

I.

HINDERED ROTATION IN
SOLID HEXAMMINECOBALT(III) CHLORIDE

II.

AUTOMATIC COULOMETRIC TITRATIONS
INVOLVING AN AMPEROMETRIC END POINT

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Henry Leopold Richter, Jr.

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ABSTRACT

I. A study has been made of the unusual behavior that solid hexamminecobalt(III) chloride exhibits when examined by the technique of nuclear magnetic resonance absorption. From the examples of substances exhibiting similar behavior to this one, the conclusion is reached that some sort of internal motion is taking place within the solid. On the basis of the structure of the hexamminecobalt(III) ion, and from information gathered on related ions, it is postulated that the motion involved is the rotation of the whole complex ion in the crystal lattice. From a study of the nuclear magnetic resonance absorption line width for the protons in the complex ion as a function of temperature, the motion is described in terms of a rate process.

The general theory of nuclear magnetic resonance is discussed, and in particular the application of this technique to the study of rate processes. The design and construction of a nuclear magnetic resonance spectrograph are described.

II. An instrument has been developed for automatic control of coulometric titrations employing the dual indicator electrode amperometric end point. The instrument is capable of detecting the end of the titration and stopping the generation, freeing the analyst of this task. The titration is stopped at a pre-set indicator current, either as a "dead stop" end point or as a preliminary operation to determining the exact end point by extrapolation of the post end point current to zero. The operation of the instrument on three different types of coulometric titrations is described.

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I. INTRODUCTION

An important discovery made in physics in the period after the close of World War II was that of nuclear magnetic resonance. Unsuccessful attempts were made to detect nuclear magnetic resonance absorption by Gorter in the 1930's.¹ In early 1946 the phenomenon was observed in two independent experiments by Felix Bloch and co-workers at Stanford University and by E. M. Purcell and associates at Harvard University. Although these two experiments were based on the same physical process, the two experimental arrangements were quite different. Bloch termed the phenomenon "nuclear induction", probably because in his apparatus the sample being studied was placed in a pair of crossed coils, and the resonating nuclei in the sample in effect coupled radio frequency energy from one coil to the other.² Purcell applied the name "nuclear magnetic resonance absorption" to describe his experiment. In his method the substance being studied is placed in a single coil and the energy absorbed from the radio frequency field of the coil is measured.³ The latter method is the one that was employed in the work to be described here. The Nobel Prize in physics for 1952 was awarded jointly to Bloch and Purcell for this work.

The field of nuclear magnetic resonance grew rapidly after 1946 as applications were found in physics and in chemistry. At the present time about one third of the groups doing nuclear magnetic resonance spectroscopy are doing what would be called chemical studies. The person who was most responsible for

finding and developing the applications of this method to the study of those properties of matter that come into the chemists' domain was Herbert Gutowsky, now at the University of Illinois.

Uses to which physicists have put nuclear magnetic resonance include studies of the nucleus itself (spin, magnetic moment and electric quadrupole moment). The techniques of nuclear magnetic resonance have been used by chemists for a variety of different types of investigations. One such use is that of an analytical tool, either for the identification of various isotopes or for the identification of the functional group in which the nucleus is located. Studies of molecular structure have been made, as well as of the structure of crystalline materials. Other uses are the study of phase transitions in solids and of internal motions in solids.

An important application of nuclear magnetic resonance is the measurement (and therefore, control) of magnetic fields with a high degree of accuracy. This in itself is a considerable advance in obtaining the accuracy of measurement which science now requires.

Another means of studying magnetic properties of the nucleus is the molecular beam magnetic resonance experiment developed by Rabi. This method is still in widespread use and is in no sense competitive to the technique of nuclear magnetic resonance, the two approaches being complementary. The molecular beam method of course excludes study of materials in liquid or solid states.

II. GENERAL THEORY OF NUCLEAR MAGNETIC RESONANCE

This section will be concerned with the general features and interpretation of nuclear magnetic resonance absorption. There are several small order effects, of chemical origin, that would modify the discussion in a minor way. These will not be treated in any detail except where they have direct bearing on the interpretation of the experiment performed. Since the phenomenon dealt with here can only be described properly in terms of quantum mechanics, most of the discussion will use that approach. Occasionally a classical analogy will be presented to aid in an explanation. The apparatus used in this investigation was of the absorption (Purcell) type and the theory will be presented from this standpoint. There are several excellent introductory papers that present the whole subject of nuclear magnetic resonance and its potentialities to the reader who is without previous background in the subject.^{4, 5, 6}

1. Properties of the Nucleus

An atomic nucleus has a number of characteristic properties. Many of these are quite familiar ones, such as mass, charge, and spin angular momentum. Other properties can arise because of the constitution and behavior of the nucleus. The combination of charge and angular momentum can be considered as the circulation of an electric current. A magnetic dipole moment is produced by such a circulation. Many nuclei also possess an electrical quadrupole moment, i. e., have electrical charge distributions that depart from spherical symmetry in a manner appropriate to an electrical quadrupole moment.

The existence of nuclear spin and nuclear magnetic moment was postulated by Pauli in 1924 to explain hyperfine structure in atomic spectra. Earlier it was believed that each component of the hyperfine pattern was emitted by a different isotope. This was clearly not the explanation, because it was found by means of the mass spectrograph that some elements exhibiting hyperfine structure consist of only one isotope. True hyperfine structure has been found to be due to a coupling between the angular momentum of the nucleus and the resultant angular momentum of the electrons.

2. Nuclear Spin and Magnetic Moment

It is required theoretically and found experimentally that nuclear spins are quantized. The spin angular momentum of a nucleus can be represented by a quantum mechanical angular momentum vector \vec{a} . It is convenient to use a dimensionless quantity \bar{I} to measure the angular momentum in units of \hbar , with \bar{I} defined by

$$\vec{a} = \hbar \bar{I} \qquad \hbar = h/2 \qquad (1)$$

The spin quantum number I of the nucleus is defined as the maximum possible component of \bar{I} in any given direction. The nuclear spin quantum number I is half-integral if the mass number of the isotope is odd and integral if the mass number is even. On somewhat obscure grounds it is believed that all nuclei composed of an even number of protons and an even number of neutrons have zero spin. This has not yet been disproved by experiment.

For this discussion the nuclear spin quantum number I will be considered in all cases as a constant of motion, since the energies involved in the processes to be described are never large enough to produce transitions to an excited state. The transitions that occur are reorientations in space of the magnetic moment vector.

The nuclear spin is commonly described in terms of its components I_x , I_y , and I_z . The non-vanishing matrix elements of the three components of the nuclear spin operator transformed to the representation in which the z component of the operator is diagonalized are⁷

$$\begin{aligned} \langle m | I_x + iI_y | m-1 \rangle &= \{(I+m)(I-m+1)\}^{\frac{1}{2}} \\ \langle m | I_x - iI_y | m+1 \rangle &= \{(I-m)(I+m+1)\}^{\frac{1}{2}} \\ \langle m | I_z | m \rangle &= m \end{aligned} \quad (2)$$

The usual commutation rules apply to the nuclear spin operators

$$\begin{aligned} [I_x, I_y] &= i\hbar I_z \\ [I_y, I_z] &= i\hbar I_x \\ [I_z, I_x] &= i\hbar I_y \end{aligned} \quad (3)$$

where $\vec{I} \cdot \vec{I} = I_x^2 + I_y^2 + I_z^2$

A nucleus has a magnetic moment vector $\vec{\mu}_I$ which can be represented as

$$\vec{\mu}_I = \gamma_I \hbar \vec{I} = g_I \mu_n \vec{I} \quad (4)$$

where γ_I and g_I are defined by the above equations and are called the nuclear magnetogyric ratio and the nuclear g factor, respectively.

μ_n is the nuclear magneton* defined as $e\hbar/2Mc$, where M is the proton mass; μ_n has the numerical value $5.04929 \cdot 10^{-24}$ erg gauss $^{-1}$. The quantity that measures the magnitude of $\bar{\mu}_I$ and is called the nuclear magnetic moment, μ_I , is

$$\mu_I = \gamma_I \hbar I \quad (5)$$

Values of the above quantities have been tabulated by Ramsey.⁸

The nuclear g factor introduced above is similar in significance to the Landé factor associated with electrons, but must not be confused with it. The Landé factor may be calculated directly from atomic theory, while present nuclear theory only puts limits on the nuclear g factor. Nuclear g factors can be measured quite precisely and present a good test for nuclear theories. The so-called Schmidt diagrams set limits for nuclear magnetic moments, and hence also for the nuclear g factor.⁹

In the presence of a magnetic field the magnetic moment vector can assume certain directions in space and the projection of the magnetic moment vector in any given direction (say, in the direction defined by the magnetic field) can have certain discrete values. The multiplicity of allowed values is determined by the spin quantum number of the nucleus, I , there being $2I+1$ values possible. It is convenient to express the magnitude of

*Not to be confused with the Bohr magneton. There is considerable confusion in notation in the literature of this subject. The Bohr magneton is generally designated as μ_β or β .

the projections in terms of a magnetic quantum number which is defined by

$$I_z = m \quad (m = I, I-1, \dots, -I) \quad (6)$$

3. The Free Spin Case

The interaction of the magnetic moment of an isolated spin with a magnetic field \overline{H}_0 gives rise to a potential energy term,

$$W_0 = - \mathbf{I} \cdot \overline{H}_0 \quad (7)$$

Different orientations of the magnetic moment vector are possible, and hence different energy levels can appear. The energy of each level is expressed as the vector dot product of the angular momentum vector and the magnetic field vector. Since the projection of the angular momentum vector on the magnetic field direction is quantized, and is characterized by the magnetic quantum number, the energy for each level is the product of the magnetic field strength and the projection of the magnetic moment vector on the field direction:

$$W_i = - I h m_i H_0 \quad (8)$$

Since $2I+1$ orientations of the magnetic moment vector are possible, $2I+1$ energy levels can exist.

These energy levels have been called nuclear Zeeman levels, from analogy with the action of a magnetic field on the energy levels that give rise to atomic spectra (the Zeeman effect). In the absence of a magnetic field only one nuclear energy level exists, which is $2I+1$ -fold degenerate. In the presence of

a magnetic field, transitions can take place between the nuclear energy levels, governed by the selection rule

$$\Delta m = \pm 1 \quad (9)$$

The $2I+1$ energy levels are equally spaced for the case under consideration. The energy difference between levels for which transitions are allowed by equation 9 is

$$\begin{aligned} \Delta E &= W_j - W_i = \gamma_I \hbar m_j H_0 - \gamma_I \hbar m_i H_0 \\ &= \gamma_I \hbar H_0 (m_j - m_i) = \gamma_I \hbar H_0 \end{aligned} \quad (10)$$

The Bohr frequency condition can now be invoked to relate the energy difference of the states between which a transition could take place to the frequency of a quantum of electromagnetic radiation:

$$\Delta E = h \nu \quad (11)$$

Now, combining equations 4, 10 and 11, we obtain

$$\begin{aligned} \Delta E &= h \nu_0 = \gamma_I \hbar H_0 \\ \nu_0 &= \gamma_I H_0 / 2\pi = \frac{g_i \mu_n H_0}{h} \end{aligned}$$

This equation gives the frequency of the radiation which is emitted if the nucleus decreases in energy or which is absorbed if the nucleus gains in energy. To give an idea of the magnitudes of quantities involved, the frequency for protons in a conveniently obtained laboratory magnetic field strength, 5000 gauss, is $21.29 \cdot 10^6$ cycles per second. This is a radiofrequency in the short-wave region.

If we were talking in terms of classical physics, this is the point at which the concept of resonance would be introduced. The relation given by equation 12 can be derived in a classical manner.⁵ A system of similar free spins with magnetogyric ratio γ_I can be imagined to be in a magnetic field H_0 . These spins can be irradiated by an electromagnetic field of frequency ν . No interaction between the spins and the electromagnetic field will take place unless $\nu = \nu_0$, corresponding to the condition set by the magnetic field H_0 of equation 12. This situation implies a condition of resonance. Sometimes the spin system is described as precessing at the Larmor frequency, ν_0 , about the magnetic field direction.

Most of the discussion to follow will be restricted to the case of nuclei of spin $\frac{1}{2}$. This is by far the simplest case to treat theoretically and to observe experimentally. The nuclear resonance work to be described here involves resonance of hydrogen nuclei, which have spin $\frac{1}{2}$.

4. Interaction With Radiation; Relaxation

For a system of free spins, the probability for a nucleus making a transition from one energy state to another is infinitesimal in the absence of a radiation field of the proper energy. The only spontaneous transitions that are possible are those to a lower state. The mean life of the upper state for protons in a magnetic field of ten kilogauss is of the order of 10^{19} years.

In the presence of radiation of the proper frequency this transition probability increases greatly. The strength of density of the electromagnetic radiation is measured by the maximum

amplitude of the magnetic component of the field, H_1 , and is described as a function $\rho(\nu)d\nu$ of the frequency. The transition probability becomes proportional to the number of quanta present when the frequency of the field is in the range $d\nu$ near ν_0 , that is, it is proportional to $\rho(\nu_0)d\nu$. In fact, the quantum mechanical transition probability obtained by perturbation theory is⁵

$$P_{(m \rightarrow m')} = \frac{2\pi}{3\hbar^2} g^2 \mu_n^2 \left| \Pi_{mm'} \right|^2 \rho(\nu_0) \quad (13)$$

The quantity $\left| \Pi_{mm'} \right|$, the matrix element of the nuclear spin, is usually of order unity when equation 9 is satisfied. Under the influence of radiation both upward and downward transitions take place. It has been shown by Rabi¹⁰ (and it seems intuitively plausible) that the transition probabilities for upward and downward transitions are equal:

$$P_{m \rightarrow m'} = P_{m' \rightarrow m} \quad (14)$$

The resonance phenomenon is detected as an absorption of energy from the radiation field, and for there to be a net absorption of energy there must be more spins in the lower state than in the upper state. For the case of spin one-half, there are two possible energy levels if a magnetic field is present, designated as spin parallel (lower) and spin antiparallel (upper) to the field. If there were equal populations for the states there would be no net absorption, because on the average there would be as many upward as downward transitions and all absorption would be cancelled by stimulated emission. The number of spins making an upward transition (absorption) is the number of spins in

the lower state, N_+ , multiplied by the upward transition probability, P_+ , namely, $N_+ P_+$. Conversely, the number of downward transitions is $N_- P_-$. If the populations were equal, the relation $N_+ = N_-$ would hold, and from equation 14, the numbers of transitions would be equal:

$$N_+ P_+ = N_- P_- \quad (15)$$

However, this is not an equilibrium situation unless the two states have the same energy. The equilibrium populations of the two states are governed by the Boltzmann thermal equilibrium equation,

$$\frac{N_+}{N_-} = \exp \left(\frac{W_- - W_+}{kT} \right) \quad (16)$$

where the W 's are the energy of the states, k is the Boltzmann factor and T is the absolute temperature of the environment. When one considers the numerical values of the variables, it is clear that $W_- - W_+ \ll kT$ and that an approximation to equation 14 is justified. For the case of protons in a magnetic field of five kilogauss, at room temperature, we obtain, on substituting equations 4 and 7 into 14, the equation

$$\frac{N_+}{N_-} = 1 + \frac{W_- - W_+}{kT} = 1 + \frac{g \mu_n H_o}{kT} = 1 + 3.5 \cdot 10^{-6} \quad (17)$$

The detection of resonance rests on the slightly larger population of the lower energy state. In the next section the population difference for protons in the earth's magnetic field is brought into the discussion. There, the ratio of the populations of the two states is about $1 + 1 \cdot 10^{-10}$. From the arguments presented

above, we see that the populations of the two states in the presence of a radiation field would soon equalize and therefore absorption of energy would cease. This usually does not happen in the actual case (although it may) because in matter a free spin never exists and a process called relaxation provides a mechanism for a spin to move from an upper state to a lower state without emitting a photon as such. The relaxation process is generally an interaction between the spin and the environment and results in a transfer of the excess energy of the spin to the lattice, where it appears as thermal energy.

From equation 16 there results the possibility of defining a "spin temperature" based on the populations of the two levels. If the relaxation process is sufficiently rapid the spin temperature remains close to the temperature of the environment, even though energy is being absorbed from the radiation field. A novel experiment of Purcell and Pound has produced a system whereby they have exhibited a situation that can be discussed in terms of "negative spin temperatures".¹¹ Some of these ideas will be encountered again when the width of the resonance line is discussed in a later section.

5. Relaxation Mechanisms

There are several relaxation mechanisms; the most common one was already mentioned in the preceding section. The speed with which the system comes to equilibrium (the relaxation time) can be described in a characteristic way, using the following case as a typical example. Consider a group of nuclei first in the earth's weak magnetic field, and then in a strong magnetic field. Because

of the earth's field, the degeneracy of the nuclear ground state is lifted and, for $I = \frac{1}{2}$, two Zeeman levels produced. However, the energy difference between the levels is small, and from equation 17 and subsequent discussion it is a close approximation to say the two levels are equally populated. These nuclei are then subjected to a strong magnetic field, and the question is asked, how much time elapses until the new populations of the two levels are established? Considering the populations of the states individually, the rate at which nuclei change energy states is described by a first-order rate equation. Considering both populations, the situation is completely analogous to a chemical reaction approaching equilibrium. If n represents the excess population of the lower state, n_0 the equilibrium value of the excess population and P the quantum mechanical transition probability (due to the relaxation process), the instantaneous rate at which equilibrium is approached is

$$\frac{dn}{dt} = 2P(n_0 - n) \quad (18)$$

The factor 2 appears because each transition changes the excess number $n = N_+ - N_-$ by two. If equation 18 is integrated, the familiar first order exponential approach to equilibrium is obtained:

$$n = n_0 \left[1 - \exp(-2Pt) \right] \quad (19)$$

The equilibrium excess number of spins in the lower state is established in a fashion analogous to the charging of a capacitor of time constant $1/2P$. A characteristic time

$$T_1 = 1/2P \quad (20)$$

is called the spin-lattice relaxation time or thermal relaxation time. Thermal relaxation times thus far measured range from 10^{-4} seconds or less in solutions containing paramagnetic ions to several hours for very pure ice crystals at liquid nitrogen temperatures. The value of T_1 for the protons in pure water at room temperature has been measured to be 2.33 seconds.

The mechanism that is commonly accepted to describe the spin-lattice relaxation process is the following, which is a qualitative review of the detailed theory proposed by Bloembergen.¹² The only kinds of interactions in which the nuclear magnetic moment can participate are those with magnetic fields oscillating at the proper frequency. The question then arises as to what kinds of oscillating magnetic fields are associated with a crystal lattice, or with the molecules in a liquid or gas. The lattice of a solid invariably contains many separated electric charges or electric dipoles. The vibrations that take place within molecules can produce transient dipole moments, even though these transient dipole moments cancel out if averaged with respect to time, leaving no net dipole moment. Lattice vibrations involving the moving of charges or ions in the lattice will produce time-varying dipole moments and hence time-varying electric fields. A varying electric field always has a varying magnetic field associated with it.

Lattice and molecular vibrations are not to be described as simple harmonic motions, but contain components at many frequencies. A convenient means of describing the vibrations and hence the spectrum of the electromagnetic fields caused by the vibrations is by a Fourier series, which gives the amplitude

of each frequency contained in the field. Undoubtedly some of the vibrations have components near the Larmor frequency ν_0 and are able to cause transitions between the nuclear states. The same type of argument can be applied to liquids and gases where the particles are in rapid motion. If the lattice or liquid contains paramagnetic substances, the magnetic fields due to these will be large and hence will have larger components at the Larmor frequency. The larger fields will cause greater transition probabilities and the relaxation time will be reduced correspondingly.

Another type of relaxation mechanism is the spin-spin relaxation process, designated by its characteristic time constant T_2 . This will be treated in a later section, and arises from interaction between the nuclear spins themselves.

6. How Resonance is Observed

The apparatus used for observing nuclear magnetic resonance absorption will be considered in detail in the section on the spectrograph itself. The substance containing the nuclei under study is placed in a coil located in the gap of a magnet. The inductance of the coil, L , is proportional to the nuclear permeability, which in turn depends on the nuclear susceptibility, χ :

$$L = L_0 (1 - 4\pi\chi) \quad (21)$$

The coil is part of a tank circuit that forms either one arm of a radio frequency bridge or is actually the tank circuit of an oscillator.

If the bridge system is used, two modes of observation

are possible. The nuclear system when at resonance with the radio frequency field of the tank circuit can produce either an absorption or a dispersion signal, depending on the way the bridge is balanced. In practice the bridge is never adjusted for complete cancellation, but an unbalance is left to allow a small output of radio frequency voltage. If the unbalance is due to an amplitude difference between the two arms of the bridge an absorption signal is observed, and if it is due to a phase difference between the two arms of the bridge a dispersion signal is observed. When the spin system is described in classical terms as a macroscopic magnetic moment vector precessing in the coil, the absorption is due to the imaginary portion of the complex nuclear susceptibility and the dispersion to the real part of the susceptibility.¹³ The observation of resonance depends on the change in the nuclear susceptibility when the resonance condition of equation 12 exists, where ν_0 represents the frequency of the field created by the currents in the coil and H_0 the magnetic field at the nucleus.

In this work, and in the field generally, only the absorption term is used. The absorption is actually observed by measuring the dissipative term associated with tank circuits. An equivalent circuit for the tank circuit is shown in Figure 1. Since nuclear

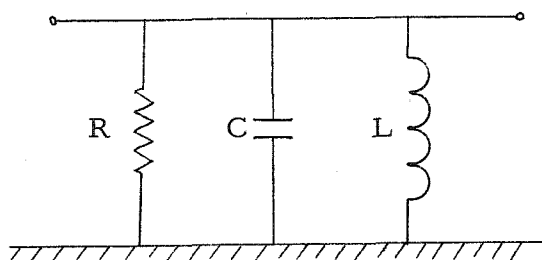


Figure 1. Equivalent tank circuit

susceptibilities are quite small and therefore the dissipative term is altered only slightly when resonance absorption takes place, certain techniques of electronic practice for the detection of small signals must be used. These will be discussed in a later section. The resistive element, R , of figure 1 represents the dissipative characteristics of the tank circuit elements, consisting of the inductance L and capacitance C . When the bridge system is used and the outputs of the two arms of the bridge nearly cancel each other, the resonance absorption, which is occurring only in one arm of the bridge, causes a change in the unbalance of the bridge and therefore a change in the output voltage. As was mentioned, the signal due to nuclear resonance is small and a severe stability requirement on the bridge components must be imposed in order that false signals are not generated by the bridge itself.

A similar situation is used for detection of the nuclear resonance when the tank circuit containing the sample is used as the feedback loop of an oscillator. The oscillator is adjusted so that it operates just on the border of oscillation. When this condition is established the negative resistance developed by the oscillator tube slightly more than balances the dissipative resistance of the tank circuit. Again the method employed is essentially that of balancing the dissipation normally present in the coil containing the sample against another resistance. In the case of the oscillator system the change in dissipation when the nuclear resonance condition exists is measured as a change in the operation of the oscillator.

7. Structure of the Resonance Line; Sources of Line Broadening

So far the only interaction between the nuclear magnetic moments and the surroundings that has been considered involves transient or oscillating magnetic fields. It is apparent from the form of equation 12, which specifies the resonance condition, that the resonance absorption line could be studied by using a constant monochromatic source of energy of frequency ν_0 and varying the magnetic field through the resonance value H_0 . However, either H_0 or ν_0 of equation 12 could be the independent variable and the magnetic field could be held constant and the frequency varied. The former method is the one in common use. When the nuclear magnetic resonance line is observed in real materials, it is neither infinitely sharp, as is implied by equation 12, nor, for a constant frequency experiment, is it centered on H_0 , where H_0 is the externally applied magnetic field. The constants in equation 12 are known quite precisely for a number of nuclei and therefore the second statement of the preceding sentence can be made with certainty.

The reason for the apparent failure of equation 12 is that we are now not being precise in using it. Equation 12 holds if the proper meaning is given to the symbols. In deriving equation 12 it was assumed that the magnetic field acting on the nucleus was just that of the externally applied magnetic field, but in actual matter two things can invalidate this assumption. The externally applied magnetic field can be modified by the shielding of the electron cloud surrounding the nucleus, causing the so-called chemical shifts observed in certain cases in nuclear resonance work. Steady magnetic fields may also be present in solids; they add vectorially

to the externally applied magnetic field. The chemical shifts are a small effect compared to the steady fields, and will not be considered further here. The field at a nucleus, H^* , is then the sum of the external field and the local fields, H_{loc}

$$H^* = H_0 - \sum H_{loc} \quad (22)$$

If the value of the local field is different from one nucleus to another the resonance frequency is different, and the line is spread over a spectrum corresponding to the variation of H_{loc} at the various nuclei. Another interaction that is not of a magnetic nature, but that can modify the nuclear energy level, is the interaction of nuclear quadrupole moments with the crystalline electric field. Since nuclei with spin $\frac{1}{2}$ do not possess quadrupole moments this influence will not be treated further.

The "natural" width of a resonance line is determined by the finite lifetime of the upper state through the uncertainty principle; it amounts to about 10^{-5} gauss. Line widths of resonance lines from liquid and gaseous substances begin to approach this value. The line structure is also affected by experimental conditions. In the discussion thus far it has been assumed that the externally applied magnetic field is constant and homogeneous over the sample of resonant nuclei. Any variation of H_0 over the sample will cause a similar variation in the resonance line.

The usual source of H_{loc} is the nuclear magnetic dipoles themselves. If we assume that only the static z components of these fields are of importance, an expression of the strength of the local field at nucleus i due to the others is

$$H_{loc} = \sum_j \mu_{zj} r_{ij}^{-3} (1 - 3 \cos^2 \theta_{ij}) \quad (23)$$

where θ_{ij} is the angle between \overline{H}_0 and the radius vector \overline{r}_{ij} connecting i and j . The field 1 Å away from and perpendicular to the magnetic vector of a proton is $\mu_p r^{-3} = 14.1$ gauss, which is a considerable contribution to line breadth.

It is easy to see how structure in the nuclear resonance line would arise by considering a simple example. Let us take as the example a perfect crystalline substance, in which the nuclei exist in pairs, one pair to a unit cell. It will be assumed that the distance between pairs is large compared to the distance between the two nuclei in a pair. Since the interaction between nuclei falls off as the inverse third power of the distance, the only significant interaction will be between the two nuclei of each pair. The crystal under consideration is such that each pair occupies the same position in the unit cell, and all internuclear vectors for the pairs are parallel. For this case it is further assumed that the two nuclei of the pair are different (but both have a nuclear spin of $\frac{1}{2}$) and that we are observing the resonance of one species, say type 1. Any structure that appears in the resonance line will be due to the influence of nucleus 2 on nucleus 1. The local magnetic field at nucleus 1 for this situation is

$$H_{loc} = \pm \mu_2 r_{12}^{-3} (1 - 3 \cos^2 \theta_{12}) \quad (24)$$

the choice of sign depending on the energy level spin 2 is occupying (or, classically, whether spin 2 is parallel or antiparallel to H_0). From equation 24 we see that two values of local field can exist. Suppose a nucleus of type 1 is considered for which the local field

is positive. To observe the resonance of this nucleus, the external field will have to be decreased by H_{loc} below the resonance field H^* for resonance to occur. For those nuclei whose local field is negative, resonance will occur when H_o is H_{loc} greater than H^* . The single resonance line expected for nucleus 1 has been split into two lines through the action of another nearby nuclear magnetic moment, each line being equidistant from H^* on either side as indicated by figure 2.

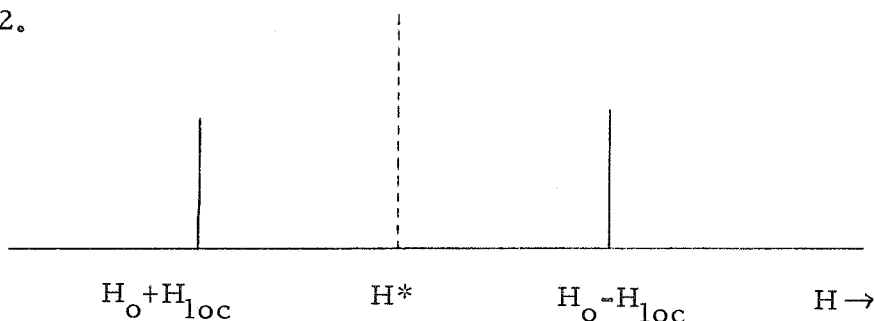


Figure 2. Spectrum for 2 spin system

This same analysis could be extended to include the effects of many nearby nuclei, but soon becomes quite complicated and useless because it is difficult to resolve close components of the absorption line. Unfortunately, the situation is never as simple as indicated by the example. The two lines shown in figure 2 as lines would be broadened considerably from the influence of the spins in the next unit cells. If the example had involved a powder sample instead of a single crystal, equation 24 would have had to be averaged over all possible orientations, and only one broad resonance line would have resulted, the edges of which would be set by the maximum value of H_{loc} given by equation 24.

Line broadening can also be caused by spin-spin interactions, as mentioned earlier. If similar nuclei are located close to each other in the solid an interaction can take place between two of them in different energy levels. Another term, a bit more descriptive, that is often applied to this process is mutual spin-spin flipping. The process is the passing of a photon between the one in the higher energy level to the one in the lower energy level. The net result is to leave the total energy of the spin system unchanged, and all that apparently happened was that two spins interchanged positions in the lattice. As mentioned earlier, this process is also characterized by a relaxation time, T_2 , which is related to the rate at which spins exchange positions in the lattice. Spin-spin interactions have no noticeable effect on the absorption line until T_2 becomes comparable to, or less than, T_1 . An influence on the line structure exists because if the relation of the lifetime of the upper state is represented by $\Delta\tau$, and the uncertainty in energy is ΔW , then, according to the Heisenberg uncertainty principle, we write

$$\Delta\tau \cdot \Delta W \sim \hbar \quad (25)$$

When a large number of spins is involved the uncertainty in energy can be looked at as a spread of energy about the expectation value of the energy. The effect of this is to impart a similar breadth to the absorption line.

One experimental situation that can broaden the absorption line is the application of sufficient radio frequency power (H_1) to saturate the spin system. When this occurs the transition probability due to the radio frequency field has become greater than that

due to the relaxation mechanism, and not only is the lifetime of the upper state again shortened, but also energy absorption from the radio frequency field is greatly diminished. The way that this is avoided in practice is to decrease the radio frequency power until further decrease has no noticeable effect on the line amplitude and structure. This technique is used to study the relaxation time and process.

The structure of the resonance line from solids is the feature of these spectra that is useful for chemical studies. By analysis of the structure of the resonance line studies have been made on molecular structure,¹⁴ crystal structure,¹⁵ phase transitions in solids,¹⁶ and hindered internal motions in solids.¹⁷

8. The Second Moment as a Measure of Line Width

The prediction of the spectrum for isolated pairs of nuclei is a simple matter; however, the addition of even one more nucleus to the situation adds a considerable complexity. The calculation of the theoretical spectrum for an actual physical situation is so tedious as to defy solution except for certain extremely symmetric configurations. Instead of making such calculations, Van Vleck formulated a theory of dipolar broadening of magnetic resonance lines in which the criterion of line width is developed from another viewpoint.¹⁸ A quantitative relation is established between the atomic configuration of the material under study and the line width expressed in terms of the so-called second moment of the distribution of the absorption line about its center. The second moment as defined by Van Vleck is the mean value of the square of the

frequency deviation from the center of the resonance, the average being taken over the shape function. The line shape, versus frequency, is taken to be a function $f(\nu)$ so normalized that

$$\int_{-\infty}^{\infty} f(\nu) d\nu = 1 \quad (26)$$

Then, with ν_0 the resonance center frequency, the second moment is

$$\langle (\Delta \nu)^2 \rangle_{av} = \int_{-\infty}^{\infty} (\nu - \nu_0)^2 f(\nu) d\nu \quad (27)$$

The relation derived by Van Vleck between the second moment expressed in gauss² (which is appropriate to the technique used in this work) and the structure of the material is

$$\begin{aligned} \langle (\Delta H)^2 \rangle_{av} = & \left(\frac{3}{2}\right) I(I+1) N_s^{-1} g^2 \mu_o^2 \sum_{j>k} (3 \cos^2 \theta_{jk} - 1)^2 r_{jk}^{-6} \\ & + \frac{\mu_o^2}{3 N_s} \sum_i \sum_f I_f(I_f+1) g_f^2 (3 \cos^2 \theta_{jf} - 1)^2 r_{jf}^{-6} \end{aligned} \quad (28)$$

$$\langle (\Delta \nu)^2 \rangle_{av} = g^2 \mu_o^2 h^2 \langle (\Delta H)^2 \rangle_{av}$$

The following list defines the symbols used in equation 28:

- | | |
|------------|--|
| g, I | Nuclear g-factor and spin for nucleus involved in the resonance |
| g_f, I_f | Nuclear g-factors and spins for other nuclear species in the sample |
| r_{st} | Length of the vector connecting nuclei s and t |
| N_s | Total number of nuclei having resonance which are present in the sub-group (molecule, ion or |

atomic complex) to which the broadening interactions are considered to be confined in computing

$$\langle (\Delta H)^2 \rangle_{av}$$

The second moment for a powder sample can be obtained from equation 28 by averaging over all orientations. Since the average value of $\cos^2 \theta$ over a sphere is $1/3$, we obtain

$$\begin{aligned} \langle (\Delta H)^2 \rangle_{av}^{powd} &= \frac{6}{5} I(I+1) N_s^{-1} g^2 \mu_o^2 \sum_{j>k} r_{jk}^{-6} \\ &+ \frac{4}{15} \mu_o^2 N_2^{-1} \sum_j \sum_f I_f(I_f+1) g_f^2 r_{jf}^{-6} \end{aligned} \quad (29)$$

The derivation of equation 27 is quantum mechanical and will not be reproduced here. One drawback to the second moment method is an experimental one. For most samples, and especially ones in powder form, the shape of the absorption line experimentally obtained is a bell-shaped curve of a gaussian nature. The extreme edges of such a curve make a considerable contribution to the width of the line when the second moment is used as a measure. This is the part of the line most difficult to resolve.

The main use of the second moment calculation is the testing of proposed structures for various substances. The dependence of the second moment on the structure as illustrated above suggests why nuclear magnetic resonance is a useful technique for studying the occurrence of phase transitions in solids. This measure of line width can be quite sensitive to changes in the molecular configuration within solids.

9. Effect of Internal Motion on Line Width

One of the reasons that the present research was undertaken is the sensitivity of the nuclear magnetic resonance line to certain motions in which nuclei might be involved. As was discussed in the preceding section, if the resonant nuclei occupy different lattice positions in the unit cell they experience different values of the local magnetic field and therefore resonate at slightly different frequencies. The spread of the absorption line indicates the spread of magnetic field over the resonant nuclei. Certain types of internal motions in the substance being studied that cause the resonant nuclei to change position in the lattice will cause the local fields adding to the main magnetic field to have a time dependence as far as these nuclei are concerned. The Larmor precession frequency of the moving nuclei varies in a manner similar to that of the magnetic field. Here it is assumed that the local fields, and hence variation in total field, are small compared to the total field, so that no difficulty as far as changing the populations of the levels is encountered. The resonance frequency observed is an average of the frequencies assumed by the nuclei during the time of measurement.

The time of measurement has to be defined carefully. The way in which this is usually done is to set a limit for the minimum time of observation. This is done by use of the uncertainty principle. In the previous discussion the uncertainty in energy of the nuclear upper energy level was related to the width of the absorption line. The sharper or narrower the absorption line, the smaller is the spread in energy that must be measured, and hence the time of observation required to measure precisely the difference

in energy increases. If the period of the motion is short compared to the time of measurement, the measurement indicates the average magnetic field experienced by the resonant nuclei, averaged over the period of observation. If, however, the motion is such that the nuclei whose resonance is being observed do not move through all possible lattice positions, but perhaps move only in a restricted portion of the unit cell (such as nuclei moving about an axis of rotation), then the width of the absorption line reflects the spread of the average field encountered by these nuclei. Considerable spread in the resonance line can remain when there is more than one group of such nuclei in each unit cell, the averaging process causing only a partial reduction in the line width.

An averaging process and a corresponding reduction in line width can be observed when experimental conditions are changed in such a manner that the rate or frequency of motion is increased beyond a certain point. This occurs when the period of the motion becomes less than the period of observation.

III. THE APPLICATION OF NUCLEAR MAGNETIC RESONANCE TO THE STUDY OF RATE PROCESSES; MOTION IN SOLIDS

1. Concept of Correlation Time

The ability to observe certain characteristic features of nuclear resonance spectra is subject to the condition that the nuclear environment appears to be stationary during what was defined as the period of observation. This condition, which sets a limit on the rate of change of the conditions to which the resonant nuclei are subjected, provides a mechanism for the study of rate processes approaching the period of observation. The effect of motion in which nuclei are involved upon the line width and structure has been discussed. In general, the periods of actual motions are not comparable to the period of observation, and in cases such as this a study by means of nuclear magnetic resonance serves to set limits for the frequencies of the motion occurring.

A concept of correlation time used by workers in this field will now be advanced. Description of processes and development of theory to explain dynamic processes in materials have been done largely in terms of the concept of rates as used by kineticists, since most people working in this field are chemists. The correlation time describes the time in which the atomic configuration around the nucleus changes appreciably. Much of the quantum mechanical treatment of the conditions under which nuclear magnetic resonance phenomena occur was developed by Bloembergen, Purcell, and Pound¹⁹ (referred to as BPP throughout

the following pages). Most of the discussion to follow deals with motions in solids, although it has been extended to study processes in solutions.²⁰

Equation 28, which relates the second moment of the absorption line to atomic configuration, contains the expression

$$\sum_j \left| (1 - 3 \cos^2 \theta_{jk}) r_{jk}^{-3} \right|^2 \quad (30)$$

Although for a rigid crystal lattice expression 30 is merely a constant dependent on geometry, another situation arises if θ_{jk} and r_{jk} are functions of time. BPP have made a statistical analysis which considers the spectrum of equation 30, expanded as a Fourier integral:

$$\left\langle \sum_j \left| (1 - 3 \cos^2 \theta_{jk}(t)) r_{jk}^{-3}(t) \right|^2 \right\rangle_{av} = J(\nu) d\nu \quad (31)$$

They find the intensity of this spectrum as a function of frequency to be

$$J(\nu) = K \frac{2 \tau_c}{1 - 4 \pi^2 \nu^2 \tau_c^2} \quad (32)$$

where τ_c is the correlation time as defined above. The reciprocal of this, $\nu_c = 1/(2\pi\tau_c)$, is the average frequency at which significant changes take place in atomic configuration. The integral of equation 31 over all frequencies is a constant, K, which implies that the area under the total nuclear magnetic resonance spectrum is constant, and therefore independent of τ_c . The width of the line is determined by what might be called static interactions; the width of the line comes from that part of $J(\nu)$ near $\nu = 0$. If $\delta\nu$ is the width of the absorption line for the rigid lattice, BPP take as the static contribution that part of the spectrum from $\nu = 0$ to $\nu = \delta\nu$. In actual usage, the spectrum from

$\nu = 0$ to $\nu = \delta\nu'$, where $\delta\nu'$ is the actual line width (narrowed or not), is considered to constitute the static portion.

The total area under the absorption line depends on the number of resonant nuclei in the volume of the sample, certain physical constants, electronic circuit parameters, and the like, but not upon the shape or width of the line. It then follows that if the correlation time is short compared to that required to observe the absorption line from a rigid lattice the line narrows and therefore increases in amplitude, conserving the area under the line. This increase in amplitude is a desirable feature from an experimental standpoint.

One experimental exploitation of the dependence of line width on correlation time is the basis of a line-narrowing experiment suggested by Bloch²¹ and executed by his co-workers. The experiment involved a narrow proton absorption line from a liquid, and is mentioned here because it provides a neat verification of the theory behind the discussion above. The limiting factor to the narrowness of absorption lines from liquids is generally the homogeneity of the external magnetic field. Bloch's experiment consisted of imparting motion to the sample by rotating or spinning the entire sample in the magnetic field; since the width of the line was only a few milligauss (frequency width about 10 cycles) the correlation time was long, comparatively speaking. By rotating the sample the magnetic field inhomogeneities over the volume of the sample could be averaged to those along the axis of rotation. Narrowing of the line was observed when the frequency

of rotation was increased past the correlation frequency set by the line width. This has since become a standard technique for high resolution nuclear magnetic resonance spectroscopy.

2. Study of Motions in Solids

The "expected normal behavior" of the resonance line for a solid can now be described. Suppose the sample consists of a "normal" solid in which no internal motions or other complicating factors are present. The width of the resonance line is generally measured as the distance between points of maximum slope, and for a solid this is expected to be on the order of several gauss. If the sample is heated while the resonance line is being observed, the line width stays constant until the temperature is reached at which the solid melts. The correlation frequency for narrowing of the resonance line from the solid would be something like 100 kc/sec. (10^5 sec^{-1}); when melting occurs the rigid lattice disappears and the particles take on motions associated with liquids. The frequencies associated with motion in a liquid are on the order of 10^{10} to 10^{12} sec^{-1} , and the motions are random and of a large scale. When melting takes place the line width is seen to suddenly narrow; cases such as this have been observed where the line width decreases a thousandfold.

A number of such cases have been observed, but a number of substances have also been observed where a partial reduction in line width occurs at a temperature far below the melting point.^{17, 22, 23, 24} Internal rotation or motion in the solid state has been ascribed to these latter substances, for the reasons set down above.

It is believed that the rate of the motion which may occur in solids is described by the Arrhenius equation,

$$A = A_0 \exp (-E/RT) \quad (33)$$

A more sophisticated treatment of the rates associated with internal motions in solids has been started by Gutowsky,²⁵ based on the theory of rate processes advanced by Glasstone, Laidler and Eyring.²⁶ This theory proposes an equation, similar in form to 33, which involves an absolute rate constant and the free energy of activation for the process. At the present state of the art, nuclear magnetic resonance information is not sufficient to provide a test of the applicability of the absolute rate theory to motions in solids. The absolute rate equation is

$$A = \frac{kT}{h} \exp (-\Delta F/RT) \quad (34)$$

If the assumption that the frequency factor represented by kT/h is correct, then the standard free energy of activation of the process can be evaluated.

The information that is derived from a nuclear magnetic resonance study of internal motions in a solid is limited to the determination of one specific rate at one specific temperature.

The experiment consists of studying the line width as a function of temperature. When the rate of the motion in the solid becomes comparable with the correlation frequency as determined by the width of the line obtained from the lattice in its apparently "rigid" form, the line narrows over a small range of the increasing

temperature. This temperature and the corresponding correlation frequency constitute just one point of the many that would be required to test equation 34.

IV. STUDY OF HINDERED ROTATION IN SOLID HEXAMMINECOBALT(III) CHLORIDE AND RELATED SUBSTANCES

1. Background

In the course of other work it was noticed by Waugh that the nuclear magnetic resonance spectrum at room temperature from the protons in hexamminecobalt(III) chloride consists of a line that is surprisingly narrow for a solid.²⁷ Other instances of narrow lines from solids are in the literature cited above, the most comparable of which is that found in solid ammonium chloride by Gutowsky and Pake, and ascribed to rotation of the ammonium ions. It was the purpose of the present investigation to study the width of the proton absorption line from hexamminecobalt(III) chloride at a series of temperatures to see if the line width behaves in a manner expected for internal rotation. Other materials related to the hexamminecobalt(III) complex ion were also studied, to see if rotational freedom could be ascribed to them and to elucidate the type of motion occurring.

2. Preparation of Samples

Hexamminecobalt(III) chloride prepared in quantity by Waugh²⁸ was used for this study after the precaution of extended drying in vacuum. Waugh has since obtained from other sources, samples of this material, which behave in the same manner as the first when studied by nuclear resonance.

Tris-ethylenediamminecobalt(III) chloride which had been

prepared by Waugh was also available.

Additional tris-ethylenediamminecobalt(III) chloride was prepared in the following manner, which is that given by Ferne-
lius²⁹ except for the method of oxidation of the cobalt from the
divalent to tervalent state, which was adapted from Palmer.³⁰
A mixture of 21 ml of ethylenediamine, 40 ml water, and 17 ml
6 N HCl is added to 24 g. of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 75 ml of water.
The oxidation is accomplished by the slow addition of 60 ml of
5% H_2O_2 . After the reaction has apparently ceased, the mix-
ture is evaporated until a crust begins to form on the surface.
The salt is precipitated by the addition of a mixture of 15 ml of
12 N HCl and 30 ml of absolute ethanol. The solid is removed
by suction filtration, washed with absolute ethanol, and dried.
The product is obtained by recrystallization from 6 N HCl. The
expected yield is 31 grams of $\text{Co(en)}_3\text{Cl}_3$ (en = ethylenediam-
mine).

The following preparations were made according to the
procedures given by Palmer:³⁰ oxalato-tetramminocobalt(III)
chloride, trans-dichloro-tetramminocobalt(III) hydrogen sulfate,
and cis-chloro-aquo-tetramminocobalt(III) sulfate. All samples
were dried in vacuum for at least one week over anhydrous cal-
cium chloride to insure complete removal of any solvents used.
The presence of a small amount of solvent could give a strong
absorption line, because of the narrowness of lines from liquids.

3. Experimental

The substances mentioned above were individually

placed in the nuclear magnetic resonance spectrometer and their spectra at room temperature were recorded. The three substances in the preceding paragraph exhibited broad absorption lines at room temperature, indicating absence of internal motions. The sample of $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ and first mentioned sample of the $\text{Co(en)}_3\text{Cl}_3$ were found to give narrow lines. The line width of the proton absorption line from $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ was then carefully studied as a function of temperature.

Because of the nature of the electronic circuitry in the spectrometer, the spectra are actually recorded as the derivative of the absorption line, plotted against magnetic field. This is the way in which broad nuclear magnetic resonance spectra are commonly obtained, and hence the measure of line width as the distance between points of maximum slope of the absorption line is as familiar as well as a convenient one. The measured widths are the separation, in gauss, of the positive and negative peak of the derivative curve. The line widths cited here have been on that basis, and although no physical significance can be attributed to this measure of width (such as could be attributed to the second moment as a measure of line width), it is useful in determining when changes take place in the absorption line.

Second-moment calculations of the absorption lines have not been attempted here because the noise and zero drift in the recorded lines would throw serious doubt upon the values obtained, and also because the crystal structure of $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ has not been determined.

Two thermostats were constructed for this work; they will be described in the section dealing with the apparatus. One was used for the temperature range from room temperature to ca. -140°C , and the other for liquid nitrogen temperature, -196°C . A gap between these temperatures remains in the data presented because no convenient means could be found to produce the intermediate temperatures. Liquid methane was tried in the liquid nitrogen thermostat, but proved unsatisfactory because the sharp absorption line from the protons in the methane dominated the spectrum, even though there was a gap of about 6 mm between the outside of the coil holding the sample and the methane.

The experimental results for $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ are shown in figure 3, the points representing the experimentally measured separation of points of maximum slope vs. temperature. Corrections need to be applied to the experimental widths to take account of artificial broadening by magnetic field modulation³¹ and magnetic field inhomogeneity. Because the determination of magnetic field inhomogeneity by magnetic measurements is an inaccurate and tedious process by present techniques, the corrections were determined by observing the width of the absorption line for the protons in a water sample of similar size and shape and subtracting this quantity from the measured widths of the absorption lines for the solid. The true width of the water line is several orders of magnitude smaller than that measured with this spectrometer, and therefore the measured width is attributed solely to instrumental broadening.

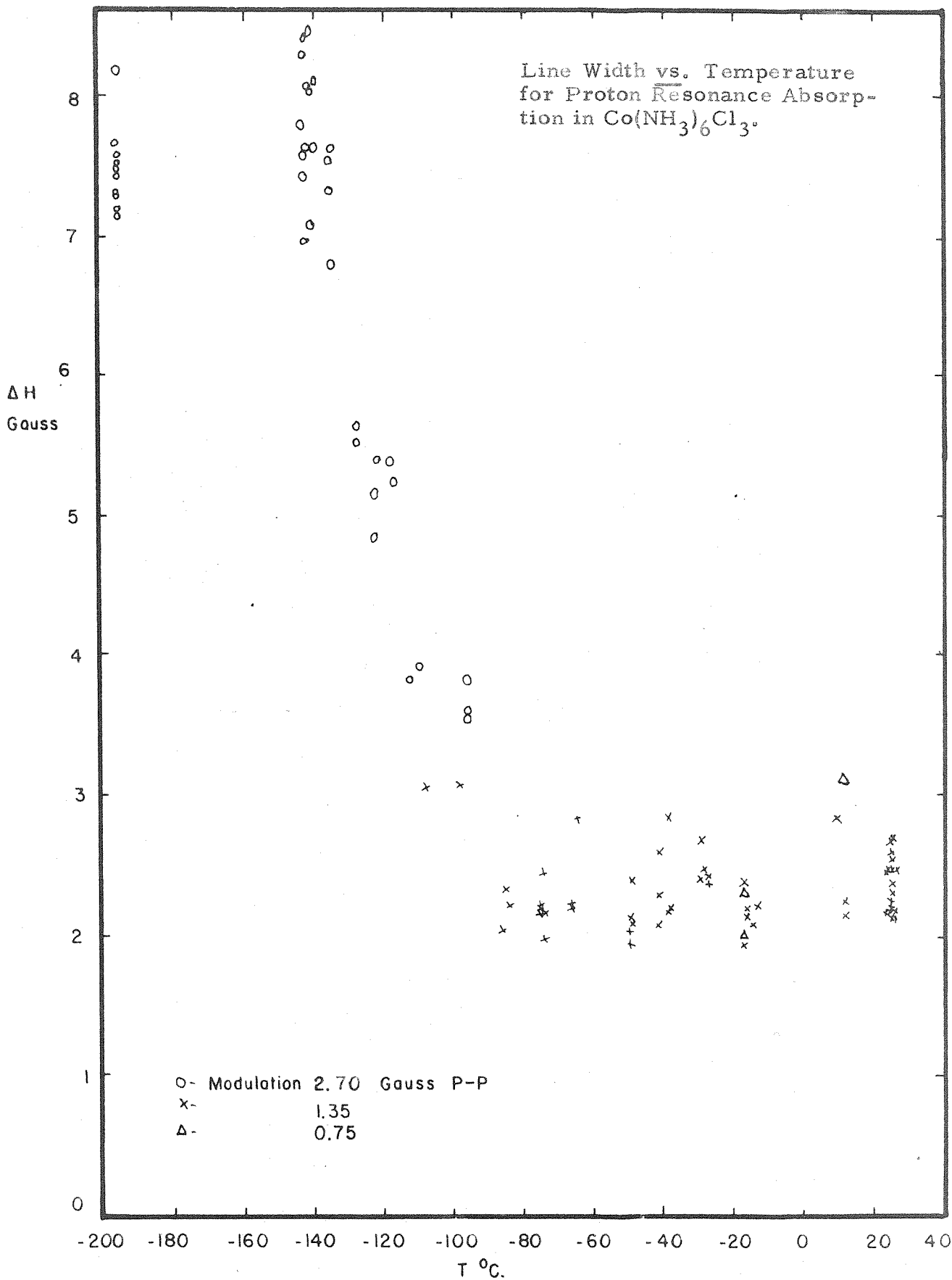


Figure 3

Figure 3 shows the transition from the broad line to narrow line happening at -120°C . The average width for the narrow portion is 2.29 gauss, and that for the broad portion 7.62 gauss. The artificial broadening present in the first value is 0.70 gauss and that in the latter is 1.70 gauss, making the corrected widths 1.59 and 5.92 gauss. It is estimated that the error involved in measuring each width is of the order of ± 0.1 gauss, and this is indicated by the size of the circles designating the experimental points of figure 3. The chance for small errors arises in locating the maxima of the derivative curve and interpolating between magnetic field markers on the chart.

The experimental work on $\text{Co(en)}_3\text{Cl}_3$ was neither reproducible nor conclusive. The first sample tried (prepared by Waugh three years earlier) was found to give a proton absorption line about 1.3 gauss wide at room temperature (uncorrected). It began to broaden at about -60°C . as the temperature was lowered. With the same sample, Waugh observed a broad absorption line at room temperature, soon after its preparation. Repeated drying did not change the behavior of this sample. The second sample as prepared above did not function satisfactorily. Apparently the sample caused pickup of the field modulation by the sample coil in this apparatus, making observation of any but the strongest of absorption lines impossible. No consistent absorption line was observed from this sample. Some of this same material when used in the M.I.T. nuclear magnetic resonance spectrograph by Waugh gave conflicting results, although a narrow line superposed on a broad was observed.³² No explanation for this behavior, which has

persisted through several dryings and pulverizations, has been advanced.

The room temperature proton resonances of the other complex compounds of cobalt mentioned above, $\text{Co}(4\text{NH}_3 \cdot \text{C}_2\text{O}_4)\text{Cl}$, trans- $\text{Co}(4\text{NH}_3 \cdot 2\text{Cl})\text{HSO}_4$ and cis- $\text{Co}(4\text{NH}_3 \cdot \text{H}_2\text{O} \cdot \text{Cl})\text{SO}_4$, were similar in appearance to the broad lines from the hexammine. The lines were weak and no attempt was made to measure the widths, visual comparison showing them to be at least as wide as 8 gauss. The iodide and bromide salts of the hexamminecobalt(III) complex ion have been recently studied by Waugh, and apparently show the same behavior as the chloride.³²

Temperatures of the thermostat and sample were measured by means of an Advance-copper thermocouple and a Leeds and Northrup precision potentiometer. The temperature of the sample did not vary more than 0.1° during a given run.

4. Conclusion

The results of this investigation show that some sort of internal motion is present in solid hexamminecobalt(III) chloride at room temperature. Two types of motion can be considered as being likely: the rotation of the whole hexamminecobalt(III) ion, and the rotation of the individual ammonia groups about their three-fold axes. The latter motion is minimized in preference to the former by this writer on two grounds. A scale model of the hexamminecobalt(III) ion was constructed from a Corey-Pauling model kit³³ based on the accepted values of covalent radii; a photograph of the model is shown as figure 4. The appearance of the model

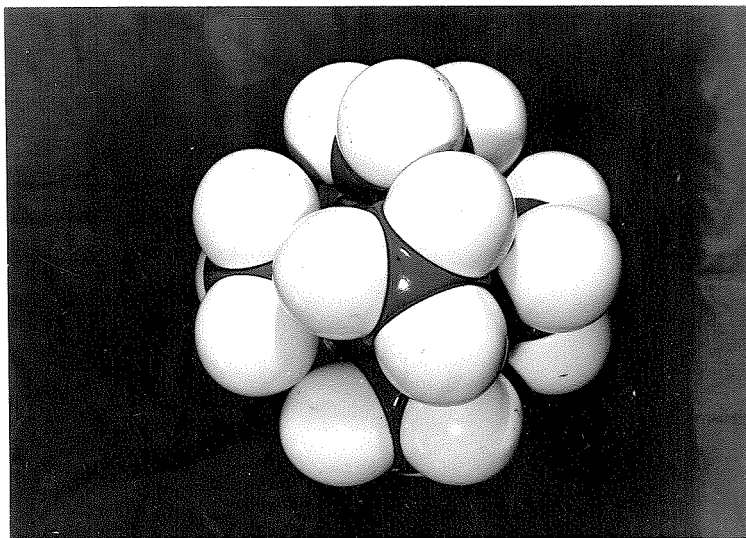


Figure 4

indicates a high degree of sphericity of the ion, the outside boundary of which is composed of 18 protons equidistant from the center. Only the ammonia groups are visible on the ion, the cobalt atom in the center being hidden by the rest. On the basis of this model a considerable amount of steric hindrance against rotation of the individual ammonia groups is present. It seems unlikely that all six of the ammonia groups would rotate in a cooperative manner, each meshing with its neighbors like a set of mechanical gears. Because of the sphericity of the ion, it is probable that the potential barriers against rotation of the whole ion are considerably lower than the barrier restricting the rotation of the individual ammonia groups.

The other consideration is that none of the bi-substituted tetramminecobalt(III) ions were found to show rotation in the solid. If the individual ammonia groups were free to rotate in the

hexammine, freedom of rotation should also be present in an ion such as the cis-dichloro-tetrammine complex ion. These a posteriori conclusions indicate that the motion is that of the whole hexammine ion.

The crystal structure of hexamminecobalt(III) iodide was determined by X-ray diffraction by Wyckoff and McCutcheon.³⁴ They reported that the positions of the nitrogen atoms could not be established with certainty. Although this difficulty could be attributed to the slight scattering power of nitrogen atoms with respect to cobalt and iodine atoms, it might instead be due to motion of the atoms. If the motion were a rapid jumping between equilibrium positions of the ion, the nitrogen atoms might spend most of the time in one of the six equivalent positions of the hexammine ion in the rigid structure, and the X-ray diffraction pattern might indicate the average positions of these atoms. The jumping from one position to another would, however, affect the phase memory of the nuclear spins, and would hence have a noticeable effect on the nuclear magnetic resonance spectrum.

Although the crystal structure of the chloride has not been determined, since the other salts of the hexamminecobalt(III) ion whose structure is known (iodide, perchlorate, bromide and chloride sulfate) possess an octahedral (Oh^5) unit cell the chloride can be discussed on this basis. Due to the three-fold symmetry of the ammonia groups, the octahedral hexamminecobalt(III) complex ion does not possess octahedral symmetry. This ion cannot fit exactly into a lattice with octahedral symmetry. Because of this circumstance, the ion will, if anything, have a greater freedom of

rotation since perfect alignment with the lattice is impossible.

With use of equation 34, the mean frequency at -120°C of the rotational motion is calculated to be $25 \cdot 10^3 \text{ sec}^{-1}$. The corresponding energy of activation is $5600 \text{ calories mole}^{-1}$. Depending on the validity of the assumptions made in deriving equation 34, the above numbers may represent only the orders of magnitude of these quantities.

If the proton absorption is a pure gaussian (error function) the width between inflection points (ΔH) can be related to the second moment (M) of the line by the following equation

$$M = 2 (\Delta H)^2 \quad (35)$$

V. DESIGN, CONSTRUCTION, AND OPERATION OF THE NUCLEAR MAGNETIC RESONANCE SPECTROGRAPH

1. General Description

As was mentioned in the introduction, two general types of nuclear magnetic resonance spectrographs are in common use. The Bloch, or nuclear induction apparatus, and the Purcell, or nuclear magnetic resonance absorption apparatus, differ in some details and each has applications to which it is the better suited. The apparatus more suitable for the observation of line shapes, or broad lines in general, is the Purcell apparatus, which has been constructed here. The Bloch apparatus has been described in the literature.³⁵

A functional diagram of the spectrometer is shown in figure 5. The various components of this apparatus will be described in the sections to follow. The writer collaborated with Dr. Humphrey in the design and construction of several pieces of apparatus which are used by both the nuclear magnetic resonance and electron paramagnetic spectrographs, and where appropriate the reader will be referred elsewhere for details.³⁶

The units shown in figure 5 constitute two nuclear magnetic resonance spectrographs sharing a common magnet. One nuclear resonance spectrograph is used to measure and control the magnetic field, and the other is used to investigate various materials. Although the two spectrographs are basically of the Purcell type, they are of different design. The magnet control spectrograph uses an oscillating detector arrangement in which the sample is coupled to the tank circuit of an oscillator. The research spectrograph is of the bridge type, the sample being coupled to a tank circuit that

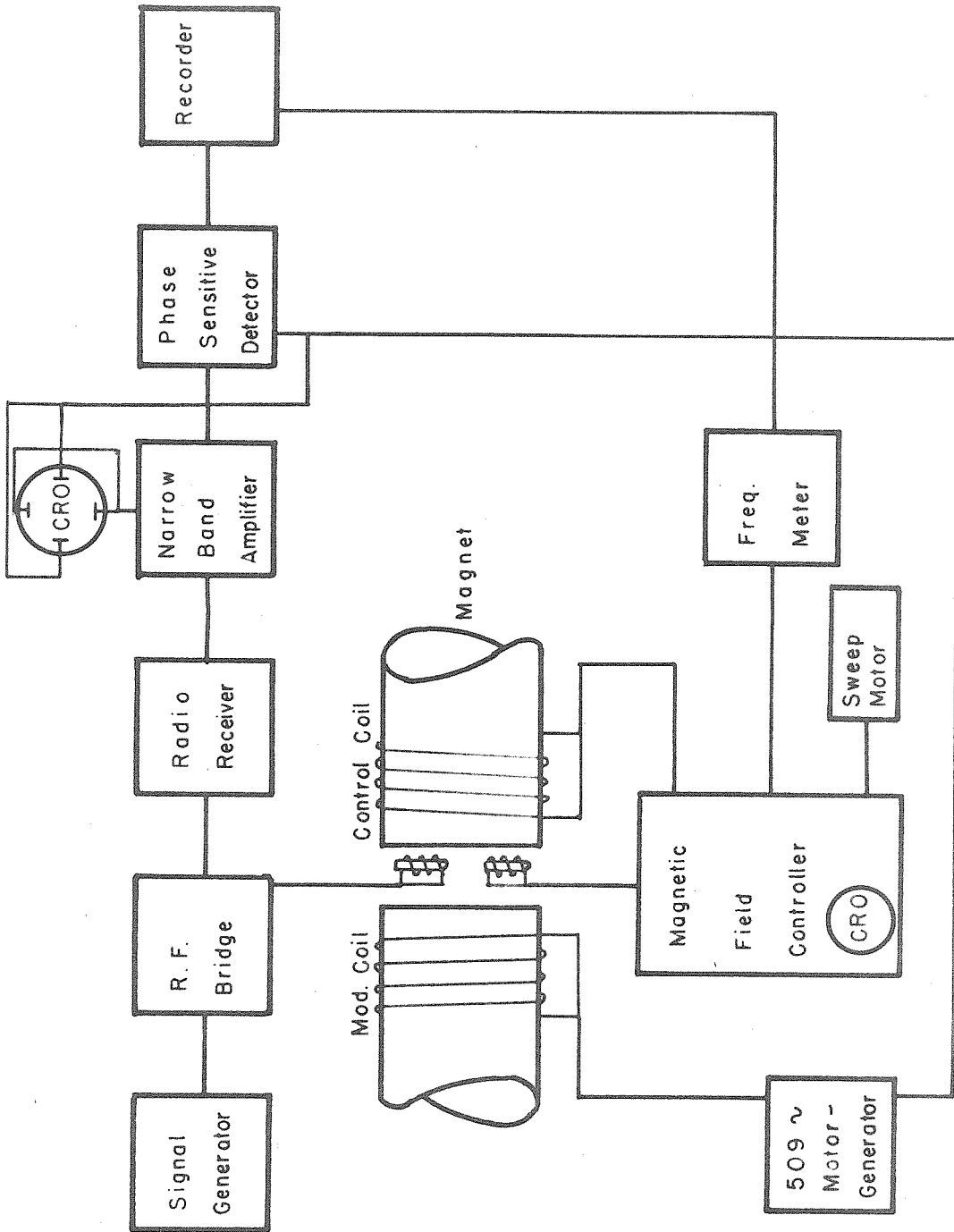


Figure 5. Block Diagram of Spectrometer

is part of a radio frequency bridge.

2. Detection of Nuclear Magnetic Resonance

The detailed operation of the two types of detectors employed will be described under their respective sections. The method of detection of the resonance other than the details of the radio frequency circuits is common to both units and will be described here. The main problem involved is that of detecting and measuring a signal that may be comparable to or smaller than the ambient noise level of the electronic circuits. The technique of making the absorption signal periodic with time and then detecting the signal because of its periodicity is in widespread use by those in the magnetic resonance fields, and is used here.

Periodicity of the absorption signal is created by modulating the magnetic field strength at an audio frequency rate. It is desirable that the nuclear resonance signal from the controller have a line width that is small compared to the line being studied by the research spectrometer. The modulation amplitude is adjusted so that it is wider than the narrow line from the controller and narrower than the wide line being studied; thus the magnetic field more than completely traverses the controlling line and only partially the other. Detection is then accomplished by means of a so-called phase sensitive detector, which correlates the signal with a reference frequency. In essence this type of detector selects only that component of a complex signal that agrees in frequency with the reference used, rejecting all else. The reference signal here is the actual voltage used to modulate the magnetic field. Circuit noise is in general a signal composed of random frequencies, and if the correlation is

done over a long enough period of time, will not be passed by the device. The basic operation of a phase sensitive detector is that of a multiplying circuit, and its operation will be discussed from that viewpoint.

It is common in electrical engineering to describe a complex signal in terms of frequency analysis; this usually is done by means of a Fourier series, and can be of the form

$$E_s = \sum_i A_i \sin(\omega_i t - \phi_i) \quad (36)$$

where E_s represents the amplitude of the signal, A_i the amplitude, ω_i the angular frequency and ϕ_i the phase of the i^{th} frequency component. Let us take the case where the reference signal is a pure sinusoid of angular frequency ω_r

$$E_r = A_r \sin \omega_r t \quad (37)$$

The action of the phase sensitive detector causes these two signals to be multiplied together, and the product integrated. If E_o is the output voltage, it may be expressed as

$$E_o = K \int_0^\tau E_s \cdot E_r dt = K \int_0^\tau A_r (\sin \omega_r t) \cdot \sum_i A_i \sin(\omega_i t - \phi_i) dt \quad (38)$$

where K is a constant describing the circuit parameters. Because of the orthogonality of sine functions, the above expression is equal to zero unless $\omega_i = \omega_r$, in which case E_o is a function of the phase angle ϕ . The cancellation of frequencies other than that of the reference will depend on the length of integration, τ , which is usually electrically adjustable.

Although the same type of circuit is employed in both spectrometers, there is a fine distinction between the application in the two cases. The magnet control nuclear resonance signal consists of an absorption line that is completely traversed by the magnetic field modulation. The position of the absorption line with respect to the center of the excursions of the field modulation can be defined in terms of a phase angle, and in this case, the output of the phase sensitive detector is proportional to this phase angle.

Ideally, the modulation is small compared to the broad absorption line being studied, and, in contrast to the former case, only a small part of this line is traversed. This is another use of the phase sensitive detector, and is known as slope detection. The result of modulating over a small portion of the line is illustrated in figure 6 where a broad absorption line is indicated in (2) with the amplitude and position of the modulation with respect to the absorption line depicted by the arrow. Part (b) of figure 6 represents an expanded portion of (a) in the vicinity of the part of the absorption line being scanned by the modulation.

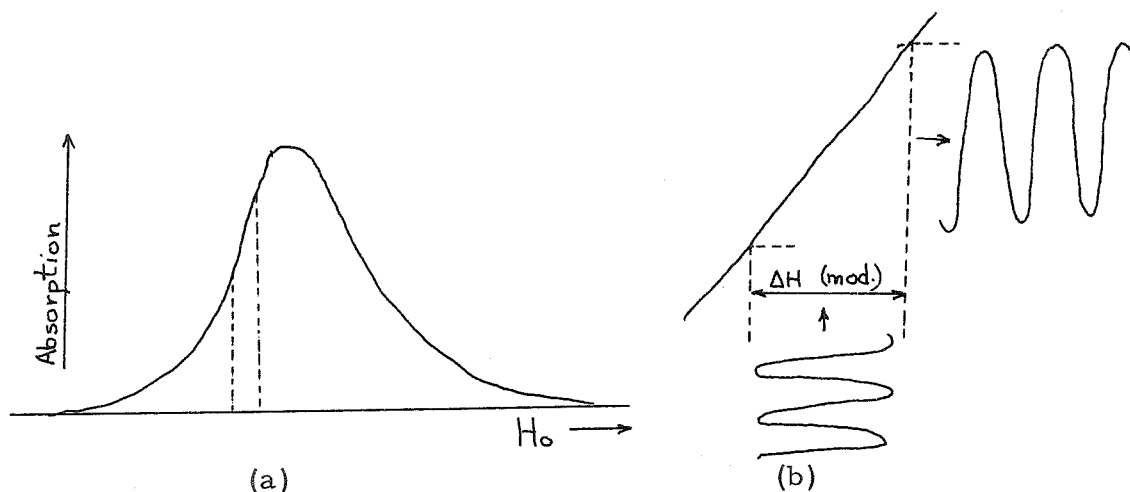


Figure 6

As the magnetic field is modulated, the amplitude of the line at the point being measured appears to move up and down the slope of the line, causing an output at the modulation frequency similar to that shown at the right of (b). The amplitude of the output sine wave will be proportional to the slope of the line in that region, and can have only one of two possible phase relationships with the modulation signal, the phase being determined by the polarity of the derivative, that is, whether the right or left side of the absorption line is being scanned. For this case E_o of equation 38 will be proportional to the amplitude of the signal, and therefore proportional to the derivative of the line. The phase relationship between the signal and the modulation voltage will determine the polarity of E_o . The output of the integrator is recorded on a strip chart, providing a record of the derivative of the absorption line.

One other necessary process is the slow changing or sweeping of the magnetic field through the absorption line. The rate of sweep of the field must be very slow compared to the modulation rate, and slow compared to the integration time. This is accomplished by a clock motor turning the tuning condenser of the control oscillator tank circuit, so that its frequency changes slowly with time. The control oscillator is part of a servo loop that serves to keep the main magnetic field at such a value that the control absorption line is always at the center of the modulation excursions. As the control oscillator slowly changes in frequency, the main magnetic field changes in a similar manner.

The next few sections will describe the functional units of the spectrometer.

3. The Magnet

The main magnetic field is produced by a large low-resistance electromagnet which was built by Safonov for cosmic ray momentum measurements.³⁷ The original pole pieces were replaced by Waugh with more suitable ones constructed of Armco magnet iron. The pole faces are six by fourteen inches, separated by a gap of 1.46 inches. The field homogeneity was improved somewhat by placing shims between the pole pieces and the magnet yoke and making small changes in the spacing and angle between the pole faces by tightening the bolts holding the pole pieces by different amounts. The field was mapped by means of sensitive coils, and then by nuclear resonance probes, to find the trends in the inhomogeneities so that corrections could be made.

Power for the magnet was furnished by two generators, one supplying a manually adjusted steady current and the other controlled by the magnetic field controller. Besides the main magnetizing windings, two auxiliary coils are on the magnet, one to provide the field modulation and which is supplied by a 5 kw. 509 cps. motor generator set, and the other is a field correction coil and is part of the controller servo system. The correction or control coil can make corrections in the field strength to compensate for changes in the d.c. generator outputs or for changes needed because of the sweeping of the magnetic field. Changes greater than 50 gauss maximum that the control coil can supply are made by an automatically controlled motor driven rheostat that adjusts the field current in the controlled d.c. generator.

4. The Magnetic Field Controller

The design and construction of the field controller have been described by Humphrey and will not be repeated here. The oscillating detector comprising the control spectrometer was adapted from that of Knoebel and Hahn⁽³⁸⁾ with two changes. The unit is a transitron oscillator with a square law detector. To impart periodicity to the absorption signal, the original circuit used a system of frequency modulation employing a vibrating condenser. This was replaced here by the magnetic field modulation system already described. The other change was the incorporation of a link coupling arrangement between the sample in the magnetic field and the oscillator tank circuit, which will be described later.

The output of the square law detector is amplified, passed through a narrow band "twin tee" electronic filter to attenuate all but that part of the signal near the modulation frequency, and then acted upon by the phase sensitive detector. The output of the phase sensitive detector is amplified by several d.c. amplifiers, and applied to the control winding on the magnet and to the circuit controlling the motor driven rheostat.

Attempts were made first using the protons in water for the controller nuclear resonance sample in the magnet. This proved to be unusable since it was desired to look at proton resonance with the research spectrometer. Since the two proton samples were in the same magnetic field they involved oscillators of the same frequency, and the oscillators of the two spectrometers were found to interact strongly in spite of precautionary measures that were taken, and the resonance absorption in both was obscured. A more workable

arrangement consisted of putting the controller proton resonance sample inside of a Helmholtz coil inside of the main magnetic field to shift it away from the main field by 10 gauss or so. This also proved unsatisfactory because a voltage source stable enough to provide an unchanging field in the Helmholtz coil could not be found. The solution proved to be a technique that was one of the first tried, and abandoned for lack of a suitable sample. This was the operation of the controller on a system of resonant nuclei other than protons. The most logical isotope to use was F^{19} , which has essentially all of the features desired. Its natural abundance is 100%, its spin is $\frac{1}{2}$, and for the same magnetic field its resonance frequency is about 6% lower than that of protons. This meant that no major changes would have to be made in the controller frequency-wise. Many compounds containing this isotope were tried as samples without success. Dr. Rex Richards, of Oxford University, suggested trifluoroacetic acid with a trace of manganous ion present to decrease the relaxation time, and this proved suitable. This sample contains both H^1 and F^{19} nuclei in sufficient quantity that either can be used as the controlling nucleus, which means that some care has to be taken to ascertain that one is on the proper absorption line.

The research spectrometer, that part of figure 5 shown above the magnet, will be described next.

5. The Radio Frequency Source.

A General Radio Co. model 1001-A radio frequency signal generator provides energy at the Larmor frequency to excite the nuclei. The frequency range of this instrument is 5 kc. to 50 mc., the output being adjustable from 0 to 200 mv. The output of this unit

was carried by means of a coaxial cable to the radio frequency bridge.

To insure frequency stability of this unit, the input line voltage was regulated by a Sola constant voltage transformer. To make certain that the oscillator components had reached their equilibrium temperatures, the power was never turned off, except for maintenance. A warming-up period of at least one day was allowed before making measurements. All the absorption lines were recorded with the signal generator operating at a frequency of 16.620 mc. at a power level of 200 mv. for the narrow, and 70 mv. for the broad lines.

6. The Radio Frequency Bridge

The radio frequency bridge used in this work is an adaptation of the bridge developed by Bloembergen¹⁹; it is shown schematically in figure 7. Two departures have been made from the original circuit. A link coupling arrangement between the sample coil and one of the tank circuits of the bridge was added and is described in exhibit 1. The bridge consists of two tank circuits, fed in parallel through small condensers to provide isolation between them. One circuit is designated as the "sample" arm of the bridge and is coupled with the sample in the magnetic field, the other is designated as the "dummy" arm and serves as a reference for the former. The two arms of the bridge are adjusted to be electrically equivalent with the sample in place and without resonance absorption taking place. The output of the two arms of the bridge will be equal in amplitude and phase. The original circuit joined the output of the two circuits by means of coaxial cables terminating in a coaxial tee connector, one coaxial cable being one-half wavelength of the frequency

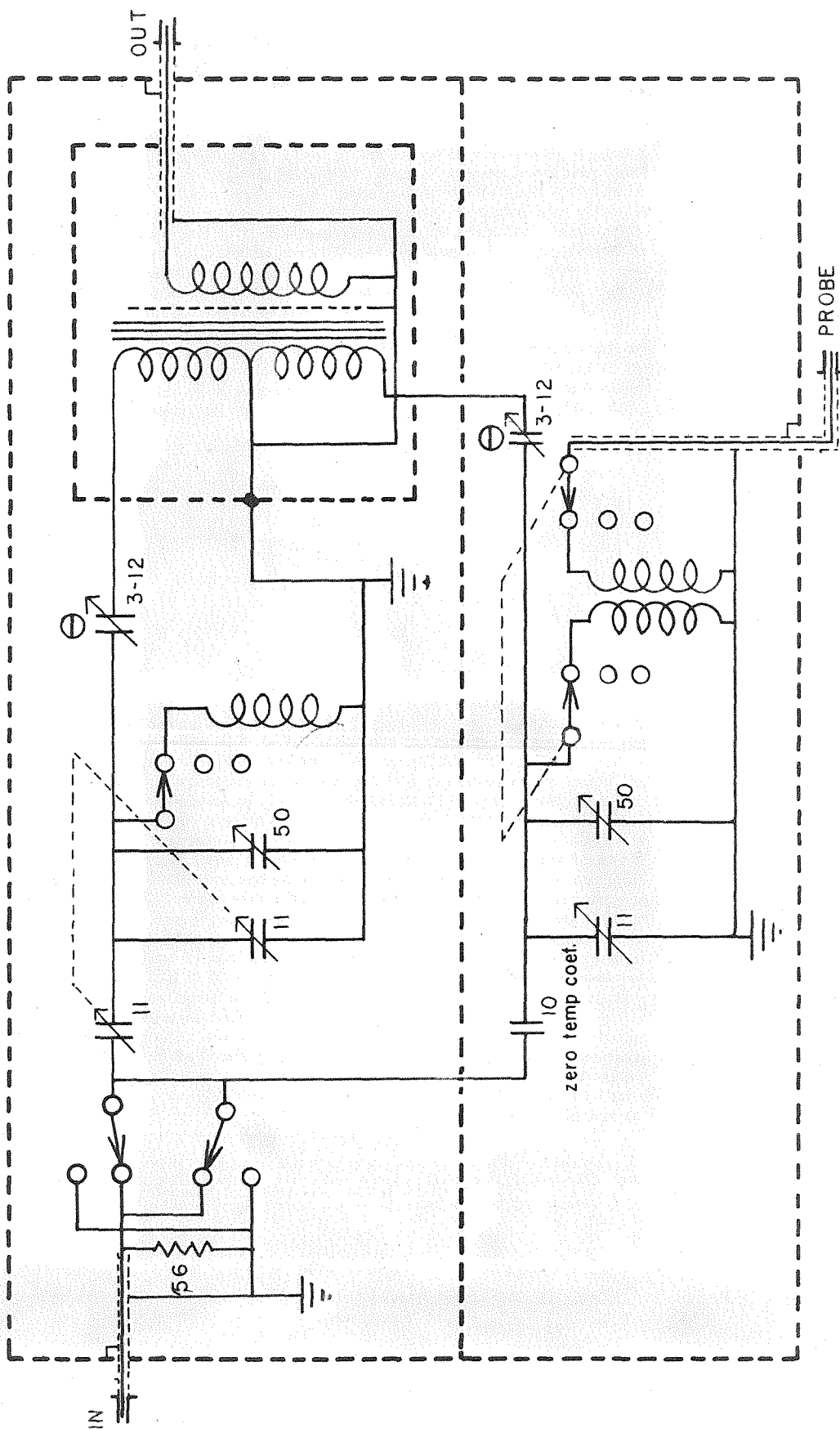


Figure 7. Schematic of radio frequency bridge

Link Coupling for Nuclear Magnetic Resonance

HENRY L. RICHTER, JR., FLOYD B. HUMPHREY, AND DON M. YOST

California Institute of Technology, Pasadena, California

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IN an attempt to use proton magnetic resonance for regulation of magnetic fields of 10 kilogauss or more, it has been found that the conventional probe sample holder used by other investigators¹ gave inadequate, if any, resonance lines above 40 mc/sec. In such arrangements, the oscillator tank coil is at the end of a coaxial probe. The weaker lines at higher frequencies are attributed to the fact that the distributed inductance of the coaxial line becomes important as frequency is increased.

To overcome this difficulty, we have employed a link-type coupling arrangement (see Fig. 1). This allows one to utilize lumped circuit elements for the oscillator tank circuit which are completely contained within the oscillator compartment of the unit. The coil containing the sample is coupled with the oscillator tank coil by means of an untuned secondary winding placed

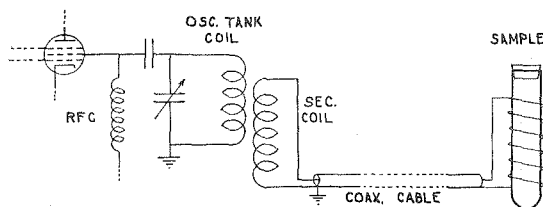


FIG. 1.

around the oscillator coil. A coaxial cable connects this secondary winding with the coil containing the sample, and this allows the sample to be many feet from the oscillator.

Experience has shown that it is not necessary to match the impedance of the coils to that of the coaxial cable. The best proton absorption lines were obtained when the secondary coil was tightly coupled to the primary and actually consisted of more turns; for example, our oscillator coil is made of 5 turns of No. 8 wire, self-supporting with a $\frac{3}{4}$ -in. diameter, 1 in. long. This is covered with a layer of Teflon tape on which the secondary is wound, consisting of 6 turns of No. 24 wire $\frac{1}{4}$ in. long. Due to impedances reflected into the oscillator tank circuit, more than one mode of oscillation is possible,² and as a result of this a dead spot of several megacycles may be expected. This dead spot can be moved by changing the length of the coaxial cable connecting the secondary and the sample coil.

The same coupling arrangement has been used on an rf bridge of the Bloembergen type³ and is presumably applicable to others. Blind spots have not been observed here since these are passive circuits. A great reduction in frequency drift and in microphonics in the rf bridge has been obtained by means of the coupling arrangement described above.

¹ H. W. Knoebel and E. L. Hahn, *Rev. Sci. Instr.* **22**, 904-911 (1951).

² H. J. Reich, *Very High-frequency Techniques* (McGraw-Hill Book Company, Inc., New York, 1947), p. 344.

³ Bloembergen, Purcell, and Pound, *Phys. Rev.* **73**, 679 (1948).

being used longer than the other. Because of the extra length of one of the cables, the signals at the output of the cables would be out of phase, and equal in amplitude, and would cancel. This device is limited to operation over a very narrow range of frequencies. A differential transformer was constructed to replace the phase reversal system using the half-wavelength line, which has an operational frequency range of many megacycles.

The differential transformer was wound on a ceramic ferrite core of the type used for winding toroids. Two separate primary windings are bifilar wound around the ring shaped core each consisting of 25 turns of 26 gauge wire in a single layer. This layer was coated with a generous quantity of "kel-f" polymer and allowed to dry thoroughly. An electrostatic shield was placed over these windings consisting of one-mil copper foil, carefully insulated so as not to constitute a shorted turn. A grounding lead was attached to the shield and the whole covered again with a liberal quantity of "kel-f" (to reduce the capacitive shunting of the transformer windings by the shield). The secondary was then wound, using 25 turns of 22 gauge wire, spaced so as to cover most of the ring. The primary windings were connected in opposition by grounding different ends of the two windings. It is important that no capacitive coupling be allowed between the primary and secondary windings, and the electrostatic shield was incorporated to prevent this. The transformer was mounted in an iron shield to prevent pickup of the modulation frequency from stray fields, which was then mounted in the bridge unit. The bridge is shown in Figure 8 with cover removed.

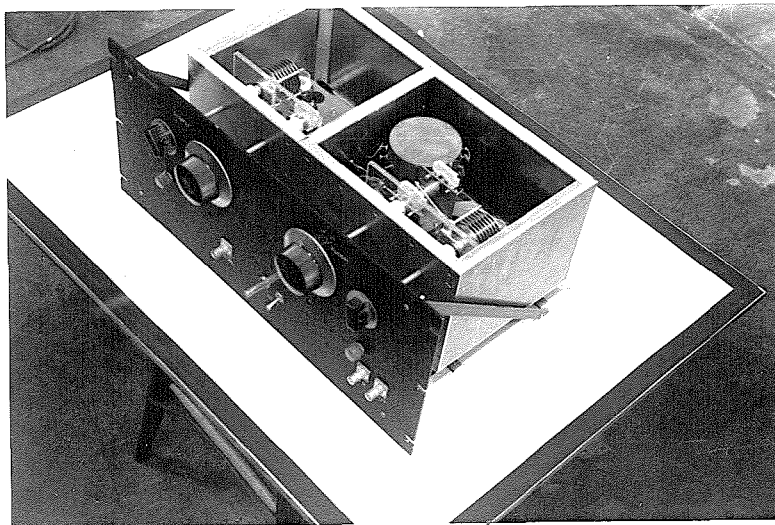


Figure 8. Radio Frequency Bridge

When balanced sharply, radio frequency bridges are quite susceptible to mechanical noise. The adjustment for balance was also found to be quite dependent on the temperature of the component parts. The bridge proper was mounted inside of a rigid aluminum box, which in turn was shock-mounted against external mechanical vibrations. Shafts for the internal controls were isolated against the transmission of mechanical noise by the use of flexible couplings. The aluminum box was mounted inside of a cabinet to restrict the flow of surrounding air, and thus gain thermal stability. Provision was made for the installation of a thermostated heater in the assembly, but this was not found to be necessary and was not done. The link coupling arrangement overcame the changing of the bridge balance by the changing of the temperature in the thermostat holding the sample and its exciting coil.

7. The Radio Frequency Receiver

The detector of the radio frequency power consists of a commercially built short-wave radio receiver (National Co. model HRO 50-T). The bridge was connected to the unbalanced antenna input of the receiver by means of a coaxial cable. A switch was provided to change the input from that of the bridge to an external antenna system for the purpose of monitoring broadcasts by radio station WWV of the National Bureau of Standards, for the purpose of frequency calibration. The HRO receiver was modified by installing a cathode follower circuit, to obtain a low impedance output, from the second detector. Figure 9 is a schematic diagram of the addition. The output of the cathode follower passes via coaxial cable to the phase sensitive detector unit.

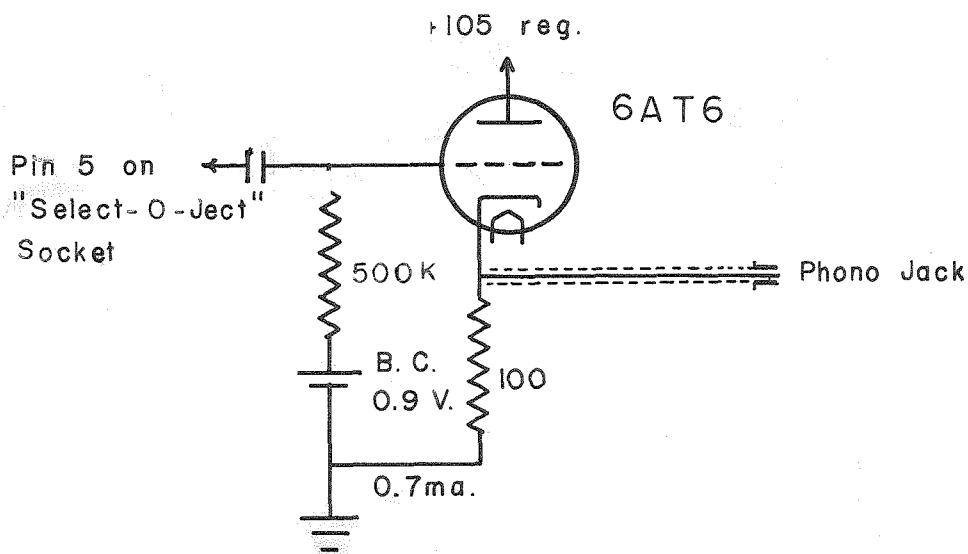


Figure 9

8. Narrow Band Amplifier and Phase Sensitive Detector

The narrow band amplifier and phase sensitive detector are combined in one piece of apparatus and are described by Humphrey (loc. cit.). The operation of the phase sensitive detector has been described above; the narrow band amplifier is used to restrict the frequency spectrum of the signal applied to the phase sensitive detector to avoid saturation of the circuits at higher input levels. The correlation in the phase sensitive detector is accomplished by a mechanical chopper switch, which is driven by the modulation voltage. The operation of the chopper can be considered as that of multiplication, the signal being multiplied by 0 or 1, according to the polarity of the exciting signal at any time. The output of the chopper is integrated by a resistance-capacitance circuit of variable cutoff frequency.

9. The Data Recording System

The integrated output of the phase sensitive detector is plotted by a Brown Electronic strip-chart recorder. As the paper chart in the recorder moves, the magnetic field is changed by the sweep motor on the controller, and a graph of the derivative of nuclear magnetic resonance absorption vs. magnetic field is obtained. The recorder is equipped with an auxiliary side-marking pen and this is used to place field markers on the chart to indicate values of the magnetic field.

The magnetic field is measured by determining the frequency of the control oscillator by means of a type BC-221 secondary frequency standard. A small amount of the radio frequency power from

the control oscillator is coupled into the frequency meter. The beat note voltage is amplified by two audio stages external to the frequency meter, displayed on an oscilloscope for visual observation and is also detected by a zero-beat detector developed by the writer (figure 10). The zero-beat detector is a vacuum tube operated relay circuit which responds to the very low audio frequencies which are present in a signal near zero-beat. A memory circuit has been incorporated in the device to prevent slow fluctuations from triggering the relay in the absence of an audio signal.

10. Low Temperature Thermostats

Two low temperature thermostats were used in this work. One consisted of the outer dewar of a liquid helium cryostat, and was used for the single temperature of a liquified gas (nitrogen). The sample was contained in a glass tube inside of the dewar to isolate it from the liquid mechanically. About an hour minimum was allowed to elapse after filling the dewar with liquid nitrogen to allow thermal equilibrium throughout the sample. A photograph of this thermostat is shown as figure 11.

After a couple of attempts at making a wide range low temperature thermostat on the basis of a conventional mechanical heat-leak,³⁹ it was conceived to try a flowing gas system as a cooling mechanism. The system developed was the following. A thermostat was constructed from Styrofoam in the form of a narrow rectangular box, that would fit between the pole pieces of the magnet. An external glass dewar vessel was fitted with a thermally insulated tube connecting it with the thermostat. Liquid nitrogen was placed

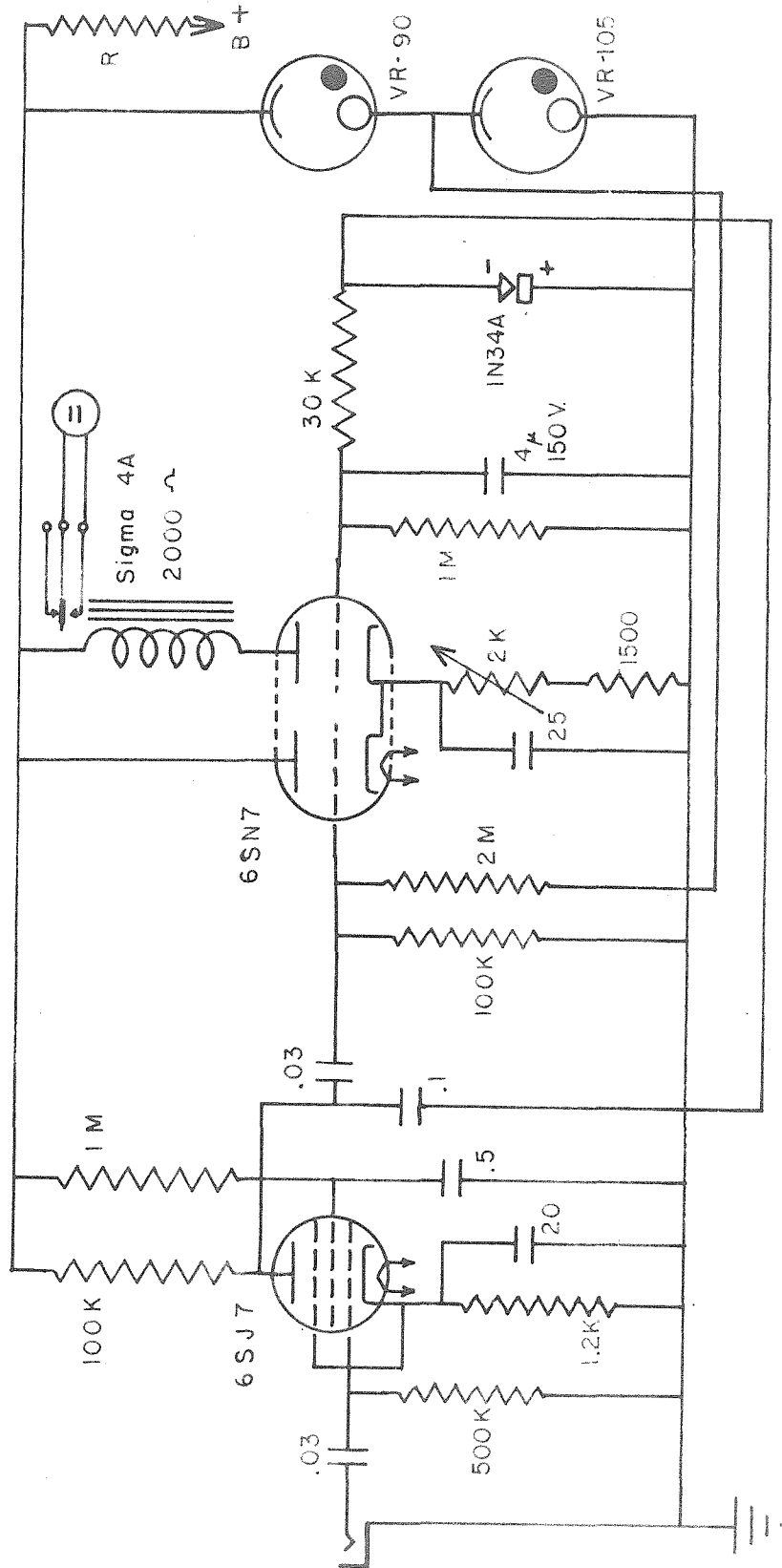


Figure 10. Zero Beat Detector

in the dewar vessel and vaporized to supply cold nitrogen gas which then passed out through the tube and circulated inside of the thermostat. The rate of vaporization could be adjusted, hence the rate of the gas flow. The heat leaking into the thermostat was balanced by the cold gas entering and a stable temperature resulted, which was dependent on the gas flow. The most efficient system would have been to bubble cylinder nitrogen gas into the dewar vessel, but because of the ease of control, heat was developed electrically beneath the surface of the liquid nitrogen, controlling the rate of vaporization. A heater was placed in the dewar consisting of three 70-ohm 10-watt resistors in parallel connection, and these were supplied with power from a Variac. Because the gas flow was very sensitive to the heater dissipation, and therefore, to the a.c. line voltage, the variac input was taken from a Sola constant voltage transformer. This system is one that would be adaptable to automatic control of temperature if so desired.

The temperature was measured by means of a thermocouple fastened to the side of the sample tube. Since the heat capacity of the circulating gas inside the thermostat is low, a period of stable temperature of at least 30 minutes was allowed to assure thermal equilibrium throughout the sample volume. This time was found to be sufficiently long; measurements taken at temperatures where the absorption line width was changing showed that thermal equilibrium was established in about 10 minutes after the attainment of a stable temperature. A photograph of this system in operating position is shown as figure 12. The range of this thermostat was from room temperature down to ca. -140° C.

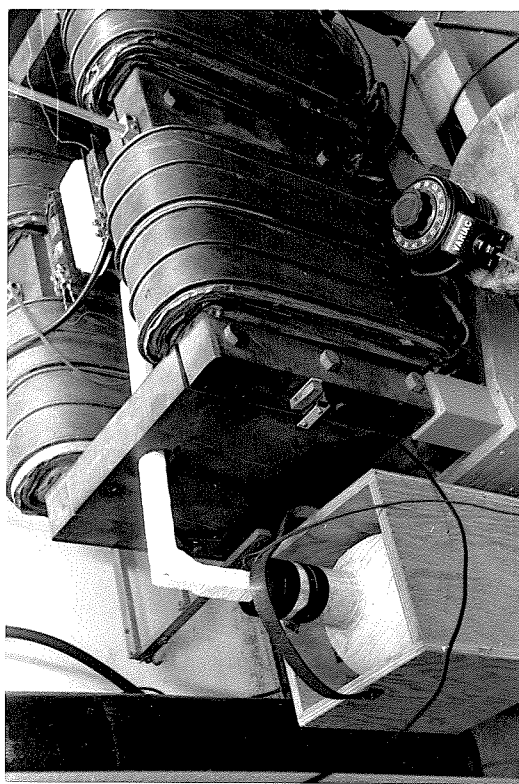


Figure 12
Gas flow thermostat

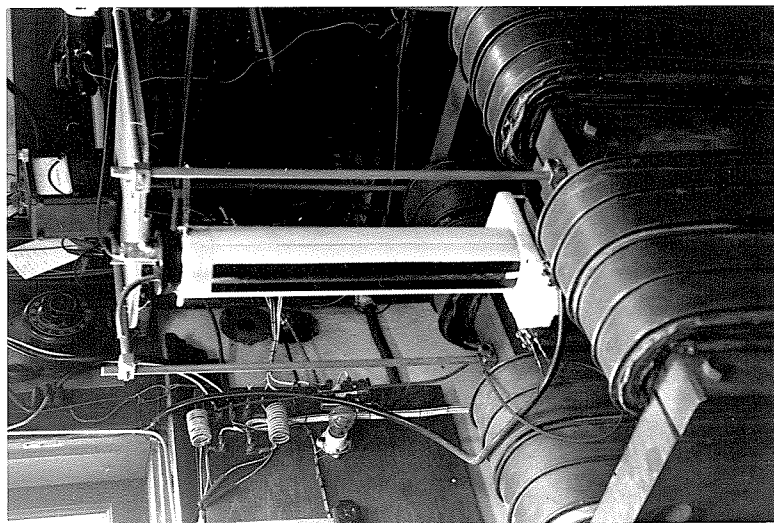


Figure 11.
Liquid nitrogen thermostat

11. Operating Procedure

The operation of the equipment for a low temperature run will be briefly described; the part dealing with low temperature procedures can be omitted if not applicable. The sample material is put in a suitable glass tube and placed in the radio frequency coil in the thermostat. The sample tubes used were of about 1/4 inch diameter and 2 inches long. The nuclear resonance magnetic field control probe is put in the gap of the magnet near the bottom, and the cryostat is placed in the gap from the top. The dewar vessel (filled with liquid nitrogen) and connecting tube for the thermostat are put in place and suitable voltage is applied to the heater in the dewar. The maximum cooling (-140° C.) was obtained with 120 volts applied to the heater. (Care must be taken to see that the heater voltage is removed when the liquid nitrogen has been consumed; a quick calculation will show that the power dissipation of the heater resistors is greatly exceeded.)

The magnetic field control system is put into operation, the steady d. c. generator being set for ca. 5 amperes (house generator G-1) and the magnet cooling water turned on. The operating frequency of the control oscillator is set using the BC-221 frequency meter and the oscillation level set to the lowest point of stable oscillation. The control generator (house generator G-9) is operated manually, changing the magnetic field slowly until the resonance line is observed on the oscilloscope on the controller. The magnetic field is swept far enough for both the H^1 and F^{19} lines to have been seen, the latter occurring at a higher field strength. The controller is then put on automatic operation on the F^{19} line. Detailed instructions for the controller are given

by Humphrey (loc. cit.).

As soon as a stable temperature appears to have been reached in the thermostat, the radio frequency bridge may be balanced. The signal generator and receiver are adjusted to the proper frequency and the bridge balanced, using the signal strength meter on the receiver for indication. The two arms of the bridge are set approximately to resonance by means of the rough tuning controls, by turning the rotary switch on the input of the bridge to select individually one arm and then the other. The amplitude adjustment of the dummy arm is made through a screwdriver adjustment available through the front panel. The rotary switch is turned to the middle position and the two arms of the bridge are balanced against each other with the fine tuning controls to give an output reading of between S-3 and S-7 on the signal strength meter with the r. f. gain control at maximum. The bridge is constructed so that the fine tuning adjustment on the sample part of the bridge controls the phase and that on the dummy arm the amplitude. The bridge is balanced in phase but a small amplitude unbalance is left.

After this is done, the phase sensitive detector can be adjusted for balance and sensitivity, and the field sweep motor and recorder started when thermal equilibrium of the sample is attained. Several runs are generally necessary to properly set sensitivity controls, integration time, sweep rate, and other adjustments.

SECTION 2

VI. AUTOMATIC COULOMETRIC TITRATIONS

INVOLVING AN AMPEROMETRIC END POINT

1. Introduction

Various coulometric titrations and the end points used in this laboratory have been described.^{40, 41, 42, 43, 44, 45 and 46}

This section is concerned with titrations which make use of dual indicator electrode amperometric end points which have been used in this laboratory (see figures 13 and 14).

The dual indicator electrode amperometric end point system forms a basis for a quite versatile titrator. The simplicity of the amperometric system, both functionally as to the physical arrangement, and in its direct application to a number of different titrations is essential in a system where different types of analyses are to be performed. The fact that the response of the indicator circuit is almost instantaneous simplifies circuit design. The dual indicator electrode system has the additional advantage that in most instances the indicator current does not change the concentration of the system being measured.

The three types of amperometric end points which have been encountered and toward which the instrument has been designed are shown in figure 13 (A, B, and C). The most common type of end point is that represented by curve A, where the indicator current has a steady or very slowly rising value until the vicinity of the end point. After the end point is passed it increases rapidly in a linear manner (when plotted against generation time as shown in figure 13). A representative end point of this type occurs in the titration of arsenic

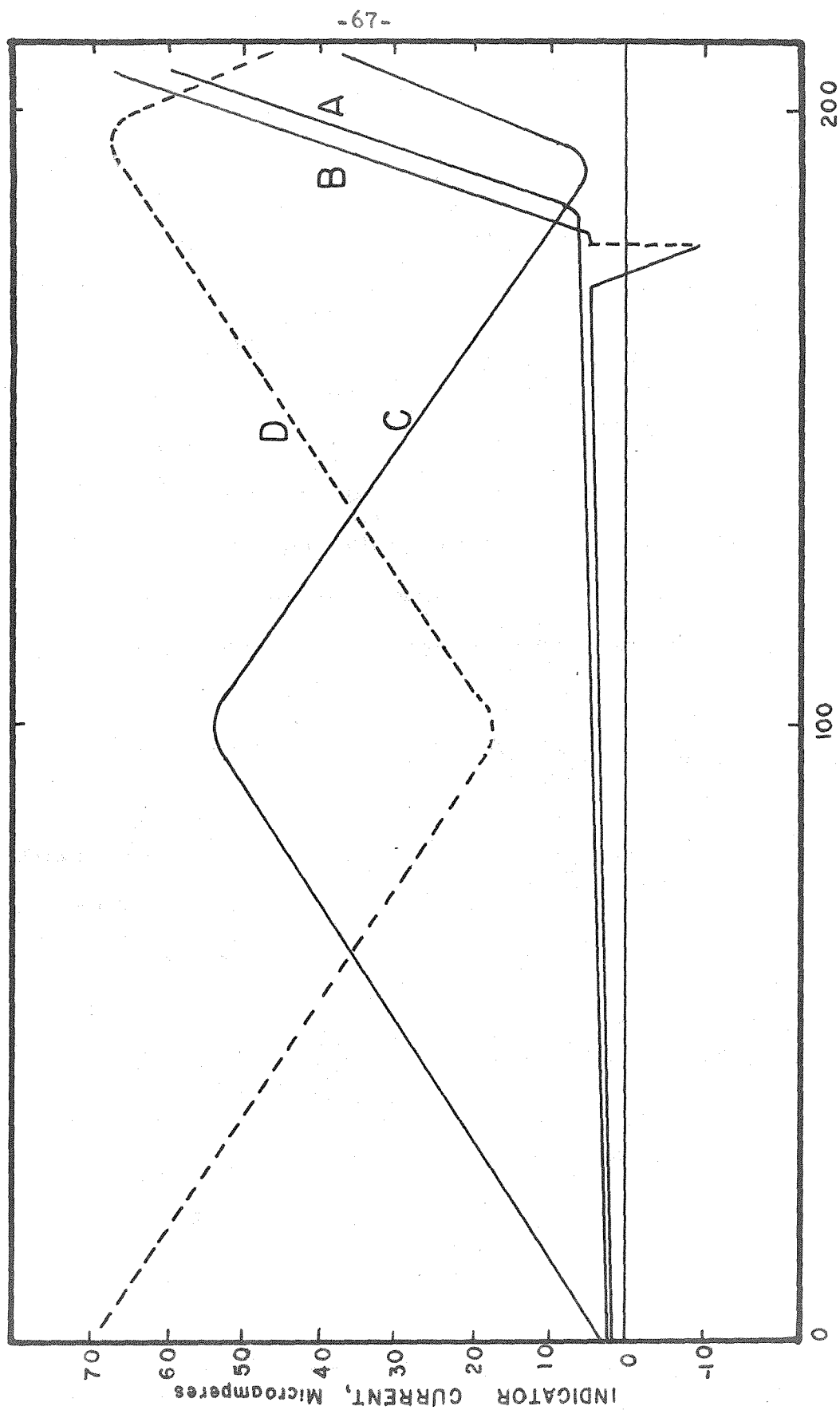


Figure 13

with electrolytically generated bromine.⁴⁹ Several authors describe automatic coulometric titrators which use this type of end point.^{47, 48 and 49} An automatic coulometric titrator which employs potentiometric detection of the end of the titration has been described.⁵⁰

Curve B represents the case where the end point is preceded by a sudden reversal of indicator current as has occasionally been experienced in titrations involving electronically generated bromine and chlorine.⁴³ This reversal is believed to be due to a shift at an electrode from one controlling half-cell to another.

Curve C represents the indicator current in a third type of titration represented by the titration of iodide with electrolytically generated bromine.⁴⁶ In this type of titration, the end point is preceded by a high maximum of indicator current.

The usual method of locating the end point has been described in detail by several authors,^{40, 43 and 46} but essentially consists in all cases of extrapolating the linearly rising post-end-point current to zero current and then applying a correction obtained from a blank titration. Thus, when used with this amperometric technique, it is not required that this instrument stop the titration exactly at the end point, for the exact end point of a titration is obtained mathematically, as indicated. The instrument which has been developed will stop a titration at any pre-set level of indicator current within its range. The analyst then records the value of this indicator current and the elapsed generation time from the timer, generated manually for one second more and again records the necessary data, from which he can calculate the slope of the indicator

current (against generation time) for the purpose of extrapolating to zero end point current. He then applies corrections obtained from a blank determination to find the corrected end point.

Although a dead-stop type of instrument is not necessary for this technique, it would be possible to use the instrument here for routine analyses as a dead-stop instrument with accuracy on the order of one percent. If a number of similar titrations were being made, it would be feasible to calculate a factor (on the basis of a blank titration) to enable the analyst to quickly compute the results of the determination on the basis of the elapsed time as indicated directly by the timer.

One other means of locating the end point would be to record the indicator current and use the automatic controller to stop the titration after end point has been passed. The end point could be obtained from the recorded indicator current in the same manner described above.

Principle of Operation

The instrument described was constructed as an accessory unit which can easily be attached to existing coulometric titrators. The basic titrator is described elsewhere⁴² and consists of a titration cell, an indicating circuit which employs two platinum electrodes in the titration cell, and the generation circuit. The latter consists of an electronically controlled constant-current power supply with an elapsed time indicator, in connection with two other platinum electrodes in the titration cell. For automatic operation, the progress of the titration is followed by measuring the current between the indicator electrodes and the potential

drop across the electrodes (the latter having an inverse relationship to the magnitude of the indicator current). The indicator current is actually measured in the form of a potential created by the flow of the indicator current through a series resistor R (Fig. 14).

Because of the magnitude of the indicator current used in the dual indicator electrode amperometric method of indication described here (0-50 microamperes) and the amount of resistance that can be placed in series with the indicator electrodes (generally 1000 ohms) the potential available for control purposes is on the order of 0 to 50 mv. The instrument therefore must contain some sort of amplifier to produce power sufficient to actuate control relays. The amplifier must be of the direct-current type, since the indicator current is of this classification, and since the direction of flow of this current is of importance. The amplifier selected for this application is a so-called "chopper amplifier" which converts a high gain, stable a. c. amplifier into a d. c. amplifier.

Block diagrams of the apparatus are shown in Figure 15. V_1 and V_2 constitute the d. c. amplifier. V_3 and V_4 are electronic relay circuits. V_4 is a cathode-coupled amplifier intended to give inversion of polarity, and which operates on a positive input (normal flow of indicator current). Vacuum tubes V_3 and V_4 actuate relays when the output of the amplifier reaches a certain pre-set value (that is, when the indicator current or potential drop between the indicator electrodes reaches a certain value). The operation of the instrument on the various end points will be discussed with the aid of the block diagrams of Figure 15.

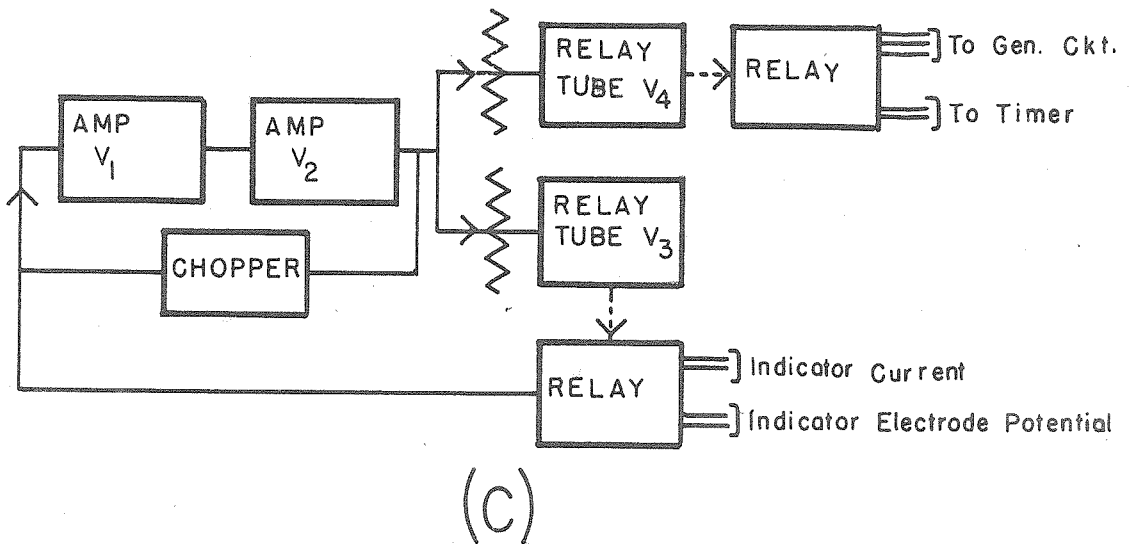
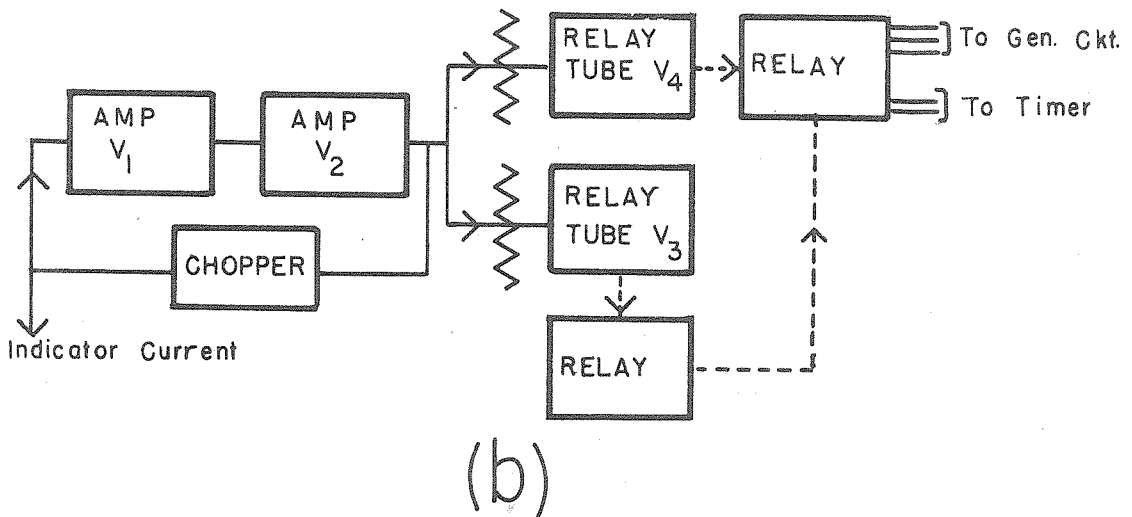
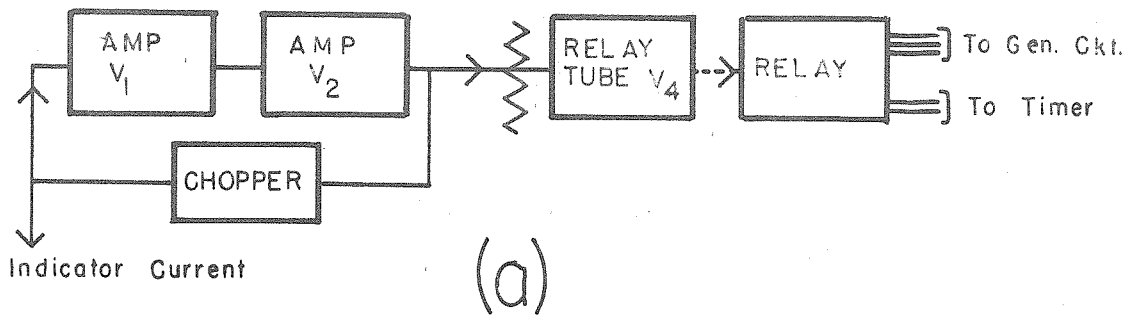


Figure 15

Titration curve A (Fig. 13) is the simplest of the three, and will be described first in a simple way, and then after titrations B and C are discussed, titration curve A will be described fully. Thus, first, circuit V_3 will be ignored. In all three types of end points shown, the termination of the titration occurs on the post-end-point linear rise of indicator current.

End point A consists only of this linear current rise. Relay tube V_4 can be pre-set to stop the titration at any desired value of indicator current, let us say 10 microamperes (Fig. 15a). The potential developed across the sensing resistor R is amplified by V_1 and V_2 and applied to V_4 . When it reaches the pre-set value, the relay in the plate circuit of V_4 closes and the titration is terminated. In actual operation with a titration made on a fast generation rate there may be a lag in the operation of the device and the final indicator current may be 15 microamperes when shut-off was set for 10.

Titration B is similar to A, but contains a sudden reversal of indicator current. When and if this occurs, it is necessary to stop the titration and give the titration system a few seconds to again attain equilibrium conditions. This reversal does not always occur. The appropriate block diagram is Figure 15b. Relay tube V_3 and V_4 are both connected to the amplifier output. V_4 again responds to a positive flow of indicator current as was described for end point A. V_3 responds to a negative flow of indicator current and is set to a low value. If a value of indicator current more negative than this is encountered, this circuit stops the titration. This can either be of the form of a permanent

termination of the titration (which is customary, since this occurs near the end point) or the machine can be set to resume the titration when the indicator current becomes more positive than the pre-set negative value for V_3 , and V_4 then terminates the titration as for end point A.

End point C of Figure 13 requires the use of the potential drop across the indicator electrodes. The appropriate block diagram is Figure 15c. Consider the circuit of Figure 14 which shows a resistance in series with the indicator electrodes. The combined resistance of the sensing resistor R and the resistance of the indicator current meter is of such a value that it is small compared to the resistance of the cell when very little indicator current is flowing and large compared to the cell resistance when 10 or more microamperes of indicator current are flowing. The potential drop across the indicator electrodes will not be constant, but because of the external resistance, will be strongly dependent on the indicator current. This potential drop is shown qualitatively by the dashed curve D of Figure 13. When very little indicator current is flowing, this potential is almost the applied indicator electrode potential. When indicator current flows during the titration, because of the potential drop across the external resistance in the indicator circuit, the potential across the indicator electrodes decreases. If the same system were used for end point C as for A, relay tube V_4 would respond at the first rise of indicator current and the titrations would be stopped quite prematurely. To avoid this, V_3 is used in such a way as to prevent application of the ampli-

fier output to V_4 until just before the end point.

The relay associated with V_3 is used to switch the amplifier input from across the indicator electrodes to across the sensing resistor R . A titration involving end point C begins with the amplifier input connected to the indicator electrodes, whose potential is chosen to be opposite in polarity to the potential across the sensing resistor R . The amplifier output is always connected to both V_3 and V_4 and, since the output of the amplifier will be negative during the first part of the titration, V_4 will not respond to the signal. V_3 does respond to a negative output and is pre-set to respond at a potential near to the applied indicator potential. The desired point of response is just before the maximum on curve D of Figure 13 which occurs just before the end point. When this happens, the relay associated with V_3 changes the input to the potential drop across the sensing resistor R and the titration completes as was described for titration A. By the process just described, the sampling of the high intermediate indicator current by the amplifier is avoided. Since V_3 would respond to the potential across the indicator electrodes at the start of the titration when it is high (Fig. 13, D), a gate tube is used for V_3 , and is disabled during the first part of the titration, effectively producing a condition replacing the initial dashed portion of curve D with that part indicated by dots.

Titration involving end point A can now be accurately described, as the same arrangement is used as for end point C. The indicator electrode potential (when plotted against generation time) bears an inverse relationship to the indicator current

(compare Fig. 13, C and D). During a titration which culminates in an A type of end point, the indicator electrode potential differences will be high until the linear rise of current denoting the end point. Thus, after the disabling of V_3 at the start of the titration, V_3 will respond at once due to the high negative input, transferring the input to the amplifier to the potential drop across the sensing resistor R . The titration will then terminate in the same manner described for end point A at the beginning of this discussion.

No changes in switching need to be made to differentiate between end points A and C. End point B requires a different arrangement; the possibility of a current reversal is known beforehand and necessary switching (from c, Fig. 15, to b) can be done. In the titrations where indicator current reversals are sometimes experienced, intermediate indicator current maxima have not been found.

Electronic Circuits:

With the instrument set for end point B, the input to the amplifier is always the potential drop across the sensing resistor R , and the response of either V_3 or V_4 can terminate the titration. With the instrument set for titration C (or A) the input to the amplifier is switched by the relay associated with V_3 and only V_4 can terminate the titration. Provision has been made for more than one value of sensing resistor to be available. The sensing resistor may be either 500 ohms or 10,000 ohms depending on the conditions of the titration. If the indicator current and its pre-end point maximum is small, R_{29} (10,000 ohms) is used. The

sensing resistance is selected by a switch (S_3).

The schematic circuit for the instrument is presented as Figure 16. With the titrations that have been discussed above, two types of end point control are available. In the case of a titration involving a slow rate of reaction, it may be desirable to have the instrument stop the generation when the pre-set value of indicator current is reached, but to resume the titration if the indicator current falls below the pre-set value of indicator current when the excess intermediate has reacted with the substance being titrated. On the other hand, it may be desirable to have the instrument permanently stop the titration when the pre-set value of indicator current has been reached. This control is accomplished by a switch (S_7) which connects holding contacts on the generation control relay (V_4) representing the "permanent stop" condition and when open is the "slow rate" position.

V_1 and V_2 of Figure 16 and associated components comprise the d. c. amplifier. V_1 and V_2 are connected in the form of a high-gain audio frequency amplifier and this is converted to a direct-current amplifier by means of the chopper indicated. The operation of this unit will not be discussed here. The d. c. amplifier was found to be the most critical part of the assembly as far as construction was concerned; careful isolation and shielding are necessary to avoid pickup. Instabilities were encountered and traced to two sources. The adjustment of the chopper is important; it is a make-before-break switch and coupling between the input and output of the a. c. amplifier occurs if the adjustment

is otherwise. It was also found necessary to bypass the plate circuits of V_1 and V_2 with small condensers to avoid oscillation (C_7 and C_{12}).

V_3 is used as a power amplifier. The sensitive relay in the plate circuit actuates a larger relay which does the necessary switching. Desensitization of V_3 at the start of the titration is accomplished by the network in the suppressor grid circuit. When switch S_4 is thrown from "manual" to "automatic," condenser C_{14} (which was charged to the supply voltage) discharges through R_{18} , with a time constant such that V_3 is gated for about ten seconds. During this time the plate current is zero and response of this stage to the output of the amplifier is avoided. The amplifier output is applied to the tube by means of R_{21} , which in effect determines the indicator electrode potential, or negative indicator current at which relay K_1 will close.

V_4 is a cathode-coupled current amplifier. The value of the cathode resistor is somewhat critical and may have to be determined by experiment to put the operation of the tube in the proper region of plate current. The maximum output of the chopper amplifier is several volts and this is fed to the grid of V_4 . The cut-off level is set by potentiometer R_{25} in the grid of the second half of the tube, which applies a negative bias. This bias is obtained from a resistor (R_{27}) in series with the negative supply connection in order to get a fairly constant voltage. A suitable filter (C_{18} , R_{26} , C_{15}) is provided to remove any ripple components that might be present.

Ordinary constructional practice for wiring has been followed. Pains as to proper shielding on the high gain and high signal parts of the chopper amplifier must be taken. A shield across the chopper socket to isolate the input and output leads of the high gain a. c. amplifier, is recommended. Most component values are not critical. Although the sensitive relays in the plate circuits of V_3 and V_4 were placed under the chassis in this instrument, an arrangement which would permit them to be accessible for adjustment in the normal operating position would be very desirable, since their operation is greatly influenced by gravity.

The amplifier used has more than ample gain, and some sort of feedback could be profitably included for the purpose of stabilization and prevention of amplifier saturation. It has not been attempted here. In the interest of reducing transients which may be produced by switching, all relay contacts carrying 110 v. current have been appropriately bypassed by capacitors, which are not shown in Fig. 16.

A lever-type telephone switch (S_2) changes the circuitry from end point B to A and C (Fig. 13), switching the input of the amplifier and the sequencing of V_3 and V_4 . A push button switch (S_6) is used as a "clearing" switch to open all relays at the start of a titration.

Experimental

Several different types of titrations have been successfully performed with the automatic instrument. The prime function of the instrument is to stop the titration in the vicinity of the end point. Although experimental results are presented, it is

emphasized that the accuracy of coulometric titrations involving dual indicator electrode amperometric end points determined as described above is not dependent upon whether the titration is performed by manual or automatic control of the generation. The crucial test was that the titration was automatically stopped at or near the proper post-end point current.

Titration of tripositive antimony by means of electrolytically generated bromine of the type described by Brown and Swift⁴⁰ have been carried out with the instrument described above by E. A. Butler of this laboratory. In every case the titration was stopped at the pre-set indicator current level, and the results of the titrations agreed within experimental error (0.2%) with the calculated amount of tripositive antimony taken.

Titration of thiosulfate with electrolytically generated iodine⁴⁴ were made by J. K. Rowley of this laboratory with both manual and automatic control of the generation. The instrument worked satisfactorily in this application, both methods of control giving similar results.

To test this instrument on an end point such as represented by C of Figure 1, titrations of iodide by electrolytically generated bromine were performed using both manual and automatic control. The titrations were done so as to duplicate the method of Wooster, Farrington and Swift⁴⁶ except that by necessity here the indicator current was allowed to flow throughout the titration. The results of one series of titrations are summarized in Table 1. Here A is the potentiometer setting which adjusts the shut-off level on V_4 , i_0 is the indicator current at the start of the titration, t_{end}

is the reading on the timer when the titration stops, i_t is the indicator current at the time of stopping, and i_{t+1} is the indicator current after one second of manual generation after stopping. The calculated time of the end point is T and W is the calculated weight of iodide found. The correction from a blank determination was negligible. The accuracy and reproducibility of the results are comparable to those in Wooster, Farrington and Swift⁴⁶ and independent of the setting of the potentiometer A.

Before making titrations with the automatic controller, as with any piece of electronic apparatus it is advisable to allow about a twenty minute warm-up period. It has been found necessary here to perform a couple of initial titrations at the beginning of each new series of runs in order to establish the two potentiometer settings required for correct shut-off points. The use of the instrument for dead stop titrations has not been explored. For a series of titrations carried out under similar conditions, it should be possible to calibrate the machine for dead-stop usage when maximum accuracy of the method is not required.

Table 1. Titrations of Iodide by Bromine

Run	A	i_o	t_{end}	i_t	i_{t+1}	T	W
1	60	1 μ amp.	87.6 ₅ sec.	29 μ a	34 μ a	81.8 ₅ sec.	546 μ g
2	60	0	87.0 ₂	31	37	81.8 ₆	546
3	51	1	85.5	22	27	81.1 ₀	541
4	51	1	85.0	22	30	82.2 ₅	549
5	51	1	85.6	22	29.5	82.6 ₇	551
6	60	1	86.0	24.5	30.5	81.8 ₈	547
7	60	1	85.9 ₂	28	35	81.9 ₀	547
8	60	1	86.2	26	32	81.8 ₇	547
9	62	0	86.1 ₈	29.5	36.5	81.9 ₇	548
10	50	0	84.7 ₈	16	21	81.5 ₈	544
11	62	1	85.8 ₈	28	35	81.8 ₈	547
548 μ g of iodide taken for each run							
ave. found							546 μ g
s.d.							2.5 μ g

Legend for Figure 16

C ₁	0.5 μ fd. 600 volt paper
C ₂	0.02 μ fd. 600 volt paper
C ₃	25 μ fd. 25 volt electrolytic
C ₄	0.1 μ fd. 400 volt paper
C ₅	0.1 μ fd. 400 volt paper
C ₆	0.05 μ fd. 600 volt paper
C ₇	100 μ m. disc ceramic
C ₈	25 μ fd. 25 volt electrolytic
C ₉	0.1 μ fd. 400 volt paper
C ₁₀	0.1 μ fd. 400 volt paper
C ₁₁	0.5 μ fd. 600 volt paper
C ₁₂	100 μ m. disc ceramic
C ₁₃	0.5 μ fd. 400 volt paper
C ₁₄	8 μ fd. volt electrolytic
C ₁₅	0.1 μ fd. 200 volt paper
C ₁₆	8 μ fd. 450 volt electrolytic
C ₁₇	8 μ fd. 450 volt electrolytic
C ₁₈	50 μ fd. 50 volt electrolytic
C ₁₉	1 μ fd. 400 volt paper
F	fuse 3 amp.
J	Test prod jack for meter
K ₁	Sensitive relay: Leach No. 1037 (1750 ohms d.c. resistance)
K ₂	Sensitive relay: Leach No. 1037 (1750 ohms d.c. resistance)
K ₃	Control relay: Leach No. 2127 (110V. A.C.)
K ₄	Control relay: Leach No. 2127 (110 V. A.C.)
L ₁	8-henry 80-ma. choke
P ₁	6.3 volt pilot light
P ₂	110 volt pilot light

R ₁	1.5 M Ω	1/2 watt
R ₂	2 M Ω	1/2 watt
R ₃	2.2 K Ω	1 watt
R ₄	100 K Ω	1/2 watt
R ₅	100 K Ω	1/2 watt
R ₆	250 K Ω	1/2 watt
R ₇	5 K Ω	1/2 watt
R ₈	1 M Ω	1/2 watt
R ₉	2.2 K Ω	1 watt
R ₁₀	100 K Ω	1/2 watt
R ₁₁	100 K Ω	1/2 watt
R ₁₂	250 K Ω	1/2 watt
R ₁₃	5 K Ω	1/2 watt
R ₁₄	1.8 M Ω	1/2 watt
R ₁₅	68 K Ω	1 watt
R ₁₆	100 K Ω	1/2 watt
R ₁₇	100 K Ω	pot. (control "B")
R ₁₈	47 K Ω	1/2 watt
R ₁₉	1 K Ω	1 watt
R ₂₀	25 K Ω	1/2 watt
R ₂₁	33 K Ω	1 watt
R ₂₂	100 K Ω	1/2 watt
R ₂₃	380 K Ω	1/2 watt
R ₂₄	560 Ω	1 watt
R ₂₅	100 K Ω	pot (control "A")
R ₂₆	33 K Ω	1/2 watt
R ₂₇	470 Ω	10 watt
R ₂₈	40 K Ω	5 watt
R ₂₉	9 K Ω	1/2 watt
R ₃₀	500 K Ω	1/2 watt
R ₃₁	dummy load (300 Ω 1 W)	

S ₁	SPST toggle switch (power on-off)
S ₂	4PDT telephone switch (titration A, C-B)
S ₃	SPST toggle switch (sensitivity low-high)
S ₄	DPDT toggle switch (automatic-manual)
S ₅	DPDT push button (manual generation)
S ₆	SPST push button (N.C.) (clearing button)
S ₇	SPST toggle switch (permanent stop)
T ₁	Power transformer: Thordarson No. T22R31
V ₁	5879
V ₂	5879
V ₃	6AS6
V ₄	6J6
V ₅	5Y3GT
X ₁	Stevens-Arnold D.C. -A.C. chopper type 243
X ₂	plug for 110 volt A.C. mains
X ₃	socket for timer power

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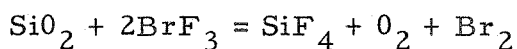
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PROPOSITIONS

1. The study of the structure of the nucleus could be carried another step by extending the observations of the angular correlation of the radioactive emission of aligned nuclei to the study of the angular correlation of neutron absorption by aligned nuclei.
2. A study of the species present in fast reactions in gaseous systems, such as flames, could be made by means of cyclotron resonance. Free electrons in particular could be easily identified by this means.
3. The study of the temperature at which the nuclear magnetic resonance line of a substance exhibiting internal motion narrows, as a function of Larmor frequency, would help to elucidate the characteristics of the motion involved. The most practical way to do this would be to make measurements at low magnetic field strengths.
4. Venkataraman and Fraenkel have found what they think is the paramagnetic resonance spectrum for the para-benzosemiquinone ion. This could be confirmed by observing the effect of saturating the proton spin system while observing the hyperfine pattern of the paramagnetic resonance spectrum.¹
5. The peaking strips² used to trigger the operation of synchrotron accelerators should be replaced by a paramagnetic resonance device.
6. It has been observed by King and Neptune that an ion containing

both chromium(III) and chromium(IV) exists in aqueous solution.³ Their spectrophotometric measurements indicate no interaction between the two forms of chromium in the ions CrCrO_4^+ and $\text{CrCrO}_4\text{H}^{++}$, but this could be further investigated using radioactive chromium to measure the exchange rate.

7. Emeleus and Woolf have proposed the quantitative reaction



as an appropriate one for the study of the heat of formation of BrF_3 .⁴ There is a strong possibility that SiF_4 would form a complex fluoride ion⁵ in liquid BrF_3 which would be undesirable for such a study.

8. Andrew has studied motions in certain solid hydrocarbons by means of nuclear magnetic resonance. His suggested cause for the reduction in proton magnetic resonance line width near the melting point of dicetyl can be replaced by a much simpler one.⁶

9. The nuclear resonance technique of spin echoes could be used in the field of electron paramagnetic resonance for the measurement of relaxation times.⁷

10. An electromagnetic system of modulation for beam pentode vacuum tube is proposed.

11. In their study of a reactive species of magnesium (presumably unipositive magnesium ion), the possibility of a significant

photochemical reaction has been ignored by Petty, Davidson and Kleinberg.⁸

12. A system of periodic visitation of undergraduate classes conducted by graduate teaching assistants in chemistry should be initiated by the course and department heads.

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