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MAGNETIC STUDIES OF NICKEL COMPLEXES
WITH SOME VIC-DIOXIMES

by

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DOCTOR OF PHILOSOPHY

Major Subject: Analytical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

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Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College
1952

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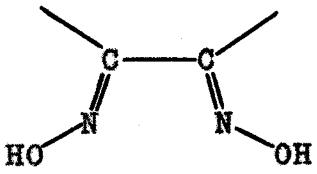
I. INTRODUCTION

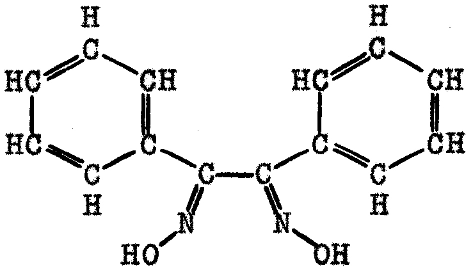
Of the rapidly growing group of organic compounds which are used as qualitative and quantitative reagents in analytical chemistry, perhaps the most familiar is dimethylglyoxime. The brilliant color and "climbing" ability of its nickel derivative are remembrances not easily forgotten by the erstwhile student of quantitative analysis. The near-specificity of the reagent for nickel and the simplicity of the gravimetric procedure in which it is most often used are more likely to be recalled by the analytical chemist, who doubtless frequently wishes that a similar reagent were available for each of the troublesome elements of the periodic table.

Dimethylglyoxime, or more properly, 2,3-butanedione-dioxime, is but one of a class of similar compounds known as the _vic_-dioximes. Also referred to as 1,2-dioximes, _ortho_-dioximes or α-dioximes, these compounds have in common the functional structure of two oxime groups attached to adjacent carbon atoms. Isomeric forms of the compounds are possible, depending on the angles at which the hydroxyl groups extend from the nitrogens of the oxime groups, but the α or _anti_ form,

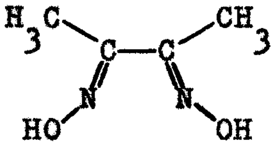


in which the hydroxyls are most distant from each other, is the structure responsible for the formation of the insoluble nickel and palladium derivatives of these reagents. The class name vic-dioxime is to be preferred, since the prefix vic-, an abbreviation of vicinal, meaning neighboring, points out the necessary adjacency of the carbons to which the reactive oximes are attached.

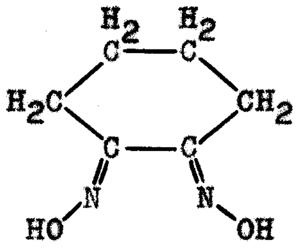
Among the numerous vic-dioximes which have been investigated for their analytical properties, there are five which have met with more frequent and useful application than the others. They are: α-benzildioxime, 2,3-butanedionedioxime (dimethylglyoxime), 1,2-cycloheptanedionedioxime, 1,2-cyclohexanedionedioxime and α-furildioxime. The structures of these reagents are indicated below.



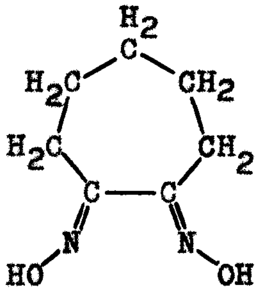
α-Benzildioxime



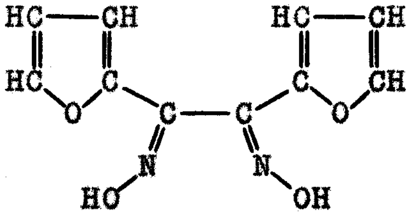
2,3-Butanedionedioxime



1,2-Cyclohexanedionedioxime



1,2-Cycloheptanedionedioxime



α-Furildioxime

The practical applications of even these five compounds have not been uniformly successful, however. Factors which in some cases have operated to the detriment of their usefulness include insufficient solubility of the reagent in water, coprecipitation of the reagent with the desired nickel derivative, and incomplete insolubility of the nickel precipitate in water, among others. Even 1,2-cycloheptanedionedioxime, which is considered to turn in the best performance in the gravimetric analysis for nickel (49), cannot assume the role of the best all-around reagent because of its definite inferiority to 2,3-butanedionedioxime or 1,2-cyclohexanedionedioxime in regard to the sensitivity of qualitative detection of nickel. The vivid red colors of the nickel compounds of the latter two reagents are the attributes which cause them to excel in this phase of analysis; the yellow color of the nickel derivative of 1,2-cycloheptanedionedioxime is definitely less easily recognized when the substance is present only in small quantities.

Although the vic-dioximes approach the concept of the ideal reagent (53) more closely than do most of the organic compounds used in chemical analysis, it is evident that there is ample room for improvement in even these highly regarded reagents. Since there are several of them which have been used for the same purpose, steps toward such improvement can obviously be guided best by (1) consideration of the results of fundamental studies not only on the reagents themselves, but on their nickel and palladium derivatives as well, and (2) correlation of these results with the practical aspects of the use of the reagents.

With the primary objective thus lying in the improvement of one of the methods of chemical analysis, a second stimulus for the intensive investigation of these compounds and their derivatives is provided by the possibility of satisfying mere curiosity. Some of the characteristics of the insoluble nickel(II) complexes of the vic-dioximes vary rather widely in view of the fact that they are probably all formed as the end-products of essentially identical reactions. For example, the colors of the nickel derivatives of four out of the five compounds listed above range from a brilliant scarlet to a dull brick-red, while the color of 1,2-bis(1,2-cycloheptanedionedioximo-*N*,*N*')nickel(II)[a] is yellow, as has already been mentioned.

Another manner in which the several *vic*-dioximes and their nickel compounds vary is in the pH range over which the latter can be precipitated in aqueous solution. 1,2-Cyclohexanedionedioxime and 1,2-cycloheptanedionedioxime can be used to separate nickel(II) at relatively low pH's (49,50) while the derivatives of the other *vic*-dioximes are insoluble only in neutral or weakly alkaline solutions (10, p. 30; 10, p. 48; 36).

Long range investigations into the basic nature of these complex compounds are indicated in order to try to find explanations for puzzling phenomena such as those which have just been mentioned. Some work along this line has recently been accomplished, using the tools of infrared spectroscopy (29) and X-ray diffraction (18).

The measurement of magnetic susceptibilities has been of great assistance in recent years in the study of the fundamental character of chemical compounds. With the

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[a] The nomenclature used here for the nickel derivatives of the *vic*-dioximes follows the recommendations of Fernelius, Larsen, Marchi and Rollinson (15).

theory of magnetic susceptibilities firmly established through the application of quantum mechanics by authorities like Van Vleck (47), the estimation of the number of unpaired electrons in a chemical compound through susceptibility measurements can be considered to be quite reliable. This estimate is of greatest interest in connection with the elements of the several transition series. In these groups of elements, where variable valence is almost the rule rather than the exception, the number of unpaired electrons often changes with the valence and also with the type of compound that the element in question forms. The determination of this number then frequently makes possible a choice between several valence states and configurations.

Though the field of magnetic studies has expanded rapidly in recent years and susceptibility measurements are not difficult to make, the technique and nomenclature used in the determination of magnetic susceptibilities are not so well known as are those employed in other types of physical study, as for example in spectrophotometry. For this reason, it is advisable to review the significance of some of the terms used in susceptibility work.

A. Definitions of Magnetic Terms[a]

If a body is placed in a magnetic field H, the intensity of the field within the body is given by B, where

$$B = H + 4\pi I.$$

The quantity I is called the intensity of magnetization. B may be either smaller or larger than H, depending on the sign of I.

If the relation above is divided through by H, the result is

$$P = \frac{B}{H} = 1 + 4\pi k,$$

where P is the permeability of the body and k is its magnetic susceptibility per unit volume. The permeability has been represented either by P or μ; the former symbol is used here to prevent confusion with quantities to be presented shortly.

Another useful relation is

$$\chi = \frac{k}{\rho},$$

where χ is the mass or gram susceptibility of the substance

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[a] Much of the material presented in this section is also given by Selwood (42).

and ρ is its density. The molar susceptibility, χ_M, can be obtained from the gram susceptibility by multiplication of the latter by the molecular weight of the substance.

If I, k and χ are negative, then the substance in question is said to be diamagnetic, and its permeability is <1. Diamagnetism has been explained (47, p. 203) to be a consequence of the orbital motion of electrons within the atom. As a result, all substances are to be credited with more or less diamagnetism, whether or not they are also paramagnetic or ferromagnetic. Diamagnetic molar susceptibilities have magnitudes in the range 10^{-4} - 10^{-6} c.g.s.u./mole, and are generally independent of temperature and the magnetic field intensity.

If I, k and χ are positive, then the material to which they apply is called paramagnetic and $P>1$. Paramagnetism has likewise been satisfactorily explained on theoretical grounds (47, p. 226-315), and is due only to the presence of unpaired electrons within the atom. Paramagnetic molar susceptibilities show values in the range 10^{-2} - 10^{-3} c.g.s.u./mole, and thus when a substance is paramagnetic, this effect is large enough to hide completely the underlying diamagnetism that is always present. Paramagnetic susceptibilities are usually inversely proportional to the absolute temperature, but independent of the magnetic field intensity.

In the special case in which the permeability is very much larger than unity, the material showing this effect is said to be ferromagnetic. Ferromagnetism is dependent upon both the temperature and the magnetic field intensity in a complicated manner. Though this effect is of great importance technologically, it occurs only rarely in nature, and is generally not considered at all in chemical applications of magnetic studies.

When the molar paramagnetism of a substance is strictly inversely proportional to the absolute temperature, it follows what is known as the Curie law:

$$\chi_M = \frac{C}{T},$$

where C is a constant. The paramagnetic susceptibilities of many materials do show this behavior, but the phenomenon is by no means universal. Other materials may adhere to a relation known as the Weiss law:

$$\chi_M = \frac{C}{T + \Delta},$$

where Δ is an additional constant sometimes called the molecular field constant.

The presence of unpaired electrons within an atom serves to give that atom a permanent magnetic moment. The value of the magnetic moment, expressed in Bohr magnetons, is given by a modification of the Curie law (2, p. 146):

$$\mu_{\text{eff.}} = 2.84\sqrt{\chi_M T} \; ;$$

or in the case that the Weiss law is followed:

$$\mu_{\text{eff.}} = 2.84\sqrt{\chi_M (T + \Delta)} \, .$$

The new quantum theory has been of aid in deducing the relation between the number of unpaired electrons and the value of the permanent magnetic moment. Although generally there are both spin and orbital contributions to the magnetic moment (this is strictly true in the case of the rare earths), in the elements of the first transition series the orbital component is apparently largely "quenched" by interactions with neighboring atoms and the value of the magnetic moment is determined principally by the spin component. For those cases in which the orbital component is completely quenched, the magnetic moment, in Bohr magnetons, is given by

$$\mu_{\text{eff.}} = \sqrt{n (n + 2)} \, ,$$

where n is the number of unpaired electrons in the atom or molecule. It is seen that a molecule containing one such electron has a moment of $\sqrt{3}$ or 1.73 Bohr magnetons, while for a molecule with two unpaired electrons the moment is $\sqrt{8}$ or 2.83 Bohr magnetons, and so on.

Proofs, rigorous or otherwise, have not been given for the several relations presented in this section of these writings. The author has felt that such proofs are unnecessary either for the understanding of the work to be discussed later or for the orientation of a reader unfamiliar with the terminology used in magnetic susceptibility studies. The latter has been the primary reason for this brief mention of magnetic terms.

B. Purpose of the Investigation

Since magnetic susceptibility studies on the complex compounds of elements of the first transition series are likely to provide much information concerning the valence of the central element and/or the configuration of the complex, through the determination of the number of unpaired electrons present, it was judged that equipment suitable for conducting such studies would make a worthwhile addition to available research facilities. Accordingly, the project of setting up such equipment was undertaken, with a view toward making the apparatus as versatile and accurate as possible without, of course, going to financial extremes. Using the equipment thus made available, the magnetic properties of the *vic*-dioxime complexes of nickel(II) were then investigated, both in the solid state and in solution, in an effort to see what fundamental differences, if any, might exist between these several complexes.

II. PART ONE: THE MAGNETIC SUSCEPTIBILITY MEASUREMENT APPARATUS

In the century which has elapsed since Michael Faraday discovered magnetism to be a universal property of matter (12, p. 69), the measurement of magnetic susceptibilities has been accomplished by methods which exhibit seemingly endless variation. The magnetic nature, physical state and availability of the material being investigated, the purpose of the measurement, and the resources of the investigator are some of the factors which have been responsible for the introduction of many of the modifications. Although special methods have been developed which differ markedly from the rest, many of the techniques can be seen at once to differ only in minor detail from the two principal methods, which are the methods of Gouy (19) and of Faraday (12, pp. 27, 497). Modern reviewers of the field, including Selwood (42), Bates (2), and others (43,22,27), have considered some six or eight variations of these two methods to be of sufficient importance to discuss in some detail.

A. Review of Principal Methods of Measurement of Magnetic Susceptibility

The sharp increase, in recent years, in the volume of published results of magnetic investigations has been marked by a concurrent increase in the number of investigators who have chosen to use the Gouy method of magnetic susceptibility measurement. The convenience, accuracy and versatility of the method have undoubtedly been responsible for its popularity, and these are the factors which led the author to select this technique for the susceptibility measurements made in the researches being reported here. For these reasons, the Gouy method will be discussed rather fully below, while other methods will receive less extensive treatment.

1. The Gouy method

The Gouy method (19) requires that the material under investigation be in the form of a long homogeneous cylinder of uniform cross-section, and is applicable regardless of the physical state of the material. Metals and alloys can be cast or machined to the required shape, and powdered solids, liquids and solutions can be packed or poured into glass sample tubes of the proper shape and dimensions. The method is not very accurate for gases, although it has been used for investigations on oxygen and other paramagnetic gases.

The cylinder of material is placed between the pole faces of an electromagnet in such a way that one end is in a region of high field strength and the other is in a region of much lower field strength. Under these conditions the cylinder will be subject to a force along its length, the magnitude of which is given by the expression:

$$f = \frac{1}{2}A(H_1^2 - H_2^2)(k_1 - k_2).^{a} \qquad (1)$$

In this equation A is the cross-sectional area of the cylinder, H_1 and H_2 are the greater and lesser magnetic fields present at the ends of the sample, respectively, and k_1 and k_2 are the volume susceptibilities of the sample and the surrounding atmosphere, respectively. The force is ordinarily measured by suspending the cylinder from one pan of a sensitive balance, weighing the cylinder in the absence of the magnetic field, then weighing it again when the field is present.

The placement of the sample is not a critical adjustment if the end of the tube in the stronger field can be placed in the homogeneous portion of the field, between flat pole faces, and if the other end of the tube extends to a region of negligible field strength. In this case H_2 can be neglected, and equation (1) reduces to:

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[a] The derivations of the equations given in these review sections are to be found in Bates (2).

$$g\Delta W = \frac{1}{2}AH_1^2(k_1 - k_2), \qquad (2)$$

where g is the acceleration of gravity and ΔW is the change in weight of the sample tube, as measured with the balance. By using a diamagnetic gas such as hydrogen, nitrogen or helium for the surrounding atmosphere, k_2 may also be made negligible, but this is not usually necessary for measurements close to room temperature, where the volume susceptibility of air is known.

It is to be seen that the Gouy method lends itself admirably to the making of both absolute and comparison measurements. For absolute measurements, the determination of the intensity of the magnetic field in the air gap between the pole faces is probably the limiting factor so far as the accuracy of the measurement is concerned. Comparison measurements in the same container require only a knowledge of the volume susceptibilities of the standard and the surrounding atmosphere. An accuracy of about 1 part per 1000 can be obtained without excessive trouble for measurements on liquids and solutions. For samples composed of powdered crystals packed into glass tubes, however, an accuracy of about 1 per cent is difficult to exceed. The primary factors responsible for this low accuracy are the uniformity and reproducibility of the packing of the sample into the tube.

The sample tubes used for the determination of the susceptibilities of liquids and powdered solids vary according to the desires of the investigator. The load capacity of most microchemical balances is only 20 grams, so that if such a balance is used, the weight of the sample and its container must be kept to a minimum. In this case the sample tube may be a simple flat-bottomed test tube of uniform diameter, although the change in weight of the empty sample tube under the influence of the magnetic field will be appreciable here and must be determined independently. If a balance of higher capacity is employed, it is convenient to use a tube which extends to regions of negligible field intensities both above and below the pole faces, so that the correction for the tube will be reduced essentially to zero. This type of tube will have a glass partition midway between the ends, of course, so that the sample will be present only in the upper half. The double-ended tube can also be used to advantage in differential measurements on solutions, the lower half being filled with solvent or a "blank" solution. In this way the change in weight due only to the component of interest can be obtained.

It is evident from the equations given above that the Gouy method leads to a determination of the volume susceptibility of the sample. In most cases the mass susceptibility is a more useful quantity, however, and therefore an independent determination of the density of the sample must be made so that the one quantity can be converted to the other. For strongly paramagnetic powdered solid samples, the "bed" density, or effective density of the packed column, is often accurate enough for these calculations, since the contribution of entrapped air to the change in weight will be extremely small in comparison to that due to the paramagnetic solid. For diamagnetic or weakly paramagnetic solids, however, the contribution of the entrapped air is no longer negligible, and the effective density of the column cannot be used to convert from volume to mass susceptibility. The contribution of the entrapped air to the effective volume susceptibility of the column is calculated, instead, and the volume susceptibility of the solid determined by taking this into account, after which the conversion to mass susceptibility is made using the crystal density of the solid.

It is often desirable to carry out magnetic investigations over a wide range of temperatures, and this is entirely possible with the Gouy method. In the vicinity of room temperatures, a simple jacket, through which water or other liquids from a constant temperature bath can be circulated, can be constructed of such form that it will fit around the sample suspension and between the pole faces.

For very low temperatures, Dewar flasks of the proper shape can be fabricated, and the usual liquefied gases used for cooling. High temperatures may be attained by placing the sample suspension inside a tubular electric furnace, although at elevated temperatures convection currents may become a problem so far as reliable use of the balance is concerned. It should be borne in mind, also, that the buoyant effect of air changes with the temperature, and that therefore the temperature of the sample tube must be controlled quite closely in order that the effective weight of the tube may be constant throughout a set of measurements.

The Gouy method for the determination of magnetic susceptibilities has been discussed very thoroughly by Selwood (42) and Bates (2).

2. The Quincke method

An adaptation of the method of Gouy which has been used rather extensively is that of Quincke (33), which is employed primarily for the measurement of the susceptibilities of liquids. The accuracy which may be expected with the method can, with careful work, approximate that of the conventional Gouy technique. Auer (1) used the Quincke method for his authoritative absolute determination of the susceptibility of water, claiming an estimated error of 7 parts per 10,000.

The method consists in placing the liquid under investigation in a container which is essentially a U-tube, one leg of which is rather narrow and of uniform diameter. The other leg is usually made with a much larger diameter, so that it acts as the reservoir for the system. Considerable changes in the height of the liquid level in the narrow leg will not affect the height of the liquid level in the wide leg very much. The narrow leg is placed between the poles of an electromagnet in such a way that the meniscus is in the homogeneous part of the magnetic field, with the tube extending down to regions of negligible field strength. When the field is excited, the meniscus will rise if the liquid is paramagnetic, and fall if it is diamagnetic. The force acting on the liquid is:

$$f = \frac{1}{2}A(k_1 - k_2)H^2, \tag{3}$$

where the terms have the same significance as in equation (2), except that k_2 now refers to the volume susceptibility of the gas above the surface of the liquid. This force is balanced by the hydrostatic pressure resulting from the change of the liquid level in the narrow leg from that of the reservoir:

$$\frac{1}{2}A(k_1 - k_2)H^2 = (d_1 - d_2)Ag\Delta h, \tag{4}$$

where d_1 and d_2 are the densities of the liquid and gas, respectively, A and g have the same significance as before, and Δh is the observed change in the height of the meniscus under the influence of the field.

If the susceptibility, k_2, and density, d_2, of the gas above the liquid are both negligible, then equation (4) reduces to:

$$\chi_1 = \frac{2g\Delta h}{H^2}, \tag{5}$$

where χ_1 is the mass susceptibility of the liquid. Under these circumstances, then, the mass susceptibility of the liquid is obtained directly, and the density need not be determined. If the proper liquid standard is chosen, k_2 will not be negligible in comparison to k_1, and the method then becomes applicable to the study of the susceptibilities of gases.

Working temperatures for the Quincke method are limited to the vicinity of room temperature, because of the nature of the materials which can be studied with the method, and also because of the inconvenience of fabricating temperature controlling apparatus to fit the sample vessel. Moderate temperatures, however, are maintained and controlled very nicely by circulating liquids from constant temperature baths.

3. The Faraday method

In contrast to the long columns of test material used in the Gouy and Quincke methods, small spherical samples are used in the Faraday method of magnetic susceptibility measurement (12, pp. 27, 497). The sample is suspended near the poles of a magnet, in such a way that it is situated in a place where the field strength is changing most rapidly with respect to the distance outward from the pole face region. The weight of the sample is usually not large; therefore a very sensitive device such as a torsion balance can be used to measure the force acting on the test body.

The force acting on the body is proportional to the rate of change of the square of the field strength with respect to the distance outward from the pole face region, so that it is desirable to place the body at the point where this rate of change is at a maximum. If flat or truncated cone pole faces are used, as in the Gouy method, this rate of change is at its maximum value over a very small region, so that reproducible positioning of the sample is critical and extremely difficult. This disadvantage of the method has been overcome to some extent by several workers, including Fereday (14) and Bates (3), who used special pole faces shaped in such a way that the rate of change of the square of the field strength was constant over a somewhat larger region.

The Faraday method is used principally for comparison measurements, since absolute measurements would require the accurate mapping of the magnetic field in the region of interest. The accuracies obtainable with the method are usually lower than with the Gouy or Quincke methods. Only small amounts of material are necessary, however, and the use of controlled high and low temperatures is not so difficult as with the other techniques, because of the relatively small volume occupied by the sample, suspension and balance.

The Faraday method was used a great deal by Pierre Curie (9) in his eminent researches on magnetic properties. The method is often referred to as the Curie method for this reason.

Two variations of the general method that have proved very successful are the Sucksmith ring balance (44) and the Foëx and Forrer translational balance (16). In the Sucksmith instrument, the sample is suspended from the bottom of a flexible phosphor bronze ring the upper side of which is fixed. An associated lamp and scale system includes two mirrors strategically placed on the ring in such positions that when the ring is distorted by the movement of the sample under the influence of the magnetic field, the movement of the image on the scale is about 150 times the sample movement. The device is suitable principally for materials of large susceptibility.

In the Foëx and Forrer balance, the sample is placed on the end of a rod which is horizontally suspended in such a way that the sample and rod can move only toward or away from specially shaped pole pieces. A coil on the other end of the rod is in close proximity to a permanent magnet system. The current through the coil can be varied so that the reaction between the permanent magnet and the coil can offset the force exerted by the magnetic field on the sample.

4. The Curie-Chéneveau balance

A technique somewhat less sensitive than those already described and therefore used only for substances of high susceptibility, such as the rare earths, is that devised by Chéneveau (8) and improved by Gray and Farquharson (20). The method is rapid, but temperature control is not easily introduced, and the measurements can be made at only one field strength, thereby limiting the usefulness of the method. Relatively small amounts of the sample are required.

The instrument is essentially a torsion balance. The sample is placed in a tube which is suspended from one end of a rod, a balancing weight being placed on the other end. The rod is supported in the middle by a torsion fibre such as a fine wire or metal ribbon. The movement of the torsion arm can conveniently be followed by a suitable mirror, lamp and scale arrangement.

A permanent horse-shoe type magnet, with parallel pole faces, is placed on another arm which can rotate about the same axis as does the torsion arm. The magnet is at such a distance from the axis that when the arm is moved, the sample tube will pass between the pole faces. If the sample tube is filled, there will be a certain attraction or repulsion between it and the magnetic field, depending on the nature of the material under investigation. When the magnet is moved past the sample tube, therefore, a certain deflection of the torsion arm will be produced which is characteristic of the sample. Corresponding deflections for the empty tube, the tube filled with a magnetic standard, and the tube filled with the unknown can be used in conjunction with the known susceptibility of the standard to derive the susceptibility of the unknown.

5. The Rankine balance

A very accurate method of magnetic susceptibility measurement suggested and used by Rankine (34), and later improved by Iskenderian (21), departs rather radically from the usual technique in that the movement of the magnet, rather than that of a sample container, is measured. In Iskenderian's form of the apparatus, a cylindrical bar magnet hangs so that its axis is parallel to the plane surface of a glass sample container.

The induced polarity on the surface of the sample causes an attraction or repulsion between it and both poles of the magnet, depending on whether the material is paramagnetic or diamagnetic. The magnet is suspended from a light horizontal torsion beam by a quartz fiber; a balancing weight is placed on the other end of the beam. The beam is supported in the middle by another quartz fiber. Although presumably the torques produced in the upper fiber could be measured with a torsion head, Iskenderian chose to place a straight conductor at the base of the apparatus and measure instead the small current necessary to restore the magnet to its original position.

The method is admirably sensitive and accurate for substances of small susceptibility, but suffers from the disadvantage of being unduly influenced by stray fields, since the primary field from the magnet is only of the order of 100 gausses, compared to fields of 10,000 - 15,000 gausses used in other methods. Extraordinary precautions must be taken to eliminate ferromagnetic impurities from the apparatus and sample material, except for the magnet, of course.

B. Structure of the Apparatus

Consideration of the preceding descriptions of the more widely used methods of magnetic susceptibility measurement shows the reasons why the Gouy method has become the most popular of these. While some of the other techniques may be better suited for certain types of special investigations and may in some cases be less expensive to set up, the versatility and precision of the Gouy method are the characteristics which lead naturally to the selection of this method for general magnetic investigations. The relative ease of maintaining temperature control, the ready availability of suitable magnetic standards, and the lack of the necessity for extreme precision in positioning of the sample are additional factors favoring this choice.

In special cases, only a very small amount of equipment is needed to carry out magnetic investigations in the Gouy manner, with no sacrifice in precision and accuracy. These special cases would be those in which the material under investigation contains no paramagnetic components and there is no danger of the presence of ferromagnetic impurities. The absence of paramagnetic materials eliminates the necessity for precise temperature control, since the susceptibilities of diamagnetic materials are essentially independent of temperature. Similarly, the absence of troublesome ferromagnetic impurities, which may completely mask the true magnetic nature of a substance, simplifies the necessary apparatus in that measurements at only one field strength are sufficient. Correction for ferromagnetic impurities, as discussed by Bates (2, pp. 133-136), is ordinarily done by a graphical method which utilizes susceptibilities determined over a range of field intensities.

For these special cases, then, the minimum amount of apparatus necessary for accurate work would include a magnet, probably of the permanent type, a balance arranged so that the sample tube can be suspended from one pan, and perhaps a shield around the sample suspension to prevent drafts from upsetting the equilibrium. If a permanent magnet were used, either it or the balance would have to be easily movable in order that the sample could be weighed in the presence and absence of the magnetic field.

In the more general case, however, the substance being studied may very well contain paramagnetic components, which means that for thorough work temperature control must be provided. Ferromagnetic impurities probably occur less often, especially with careful work, but they can crop up most unexpectedly and therefore measurements should always be made at several field intensities, if possible. The susceptibilities of paramagnetic and diamagnetic materials are independent of the magnitude of the field, while the susceptibility of a ferromagnetic substance varies with the field intensity; therefore ferromagnetic impurities are easily discovered in this way. Magnetic fields of several different intensities are most conveniently obtained through the use of an electromagnet, of course, and once again the apparatus has become more complicated, since the electromagnet must be supplied with current, and either this current or the field must be stabilized and measured.

In setting up an assembly of apparatus of such nature that it will be useful for investigating a variety of magnetic phenomena over a period of years, the effects mentioned above must of course be considered. The major items of equipment necessary for an apparatus of this type, then, include the following: an electromagnet with its associated power supply, a balance of the proper sensitivity, the sample suspension, the current measuring device, and the sample temperature controlling apparatus. The complete assembly of this equipment is pictured in Figures 1 and 2.

1. Electromagnet and power supply

Although Selwood (42, p. 25) states that most investigators of magnetic properties have used magnets of their own design, a unit which was placed on the market after the publication of his book appeared to be very satisfactory for the type of apparatus considered here. Such a magnet, the Consolidated Engineering Corporation Type 23-104A, has now been used for over two years in the author's laboratory, and no serious complaints can yet be lodged against it. The shape and construction of the magnet can be seen in Figure 2.

The air gap of the magnet can be varied from practically

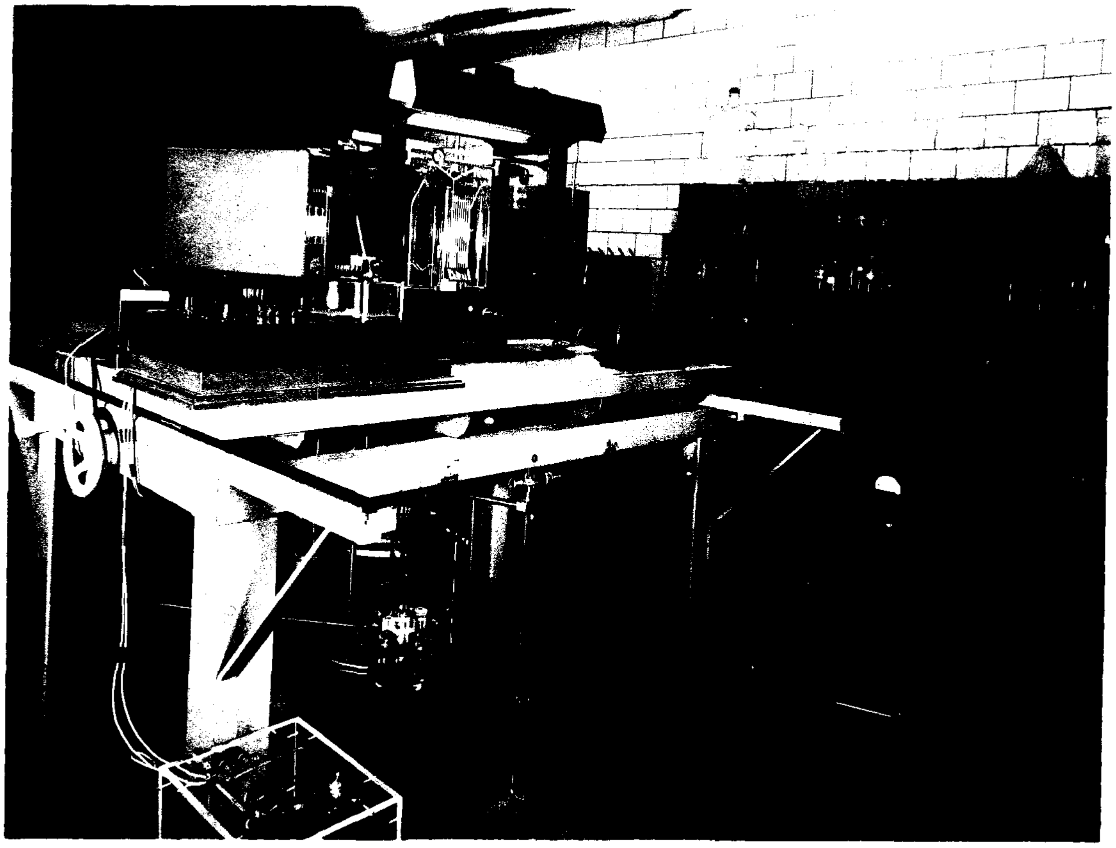


Fig. 1. Magnetic Susceptibility Apparatus, Front View.

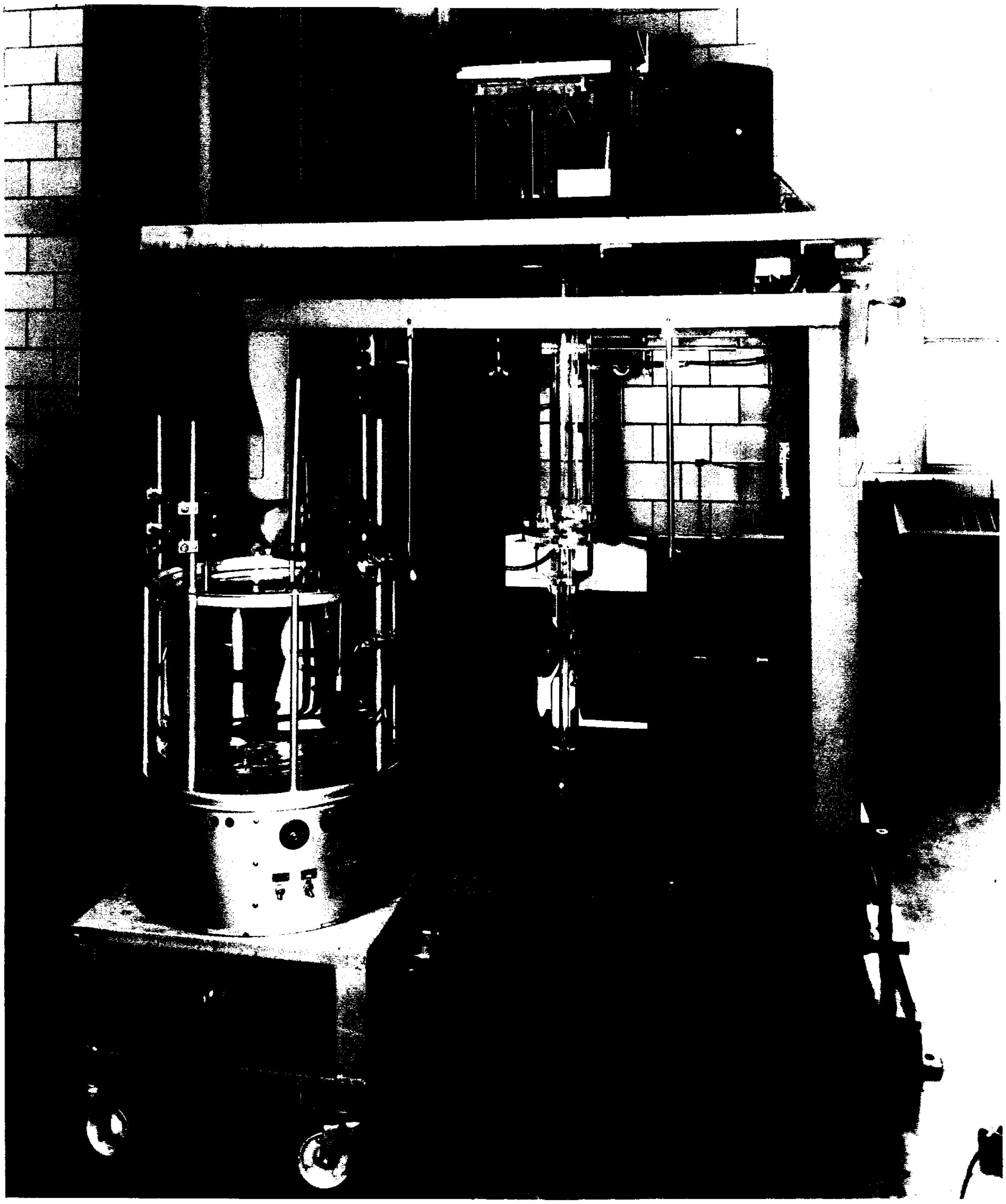


Fig. 2. Magnetic Susceptibility Apparatus, Rear View.

zero up to a maximum of about 4 inches, depending on the particular pole faces employed. The maximum field intensities available, under the limitations of the power supply, range from more than 16 kilogausses at gaps of less than 0.5 inch down to about 4 kilogausses at the widest gap widths. The pole faces are easily interchangeable, since they screw into threaded sockets in the ends of the coil cores. For the work being reported here, the air gap was set at 1 inch and pole faces in the shape of truncated cones were used, the outer flat surfaces being 2 inches in diameter. Using these pole tips, the field was apparently homogeneous over an area somewhat more than an inch in diameter. This of course meant that the positioning of the sample tube did not need to be extremely precise.

The distance from the centers of the pole tips down to the top of the yoke is 9 inches. This is ample room for most sample tubes and temperature controlling devices, for when the field intensity between the pole is at a maximum, the field strength decreases radially until it is negligible at a distance of about 7 inches from the pole face centers. A leeway of about 2 inches is thus allowed for the ends of the sample tubes and the bottom end of the temperature control apparatus.

No provisions have been made for cooling the windings and cores of the electromagnet, contrary to the usual practice with instruments of this type. The temperature of the end plates on the coils does not undergo any detectable change when the maximum current of 10 amperes is drawn for periods of 20 minutes or so, however, so apparently no cooling is ordinarily needed. For experiments carried out over very long periods at high currents, or for currents in excess of the rated capacity of the power supply, it is possible that the temperature rise in the windings might be excessive and cooling would then have to be provided.

The D.C. power supply for the electromagnet, Consolidated Engineering Corporation Type 3-121A, is more or less conventional. A variable auto-transformer (the coarse voltage control), fed from the 110 volt A.C. line, leads to an isolation transformer, which in turn feeds a selenium rectifier bridge circuit. This effects full wave rectification and furnishes the D.C. output. A covered reversing switch is located in the output circuit; the cover is interlocked with the primary A.C. circuit in such fashion that when it is removed, as is necessary in order to throw the reversing switch, the A.C. power to the whole unit is cut off. This feature is a precaution against the possibility that an attempt might be made to reverse the direction of current flow while the magnet is still energized.

The rated capacity of the power supply is 10 amperes at

72 volts D.C. When currents of 5 amperes or less were drawn from the power supply, the output seemed to be quite stable. When currents approaching the limit of 10 amperes were used for more than a few minutes, however, several of the components of the power supply seemed unable to dissipate heat fast enough, and the stability of the output current deteriorated. A small fan, placed beneath the chassis and blowing air upward past these components, improved the stability somewhat, especially at the higher loads. A further aid to the stability of the output of the power supply was rendered by an electronic A.C. line voltage regulator, a Superior Electric Company Type IE5105, placed between the A.C. power source and the D.C. power supply.

The original circuit of the power supply was altered in several minor ways in order to make its use more convenient and reliable. First of all, an indicator circuit using two panel lamps was added. This circuit has the function of indicating the position of the reversing switch, so that the operator may be consistent on this point. Secondly, one side of the D.C. output circuit was brought to a set of terminals on the front panel. An external ammeter, used for measuring reversing and saturation currents, and the shunt for the potentiometer were connected in series across these terminals. The total magnet current thus flowed through each of these components.

A third change in the power supply circuit involved the addition of 2 large (500 µfd. each) capacitors, connected across the D.C. output voltage line immediately following the rectifier bridge. The addition of the capacitors was occasioned by the discovery that the magnetic field present at the poles of the electromagnet included an alternating component whose magnitude was nearly 1 per cent of the total field. Since the frequency involved here was presumably 120 cycles per second, it was unlikely that this component could cause any trouble with the present form of the apparatus, but the capacitors were added as a precaution against that possibility. The magnitude of the alternating component of the field was reduced to less than 0.2 per cent of the total by the filtering action of the capacitors. The electrical circuit for the electromagnet and power supply, including the revisions just mentioned, is presented in Figure 3.

It was found that a residual field of some 130 gausses remained in the space between the pole faces after a coil current of 10 amperes had been used. With some highly paramagnetic materials, this residual field could of course lead to an incorrect value of the initial weight, so it therefore had to be done away with, if possible. A current of approximately 0.75 amperes in the reverse direction was found, when shut off, to leave a residual field of less than

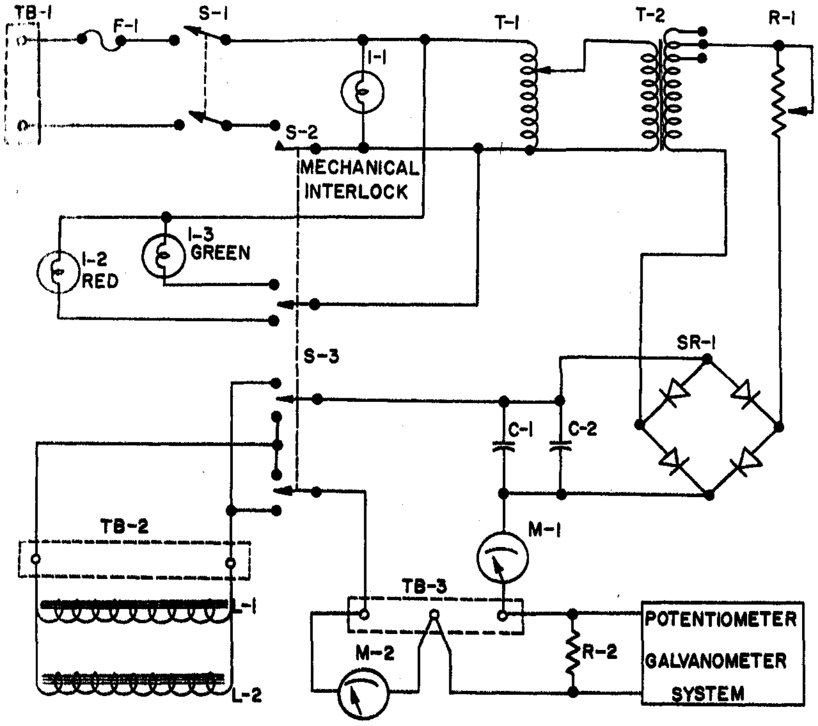


FIG. 3 ELECTRICAL CIRCUIT
FOR ELECTROMAGNET AND POWER SUPPLY

C-1,2	500μFD. 200V. CAPACITORS	S-1	MAIN POWER SWITCH DPST
F-1	15A. FUSE	S-2	SAFETY SWITCH, INTERLOCKED
I-1,2,3	6W. 110V. INDICATOR LAMPS	S-3	REVERSING SWITCH, 3PDT
L-1,2	ELECTROMAGNET WINDINGS	SR-1	SELENIUM RECTIFIER BRIDGE
M-1	PANEL D.C. AMMETER, 0-10A.	T-1	V-10 VARIAC "COARSE VOLTAGE ADJUST"
M-2	EXTERNAL D.C. AMMETER, 0-10A.	T-2	ISOLATION TRANSFORMER
R-1	0.5Ω 100W. RHEOSTAT	TB-1	A.C. INPUT TERMINAL BOARD
	"FINE VOLTAGE ADJUST"	TB-2	D.C. OUTPUT TERMINAL BOARD
R-2	0.01Ω 15A. CURRENT SHUNT	TB-3	FRONT PANEL TERMINALS

5 gausses. A reversed current of this magnitude was consequently used at the end of each set of measurements made since the time of the discovery of its effect.

The electromagnet was mounted on the lower level of a sturdy angle iron table assembly, as seen in Figures 1 and 2. Although this table was built in such a way that the apparatus could have been rather easily moved, this quality was decreased somewhat by the fact that it became necessary to mount the table itself on devices which reduce the transmission of building vibrations to the apparatus, and which thus protect the knife edges of the balance to some extent.

2. Balance and sample suspension

A modified semimicro balance of the keyboard type, the Ainsworth Type TCX, was used as the force-measuring device of the susceptibility apparatus. Special features which fit the balance for this work and which are not standard on the TCX include double magnetic dampers, a hook on the bottom of the left pan, a hole through the floor and lower case of the balance beneath the left pan, and a special pan rest under the left pan, shaped so as not to interfere with the hook. The capacity of this balance (100 grams on each pan) is large enough that relatively large sample tubes could be used, and the sensitivity (about 0.10 milligram per division, damped) is sufficient that changes in weight of the order of a few milligrams could be measured as accurately as could the other variables concerned.

The sample tube suspension system began with a hook, which, during a set of measurements, was suspended from the left pan of balance. This piece of the suspension was made of silver wire. It extended some 10 inches down through the table top into the draft shield, where it terminated in a small aluminum pulley. A thin silver chain, looped around the pulley and hooked into itself, reached from the pulley down into the central chamber of the constant temperature jacket. The sample tube itself hung from another hook, also of silver, at the lower end of the chain. The links of the chain were 1/16 inch long, which meant that the vertical position of the sample tube could be adjusted by increments of half this distance.

The sample tubes used were approximately 16 inches long and were prepared from Fischer and Porter Company precision Pyrex tubing. Each tube had a partition at its center, and was fitted with \$ 7/15 outer joints at each end. Care was taken in the preparation of these tubes to affix the end joints at such distances from the partition that the precise internal diameter of the tubes would remain undistorted for a distance of at least 7 inches from the partition; a length of 7 inches had been determined to be sufficient for the column to reach to negligible field intensities. The lower half of each tube was filled with dry air, stoppered and sealed with Pyseal.

A platinum wire collar with two loops or "ears" extending upwards was fastened in place around the neck of the ₮ joint at the upper end of each tube, using either Pyseal or Sauereisen cement. A platinum wire stirrup was hooked into the "ears" of the collar, and a loop at the center of the stirrup fitted onto the hook at the lower end of the silver chain mentioned above. After these wire fittings were permanently attached, the tube was hung from the loop in the stirrup and the fittings adjusted so that the tube hung in as vertical a position as possible.

3. Current measurement

It became apparent fairly early in the setting up of the apparatus that it would be a much easier process to measure the coil current to the required accuracy rather than to try to set the current to a definite value with comparative accuracy. Accordingly, no attempt has since been made to reproduce a measurement by adjusting the current. What was done, instead, was to set the coarse voltage control at points which would yield currents in the desired ranges; these currents were then measured by a shunt-potentiometer system to an accuracy of 0.1 per cent or better.

A current shunt of 0.01 ohm resistance and 15 ampere capacity was connected into the D.C. current line as described above in connection with the power supply. The voltage available at the "Potential" terminals of the shunt was measured by means of a Leeds and Northrup Type K-2 potentiometer. Since no attempt was being made here to obtain the absolute value of the current, the resistance of the shunt was taken as exactly 0.01 ohm and the reading on the potentiometer gave the current directly. A Leeds and Northrup Type 2430-C galvanometer was used with the potentiometer as the balance-indicating device. The short period (2.5 seconds) of this galvanometer proved to be an aid in the smooth operation of the whole apparatus. It permitted exceptionally rapid balancing of the potentiometer, which helped in that time was thus left free to attend to the operation of the semimicro balance.

In order to make the current measurements more independent of room temperature , the lower part of the case of the current shunt was wrapped in aluminum foil and then placed inside a few turns of copper tubing, coiled to fit the case. Water from the constant temperature bath, which was maintained at 20° C., was passed through the tubing. The heat transfer here was probably not very efficient, but the current measurements did seem to be more consistent and independent of the room temperature.

For less precise measurements of the coil current, as for example in the setting of the reverse and saturation currents, a Weston Model 901 D.C. ammeter was used. This meter, with its 5.5 inch scale, could be conveniently used to estimate currents to within about 0.02 ampere, although the values obtained were subject to slight fluctuations with room temperature.

4. Temperature control

Since the Gouy method of measuring magnetic susceptibilities can be applied over a very wide range of temperatures, provided that these temperatures can be accurately controlled, an arrangement of apparatus which utilizes the Gouy method to best advantage must also provide flexibility of temperature control. In its present form the apparatus being discussed here can be used only at temperatures which vary not too widely from room temperature. An attempt was made, however, to design and mount the components of the present temperature control system in a way that will permit relatively easy substitution of equipment designed for maintaining higher and lower temperatures.

The system used involved the pumping of water from a constant temperature water bath, a Precision Scientific Company No. 6548, through a glass jacket surrounding the chamber in which the sample tube hung. The system as a whole can be seen in Figure 2, and the jacketed sample chamber is presented in Figure 4. The bath was set at 20.1 ± 0.05° C. for the present work, and the temperature of the central chamber inside the jacket varied no more than 0.1° from this point. The pumping of the water from the bath through the jacket apparently did not interfere with the magnetic measurements, and consequently was done continuously.

A Lucite plate was attached to the top of the jacketed chamber, as seen in Figure 4. A similar plate was placed at the bottom of a Lucite draft shield assembly which extended from the glass water jacket up to the lower surface of the top of the table. The two plates were held together by three adjustable bolts which were the sole support of the water jacket and were also the means by which the vertical and horizontal adjustment of the position of this unit were made. The jacketed sample chamber could thus be removed very easily to make way for other means of temperature control. The plate on the bottom of the draft shield could serve as a point of attachment for suitably shaped Dewar flasks, for low temperature work.

The draft shield assembly was supported, in turn, by brass rods which were bolted to the frame of the table. The upper tubular portion of the draft shield was split and hinged, and thus formed the opening in which the measuring tubes could be inserted and hung from the chain in the sample chamber.

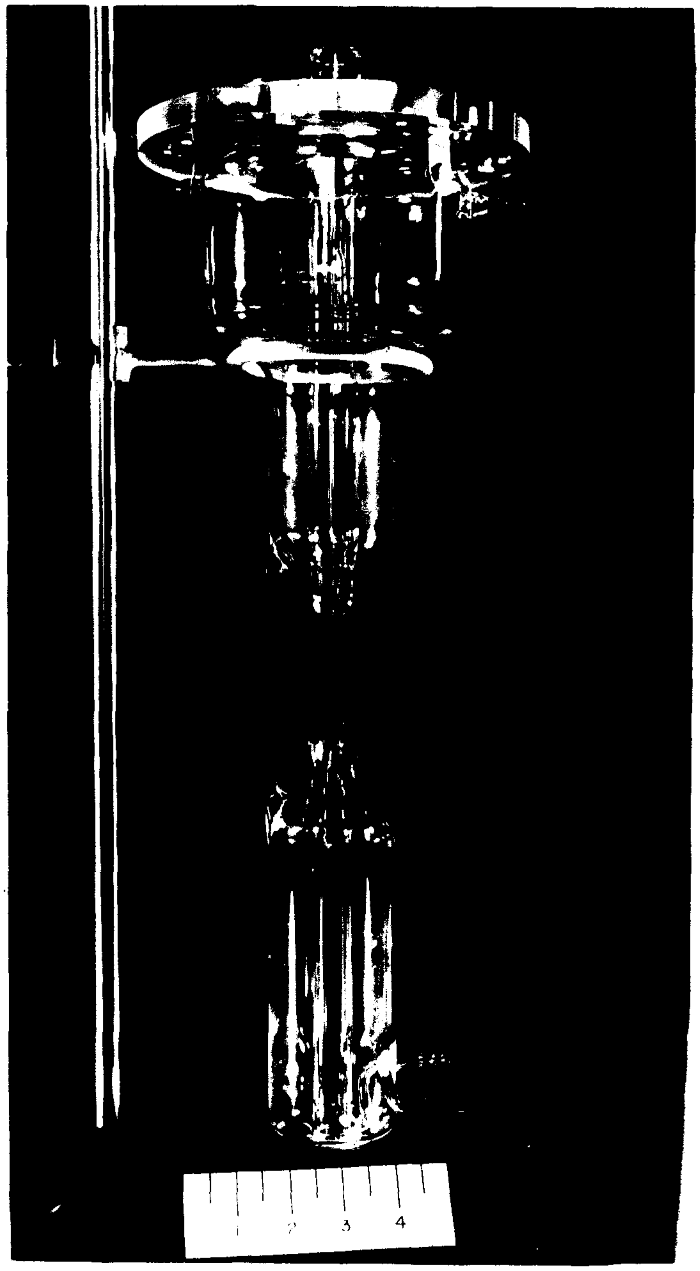


Fig. 4. Jacketed Chamber for Susceptibility Tubes.

It may be seen from Figure 4 that, at the bottom of the central tube in the water jacket unit, there is a small side tube leading through the jacket. This entrance into the sample chamber was useful for admitting cooled air for the purpose of bringing the sample tube to thermal equilibrium more quickly, for admitting an inert gas, if such an atmosphere was desired, and for draining such liquids as were used to rinse down the walls of the sample chamber.

C. Calibration

In the measurement of magnetic susceptibilities, as in the determination of any physical property, the value of the results is largely determined by the accuracy with which the measuring apparatus can be calibrated. Relative or comparison measurements of magnetic properties can often be made quite precisely, but the difficulties encountered in making absolute determinations limit the accuracy with which these properties may be known. The apparatus being dealt with in this discussion was used for comparison measurements only, and its calibration was therefore of the utmost importance. Both the standards used and the method of calibration employed should be considered.

1. Standards

Some care should be exercised in choosing a standard for the calibration of a Gouy type susceptibility apparatus. The numerical value of the volume susceptibility of the standard should be greater than that of any other solution or solid that is to be subjected to measurement, in order that a column which extends to negligible field strengths in the case of the standard shall also extend to negligible field strengths in the case of the unknown. A standard which met this requirement for the present work and was, in addition, readily obtained and easily prepared, was a solution of nickel chloride of a concentration in the neighborhood of 30 per cent by weight. Selwood (42, p. 29) reports the gram susceptibility at 20° C. for a solution in this concentration range as being given by the relation:

$$\chi = \left[\frac{4433 \pm 12}{129.6} p - 0.720 (1 - p)\right] \times 10^{-6}, \qquad (6)$$

where p is the weight fraction of nickel chloride present.

Several other calibrating agents, whose susceptibilities lie in ranges removed from that of the nickel chloride solutions and are therefore suitable for investigations of a slightly different nature, are also suggested by Selwood. A standard often used for work with gases is oxygen, whose volume susceptibility he gives as $(0.1434 \pm 0.0004) \times 10^{-6}$ at 20° C. and 760 mm. The magnetic susceptibility of water has been investigated many times, and this substance is usually employed when a calibrating agent of relatively low susceptibility ($\chi = -0.720 \times 10^{-6}$ at 20° C.) is needed. The water must be free of dissolved air, because of the paramagnetic oxygen present in air. For work with materials of extremely high susceptibilities, Selwood suggests the use of Mohr's salt, hydrated ferrous ammonium sulfate, whose molar susceptibility is $9500 \times 10^{-6}/(T + 1)$, where T is the absolute temperature.

The standard nickel chloride solution was prepared from special reagent grade material (J. T. Baker Chemical Company, Phillipsburg, New Jersey) with a very low cobalt content. The hexahydrated salt was not recrystallized before use, this being deemed unnecessary. The solution was made up by dissolving 1489 grams of the salt in water, filtering, and diluting to 2 liters. It was stored in a Pyrex bottle bearing an all-glass siphon system.

Standardization of the solution was done electrolytically, in the usual manner (41) except that 10 grams of ammonium chloride were added to each sample taken for analysis, in lieu of the ammonium sulfate that accumulates in the ordinary analytical procedure for nickel in its alloys. The samples taken for the analyses were weighed out with a weight burette, and the necessary buoyancy corrections were made. The solution residues left after the electrolyses were tested for nickel with a saturated solution of 1,2-cyclohexanedionedioxime at a pH of 4; those showing more than a negligible amount of the red compound were discarded.

As a result of these analyses, the standard solution was found to contain 29.98 per cent nickel chloride by weight. Using this figure in equation (6) led to a value of $\chi = 9.751 \times 10^{-6}$ c.g.s.u./g. for the mass susceptibility of the solution. The density of the solution was measured with a Westphal balance (L. W. Hohwald Company, Jersey City, New Jersey) and checked by use of a specific gravity bottle; it was determined to be 1.345 g./ml. The product of the mass susceptibility and the density is equal to the volume susceptibility; the value of $k = 13.115 \times 10^{-6}$ c.g.s.u./ml. was thus obtained for the latter quantity.

2. Method of calibration

The best and most direct method of calibration of a susceptibility-measuring apparatus using the Gouy technique would be to determine the changes in weight of a sample tube, filled with the standard, for various values of the square of the magnetic field intensity in the air gap of the electromagnet. The changes in weight so produced would have to be corrected for the changes in weight undergone by the empty tube at the same fields, of course. However, the direct measurement and control of the magnetic field is not so easily done, to the desired precision, as is the measurement and control of the current through the coils of the electromagnet. If some attention is paid to the hysteresis of the core, and if the coils are cooled or run at low enough power that they remain cool, the current can often be taken as proportional to the field. The process of finding changes in weight of the standard-filled sample tube for various values of the current is sufficient for calibration, in this case, and this is the practice that was followed here.

In the case of a system of apparatus in which the current can readily be reproduced to 0.1 per cent or so, the process of calibration is relatively simple. The values of the weight changes of the standard-filled sample tube can be determined for the several desired currents and the process is complete. For the system under consideration here, however, in which the power supply was not stable enough that the current could accurately be reproduced and in which therefore the current was measured rather than set, calibration was more complex. Since the current drawn when a measurement of an unknown was being made very rarely duplicated the current used for any of the calibration points, what was needed here was a continuous plot of the change in weight for the standard against the current. In this manner the change in weight for the sample tube filled with the standard solution could be found for any and all values of the current.

This scheme was indeed used for the calibration of sample tubes in the first part of this work. Some 40 or more observations of the change in weight for the standard solution, at various values of the current over the whole range of 0-10 amperes, were taken for each tube; a large plot of ΔW vs. I was then made. This served as the calibration curve for that tube.

This process was very cumbersome, time-consuming and somewhat lacking in precision. Its unwieldiness is shown by the fact that if a typical calibration curve had been plotted on a single piece of cross-section paper on a scale commensurate with the accuracy of the individual observations, that piece of paper would have measured some 7 by 10 feet. This type of plot was also unsatisfactory in that even though more than 40 observations were used in its preparation, the individual points were still so widely spaced that it was difficult to draw a smooth curve through them.

It became apparent, after several tubes had been calibrated in this manner, that the shape of the curve was nearly the same in each case, though the magnitude of the ΔW values varied somewhat from tube to tube. Point to point comparison of the curves for two tubes of grossly different diameters revealed the fact that, while the heights of the two elongated S-shaped curves were different, the ratio of

ΔW values from one curve to those from the other, for the same currents, was constant. It appeared that the calibration curve for one tube could be used for the other if this ratio were once accurately determined and used as a calibration factor.

Consideration of equation (2), reproduced here for convenience,

$$g\Delta W = \frac{1}{2}AH_1^2(k_1 - k_2), \tag{2}$$

shows that the facts mentioned in the preceding paragraph should indeed be true. For a given solution in the tube, which fixes the value of the term in parenthesis, the shape of the curve should be determined by the manner in which H_1^2 varies with the current through the coils of the magnet, if the cross-sectional area of the tube is constant throughout its length. The discovery of the constant ratio mentioned above indicates that the cross-sectional areas of the two tubes were constant within experimental error. It is unlikely that if variations in these areas had been present, such variations would have been the same for both tubes.

The calibration system used for the major portion of this work took advantage of the situation discussed above. Some 61 observations of the change in weight of one of the sample tubes filled with the standard solution, at various values of the current, were obtained to be used as the basis for the "master" calibration curve. These data were plotted on very large cross-section paper. It would have been desirable to smooth out the curve by fitting the data to some relatively simple mathematical relation, but inspection of the plot made it apparent that the equation for the curve would not be simple nor easily found. In lieu of this procedure, the plot was split into 4 sections, the division being based on the appearance of the curve and made in such a way that each section so produced would be as symmetrical as possible. Each section, with the exception of the first, was then fitted to a quadratic equation by the method of least squares. As the last step in the process, the equations were then used to calculate ΔW values for currents over the whole range of 0-10 amperes, in 0.01 ampere steps. These values were arranged in tabular form, to be used as the master calibration table.

The first section of the curve could not be accurately fitted to a quadratic or other simple expression. Since it was relatively smoother than the other sections anyway, the values from this portion of the curve were simply read off the plot and inserted in the table without further treatment.

Once the master calibration table had been prepared, calibration of sample tubes was reduced to a very simple process. Each tube was filled with the standard nickel chloride solution. The changes in weight, measured to the nearest 0.05 mg., for the tube so filled were determined at some half-dozen different currents, measured to the nearest 0.001 ampere. The master table was then entered to obtain the ΔW's listed there for the same currents. The average ratio of the experimental to the tabular values of ΔW was taken as the calibration factor for that particular tube.

When a tube was used for the measurement of the susceptibility of some unknown material, the raw data consisted of a number of ΔW values and the corresponding currents at which they were obtained. Since the basis of the method lay in a comparison with a standard, the ΔW values for the tube filled with the standard solution, at the same currents, were needed. These were obtained by entering the master calibration table, noting the values listed therein for the specified currents, and multiplying the tabular ΔW values by the calibration factor for the tube used.

The system of tube calibration using the master table was found to be very much more satisfactory than the original method, especially when the factors of time savings, accuracy and convenience are considered. An additional consideration favoring this system is the fact that the use of the table will still be valid when it becomes necessary or desirable to use a different magnetic standard, provided that the volume susceptibility of the new standard is no greater than that of the nickel chloride solution used in setting up the table. The calibration factors for the sample tubes would be determined in exactly the same fashion as described above; the tubes being filled with the new standard, of course. The only other alteration necessary in the whole procedure of calibration and measurement would be that the volume susceptibility of the new standard would be used in equation (2), in the calculation of the susceptibility of the sample material.

D. Method of Operation of the Apparatus

The successful operation of the magnetic susceptibility apparatus requires patient, careful attention to a host of details. Results can be obtained which are precise to better than 1 part per 1000, but the precision deteriorates rapidly as the haste of the operator increases.

Several steps in the operating procedure are carried out prior to the actual taking of data in order to insure smooth operation. The constant temperature bath and circulating pump, which are ordinarily left running continuously, are checked occasionally to see that the sample chamber is being maintained at 20° C. The storage battery supplying current to the potentiometer is connected at least 2 hours before the measurements, in order that its voltage may be sensibly constant. The sample tube should be filled, wiped off with acetone or methanol, and placed in the sample chamber a minimum of 1.5 hours before the taking of any data, so that its weight will not be changing too rapidly. At the time the tube is placed in the chamber, the suspension should be hung from the pan of the balance for a few minutes while the position of the tube is adjusted; the partition at the center of the tube must match the centers of the pole faces. A few minutes before the measurement is to begin, the balance lamp, the galvanometer lamp, the line voltage regulator and the small fan beneath the power supply are all turned on.

The sequence of operations during the measurements can probably be best understood by following numbered steps in the procedure, as would be given on an instruction sheet. Explanatory comments on some of the steps will be found immediately following the procedure.

1. Check balance action for irregularities.
2. Engage hook on suspension with hook under left pan; make sure tube is freely suspended.
3. Weigh tube and suspension to 0.01 mg.; note time when weighing is completed.
4. Throw main power supply switch on; using "Coarse Voltage" control, run current up to 10.0 amps.; throw main power supply switch off.
5. Repeat step 4, allowing current to remain at 10.0 amps. for 20 to 30 seconds this time.
6. While waiting for 20 to 30 second period in step 5, standardize potentiometer against standard cell.

7. Set "Coarse Voltage" control at point to give current of desired magnitude; throw main power supply switch on.
8. Reweigh sample tube, measuring current with potentiometer at same time; note time when both measurements are complete.
9. Increase current to 10.0 amps.; throw main power supply switch off.
10. Repeat steps 7-9 for each additional ΔW *vs.* I value wanted.
11. Make sure main power supply switch is off; decrease "Coarse Voltage" control to 0; throw reversing switch.
12. Throw main power supply switch on; increase current to 0.75 amp. using "Coarse Voltage" control; when this current is reached, throw main power supply switch off.
13. Throw reversing switch to original position.
14. Reweigh sample tube; note time when weighing is complete.
15. Disengage sample suspension from balance; unload balance; turn off all powered components except the thermostat and circulating pump.

The initial and final weights of the sample tube will rarely be identical. They will often differ by 0.02 or 0.03 mg., and may infrequently differ by 0.10 mg. or more. The weighing operations are all timed so that the zero-field weight of the tube at the time of a measurement may be found by interpolation between the initial and final weights.

The ΔW values for strongly paramagnetic samples are usually large enough that the sample tube weights in these cases need be obtained only to the nearest 0.05 mg., while the currents corresponding to these weights should be measured to 0.001 ampere, if possible. For diamagnetic samples, on the other hand, the reverse of this situation holds: the currents need be accurate only to about 0.005 ampere, while the sample tube weights should be measured down to the nearest 0.01 mg. The changes in weight are small for diamagnetic samples, so that the weight estimations are the factors which limit precision and accuracy here.

The setting of the current at its maximum value in steps 4 and 5 is done to avoid uncertainties in the magnetic field due to the hysteresis of the cores. While 10.0 amperes is not sufficient to saturate the cores, it is apparently enough that the magnet operates on the upper portion of the hysteresis loop after this current is drawn, and the current can more accurately be taken to be representative of the field produced. The setting of the current at 10.0 amperes after a measurement at a lower current is likewise a precaution taken to keep the magnet operating on the same portion of the hysteresis loop.

The reverse current of 0.75 ampere has been discussed previously; its function is to remove the residual field between the pole faces so that the final and initial weights of the sample tube will be true zero-field weights.

E. Treatment of Data

The raw data obtained by operating the apparatus as described above consists of the initial and final weights of the sample tube, the weights of the sample tube at various currents through the magnet, the values of those currents, and the times at which the data were obtained. Additional information needed to convert these data into the volume susceptibility of the material being investigated include the calibration factor for the tube, the master calibration table, and the volume susceptibility of the standard solution.

The recorded times of the initial and final zero-field weights of the filled sample tube allow the estimation of its weight at any intermediate time, by interpolation. Zero-field weights of the tube at the times of the observations made with the magnet energized are obtained in this way. The differences between these interpolated zero-field weights and the actual weights in the presence of the various magnitudes of the magnetic field are then secured by subtraction, respecting the sign of the change; these are the true ΔW values for the unknown.

The uncorrected ΔW values for the standard solution, corresponding to the ΔW's for the unknown, are next obtained from the master calibration table, using the recorded experimental values of the current. These standard values are corrected for the particular tube used by multiplication by the calibration factor for that tube.

Equation (2) of course holds true in the case where the tube is filled with the unknown material as well as in the case where it is filled with the standard solution. If it is set up for these two cases and then the first equation divided by the second, the square of the field intensity, the cross-sectional area of the tube, the acceleration of gravity and the numerical coefficient will all cancel, and the result will be:

$$\frac{\Delta W_x}{\Delta W_s} = \frac{k_x - k_a}{k_s - k_a}. \qquad (7)$$

Here ΔW_x is the experimental value of the change in weight for the unknown, ΔW_s is the corrected change in weight for the standard solution, and k_x, k_s, and k_a are the volume susceptibilities of the unknown, the standard solution and air, respectively. Since all of the factors here are known except the volume susceptibility of the material being investigated, k_x, the equation can be solved for this quantity.

Strictly speaking, the quantity k_x obtained in this fashion is the volume susceptibility of the column of material subjected to measurement. If the material is a liquid, the tube is of course filled completely and the quantity k_x

is actually the volume susceptibility of that liquid. The gram susceptibility of the liquid can be found by dividing the volume susceptibility by the density, which must be determined independently.

If the material under investigation is a powdered solid, however, k_x cannot be considered to be the volume susceptibility of the unknown. Here it is strictly the volume susceptibility of the packed column, and must be corrected for the air also contained in the column with the solid. If the density of the solid, the volume of the tube and the weight of the solid in the tube are known, these factors can be used with the volume susceptibility of air to calculate first the fraction of the tube volume occupied by the solid and then the volume susceptibility of the powdered material itself. Once this is known, conversion to the mass susceptibility may be done by dividing the density, as before.

In the case that the unknown material is a powdered solid which is evidently quite highly paramagnetic, judging from the magnitude of the ΔW values, the correction for the air in the packed column becomes negligible. Although k_x is still only the volume susceptibility of the packed column, a very satisfactory approximation to the gram susceptibility of the solid can be obtained by dividing k_x by the "bed" density of the column, "bed" density being equal to the weight of the solid contained in the sample tube divided by the volume of the tube. The process of finding the susceptibility of the material is somewhat simpler, in this case, since an independent measurement of the density is unnecessary.

III. PART TWO: MAGNETIC STUDIES ON THE CRYSTALLINE COMPLEXES OF NICKEL(II) WITH SOME *VIC*-DIOXIMES

Studies of the behavior of similar substances when they are present in solutions are almost certain to provide more information about the comparative stabilities and reactivities of those substances than will investigations of the isolated pure materials. At the same time, the basic information derived from the latter type of study is needed in order to decide whether or not the substances are indeed similar enough that the solution studies will have any meaning.

Both types of investigation have been carried out here. They are very closely allied, but the techniques of measurement are sufficiently dissimilar that it has been judged advisable to consider them separately. The review of literature pertinent to the magnetic study of solutions of nickel(II) complexes with the *vic*-dioximes is presented in Part Three.

A. Review of the Literature

The nickel(II) ion possesses 26 electrons, 8 of which must somehow be distributed among the available orbitals in the 3d shell. In the normal ion, all 5 of these orbitals are available, with the result that 3 become occupied by a pair of electrons each, while the remaining 2 orbitals contain a single unpaired electron in each case. The latter two unpaired electrons give the ion a permanent magnetic moment. According to the relation presented previously, this moment will have the value of $\sqrt{n(n+2)}$ Bohr magnetons, where n is the number of unpaired electrons, if the "spin only" formula can be followed. This leads to a value of $\mu_{eff.} = 2.83$ Bohr magnetons. Measured values of this moment for the simple nickel(II) ion range from 3.0 to 3.4 Bohr magnetons (29), however, indicating that a sizeable orbital component is present.

The electronic and spatial configurations that become possible when nickel(II) is tied up in some of its complex compounds are very thoroughly presented by Pauling (30, pp. 81-123), using the well-known hybrid bond orbital theory. It is sufficient here to mention them only briefly.

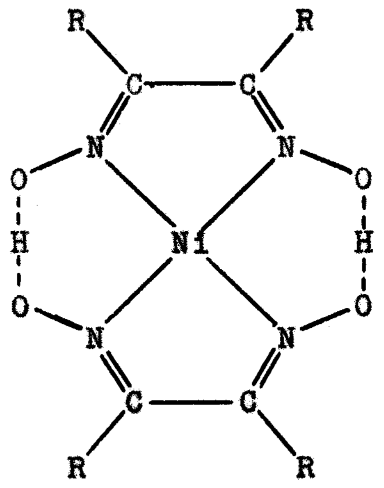
One of the possibilities that arises is that four bonds may be formed between the nickel atom and the attached groups which are either ionic or utilize the 4s and the three 4p orbitals in weak covalent bonds. These bonds have been considered to be directed toward the corners of a regular tetrahedron. The 8 electrons in the 3d shell are undisturbed and there are yet 2 unpaired electrons in this type of complex. The orbital contribution to the magnetic moment appears to be more completely quenched, however, and the values for $\mu_{eff.}$ range from 2.6 to 3.2 (42, p. 176). Examples of compounds which exhibit the tetrahedral configuration include the nickel(II) complex with acetylacetone (5) and tetraamminenickel(II) sulfate (39).

The second type of bonding encountered in nickel complexes is that in which 4 covalent bonds are formed that utilize one 3d, the 4s and 2 of the three 4p orbitals. The bonds are directed to the corners of a square and the four coordinating atoms as well as the metal atom lie in a common plane. Since the fifth 3d orbital is used for bond formation, this means that the 8 electrons originally present in the 3d shell must now distribute themselves among the 4 remaining orbitals, with the result that they all become paired. Compounds involving bonding of this type should therefore be diamagnetic. Two of the many representatives of this group are the nickel(II) complexes with o-aminophenol and salicylaldoxime (26).

A third configuration which may occur is that in which 6 bonds directed to the corners of a regular octahedron are formed. The bonds are probably ionic in nature, for nickel(II) complexes which show this coordination number are in general paramagnetic, with 2 unpaired electrons indicated.

The electronic configuration of the octahedral state for nickel(II) has not been discussed very thoroughly in the literature, although Emeléus and Anderson suggest that 2 electrons are promoted to the 5s level (11, p. 177). The foremost examples of this group of compounds are the hexaamminenickel(II) halogenides, some of which have been demonstrated to be octahedral by Wyckoff (55).

The inner complex compounds of divalent nickel with the vic-dioximes fall into the second group of coordination compounds mentioned above. Much of the evidence for their square, coplanar structure has been very ably reviewed by Diehl (10). Recent X-ray work by Godycki and co-workers on the structure of 1,2-bis(2,3-butanedionedioxime-N,N')nickel(II) (18), as well as the infrared study by Voter, et al. (51) on this compound and several similar to it, have indicated that this configuration in the neighborhood of the nickel atom is symmetrical even to the positions of the hydrogens in the hydrogen bonds. The structural formula below, the gross features of which were first suggested by Pfeiffer (31,32), represents the configuration now commonly accepted for the 1,2-bis(vic-dioximo-N,N')nickel(II) compounds. It is to be noted that the bonds from the nitrogens to the nickel atom must be regarded as being all equivalent; a similar situation



holds for the bonds between the nitrogens and the oxygens.

Pauling's theory for the 4-coordinate square complexes of nickel includes the prediction that they be diamagnetic. The several investigations into the magnetic character of the vic-dioxime complexes of nickel(II) over the past 2 decades have borne out the accuracy of this prediction, with no exceptions. Thus, Klemm, Jacobi and Tilk (23) reported in 1931 that they had found 1,2-bis(2,3-butanedionedioxime-N,N')nickel(II) to be diamagnetic, with $\chi = -0.53 \times 10^{-6}$. In the same year, Cambi and Szegő (5) published the results of their researches on a number of nickel complexes; their value for the gram susceptibility of the same compound was -0.335×10^{-6}. They included 1,2-bis(α-benzildioximo-N,N')nickel(II) in their survey, and reported this compound to be diamagnetic also, with $\chi = -0.476 \times 10^{-6}$.

Sugden (45) and Cavell and Sugden (6) carried out an extensive series of studies with the primary aim of investigating the cis-trans isomerism of nickel complexes with unsymmetrical vic-dioximes. They were successful in isolating 2 forms each of 1,2-bis(1-phenyl-2,3-butanedionedioximo-N,N')nickel(II), 1,2-bis(2,3-hexanedionedioximo-N,N')nickel(II), and 1,2-bis(2,3-heptanedionedioximo-N,N')nickel(II), among others. The higher-melting forms of each pair were assigned the trans configuration on the basis of electric dipole measurements. All of the isomers which they subjected to magnetic susceptibility measurement were found to be diamagnetic.

The nickel(II) complex of o-naphthoquinonedioxime was reported by Mellor and Craig (26) to be diamagnetic. It was pointed out by Voter (48) that this result violates Feigl's statement (13) that aromatic rings destroy the specific activity of the vic-dioxime grouping and that the oxime groups would, in this case, behave merely as acids. Since the empirical formula which Mellor and Craig reported for their product corresponds to the normal vic-dioxime complex and not to the salt of a dibasic acid, Voter suggested that a reappraisal of the situation would be in order.

The light orange compound resulting from the reaction of nickel(II) with 1,2-diaminoethanedionedioxime in ammoniacal solution was prepared in 1941 by Chatterjee (7) and found to be diamagnetic, $\chi = -0.393 \times 10^{-6}$. The same two reactants, however, when added in slightly acid solution gave blue crystals which were paramagnetic. Chatterjee found the empirical formula $Ni(C_2H_6N_4O_2)_2Cl_2 \cdot 6H_2O$ for the latter compound, which of course does not conform to that expected for the normal vic-dioxime complexes.

In a study designed to compare the susceptibilities of nickel complexes in the solid state with those of the same complexes in solution, Willis and Mellor (54) in 1947 prepared 1,2-bis(1,2-propanedionedioximo-N,N')nickel(II). They found the compound to be diamagnetic in the solid state, but paramagnetic when dissolved in pyridine. This study has a special bearing on Part Three of this discussion and will be treated in more detail there.

In view of the results of the investigations just cited, it would be logical to assume that all normal inner complex compounds of nickel(II) ions with the vic-dioximes would be diamagnetic, at least in the solid state. If the elemental analysis of a new compound showed it to conform to the normal 2:1 ratio of organic reagent to nickel, if other physical characteristics were similar to those of compounds which had been demonstrated to be diamagnetic, and if the parent organic reagent had unmistakably been a vic-dioxime, then such an assumption would probably be sound. The investigator who desired to do further work with the compound, based on this assumption, could proceed with a fair amount of confidence.

There is always the chance, however, that things may not be quite what they seem. Willis and Mellor, in reporting on their work with solutions of nickel complexes (54), suggested that the energy differences between the planar and tetrahedral states may be quite small. In the light of this suggestion, the small but real differences in the physical characteristics and chemical reactivities of the several bis(*vic*-dioximo-*N*,*N*')nickel(II) complexes that were dealt with in these researches would indeed be reason enough for investigating their magnetic nature. The facts that the values for their susceptibilities were also needed for subsequent work and that published values for one of the compounds were somewhat discordant served to broaden the justification for the work, if such justification was needed.

B. Materials

Where not otherwise specified, reagent-grade chemicals were employed. The nickel chloride used for the preparation of the compounds was the same (J. T. Baker, low cobalt) as that used in the preparation of the magnetic standard solution. Demineralized water was used throughout for making up solutions, washing, etc., in an effort to keep the materials free from traces of iron.

1,2-Bis(2,3-butanedionedioximo-N,N')nickel(II). 2,3-Butanedionedioxime (dimethylglyoxime) obtained from the Matheson Company was used to prepare this compound in a straightforward scale-up (0.15 g. to 20 g.) from the standard analytical procedure (10, p. 30). The dried precipitated material was recrystallized from o-dichlorobenzene.

1,2-Bis(α-benzildioximo-N,N')nickel(II). The insolubility of the reagent, α-benzildioxime, in water and the usual solvents precluded the possibility of obtaining this compound in any sizeable quantity by the usual analytical procedure. The following scheme was used to prepare 20 g. of the material in a manner which avoided the excessive volumes of solutions which otherwise would have been necessary.

A dropping funnel, a Soxhlet extractor and an electric heating mantle were fitted to a 5 l. 3-neck flask. A solution containing 16.0 g. of 30 per cent aqueous nickel chloride solution in 500 ml. of 95 per cent ethanol was prepared and placed in the dropping funnel. The extractor was charged with 19.0 g. of Eastman white label α-benzildioxime, while the flask was filled with 3.5 l. of acetone and 50 ml. of concentrated ammonia solution. The acetone solution in the flask was heated to boiling and the extraction process was thereby begun. When the first several portions of the vic-dioxime had been added to the reaction mixture in the flask, the addition of the nickel chloride-ethanol solution was started, very slowly. This latter addition was completed over a period of 12 hours. The extraction process was complete in about 2 days; the extractor was then replaced by a reflux condenser and refluxing was continued for another day. At the end of this time, the orange product was filtered off, dried and recrystallized from o-dichlorobenzene.

1,2-Bis(1,2-cycloheptanedionedioximo-N,N')nickel(II). 1,2-Cycloheptanedionedioxime was synthesized according to published directions (46) and used to prepare the nickel(II) compound by a procedure scaled up (0.25 g. to 6 g.) from the usual analytical precipitation (49). The dried precipitate was recrystallized from nitrobenzene.

1,2-Bis(1,2-cyclohexanedionedioximo-N,N')nickel(II). 1,2-Cyclohexanedionedioxime was synthesized following the selenium dioxide oxidation procedure of Rauh, Smith, Banks and Diehl (35). The nickel(II) compound was prepared by a scale-up (0.25 g. to 6 g.) of the standard gravimetric procedure for nickel (50). The product was recrystallized in part from bromobenzene, in part from o-dichlorobenzene.

1,2-Bis(α-furildioximo-N,N')nickel(II). The procedure of Reed, Banks and Diehl (37) was used for the preparation of the reagent, α-furildioxime. The nickel(II) compound was obtained by use of a method which resembled an enlarged version (0.25 g. to 12 g.) of the gravimetric procedure for nickel using this reagent (36), but with some minor changes. The quantitative precipitation of nickel is ordinarily done in the presence of 200 per cent excess of the reagent; to conserve the latter, 50 per cent excess was used, with subsequent especially thorough washing of the precipitate. The vic-dioxime was dissolved in a 10 per cent ethanol-water mixture to reduce the volume of the reagent solution somewhat. The order of addition of the reagents was also reversed; that is, the dilute solution of nickel chloride was added to the reagent solution, in order to effect as complete precipitation as possible. The dried precipitated material was recrystallized from o-dichlorobenzene.

The recrystallized compounds were analyzed gravimetrically for their nickel contents. This was done to check their conformity with the respective formulae established for the normal nickel(II) complexes with the vic-dioximes. It was not certain beforehand that the recrystallization process, which was necessary in order to obtain easily handled forms of the compounds, would leave their fundamental nature unchanged. Weighed samples of the compounds were treated with nitric acid and then with perchloric acid to bring them completely into solution. The perchlorate solutions were analyzed for nickel according to the 1,2-cycloheptanedionedioxime method of Voter and Banks (49). The results of the analyses are to be found in Table 1.

Other pertinent data given in Table 1 include the colors of the complexes when precipitated from aqueous solution and also after recrystallization from the organic solvents mentioned above, the theoretical molecular weights, the theoretical nickel contents, and the densities of the compounds. Estimates for the last-named item were obtained by the liquid displacement method of measuring densities of solids (4). Pycnometers of 50 ml. capacity (Kimble No. 15123) were used, and the liquid employed was 95 per cent ethanol. Water would be suitable for this purpose except that it does not wet the crystals well; some tend to float to the surface.

C. Magnetic Susceptibility Measurements

The *vic*-dioxime complexes of nickel(II) as obtained from precipitation in aqueous solution proved to be nearly impossible to manipulate satisfactorily. The particles collected static charges very easily and clumped together at the slightest touch. Quantitative transfer in the dry state could not be effected. Through slow crystallization from organic solvents, however, the particle size was evidently increased enough that the materials behaved more like

Table 1.

Physical Data for the 1,2-Bis(*vic*-dioximo-*N*,*N'*)nickel(II) Complexes

Compound	Color		% Nickel		Mol. Wt.	Density, g./ml.
	Aq. Ppt.	Recryst.	Calc.	Obs.		
1,2-Bis(α-benzil-dioximo-*N*,*N'*)nickel(II)	Red-or.	Red-br.	10.92	10.97	537.2	1.509
1,2-Bis(2,3-butanedione-dioximo-*N*,*N'*)nickel(II)	Red	Brown	20.32	20.47	288.9	1.715
1,2-Bis(1,2-cycloheptane-dionedioximo-*N*,*N'*)nickel(II)	Yellow	Orange	15.90	15.88	369.0	1.619
1,2-Bis(1,2-cyclohexane-dionedioximo-*N*,*N'*)nickel(II)	Red	Brown	17.21	17.30	341.0	1.703
1,2-Bis(α-furil-dioximo-*N*,*N'*)nickel(II)	Red-br.	Br.-blk.	11.81	11.87	497.1	1.747

crystalline bodies. They still showed a slight tendency to clump together, but this effect had been reduced to a point where the substances were quite easily worked with. The recrystallized compounds were used for all magnetic susceptibility measurements.

The usual double-length sample tubes with central partitions and 0.50 or 0.75 cm. inner diameters were used for magnetic measurements on the 5 crystalline complexes. The lower half of each sample tube used was filled with dry air, stoppered and sealed. The filling of the upper compartment of the sample tube was done by adding several very small portions at a time, then vertically tapping the tube on the bench or table top about 100 times or until the volume of packed solid appeared to be constant. The process was relatively tedious. The height of the material in the tube was brought to the calibration mark at the top as closely as possible.

Two sets of measurements, independent even to the packing of the sample tube, were made on each complex compound in the manner set forth in Part One of these writings. Each set included observations of the change in weight of the sample tube at 9 or 10 different currents over the whole range of 0-10 amperes.

In the treatment of the data from a single, typical set of measurements, the changes in weight for the sample tube filled with the complex were first plotted against the standard changes in weight for the same tube, as obtained through the use of the calibration table and the factor for the tube. This plot was made in order to ascertain whether or not the complex was contaminated with ferromagnetic impurities; the presence of these would cause the plot to deviate from linearity, as would the presence of non-uniform packing in the sample tube. Invariably the curve produced on such a plot had a slight amount of curvature at the lower values of the coordinates, but was linear for the latter 75 per cent or more.

The value of the average ratio of the change in weight of the unknown to that of the standard was desired here. This was given by the slope of the linear portion of the curve. With this ratio thus determined, the volume susceptibility of the packed column was calculated by the use of the relation

$$R = \left(\frac{\Delta W_x}{\Delta W_s}\right)_{\text{ave.}} = \frac{k_x - k_a}{k_s - k_a}, \qquad (8)$$

where R is the ratio just mentioned, and the other terms have the same significance as in equation (7) of Part One. The volume susceptibility of the nickel(II) complex was derived from that of the packed column by correction of the latter for the contribution of the air in the column. Division of the volume susceptibility of the complex by its density of course led to the gram susceptibility, which in turn gave the molar susceptibility when multiplied by the molecular weight.

The mass and molar susceptibilities of the 5 complex compounds were measured and calculated in the manner just described. The average values of these data for each compound are to be found in Table 2. Individual observations differed from the average values by approximately ± 3 per cent, in general.

The rather low precision of the results is to be ascribed principally to the poor uniformity and reproducibility of the packing of the sample tubes. The complex compounds crystallized in needles, the length of some of which approached half the diameter of the sample tube. This factor, coupled with the clumping tendency mentioned earlier, prevented satisfactory packing. The latter process is most conveniently done with powders, or more nearly spherical particles.

D. Conclusions

The results of magnetic measurements on the 5 vic-dioxime complexes of nickel(II) show them all to be definitely diamagnetic in the solid state. These results also indicate that they are to be assigned the square planar structure, since

Table 2.

Magnetic Susceptibilities of the 1,2-Bis(vic-dioximo-N,N')nickel(II) Complexes at 20° C.

Compound	Gram susceptibility, χ, x 10^6	Molar susceptibility, χ_M, x 10^6
1,2-Bis(α-benzildioximo-N,N')nickel(II)	-0.488	-262
1,2-Bis(2,3-butanedionedioximo-N,N')nickel(II)	-0.374	-108
1,2-Bis(1,2-cycloheptanedionedioximo-N,N')nickel(II)	-0.469	-173
1,2-Bis(1,2-cyclohexanedionedioximo-N,N')nickel(II)	-0.393	-134
1,2-Bis(α-furildioximo-N,N')nickel(II)	-0.388	-193

the lack of any unpaired electrons in the molecules signifies the assumption of the dsp^2 electronic configuration by the central nickel atom in these compounds. These facts being established, it is to be recognized that the 5 complexes studied here can be considered examples of the normal 1,2-bis(vic-dioximo-N,N')nickel(II) compound.

The value found for the diamagnetic susceptibility of 1,2-bis(α-benzildioximo-N,N')nickel(II), -0.488×10^{-6}, is about 2.5 per cent higher than the figure of -0.476×10^{-6} reported by Cambi and Szegö (5). The author's finding for the susceptibility of 1,2-bis(2,3-butanedionedioximo-N,N')nickel(II), -0.374×10^{-6}, is about 11 per cent higher than the figure of -0.335×10^{-6} given by the same workers for this compound, but is some 0.16×10^{-6} lower than the value of -0.53×10^{-6} reported by Klemm, Jacobi and Tilk (23). The relative concordance between the measurements of Cambi and Szegö and those of the author, for the latter compound, casts some doubt on the accuracy of the result published by the last-named trio of workers. Comparison of the Cambi and Szegö values, for both compounds, with those of the author suggests higher purity of the latter's compounds.

It would be instructive to be able to compare the experimental susceptibility values reported here with theoretical or empirical susceptibilities for the nickel(II) complexes. Empirical estimates for organic compounds can often be made through the use of the Pascal atomic susceptibility constants, a table of which is given by Selwood (42, p. 52). The constants vary according to the manner in which the atoms are combined in their various compounds, however, and constants are not listed for some of the atomic groupings present in the vic-dioxime complexes of nickel(II), so such estimates for the latter compounds would be very inaccurate and the comparison with experimental values meaningless.

IV. PART THREE: STUDIES ON NON-AQUEOUS SOLUTIONS OF THE COMPLEXES OF NICKEL WITH THE VIC-DIOXIMES

The magnetic studies which proved the several crystalline bis(vic-dioximo-N,N')nickel(II) compounds to be structurally similar brought forth no significant deviations which could be correlated with the variations of other characteristics of the compounds. As has been stated previously, investigations into the behavior of these substances when present in solution would be more likely to yield information of this sort, and this was the primary reason for this part of these researches.

The extreme insolubility of these compounds in water is one of their foremost attributes, since it is one of the factors responsible for their usefulness as reagents in the gravimetric determinations of nickel and palladium. By the same token, water is automatically excluded from the list of solvents in which the reactions of these complexes can be studied. Their non-ionic nature indicates that perhaps a great variety of organic solvents would be suitable for this purpose, but only limited solubility is exhibited by the compounds in all but a few of these. The scope of the magnetic studies, for which reasonably concentrated solutions must be used, was limited by this effect, but the intense color of even very dilute solutions of the complexes pointed to the possibility of using spectrophotometric techniques to extend the limits of the investigation.

A. Review of the Literature

Within the last decade, it has been demonstrated by several investigators that the magnetic character and presumably, also, the basic structure shown by a number of nickel(II) complexes in the solid state are not always retained when these same compounds are dissolved in organic solvents. The first instance of this behavior was apparently noted by French, Magee and Sheffield in 1942 (17). These workers investigated a number of nickel complexes, both from the magnetic standpoint and with reference to their visible and ultraviolet absorption spectra. One of the compounds that was included in their study was bis(formylcamphor)ethylenediamine nickel, which was diamagnetic in the solid state, but showed a magnetic moment of 1.9 Bohr magnetons in methyl alcohol solution. The normal moment for paramagnetic nickel(II) is 2.83 Bohr magnetons or more, of course, so these authors postulated an equilibrium between planar and tetrahedral forms of the complex. They reasoned that the planar form was under some strain, even in the crystalline state, due to the presence of the asymmetric centers in the camphor rings, and that the influence of solvent molecules was sufficient to make possible the transformation of about one third of the molecules into the tetrahedral forms.

The same compound was later subjected to study by Lifschitz, who in 1947 reported that the observations of the former workers were correct (24). Furthermore, he found that the complex was also partially paramagnetic in nitrobenzene and acetonitrile, but diamagnetic in benzene and acetone. Lifschitz stated that there was apparently no simple relation between the susceptibility of the solute and the various characteristics of the several solvents which he used, but it is to be noted that his figures for the dielectric constants of these solvents were highest for those in which a paramagnetic moment was shown by the nickel complex.

Willis and Mellor in 1947 concluded an extensive survey of the magnetic behavior of nickel complexes in solution, using organic solvents (54). A total of 12 compounds were studied, 2 of these being paramagnetic and the rest diamagnetic in the solid state. The paramagnetic compounds were observed only in pyridine solution, and the magnetic moment of the nickel atom was unaffected by the dissolution in each case.

Each of the 10 diamagnetic solids, however, showed a partial conversion to a paramagnetic form in at least 1 of the 6 solvents used, and in 3 cases this conversion was essentially complete, with magnetic moments of more than 3.00 Bohr magnetons being reported. None of the solvents seemed to influence the magnetic character of all of the solutes in any consistent manner, although pyridine effected the conversion more often than most, and was the solvent present in the 3 cases of complete conversion.

These authors suggested, in the case of the pyridine solutions, that the change in the magnetic moment of the nickel atom upon entering solution was due to the setting up of an equilibrium between the original square coplanar state and an octahedral configuration involving the addition of 2 pyridine molecules to the original compound. They further suggested that an equilibrium between square and tetrahedral configurations was the cause of the change in magnetic moment in the non-pyridine solutions, the influence of the solvent molecules being responsible for any conversion that was produced. This is, of course, the explanation offered by French and co-workers for the same phenomenon.

It is interesting to note that Willis and Mellor included in their survey the same bis(formylcamphor)ethylenediamine complex that had previously been investigated by French, et al., and which was apparently studied by Lifschitz at about the same time as Willis and Mellor did their work. In general, the findings of all three groups of authors are in agreement, with the exception that Lifschitz found the compound to be diamagnetic in benzene solution, whereas Willis and Mellor noted that it showed some paramagnetism in the same solvent.

The compound bis(methylglyoxime)nickel, or better, 1,2-bis(1,2-propanedionedioximo-N,N')nickel(II) was listed among the diamagnetic solids investigated by Willis and Mellor. This complex which by its diamagnetic nature must be a typical square coplanar compound in the solid state, was studied in pyridine solution. The magnetic moment of the central nickel atom was found to be 1.5 Bohr magnetons at the particular concentration used, signifying that an equilibrium between the diamagnetic form and some paramagnetic structure was being observed. Since for complete conversion into the latter the nickel should have had a molar susceptibility of at least $+3400 \times 10^{-6}$ and could have exhibited a value as high as $+4400 \times 10^{-6}$ or so, the molar susceptibility of $+990 \times 10^{-6}$ found in the solution indicates an amount of conversion in the range 22 to 29 per cent. The authors of the paper made no statements or suggestions specific for this compound, but since the solvent was pyridine, it is to be assumed that they considered the paramagnetic form to be an octahedral structure involving 2 molecules of pyridine.

The discovery of an equilibrium of this type for a vic-dioxime complex of nickel(II) points at once to the possibility of using the reaction with pyridine as a measure of the stability of the several vic-dioxime complexes used in the work being reported here. The compound used by Willis and Mellor differs somewhat from the 5 compounds used in this work in that the parent vic-dioxime is unsymmetrical, but it was felt that the reaction is probably essentially characteristic of the coordination center of the molecule, and that such structural differences might influence the degree to which the reaction proceeds but not its fundamental nature. It was also felt that other basic solvents might react with the vic-dioxime complexes in similar fashions. For these reasons, then, it was determined to make an investigation of the magnetic properties of the bis(vic-dioximo-N,N')nickel(II) complexes in pyridine and other organic solvents, with a view toward the estimation of their relative stabilities.

The spectrophotometric extension of the results of the magnetic studies to those compounds too insoluble to permit creditable magnetic measurements seemed feasible after consideration of recent correlations of absorption spectra and magnetic properties. Selwood has pointed out (42, p. 179) that while in general solid diamagnetic compounds of nickel show colors ranging from red through brown to yellow and paramagnetic complexes exhibit shades of green or blue, absolute reliance cannot be placed in this rule since there are several rather striking exceptions (28). Mills and Mellor (28) and McKenzie, Mellor, Mills and Short (25) have shown, however, that somewhat more confidence can be placed in the visible and ultraviolet absorption spectra of solutions of nickel. They found, with very few exceptions, that the presence of square diamagnetic complexes in solution led to the appearance of an absorption band in the vicinity of 400 mμ. which was not found in solutions of paramagnetic complexes. The intensity of this "nickel band" was very great in all cases, with the molar absorbancy indices ranging from 3,000 to 12,000. The deviations from this standard behavior were only partially explained by these workers, but it is to be noted that the parent reagents were also very highly colored in each of these cases.

The absorption spectra of α-benzildioxime, in chloroform, and the nickel(II) complex of this reagent, in absolute alcohol, were presented by the latter group of authors. The former spectrum was characterized by very little absorption at wavelengths above 300 mμ., while that of the latter compound exhibited strong absorption up to about 475 mμ., with the characteristic "nickel band" showing a maximum at 405 mμ.

In view of the results of the spectral studies conducted by Mellor and co-workers on nickel(II) complexes, it appeared likely that the nickel(II) compounds of the 5 vic-dioximes considered in the present work would exhibit spectra characterized by the "nickel band" when dissolved in nonreactive liquids, but that this absorption band would be expected to be diminished or perhaps even eliminated in solvents such as pyridine or other amines, in which the structure of the complexes might be altered. The inherent sensitivity of spectrophotometric methods for highly colored systems such as these would be useful, also, in helping to establish the nature of the reaction.

B. Materials and Apparatus

The preparation, purification and analysis of the five 1,2-bis(vic-dioximo-N,N')nickel(II) compounds were described in Part Two. Diamagnetic susceptibility data used here in calculations relevant to these compounds are to be found in Table 2 of Part Two.

Pyridine, n-butylamine, chloroform, o-dichlorobenzene. Reagent grades, where obtainable at moderate cost, or good technical grades of these solvents were used without further purification. Where redistillation was indicated for the sake of conservation of solvent, this was done through a column 1.5 inches in diameter and 16 inches long, packed with glass Raschig rings.

Magnetic susceptibility measurements were made using the apparatus and technique described in Part One. Densities of the solutions, necessary for the susceptibility calculations, were obtained through the use of a chain-type Westphal balance, L. W. Hohwald, Jersey City, New Jersey.

Spectrophotometric absorption curves were secured with a Cary Recording Spectrophotometer, Model 12, Serial 72, Applied Physics Corporation, Pasadena, California. Matched Corex cells were used in this instrument for the measurements in the visible region down to 340 mμ; matched silica cells were used for work in the ultraviolet portion of the spectrum. Direct control of the temperatures of the cells and solutions contained therein was not provided, but the temperature of the room was maintained at 25° C., so that the temperatures of the samples probably varied only slightly from this point.

Specific conductivity measurements were made with a portable conductivity apparatus, Leeds and Northrup Model 4866, Philadelphia, Pennsylvania, using a Leeds and Northrup No. 4920 dip cell electrode assembly designed for use with solutions of low conductivity. Since in general only the order of magnitude was desired in the conductivity measurements, rigid temperature control was not always employed, although the temperatures of most of the samples were fixed by placing them in the 20° C. bath of the magnetic susceptibility apparatus.

C. Experimental

The experimental measurements described here were made for one or both of two purposes: (1) to assist in the comparison of the reactivities or stabilities of the several vic-dioxime complexes of nickel(II); (2) to obtain information relative to an estimation of the nature of the reactions between 1,2-bis(α-furildioximo-N,N')nickel(II) and pyridine or n-butylamine. The methods used, however, can most concisely and clearly be described by following the natural division into magnetic and spectrophotometric studies, ignoring, for the present, the ultimate use of the results of the measurements.

1. Magnetic measurements

The solutions prepared for the magnetic studies were made up by dissolving weighed samples in the desired solvent and diluting to 100 ml. at 20° C., with the exception of the chloroform and n-butylamine solutions containing bis(1,2-cycloheptanedionedioximo-N,N')nickel(II). The latter were solutions saturated with the complex at 20° C., and were analyzed subsequent to the magnetic measurements on them. The specific gravities of all the solutions were measured with the Westphal balance immediately following their several preparations, before any samples were taken for magnetic or other measurements. The densities derived from the specific gravity readings were assumed to be constant throughout the remainder of the work with the solutions.

The susceptibility of each of the solutions studied was determined at least twice, and some of the solutions for which it was difficult to obtain reproducible values were subjected to this measurement as often as 6 or 8 times. Each determination of the susceptibility was carried out by measuring the change in weight of the solution-filled sample tube at 6 or more different magnet currents. The changes in weight for the standard nickel chloride solution at these currents were obtained by reference to the calibration table and the calibration factor for the tube. The average ratio of the changes in weight for the unknown and the standard was obtained by calculation, the individual values of the ratio being sufficiently consistent that no plotting of the data was necessary. The individual ratios differed from the average by an average deviation of ±0.1 per cent, in general.

The volume susceptibilities of the solutions were calculated with the now-familiar relation

$$R = \left(\frac{\Delta W_x}{\Delta W_s}\right)_{\text{ave.}} = \frac{k_x - k_a}{k_s - k_a}, \qquad (9)$$

where R is the average ratio again, and the other terms continue to have their usual significance. The volume susceptibilities, k_x, were converted to the mass susceptibilities, χ_x, by dividing the former by the respective densities.

The experimental values for the mass susceptibilities of the solutes were obtained by use of the equation

$$\chi_{soln} = w_1\chi_1 + w_2\chi_2, \qquad (10)$$

where χ_{soln}, χ_1 and χ_2 are the mass susceptibilities of the solution, solute and solvent, respectively, and w_1 and w_2 are the weight fractions of the solute and solvent. These calculations of course assume the linear additivity of susceptibilities according to weight. The gram susceptibilities of the solvents were needed for this work; they were determined to be as follows: chloroform, -0.4985×10^{-6}; pyridine, -0.6084×10^{-6}; n-butylamine, -0.8175×10^{-6}. The gram susceptibilities of the solutes were converted to molar susceptibilities by multiplication by the respective molecular weights.

Since in many of the solutions some conversion to paramagnetic forms did occur, it was desirable to obtain the molar susceptibilities of the central nickel atoms in the various compounds. These were derived from the total molar susceptibilities of the complexes in solution by subtracting from the latter the molar diamagnetic susceptibilities of the original compounds, as listed in Table 2, Part Two. The molar susceptibilities for the nickel are to be found in Table 3, in the column headed χ_A.

The primary interest in the latter quantities lay in the possibility of using them for estimating the amounts of conversion that had taken place. Divalent nickel theoretically has but 2 possible magnetic states, one in which there are 2 unpaired electrons and one in which there are none. A molar susceptibility for nickel which lies between 0 and $+3400 \times 10^{-6}$, the value calculated for 2 unpaired electrons at 20° C., will therefore indicate the position of an equilibrium between the 2 states. Because of the usual orbital contribution, however, the actual molar susceptibility of nickel(II) in its paramagnetic state always lies somewhat above $+3400 \times 10^{-6}$, and may be as large as $+4500 \times 10^{-6}$ or $+4600 \times 10^{-6}$.

Because of this uncertainty in the susceptibility of the nickel in the paramagnetic complex, the indications presented by the experimentally measured susceptibilities as to the amounts of conversion can only be approximate. For consistency and for lack of a better basis for calculation, the molar susceptibility of the nickel in the paramagnetic form was assumed in all cases to be $+3400 \times 10^{-6}$, and the ratios of the experimental values to the latter figure were taken to be measures of the amounts of conversion.

Table 3.

Magnetic Data for Solutions of Nickel(II) Complexes at 20° C.

Solute	Soln. No.	Solvent	Conc., g./100ml.	χ_A x 10^6	Per Cent Conversion	$\mu_{eff.}$ B.m.
I[a]	1	C_5H_5N	0.850	140	4 ± 2	0.6
II[b]	2	C_5H_5N	0.056	∼0	∼0	0
III[c]	3	C_5H_5N	0.309	120	4 ± 2	0.5
	4	$CHCl_3$	0.235	∼0	∼0	0
	5	n-$BuNH_2$	0.055	740	22 ± 6	1.3
IV[d]	6	C_5H_5N	0.971	1190	35	1.68
	7	C_5H_5N	0.888	1180	35	1.67
	8	C_5H_5N	0.671	1080	32	1.60
	9	C_5H_5N	0.485	1030	30	1.56
	10	n-$BuNH_2$	0.977	870	26	1.43
	11	n-$BuNH_2$	0.961	940	28	1.49
	12	n-$BuNH_2$	0.706	1300	38	1.75
	13	n-$BuNH_2$	0.531	1040	31	1.56
	14	n-$BuNH_2$	0.361	1500	44	1.88

[a] I = 1,2-Bis(α-benzildioximo-N,N')nickel(II).

[b] II = 1,2-Bis(2,3-butanedionedioximo-N,N')nickel(II).

[c] III= 1,2-Bis(1,2-cycloheptanedionedioximo-N,N')nickel(II).

[d] IV = 1,2-Bis(α-furildioximo-N,N')nickel(II).

These ratios, times 100, are listed in Table 3 under the heading "Per Cent Conversion". The figures presented thereunder are to be regarded only as estimates for the upper limits of the amounts of reaction that have apparently taken place, because of the uncertainty mentioned above.

The effective magnetic moments for the nickel present in the solutions were calculated from the Curie law (2, p. 146):

$$\mu_{\text{eff.}} = 2.84\sqrt{\chi_A T}, \qquad (11)$$

where $\mu_{\text{eff.}}$ is the moment expressed in Bohr magnetons, χ_A is the molar susceptibility of the nickel and T is the absolute temperature.

No magnetic data are given for solutions of 1,2-bis(1,2-cyclohexanedionedioximo-N,N')nickel(II) because of the limited solubility of this compound in all of the solvents tested.

The concentrations of solutions 2 and 5 in Table 3 are considerably lower than those of the other solutions studied and are about at the lowest limit permissible for work of this type, in which the detection of a paramagnetic element is desired. The results tabulated for these two solutions are to be regarded as qualitative indications only; the data for the other solutions are much more exact.

Consideration of the evidence presented in Table 3 permits the following conclusions to be drawn immediately: (1) 1,2-bis(α-furildioximo-N,N')nickel(II) unmistakably reacts to a considerable extent with the solvents pyridine and n-butylamine; (2) 1,2-bis(1,2-cycloheptanedionedioximo-N,N')nickel(II) reacts only slightly with pyridine, probably is changed somewhat more in n-butylamine, and dissolves in chloroform unchanged from its original diamagnetic state; (3) 1,2-bis(α-benzildioximo-N,N')nickel(II), though quite soluble in pyridine, is only slightly affected by this solvent; and (4) 1,2-bis(2,3-butanedionedioximo-N,N')nickel(II) probably does not react with pyridine.

The magnetic measurements on these solutions were in each case completed within a week after their respective preparations. It was noticed some time later, however, that the colors of some of the solutions had faded considerably. In pursuit of a reason for this behavior, the susceptibilities of those solutions that had not already been discarded were measured again. Table 4 presents the comparison between the results of the original measurements and those of the second determinations. The calculations for the magnetic quantities were made in the same fashion for both sets of results. The column headed "Days Lapsed" indicates for each solution the time delay between its preparation and susceptibility determination.

The second determinations for the last three solutions

Table 4.

Comparison of Magnetic Data for Fresh and Aged Solutions of Nickel(II) Complexes at 20° C.

Solute	Soln. No.[a]	Solvent	Days Lapsed	$\chi_A \times 10^6$	Per Cent Conversion	$\mu_{eff.}$ B.m.
III[b]	5	$\underline{n}$-BuNH$_2$	4	740	22 ± 6	1.3
			30	4170	120 ± 15	3.1
IV[c]	6	C_5H_5N	2	1190	35	1.68
			14	1370	40	1.80
	8	C_5H_5N	2	1080	32	1.60
			20	1370	40	1.80
	9	C_5H_5N	4	1030	30	1.56
			20	1210	36	1.69
	10(a)	$\underline{n}$-BuNH$_2$	3	870	26	1.43
			12	870	26	1.43
	10(b)	$\underline{n}$-BuNH$_2$	(3)	(870)	(26)	(1.43)
			15	2410	71	2.38
	12	$\underline{n}$-BuNH$_2$	3	1300	38	1.75
			28	3590	106	2.91
	13	$\underline{n}$-BuNH$_2$	4	1040	31	1.56
			20	3680	108	2.95
	14	$\underline{n}$-BuNH$_2$	7	1500	44	1.88
			22	4090	120	3.11

---

[a] Concentration data for these solutions are to be found in Table 3.

[b] III = 1,2-Bis(1,2-cycloheptanedionedioximo-$\underline{N}$,$\underline{N}$')nickel(II).

[c] IV = 1,2-Bis(α-furildioximo-$\underline{N}$,$\underline{N}$')nickel(II).

illustrate the error in assuming the value $+3400 \times 10^{-6}$ for the susceptibility of the nickel in the paramagnetic complex. Amounts of conversion greater than 100 per cent are impossible and therefore not especially illuminating in comparison to previously determined values for the same solutions. Because of the complete consumption of these solutions, it was not possible to inquire further into whether or not they were finally at equilibrium. For this reason, it was not considered worthwhile to recalculate all of the results, since this process would shed no further light on the comparison of fresh and aged solutions.

Table 4 shows that the fading of the color of the solutions was accompanied by an aging effect of considerable magnitude in the case of the n-butylamine solutions and of lesser consequence in the pyridine solutions. Unfortunately, the solutions were all so nearly opaque that it was impossible to study the color changes spectrophotometrically except perhaps with very short cells, which were not available.

The results of two remote sets of measurements on each solution do not give sufficient information to allow any decision to be made about the nature of this aging effect. The results can be explained in at least two ways. The solutions could come to some sort of quasi-equilibrium almost immediately, with amounts of conversion approximately equal to those given by the first measurements, and could then change slowly under the influence of some secondary reaction. This behavior appears to be the more probable in the case of the pyridine solutions. Alternatively, the results could be explained by a rather slow logarithmic approach to equilibrium. The latter speculation would seem to be better suited for the n-butylamine solutions.

Solutions 6 and 10, which contain 1,2-bis(α-furildioximo-N,N')nickel(II) in pyridine and n-butylamine, respectively, were prepared expressly for a more complete investigation of the aging effect. The magnetic and other measurements on these two solutions will be considered shortly.

In casting about for more information on what might have been happening in the solutions in which some conversion had taken place, rough conductivity measurements were made on some of those listed in Table 3. The results indicated that while the dissolution of 1,2-bis(1,2-cycloheptanedionedioximo-N,N')nickel(II) in chloroform apparently did not raise the specific conductance of the latter at all, pyridine and n-butylamine solutions of this compound and 1,2-bis(α-furildioximo-N,N')nickel(II) exhibited specific conductances which were measurably greater than those of the pure solvents. Furthermore, the conductivities of several of the solutions of the last-named complex in n-butylamine appeared to have risen in direct proportion to the analytical concentration of the complex. Numerical values for these quantities are not quoted here because the subsequent discovery of the aging effect has rendered their comparison somewhat less valid and therefore less useful.

The specific conductances of the n-butylamine solutions lay in the range 10^{-6} to 10^{-7} mhos/cm., while those of the pyridine solutions generally were slightly greater than 10^{-6}mhos/cm. The specific conductance of pure n-butylamine was found to be $< 10^{-7}$, and that of n-butylamine to which sufficient perchloric acid had been added to make concentration of the latter 0.02M was 5.6×10^{-6}. The pyridine available showed a specific conductance of 4.3×10^{-7}, and a 0.02M perchloric acid-pyridine solution gave a value of 6.8×10^{-4} mhos/cm. Thus, although the actual conductivities of the solutions of nickel(II) complexes in these basic solvents were very low, comparison with the values for the pure solvents and for the solutions containing perchloric acid leads to the conclusion that a measurable amount of ionization must have taken place.

It was desirable to know whether the conductivities of the solutions were affected by the age of the latter and if so, whether the change in conductivity could be considered to run a course parallel to the change in the amount of conversion in any or all of the solutions. For these reasons, also, solutions 6 and 10 were prepared and investigated.

One portion (sample (a)) of each of these two solutions was placed in a susceptibility sample tube. Both of these tubes were then stoppered and left intact for a period of 2 weeks, during which the susceptibilities of the enclosed samples were measured daily. Another portion (sample (b)) of each solution was placed in a vessel suitable for conductivity measurements. The specific conductances of these two samples were also measured daily for the same two week period, at roughly the same times as the magnetic measurements on their twins were being conducted. At the end of the period, the conductivities of the samples (a) and the susceptibilities of both samples (b) were determined.

The susceptibility of sample (a) (reserved for magnetic work) of solution 6 (pyridine solution) was constant, for nearly a week, at a value which indicated some 35 per cent conversion of the solute, and then rose slowly until, at the end of the period, some 40 per cent of the solute had apparently reacted. The conductivity of sample (b) of solution 6 rose almost linearly from an initial value of about 6.5×10^{-7} mhos/cm. to about 3.5×10^{-6} at the end of the study. The final susceptibilities of samples (a) and (b) were very nearly equal, as was likewise true for their conductivities. The rise in the specific conductance of (b) did not exactly parallel the change in the amount of conversion for (a), but aside from this one small difference, apparently the two samples were not to be distinguished from each other. For this reason they were not listed separately in Table 4.

n-Butylamine solution 10 showed an unexpectedly different behavior. The susceptibility of sample (a) (reserved for magnetic work) fell slightly during the first few days, then remained constant for the remainder of the 2 week period at a value which corresponded to 26 per cent conversion of the original complex. The specific conductance of sample (b) rose, relatively rapidly at first, then more slowly, from 1.5×10^{-7} to 5.1×10^{-7} mhos/cm. over the same period. The specific conductance of sample (a) at the end of the study, however, was only 1.2×10^{-7} mhos/cm., or slightly less than the initial value of this quantity for sample (b). The susceptibility of sample (b) at the end of the 2 weeks, moreover, had risen to a figure which indicated about 71 per cent conversion. Since (a) had been completely isolated during this period while (b) had been repeatedly exposed to and mixed with air, through the frequent insertions of the electrode assembly, the logical conclusion is that some component of the atmosphere is of some influence on the reaction between n-butylamine and 1,2-bis(α-furildioximo-N,N')nickel(II).

2. Spectrophotometric measurements

With two exceptions to be discussed later, the solutions of nickel(II) complexes used for the recording of spectral absorption curves were made up by dilution of measured volumes of stock solutions with the desired reactive solvents. Chloroform was employed as the solvent in all of the stock solutions except that of 1,2-bis(1,2-cyclohexanedionedioximo-N,N')nickel(II), for which o-dichlorobenzene was used. The chloroform stock solutions were prepared by dissolving weighed samples of the crystalline vic-dioxime complexes of nickel in this solvent and diluting to volume at room temperature.

The stock solution of 1,2-bis(1,2-cyclohexanedionedioximo-N,N')nickel(II) in o-dichlorobenzene was made up by introducing a weighed sample of the solid into a measured volume of the solvent and allowing the mixture to come to equilibrium. The excess nickel complex was then filtered off, dried and weighed. The difference between the two weights divided by the volume of solvent used was taken as the concentration of complex in solution.

Chloroform was chosen as the solvent for most of the stock solutions not only because 4 of the 5 complex compounds were soluble enough in this medium for spectrophotometric work, but also because one of them, 1,2-bis(1,2-cycloheptanedionedioximo-N,N')nickel(II), had been shown to be diamagnetic when present in chloroform solution. It is unfortunate that this condition could not be checked for all of the complexes, in particular for the α-furildioxime complexes.

The absorption curves were obtained by using the Cary spectrophotometer strictly according to the manufacturer's directions. The sample cells were cleaned, rinsed with acetone and dried before use. The instrument was balanced, for the particular pair of cells used, before each set of curves was made. Care was taken always to use the cells in the same positions as those for which the instrument had been balanced.

The absorption curve of each of the solutions was measured against a "blank" composed of the same solvent or solvent mixture as that present in the solution of interest. By using this "blank", the spectral absorption due only to the nickel compound was recorded.

The spectrophotometric absorption curves as obtained for solutions of the 5 vic-dioxime complexes of nickel(II) are to be found in Figures 5-9. Concentration data and the composition of the solvent mixtures for each solution accompany the curves. The lengths of the particular cells used are also recorded. It is to be seen that each of the complexes was observed in (a) an unreactive solvent; (b) a solvent mixture composed largely of n-butylamine; and (c) a solvent mixture containing a large amount of pyridine.

Comparison of the curves (a) in Figures 5-9 shows that in the unreactive solvents (chloroform or o-dichlorobenzene) a double-peaked absorption band is present in every case. The two peaks of this band are very nearly 45 mμ. apart for each of the complexes, although the positions of the peaks with respect to wavelength and the relative heights of the two maxima vary somewhat from compound to compound. It is believed that this absorption band can be considered equivalent to the "nickel band" of Mc Kenzie, et al. (49).

The presence of a large amount of n-butylamine in the solutions represented by curves (b) in Figures 5, 6 and 9 apparently affected the α-benzildioxime, 2,3-butanedionedioxime and α-furildioxime complexes to a considerable extent, since in these cases the principal absorption band has essentially disappeared. n-Butylamine evidently had a lesser effect on the 1,2-cycloheptanedionedioxime compound, for the magnitude of the absorption band here (curve (b), Figure 7) has been reduced only some 20 per cent or so. In the case of the 1,2-cyclohexanedionedioxime complex, the maxima of the principal band have been only very slightly affected by the presence of the basic solvent (curve (b), Figure 8).

It may be said that in general, pyridine affected the several solutes in these solutions much less than did n-butylamine. Only in the case of the α-furildioxime

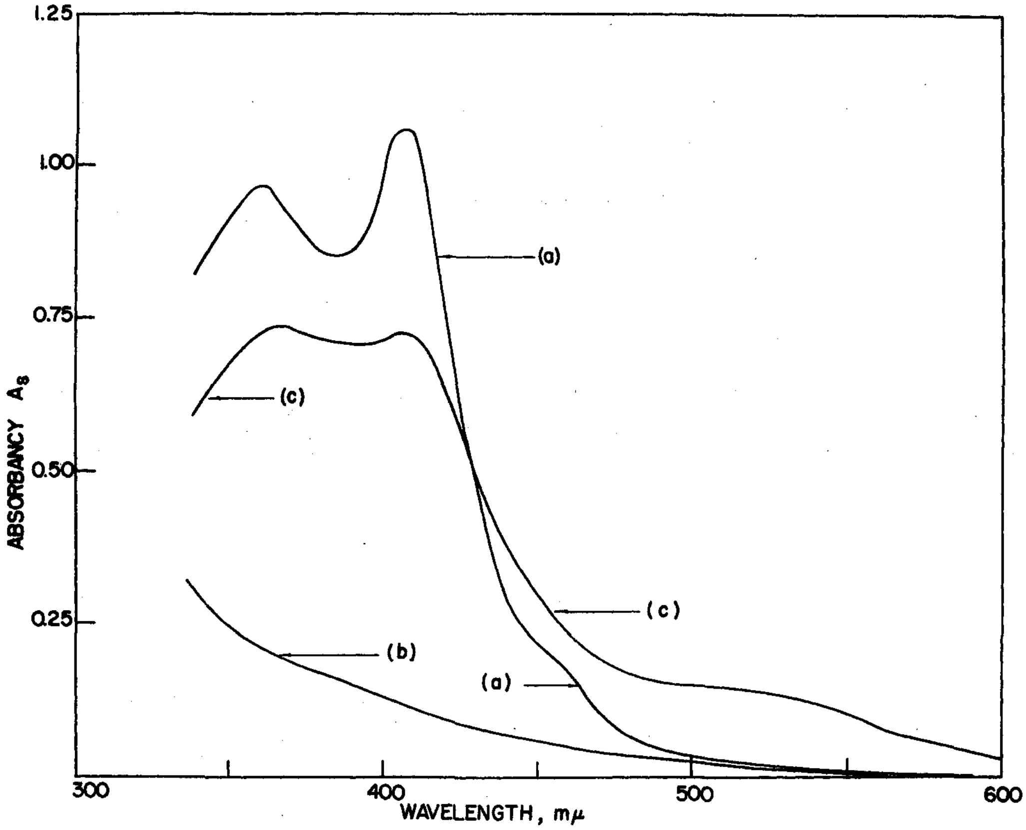


Fig. 5. Spectrophotometric Absorption Curves for 1,2-Bis(α-benzildioximo-*N*,*N*')nickel(II) in:

(a) 100% chloroform
(b) 10% chloroform, 90% *n*-butylamine
(c) 10% chloroform, 90% pyridine

Complex concentration: 1.0×10^{-4} M.
Cell length: 1.00 cm.

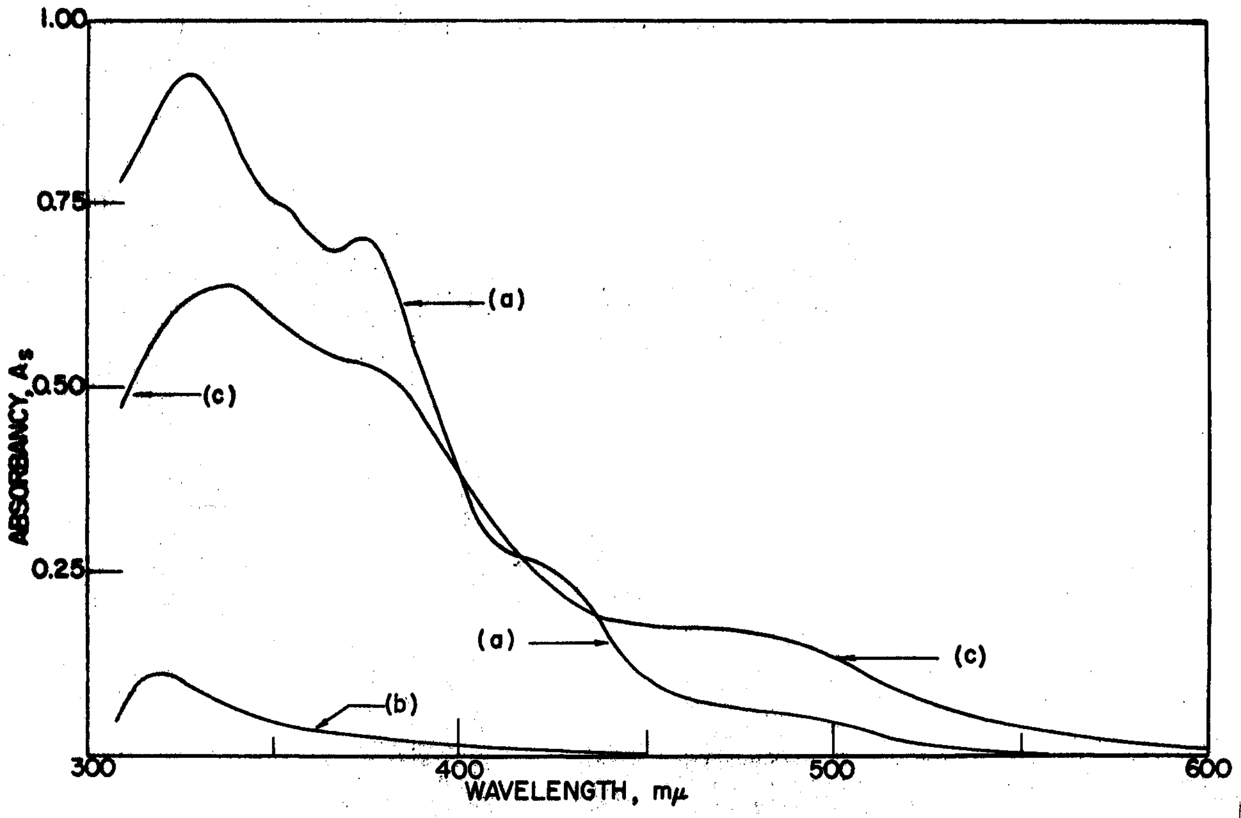


Fig. 6. Spectrophotometric Absorption Curves for 1,2-Bis(2,3-butanedionedioximo-N,N')nickel(II) in:

(a) 100% chloroform
(b) 10% chloroform, 90% n-butylamine
(c) 10% chloroform, 90% pyridine

Complex concentration: 4.0×10^{-5} M.
Cell length: 5.00 cm.

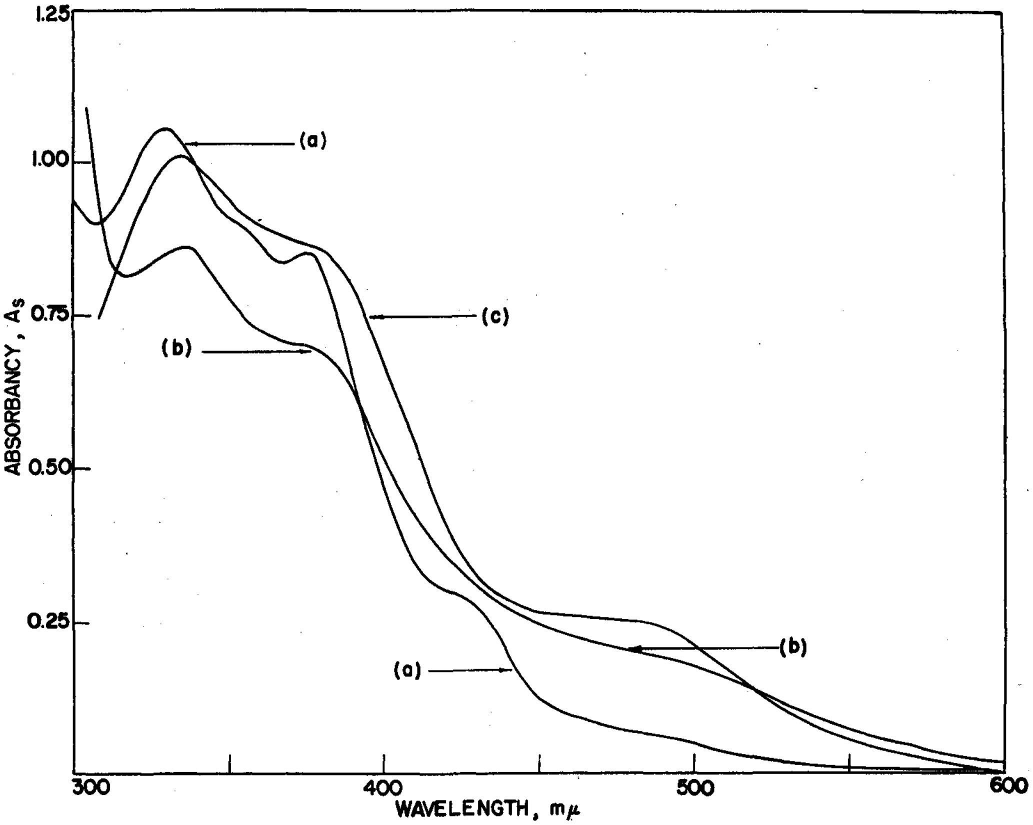


Fig. 7. Spectrophotometric Absorption Curves for 1,2-Bis(1,2-cycloheptanedionedioximo-N,N')nickel(II) in:

(a) 100% chloroform
(b) 10% chloroform, 90% n-butylamine
(c) 10% chloroform, 90% pyridine

Complex concentration: 1.0×10^{-4} M.
Cell length: 1.00 cm.

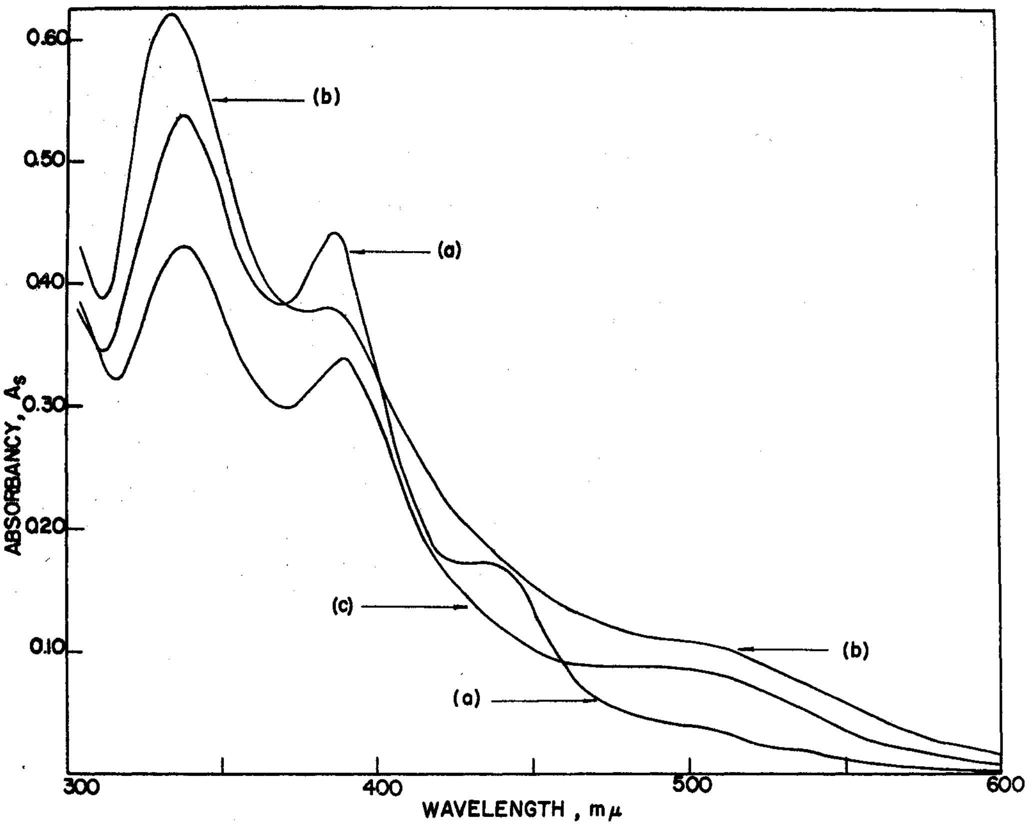


Fig. 8. Spectrophotometric Absorption Curves for 1,2-Bis(1,2-cyclohexanedionedioximo-*N*,*N*')nickel(II) in:

(a) 100% *o*-dichlorobenzene
(b) 50% *o*-dichlorobenzene, 50% *n*-butylamine
(c) 50% *o*-dichlorobenzene, 50% pyridine

Complex concentration: 1.1 x 10^{-5} M.
Cell length: 10.00 cm.

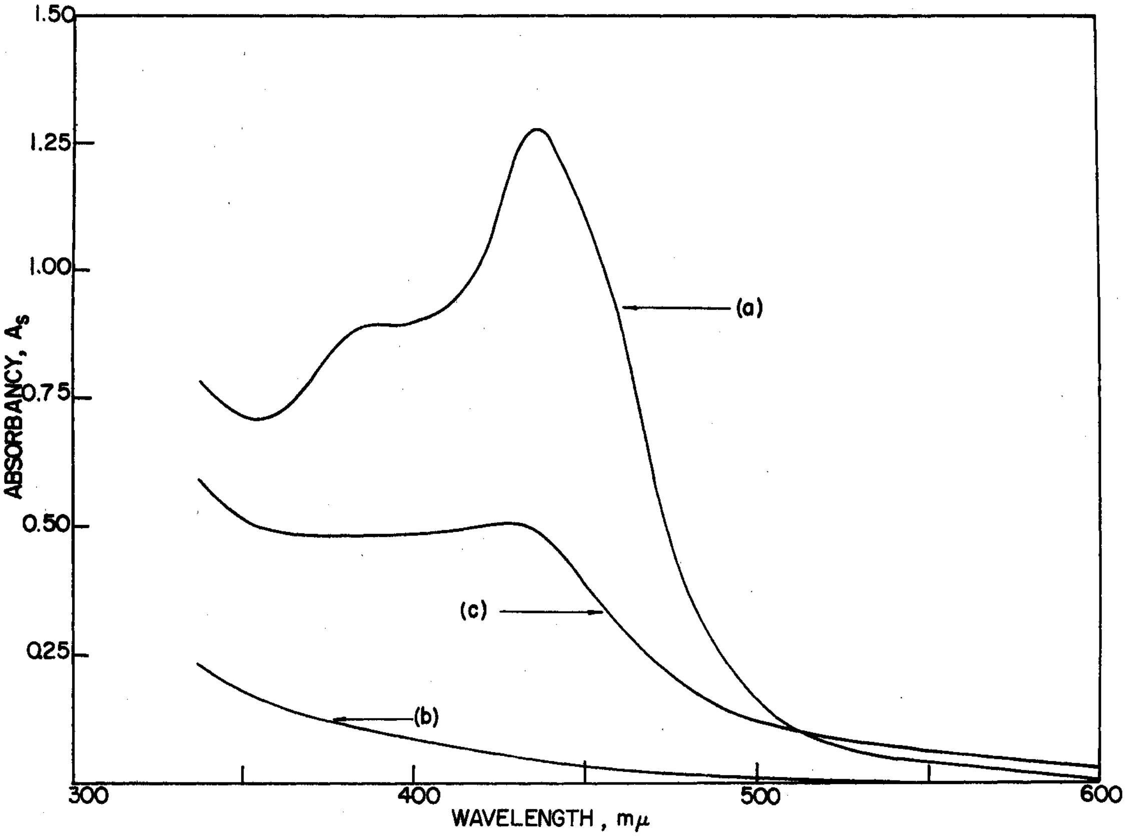


Fig. 9. Spectrophotometric Absorption Curves for 1,2-Bis(α-furildioximo-N,N')nickel(II) in:

(a) 100% chloroform
(b) 15% chloroform, 85% n-butylamine
(c) 15% chloroform, 85% pyridine

Complex concentration: 7.5×10^{-5} M.
Cell length: 1.00 cm.

compound (curve (c), Figure 9) were the absorption maxima very greatly reduced, and even here they were reduced only by about 50 per cent. Curve (c), Figure 5, shows that the peaks for the α-benzildioxime complex have decreased some 30 per cent as a result of the presence of pyridine in the solution, while the absorption spectra of the other 3 compounds, as presented in Figures 5-8, have been affected very little by this factor.

All of the spectrophotometric measurements represented in Figures 5-9 were made within 2 days, at the very latest, after the solutions had been prepared. As in the solutions used in the magnetic work, some fading was later noticed in some of the n-butylamine solutions, but this effect was not investigated here.

Several attempts were made to obtain equilibrium data for the reaction of n-butylamine with the α-furildioxime complex by recording absorption spectra of solutions containing a constant amount of the complex and varying amounts of the amine. The spectra of such solutions were not easily reproduced, however, because of the unpredictable fading of the colors of the solutions. It was felt, therefore, that any calculations based on these data probably would have been in error and might have been seriously misleading.

The appearance of a broad absorption band of relatively low intensity in the range 450 to 550 mμ. was noted in several of the curves (b) and (c) in Figures 5-9. It was felt that perhaps this band was due to the presence of the simple hexapyridinenickel(II) complex, in the pyridine solutions, or the hexa-n-butylaminenickel(II) complex, in the n-butylamine solutions. To check on this matter, the absorption spectra of these two simple complexes, in pyridine and n-butylamine, respectively, were determined.

Hydrated nickel chloride was heated for several hours at >100° C. until all traces of the original green color had disappeared and the material had assumed the yellow color of the anhydrous salt. Portions of this material, in excess, were then introduced into pyridine and n-butylamine in order to form saturated solutions of the two complexes. In the case of the pyridine-nickel chloride mixture, the solution became bluish-green and the excess salt was largely converted to a light blue powder. The n-butylamine-nickel chloride solution assumed a deep blue color, while the excess solid material was completely transformed into large, transparent, deep-blue crystals. Neither of the new blue solid forms was stable in the absence of excess solvent; both changed more or less rapidly into a yellow-green mixture of anhydrous and hydrated nickel chloride when exposed to air. The nickel content of each of the two solutions was determined gravimetrically.

The absorption spectra of the two solutions were determined with the Cary spectrophotometer and are presented in Figure 10, along with concentration and cell length data. Consideration of the two curves shows that these two complexes are not responsible for the broad absorption band previously mentioned, for the wavelength region in which the latter appeared is almost precisely that in which these two simple complexes exhibit the least absorption.

It is of interest to note that these two complexes have absorption maxima in the neighborhood of 400 mμ. This, of course, is the very region in which the "nickel band" of diamagnetic nickel complexes is most prominent. The molar absorbancy indices for the latter type of absorption band are usually greater than 1000, however, while the indices for the absorption bands of the simpler complexes, as can be calculated from Figure 10, will only be in the neighborhood of 10 or 15. On the basis of this comparison, it is evident that the presence of these simpler nickel complexes cannot be detected in solutions of the diamagnetic nickel(II) compounds by reference to absorption spectra.

D. Discussion and Conclusions

The various items of magnetic and spectrophotometric evidence presented in the preceding sections are, for the most part, quite interesting and in some cases relatively informative. The picture which they help to paint is still

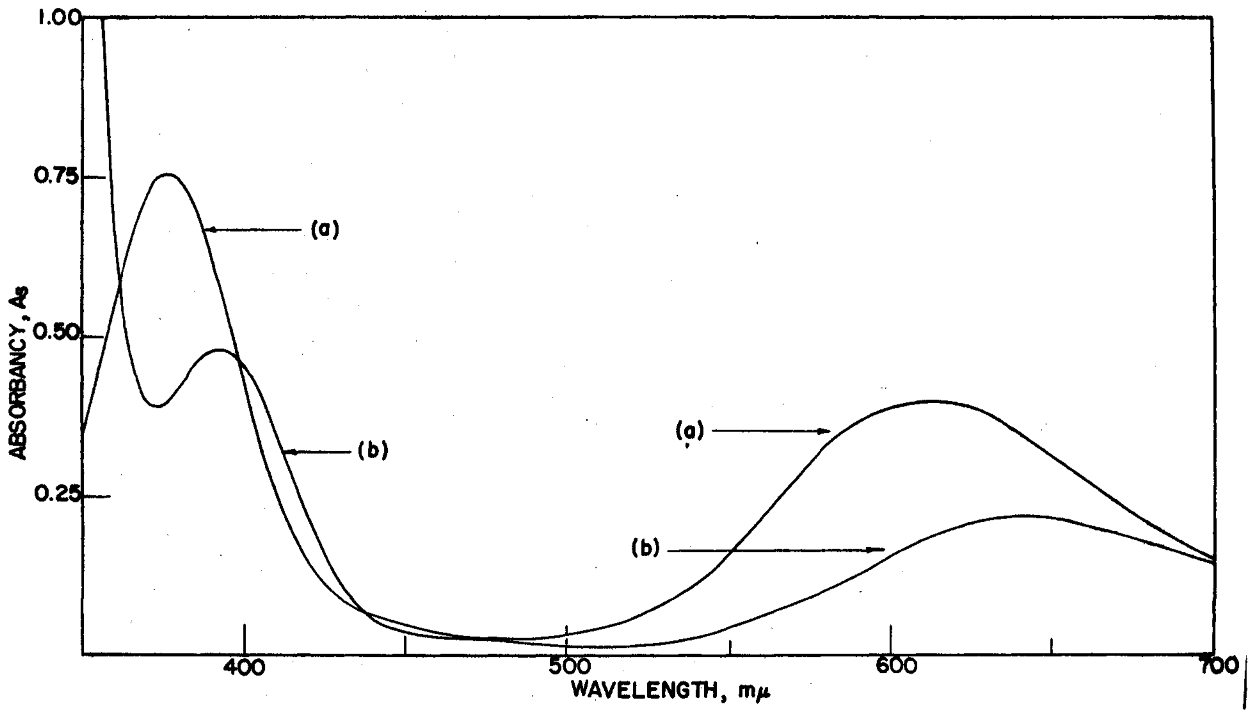


Fig. 10. Spectrophotometric Absorption Curves for:

(a) 0.0243 M. $NiCl_2$ (anhyd.) in n-butylamine
(b) 0.0204 M. $NiCl_2$ (anhyd.) in pyridine

Cell length: 2.00 cm.

incomplete, however, and for the present, at least, only tentative conclusions can be drawn concerning the relative stabilities of the *vic*-dioxime complexes of nickel(II) and the nature of the reaction between these and certain basic solvents.

1. Comparative stabilities of the *vic*-dioxime complexes

Magnetic susceptibility measurements on pyridine solutions of the bis(*vic*-dioximo-*N*,*N*')nickel(II) compounds have clearly established the fact that 1,2-bis(α-furildioximo-*N*,*N*')nickel(II) was considerably more affected by this solvent than were any of the other complexes on which these measurements could be made. It can also definitely be stated that the α-benzildioxime and 1,2-cycloheptanedionedioxime complexes of nickel(II) showed very little reactivity toward this reagent, on the basis of the magnetic evidence. The 1,2-cyclohexanedionedioxime compound was too insoluble to permit a study of its pyridine solution, and the complex of 2,3-butanedionedioxime was only soluble enough that similar unreactivity was indicated, but not proved.

Spectrophotometric observations of solutions in which these compounds were present and which also contained large excesses of pyridine corroborate, in general, the conclusions based on magnetic evidence. It is logical to assume that the principal absorption band in the region 350-400 mμ., which is shown by all of the complexes when dissolved in unreactive solvents, is characteristic of the diamagnetic square nature of these complexes, in view of the work of Mc Kenzie, *et al*. (25) and the magnetic data presented for a chloroform solution of one of them. If this assumption is accepted, then it would follow that a major change in the height or shape of this absorption band would probably indicate a change in the fundamental character of the compound.

On this basis, then, 1,2-bis(α-furildioximo-*N*,*N*')nickel(II) must again be considered to be the least stable toward reaction with pyridine, since its principal absorption band suffered the greatest reduction in height, as a result of the presence of this solvent, of all the complexes studied. The next least stable, judging by the same standard, is the α-benzildioxime compound. The absorption spectra of the remaining 3 *vic*-dioxime complexes were so little affected by pyridine that no one of them can be said to be more or less stable than the other two. As a group, they are evidently more stable toward pyridine than either of the other complex compounds named above.

Russell, Cooper and Vosburgh (40) and Roberts and Field (38) have demonstrated correlations between absorption spectra and stabilities of several complexes of nickel, copper and cobalt in aqueous solution. In these complexes, the wavelength of maximum absorption decreased as the stability increased; apparently the absorption bands studied could, in these cases, be taken as characteristic of the metal-ligand bonds.

Comparison of the absorption spectra measured for solutions of the vic-dioxime complexes of nickel(II) in chloroform and o-dichlorobenzene gives rise to the speculation that a similar correlation may be made here. If the double-peaked principal absorption band is characteristic of the diamagnetic square coplanar nature of the complexes and therefore probably characteristic also of the bonds within the coordination sphere of the nickel atom, then perhaps the wavelength region at which the band occurs may be indicative of the strength of those bonds.

The mean wavelength of the principal absorption band (the average of the wavelengths corresponding to the two peaks) was calculated for each of the 5 nickel complexes considered here. They are as follows, in order of decreasing wavelength: α-furildioxime complex, 413 mμ.; α-benzildioxime complex, 384 mμ.; 1,2-cyclohexanedionedioxime complex, 362 mμ.; 1,2-cycloheptanedionedioxime complex, 354 mμ.; 2,3-butanedionedioxime complex, 351 mμ.

The fact that the order in which the compounds are listed here is the same as that found for their stabilities against the reaction with pyridine makes this correlation more plausible. If the correlation is sound and if the magnitude of the separation of the mean wavelengths of the various complexes has any bearing on their relative stabilities, then the bonds within the α-furildioxime complex must be the weakest and those of the α-benzildioxime complex somewhat stronger. The mean wavelengths for the principal bands of the other 3 complexes are quite closely bunched, so that there is probably little distinction to be made between the strengths of the bonds in these compounds.

No such nicely ordered inferences as those presented above can be drawn from the studies of solutions of nickel(II) vic-dioxime complexes where n-butylamine was employed as the reagent or reactive solvent. The magnetic evidence indicates that 1,2-bis(α-furildioximo-N,N')nickel(II) reacts with or is affected in some way by this solvent to a considerable extent, and that 1,2-bis(1,2-cycloheptanedionedioximo-N,N')nickel(II) probably enters into a similar reaction to a lesser degree or perhaps only more slowly.

In view of the effects observed in the pyridine solutions, it was not surprising to learn that the absorption spectra of the α-furildioxime and α-benzildioxime complexes exhibited radical changes when n-butylamine was added in excess to their respective solutions. It was also not unexpected when the absorption spectra of solutions of the 1,2-cyclohexanedionedioxime complex were but little affected by the presence of this amine. The slight change in the spectrum of the 1,2-cycloheptanedionedioxime compound in solutions containing n-butylamine was not to be predicted, but it was to be regarded as significant since it could be correlated with magnetic data.

The complete disappearance of the "nickel band" from the absorption spectrum of 2,3-butanedionedioxime in solutions where n-butylamine was added came, therefore, entirely without warning. This behavior was completely out of line with previously observed evidences of relative stabilities among the vic-dioxime complexes, and cannot at present be easily explained.

The effect of n-butylamine on the absorption spectra of solutions of the various vic-dioxime complexes can be correlated with one other item of their behavior, but the true relation, if any, between these phenomena is unknown at the present time. Thus, it has been reported that quantitative precipitation of nickel(II) with α-furildioxime (36), α-benzildioxime (10, p. 48), and 2,3-butanedionedioxime (10, p. 30) in aqueous media occurs only in neutral or slightly alkaline solutions, whereas the same type of precipitation can be made with 1,2-cycloheptanedionedioxime (49) or 1,2-cyclohexanedionedioxime (50) in distinctly acid solutions, or down to a pH of about 3. The nickel(II) complexes formed by the first 3 of the reagents named are those which are apparently most greatly affected by n-butylamine. The fact that this amine is a much stronger base than pyridine may be of some consequence in the latter phenomenon.

2. Nature of the reactions

A number of speculations may be made as to the manner in which pyridine or n-butylamine reacts with 1,2-bis(α-furildioximo-N,N')nickel(II). One of the first that comes to mind is that in which 2 molecules of the solvent are added to the square complex, forming a paramagnetic octahedral structure:

$$Ni(DH)_2 + 2\ R_3N \rightleftharpoons Ni(DH)_2(R_3N)_2$$

The symbol DH_2 is more or less universally used to represent a vic-dioxime; DH^- then indicates the anion of the reagent and is so used here. This equilibrium is the same as that suggested by Willis and Mellor for the reaction between 1,2-bis(1,2-propanedionedioximo-N,N')nickel(II) and pyridine (54).

The infrared absorption studies by Voter, et al. (51) on the nickel and palladium derivatives of the vic-dioximes have demonstrated the absence of absorption bands which may be ascribed to hydroxyl groups; they suggested, by way of explanation, that this effect was due to the symmetry of the O··H··O bonding in the diamagnetic square complexes. The same authors have also shown (52) that when these compounds are dissolved in pyridine, an absorption band appears at a wavelength at which bands due either to O-H or N-H bonding usually occur.

In view of the latter observation, it is not unreasonable to suppose that the presence of the solvent molecules, in the product of the reaction postulated above, is sufficient to destroy the symmetry of the O··H··O bonding. If the disturbance were great enough, the hydrogen bond might in effect be broken. Since the hydrogen of an oxime hydroxyl group is quite active, it is possible that, with the hydrogen bond broken, the basic character of the solvent would cause the removal of this hydrogen. This process could take place simultaneously with the reaction suggested above, or subsequent to it.

$$\mathrm{Ni(DH)_2 + 3\ R_3N \rightleftharpoons NiD(DH)(R_3N)_2^- + R_3NH^+}$$

$$\mathrm{Ni(DH)_2 + 2\ R_3N \rightleftharpoons Ni(DH)_2(R_3N)_2}$$

$$\mathrm{Ni(DH)_2(R_3N)_2 + R_3N \rightleftharpoons NiD(DH)(R_3N)_2^- + R_3NH^+}$$

A second possibility for the manner in which n-butylamine or pyridine might cause a change in the magnetic character and the absorption spectrum of 1,2-bis(α-furildioximo-N,N')nickel(II) is that some nebulous "solvent effect" is of sufficient influence to effect a simple conversion from the square configuration to a tetrahedral form.

$$\mathrm{Ni(DH)_2(square\ planar) \rightleftharpoons Ni(DH)_2(tetrahedral)}$$

With the molecule thus distorted, the same hydrogen-bond-breaking and ionization processes as those mentioned above could presumably occur, again either simultaneously or subsequently. The "solvent effect" theory was proposed by Willis and Mellor (54), but for cases specifically not involving pyridine. It was also suggested by French, Magee and Sheffield (17).

A third behavior which may be postulated is that of a simple competition between solvent molecules and the <u>vic</u>-dioxime groups for the coordination positions about the nickel atom. No decision can definitely be made as to

$$\mathrm{Ni(DH)_2 + 6\ R_3N \rightleftharpoons Ni(R_3N)_6^{++} + 2\ DH^-}$$

whether the product of this reaction would be tetrahedral (4-coordinate) or octahedral (6-coordinate). The tendency of nickel to form octahedral complexes with pyridine, ammonia and other reagents in aqueous solution, however, points toward the sixfold coordination (40).

The reaction type last presented appears to be the least probable of the three suggested here. This sort of equilibrium was considered by Willis and Mellor (54), but dismissed on the grounds that the inherent stabilities of covalent nickel complexes are too high and those of octahedral complexes too low to permit this kind of competition to take place to any great extent. This argument is reinforced by the fact that the simple nickel-pyridine and nickel-n-butylamine complex compounds are not stable enough to exist in the absence of excess solvent. To be allied with this, also, is the inability of n-butylamine to keep nickel from precipitating as the hydroxide in aqueous solutions. Ammonia, of course, accomplishes this task quite nicely.

No very strong arguments can be quoted either in support of or against the second of the reaction types proposed above. The tendencies of pyridine and n-butylamine to coordinate with nickel, however, make the proposal implausible in that it is hard to believe that such a conversion could take place, in the presence of these molecules, without the occurrence of some more direct interaction or coordination.

Lacking more complete evidence on the nature of this reaction, the process first postulated above is to be regarded as the most acceptable of those presented here. The objections which were raised in connection with the other two possibilities are satisfied and, in addition, this type of behavior is believed to offer a plausible explanation for some of the experimental observations.

The conductivity measurements on some of the pyridine and n-butylamine solutions of the α-furildioxime complex indicate that some ionization takes place in the reactions. When the magnitudes of these observations are compared to the specific conductances obtained when perchloric acid was dissolved in these two solvents, however, the fact is revealed that probably a good deal less ionization occurs in the reaction with pyridine than in that with n-butylamine. Since in freshly prepared solutions the amounts of conversion were roughly the same for the two cases, the conclusion to be drawn is that the ionization process is secondary to the addition reaction. The greater basicity of n-butylamine, compared to pyridine, would explain the difference in amounts of ionization.

The possibilities for ionization are indicated in all three of the proposed processes, but only in the first and second of these is the production of ions a secondary reaction. The first process is to be preferred over the second because of the utilization of the solvent molecules in the coordination sphere of the nickel atom.

All three of the processes would likewise explain the reappearance of the infrared absorption band at a position indicative of O-H or N-H bonding. If a choice could be made between these two types of bonding, through further infrared absorption studies, perhaps, this fact would be of great assistance in making a decision on the nature of the reaction.

It is not yet by any means a certainty that the reaction of the α-furildioxime complex with pyridine is entirely similar to that with n-butylamine. From Table 4, for example, it is to be noted that in pyridine, greater concentrations of the complex lead to larger amounts of conversion, whereas in n-butylamine, the reverse of this effect is indicated.

Another difference between the reactions taking place in the two solvents is in the apparent influence of some component of the atmosphere on the conversion of the solute. Though of considerable magnitude in the n-butylamine solutions, this effect is exhibited to a far lesser degree in the pyridine solutions, if indeed it is present at all. The fact that the complex shows a satisfactorily steady magnetic state when isolated from the atmosphere, either in pyridine or n-butylamine, indicates that perhaps the effect of the atmosphere is secondary, and that the principal reactions are similar.

It is evident that no unequivocal decision can at present be made regarding the nature of the reactions between 1,2-bis(α-furildioximo-N,N')nickel(II) and the two solvents pyridine and n-butylamine. The arguments and experimental observations presented here have not been particularly illuminating in this connection. As a result of this evidence, however, the addition of two solvent molecules to the original square complex, possibly followed by more or less ionization, now appears to be the most probable formulation.

V. SUMMARY

In response to the feeling that magnetic susceptibility measurements would be of considerable value in the studies of the fundamental nature of complex compounds of the elements of the first transition series, an apparatus suitable for obtaining these data was constructed. The Gouy method of susceptibility determination was employed as the basis for the design and operation of the equipment. The assembly of the various components was made as flexible as possible, so as to permit a maximum of versatility in future use of the apparatus. An electromagnet, its power supply, a semimicro balance and a current-measuring device comprise the major units of the equipment. A calibration method was devised which is believed to allow measurements on liquid samples to be made with a precision of 0.1 per cent or better and with an accuracy of the same order of magnitude.

The magnetic susceptibilities of the water-insoluble nickel(II) complexes of α-benzildioxime, 2,3-butanedionedioxime, 1,2-cycloheptanedionedioxime, 1,2-cyclohexanedionedioxime, and α-furildioxime were measured. All of these compounds, which were transformed into more easily manipulated forms by recrystallization from organic solvents, were found to be diamagnetic. The values obtained for two of the complexes corresponded fairly well to susceptibility figures previously reported in the literature for the same compounds. The conclusion drawn from the results of these measurements was that the five compounds are all to be considered as normal square coplanar complexes of nickel(II), at least in the crystalline state.

Magnetic and allied spectrophotometric studies were carried out on solutions of the same five nickel(II) complexes, in both reactive and nonreactive organic solvents. These studies established definitely the fact that 1,2-bis(α-furildioximo-N,N')nickel(II) is the least stable of these compounds toward reaction with pyridine and n-butylamine to form an unknown paramagnetic complex. The results of the observations on the pyridine and n-butylamine solutions of the other four compounds were not entirely in agreement, but they indicated that 1,2-bis(α-benzildioximo-N,N')nickel(II) is the next least stable. Some tentative suggestions were made as to the nature of the reactions of 1,2-bis(α-furildioximo-N,N')nickel(II) with pyridine and n-butylamine, on the basis of magnetic and conductance measurements carried out on solutions of this complex in the two solvents. The addition of two molecules of the solvent to the original square complex to form an octahedral paramagnetic configuration was regarded as the most probable course for these reactions to take.

VI. SUGGESTIONS FOR FUTURE WORK

Determinations of the magnetic susceptibilities of diamagnetic samples with the apparatus described previously have not been as precise as it is believed that they could be. One factor which may have been responsible for this is the assumption of a constant value for the susceptibility of air. This quantity should vary as atmospheric conditions change, and these variations may be great enough to influence the calculations in which the susceptibility of air is used, in the case of diamagnetic materials. It is recommended that an investigation of the variation of the susceptibility of some diamagnetic standard, such as water, with changes in atmospheric pressure and room temperature be undertaken. If this effect should be found to be serious and not easily offset by using varying values for the susceptibility of air in the calculations, the possibility of substituting nitrogen or some other diamagnetic gas for the air surrounding the sample tube should be explored.

A structural change in the apparatus which would increase its flexibility somewhat is the alteration of the position of the electromagnet. This unit now rests on the bottom of the yoke, but if it were mounted so as to lie on its side, considerably more room would be available below the poles.

This additional space would not only facilitate the dismounting of the jacketed sample chamber for cleaning, but would also make somewhat easier the construction of other temperature control units which may be needed in the future.

The chemical problems left unanswered by this investigation are numerous. One effect that should certainly be examined more closely is the influence of air or oxygen on the reaction of 1,2-bis(α-furildioximo-N,N')nickel(II) with n-butylamine. If the nature of the effect can be established, then perhaps a repetition of some of the measurements reported here will permit the drawing of more valid and complete conclusions concerning the reaction of the nickel complex with the amine.

It is possible that more satisfactory magnetic studies on the reaction of 1,2-bis(1,2-cycloheptanedionedioximo-N,N')nickel(II) with n-butylamine can be carried out by adding various amounts of the amine to chloroform solutions of the nickel complex and measuring the susceptibilities of the resultant mixtures. The greater solubility of the complex in chloroform compared to its solubility in n-butylamine points toward this move.

Once the effect of air or oxygen on these reactions is determined, then perhaps a more thorough spectrophotometric investigation of the reaction of 1,2-bis(α-furildioximo-N,N')nickel(II) with n-butylamine can be made. This type of study might establish the number of amine molecules taking part in the reaction and the order of magnitude of the stability constant.

Limited spectrophotometric observations have indicated that dioxane also causes considerable fading of chloroform solutions of some of the nickel(II) complexes. Magnetic and additional spectrophotometric studies might be expected to yield interesting information on this phenomenon.

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