carbon dioxide. The mean values calculated as described later are shown in table 11 below.

Table 11.

Mean Pressure	Mean M'	Temperature.
71.5836	44.2011	297
48.7320	44.1410	297
24.5314	44.0738	297
70.7154	44.2774	273
49.6776	44.1912	273
24.8303	44.1040	273
70.8560	44.3945	242
45.1095	44.2510	242
25.9265	44.1585	242
68.7685	44.1685	322
69.1566	44.1196	350

Results for Sulphur Dioxide.

Table 12.

Pressure	Temperature	Volume	Weight	M'.
69.621	298.33	5444.6	13.2524	65.039
68.092	298.33	5444.6	12.9572	65.019
45.768	298.36	5444.4	8.6660	64.702
46.145	298.40	5444.4	8.7357	64.699
23.961	298.41	5444.1	4.5157	64.383
23.137	298.41	5444.1	4.3606	64.389

Table 13.

Pressure	Temperature	Volume	Weight	M'.
70.978	273.18	5443.3	14.8484	65.467
72.015	273.18	5443.3	15.0735	65.501
43.422	273.18	5443.1	9.0066	64.912
43.698	273.18	5443.1	9.0655	64.924
23.787	273.18	5442.9	4.9067	64.555
23.975	273.18	5442.9	4.9480	64.585
24.555	273.18	5442.9	5.0652	64.557
23.776	273.18	5442.9	4.9065	64.583
24.279	273.18	5442.9	5.0091	64.569

Table 14.

Pressure	Temperature	Volume	Weight	M'
67.523	265.46	5442.8	14.5541	65.566
67.891	265.36	5442.8	14.6435	65.571
41.499	265.36	5442.8	8.8531	64.952
41.932	265.36	5442.6	8.9598	64.963
23.159	265.36	5442.4	4.9179	64.588
22.972	265.36	5442.4	4.8790	64.575

Table 15.

Pressure	Temperature	Volume	Weight	M'.
68.916	323.18	5445.9	12.0659	64.786
68.998	323.19	5445.9	12.0791	64.780
68.074	345.65	5447.1	11.1186	64.626
68.746	345.65	5447.1	11.2302	64.635

Table 16.

Mean values of molecular weights- sulphur dioxide, calculated from results in tables 12-15.

Temperature	Pressure	M'.
265.36	67.707	65.570
265.36	41.690	64.957
265.36	23.065	64.581
273.18	71.496	65.488
273.18	43.560	64.918
273.18	24.074	64.570
298.36	68.856	65.029
298.36	45.956	64.700
298.36	23.549	64.386

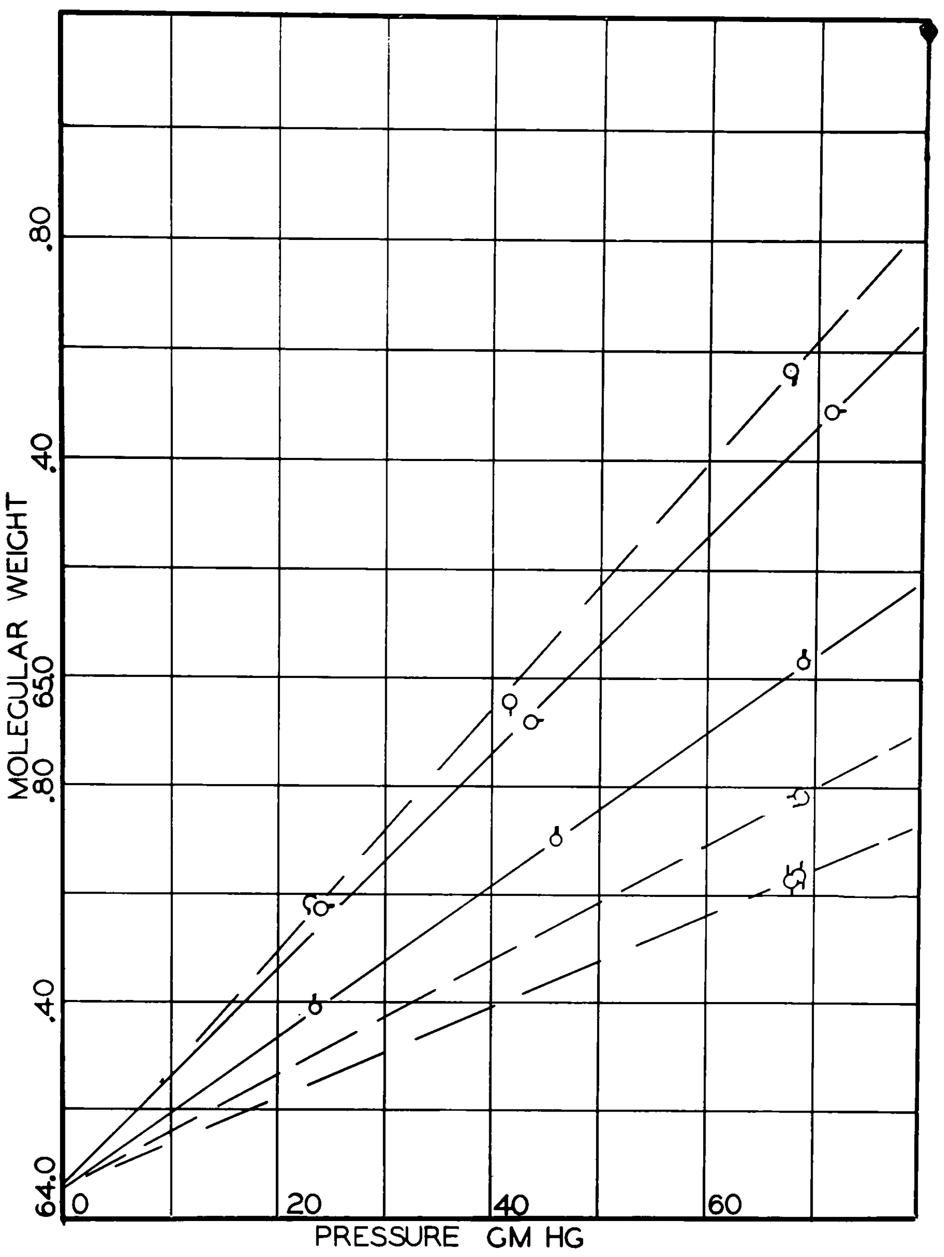

Figure 5.

The Molecular Weight of Sulphur Dioxide.

DISCUSSION OF RESULTS.

Discussion of Results.

The discussion of the results is divided into three sections. The first is a discussion of errors which gives some indication of the value of the numerical results. The second is the discussion from the point of view of the determination of atomic weights, and the third from the point of view of the ideal gas law equation and deviations from it. A new equation of state for a gas at relatively low densities is put forward in the latter section.

Discussion of Errors.

Errors are calculated by two methods, namely the maximum error, and the average deviation of the mean. Each makes a definite contribution to a furthur discussion of results. This method of expressing errors is recommended by Birge for the type of experimental work involved.

The first, or maximum error, gives an indication of the maximum deviation to be expected between any single determination of the apparent molecular weight and the mean value at the same temperature and pressure. The second indicates the reliance that may be placed on the absolute numerical value of the mean. This value depends on the assumption that the residual errors are negligible, and constant errors absent. The first is approximately true for all isothermals except those in which the temperature was uncertain to greater than 0.01°C, for which allowances have been made, and every precaution was taken to eliminate the second. The fact that the numerical results for the atomic weights of the elements sulphur and carbon, are about equally spaced about the usually accepted value gives an added assurance that all constant errors were eliminated.

No attempt is made to discuss the probable or mean error the number of determinations required being beyond the possibility of completion at present. In the case of sulphur dioxide the number of determinations at each point were insufficient to justify a discussion of the deviation measure of the mean.

The Maximum Error.

The maximum error arises directly from a consideration of the various measuring instruments, and experiments especially designed to determine the contribution to it of each factor involved.

Reference to each section on the discussion of apparatus will show that of the four measurements necessary the following deviations may be assigned to each one.-

Temperature of gas	-30° C	± 0025
Temperature of gas	-7.82° C	± 0.01
Temperature of gas	0° C	± 0.005
Temperature of gas	25° C	± 0.01
Temperature of gas	50° C	± 0.03
Temperature of gas	75° C	± 0.02
Pressure of gas		0.006 cm.
Volume of gas		0.10 ml.
Weight of gas		0.0003 gm.

The value assigned to the error in weight is probably a maximum one and in many cases must have been less. The final method adopted for opening the tubes does not allow an accurate guess of the amount of the deviation contributed by this factor, but the above is probably a generous one.

Since the four measurements enter the equation directly, maximum errors in the apparent molecular weight may be calculated with ease. These are found to vary at 25° C and 0° C from 0.015 % at high pressures to 0.035 % at the lowest pressure. Examination of the tables shows that these are the the maximum deviations between any single value and the mean if the values be compared at the same temperature and pressure

The Average Deviation of the Mean.

The average deviation of the mean for any values at the same temperature and pressure may be calculated as follows.

Inspection of the general form of curve obtained shows them to be straight lines to within the limits of experimental error. They may be represented by the general equation

$$M = aP + M_0$$

This permits an averaging of results along any isotherm according to the following method. The mean of the pressures and the corresponding molecular weight at each gives a value for the molecular weight measured at the mean value of the pressures. This value is plotted and the equation for the straight line drawn to any tentative value of the molecular weight at zero pressure obtained. The value of the molecular weight at any point near the mean is then corrected to its value at the mean value of the pressure. Table 17 below gives an example of how the apparent molecular weight is obtained for a mean pressure. The data is taken from table 6.

Table 17.

Calculation of the Deviation of the Mean.

Pressures read.	Mol. Weights calc.	Correction to mean	Value of M' at mean	Deviations from mean M'.
75.427	44.216	-.0107	44.2053	+.0042
72.772	44.209	-.0033	44.2056	+.0045
72.366	44.198	-.0022	44.1958	-.0053
71.168	44.194	+.0012	44.1952	-.0059
69.366	44.199	+.0059	44.2049	+.0038
68.403	44.191	+.0089	44.1998	-.0013

Mean pressure 71.5863 Mean molecular weight 44.2011
Deviation of mean 0.0036 %

The last column in the above table gives the deviations from the mean value which makes it possible to calculate the deviation of the mean in the usual manner. The deviation of the mean in this case is .0036 %. All the data on carbon dioxide has been treated in the same manner and are tabulated below.

Table 18.

Mean Pressure	Mean M'.	Temperature	Deviation of Mean %.
71.5836	44.2011	297	.0038
48.7320	44.1410	297	.0038
24.5314	44.0738	297	.0050
70.7154	44.2774	293	.0043
49.6776	44.1912	293	.0036
24.8303	44.1040	293	.017
70.8560	44.3945	242	.0014
45.1095	44.2510	242	.0041
25.9265	44.1585	242	.0062
68.7685	44.1585	322	.0036
69.1566	44.1196	350	.0063

II.

The Determination of Molecular and Atomic Weights.

The first interest in the application of the results lies in the possibility of obtaining theoretical molecular weights from them without the use of any equation such as that used by Guye and Frederich which is mentioned in the introduction.

From the general graphs of the results it is seen that all isothermals which are drawn as full lines have been set by a number of values at each of three pressures. These are straight lines to within the limits of experimental error, and can be extrapolated to zero pressure with some exactitude.

The results along any isothermal may be represented by an equation of the form

$$M = aP + M_0$$

where a is the slope of the line, and M_0 the theoretical molecular weight at zero pressure. The determination of M_0 depends on the determinations of a which are made as follows.

In the case of carbon dioxide it is possible to calculate weights for each point on an isothermal. This is done in the usual manner from the average deviation of the mean. The mean values are plotted and a straight line drawn through them such that the residual of any mean is distant from the line an amount proportional to its weight. In general the point at or near atmospheric pressure showed the greatest calculated accuracy, but in some cases the larger number of determinations at the lower pressures gave to the means almost equal weights. Examples of the first are seen in the -30°C isothermal for carbon dioxide, and for the second in the 25°C isotherm of the same gas.

In the case of sulphur dioxide the method employed differed somewhat. The number of determinations at each point did not warrant calculations of the various average deviations, and in consequence it was not thought advisable to assign to each point a calculated set of weights. The points were weighed roughly as the maximum error would require. This agreed fairly well with the experimental results obtained. Moreover distinct evidence of adsorption on the wall of the known volume bulb is seen in the -7.82°C isothermal. This would tend to make all the low pressure molecular weights too high. This isothermal was not considered in the extrapolation for the molecular weight of sulphur dioxide.

The method of plotting used is that recommended by Goodwin.

The values of a and M_o are shown below.

Table 19.

Gas	Temp	a	M.
C			
CO_2	25°C	2.706×10^{-3}	44.0083
	0°C	3.907×10^{-3}	44.0001
	30°C	5.446×10^{-3}	44.0079
SO_2	0°C	2.009×10^{-2}	64.064
	25.2°C	1.418×10^{-2}	65.054

The mean values for each are

$SO_2 = 65.059$
$CO_2 = 44.0055$

The mean value for carbon dioxide must be changed slightly for this reason. In the calculation of the average deviation of the mean no allowance was made for the residual error contributed by the uncertainty in the measurement of the absolute temperature. The three values from which the mean have been calculated should not be assigned the same weight. Assigning equal values to the weight of the 25°C and 0°C isothermals and a weight of 1/3 to the -30°C isothermal the calculated value of the atomic weight of carbon is 12.004.

With an estimated accuracy of something better than 0.01% in the molecular weight from all data this gives an estimated accuracy of 0.03 % in the atomic weights.

The values given above agree within experimental error with those usually accepted ones given by Baxter, Birge, yearly reports of the Americal Chemical Society, and others.

It is not intended that the values given for the atomic weights should be considered more accurate than those usually accepted ones, but of equal importance. The main interest lies in the determinations of the slopes of the isothermals and the proof that these are straight lines, as this is of especial importance from the point of view of the kinetic theory. Another consideration is that by this method the atomic weights of some elements may be determined from gaseous densities without the use of any equation involving assumptions or empirical constants. The experimental results give at the same time the numerical value and the justification for making the extrapolation.

In a planned extension of the experimental work the slopes of these curves will be used with more determinations to give a value for the atomic weights which will be ten times as accurate. This will be done by replacing the present volume with one of fifty litre capacity, and the present manometer liquid with another of less density. By this arrangement it will be possible to determine a point at or near one cm. of mercury. The extrapolation may then be made over the shorter range with a much greater accuracy using the slopes already obtained.

It is pointed out that the ultimate accuracy in measurements on gas densities near atmospheric pressure has been reached in these experiments. No furthur increase in accuracy is possible until the design of a new manometer allows readings of pressure closer than .001 cm. At the same time this would require a new international pressure standard.

III.

The measured aberrations from the ideal gas laws obtained in these observations may be used to test the rigidity of equations of state at low pressures to a degree that has hitherto been impossible. A new equation of state for gases at low pressures is used and tested in comparison with several others.

Investigation of low pressure deviations offers more possibility for theoretical discussion than the examination of those at high pressures. Similarly the physical interpretation of equations of state designed to hold at low pressures over a long temperature range can usually be more sound than the inferences drawn from equations designed to hold at high pressures. These statements may be verified roughly by some such considerations as are outlined below.

A gas, the pressure of which is infinitely close to zero, obeys the ideal gas law. As the pressure increases the ideal gas law fails, and aberrations become more pronounced. A representation of these deviations by some correction terms applied to the ideal gas law presupposes partially analagous conditions in the actual gas under treatment to those in the ideal gas. In order to assume analagous conditions the actual gas must be at low pressures where the terms molecular volume, mean free path, and molecular attraction retain some significance which they lose or which vary at high pressures. In other words the conditions in the interior of a gas at high pressure are relatively unknown, and but few simplifying assumptions such as those used in the development of the ideal gas law are possible. It is therefore more suitable to base equations of state and theoretical reasoning on data for gases at low pressures.

The larger number of equations have been developed to account for aberrations at high pressures and temperatures, and usually fail at the lower ranges. This is probably due to the fact that accurate data for the deviations at low pressures have been unavailable hitherto.until the completion of this present work. The data included in the results allow critical examination of equations of state for low pressures, and are capable of indicating deviations of the order of 0.01%.

The development of a low pressure gas equation of state may follow two methods, that of Van der Waals, and that of Jones and others. The difference lies in the consideration of the physical structure of the molecule. The Van der Waals' molecule consists of a sphere of nearly definite radius possessing mass, and an attractive field of force. The idea has undergone some change but the substitution of the term "collision radius" for radius, and the recognition that a change in this is apparently only a second or third order correction at low pressures and temperatures, allows the same general method of treatment. The second picture requires nothing of a molecule but an attractive and repulsive field. If one considers as the collision radius the distance from the mathematical centre of a molecule at which the repulsive field becomes numerically equal to the attractive field the two pictures may be brought into a displaced juxtraposition. In this case the variance in the aberrations may be considered to be caused by a change in the collision radius where no separation of the correction constant into a Van der Waals' radius and attractive field is possible.

The supposition is, that at low pressures the attractive field is nearly constant so far as the pressure is concerned, and the collision radius of a Van der Waals' molecule introduces only a second order correction since the mean free path is relatively large. It is advisable therefore to use this model in the development of an equation of state for gases at low pressures. The fact that the second method of treatment fails at low temperatures increases the confidence that the development on a Van der Waals' molecule is more suitable.

Development of an Equation of State.

Maass and Mennie have shown that the pressure of an ideal gas on a manometer may be representated by the equation

$$\left(P+\frac{a'}{V^2}\right)V = RT\left(1+\frac{2r}{\ell}\right) \qquad \text{-----(9).}$$

where r is the molecular radius, ℓ the mean free path, and a' the Van der Waals' constant of attraction.

It is known that ℓ does not remain constant, and assuming a' and r to remain so at low pressures the variation in the last term is caused only by a change in ℓ. This may be shown more clearly by writing the equation in the form

$$(PV - RT) = \left(RT\frac{2r}{\ell} - \frac{a'}{V}\right) \qquad \text{-----(10).}$$

The change in ℓ may be observed by viscosity measurements, in which case if Sutherland's viscosity equation holds the above may be changed to the form shown by Maass and Mennie

$$PV^2 - RTV + a' - RT\xi\left(1+\frac{c}{T}\right) = 0 \qquad \text{--------(11).}$$

where $\xi = \dfrac{8\sqrt{2}\,\pi r^3 N}{1+\frac{c}{273}}$

or

$$PV^2 - RTV + a' - RTb' = 0 \qquad \text{-----(12).}$$

Equation (11) fails at low temperatures. If the assumptions are correct this inexactness is due to the known fact that Sutherland's formula does not represent accurately the change in viscosity at low temperatures. It remains therefore to seek a new function of ℓ which is rigid over a long temperature range.

The mean free path, ℓ, may be related to the viscosity, η, by some formula such that

$$\eta = K_1 m n x \ell \qquad \text{-----(13).}$$

or more accurately since viscosity changes more rapidly with temperature than $\sqrt{T}$.

$$\eta = K_1 m n x \ell f(T)$$

and since $x \propto \sqrt{T}$

$$\eta = K_2 m n \sqrt{T} \ell f(T)$$

but

$$l_o = \frac{\psi}{4\sqrt{2}\pi r^2 n}$$

where ψ=some constant

and $l = l_o$ when $\eta = \eta_o$ assuming as before that the total change in η is caused by a change in l ,

therefore

$$\eta_o = \frac{\psi K_2 m n \sqrt{T} f(T)}{4\sqrt{2}\pi r^2 n} \qquad \text{-----(14).}$$

whence

$$\eta = K_3 \sqrt{T} f(T) \qquad \text{-----(15).}$$

where $K_3 = \dfrac{\psi K_2 m}{4\sqrt{2}\pi r^2}$

or $\dfrac{\eta}{\sqrt{T}} = K_2 f(T)$

The most accurate data of B. P. Sutherland was used to plot $\dfrac{\eta}{\sqrt{T}}$ vs T and $f(T)$ was found to be a straight line;

therefore

$$\frac{\eta}{\sqrt{T}} = (1 + KT) \qquad \text{-----(16).}$$

and we may write

$$l = \frac{l_o (1+KT_o)}{(1+KT_o)}$$

where $T_o = 0°$ and $l = l_o$ at $T = T_o$

substitution in (9) gives

$$\left(p + \frac{a}{v^2}\right)v = RT\left[1 + \frac{2r(1+KT_o)}{l_o(1+KT)}\right] \qquad \text{-----(17).}$$

but

$$\ell_0 = \frac{\psi}{4\sqrt{2}\,\pi r^2 n}$$

therefore

$$\left(p+\frac{a}{v^2}\right)v = RT\left[1+\frac{8\sqrt{2}\,\pi r^3 n\,(1+KT_0)}{\psi\,(1+KT)}\right]$$

or

$$\left(p+\frac{a}{v^2}\right)v = RT\left[1+\frac{8\sqrt{2}\,\pi r^3 N\,(1+KT_0)}{\psi\, V(1+KT)}\right] \qquad \text{---(18).}$$

since $n = \dfrac{N}{V}$

i.e. $$pv+\frac{a}{v} = RT+\frac{RTb\,(1+KT_0)}{v\,(1+KT)} \qquad \text{---(19)}$$

$$pv^2+a-RTv-\frac{RTb\,(1+KT_0)}{1+KT} = 0$$

where $b = \dfrac{8\sqrt{2}\,\pi v^3 N}{\psi}$

---(20).

and this may be written

$$v(1+KT)(pv-RT) = b^0T-a+aKT$$

where $b^0 = b(1+K_0T_0) = \text{const.}$

or $$V(1+KT)(pv-RT) = \mathcal{H}\,T-a \qquad \text{---(21)}$$

where $\mathcal{H} = b^0+aK = \text{const}$

This is the equation that has been applied to the experimental data.

The equation may be tested for rigidity very simply. Inspection shows that if the function of the right hand side is plotted against the temperature a straight line should result. This is true. The equation therefore holds over the range of temperature and pressure measured to within the limits of experimental accuracy. The evaluation of the only unknown constant, the Van der Waals' constant of attraction may be made very readily from this line. The value of K may be determined from viscosity data by the use of equation (16).

The function was calculated as follows. The volume $\bar{V}$ may be calculated from the apparent molecular weights by the use of the equation

$$\bar{V} = \frac{M}{M'} \frac{RT}{P}$$

where $\bar{V}$ represents the volume that would be contained by a theoretical molecular weight of the actual gas used at the corresponding conditions of T and P. The results are shown in table 20. The value of RT may be calculated for each temperature in the usual manner, and the value of $(1+KT)$ calcylated from the viscosity line obtained from equation (16). the constants of which are,

$$1 + 4.0938 \times 10^{-3} T$$

The results lie on a straight line the equation of which is

$$\chi T - a = 1.616 \times 10^{-2} - 11.34$$

The numerical value of the results are shown in table 21. The equation therefore holds at all points. This is demonstrated furthur by a direct calculation of V shown in comparison with those calculated from some other equations in table 22.

The equation for carbon dioxide is therefore

$$V\left(1 + 4.0983 \times 10^{-3} T\right)\left(PV - RT\right) = 1.616 \times 10^{-2} T - 11.34$$

or written in a slightly different form

$$PV^2 + 11.34 - RTV - RT \, \frac{0.3596\left(1 + 4.6983 \times 10^{-3} T_0\right)}{1 + 4.0983 \times 10^{-3} T}$$

Table 20.
Calculation of the observed volumes. The values of M' were read from a smooth curve of M' vs. T.

Temperature	M'	V obs.
243.18	44.422	19.764
273.18	44.295	22.266
293.18	44.232	23.930
323.18	44.167	26.418
343.13	44.138	28.071

Table 21.
Measured deviation from the ideal gas law and value of the function $v(1+\kappa T)(pv-RT)$

Temperature	Pressure	PV/RT	$v(1+\kappa T)(pv-RT)$
243.18	1.0000	-0.188	-7.42
273.18	1.0000	-0.148	-7.24
293.18	1.0000	-0.125	-6.62
323.18	1.0000	-0.099	-6.10
343.18	1.0000	-0.086	-5.81

If the equation is written in the form of an isothermal by substitution of

$$\tilde{V} = \frac{M}{M'} \cdot \frac{RT}{p}$$

we have by expansion by the binomial theorem

$$\frac{M'}{M} = 1 + \left(\frac{a - \frac{RTb^{o}}{1+\kappa T}}{R^2T^2} \right) p + 2\left(\frac{a - \frac{RTb^{o}}{1+\kappa T}}{R^2T^2} \right) p^2 + \ldots$$

where $b^{o} = b(1+\kappa T_0)$

The second term represents the slopes of the isothermals which at low pressures are known to be straight lines From the known constants in this term it should be possible to calculate the slope of any isothermal. This has been done in the case of the one at 0°C and shows a calculated slope of 6.53×10^{-3} against a measured value of 6.54×10^{-3}. A variation of 0.01% in the highest molecular weight of any isothermal causes a change in the slope of 18% so the calculated value is well within the error of measurement.

A calculation of the second term of the expansion, which allows for a curvature in the isothermal at higher pressures shows that it does not become effective until five atmospheres where it affects the results by 0.01%.

The expressions obtained by the expansion of the equations of Maass and Mennie, and Van der Waals' are given for comparison.

In the case of Van der Waals' equation a first order approximation that PV = RT was required in order to preform the expansion.

Maass and Mennie.

$$\frac{M'}{M} = 1 + \left(\frac{a - RTb'}{R^2T^2}\right)p + 2\left(\frac{a - RTb'}{R^2T^2}\right)^2 p^2 + \cdots$$

Van der Waals. $\left(P + \frac{\alpha}{V^2}\right)(v - \beta) = RT$

$$\frac{M'}{M} = 1 + \frac{a - R\beta T}{R^2T^2}\,p + \cdots$$

A second method of treatment of the expanded form will be discussed later.

A comparison of several equations is made in tables 22 to 24.

Table 22 shows the calculated volumes against those observed. The values for the equation of Maass and Mennie, shown as V2 , were calculated by their original method using the data obtained herein. The discrepancy at -30°C is well outside the limit of experimental error.

Table 22.
Comparison of results Vobs. vs. V cal. at various temperatures. Pressure = one atmosphere.

V_1 new equation; V_2 Maass and Mennie; V_3 gas law.

Temperature	V obs.	V_1	V_2	V_3
243.18	19.764	19.764	19.772	19.952
273.18	22.266	22.266	22.265	22.414
293.18	23.930	23.930	23.930	24.055
323.18	26.418	26.418	26.418	26.517
343.18	28.071	28.071	28.069	28.157

Table 23 shows a comparison of the observed data with those calculated from the equation of Bridgeman. for carbon dioxide gas. The comparisons are made in the form of an isobar in which form Bridgeman gives his constants. The discrepancies at the lower temperatures are outside the limits of error.

Table 23.
Comparison of results from Bridgemans equation for an isostere at V= 23.930 l.

Temperature	P obs.	Pcalc.
243.18	0.82730	0.82664
273.18	0.93098	0.93046
293.18	1.00000	0.99970
323.18	1.1035	1.1032
343.18	1.1724	1.1723

Table 24 requires some considerable discussion. Considerable interest is attached to the values of the constants of Van der Waals equation. Algebracially they are unique, that is only one value of each α, and β should satisfy the experimental results

The use of a slightly different α with a β calculated to correspond alters the calculated volume very slightly. This is due to the nature of the equation. Hitherto it has been impossible to detect differences in the calculated values even with considerable differences in the constants used because of the fact that the experimental data were not sufficiently accurate. The data given above allows a calculation of the limits of variation in the constants. This is shown in Table 24. A variation of 7% in the value of α causes a noticible discrepancy at the extreme temperatures when the volumes are calculated by use of a corresponding β.

In a simultaneous solution of Van der Waals equation using the data given above the following values for the constants were determined; $\alpha = 7.06$ $\beta = .166$. The pressures calculated with the use of these constants follow the experimental values. They are shown in column 4. Column 6 shows the pressures calculated from the best representative values of the constants based on the work of Andrews and Amagat, and quoted by Jellinek. The discrepancies vary between 0.2% at low temperatures to 0.03% at the highest. Van der Waals equation does not hold over the whole range.

The effect of a variation in constants is shown in columns 3 and 5. In column 3 the results were calculated by substituting the best representative value of α in one set of the results and calculating the corresponding value of β. Discrepancies of the order of 0.1% are noticible at temperatures fartherest removed from the substitution one. In column 5 a value of 7.56 for α was assumed and a corresponding value of β calculated. This shows that a change of 7% in α makes a noticible difference between the calculated and observed values. Thus a change in the constants of a Van der Waals equation makes the equation entirely inapplicable to calculations of the highest accuracy. This if the first demonstration of this fact.

Table 24.
Comparison of the observed pressures with those calculated from Van der Waals' equation using different values for the constants α and β.

Temp.	Pressure obs.	3	4	5	6.
		$\alpha =$ 4.208	7.06	7.56	4.208
		$\beta =$ .050	.166	.188	.0712.
243.18	1.0000	1.0013	1.0000	1.0003	1.0024
273.18	1.0000	1.0005	1.0000	.9999	1.0014
293.18	1.0000	(1.0000)	1.0000	(1.0000)	1.0009
323.18	1.0000	.9996	1.0000	1.0001	1.0004
343.18	1.0000	.9995	1.0000	1.0003	1.0004

Critical comparison of the three equations i.e. those of Maass and Mennie, Van der Waals, and Maass and Cooper, is aided by writing them in the following forms:-

Maass and Mennie

$$pv^2 + a' - RTV - Rb'T = 0$$

Van der Waals

$$pv^2 + \alpha - RTv - pv\beta - \frac{\alpha\beta}{V} = 0$$

Maass and Cooper.

$$pv^2 + a - RTv - \frac{Rb^\circ T}{1+KT}$$

The equations are similar when

$$RTb' = pv\beta - \frac{\alpha\beta}{V} = \frac{Rb^\circ T}{1+KT}$$

or making the first order approximation that PV = RT

$$RTb' = RT\beta - \frac{\alpha\beta}{V} = \frac{RTb^\circ}{1+KT}$$

The term $\frac{\alpha\beta}{V}$ affects the results to 1/6000 and neglecting this

$$RTb' = RT\beta = \frac{RTb^\circ}{1+KT}$$

i.e. $b' = \beta = \frac{b^\circ}{1+KT}$

at 0°C where $\frac{b^\circ}{1+KT} = b''$ we have $b' = \beta = b''$

and the equation becomes identical with that of Maass and Mennie. At all other temperatures the first two suppose a constant correction term whilst the latter demands a variable one.

It has been shown that Van der Waals equation may be made to fit the experimental data by a proper choice of constants. The same must be true of that of Maass and Mennie since they are the same to within the first order. A difference between these two and the new equation is apparent on consideration of the range over which the equation holds. This is shown in table 25 in which the values obtained by Van der Waals equation by use of the constants determined at low pressures are compared against the experimental values and those calculated by the new equation.

Table 25.
Comparison of Vobs vs V cal. at high pressures.

Pressure obs.	Pressure V.der V.	Pressure New.
12.01	12.12	12.012
13.22	13.35	13.197
14.68	14.86	14.663
20.01	20.74	19.945
34.49	30.86	33.297

Furthurmore whilst the constants of Van der Waals equation must be determined by some simultaneous solution involving a quadratic in V, those of the new equation may be determined very simply as explained above, and yield unique values, for if K be changed 100% i.e. be placed equal to zero the calculated values of V do not agree with those determined experimentally. This is shown in table 26.

Table 26.
Effect of change in K.

Temperature	Pobs.	P.	Pcalc.
		k = 0	k = 4.50
243.18	1.0000	.99884	1.00004
343.18	1.0000	1.0015	.9999

The forms of the equations of the isothermals allow another differentiation. The new equation allows calculations for the slopes as shown above, Van der Waals equation has no such application due to the substitution of PV By RT.

Comparison with the equation of Bridgeman is more difficult to make on account of the relative large number of semi empirical constants. Examination of table 23 shows that Bridgeman's equation probably crosses the new at approximately 0°C. Whilst somewhat similar in form it fails at low temperatures and pressures but as Bridgeman has pointed out is quite satisfactory at high pressures, and temperatures above 0°C.

A more apparent difference may be detected by writing the equations in the form of isosteres thus for Maass and Mennie, and Van der Waals we have

$$p = BT - a'$$

and for the recently proposed equation

$$p = B_1 T + \frac{C_1}{1+KT} - A$$

The first two equations demand that the

the isosteres to be straight lines, whilst the new equation allows for a curvature. In this respect the new equation probably represents the facts to a greater degree of exactness since isosteres ar known to possess a curvature(6) at higher pressures. No departure from a straight line can be detected in the results given herein, so no real value of C_1 can be calculated. An upper limit was calculated and found to be of the order of 1×10^{-4}.

The equation lends itself to two furthur applications, namely the calculation of the molecular radius ,r, and the calculation of the viscosity constant K, as defined by equation (16). A knowledge of ,r, permits the calculation of the viscosity of the gas under examination at 0°C, and this combined with equation (16) permits the calculation at any other temperature at which the equation holds. In so far as the second application is concerned this is the first time that PVT results have enabled the calculation of viscosity at different temperatures.

The calculation of the molecular radius may be carried out as follows.

From equation (20) we have

$$pv^2 + a - RTv - \frac{RTb(1+kT_0)}{\psi(1+kT)} = 0$$

where $b = 8\sqrt{2}\pi r^3 N$

therefore $b = 6\sqrt{2} V_0$

where V_0 is the total volume of the molecules, and ψ is a correction factor due to the fact that the molecules are elastic spheres, and allowing for a persistence of velocity. Using Jeans(14) calculation of ψ we have

$$pv^2 + a - RTv - \frac{6\sqrt{2}\,V_0(1+KT_0)}{1.342(1+KT)}$$

from which ,r, is 2.28×10^{-8} cm. The viscosity at zero degrees is therefore .000133 which differs from the experimental value of .00013$\overset{5}{4}$ by 0.15%

The second application, namely the calculation of ,K, from PVT data may be carried out as follows.

From the expanded form of the isothermal we have

$$\frac{M'}{M_0} = 1 + \frac{a - \frac{RTb^\circ}{1+KT}}{R^2T^2}\,p$$

but $M' = M_0 + \alpha p$

therefore $\frac{M'}{M_0} = 1 + \frac{\alpha}{M_0}\,p$

and equating equal coefficients

$$\lambda = a - \frac{\beta T}{1+KT}$$

where $\lambda = \frac{\alpha}{M_0} R^2T^2$ and $\beta = Rb^\circ$

The solution for K? may be made as follows.

Defining some quantity θ such that $\theta = \frac{1}{T}$

then $A - \frac{B}{\theta + K} = \lambda$

and A may be eliminated between two such equations whence $$\frac{\beta(\theta_2-\theta_1)}{(\theta_1+K)(\theta_2+K)} = \lambda_1 - \lambda_2$$

similarly
$$\frac{\beta(\theta_3-\theta_1)}{(\theta_1+K)(\theta_3+K)} = \lambda_1 - \lambda_3$$
and by division
$$\frac{(\theta_1-\theta_2)(\theta_3+k)}{(\theta_1-\theta_3)(\theta_2+k)} = \frac{\lambda_1-\lambda_2}{\lambda_1-\lambda_3}$$
and since λ may be evaluated for each experimental isothermal K, may be calculated directly.

The nature of the equation is such that K, may be calculated to one significant figure only. It is found to be 5×10^{-3}. Using this value for a calculation of b we have b = .412 from which the viscosity at zero = .000131 against a measured value of .00013$\overset{5}{\wedge}$4. Using the value of K, obtained above the viscosity at -60°C is found to be .000116 against a measured value of .0001160. Thus without the use of any values other than the purely experimental ones used to determine the slopes of the isothermals viscosities may be calculated over a long temperature range to about 2%.

Application of the equation to sulphur dioxide.

The equation was not applied to the results obtained for sulphur dioxide. This is due to the fact that viscosity measurements for sulphur dioxide agree neither with one another, not are any set of results consistent among themselves. Measurements are now in progress in this laboratory which will give sufficiently accutate data, and when these are obtained the equation will be applied to sulphur dioxide using the PVT data obtained here.

The application should be one of considerable interest in view of the fact that the PVT measurements are made very near the boiling point of the gas at which temperature aberrations may be expected to be greatest. Furthurmore the molecule of sulphur dioxide is considerably "softer" than that of carbon dioxide, and will probably disclose whether or not the assumption of a constant molecular radius was justifiable.

In connection with the determination of molecular weights at infinitely small pressures, experiments in progress will yield points for M8 near 3cm. of mercury with the same accuracy as the other results. These will enable an extrapolation to zero pressure to be made with much greater accuracy using the isothermals already obtained.

In these experiments the five litre bulb used heretofor is being replaced by one of fifty litre capacity, and the mercury of the manometers by a much lighter substance of very low vapor pressure. This will give approximately the same accuracy in determining both the pressures and the weights.

SUMMARY.

The densities of carbon dioxide and sulphur dioxide have been measured with an accuracy of better than .01% at pressures up to one atmosphere and over a temperature range of approximately 100°C.

The accuracy of the results permitted a direct extrapolation to zero pressure for the theoretical molecular weight of the gas, and the atomic weights of carbon and sulphur. This was done without the use of any equation and is the first experimental demonstration of the validity of Berthelot's hypothesis.

A new equation of state is proposed, This involves a new function for the change in viscosity with temperature. The constants of the equation have been determined for carbon dioxide.

A demonstration of the effect of a change in value of the Van der Waals constants is shown.

An equation is given which permits the calculation of the slope of any isothermal provided the constants of the equation are known.

An entirely new application of PVT data is demonstrated, that is the calculation of viscosities of the gas under consideration at any temperature.

TABLE OF REFERENCES.

Table of References.

1.--- Note References should be consulted by name. The text is numbered only in cases of two different references to the same name, or when no name is given. The numbers in the text refer to those opposite the names below.

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Footnote.

A complete summary of atomic weight determinations is given by Clarke-"A Redetermination of Atomic Weights." 4th. ed., 1920. Published as Part 3, Vol. 16, Mem. Nat. Acad. of Sci. U. S. A.