THE MAGNETIC SUSCEPTIBILITY OF OXYGEN AND NITRIC OXIDE AT LOW FIELD STRENGTHS

By

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INTRODUCTION

A. Magnetic Materials. Susceptibility.

With respect to their magnetic properties material substances may be classified as ferromagnetic, paramagnetic, and diamagnetic. When placed in a magnetic field, ferro- and paramagnetic materials acquire a net magnetic moment in the direction of the applied field. Diamagnetic materials acquire a magnetic moment opposite to the applied field.

The magnetic moment per unit volume per unit applied field strength, usually denoted by κ , is defined as the volume susceptibility of the material. The corresponding quantity, χ , per unit mass is called the specific or mass susceptibility. Another quantity, χ_M, the molar susceptibility, is defined as the magnetic moment per mol per unit field strength. These quantities vary widely for the different types of magnetic materials and are negative for diamagnetic materials and positive for para- and ferromagnetics.

Bismuth, which is one of the most strongly diamagnetic materials, acquires a moment very small in comparison to that exhibited by many paramagnetic materials. In turn, most paramagnetic materials exhibit moments very small in comparison to those acquired by ferromagnetic materials, such as iron cobalt and nickel. For purposes of comparison the following table of approximate values is given:

Table 1. Approximate value of the susceptibility for various types of magnetic materials.

Material	Type	Susceptibility
Water	diamagnetic	7.200×10^{-7}
Oxygen	paramagnetic	1.06×10^{-4}
Nickel	ferromagnetic	3.0
Iron	ferromagnetic	2.5×10^{2}

According to the molecular theory of magnetism, each molecule or atom is assumed to be a magnetic dipole. In the case of diamagnetic materials the dipoles are created by the applied magnetic field. In paramagnetic materials, on the other hand, the atoms or molecules are supposed to be permanent dipoles which are oriented at random in the unmagnetized state and thus produce no external magnetic effects. When a magnetic field is impressed the magnetic moment vector of the atom or molecule is caused to precess about the field direction, giving rise to a net moment in the direction of the applied field.

Diamagnetism may be accounted for on the basis of Amperian currents within the atom. An electron revolving about its nucleus is equivalent to a circular current; the strength of which, depends upon the angular velocity of the electron. Such a circular current gives rise to a magnetic moment, whose value depends upon the angular velocity of the electron. In the absence of an impressed field a diamagnetic atom exhibits no net magnetic moment due to orbital or spin moment of its electrons. The absence of a permanent moment is associated with the fact that the number of electrons in the molecule, in a great majority of cases, is even and the electron spins are balanced in pairs. The orbital moments either compensate each other or do not change their orientation in an applied field owing to strong electrostatic forces within the molecule. However, if an external field is applied there will be in general a component normal to the plane of a particular electron orbit. When a field is applied normal to the plane of an electron orbit and in the direction of the angular velocity vector, the angular velocity of the electron is decreased without changing the size of the orbit. This results in a decrease in the moment in the direction of the field. A field applied opposite to the direction of the angular velocity vector increases the angular velocity, thereby increasing the moment opposite to the field direction. For a group of Amperian currents oriented at random the effect is a net magnetic moment opposite to the field direction. Such a result is also predicted by Lenz's law, for the induced moment would necessarily be opposite to the inducing field if no permanent dipoles were present. All materials, therefore, tend to be diamagnetic, but this tendency is completely masked in certain materials (para- and ferromagnetic) by the much larger effect due to permanent dipoles.

Since diamagnetism is a fundamental property of the atom, the effect does not vary appreciably with temperature. No variation in the diamagnetic susceptibility with field strength is expected for saturation is not approached with fields obtained in the laboratory. Likewise, paramagnetic materials are not saturated with fields obtained in the laboratory, but the susceptibility does vary with temperature. This is due to the thermal agitation which reduces the effective component of the permanent magnetic moment in the direction of the applied field. On the other hand, the ferromagnetic susceptibility varies widely with both temperature and field strength. For this reason the theoretical treatment of such materials is more difficult than for para- and diamagnetic substances.

This thesis deals with the experimental determination of the susceptibility of oxygen and nitric oxide at low field strengths. These are the only two common gases which have a permanent magnetic moment. They are both therefore paramagnetic and the theoretical value of the susceptibility has been calculated in each case.

B. Calculations From Theory.

1. Oxygen.

In 1905 Langevin (1) derived, on the basis of classical electrodynamics, the formula

$$K = N\left[\alpha + \frac{\mu^2}{3KT}\right]$$

for the susceptibility of a paramagnetic material. In this equation K is the volume susceptibility, N the number of atoms or molecules per unit volume, μ the magnetic moment of the atom or molecule, k Boltzmann's constant, and T the absolute temperature. α is a constant independent of the absolute temperature and represents the induced diamagnetic moment. α is usually negative and small in comparison to $\frac{\mu^2}{3KT}$. It is generally neglected in paramagnetic calculations. Van Vleck (2) has shown that the above equation can be derived quite generally on the basis of the new quantum mechanics. He has considered the special cases of oxygen and nitric oxide (3) from the quantum mechanical standpoint. For oxygen, the formula obtained is

$$\kappa = N\left[4S(S+1) + \sigma_K^2\right]\frac{\beta^2}{3KT} \tag{1a}$$

When applied to molecules, the quantities in the above equation have the following significance: κ is the volume susceptibility of the gas, N the number of molecules per unit volume, s the total spin moment, σ_K the resolved electronic angular momentum along the nuclear axis, and β the magnetic moment of one Bohr magneton. The measured value of the susceptibility indicates that the ground state for the oxygen molecule is a $^3\Sigma$ state, for which s = 1 and $\sigma_K = 0$. This ground state has been confirmed by analysis of the oxygen bands. If these values of s and σ_K are substituted in the above formula, the equation may be written

$$\chi_M = \frac{8L\beta^2}{3KT}$$

where χ_M is the molar susceptibility of the gas and L is Avagadro's number. The product $\chi_M T$ is therefore given by

$$\chi_M T = \frac{8L\beta^2}{3K} \tag{1b}$$

$\chi_M T$ is easily calculated from fundamental constants and is therefore convenient for comparison of experiment with theory. Equation (1b) is a mathematical statement of Curie's law, that is, that the molar susceptibility of a paramagnetic material is inversely proportional to the absolute temperature.

Using recent values of the physical constants (4) in the calculations, Equation (1a) gives 0.142 x 10^{-6} for the volume susceptibility of oxygen at 20°C and 760 mm pressure. From Equation (1b), the value of $\chi_m T$ is 1.000. It should be pointed out that this result is somewhat larger than the value 0.993, as given by Van Vleck (5). The difference results from slightly different values of the physical constants in the calculations.

2. Nitric Oxide.

Nitric oxide requires special consideration since the separation of the energy levels in the ground state of the molecule is comparable to the equipartition allowance kT. It is known from band spectra data that the multiplet width is about 120.9 cm^{-1}, which results in an energy separation of about 0.6 kT. In the case of oxygen the multiplet width is less than 1 cm^{-1}. The corresponding energy separation is therefore small in comparison to kT and can be neglected in the derivation of the susceptibility formula.

An inclusion of these so-called "medium frequency terms" results in the formula

$$\left.\begin{array}{ll} & \kappa = \dfrac{N\Theta^2}{3KT} \\[2ex] \text{where} & \Theta^2 = 4\beta^2 \dfrac{1 - e^{x} + Xe^{-X}}{X + Xe^{-X}} \\[4ex] \text{and} & X = \dfrac{h\Delta\nu}{KT} \end{array}\right\} \qquad (2)$$

for the volume susceptibility, κ , of nitric oxide.

In these equations $\Delta\nu$ is the separation, in wave numbers, of the two component normal states of the molecule and h is Planck's constant. The other symbols have the same meaning as in the previous equations.

A calculation of κ, using Equations (2), gives 0.0597×10^{-6} for the volume susceptibility of nitric oxide at 20°C and 760 mm pressure. This value rather than 0.0600×10^{-6}, as given by Van Vleck (3), results from the use of more recent values of the physical constants in the calculations.

The value of the apparent Bohr magneton number, $\frac{\Theta}{\beta}$, as calculated from Equations (2), with $\Delta\nu = 120.9$ cm^{-1}, is 1.836 at 20°C. This quantity changes somewhat with temperature and is a measure of the deviation of the susceptibility of nitric oxide from Curie's law.

C. Measurement of Magnetic Susceptibility.

The most common procedure in determining the susceptibility of para- and diamagnetic materials is by means of the non-uniform field method. With proper modification of the apparatus either absolute or relative measurements may be made on solids, liquids or gases. In principle the method depends upon the fact that when a specimen is placed in a non-uniform magnetic field a force acts on it which is proportional to the difference between the susceptibility of the specimen and that of the surrounding medium. If the specimen is paramagnetic it tends to move into the more intense field and in the opposite direction if diamagnetic. Actual measurements involve the use of some type of balance to determine the force acting on the specimen, or at least a quantity proportional to the force.

For measurements on liquids a simple form of the apparatus is a U-tube partially filled with the liquid to be tested and so placed that one meniscus is between the pole pieces of a powerful electromagnet. When the field H is turned on the level of the meniscus is altered. If V is the small change of volume of liquid in the field, K_l, and K_a, the susceptibility of the liquid and air respectively, then the change in magnetic energy is

$$\frac{1}{2} V H^2 (K_l - K_a)$$

The change in gravitational potential energy is

$$\int_0^h 2 g \rho A x \, dx = g \rho A h^2$$

where ρ is the density of the liquid (air neglected), A the cross-sectional area of the tube, and h the change in height of the meniscus. Equating the two gives

$$K_l - K_a = \frac{2 g \rho h}{H^2}$$

from which K_l may be calculated if K_a is known.

This type of balance, known as the manometric balance, has been greatly improved by Wills and Hector (6) for measurements on gases. In this method the gas is balanced magnetically against a solution of known susceptibility. Instead of observing the motion of the meniscus directly, the motion of gum-mastic particles in a constricted portion of the tube was observed with a microscope. This indicator is very sensitive and an accurate balance can be obtained.

Wills and Boeker (7) have further modified this form of balance in their work on the variation of the susceptibility of water with temperature. In this experiment the water in one arm of the balance was heated to various temperatures and balanced magnetically against the water in the other arm, which was kept at the reference temperature. From the measurements, the ratio of the susceptibility at temperature t to that at the reference temperature could be calculated.

In the method devised by Curie (8) for determining the susceptibility of solids, a small sample of material of volume V and susceptibility κ_s is attached to the arm of a balance and suspended in a non-uniform magnetic field H in air. The force, which is measured with the balance, may be derived from the change in magnetic energy. This force, say in the x-direction, is given by

$$F_x = (\kappa_s - \kappa_a) V H_x \frac{\partial H_x}{\partial x}$$

Knowing κ_a, the field H and its gradient, the susceptibility of the solid can be calculated.

Soné (9) has used the principle of the Curie balance to determine the susceptibility of several gases, including nitric oxide, relative to water. In this case the solid was replaced by a rather long capsule into which the gases could be introduced. From a measurement of the force exerted on the capsule when evacuated, when filled with the gas, and when filled with air the susceptibility of the gas relative to air could be deduced. Knowing the susceptibility of air with respect to water the results could be referred to water as a standard. Since the magnetic effect of gasses is small, the measurements were made with the gas under several atmospheres pressure.

Another method for gases for which high sensitivity is claimed is the Faraday test body method. A light test body is suspended, by means of a fine torsion fiber, in a gas in a suitable container placed in a non-uniform magnetic field. Under these conditions a torque acts on the test body which is proportional to the difference between the susceptibility of the test body and that of the surrounding medium. If $T_x - T_o$ is the difference between the torque on the test body when surrounded by the gas under test and when in an evacuated space, and $T_s - T_o$ the corresponding quantity for the standard gas, it is easily shown that

$$\frac{\kappa_x}{\kappa_s} = \frac{T_x - T_o}{T_s - T_o}$$

where κ_x and κ_s are the susceptibilities of the gas under test and the standard gas respectively. The calculation for κ_x is carried out by replacing the torques in the above equation by the corresponding angular twists of the fiber necessary to restore the test body to its initial position. For high sensitivity the test body should be made as nearly magnetically neutral as possible.

Havens (10) has used this method to determine the magnetic susceptibility of nitrogen dioxide relative to oxygen. The test body consisted of two small evacuated glass bulbs attached together, with a compensating cross-piece of quartz. By the use of fine quartz fibers for the suspension a sensitivity of 3×10^{-15} was reported for volume susceptibility measurements.

In general, relative measurements of this sort are more easily carried out and are more accurate than absolute measurements since a knowledge of the field or its gradient is not necessary.

In all of the methods described above the sample is either suspended, or placed in some manner in a strong, fixed magnetic field. This appears necessary because the magnetic effect of para- and diamagnetic materials is extremely small. However, in 1933 Rankine (11) described a novel form of balance designed for measurements at low field strengths. He later constructed such a balance, but it failed to function with the requisite sensitivity, largely because of ferromagnetic impurities in some of the materials used in the construction (12). The principle of this balance is fundamentally different from the others in that the sample is fixed while the magnetic field is supplied by a small suspended bar magnet. This type of balance, as improved by Iskenderian (13), is used in the present experiment and will be subsequently described in detail.

For a more detailed discussion of the various other methods for measuring magnetic susceptibility see E. C. Stoner, Magnetism and Matter, Chapter III. (Methuen & Co. Ltd., London. 1934)

D. Other Measurements on Oxygen and Nitric Oxide.

1. Oxygen.

The susceptibility of oxygen has been the subject of a good many investigations. The gas was particularly well suited to early and less refined methods, for it is strongly paramagnetic and may be prepared in a pure state with little difficulty. The variation of the susceptibility with temperature follows Curie's law quite closely over a very wide temperature range. The theoretical value of the product $\chi_M T$ is accurately known and so furnishes an excellent means of checking various experimental methods.

The experimental values of $\chi_M T$ from several independent investigations at high field strengths are in essential agreement with the theoretical value. Some of the results obtained are as follows: (14) 0.983 (Curie), 0.970 (Onnes and Oosterhuis), 0.975 (Soné), 1.001 (Bauer and Piccard), 1.021 (Wills and Hector), 0.979 (Lehrer), 1.002 (Woltjer, Coppoolse, and Wiersma).

Iskenderian (15) has used the Rankine balance to make measurements on oxygen at a field strength of about 40 oersteds. Previous measurements on the gas had usually been made at field strengths of the order of several thousand oersteds. He obtained the value 0.979 for $\chi_M T$, which is definitely lower than the theoretical value. The low value is apparently due to the fact that the gas used was tank oxygen which, as he points out, probably contained some diamagnetic impurities. From his results it appears that there is no appreciable change in the susceptibility over the range of field strengths of from several thousand to some 40 oersteds.

On the other hand, Hector and Peck (16) have used an improved form of the Hughes induction balance to make measurements on oxygen and several liquids at field strengths of from 5 to 35 oersteds. They have reported finding oxygen approximately 7 per cent more paramagnetic and water about 6 per cent more diamagnetic in these fields than in strong fields. Following a suggestion by G. Temple (17), Meeks and Jamison (18) used a modified form of the Rankine balance which makes possible absolute as well as relative measurements if the distribution of magnetism in the suspended magnet is known. Relative measurements were made on carbon tetrachloride, benzene, and toluene using very pure samples. Measurements on each of these three liquids gave values (assuming -0.7200×10^{-6} for water) which were in excellent agreement with those reported by others using strong fields, indicating that a discrepancy of 6 per cent did not exist between the susceptibility of water in high and low fields. This makes the reported variation for oxygen appear very questionable. Jamison (19) later reported that preliminary absolute measurements on water yielded a value a few per cent below that obtained at high fields, but stated that refinements in experimental technique and computations might well bring the two values into agreement.

2. Nitric Oxide.

Relatively few measurements of the susceptibility of nitric oxide have been carried out. The gas is rather strongly paramagnetic, its susceptibility being a little less than half that of oxygen. However, it is somewhat difficult to prepare in a pure state and is not easily handled since it combines readily with oxygen to form the dioxide. The few reliable values of the susceptibility available have been obtained from measurements on the more or less impure gas with corrections applied for the susceptibility of the impurities. No previous measurements on this gas at low fields have been reported. Values of the mass susceptibility of nitric oxide, from measurements at high field strengths, have been reported as follows: 46.68×10^{-6} (Weiss and Piccard (20)), 48.7×10^{-6} (Bauer, Weiss and Piccard (21)), 48.80×10^{-6} (Soné (22)). The corresponding values of the volume susceptibility, κ , at 20°C and 760 mm pressure are 0.0583×10^{-6}, 0.0609×10^{-6}, and 0.0610×10^{-6} respectively, or approximately within 2 per cent of the theoretical value.

II. The Rankine Balance

If a bar magnet is placed parallel to the surface of a magnetizable material a force is exerted on the magnet due to a distortion of its field by the material. This force is an attraction if the material is paramagnetic, and a repulsion if diamagnetic. The force is proportional to the susceptibility of the sample and is given approximately by the equation (23)

$$F = \frac{\pi m^2 \kappa}{2x^2}$$

where m is the pole strength of the magnet, κ the volume susceptibility of the sample, and x the distance from the magnet to the surface of the material. To make use of this effect in the determination of susceptibility, an apparatus such as that pictured schematically in Fig. 1 is used.

In this arrangement the magnet M is suspended close to the cell C, into which liquids or gases may be placed. The suspension is made by means of a fine quartz fiber F attached to a short and very light beam B. The magnet is counter balanced by the weight W. The beam is in turn supported by another quartz fiber attached to a torsion head above.

The deflection of the suspended system is measured by means of the mirror O. Current in the control wire N is used to return the magnet to its original position against the force exerted by the sample. This type of suspension is designed to reduce the control on the system from extraneous magnetic fields, which may in some cases entirely mask the effect sought. Unless the magnet has a horizontal magnetic moment, a uniform magnetic field does not exert any directive torque on the beam. However, it is found in practice that the poles of the suspended magnet do not in general lie on a vertical line even when the axis of the magnet is vertical. This introduces a horizontal moment and therefore a directive torque on the beam in a uniform magnetic field. In general the axis of the magnet will not be exactly vertical because of a slight tilt due to the earth's field. This effect also contributes to a horizontal moment.

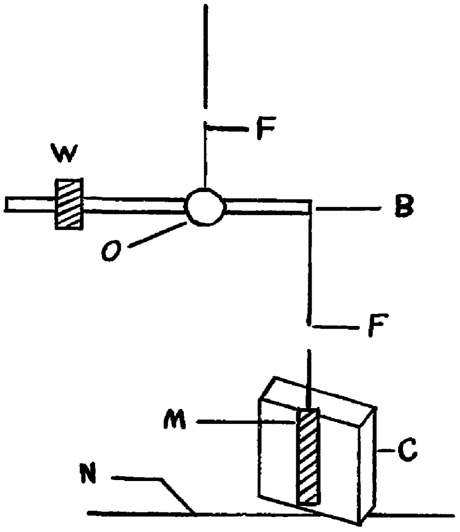


Fig. 1

By making the torsion constant of the lower fiber small in comparison to that of the upper fiber, the torque on the beam due to extraneous fields can be considerably reduced. Rankine (24) has shown that the effective torsional coefficient of such a system is given by

$$\tau = \tau' + \left(\frac{1}{\tau''} + \frac{1}{\mu' H}\right)^{-1}$$

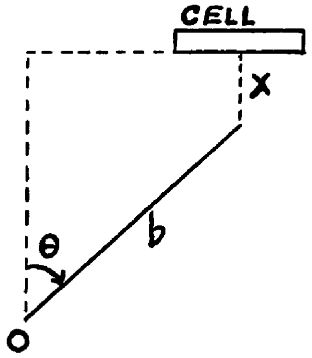
where τ is the ratio of the torque on the beam (due to the force between the specimen and magnet) to the resulting angular displacement, τ' and τ'' the torsion coefficients of the upper and lower fibers respectively, μ' the horizontal moment of the magnet, and H the extraneous uniform magnetic field. In practice $1/\mu' H$ is small compared to $1/\tau''$ and may be neglected. The expression then reduces to $\tau = \tau' + \tau''$ and if τ'' is made small in comparison to τ', the effective torsional coefficient is nearly that of the upper fiber.

Iskenderian (13) has further reduced the effect of the extraneous fields by suspending the magnet as follows; A Duralumin hook is attached to the magnet so that the point of the hook lies on the extended axis of the magnet. The point of this hook is tungsten tipped and rests in a jewel set in a Duralumin ring attached to the upper fiber.

It was found early that all ferromagnetic materials must be avoided in the construction and in the immediate neighborhood of the balance. Such materials distort the otherwise practically uniform earth's field and exert a torque on the beam, which may be greater than that exerted by the sample. The effect of such materials is to impair the sensitivity of the instrument. That the balance be constructed of materials free from ferromagnetic impurities seems to be one of the most important specifications in the design of a successful instrument.

The factors which determine the sensitivity of the balance can be deduced from Fig. 2, which shows the arrangement viewed from above. In this figure the beam is supported at O. b is the arm of the balance which carries the magnet represented by m, at a distance x from the face of the cell.

The equilibrium condition for the beam is



Fib. 2

$$T_0 + T + \frac{\pi m^2 b \sin\theta K}{2X^2} + \tau(\theta + \theta_0) = 0$$

where T_0 is the torque due to extraneous fields and to the magnetization of the cell by the magnet, T the torque due to the current in the control wire, and θ_0 an unknown angular displacement of the beam.

If T_0 and T are held constant, then

$$\frac{\Delta K}{\Delta\theta} = \frac{X^2}{\pi m^2 b \sin\theta}\left[\frac{2b\sin^2\theta - X\cos\theta}{X^3}\pi m^2 b K - 2\tau\right]$$

The precision in a measurement of K will be greatest when the above expression is a ninimum. In the balance designed by Iskenderian (25) the optimum value of θ was found to be about 29°, but due to accidental disturbances, an effort to obtain greater sensitivity than that for which $\theta = 90^\circ$ was not justified. When $\theta = 90^\circ$, we have

$$\frac{\Delta K}{\Delta\theta} = \frac{X^2}{\pi m^2 b}\left[\frac{2b^2\pi m^2 K}{X^3} - 2T\right]$$

For the balances yet constructed the last term in the parenthesis is small compared to the first and may be neglected, giving

$$\Delta K = \frac{2bK}{X}\Delta\theta \qquad (3)$$

For the balance used by Iskenderian (13) and also for that used in the present work, the sensitivity is of the order of 10^{-10} for susceptibilities of the order of 10^{-6}.

The relative susceptibility, κ , of a liquid or gas may be determined from the following considerations:

With the cell evacuated, the equilibrium equation for the beam is

$$T_0 + c\,i_0 + \tau\theta_0 = 0 \qquad (4)$$

where i_0 is the control current necessary to keep the magnet in its fiducial position near the cell, and c is a constant whose value depends upon the magnetic moment of the magnet and the distance from the magnet to the control wire. The other symbols have the same meaning as in previous equations.

When the cell is filled with the standard liquid, the equilibrium equation is

$$T_0 + c'\kappa_s + c\,i_s + \tau\theta_0 = 0 \qquad (5)$$

where i_s is the control current which returns the magnet to its original position, and $c'\kappa_s$ is the torque exerted by the standard liquid of susceptibility κ_s ; c' is a constant depending upon the pole strength of the magnet and its position with respect to the cell.

When the cell is filled with a liquid or gas of susceptibility κ_x , the equilibrium equation becomes

$$T_0 + c'\kappa_x + c\,i_x + \tau\theta_0 = 0 \qquad (6)$$

where i_x is the current which again returns the magnet to its predetermined position with respect to the cell.

From equations (4) and (5), considering the magnitudes of the currents without regard to sign, we have

$$C'\kappa_s = c(i_s - i_o) \tag{7}$$

From equations (4) and (6) we obtain

$$C'\kappa_x = c(i_x - i_o) \tag{8}$$

Combining equations (7) and (8) we have for the susceptibility κ_x, of the test specimen

$$\kappa_x = \frac{i_x - i_o}{i_s - i_o}\,\kappa_s \tag{9}$$

III. Apparatus.

A. The magnetic balance.

1. Construction.

The general form of the Rankine balance used in this experiment to determine the susceptibility of oxygen and nitric oxide, is similar to that used by Iskenderian (13) in his work on the susceptibility of H_2O, D_2O and HDO. However, the construction differs in some respects and will be described in detail.

The moving system is suspended from a torsion head A, as indicated in Fig. 3. To avoid any ferromagnetic materials in the construction this torsion head was fashioned from OFHC copper. By means of

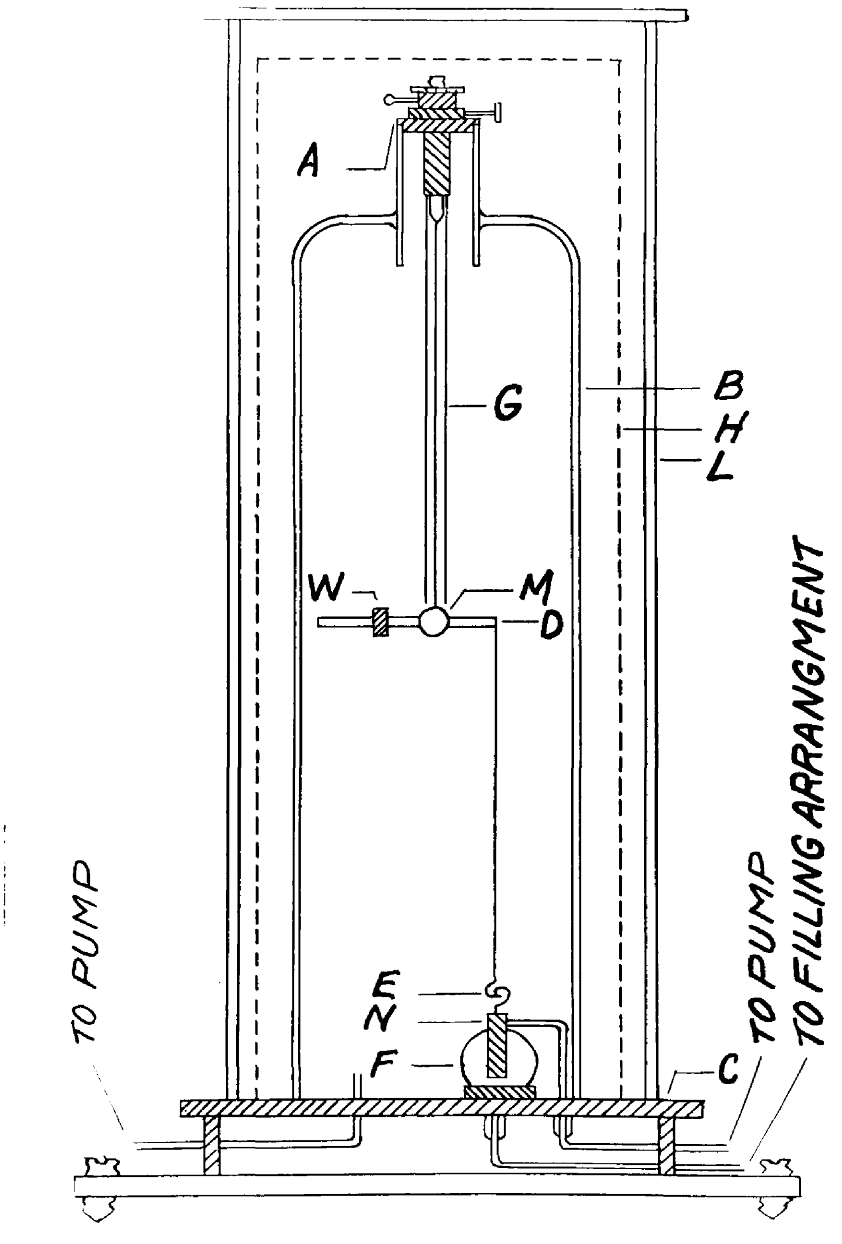


Fig. 3. The Magnetic Balance

this head the whole moving system may be raised or lowered to adjust the magnet above the base plate, and also a twist may be applied to the upper fiber if desired.

The torsion head is supported by the tripod B which is made entirely of pyrex glass. The over all height is approximately 55 cm, and the diameter of the circle containing the base about 15 cm. The support was made by sealing three 11 mm pyrex tubes radially into a short length of 45 mm tubing then bending these over to form a tripod. To secure the tripod the ends of the legs were waxed into shallow holes in the base plate C.

The base plate is also of OFHC copper and is about 8 in. square and 3/8 in. thick. It is secured to a heavy hardwood board somewhat larger than the plate by means of four short OFHC copper legs. The board is fitted with three large OFHC copper leveling screws. In use the instrument was placed on a concrete pier.

The balance beam D is made of a narrow strip of Duralumin. It is 6 cm long and the point of attachment of the upper fiber is about 2 cm from the end which carries the magnet. The counter weight W is a small strip of copper bent to ride on the beam. The mirror M is a small plane electrometer mirror fastened to the beam with shellac.

2. The magnet.

The magnet N is of an alloy called Nipermag and was obtained from Cinaudagraph Corporation. It is in the form of a right circular cylinder 24 mm long and 2 mm in diameter. Its weight is 0.5 gm and its pole strength about 10 emu. The magnet is attached to the lower fiber by the arrangement shown at E. The pointed end of the hook attached to the magnet rests in an indentation in a small glass bead set in the upper hook. These hooks were made from No. 30 Duralumin wire. The arrangement allows the magnet to take up its preferred orientation about its vertical axis with respect to extraneous magnetic fields, thereby reducing the torque exerted on the suspension fiber. It is doubtful if such an arrangement is of any great value in the present case since the torsion coefficient of the lower fiber is quite small in comparison to that of the upper fiber. However, this manner of suspension does greatly facilitate setting up the suspension or replacing quartz fibers.

The lengths of the upper and lower quartz fibers are about 24 cm and 17 cm respectively, and their torsion constants of the order 10^{-4} and 10^{-6} dyne-cm per radian. The production and measurement of quartz fibers will be described later in this section. The torsion constants of the fibers used in obtaining the data presented in this thesis were not actually measured but were estimated from actual measurements on fibers drawn under similar conditions.

The total weight of the suspended system is slightly over 1 gm. The deflection of the beam was measured by means of a telescope and scale arrangement. The mirror-to-scale distance in the present setup is slightly more than two meters.

3. The test cell.

The construction of a suitable test cell offered some difficulty as did the electrostatic shielding of the cell from the magnet. The test cell finally adopted was made by sawing off two 50 ml pyrex beakers a short distance from the bottom. These halves of the cell were finely ground and partially polished then fused together. While sealing these two parts together, entrance and exit tubes of small tubing were also sealed in. The cell so formed is approximately a cylinder about 4 cm in diameter and 1.5 cm long. It was supported in the proper position with respect to the magnet by sealing the connecting tubes through holes drilled in the base plate. The entrance and exit tubes were not in direct contact with the base plate but were ring sealed into short lengths of larger tubing which were set into counter sunk holes underneath the base plate and held rigidly by sealing with hard wax. The test cell and method of supporting is shown at F in Fig. 1. For purposes of clarity of the diagram, the exit tube is shown leaving through the base plate to the right, actually the exit is made directly behind the test cell.

It was found that in cleaning or in admitting air to the cell electrostatic charges were sometimes built up which completely vitiated the effect of the sample. To remedy this, a thin copper box was made to just fit over the test cell and the portion of the exit tube which extended above the base plate. The shielding was apparently complete, but the box, which was not of OFHC copper, attracted and held the magnet to it. To neutralize this effect a thin piece of cover glass was attached to the side of the box facing the magnet. This arrangement proved to be quite satisfactory and apparently did not appreciably decrease the sensitivity of the balance.

4. Cell filling arrangement.

The arrangement for filling the test cell is shown schematically in Fig. 4. From the bulb B the cell and connecting tubes may be evacuated, as well as the gas train when first put into use. The bulb B serves mainly to facilitate cleaning the test cell, for cleaning solution or other liquids may be introduced into C and drawn through the cell into B, from which they are easily removed. The connection to the gas train is a small copper tube which is soldered into a brass plate D. Both the plate and the top of the tube C were ground and sealed with stopcock grease. The tube is sufficiently flexible that it may simply be lifted up slightly and turned to one side when liquids are to be introduced into the test cell. Liquids were introduced into C by means of a pipette calibrated to deliver a volume sufficient to fill the test cell and exit tube to some point A. The volume of liquid required was about 26 ml. Liquids were also drawn out of the cell by means of the pipette, the entrance tube being slightly inclined to facilitate removal.

5. The control circuit.

At first the control circuit consisted of a single wire, mounted directly beneath the copper base plate, in series with one cell of a 6 volt storage battery, variable resistance, and a 10 ohm standard resistance. The current was measured by means of a L and N Type K

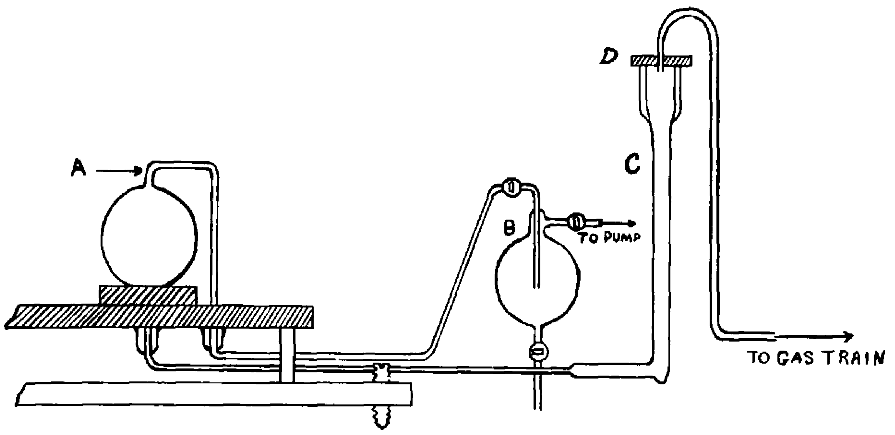


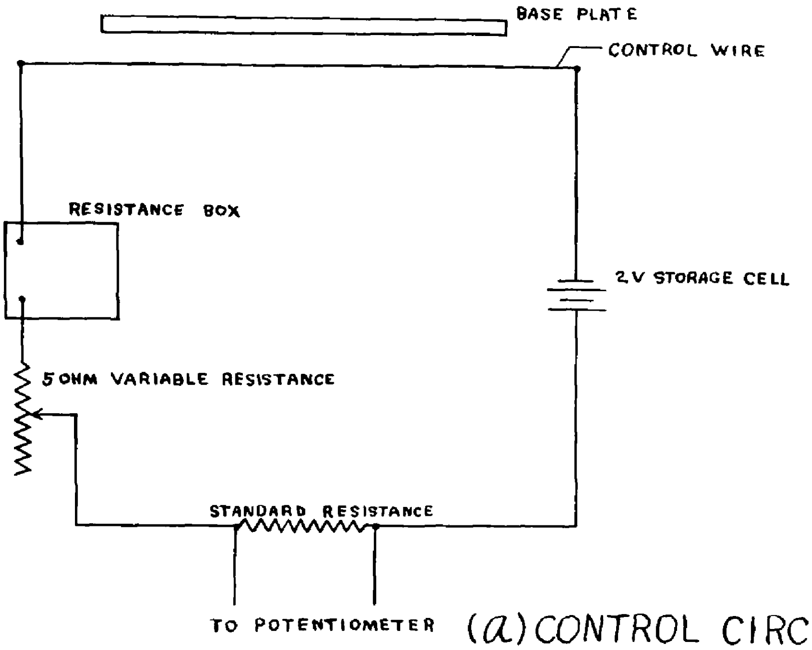
Fig. 4. Cell Filling Arrangement.

potentiometer by measuring the potential difference across the standard resistance. Later the mounting of the control wire was improved to insure its remaining in the same position, and a second wire mounted parallel to the first and just below it. Both wires were mounted in the plane of the beam in its zero position. The current in the second wire was used to bring the beam to its zero position making it possible to begin each determination with the same zero current in the upper wire. This was done since it was thought that perhaps more consistent readings might be obtained if the magnet were subjected to approximately the same field gradients at the beginning of each run. The results did not indicate that there was any particular advantage in using this second wire. So far as control over the motion of the beam was concerned, a single wire was found quite sufficient and adjustments were more easily made than when two wires were used.

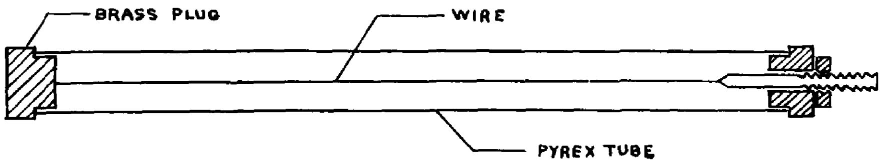
The control circuit and the method of mounting the wire is shown in Fig. 5. All variable resistances for controlling the current, as well as the potentiometer, were placed in an adjoining room so that it was only necessary to enter the constant temperature room to change samples.

6. Temperature effects and control.

One of the most serious problems in connection with the operation of the balance was that of disturbing temperature effects. It was noted early in the work that light falling on the fiber caused



(a) CONTROL CIRCUIT



(b) CONTROL WIRE MOUNTING

Fig. 5. Control Wire Mounting.

an immediate deflection of the beam. To guard against this, the upper fiber was surrounded with a heavy walled copper tube G (Fig. 3). A polished copper cylinder H, with only a small hole for viewing the mirror, was made to fit just inside the pyrex cylinder L which housed the balance. The whole was then surrounded with a Celotex box coated with aluminum paint.

To operate at the desired temperature and in order to control the temperature of the room it was necessary to provide both a heating and cooling arrangement. The cooling was accomplished by placing a large fan behind an auto radiator through which tap water could be circulated. To furnish the heating a 550 watt heater element was unwound and stretched in the form of a grid directly in front of the radiator. Water was allowed to flow continuously through the radiator while the temperature control was effected with the heater. The current in the heater was controlled by means of a sensitive thermostat in connection with a vacuum tube arrangement. The thermostat was mounted on the Celotex box surrounding the balance. The current through it was only one or two microamperes which did not affect the balance, and also made for better operation of the thermostat. The vacuum tube circuit and control relays were located in an adjoining room well away from the instrument. All of the relays were alternating current operated except for the one in the plate circuit.

In spite of the precautions mentioned to protect the instrument against temperature fluctuations, it did not operate satisfactorily although some preliminary data were taken with benzene as the test liquid. The expedient of thoroughly insulating the balance was first tried. The base was packed with rock wool and a double walled Celotex box prepared which was also packed with rock wool and placed over the instrument. This increased insulation did not much improve the performance of the balance and in addition greatly increased the time necessary for it to come to equilibrium when for any reason the temperature of the room had to be changed.

At this point a series of experiments were performed in an attempt to locate the basic cause of these disturbing temperature effects. With the base alone insulated, the temperature of the room was allowed to increase slowly while the deflection readings were taken every few minutes for about an hour. The temperature increase was only about 1.3° C, but the deflections were surprisingly large. To illustrate the magnitude of the effect the results of this test are shown in Fig. 6. Graph I shows the effect of increasing the temperature and Graph II the effect of decreasing the temperature. When the insulation was removed from the base similar results were obtained but with deflections in the opposite sense. With the copper cylinder removed the deflection took place more rapidly and reversed its direction after several minutes.

Although it was not possible to isolate specific factors which contributed to the temperature effect, the results of the tests proved of value in other respects. In all cases the extreme temperature sensitivity of the instrument was apparent, which explained why it failed to function satisfactorily even when reasonable precautions

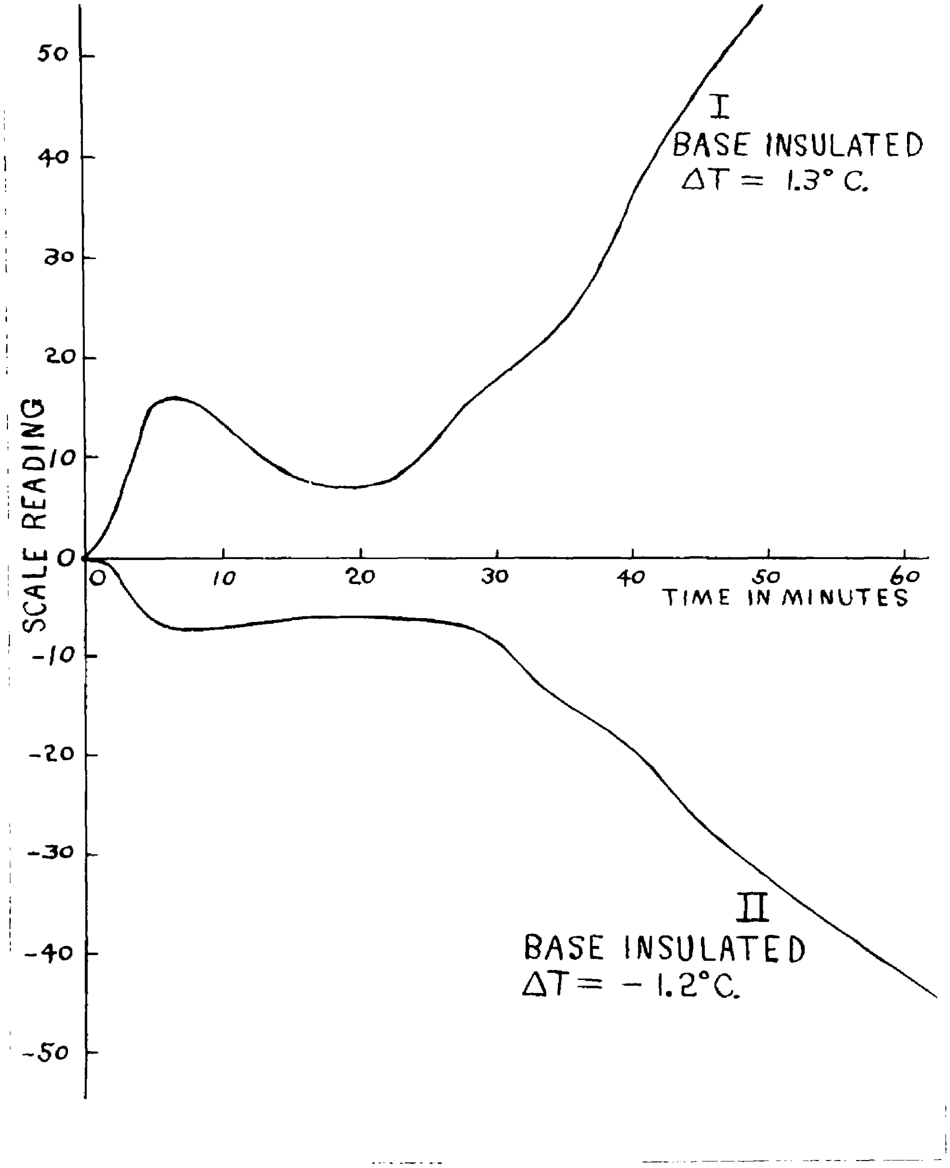

50
40
30
20
10
0
-10
-20
-30
-40
-50
SCALE READING
0
10
20
30
40
50
60
TIME IN MINUTES
I
BASE INSULATED
ΔT = 1.3° C.
II
BASE INSULATED
ΔT = − 1.2°C.

Fig. 6.

were taken. However, the most significant observation made during the series of tests was the fact that if sufficient time (a matter of hours) were allowed, the beam returned in each case to approximately its original position even at the higher or lower temperature.

This was taken as an indication that practically all of the trouble was due to temperature gradients set up over the instrument.

With the thought in mind to eliminate as far as possible temperature gradients, all of the old insulation was removed. A wood form about four inches high was built around the base of the instrument and also around the cell-connecting tubes and filling arrangement, leaving sufficient space for free circulation of air. The inside of this form was lined with Celotex. A single walled Celotex box which rested on the form was placed over the balance and a similar box over the cell filling arrangement. To provide for circulation of air a small rubber fan was placed in each box. The fans were mounted on a common shaft which extended through bearings in the wooden form. The fans were driven rather slowly from outside by means of a small motor belted to the shaft. A baffle was arranged in the large box to provide for vertical circulation of air about the instrument. An auxiliary fan was used in the room to insure a better mixing of the air. This improved the temperature control considerably.

With the arrangement just described the performance of the balance proved satisfactory and consistent readings were obtained for the first time.

7. Sensitivity and stability.

Fig. 7 shows the relation between deflection in terms of scale divisions and control current in the neighborhood of zero on the scale, with water in the test cell. The data were obtained by changing the control resistance in steps of 1 ohm. From this graph, the current change which produces a deflection of one scale division is about 6×10^{-6} amp. Deflections could be estimated to 1/10 of a scale division, corresponding to a current change of about 6×10^{-7} amp. The value is somewhat smaller with the test cell empty or when filled with oxygen or nitric oxide, but still of the same order of magnitude.

A typical value of i_w is 0.0030960 amp. Thus the uncertainty in reading the deflection is about 6 in the last place. This relatively more important in the case of nitric oxide where the current difference contains only three significant figures instead of four as in the case of water and oxygen. However, the uncertainty introduced in reading the current and deflection is far less than that due to extraneous effects which could not be controlled. Since the balance was used as a null instrument, with settings made on a particular zero mark on the scale, it is probable that the error introduced in the process of determining the fiducial current is less than that mentioned above.

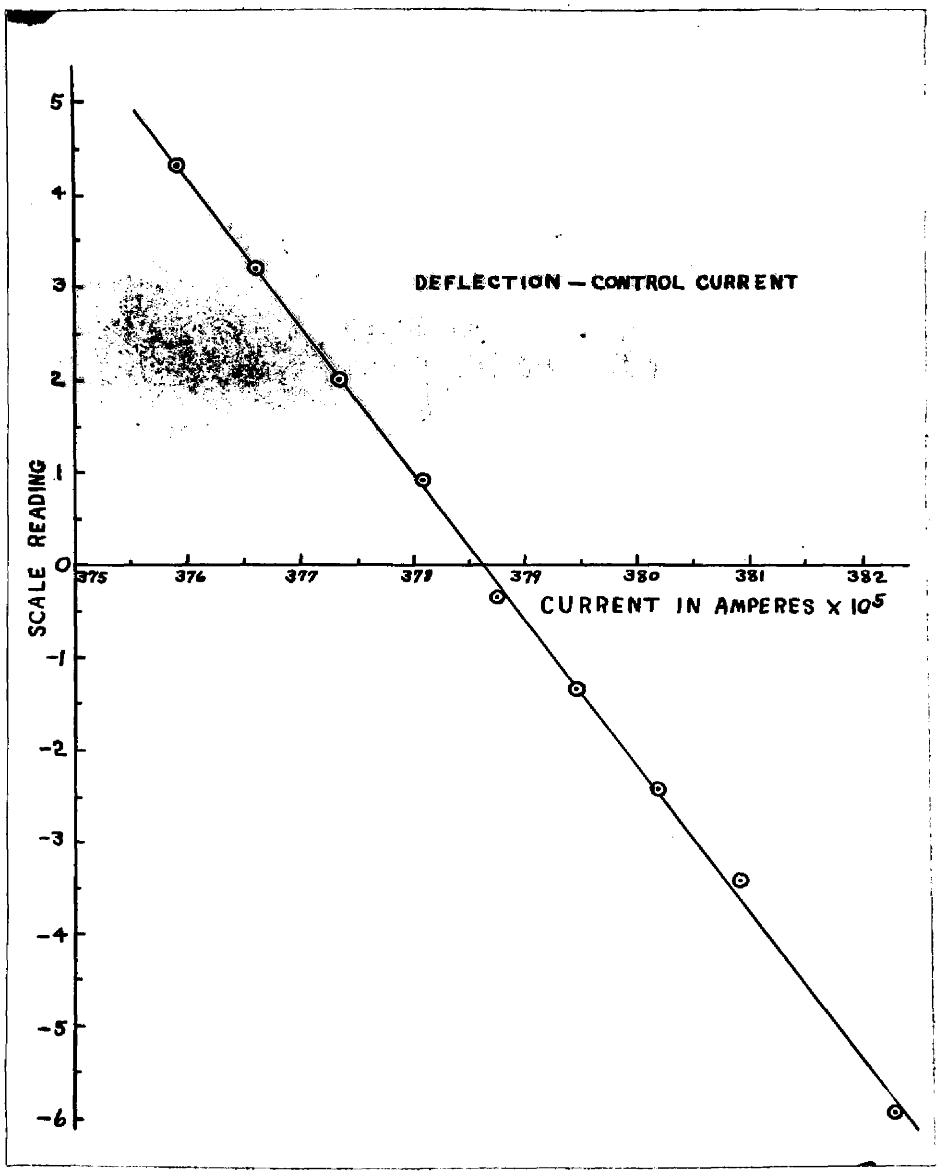

DEFLECTION — CONTROL CURRENT
SCALE READING
5
4
3
2
1
0
-1
-2
-3
-4
-5
-6
375
376
377
378
379
380
381
382
CURRENT IN AMPERES X 10^5

Fig. 7

B. Production of Quartz Fibers.

Some preliminary work was done on the production and measurement of quartz fibers used in connection with the magnetic balance. Fig. 8a is a photograph of the apparatus used in drawing the fibers. The method is a variation of the elastic catapult method used by Holbourn (26). Instead of using a long length of elastic to supply the drawing force, a window shade spring was employed as shown in Fig. 8b. By means of the wheel and axle arrangement the motion of the spring was amplified so as to swiftly separate the two pieces of quartz. The guide for the upper quartz holder was mounted on a rack and could be easily adjusted for height by the hand wheel shown at the right of Fig. 8a. The guide is fitted with a catch which is released by an electromagnet when a foot switch is closed. With the hand wheel adjustment and magnetic release the proper moment for releasing the upper quartz is more easily controlled than in the apparatus described by Holbourn.

To catch the fiber, two short lengths of heavy wire were inserted perpendicular to the back board and close to the line of flight of the upper quartz. These were placed about 50 cm apart and were covered with a sticky compound made by melting together rosin and castor oil as recommended by Holbourn. A sheet of air from a wing top was blown under each wire, so that as the fiber is drawn it is blown against the wires and held.

To fasten the upper quartz in the holder the sides of the holder were filed through so as to expose the rod. This section was first wrapped with a narrow strip of cellulose tape then tightly with fine thread. The method of securing the upper quartz in the holder is shown in

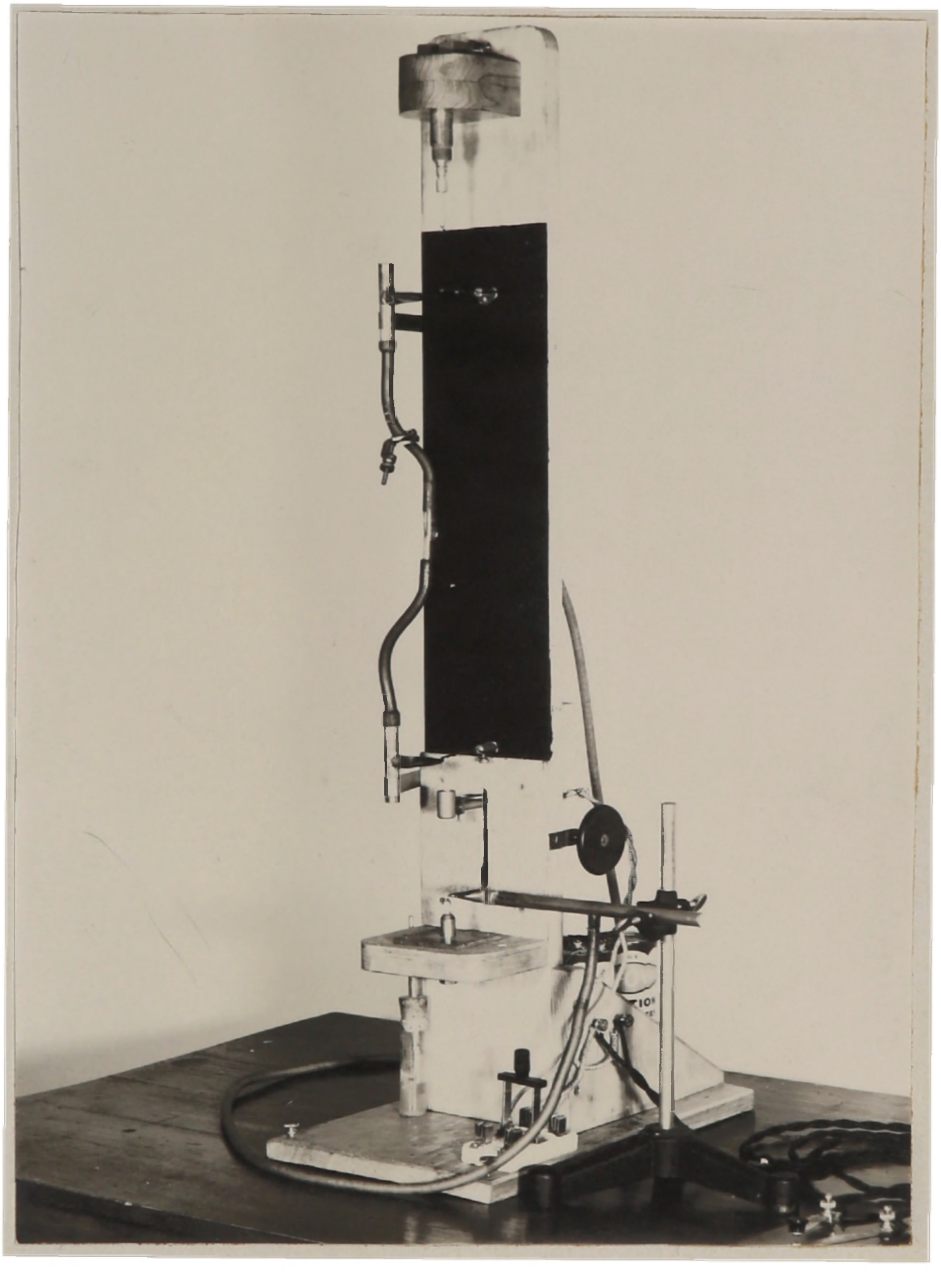


Fig. 8a. Quartz Fiber Apparatus.

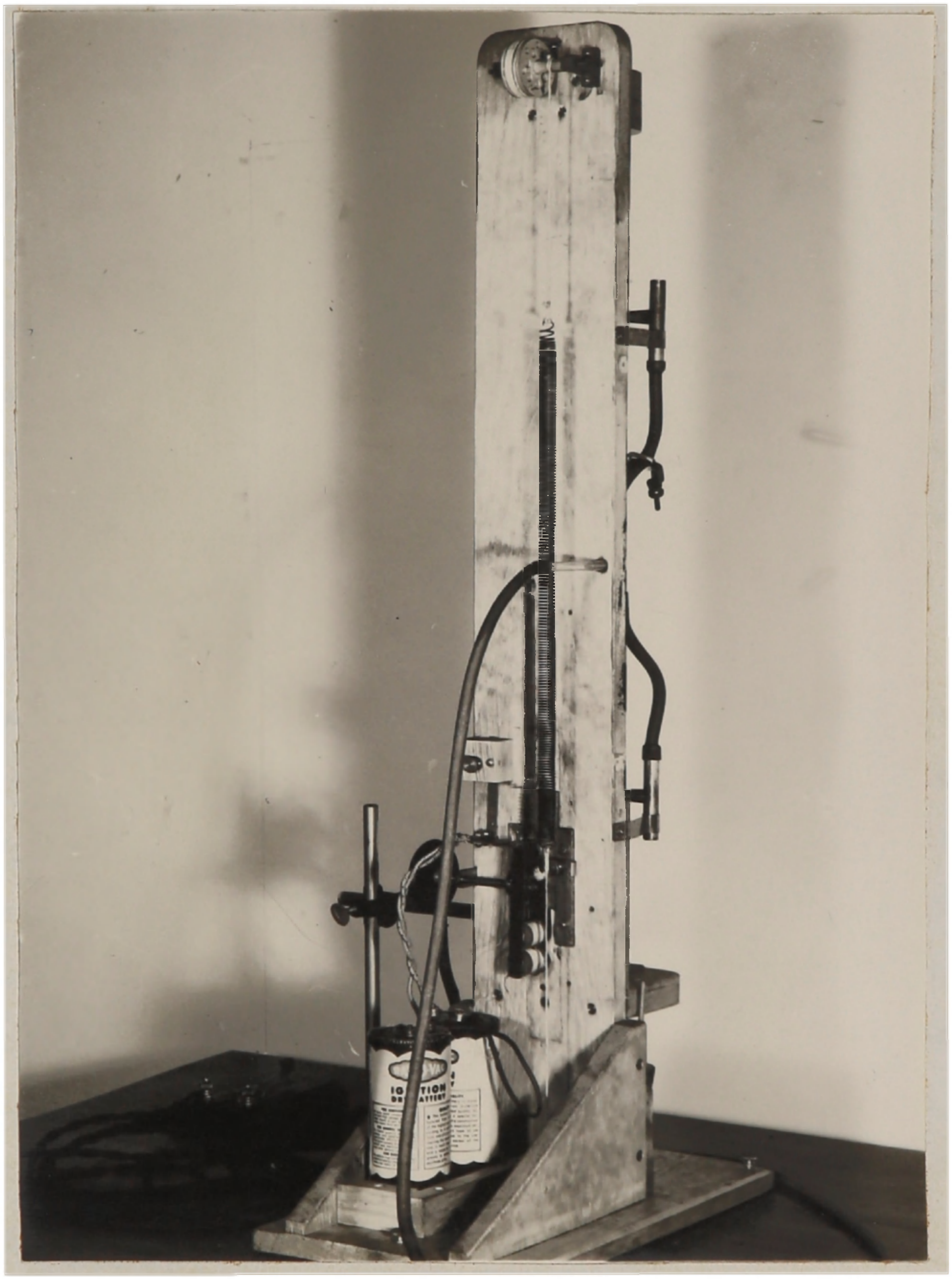


Fig. 8b. Quartz Fiber Apparatus.

Fig. 9a. Fig. 9b shows the method of holding the lower quartz; the end of the rod was swelled in an oxygen flame then inserted from the bottom of the holder. Quarter inch quartz rods were used.

To draw a fiber, a needle a fraction of a millimeter or so is first drawn on the upper quartz. A strong oxygen flame is then directed over the rounded top of the lower quartz until it is red hot. The upper quartz is quickly lowered by means of the hand wheel and the needle stuck to the lower quartz, then immediately released by pressing the foot switch.

In drawing a small fiber it is necessary to use a small needle which is sometimes melted away before it can be stuck to the lower quartz. In such case it was found helpful to direct a sheet of air from a wing top just over the top of the lower quartz to confine the flame to a thin sheet. This attachment is shown in Fig. 8a.

It was found that the diameter of the fiber is controlled largely by the size of the needle from which it is drawn, although for fine needles the tension in the spring must be increased somewhat.

This apparatus proved to be quite satisfactory and easy to use. It is compact and can be moved and used wherever gas, air, and oxygen are available. Fibers may be quickly made as needed making it unnecessary to store them. With the present apparatus the length of the fiber which can be drawn is limited to about 50 cm, but by increasing the height of the instrument longer fibers could certainly be drawn.

Several common methods for measuring the diameter of fibers were tried. In general, the results on the same fiber by various methods were not in particularly good agreement. The elastic straining method described by

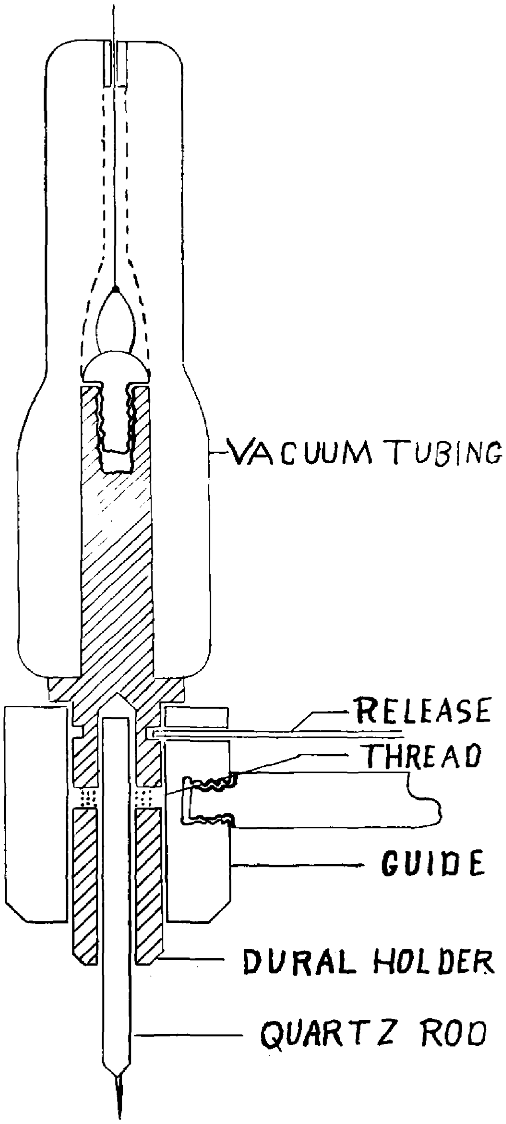


Fig. 9a. Upper Quartz Holder.

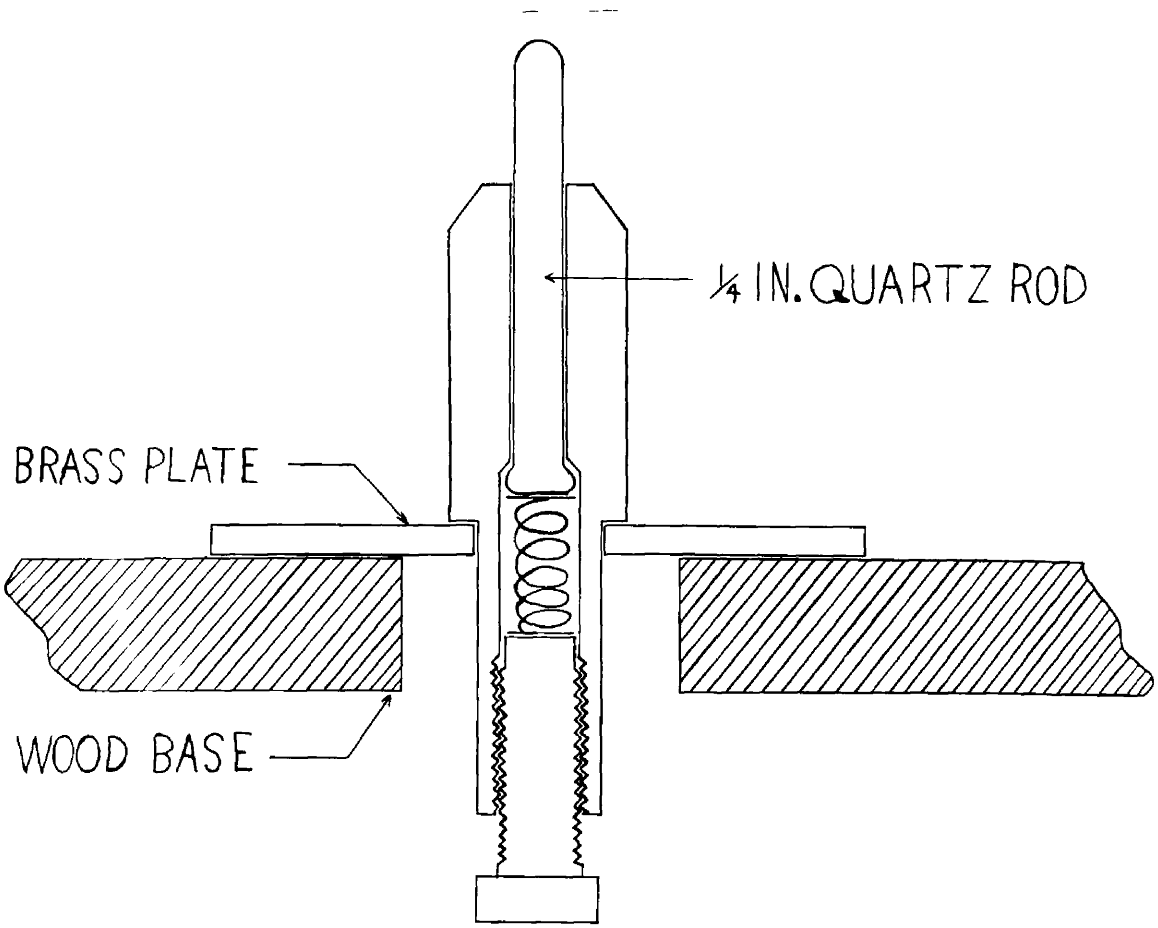


Fig. 9b. Lower Quartz Holder.

Rolt (27) proved to be the simplest and was the one generally used. In this method the fiber is held in a horizontal position and small weights hung at its center. The corresponding depressions from the horizontal position are measured with a cathetometer. From these data and knowing Young's modulus for quartz and the length of the fiber the diameter can be calculated. The smallest fiber measured in this work was about 0.6μ in diameter.

IV. Experimental Procedure.

A. Liquids.

In preparation for taking a reading the pyrex cylinder surrounding the instrument was first evacuated using a fore pump. The vacuum in the cylinder was maintained by continuous pumping in order to avoid any disturbances which might have resulted from small pressure changes. The test cell was then evacuated using a separate pump. After allowing sufficient time, usually an hour or more, for the instrument to settle down, the current i_o was noted which brought the magnet to its predetermined position with respect to the test cell. When benzene was used as the test liquid it was introduced before the water sample since it could be removed with less disturbance to the instrument than could water. To introduce the benzene, air was first admitted to the test cell, then the proper volume of liquid was drawn up into the pipette which was then inserted into the filling tube C (Fig. 4). It was then carefully released in order to avoid air bubbles and allowed to fill the cell. The current i_B was then noted which brought the magnet back to its original position. After removing the benzene the test cell was dried and the procedure repeated for water.

Even the removal of benzene from the test cell so disturbed the balance that two hours or more were usually required for it to again reach equilibrium. For this reason a new zero current reading was usually taken before introducing the water sample. In view of the time required for a complete set of readings, the procedure finally adopted was to take the benzene reading one night and a reading on water the next. It was found necessary to take readings at night since accidental disturbances could not be avoided during the day.

B. Gases.

The procedure for gases was considerably simpler and all of the data for a complete calculation could be obtained in one evening. The pressure of the gas in the collection bulb was first built up to about 15 cm of mercury, which was sufficient to fill the cell to a pressure somewhat above atmospheric. After noting the current reading with the cell evacuated the gas was introduced and the pressure subsequently reduced to atmospheric. After obtaining the current reading for the gas the cap of the cell-filling arrangement was removed, a little air drawn through the cell, and the water sample introduced.

The time required for a complete run on oxygen or nitric oxide was about two hours, but a much longer time was necessary for the balance to come to equilibrium after removing the water and pumping the test cell in preparation for the next run.

C. Preparation of Gases.

1. Oxygen.

Fib. 10 shows the plan of the apparatus used in preparing the oxygen. The gas was generated in an ordinary demonstration electrolysis apparatus using about a 10 per cent sulfuric acid solution. The tank shown at the left of the figure is a gallon can connected to a manometer and also to the bulb of the electrolysis apparatus. Tank oxygen was allowed to flow through this part of the system to flush out the air from above the solution in the bulb and from the

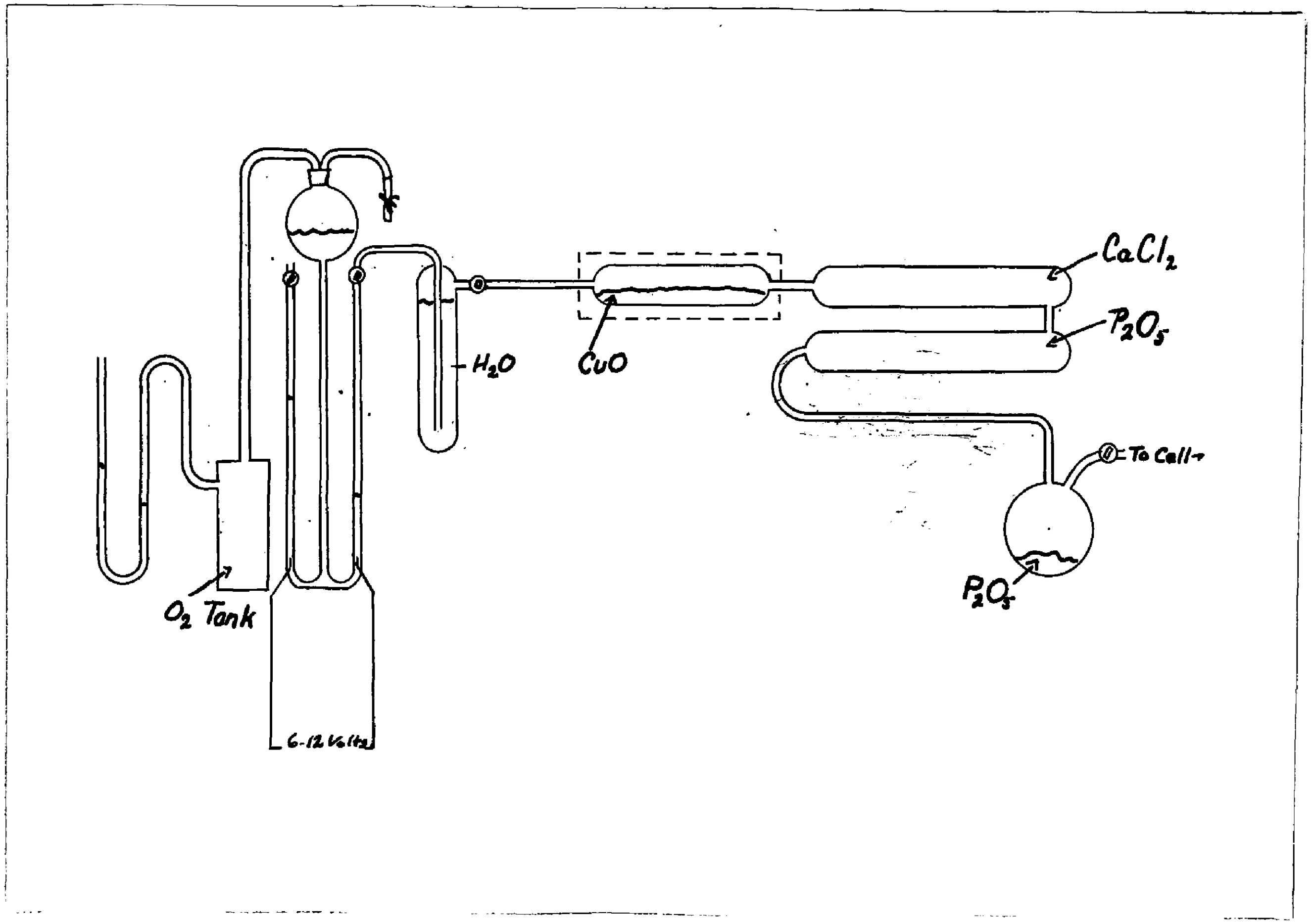


Fig. 10. Apparatus for Preparing Oxygen.

tank. The pressure was then built up sufficiently to give the necessary pressure in the collection bulb. Besides furnishing the necessary pressure, tank oxygen was used above the electrolyte to avoid dissolved air.

The generated gas was first bubbled through a tall column of distilled water to remove sulfuric acid vapor, then passed over hot copper oxide in an electrically heated furnace to remove any hydrogen which might have washed over into the oxygen side of the system. The gas was then passed through tubes containing calcium chloride and phosphorus pentoxide respectively, into the collection bulb.

2. Nitric oxide.

Several methods which reportedly gave pure or very nearly pure nitric oxide were investigated. Since the volume of gas required was rather small, the method of Emich (28) seemed most promising. In this method the gas is formed by the reduction of nitrous acid by mercury in a sulfuric acid solution. The solution recommended by him is one of pure sulfuric acid containing 2 per cent of sodium nitrite. When mercury is added the reaction takes place at the mercury surface. The evolved gas is freed of $N_2 O_3$ by passing over potassium hydroxide. In experimenting with this method it was found that apparently a better gas could be obtained using a less concentrated surfuric acid solution. It was also observed that when the gas was bubbled through and collected over mercury the purity was much improved. A reaction with the mercury was noted and attributed to NO_2 in the evolved gas. The dilute solution, aside from requiring much less sulfuric acid, was more easily handled. The reaction takes place without shaking since the heavy precipitate does not form on the mercury surface as it does when the concentrated solution is used.

The mixture finally adopted was a 20 per cent sulfuric acid solution containing 2 per cent of sodium nitrite with enough mercury to provide the necessary surface for a reasonable rate of evolution of gas. Fig. 11 shows the plan of the apparatus used. The acid solution containing the sodium nitrite is placed in flask B, leaving only a little space above the liquid. The mercury is placed in flask A. To generate the gas some of the mercury is allowed to flow through the stop cock into the lower flask. C is a double mercury bubbler through which the gas must pass. The mercury serves to remove the nitrogen dioxide and probably some of the higher oxides which may be present; it also aids in preventing too violent a reaction by maintaining a few centimeters pressure on the solution in the lower flask. D is a drying tube containing phosphorus pentoxide. At E the gas may be led outside for test or through the drying tube into the collection bulb G.

D. Analysis of Nitric Oxide.

Many solutions are known to absorb nitric oxide and are used in the analysis of the gas. In some cases the gas is merely absorbed and can be driven out by heating as is the case with ferrous sulphate. In others a chemical reaction takes place as when the gas is absorbed in $KMnO_4$. Solutions which react chemically with the gas are to be preferred since in the case of true absorption an equilibrium may be set up with some of the

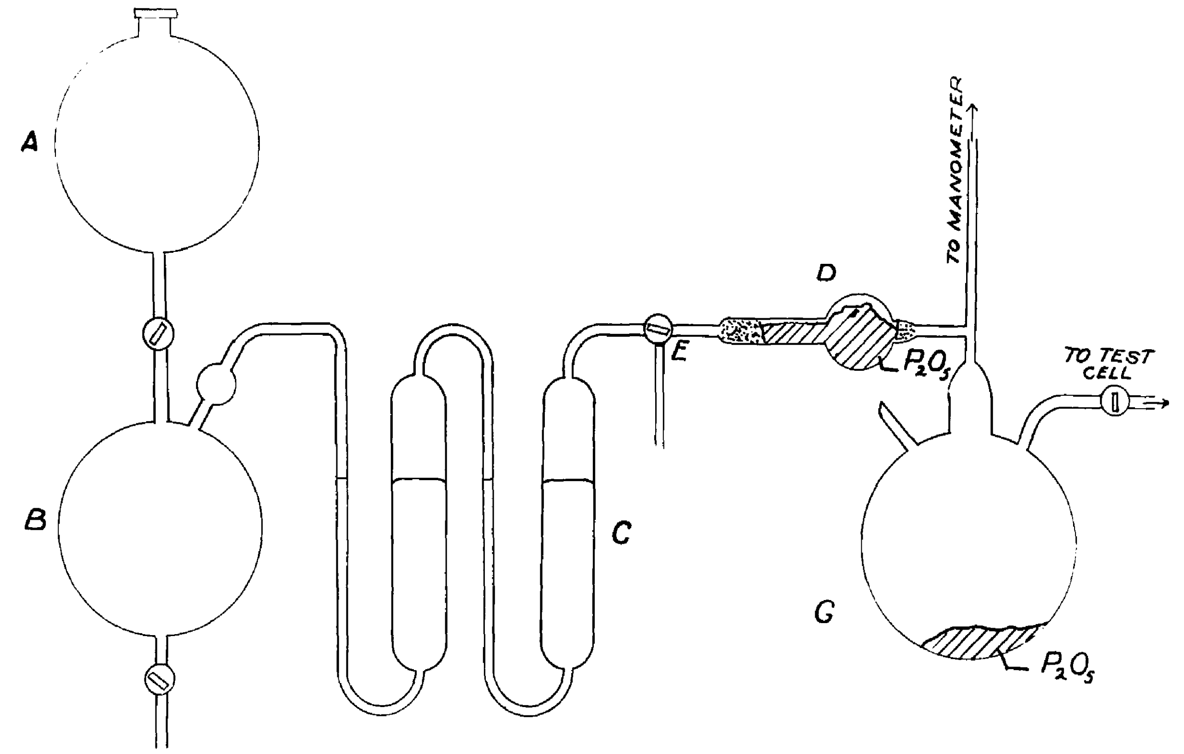


Fig. 11. Apparatus for Preparing Nitric Oxide.

gas unabsorbed.

Two solutions which react chemically with the gas were used in the present analysis. The first was a saturated solution of sodium sulphite made slightly alkaline with potassium hydroxide, and the second a solution of potassium dichromate to which was added one-fifth its volume of concentrated sulfuric acid. The analysis was carried out by collecting the gas over water in 11 mm glass tubes about 50 cm long, then placing them with the open end under the absorbing solution. As the gas is absorbed the solution rises in the tube and the remaining volume of unabsorbed gas gives a measure of the purity. It has been found that nitric oxide is slowly decomposed by contact with water. For this reason a special absorption tube was constructed for collecting the gas over mercury. The tube was similar to the others but had a three-way stopcock at the upper end. To collect the gas, the lower end was placed in a dish of mercury and the tube pumped until filled with mercury to the stopcock. The gas was then admitted above the mercury, with which it was in contact for only a few seconds. The results obtained with the two solutions and with the different absorbing tubes were in excellent agreement.

The average purity of the gas used in the measurements, as indicated by this method of analysis, was 99 per cent nitric oxide with very little variation.

A single attempt at titration of the potassium dichromate solution, which had absorbed nitric oxide, gave a somewhat divergent result. However, the accuracy of the one determination was not considered sufficient to form any good basis of comparison with the other values. Time did not permit any further work with this method of analysis.

V. Experimental Results.

A. Benzene.

Benzene was used in the preliminary work merely to test the performance of the balance and the results are not to be considered as giving an accurate value for the susceptibility of that liquid. These measurements were made under rather poor conditions before a suitable temperature control had been installed.

The measurements in Table 2 were made on thiophene free benzene at a temperature of about 25° C. In the calculations the mass susceptibility of water was assumed to be -0.7200×10^{-6} at 20° C, which gave -0.7179×10^{-6} for the volume susceptibility at the temperature of measurement. The density of benzene at 25° C. was taken to be 0.8734 gm/ml.

Table 2. Preliminary Measurements on Benzene.

Trial	$i_o \times 10^7$	$i_B \times 10^7$	$i_w \times 10^7$	$\Delta i_B \times 10^7$	$\Delta i_w \times 10^7$	$\chi \times 10^6$
1	22963	31966	33312	9003	10349	7150
2	14567	21830	23178	7263	8611	6933
3a	13510	20728		7218		
3b	13700		22080		8380	7080
4	13761	20301	21317	6540	7616	7035
Mean value (mass susceptibility)						7049

In the above table i_o, i_b, and i_w denote the control currents, in amperes, with the cell evacuated, with benzene in the cell, and with water in the cell, respectively.

Δi_B and Δi_w denote the quantities $i_B - i_0$ and $i_w - i_0$. χ represents the mass susceptibility of benzene at the temperature of measurement. Although the variation is rather large, the mean value is in good agreement with the value $\chi = (0.7036 \pm 0.0012) \times 10^{-6}$ as obtained by Meeks and Jamison (18) using a similar balance.

B. Oxygen.

1. Undried tank oxygen.

The following set of measurements was made using tank oxygen. The gas was taken directly from the tank without being dried.

Table 3. Measurements on Undried Tank Oxygen.

Trial	$i_0 \times 10^7$	$i_{O_2} \times 10^7$	$\Delta i_{O_2} \times 10^7$	$\Delta i_w \times 10^7$	$\chi_M T$
1	28502	26754	1748		
2	28499	26747	1752		
3	28526	26766	1760		
4	28549	26755	1794		
Mean Values			1764	9589	0.968

In the above table i_{O_2} refers to the control current with oxygen in the test cell. Δi_{O_2} denotes the quantity $i_{O_2} - i_0$. $\chi_M T$ is the product of the molar susceptibility by the absolute temperature; for pure oxygen the theoretical value is 1.000.

The above data were taken with the balance in essentially its final form. The temperature control had been improved so that the temperature of the room could be kept constant to within 0.1° C. Fans had been installed in the housing to prevent temperature gradients from being set up over the balance. Instead of taking a reading on water following one on oxygen, the average value of $\Delta i_w = 9589 \times 10^{-7}$ was used. This value was the mean of six separate measurements on water taken over as many days. The average deviation from the mean was only 0.04 per cent. In view of the constancy of these readings it did not appear necessary to repeat readings on water with each test on oxygen. The temperature of measurement was 21.8° C. at which temperature the volume susceptibility of water is -0.7184×10^{-6}. The density of oxygen was calculated for the temperature and pressure of measurement from the value of 1.4290 gm/l at 0° C. and 760 mm pressure.

2. Dried tank oxygen.

For the next set of measurements, oxygen was taken from the same tank and run through a drying tube before being admitted to the test cell. Table 4 shows the results of four determinations on the dried gas.

Table 4. Measurements on Dried Tank Oxygen.

Trial	$i_0 \times 10^7$	$i_{O_2} \times 10^7$	$\Delta i_{O_2} \times 10^7$	$\Delta i_w \times 10^7$	$\chi_M T$
1	28563	26761	1802		
2	28517	26733	1784		
3	28552	26740	1812		
4	28595	26803	1792		
Mean Values			1798	9589	0.987

A comparison of the above data with that of Table 3 would indicate that water vapor may be the chief diamagnetic impurity in the tank oxygen used. However, some measurements were made later on the dried gas from another tank and a value considerably lower than the one above obtained, indicating a variation in purity from one tank of the gas to another.

3. Electrolytic oxygen.

Table 5 shows the results of the final measurements on oxygen. The gas used was electrolytic oxygen, purified and carefully dried by passing over calcium chloride and phosphorus pentoxide. The conditions of measurement were kept as nearly constant as possible throughout the series of runs. Except in one or two cases a reading was taken on water immediately following the one on oxygen. The temperature of measurement was 21° C.

Table 5. Measurements on Electrolytic Oxygen. (20° C.)

Trial	$\Delta i_{O_2} \times 10^7$	$\Delta i_w \times 10^7$	$K_{O_2} \times 10^6$	$\chi_{O_2} \times 10^6$	$\chi_m T$
1	1893	9959	0.1407	105.7	0.992
2	1907	9830	0.1429	107.3	1.007
3	1909	9830	0.1437	107.9	1.012
4	1857	9821	0.1395	104.8	0.983
5	1878	9866	0.1407	105.9	0.994
6	1890	9867	0.1420	106.6	1.000
7	1887	9867	0.1418	106.5	0.999
8	1876	9897	0.1409	105.6	0.993
9*	1857	9892	0.1389	104.3	0.979
10*	1860	9943	0.1382	103.8	0.974
11*	1840	9826	0.1384	104.0	0.976
12	1893	9779	0.1430	107.4	1.008
13	1863	9829	0.1397	104.9	0.984
	Mean Values		0.1415	106.3	0.997
	Av. Deviation From Mean		0.0012	0.9	0.008
	Probable Error in Mean		0.0003	0.2	0.002

* Deleted from the final calculations.

In the above table K_{O_2} and χ_{O_2} denote the relative volume and mass susceptibilities respectively. The values of K_{O_2} and χ_{O_2} have been reduced to 20° C. and 760 mm pressure.

Those trials marked with an asterik have been deleted in calculating the mean values and probable error. There was reason to believe that the gas had become contaminated when these measurements were made. Before making the next run (No. 12), the entire system was pumped out and refilled with oxygen.

C. Nitric Oxide.

Table 6. Measurements on Nitric Oxide.

Trial	$\Delta i_{NO} \times 10^7$	$\Delta i_w \times 10^7$	$\chi_{NO} \times 10^6$	$\kappa_{NO} \times 10^6$
1	756	9796	46.5	0.0581
2*	699	9740	43.2	0.0540
3	789	9740	48.5	0.0606
4	757	9534	47.4	0.0592
5	742	9538	46.4	0.0580
6	763	9580	47.6	0.0594
7	748	9551	47.0	0.0587
Mean Values			47.2	0.0590
Average Deviation From Mean			0.6	0.0007

* Deleted from the final calculations.

The results shown in Table 6 are those obtained for nitric oxide, using a gas which was shown by analysis to be 99 per cent pure.

Δi_{NO} in the above table denotes the value of $i_{NO} - i_0$, χ_{NO} the mass susceptibility, and κ_{NO} the volume susceptibility of nitric oxide. These values have been corrected for 1 per cent nitrogen and reduced to 20° C. The density of nitric oxide at the temperature and pressure of measurement was calculated from the value 1.3402 gm/l at 0° C. and 760 mm pressure. The density of nitrogen at 0° C. and 760 mm pressure was taken to be 1.2505 gm/l, and the mass susceptibility at 20° C. to be -0.27×10^{-6}.

Trial No. 2 is definitely out of line with the other values and has been deleted in determining the mean and average deviation from the mean.

VI. Calculations.

A. Oxygen.

In every case, whether the test specimen is a liquid or a gas, the first step in the calculations is to find the volume susceptibility relative to water at the temperature of measurement. This is carried out using Equation (9), in which κ_s now becomes the volume susceptibility of water and must be calculated from the known mass susceptibility.

κ_w is determined as follows: The mass susceptibility of water at 20° C. is assumed to be -0.7200×10^{-6}. The volume susceptibility is given by $\kappa_w = \chi\rho$, where ρ is the density of water at the temperature of measurement. Having thus found the volume susceptibility, κ_x, of the test specimen, the mass susceptibility is given by $\chi_x = \dfrac{\kappa_x}{\rho}$, where ρ is the density of the test specimen at the temperature and pressure of measurement.

In the case of oxygen the mass susceptibility at 20° C. was calculated from the value of 21° C. assuming that χ is inversely proportional to the absolute temperature. κ, at 20° C., was then determined from the value of χ at 20° C., using $\kappa = \chi\rho$, where ρ is now the density of the gas at 20° C. and 760 mm pressure. $\chi_M T$ is the product of the mass susceptibility, the molecular weight, and the absolute temperature.

It will be noted that -0.7200×10^{-6} is taken for the mass susceptibility of water at temperatures other than 20° C. for which it is given. In case of the measurements on benzene this value is taken at 25° C., and also at 21° C. at which temperature the final measurements on oxygen and nitric oxide were made. Experiments indicate that there is very little if any variation of this quantity with temperature, and that the variation observed depends upon the previous treatment of the water, that is, whether or not it has been standing in contact with air or some other gas.

Wills and Boeker (7) have made measurements on water over the temperature range from 20° C. to about 70° C. They found that boiled water indicated less diamagnetism at temperatures higher than 23.5° C. and more diamagnetism above that temperature when the water had stood in contact with helium gas for several days before measurement. The variation, which is less than 1 per cent in either case, is erratic and difficult to account for. This paper also gives a good summary of the previous work on the variation of the susceptibility of water with temperature.

B. Nitric Oxide.

The method of calculating the observed susceptibility of nitric oxide is the same as that used for oxygen. However, this gas requires special consideration in that a correction must be made for the impurity in the gas. The calculation is as follows: Assuming that the constituent susceptibilities are additive and that the impurity is entirely nitrogen, we have

$$\chi_{obs.}(m_{NO}+m_{N_2}) = \chi_{NO}m_{NO} + \chi_{N_2}m_{N_2}$$

Putting the mass of each gas in terms of volume and density, we obtain

$$\chi_{NO} = \chi_{OBS.} + \frac{V_{N_2}/\rho_{N_2}}{V_{NO}/\rho_{NO}} \left(\chi_{OBS} - \chi_{N_2} \right)$$

Assuming Soné's value (29) of -0.27×10^{-6} for the mass susceptibility of nitrogen, the correction to the observed value amounts to about 1 per cent in this particular case.

It may be mentioned that the temperature variation is here assumed to be the same as that for oxygen. However, theory predicts that the susceptibility of nitric oxide, unlike that of oxygen, should not strictly follow Curie's law. The deviation is very small and certainly would not be detected over the temperature range involved here.

It was also assumed that the residual gas was entirely nitrogen. This seems a rather bold assumption, but is supported by the work of Moser (30), Weiss and Piccard (20), and Soné (22). Unless oxygen or water vapor, for example, are present in appreciable quantities in the residual gas, the correction due to the actual susceptibility of the impurity is of little consequence in a gas which is 99 per cent nitric oxide.

VII. Discussion.

A. Preliminary Results.

The performance of the Rankine balance in this experiment has been found thoroughly satisfactory, with the precision in a single determination limited largely by accidental disturbances which could not be completely controlled. The average deviation from the mean of a number of determinations on oxygen is practically the same as that reported by

Iskenderian (15).

Equation (3) with $b = 2$ cm, $x = 0.5$ cm, and $\kappa = 0.1400 \times 10^{-6}$ shows that the theoretical sensitivity of the present balance for measurements on oxygen is about 2×10^{-10}. This sensitivity is not attained in a single determination, but the probable error in the mean of measurements on oxygen is but 3×10^{-10}. The data shows that the effect of these accidental disturbances is entirely a random one, with the maximum deviation of any one measurement from the mean of about 2 per cent and the average deviation 1 per cent. It is felt that considerable significance may therefore be attached to the mean values given here. These values are, in the author's opinion, about as precise as can be obtained with the balance in its present form and used under usual laboratory conditions.

From the preliminary measurements on tank oxygen, four determinations on the gas taken directly from the tank gave 0.968 for $\chi_M T$; when the gas was carefully dried the same number of determinations gave the value of 0.987. However, some later measurements on the dried gas from another tank gave a considerably lower value. It is thus apparent that the somewhat low value obtained by Iskenderian (15) is accounted for on the basis of impurities in the gas; also that a variation in the purity of the gas from tank to tank may be expected. It is evident that one of the impurities is water vapor which is strongly diamagnetic and would, therefore, be particularly effective in lowering the observed value. However, other likely impurities in the gas have susceptibilities small in comparison to that of oxygen. These impurities, even though their magnetic effects are small, displace oxygen in the test cell and also contribute to a lower observed value.

B. Electrolytic Oxygen.

Measurements on electrolytic oxygen in the present research give a mean value of 0.997 for $\chi_M T$, which is in excellent agreement with the theoretical value of 1.000. The agreement with the results obtained by other methods using high field strengths is also good. The average of the results of seven other investigations (14), using a different method, is 0.990, with a maximum deviation from the mean of about 3 per cent.

C. Nitric Oxide.

In view of the results on oxygen it is difficult to reconcile, on the basis of experimental error, the 3 per cent difference between the value obtained here and that obtained by Soné (22) for nitric oxide. The highest single value obtained in the present work is a little more than 0.5 per cent below that reported by Soné.

An important factor which enters into measurements on nitric oxide is the question of the purity of the gas. Most measurements have been made on the more or less impure gas and the observed value of the susceptibility corrected for the impurities. In the present analysis of the gas the two different absorbing solutions used gave results in agreement to 0.2 per cent. Since it is generally agreed that absorption methods are reliable, especially when used on a gas of rather high purity, it is probable that the 99 per cent purity stated is very close to the correct value. It therefore seems improbable that a more accurate analysis of the gas would change the value of the susceptibility by more than a fraction of 1 per cent.

The gas used by Soné was about 95 per cent nitric oxide by volume. In his paper he states: "....... thus the correction for the susceptibility due to nitrogen was about 3 per cent." According to the author's calculations the correction would be nearer 5 than 3 per cent. However, this would result in an even greater discrepancy between the two values.

It will also be noted that the volume susceptibility obtained here is about 1.2 per cent below the theoretical value. Van Vleck (3) points out in his paper that x in Equation (2) should be about 5 per cent larger, due to the fact that the constant B, in the term value, is different in the two component normal states of the molecule. He states that by a crude estimate this would affect the susceptibility by about 1 per cent. It is apparent from his final equation that an increase in x lowers the susceptibility. Hence, it is entirely possible that his value 0.0597×10^{-6} may be as much as 1 per cent too high. This would bring the value 0.0590×10^{-6} into excellent agreement with the theoretical value, while it would appear that 0.0610×10^{-6} obtained by Soné is too high.

At the beginning of the present work it was thought that the balance might be adapted to making measurements over a temperature range. It appears that this would be almost impossible with the present arrangement for the balance itself was found very sensitive to temperature changes. It would be necessary to thermally insulate the test cell from the magnet which would introduce many difficulties since the magnet must be kept quite close to the test cell. Nitric oxide would be particularly interesting in this respect for the theoretical deviation from Curie's law could be tested at low field strengths. Van Vleck (3) has calculated the value of the apparent Bohr magneton number for various temperatures ranging from 0° K to an infinite temperature. The value varies from 0 at absolute zero to 2.000 at an infinite temperature. Assuming that the same precision could be attained for nitric oxide as in the present work, measurements over a temperature range of 100° C. or so, about room temperature, would be sufficient to at least show the deviation. Measurements over a much larger temperature range would be desirable.

A number of investigations (31) of the relative susceptibility at different temperatures have been made by other methods. The temperature range extended from 113° K, which is below the boiling point of nitric oxide, to about 300° K. The experimental values agree with those calculated over the entire range investigated to within 1 per cent.

The value of the apparent Bohr magneton number ($\frac{\theta}{\beta}$ in Equations (2)) as calculated from the value 0.0590×10^{-6} obtained here is 1.82 at 293° K. The value obtained by Van Vleck (3) at the same temperature is 1.836. The value from Soné's data is 1.85.

VIII. Conclusions.

1. The results demonstrate that the performance of the balance is satisfactory under usual laboratory conditions if measurements are made at night when conditions are best. The precision in a single determination is limited by accidental disturbances which at present cannot be controlled.

2. Results show that the high theoretical sensitivity of this type

of instrument is not attained, but the probable error in the mean of a large number of determinations does approach the theoretical sensitivity. The values, particularly those for oxygen, are therefore about as precise as can be obtained with the balance in its present form.

3. The instrument is very sensitive to temperature gradients, but with proper precautions their effects can be controlled.

4. The value of $\chi_M T$, reported by Iskenderian for oxygen, is too low because of impurities in the gas. The value for electrolytic oxygen is in excellent agreement with the theoretical value and with the average of the results of several other investigators using intense fields. It is apparent that the susceptibility of water shows no appreciable change in passing from high to low field strengths.

5. The susceptibility of nitric oxide is in essential agreement with the theoretical value, but definitely lower than that obtained by Soné. The discrepancy does not seem to be accounted for on the basis of experimental error. Whether or not it is due to an actual change in susceptibility with field strength is questionable.

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