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THE STRUCTURE AND ACTIVITY OF CATALYTICALLY ACTIVE SOLIDS

FOURTH TECHNICAL REPORT

Project NR 057 143

Contract N7 onr-45003

Period Covered: 1 October 1951 to 30 September 1952

by

P. W. Selwood, Chief Investigator
Thomas Freund, Research Associate
Elizabeth Wier Toor, Research Associate
Frank DeBoer, Research Assistant
Stephen Adler, Research Assistant
Louise Moore, Research Assistant

The Department of Chemistry
Northwestern University
Evanston, Illinois

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SUMMARY

This report covers work on the structure of glass, on thermomagnetic analysis, and on supported palladium catalysts, together with a note on purple sulfur.

It has been found that the anomalous magnetic moment of ions of nickel, cobalt, and uranium in silicate glasses, as previously reported, may probably be interpreted in terms of the relative contributions of these ions as being tetrahedrally coordinated integral parts of the net-work, or as octahedrally coordinated net-work modifiers. This observation appears to open a useful field of application of magnetic methods in glass chemistry.

Thermomagnetic analysis of the solid state reaction γ-Fe_2O_3 to α-Fe_2O_3 has given definite evidence that the activation energy for this reaction is not related to particle size. Other variables are being investigated.

Supported palladium metal on high-area alumina has been shown to yield no enhancement of magnetic susceptibility and thus not to show the dispersion effect exhibited by many paramagnetic oxides in supported condition.

"Purple" sulfur, made by the method of Rice and Sparrow, by freezing the vapor from 450° C onto a finger cooled in liquid nitrogen, has been shown to be paramagnetic.

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Part I. The Magnetic Anisotropy of Nickel-Containing Glass
by Elizabeth Weir Toor

Previous measurements made in this laboratory of the magnetic susceptibilities of a series of nickel-containing glasses have shown that nickel has an unusually high magnetic moment in such glasses. This could be explained by either of two possibilities, that the nickel is in the plus three oxidation state, or that the orbital component of the moment is not quenched to the same extent in the glass as in most nickel salts because of some difference in the electrical fields surrounding the nickel ion. Possibly the fields are more symmetric in the glasses. If this second alternative were actually the case, it might be possible to detect paramagnetic anisotropy in the glasses under certain conditions. If a field surrounding a nickel ion could be made less symmetric, the susceptibility would vary with direction. Therefore pieces of a nickel-containing glass were drawn out in a flame as rapidly as possible and cooled quickly. The anisotropies of small sections of the resulting rods were measured. The effect of annealing on the anisotropy was also studied and the susceptibility of one sample was measured at different field strengths to determine whether or not it was ferromagnetic.

Procedure:

(a) Making Samples for Anisotropy Measurements: -- The nickel-containing glass used was one of a series supplied by Dr. W. Weyl, of Pennsylvania State College and was designated as M-6. Its susceptibility and moment had been measured previously. This glass contained 15.6% nickel by weight and the composition corresponded to $NiO.Na_2O.4SiO_2$. A lump of this glass was held over an oxygen-methane flame, and as small portions melted they were drawn out into threads very rapidly with a quartz rod. Sections of these threads, a few millimeters long, were then broken off and used in magnetic anisotropy measurements.

Similar samples were made of a glass designated as M-2, which contained magnesium instead of nickel, and had the composition $MgO.Na_2O.4SiO_2$. To make these samples it was necessary to powder the glass and melt it in a platinum crucible, then to draw out threads with a quartz rod.

(b) Measurement of Magnetic Anisotropy: -- The cylindrical glass-shaped rods were attached to a glass rod at the end of a quartz suspension so that the long dimension of the sample was perpendicular to the quartz suspension. The anisotropy of the sample, the difference between the susceptibilities parallel and perpendicular to the long axis of the sample, was then measured by the Krishnan swing method. When the glass rods or fibres were too fine to be measured singly, several of about the same radius were tied together into bundles with pieces of hair and the bundle was then used in the same way as a single rod-shaped sample. All samples were weighed and the diameters were measured with a micrometer, excepting for those which were used as bundles. For a number of the samples, the anisotropy was measured several times at intervals of a few days.

(c) Annealing of Samples: -- Several of the samples were annealed after their anisotropies had been measured. A sample, in a platinum crucible, was placed in a muffle furnace which had previously been heated to the desired temperature.

The sample was then kept at that temperature for several hours. The furnace was then cooled to room temperature at a rate of about 56°C. per hour. The anisotropy of the sample was then re-measured. The annealing process was repeated at progressively higher temperatures, up to about 700°C.

(d) Detection of Ferromagnetism: -- To determine whether or not the samples were ferromagnetic, the susceptibility of one rod was measured over a range of field strengths with a Faraday balance. In this balance, a small glass bucket hangs from the end of a long glass rod which in turn is attached to a quartz spiral. The bucket hangs vertically between the pole-pieces of a magnet and the apparatus can be adjusted so that the bucket hangs in a region of constant dH/dx. The height of a mark on the long glass rod is measured with the field off and on, by means of a telescope with a vernier. By comparing the change in height found for an unknown sample to that found for a material the susceptibility of which is known, the susceptibility of the unknown sample can be calculated, providing the weights of both materials are known. If the substance is ferromagnetic, the susceptibility at one temperature will vary with the field strength.

The susceptibility of the empty bucket was measured over a range of field strengths, at room temperature and in a bath of dry ice and acetone. The susceptibility of the bucket containing a weighed amount of sucrose, the susceptibility of which had previously been measured, was determined over the same range of field strengths at room temperature. The glass sample, M-6 #10, was then inserted upright into the sugar in the bucket, and the susceptibility again measured at room temperature and at -85°C.

Results:

In Table I are listed the weights, radii, and anisotropies, $\Delta\chi$, of all samples of the glasses M-6 and M-1. Table II shows the change in anisotropy with time and with annealing for five samples of the nickel glass M-6. The period between the drawing of the glass into a fibre and the measurement of the anisotropy is given in days. The temperature given is the temperature at which the furnace was held, and the time during which the sample was held at this temperature is given in hours.

All M-6 samples were paramagnetic, and the long axis lay parallel to the field, generally, although it was sometimes inclined at a slight angle. The M-2 samples appeared to be diamagnetic, and took up an equilibrium position which varied from one sample to another.

Above 700°C., all samples turned greenish, though the color faded rapidly when the samples had been removed from the furnace. The thinner samples, #11 and #3, became bent and had apparently softened at the high temperature.

At room temperature, for M-6, χ_{Ni} /gm. was 89.0×10^{-6} and for M-2 was -0.28×10^{-6} per gram of glass.

In Graph #1 the anisotropy initially found for each sample is plotted versus the radius of the sample for all samples of M-6.

In Table III the results of measurements with the Faraday balance are given. The average changes in height, field off and field on, of the marker on the glass rod are listed for the empty bucket, Δ_1 , the bucket containing sugar, Δ_2, and the bucket containing sugar plus the sample M-6 #10, Δ_3 . These average changes in height are given at two temperatures and different field strengths, or rather at different currents. The relationship between current and field strength is known approximately. For each value of the current, at least four measurements were made to determine the average value of . The units of Δ are arbitrary and the changes were in the same direction for all measurements, i.e., the bucket moved out of the field when the current was turned on.

The weight of the bucket was 0.0351 gm.
The weight of the sugar was 0.0381 gm.
The weight of M-6 #10 was 0.00061 gm.

Table I. Variation of Anisotropy of Glasses with Sample Radius

Sample	Weight (mg.)	Radius (mm.)	$\Delta\chi_{Ni}$/gm. x10^6
M-6 #1	16.10	0.58	1.50
M-6 #2	3.67	0.34	0.33
M-6 #3	1.21	0.21	0.80
M-6 #4	9.61	0.44	0.33
M-6 #5	3.08	0.31	0.21
M-6 #6	3.55	0.27	0.48
M-6 #7	8.92	0.46	0.28
M-6 #8	3.08	0.29	0.43
M-6 #9	5.83	0.31	0.27
M-6 #10	0.61	0.16	24.6
M-6 #11	7.67	0.47	1.87
M-6 #12	1.11	0.16	0.53
M-6 #13	0.84	0.15	1.58
M-6 #14	1.19	0.09	4.34
M-6 #15	0.90	0.09	4.72
M-6 #16	0.77	0.09	2.41
M-6 #17	1.61	0.08	8.78
M-6 #18	0.78		3.01
M-2 #1	8.94	0.34	0.012 per g. sample
M-2 #2	3.62	0.24	0.012
M-2 #3	3.45	0.21	0.011
M-2 #4	2.48	0.27	0.013

Table II. Variation of Anisotropy with Time and with Annealing

Sample	Time (days)	Annealing Temp.°C.	Annealing Time (hrs.)	$\Delta\chi_{Ni}$/gm.x10^6
M-6 #1	1			0.08
	3			1.07
	27			1.56
	30			1.65
	50			1.86

Table II. (continued)

Sample	Time (days)	Annealing Temp. °C.	Annealing Time (hrs.)	$\Delta\chi_{Ni}$/gm.x10^6
	55	193	16	1.86
	56	243	5	0.08
	58	238	3	1.67
	59	293	5	0.35
	63	366	16	1.76
	66	504	16	1.74
	71	595	5	1.00
	76	660	22	0.19
	80	722	20	0.00
M-6 #2	1			0.64
	3			0.47
	27			0.39
	52			0.41
	56	243	5	0.35
	62	293	5	0.40
	66	504	16	0.08
	70	595	5	0.13
	77	660	22	0.03
M-6 #3	2			1.15
	28			0.86
	52			0.05
	62	243	5	0.04
	66	504	16	0.03
	70	595	5	0.24
M-6 #10	6			24.6
	22			17.1
	27			15.5
	29			13.9
	40	266	7	25.7
	43	377	17	25.0
	49	432	19	29.4
	54	544	3	17.9
	61	544	22	27.4
	64	643	18	16.6
	70	715	4	9.6
M-6 #11	6			1.86
	23			2.19
	36			1.55
	40	266	7	2.55
	43	377	17	2.59
	49	432	19	2.23
	55	544	3	1.64
	61	544	22	1.78
	64	643	18	1.23
	71	715	4	1.33

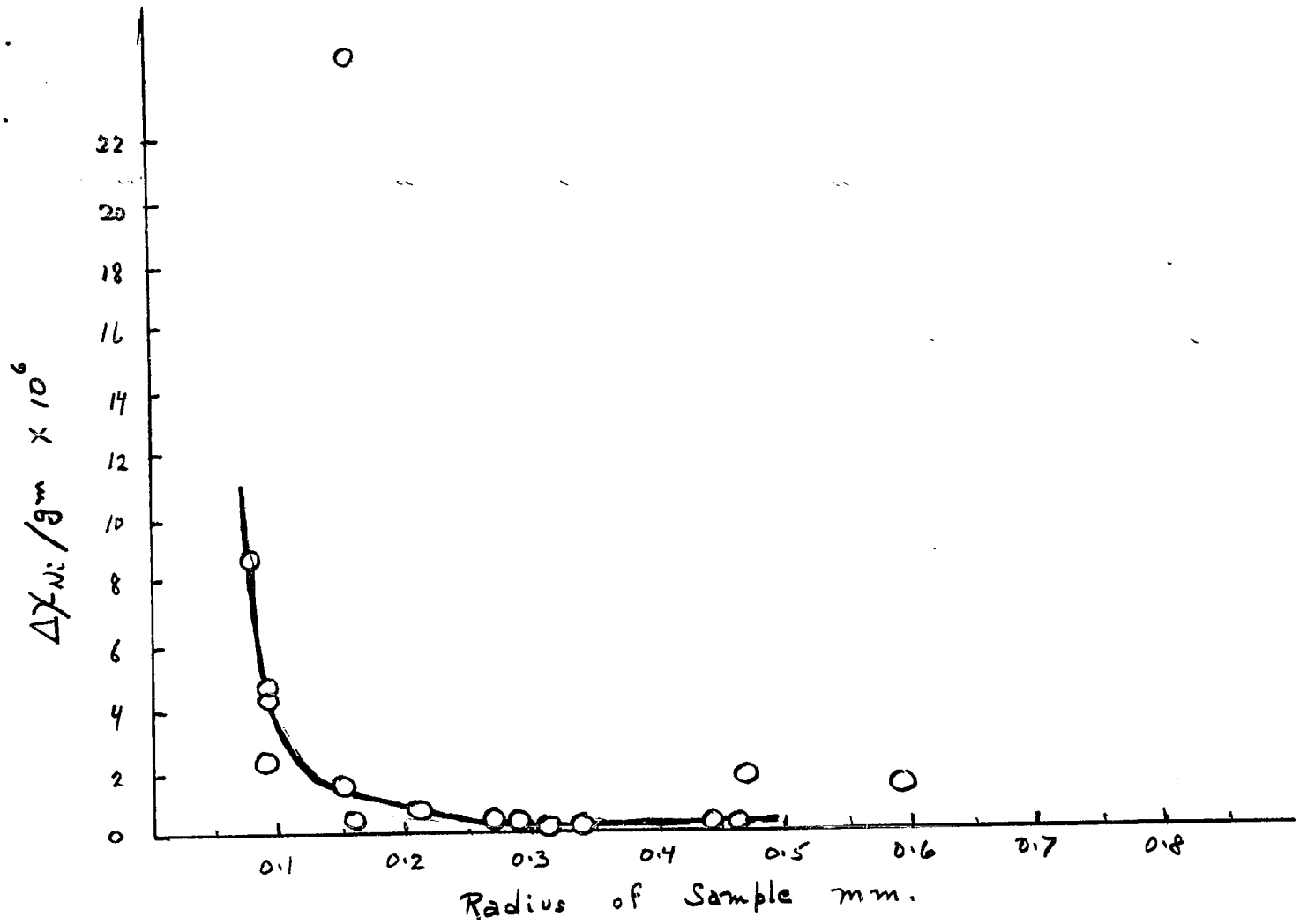


Fig. 1 Anisotropy vs. Sample Radius for Nickel Glass M-6.

Table III. Measurement of Susceptibility with the Faraday Balance

Temperature	Current (amps.)	Average Change in Height of Marker Δ_1	Δ_2	Δ_3
300°K.	10	0.329	0.851	0.566
	8	0.265	0.662	0.503
	6	0.150	0.539	0.397
	4	0.091	0.317	0.231
	2	0.024	0.093	———
184°K.	10	0.252	———	0.474
	8	0.153	———	0.331
	6	0.099	———	0.256
	4	0.059	———	0.150
	2	0.034	———	0.028

In Table IV are shown the values obtained for $\Delta_2-\Delta_1$, the change in height due to the sugar alone, and $\Delta_3-\Delta_2$, the change due to the nickel glass, as well as the ratio $(\Delta_3-\Delta_2)/(\Delta_2-\Delta_1)$. From this the susceptibility of the nickel in the glass is calculated by the following equation:

$$\chi_{Ni}/\text{gm.} = \frac{100}{15.6} \cdot \chi\,\text{sugar/gm.} \cdot \frac{\Delta\ \text{glass}}{\Delta\ \text{sugar}} \cdot \frac{\text{weight of sugar}}{\text{weight of glass}}$$

Table IV also includes these calculated susceptibilities, the current and the corresponding values of 1/H. In Graph #2 the susceptibilities are plotted versus 1/H.

Table IV. Calculation of Susceptibilities with Faraday Balance

Temp.	$(\Delta_2-\Delta_1)$	$(\Delta_3-\Delta_2)$	$(\Delta_3-\Delta_2)/(\Delta_2-\Delta_1)$	χ_{Ni}/gm.	I amps.	1/H $\times 10^3$
300°K.	0.52	-0.29	-0.56	126.4	10	0.100
	0.40	-0.16	-0.40	91	8	0.105
	0.41	-0.16	-0.39	88	6	0.121
	0.23	-0.09	-0.39	89	4	0.159
184°K.	0.60	-0.38	-0.63	144	10	0.100
	0.46	-0.28	-0.61	138	8	0.105
	0.46	-0.30	-0.65	148	6	0.121
	0.27	-0.17	-0.64	145	4	0.159
	0.06	-0.07	-1.17	264	2	0.303

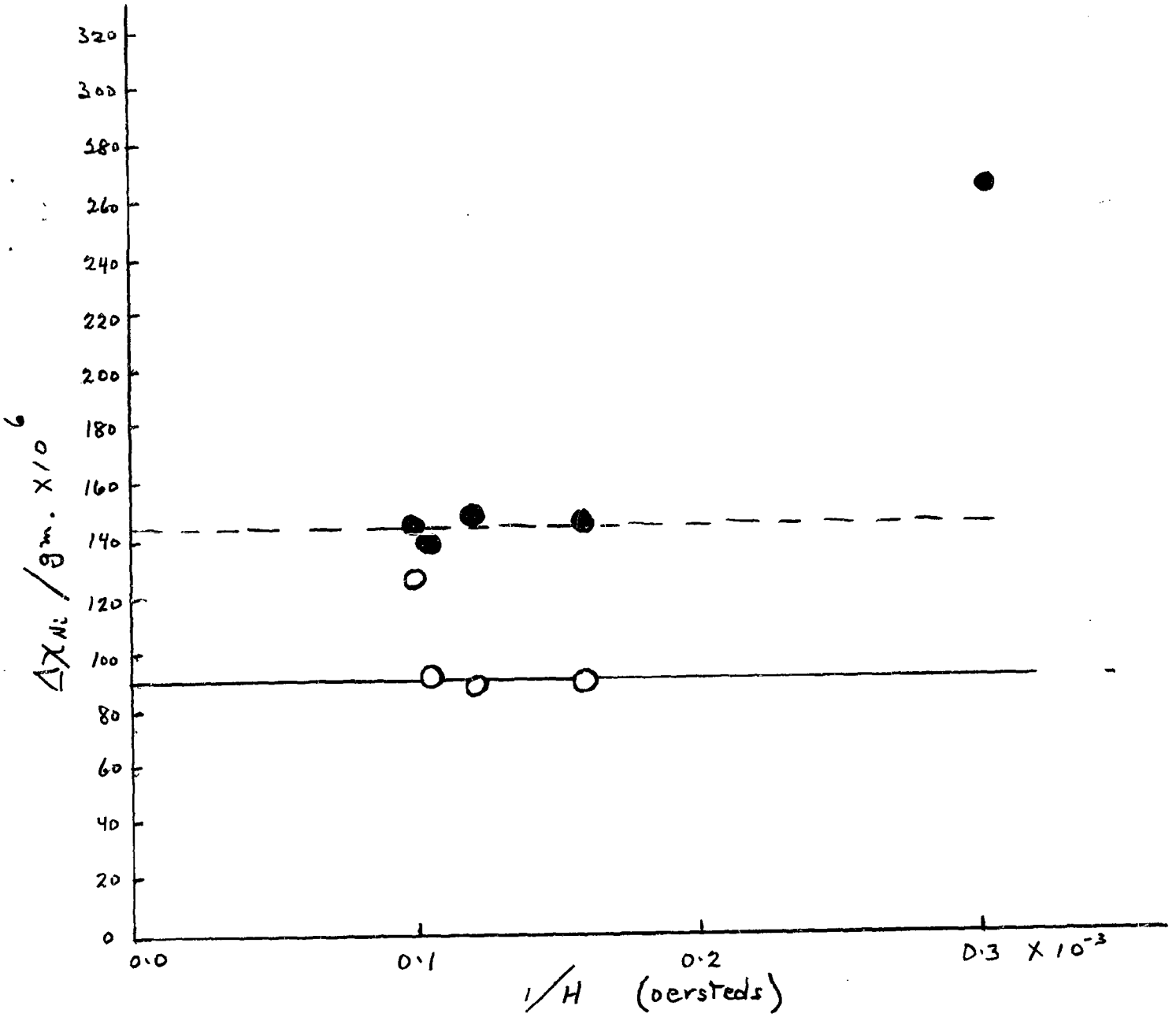


Fig. 2 Susceptibility of M-6 #10 vs. Reciprocal Field

Discussion of Results:

The problem is two-fold; first, the reason for the anomalous magnetic moments of nickel and cobalt in glasses is to be found, and second, the anisotropy of drawn nickel glass must be explained. The abnormally high moment of nickel and the corresponding low moment of cobalt will be considered first.

Since drawn nickel glass showed magnetic anisotropy, it appears that the unusual moment of nickel is caused by abnormal quenching effects, rather than by a high oxidation state. The low moment of cobalt should also arise from the same quenching effects. In Table V, the calculated and experimental moments of cobalt, nickel, and copper ions are compared, in solid salts, in solution, and in glass. Copper, as well as cobalt, has a lower moment in glass than in solid salts or in solutions.

Table V. Magnetic Moments of Cobalt, Nickel and Copper
(in Bohr magnetons)

	μ calculated		μ experimental		
	Spin only	Spin plus orbital	In solution (1)	In solid salts(1)	In glass(2)
Co	3.87	5.20	4.4-5.2	4.4-5.2	4.5-4.7
Ni	2.83	4.47	3.2	3.2-3.4	3.5-3.6
Cu	1.73	3.00	1.8-2.0	1.8-2.0	1.5-1.8

The nickel, cobalt, and copper ions must occupy equivalent positions in the three series of glasses, like a series of isomorphous salts. According to Weyl,(3) cobalt and nickel ions, because of their size and charge, would be expected to occupy "net-work modifying" (N.W.M.) or interstitial positions, in which the nickel or cobalt ion has a coordination number of six, i.e., the transition ions are in positions of octahedral symmetry. However, it is also possible for these ions to occupy "net-work forming" (N.W.F.) positions, as CoO_4 or NiO_4 complexes, these complexes being part of the actual silica network. In this case, the transition ions are in positions of tetrahedral symmetry. These considerations should apply to copper as well as to nickel and to cobalt. Weyl says that the proportion of NiO_4 or CoO_4 groups may be very small, but that these groups possess very intensive light absorption, NiO_4 causing the purple coloration in some nickel glasses.

Only ions, atoms, or molecules having a resultant orbital or spin moment are paramagnetic, since the paramagnetic moment arises from the tendency of the external field to orientate the ions so that their magnetic axes are parallel to the direction of the field. Such alignment is opposed by thermal motion of the ions, by interaction between neighboring paramagnetic ions, and by the "quenching" of the moment by an imposed electric field such as the internal field of a crystal. In the glasses, the nickel and cobalt ions are sufficiently magnetically dilute that only the first and third factors can affect the moments. The possible effects of a crystalline field will now be considered.

In a free ion of quantum number j, there will be 2j+1 states of equal energy, which split in a magnetic field into 2j+1 states of different energies. The distribution of the ions in these varying energy levels gives a resultant magnetic moment along the field. The effect of a local field, such as a crystalline field, is to remove the degeneracy of the free ion by Stark splitting of the 2j+1 states. Thus the response of an ion in a crystal to a magnetic field must be less than that of a free ion, and the paramagnetic moment is decreased. If the degeneracy were completely removed by the crystalline field, the ions would cease to be paramagnetic. In general however, the spin moment is left free, and the orbital moment is partially or fully quenched by the crystalline field, or by local fields in a solution. Therefore many ions in solid salts or in solutions have moments corresponding to the "spin only" value, or between the "spin only" and the "spin plus orbital" moments. Nickel salts, in general, have stronger internal fields than cobalt salts, since the orbital moment of nickel salts is more nearly quenched. However this behaviour appears to be reversed in glasses.

Bethe[4] has calculated the splitting of energy levels which will occur in internal fields of different symmetry. The symmetry of the field surrounding a given atom is not necessarily that of the crystal itself. Instead, the field seems to have the symmetry character of the position of the atom or ion. For example, the $NiSO_4.6H_2O$[8] crystal is tetragonal, but six water molecules surround each nickel ion octahedrally, producing a nearly cubic field about the nickel ion. Similarly, it is possible that in solution the field acting upon a paramagnetic ion has the symmetry of the coordination group, again six water molecules for the nickel ion. Thus the magnetic moments in the solid salt and in solution will be similar. Probably the lack of a definite crystalline structure in a glass does not affect the moments of paramagnetic ions in the glass. Only the symmetry of the neighboring ions will influence the magnetic moment. Thus it is necessary to determine the effect of both octahedral and tetrahedral symmetry upon the moments of the cobalt and nickel ions. Penney and Schlapp[5] have made detailed calculations of the effects of various fields upon magnetic susceptibilities, with special reference to nickel and cobalt. Van Vleck[6] has summarized their results, some of which are given below.

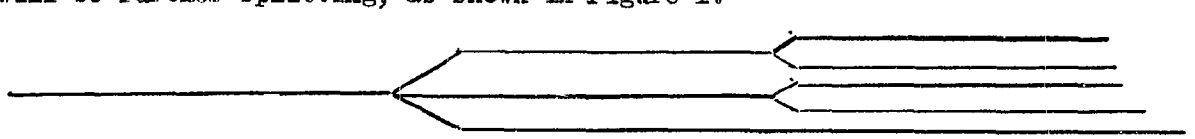
The potential energy, ψ, caused by the surrounding ionic field, at a given ion, may be expressed as a power series of the coordinates x_i, y_i, z_i, of the surrounding ions with the given ion as the origin of coordinates:

$$(1) \;\ldots\ldots\; \psi = \sum_i \left\{ A x_i^2 + B y_i^2 - (A+B) z_i^2 + D(x_i^4 + y_i^4 + z_i^4) \right\}$$

All uneven terms drop out when there is a two-fold symmetry axis in the z-direction. For cubic symmetry, $x_i^2 = y_i^2 = z_i^2$ and

$$(2) \;\ldots\ldots\; \psi = D(x_i^4 + y_i^4 + z_i^4) = 3Dz_i^4$$

If the cubic field is dominant, then the F terms split up into three terms, Γ_2, Γ_4, and Γ_5, as in Figure 1. If a weak rhombic field is superimposed, there will be further splitting, as shown in Figure 1.



free ion cubic field weak rhombic field

Figure 1. Splitting of F terms in cubic and rhombic fields.

In a purely cubic field Γ_4 and Γ_5 would be triply degenerate, but in a weak rhombic field the degeneracy is removed, and the orbital moment is at least partially quenched. Ni^{++} is in a $^3F_4$ state and Co^{++} is in a $^4F_{9/2}$ state. Therefore, the splitting of the F-terms determines the values of their moments. For Ni^{++} salts, the singlet level, Γ_2, has been found to lie below all others, as in Figure 1. This symmetry of the field is roughly that expected for a Ni^{++} ion in a position of octahedral symmetry, as in certain salts, in solution, or in N.W.M. positions in a glass. The dominant cubic field is caused by the immediately surrounding ions or atoms, and the weak rhombic field by less symmetrically placed more distant neighbors. On the other hand, Van Vleck(6) shows that for the same signs of A,B, and D, in Equation (1), the pattern for cobalt will be inverted relative to that for nickel, i.e., it will be Figure 1 upside down. A low singlet level indicates a small anisotropy and conformity to Curie's law down to low temperatures, as is found for nickel salts. A low triplet level corresponds to a larger anisotropy, deviations from Curie's law, and less quenching of orbital moment, which describes the normal behaviour of cobalt ions in positions of octahedral symmetry, as in the hydrated sulfates.

However, for a field of four negative charges tetrahedrally surrounding the paramagnetic ion, the sign of D is reversed, and the Stark pattern is therefore inverted. This means that the behaviour of Co^{++} and of Ni^{++} will be reversed, and that nickel will have a moment quenched less than that of cobalt, when in a position of tetrahedral symmetry. These theoretical predictions have been confirmed in the case of cobalt by Krishnan and Mookherji,(7) who measured the anisotropy of single crystals of $Cs_2[CoCl_4]$ and $Cs_2[CoCl_4]Cl$, in which the four chlorine atoms surround the cobalt ions tetrahedrally. The anisotropy of both salts was found to be very small, like that of nickel salts.

Thus the behaviour of cobalt and nickel in glasses can be explained quite satisfactorily by the assumption that the paramagnetic ions are distributed in both octahedral and tetrahedral positions. Even if only a small percentage of the ions are in tetrahedral positions, the moment of cobalt will be lower than normal and that of nickel will be higher. It might be possible to predict the number of ions in tetrahedral positions, at least for cobalt glasses, by comparing the moment of the cobalt in the glass to that of a normal cobalt salt such as $CoSO_4.7\ H_2O$, and to that for $Cs_2[CoCl_4]$.

The same sort of reversal of magnetic properties might be expected for other pairs of transition elements when the paramagnetic ions are in tetrahedral positions. $Cu^{++}(^2D_{5/2})$ and $Fe^{++}(^5D_4)$ are one such pair. According to Van Vleck,(6) the effects for this pair will be much more complicated than for cobalt and nickel, since iron and copper are less closely related and would not be expected to have almost identical crystalline fields. It is possible that this effect accounts for the low moment of copper in glass.

The second problem is to explain the anisotropy of drawn nickel glass. Nickel salts in which the nickel ions have positions of octahedral symmetry have an anisotropy which is about three per cent of the average susceptibility, while isomorphous cobalt salts have anisotropies which are about twenty per cent of the average susceptibility. Therefore nickel ions in octahedral positions in glass will have a very small anisotropy, while those in tetrahedral positions will have a much larger anisotropy. In the unstrained glass network, both the tetrahedral and octahedral positions of the nickel atoms are oriented randomly so that the glass has no resultant anisotropy.

To obtain the anisotropic glass rods, the glass was heated and rapidly drawn out, being allowed to cool rapidly to room temperature. This procedure must distort the original structure of the glass. It is probable that the octahedral holes are drawn out along the direction of pulling of the glass fibre. This would have the overall effect of changing some of the octahedral holes into positions of tetragonal symmetry, with one axis elongated along the direction of drawing. If this elongation is not too large, the conditions would still correspond to a predominantly cubic field with a weak rhombic field superimposed, which would leave the nickel ion with a small anisotropy, not much different from that of the ion in the strictly octahedral position. But here all the imposed local fields will be oriented in nearly the same direction, and as a result, the glass will show anisotropy, of the same order as that of $NiSO_4.6\ H_2O$. On the other hand, if the elongation of the cubic axis parallel to the direction of drawing is large, it is possible that the symmetry of the octahedral holes might change to something approaching tetrahedral symmetry, but this is rather unlikely.

It is more difficult to conceive of a way in which the tetrahedrally coordinated nickel ions in N.W.F. positions could be oriented in the drawn glass so that there could be a large resultant anisotropy. Probably such an orientation would lead to a distortion of the tetrahedral symmetry, possibly to a degree which could cause the crystalline fields to become so unsymmetric as to remove all degeneracy in the energy levels, causing the moment to drop to the spin-only value for those particular ions. Thus it is difficult to account for any large anisotropy which arises in a drawn glass. However, according to Weyl,(3) more nickel ions will be present as tetrahedrally coordinated ions when the glass is raised to a high temperature, and also in the unannealed glass. If there is any orientation of these tetrahedrally coordinated nickel ions in the glass network, there could be quite a substantial anisotropy.

For most of the samples of the nickel-containing glass M-6, the measured anisotropy was small. Only two samples had an anisotropy larger than about five per cent of the average susceptibility. These two exceptions, M-6 #10 and M-6 #17, have anisotropies which are about 25% and 10%, respectively, of the average susceptibility. An anisotropy of from 2% to 5% would be expected for octahedrally coordinated nickel ions, if all such ions were oriented in the same way in the glass. For oriented tetrahedrally coordinated nickel ions, an anisotropy of 20% to 30% would be expected, comparable to those found for octahedrally coordinated cobalt salts. For most of the samples the anisotropy is less than one per cent of the average susceptibility of 89 c.g.s. e.m. units per gram at room temperature. The anisotropy increases as the radius of the samples decreases. If the amount of distortion in the glass increases as the radius of the sample is decreased, then the anisotropy increases as the amount of distortion increases. As shown in Graph I, the anisotropy tends to increase to above 5% of the average susceptibility for samples of very small radius. Therefore the anisotropy must be partly caused by tetrahedrally coordinated nickel ions, as well as by the octahedrally coordinated ions, and some at least of the tetrahedrally coordinated ions must be non-randomly oriented. Sample M-6 #10 does not fit the curve of Graph I, and its anisotropy is extremely high, equal to that which would correspond to all the nickel ions being tetrahedrally coordinated and similarly oriented. The reason for this behaviour is unknown. The susceptibility of the sample is normal, after annealing, so that an impurity does not seem to be the cause.

Annealing should decrease strain, and increase the randomness of orientation, thus decreasing the anisotropy of the glass samples, as was found experimentally. Since conditions were not the same for the annealing of all samples, it is not surprising that the results are rather erratic.

From the measurements with the Faraday balance, it can be concluded that M-6 #10 was not ferromagnetic, at least after annealing, since its susceptibility agrees, at both temperatures, with that found previously for the glass M-6. Since this sample showed the largest anisotropy, it is unlikely that any of the other samples were anisotropic because of the formation of ferromagnetic substances.

No further measurements have been made on the uranium glass, previously reported from this Laboratory as showing zero magnetic moment, although optical evidence suggests that the uranium is in the +4 oxidation state. There is, however, one electronic state for U^{+4} which yields zero moment. In view of the proposed explanation given above for the anomalous moments of nickel and cobalt in glass, it seems not impossible that +4 uranium may assume a diamagnetic state under similar conditions.

Summary:

It has been suggested that the abnormally high moment of nickel and the abnormally low moment of cobalt in glass are due to the presence of the paramagnetic ions in positions of tetrahedral symmetry. Local fields of tetrahedral symmetry will give nickel magnetic properties like those of cobalt in fields of octahedral symmetry, and will give cobalt magnetic properties like those of nickel. This inversion of magnetic properties could occur with other pairs of transition elements in glasses. Therefore the use of magnetic measurements to determine the oxidation states of paramagnetic ions in glasses may be complicated by the fact that the paramagnetic ion has a changed moment in the glass.

Suggestions for further work:

It would be interesting to make similar measurements upon a cobalt glass. If the anisotropy found were much larger than for nickel glasses, in samples of the same radius, the anisotropy would be caused by paramagnetic ions in octahedral positions; if it were smaller, the anisotropy would be caused by paramagnetic ions in tetrahedral positions. Comparison with a salt in which nickel is tetrahedrally coordinated would also be revealing as well. It would be advisable to control the conditions of drawing and of annealing much more closely than in the present work, if further measurements are made upon glasses.

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(3) Weyl, Journal of Applied Physics, 17, 628 (1946)

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Part II. The Reaction γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ (Status Report)

By Frank E. De Boer

(a) The object of this research is the investigation of the solid phase transformation of γ-Fe_2O_3 to α-Fe_2O_3. In the course of this research the effect which surface area, length of time of preliminary heating, the presence and type of foreign ions, and the method of preparation have upon the activation energy of the reaction will be studied. The properties which allow measurement of the amounts of the two phases present, and thus of the kinetics of the reaction, are; the γ phase is ferromagnetic while the α phase is non-ferromagnetic (at least its ferromagnetism is very slight) and the x-radiograms of the phases differ, the γ-oxide is a spinel whereas the α has the corundum structure.

The apparatus which has been used for the measurement of the kinetics of this reaction is that built by R.F.S. Robertson and described by Robertson and Selwood, The Review of Scientific Instruments, Vol. 22, No. 3, 146-152. If the magnetization of a sample is too low at the transition temperature, the measurements will be made by following the rise or fall of an x-ray diffraction peak using a Philips-North American X-ray diffraction apparatus with a high temperature furnace attached. Surface areas were measured with a B.E.T. type instrument.

(b) Preparation and Analysis: -- A-series: 31.5 g. $Fe_2(SO_4)_3$ and 22.0 g. $FeSO_4.7H_2O$ were suspended in water and then poured into a boiling solution of NaOH (this addition was not quantitative.) The precipitate was washed by decantation several times with cold water until neutral to litmus. It was partly dried by placing over $CaCl_2$; this method was quite unsatisfactory. The sample was divided into two parts; nothing further of any significance was done with the first part, A-1. A-2 was heated in the oven for several days at 110°, crushed with an agate mortar and pestle, and heated in an atmosphere of oxygen at 225° for ninety hours. The X-radiogram corresponded closely to that for γ-Fe_2O_3 given in the ASTM card catalogue. The percentage of iron in the sample was found by the permanganate method to be 66.2%. The sample was then dried over P_2O_5 in vacuo for two days; re-analysis showed the sample contained 69.7% iron (theoretical is 69.94%.)

B-1: γ-Fe_2O_3 was prepared from tetrapyridino-ferrous chloride by the method of Inorganic Synthesis, Vol. I, pp. 184-186. The X-radiogram corresponded to that for γ-Fe_2O_3 but the peaks were very small. The sample was analyzed by the permanganate method: results showed 66.2% iron. It was dried over P_2O_5 in vacuo for two days; re-analysis showed the sample contained 69.75% iron

A-26: This sample was prepared in a manner identical to that used in the preparation of A-2 except that it was dried in the oven at 110° for twelve hours and was oxidized under oxygen at 230° for only 35 hours. It was analyzed with 0.04 N $Ce(SO_4)_2$ by L. Moore and was found to contain 70.7 ± 0.7% Fe with about 1% of the iron being in the plus two oxidation state.

C-series: About 400 ml. of a concentrated solution containing equal amounts (by weight) of $Fe_2(SO_4)_3$ and $FeSO_4.6NH_3$ were added to water solutions which contained varying amounts of NaOH (see Table 1.)

Table 1

Sample	Amount of NaOH per liter H_2O
C-1	33 g.
C-2	30
C-3	27
C-4	24
C-5	21
C-6	16
C-7	12
C-8	9
C-9	5
C-10	2

All the precipitates were black except C-10 which was green (the specific magnetization of C-10 was also very low.) The samples were washed until neutral to litmus, plus a few times more, dried at 110°, crushed, and oxidized in air at 250°. The samples were analyzed as follows: the samples were weighed into porcelain crucibles which had been ignited, dried at 110° overnight, weighed again, heated at 950° for an hour, weighed, and then the analysis for iron was done by the permanganate method. Table 2 shows the results of this analysis.

Table 2

Sample	Loss of weight by drying in mg. per g. of sample put into crucible	Loss of weight by ignition in mg. per g. dry sample	percent Fe in ignited sample
C-1	11.0	14.1	69.6 ± 0.2
C-2	5.8	12.8	69.3
C-3	10.4	12.5	69.5
C-4	7.7	11.9	69.5
C-7	14.4	15.4	69.6
C-8	8.3	16.4	69.5

D-series: This series was made in order to make sure that there was no sodium in the samples. 50 g. $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in about one-half liter boiling water was added to 61.5 g. $Fe(NH_4)(SO_4)_2$ in the same amount of boiling water (the solution turned brown but no precipitate could be noticed.) This mixture was poured into two liters of dilute ammonium hydroxide. The resulting jet black precipitate was washed by decantation six times with four liters of water each time, filtered, dried at 110° for several hours, crushed to pass a 150 mesh screen, and oxidized at 230° for varying lengths of time as shown in Table 3.

Table 3

Sample	Time of oxidation
D-1	1.5 hours
D-2	2.75 "
D-3	5.25 "
D-4	16.5 "
D-5	22.75 "
D-6	48.0 "

Sample D-5 was in addition heated at 300° for 24 hours.

Analysis was carried out in a manner similar to that used for series C and the results are listed in Table 4.

Table 4

Sample	Loss of weight by drying, in mg. per g. of sample put in the crucible	Loss of weight by heating to 480°, in mg. per g. dried sample	Loss of weight by heating to 950°, in mg. per g. of dried sample	Per cent Fe in ignited sample
D-1	10.4	13.6	----	68.8
D-4	7.9	9.4	11.7	68.6
D-5	14.6	8.8	13.6	68.6
D-6	16.3	10.0	13.3	69.4

One of the spaces in the D-1 row is vacant because the crucible broke. The samples would not completely dissolve in concentrated HCl so that the iron determinations are low. (The samples can still be analyzed by the potassium carbonate fusion method if necessary.)

E-series:

1 and 2: 70 g. Fe $SO_4 \cdot 7H_2O$ (reagent grade) was added to 1100 ml. H_2O, heated almost to boiling, 88 ml. conc. NH_3 solution and a few grams of NaOH were added, the resulting precipitate was dark green; the mixture was stirred continuously throughout the preparation. 12.3 g. $NaNO_3$ in a little water was added dropwise to the hot solution whereupon the precipitate turned jet black after boiling for an hour. The mixture was separated into two parts, both were filtered; the first part, E-1, was not washed, the other, E-2, was washed once by decantation.

3 and 4: Made by the same method as above except that 110 g. $FeSO_4 \cdot 7H_2O$, 10.4 g. $NaNO_3$, and no NaOH were used. E-3 was not washed; E-4 was washed by decantation once.

5: This was made by the same method as E-3 except that the precipitate was washed by decantation eight times.

All the samples were dried in the oven at 100°, heated at about 750° in vacuo, and crushed to pass a 150 mesh screen. These samples were then analyzed thermomagnetically in vacuo. In each case the magnetization decreased to about 3/4 its original value after one heating and cooling cycle (the maximum temperature of a cycle was between 600° and 650°, the time that a sample was above 600° in no case was longer than twenty minutes.) On the second cycle curves of samples 1 and 2 were reversible, those for samples 3 and 4 were irreversible; only one cycle was made for sample 5. The cooling curves of the irreversible cycles are a little lower than the heating curves (graph is magnetization versus temperature.) The Curie temperatures for samples 1, 2, and 5 are 575°; the Curie temperature of E-3 decreases progressively from 572° to 568° to 562°; the Curie temperature of E-4 was 564° on the first cycle and 560° on the second cycle. All the samples were then heated in air at 230° for 24 hours; thermomagnetic runs in vacuo showed that E-5 had about one-ninth its ferromagnetism left even though the temperature had risen well above 600°; E-1 under similar conditions had about one-sixth its ferromagnetism left. The samples were next heated at 250° for six hours; a vacuum thermomagnetic run on E-5 showed that it still had about one-ninth its ferromagnetism left at the end of the run. The samples were heated at 275° for seven hours; a vacuum thermomagnetic run showed that E-5 had about one-twelfth its ferromagnetism left at the end of the run, the temperature had risen above 700° during the run. The sample tube was opened and a thermomagnetic run made; the magnetization decreased to zero and did not increase at all on cooling to room temperature. The samples were heated to 300° for 23 hours; vacuum thermomagnetic analysis again showed the sample had one-twelfth its ferromagnetism left after cooling.

Chemical analysis of series E is shown in Table 5

Table 5

Sample	Percent iron
E-1	68.8
E-2	69.2
E-3	69.45
E-4	69.5
E-5	69.9

The samples will be analyzed for sodium by the following method. (Specific directions are those of Mr. Cohn of the U.S. Bureau of Mines.) The oxide, after having been ignited at 900°, is dissolved in 20 ml. 8 N HCl over a steam bath. When completely dissolved, water or HCl is added to bring the solution to 6.7 N with respect to HCl. The ferric chloride is extracted from the solution by using three portions of ethyl ether, in each extraction one uses one and one-half the volume of the water solution of ethyl ether. The water solution is evaporated over a low temperature hotplate and -- after evaporation of the small amount of ether -- under an infra-red lamp. The residue is taken up with a measured amount of water and photometered.

RESULTS

The kinetics of most of the samples have been run. Until quite recently it was uncertain as to how to determine a meaningful activation energy. The theory of the method to be used will be found in the appendix. The crux of this method is that one determines the time that it takes for the reaction to reach a given value of the specific magnetization at various temperatures, and plots the logarithm of the time versus the reciprocal temperature. Then the activation energy is equal to the slope (if 1/T is plotted on the abcissa) multiplied by 2.303R, where R is the gas constant. This method has been used to find the activation energies of the D-series and will be applied to the other samples as soon as possible. The results for the D-series will be found in Table 6 and in graph 5. Graphs 1 to 4 are the plots from which the D-series activation energies were found.

Table 6

Sample	Activation Energy	Specific Magnetization at room temperature	Specific Surface Area
D-1	58.7 kcal.	0.507 spaces/mg.	57.8 m^2/g.
D-4	51.5	0.493	----
D-5	35.1	0.460	58.7
D-6	51.6	0.486	53.1

This table shows rather well that there is no relation between the surface area (or particle size) and activation energy, although there might be near the extremes; the graph shows almost a straight line relationship between activation energy and specific magnetization. The specific magnetization of these sodium-free samples decreased as the time of preliminary heating increased; this is probably not due to formation of the α oxide, since the heating was done at much lower temperatures than those at which the kinetics were measureable and since the reaction has an appreciable activation energy, but rather to the crystal lattices becoming more ordered. This hypothesis might be tested by x-ray diffraction.

The kinetics of the E-series have as yet not been studied.

Projected Work

1. To study the E-series
2. To study a series containing aluminum
3. To study a series made by the pyridine method
4. To make and study a very low surface area sample

Appendix

The following is the derivation of the method for finding activation energy without knowing the order of the reaction as developed by W.E. Parkins, G.J. Dienes, and F.W. Brown, J. Appl. Phys. 22, 1012 (1951). If one takes

$$\frac{dn}{dt} = -K_o n^{\gamma} e^{-E/kT} \qquad (1)$$

the general rate expression where n is the amount of the reacting substance, t is time, K_o is a constant, γ is the order of reaction, E is activation energy, k is Boltzmann's constant, T is the absolute temperature. If p is the physical property being measured, then $p = g(n)$ .... (2), where g(n) must be a single valued function of p. If $\gamma \neq 1$ and E and T are constant (isothermal conditions for each run), then the rate expression integrates to $n_o^{1-\gamma} - n^{1-\gamma} = K_o(1-\gamma)\, e^{-E/kT}\, t$ .... (3), where n_o is the value of n at t=0. If one lets h(p) be an unspecified function of n and substitutes this for $n^{1-\gamma}$ in equation (3),

$$\frac{1}{K_o(1-\gamma)}\left[h(p_o) - h(p)\right] = t\, e^{-E/kT} = u \text{ .... (4)}.$$

If identical samples are exposed to varying temperatures and p is measured as a function of time then E can be determined. That is if p_o and p are constants for a series of runs, then the left side of (4) is a constant. t is the time required from p_o to $p = c_1$. Then $t\, e^{-E/kT} = c_2$; or $\log t = \log c_2 + \frac{E}{2.303kT}$ ... (5). E should be independent of the value of p taken, if not the method is inapplicable.

Thanks are due to Mr. Cohn of the U.S. Bureau of Mines for bringing the above to our attention and for the specific directions for the sodium analysis. Thanks are due Dr. Klotz of this department for the use of his flame photometer.

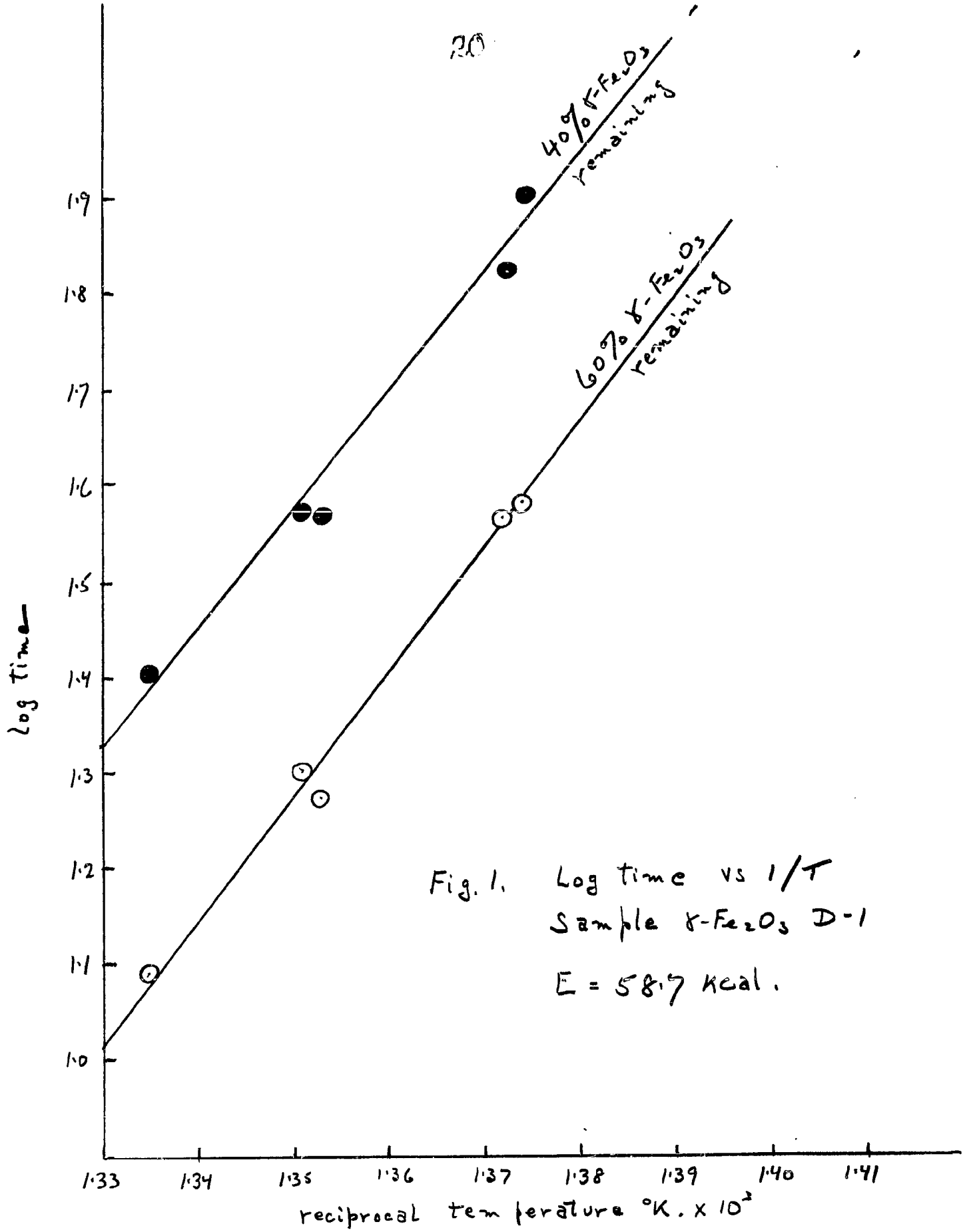

Fig. 1. Log time vs 1/T
Sample γ-Fe_2O_3 D-1
E = 58·7 Kcal.

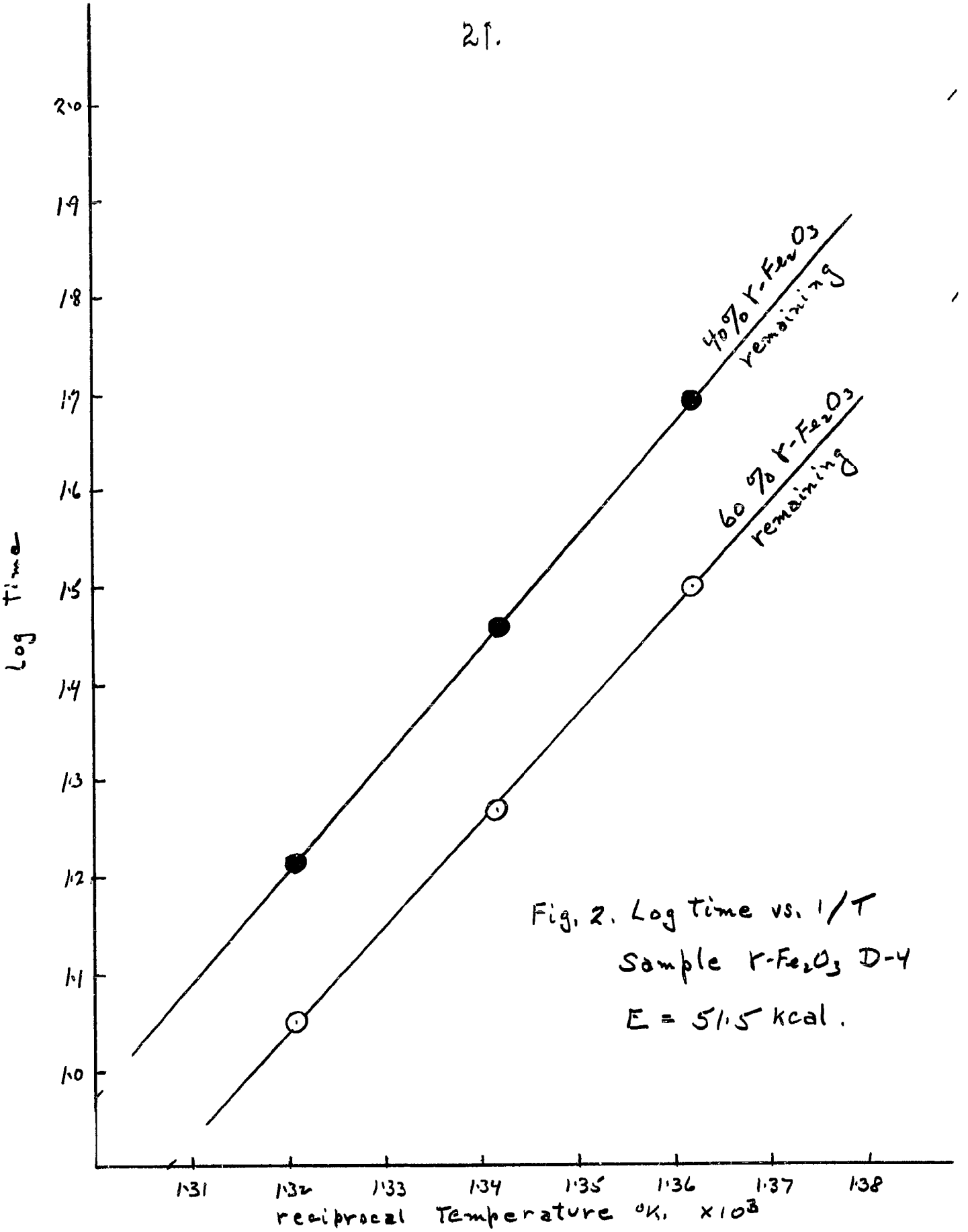

Fig. 2. Log time vs. 1/T
Sample γ-Fe_2O_3 D-4
E = 51.5 kcal.

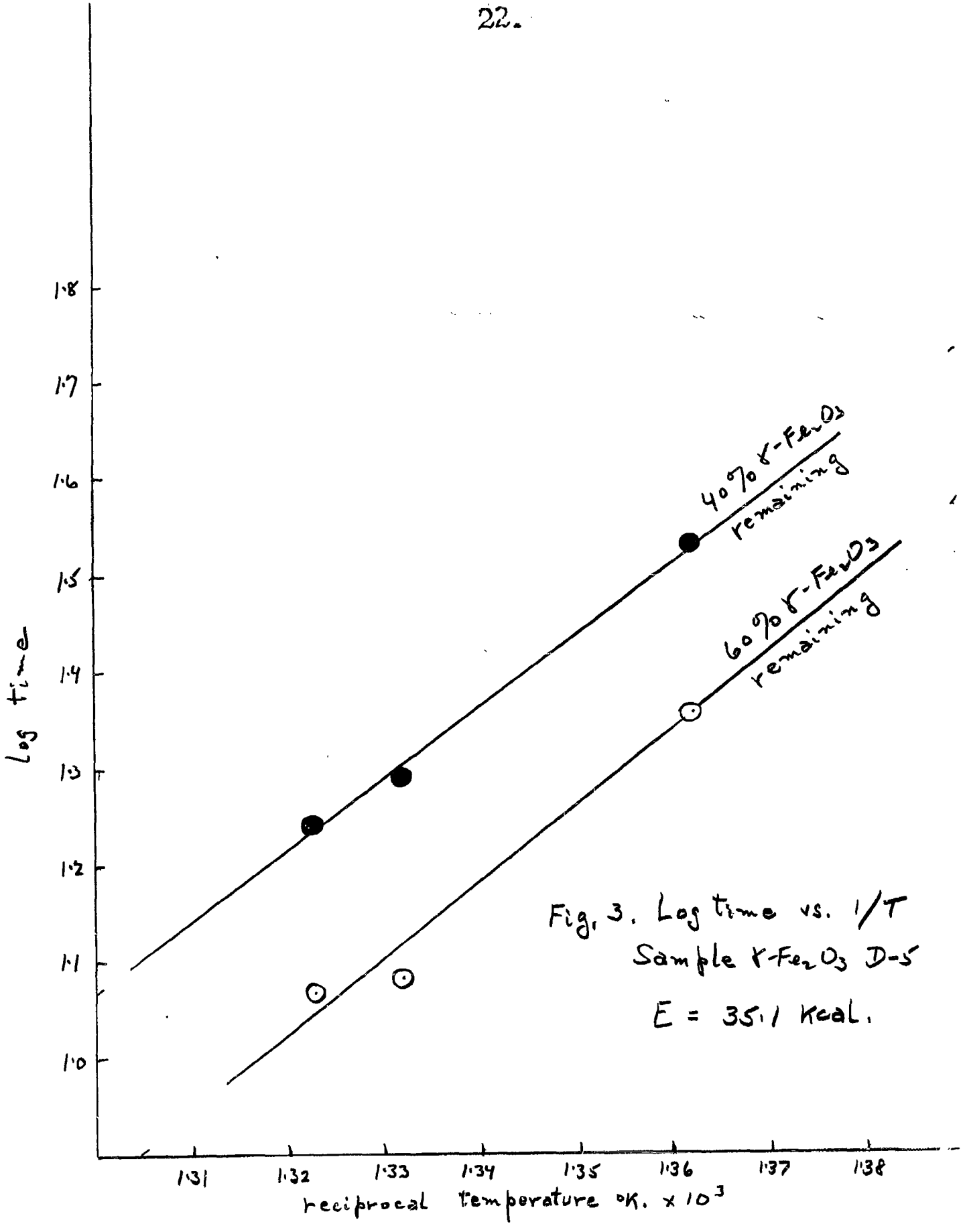

Fig. 3. Log time vs. 1/T
Sample γ-Fe_2O_3 D-5
E = 35.1 Kcal.

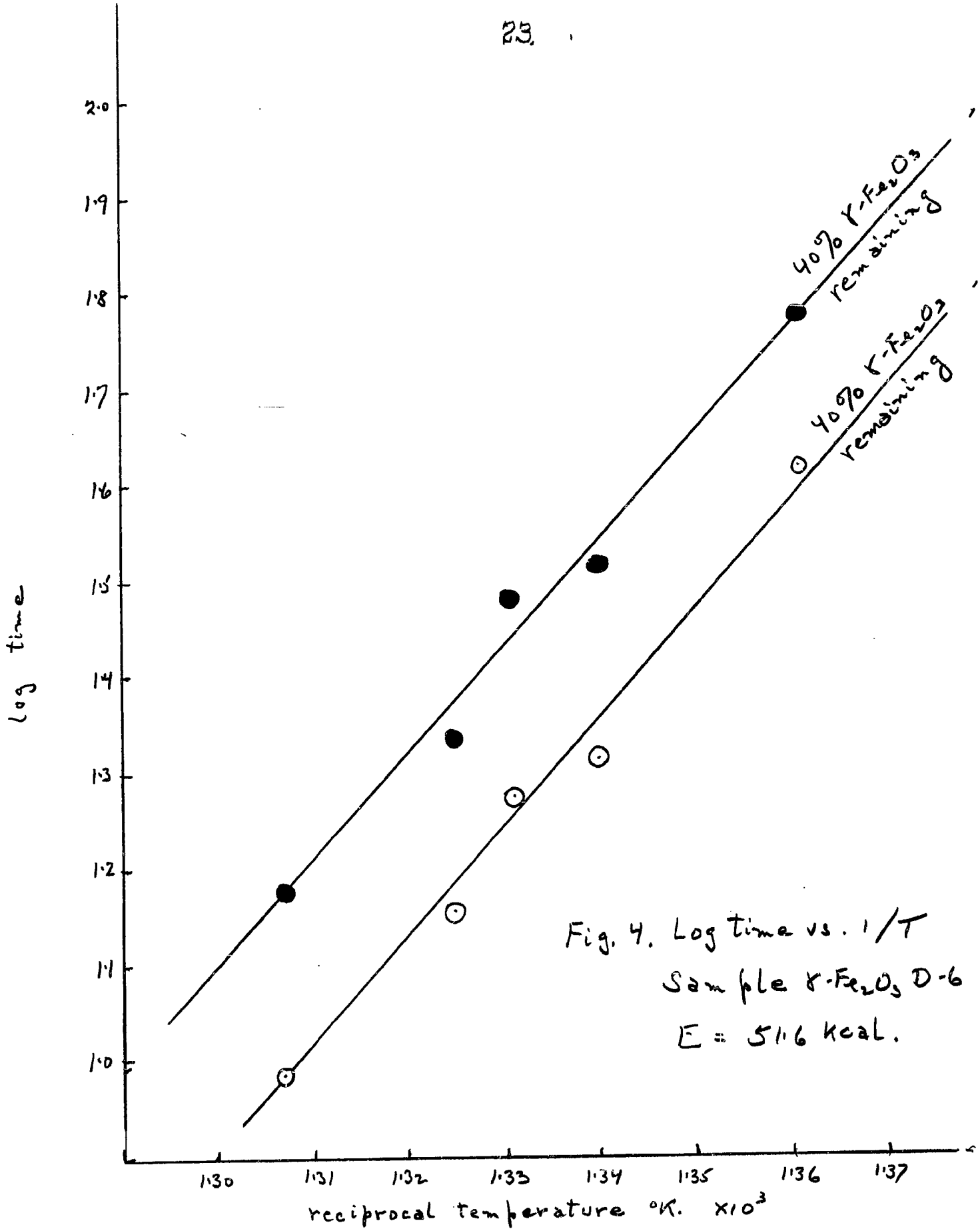

Fig. 4. Log time vs. 1/T
Sample γ-Fe_2O_3 D-6
E = 51.6 kcal.

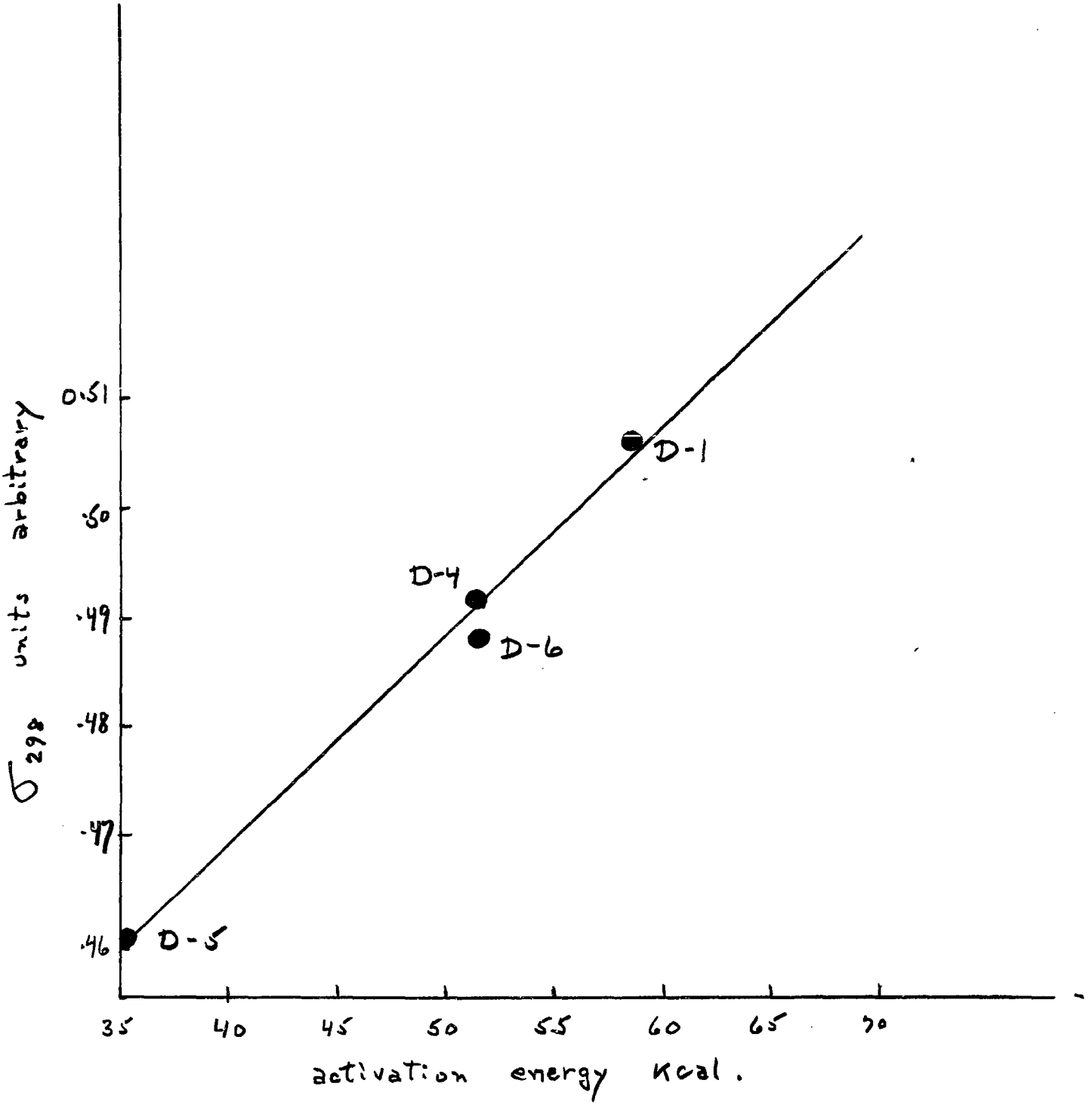

Fig. 5. Activation energy vs. specific magnetization.

Part III Supported Palladium
by P. W. Selwood

The purpose of this work was to see if metallic palladium supported at low concentrations on high surface area alumina shows the increase of magnetic susceptibility shown by supported chromia, copper oxide, and other paramagnetic systems. The answer to this question being found to be in the negative, some further experiments were done on the magnetic properties of hydrogenized supported palladium.

Experimental Part

Magnetic measurements: Magnetic susceptibilities were measured by the Gouy method, with a sample tube of about 25 cc. capacity. The tube was fitted with a cap made up of a micro stopcock and two standard taper joints in such a way that the powdered samples could readily be changed, evacuated, or attached to a gas burette system for quantitative absorption of hydrogen. Part of the apparatus is shown in Fig. 1. All magnetic measurements were made at 25°C. The apparatus was calibrated with water. All measurements were made at fields of 5830, 6360, and 7250 oersteds.

Alumina: So-called "gamma"-alumina prepared by Mr. Paul Jacobson was used for the palladium support. This had a surface area of 190 m^2g^{-1} and a magnetic susceptibility of -0.39×10^{-6}, which was independent of field strength within experimental error. After being degassed for several hours in high vacuum at 200°C., the alumina had a susceptibility of -0.38×10^{-6}.

Palladium-Alumina: The absorptive capacity of the alumina having previously been determined, 30 g. of the alumina was treated with 30 cc. of a water solution of palladous chloride to which had been added a few drops of dilute hydrochloric acid. The alumina took up all the solution, which contained 1.70g. of palladous chloride. This mixture was dried at 100°C. The susceptibility was found to be -0.30×10^{-6}, showing, as expected, no appreciable paramagnetism in the supported palladous chloride.

The mixture was now heated to 140°C. in hydrogen for ten hours, until the exit gases contained no hydrogen chloride as determined by bubbling through silver nitrate solution. As previously known, reduction of the palladous chloride started at room temperature.

The mixture was now cooled in hydrogen; the hydrogen was replaced by helium; and the susceptibility was measured. The susceptibility was -0.11×10^{-6}. After being heated in high vacuum at 150°C. for five hours, the sample had a susceptibility of -0.14×10^{-6}. As the sample contained 1.02g. palladium, the susceptibility per gram of supported palladium was 7.1×10^{-6}. This sample was strongly active toward hydrogen in air.

Hydrogen Absorption: The sample, weighing 25 g. was pumped out for one hour at room temperature. The dead-space was found with helium to be 22.7 cc. at 747 mm. and 24.2°C. The sample was again pumped out, then hydrogen was admitted. The absorption of hydrogen was at first very rapid. This was followed by an extremely slow absorption extending over several weeks. The hydrogen absorption results are shown in Fig. 2.

At intervals the sample tube was removed from the gas burette for measurement of the magnetic susceptibility. The data are presented in Table 1 which gives the Pd-H proportion, the measured susceptibility, and the susceptibility per gram of the palladium-hydrogen system. It will be noted that the susceptibility for $PdH_{1.0}$ was approximately 3.0×10^{-6}.

Table 1

Magnetic Susceptibility of the Supported

Palladium-Hydrogen System

$Pd\text{-}H_x$	$X_x 10^6$	$X_{Pd\text{-}H_x} \times 10^6$
$Pd\text{-}H_0$	-0.14	7.1
$Pd\text{-}H_{0.5}$	-0.26	3.4
$Pd\text{-}H_{0.7}$	-0.26	3.4
$Pd\text{-}H_{1.2}$	-0.28	2.9
$Pd\text{-}H_0$	-0.12	7.6

At the end of several weeks the sample was evacuated for five hours at 150°C. The susceptibility per gram of sample was found to have returned to -0.12×10^{-6}.

Discussion of Results

Palladium, together with manganese, is unusual among common elements for showing a high magnetic susceptibility in the elementary state. It was, therefore, felt that there was a definite possibility of palladium showing the "dispersion effect" previously described in several communications from this laboratory[1]. The fact that the susceptibility of supported palladium at fairly low concentration was found to be only slightly larger than that of massive palladium ($\sim 5.4 \times 10^{-6}$) shows that palladium resembles molybdenum dioxide, in which the dispersion effect is absent or obscured. It is hence not possible to use magnetic measurements to estimate the degree to which palladium is dispersed in the form of an active supported catalyst, but whether this is due to some intrinsic property of supported palladium, or to failure to effect a good dispersion, is not clear.

The effect of absorbed hydrogen on the magnetic susceptibility of palladium is an old problem[2]. Previous results agree that in the neighborhood of $PdH_{0.60}$ the system becomes diamagnetic and this is taken to show that there is approximately 0.6 electron hole in the d-band of metallic palladium.

It might be expected that supported palladium would show some quantitative differences from massive palladium in this respect. The results presented here on supported palladium show a rapid decrease of paramagnetism to $PdH_{0.5}$, but virtually no further change during the very slow ensuing absorption of hydrogen. But at $PdH_{0.5}$ the susceptibility is still some distance from zero.

Further work will be necessary before the significance of these results on the susceptibility of the supported palladium-hydrogen system becomes clear.

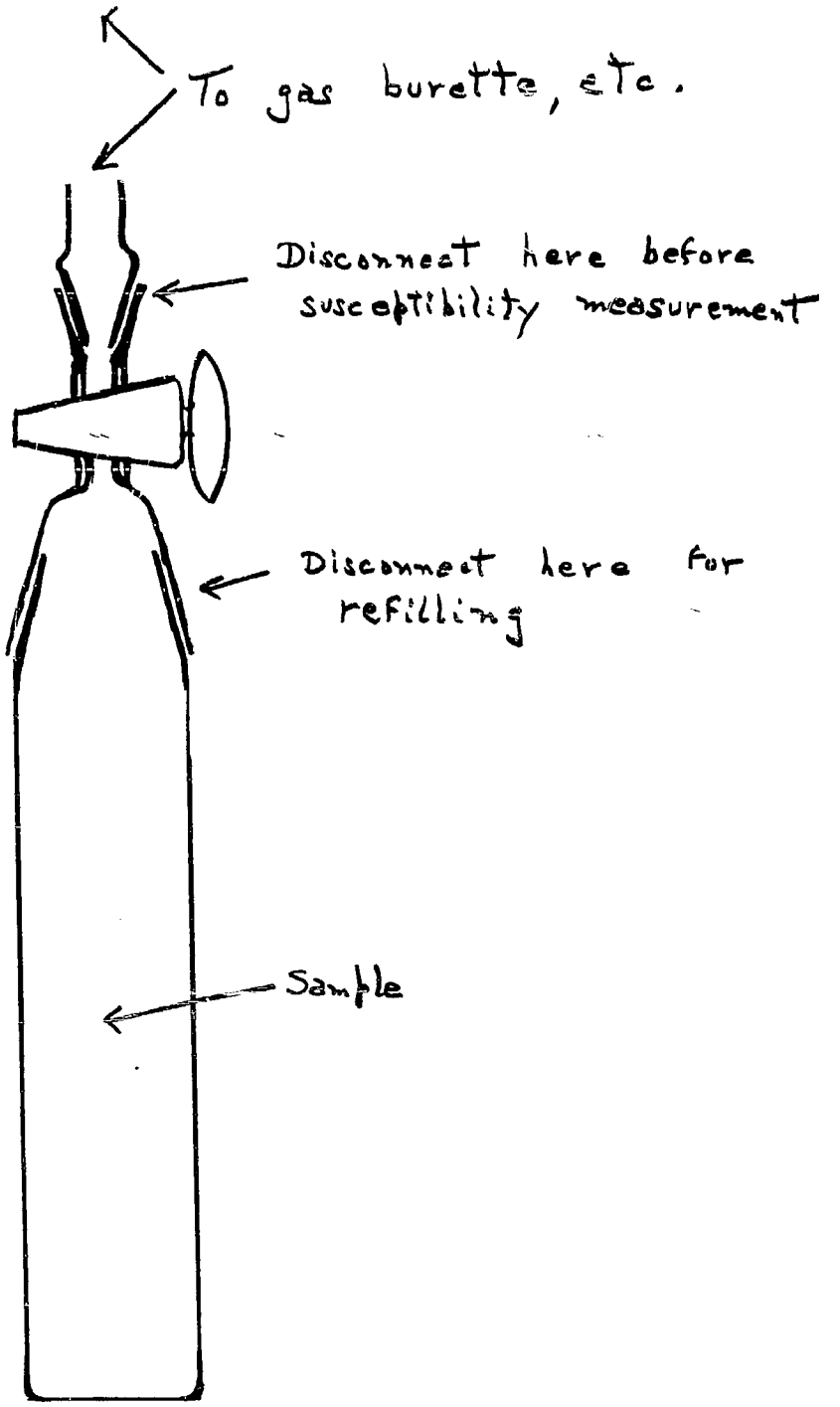

Fig. 1. Sample tube for susceptibility measurements on hydrogenized supported palladium.

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2. Smith, D. P., "Hydrogen in Metals" University of Chicago Press (1948) p. 214.

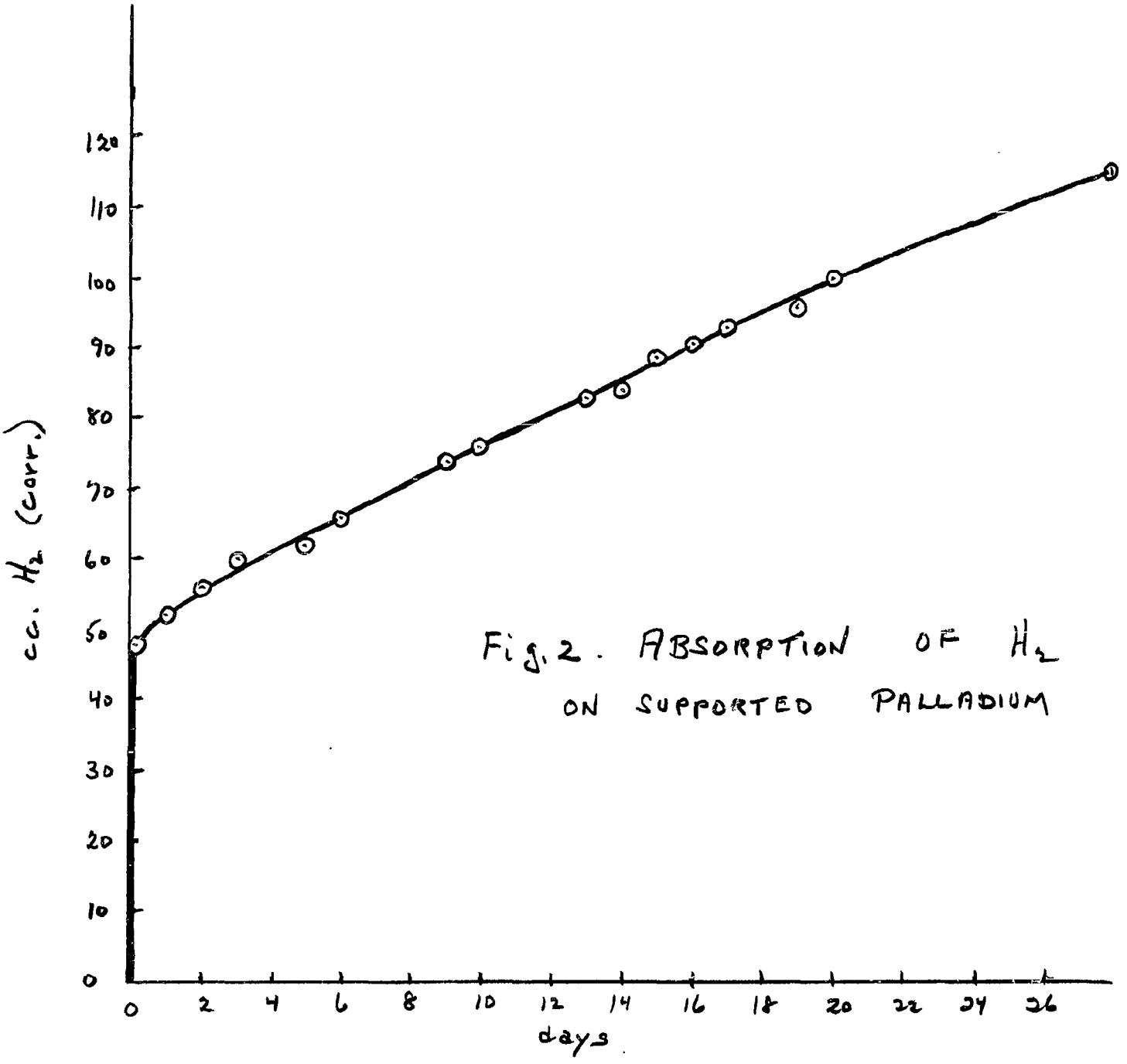

Fig. 2. ABSORPTION OF H_2 ON SUPPORTED PALLADIUM

Part IV A Preliminary Magnetic Study of Purple Sulfur
by T. Freund, S. Adler, and C.N. Sparrow

Recently F. O. Rice and C. N. Sparrow (in press) have succeeded in preparing a purple meta-stable modification of sulfur. It is prepared in a vacuum system by passing sulfur vapor from flowers of sulfur through a furnace at 450°C and freezing the product on a liquid nitrogen cold finger. This new modification of sulfur upon being allowed to come to room temperature rapidly undergoes a transition to ordinary yellow sulfur.

A suitable apparatus for the preparation of the material was constructed and the technique of filling a very small glass bucket for the magnetic balance was devised. The magnetic measurements show that purple sulfur is strongly paramagnetic. Unfortunately, it was not possible to prepare pure purple sulfur. The material prepared contained a large amount of yellow sulfur.

The purple sulfur was transferred from the cold finger to the bucket by carrying out the operation in fresh liquid nitrogen.

The magnetic measurements were carried out in an atmosphere of dry helium on a Faraday type balance at a field strength of about 7500 gauss. One preliminary measurement was made using a very small sample of about 3 mg. This indicated that the substance was strongly paramagnetic. A new preparation of purple sulfur was made and the susceptibility was measured on a 17.6 mg. sample.

The calculations were made from:

$$\frac{-(\delta_s)(\Theta)}{g} = Xg$$

where δ_s is the deflection on the balance due to the magnetic field corrected for the diamagnetism of the bucket, g is the weight in grams of the sample, Xg is the gram susceptibility, and Θ is the calibration factor for this balance from sugar measurements. The sugar used had a known gram susceptibility of -0.566×10^{-6} at 300°K. δ_T is the total deflection due to the bucket plus sample and δ_B is the deflection due to the bucket alone. A negative δ indicates paramagnetism. All δ values reported are the average of four or more readings. Θ is 1.48×10^{-8}, g is 0.0176, and δ_B at 77°K is 0.423 and at 300°K is 0.755.

The method of measurement is described with the data below.

(1) The balance case was flushed at room temperature with dry helium for one-half hour. Then the case was cooled with a dewar of liquid nitrogen for one-half hour while continuing to flush very slowly with helium.

(2) The bucket containing the sample was quickly placed in the balance case. Afterwards the helium was shut off and the sample allowed to stand for one-quarter of an hour.

(3) The susceptibility was measured at 77°K.

$\delta_T = -11.6$

$\delta_B = 0.4$ $\qquad$ $X_g = 10 \times 10^{-6}$

$\delta_S = -12.0$

(4) The liquid nitrogen dewar was replaced with liquid oxygen and the system slowly flushed for fifteen minutes with dry helium. This should remove most of the oxygen from the sample.

(5) The liquid oxygen dewar was replaced with liquid nitrogen and the helium turned off. The sample was allowed to stand for quarter of an hour at the liquid nitrogen temperature.

(6) The susceptibility was measured at 77°K.

$\delta_T = -10.2$

$\delta_B = 0.4$ $\qquad$ $X_g = 9.3 \times 10^{-6}$

$\delta_S = 10.6$

(7) The liquid nitrogen dewar was removed and the sample was allowed to stand for one hour while slowly flushing with helium. The sample turned yellow.

(8) The case was immersed in liquid nitrogen, the helium turned off, and the sample allowed to stand for ten minutes.

(9) The susceptibility was measured at 77°K.

$\delta_T = 0.786$

$\delta_B = 0.423$ $\qquad$ $X_g = -0.305 \times 10^{-6}$

$\delta_S = 0.363$

(10) The susceptibility of the sample of yellow sulfur was measured at room temperature, 300°K.

$\delta_T = 1.264$

$\delta_B = 0.755$ $\qquad$ $X_g = -.427 \times 10^{-6}$

$\delta_S = 0.509$

(11) The liquid nitrogen temperature measurement of the yellow sulfur was repeated.

$\delta_T = 0.897$

$\delta_B = 0.423$ $\qquad$ $X_g = -0.398 \times 10^{-6}$

$\delta_S = 0.474$

(12) The room temperature measurement was repeated on the yellow sulfur with excellent agreement.

$\delta_T = 1.264$

$\delta_B = 0.755$ $\qquad$ $Xg = -.427 \times 10^{-6}$

$\delta_S = 0.509$

The gram susceptibility of sulfur is -0.49×10^{-6} (International Critical Tables). This indicates a small impurity in the yellow sulfur. Correcting the measured gram susceptibility of the impure purple sulfur by the low temperature diamagnetic value of the yellow sulfur gives a molar susceptibility for diatomic sulfur at 77°K of purple sulfur of 7×10^{-4}. Recently A.B. Scott (JACS 71, 3145(1949)) measured the susceptibility of diatomic sulfur vapor at elevated temperatures and found the Curie constant to be 0.93. The molar susceptibility at 77°K corresponding to this is 120×10^{-4}. Scott's value agrees well with the calculated value for $^3\Sigma$. The $^3\Sigma$ state is the ground level for diatomic sulfur.

While the values of the paramagnetic susceptibility of the impure purple sulfur were very low for diatomic sulfur, it is felt that some improvement in the technique of preparation of the purple sulfur would increase the values several fold. The main danger in this experiment is oxygen contamination. Possibly greater precautions can be taken. For the measured paramagnetism to be due to oxygen entirely the oxygen would have to be at least 10 mole per cent.

Part V

A program is under way for study of the Catalytic activity of several series of catalysts which have been investigated by magnetic susceptibility methods in this laboratory. This program is expected to be completed during the coming year.

A study has been made of the supported titanium sesquioxide. This work will be reported in detail in a forthcoming report.

The use of nuclear induction as a tool in catalyst research is being further explored by Thomas Hickmott who now holds a National Science Foundation Fellowship at Harvard University.

A magnetic study of chemisorbed carbon monoxide on supported iron is being initiated by Dr. M.J. Hulatt at Harvard.

P.W. Selwood, Project Director will be at Harvard as a Visiting Lecturer until next June.