The dielectric relaxation of V$_2$O$_5$ was investigated using the method of Davidson and Cole. By means of an Argand diagram, deviation from an exact Debye dielectric was established. This was done with the parameter $\beta$. For a Debye dielectric $\beta = 1$. The largest value of $\beta$ for V$_2$O$_5$ was 0.50.

The activation energy of the dielectric relaxation process was determined as 0.16 eV.

The average activation energy of d-c conduction was determined to be 0.23 eV. This was measured by means of a two-electrometer system designed by the author.

The process of polaron hopping was discounted as the process of dielectric relaxation. This was attributed to the high critical temperature requirement set down by Sewell. In place of the hopping model, tunneling is accepted as the means of dipolar reorientation. The value of the d-c activation
energy is 0.07 eV larger than the a-c related process. This is the additional energy required for ionization of an electron from a positive defect, such as an interstitial impurity cation or oxide-ion vacancy, to which it experiences Coulombic attraction.
DONOR CENTERS IN VANADIUM PENTOXIDE

by

John Fredric Yerke

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It would be impossible to express my gratitude to the many people who have helped make this thesis a reality; may this thesis serve in some way to do so.

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DEDICATION

to my wife,

Kathy
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DONOR CENTERS IN VANADIUM PENTOXIDE

I. INTRODUCTION

Single crystalline vanadium pentoxide, when grown from the melt, has been shown to be a low-mobility n-type semiconductor, which if pure and stoichiometric, would be an insulator. Conduction is due to either the loss of oxygen at the melting point or the presence of impurities. The electron mobility is 0.1 to 0.001 cm²/V sec.

The structure of V₂O₅ is orthorhombic with space group Pmmn.

Although V₂O₅ is anisotropic, all measurements to be reported here were made with the field parallel to the b-axis only, due to the thinness of samples.

The existence of a dipolar center with an activation energy of 0.24 eV for dipolar reorientation has been reported by Mar (10). In addition, he reports the relaxation process to be approximately Debye-type. It will be shown that the relaxation process approaches a Debye representation but is characterized more adequately by a Cole-Davidson (3) treatment, in which a distribution of relaxation times is assumed.

By both oxygenating at high temperature and pressure, and doping with copper, the effect upon the d-c conduction is examined. The d-c conduction is measured by a unique two electrometer system which adds to the accuracy of the measurement.

By comparison of the activation energies for dielectric
relaxation and d-c conduction, the process of electron migration can be clarified. ESR measurements are used to support the conclusions. Previously, (10) it has been assumed that the process of dielectric relaxation was one of thermally activated polaron hopping; however, in the temperature range of interest here, there is good reason to believe the process is more likely one of thermally activated tunnelling as will be shown.
II. THEORY OF DEBYE TYPE DIELECTRIC RELAXATION

Macroscopic Derivation of Debye Equations

The response of a dielectric to an electric field on a macroscopic scale is best understood by use of the Debye equations. The basis for the Debye equation is the differential equation (2.8).

When a parallel plate capacitor in vacuum is connected to an external voltage source, an electrical field, $E$, results in the cavity between the plates. The electric field is given by

$$E = 4\pi \sigma_0$$  \hspace{1cm} (2.1)

where $\sigma_0$ is the charge per unit area for the capacitor in vacuo.

If a dielectric is introduced into the capacitor and the external voltage maintained constant, more charge will flow into the capacitor. The dielectric reacts by increasing the charge density ($\sigma$) on the capacitor plates, giving

$$\sigma = \varepsilon_s \sigma_0$$  \hspace{1cm} (2.2)

where $\varepsilon_s$ is the static dielectric constant, which represents equilibrium after an infinite amount of time. The polarization and external field combine to hold the charge on the electrodes. From this, the definition of polarization, $P$, is obtained as

$$\sigma_0 + P = \sigma.$$  \hspace{1cm} (2.3)
By combining the previous equations, the definition of the static dielectric constant

\[ \varepsilon_s - 1 = \frac{4\pi P_s}{E} \]  

(2.4)
is obtained. The polarization, \( P_s \), is the static value.

If \( E \) is a function of time, then as the value of time approaches infinity, the polarization approaches the static or equilibrium value. A reasonable, and commonly made assumption is that the rate of approach to equilibrium is proportional to the distance from equilibrium, or

\[ \tau \frac{dP(t)}{dt} = P_s - P(t) \]

(2.5)

where \( \tau \) is constant.

By assuming the static polarization to consist of only an optical and static dipolar polarization, which are referred to as \( P_{\text{opt}} \) and \( P_{\text{Do}} \), respectively, the time-independent polarization may be separated in Equation (2.4). This is possible because the optical polarization refers to a changing field in negligible time at all frequencies used for electrical measurements. Thus, Equation (2.4) becomes

\[ \varepsilon_s - 1 = \frac{4\pi}{E} (P_{\text{Do}} + P_{\text{opt}}) \]

(2.6)
The definition of the optical dielectric constant, \( \varepsilon_{\text{opt}} \), is now obtained as

\[ \varepsilon_{\text{opt}} - 1 = \frac{4\pi P_{\text{opt}}}{E} \]

(2.7)
where $\varepsilon_{\text{opt}}$ is measured at frequencies of optical interest. Let the time-dependent dipolar polarization be $P_D$. If an electric field, $E(t)$, is applied to a dielectric, $P_D$ then responds according to the differential equation

$$\tau \frac{dP_D(t)}{dt} + P_D(t) = P_D(0)$$

(2.8)

By combining Equations (2.6) and (2.7), the equilibrium value of $P_D(0)$ is obtained for the field $E(t)$. When substituted into Equation (2.8), the result is

$$\tau \frac{dP_D}{dt} + P_D(t) = (\varepsilon_s - \varepsilon_\infty) \frac{E(t)}{4\pi}$$

(2.9)

where $\varepsilon_\infty$ is the dielectric constant at frequencies much greater than the frequency of dipolar reorientation.

The general solution of Equation (2.9) is obtained for a periodic field

$$E^*(t) = E_0 \exp(1\omega t)$$

(2.10)

and is expressed as a complex quantity, $P_D^*$, for the dipolarization

$$P_D^*(t) = K e^{-\gamma t} + \frac{1}{4\pi} \frac{\varepsilon_s - \varepsilon_\infty}{1+i\omega \tau} E_0 e^{i\omega t}$$

(2.11)

where $K$ represents any initial polarization. The first term decays with time and for alternating current measurements may be neglected when compared with the second term. This enables the complex dielectric constant, $\varepsilon^*(\omega)$ to be defined by

$$\varepsilon^*(\omega) - \varepsilon_\infty = \frac{4\pi}{E^*} \frac{P_D^*(\omega, t)}{E^*(\omega, t)}$$

(2.12)
For $K = 0$, Equation (2.11), when substituted into (2.12), yields

$$\epsilon^*(\omega) - \epsilon_\infty = \frac{\epsilon_s - \epsilon_\infty}{1 + i\omega \tau} \quad (2.13)$$

If $\epsilon^*(\omega)$ is separated into its real ($\epsilon_1(\omega)$) and imaginary ($\epsilon_2(\omega)$) parts, the Debye equations result:

$$\epsilon_1(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2 \tau^2} \quad (2.14)$$

$$\epsilon_2(\omega) = (\epsilon_s - \epsilon_\infty) \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (2.15)$$

Experimentally, the measured values are $\epsilon_1(\omega)$ and the loss tangent,

$$\tan \delta = \frac{\epsilon_2(\omega)}{\epsilon_1(\omega)} \quad (2.16)$$

Expressed in terms of the Debye equations, $\tan \delta$ is given by:

$$\tan \delta = \frac{(\epsilon_s - \epsilon_\infty) \omega \tau}{\epsilon_s + \epsilon_\infty \omega^2 \tau^2} \quad (2.17)$$

**Molecular Derivation of Debye Equations**

The Debye equations are also obtainable from a molecular model with a single relaxation time. An example of this model, which is simple and useful, is known as the bistable model; it is treated by Frohlich (5) and Daniel (2).

The effective field acting on a dipole is generally not solely the externally applied field, $E$, but a contribution of it and the field due to dipolar interaction. The
field acting on the dipole is $E_i$, where $E_i \geq E$. The bistable model begins with the assumption of negligible electrostatic interaction (i.e. $E_i = E$). To neglect the dipolar interaction, a low concentration of $N$ bistable dipoles per unit volume must be assumed. The bistable model assumes that a particle of charge, $e$, may be in one of two sites, 1 and 2, separated by a distance, $b$. These sites are the minima of potential energy wells. When an electric field, $E(t)$, is applied to the system, a difference in potential energy of the two sites results. Figure 1, which illustrates the bistable model, is drawn with solid lines representing the condition without the applied field and dashed lines representing the presence of the field.

The potential energy due to the applied field is

$$\phi = \phi_1 - \phi_2 = ebE(t) = ebE(t) \cos \theta \quad (2.18)$$

where $\theta$ is the angle between line 1-2 in Figure 1 and the direction of the field. The bistable model requires the assumption that $\cos \theta = 1$ and constant activation energy for dipolar reorientation.

This model is equivalent to a dipole since a movement of the charge from one energy well to the other is equivalent to a 180-degree reorientation of the dipole moment. The magnitude of the moment is $eb/2$ and can be imagined to be hinged about the center point 0.

In the microscopic assembly, $N$ bistable dipoles are imagined as being in a heat reservoir, where spontaneously
Figure 1. Bistable model: the potential energy as a function of distance.
active particles exchange energy with each other and the dipoles. When a charge in one well has obtained enough energy, the dipole reorients. Once in the other energy well, the energy of the charge is dissipated to that heat reservoir and the process is ultimately repeated.

If \( E(t) \) is applied in the direction shown, the frequency of dipoles jumping from Well 1 to Well 2 is given by the difference in potential energy between the two wells as

\[
W = A \exp \left[ -\frac{H - \mu E(t)}{kT} \right]
\]

(2.19)

where \( T \) is the absolute temperature, \( k \) is the Boltzmann constant, and \( H \) is the activation energy, that is, the height of the potential barrier in zero field. The quantity \( A \) represents the frequency of attempts to overcome the potential barrier and is independent of temperature.

Equation (2.19) can be simplified by examining the magnitude of \( E(t) \). For dipoles in normal dielectrics, \( \mu \) is in the vicinity of \( 10^{-18} \) e.s.u., and \( E \) for fields below breakdown strength is always less than \( 10^5 \) e.s.u. Therefore, if

\[
\frac{\mu E(t)}{kT} \ll 1
\]

(2.20)

and the frequency of jumps in the absence of an applied field is expressed as

\[
W = A \exp \left[ -\frac{H}{kT} \right],
\]

expansion of the exponential in (2.19) leads to

\[
W_{12} = W \left[ 1 - \frac{\mu E(t)}{kT} \right]
\]

(2.21)
\[ W_{21} = W \left[ 1 + \frac{\mu E(t)}{kT} \right], \quad (2.22) \]

where \( W_{21} \) is the frequency of jumps from well 2 to well 1, and vice versa for \( W_{12} \).

The total number of charged bistable dipoles, \( N \), is comprised of \( N_1 \) and \( N_2 \) charges, which occupy well 1 and 2, respectively. By assuming the number of charges leaving one well equals the number of charges entering it, \( N_1 \) and \( N_2 \) will remain constant. This is expressed as

\[ N_1 W_{12} = N_2 W_{21} \quad (2.23) \]

The change in the number of dipoles in well 1, with respect to time is

\[ \frac{dN_1}{dt} = N_2 W_{21} - N_1 W_{12} \quad (2.24) \]

The constancy of jumps implies

\[ \frac{d(N_1 - N_2)}{dt} = 2 \frac{dN_1}{dt} \quad . \quad (2.25) \]

Equations (2.24) and (2.25), when combined with the derived expressions for \( W_{12} \) and \( W_{21} \), yield

\[ \frac{1}{2} \frac{d(N_1 - N_2)}{dt} = - N_1 W_{12} + N_2 W_{21} \quad (2.26) \]

By multiplying Equation (2.26) by \( \mu \) and substituting

\[ P_D = \mu (N_1 - N_2) \]

\[ T_D \frac{dP_D(t)}{dt} + P_D(t) = \frac{N\mu^2}{kT} E(t) \quad (2.27) \]

where

\[ T_D = \frac{1}{2W} = \frac{1}{2A} \exp \left[ -\frac{H}{kT} \right] = T_H \exp \left( -\frac{H}{kT} \right) . \quad (2.28) \]
Equation (2.27) is now in the form of a characteristic linear differential equation for a single relaxation time. 

$\tau_D$ is the time for the relaxation process and depends only on temperature. It may be expressed physically as the reciprocal of the frequency of jumps across the potential hill. 

$\tau_H$ is also temperature dependent, but $H$ is assumed not to be. 

The solution of Equation (2.27), in terms of quantities relating to the experimental measurements, is Equation (2.13), which gives the Debye Equations (2.14) and (2.15).

**EMPIRICAL METHODS FOR EVALUATION OF DIELECTRIC MEASUREMENTS**

**Cole-Cole Plot (Argand Diagram)**

An equation analogous to Equation (2.13) may be written in an attempt to fit experimental observations in the form

$$\varepsilon^*(\omega) = \varepsilon_1 - i \varepsilon_2 = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1+i\omega\tau_0)} \beta$$

(2.29)

$\varepsilon_s$ and $\varepsilon_\infty$ are the limiting low and high-frequency dielectric constants, respectively, and $\tau_0$ is a relaxation time. The parameter $\beta$ assumes values between zero and one. When $\beta = 1$, Equation (2.29) conforms exactly to the Debye result. If Equation (2.29) is separated into its real and imaginary portions, the result is:

$$\varepsilon_1 - \varepsilon_\infty = (\varepsilon_s - \varepsilon_\infty)(\cos \phi) \beta \cos \beta \phi$$

(2.30)

$$\varepsilon_2 = (\varepsilon_s - \varepsilon_1)(\cos \phi) \beta \sin \beta \phi$$

(2.31)
where the \( \tan \phi = \omega \tau_0 \). Similarly, if \( \beta \) is set equal to one and the value of \( \phi \) substituted into Equations (2.30) and (2.31), the Debye equations are obtained.

The analysis of experimental data may be facilitated by certain graphical methods which permit the derivation of parameters by geometric construction. One of the most useful plots concerning dielectrics is constructed by plotting \( \epsilon_2(\omega) \) against \( \epsilon_1(\omega) \) at the same frequency, in either Cartesian or complex coordinates. This type of plot is referred to as a Cole-Cole plot or Argand diagram (2). Two examples of the Cole-Cole plot are shown in Figure 2. By assuming Equation (2.29) to be valid, the Cole-Cole plot allows a determination of the values \( \epsilon_s, \epsilon_\infty, \) and \( \beta \), and indirectly \( \tau_0 \).

When Equations (2.30) and (2.31) are written in polar coordinates

\[
r = \left[ (\epsilon_1 - \epsilon_\infty)^2 + \epsilon_2^2 \right]^{\frac{1}{2}}
\]

and

\[
\theta = \tan^{-1} \left[ \frac{\epsilon_2}{\epsilon_1 - \epsilon_\infty} \right].
\]

With the appropriate substitution, one obtains

\[
r = (\epsilon_s - \epsilon_\infty) \left[ \cos(\theta/\beta) \right]^{\beta} \tag{2.32}
\]

and

\[
\tan \theta = \tan \beta \theta, \text{ or } \omega \tau_0 = \tan(\theta/\beta). \tag{2.33}
\]

For \( \beta < 1 \) (e.g. 0.55), the Cole-Cole plot of Figure 2a is obtained. The values of \( \epsilon_s \) and \( \epsilon_\infty \) are specified where the arc intercepts the axis. In other words, the locus of Equation (2.32) in the complex plane, is the limiting curve. As \( \omega \to 0 \), a semi-circle with its center on the real axis is
Figure 2. General Cole-Cole plots for (a) $\beta = 0.55$ for (b) $\beta = 1.0$
obtained, and as $\omega \to \infty$, a straight line, which makes an angle $\beta \pi/2$ with the $\varepsilon_1$-axis, is obtained. For a material which is an exact Debye dielectric, Figure 2b is expected. In this figure, $\beta \pi/2$ is equal to 90 degrees, which gives $\beta = 1$ and agrees with earlier statements.

$\tau_0$ is determined by plotting $\tan(\theta/\beta) = \tan \left[ \frac{\varepsilon_2}{(\varepsilon_1 - \varepsilon_\infty)^2} \right]$ against frequency. This gives a straight line. Where this line crosses $\tan(\theta/\beta) = 1$, the value of the frequency, $f_c$, is obtained and gives

$$\tau_0 = \frac{1}{2} \pi f_c \quad (2.34)$$

For Figure 2a, $f_c$ does not correspond to the maximum value of $\varepsilon_2$, but to the point on the complex plane locus for which $\theta = \beta \pi/4$. However, Figure 2b, which is for an exact Debye dielectric, does have the maximum value of $\varepsilon_2$ at $\theta = \beta \pi/4$, as would be expected. This will be discussed later.

For a Debye dielectric ($\beta = 1$), a useful and relatively accurate determination of $\tau$, with respect to the real Debye equations, is obtained from a dispersion curve. A dispersion curve is a graph of the frequency dependence of the real or imaginary dielectric constant. An example of such a graph of $\varepsilon_1$ vs. $\log \omega$, is shown in Figure 3. To obtain $\tau$, Equation (2.14) is used. The value of $\varepsilon_1(\omega)$ is $\varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)/2$ and the respective frequency is substituted into Equation (2.14) with $\varepsilon_\infty$ and $\varepsilon_s$, and $\tau$ is then calculated. The main requirement for such a calculation is well
Figure 3. General dielectric dispersion curve
defined high and low frequency regions.

**Distribution of Relaxation Times**

The dispersion of a Debye dielectric may be represented by a simple relaxation process (i.e. a single relaxation time), which is characterized by a distribution function, \( y(\tau) = \frac{d\varepsilon_s}{d\tau} \). An example of this function is the physically simple model developed by Frohlich (5).

\( \tau \) is dependent on temperature according to Equation (2.28). By assuming that the activation energy varies from \( H \) to \( H + \nu_1 \), the relaxation time varies between

\[
\tau_0 = A \exp \left[ \frac{H}{kT} \right] \quad (2.35)
\]

and

\[
\tau_1 = A \exp \left[ \frac{H + \nu_1}{kT} \right] \quad (2.36)
\]

where \( A \) is the reciprocal of the frequency of jumps.

Frohlich assumes that the dipoles in an energy interval, \( d\nu \), contribute to the static dielectric constant, a term,

\[
d\varepsilon_s = (\varepsilon_s - \varepsilon_\infty) \frac{d\nu}{\nu_1} \quad (2.37)
\]

which is independent of the position of the interval \( d\nu \). The definition of the distribution function then gives

\[
d\varepsilon_s = y(\tau) \frac{d\tau}{d\nu} \frac{d\nu}{d\tau}. \quad (2.38)
\]

The differentiation of Equation (2.36) with variable \( \nu \) and use of the appropriate substitution yields

\[
y(\tau) = (\varepsilon_s - \varepsilon_\infty) \frac{kT}{\nu_1} \frac{1}{\tau} \quad \text{for} \quad \tau_0 < \tau < \tau_1, \quad (2.39)
\]
\[ y'(\tau) = 0 \quad \text{for} \quad \tau < \tau_1 \quad \text{and} \quad \tau > \tau_1, \] (2.40)

the distribution function for a Debye dielectric.

However, few dielectrics are truly Debye-type, and instead, exhibit dispersion over much higher or lower frequencies and over broader frequency ranges. The broader dispersion may also be represented in terms of the distribution of simple relaxation processes. Davidson and Cole (3) characterize this with the distribution function \( F(\tau/\tau_0) \) for relaxation times \( \tau \). The time, \( \tau_0 \) is the relaxation time of Equation (2.28). The function is

\[ F(\tau/\tau_0) = \frac{\sin \beta \pi}{\pi} \frac{\tau}{\tau_0 - \tau}, \quad \text{for} \quad \tau > \tau_0 \] (2.41)

Written in an analogous form, the fraction, \( f \), of relaxation processes with relaxation time less than a specified \( \tau \) is

\[ f(\tau/\tau_0) = \left( \frac{\sin \beta \pi}{\pi} \right) \frac{\tau}{\tau_0} \frac{\beta}{\beta - 1}, \quad \text{for} \quad \tau < \tau_0 \] (2.43)

where \( \beta \) is the incomplete beta function.

Figure 4a shows the fraction, \( f(\tau/\tau_0) \) of relaxation time less than \( \tau \) computed for \( \beta = 0.60 \). For example, one sees that ten percent of assumed processes must have \( \tau \) less than \( \tau_0/20 \).

If \( \beta \) were equal to one, then Equation (2.39) and (2.40) would be used to show the distribution of relaxation times. When expressed in terms of fraction of relaxation processes, Figure 4b best explains that distribution.
Figure 4. Cole-Davidson distribution of relaxation times for (a) $\beta = 0.6$, and (b) $\beta = 1.0$
III. DEBYE TYPE RELAXATION DUE TO TRAPPED ELECTRONS

The Center

Debye type dielectric loss due to trapped electrons is explained by Fröhlich (6). He proposes a center which consists of a charge carrier (electron or hole) which is trapped in the field of a crystalline defect or impurity atom or ion. For dielectric loss to exist, two conditions must be met: 1) at least two available levels must exist so that transition between the two levels results in the reorientation of the electric moment of the center, and 2) the energy levels are required to have, at a temperature $T$, an energy spread considerably less than $kT$. The second condition implies that the electronic states could be superposed to form the required localized states in a quasi-classical way.

The quasi-classical behavior results from the interaction of the electron with its neighboring ions (7). Since these ions become displaced, the wave function of the entire system should be considered, not the electron alone. This reaction then reduces the spread of energy levels by a factor of the order of

$$F = \exp\left(-\frac{\Delta^2}{d^2}\right)$$ (3.44)

where $\Delta$ is the displacement of an ion to a neighboring electron and $d$ is the zero point amplitude of the ion. If the condition is fulfilled, an electron behaves nearly classically in the sense that it can be assumed localized at a positive
ion near a defect, with a chance of jumping to an equivalent neighboring one.

**Hopping Polaron Model**

An electron-phonon interaction leads to the formation of a polaron, comprising the electron and its accompanying polarization. Since the original electron-lattice interaction is not completely accounted for in the formation of a polaron, it may move from site to site as a result of weak residual interactions. Movement between sites is by either tunneling or phonon-activated jumping. At high enough temperature, the latter will predominate and the particle is considered to hop from site to site in a random manner (12). Since hopping is facilitated by the thermal motion of ions, the mobility will then increase with an increase in temperature (7). Originally, the mobility should be less than $1 \text{cm}^2/\text{sec}^{-1} \text{volt}^{-1}(2)$; otherwise the band model may be more appropriate.

Sewell (12) calculated the dielectric properties quantum-mechanically for a simple idealized two-site model with small polaron properties. Sewell's quantum mechanical calculation of the polarization response, $K(t)$, to a classically applied field is similar to the classically defined polarization decay function, $X(t)$, of Fröhlich (5), if $T > T_c$, the critical temperature. Sewell's conclusions were that if thermally activated processes predominate over tunneling
(T > T_c), the system behaves as a Debye dielectric and leads to appreciable dielectric losses whenever the applied field becomes comparable with the jump frequency. If the tunneling processes predominate (T < T_c), the system absorbs energy very strongly from fields whose frequencies are close to the tunneling frequency (i.e. resonance absorption).
IV. EXPERIMENTAL

Sample Preparation

Crystal Growth

Undoped V$_2$O$_5$ crystals were grown in two purities. The first method used Baker Analyzed V$_2$O$_5$ with an assay of 99.5% V$_2$O$_5$, 0.10% chlorine, and 0.30% CO$_2$. The second method employed Matheson, Coleman and Bell's reagent grade ammonium metavanadate. The assay was 99.0% NH$_4$VO$_3$, 0.3% CO$_3$, 0.2% chloride and 0.02% sulfate. By heating ammonium metavanadate at 600°C for approximately six to ten hours, the ammonia and water are released to the atmosphere and V$_2$O$_5$ is formed.

Crystal growth was performed in the open atmosphere, by positioning a V$_2$O$_5$ or NH$_4$VO$_3$-filled platinum crucible in a Heavy-Duty Electric Company Furnace, Type 86. The temperature was controlled by a Barber-Coleman Power controller (Series 622) and Millivolt Indicator Controller (Model 177), but visually read by a more accurate Hewlett Packard Model 7100B Chart Recorder. A hatch cover, of Pyrex glass, was used to cover the inlet on the top of the furnace; this jointly served to limit the loss of heat and provide a viewing window.

The V$_2$O$_5$ sample was melted at approximately 670°C.
Two methods were used for growing crystals from the melt. The first was the procedure practiced by K.M. Mar (10). He seeded the melt with a small piece of a previously grown crystal which floated on the surface of the melt. The immediate area of the seed solidified quickly and the hatch, which was opened for seeding, was closed and the previously solidified portion was melted away. This left "a small single crystallite." The temperature was then held constant for approximately twenty minutes and then cooled at an approximate rate of 0.6°C per minute by adjusting the Barber-Coleman Power Controller. The crystal floated on the surface during the growth period.

When the desired size had been obtained, the crystal was removed with tongs. When the tongs were placed in the molten solution, the crystal quickly froze to them. It was then lifted out of the crucible.

The other process involved cooling the melt until a small solidified portion appeared on the surface of the melt. The temperature was then increased until once again "a small single crystallite" was formed. The remainder of the second process was identical to that of the first.

Crystal growth in the direction of the c-axis occurred at a higher rate than for the a and b axes. The final shape of the crystal was usually rectangular with rounded corners and the upward surface was always extremely reflective. Occasionally, a twin crystal was grown with a visual line
of division down the center of the crystal, perpendicular and parallel to the b and c-axes, respectively. The crystal was always cleaved at this position, rendering two good samples. Twins were exceptionally valuable samples because of the data which is obtainable from two samples of identical purity.

Samples doped with copper were also grown. Phase studies done by Flood, Krog, and Sorum (4) have shown that the addition of monovalent metals to V$_2$O$_5$ produced a series of new phases; M$_x$V$_2$O$_5$, each phase being characterized by a range of X. If X $\leq$ 0.02, the gross V$_2$O$_5$ structure is maintained. For this reason, the stoichiometric ratio of copper was always kept below 0.02.

The pre-weighed copper was added to the NH$_4$VO$_3$-filled crucible before melting. The procedure for growing doped samples does not differ from that of undoped ones.

Although a certain stoichiometric ratio (i.e. Cu$_x$V$_2$O$_5$) exists in the copper and NH$_4$VO$_3$ melt, it is unlikely the resulting crystal will have the same stoichiometric ratio with respect to copper.

**Oxygen Treatment of V$_2$O$_5$ Samples**

Vanadium pentoxide crystals, when grown from the melt, experience a loss of oxygen, and thus a deviation from the stoichiometric ratio. By subjecting samples to a high temperature and an O$_2$ pressure of approximately 20 atm, the
correct stoichiometric ratio may be approached.

The process of oxygenation was done in a Parr Bomb No. 4740, which has a maximum pressure limit of 5400 psig at 600°C. The samples to be treated with oxygen were done so just prior to the application of electrodes, which is discussed later.

The crystal was placed in a Pyrex test tube inside the bomb. The bomb was then sealed and flushed a minimum of twenty times with oxygen to insure only an oxygen atmosphere. A pressure gauge mounted on the lid of the bomb monitored the pressure within.

The bomb was then placed in a Marshall High Temperature Testing Furnace with the pressure gauge protruding. An iron-Constantan thermocouple located between the furnace wall and the bomb was connected to a Hewlett Packard Model 7100B Chart Recorder for determination of temperature, which was 600°C.

The total time of oxygenation varied from four to five days. Electrodes were applied immediately after removal of the sample from the bomb.

**Capacitor Construction**

The capacitor was constructed by application of the three electrode system suggested by A. Von Hippel (9) and used by K.M. Mar (10). If a two-parallel-plate capacitor is used, the capacitance between them is greater than that
defined by the electrodes proper owing to the edge capacitance beyond the electrodes and the capacitance to ground of the high electrode. As seen in Figure 5, the three terminal system has the added guard electrode surrounding the measuring electrode, both being parallel to the unguarded electrode. The guard electrode has the versatility of being either an electrode which is actively used or connected to ground. Our apparatus is such that a-c measurements require a grounded guard electrode and d-c, an active electrode, as will be seen later. The guard and unguarded electrodes go to the low and high terminals, respectively.

The most efficient results for an electrode system of the type used for a-c measurements require that the width of the guard electrode be at least twice the thickness of the specimen, and the unguarded electrode extend to the outer edge of the guard electrode. The gap between the guard and guarded electrode should be as small as possible. In calculating the vacuum-capacitance of the electrodes, the effective radius of the guarded electrode is given by Ammey (1) as:

\[ r = r_1 + \frac{g}{2} - \delta \]  

(4.45)

where

\[ g = r_2 - r_1 \quad \text{and} \quad \delta = \frac{2t}{\pi} \ln \cosh \left( \frac{\pi k}{4t} \right) \]  

(4.46)

Figure 5 shows the significance of the above symbols.

The guard and guarded electrodes were made parallel to the unguarded electrode by means of an American Optical
Figure 5. Three-terminal capacitor

Figure 6. Necessary measurements for obtaining the effective radius
Company Microtome Model 860. The preparation and technique used were similar to those of K.M. Mar. \( V_2O_5 \) crystals (high luster side down) were prepared for microtoming by cementing them with Duco Cement directly to a pedestal. After microtoming, the crystal was removed from the pedestal by placing the combination in trichloroethylene and boiling to remove. The crystal thickness at the location of the guarded electrode was measured with a micrometer and ranged from 0.02159 to 0.04956 cm. For any one sample, the thickness in the electrode area was uniform within 0.0002 cm.

Electrodes were applied to the crystals by evaporating gold on to the crystal surfaces. Prior to evaporation, the samples were cleaned by suspending them for approximately thirty minutes each in four separate boiling solvents. The solvents used were trichloroethylene, petroleum ether, 100% ethanol and acetone, respectively. The apparatus used for evaporation was a Mikros VE-10 Vacuum Evaporator with a modified current source, which was made available by Dr. J.C. Looney. The vacuum obtained for gold plating was 0.03 to 0.01.

The guarded and guard electrodes were applied simultaneously. This was done by laying a precision-made, ring-shaped mask in the pre-selected site and gold plating the exposed surface. The mask had a thickness of 0.066 cm and an inside and outside diameter of 0.4724 cm and 0.6096 cm, respectively. After the guard and guarded electrodes were applied,
the mask was removed, the crystal turned over and that entire surface gold plated. This produced the unguarded electrode.

The gold which had plated out on the edges of the crystal was removed by cleaving and scraping. An American Optical Cycloptic Stereoscopic Microscope was used to verify that no gold remained on the edges of the crystal.

Cryostat

The cryostat originally used was that of K.M. Mar (10). It was well suited for vacuum and low-temperature work and was used by this author for the first d-c conductivity tests, with one change. The guard electrode was freed from ground, rendering it an active electrode, as will be discussed later in the d-c circuitry section.

A new cryostat was designed, using the internal portion of Mar's as a basis. The purpose of the new cryostat was the minimization of sample handling time during installation of the sample into the cryostat.

The major internal change replaced the soldering of electrical leads to the capacitor. This was done by installing two spring loaded gold plated caps. (see Figure 7) To ensure that the caps did not scratch or injure the capacitor in any way, 0.01 inch thick gold disks, with a diameter of 2.5mm, were placed between the caps and the capacitor. The disks were not mounted permanently and were easy to insert
Figure 7. Sample holding unit: 1. spring loaded gold plated electrodes, 2. unguarded electrode contact, 3. BeO disk, 4. brass block, 5. thermocouple bead pressed between Teflon blocks, 6. brass shoulder, 7. swing bridge, 8. guard electrode and guarded electrode leads, 9. cold finger, 10. aluminum radiation shield, 11. vacuum cell, 12. unguarded electrode lead, 13. the V$_2$O$_5$ three-terminal capacitor
with each sample change. Excellent electrical contact was obtained when mechanical pressure was applied by use of the sample positioning screw.

The new method of electrical contact was constructed by bolting two screws to a piece of Teflon. The screws were counter sunk to give a flush fit with the upper Be0 block. The threads were then ground off, leaving a separation of 1.5cm between the two ground screws. Springs from a ball point pen were cut to a desired size and soldered to the nut. The caps slid onto the shafts and the upper edges snapped under the first coil or two of the springs. Electrical leads were soldered to the point of spring and gold cap contact.

Electrical contact with the unguarded electrode was obtained in a similar manner. A thin piece of gold plate, the same diameter as the lower Be0 block, was cemented with epoxy resin to the Be0 block. An electrical lead was then soldered to the edge of the gold. The unguarded terminal rested on the gold plate and again the pressure from the sample adjustment screw gave good electrical contact at all temperatures used.

A copper-constantan thermocouple was placed in the same location as Mar's. The output was measured by means of a Leeds and Northrup millivolt potentiometer. The temperature was usually maintained at a constant value by the use of freezing baths.

The vacuum cell (Figure 7) was built by C.W. Woods.
The material used was brass because of its durability and added shielding. The size was such to enable the entire body to become completely immersed in a cold bath provided by a one-liter wide-mouth Dewar flask.

Use was made of the cold finger construction designed by K.M. Mar. The connection between the crystal holder and the vacuum cell was done in the same fashion as was done by Mar. A brass tube was soldered to the base of the cold finger and the lid of the vacuum cell.

The lid of the vacuum cell had holes for the BNC connectors, thermocouple wires and the tube to the vacuum. Three o-ring-sealed vacuum BNC connectors were positioned around the lid, 90° apart. On the inside of the lid, after the leads from the three terminal capacitor were soldered to their respective BNC connectors, each connection was sealed with Torr-Seal. The remaining 90° position was occupied by the vacuum lead. Between it and a BNC connector was a small hole for the thermocouple wires, which was also sealed with Torr-Seal. The lid of the cryostat was secured to it and to the body by four screws and was made vacuum tight by the use of an o-ring.

Mating BNC connectors to those on the lid were affixed to co-axial cables, which in turn led to the electronic measuring apparatus. When temperatures less than about -30°C were reached, water from the ice formed on the BNC couplings would cause a partial short circuit between the casing
(ground) and all leads to the capacitor. This was solved by having all couplings housed in rubber tubing which was then filled with drierite and tightly clamped. No short circuits were observed after this procedure was followed.

**Circuitry**

**Capacitor Circuit**

The capacitor can be resolved into a circuit consisting of three resistors (see Figure 8). The first of these is between the guarded and guard electrodes and is known as the "gap resistance", $R_r$. Second is the resistance between the guarded and unguarded electrodes, $R_c$. It is the measurement of this resistor on which primary concern is focused. Last is the resistance between the guard and unguarded electrodes, which is named the guard resistance, $R_g$.

Since only $R_c$ and its characteristics are desired, means must be taken to insure that the other resistances present, $R_r$ and $R_g$, do not affect the measurement of $R_c$.

**Two Electrometer System**

A two electrometer system, as shown in Figure 9, was devised to make the gap current, $I_r$, zero at all times. Figure 10 is the same circuit as Figure 9, but the three terminal capacitor has been resolved into its resistors and the circuit slightly rearranged. The two electrometers and three terminal capacitor contained in Figure 10 constitute
Figure 8. Resolution of the capacitor to a simple circuit
Figure 9. Two-electrometer system
Figure 10. Two-electrometer system as a Wheatstone bridge
a Wheatstone bridge. Therefore, a balance condition of \( I_r = 0 \) must be satisfied in order to obtain a correct value of \( R_c \). Only when \( V_{ac} \) is equal to \( V_{ad} \) is this balance condition obtained.

Figures 9 and 10 have several components which should be clarified. \( K_1 \) and \( K_2 \) are identical Keithley Model 610-A Electrometers. The accuracy of the electrometer is 2% of full scale when reading voltages. The accuracy with respect to current measurement is 3% of full scale from 3 to \( 10^{-10} \) A and 4% of full scale from \( 3 \times 10^{-10} \) A to \( 10^{-13} \) A. The accuracy of resistance measurement is 3% of full scale from \( 10 \ \Omega \) to \( 10^{10} \ \Omega \) and 5% of full scale from \( 3 \times 10^{10} \ \Omega \) to \( 10^{14} \ \Omega \). \( R_v \) is a Heathkit Decade Resistance box with a range from 0 to 999,999 ohms. \( E \) is the power supply. Two different supplies were used, a Keithley Model 240-A and a Keithley Model 241 regulated power supply. The first has an accuracy of \( \pm \)1% of the dial setting and the latter \( \pm 0.05\% \) above two volts and within one millivolt below two volts.

For the balance condition, the potential at points c and d must be equal. This is done by adjusting the voltage drop across the parallel resistance created by \( R_2 \) and \( R_v \). This resistance is defined as \( R \). The construction of the Keithley 610-A Electrometer is such that when "volts" is dialed, high impedance exists. \( K_2 \) was always set to high impedance. Therefore, \( R_2 \) is much larger than \( R_v \). The resistance, \( R \), then becomes:
\[ R = \frac{R_c R_v}{R_c + R_v} = R_v \]  

(4.47)

Thus, by varying \( R_v \), \( V_{ad} \) is varied and is read directly from the meter display of Keithley - 2.

The voltage drop, \( V_{ac} \), is obtained directly from the display of \( K_1 \), but in a slightly different manner than \( V_{ad} \). The primary step required to determine \( V_{ac} \) is to first obtain the current, \( I \). (see Figure 10) This is done by adjusting the amperes section of the dial on \( K_1 \) until the meter display registers a value. The dial range is from \( 10^{-1} \) to \( 10^{-11} \) A. The inverse of the dial value alone is the resistance across which the current obtained flows. Therefore, the display shows the voltage drop across \( R_1 \). (see Figure 10) For example, if the current reading is \( 2.5 \times 10^{-4} \) A, with \( 10^{-4} \) being the dial value, then the resistance, \( R_1 \), is \( 10^4 \) ohms and the voltage drop, \( V_{ac} \), is 2.5V.

The sensitivities of the two electrometers must always be at the same setting. The adjustment of \( R_v \), the Heathkit Decade Resistance Box, until the two electrometers have the same voltages, gives the previously stated balance condition, i.e. \( V_{ac} = V_{ad} \).

After satisfying the balance condition, Kirchoff's Law may be used to write

\[ E = I_1 (R_C + R_1) \]  

(4.48)

where \( E \) is read from the power supply, and \( I_1 \) and \( R_1 \) are obtained from \( K_1 \).
Impedance Bridge

A General Radio Type 1608-A Impedance Bridge was used to study the dielectric properties of $V_2O_5$ crystals. The bridge is a self-contained impedance-measuring system, which includes six bridges for the measurement of capacitance, conductance, resistance and inductance as well as the generators and detectors necessary for d-c and 1-kHz a-c measurements. To extend the a-c frequency beyond kHz, an Electro-Scientific Industries Model 861A alternating current generator was used with the impedance bridge. The unit provides a continuous frequency variation in three ranges from 20 to 20,000 Hz. The frequency was monitored by a more accurate Transistor Specialties Inc. Model 361R frequency counter. The basic bridge accuracy is 0.1%.

Measurements were made by grounding the guard electrode and once again the high and low terminals were the unguarded and guarded electrodes, respectively. All of the electrical leads from the cryostat were shielded except for that of the guarded electrode. This is done to help reduce capacitance-to-ground leakage, as called for by the bridge operation manual. Of the available bridges, $G_p$ and $C_p$ were used exclusively. The bridge, $C_p$, is used when the dissipation factor, D (same as loss tangent), is in the range 0.02 to 2. $G_p$ is used for a range of Q between 0 and 1.2. Q is the quality factor or the inverse of the dissipation factor. As is evident, there is some overlap in the regions
Figure 11. Simulation sample: sub-letters C, G, and R refer to guarded, guard and gap related variables.
covered by the separate bridges. The measured quantities from the $C_p$ bridge are the parallel capacitance, $C_p$, and the dissipation factor. $G_p$ measures the parallel conductance, $G_p$, and quality factor. Both bridges render either directly or indirectly $C_p$, $D$ and $G_p$. All readings were corrected for errors caused by terminal and lead impedances as well as capacitance-to-ground leakage. The $C_p$ bridge uses the following equation to relate the corrected measured values:

$$D = \frac{1}{\omega C_p R_p}$$

(4.49)

where $\omega$ is the angular frequency and $R_p(=1/G_p)$ is the only unknown. The corrected measured values resulting from the $G_p$ bridge are related by

$$Q = \frac{\omega C_p}{G_p}$$

(4.50)

where only $C_p$ is unknown.

A simulation circuit, constructed from various known resistors and capacitors and housed in a "mini-box" for shielding, was used to test the bridge performance. Figure 11 shows the circuit of the simulation sample. When measured with the bridge, the conductances and capacitances of the respective components of interest agreed. The high and low ends of the frequency range (i.e. 50Hz and 20,000Hz) were especially studied.
Procedures of Making Measurements

Temperature Control

The cryostat was evacuated with a mechanical fore-pump to a pressure of $10^{-2}$ mm. Nitrogen gas was used to help rid the cryostat of any water vapor. After six hours of evacuation, the cryostat was placed in a one-liter wide-mouth Dewar flask where it was immersed in a constant-temperature bath.

By the use of ice, organic freezing baths, dry ice and liquid nitrogen, constant temperatures were obtained. Capacitance readings from the impedance bridge were obtained from a temperature range between 100K and 175K, depending on the sample. Freezing baths and liquid nitrogen fulfilled this temperature requirement. D-C measurements done in the temperature range between 273K and approximately 80K made use of all temperature controlling schemes. After the cryostat was at constant temperature for five minutes, measurements were taken. The temperature was checked before, during and after the experiment for constancy by use of the previously mentioned thermocouple and potentiometer.

Periodically during an experiment, the electrical connections were checked for short circuits. At no time during an experiment were shorts found.
V. RESULTS AND INTERPRETATION

Data Evaluation and Results

Dielectric Relaxation

The various types of V₂O₅ samples investigated with respect to dielectric relaxation were NH₄VO₃ type, oxygen treated NH₄VO₃ type, copper doped and reagent grade V₂O₅. The samples were 6A, 6B, 5 and C-2, respectively.

The vacuum capacitance required to obtain the real dielectric constant is obtained from an equation given by von Hippel (9) for three-terminal capacitors. The equation is

\[ C₀ = 0.06954 \frac{d²}{t} \text{ Pf} , \]  \hspace{1cm} (5.51)

where \( d \) is the diameter of the unguarded electrode and \( t \), the thickness of the sample between the guarded and unguarded electrodes. Both \( d \) and \( t \) are in centimeters.

Figure 12 and 13 show the dielectric dispersion of sample 6-A and 6-B at various constant temperatures. The dispersion of sample 5 showed that \( \varepsilon₁ \) was less than one at high frequency. This is caused by the poor application of electrodes. This data was not used.

Both of the Debye equations (see Equations 2.14 and 2.15) are functions of the relaxation time; however, only \( \varepsilon₂ \) yields information about the process. This is implied by the equation

\[ \sigma_{Dielectric}(\omega,T) = \frac{\omega\varepsilon₂(\omega,T)}{\varepsilon₀} \]  \hspace{1cm} (5.52)
Figure 12. Dielectric dispersion of sample 6-A at various temperatures
Figure 13. Dielectric dispersion of sample 6-B at various temperatures.

Dielectric dispersion of sample 6-B at various temperatures.
where \( \varepsilon_0 \) is the permittivity of free space and \( \delta_{\text{Die}}(\omega,T) \) is the dielectric conductivity, which cannot be directly measured. It is obtained from the a-c conductivity, \( \delta_{\text{ac}}(\omega,T) \), which is the linear sum of \( \delta_{\text{dc}}(T) \) and \( \delta_{\text{Die}}(\omega,T) \).

The d-c conductivity is obtainable by three methods in our laboratory. One way is to extrapolate \( \delta_{\text{ac}}(\omega,T) \) to \( \omega = 0 \). At that point \( \delta_{\text{ac}}(0,T) = \delta_{\text{dc}}(T) \). A second method is the direct measurement of \( \delta_{\text{dc}}(T) \) simultaneously with the determination of \( C_p \) or \( G_p \) and \( D \). The third method obtains \( \delta_{\text{dc}}(T) \) with the two electrometer system. From the data obtained, \( \delta_{\text{dc}}(T) \) is plotted against \( T^{-1} \), in degrees K and a straight line is obtained. From this line, the Arrhenius equation,

\[
\delta_{\text{dc}}(T) = \delta_0 \exp\left(-\frac{E_{\text{dc}}}{kT}\right)
\]

is used to obtain the activation energy, \( E_{\text{dc}} \), as will be done later. This gives \( \delta_{\text{dc}}(T) \) in the temperature range 273K to 120K, and less than 120K in some instances. Unfortunately, the three methods all yielded different results except at low temperatures. To determine the discrepancy, the simulation sample was used. It revealed the three methods to be identically correct. Therefore, the reason for the discrepancy in the methods is unknown. The first method was chosen for determining the \( \delta_{\text{dc}}(T) \), because the latter methods gave values greater than the smaller values of \( \delta_{\text{ac}}(\omega,T) \) obtained.

At low frequencies (i.e. \( f < 400 \)), the conductance decreases with frequency rather than increases. Due to this unexplained occurrence, the points taken for the extrapolation
to zero frequency exclude those which manifest this behavior. In some cases this variation was at such a high frequency and the points were so scattered, extrapolation was not attempted.

Figure 14 shows the extrapolated graph for sample 6-A at $T = 150K$. Extrapolation was done with a Hewlett Packard Model 9500 calculator, using a non-linear least squares curve fitting program, both furnished by Dr. W.J. Fredericks. From Figure 14, it should be noted that the increase of $\delta_{ac}(\omega, T)$ with increasing frequency signifies that at infinite frequency all of the field energy is dissipated as heat.

Knowing $\delta_{Dielectric}(\omega, T), \epsilon_2(\omega, T)$ may be calculated and plotted against $\epsilon_1(\omega, T)$ to obtain an Argand diagram. Figures 15, 16 and 17 are representative plots of those samples examined. At the lower frequencies in all Argand diagrams, the accuracy of the points decreases. This is believed to be due to errors in the determination of $\delta_{ac}(\omega, T)$ and the value used for $\delta_{ac}(0, T) = \delta_{dc}(T)$.

Extrapolation of the high frequency regions for the Argand diagrams to the $\epsilon_1(\omega, T)$ axis, defines $\beta$ and $\epsilon_{\infty}$ for each. Programmed curve fitting techniques were used for the extrapolation. Table I summarizes these values.

By graphing $\ln \left[ \tan \left( \frac{\theta}{\beta} \right) \right]$ against $\ln(f)$, the frequency, as discussed in Chapter three, the cross-over frequency, $f_C$ is obtained. This then gives the relaxation time ($T$). These values are summarized in Table I for the samples studied.
Figure 14. Extrapolation of a-c conductivity to zero frequency where the conductivity has been divided by cm$^{-1}$
Figure 15. Cole-Cole plot of sample 6-A at $T = 150K$
Figure 16. Cole-Cole plot of sample 6-B at $T = 155K$
Figure 17. Cole-Cole plot of sample C-2 at T = 152K
The shape of the Cole-Cole plot, characterized by $\beta$ for each plot, far from resembles the plots of true Debye dielectrics where $\beta = 1$. For this reason, a single relaxation time cannot be used to represent the relaxation process. Instead, a distribution function similar to that in Figure 4a should be used. Figure 18 shows distribution of relaxation times for sample 6-B at $T = 165K$.

Equation (2.28) may be used to calculate $H$, the activation energy of the relaxation process. To do so, the $\ln (\tau(T))$ is plotted against $T^{-1}$, and $H$ is determined from the slope of the plot. The plot for the samples in Table I is given in Figure 19. The activation energy is 0.16 eV.

**D-C Conductivity**

To obtain the activation energy of the d-c conduction, the two electrometer system was used. From the results, $\delta_{dc}(T)$ was plotted against the inverse of the temperature in degrees, K. Equation (5.53) was used to obtain the activation energy from the slope. The plots for the various samples are given in Figures 20 and 21. The values of $E_{dc}$ for the samples measured are in Table II. The average $E_{dc}$ is 0.23 eV.

Reagent grade $V_2O_5$ is the basis for the distribution of sample purities, as given in Figures 20 and 21. From this basis, the conductivity was increased or decreased by doping. $NH_4VO_3$ was also used as a starting material to change the
Figure 18. Distribution of relaxation times for sample 6-B at T = 165K
<table>
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<tr>
<th>Sample</th>
<th>T, K</th>
<th>1000/\text{T, K}^{-1}</th>
<th>\varepsilon_\infty</th>
<th>\beta</th>
<th>f_c (\text{Hz})</th>
<th>(\tau), \text{sec}</th>
<th>-ln (\tau)</th>
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<tbody>
<tr>
<td>6-A</td>
<td>140</td>
<td>7.14</td>
<td>3.51</td>
<td>0.38</td>
<td>105 ±10</td>
<td>1.52 \times 10^{-3}</td>
<td>6.49</td>
</tr>
<tr>
<td>6-A</td>
<td>150</td>
<td>6.67</td>
<td>3.66</td>
<td>0.48</td>
<td>174 ±50</td>
<td>9.14 \times 10^{-4}</td>
<td>7.00</td>
</tr>
<tr>
<td>6-A</td>
<td>160</td>
<td>6.25</td>
<td>2.42</td>
<td>0.51</td>
<td>317 ±10</td>
<td>5.03 \times 10^{-4}</td>
<td>7.59</td>
</tr>
<tr>
<td>6-B</td>
<td>143</td>
<td>6.99</td>
<td>3.65</td>
<td>0.32</td>
<td>171 ±20</td>
<td>9.30 \times 10^{-4}</td>
<td>6.98</td>
</tr>
<tr>
<td>6-B</td>
<td>155</td>
<td>6.45</td>
<td>3.55</td>
<td>0.37</td>
<td>389 ±20</td>
<td>4.09 \times 10^{-4}</td>
<td>7.80</td>
</tr>
<tr>
<td>6-B</td>
<td>165</td>
<td>6.06</td>
<td>3.65</td>
<td>0.50</td>
<td>1287 ±20</td>
<td>1.24 \times 10^{-4}</td>
<td>9.00</td>
</tr>
<tr>
<td>C-2</td>
<td>125</td>
<td>8.00</td>
<td>2.89</td>
<td>0.39</td>
<td>20 ±10</td>
<td>7.82 \times 10^{-3}</td>
<td>4.85</td>
</tr>
<tr>
<td>C-2</td>
<td>146</td>
<td>6.85</td>
<td>3.55</td>
<td>0.53</td>
<td>300 ±100</td>
<td>5.30 \times 10^{-4}</td>
<td>7.54</td>
</tr>
<tr>
<td>C-2</td>
<td>152</td>
<td>6.58</td>
<td>1.76</td>
<td>0.32</td>
<td>400 ±100</td>
<td>3.90 \times 10^{-4}</td>
<td>7.85</td>
</tr>
</tbody>
</table>
Figure 19. $\ln \tau$ as a function of reciprocal temperature for values in Table 1
basis. Doping with copper adds electrons to the donor levels of the crystal and increases the d-c conductivity. Oxygen doping does the opposite; since it is an acceptor, it decreases the concentration of donor electrons already present in a particular sample and in turn decreases the d-c conductivity. In other words, oxygenation increases the stoichiometric ratio of $V_2O_5$ in the direction of an electrical insulator, which it would be if exactly stoichiometric. The order of the d-c conductivities, at 297K, agrees with expectation for the samples listed in Table II and plotted in Figures 20 and 21.

**The Dielectric Relaxation Process**

Various mechanisms of the relaxation process are discussed by K.M. Mar (10). He discounts all except the hopping polaron theory, as an acceptable model for dipolar relaxation in $V_2O_5$. The hopping polaron theory, with a center consisting of either an impurity ion or vacancy, has been shown to account qualitatively for observations of Debye losses of some transition metal oxides (13). The center described is created by either doping or through reduction by increasing the nonstoichiometry of the original sample. The range of activation energies reported for these oxides varied from 0.001ev to 0.43ev.

It has been determined by thermal emf measurements that the charge carrier in $V_2O_5$ is the electron. The carriers are
Table II. Activation Energy of d-c Conduction for Samples Tested

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type of Sample</th>
<th>$E_{dc}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>$O_2$ treated reagent grade $V_2O_5$</td>
<td>0.25 ±0.01</td>
</tr>
<tr>
<td>6-A</td>
<td>$NH_4VO_3$ type $V_2O_5$</td>
<td>0.27 ±0.01</td>
</tr>
<tr>
<td>6-B</td>
<td>$O_2$ treated $NH_4VO_3$ type $V_2O_5$</td>
<td>0.21 ±0.01</td>
</tr>
<tr>
<td>5</td>
<td>$NH_4VO_3$ type Cu doped $V_2O_5$ $(Cu_{0.02}V_2O_5)^3$</td>
<td>0.21 ±0.01</td>
</tr>
<tr>
<td>3</td>
<td>$NH_4VO_3$ type $V_2O_5$</td>
<td>0.24 ±0.01</td>
</tr>
<tr>
<td>C-2</td>
<td>Reagent grade $V_2O_5$</td>
<td>0.25 ±0.01</td>
</tr>
<tr>
<td>G²</td>
<td>Cu doped reagent grade $V_2O_5$ $(Cu_{0.01}V_2O_5)^3$</td>
<td>0.21 ±0.01</td>
</tr>
</tbody>
</table>

1. Twin samples
2. Measurement taken with slightly modified electrometer system
3. Dopped to copper content given
Figure 20. The d-c conductivities of samples G, 5, C-2 and 3, as a function of reciprocal temperature.
Figure 21. The d-c conductivities of samples 6-A, 6-B and 7, as a function of reciprocal temperature; Add 1 to the ln for sample 6-B
created either by loss of oxygen at the melting point or incorporation of impurities.

Milan (11) has accounted for the former by showing that molten $V_2O_5$, at the melting point, dissociates according to

$$V_2O_5 = V_2O_5_{-x} + \frac{x}{2} O_2$$

where $x$ increases with increasing temperature. For every atom of oxygen evolved, two electrons are left behind. These electrons can either be trapped at separate $V^{+5}$ centers, yielding $V^{+4}$ centers, or be trapped at one $V^{+5}$ center, thus giving rise to one $V^{+3}$ center. Only a highly reducing atmosphere would result in the formation of a $V^{+3}$ ion. Therefore, the former is assumed.

An impurity could be incorporated into the sample when $V_2O_5$ is in its molten state. It also might enter a sample by being oxidized by $V^{+5}$ and then experiencing bipolar diffusion into the lattice.

**Dipolar and Donor Centers**

ESR studies of $V_2O_5$ crystals by Mar (10) and Gilles and Boesman (8) reveal a 15-line spectrum. The nuclear spin of $^{51}V$ is $7/2$. An electron trapped equally by two $V^{+5}$ ions would give rise to that number of hyper-fine lines. This may be viewed as a localized center. A neighboring positive defect, such as an oxide-ion vacancy or interstitial impurity cation, may form a dipolar center by binding the electronic
center in its field. The hopping motion or tunneling of the electron between two localized centers results in the reorientation of the dipole.

One should note that if the positive defect is an oxide-ion vacancy, this accounts for only one of the two electrons made available by the loss of an atom of oxygen. It is not known what other center results.

Unpublished results from this laboratory show that NH4VO3-type V2O5 samples display an 8-line ESR spectrum. This implies that the unpaired electron is trapped on a single V4+-5 ion. In other respects, the dipolar center would be described as above.

The activation energy of dipolar reorientation is to be identified with the observed value for the relaxation process, namely 0.16 eV. This energy is in the region of previously reported activation energies for transition metal oxides.

The mobility of V2O5 has been reported in the range 0.1 to 0.001 cm²/V sec, which is in the observed range for polaron hopping. However, the temperature must be greater than θ_D/2 for dielectric relaxation to occur by hopping; θ_D is the Debye temperature. The value of θ_D for V2O5 is not known, but by comparison with other oxides, e.g. TiO2 and Fe2O3 for which θ_D is 758K and 660, respectively, it must be assumed that the experimental temperature was less than θ_D/2.

With the temperature less than θ_D/2, tunneling is assumed to be the process of electron movement. The acti-
vation energy of 0.16 eV indicates that the electrons require energy before the probability of tunneling becomes significant.

The average activation energy of d-c conduction, for the samples whose dielectric properties were studied, is 0.23 eV. This activation energy includes the energy required for carrier production (i.e. the ionization energy). This indicates that an energy of 0.07 eV is required to remove the electron from the positive defect to infinity.

As shown in Figure 19, there is a large error in the value of the dielectric relaxation times, required to determine the activation energy. Mar reported a value 0.24 eV for H; if H and $E_{d-c}$ were identical, then it could be assumed that the ionization energy of the dipolar center is zero. The error in the present experiment is such that the ionization energy cannot be established with confidence; the data support the conclusion that it is small, but not zero.


