STUDIES ON ALKALI AND ALKALINE EARTH NIOBATES, NIOBIUM COMPLEXES WITH SOME ORGANIC LIGANDS AND THEIR SEMICONDUCTING PROPERTIES

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CERTIFICATE

This is to certify that the thesis entitled 'Studies on Alkali and Alkaline earth niobates, niobium complexes with some organic ligands and their semiconducting properties" submitted by Shri S.K. Arya, ID No. 74S83003, for award of Ph.D. degree of the Institute, embodies original work done by him under my supervision.

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PREFACE

The thesis entitled "Studies on Alkali and Alkaline earth niobates, niobium complexes with some organic ligands and their semiconducting properties" deals with the systematic studies on the formation of alkali and alkaline earth niobates at high temperature and some aspects of complex forming ability of niobium (V) with organic ligands containing sulphur, oxygen and nitrogen donor atoms.

The electrical conductivity of the prepared niobates and niobium complexes have been measured in the range of 40-250°C and 30-150°C respectively. Activation energies of niobates and niobium complexes have been calculated. Seebeck coefficients of the above compounds was also measured.

First chapter contains a brief survey of the literature on the studies of niobates and niobium complexes.

Chapter two deals with the formation of lithium, potassium,calcium, strontium and barium niobates in the range of 500-1200°C. Following niobates have been prepared: $Li_2O.Nb_2O_5$, $2Li_2O.Nb_2O_5$, $3Li_2O.Nb_2O_5$, $K_2O.Nb_2O_5$, $CaO.\ 2Nb_2O_5$, $CaO.Nb_2O_5$, $SrO.2Nb_2O_5$, $SrO.Nb_2O_5$, $2SrO.Nb_2O_5$, $3SrO.\ Nb_2O_5$, $4SrO.\ Nb_2O_5$, $BaO.2Nb_2O_5$ and $Bao.\ Nb_2O_5$.

The formation of these niobates was confirmed by analytical results. The electrical conductivity of these niobates has been measured at different temperatures, from which their activation energies have been calculated. The Seebeck coefficient measurements were also made with each niobate.

Chapter three deals with the isolation and characterization of complexes of niobium(V) with N-aryl N'-2(4,5,6-monosubstituted pyridyl) thioureas; 1,5-disubstituted 2,4-dithiobiurets, 1,5-disubstituted 2-thiobiurets, benzimidazole and acridine. The structure of these complexes have been confirmed by infra-red spectra, magnetic susceptibility, molar conductance and electrical measurements. From the electrical conductivity of these complexes, measured at different temperatures, their band gaps have been calculated.

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CONTENTS

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CHAPTER - I

GENERAL INTRODUCTION

GENERAL INTRODUCTION

Niobium is one of the heaviest elements of V A Group of the periodic table. It exhibits oxidation states ranging from 2 to 5. The pentavalent being most stable. Niobium forms a number of oxides such as NbO, Nb_2O_3, NbO_2 and Nb_2O_5. It also forms halides of the type NbX_2 (X = Clor I), NbX_3, NbX_4 and Nb X_5 (F, Cl, Bror I).

Dela fontaine[1] and Grube[2] obtained NbO by the reduction of niobium pentoxide with hydrogen at 1300 - 1750°C, or reduction of niobium tetraoxide with niobium metal in the atmosphere of argon at 1600 - 1700°C.

Nb_2O_3 was prepared by Smith and Maas[3] by heating niobium pentoxide with five times its weight of magnesium at 1200 - 1300°C. Brauer[4] and Grube[2] obtained NbO_2 by the reduction of niobium pentoxide with hydrogen at 1000-1200°C. Niobium pentoxide[5] is formed on heating niobium metal, lower oxides, niobium hydride, niobium oxysulphide or oxalatoniobic acid in oxygen or air.

Brauer[4] reported that Nb_2O_5 exists in three crystalline modifications i.e. α , β and γ . On heating transformations between these forms takes place as: amorphous to γ at 500°C,

γ to β at 1000°C and β to α at 1100°C. Holtzberg et al[6] comfirmed the existence of only two modifications i.e. α and γ and the possible existence of third δ - modification was proved to be poorly crystallized state of γ -phase. They proposed that α and β - phases are identical with β - modification existing as a two dimensional array, the transformation temperatures were observed to be amorphous to γ , 435°C and γ to α 830°C. X-ray investigation by Goldschmidt[7] confirmed that β - modification was stable only above 900°C.

The preparation, structure and thermal properties of various polymorphic forms of Nb_2O_5 have been reviewed in detail by Schafer and coworkers.[8-11]

α - modification suggested by Brauer[4] has been accepted by most of the investigators[12-18] . Greener et al[12] measured the electrical conductivity of α - Nb_2O_5 single crystals and sintered specimens under a constant oxygen pressure and in the temperature range of 573-1173°K. They observed exponential temperature dependence with an activation energy of 1.65 eV in both the cases.

Greener and Hirthe[15] measured the electrical conductivity of single crystal and sintered specimen of α- Nb_2O_5 after prior reduction in 10^{-6} atom of air at temperatures varying from 350° to 1150°K. The conductivity of single crystals as well as sintered specimens was found to be exponentially dependent on temperature. The activation energy of single crystals was found to be 0.91 eV in the range of 650° - 1150°K and 0.2 eV in the range of 350-650°K. The activation energy of sintered specimen varied from 1.0eV for the smallest degree of reduction to almost zero at the highest degree of reduction.

On the other hand Chen and Swalin[18] re-examined the temperature dependence of electrical conductivity using α- Nb_2O_5 single crystals in an oxygen pressure range of 1 atm to 10^{-6} atm and temperature range of 873-1623°K. They observed that at high temperatures the activation energy is 1.4 eV, whereas below 1073°K it is 0.4 eV.

Niobium pentoxide reacts with basic oxides to form compounds known as niobates. Numerous anhydrous as well as hydrated niobates are known. Certain aspects of their chemistry is reviewed by Fairbrother[19] and Wycoff.[20]

The formation of several lithium, sodium and potassium niobates has been reported by many investigators.[21-31]

Balke and Smith[32] prepared silver niobate $Ag_2O \cdot Nb_2O_5 \cdot 2H_2O$ by adding a solution of silver nitrate to a solution of silver niobate in 1:1 proportion. They also prepared rubidium niobate, $4\ Rb_2O \cdot 3Nb_2O_5 \cdot 14H_2O$ and cesium niobates 4 Cs_2O. $3Nb_2O_5$. $14H_2O$ by fusing Nb_2O_5 with rubidium and cesium carbonates respectively.

Balke and Smith[32] also obtained aluminium metaniobate $Al(NbO_3)_3 \cdot 6H_2O$ by adding a solution of alum to sodium niobate. He observed that the same compound is formed when niobium pentoxide is fused with alum. Kvashenko[31] et al studied the formation of aluminum ortho and meta-niobate conductometrically and potentiometrically. They also observed that dielectric constant and dielectric conductivity of $Nb\,AlO_4$ is dependent on temperature.

Niobates of the type $Nb_2M^{II}O_6$ (M^{II} = Mg, Mn, Fe, Co, Ni, Zn and Cd) are known to possess orthorhombic type of structure $\left[Nb_2\ (Fe,Mn)O_6\right]$, in which each metal atom is surrounded by nearly regular octahedron of oxygen atoms.

Rose[21] prepared $MgO.Nb_2O_5.4H_2O$, $2Fe_2O_3.\ 3Nb_2O_5.8H_2O$, $CuO.Nb_2O_5.2H_2O$ and $Hg_2O.Nb_2O_5.3H_2O$ by fusing Nb_2O_5 with respective chloride of the metals.

Joly[33] obtained a number of niobates by heating Nb_2O_5 with metallic chloride at temperatures somewhat below the volatilization temperature of the respective chlorides. The following niobates were prepared: 2 $MgO.Nb_2O_5$, 3 $MgO.Nb_2O_5$, 4 $MgO.Nb_2O_5$, $MnO.Nb_2O_5$, $FeO.Nb_2O_5$ and $YO.Nb_2O_5$.

Larsson[34] also prepared a number of amorphous niobates by fusing Nb_2O_5 with chlorides of corresponding metal. The niobates obtained were: $MgO. Nb_2O_5$, $4 MgO. Nb_2O_5$, $3 MnO. Nb_2O_5$, $CoO. Nb_2O_5$, $NiO. Nb_2O_5$, $CuO. Nb_2O_5$, $ZnO. Nb_2O_5$, $Y_2O_2. Nb_2O_5$, $Y_2O_3. Nb_2O_5$, $ZrO_2. 5 Nb_2O_5$, $CdO. Nb_2O_5$ and $ThO_2. 16 Nb_2O_5$.

By adding a zinc sulphate solution to a solution of sodium metaniobate Bedford[35] obtained zinc ortho dodecaniobate $7 ZnO. 6 Nb_2O_5. 25 H_2O$. Antimony orthoniobate was synthesised from a solution of potassium niobate with antimony carbonate.[36]

Goldschmidt[37] investigated the systems between niobium pentoxide and certain metal oxides which include MgO, Al_2O_3, SiO_2, CaO, TiO_2, V_2O_5, Cr_2O_7, Fe_2O_3, Co_3O_4, NiO, SrO, ZrO_2, MoO_3, BaO, Ta_2O_5, WO_3 and CeO_2 by x-ray and observed the formation of 1:1 niobates. He also observed the formation of $2 Nb_2O_5. Co_3O_4$ and $6 ZrO.Nb_2O_5$ besides 1:1 niobates. These niobates form rutile, columbite, hematite or perovskite type structures.

Electrical conductivities of binary systems of oxides based on niobium pentoxide are reported by Manakov et al.[38] Systems studied are Nb_2O_5 – $NMxOy$ (in which N varied from zero to fifty mole percent for M=K,Li,Ca,Al,Fe & V) showed that in Nb_2O_5-Fe_2O_3, Nb_2O_5 - V_2O_5 and pure Nb_2O_5, transition from electronic to ionic takes place with the increase in content of Mx Oy. The structure and temperature dependence of electrical resistivity of metaniobates of manganese, iron, cobalt, nickel and copper was studied by Bazuev and Krylov.[39]

Niobium like other members of V Group forms a large number of complex compounds in oxidation states of 2 to 5. The complex compounds of niobium halides are probably the most extensively studied compounds. Known halides are NbY_2 (Y = Clor I), NbX_3, NbX_4 and $Nb X_5$ (X = F,Cl,Br or I).

Lower halides are generally obtained by reduction or thermal decomposition of the pentahalides. The ease of reduction increases from fluoride to iodide. By varying reaction conditions it is possible to obtain a variety of products using MCl_5 + M (M = Nb, Ta) reaction and different temperature gradient for reaction. Schafer and his colleagues[40-47] prepared various chlorides.

Niobium (II) fluoride and bromide are not yet known whereas niobium (II) chloride was prepared by Schafer and Dohmann[44] on heating stoichiometric quantities of niobium metal powder and niobium trichloride at 800°C.

Corbet and Seabaugh[47] obtained niobium (II) iodide by heating niobium tri-iodide in a stream of pure hydrogen at 400°C.

Niobium trichloride, tribromide and tri-iodide are obtained[19,48,49] by reduction of the respective penta halides with hydrogen, aluminium or niobium metal. In certain instances, thermal decomposition of the tetrahalides to respective trihalides was used.

Monomeric cyclopentadiene complexes of niobium (III) are reported e.g. $(\pi - C_5H_5)_2$ Nb HL where L = CO, PR_3, C_2H_4[50] and RC ≡ CR'[51].

Maas and McCarley[52] prepared niobium (III) halide complexes of the type $Nb_2 X_6 (SC_4 H_8)_3$ (X = Cl, Br, I) and $[Nb_2 Cl_8(S C_4 H_8)]^{2-}$.

Recently a convenient synthetic route to niobium (III) halo complexes has been discovered by Allen and Naito[53]. They observed that on treating niobium pentachloride with borane-dimethyl sulphide complex and a stoichiometric amount of sodium/potassium alloy in toluene at room temperature forms $Nb_2 Cl_6 (SMe_2)_3$ which can be converted to $Nb_2 Cl_6 (L-L)_2$, where L-L is a chelating diphosphine or diarsine.

NbF_4, $NbCl_4$ and $NbBr_4$ can be conveniently prepared by the reduction of corresponding pentahalides under controlled conditions at elevated temperatures with either niobium, iron, aluminium or hydrogen.

Niobium tetraiodide[54] was prepared by thermal decomposition of pentaiodide at 270°C in a sealed tube.

Blight and Kepert[55] observed that the electrical conductivity of niobium tetrachloride increases sharply by a factor of 10^4-10^5 at 533°K and the temperature dependence is typical for it.

Fowles et al[56] reported the formation of niobium (IV) halide complexes of type $NbX_4.2L$ (X = Cl, Br and I; L = methyl cyanide, γ-picoline, diarsine, thiourea, triphenyl phosphine and 1:4 dioxane), $NbX_4.2L$ (X = Cl and Br; L = tetrahydrofuran and tetrahydropyran). $NbX_4.L$ (X = Cl, Br and I; L = 2,2' bipyridyl, 1:10 phenanthroline triethylamine and NNN'N'-tetramethylene diamine) type of complexes are reported by Brown et al.[57] In non aqueous solvents, Deutsher et al[58] and Hamilton et al[59] prepared complexes of type NbL_4 (where L = 1,2-dimethyl thioethane, benzoyl tri fluoroacetone, theonyl trifluoroacetone, dibenzylmethane, tropolone and 8-hydroxyquinoline) by the reaction of niobium tetrachloride with respective ligands. They concluded on the basis of spectral results that complexes of β- diketonates are dodecahedral and dimethyl thioethanes are triangular dodecahedral.

Green dimeric compounds with composition $NbX_3(MeCN)_3$ (X = Cl or Br) were prepared by zinc reduction of $NbCl_4$ in methyl cyanide, containing a new bridging ligand $C_4H_6N_2$ which was proposed as $[Nb_2Cl_6\ (NCMe)_4\ C_4H_6N_2]$ by Schaefer et al.[60] Upon replacement of 2 or 4 of the coordinated methyl cyanide molecules with chloride salts gave $[Nb_2Cl_8(MeCN)_4\ C_4H_6N_2]^{2-}$ and $[Nb_2Cl_{10}\ (C_4H_6N_2)]^{4-}$ anions respectively.

A nine coordinated acetylacetone complex Nb ac ac_4. dioxan having spin only magnetic moment of 1.73 B.M. was prepared by Deutscher and Kepert.[61]

Recently Malhotra and Chaudhry[62] have isolated complexes of type M Cl_4.Benz., M Cl_3. 2 Benz. and M Cl_2. 3 Benz. (M = Nb, Ta & Mo) by the reaction of pentachlorides with benzoins in carbon tetrachloride on the basis of molar conductance, molecular weight, magnetic susceptibility and i.r. spectral results they proposed the structure of the compounds to be octahedral.

All the pentahalides are most conveniently obtained by direct combination of the elements at elevated temperatures (230 - 300°C). Care is necessary during the preparation of Nb I_5 because of its ready thermal decomposition. Alternative methods have also been reported for the preparation of pentahalides.[49,63,64] Niobium pentachloride exists as a dimeric unit in the solid state.[65]

All the pentahalides form stable 1:1 complexes with a variety of ligands. Most of these complexes have been discussed by Fairbrother.[19,48] Glushkova et al[66] prepared pentafluoride amine complexes whereas Brown et al[67] prepared pentahalide triphenyl phosphene sulphide and triphenyl phosphene selenide complexes.

By the reaction of niobium pentachloride with 1,4-selenoxan and thioxan in chloroform Fowles and Baker[68] obtained 1:1 red coloured complexes in which bonding is through sulphur or selenium and not through oxygen.

Elinson and Maltseva[69] studied the optical properties of coloured complexes of o-(pyridylazo) cresol, (pyridylazo) (ethylamino) p-cresol, (pyridylazo)(diethylamino) phenol and their bromo and dibromo derivatives with niobium pentachloride.

By the reaction of 8-quinolinol (OXH) with niobium pentachloride and pentabromide Frazer et al[70] obtained compounds with composition $NbX_5 \cdot n(OXH)$ ($n = 2$-6, 8 & 10), which on heating gave compounds of type $MX_m(OX)_{5-m}$ ($m = 1$-4). $Nb\,Br_2(OX)_3$ and $Nb\,Br(OX)_4$- do not form similar compounds on heating. Infrared and conductance measurements studies indicated these compounds to be having coordination numbers of 9,8,7 & 6 for m = 1-4.

Ackermann and Koch[71] studied spectrophotometrically the formation of Nb (V) mix ligand complexes of type Nb (V) L-L' (L = pyrocatechol, pyrogallol, gallic acid, dibromogallic acid and L'= EDTA or 1,2 diamino cyclohexane tetra acetic acid) at pH 1.6 - 3.7. They observed that these complexes have 1:1:1 composition and can be used for the estimation of niobium in aqueous solutions.

McCarley et al[72] reported synthetic methods for the preparation of hydrated halides and halo complexes of $Nb_6X_{12}^{n+}$ (X = Cl or Br) cluster in the stable oxidation state n = 2-4, by reduction of anhydrous niobium penta chloride in the presence of alkali metal chloride at high temperatures.

By the reaction of niobium halides with acetonitrile Fowles and Gadd[73] obtained three type of complexes. $NbX_5 \cdot C_2H_3CN$ (X = Cl or Br) $NbX_4 \cdot 2C_2H_3CN$ and $NbX_3 \cdot 3C_2H_3CN$. Spectroscopic and magnetic measurements showed that bonding is through nitrogen atom rather than double bond and complexes are consistent with 6-coordinated structures.

Raman spectra of crystalline complexes of type MX_5L (M = Nb or Ta; X = Cl or Br and L = dimethyl sulfide or acrylonitrile) were also studied by Fowles et al[74], results were compared with model species $[MX_5\ Y]$ (M = Nb or Ta, X = Cl or Br and Y = Cl, Br or I) and MX_5. MeCN. By studying x-ray structural analysis of niobium (V) complexes, a new type of carbon-bridging group was found in crystals of bis - μ (trimethyl silyl methylidine) - tetrakis (trimethyl silyl methyl) - diniobium (V) by Huq et al.[75]

The complexes of niobium (V) with wide range of Schiff bases containing a variety of donor sites have been prepared.[76,77,78] Chang and Savich[76] and Chang and Lapitskii[78] have shown that in almost all the complexes the coordination number of niobium is seven.

Parasher and Tondon[79] reported hexa and octa-coordinated Schiff base complexes of niobium (V). Biradar et al[80,81] used aromatic Schiff bases of type N-N'-disalcylidene ethylene diamine, bis-[p-(salicylidene amino) phenyl] sulphide, 4,4'-bis (salicylidene amino) diphenyl amine bis [o-(salicylidene amino) phenyl] disulphide, salicylidine - aniline, salicylidine-p-chloro aniline, salicylidine-p-toluidine, salicylidine-p-anisidine, benzylidene-p-aminodiphenylamine and anisylidene p-amino diphenylamine for their studies. They observed that Nb (V) has coordination number seven in all the complexes formed by the above mentioned bases.

Niobium pentafluoride xenon difluoride adducts $NbF_5 . 2XeF_2$ and $NbF_5 . XeF_2$ have been prepared by direct combination of the niobium halide in hydrofluoric acid by Lawrence and Sturgeon[82] and, Holloway and Knowles.[83] Thermal decomposition was found to proceed with an intermediate compound formation of 2:1 adducts. Edwards and Jones[84], on interacting niobium pentafluoride and selenium tetrafluoride found the major product to be $SeF_4 . 2NbF_5$. The complexes $SeF_4 . NbF_5$ and $SeOF_2 . NbF_5$ were obtained as minor products of this reaction.

With mono, di and trialkylamines, niobium pentafluoride forms simple 1:1 adducts wereas, with methylamine, dimethyle amine and diethylamine the niobium pentachloride and bromide undergo replacement reactions to yield compounds of types $NbCl_2 (NHCH_3)_3$, $NbCl_3 (NHR)_2 NH_2R$ and $NbCl_3(NR_2) . NHR_2$. Whereas with trimethylamine 1:2 complexes viz $NbCl_5 . 2 N(CH_3)_3$ and $NbBr_5 . 2N(Ch_3)_3$ were isolated.

Niobium penta fluoride form stable 1:2 complexes, whereas depending on reaction conditions, the other pentahalides either form 1:1 complexes or undergo reduction to give tetrahalide complexes of type $NbX_4 . nL$ (X = Cl, Br and I; L = monodentate ligand; n = 1-3).

It is also reported[80] that niobium pentachloride is reduced in the presence of lithium dialkylamides with the formation of tetravalent complexes such as $Nb(NR_2)_4$ (R = Me, Et, ^nPr, ^nBu etc.), the extent of reduction increases with the length of alkyl chain. Electrolytic reduction of pentachloride in presence of pyridine, Wentworth and Brubaker[87] obtained a dimeric complex of type $[NbCl(OEt)_3 \cdot C_5H_5N]_2$ which on adding alcoholic pyridium chloride solution was converted to another complex $(C_5H_6N)_2[Nb(OEt)Cl_5]$.

The present work was, therefore undertaken with a view to study systematically the formation of alkali and alkaline earth niobates between 500 - 1200°C. Preparation of complex compounds of Nb(V) with the ligands containing sulphur, nitrogen and oxygen as donor atoms in tetrahydro furane aqueous medium, structures of these compounds have been studied using analytical and physico-chemical methods. Semiconducting properties of the prepared niobates and complexes have also been studied by measuring electrical conductivity and Seebeck coefficients.

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CHAPTER - II

NIOBATES OF LITHIUM, POTASSIUM CALCIUM, STRONTIUM AND BARIUM.

INTRODUCTION

The potential use of niobium for high temperature service has focussed attention on its oxides and niobates, particularly of lithium, since oxides make up the barrier layer between the metal and gas phase during oxidation.

Niobates find their use in ceramics[1], piezoelectric meterials[2], electro-optic modulators[3], ferroelectric materials[4] and superconductors[5].

Hofmann and Kohlschutter[6] obtained hydroxylamine niobate, $3(NH_2OH).HNbO_3$, by digesting a mixture of potassium deutrohexaniobate, $K_2 Nb_4O_{12}. 5\frac{1}{2} H_2O$ with conc. ammonia and hydroxylamine chloride. They also prepared another hydroxyl amine niobate, $5 NH_2OH. Nb_2O_5. 2H_2O$ which had different composition.

Evnalova and Rashkovich[7] prepared lithium metaniobate, $LiNbO_3$ by baking stoichiometric mixture of Li_2CO_3 and Nb_2O_5 at 1000°C for 3 hours and determined the domain structure of crystals. Robert[8] obtained lithium metaniobate, $LiNbO_3$ by sintering Li_2CO_3 and Nb_2O_5 for 12-15 hours at 950°C. He also prepared single crystals by carrying out the reaction at 1300°C.

Roitberg et al´ measured the pyroelectric and electrical conductivity of lithium metaniobate single crystals in the range of 20 - 250°C. Novik[10] et al measured thermoelectric effects in lithium metaniobate whereas Cermak Karel[11] studied optical properties in the near ultravoilet spectral region.

Large single crystals of lithium niobate were grown using an automated puller by Zydzik G.[12] Byer et al[13] used lithium metaniobate in electro optical switch and second harmonic generation. Recently single crystals of lithium metaniobate have been grown by many investigators using different techniques.[14-17]

Rose[18] obtained hydrated sodium metaniobate, $Na_2O.\ Nb_2O_5.\ 9H_2O$, by heating a solution of NaOH containing niobium hydroxide in suspension. He also prepared 3 $Na_2O.\ Nb_2O_5$, 4 $Na_2O.\ Nb_2O_5.$ 4 $OH_2O.\ Na_2O.$ 4 $Nb_2O_5.\ 5H_2O$ by expelling CO_2 on fusing Nb_2O_5 with $Na_2\ CO_3$ in different proportions.

Holmquist[19] isolated cubic and hexahedral crystals of sodium pyroniobate, $Na_4\ Nb_2\ O_7$ by melting a mixture of sodium carbonate, niobium pentoxide and sodium fluoride.

Small crystals of sodium deutro hexaniobate, $Na_4\ Nb_6\ O_{17}.\ 9H_2O$, were isolated by Santesson[20] from a boiling aqueous solution of a fused mixture of Nb_2O_5 and KOH, but Bedford[21] could not confirm the findings of Santesson.

When sodium hydroxide is added to a hot solution of potassium oxyfluoro niobate, sodium orthoniobate $Na_{10}Nb_{28}O_{25} \cdot 21\,H_2O$ is obtained.[22]

Bouilland[23] studied Na_2O-Nb_2O_5 systems by heating Nb_2O_5 and Na_2CO_3 or Nb_2O_5 and $NaNO_3$ in mole ratio 1:1 and 1:2 respectively, in argon atmosphere at 1100°C and obtained $NaNbO_3$. It was also observed that at the same temperature the reaction in the latter system proceeded faster in contrary to the data of Spitsyn and Lapitskii.[24]

Na_2O-Nb_2O_5 system was again studied by Pietro[25] who on heating Nb_2O_5 and $NaNO_3$ at temperatures between 800-1200°C for 100-500 hours, obtained five compounds : $Na_2O \cdot 13\,Nb_2O_5$, $Na_2O \cdot 7\,Nb_2O_5$, $Na_2O \cdot 3\,Nb_2O_5$, $Na_2O \cdot 4Nb_2O_5$ and $Na_2O \cdot 2\,Nb_2O_5$.

Joly[26] obtained potassium metaniobate, $KNbO_3$, by fusing equimolar parts of potassium and niobium pentoxide with calcium fluoride in a platinum crucible.

The formation of potassium orthoniobate K_3NbO_4 was confirmed by Rose[18] from the amount of carbondioxide evolved when niobium pentoxide was fused with potassium carbonate.

Preparation of pure potassium metaniobate, $KNbO_3$, has been reported by Riesmann et al.[27] They observed the formation of potassium metaniobate at 1075°C. Impurity segregations and their interaction with domains and dislocations in potassium metaniobate single crystals were studied by Mishra and Ingle.[28] Dielectric and conductivity measurements were made by Deshmukh and Ingle.[29] In recent years single crystals of potassium metaniobate have been grown by Quittet et al[30] and Gaffar et al.[31]

Jander and Frey[32] studied the reactions of Nb_2O_5 with various oxides such as BaO. SrO, CaO, MgO, ZnO and CuO and reported the formation of some niobates. Ibrahim et al[33] studied $CaO-Nb_2O_5$ systems and observed the formation of two calcium niobates, $CaO.Nb_2O_5$ and $3CaO.Nb_2O_5$, at higher temperatures. Calcium orthoniobate $3CaO. Nb_2O_5$ exists in both cubic and orthorhombic forms.

By using heavy atom method Cummings[34] determined the crystal structure of calcium metaniobate and observed that the structure consists of calcium and niobium atoms surrounded by oxygen atoms in polyhedral arrangement. Carpy et al[35] determined the crystal structure of calcium pyroniobate, $Ca(NbO_3)_2$ by x-ray method.

The crystal structure of strontium niobate was reported by Ishizawa et al[36] as a compound of perovskite type slabs. Thisstructure was confirmed by 3-dimensional x-ray diffraction method.

Thermogravimetric, x-ray and chemical analysis of solid phase reaction of a 1:1, $BaCO_3:Nb_2O_5$ mixture was carried out by Gonslavskii et al[37] and they observed that barium metaniobate is formed at a very high temperature although the decomposition of $BaCO_3$ in presence of Nb_2O_5 occurs at 700°C.

The crystal structure of common highly conducting metals like copper, aluminium and silver is such that the outer atomic electrons are shared by all the atoms. These electrons are actually free to wander throughout the substance and this remains true over a wide temperature range. In most metals each atom supplies one such free electron and electrical conduction takes place as a result of the motion of the free electrons under the action of an applied electric field.

In contrast to good conductors, the structure of solid insulators is such that over a wide temperature range almost all the electrons remain bound to their respective atoms, therefore insulators have no appreciable electrical conductivity.

There are substances which normally behave like insulators but start conducting if some energy is supplied to them. These are known as semiconductors. Semiconductors[38] generally have electrical conductivity in the range of 10^{2} to 10^{-9} ohm^{-1} cm^{-1} at R.T. (Room Temperature) intermediate between good conductors (10^{6} ohm^{-1} cm^{-1}) and insulators (10^{-14} to 10^{-22} ohm^{-1} cm^{-1}).

Conductor, semiconductor and insulator have also been distinguished on the basis of the band gap[39], Eg., the energy difference between valence band which refers to the fully occupied energy band (and corresponds to all bonding molecular orbitals) and conduction band (corresponds to the antibonding molecular orbitals). Most semiconductors[40] have an energy gap of the order of 1 eV, although many thermoelectric and infrared materials have band gap (Eg) in the neighbourhood of 0.1 eV. Energy gap values of more than about 3 eV is found in the case of insulators and such substances are useful in phosphors and luminescent materials.[41]

The development of semiconductors requires an ever great application and this demand cannot be fully met by handful of elements having semiconducting properties, nor by few relevant chemical compounds, which are already understood. Therefore, increasing attention is being paid to studies on less known compounds able to act as semiconductors. Among them compounds of metals or semiconducting elements with oxygen may be considered as most promising because semiconducting properties of oxides originate generally from the presence of lattice defects. Although the application of oxide semiconductors is abreast of the use of germanium and silicon in technology. For example, NiO is frequently used in thermisters.

Different conduction mechanisms have been proposed for semiconductors depending on the nature of system under study. Generally, Band model[42] is extended to the conduction processes where hopping of electrons takes place from valence band to conduction band. Tunneling models[43,44] have also been proposed for many systems in which the electrons or holes penetrate through a potential barrier. A special theory has been developed known as small polaron theory[45] for materials in which mobility of electrons or holes is in the region of about 1 cm^2/Vs or lower.

The current knowledge of oxide materials is rather limited and very less work is reported in literature.[46-52]

A critical survey of literature showed that no systematic work has been done on the formation of niobates of alkali and alkaline earth, and therefore the present investigation was undertaken with a view to study systematically the formation of alkali and alkaline earth niobates in the temperature range 500-1200°C.

Various workers observed that activation energy of α- Nb_2O_5 increases with rise of temperature[53-55] which is contrary to the general behavior of semiconductors. It was therefore thought worthwhile to study the semiconducting properties of various niobates formed at various temperatures. Seebeck coefficients were also determined to ascertain the type of conduction.

2.2. EXPERIMENTAL

2.21 Preparation of α, β & γ - forms of Nb_2O_5

α, β and γ forms of Nb_2O_5 were obtained by heating amorphous Nb_2O_5 at 1200, 1000 and 800°C respectively. These transformations were confirmed by Differential thermal analysis (DTA) as shown in Fig. 1.

2.22 General method of preparation of Alkali niobates :

All the chemicals used were of B.D.H. Fluka or Analar quality.

Several mixtures were prepared by weighing accurately niobium pentoxide and alkali carbonates in different

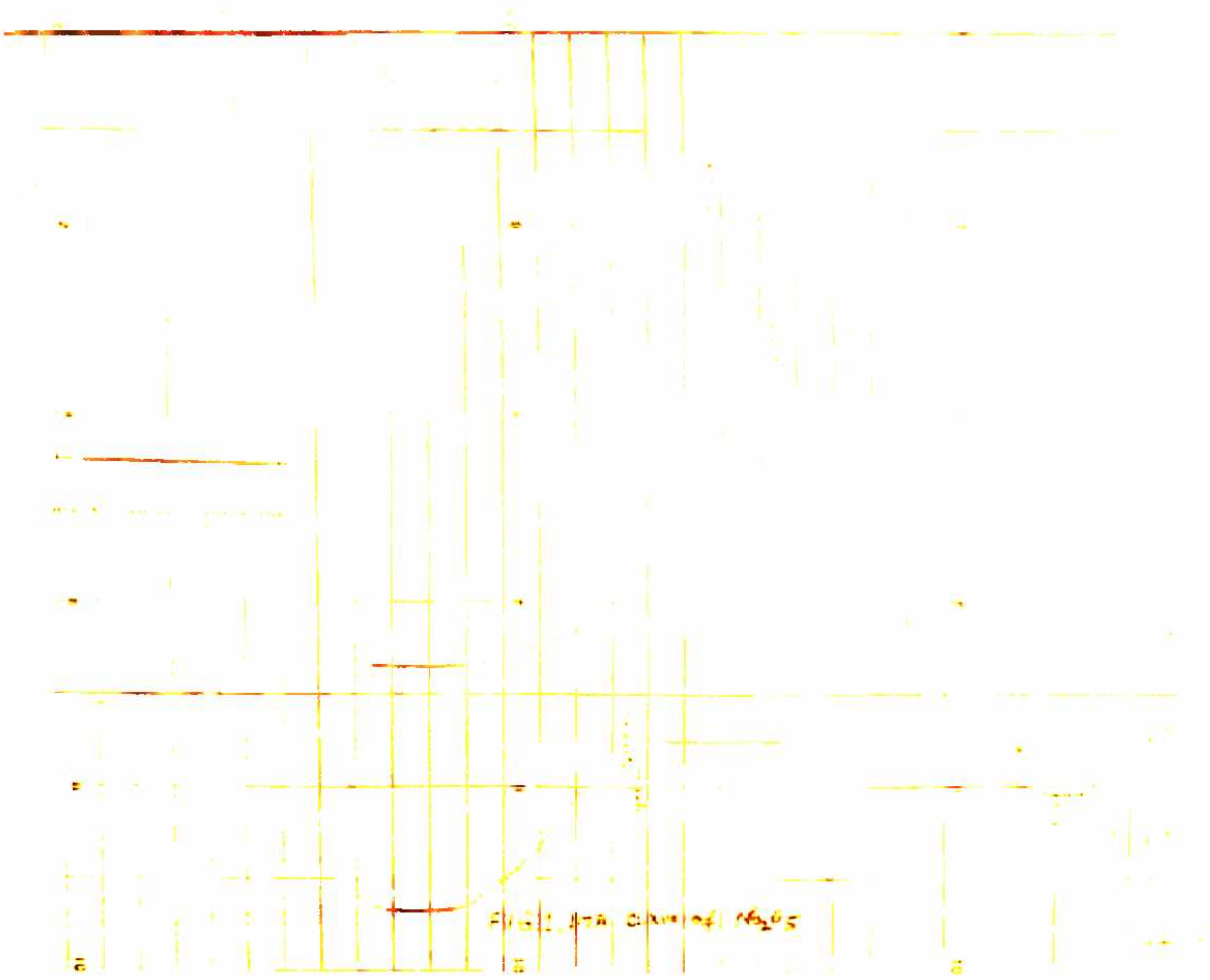

FIG. 1. J-E Curve of Nb_2O_5

proportions (1:1.2, 1:2, 1:3, 1:4, 1:5 and 1:10). These were mixed separately in an agate pestle and mortar, transferred into porcelain or platinum crucible and heated at a fixed temperature for three hours. The heated mass was taken out, powdered well and weighed. Weighed quantity of the reacted mass was transferred into a conical flask and washed with CO_2 free hot water till it was free of unreacted oxides. Pure niobates thus obtained was dried in air oven at 110-120°C till its weight was constant and then cooled in a desciccator containing potassium hydroxide pellets. Yield was ~ 80-85%.

2.23 General method of preparation of Alkaline earth niobates :

Several mixtures were prepared by weighing accurately niobium pentoxide and alkaline earth carbonate or acetate* in different proportions (1:1, 1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, 1:9 and 1:10). These were mixed separately in an Agate

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* Goslavskii et al[37] observed that barium metaniobate is formed at a very high temperature although the decomposition of $BaCO_3$ in presence of Nb_2O_5 occurs at 700°C, therefore $Ba(OAc)_2$ was preferred.

pestle and mortar transferred into a platinumor porcelain crucible and heated at a fixed temperature for fixed interval of time.

The heated mass was taken out, powdered well and weighed. Weighed quantity of the reacted mass was transferred into a conical flask, washed free of unreacted oxides, first with 0.05 N HCl and finally with CO_2 free hot water till it was free of chloride ions. Pure niobate thus obtained was dried in an air oven at 110-120°C till its weight was constant and then cooled in a desciccator containing potassium hydroxide pellets. Yield was $\sim$ 80-85%.

2.24 Analysis of Alkali niobates :

A weighed quantity of the washed dry product was decomposed with standard hydrochloric acid solution and alkali oxides were estimated by standard methods. Precipitate of hydrated niobium pentoxide was obtained by adding ammonium hydroxide till the pH of the solution was between 7-8. Precipitate thus obtained was filtered, washed free of chloride ions, ignited to a constant weight. The results are reported in Tables 2.01 - 2.04. An alternative scheme for formation of Alkali niobates as a function of temperature is given in Fig. 2.

2.25 Analysis of Alkaline earth niobates :

A weighed quantity of the washed and dry product was decomposed by fusion with potassium hydroxide. The melt so obtained was extracted with water, neutralized with dil hydrochloric acid and then hydrated niobium pentoxide precipitated by adding ammonium hydroxide till the pH of solution was between 7 and 8. Precipitate of hydrated niobium pentoxide was filtered, washed free of chloride ions and then again fused with potassium pyrosulphate and finally washed free of sulphate ions, ignited and weighed till constant weight. Alkaline earth oxides were estimated by standard methods.[56,57] The results are reported in Tables 2.05 - 2.17.

An alternate scheme for formation of Alkaline earth niobates as a function of temperature is given in Figs. 3, 4 and 5.

2.26 ELECTRICAL MEASUREMENT

The electrical conductivities of the samples in the form of cylindrical pellets as reported by Rao et al[58] (1 cm diameter and 1-2 mm thick, shown in Fig. 6) were measured. The pellets were prepared by applying a pressure of $2x10^7$ Kgs per sq. m. Two thin steel foils were placed on both the sides of the pellets prior to the application of pressure to avoid any contamination. Pellets thus obtained were coated with silver paint[+] and heated in an inert atmosphere of nitrogen at 500-550°C for ohmic contact. The electrical conductivity (σ) of the pellets of niobates were measured by employing a conductivity cell fabricated at B.I.T.S. workshop (Fig. 6). The conductivity cell (2-3" diameter and 25" long) was made of glass and electrodes were made of stainless stell. In this apparatus measurements could be made in the temperature range of 0-500°C. The electrical conductivity measurements of prepared niobates were made in the range of 40-250°C by means of a Digital Picoammeter (DSA 813 Electronics Corporation of India Limited). The temperature of the samples was measured with the help of contact thermometer attached to the thermostat U-10 (VEB MLW Model No. 22146 GDR) in which the cell was placed.

The temperature dependence of the electrical conductivity is given by the equation[59]

$$\sigma = \sigma_0 \, e^{-E_a/kT} \quad \ldots\ldots\ldots \quad (1)$$

where σ is conductivity in $Ohm^{-1}\ cm^{-1}$ at T°K, σ_0 is a constant, Ea is the activation energy, k the Boltzmann's constant. The Ea values were obtained from the linear plots of log σ versus $^1/_T$.

[+] Obtained from: Transene Company Inc. Rowley, MASS, U.S.A.

The Seebeck coefficient α, of a semiconductor is given as

$$\alpha = \lim_{\Delta T \to 0} \left(\frac{\Delta E}{\Delta T} \right) ; \qquad (2)$$

where ΔE is the thermal emf set up due to a thermal gradient ΔT between the two ends of a semiconducting specimen. In order to measure α as accurately as possible we measured a number of ΔE values arising from several ΔT values, using a D.C. Microvoltmeter (Philips GM 6020). Fig 7.

2.3 RESULTS AND DISCUSSION

Alkali niobates :

To start with the formation of niobates some preliminary experiments were conducted to obtain optimum time of reaction as shown in Table 2.01(a). It was observed that the reactions were almost complete when the mixtures were heated for three hours, therefore this time of heating was kept constant for carrying out the reactions.

The temperature at which sample is prepared should be suitably high to allow rapid establishment of the state of thermodynamic equilibrium between the two mixtures and the surroundings. Therefore, when mixtures containing Nb_2O_5 and lithium or potassium carbonate in varying proportions, were heated at high temperatures (500-1000°C),

TABLE - 2.01(a)

S.N.	Weight of Nb_2O_5 taken (gm)	Weight of M_2CO_3 taken (M = Li or K)	Molar ratio $Nb_2O_5 : M_2CO_3$	Temperature °C ± 20	Time of heating (hours)	% M_2O	[illegible]	Ratio [illegible]	Compound
1.	0.4998	0.1646 L	1:1.2	700	1	4.20	[illegible]	V. less reaction	
2.	0.4989	0.1624 L	1:1.2	700	2	[illegible]	[illegible]	V. less reaction	
3.	0.5015	0.1689 L	1:1.2	700	3	[illegible]	[illegible]	V. less reaction	
4.	0.5003	0.1653 L	1:1.2	700	4	5.74	[illegible]	Less reaction	
5.	0.4986	0.1671 L	1:1.2	700	5	[illegible]	[illegible]	Less reaction	
6.	0.5006	0.2826 L	1:2	700	1	[illegible]	[illegible]	V. less reaction	
7.	0.5001	0.2798 L	1:2	700	2	5.23	[illegible]	V. less reaction	
8.	0.5006	0.2802 L	1:2	700	3	[illegible]	[illegible]	[illegible] : 1	$Li_2O . Nb_2O_5$
9.	0.4991	0.2812 L	1:2	700	4	[illegible]	[illegible]	[illegible] : 1	$Li_2O . Nb_2O_5$
10.	0.4985	0.1676 L	1:1.2	1000	2	[illegible]	[illegible]	Less reaction	
11.	0.4995	0.1689 L	1:1.2	1000	3	[illegible]	[illegible]	[illegible] : 1	$Li_2O . Nb_2O_5$
12.	0.5008	0.3125 K	1:1.2	700	2	[illegible]	[illegible]	0.34 : 1	Less reaction
13.	0.5027	0.3139 K	1:1.2	700	3	25.00	[illegible]	[illegible] : 1	$K_2O . Nb_2O_5$
14.	0.4992	0.3126 K	1:1.2	700	4	[illegible]	[illegible]	0.94 : 1	$K_2O . Nb_2O_5$
15.	0.5005	0.3108 K	1:2	1000	2	[illegible]	[illegible]		Less reaction
16.	0.4987	0.3163 K	1:2	1000	3	[illegible]	[illegible]	[illegible] : 1	$K_2O . Nb_2O_5$

L = Lithium K = Potassium

TABLE - 2.01(b)

S.N.	Weight of Nb_2O_5 taken (gm)	Weight of MCO_3 taken(M= Ca, Sr, Ba)	Molar ratio $Nb_2O_5 : MCO_3$	Temperature °C ± 20	Time of heating (hours)	% M	% Nb_2O_5	Ratio formed	Compound
1.	0.4992	0.1875 C	1:1	1000	1	4.92	94.32	V. less reaction	
2.	0.4980	0.3724 C	1:2	1000	1	5.[illegible]	[illegible].12	V. less reaction	
3.	0.5012	0.3800 C	1:2	1000	2	[illegible].10	[illegible]1.81	Less reaction	
4.	0.5001	0.3815 C	1:2	1000	3	[illegible].50	[illegible].41	1.0[illegible]:2	$CaO.2Nb_2O_5$
5.	0.4996	0.3784 C	1:2	1000	4	9.01	90.15	1.0[illegible]:2	$CaO.2Nb_2O_5$
6.	0.5019	0.3756 C	1:2	1000	5	[illegible].58	[illegible]0.25	1.0[illegible]:2	$CaO.2Nb_2O_5$
7.	0.5006	0.3825 C	1:2	1200	2	6.21	[illegible].41	V. less reaction	
8.	0.5007	0.1852 C	1:1	1200	3	17.28	82.5[illegible]	1.[illegible]:1	$CaO.Nb_2O_5$
9.	0.5046	0.1886 C	1:1	1200	4	17.37	82.40	1 : 1	$CaO.Nb_2O_5$
10.	0.5002	0.1875 C	1:1	1200	5	17.44	82.13	1 : 1	$CaO.Nb_2O_5$
11.	0.5022	0.2695 S	1:1	1200	2	7.18	91.67	V. less reaction	
12.	0.4995	1.1106 S	1:4	1200	2	8.30	91.34	V. less reaction	
13.	0.5034	0.2789 S	1:1	1200	3	10.55	89.06	1.02:2	$SrO.2Nb_2O_5$
14.	0.5027	0.2748 S	1:1	1200	5	16.52	83.04	1.02:2	$SrO.2Nb_2O_5$
15.	0.5026	1.1126 S	1:4	1200	3	44.08	55.25	2 : 1	$2SrO.Nb_2O_5$
16.	0.5002	0.3745 B	1:1	1200	3	4.49	94.97	V. less reaction	
17.	0.5015	1.5002 B	1:4	1200	3	6.42	92.18	V. less reaction	

C - Calcium; S - Strontium; B - Barium.

TABLE - 2.01

LITHIUM NIOBATES

Time of heating - 3 hrs.

S.N.	Weight of Nb_2O_5 taken (gm)	Weight of Li_2CO_2 taken (gm)	Molar ratio Nb_2O_5:Li_2Co_3	% Li_2O	% Nb_2O_5	Ratio formed Li_2O:Nb_2O_5	Compound
Temperature of Reaction - 500 +20°C							
1.	0.5046	0.1688	1:1.2	1.08	98.56	almost no reaction	
2.	0.5008	0.2806	1:2	2.13	97.45	almost no reaction	
3.	0.5008	0.4137	1:3	2.84	96.38	almost no reaction	
4.	0.4981	0.5608	1:4	4.58	94.61	almost no reaction	
5.	0.5002	0.6921	1:5	4.89	94.01	almost no reaction	
6.	0.5016	1.3926	1:10	4.78	94.00	almost no reaction	
Temperature of Reaction - 600 ± 20°C							
1.	0.5010	0.1618	1:1.2	2.00	97.58	almost no reaction	
2.	0.5011	0.2763	1:2	2.75	96.91	almost no reaction	
3.	0.4930	0.4160	1:3	11.29	88.06	1.13:1	$Li_2O.Nb_2O_5$
4.	0.4987	0.5606	1:4	11.09	88.36	1.07:1	$Li_2O.Nb_2O_5$
5.	0.5007	0.7016	1:5	16.86	82.47	1.81:1	$2Li_2O.Nb_2O_5$
6.	0.5021	1.3998	1:10	16.02	83.31	1.84:1	$2Li_2O.Nb_2O_5$

TABLE - 2.02

LITHIUM NIOBATES   Time of heating - 3 hrs.

S.N.	Weight of Nb_2O_5 taken (gm)	Weight of Li_2Co_3 taken (gm)	Molar ratio $Nb_2C_5:Li_2Co_3$	% Li_2O	%Nb_2O_5	Ratio formed $Li_2O:Nb_2O_5$	Compound
Temperature of Reaction - 700 ±20°C							
1.	0.5015	0.1689	1:1.2	5.48	93.96	V less reaction	
2.	0.5006	0.2802	1:2	8.62	91.00	0.85:1	$Li_2O.Nb_2O_5$
3.	0.5001	0.4163	1:3	16.32	82.98	1.73:1	$2Li_2O.Nb_2O_5$
4.	0.4998	0.5482	1:4	17.06	82.12	1.84:1	$2Li_2O.Nb_2O_5$
5.	0.5006	0.6883	1:5	17.13	82.02	1.85:1	$2Li_2O.Nb_2O_5$
6.	0.4998	1.3862	1:10	17.31	82.00	1.87:1	$2Li_2O.Nb_2O_5$
Temperature of Reaction - 800 ±20°C							
1.	0.4998	0.1610	1:1.2	8.61	90.94	0.84:1	$Li_2O.Nb_2O_5$
2.	0.4998	0.2813	1:2	9.01	90.78	0.88:1	$Li_2O.Nb_2O_5$
3.	0.4997	0.4210	1:3	16.96	82.31	1.83:1	$2Li_2O.Nb_2O_5$
4.	0.5019	0.5611	1:4	16.98	82.28	1.83:1	$2Li_2O.Nb_2O_5$
5.	0.4991	0.6814	1:5	17.08	82.12	1.88:1	$2Li_2O.Nb_2O_5$
6.	0.5002	1.3819	1:10	17.24	82.01	1.86:1	$2Li_2O.Nb_2O_5$

TABLE - 2.03

LITHIUM NIOBATES

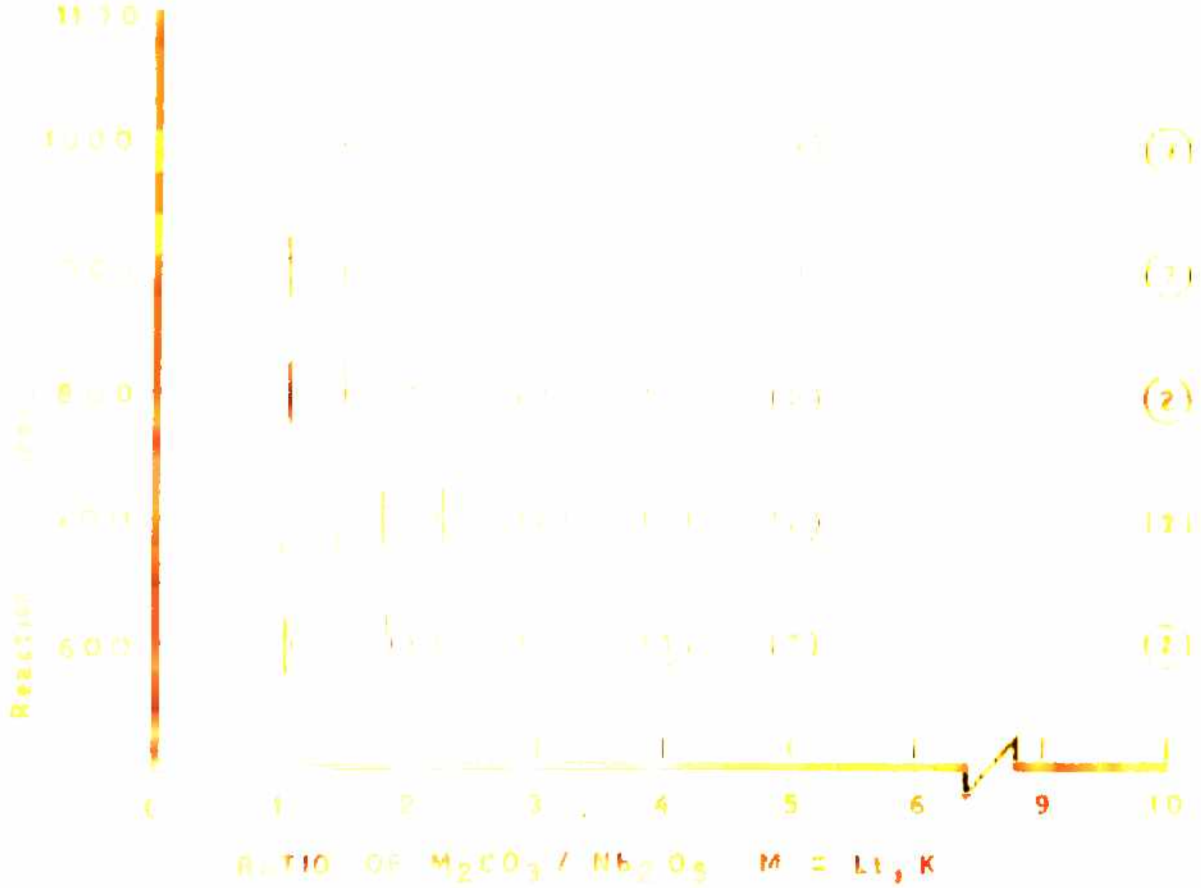
Time of heating - 3 hrs.

S.N.	Weight of Nb_2O_5 taken (gm)	Weight of Li_2Co_3 taken (gm)	Molar ratio $Nb_2O_5:Li_2Co_3$	% Li_2O	% Nb_2O_5	Ratio formed $Li_2O:Nb_2O_5$	Compound
Temperature of Reaction - 900 ±20°C							
1.	0.5023	0.1661	1:1.2	9.24	90.29	0.91:1	$Li_2O.Nb_2O_5$
2.	0.5002	0.2805	1:2	17.30	82.02	1.87:1	$2Li_2O.Nb_2O_5$
3.	0.4970	0.4202	1:3	18.84	81.10	2.06:1	$2Li_2O.Nb_2O_5$
4.	0.5016	0.5589	1:4	23.46	75.92	2.71:1	$3Li_2O.Nb_2O_5$
5.	0.4975	0.7031	1:5	23.88	75.67	2.80:1	$3Li_2O.Nb_2O_5$
6.	0.5003	1.3873	1:10	24.62	74.86	2.91:1	$3Li_2O.Nb_2O_5$
Temperature of Reaction - 1000 ±20°C							
1.	0.4995	0.1689	1:1.2	10.06	89.62	0.99:1	$Li_2O.Nb_2O_5$
2.	0.5051	0.2678	1:2	18.06	81.61	1.96:1	$2Li_2O.Nb_2O_5$
3.	0.4973	0.4161	1:3	18.90	81.06	2.06:1	$2Li_2O.Nb_2O_5$
4.	0.5014	0.5572	1:4	25.12	74.29	2.78:1	$3Li_2O.Nb_2O_5$
5.	0.4979	0.6980	1:5	25.68	74.02	2.96:1	$3Li_2O.Nb_2O_5$
6.	0.4997	1.3922	1:10	25.14	74.50	2.99:1	$3Li_2O.Nb_2O_5$

TABLE - 2.04

POTASSIUM NIOBATES Time of heating = 3 hours.

S.N.	Weight of Nb_2O_5 taken (gm)	Weight of K_2CO_3 taken (gm)	Molar ratio $Nb_2O_5:K_2CO_3$	Temperature °C ±20	% K_2O	% Nb_2O_5	Ratio formed $K_2O:Nb_2O_5$	Compound
1.	0.5023	0.3162	1:1.2	500	-	99.08	No reaction	
2.	0.4986	0.5108	1:2	500	2.10	97.54	Almost no reaction	
3.	0.5013	0.3126	1:1.2	600	1.42	98.26	Almost no reaction	
4.	0.4921	0.5263	1:2	600	4.92	94.61	V.less reaction	
5.	0.5027	0.3139	1:1.2	700	25.00	74.61	0.95:1	$K_2O.Nb_2O_5$
6.	0.4992	0.5251	1:2	700	25.23	74.01	0.96:1	$K_2O.Nb_2O_5$
7.	0.5003	0.3112	1:1.2	800	24.91	74.81	0.94:1	$K_2O.Nb_2O_5$
8.	0.4953	0.3135	1:1.2	900	25.08	74.46	0.95:1	$K_2O.Nb_2O_5$
9.	0.4987	0.3163	1:1.2	1000	26.43	73.26	1.02:1	$K_2O.Nb_2O_5$



2 Formation of Lithium and Potassium niobates as f(T).

○ refers to Li and □ refers to K compound, Time of heating = 3 hrs.

no compound formation

1 = metaniobates $M_2O \cdot Nb_2O_5$

2 = Pyroniobates [illegible] Nb_2O_5

3 = ortho niobates, $3Li_2O$ Nb_2O_5

TABLE - 2.05

CALCIUM NIOBATES

Time of heating - 3 hrs

S.N.	Weight of Nb_2O_5 taken (gm)	Weight of $CaCO_3$ taken	Molar ratio Nb_2O_5:$CaCO_3$	% CaO	% Nb_2O_5	Ratio formed CaO.Nb_2O_5	Compound
Temperature of Reaction - 500 ± 20°C							
1.	0.4938	0.3716	1:2	5.94	94.02	V. less reaction	
2.	0.5054	0.5604	1:3	5.44	93.21	V. less reaction	
3.	0.5034	0.7390	1:4	6.79	93.20	V. less reaction	
4.	0.4986	1.1373	1:6	7.01	92.69	V. less reaction	
5.	0.4966	1.8524	1:10	8.48	91.22	0.88:2	CaO.2Nb_2O_5
6.	0.5021	3.7455	1:20	9.02	91.01	0.94:2	CaO.2Nb_2O_5
Temperature of Reaction - 600 ±20°C							
1.	0.5003	0.3681	1:2	9.02	90.86	0.94:2	CaO.2Nb_2O_5
2.	0.4992	0.5486	1:3	9.42	90.51	0.99:2	CaO.2Nb_2O_5
3.	0.5010	0.7432	1:4	18.14	81.36	1.05:1	CaO.Nb_2O_5
4.	0.4986	0.9262	1:5	18.29	81.48	1.05:1	CaO.Nb_2O_5

TABLE - 2.06

CALCIUM NIOBATES

Time of heating - 3 hrs.

S.N.	Weight of Nb_2O_5 taken (gm)	Weight of $CaCO_3$ taken (gm)	Molar ratio $Nb_2O_5:CaCO_3$	% CaO	% Nb_2O_5	Ratio formed $CaO:Nb_2O_5$	Compound
Temperature of Reaction - 700 ±20°C							
1.	0.4998	0.1850	1:1	1.00	98.96	Almost no reaction	
2.	0.4998	0.3686	1:2	8.49	91.38	0.82:2	$CaO.2Nb_2O_5$
3.	0.5006	0.5501	1:3	9.02	90.87	0.94:2	$CaO.2Nb_2O_5$
4.	0.5001	0.7379	1:4	17.37	81.81	1.04:1	$CaO.Nb_2O_5$
5.	0.4996	0.9287	1:5	17.57	82.16	1.01:1	$CaO.Nb_2O_5$
Temperature of Reaction - 800 ±20°C							
1.	0.5008	0.1848	1:1	1.14	98.80	Almost no reaction	
2.	0.4996	0.3702	1:2	9.06	91.18	0.95:2	$CaO.2Nb_2O_5$
3.	0.4989	0.5530	1:3	9.02	90.98	0.95:2	$CaO.2Nb_2O_5$
4.	0.5013	0.7406	1:4	17.06	82.98	0.98:1	$CaO.Nb_2O_5$
5.	0.4979	0.9306	1:5	17.00	82.86	0.98:1	$CaO.Nb_2O_5$

TABLE - 2.07

CALCIUM NIOBATES

Time of heating - 3 hrs.

S.N.	Weight of Nb_2O_5 taken (gm)	Weight of $CaCO_3$ taken (gm)	Molar ratio $Nb_2O_5:CaCO_3$	% CaO	% Nb_2O_5	Ratio formed $CaO:Nb_2O_5$	Compound
Temperature of Reaction - 900 ±20°C							
1.	0.4999	0.1846	1:1	1.32	98.60	Almost no reaction	
2.	0.4979	0.3648	1:2	8.90	90.30	0.94:2	$CaO.2Nb_2O_5$
3.	0.5017	0.5552	1:3	9.06	90.82	0.94:2	$CaO.2Nb_2O_5$
4.	0.5062	0.7446	1:4	16.90	82.90	0.96:1	$CaO.Nb_2O_5$
5.	0.5001	0.9324	1:5	17.10	82.10	0.99:1	$CaO.Nb_2O_5$
Temperature of Reaction - 1000 ± 20°C							
1.	0.5048	0.1892	1:1	3.20	96.56	Almost no reaction	
2.	0.5057	0.3732	1:2	9.50	90.42	0.99:2	$CaO.2Nb_2O_5$
3.	0.5020	0.5612	1:3	9.12	90.83	0.96:2	$CaO.2Nb_2O_5$
4.	0.5070	0.7424	1:4	17.92	81.91	1.03:1	$CaO.Nb_2O_5$
5.	0.5088	0.9374	1:5	16.90	83.10	0.96:1	$CaO.Nb_2O_5$

TABLE - 2.08

CALCIUM NIOBATES

Time of heating - 3 hrs.

S.N.	Weight of Nb_2O_5 taken (gm)	Weight of $CaCO_3$ taken (gm)	Molar ratio $Nb_2O_5:CaCO_3$	% CaO	% Nb_2O_5	Ratio formed $CaO:Nb_2O_5$	Compound
Temperature of Reaction 1100 ± 20°C							
1.	0.5037	0.1889	1:1	16.92	82.81	0.97:1	$CaO.Nb_2O_5$
2.	0.5009	0.3810	1:2	17.31	82.47	0.99:1	$CaO.Nb_2O_5$
3.	0.5008	0.5581	1:3	17.85	81.96	1.03:1	$CaO.Nb_2O_5$
4.	0.5028	0.7313	1:4	18.60	81.21	1.06:1	$CaO.Nb_2O_5$
5.	0.5021	0.9331	1:5	18.12	81.82	1.05:1	$CaO.Nb_2O_5$
Temperature of Reaction = 1200 ±20°C							
1.	0.5007	0.1852	1:1	17.28	82.56	1:1	$CaO.Nb_2O_5$
2.	0.5035	0.3712	1:2	18.10	81.72	1.05:1	$CaO.Nb_2O_5$
3.	0.5038	0.5691	1:3	16.56	83.66	0.94:1	$CaO.Nb_2O_5$
4.	0.5043	0.7421	1:4	17.56	82.00	1.02:1	$CaO.Nb_2O_5$
5.	0.5012	0.9301	1:5	17.32	82.46	0.99:1	$CaO.Nb_2O_5$

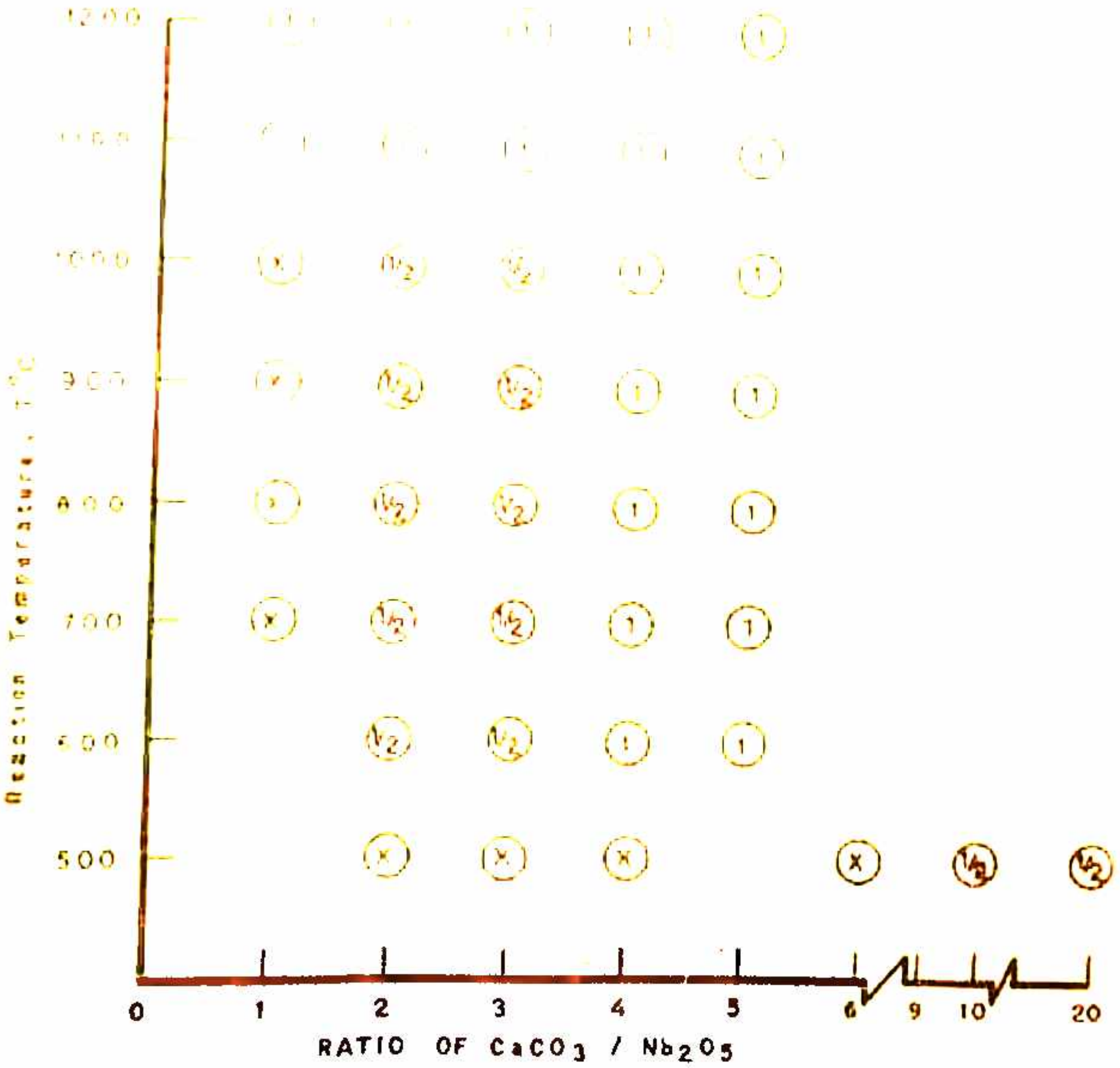


FIG.3 Formation of Calcium niobates as f(T).

Time of heating = 3 hrs.

(X) = no compound formation

(1/2) = $CaO \cdot 2Nb_2O_5$

(1) = $CaO \cdot Nb_2O_5$

TABLE - 2.09

STRONTIUM NIOBATES

Time of heating - 3 hrs.

S.N.	Weight of Nb_2O_5 taken (gm)	Weight of $SrCO_3$ taken (gm)	Molar ratio Nb_2O_5:$SrCO_3$	% SrO	% Nb_2O_5	Ratio formed	Compound
Temperature of Reaction - 500 ± 20°C							
1.	0.5010	0.5550	1:2	4.14	94.82	Almost no reaction	
2.	0.5019	1.1102	1:4	4.78	94.12	Almost no reaction	
3.	0.4955	2.7689	1:10	5.21	93.62	Almost no reaction	
Temperature of Reaction - 600 ± 20°C							
1.	0.5001	0.5541	1:2	27.10	72.02	0.96:1	$SrO.Nb_2O_5$
2.	0.5001	1.1096	1:4	27.38	72.26	0.97:1	$SrO.Nb_2O_5$
3.	0.5018	2.7781	1:10	27.56	72.16	0.97:1	$SrO.Nb_2O_5$

TABLE - 2.10

STRONTIUM NIOBATES

Time of heating - 3 hrs.

S.N.	Weight of Nb_2O_5 taken (gm)	Weight of $SrCO_3$ taken (gm)	Molar ratio Nb_2O_5:$SrCO_3$	% SrO	% Nb_2O_5	Ratio formed	Compound
Temperature of Reaction - 700 ± 20°C							
1.	0.5011	0.2783	1:1	3.01	96.02	Almost no reaction	
2.	0.5005	0.5562	1:2	27.36	72.29	0.97:1	$SrO.Nb_2O_5$
3.	0.4998	1.1070	1:4	43.10	56.52	1.90:1	$2SrO.Nb_2O_5$
4.	0.4990	1.6600	1:6	43.40	56.48	2.01:1	$2SrO.Nb_2O_5$
5.	0.4972	2.7663	1:10	43.52	56.31	1.98:1	$2SrO.Nb_2O_5$
Temperature of Reaction - 800 ±20°C							
1.	0.5010	0.2782	1:1	3.22	95.81	Almost no reaction	
2.	0.4990	0.5500	1:2	27.80	72.09	0.98:1	$SrO.Nb_2O_5$
3.	0.5022	1.1051	1:4	43.24	56.65	1.95:1	$2SrO.Nb_2O_5$
4.	0.5016	1.6649	1:6	53.01	46.59	2.90:1	$3SrO.Nb_2O_5$
5.	0.5011	2.7700	1.10	53.10	46.78	2.89:1	$3SrO.Nb_2O_5$

TABLE - 2.11

STRONTIUM NIOBATES

Time of heating - 3 hrs.

Temperature of Reaction - 900±20°C

S.N.	Weight of Nb_2O_5 taken (gm)	Weight of $SrCO_3$ taken (gm)	Molar ratio $Nb_2O_5:SrCO_3$	% SrO	% Nb_2O_5	Ratio formed	Compound
1.	0.5011	0.2798	1:1	5.29	94.02	Almost no reaction	
2.	0.4983	0.5604	1:2	28.23	71.45	1.01:1	$SrO.Nb_2O_5$
3.	0.4990	0.8302	1:3	43.81	55.51	2.08:1	$2SrO.Nb_2O_5$
4.	0.4998	1.097	1:4	43.82	55.09	2.10:1	$2SrO.Nb_2O_5$
5.	0.4991	1.3760	1:5	54.09	46.22	3.01:1	$3SrO.Nb_2O_5$
6.	0.4961	1.6556	1:6	54.06	46.34	2.98:1	$3SrO.Nb_2O_5$
7.	0.5014	1.9400	1:7	61.08	39.21	4.04:1	$4SrO.Nb_2O_5$
8.	0.4997	2.2018	1:8	61.40	38.81	4.06:1	$4SrO.Nb_2O_5$
9.	0.5048	2.5006	1:9	61.62	38.61	4.08:1	$4SrO.Nb_2O_5$
10.	0.5050	2.7628	1:10	61.03	38.51	4.05:1	$4SrO.Nb_2O_5$

TABLE - 2.12

STRONTIUM NIOBATES

Time of heating = 3 hrs.

S.N.	Weight of Nb_2O_5 taken (gm)	Weight of $SrCO_3$ taken (gm)	Molar ratio $Nb_2O_5:SrCO_3$	% SrO	% Nb_2O_5	Ratio formed $SrO:Nb_2O_5$	Compound
Temperature of Reaction = 1000 ±20°C							
1.	0.5076	0.2782	1:1	7.09	92.45	V. less reaction	
2.	0.5019	0.5601	1:2	29.01	70.26	1.05:1	$SrO.Nb_2O_5$
3.	0.5010	1.1101	1:4	44.12	55.34	2.04:1	$2SrO.Nb_2O_5$
4.	0.5010	1.6704	1:6	53.12	46.23	2.94:1	$3SrO.Nb_2O_5$
5.	0.5006	2.7742	1:10	61.92	38.00	4.07:1	$4SrO.Nb_2O_5$
Temperature of Reaction = 1100 ±20°C							
1.	0.4992	0.2780	1:1	16.12	83.04	0.99:2	$SrO.2Nb_2O_5$
2.	0.5012	0.5612	1:2	27.90	72.51	0.98:1	$SrO.Nb_2O_5$
3.	0.5013	1.1091	1:4	45.62	54.55	2.1:1	$2SrO.Nb_2O_5$
4.	0.5036	1.6736	1:6	47.06	53.35	2.90:1	$3SrO.Nb_2O_5$
5.	0.5014	2.2422	1:8	61.24	38.82	4.04:1	$4SrO.Nb_2O_5$
6.	0.5016	2.7921	1:10	61.81	38.45	4.12:1	$4SrO.Nb_2O_5$

TABLE - 2.13

STRONTIUM NIOBATES

Time of heating = 3 hrs

Temperature of Reaction = 1200±20°C

S.N.	Weight of Nb_2O_5 taken (gm)	Weight of $SrCO_3$ taken (gm)	Molar ratio $Nb_2O_5:SrCO_3$	% SrO	% Nb_2O_5	Ratio formed $SrO:Nb_2O_5$	Compound
1.	0.5034	0.2789	1:1	16.55	83.06	1.02:2	$SrO.2Nb_2O_5$
2.	0.5029	0.5534	1:2	28.22	71.69	1.01:1	$SrO.Nb_2O_5$
3.	0.4994	0.8310	1:3	43.42	56.82	1.96:1	$2SrO.Nb_2O_5$
4.	0.5026	1.1126	1:4	44.08	56.25	2.00:1	$2SrO.Nb_2O_5$
5.	0.5008	1.2906	1:5	52.45	47.87	2.85:1	$3SrO.Nb_2O_5$
6.	0.5067	1.6721	1:6	54.23	45.66	3.04:1	$3SrO.Nb_2O_5$
7.	0.5054	1.9402	1:7	60.98	39.46	3.96:1	$4SrO.Nb_2O_5$
8.	0.5023	2.2171	1:8	61.80	38.62	4.12:1	$4SrO.Nb_2O_5$
9.	0.5034	2.5035	1:9	62.01	39.51	4.02:1	$4SrO.Nb_2O_5$
10.	0.5056	2.7728	1:10	62.12	38.24	4.16:1	$4SrO.Nb_2O_5$

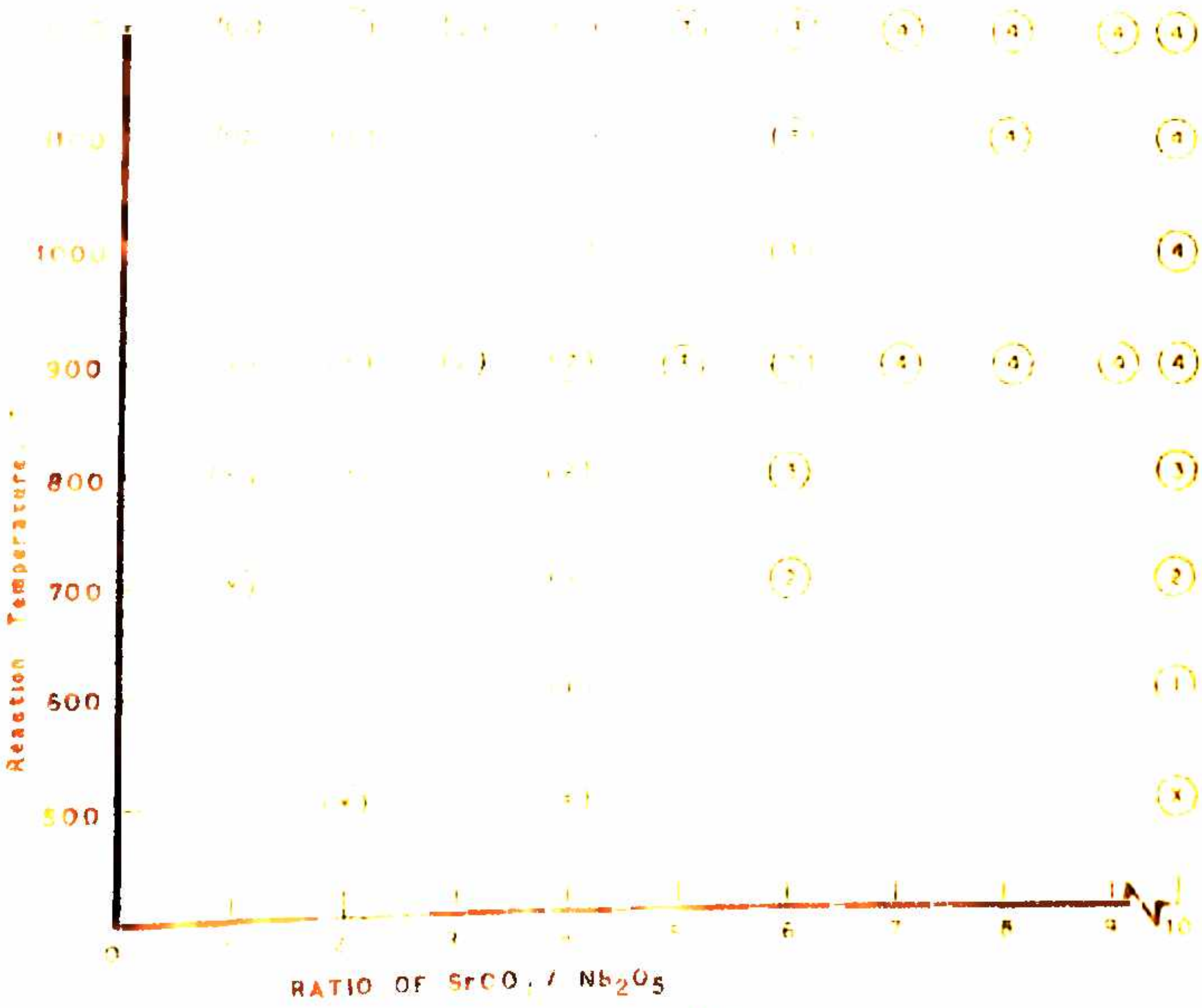


FIG 4. Formation of Strontium niobates as f (T).

Time of heating = 3 hrs.

Ⓧ No compound formation

(1/2) = $SrO.2Nb_2O_5$

① = $SrO.Nb_2O_5$

② = $2SrO.Nb_2O_5$

3 = $5SrO.2Nb_2O_5$

4 = $4SrO.Nb_2O_5$

TABLE - 2.14

BARIUM NIOBATES

Time of heating - 3 hrs.

S.N.	Weight of Nb_2O_5 taken (gm)	Weight of $Ba(OAc)_2$ taken (gm)	Molar ratio $Nb_2O_5:Ba(OAc)_2$	% BaO	%Nb_2O_5	Ratio formed $BaO:Nb_2O_5$	Compound
Temperature of Reaction - 500±20°C							
1.	0.4985	0.9646	1:2	-	99.10		No reaction
2.	0.5010	1.4396	1:3	1.02	98.70		Almost no reaction
3.	0.4996	1.9202	1:4	1.10	98.60		Almost no reaction
4.	0.5020	2.3963	1:5	2.69	96.80		Almost no reaction
5.	0.5011	4.7988	1:10	2.72	96.76		Almost no reaction
6.	0.5000	9.6004	1:20	3.44	95.94		Almost no reaction
Temperature of Reaction - 600 ± 20°C							
1.	0.5010	0.9652	1:2	8.29	90.72		V. less reaction
2.	0.4992	1.4463	1:3	8.86	90.12		V. less reaction
3.	0.5038	1.9196	1:4	11.32	87.66		Less reaction
4.	0.5011	2.3922	1:5	12.59	86.06		Less reaction
5.	0.4992	4.7961	1:10	15.90	83.54		Less reaction
6.	0.5011	9.5621	1:20	16.02	83.03		Less reaction

TABLE - 2.15

BARIUM NIOBATES

Time of heating - 3 hrs.

S.N.	Weight of Nb_2O_5 taken (gm)	Weight of $Ba(OAc)_2$ taken (gm)	Molar ratio Nb_2O_5:$Ba(OAc)_2$	% BaO	% Nb_2O_5	Ratio formed	Compound
Temperature of Raction - 700 ±20°C							
1.	0.4987	0.9633	1:2	21.00	78.60	0.92:2	$BaO.2Nb_2O_5$
2.	0.4997	1.4495	1:3	23.12	76.90	1.04:2	$BaO.2Nb_2O_5$
3.	0.5084	1.9260	1:4	37.58	62.02	1.05:1	$BaO.Nb_2O_5$
4.	0.5011	2.4106	1:5	37.28	63.02	1.03:1	$BaO.Nb_2O_5$
Temperature of Reaction - 800 ±20°C							
1.	0.5011	0.4802	1:1	1.52	98.01	Almost no reaction	
2.	0.4979	0.9582	1:2	23.70	76.02	1.06:2	$BaO.2Nb_2O_5$
3.	0.5010	1.4429	1:3	22.91	76.42	1.04:2	$BaO.2Nb_2O_5$
4.	0.4989	1.9162	1:4	37.62	62.02	1.05:1	$BaO.Nb_2O_5$
5.	0.5012	2.3990	1:5	36.50	63.20	1:1	$BaO.Nb_2O_5$

TABLE - 2.16

BARIUM NIOBATES

Time of heating - 3 hrs.

S.N.	Weight of Nb_2O_5 taken (gm)	Weight of $Ba(OAc)_2$ taken (gm)	Molar ratio	% BaO	% Nb_2O_5	Ratio formed $BaO:Nb_2O_5$	Compound
Temperature of Reaction - 900±20°C							
1.	0.5001	0.4842	1:1	2.06	98.12	Almost no reaction	
2.	0.5047	0.9626	1:2	22.51	77.10	1.01:2	$BaO.2Nb_2O_5$
3.	0.4988	1.4380	1:3	22.44	77.07	1.02:2	$BaO.2Nb_2O_5$
4.	0.5011	1.9251	1:4	36.50	63.01	1:1	$BaO.Nb_2O_5$
5.	0.5012	2.3990	1:5	36.50	63.20	1:1	$BaO.Nb_2O_5$
Temperature of Reaction - 1000 +20°C							
1.	0.5010	0.4808	1:1	5.12	94.16	V. less reaction	
2.	0.5015	0.9620	1:2	37.20	62.98	1.02:1	$BaO.Nb_2O_5$
3.	0.5020	1.4411	1:3	37.38	63.02	1.03:1	$BaO.Nb_2O_5$
4.	0.5026	1.9398	1:4	37.01	62.81	1.02:1	$BaO.Nb_2O_5$
5.	0.5001	2.4006	1:5	36.38	62.69	1.01:1	$BaO.Nb_2O_5$

TABLE - 2.17

BARIUM NIOBATES

Time of heating = 3 hrs.

S.N.	Weight of Nb_2O_5 taken (gm)	Weight of $Ba(OAc)_2$ taken (gm)	Molar ratio Nb_2O_5:$Ba(OAc)_2$	% BaO	% Nb_2O_5	Ratio formed	Compound
Temperature of Reaction = 1100 ± 20°C							
1.	0.5064	0.4745	1:1	21.97	77.61	0.94:2	$BaO.2Nb_2O_5$
2.	0.5058	0.9622	1:2	35.81	63.83	0.92:1	$BaO.Nb_2O_5$
3.	0.5075	1.4476	1:3	35.92	63.95	0.98:1	$BaO.Nb_2O_5$
4.	0.5058	1.9295	1:4	36.40	62.80	1.01:1	$BaO.Nb_2O_5$
5.	0.4977	2.3960	1:5	37.08	62.12	1.03:1	$BaO.Nb_2O_5$
Temperature of Reaction = 1200 ± 20°C							
1.	0.4964	0.4830	1:1	21.40	75.20	0.95:2	$BaO.2Nb_2O_5$
2.	0.5005	0.9697	1:2	36.80	63.10	1.02:1	$BaO.Nb_2O_5$
3.	0.5071	1.4338	1:3	36.49	63.06	1:1	$BaO.Nb_2O_5$
4.	0.5029	1.9337	1:4	37.73	62.07	1.05:1	$BaO.Nb_2O_5$
5.	0.5003	2.4042	1:5	36.49	63.00	1:1	$BaO.Nb_2O_5$

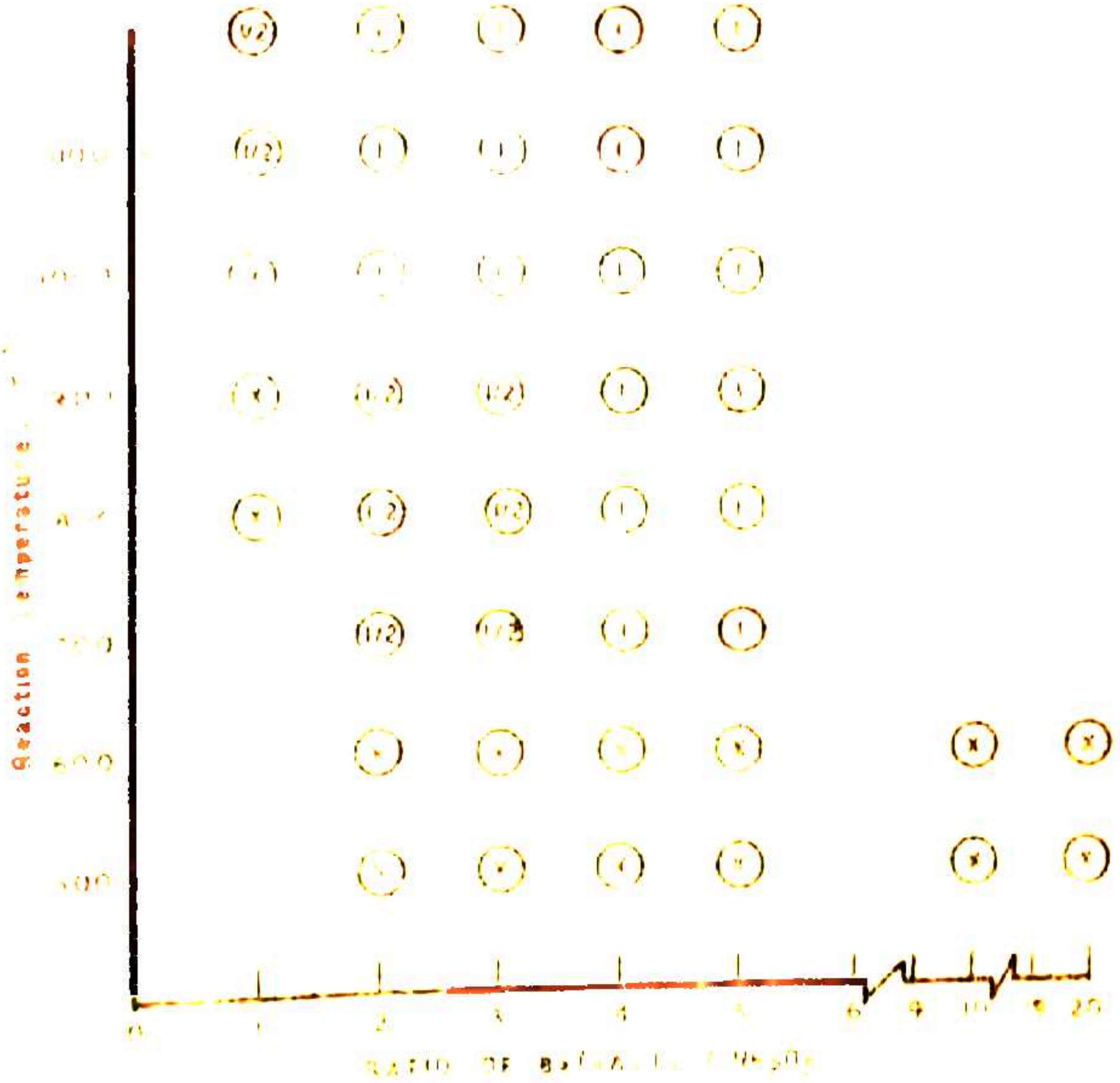


FIG. 5 Formation of Barium niobates as f(T)

Time heating = 3 hrs

(X) - no compound formation

(1:2) - $BaO \cdot 2Nb_2O_5$

(1) = $BaO \cdot Nb_2O_5$

various insoluble niobates were formed. Their compositions depend on the proportions of the constituents in the mixtures and temperature of heating.

It is interesting to note that lithium formed three insoluble niobates, whereas potassium formed only one insoluble niobate. For other ratios and temperatures the niobates formed were soluble in hot water. An attempt was also made to prepared sodium niobates but the niobates formed were soluble in hot water which prevented us to continue further.

It is evident from the results reported in Tables 2.01 and 2.04 that almost no reaction takes place at 500°C whatever may be the ratio of constituents. On increasing the temperature to 600°C, when Nb_2O_5 : Li_2CO_3 is 1:3, lithium metaniobate, $Li_2O \cdot Nb_2O_5$, is formed. On increasing this ratio to 1:5 or more, another niobate, lithium pyroniobate, $2Li_2O \cdot Nb_2O_5$, is formed. This niobate is reported for the first time.

At 700°C lithium metaniobate is formed when Li_2CO_3 : Nb_2O_5 ratio is only 1:2 and with higher ratios lithium pyroniobate was isolated. On further increasing the temperature to 800°-1000°C lithium meta niobate is formed at lowest ratio of 1:1.2 (Tables 2.02, 2.03).

Lithium orthoniobate, $3Li_2O.\ Nb_2O_5$, was obtained on taking $Nb_2O_5 : Li_2CO_3$ ratio 1:4 or higher (Table 2.03).

Potassium metaniobate ($K_2O.\ Nb_2O_5$) was obtained in the range of 700°- 1000°C with ratio 1:1.2 of Nb_2O_5 and K_2CO_3 as shown in Table 2.04. It also formed at 700°C when reaction mixture of Nb_2O_5 and K_2CO_3 was taken in the ratio 1:2.

On taking higher ratios reaction product was observed to be soluble in hot water due to formation of soluble niobates.

Alkaline earth niobates :

It was observed in these cases also that the reactions were almost complete when the mixtures were heated for three hours, therefore this time of heating was chosen for carrying out these reactions as well (cf. Table 2.01(b) .

When the mixtures containing Nb_2O_5 and carbonate or acetate of calcium, strontium and barium in varying proportions were heated at high temperatures (500-1200°C), various insoluble niobates were formed. Their compositions depend on the proportions of the constituents in the mixtures and temperature of heating.

It is interesting to note that calcium and barium both formed two stable compounds $XO.\ Nb_2O_5$ and $XO.\ 2Nb_2O_5$ (X = Ca or Ba), whereas strontium formed five different niobates, $Y\ SrO.\ Nb_2O_5$ (Y = 1,2,3 & 4) and $SrO.\ 2Nb_2O_5$.

Calcium niobates :

From the results reported in Table 2.05 it is evident that when $Nb_2O_5 : CaCO_3$ were heated in ratios 1:2, 1:3, 1:4 and 1:6 at 500°C, very little reaction was observed, unless a large excess (10 to 20 times) of $CaCO_3$ was used in the reaction mixture. The compound finally formed was $CaO.\ 2Nb_2O_5$.

On further increasing the temperature from 600 to 1000°C the same niobate was obtained with $Nb_2O_5 : CaCO_3$ ratio of 1:2 and 1:3 (Tables 2.06 and 2.07), whereas for 1:1 ratio very less reaction was observed upto 1000°C. Calcium metaniobate, $CaO.\ Nb_2O_5$, was observed to be formed in above mentioned temperature range but with $Nb_2O_5 : CaCO_3$ ratio of 1:4 and 1:5 (Tables 2.06 and 2.07).

Calcium metaniobate was also isolated in the range of 1100-1200°C when Nb_2O_5 and $CaCO_3$ mixtures were heated in any ratio ranging from 1:1 to 1:5.

Strontium niobates :

It is clear from Table 2.09 that almost no reaction was observed when Nb_2O_5 and $SrCO_3$ mixtures were heated in the ratios 1:2, 1:4 or 1:10, but at 600°C strontium metaniobate SrO. Nb_2O_5, was obtained with same ratios. On higher temperatures i.e. from 700 to 1200°C, it was isolated, when Nb_2O_5 : $SrCO_3$ ratio was 1:2 only.

Strontium pyroniobate 2SrO. Nb_2O_5 was isolated at 700°C when Nb_2O_5 and $SrCO_3$ mixtures were taken in ratios 1:4, 1:6 or 1:10 (Table 2.10). It also formed in the temperature range 700-1200°C, when Nb_2O_5 : $SrCO_3$ was only in the ratio 1:3 and 1:4 (Table 2.10-2.13).

Strontium orthoniobate 3SrO. Nb_2O_5 was obtained when Nb_2O_5 : $SrCO_3$ was taken in the ratio 1:10 and heated 800°C. It was also obtained when reaction mixture having Nb_2O_5 and $SrCO_3$ in the ratio 1:5 or 1:6 were heated at 800-1200°C. (Table 2.10-2.13).

Strontium niobate 4SrO. Nb_2O_5, formed in the range temperature range of 900-1200°C when Nb_2O_5 and $SrCO_3$ mixtures were taken in ratio 1:7 or more (Table 2.11-2.13).

Another strontium niobate, SrO. $2Nb_2O_5$ was obtained when Nb_2O_5 and $SrCO_3$ mixtures were heated in the temperature range of 1100-1200°C with 1:1 ratio (Table 2.12 & 2.13).

Barium niobates :

It was observed that no Barium niobate was formed even on heating Nb_2O_5 and $BaCO_3$ at 1200°C (cf Table 2.01 b) Therefore Barium acetate was preferred for the formation of barium niobates.

From the results reported in Table 2.14 it is evident that no Barium niobate was isolated on heating Nb_2O_5 and Ba $(OAc)_2$ mixtures at 500 or 600°C in any ratio. But two stable niobates BaO. $2Nb_2O_5$ and BaO. Nb_2O_5 were obtained when the mixtures were heated in the temperature range 700-900°C with 1:2, 1:3, 1:4 and 1:5 ratio of Nb_2O_5 and Ba $(OAc)_2$ (cf Tables 2.15 and 2.16).

Barium metaniobate, BaO. Nb_2O_5, also formed when reaction was carried out between 1000-1200°C with various ratios of Nb_2O_5 and $Ba(OAc)_2$, except 1:1 in which case almost no reaction was observed as is shown in Tables 2.16 and 2.17.

The formation of CaO. $2Nb_2O_5$, SrO. $2Nb_2O_5$, 3SrO. Nb_2O_5 and BaO. $2Nb_2O_5$ is reported here for the first time.

2.4 Semiconducting properties of alkali niobates :

In tables 2.18 to 2.24 the measured values of electrical conductivity of various forms of Nb_2O_5 and

TABLE - 2.18

Electrical Conductivity of α-Nb_2O_5 at different temperatures.

S.N.	Temperature (^oK) (T)	$\frac{1}{T} \times 10^3$ ($^oK^{-1}$)	σ ($Ohm^{-1}Cm^{-1}$)	Log σ ($Ohm^{-1}Cm^{-1}$)
1.	313	3.20	1.10×10^{-7}	$\bar{7}.04$
2.	323	3.10	1.29×10^{-7}	$\bar{7}.11$
3.	333	3.00	1.51×10^{-7}	$\bar{7}.18$
4.	343	2.92	1.86×10^{-7}	$\bar{7}.27$
5.	353	2.83	1.99×10^{-7}	$\bar{7}.30$
6.	363	2.76	2.14×10^{-7}	$\bar{7}.33$
7.	373	2.68	2.69×10^{-7}	$\bar{7}.43$
8.	383	2.61	3.24×10^{-7}	$\bar{7}.51$
9.	393	2.54	3.55×10^{-7}	$\bar{7}.55$
10.	403	2.48	4.79×10^{-7}	$\bar{7}.68$
11.	413	2.42	6.76×10^{-7}	$\bar{7}.83$
12.	423	2.36	1.41×10^{-6}	$\bar{6}.15$
13.	433	2.31	3.71×10^{-6}	$\bar{6}.57$
14.	443	2.26	6.61×10^{-6}	$\bar{6}.82$
15.	453	2.21	1.20×10^{-5}	$\bar{5}.08$
16.	463	2.16	1.51×10^{-5}	$\bar{5}.18$
17.	473	2.11	2.19×10^{-5}	$\bar{5}.34$
18.	483	2.07	4.17×10^{-5}	$\bar{5}.62$
19.	493	2.03	5.76×10^{-5}	$\bar{5}.76$
20.	503	1.99	8.71×10^{-5}	$\bar{5}.94$
21.	513	1.95	1.35×10^{-4}	$\bar{4}.13$
22.	523	1.91	1.95×10^{-4}	$\bar{4}.29$

TABLE - 2.19

Electrical Conductivity of β-Nb_2O_5 at different temperatures

S.N.	Temperature (^oK) (T)	$^1/_T \times 10^3$ ($^oK^{-1}$)	σ ($Ohm^{-1}cm^{-1}$)	Log σ ($Ohm^{-1}cm^{-1}$)
1.	313	3.20	6.31×10^{-8}	$\bar{8}.80$
2.	323	3.10	8.71×10^{-8}	$\bar{8}.44$
3.	333	3.00	1.10×10^{-7}	$\bar{7}.04$
4.	343	2.92	1.15×10^{-7}	$\bar{7}.06$
5.	353	2.83	1.35×10^{-7}	$\bar{7}.13$
6.	363	2.76	1.70×10^{-7}	$\bar{7}.23$
7.	373	2.68	2.24×10^{-7}	$\bar{7}.35$
8.	383	2.61	2.75×10^{-7}	$\bar{7}.44$
9.	393	2.54	3.16×10^{-7}	$\bar{7}.50$
10.	403	2.48	3.31×10^{-7}	$\bar{7}.52$
11.	413	2.42	3.98×10^{-7}	$\bar{7}.60$
12.	423	2.36	8.51×10^{-7}	$\bar{7}.93$
13.	433	2.31	1.35×10^{-6}	$\bar{6}.13$
14.	443	2.26	2.40×10^{-6}	$\bar{6}.38$
15.	453	2.21	4.90×10^{-6}	$\bar{6}.69$
16.	463	2.16	8.51×10^{-6}	$\bar{6}.93$
17.	473	2.11	1.15×10^{-5}	$\bar{5}.18$
18.	483	2.07	1.95×10^{-5}	$\bar{5}.29$
19.	493	2.03	3.24×10^{-5}	$\bar{5}.51$
20.	503	1.99	4.37×10^{-5}	$\bar{5}.64$
21.	513	1.95	6.31×10^{-5}	$\bar{5}.80$
22.	523	1.91	8.71×10^{-5}	$\bar{5}.94$

TABLE - 2.20

Electrical Conductivity of γ-Nb_2O_5 at different temperatures

S.N.	Temperature (°K) (T)	$\frac{1}{T} \times 10^3$ (°K^{-1})	σ ($Ohm^{-1}cm^{-1}$)	Log σ ($Ohm^{-1}cm^{-1}$)
1.	313	3.20	3.17×10^{-12}	$\overline{11}.50$
2.	323	3.10	3.17×10^{-12}	$\overline{11}.50$
3.	333	3.00	3.91×10^{-11}	$\overline{11}.59$
4.	343	2.92	1.62×10^{-10}	$\overline{10}.21$
5.	353	2.83	3.72×10^{-10}	$\overline{10}.57$
6.	363	2.76	8.36×10^{-10}	$\overline{10}.92$
7.	373	2.68	2.15×10^{-9}	$\overline{9}.33$
8.	383	2.61	5.05×10^{-9}	$\overline{9}.70$
9.	393	2.54	1.55×10^{-8}	$\overline{8}.19$
10.	403	2.48	3.82×10^{-8}	$\overline{8}.58$
11.	413	2.42	8.36×10^{-8}	$\overline{8}.92$
12.	423	2.36	1.20×10^{-7}	$\overline{7}.08$
13.	433	2.31	3.24×10^{-7}	$\overline{7}.51$
14.	443	2.26	4.49×10^{-7}	$\overline{7}.65$
15.	453	2.21	8.95×10^{-7}	$\overline{7}.95$
16.	463	2.16	1.36×10^{-6}	$\overline{6}.13$
17.	473	2.11	2.35×10^{-6}	$\overline{6}.37$
18.	483	2.07	3.10×10^{-6}	$\overline{6}.49$
19.	493	2.03	5.03×10^{-6}	$\overline{6}.70$
20.	503	1.99	7.41×10^{-6}	$\overline{6}.87$
21.	513	1.95	1.05×10^{-5}	$\overline{5}.02$
22.	523	1.91	1.63×10^{-5}	$\overline{5}.21$

TABLE - 2.21

Electrical conductivity of $Li_2O.Nb_2O_5$ at different temperatures

S.N.	Temperature (°K) (T)	$\frac{1}{T}$ ($^oK^{-1}$)	σ (Ohm^{-1} cm^{-1})	Logσ ($Ohm^{-1}cm^{-1}$)
1.	313	3.20	9.77×10^{-11}	$\overline{11}.99$
2.	333	3.00	9.77×10^{-11}	$\overline{11}.99$
3.	353	2.83	9.77×10^{-11}	$\overline{11}.99$
4.	373	2.68	9.77×10^{-11}	$\overline{11}.99$
5.	393	2.54	9.77×10^{-11}	$\overline{11}.99$
6.	413	2.42	9.77×10^{-11}	$\overline{11}.99$
7.	433	2.31	9.77×10^{-11}	$\overline{11}.99$
8.	453	2.21	9.77×10^{-11}	$\overline{11}.99$
9.	473	2.11	9.77×10^{-11}	$\overline{11}.99$
10.	483	2.07	1.92×10^{-10}	$\overline{10}.28$
11.	493	2.03	3.18×10^{-10}	$\overline{10}.50$
12.	503	1.99	5.05×10^{-10}	$\overline{10}.70$
13.	513	1.95	1.19×10^{-9}	$\overline{9}.07$
14.	523	1.91	2.30×10^{-9}	$\overline{9}.36$

TABLE - 2.22

Electrical conductivity of $2Li_2O.Nb_2O_5$ at different temperatures

S.N.	Temperature (^{o}K) (T)	$\frac{1}{T} \times 10^{-3} (^{o}K^{-1})$	$\sigma (Ohm^{-1}cm^{-1})$	$Log\sigma (Ohm^{-1}cm^{-1})$
1.	313	3.20	1.32×10^{-10}	$\overline{10}.12$
2.	333	3.00	1.32×10^{-10}	$\overline{10}.12$
3.	353	2.83	1.32×10^{-10}	$\overline{10}.12$
4.	373	2.68	1.32×10^{-10}	$\overline{10}.12$
5.	393	2.54	1.32×10^{-10}	$\overline{10}.12$
6.	413	2.42	1.32×10^{-10}	$\overline{10}.12$
7.	433	2.31	1.32×10^{-10}	$\overline{10}.12$
8.	443	2.26	2.25×10^{-10}	$\overline{10}.35$
9.	453	2.21	5.86×10^{-10}	$\overline{10}.77$
10.	463	2.16	9.16×10^{-10}	$\overline{10}.96$
11.	473	2.11	1.49×10^{-9}	$\overline{9}.17$
12.	483	2.07	4.19×10^{-9}	$\overline{9}.62$
13.	493	2.03	5.82×10^{-9}	$\overline{9}.76$
14.	503	1.99	1.16×10^{-8}	$\overline{8}.06$
15.	513	1.95	1.46×10^{-8}	$\overline{8}.16$
16.	523	1.91	3.04×10^{-8}	$\overline{8}.48$

TABLE - 2.23

Electrical conductivity of $3Li_2O.Nb_2O_5$ at different temperatures

S.N.	Temperature (°K) (T)	$\frac{1}{T} \times 10^3 (^oK^{-1})$	σ $(Ohm^{-1}cm^{-1})$	Log σ $(Ohm^{-1}cm^{-1})$
1.	313	3.20	3.23×10^{-10}	$\overline{10}.51$
2.	323	3.10	3.23×10^{-10}	$\overline{10}.51$
3.	333	3.00	3.23×10^{-10}	$\overline{10}.51$
4.	343	2.92	3.23×10^{-10}	$\overline{10}.51$
5.	353	2.83	3.23×10^{-10}	$\overline{10}.51$
6.	363	2.76	6.92×10^{-10}	$\overline{10}.84$
7.	373	2.68	1.64×10^{-9}	$\overline{9}.21$
8.	383	2.61	3.31×10^{-9}	9.52
9.	393	2.54	6.78×10^{-9}	$\overline{9}.83$
10.	403	2.48	1.92×10^{-8}	$\overline{8}.28$
11.	413	2.42	3.04×10^{-8}	$\overline{8}.48$
12.	423	2.36	7.28×10^{-8}	$\overline{8}.86$
13.	433	2.31	1.18×10^{-7}	$\overline{7}.07$
14.	443	2.26	1.83×10^{-7}	$\overline{7}.26$
15.	453	2.21	3.56×10^{-7}	$\overline{7}.55$
16.	463	2.16	6.19×10^{-7}	$\overline{7}.79$
17.	473	2.11	9.86×10^{-7}	$\overline{7}.99$
18.	483	2.07	1.49×10^{-6}	$\overline{6}.17$
19.	493	2.03	2.25×10^{-6}	$\overline{6}.35$
20.	503	1.99	3.65×10^{-6}	$\overline{6}.56$
21.	513	1.95	5.15×10^{-6}	$\overline{6}.71$
22.	523	1.91	7.45×10^{-6}	$\overline{6}.87$

TABLE - 2.24

Electrical conductivity of $K_2O.Nb_2O_5$ at different temperatures

S.N.	Temperature (°K) (T)	$\frac{1}{T} \times 10^3 (°K^{-1})$	σ (Ohm^{-1} cm^{-1})	Log σ(Ohm^{-1}cm^{-1})
1.	313	3.20	3.12×10^{-10}	$\overline{10}.49$
2.	323	3.10	3.12×10^{-10}	$\overline{10}.49$
3.	333	3.00	3.12×10^{-10}	$\overline{10}.49$
4.	343	2.92	6.79×10^{-10}	$\overline{10}.83$
5.	353	2.83	1.85×10^{-9}	$\bar{9}.27$
6.	363	2.76	5.27×10^{-9}	$\bar{9}.72$
7.	373	2.68	8.44×10^{-9}	$\bar{9}.93$
8.	383	2.61	2.41×10^{-8}	$\bar{8}.38$
9.	393	2.54	4.32×10^{-8}	$\bar{8}.64$
10.	403	2.48	7.84×10^{-8}	$\bar{8}.89$
11.	413	2.42	1.71×10^{-7}	$\bar{7}.23$
12.	423	2.36	3.82×10^{-7}	$\bar{7}.58$
13.	433	2.31	5.33×10^{-7}	$\bar{7}.77$
14.	443	2.26	7.99×10^{-7}	$\bar{7}.90$
15.	453	2.21	1.62×10^{-6}	$\bar{6}.21$
16.	463	2.16	2.05×10^{-6}	$\bar{6}.31$
17.	473	2.11	4.82×10^{-6}	$\bar{6}.68$
18.	483	2.07	5.51×10^{-6}	$\bar{6}.74$
19.	493	2.03	9.21×10^{-6}	$\bar{6}.96$
20.	503	1.99	1.97×10^{-5}	$\bar{5}.29$
21.	513	1.95	2.76×10^{-5}	$\bar{5}.44$
22.	523	1.91	4.82×10^{-5}	$\bar{5}.68$

TABLE - 2.25

Electrical conductivity of $CaO.2Nb_2O_5$ at different temperatures

S.N.	Tempera-ture (^oK) (T)	$\frac{1}{T}x10^3(^oK^{-1})$	σ ($Ohm^{-1}cm^{-1}$)	Log σ ($Ohm^{-1}cm^{-1}$)
1.	313	3.20	6.16×10^{-13}	$\overline{13}.79$
2.	323	3.10	8.14×10^{-13}	$\overline{13}.91$
3.	333	3.00	1.05×10^{-12}	$\overline{12}.02$
4.	343	2.92	4.79×10^{-12}	$\overline{12}.68$
5.	353	2.83	1.95×10^{-11}	$\overline{11}.29$
6.	363	2.76	5.25×10^{-11}	$\overline{11}.72$
7.	373	2.68	8.71×10^{-11}	$\overline{11}.94$
8.	383	2.61	4.89×10^{-10}	$\overline{10}.69$
9.	393	2.54	1.38×10^{-9}	$\overline{9}.14$
10.	403	2.48	4.47×10^{-9}	$\overline{9}.65$
11.	413	2.42	8.51×10^{-9}	$\overline{9}.93$
12.	423	2.36	2.57×10^{-8}	$\overline{8}.41$
13.	433	2.31	6.31×10^{-8}	$\overline{8}.80$
14.	443	2.26	9.55×10^{-8}	$\overline{8}.98$
15.	453	2.21	2.51×10^{-7}	$\overline{7}.40$
16.	463	2.16	5.13×10^{-7}	$\overline{7}.71$
17.	473	2.11	1.20×10^{-6}	$\overline{6}.08$
18.	483	2.07	1.51×10^{-6}	$\overline{6}.18$
19.	493	2.03	1.78×10^{-6}	$\overline{6}.25$
20.	503	1.99	5.37×10^{-6}	$\overline{6}.73$
21.	513	1.95	6.61×10^{-6}	$\overline{6}.82$
22.	523	1.91	1.10×10^{-5}	$\overline{5}.04$

TABLE - 2.26

Electrical conductivity of $CaO.Nb_2O_5$ at different temperatures

S.N.	Temperatures (^oK) (T)	$\frac{1}{T}x10^3$ ($^oK^{-1}$)	σ ($Ohm^{-1}cm^{-1}$)	Log σ ($Ohm^{-1}cm^{-1}$)
1.	313	3.20	1.34×10^{-12}	$\overline{12}.13$
2.	323	3.10	1.45×10^{-12}	$\overline{12}.16$
3.	333	3.00	1.66×10^{-12}	$\overline{12}.22$
4.	343	2.92	2.19×10^{-12}	$\overline{12}.34$
5.	353	2.83	2.47×10^{-12}	$\overline{12}.39$
6.	363	2.76	7.28×10^{-12}	$\overline{12}.86$
7.	373	2.68	1.97×10^{-11}	$\overline{11}.29$
8.	383	2.61	7.11×10^{-11}	$\overline{11}.85$
9.	393	2.54	9.61×10^{-11}	$\overline{11}.98$
10.	403	2.48	2.15×10^{-10}	$\overline{10}.33$
11.	413	2.42	4.19×10^{-10}	$\overline{10}.62$
12.	423	2.36	8.53×10^{-10}	$\overline{10}.93$
13.	433	2.31	2.25×10^{-9}	$\overline{9}.35$
14.	443	2.26	5.63×10^{-9}	$\overline{9}.75$
15.	453	2.21	7.94×10^{-9}	$\overline{9}.90$
16.	463	2.16	1.21×10^{-8}	$\overline{8}.08$
17.	473	2.11	2.00×10^{-8}	$\overline{8}.30$
18.	483	2.07	3.73×10^{-8}	$\overline{8}.57$
19.	493	2.03	6.95×10^{-8}	$\overline{8}.84$
20.	503	1.99	1.15×10^{-7}	$\overline{7}.06$
21.	513	1.95	1.56×10^{-7}	$\overline{7}.19$
22.	523	1.91	3.04×10^{-7}	$\overline{7}.48$

TABLE - 2.27

Electrical conductivity of $SrO.2Nb_2O_5$ at different temperatures

S.N.	Temperature (°K) (T)	$\frac{1}{T}x10^3(^oK^{-1})$	$\sigma(Ohm^{-1}cm^{-1})$	$Log\,\sigma(Ohm^{-1}cm^{-1})$
1.	313	3.20	8.91×10^{-14}	$\overline{14}.95$
2.	323	3.10	8.91×10^{-14}	$\overline{14}.95$
3.	333	3.00	1.05×10^{-13}	$\overline{13}.02$
4.	343	2.92	2.40×10^{-13}	$\overline{13}.38$
5.	353	2.83	6.76×10^{-13}	$\overline{13}.83$
6.	363	2.76	2.57×10^{-12}	$\overline{12}.41$
7.	373	2.68	1.55×10^{-11}	$\overline{11}.19$
8.	383	2.61	4.37×10^{-11}	$\overline{11}.64$
9.	393	2.54	1.02×10^{-10}	$\overline{10}.01$
10.	403	2.48	1.74×10^{-10}	$\overline{10}.24$
11.	413	2.42	3.63×10^{-10}	$\overline{10}.56$
12.	423	2.36	7.59×10^{-10}	$\overline{10}.88$
13.	433	2.31	1.62×10^{-9}	$\overline{9}.21$
14.	443	2.26	3.39×10^{-9}	$\overline{9}.53$
15.	453	2.21	5.25×10^{-9}	$\overline{9}.72$
16.	463	2.16	1.32×10^{-8}	$\overline{8}.12$
17.	473	2.11	2.95×10^{-8}	$\overline{8}.47$
18.	483	2.07	5.37×10^{-8}	$\overline{8}.73$
19.	493	2.03	1.10×10^{-7}	$\overline{7}.04$
20.	503	1.99	2.24×10^{-7}	$\overline{7}.35$
21.	513	1.95	3.31×10^{-7}	$\overline{7}.52$
22.	523	1.91	4.89×10^{-7}	$\overline{7}.69$

TABLE - 2.28

Electrical conductivity of $SrO.Nb_2O_5$ at different temperatures

S.N.	Temperature(^oK) (T)	$\frac{1}{T} \times 10^3 (^oK^{-1})$	$\sigma (Ohm^{-1}cm^{-1})$	$Log\, \sigma (Ohm^{-1}cm^{-1})$
1.	313	3.20	1.05×10^{-12}	$\overline{12}.02$
2.	323	3.10	1.05×10^{-12}	$\overline{12}.02$
3.	333	3.00	1.05×10^{-12}	$\overline{12}.02$
4.	343	2.92	1.49×10^{-12}	$\overline{12}.17$
5.	353	2.83	5.27×10^{-12}	$\overline{12}.72$
6.	363	2.76	2.10×10^{-11}	$\overline{11}.32$
7.	373	2.68	3.49×10^{-11}	$\overline{11}.54$
8.	383	2.61	1.07×10^{-10}	$\overline{10}.03$
9.	393	2.54	2.90×10^{-10}	$\overline{10}.46$
10.	403	2.48	6.97×10^{-10}	$\overline{10}.84$
11.	413	2.42	1.33×10^{-9}	$\overline{9}.12$
12.	423	2.36	2.26×10^{-9}	$\overline{9}.35$
13.	433	2.31	4.82×10^{-9}	$\overline{9}.68$
14.	443	2.26	8.57×10^{-9}	$\overline{9}.93$
15.	453	2.21	2.06×10^{-8}	$\overline{8}.31$
16.	463	2.16	4.91×10^{-8}	$\overline{8}.69$
17.	473	2.11	1.16×10^{-7}	$\overline{7}.06$
18.	483	2.07	1.71×10^{-7}	$\overline{7}.23$
19.	493	2.03	4.22×10^{-7}	$\overline{7}.62$
20.	503	1.99	6.37×10^{-7}	$\overline{7}.80$
21.	513	1.95	1.30×10^{-6}	$\overline{6}.11$
22.	523	1.91	2.36×10^{-6}	$\overline{6}.37$

TABLE - 2.29

Electrical conductivity of $2SrO.Nb_2O_5$ at different temperatures

S.N.	Temperature ($^oK^{-1}$) (T)	$\frac{1}{T}$x10^3($^oK^{-1}$)	σ(Ohm^{-1}cm^{-1})	Log σ (Ohm^{-1}cm^{-1})
1.	313	3.20	3.24×10^{-12}	$\overline{12}.51$
2.	323	3.10	3.24×10^{-12}	$\overline{12}.51$
3.	333	3.00	7.62×10^{-12}	$\overline{12}.88$
4.	343	2.92	1.83×10^{-11}	$\overline{11}.26$
5.	353	2.83	5.52×10^{-11}	$\overline{11}.74$
6.	363	2.76	1.42×10^{-10}	$\overline{10}.15$
7.	373	2.68	6.50×10^{-10}	$\overline{10}.81$
8.	383	2.61	2.90×10^{-9}	$\bar{9}.46$
9.	393	2.54	3.92×10^{-9}	$\bar{9}.59$
10.	403	2.48	1.59×10^{-8}	$\bar{8}.20$
11.	413	2.42	4.49×10^{-8}	$\bar{8}.65$
12.	423	2.36	8.79×10^{-8}	$\bar{8}.94$
13.	433	2.31	2.58×10^{-7}	$\bar{7}.41$
14.	443	2.26	4.19×10^{-7}	$\bar{7}.62$
15.	453	2.21	6.34×10^{-7}	$\bar{7}.80$
16.	463	2.16	1.04×10^{-6}	$\bar{6}.02$
17.	473	2.11	1.64×10^{-6}	$\bar{6}.21$
18.	483	2.07	2.98×10^{-6}	$\bar{6}.47$
19.	493	2.03	7.11×10^{-6}	$\bar{6}.85$
20.	503	1.99	9.88×10^{-6}	$\bar{6}.99$
21.	513	1.95	1.33×10^{-5}	$\bar{5}.12$
22.	523	1.91	1.70×10^{-5}	$\bar{5}.23$

TABLE - 2.29(b)

Electrical Conductivity of $2SrO.Nb_2O_5$ (formed at 800°C, 4:1) at different Temperatures

S.N.	Temperature (°K) (T)	$\frac{1}{T} \times 10^3 (°K^{-1})$	σ $(Ohm^{-1}Cm^{-1})$	Log σ $(Ohm^{-1}Cm^{-1})$
1.	313	3.20	2.82×10^{-12}	$\overline{12}.45$
2.	323	3.10	3.18×10^{-12}	$\overline{12}.50$
3.	333	3.00	7.60×10^{-12}	$\overline{12}.88$
4.	343	2.92	1.42×10^{-11}	$\overline{11}.15$
5.	353	2.83	4.47×10^{-11}	$\overline{11}.65$
6.	363	2.76	1.26×10^{-10}	$\overline{10}.10$
7.	373	2.68	5.02×10^{-10}	$\overline{10}.70$
8.	383	2.61	2.52×10^{-9}	$\overline{9}.40$
9.	393	2.54	7.96×10^{-9}	$\overline{9}.90$
10.	403	2.48	1.42×10^{-8}	$\overline{8}.15$
11.	413	2.42	4.08×10^{-8}	$\overline{8}.61$
12.	423	2.36	8.32×10^{-8}	$\overline{8}.92$
13.	433	2.31	2.52×10^{-7}	$\overline{7}.40$
14.	443	2.26	3.57×10^{-7}	$\overline{7}.55$
15.	453	2.21	6.31×10^{-7}	$\overline{7}.80$
16.	463	2.16	1.00×10^{-6}	$\overline{6}.00$
17.	473	2.11	1.59×10^{-6}	$\overline{6}.20$
18.	483	2.07	2.57×10^{-6}	$\overline{6}.41$
19.	493	2.03	6.45×10^{-6}	$\overline{6}.81$
20.	503	1.99	9.57×10^{-6}	$\overline{6}.98$
21.	513	1.95	1.18×10^{-5}	$\overline{5}.07$
22.	523	1.91	1.45×10^{-5}	$\overline{5}.16$

TABLE - 2.30

Electrical conductivity of $3SrO.Nb_2O_5$ at different Temperatures.

S.N.	Temperature ($^{o}K^{-1}$) (T)	$\frac{1}{T} \times 10^3$ ($^{o}K^{-1}$)	σ ($Ohm^{-1}cm^{-1}$)	Log σ ($Ohm^{-1}cm^{-1}$)
1.	313	3.20	5.50×10^{-12}	$\overline{12}.74$
2.	323	3.10	5.50×10^{-12}	$\overline{12}.74$
3.	333	3.00	4.36×10^{-11}	$\overline{11}.64$
4.	343	2.92	1.82×10^{-10}	$\overline{10}.26$
5.	353	2.83	2.95×10^{-10}	$\overline{10}.47$
6.	363	2.76	2.40×10^{-9}	$\overline{9}.38$
7.	373	2.68	3.98×10^{-9}	$\overline{9}.60$
8.	383	2.61	1.29×10^{-8}	$\overline{8}.11$
9.	393	2.54	1.81×10^{-8}	$\overline{8}.26$
10.	403	2.48	2.63×10^{-8}	$\overline{8}.42$
11.	413	2.42	7.08×10^{-8}	$\overline{8}.85$
12.	423	2.36	1.95×10^{-7}	$\overline{7}.29$
13.	433	2.31	4.78×10^{-7}	$\overline{7}.68$
14.	443	2.26	6.92×10^{-7}	$\overline{7}.84$
15.	453	2.21	1.38×10^{-6}	$\overline{6}.14$
16.	463	2.16	2.51×10^{-6}	$\overline{6}.40$
17.	473	2.11	5.37×10^{-6}	$\overline{6}.73$
18.	483	2.07	6.91×10^{-6}	$\overline{6}.84$
19.	493	2.03	9.55×10^{-6}	$\overline{6}.98$
20.	503	1.99	1.09×10^{-5}	$\overline{5}.04$
21.	513	1.95	1.82×10^{-5}	$\overline{5}.26$
22.	523	1.91	2.40×10^{-5}	$\overline{5}.38$

TABLE - 2.31

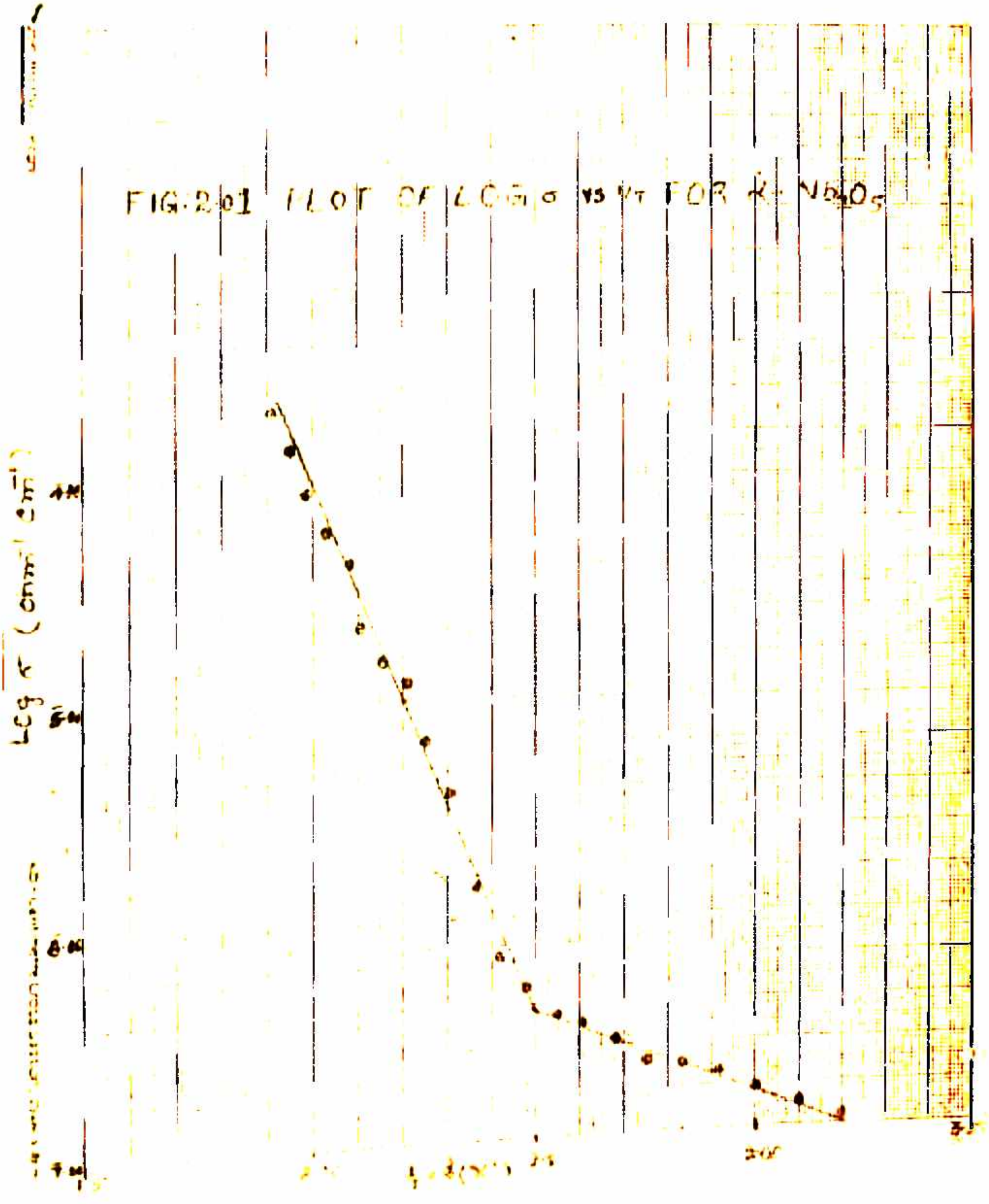
Electrical conductivity of $4SrO.Nb_2O_5$ at different Temperatures

S.N.	Temperature(^oK) (T)	$\frac{1}{T} \times 10^3 (^oK^{-1})$	σ ($Ohm^{-1}cm^{-1}$)	Logσ ($Ohm^{-1}cm^{-1}$)
1.	313	3.20	3.55×10^{-11}	$\overline{11}.55$
2.	323	3.10	9.81×10^{-11}	$\overline{11}.99$
3.	333	3.00	3.81×10^{-10}	$\overline{10}.58$
4.	343	2.92	1.13×10^{-9}	$\overline{9}.05$
5.	353	2.83	1.95×10^{-9}	$\overline{9}.29$
6.	363	2.76	4.07×10^{-9}	$\overline{9}.61$
7.	373	2.68	7.98×10^{-9}	$\overline{9}.90$
8.	383	2.61	2.65×10^{-8}	$\overline{8}.42$
9.	393	2.54	4.60×10^{-8}	$\overline{8}.66$
10.	403	2.48	1.26×10^{-7}	$\overline{7}.10$
11.	413	2.42	2.84×10^{-7}	$\overline{7}.45$
12.	423	2.36	5.16×10^{-7}	$\overline{7}.71$
13.	433	2.31	1.09×10^{-6}	$\overline{6}.04$
14.	443	2.26	1.38×10^{-6}	$\overline{6}.14$
15.	453	2.21	2.65×10^{-6}	$\overline{6}.42$
16.	463	2.16	4.40×10^{-6}	$\overline{6}.64$
17.	473	2.11	6.50×10^{-6}	$\overline{6}.81$
18.	483	2.07	7.98×10^{-6}	$\overline{6}.90$
19.	493	2.03	1.29×10^{-5}	$\overline{5}.11$
20.	503	1.99	2.83×10^{-5}	$\overline{5}.45$
21.	513	1.95	3.10×10^{-5}	$\overline{5}.49$
22.	523	1.91	4.59×10^{-5}	$\overline{5}.66$

TABLE - 2.31(b)

Electrical Conductivity of $4SrO.Nb_2O_5$ (formed at 900°C, 8:1) at different temperatures

S.N.	Temperature (°K) (T)	$\frac{1}{T} \times 10^3 (°K^{-1})$	σ $(Ohm^{-1}Cm^{-1})$	Log σ $(Ohm^{-1}Cm^{-1})$
1.	313	3.20	3.81×10^{-11}	$\overline{11}.58$
2.	323	3.10	8.93×10^{-11}	$\overline{11}.95$
3.	333	3.00	4.08×10^{-10}	$\overline{10}.61$
4.	343	2.92	8.94×10^{-10}	$\overline{10}.95$
5.	353	2.83	2.25×10^{-9}	$\bar{9}.35$
6.	363	2.76	3.99×10^{-9}	$\bar{9}.60$
7.	373	2.68	6.95×10^{-9}	$\bar{9}.84$
8.	383	2.61	2.25×10^{-8}	$\bar{8}.35$
9.	393	2.54	5.15×10^{-8}	$\bar{8}.71$
10.	403	2.48	8.35×10^{-8}	$\bar{8}.92$
11.	413	2.42	2.25×10^{-7}	$\bar{7}.35$
12.	423	2.36	4.08×10^{-7}	$\bar{7}.61$
13.	433	2.31	7.26×10^{-7}	$\bar{7}.86$
14.	443	2.26	8.93×10^{-7}	$\bar{7}.95$
15.	453	2.21	2.00×10^{-6}	$\bar{6}.30$
16.	463	2.16	4.48×10^{-6}	$\bar{6}.65$
17.	473	2.11	6.93×10^{-6}	$\bar{6}.84$
18.	483	2.07	8.95×10^{-6}	$\bar{6}.95$
19.	493	2.03	1.13×10^{-5}	$\bar{5}.05$
20.	503	1.99	2.52×10^{-5}	$\bar{5}.40$
21.	513	1.95	3.24×10^{-5}	$\bar{5}.51$
22.	523	1.91	4.18×10^{-5}	$\bar{5}.62$



FIG·2·01 PLOT OF LOG σ vs $1/T$ FOR K-Nb_2O_5

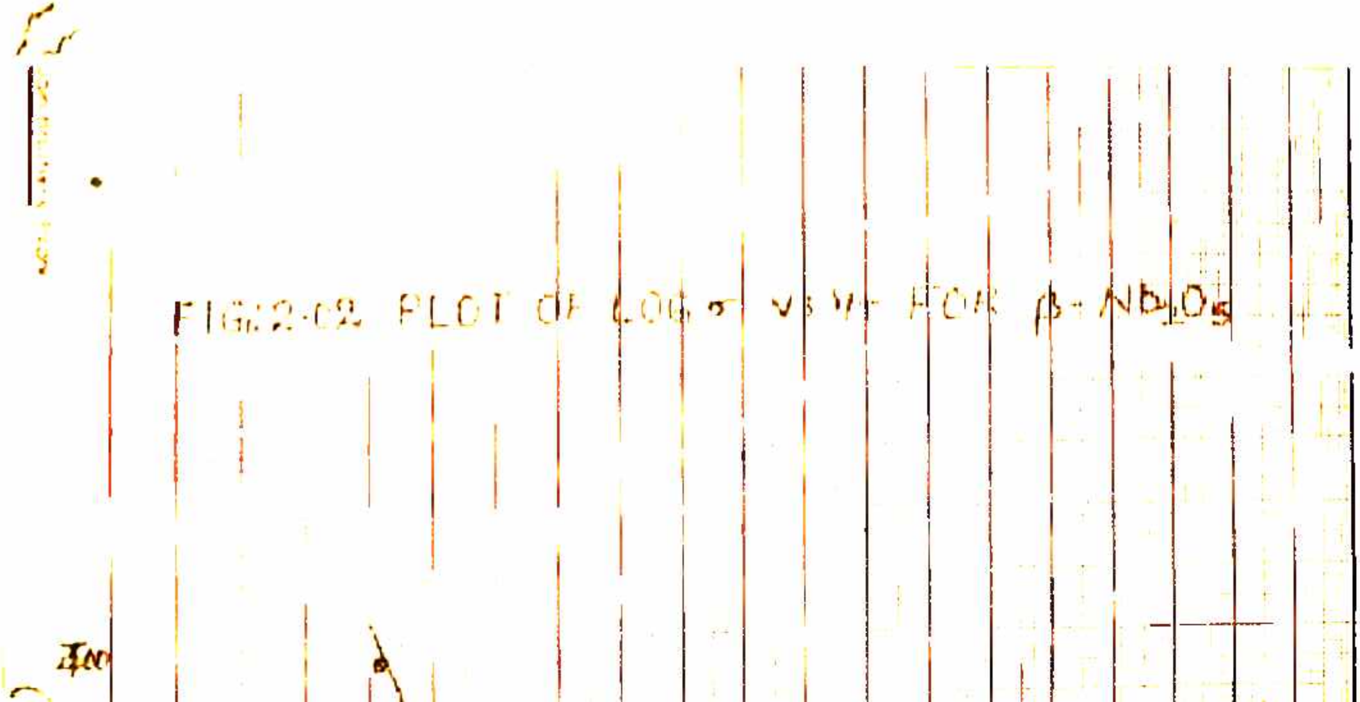
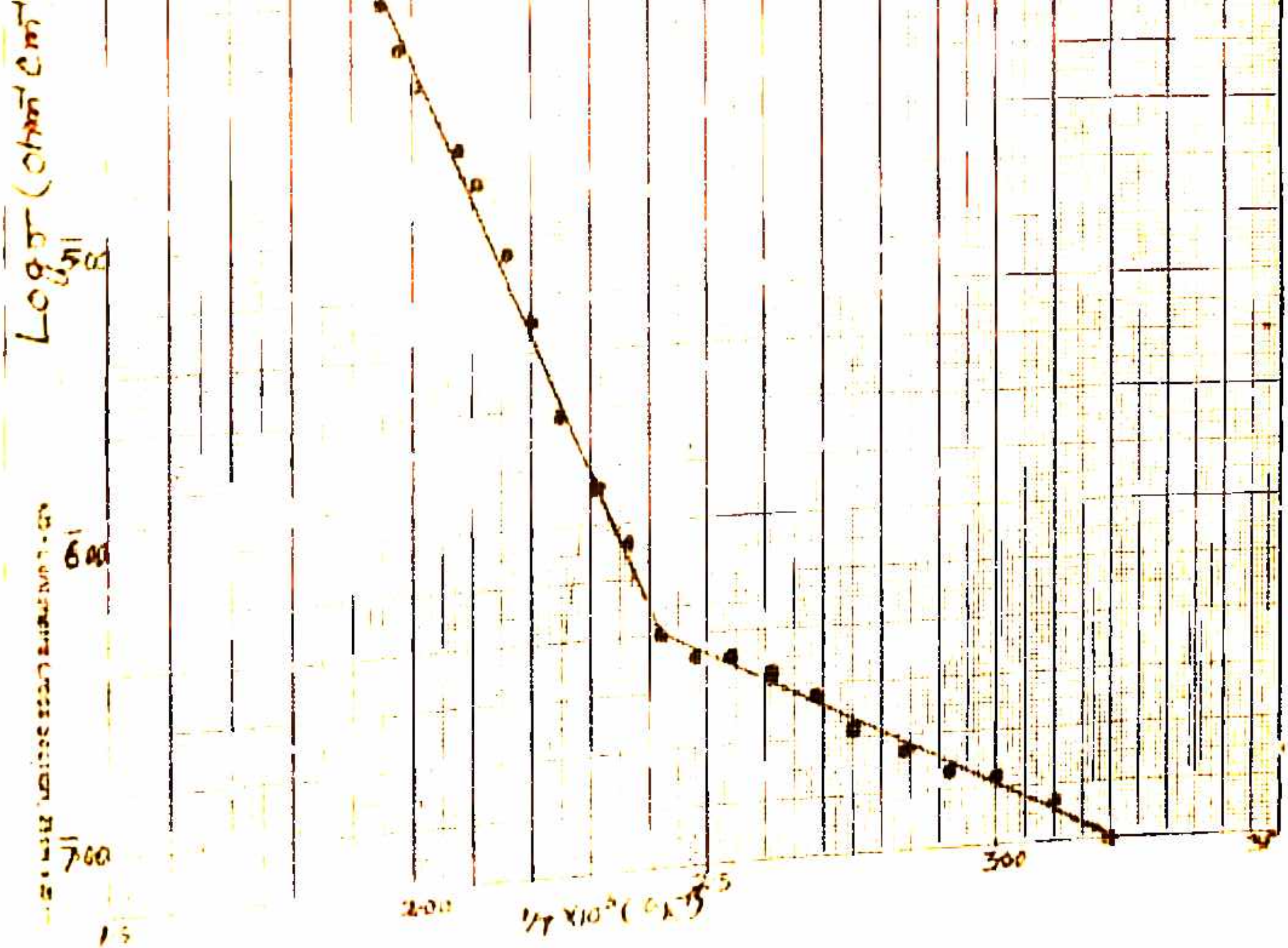
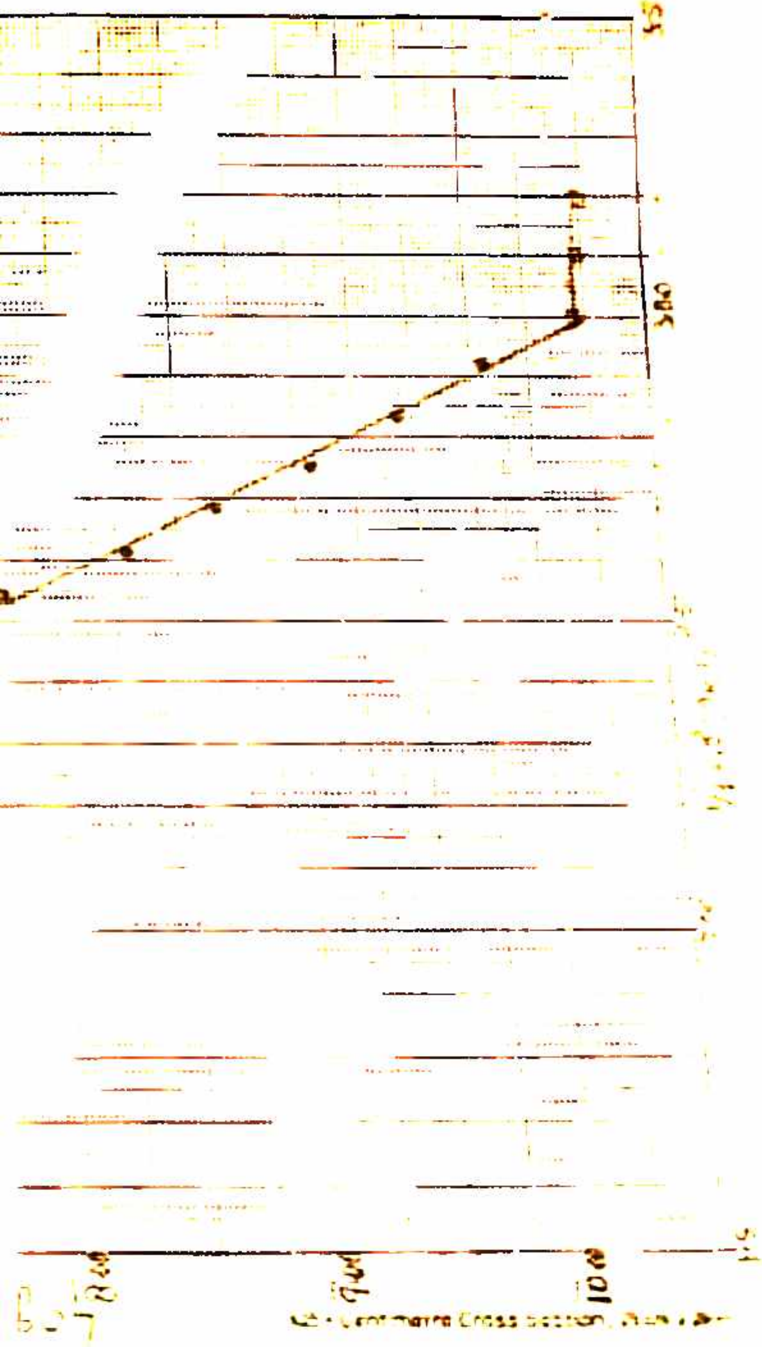
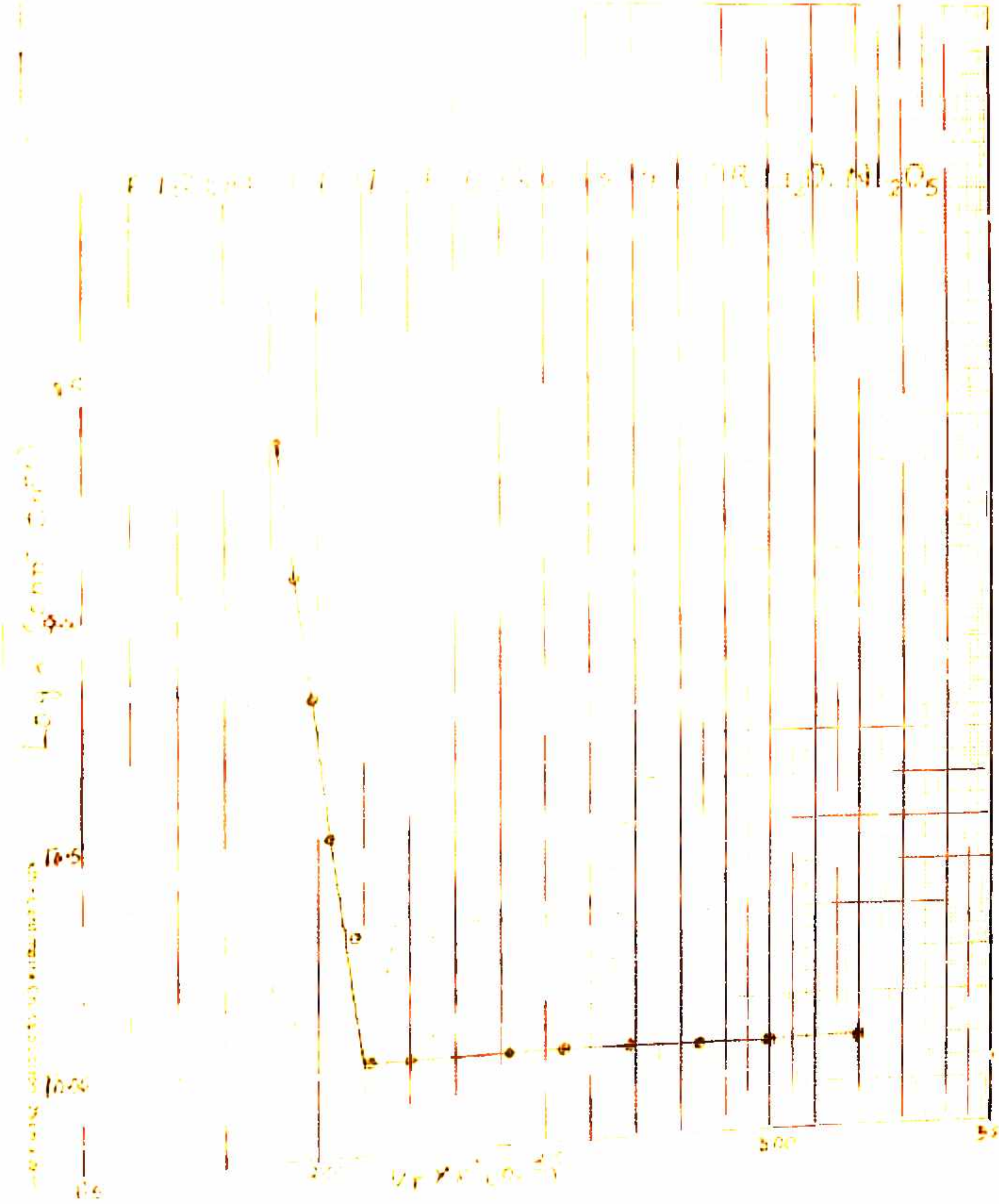


FIG. 2.02 PLOT OF LOG σ VS 1/T FOR β-Nb_2O_5

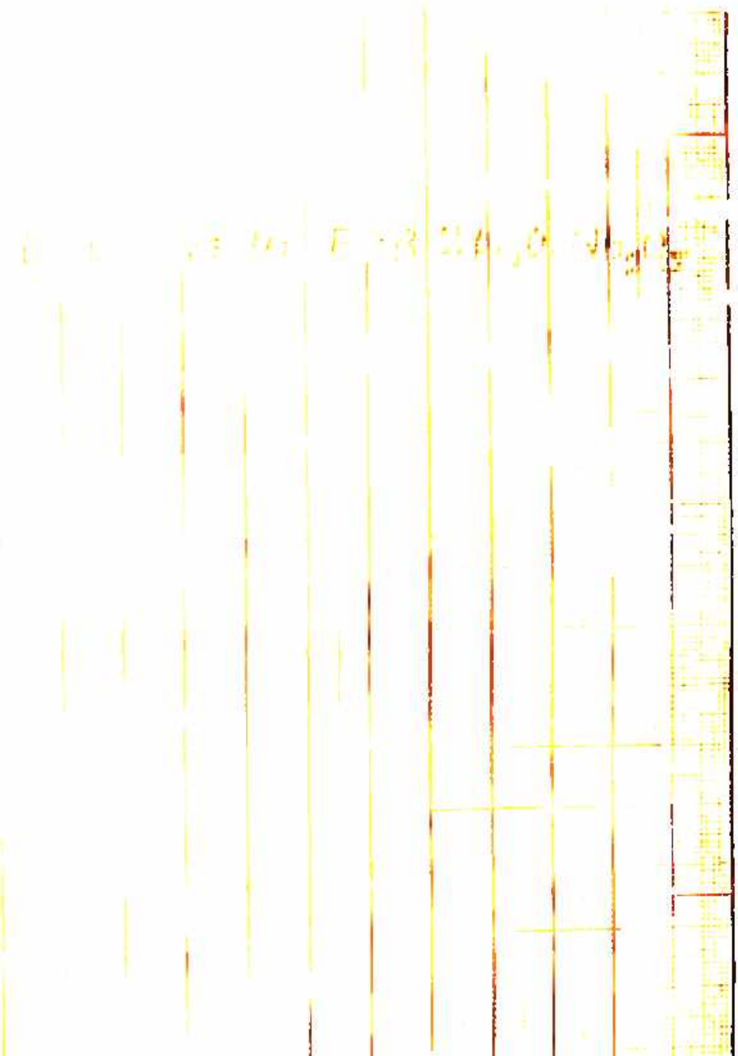

Log σ (ohm⁻¹ cm⁻¹)
5̄00
6̄00
7̄00
1.5
2.00
2.5
3.00
1/T x10³ (°K)⁻¹

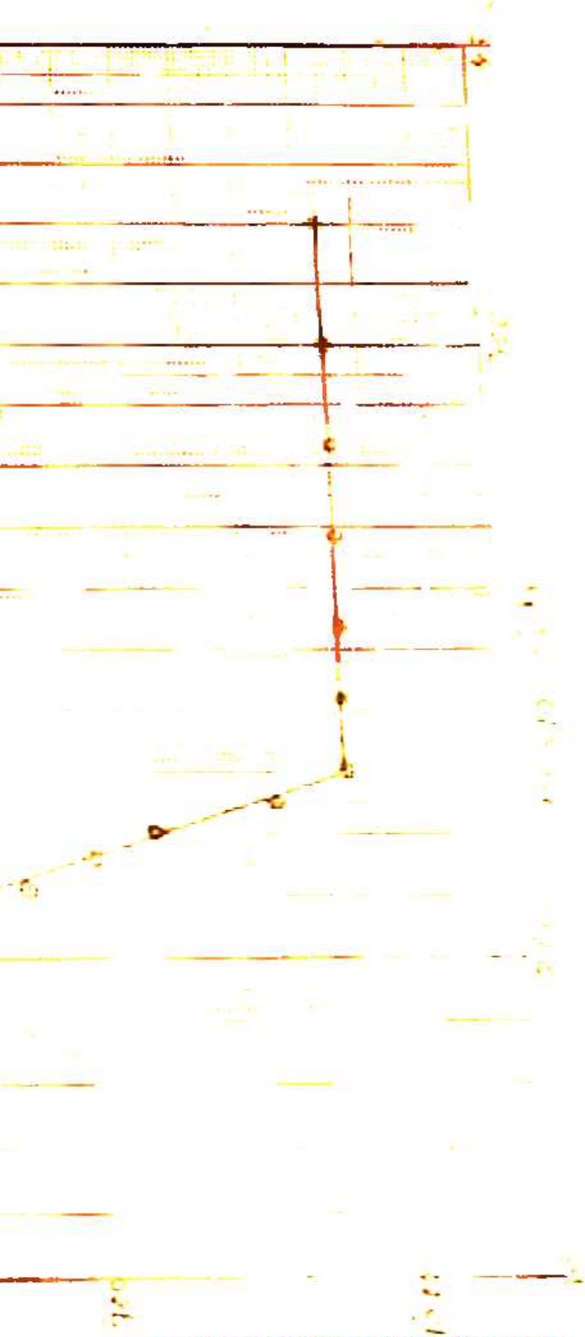

vs 1/T FOR
T- Nb_2O_5


55
380
45
840
940
1040
Centimetre Cross section

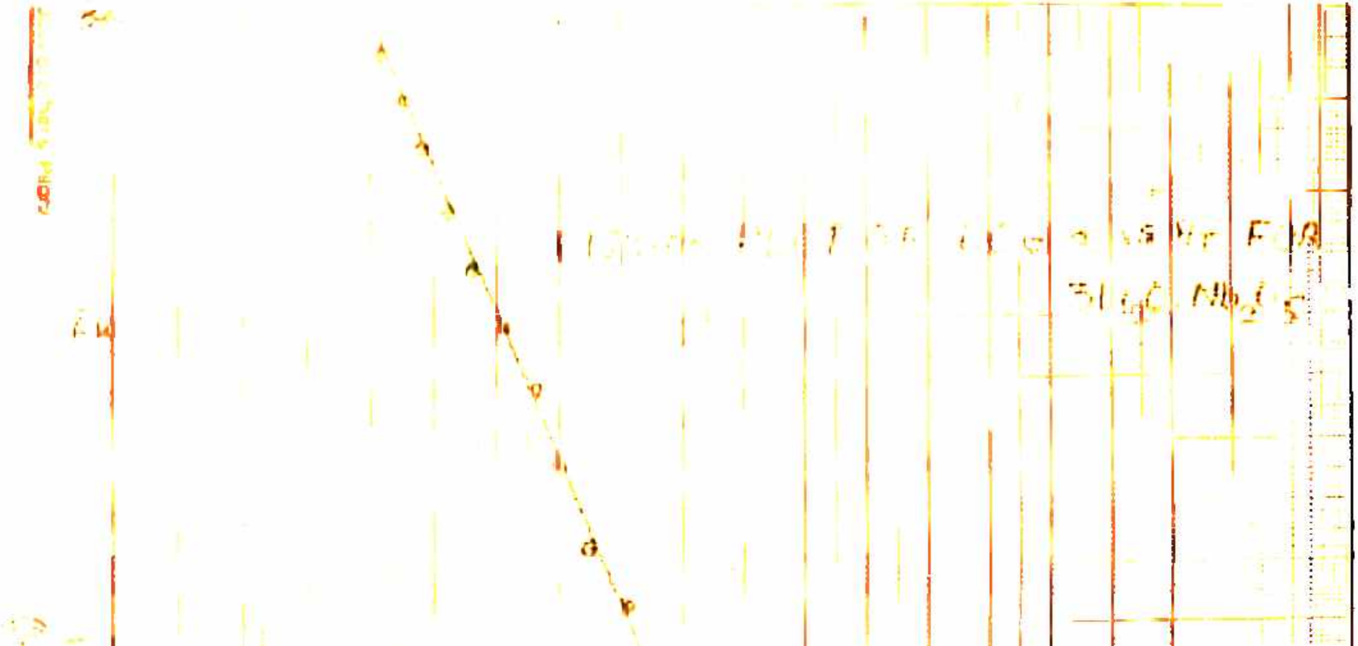


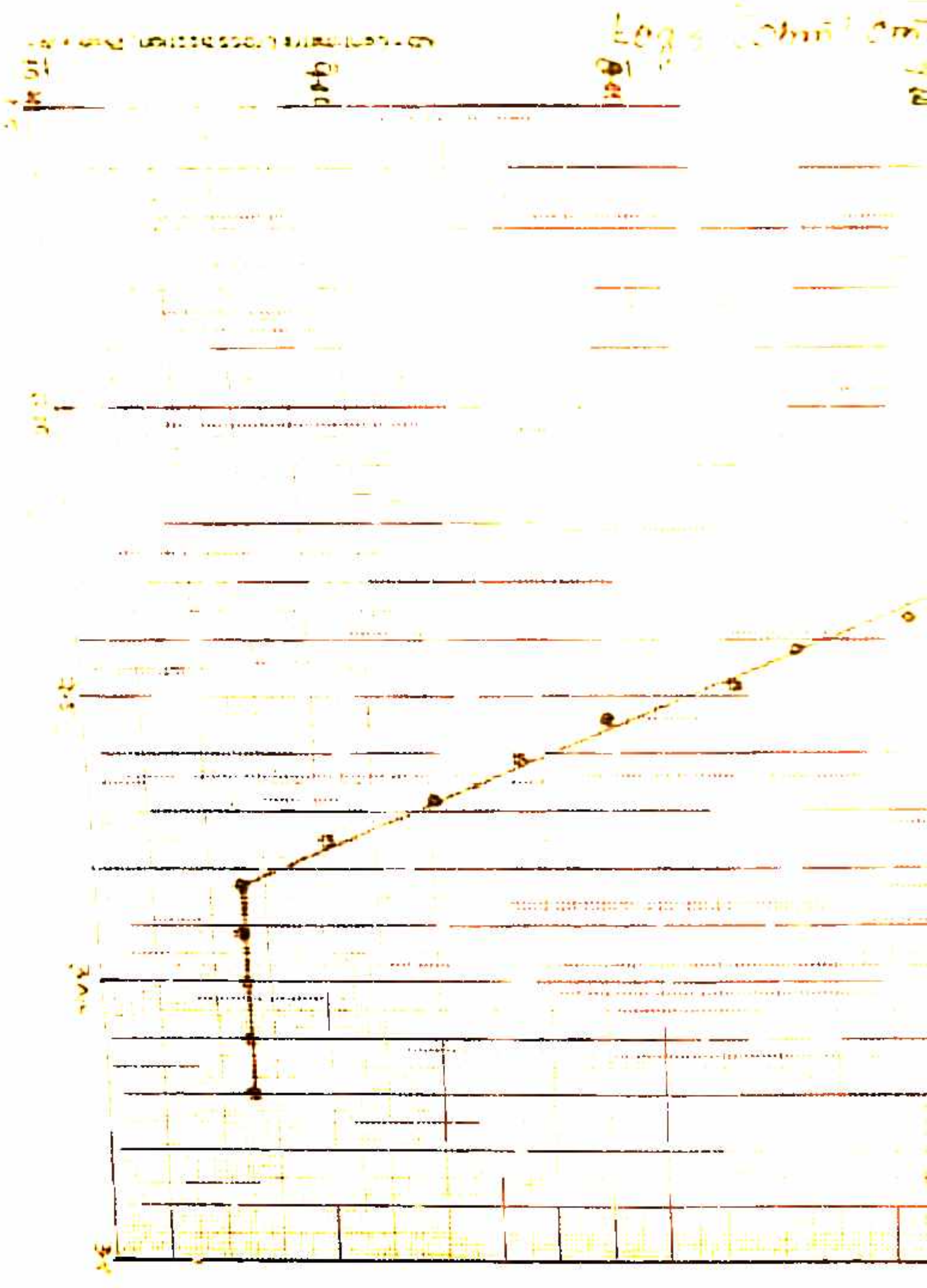
N_2O_5
Log
10·5
10·00
500





Centimetre Cross Section, 25cm x 28cm


vs Vr FOR


Log Ohm⁻¹ cm

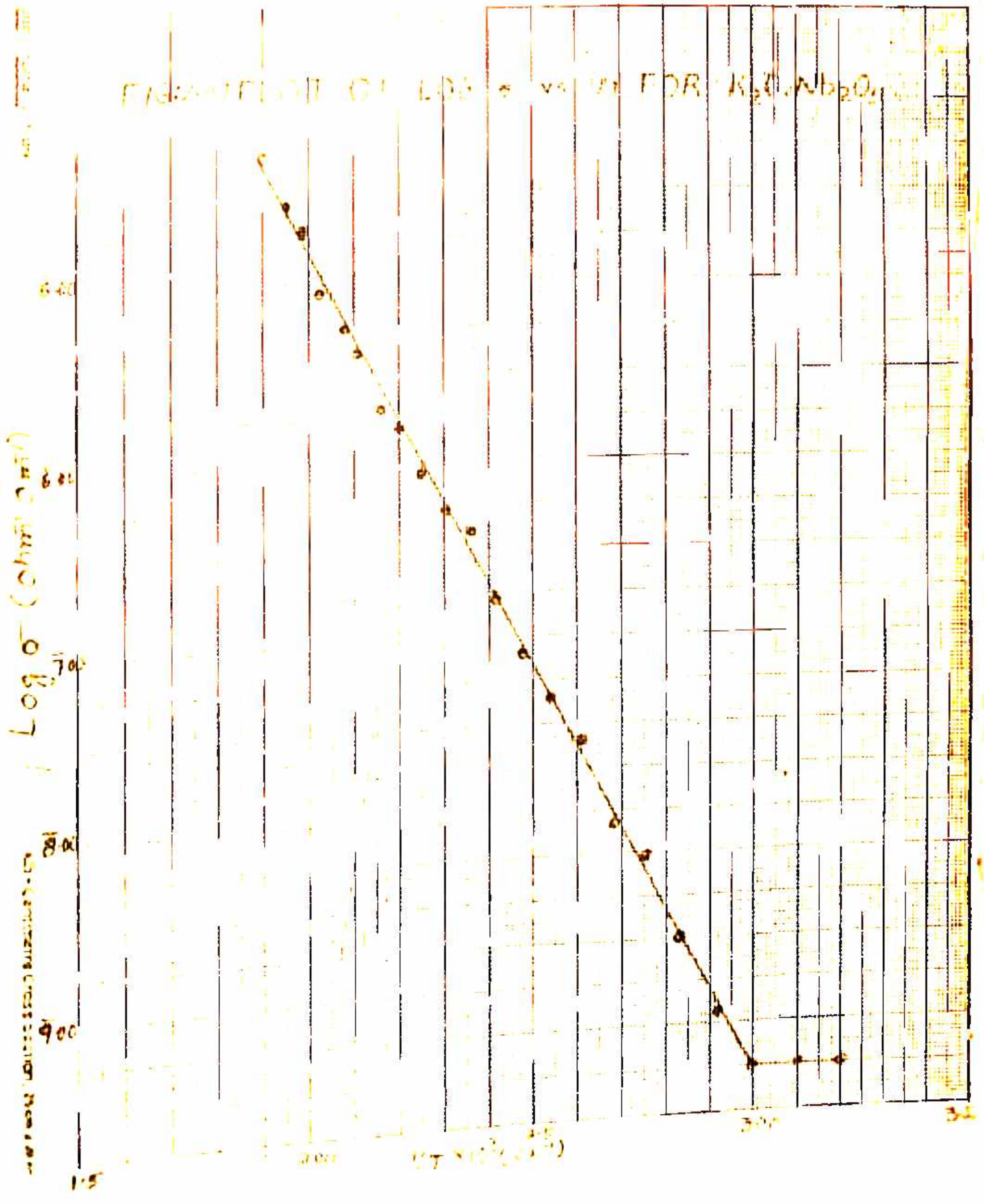


FIG. PLOT OF LOG σ vs 1/T FOR $K_2O.Nb_2O_5$

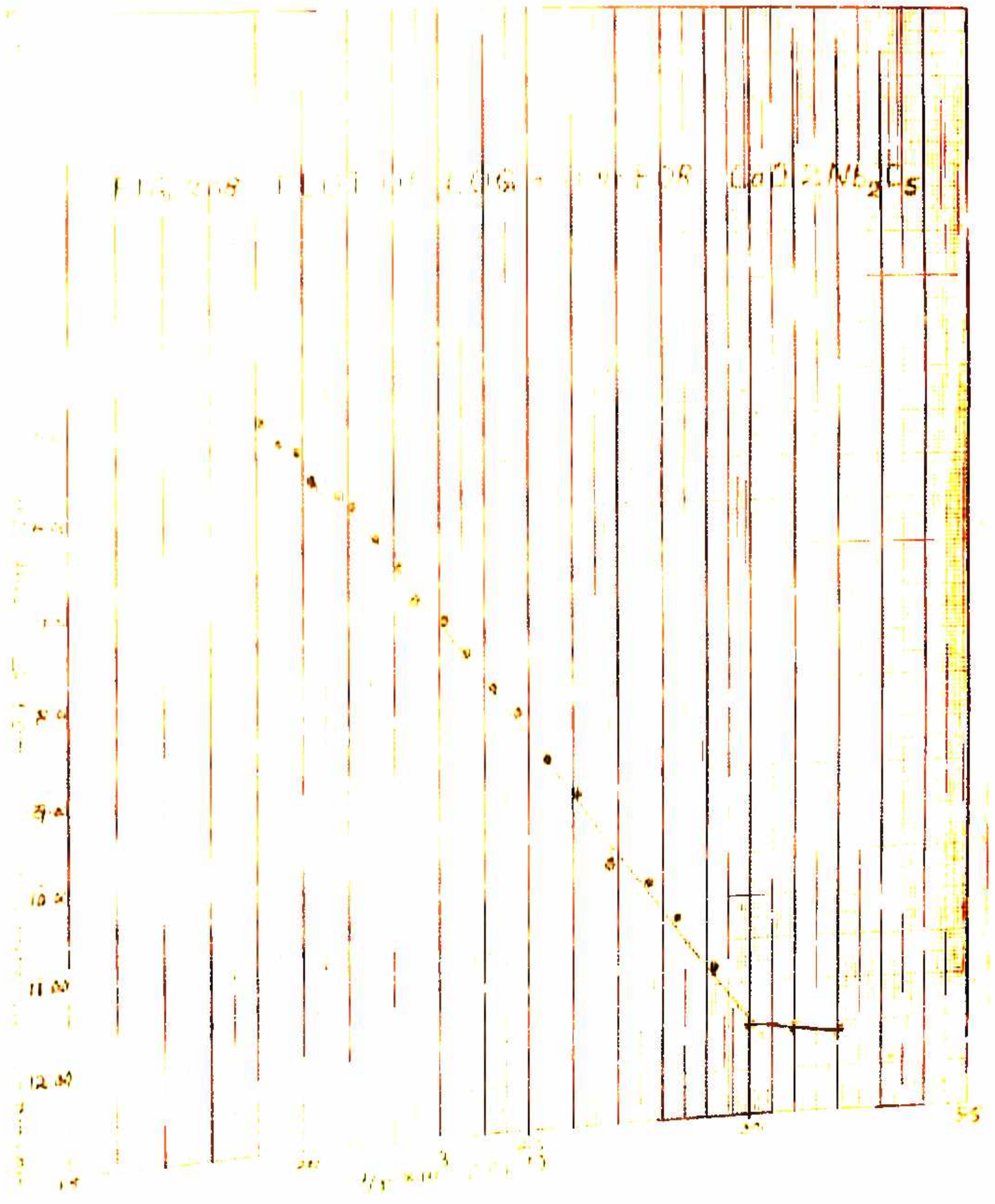


FIG. 2.8 PLOT OF LOG [illegible] FOR CaO:2Nb$_2$O$_5$

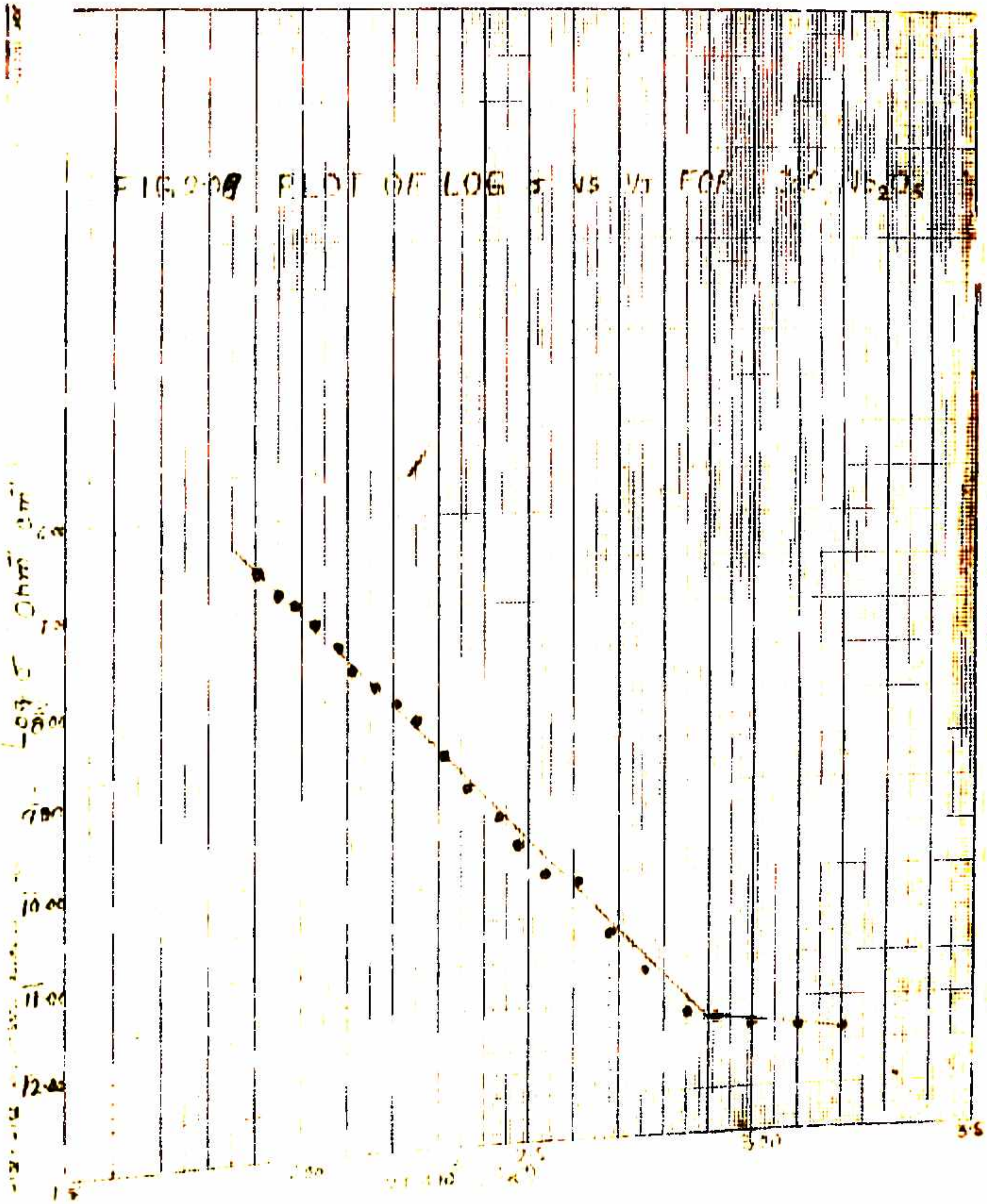


FIG.2.08 PLOT OF LOG σ VS 1/T FOR [illegible] V_2O_5

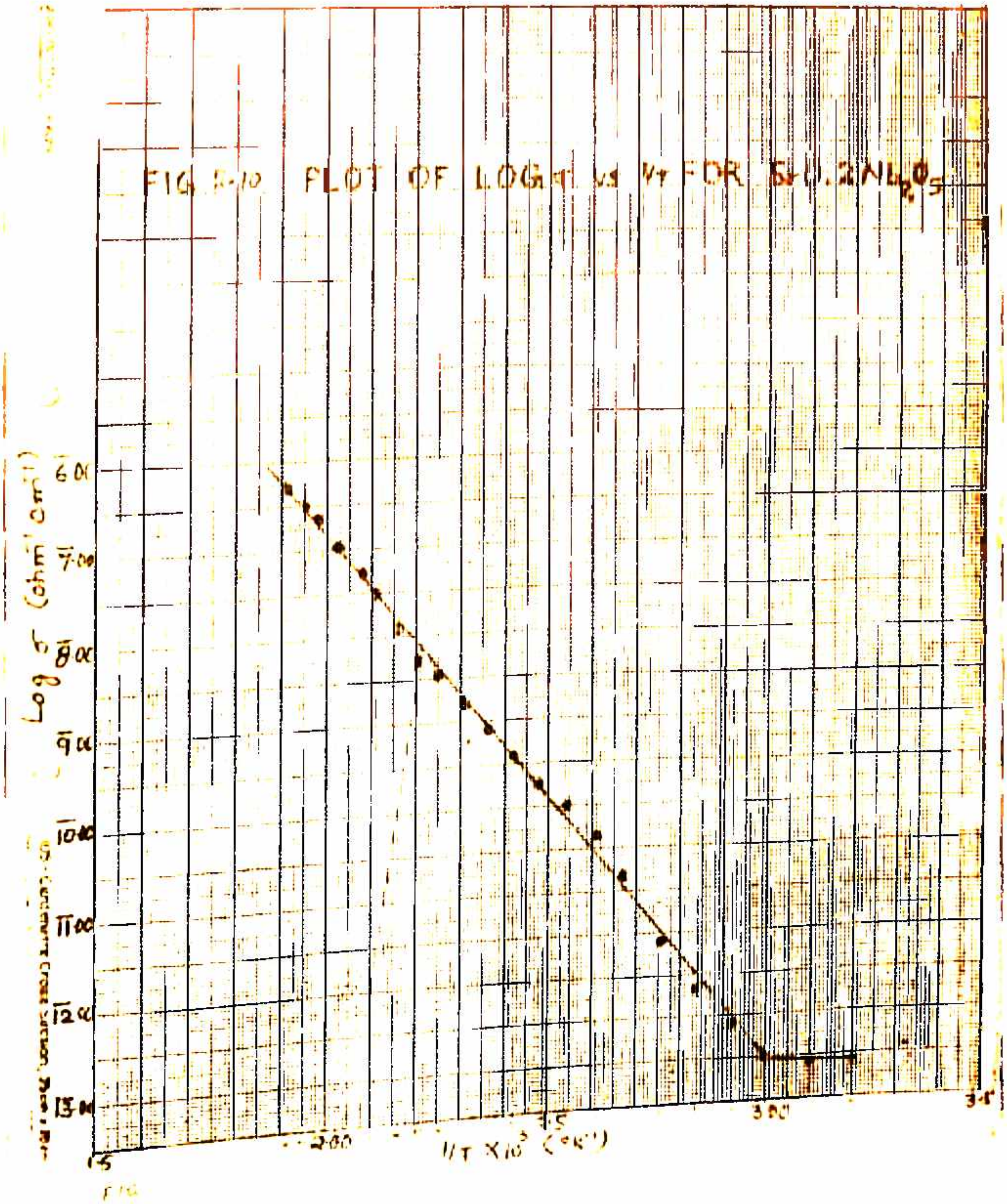


FIG 5-10 PLOT OF LOG σ vs 1/T FOR SrO.2Nb₂O₅

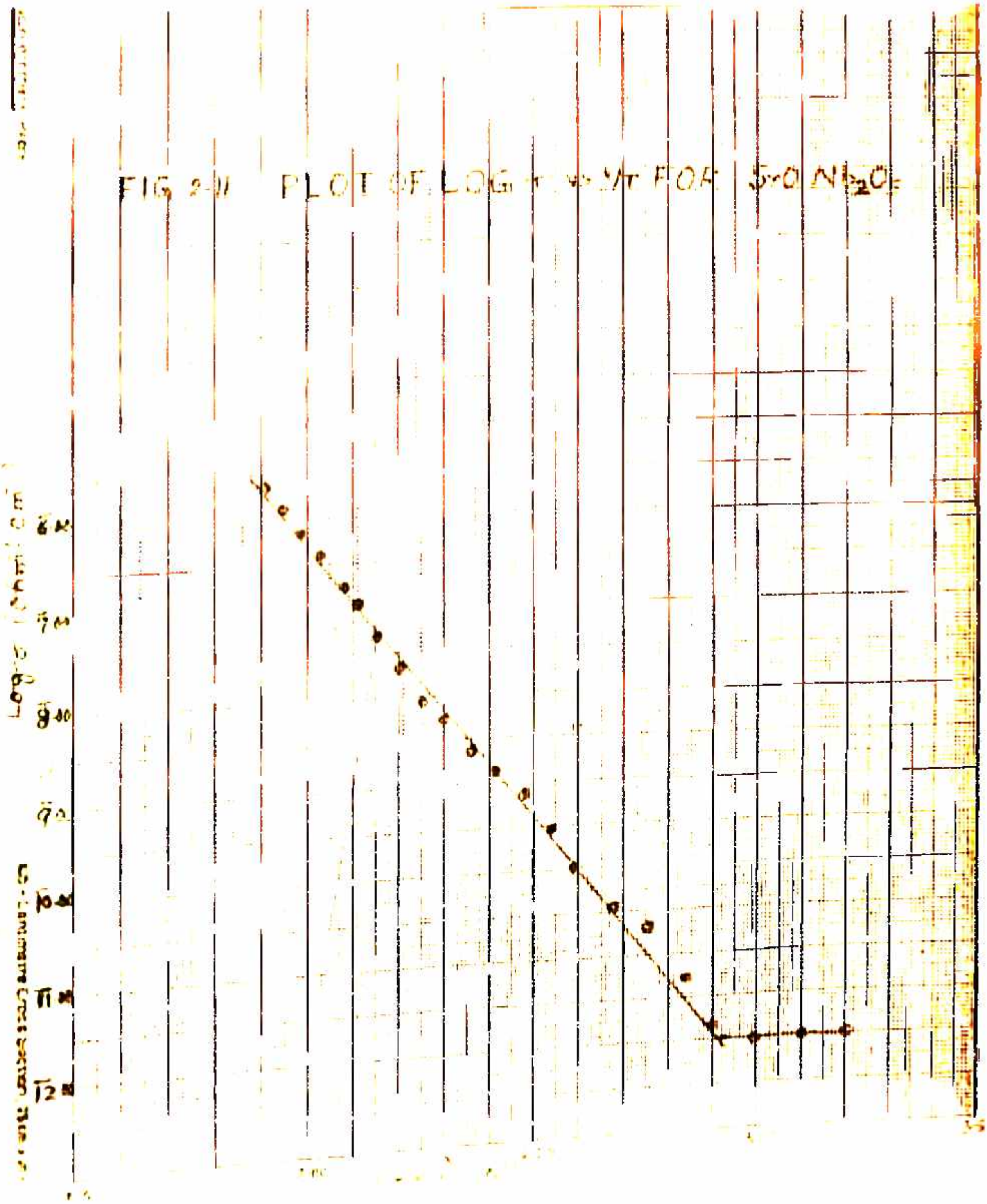
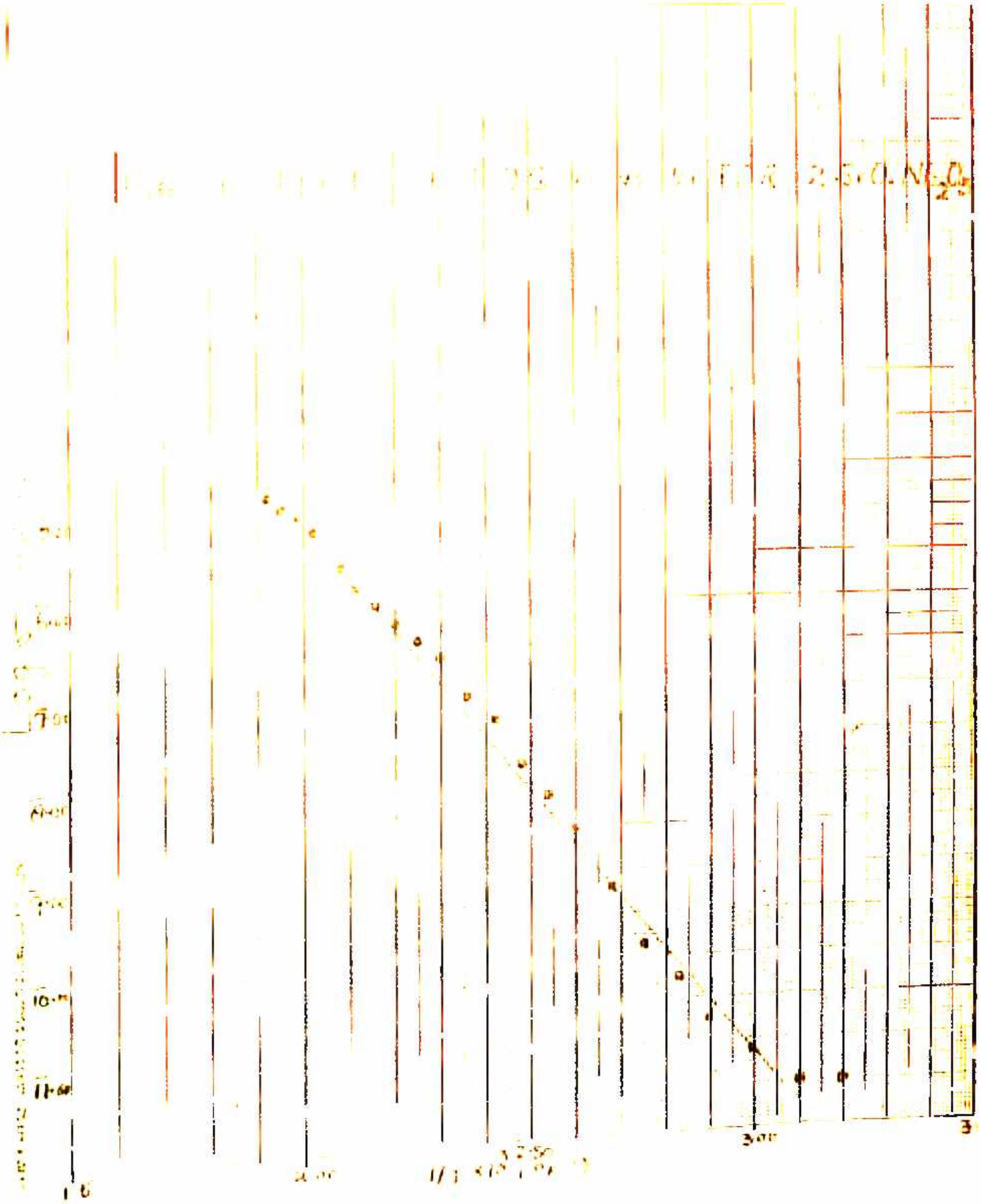


FIG 2-11 PLOT OF LOG σ vs 1/T FOR 5% Nb$_2$O$_5$


N2O5
7.00
8.00
10.00
11.00
1.6
2.00
1/T × 10^3
3.00
3

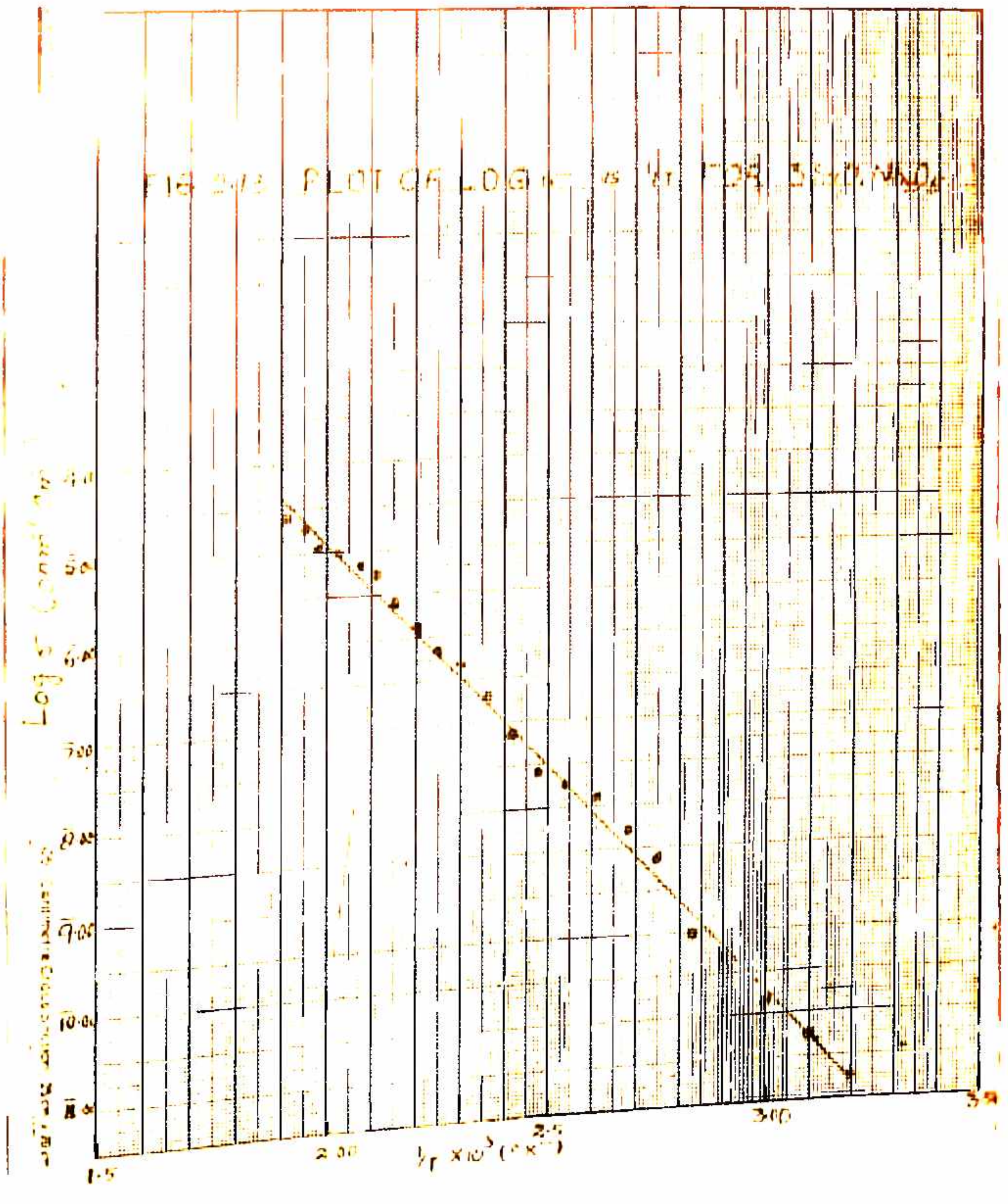


FIG 2·13 PLOT OF LOG σ vs 1/T FOR [illegible]

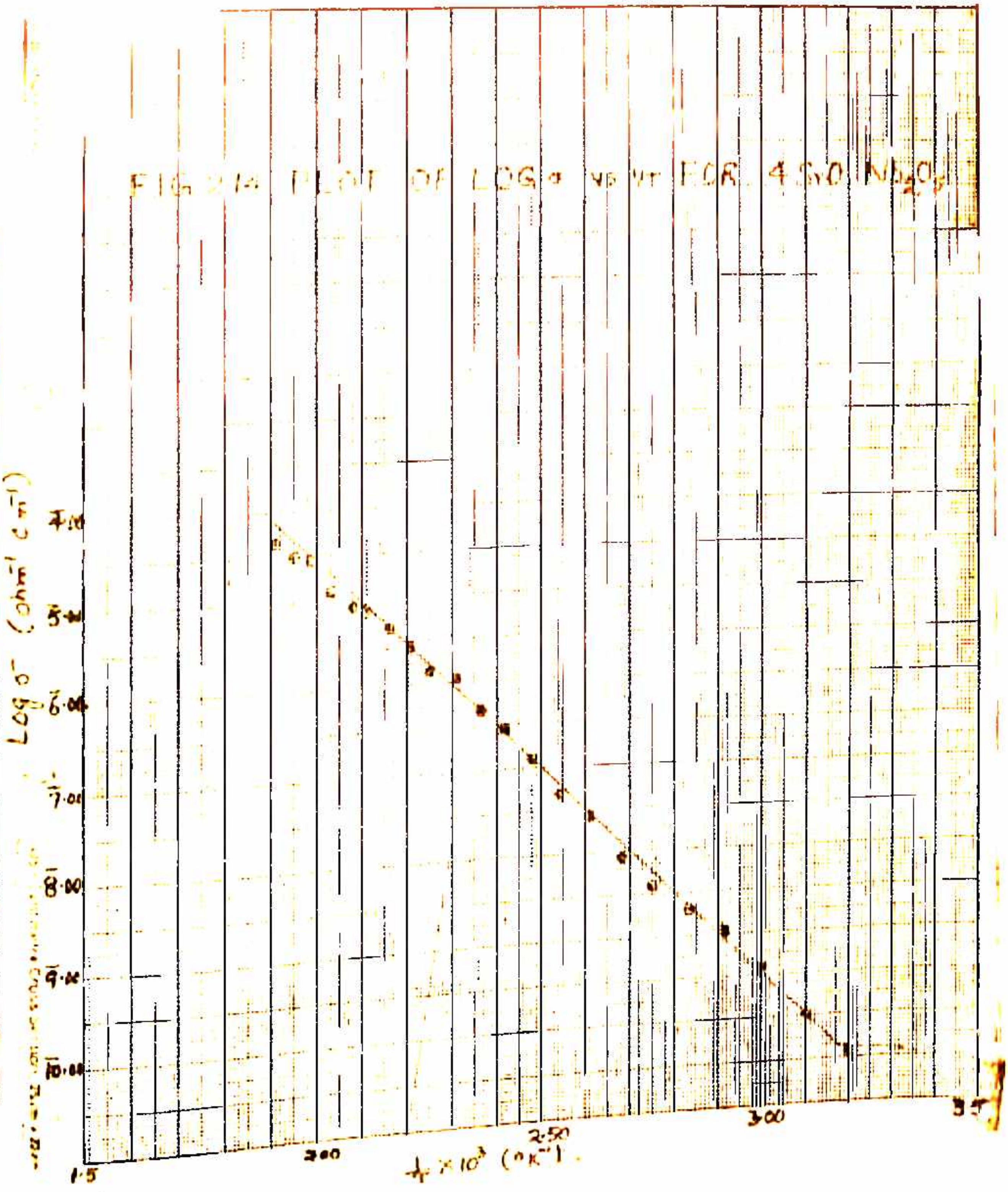
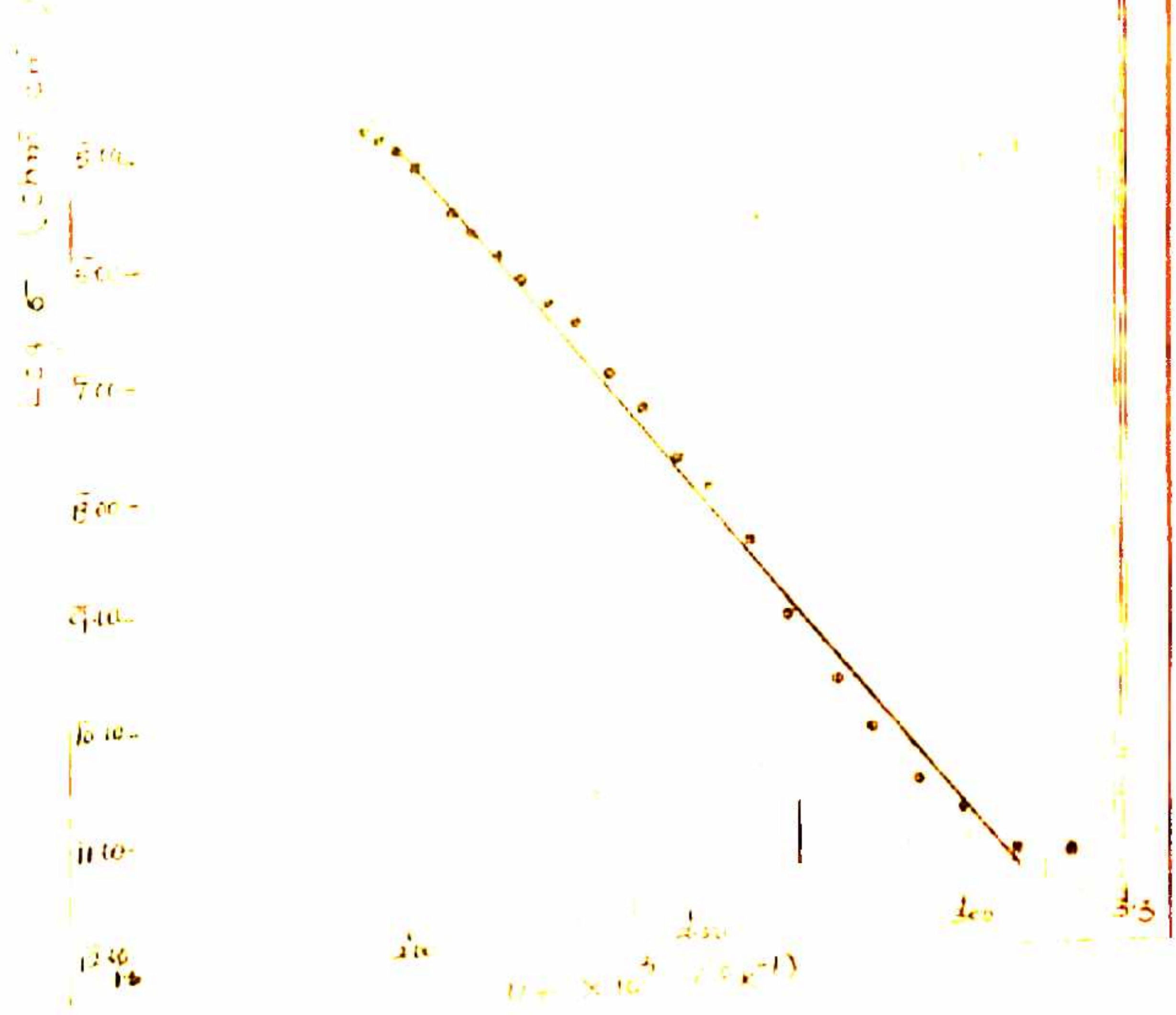


FIG 2.14 PLOT OF LOG σ vs 1/T FOR 4.50 Nd_2O_3

FIG 2 [illegible] FOR 23.0 Nb_2O_5
(FORMED AT [illegible]°C, 1:4)



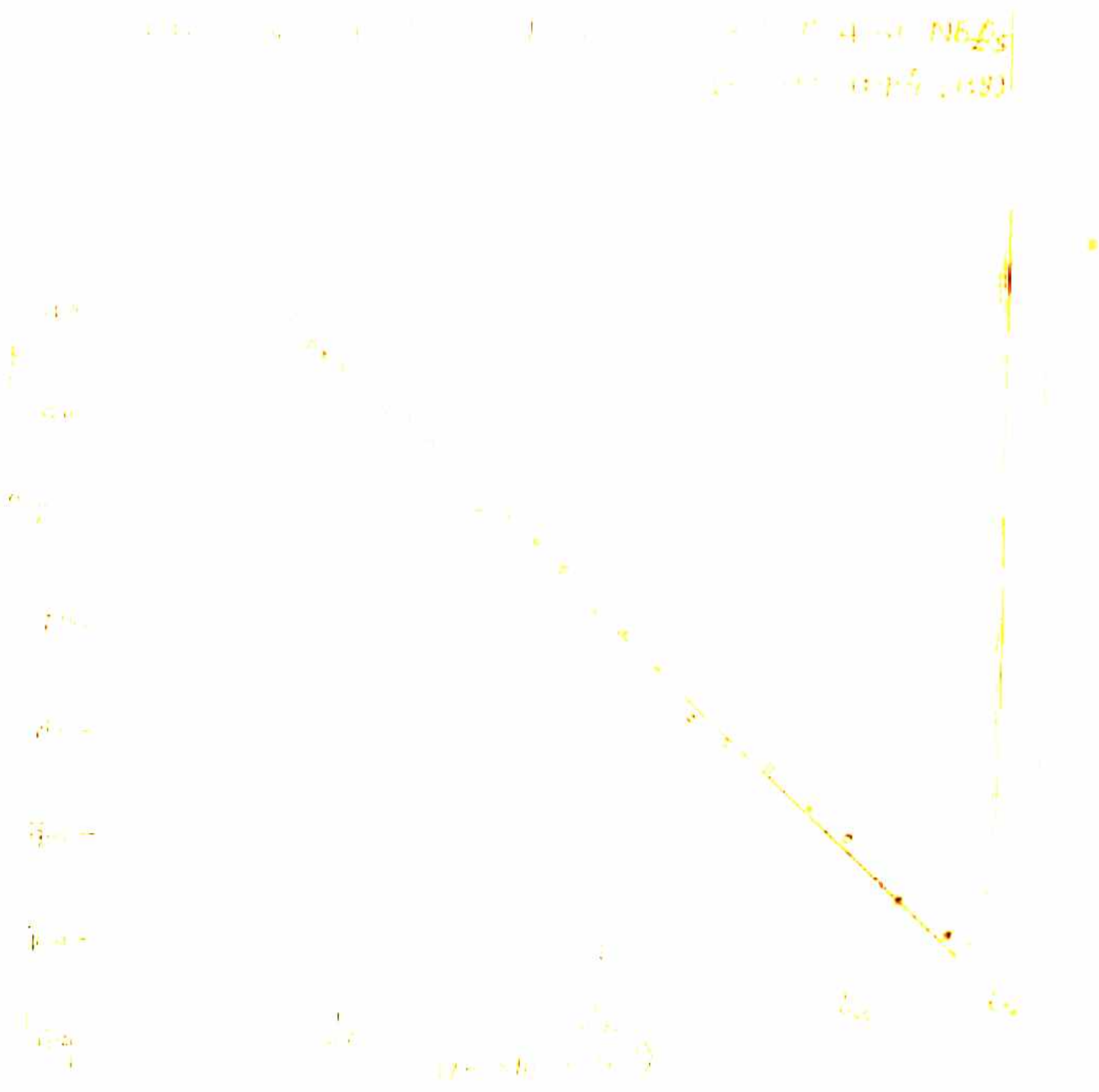


TABLE - 2.32

Activation Energies of Alkali Niobates

S.N.	Niobate	Ea in eV
1.	$\alpha - Nb_2O_5$	0.91
2.	$\beta - Nb_2O_5$	0.94
3.	$\gamma - Nb_2O_5$	1.04
4.	$Li_2O.\ Nb_2O_5$	1.45
5.	$2Li_2O.\ Nb_2O_5$	1.24
6.	$3Li_2O.\ Nb_2O_5$	1.15
7.	$K_2O.Nb_2O_5$	0.97

TABLE - 2.33

Activation Energies of Alkaline Earth Niobates

S.N.	Niobate	Ea in eV
1.	$CaO.\ 2Nb_2O_5$	1.25
2.	$CaO.\ Nb_2O_5$	1.38
3.	$SrO.\ 2Nb_2O_5$	1.21
4.	$SrO.\ Nb_2O_5$	1.16
5.	$2SrO.\ Nb_2O_5$	1.13
6.	$3SrO.\ Nb_2O_5$	1.08
7.	$4SrO.\ Nb_2O_5$	1.02

TABLE - 2.34

Seebeck Coefficients of Alkali Niobates

S.N.	Compound	α in $\mu V/^{o}C$
1.	$\alpha - Nb_2O_5$	- 350
2.	$\beta - Nb_2O_5$	- 300
3.	$\gamma - Nb_2O_5$	- 265
4.	$Li_2O.\ Nb_2O_5$	- 270
5.	$2Li_2O.\ Nb_2O_5$	+ 354
6.	$3Li_2O.\ Nb_2O_5$	+ 370
7.	$K_2O.\ Nb_2O_5$	- 380

TABLE - 2.35

Seebeck Coefficients of Alkaline Earth Niobates

S.N.	Compound	α in $\mu V/^{o}C$
1.	$CaO. 2Nb_2O_5$	+ 60
2.	$CaO. Nb_2O_5$	+ 116
3.	$SrO. 2Nb_2O_5$	+ 20
4.	$SrO. Nb_2O_5$	+ 77
5.	$2SrO. Nb_2O_5$	+ 177
6.	$3SrO. Nb_2O_5$	+ 154
7.	$4SrO. Nb_2O_5$	+ 197
8.	$BaO. 2Nb_2O_5$	+ 26
9.	$BaO. Nb_2O_5$	+ 58

alkali niobates at different temperatures are given. In Figs. 2.01 to 2.07 plots of logarithm of electrical conductivity (log σ) of niobates against reciprocal of temperature (T^{-1}) in $^{\circ}K^{-1}$ are shown. The values of activation energy, Ea, for the conduction process were calculated using the equation[59]

$$\sigma = \sigma_0 \, e^{-Ea/kT} \qquad (1)$$

where σ is conductivity at $T^{\circ}K$, σ_0 is a constant and k is Boltzmann's constant. The slopes of the log σ vs $^1/_T$

hence it could not be compared with any other data. The activation energies for niobates and different forms of Nb_2O_5 are given in table 2.32.

In all the cases a common feature in the variation of electrical conductivity with temperature is that the conductivity first remains constant over certain range of temperature and then it increases rapidly. It seems probable that the applied energy is not sufficient to excite the charge carriers initially but when the temperature goes beyond certain value the available energy excites the charge carriers sufficiently and thus they are able to conduct electricity.

The ranges over which conductivity remains constant are 313-473°K, 313-433°K, 313-353°K and 313-333°K for lithium meta, pyro and orthoniobates and potassium niobates respectively.

It is evident from Figs. 2.04-2.06 that with the increase in concentration of lithium oxide, the electrical conductivity increases and subsequently activation energy decreases (cf. Tables 2.21-2.23).

In case of lithium metaniobate, $LiNbO_3$, activation energy is found to be the highest (1.45 eV) and it is in good agreement with results of Roitberg et al[9] and alkali niobates at different temperatures are given. In Figs. 2.01 to 2.07 plots of logarithm of electrical conductivity (log σ) of niobates against reciprocal of temperature (T^{-1}) in $^{\circ}K^{-1}$ are shown. The values of activation energy, Ea, for the conduction process were calculated using the equation[59]

$$\sigma = \sigma_0 \ e^{-Ea/kT} \qquad (1)$$

where σ is conductivity at $T^{\circ}K$, σ_0 is a constant and k is Boltzmann's constant. The slopes of the log σ vs $1/T$ straight lines were accurately determined using the least square method.

On measuring the electrical conductivity of α, β and γ forms of Nb_2O_5 and also niobates at various temperatures it was observed that conductivity is exponentially dependent on temperature. The activation energy of α form is observed to be 0.91 eV in the temperature range 398-523°K, which is in good agreement with the observation of Greener and Hirthe[54] and it is 0.14 eV in the range of 313-398°K. The value of the activation energy for β form is found to be 0.95 eV in the range 413-523°K and 0.21 eV between 313°K and 413°K. On the other hand γ form has shown only one activation energy that is 1.04 eV between 313°K and 523°K. The activation energies for β and γ forms were determined for the first time and hence it could not be compared with any other data. The activation energies for niobates and different forms of Nb_2O_5 are given in table 2.32.

In all the cases a common feature in the variation of electrical conductivity with temperature is that the conductivity first remains constant over certain range of temperature and then it increases rapidly. It seems probable that the applied energy is not sufficient to excite the charge carriers initially but when the temperature goes beyond certain value the available energy excites the charge carriers sufficiently and thus they are able to conduct electricity.

The ranges over which conductivity remains constant are 313-473°K, 313-433°K, 313-353°K and 313-333°K for lithium meta, pyro and orthoniobates and potassium niobates respectively.

It is evident from Figs. 2.04-2.06 that with the increase in concentration of lithium oxide, the electrical conductivity increases and subsequently activation energy decreases (cf. Tables 2.21-2.23).

In case of lithium metaniobate, $LiNbO_3$, activation energy is found to be the highest (1.45 eV) and it is in good agreement with results of Roitberg et al[9] and

Bergmann.[60] We see from the results reported in table 2.32 that the activation energy of lithium pyro and orthoniobates is less (1.24 eV and 1.15 eV) as compared to that of lithium metaniobate (1.45 eV). A possible explanation for this may be that in the case of lithium metaniobate the lithium ions mostly occupy the vacancies in the crystal lattice whereas in lithium pyro- and orthoniobates they occupy interstitial sites and are therefore able to conduct easily.

The activation energy (Ea) of potassium metaniobate (0.97 eV) is much lower as compared to the observed activation energy of lithium metaniobate (1.45 eV). This difference may also be due to occupation of interstitial sites by the potassium ions in potassium metaniobate crystal lattice.

Seebeck coefficient (α) measurements in Table 2.34 show that $Li_2O.Nb_2O_5$ and $K_2O.Nb_2O_5$ have negative values of α, which means that these are n-type semiconductors i.e. electrical conduction here is mainly through electrons. The values of α in the case of $2Li_2O.\ Nb_2O_5$ and $3Li_2O.\ Nb_2O_5$ are found to be positive thereby proving that these are p-type semiconductors i.e. conduction is mainly through holes.

Semiconducting properties of alkaline earth niobates

The electrical conductivity (σ) at different temperatures of calcium and strontium niobates are given in tables 2.25-2.31 and plots of logarithm of electrical conductivity against reciprocal of temperature in °K is presented in Figs. 2.08 to 2.14. The activation energy, Ec, for the conduction process for these niobates was also calculated using the equation (1).

The slopes of the log σ versus $^1/_T$ straight line curves were accurately determined using the least square method. It is observed that there is very little change in the electrical conductivity values for the niobates formed at 800° or 1200°C and 900° or 1200°C (compare table 2.29, 2.29(b), 2.31 and 2.31(b) and Figs. 2.12, 2.15, 2.14 and 2.16), indicating that the niobate formed at 800° or 1200°C and 900° or 1200°C should have the same activation energies. This proves that once a niobate is formed it should have the same value of activation energy irrespective of its temperature of formation and Nb_2O_5 loses its forms (α, β or γ). The little change in electrical conductivity values can be due experimental errors.

From the results reported in Table 2.33 it is observed that in case of $Ca\ Nb_4O_{11}$ (or $CaO.\ 2Nb_2O_5$) the activation energy is small which is probably because the number of vacancies occupied by calcium ions in the niobate lattice is less, whereas when the calcium metaniobate $Ca(NbO_3)_2$ (or $Cao.\ Nb_2O5$) is formed the activation energy is found larger and correspondingly conductivity decreases,(Fig.2.09) because perhaps more of vacancies are occupied by calcium ions in $Ca(NbO_3)_2$ lattice to form polyhedral type of arrangement[34] and are unable to conduct well.

In the case of strontium niobates as the ratio of $SrO:Nb_2O_5$ increases it is observed that activation energy decreases (table 2.33). It may be that the strontium ions occupy more and more interstitial sites in the lattices to form distorted perovskite structure.

It is further ascertained that SrO. having more conductivity than CaO[61,62] forms niobates having less activation energies.

The electrical conductivity of both the barium niobates $Ba\,Nb_4O_{11}$ and $Ba\,(NbO_3)_2$ was observed to be constant ($BaO.\ 2Nb_2O_5$; $\sigma = 4.20 \times 10^{-11}$ $ohm^{-1}Cm^{-1}$; $BaO.\ Nb_2O_5$; $\sigma = 1.02 \times 10^{-12}$ $ohm^{-1}cm^{-1}$) in the temperature range 313 to 523°K, therefore their activation energies cannot be calculated. It is because the energy available upto 523°K may not be sufficient to excite the charge carriers.

Seebeck coefficient (α) measurements as reported in Table 2.35 show that all the alkaline earth niobates are p-type semiconductors i.e. conduction is chiefly by means of holes.

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CHAPTER - III

COMPLEX COMPOUNDS OF NIOBIUM PENTACHLORIDE WITH ORGANIC LIGANDS.

INTRODUCTION

Complex compounds are defined as the combination of two or more atoms, ions or molecules, which arise as a result of the formation of bonds by sharing pairs of electrons originally associated with the different components (ligands), and which possess some identifiable physical or chemical characteristics of a distinct species. Ligands are classified as monodentate, bidentate, tridentate etc. depending upon the number of donor groups. Bidentate or polydentate ligands, whose structures permit the attachment of two or more donor atoms to the same metal ion simultaneously, thus closing one or more ring, are called chelate Usually chelation having five or six membered ring is favoured due to low strain.

The origin of chemistry of coordination compounds begins with Werner's theory[1] of complexes, which is based on the concept of secondary valencies and for which he was awarded Nobel prize in chemistry. Lowry[2] and Sidgwik[3] gave a new impetus to the subject by putting forward the electronic interpretation of coordinate bond. According to this theory every coordinating molecule or group possesses a donor atom with a lone pair of electrons, which it can donate to the central atom forming a coordinate bond. The

The central atom accepts the lone pair of electrons till its effective atomic number assumes the next inert gas configuration.

The valence band theory of Pauling[4] introduced the concept of hybridization of orbitals to explain the sterio-chemistry and magnetic properties of complexes. This theory is limited toa a qualitative treatment and cannot predict the relative energies of different structures. It cannot interpret or predict the spectra and also in many instances fails to explain detailed magnetic properties of the complexes.

The ligand field theory as we have it today evolved out of a purely electrostatic theory called crystal field theory, which was first expounded in 1929 by Bethe. This theory was further developed by Penney and Schlapp[5], Van Vleck[6], Van Vleck and Penney[7] and Kotani[8] to explain magnetic and optical properties in complex compounds, but partly covalent bonding has been neglected, and therefore whatever effects and phenomena stem directly from covalency are entirely inexplicable in simple crystal field theory. On the other hand crystal field theory provides a very simple and easy way to treat numarically many aspects of the electronic structure of complexes, i.e. it treats a complex as a positively charged metal ion surrounded by a number of ligands (equal to coordination number of metal ion), which are considered as negative point charges or almost point dipoles with the negative end orientation towards the metal ion. Under these circumstances the degeneracy of the metal d orbitals is lifted. Thus in an octahedral complex the d-orbitals are split into two sets of orbitals consisting of d_{z^2} and $d_{x^2-y^2}$ orbitals, which are designated as eg, and the other consisting of d_{xy}, d_{yz} and d_{xz} orbitals designated as t_{2g}.

The eg orbitals are higher in energy than t_{2g} orbitals. This theory has been widely used to explain the so-called d-d spectra of complexes in visible region and in the prediction of properties of ionic complexes. Orgel[9-11] was first to draw attention to the effect of crystal field splitting on the stability of coordination compounds of transition metals.

The molecular orbital theory developed by Van Vleck[12] starts with the premise that overlap of orbitals will occur to some degree, whenever symmetry permits. It thus includes the electrostatic situation (no overlap) as one extreme, maximum overlapping of orbitals as the other extreme, and all intermediate degree of overlap in its scope. It explains the energy considerations which were neglected in valence bond approach and also treated the electron as moving in the potential field set up by the nuclei of all atoms in the molecule. It explains the formation of molecular orbital by the combination of atomic orbitals in two different ways, firstly by bonding where the electrons have lower potential energy in the molecule than in the original atom and secondly by antibonding orbitals where electrons have been excited to the higher energy level. During the formation of a molecule, an interaction occurs between the electrons from the individual atoms whereby the structure of a molecule is stabilized. These interactions produce three electronic conbinations known as σ, π & δ bonds and the electrons which form the bonds are designated by the same symbols.

The ligand field theory developed by Orgel[13], Griffith[14] and Ballhausen[15] is a more recent approach. The theory generalizes certain features of the molecular orbital theory. It thus gives more rigid treatment of the effect of the coordinating atom in the ligand on the orbitals of the central atom to which it is attached and of the effect this interaction has on the stereochemistry of the complexes. It leads to a more complete understanding of electronic spectra and magnetic properties.

The usefulness of metal complexes in theoretical and applied chemistry and in technology is well recognized. A large amount of work has been done on the reactions of transition metal halides with ligands containing nitrogen, sulphur and oxygen donor atoms.

Thiourea complexes have been a subject of study for many investigators.[16-27] These workers while working on Ti (IV), Ni (II), Cu (I), Mo (III), Ag (I), Sn (IV), Au (I), Hg (II), Tl (II) and Pb (II) complexes with thioureas observed that coordination occurs through sulphur.

Metal complexes of substituted thioureas have also received considerable attention of chemists.[28-38] Complexes of Co (II), Ni (II), Cu (I), Ag (I), Te (II) and Te (IV) with substituted thioureas have also been found to coordinate through sulphur. More recently substituted thioureas having a heterocyclic group as a substituent have also been studied by various workers.[39-42] In these compounds nitrogen in heterocyclic ring and sulphur are found to be donor atoms to form a quite stable chelate as a six membered ring.

Interest in sulphur donor ligands and their related metal complexes has grown rapidly and number of chemical studies in this area has increased to a considerable extent. A number of excellent reviews dealing with different aspects of the field have appeared. The discussions by Livingston,[43] Harris and Livingstone,[44] McCleverty,[45] Gray[46] and Jorgensen[47] deal with sulphur and sulphur and oxygen ligand complexes in general. A review by Eisenberg[48] deals with structural systems of 1,1- and 1,2- dithiolatochelates of iron, cobalt, nickel, copper, palladium, platinum and gold and other related systems.

Like other transition elements, niobium forms a large number of compounds due to the presence of vacant '4d' orbital. It has the electronic configuration as $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^4\ 5s^1$. Usually niobium exhibits covalency of six, seven and eight in its complexes.

Complexes of niobium pentachloride with acetophenone and benzophenone gives the moisture sensitive complexes of type $Nb\ Cl_5.L.$[49] The carbonyl stretching frequency was lowered in complexes indicating that co-ordination is taking place through oxygen of acetophenone and benzophenone.

Gadd and Fowles[50] prepared 2,2'-bipyridyl complexes of niobium (V) at 0°C in methyl cyanide. Theyobserved the formation of 1:1 complexes. The infrared spectra and magnetic measurements showed that complexes are diamagnetic with coordination number six.

Polymeric oxochloroalkoxo dipyridyl derivatives of formula $Nb_4O_7\ Cl_4(O\ Et)_4\ (dipy)_2 \cdot 2H_2O$ were isolated from ethanolic solution of $NbCl_5$ containing dipyridyl.[51] Polymeric complex cationic species of Nb (V) of the formula $[Nb_4\ O_6$ [illegible] $(dipy)_2 \cdot H_2O]^{+}$ was precipitated from alcoholic solution of these polymers. In these cations chloro ligands are replaced on hydrolysis by hydroxo groups.

Complexes of niobium (V) with wide range of Schiff bases containing a variety of donor sites have been reported.[52-54] It has been observed that in almost all the complexes the co-ordination number of niobium is seven. Parasher and Tondon[55] have reported hexa and octa coordinated Schiff base complexes of niobium (V). Later Biradar et al[56,57] reported co-ordination number seven for some schiff base complexes of niobium.

Johnson and Ilmair[58] reported the formation of new compounds Nb $(BPHA)_4$ Cl and Nb $O(DEDTC)_3$ (where BPHA and DEDTC are the anions of benzoyl phenyl hydroxyl amine and diethyl dithiocarbamic acid). Bradley et al[59] observed that niobium (V) pentakis dialkylamide (R=Me & Et) reacts with carbon disulphide in cyclohexane to yield tetravalent dialkyl dithiocarbamates of general formula $Nb(S_2CNR_2)_4$, but Johnson and Pantaleo[60] observed that if the reaction is carried out in methyl alcohol the compounds formed are $NbX(OMe)_2(S_2CNR_2)_2$ (X = Cl, Br, NCS; R = Me,Et & CH_2Ph).

Crystal and molecular structures of dichloro (OXO) 2,2' bipyridyl ethoxy niobium (V) and tetra phenyl arsonium oxopenta thiocyanato niobium (V) have been reported by Kamenar and Prout.[61] They observed that both complexes contain octahedrally co-ordinated nitrogen and oxygen atoms multiply bonded to niobium atom. The bond distance of each nitrogen and oxygen atom with respect to niobium is reported. Reactions of Nb (V) chlorides with bidentate ligands such as dithiane, $S\ Ph_2$, $O-(MeO)_2\ C_6\ H_4$ $[(Ph_2\ P)_2\ CH_2]_2$ and dithio ethane gave 2:1 or 1:1 complexes.[62] Some complexes contained ligand bridging two 6-coordinated metal atoms.[62]

Fowles and co-workers[63-66] have been continuously working on niobium complexes and have recently reported the crystal structure of 1:1 adduct of trichloro sulphidoniobium(V) with triphenyl phosphene sulphide.[67] The unit cell contains 2 identical monomers of $NbCl_3S.S\ PPh_3$ and a centrosymmetric dimer of $[NbCl_3S.SPPh_3]_2$. It was also observed that in monomer Nb atom is 5 co-ordinated and in dimer it is 6 co-ordinated. Semiconducting properties of several other metal (Cu(II), Co(II), Ni(II) and Pt(II)) phthalocyanin complexes[68] have been reported and they have almost same activation energies E_a = 0.75 to 0.9 eV.[69,70] The Hall mobility of copper phthalocyanine has been found to be about two orders of magnitude greater than that of the metal free compounds.[71]

The Etiporphyrine and metal Cu(II), Co(II), Ni(II) and Mg(II) complexes have Ea in the range of 0.9 to 1.0 eV; this shows the absence of any marked effect of the metal atoms on the conductivity.[72]

Dipyromethane complexes of Cu(II) and Co(II) complexes have Ea=0.9 eV, which is very close to the values for the porphyrins.[73] Resistivity measurements on the Cu(II) complex of the Schiff base, formed from salicylaldehyde and p-anisidine, in which the metal forms a bridge between the bidentate ligands, have revealed that the complex has a resistivity of the same order as that of the ligand, log R (R = Resistance) at 127°C being 11.6 and 11.1 respectively.[74] However Ea is increased from 1.6 to 2.7 eV when the metal is present.

The resistivity of the Schiff bases formed from salicyldehyde and ethylenediamine or phenylene diamine is increased by four to six orders of magnitude when Cu(II) or Ni(II) complex is formed.

It has been found that the delocalization of π-electrons in a simple organic molecule possessing a conjugated system of double bonds, is more pronounced in a planar polycyclic aromatic structure than in a linear or branched chain polyene.[75,76] Electron transport through co-ordinated metal groups in a polymeric system should therefore be enhanced if the ligands have conjugated planar polycyclic structure, particularly if the metal is chelated and the chelate rings are coplanar with the ligands. Hence, metals forming square planar complexes are preferred, although coplanar situations are possible in octahedral complexes if the fifth and sixth coordination positions are filled by other donors. Therefore the observation of conductivity in co-ordination compounds is of great interest.

Of great value is the observation of high conductivity in polymeric metal complexes of 2,2'-dipyridyl, 1,10-phenanthroline[77], polyacrilonitrile,[78] ferrocene[79,80], tetracyano-ethylene[81] and dithio-oxamide metal complexes.[82,83] Extended polymers of double ligands, such as polymeric metal complexes of the dioxime of 1,5-diacetyl-2,6-dihydroxy naphthalene have also been found to be good semiconductors.[84]

It is evident from the survey of literature that practically no work has been done on the complex formation of $NbCl_5$ with N-Aryl N'-2(4,5,6-monosubstituted pyridyl) thioureas, 1,5-disubstituted 2,4-dithiobiurets; 1,5-disubstituted 2-thiobiurets, acridine, benzimidazole and imidazole.

The present investigations were therefore, undertaken with a view to study the formation of complex compounds of niobium pentachloride with above mentioned ligands in tetrahydrofuran. The magnetic properties, molar conductance measurements, i.r. spectral results and semiconducting properties have also been studied.

3.2 EXPERIMENTAL

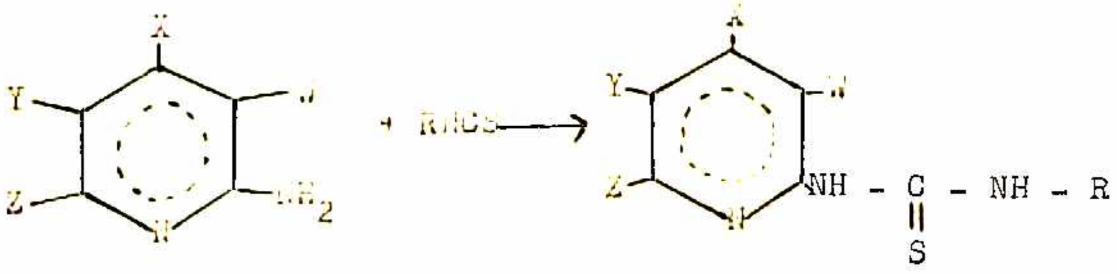
3.21 Chemicals and Instruments :

All the reagents used were of BDH Analar, E. Merck GR or Fluka extra pure quality. Solvents used were purified by distillation after drying.[85,86] All the solutions were made immediately before use. The i.r. spectra were recorded on a Perkin Elmer Infrared Grating Spectrophotometer (Model 237B) using KBr pellet technique. Conductance measurements were made on conductivity meter type LBR of Wissenschaftlich technique (Warkstatten, Germany), using dip type cell. Magnetic measurements were made on a Gouy's balance using Hg Co $(CNS)_4$ as the standard. Electrical conductivity measurements were made by using conductivity cell (Fig.6) and Digital Picoammeter (ESA 813 Electronic Corporation of India) and Seebeck coefficients were obtained by using a D.C. Microvoltmeter (Philips GM 6020). 2-amino-4-methyl pyridine and 2 amino-6-methyl pyridine of Aldrich chemicals were used for the preparation of ligands. Niobium pentachloride of Fluka was used in all the experiments.

Acridine of BDH, Imidazole of E.Merck and Benzimidazole of Koch light were used.

3.22 Synthesis of N-substituted N'-2(4,5,6-substituted pyridyl) thioureas :

Equimolar amounts of the 2-amino 4-methyl, 2 amino-6-methyl pyridine and aryl isothiocyanate were taken in ethanol. The mixture was refluxed for about three hours. The product i.e., substituted thioureas started separating out even in the boiling ethanol because of their low solubility in ethanol. The precipitate was filtered and washed with hot ethanol. The formation of substituted thioureas can be represented by the following equations:



substituted thiourea

where

R = - C_6H_5 ; - $C_6H_4(CH_3)$ ortho ; - $C_6H_4(CH_3)$ para

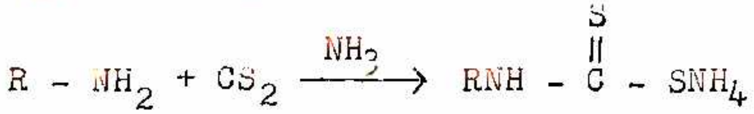
& W = H X = CH_3; Y = H ; Z = H

or W = H X = H ; Y = H ; Z = $-CH_3$

The compounds were found to have high and sharp melting points.

3.23 Synthesis of Phenyl, o-tolyl and p-tolyl isothiocyanates

Phenyl, orthotolyl and paratolyl isothiocyanates were prepared by the method described by Vogel.[85] The reaction taking place in the preparation of the mustard oils are given below:



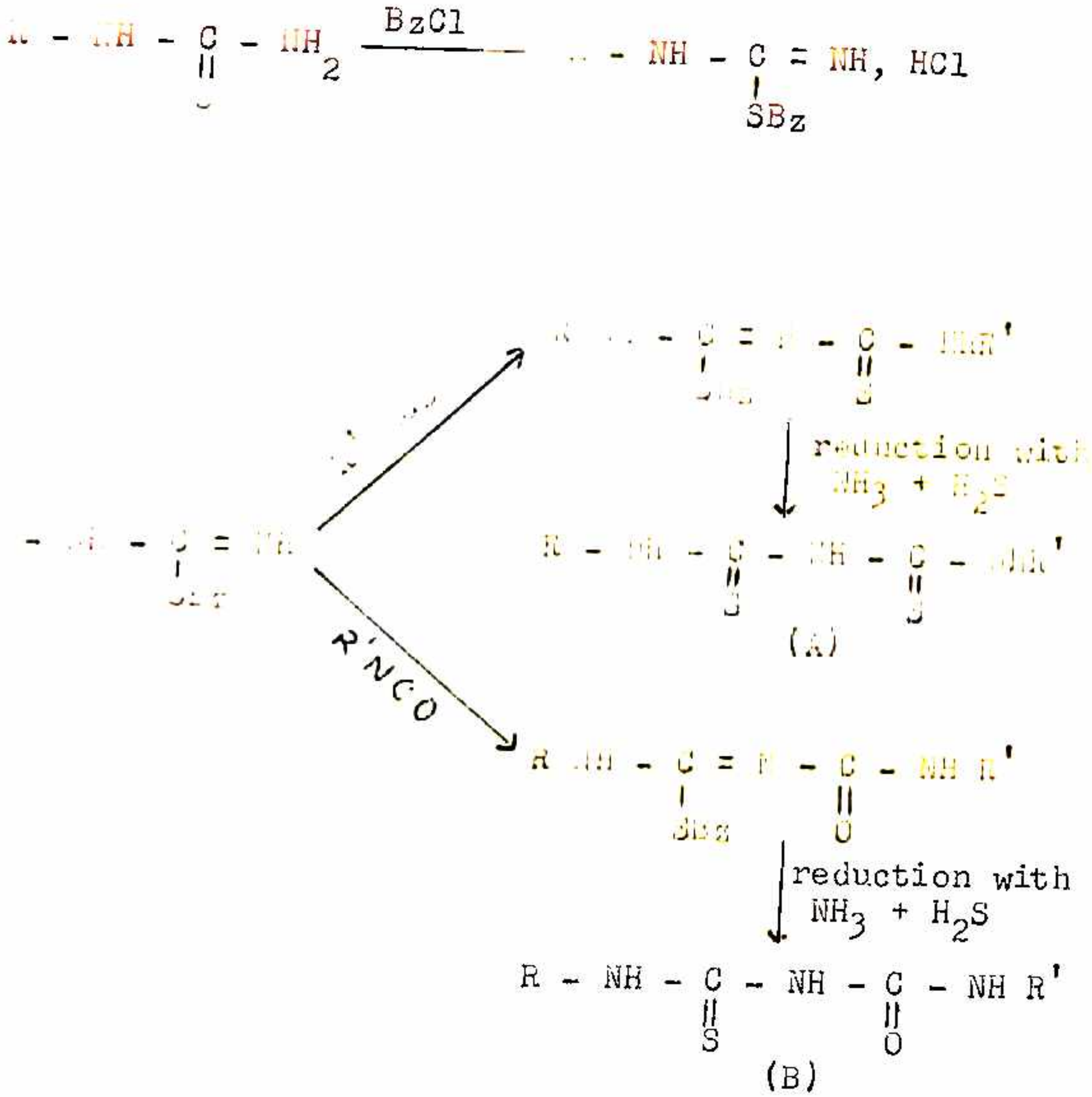
$$R - NH_2 + CS_2 \xrightarrow{NH_3} RNH - \overset{\overset{S}{\|}}{C} - SNH_4$$

$$R\ NH\ CSSNH_4 + Pb(NO_3)_2 \longrightarrow RNCS + NH_4NO_3 + HNO_3 + PbS$$

(R= Phenyl, orthotolyl and paratolyl).

3.24 Synthesis of 1,5-diaryl substituted 2,4-dithiobiurets and 1,5 diaryl substituted 2 thiobiurets.

The ligands 1,5-diphenyl 2,4-dithiobiuret (DPDTB); 1,5-diphenyl-2-thiobiuret (DPTB); 1,5-diorthotolyl 2,4-dithiobiuret (D-o-TDTB); 1,5-diparatolyl 2,4-dithiobiuret (D-p-TDTB); 1-phenyl 5-orthotolyl 2,4-dithiobiuret (P-o-TDTB); 1-phenyl 5-paratolyl 2,4-dithiobiuret (P-p-TDTB); 1-phenyl 5-orthotolyl 2-thiobiuret (P-o-TTB) and 1-phenyl 5-paratolyl 2-thiobiuret (P-p-TTB) were prepared by the method of Dixit.[87] A general scheme of the reaction is given below:



(A) = 1,5-diaryl substituted 2,4-dithiobiuret

(B) = 1,5-diaryl substituted 2-thiobiuret.

R,R'= Phenyl, orthotolyl or paratolyl

Bz = Benzyl.

3.25 General Method of Preparation of Complexes:

To a solution (0.01 M) of niobium pentachloride in tetrahydrofuran was added in slight excess (mole ration 1:1.3

except benzimidazole), mole ratio 1:5 in case of benzimidazole) in the same solvent (but Acridine in chloroform) with vigorous shaking and sufficient time was allowed for the precipitate to settle down. The flask containing reaction mixture was kept at 1C^{o}C. The complex thus settled was filtered, washed with either chloroform or tetrahydrofuran, then with dry ether and finally dried in vacuum.

All the preparations were carried out in a dry box in the absence of moisture.

3.26 Analysis of the Complexes.

The composition of the complexes were determined by the estimation of elements. A weighed quantity of the complex was fused with 1:1 mixture of sodium peroxide and sodium carbonate in nickel crucible. The fused mass was extracted with water and then neutralized with nitric acid. Hydrated niobium pentoxide precipitated by adding ammonium hydroxide while the pH was maintained between 7 and 8. This precipitate was filtered and washed with hot water. The filterate so obtained was divided into two equal portions I and II. For estimation of chloride, silver nitrate was added to solution I, kept overnight, filtered and washed with water containing (1-2%) nitric acid, dried and weighed as silver chloride. For the estimation of sulphur, solution II was evaporated to dryness 3-4 times with hydrochloric acid and then Barium chloride was added to it. The precipitate of $BaSO_4$ was filtered, washed free of chloride ions ignited and weighed.

Complexes with acridine and Benzimidazole were analysed for niobium and chloride by the same method as adopted above and the nitrogen was estimated by semi-micro Kjeldahl's method.

3.27 Electrical Measurements :

The electrical conductivities of the samples in the form of cylindrical pellets (1 cm diameter, 1-2 mm thick, shown in Fig. 6) as followed by Rao et al[88] were measured. The pellets were prepared by applying a pressure of 2×10^7 kgs per sq.m. Two thin steel foils were placed on both the sides of the pellets prior to the application of pressure to avoid any contamination. Pellets thus obtained were coated with silver paste* and heated in air oven at 50-60°C for ohmic contact. The electrical conductivity (σ) of the pellets of complexes were measured by employing a conductivity cell (Fig. 6) and Digital Picoammeter (ESA 813 Electronic Corporation of India Limited). The temperatures

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*Obtained from Epoxy Technology Incorporation, 65 Groove Street, Watertown, MASS 02172 U.S.A.

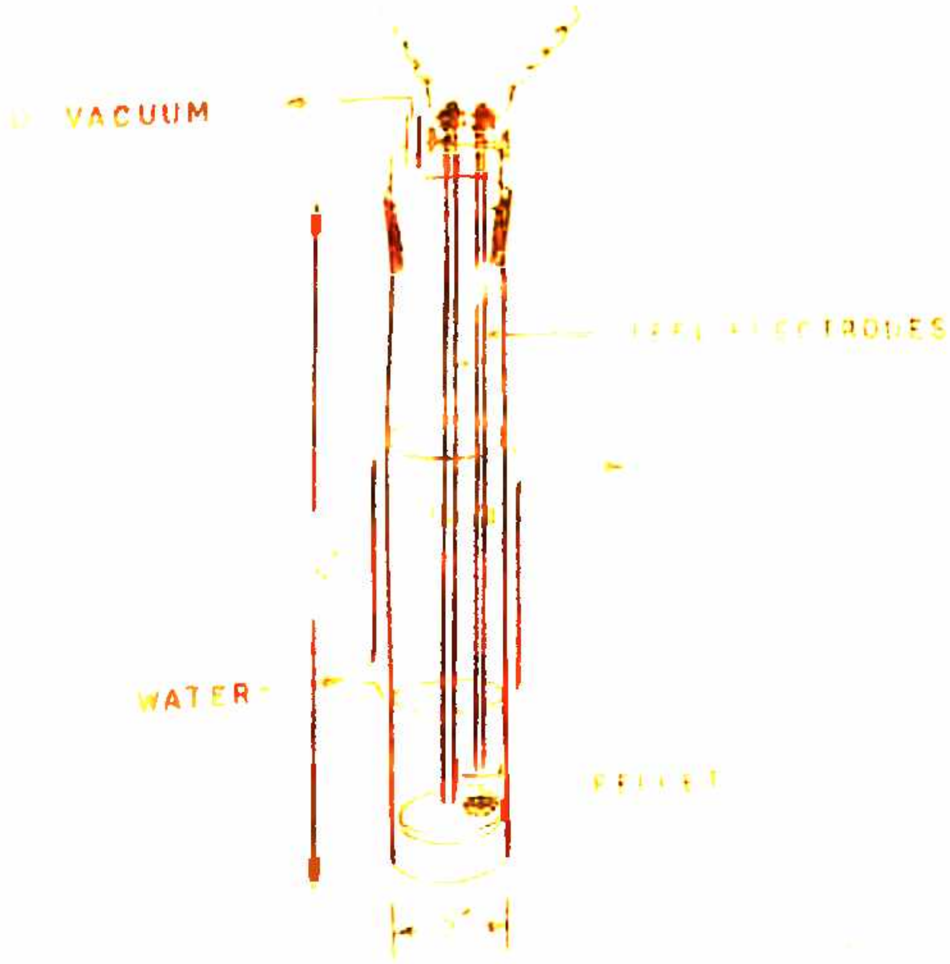


FIG. 6 CONDUCTIVITY CELL

of the samples were measured with the help of contact thermometer attached to the Thermostat U-10 (VEB MLW Model No. 22146 GDR) in which the cell was placed.

The temperature dependence of the electrical conductivity is given by the following equation[89] already used in Chapter II with $Eg/_2 = Ea$

$$\sigma = \sigma_0 \; e^{-Eg/_2 kT} \qquad \ldots\ldots \quad (3)$$

The values of the Seebeck coefficient, α, of the complexes were obtained by using equation (2). The set up used for this measurement is shown in Fig. 7.

FIG. 7 SET UP FOR SEEBECK COEFFICIENT DETERMINATION

TABLE - 3.01

Analytical results of the complex compounds of NbCl5 with aryl N'-2(4,6-dimethyl pyrimidyl) thioureas

S.N.	Complex	M.Pt. °C	Colour	Molecular formula	Analysis of complex compounds % Calculated Nb			% Found Nb		
					Nb	S	Cl	Nb	S	Cl
1.	$NbCl_5$.PTU	170	Light green	$NbCl_5. C_{12}H_{11}N_3S$	18.62	6.41	35.54	18.40	6.72	35.55
2.	$NbCl_5$.o TTU	182	Grey	$NbCl_5. C_{13}H_{13}N_3S$	18.13	6.23	34.57	18.25	6.40	34.70
3.	$NbCl_5$.p-TTU	190	Green	$NbCl_5. C_{13}H_{13}N_3S$	18.13	6.23	34.57	18.32	6.43	34.92
4.	$NbCl_5$.P4MeTU	185	Brown	$NbCl_5. C_{13}H_{13}N_3S$	18.13	6.23	35.54	18.24	6.33	35.68
5.	$NbCl_5$.o-T4MeTU	189	Reddish brown	$NbCl_5. C_{14}H_{15}N_3S$	17.63	6.06	33.65	17.40	6.18	33.42
6.	$NbCl_5$.p T4MeTU	209	Brown	$NbCl_5. C_{14}H_{15}N_3S$	17.63	6.06	33.65	17.75	6.30	33.61
7.	$NbCl_5$.P6Me TU	198	Light brown	$NbCl_5. C_{13}H_{13}N_3S$	18.13	6.23	34.57	18.28	6.14	34.56
8.	$NbCl_5$.o T6MeTU	222	Grey	$NbCl_5. C_{14}H_{15}N_3S$	17.63	6.06	33.65	17.10	6.44	33.22
9.	$NbCl_5$.p T6MeTU	208	Light Green	$NbCl_5. C_{14}H_{15}N_3S$	17.63	6.06	33.65	17.44	6.21	33.38

TABLE - 3.02

Analytical results of complex compounds of NbCl$_5$ with 1,5 di-substituted 2,4-dithiobiurets and 1,5-disubstituted 2-thiobiurets

S.N.	Complex	M.Pt. °C	Colour	Molecular formula	Analysis of [illegible] % Calculated			Found		
					Nb	S	Cl	Nb	S	Cl
1.	NbCl$_5$.DPDTB	259d	Light Yellow	$NbCl_5.C_{14}H_{13}N_3S_2$	16.64	11.48	31.84	16.85	11.65	32.0[illegible]
2.	NbCl$_5$.DPTB	290d	Yellow	$NbCl_5.C_{14}H_{13}N_3SO$	17.18	5.91	32.78	17.52	6.12	3[illegible]
3.	NbCl$_5$.D-o-TDTB	216d	Yellow	$NbCl_5.C_{16}H_{17}N_3S_2$	15.88	10.92	30.31	16.14	11.10	30.45
••	NbCl$_4$.D-p-TDTB	204d	Light yellow	$NbCl_5.C_{16}H_{17}N_3S_2$	15.88	10.92	30.31	16.20	11.15	30.42
5.	NbCl$_5$.P-o-TDTB	197d	Yellow	$NbCl_5.C_{15}H_{15}N_3S_2$	16.28	11.18	32.45	16.42	11.35	32.64
6.	NbCl$_5$.P-p-TDTB	212d	Grey	$NbCl_5.C_{15}H_{15}N_3S_2$	16.28	11.18	32.45	16.38	11.38	32.70
7.	NbCl$_5$.P-o-TTB	184d	White	$NbCl_5.C_{15}H_{15}N_3SO$	16.74	5.76	31.95	16.96	5.92	32.28
8.	NbCl$_5$.P-p-TTB	152d	White	$NbCl_5.C_{15}H_{15}N_3SO$	16.74	5.76	31.96	17.04	5.96	32.20

TABLE - 3. 13

Analytical results, conductance and magnetic measurements of NbCl5 complexes with organic semi-conductors

S.N.	Complex	M.Pt. °C	Colour	Molecular formula		% Nb	% N	% Cl	Conduc- tance	Magnetic suscepti- bility (C.G.S.) x 10^{-6}
1.	Nb $(C_7H_6N_2)_4$ Cl_5	274	Cream	$NbC_{28}H_{24}N_8Cl_5$	Found	13.31	15.44	24.15	172.00	-0.1342
					Calc.	12.52	15.10	23.92		
2.	$NbCl_5.C_6H_4CHC_6H_4N$	324	Yellow	Nb $C_{13}H_9N$ Cl_5	Found	21.02	3.28	40.02	10.42	-0.8588
					Calc.	21.07	3.12	39.50		

TABLE - 3.04

I.R. Spectral peaks of ligands (cm^{-1})

Compound	δ_{as} (NH)	ν(C = S)	ν([illegible] - [illegible])	ν([illegible])	δ [illegible]
PTU	1565 s	765 b	1010 s	[illegible]	[illegible]
o-TTU	1530 s	752 s	-	[illegible]	[illegible]
p-TTU	1590 m	-	-	[illegible]	[illegible]
P 4MeTU	1550s,1494s	775 w	[illegible]	[illegible]	[illegible]
o.T4MeTU	1535s	755 s	[illegible]	1010 m	[illegible]
p.T 4MeTU	1527 m	760 w	1060 m	1520 s	1370 m
P 6MeTU	1512 m	765 m	1020 w	1010 s	[illegible],1325m
o T 6MeTU	1550 s	775 m	1152 m	1025 s	[illegible]
p T 6MeTU	1525 m	760 m	1050 m	1025 m	[illegible]

s=strong; m=medium; w=weak; b=broad.

TABLE - 3.07

I.R. Spectral peaks of ligands (cm⁻¹)

Compound	N-H strech	N-H bend	N-H bend + ν(C-N) + (C=S) strech	ν(C [illegible])	[illegible]	C [illegible] strech
DPLTB	3120 m	1015 m	1480 m	1[illegible] s	7[illegible]	-
DPTB	3230 s	1000 s	1435 m	1[illegible]	[illegible]	17[illegible]
D-o-TDTB	3215 m	1025 s	1500 s	13[illegible]	75[illegible] s	-
D-p-TDTB	3160 m	1025 m	1495 m	1255 m	735 w	-
P-o-TDTB	3235 m	1015 m	1450 b	1240 s	735 m	-
P-p-TDTB	3225 s	1000 s	1465 m	1240 m	770 w	-
P-o TTB	3250 s	1020 s	1450 s	1245 s,b	755 s	1715 m
P-p-TTB	3196 m	1020 s	1460 m	1295 m	755 w	1715 s

w=weak; m=medium; s=strong; b=broad

TABLE - 3.05

I.R.spectral data of benzimidazole, acridine and their complexes (cm^{-1})

Compound	Molecular formulae	ν(C [illegible]	[illegible]
Benzimidazole	$C_7H_6N_2$	1600 s	1[illegible] s
Benzimidazole complex	$NbC_{28}H_{24}N_8Cl_5$	16[illegible] s	142[illegible] s
Acridine	$C_6H_4CHC_6H_4N$	1610 m	1362 m
Acridine complex	$NbC_{13}H_9NCl_5$	1625 b	1375 m

s = strong m = medium b = broad

TABLE - 3.07

I.R. Spectral peaks of $NbCl_5$ Complexes (cm^{-1})

Compound	ν_s (NH)	δ_{as} (NH)	ν([illegible])	ν([illegible])	ν([illegible])	δ ([illegible])
$NbCl_5$. PTU	-	1565 s 1515 b	700 b	1135 m 1160 m	[illegible]	[illegible]
$NbCl_5$. o TTU	-	1545 b	735 m,b	1110 vw 1125 m	[illegible]	[illegible]
$NbCl_5$. p TTU	3150 m	1564 s	770 vw	1210 m 1105 m,b	1550 m	[illegible]
$NbCl_5$. P4MeTU	-	1539 m	-	1104 m	1620 vw	[illegible] m [illegible] w
$NbCl_5$. o T4MeTU	-	1520 s	735 w	111[illegible] m,b 1150 m	-	1334 m
$NbCl_5$. p T4MeTU	3090 vb	1577 s	720 vb	1138 m 1304 m,b	1636 m 1572 s	1285 b
$NbCl_5$. P6MeTU	-	1590 b	-	1130 s	-	1260 m,b
$NbCl_5$. o T6MeTU	-	-	740 b	1130 b	1600 b	1270 m
$NbCl_5$. p T6MeTU	3120 m	1514 m,b	715 w	1140 m	-	1275 m,b

s=strong; m=medium w=weak b=broad

TABLE - 3.08

I.R. Spectra of Complexes (Cm^{-1})

Compound	N - H stretch	N - H bend	C-H bend + ν(C-N) + (C=S)stretch	ν(C = S)	C - S stretch	C = O stretch
$NbCl_5$. DPDTB	3170 b	1590 m	1450 m	1230 m	7[illegible]0 w	-
$NbCl_5$. DPTB	3050 b	1577 m	1425 m	1200 b 1275 w	743 s	1[illegible]42 m
$NbCl_5$. D-o TDTB	-	1600 m	1450 m	1240 m	740 m	-
$NbCl_5$. D-p-TDTB	-	1615 m	1450 m	1220	730 m	-
$NbCl_5$. P-o-TDTB	-	1585 m	1415 m	1210 m	750 w	-
$NbCl_5$. P-p TDTB	-	1615 m	1400 m	1200 b	700 w	-
$NbCl_5$. P-o TTB	-	1625 s	1480 m	1325 s	725 b	1710 s
$NbCl_5$. P-p-TTB	3125 m	1610 s	1475 m	1340 m	770 w	1640

s = strong; m = medium; w = weak; b = broad.

TABLE - 3.0

S.N.	Compound	Molar Conductance of the complexes in DMF Conc. x $10^{-[illegible]}$	 λ_M $Cm^2mole^{-1}ohm^{-1}$	Susceptibility X x 10^{-5}
1.	$NbCl_5$. PTU	0.11	90.76	- 0.574
2.	$NbCl_5$. o TTU	0.11	90.76	- 0.446
3.	$NbCl_5$. pTTU	0.11	74.95	- 0.275
4.	$NbCl_5$. P4MeTU	0.13	81.43	- 0.356
5.	$NbCl_5$. o-T4MeTU	0.10	83.20	-00.525
6.	$NbCl_5$. p-T4MeTU	0.12	84.61	- 0.210
7.	$NbCl_5$. P6MeTU	0.10	91.52	- 0.430
8.	$NbCl_5$. o T6MeTU	0.10	80.77	- 0.714
9.	$NbCl_5$. p-T6MeTU	0.10	89.46	- 0.256

TABLE - 3.10

S.N.	Formula	Molar conductance of the complexes in DMF		Susceptibility.
		Concentration $\times 10^{-2}$ M	λ_M Cm^2 $mole^{-1}$ ohm^{-1}	$X \times 10^{-5}$
1.	$NbCl_5$. DPDTB.	.10	80.66	- 0.299
2.	$NbCl_5$. DPTB	.10	87.16	- 0.294
3.	$NbCl_5$. D-o-TDTB	.099	91.52	- 0.352
4.	$NbCl_5$. D-p-TDTB	.098	85.07	- 0.298
5.	$NbCl_5$. P-o-TDTB	-	Insoluble	- 0.373
6.	$NbCl_5$. P-p-TDTB	.12	93.22	- 0.481
7.	$NbCl_5$. P-o-TTB	.10	92.44	- 0.543
8.	$NbCl_5$. P-p-TTB	-	Insoluble	- 0.429

3.2 RESULTS AND DISCUSSIONS :

The results of the elemental analysis, molar conductance and magnetic measurement data are recorded in tables 3.01 to 3.03 and 3.09 to 3.10. The i.r. spectra of ligands and complexes are in Figs. 3.01 to 3.30. The relative i.r. [illegible] are recorded in tables 3.04 to 3.08. The electrical conductivity is reported in tables 3.11 to 3.29 and log σ vs $^{1}/_{T}$ plots are shown in Figs. 3.32 to 3.50. The seebeck coefficient data are recorded in tables 3.32 to 3.34.

3.31 General properties of the Complexes

The complexes of Nb(V) chloride with P4MeTU, oT4MeTU, pT4MeTU and PoMeTU are brown in colour, while that of PTU, pTTU and pT6MeTU are green. The complexes of DPDTB, DPTB, D-o-TDTB, D-p-TDTB, P-o-TDTB and acridine are yellow in colour whereas P-OTTB, P-pTTB and Benzimidazole are white or cream coloured.

All these complexes are insoluble in common organic solvents like Benzene, Chloroform, Carbon tetrachloride, ether, alcohol, nitrobenzene and Tetrahydrofuran. All these complexes are highly soluble in Dimethyl formamide. Melting points of these complexes are reported in tables 3.01, 3.02 and 3.03.

3.32 Magnetic Measurements :

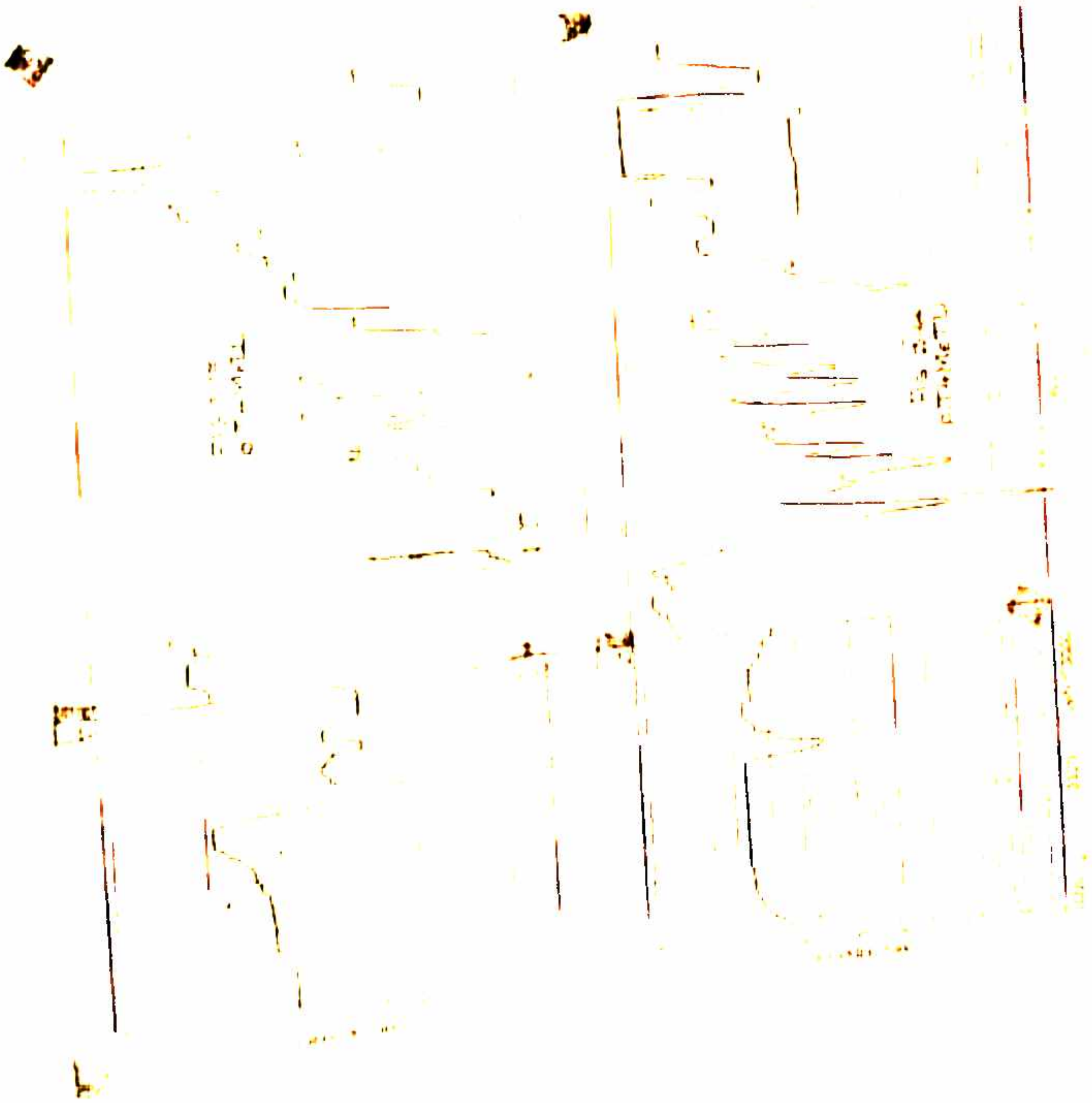
Magnetic susceptibilities of the complexes were determined by Guoy's magnetic balance, applying a field strength of about 1.[illegible] $\times 10^3$ gauss. The Guoy's balance was calibrated using mercury tetrathiocyanato cobaltate, $Hg[Co(CNS)_4]$ (standard). The values of magnetic susceptibility of the complexes are recorded in tables 3.03, 3.09 and 3.10.

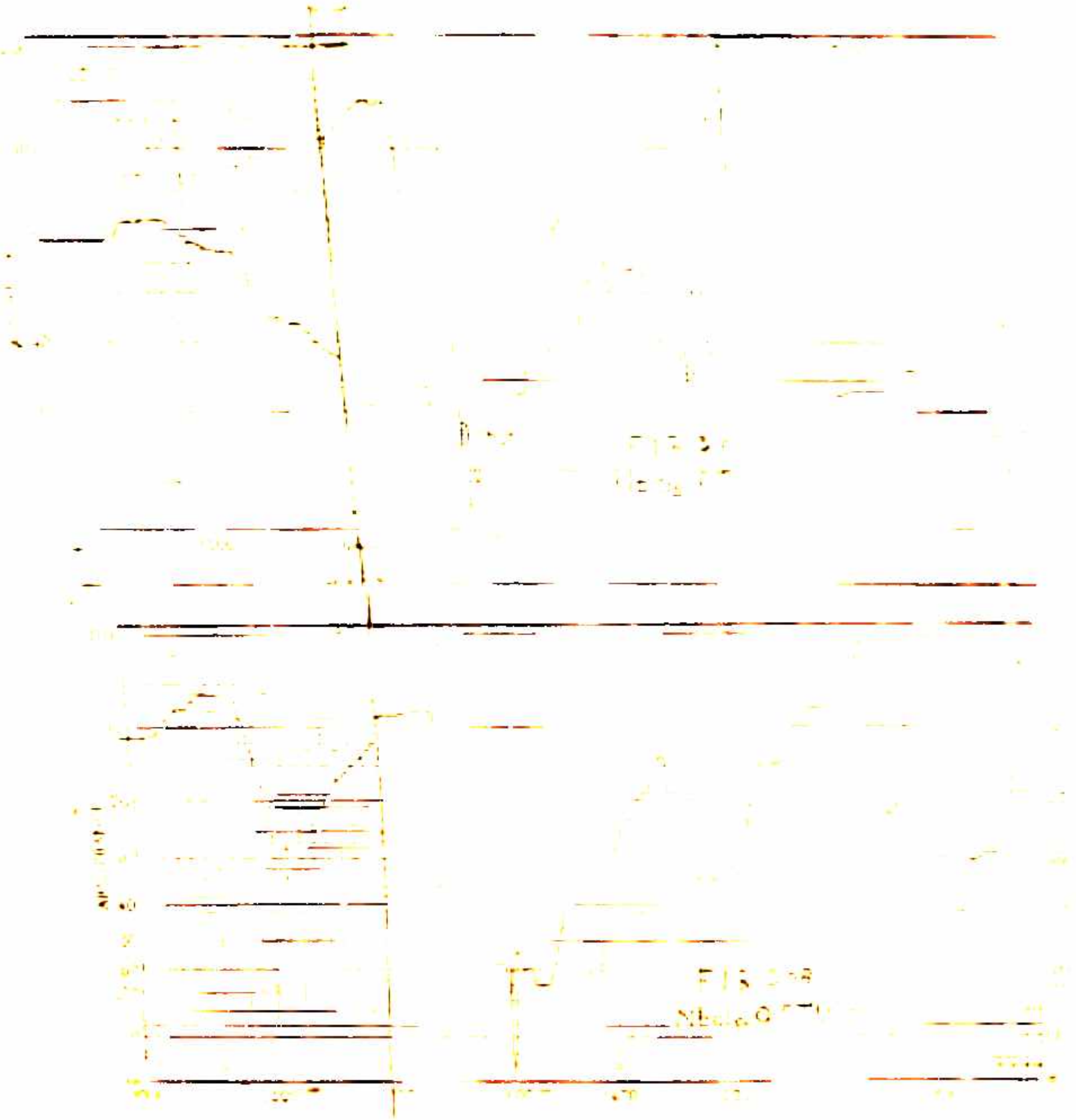
3.33 Conductance Measurements :

The molar conductance of all the complexes was determined in Dimethyl formamide. The instrument used was conductivity meter type LBR of Wissenchaffich Technische Werstatten, Germany, with a dip type cell. The distilled Dimethyl formamide was used and the solutions were prepared immediately before use.

3.34 I.R. Measurements

All the infrared spectra were recorded on Perkin Elmer's Grating Infrared Spectrophotometer model 237 B at medium scanning speed. The spectra of $NbCl_5$ complexes and ligands were recorded by KBr Pellet Technique. It is clear from the figures that the spectra of ligands and their metal complexes are quite complicated. The peaks that could be assigned with reasonable certainty are recorded in tables 3.04 to 3.08.





[illegible]

FIG. 5.10

Indole [illegible]

FIG. 5.11

[illegible]

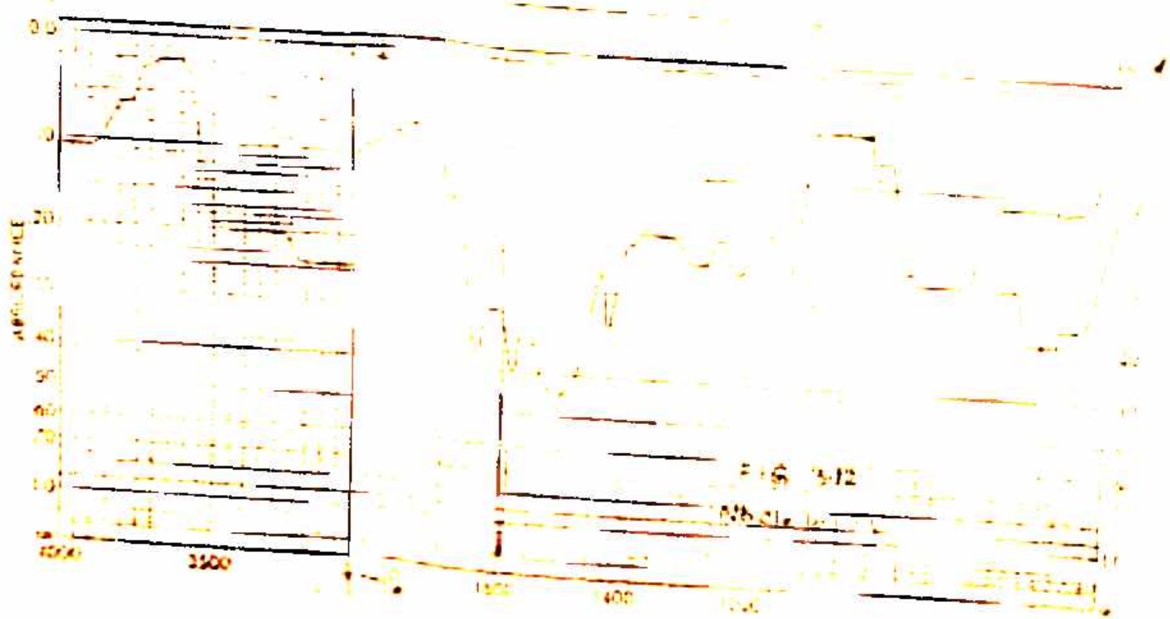


FIG. 5.12

[illegible]

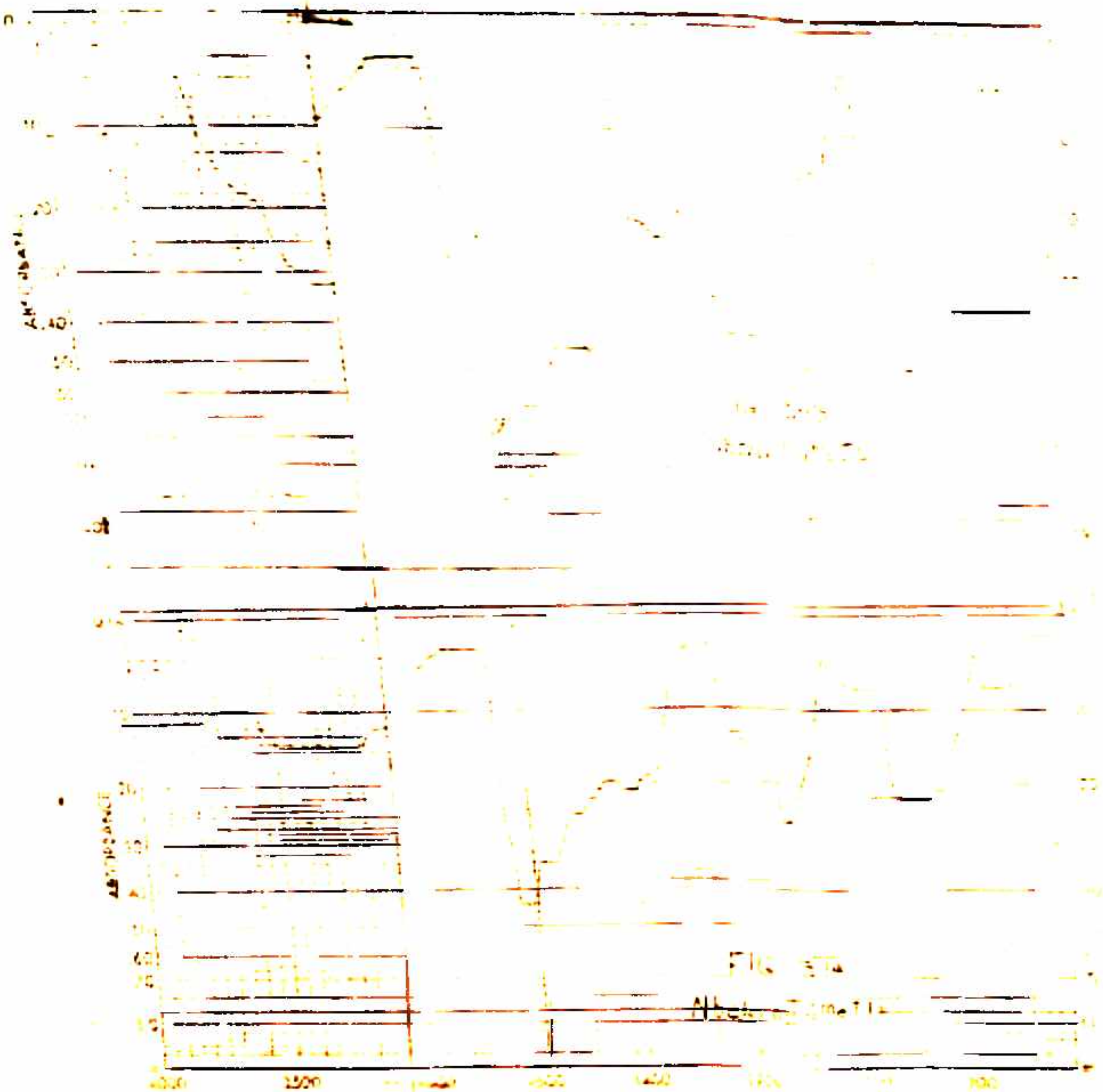


FIG. [illegible]

[illegible]


ABSORBANCE
0
.10
.20
.30
.40
.50
.60
1.0
3500
3000

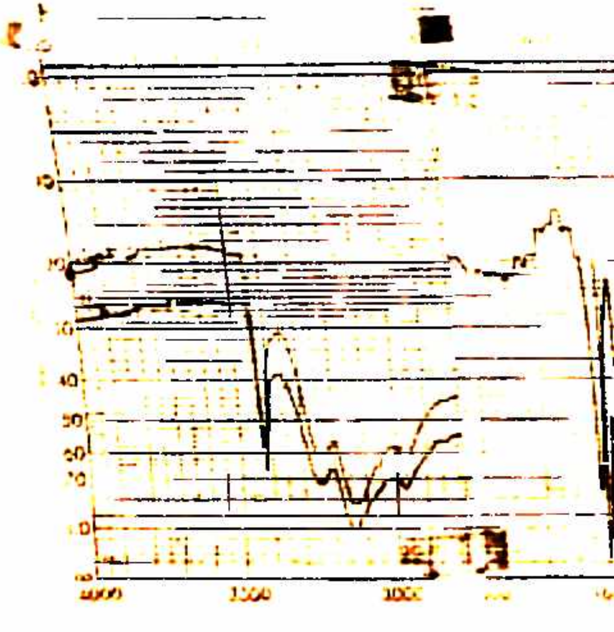

0
.10
.20
.30
.40
.50
.60
.70
1.0
4000
3500
3000

FIG 3-17
Meo-p-TAMTU

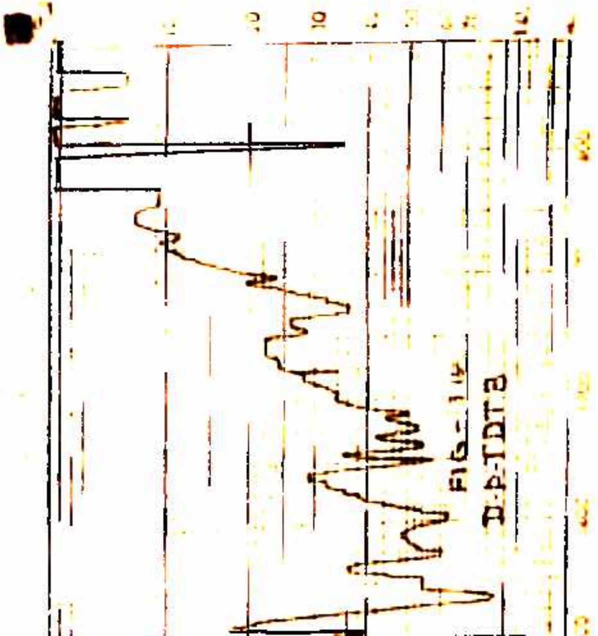


FIG - 3-18
D-P-TDTB

[illegible]

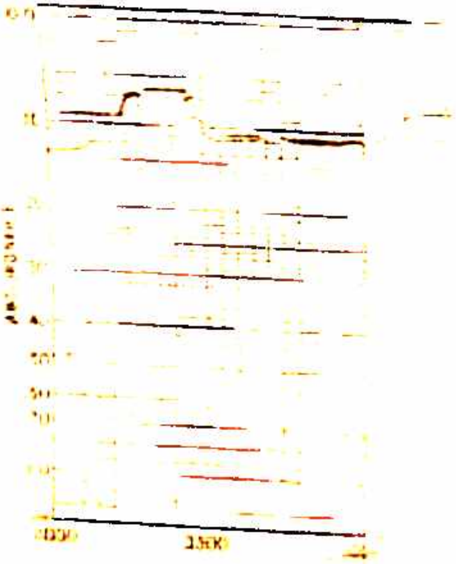
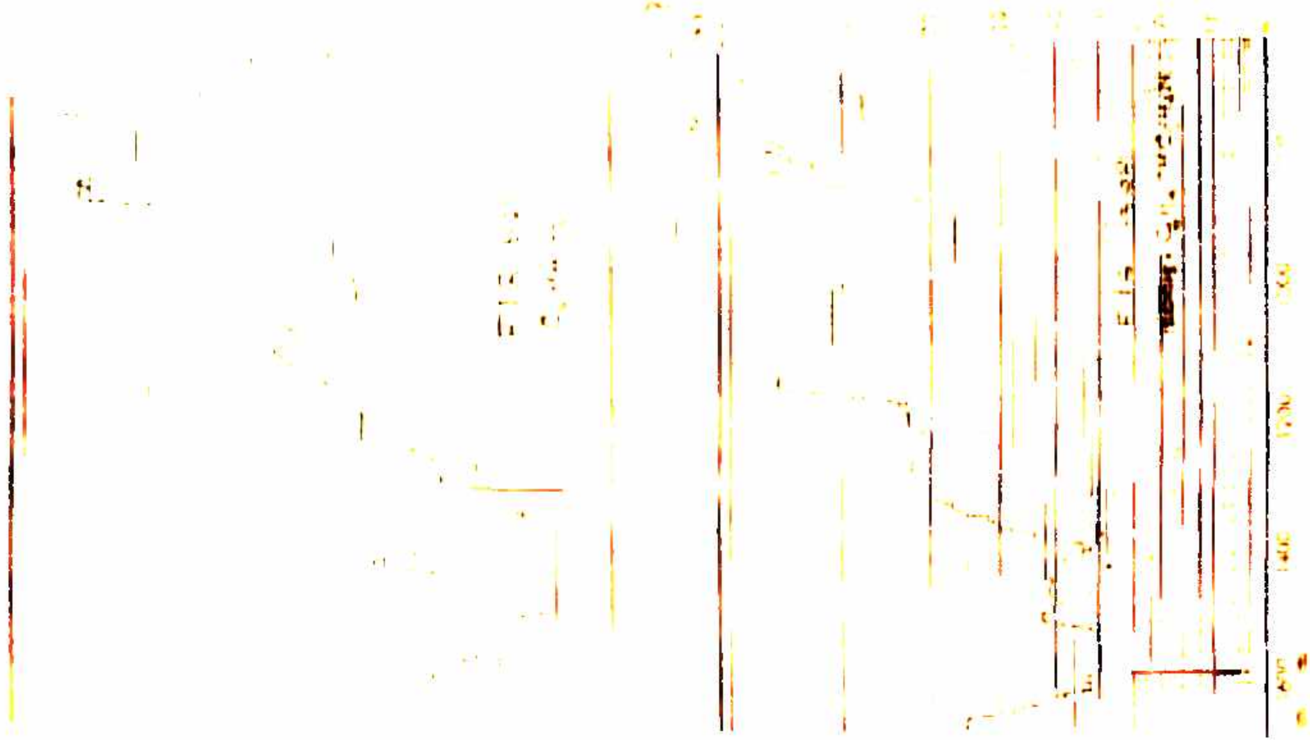
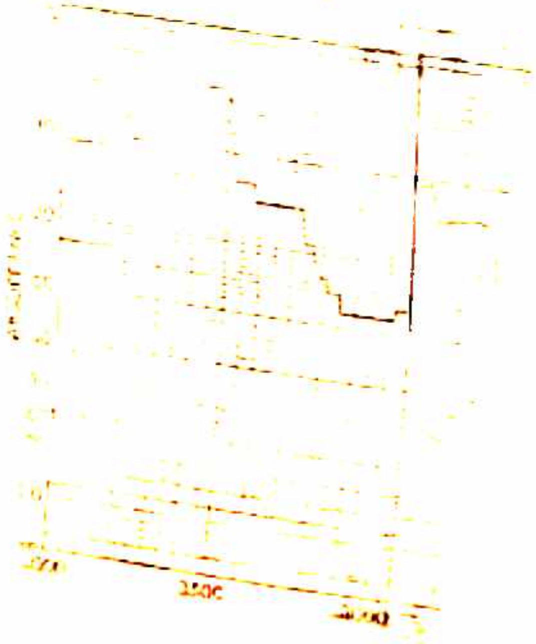


FIG. [illegible]
Nb-1s DP1B

FIG. [illegible]
[illegible] DP1B





[illegible] PENTACHLORIDE COMPLEXES :

The composition, melting points and percentage of various elements of the complexes obtained by the reaction of anhydrous $NbCl_5$ with N-Aryl-N'-2(4,5,6-monosubstituted Pyridyl) thiourea are reported in table 3.01. The analytical results of these complexes correspond to general emperical formula $NbCl_5.L$ where L is a molecule of bidentate ligand.

The molar conductance measurements of these complexes in freshly distilled dimethyl formamide are found to be 74.95 to 91.52 mhos (Table 3.09). These results indicate the electrolytic nature of complexes corresponding to 1:1 electrolytes.[90]

The magnetic susceptibility of these complexes at 25°C were observed to be in the range of $- .210 \times 10^{-5}$ to $- .714 \times 10^{-5}$ (Table 3.09). Negative values of the susceptibility indicate that all the complexes are diamagnetic showing thereby that all the electrons are paired.

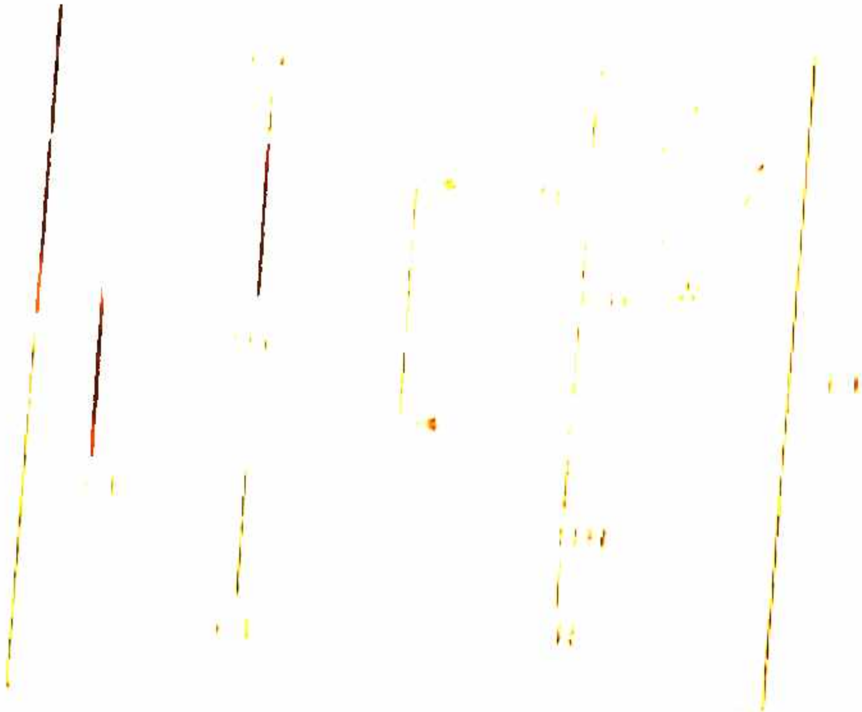
On examination of i.r. spectra of ligands and their niobium pentachloride complexes (Tables 3.04 and 3.07 and Figs. 3.01 to 3.15) it has been observed that bands appearing around 3090-3160 have been assigned to $\nu_s(NH)$ and $\nu_{as}(NH)$. A medium broad band appearing $\sim$ 3000 - 3100 cm^{-1} has been assigned to 2-aminopyridine vibrations. Bands appearing

1000 cm^{-1} and 1640 cm^{-1} have been assigned to $\nu(C = C + C = N)$ of aryl group. In case of the metal complexes there is a little change in these bands. The band appearing around 1152 to 1005 cm^{-1} has been assigned to $\nu(N - C - N + C = S)$ modes in case of ligands. These bands are either reduced in intensity or shifted to a higher frequency in most of the spectra of metal complexes. The mode $\nu(C = S)$ occurring at 752 - 775 cm^{-1} in ligands is also reduced in intensity or shifted to a lower frequencies (13 - 65 cm^{-1}) in metal complexes, showing that coordination is taking place through sulphur atom of ligand.

In addition to the above bands the following bands have also been assigned. The bands appearing ~ 1512 - 1590cm^{-1} and ~1270 - 1390 cm^{-1} have been assigned to δ_{as} (NH) and δ_{s} (NH), respectively.

Assigning the band for $\nu(C = C + C = N)$ is very important in deciding whether the heterocyclic nitrogen is involved in coordination or not. This band has been reported to be shifted to higher frequencies in case of coordinated pyridyl nitrogen.[40] An increase by 20 - 52 cm^{-1} in $\nu(C = C + C = N)$ shows that pyridyl ring nitrogen is involved in bond formation.

The other possible sites for co-ordination are nitrogen and sulphur in the ligand. A shift 13 - 65 cm^{-1} of $\nu(C = S)$ in complexes and lowering of intensity favour coordination through sulphur of the thiourea unit making thereby d^2sp^3 hybridization having octahedral structure. Hence, the possible structure of complex compounds can be represented by structure I. Insolubility of thesese complexes in suitable solvents precluded the molecular weight determination.



STRUCTURE I COMPLEX STRUCTURE OF $NbCl_5$ WITH N-ARYL N-2 (MONOSUBSTITUTED PYRIDYL) THIOUREAS.

FOR :—

$[NbCl_4 . PTU]Cl$; $R = -C_6H_5$; $W = H$; $X = H$; $Y = H$; $Z = H$

$[NbCl_4 . P4MeTU]Cl$; $R = -C_6H_5$; $W = H$; $X = CH_3$; $Y = H$; $Z = H$

$[NbCl_4 . P6MeTU]Cl$; $R = -C_6H_5$; $W = H$; $X = H$; $Y = H$; $Z = CH_3$

$[NbCl_4 . oTTU]Cl$; $R = -C_6H_4\underset{ortho}{(CH_3)}$; $W = H$; $X = H$; $Y = H$; $Z = H$

$[NbCl_4 . oT4MeTU]Cl$; $R = -C_6H_5\underset{ortho}{(CH_3)}$; $W = H$; $X = CH_3$; $Y = H$; $Z = H$

$[NbCl_4 . oT6MeTU]Cl$; $R = -C_6H_4\underset{ortho}{(CH_3)}$; $W = H$; $X = H$; $Y = H$; $Z = -CH_3$

$[NbCl_4 . pTTU]Cl$; $R = -C_6H_4\underset{para}{(CH_3)}$; $W = H$; $X = H$; $Y = H$; $Z = CH_3$

$[NbCl_4 . pT4MeTU]Cl$; $R = -C_6H_4\underset{para}{(CH_3)}$; $W = H$; $X = -CH_3$; $Y = H$; $Z = H$

$[NbCl_4 . pT6MeTU]Cl$; $R = -C_6H_4\underset{para}{(CH_3)}$; $W = H$; $X = H$; $Y = H$; $Z = -CH_3$

$NbCl_5$ also formed complexes with 1,5 disubstituted 2,4-dithiobiurets and 1,5 disubstituted 2-thioubiurets in tetra hydrofuran medium. Their compositions, melting points and percentages of various elements are reported in table 3.02, indicating the general emperical formula $NbCl_5 \cdot L$, where L is a molecule of bidentate ligand.

The conductance studies in freshly distilled N,N-dimethyl formamide indicate the electrolytic nature of the complexes. The molar conductance values are in the range of 80.66 - 93.22 mhos, which corresponds to 1:1 electrolyte in this solvent.[90] The negative values of magnetic susceptibility $-.294 \times 10^{-5}$ to $-.543 \times 10^{-5}$ (Table 3.10) suggests that complexes are diamagnetic and all the electrons are paired as was observed in the case of substituted thioureas complexes also.

On examination of the spectra of ligands and their niobium pentachloride complexes (Table 3.05 and 3.08) it has been observed that a medium strong band is present at 3120 - 3250 cm^{-1} which may be assigned to $\nu_s(NH)$ and $\nu_{as}(NH)$. In complexes $\nu(NH)$ stretching bands are observed at 3125 - 3170 cm^{-1} which are 5-25 cm^{-1} lower than those of the ligands. A similar observation for the $\nu(NH)$ stretch at 3250-3200 cm^{-1} was made by Stephen and Townshend[91] in the case of dithiobiurets and their silver complexes.

A medium strong intensity band is also observed at 1[illegible] - 1025 cm^{-1} in ligands and 1585 - 1020 cm^{-1} in complexes, which may be assigned to N-H bending vibrations. Another strong band appearing at 1435 - 1502 cm^{-1} in ligands and 1415 - 1480 cm^{-1} in complexes may be mixed band of N-H bending, C-N stretching and C=S stretching vibrations.

A medium intensity band appearing at 1227 - 1295 cm^{-1} in dithiobiurets shifted to 1200 - 1275 cm^{-1} with medium intensity in complexes appears to be due to C = S vibrations. The band at 745 - 795 cm^{-1} in DPDTB, D-o-TDTB, D-p-TDTB, P-o-TDTB and p-TPDTB is mainly due to C=S stretching vibrations, having a little contribution of C-N stretching vibrations. This band has been observed at 700-780 cm^{-1} (15-45 cm^{-1} lower than in ligands) with medium or weak intensity in the complexes (Tables 3.05 and 3.08) indicating coordination is taking place through sulphur atom of the ligand.

In thiobiurets a band of medium intensity occurs in the region 1710-1715 cm^{-1}, which is observed to be stronger than usual ketone C=O band. On chelation with $NbCl_5$ this peak is shifted to lower frequency 1640 -.1710 (~75 cm^{-1}), indicating chelation through C=O group.

On comparing the i.r. spectra of ligands and complexes the donor sites present are two sulphur atoms of thiocarbonyl groups in 1,5-disubstituted 2,4-dithiobiurets, [illegible] and oxygen atoms in 1,5-disubstituted 2-thiobiurets and one of the nitrogen of the NH groups.

The decrease in C=S stretching frequencies (15-45 cm^{-1}) on complexation is more than the decrease in N-H stretching (5-15 cm^{-1}) and NH bending vibrations (Table 305) Thus the nitrogen of the NH group as a donor is not favoured.

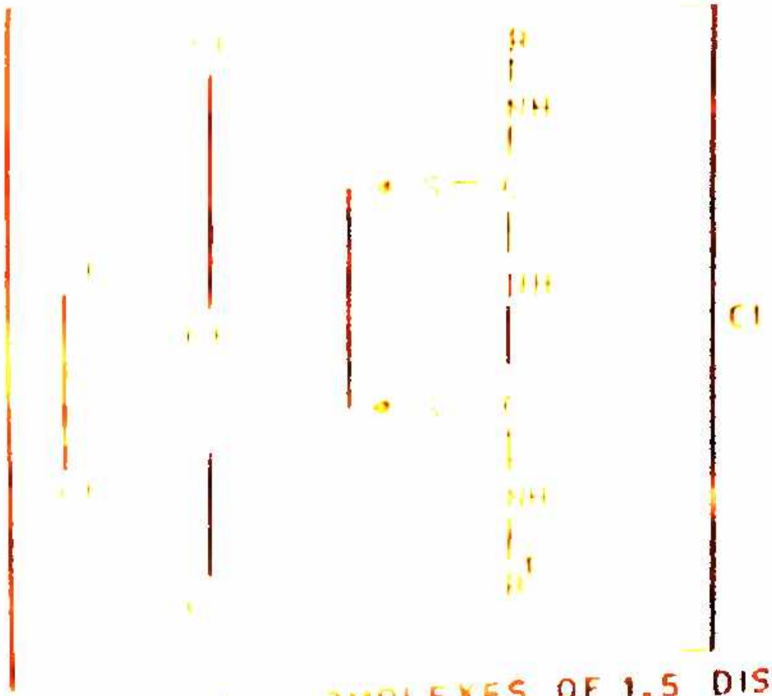
Srivastava and Agarwal[92] showed by their potentiometric studies on the oxidation of dithiobiurets and their complexes that ligands are oxidized by iodine to dithiazolidine, but in the case of complexes no oxidation to dithiazolidines occurred. This is because of the chelation through sulphur atoms of the two thiocarbonyl groups giving a very stable complex.

Insolubility of these complexes in suitable solvents precluded the molecular weight determination.

On the basis of the results of elemental analysis, molar conductance magnetic susceptibility and i.r. spectra, it seems that complexes with 1,5 disubstituted 2,4 dithiobiuret and 1,5 disubstituted 2 thiobiurets are formed. All the complexes seem to have $d^2 sp^3$ hybridization having octahedral structure.

The complex compounds may be represented as structure II & III.

In these complexes chelation takes place through two sulphur atoms in dithiobiurets and sulphur and oxygen atoms in thiobiurets respectively.



STRUCTURE II NbCl$_4$ COMPLEXES OF 1,5 DISUBSTITUTED 2,4 DITHIOBIURETS.

[illegible]

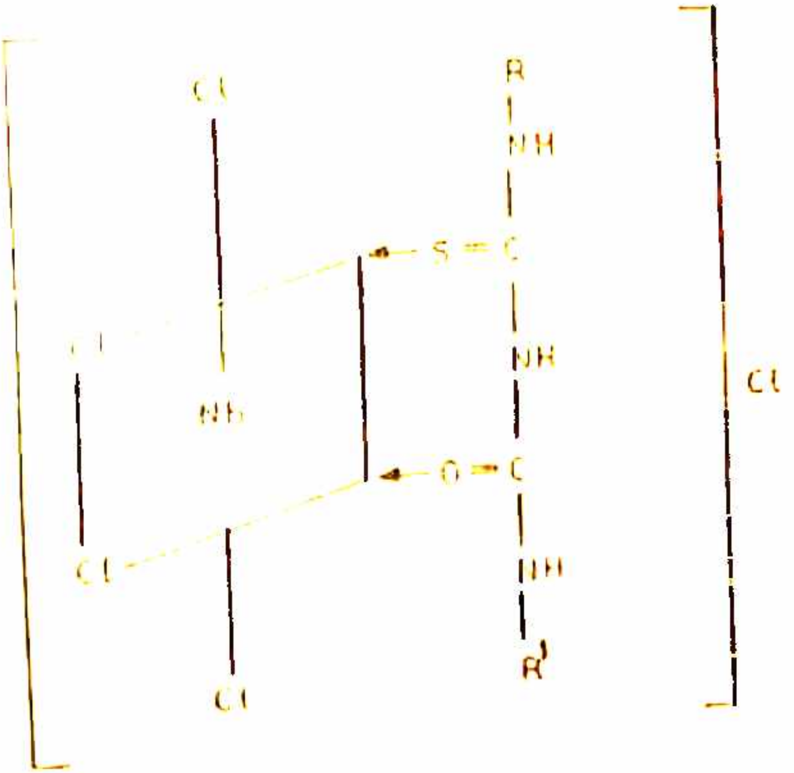
[illegible] | [illegible], R = -C_6H_5, R^1 = -C_6H_5

[illegible] | [illegible], R = -C_6H_5, R^1 = -$C_6H_4(CH_3)$ ortho

[NbCl$_4$ [illegible]] | Cl, R = -C_6H_5, R^1 = -$C_6H_4(CH_3)$ para

NbCl$_4$ (O-O [illegible]) | Cl, R = -$C_6H_4(CH_3)$ ortho, R^1 = -$C_6H_4(CH_3)$ ortho

[NbCl$_4$ [illegible]] | Cl, R = -$C_6H_4(CH_3)$ para, R^1 = -$C_6H_4(CH_3)$ para



STRUCTURE. III — $NbCl_5$ COMPLEXES OF 1,5 DISUBSTITUTED 2 — THIOBIURETS.

FOR :-

[$NbCl_4$. DPTB] Cl, R = $-C_6H_5$; R' = $-C_6H_5$

[$NbCl_4$ P-o-TTB] Cl; R = $-C_6H_5$; R' = $-C_6H_4(CH_3)$ ortho

[$NbCl_4$. P-p-TTB] Cl; R = $-C_6H_4(CH_3)$ para ; R' = $-C_6H_5$

$NbCl_5$ also formed complexes with benzimidazole and acridine. The composition, melting points and percentages of various elements are reported in table 3.03, showing that benzimidazole formed complex with 1:4 stoichiometry, whereas acridine formed complex with 1:1 stoichiometry (Table 3.03)

The molar conductance of benzimidazole and acridine complex in dimethyl formamide at the concentration of 10^{-3}M are 172.00 and 90.42 indicating 1:2[93] and 1:1[90] electrolytes respectively (Table 3.10). The negative values of magnetic susceptibility -0.434×10^{-6} and -0.868×10^{-6} indicate that complexes are diamagnetic and therefore all the electrons are paired.

On comparing i.r. spectra of benzimidazole and its complex with $NbCl_5$ (Table 3.06, Fig. 3.27 to 3.30), it is observed that a broad band ~ 3505 cm^{-1} appears in ligand, whereas a medium intensity appears at 3500 cm^{-1} in complex, these bands are due to N-H stretch of - NH group of benzimidazole. A weak band in the case of complex indicates that O-H band of moisture (either from KBr or complex) is overlapping with N-H band, which is confirmed by appearance of a weak band at 3000 cm^{-1}. A similar observation was made by Srivastava[93] while studying molybdenum amine complexes.

A sharp band at 1600 cm^{-1} in benzimidazole is assigned to $C = N + C = C$ stretching vibration in view of the previous assignments by Morgan[94] and Harkins et al.[95] This band appears around 1615 cm^{-1}, an increase by 15 cm^{-1}, indicating that coordination is taking place through unsaturated nitrogen of the imidazole ring of ligand as was observed by Biradar and Gaudar.[0]

In addition to the bands assigned above, a band appearing at 1225 cm^{-1} in ligand and at 1220 cm^{-1} in complex can be assigned to C-N stretch vibrations.

Since benzimidazole complex has $NbCl_5$: ligand stoichiometry as 1:4 and corresponds to 1:2 electrolyte and coordinates through unsaturated nitrogen of imidazole ring, it is very difficult to assign a definite structure to the complex. It seems probable that in this complex $NbCl_5$ forms a seven co-ordinated complex. On comparing i.r. spectra of acridine and its complex, it is observed that a band appearing at 1610 cm^{-1} in acridine, which may be assigned to C=C+C=N stretching vibrations is shifted to 1625 cm^{-1} in complex. An increase of 15 cm^{-1} shows coordination through nitrogen atom.

It is further confirmed by a band appearing at 1362 cm^{-1} in ligand, which may be assigned to C-N stretching vibrations, is observed at 1375 cm^{-1} in complex, which means an increase of 13 cm^{-1}. Since acridine contains only one donor atom there is no possibility of coordination with any other atom except nitrogen of ligand.

From table 3.03 it is evident that acridine also formed 1:1 complex as in case of substituted thioureas, 1,5 disubstituted 2,4 dithiobiuret and 1,5-disubstituted 2-thiobiurets and also corresponds to 1:1 electrolyte. From the above data it appears that acridine complex is a plymeric one, in which Niobium atom has metal-metal bonding.

TABLE - 3.11

Electrical Conductivity of $NbCl_5$.PTU Complex at different Temperatures

S.N.	Temperature (^oK) (T)	$\frac{1}{T} \times 10^3 (^oK^{-1})$	σ ($Ohm^{-1}Cm^{-1}$)	Logσ ($Ohm^{-1}Cm^{-1}$)
1.	303	3.30	3.25×10^{-15}	$\overline{15}.51$
2.	313	3.20	2.25×10^{-14}	$\overline{14}.35$
3.	323	3.10	6.95×10^{-14}	$\overline{14}.84$
4.	333	3.00	3.18×10^{-13}	$\overline{13}.50$
5.	343	2.92	8.34×10^{-13}	$\overline{13}.92$
6.	353	2.83	2.25×10^{-12}	$\overline{12}.35$
7.	363	2.76	8.17×10^{-12}	$\overline{12}.91$
8.	373	2.68	2.53×10^{-11}	$\overline{11}.40$
9.	383	2.61	8.34×10^{-11}	$\overline{11}.92$
10.	393	2.54	2.83×10^{-10}	$\overline{10}.45$
11.	403	2.48	6.47×10^{-10}	$\overline{10}.81$
12.	413	2.42	1.26×10^{-9}	$\overline{9}.10$
13.	423	2.36	2.52×10^{-9}	$\overline{9}.40$

TABLE - 3.12

Electrical Conductivity of $NbCl_5$.oTTU Complex at different Temperatures

S.N.	Temperature(°K) (T)	$\frac{1}{T} \times 10^3 (°K^{-1})$	$\sigma (Ohm^{-1}cm^{-1})$	$\log \sigma (Ohm^{-1}cm^{-1})$
1.	303	3.30	7.43×10^{-15}	$\overline{15}.87$
2.	313	3.20	4.08×10^{-14}	$\overline{14}.61$
3.	323	3.10	1.45×10^{-13}	$\overline{13}.16$
4.	333	3.00	4.58×10^{-13}	$\overline{13}.66$
5.	343	2.92	1.32×10^{-12}	$\overline{12}.12$
6.	353	2.83	6.46×10^{-12}	$\overline{12}.81$
7.	363	2.76	1.45×10^{-11}	$\overline{11}.16$
8.	373	2.68	6.93×10^{-11}	$\overline{11}.84$
9.	383	2.61	1.42×10^{-10}	$\overline{10}.15$
10.	393	2.54	3.19×10^{-10}	$\overline{10}.50$
11.	403	2.48	1.03×10^{-9}	$\overline{9}.01$
12.	413	2.42	2.30×10^{-9}	$\overline{9}.36$
13.	423	2.36	5.15×10^{-9}	$\overline{9}.71$

TABLE - 3.13

Electrical Conductivity of $NbCl_5$.p TTU Complex at different Temperatures

S.N.	Temperature(^oK) (T)	$\frac{1}{T} \times 10^3 (^oK^{-1})$	$\sigma (Ohm^{-1}cm^{-1})$	$Log\sigma (Ohm^{-1}cm^{-1})$
1.	303	3.30	6.18×10^{-14}	$\bar{14}.79$
2.	313	3.20	1.70×10^{-13}	$\bar{13}.23$
3.	323	3.10	7.60×10^{-13}	$\bar{13}.88$
4.	333	3.00	2.58×10^{-12}	$\bar{12}.41$
5.	343	2.92	6.49×10^{-12}	$\bar{12}.81$
6.	353	2.83	2.24×10^{-11}	$\bar{11}.35$
7.	363	2.76	4.92×10^{-11}	$\bar{11}.69$
8.	373	2.68	1.24×10^{-10}	$\bar{10}.09$
9.	383	2.61	2.05×10^{-10}	$\bar{10}.31$
10.	393	2.54	6.61×10^{-10}	$\bar{10}.82$
11.	403	2.48	2.04×10^{-9}	$\bar{9}.31$
12.	413	2.42	4.92×10^{-9}	$\bar{9}.69$
13.	423	2.36	9.55×10^{-9}	$\bar{9}.98$

TABLE - 3.14

Electrical conductivity of $NbCl_5$.P4Me.TU Complex at different Temperatures

S.N.	Temperature (^{o}K) (T)	$\frac{1}{T} \times 10^3$ ($^{o}K^{-1}$)	σ ($Ohm^{-1}Cm^{-1}$)	Log σ ($Ohm^{-1}Cm^{-1}$)
1.	303	3.30	1.42×10^{-10}	$\overline{10}.15$
2.	313	3.20	2.97×10^{-10}	$\overline{10}.47$
3.	323	3.10	8.36×10^{-10}	$\overline{10}.92$
4.	333	3.00	1.79×10^{-9}	$\overline{9}.25$
5.	343	2.92	3.99×10^{-9}	$\overline{9}.60$
6.	353	2.83	7.62×10^{-9}	$\overline{9}.88$
7.	363	2.76	1.87×10^{-8}	$\overline{8}.27$
8.	373	2.68	2.97×10^{-8}	$\overline{8}.47$
9.	383	2.61	5.64×10^{-8}	$\overline{8}.75$
10.	393	2.54	1.59×10^{-7}	$\overline{7}.20$
11.	403	2.48	2.71×10^{-7}	$\overline{7}.43$
12.	413	2.42	4.18×10^{-7}	$\overline{7}.62$
13.	423	2.36	5.65×10^{-7}	$\overline{7}.75$

TABLE - 3.15

Electrical Conductivity of $NbCl_5$.o T 4MeTU Complex at different Temperatures

S.N.	Temperature (°K) (T)	$\frac{1}{T} \times 10^3 (^oK^{-1})$	σ $(Ohm^{-1}Cm^{-1})$	Logσ $(Ohm^{-1}Cm^{-1})$
1.	303	3.30	2.05×10^{-10}	$\overline{10}.31$
2.	313	3.20	4.28×10^{-10}	$\overline{10}.63$
3.	323	3.10	1.56×10^{-9}	$\overline{9}.19$
4.	333	3.00	4.19×10^{-9}	$\overline{9}.62$
5.	343	2.92	6.85×10^{-9}	$\overline{9}.83$
6.	353	2.83	1.66×10^{-8}	$\overline{8}.22$
7.	363	2.76	4.37×10^{-8}	$\overline{8}.64$
8.	373	2.68	9.35×10^{-8}	$\overline{8}.97$
9.	383	2.61	1.56×10^{-7}	$\overline{7}.19$
10.	393	2.54	2.35×10^{-7}	$\overline{7}.37$
11.	403	2.48	4.17×10^{-7}	$\overline{7}.62$
12.	413	2.42	7.30×10^{-7}	$\overline{7}.86$
13.	423	2.36	1.21×10^{-6}	$\overline{6}.08$

TABLE - 3.16

Electrical Conductivity of $NbCl_5 \cdot pT4MeTU$ Complex at different Temperatures

S.N.	Temperature (^{o}K) (T)	$\frac{1}{T} \times 10^{3}$ ($^{o}K^{-1}$)	σ ($Ohm^{-1}Cm^{-1}$)	Log σ ($Ohm^{-1}Cm^{-1}$)
1.	303	3.30	5.28×10^{-10}	$\overline{10}.72$
2.	313	3.20	1.05×10^{-9}	$\overline{9}.02$
3.	323	3.10	3.04×10^{-9}	$\overline{9}.48$
4.	333	3.00	5.91×10^{-9}	$\overline{9}.77$
5.	343	2.92	1.33×10^{-8}	$\overline{8}.12$
6.	353	2.83	3.48×10^{-8}	$\overline{8}.54$
7.	363	2.76	8.75×10^{-8}	$\overline{8}.94$
8.	373	2.68	1.38×10^{-7}	$\overline{7}.14$
9.	383	2.61	2.25×10^{-7}	$\overline{7}.35$
10.	393	2.54	4.18×10^{-7}	$\overline{7}.62$
11.	403	2.48	5.66×10^{-7}	$\overline{7}.75$
12.	413	2.42	7.46×10^{-7}	$\overline{7}.87$
13.	423	2.36	2.19×10^{-6}	$\overline{6}.14$

TABLE - 3.17

Electrical Conductivity of $NbCl_5$. P6MeTU complex at different Temperatures

S.N.	Temperature (^oK) (T)	$\frac{1}{T} \times 10^3 (^oK^{-1})$	$\sigma (Ohm^{-1}Cm^{-1})$	$Log \sigma (Ohm^{-1}Cm^{-1})$
1.	303	3.30	2.24×10^{-15}	$\overline{15}.35$
2.	313	3.20	9.55×10^{-15}	$\overline{15}.98$
3.	323	3.10	4.79×10^{-14}	$\overline{14}.68$
4.	333	3.00	2.05×10^{-13}	$\overline{13}.31$
5.	343	2.92	5.65×10^{-13}	$\overline{13}.75$
6.	353	2.83	2.19×10^{-12}	$\overline{12}.34$
7.	363	2.76	7.08×10^{-12}	$\overline{12}.85$
8.	373	2.68	2.57×10^{-11}	$\overline{11}.41$
9.	383	2.61	1.15×10^{-10}	$\overline{10}.06$
10.	393	2.54	4.19×10^{-10}	$\overline{10}.62$
11.	403	2.48	9.16×10^{-10}	$\overline{10}.96$
12.	413	2.42	1.82×10^{-9}	$\overline{9}.26$
13.	423	2.36	4.09×10^{-9}	$\overline{9}.61$

TABLE - 3.18

Electrical Conductivity of $NbCl_5$. oT 6MeTU Complex at different Temperatures

S.N.	Temperature (°K) (T)	$\frac{1}{T} \times 10^3 (^oK^{-1})$	σ (Ohm^{-1}cm^{-1})	Log σ (Ohm^{-1}cm^{-1})
1.	303	3.30	8.73×10^{-14}	$\overline{14}.94$
2.	313	3.20	4.18×10^{-13}	$\overline{13}.62$
3.	323	3.10	1.35×10^{-12}	$\overline{12}.13$
4.	333	3.00	4.37×10^{-12}	$\overline{12}.64$
5.	343	2.92	1.03×10^{-11}	$\overline{11}.01$
6.	353	2.83	3.48×10^{-11}	$\overline{11}.54$
7.	363	2.76	1.15×10^{-10}	$\overline{10}.06$
8.	373	2.68	4.58×10^{-10}	$\overline{10}.66$
9.	383	2.61	8.55×10^{-10}	$\overline{10}.93$
10.	393	2.54	3.80×10^{-9}	$\overline{9}.58$
11.	403	2.48	8.17×10^{-9}	$\overline{9}.91$
12.	413	2.42	1.42×10^{-8}	$\overline{8}.15$
13.	423	2.36	2.57×10^{-8}	$\overline{8}.41$

TABLE - 3.19

Electrical Conductivity of $NbCl_5$.pT6MeTUT Complex at different Temperatures

S.N.	Temperature(°K) (T)	$\frac{1}{T} \times 10^3 (^\circ K^{-1})$	σ (Ohm^{-1}cm^{-1})	Logσ (Ohm^{-1}cm^{-1}
1.	303	3.30	3.03×10^{-13}	$\overline{13}.48$
2.	313	3.20	7.11×10^{-3}	$\overline{13}.85$
3.	323	3.10	2.52×10^{-12}	$\overline{12}.40$
4.	333	3.00	9.55×10^{-12}	$\overline{12}.98$
5.	343	2.92	2.41×10^{-11}	$\overline{11}.38$
6.	353	2.83	8.95×10^{-11}	$\overline{11}.95$
7.	363	2.76	2.35×10^{-10}	$\overline{10}.37$
8.	373	2.68	4.92×10^{-10}	$\overline{10}.69$
9.	383	2.61	1.92×10^{-9}	$\overline{9}.28$
10.	393	2.54	5.28×10^{-9}	$\overline{9}.72$
11.	403	2.48	9.35×10^{-9}	$\overline{9}.97$
12.	413	2.42	1.36×10^{-8}	$\overline{8}.13$
13.	423	2.36	3.33×10^{-8}	$\overline{8}.52$

TABLE - 3.20

Electrical Conductivity of $NbCl_5$. DPDTB Complex at different Temperatures

S.N.	Temperature(^oK) (T)	$\frac{1}{T} \times 10^3 (^oK^{-1})$	$\sigma\ (Ohm^{-1}Cm^{-1})$	$Log\sigma\ (Ohm^{-1}Cm^{-1})$
1.	303	3.30	1.95×10^{-8}	$\bar{8}.29$
2.	313	3.20	4.48×10^{-8}	$\bar{8}.65$
3.	323	3.10	1.32×10^{-7}	$\bar{7}.12$
4.	333	3.00	3.40×10^{-7}	$\bar{7}.53$
5.	343	2.92	6.04×10^{-7}	$\bar{7}.78$
6.	353	2.83	1.13×10^{-6}	$\bar{6}.05$
7.	363	2.76	2.52×10^{-6}	$\bar{6}.40$
8.	373	2.68	4.19×10^{-6}	$\bar{6}.62$
9.	383	2.61	6.78×10^{-6}	$\bar{6}.83$
10.	393	2.54	1.13×10^{-5}	$\bar{5}.05$
11.	403	2.48	1.78×10^{-5}	$\bar{5}.25$
12.	413	2.42	2.90×10^{-5}	$\bar{5}.46$
13.	423	2.36	4.69×10^{-5}	$\bar{5}.67$

TABLE - 3.21

Electrical Conductivity of $NbCl_5$. DPTB Complex at different Temperatures.

S.N.	Temperature(^{o}K) (T)	$\frac{1}{T}x10^3(^{o}K^{-1})$	σ (Ohm^{-1}Cm^{-1})	Log σ (Ohm^{-1}Cm^{-1})
1.	303	3.30	1.55×10^{-8}	$\bar{8}.19$
2.	313	3.20	3.64×10^{-8}	$\bar{8}.56$
3.	323	3.10	8.15×10^{-8}	$\bar{8}.91$
4.	333	3.00	1.87×10^{-7}	$\bar{7}.27$
5.	343	2.92	3.56×10^{-7}	$\bar{7}.55$
6.	353	2.83	7.60×10^{-7}	$\bar{7}.88$
7.	363	2.76	1.23×10^{-6}	$\bar{6}.09$
8.	373	2.68	2.25×10^{-6}	$\bar{6}.35$
9.	383	2.61	3.72×10^{-6}	$\bar{6}.57$
10.	393	2.54	5.90×10^{-6}	$\bar{6}.77$
11.	403	2.48	1.03×10^{-5}	$\bar{5}.01$
12.	413	2.42	1.59×10^{-5}	$\bar{5}.20$
13.	423	2.36	2.64×10^{-5}	$\bar{5}.42$

TABLE - 3.22

Electrical Conductivity of $NbCl_5$.D-o-TDTB Complex at different Temperatures

S.N.	Temperature (°K) (T)	$\frac{1}{T} \times 10^3$ (°K^{-1})	σ ($Ohm^{-1}cm^{-1}$)	Logσ ($Ohm^{-1}cm^{-1}$)
1.	303	3.30	2.64×10^{-8}	$\bar{8}.42$
2.	313	3.20	5.14×10^{-8}	$\bar{8}.71$
3.	323	3.10	8.95×10^{-8}	$\bar{8}.95$
4.	333	3.00	1.74×10^{-7}	$\bar{7}.24$
5.	343	2.92	3.25×10^{-7}	$\bar{7}.51$
6.	353	2.83	6.47×10^{-7}	$\bar{7}.81$
7.	363	2.76	1.26×10^{-6}	$\bar{6}.09$
8.	373	2.68	2.40×10^{-6}	$\bar{6}.38$
9.	383	2.61	4.80×10^{-6}	$\bar{6}.68$
10.	393	2.54	8.15×10^{-6}	$\bar{6}.91$
11.	403	2.48	1.45×10^{-5}	$\bar{5}.16$
12.	413	2.42	2.14×10^{-5}	$\bar{5}.33$
13.	423	2.36	3.10×10^{-5}	$\bar{5}.49$

TABLE - 3.23

Electrical Conductivity of $NbCl_5$.D-p-TDTB Complex at different Temperatures

S.N.	Temperature (^oK) (T)	$\frac{1}{T} \times 10^3 (^oK^{-1})$	σ ($Ohm^{-1} cm^{-1}$)	Log σ ($Ohm^{-1} cm^{-1}$)
1.	303	3.30	1.66×10^{-7}	$\bar{7}.22$
2.	313	3.20	3.81×10^{-7}	$\bar{7}.58$
3.	323	3.10	7.60×10^{-7}	$\bar{7}.88$
4.	333	3.00	1.45×10^{-6}	$\bar{6}.16$
5.	343	2.92	2.25×10^{-6}	$\bar{6}.35$
6.	353	2.83	3.56×10^{-6}	$\bar{6}.55$
7.	363	2.76	6.31×10^{-6}	$\bar{6}.80$
8.	373	2.68	1.00×10^{-5}	$\bar{5}.00$
9.	383	2.61	1.35×10^{-5}	$\bar{5}.13$
10.	393	2.54	1.78×10^{-5}	$\bar{5}.25$
11.	403	2.48	3.48×10^{-5}	$\bar{5}.54$
12.	413	2.42	1.00×10^{-4}	$\bar{4}.00$
13.	423	2.36	1.36×10^{-4}	$\bar{4}.13$

TABLE - I.24

Electrical conductivity of $NbCl_5$. P-o-TDTB Complex at different Temperatures

S.N.	Temperature(^oK) (T)	$\frac{1}{T} \times 10^3 (^oK^{-1})$	σ ($Ohm^{-1}cm^{-1}$)	Logσ ($Ohm^{-1}cm^{-1}$)
1.	303	3.30	2.51×10^{-7}	$\bar{7}.40$
2.	313	3.20	4.78×10^{-7}	$\bar{7}.68$
3.	323	3.10	1.00×10^{-6}	$\bar{6}.00$
4.	333	3.00	2.35×10^{-6}	$\bar{6}.37$
5.	343	2.92	4.80×10^{-6}	$\bar{6}.68$
6.	353	2.83	1.05×10^{-5}	$\bar{5}.02$
7.	363	2.76	1.78×10^{-5}	$\bar{5}.25$
8.	373	2.68	2.63×10^{-5}	$\bar{5}.42$
9.	383	2.61	4.18×10^{-5}	$\bar{5}.62$
10.	393	2.54	6.47×10^{-5}	$\bar{5}.81$
11.	403	2.48	9.57×10^{-5}	$\bar{5}.98$
12.	413	2.42	1.42×10^{-4}	$\bar{4}.15$
13.	423	2.36	2.14×10^{-4}	$\bar{4}.33$

TABLE - 3.25

[illegible] Conductivity of $NbCl_5$.P-p-TDTB Complex at different Temperatures

S.N.	Temperature (°K) (T)	$\frac{1}{T} \times 10^3$ (°K^{-1})	σ ($Ohm^{-1}cm^{-1}$)	Log σ ($Ohm^{-1}cm^{-1}$)
1.	303	3.30	1.07×10^{-7}	$\bar{7}.03$
2.	313	3.20	2.05×10^{-7}	$\bar{7}.31$
3.	323	3.10	5.15×10^{-7}	$\bar{7}.71$
4.	333	3.00	1.26×10^{-6}	$\bar{6}.10$
5.	343	2.92	2.51×10^{-6}	$\bar{6}.40$
6.	353	2.83	5.64×10^{-6}	$\bar{6}.75$
7.	363	2.76	1.32×10^{-5}	$\bar{5}.12$
8.	373	2.68	2.69×10^{-5}	$\bar{5}.43$
9.	383	2.61	5.14×10^{-5}	$\bar{5}.71$
10.	393	2.54	7.96×10^{-5}	$\bar{5}.90$
11.	403	2.48	1.32×10^{-4}	$\bar{4}.12$
12.	413	2.42	1.78×10^{-4}	$\bar{4}.25$
13.	423	2.36	2.35×10^{-4}	$\bar{4}.37$

TABLE - 3.26

Electrical Conductivity of $NbCl_5$. H-o-TTB Complex at different Temperatures

S.N.	Temperature(°K) (T)	$\frac{1}{T} \times 10^3 (^oK^{-1})$	σ (Ohm^{-1}cm^{-1})	Log σ (Ohm^{-1}cm^{-1})
1.	303	3.30	1.55×10^{-7}	$\bar{7}.19$
2.	313	3.20	3.02×10^{-7}	$\bar{7}.48$
3.	323	3.10	4.69×10^{-7}	$\bar{7}.67$
4.	333	3.00	8.15×10^{-7}	$\bar{7}.91$
5.	343	2.92	1.35×10^{-6}	$\bar{6}.13$
6.	353	2.83	2.35×10^{-6}	$\bar{6}.37$
7.	363	2.76	3.82×10^{-6}	$\bar{6}.58$
8.	373	2.68	6.76×10^{-6}	$\bar{6}.83$
9.	383	2.61	1.20×10^{-5}	$\bar{5}.08$
10.	393	2.54	2.00×10^{-5}	$\bar{5}.30$
11.	403	2.48	3.32×10^{-5}	$\bar{5}.52$
12.	413	2.42	4.27×10^{-5}	$\bar{5}.63$
13.	423	2.36	6.78×10^{-5}	$\bar{5}.83$

TABLE - 3.27

Electrical Conductivity of $NbCl_5$. P-p-TTB Complex at different Temperatures

S.N.	Temperature(°K) (T)	$\frac{1}{T} \times 10^3 (°K^{-1})$	$\sigma (Ohm^{-1} cm^{-1})$	$Log\,\sigma (Ohm^{-1} cm^{-1})$
1.	303	3.30	1.42×10^{-7}	$\bar{7}.15$
2.	313	3.20	3.18×10^{-7}	$\bar{7}.50$
3.	323	3.10	6.62×10^{-7}	$\bar{7}.82$
4.	333	3.00	1.49×10^{-6}	$\bar{6}.17$
5.	343	2.92	2.83×10^{-6}	$\bar{6}.45$
6.	353	2.83	4.18×10^{-6}	$\bar{6}.62$
7.	363	2.76	6.02×10^{-6}	$\bar{6}.82$
8.	373	2.68	9.33×10^{-6}	$\bar{6}.97$
9.	383	2.61	1.42×10^{-5}	$\bar{5}.15$
10.	393	2.54	2.10×10^{-5}	$\bar{5}.32$
11.	403	2.48	3.03×10^{-5}	$\bar{5}.48$
12.	413	2.42	4.48×10^{-5}	$\bar{5}.65$
13.	423	2.36	7.13×10^{-5}	$\bar{5}.85$

TABLE - 3.28

Electrical Conductivity of $Nb(C_7H_6N_2)_4Cl_5$ complex at different Temperatures

S.N.	Temperature(^oK) (T)	$\frac{1}{T} \times 10^3 (^oK^{-1})$	$(Ohm^{-1}cm^{-1})$	Log $(Ohm^{-1}cm^{-1})$
1.	303	3.30	5.62×10^{-9}	$\bar{9}.75$
2.	313	3.20	1.09×10^{-8}	$\bar{8}.04$
3.	323	3.10	2.24×10^{-8}	$\bar{8}.35$
4.	333	3.00	4.17×10^{-8}	$\bar{8}.62$
5.	343	2.92	7.41×10^{-8}	$\bar{8}.87$
6.	353	2.83	1.10×10^{-7}	$\bar{7}.04$
7.	363	2.76	1.95×10^{-7}	$\bar{7}.29$
8.	373	2.68	3.31×10^{-7}	$\bar{7}.52$
9.	383	2.61	6.03×10^{-7}	$\bar{7}.78$
10.	393	2.54	1.15×10^{-6}	$\bar{6}.06$
11.	403	2.48	2.19×10^{-6}	$\bar{6}.34$
12.	413	2.42	3.31×10^{-6}	$\bar{6}.52$
13.	423	2.36	4.90×10^{-6}	$\bar{6}.69$

TABLE - 3.29

Electrical Conductivity of $NbCl_5.C_6H_4$ CHC_6H_4N Complex at different Temperatures

S.N.	Temperature (^oK) (T)	$\frac{1}{T}$ X 10^3 ($^oK^{-1}$)	σ ($Ohm^{-1}Cm^{-1}$)	Log σ ($Ohm^{-1}Cm^{-1}$)
1.	303	3.30	8.13×10^{-11}	$\overline{11}.91$
2.	313	3.20	2.75×10^{-11}	$\overline{10}.44$
3.	323	3.10	4.89×10^{-10}	$\overline{10}.69$
4.	333	3.00	1.15×10^{-9}	$\overline{9}.06$
5.	343	2.92	2.19×10^{-9}	$\overline{9}.34$
6.	353	2.83	6.76×10^{-9}	$\overline{9}.83$
7.	363	2.76	1.48×10^{-8}	$\overline{8}.17$
8.	373	2.68	2.82×10^{-8}	$\overline{8}.45$
9.	383	2.61	4.89×10^{-8}	$\overline{8}.69$
10.	393	2.54	7.76×10^{-8}	$\overline{8}.89$
11.	403	2.48	1.41×10^{-7}	$\overline{7}.15$
12.	413	2.42	2.24×10^{-7}	$\overline{7}.35$
13.	423	2.36	3.02×10^{-7}	$\overline{7}.48$

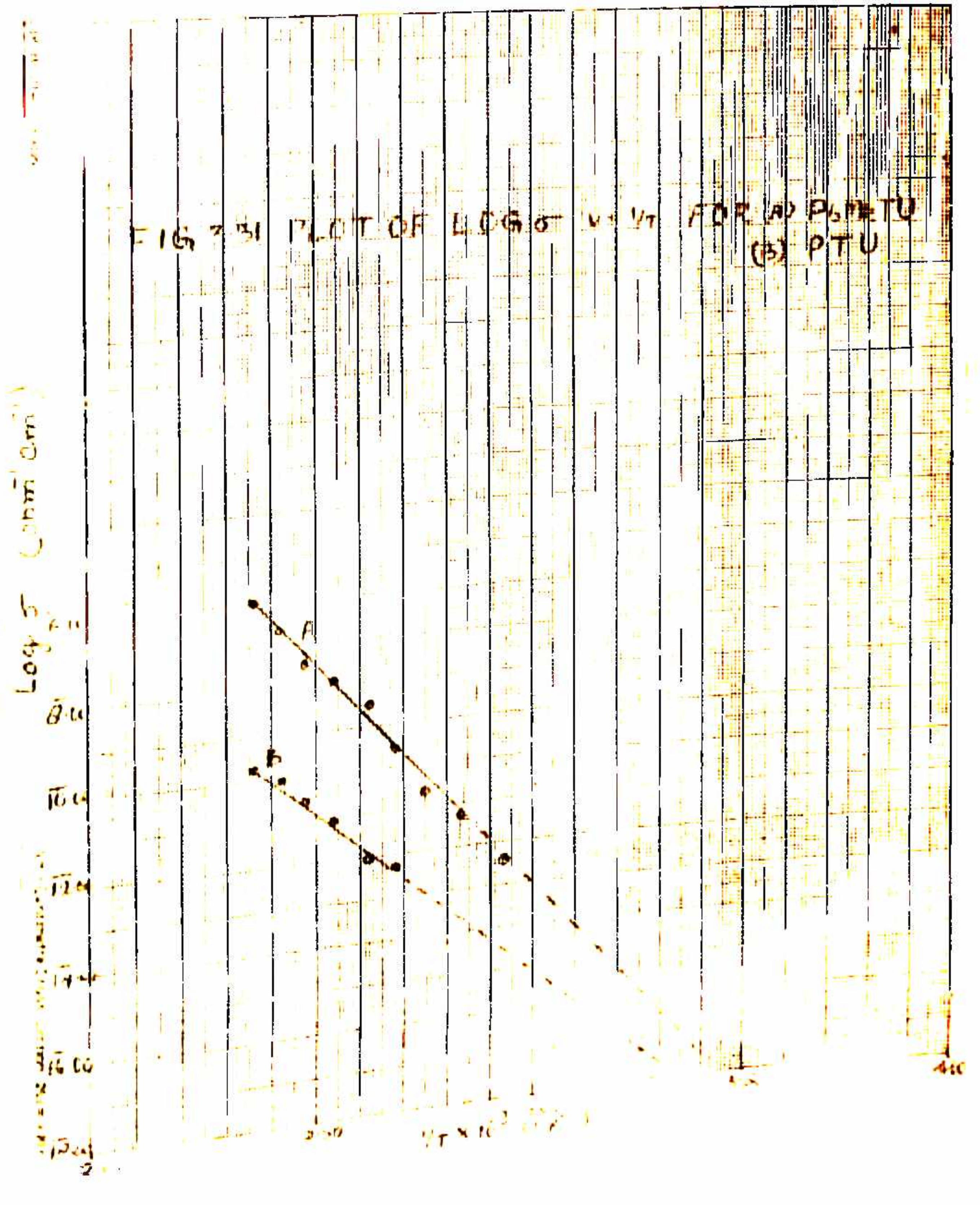


FIG 7.31 PLOT OF LOG σ v 1/T FOR (A) P6MeTU
(B) PTU

FIG 5·32 PLOT OF LOG σ vs 1/T FOR Nbcl5·PTU

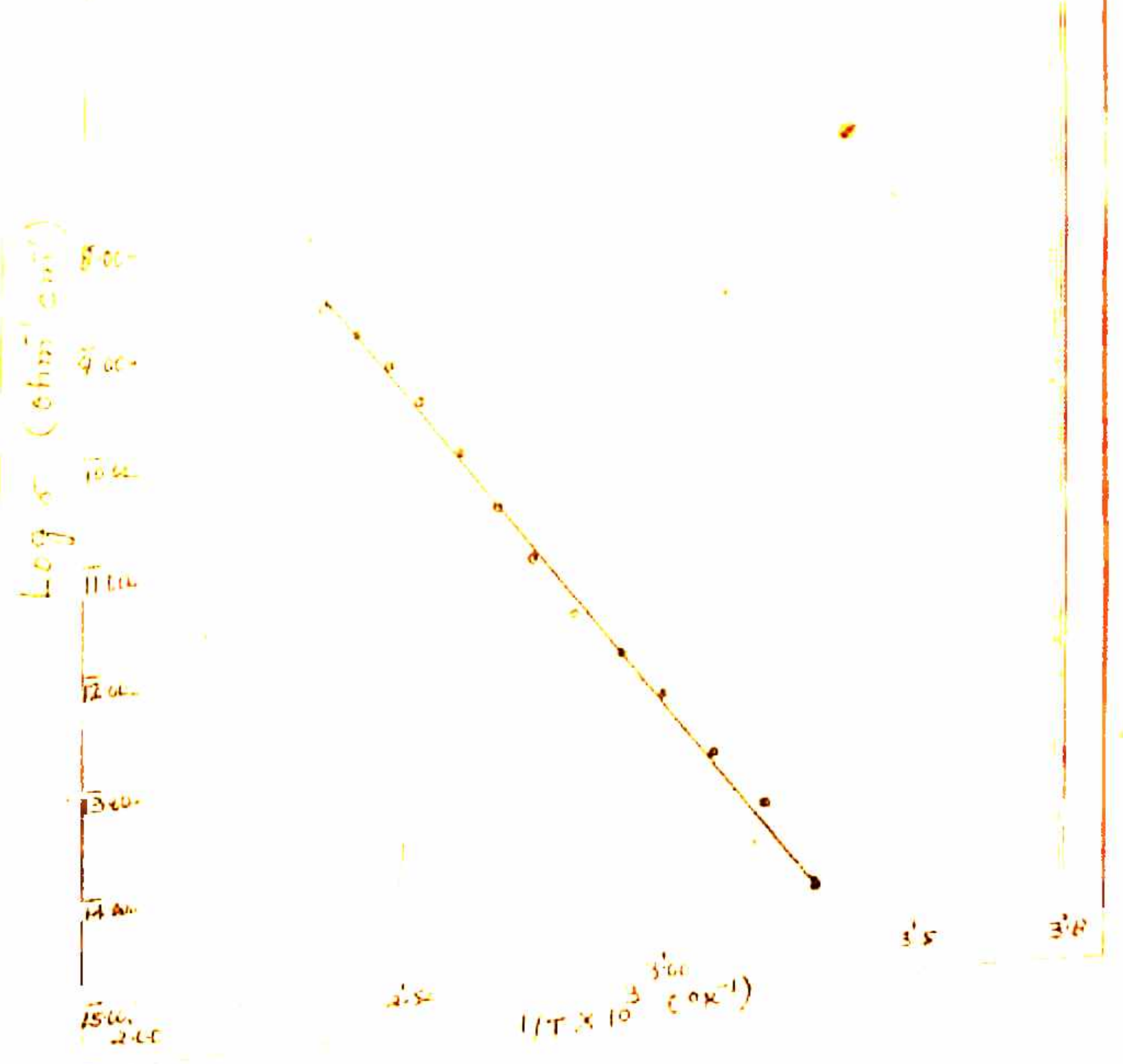


FIG. [illegible] PLOT OF LOG σ vs 1/T FOR NbCl5 oTTU

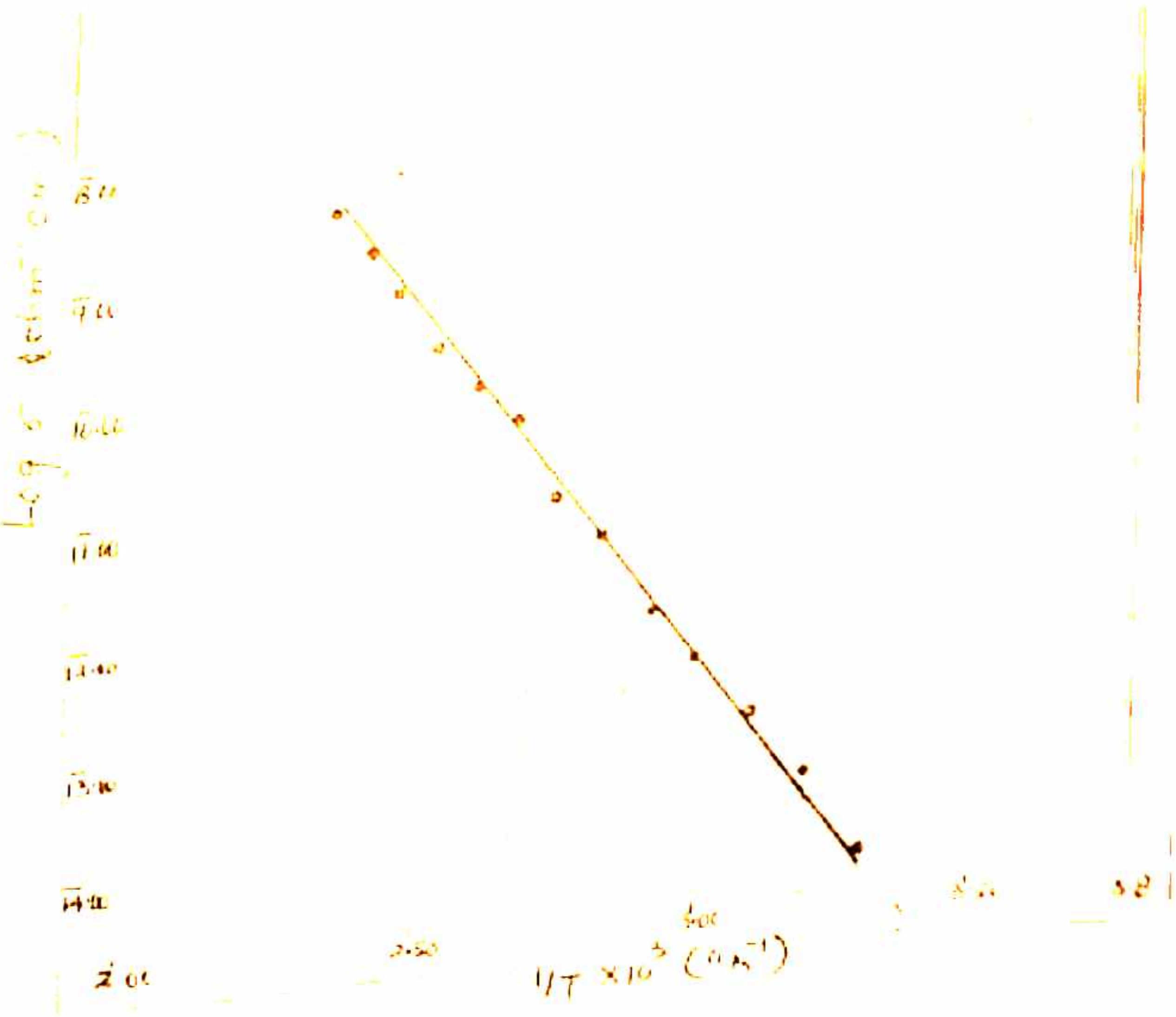


FIG 3.14 PLOT OF LOG σ vs 1/T FOR NbCl$_5$.HTTU

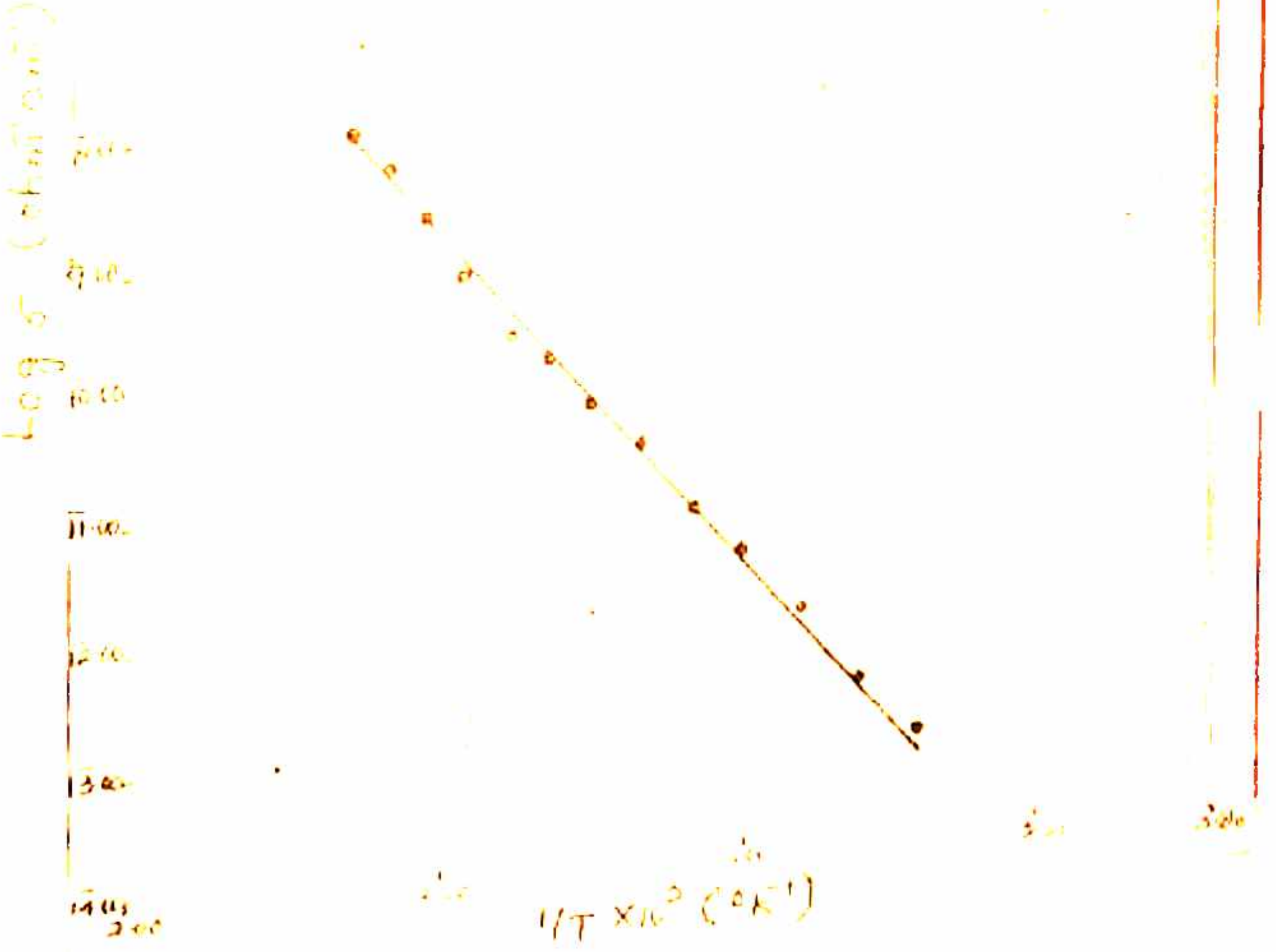
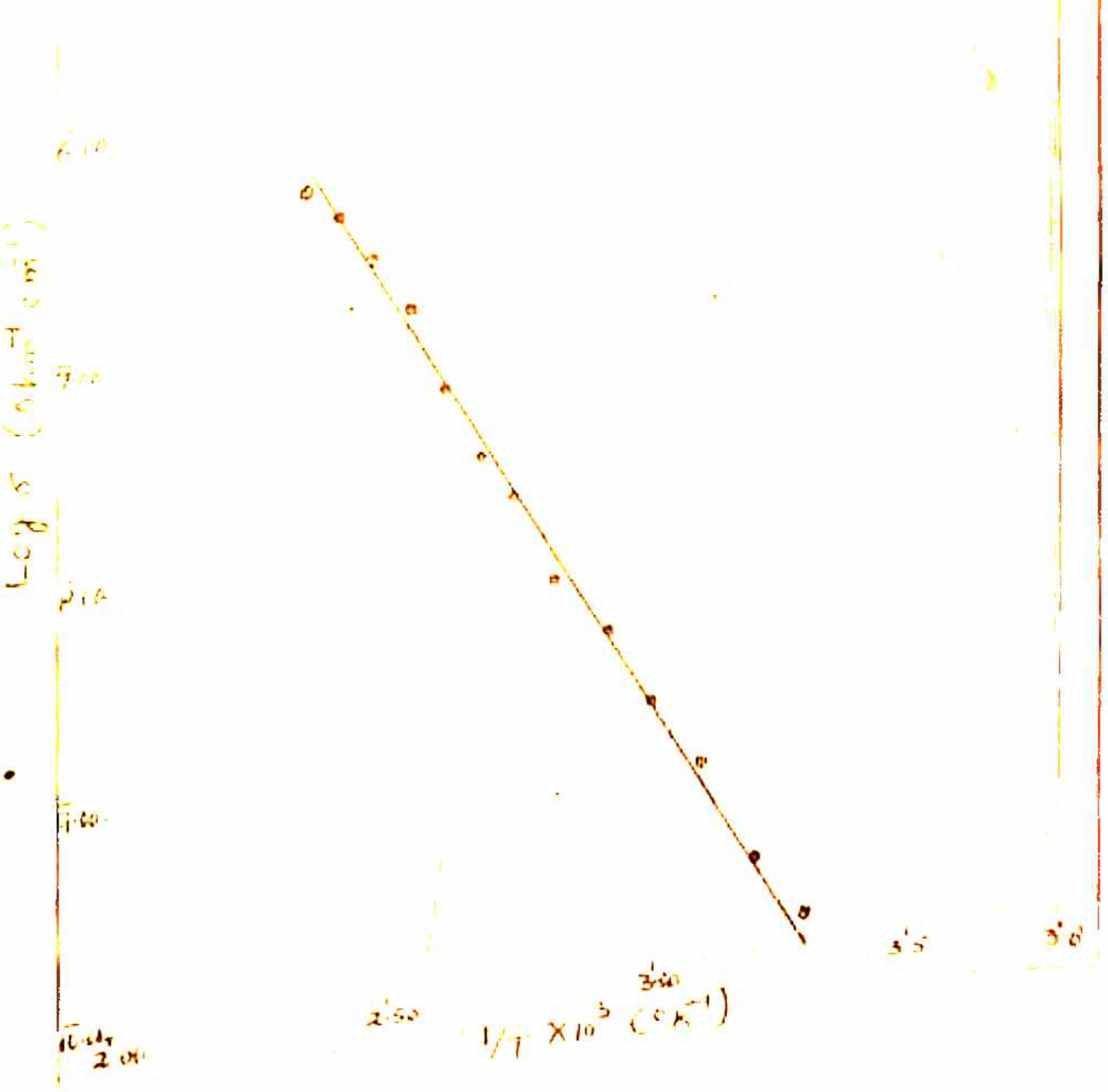


FIG 3.55 PLOT OF LOG σ vs 1/T FOR NbI$_5$ PAMTU



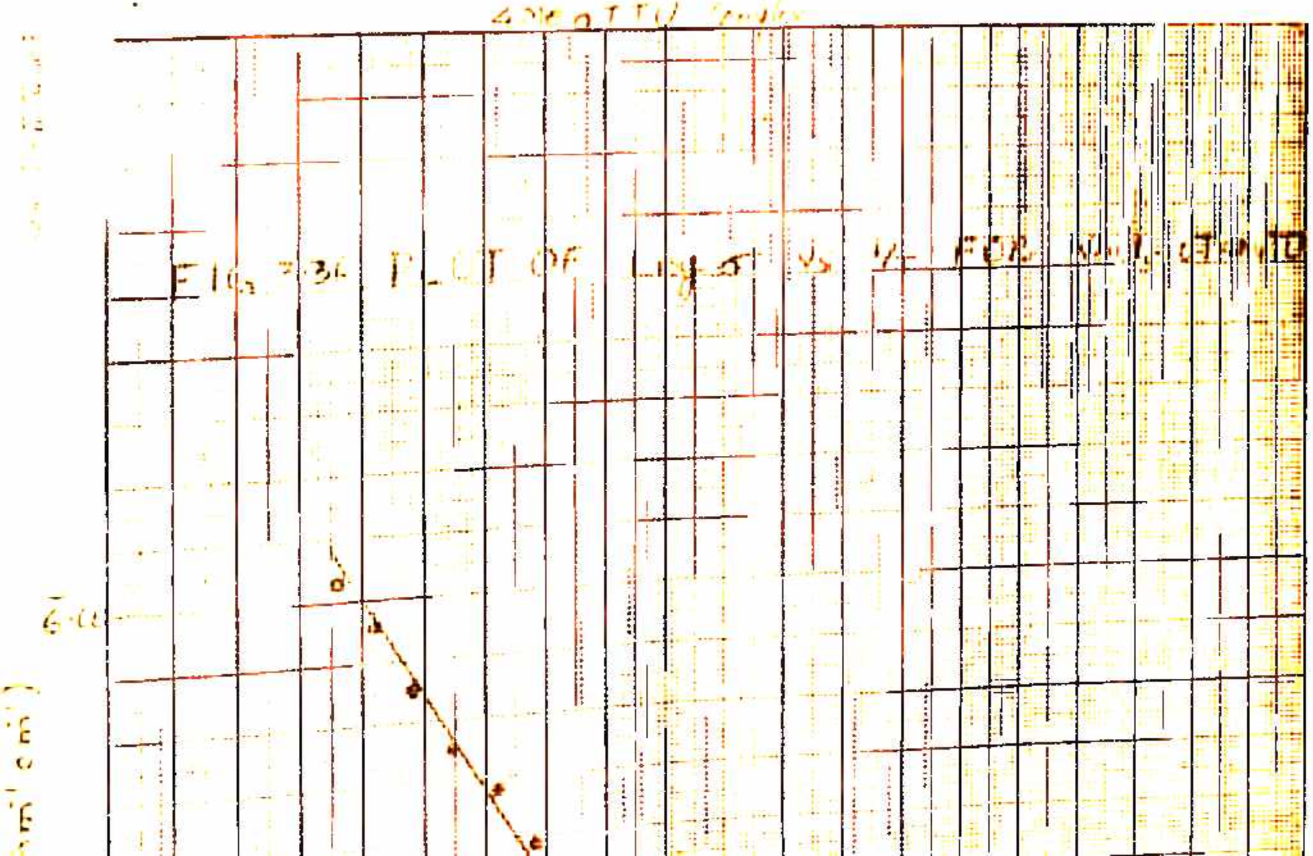
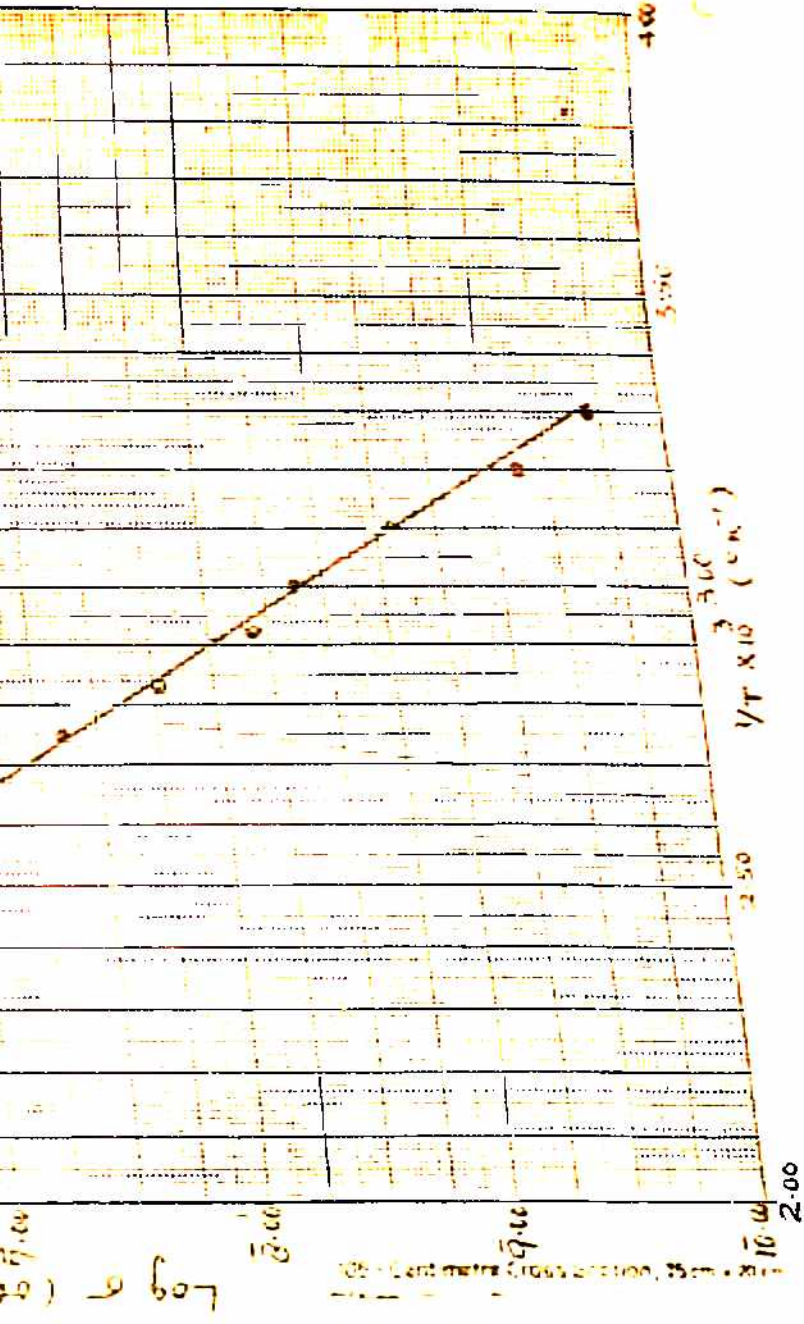


FIG. 7.36 PLOT OF Log σ Vs 1/T FOR [illegible]


4.00
3.50
3.00
2.50
2.00
1/T × 10³ (°K⁻¹)
1̄0.00
9̄.00
8̄.00
7̄.00
Log σ (
10 × Centimetre Cross section, 25cm × 20

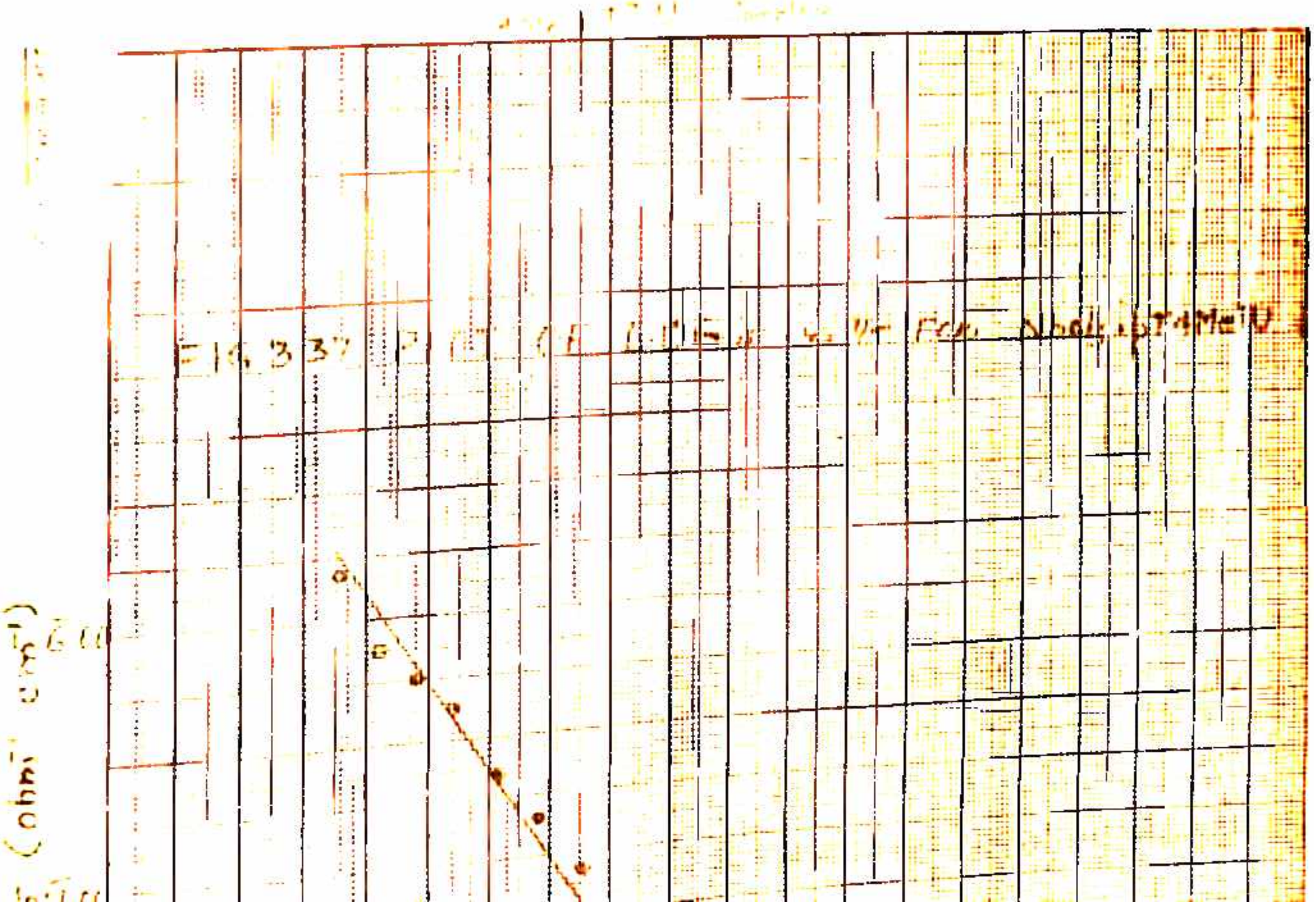
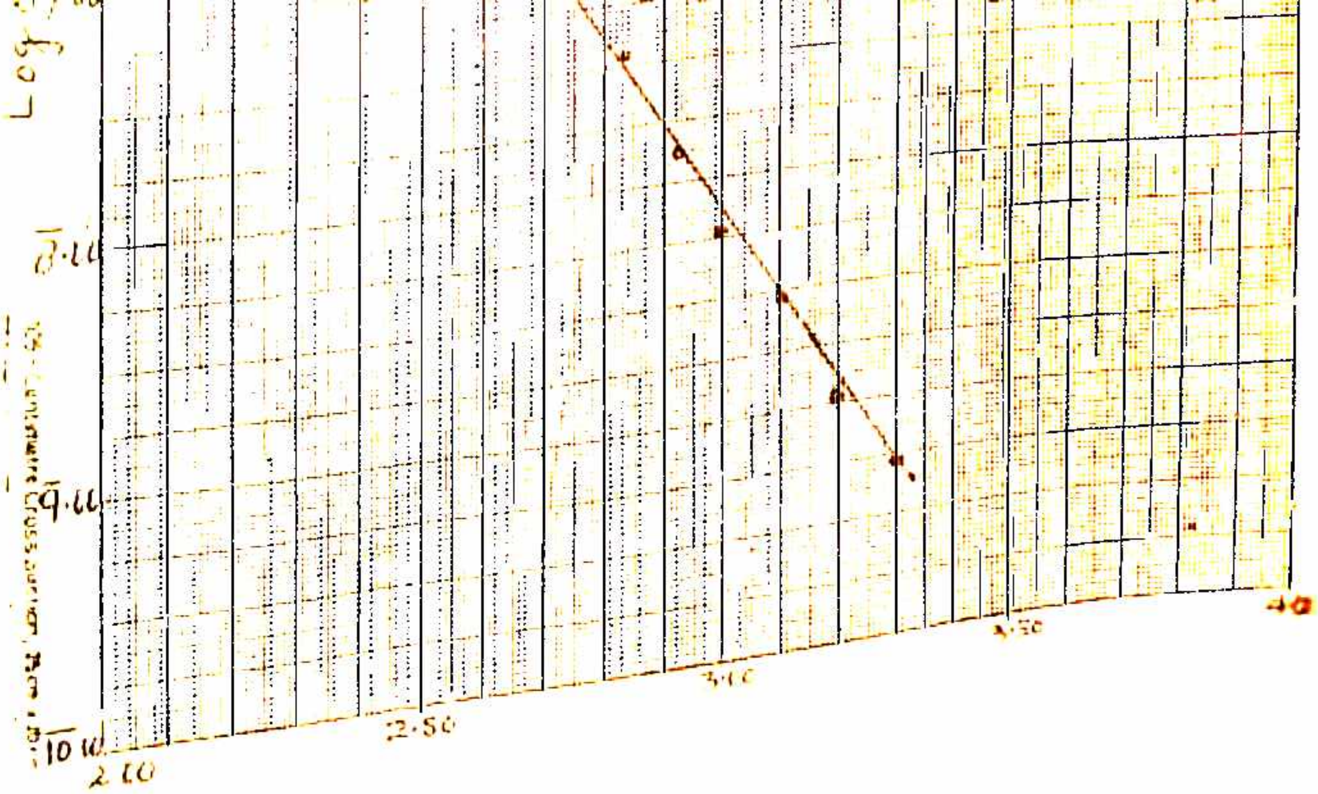


FIG. 3.37 PLOT OF [illegible] vs 1/T FOR [illegible] 4 MeV



Log
$\bar{8}.44$
$\bar{9}.44$
$\overline{10}.44$
Centimetre Cross section
2.00
2.50
3.00
3.50
4.0

FIG 3.38 PLOT OF LOG σ vs 1/T FOR Nbcl$_5$. P6mTU

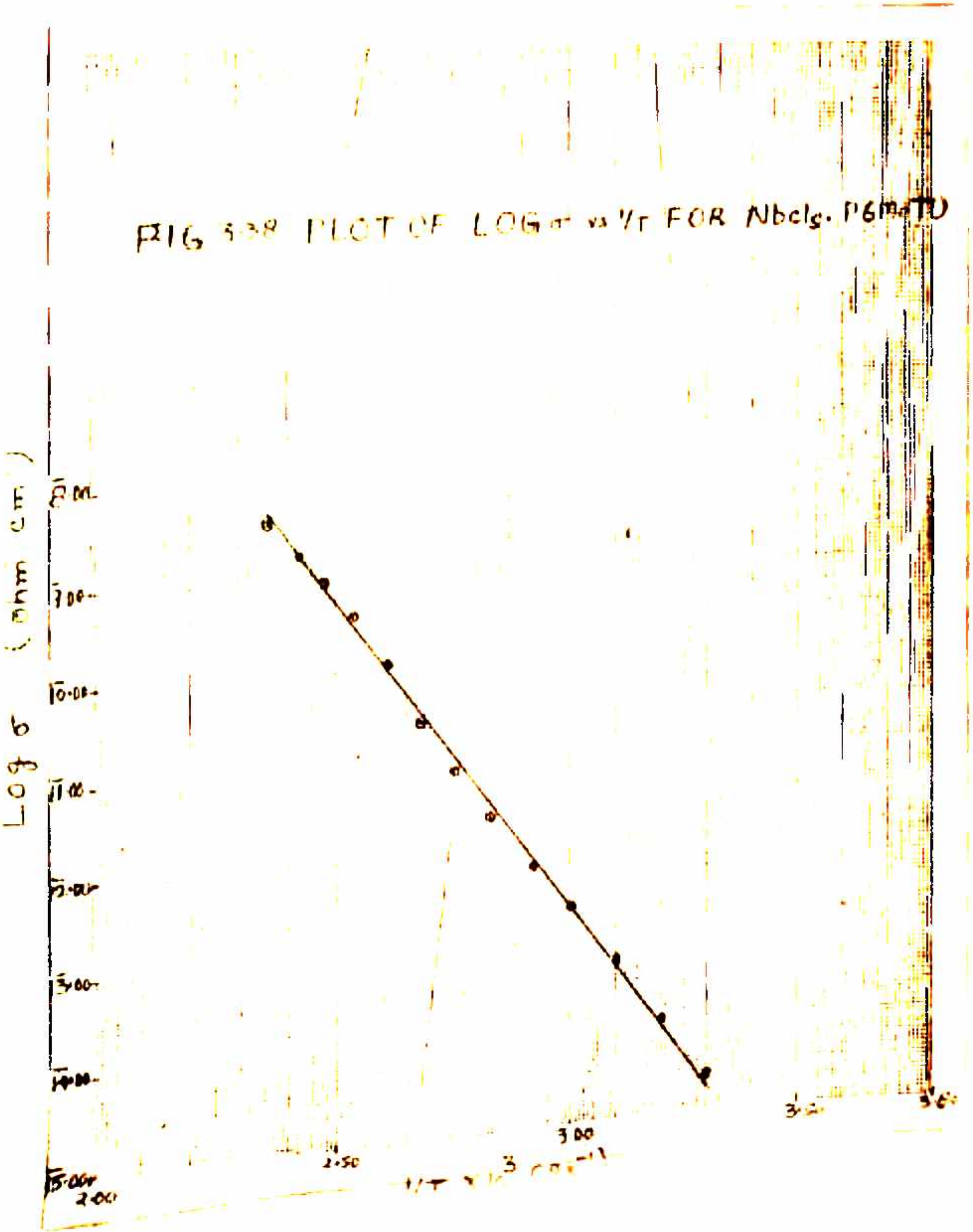
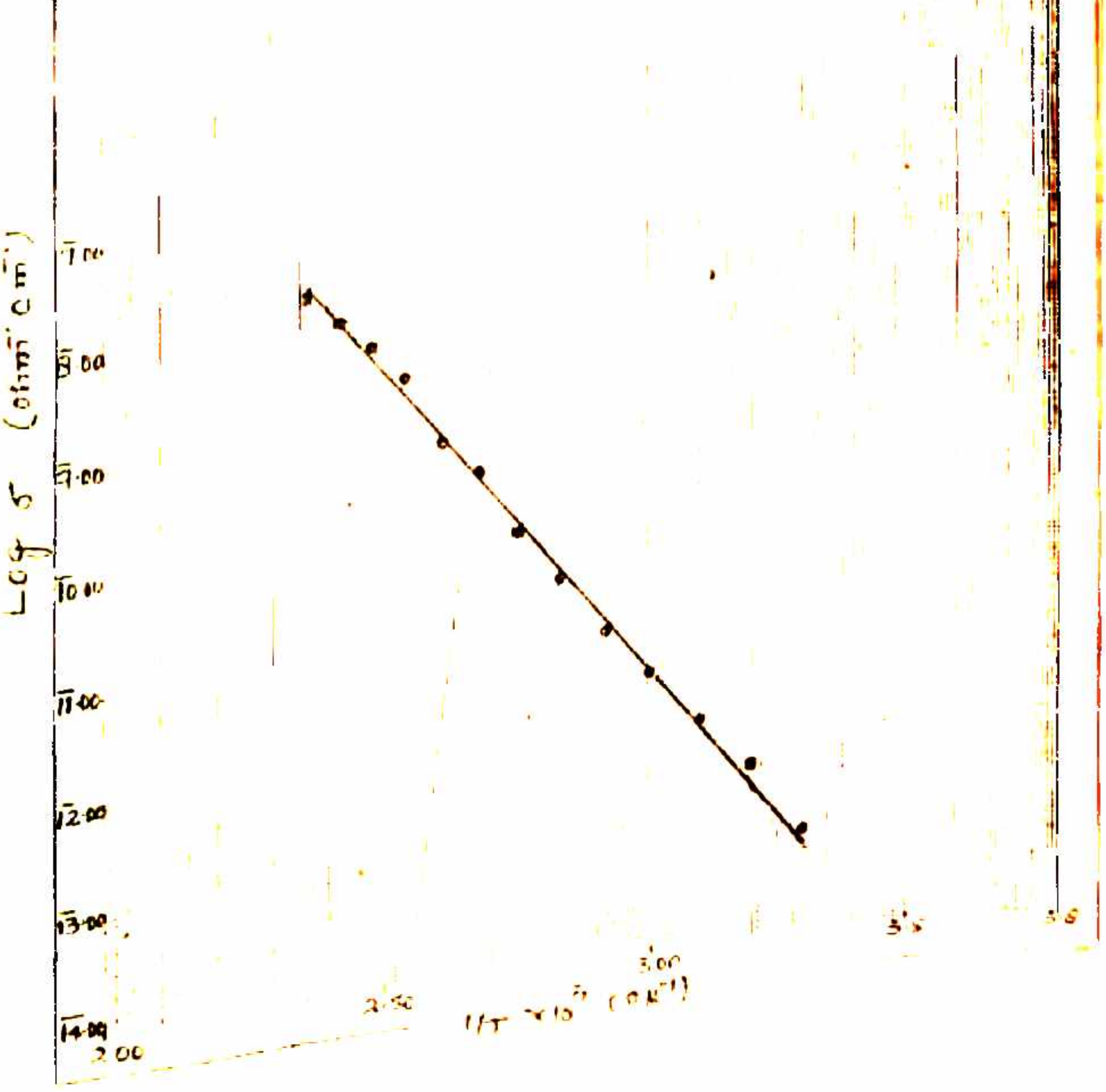


FIG 3·37 PLOT OF LOG σ vs 1/T FOR $NbCl_5$ OT6Mo TU



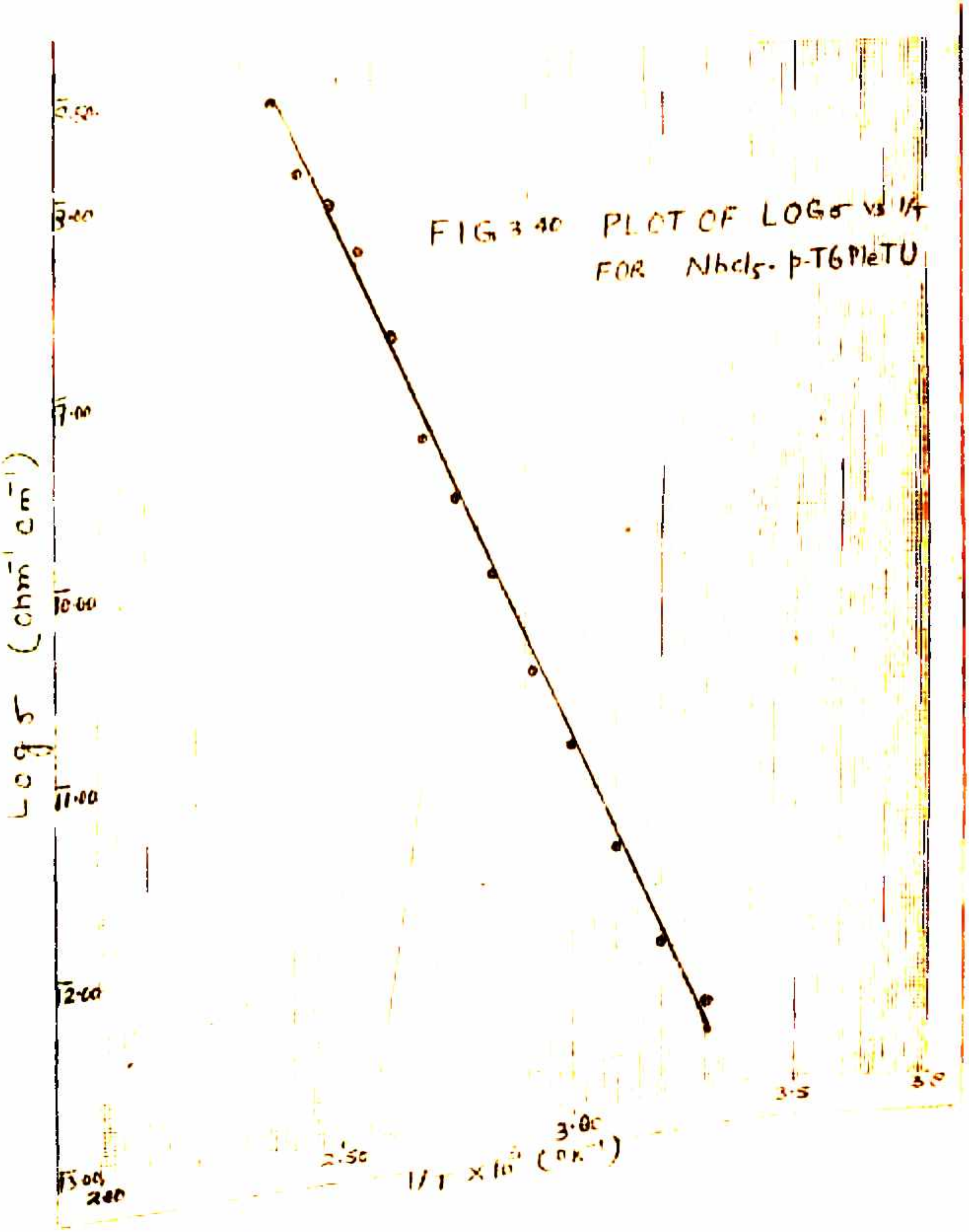
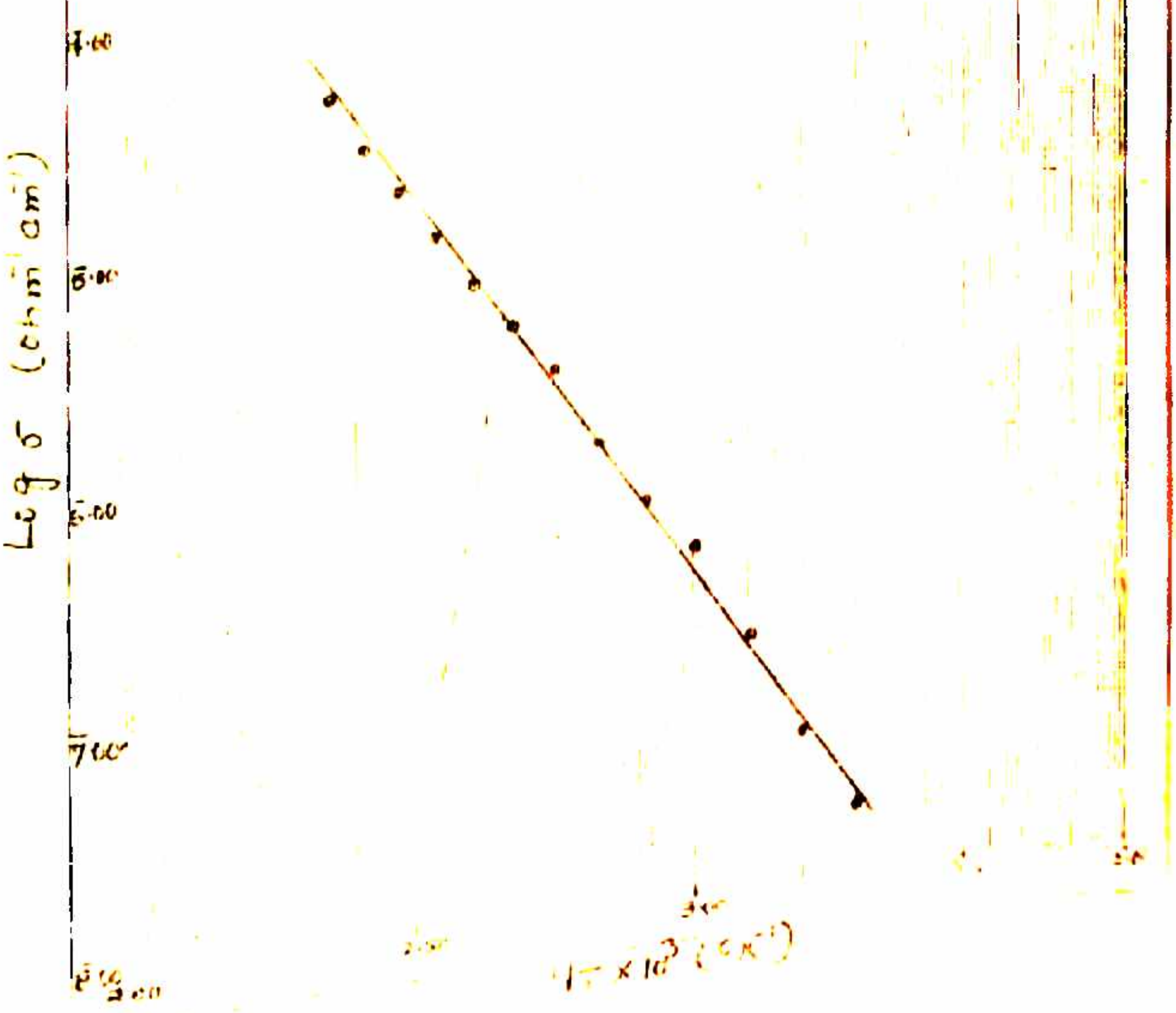


FIG 3.40 PLOT OF LOGσ vs 1/T
FOR NbCl5· p-TGMeTU

FIG 3.41 PLOT OF LOG σ vs 1/T FOR $NbCl_5$-DPDTB



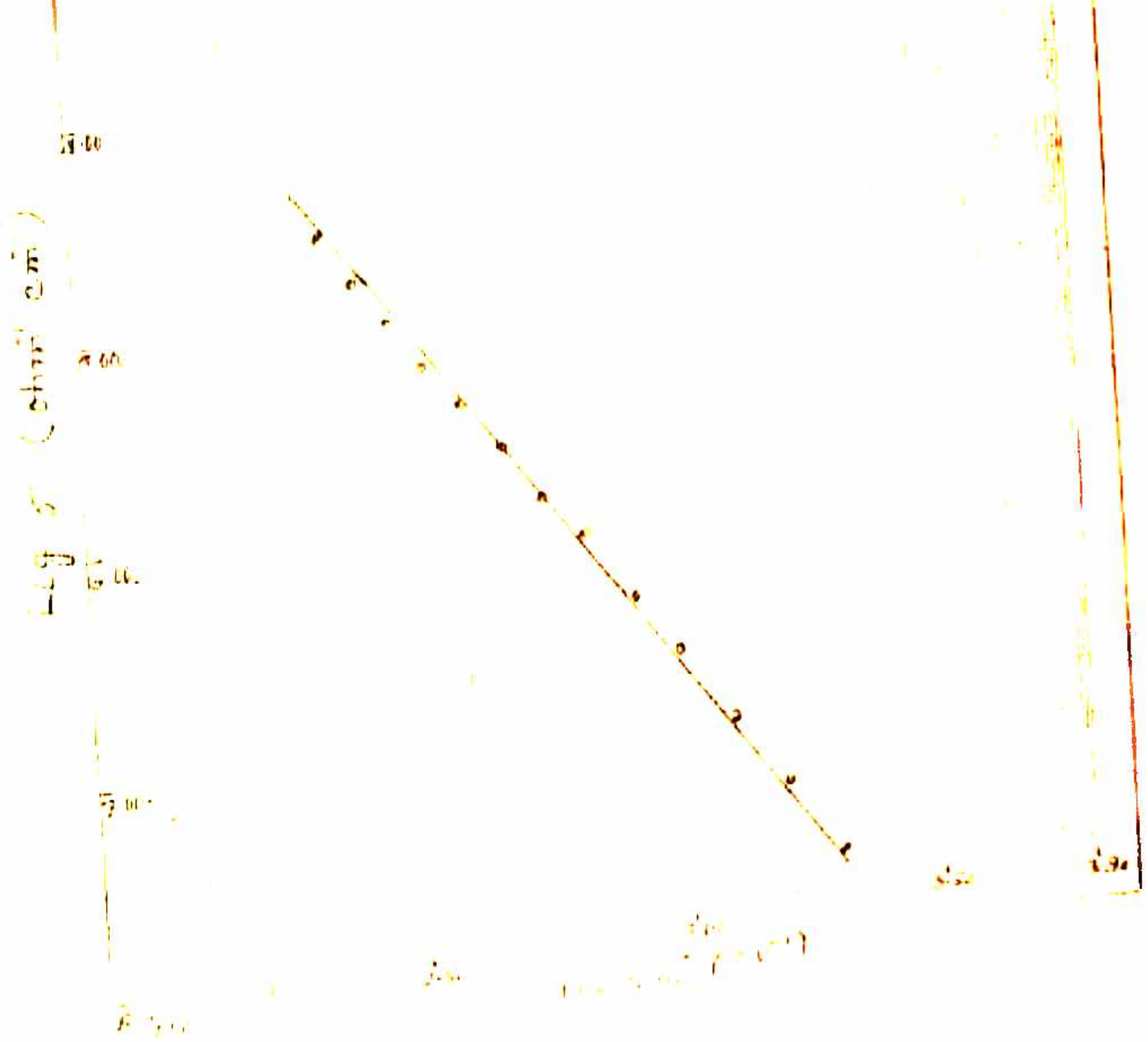
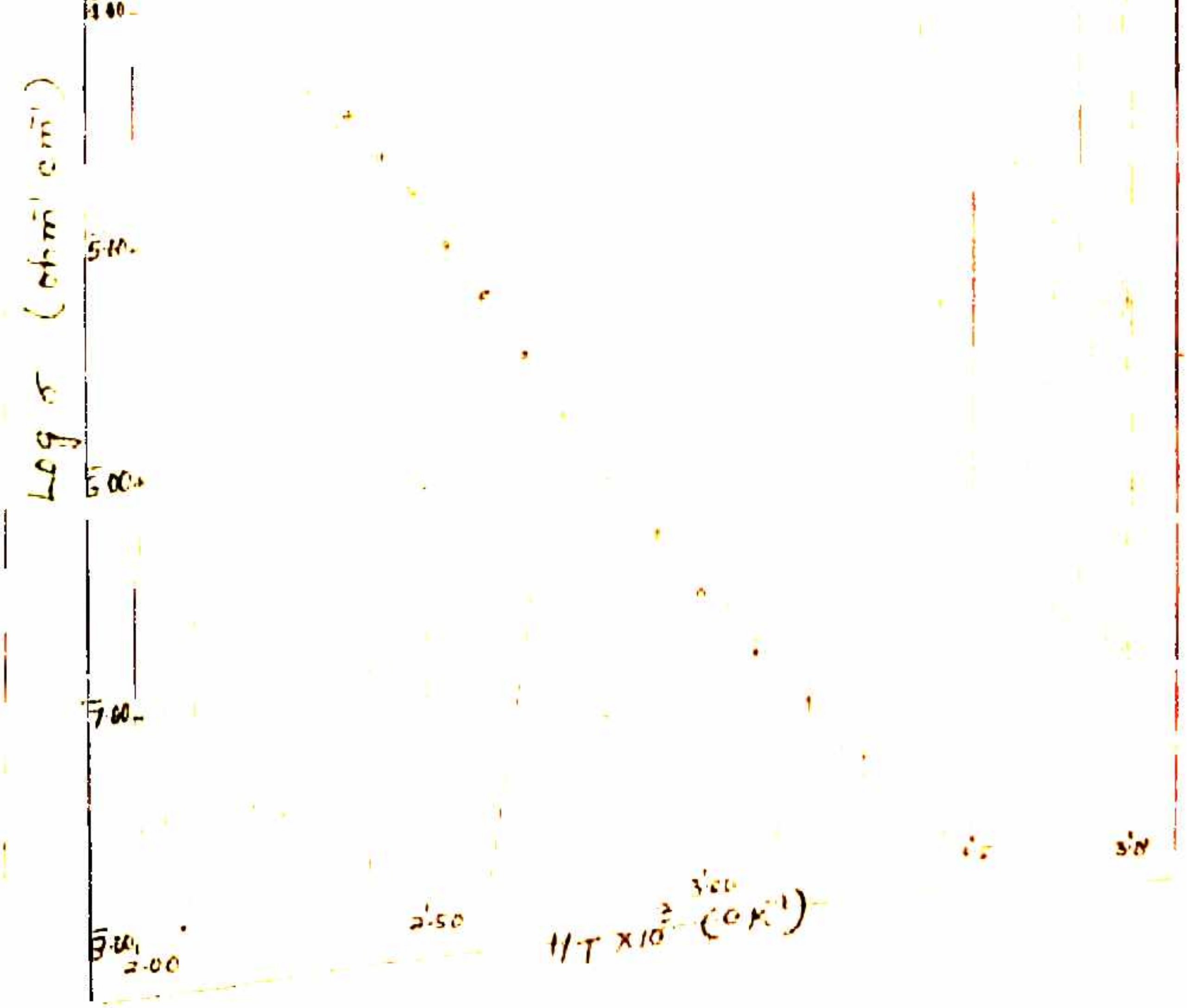


FIG 3.49 PLOT OF LOG σ vs 1/T FOR NbCl$_5$ DPTB

FIG 3.42 PLOT OF LOG σ vs 1/T FOR NbCl5. Di-o-TDTB



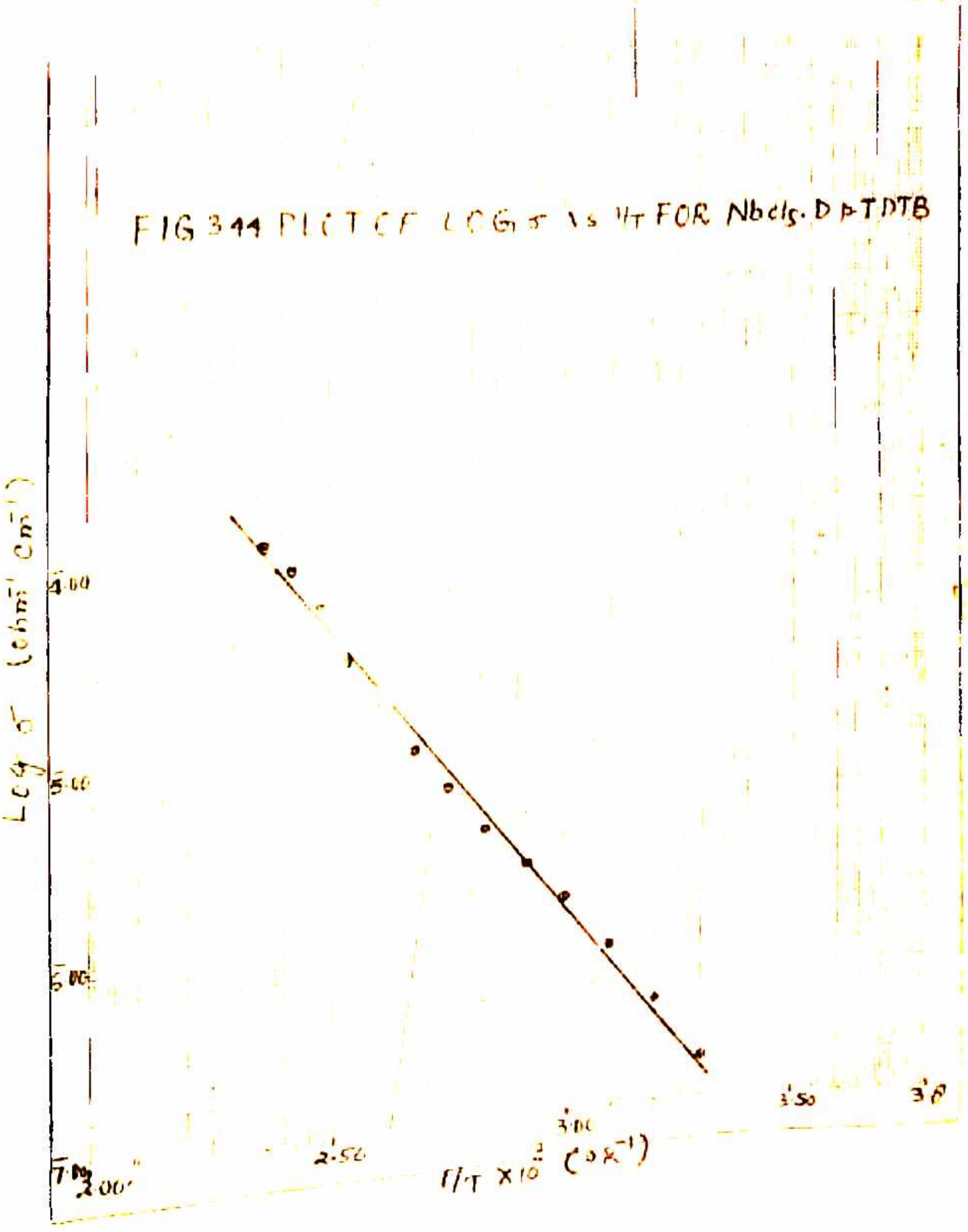
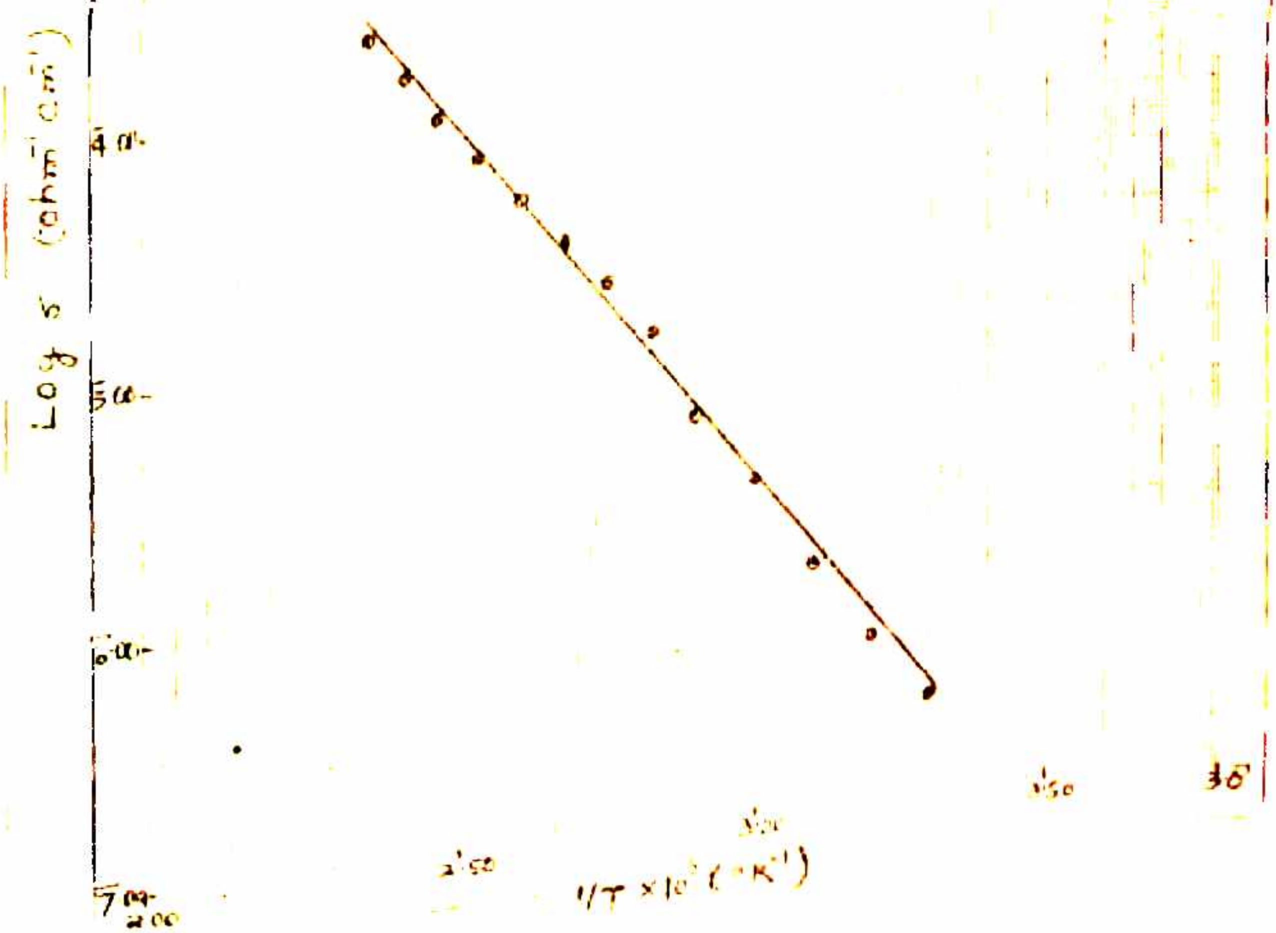


FIG 3.44 PLOT OF LOG σ Vs 1/T FOR $NbCl_5$.DPTDTB

FIG 3.45 PLOT OF LOG σ vs $1/T$ FOR NbCl$_5$ P..TDTB



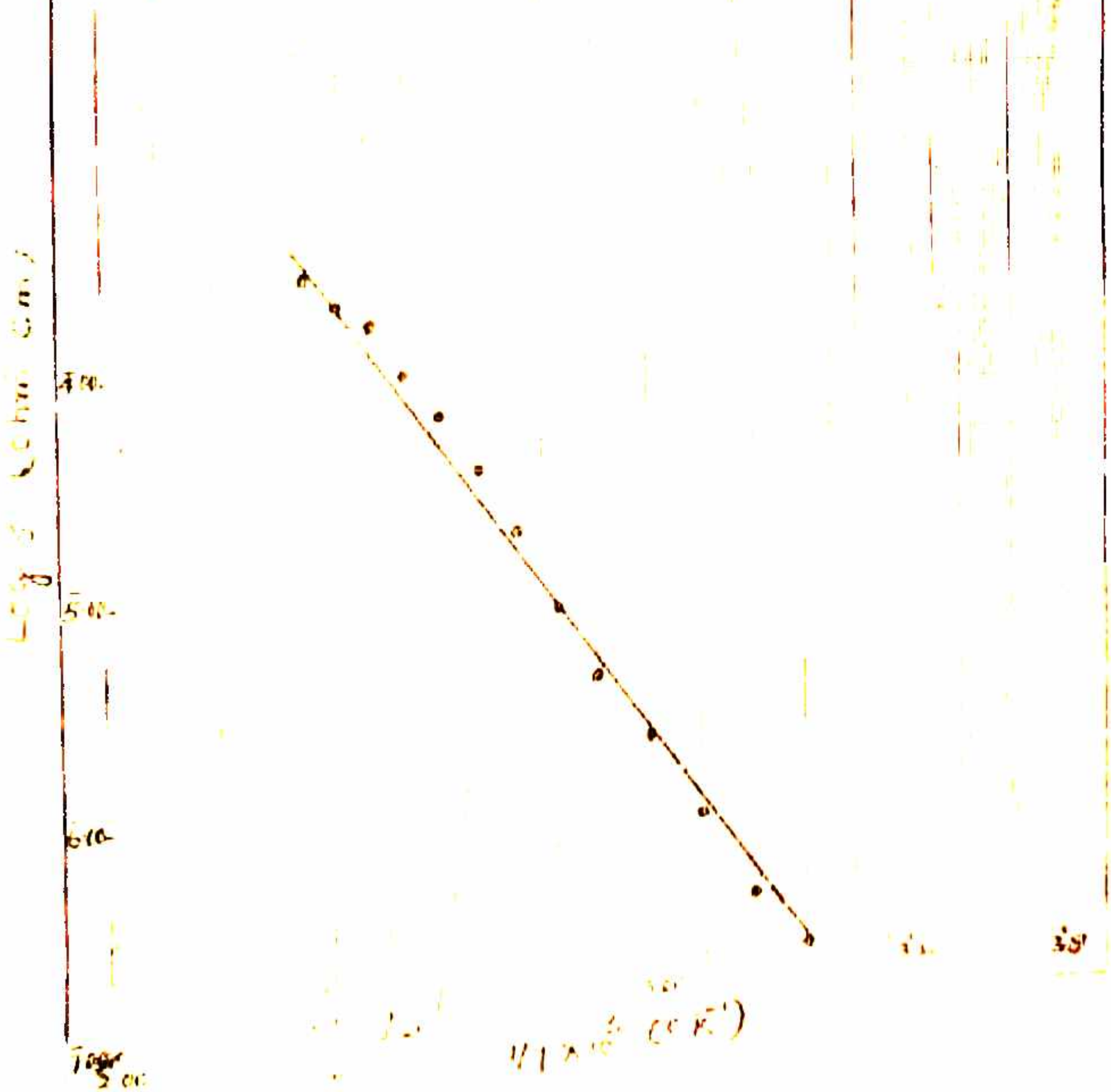


FIG 3.46 PLOT OF LOG σ vs 1/T FOR $NbCl_5$-P.P-TDTB

FIG 3.47 PLOT OF LOG σ vs 1/T FOR $NbCl_5$. PaTTB

FIG 3.40 PLOT OF LOG σ vs 1/T FOR $NbCl_5$.Py-TTB

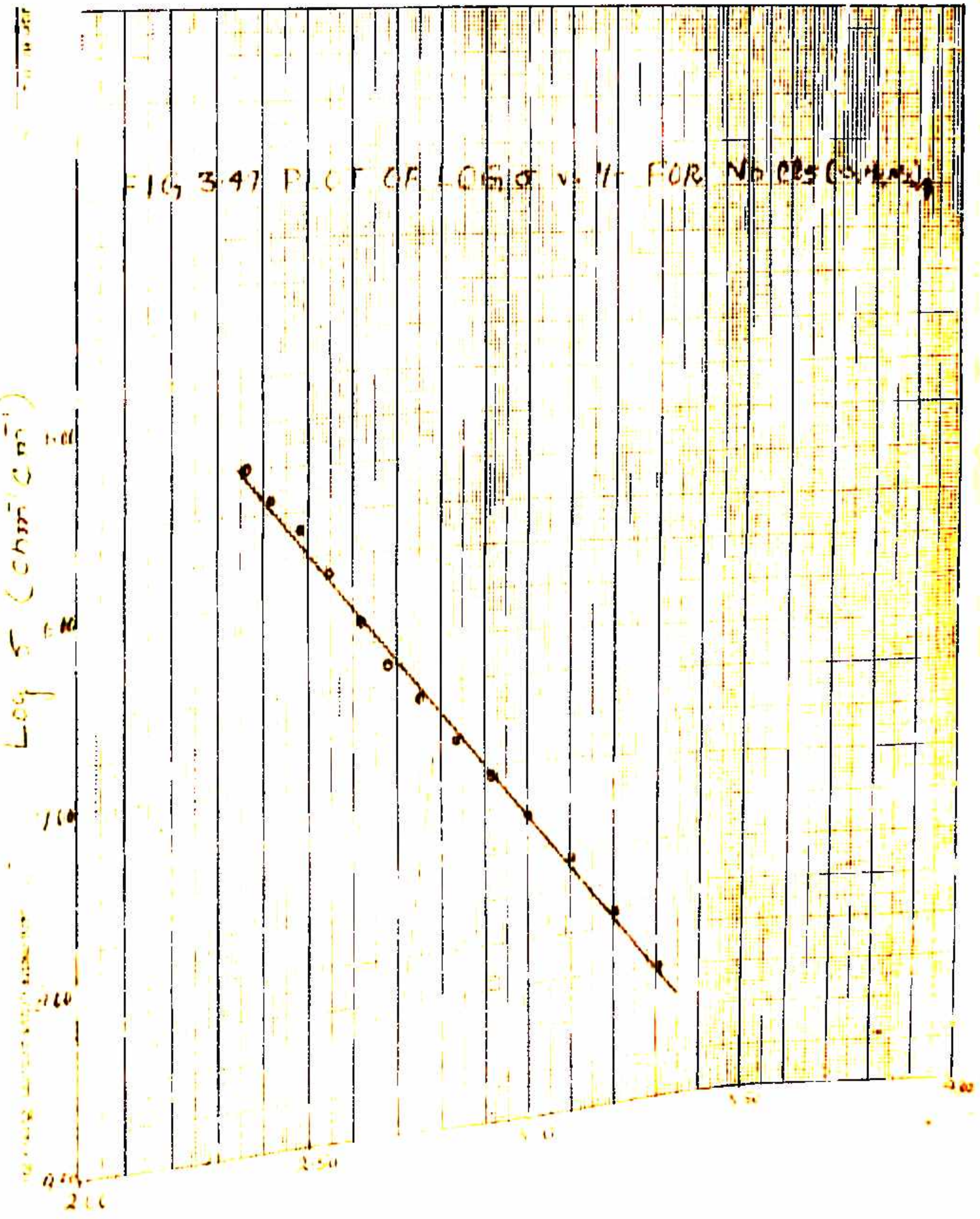


FIG 3.47 PLOT OF LOG σ vs 1/T FOR Nb CBS ([illegible])

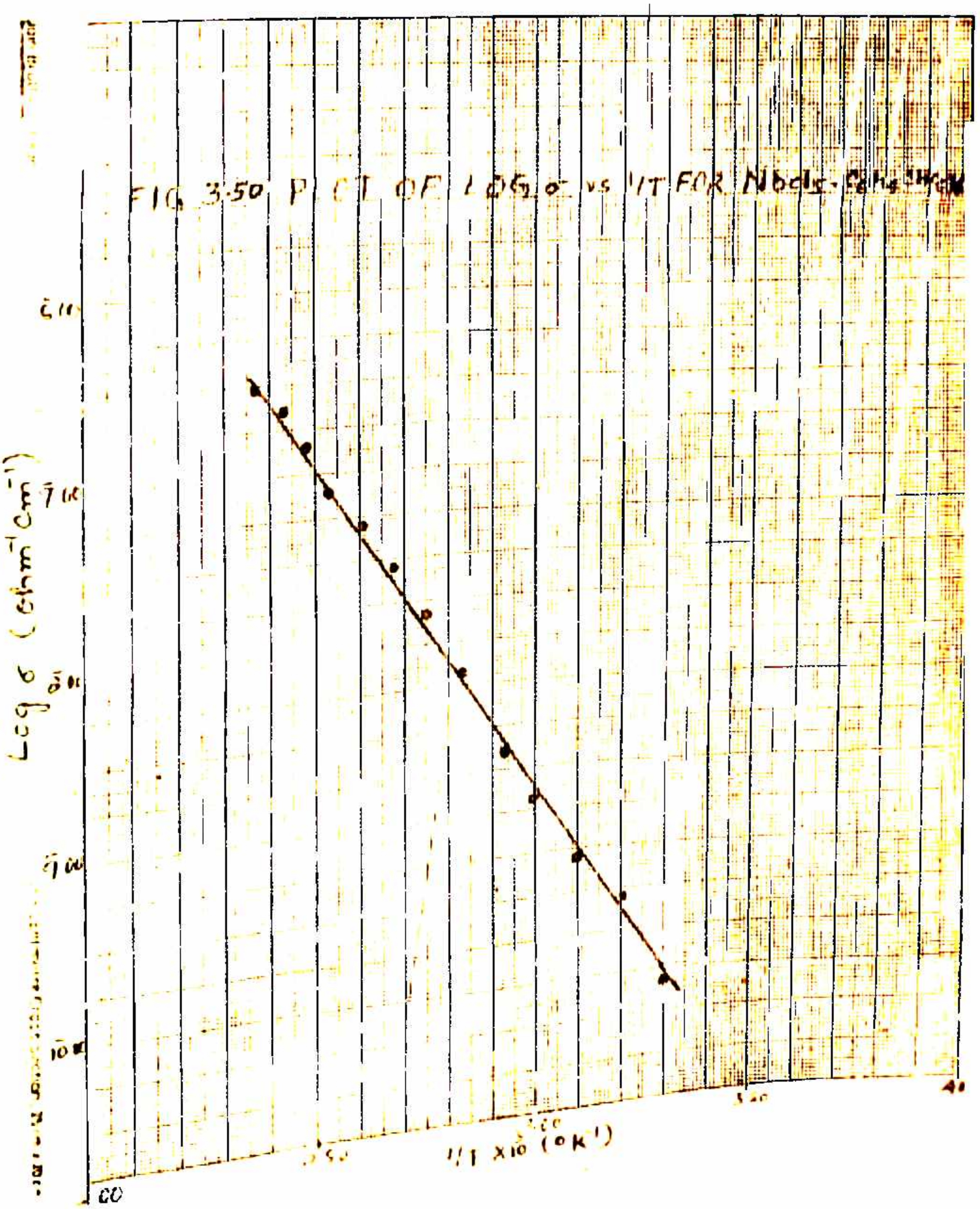


FIG 3.50 PLOT OF LOG$_{10}$ σ vs 1/T FOR NbCl$_5$·[illegible]

TABLE - 1.30

Band Gaps of N-Aryl-N'-2(4,5,6-monosubstituted pyridyl) thiourea Complexes

S.N.	Compound	Eg in eV
1.	Nb Cl_5. PTU	2.49
2.	Nb Cl_5. oTTU	2.46
3.	Nb Cl_5. pTTU	2.18
4.	Nb Cl_5. P 4Me TU	1.57
5.	Nb Cl_5. o T 4Me TU	1.60
6.	Nb Cl_5. pT 4Me TU	1.56
7.	Nb Cl_5. P 6Me TU	2.70
8.	Nb Cl_5. oT6Me TU	2.36
9.	Nb Cl_5. pT6Me TU	2.20

TABLE - [illegible].31

Band Gaps of 1,5-disubstituted 2,4-dithiobiuret and 1,5-disubstituted 2-thiobiuret Complexes

S.N.	Compound	E_g in eV
1.	$NbCl_5$. DPDTB	1.41
2.	$NbCl_5$. DPTB	1.34
3.	$NbCl_5$. D-o TDTB	1.34
4.	$NbCl_5$. D-p TDTB	1.15
5.	$NbCl_5$. P-o TDTB	1.25
6.	$NbCl_5$. P-pTDTB	1.59
7.	$NbCl_5$. P-oTTB	1.13
8.	$NbCl_5$. P-pTTB	1.09

TABLE - 3.32

Seebeck Coefficients of N-aryl N'-2(4,5,6-monosubstituted pyridyl) thiourea complexes

S.N.	Compound	α in μV/°C
1.	$NbCl_5$. PTU	+ 544
2.	$NbCl_5$. OTTU	+ 428
3.	$NbCl_5$. pTTU	+ 206
4.	$NbCl_5$. P4MeTU	+ 532
5.	$NbCl_5$. oT 4MeTU	- 220
6.	$NbCl_5$. pT4MeTU	- 250
7.	$NbCl_5$. P6MeTU	+ 260
8.	$NbCl_5$. oT6MeTU	+ 312
9.	$NbCl_5$. pT6MeTU	+ 256

TABLE - 3.33

Seebeck Coefficients of 1,5-disubstituted 2,4-dithiobiuret and 1,5-disubstituted 2-thiobiuret complexes.

S.N.	Compound	α in $\mu V/^{o}C$
1.	$NbCl_5$. DPDTB	+ 376
2.	$NbCl_5$. DPTB	+ 212
3.	$NbCl_5$. D-oTDTB	- 285
4.	$NbCl_5$. D-p TDTB	+ 450
5.	$NbCl_5$. P-oTDTB	+ 146
6.	$NbCl_5$. P-p TDTB	+ 180
7.	$NbCl_5$. P-o TTB	- 178
8.	$NbCl_5$. P-pTTB	- 240

TABLE - 3.34

Band Gaps and Seebeck coefficients of Benzimidazole and Acridine Complexes

S.N.	Compound	Eg in eV	α in μV/°C
1.	$Nb(C_7H_6N_2)_4Cl_5$	1.24	- 225
2.	$NbCl_5 \cdot C_6H_4CHC_6H_4N$	1.53	- 340

SEMICONDUCTING PROPERTIES OF COMPLEXES

3.41 Semiconducting properties of N-Aryl N'-2(4,5,6-mono-substituted pyridyl) thiourea complexes.

The electrical conductivity (σ) at different temperatures of the complexes are given in Tables 3.11 to 3.19 and the plots of logarithm of electrical conductivity against reciprocal of temperature in ^{o}K are presented in Figs. 3.32 to 3.40. The band gap, Eg, for the conduction process was calculated using the equation[89]

$$\sigma = \sigma_0 \quad e^{-Eg/2kT} \qquad (3).$$

where σ is conductivity at $T^{o}K$, σ_0 is a constant and k is Boltzmann's constant. The slopes of log σ vs $^{1}/_{T}$ straight line curves were accurately determined using least square method.

From the results reported in Tables 3.11 to 3.19 it is observed that electrical conductivities of these complexes are in ther range 10^{-10} to 10^{-15} $ohm^{-1}cm^{-1}$ at room temperature whereas the electrical conductivity of ligands is in the range of 10^{-15} to 10^{-18} ohm^{-1} cm^{-1} at room temperature (Fig. 3.31), proving thereby that increase in electrical conductivity is associated with complex formation. Labes et al[97], while studying electrical resistivity of substituted hydrocarbons complexed with benzoquinones, observed that lowering of electrical resistivity is associated with complex formation.

From Table 3.30 it is observed that band gaps of NbCl$_5$.oT4MeTU, NbCl$_5$.mT4MeTU and NbCl$_5$.P4MeTU are in the range of 1.56 to 1.60 eV, whereas for others the range is 2.18 to 2.70 eV. The reason seems to be that the substituent (methyl group) at position four donates electrons to the pyridyl ring which increases the mobility of the charge carriers. On the other hand substituent at position six have been found to behave in different manner.

A series of polymers has been obtained from 4,4' bis(α-thioaldyl pyridineamido) diphenyl having various substituents in diphenyl by Rukhadze and co-workers[98-100] who observed that Co(II), Ni(II), Cu(II) and Zn(II) polymers are insulators at room temperatures, but at 110°C Cu(II) derivative was found to be best conductor.

It has been observed in these complexes also that these are insulators at room temperature, but four substituent complexes are semiconductors at ~ 40°C, whereas others are semiconductors at ~ 110°C.

Seebeck coefficients (α) were obtained by eq. (2). It is observed that α values are negative for oT4MeTU and pT4MeTU complexes of NbCl$_5$ (Tables 3.32) which means these are n-type semiconductors, i.e., conduction is by means of electrons. On the other hand α-values for other complexes are positive (p-type semiconductors), i.e., conduction is mainly through holes.

3.42 Semiconducting properties of 1,5-disubstituted 2,4 dithiobiuret and 1,5 disubstituted 2-thiobiuret complexes

The electrical conductivities of these complexes at different temperatures are given in tables 3.20 - 3.27 and the plots of logarithm of electrical conductivity against reciprocal of temperature in °K are represented in Fig. 3.41 to 3.48. The band gap, Eg, for the conduction process was calculated using the equation (3).

The slopes of log σ vs $^{1}/_{T}$ straight line curves were accurately determined using least square method as was adopted in the case of other compounds.

The electrical conductivities of 1,5-disubstituted 2,4-dithiobiurets (DSDTB) and 1,5-disubstituted 2-thiobiurets (DSTB) complexes are in the ranges 10^{-8} to 10^{-5} ohm^{-1} cm^{-1} and 10^{-7} to 10^{-4} ohm^{-1}cm^{-1} (figs. 3.41 to 3.48), on comparing these ranges with the electrical conductivity range of the semiconductors given as by Kittel[101] it is observed that DSDTB and DSTB complexes are good semiconductors with band gaps ranging from 1.09 to 1.47 eV (Table 3.33).

The electrical conductivity of these complexes is much higher as compared to the electrical conductivity of substituted thiourea complexes. The reason seems to be that the increase in sulphur content increases the electrical conductivity of complexes (compare tables 3.01 & table 3.02).

Our observation is in agreement with the observation of Inoue et al.[102] They also observed that electrical conductivity of aniline black increases with increasing sulphur content.

It has also been observed that resistivity of coordination polymers formed from ligands having sulphur or sulphur and nitrogen containing donor groups, are dependent more on the concentration of metal groups than on the nature of the metal.[103] The materials studied include Cu(I) derivative of substituted bis (dithiocarbamic acids), Cu(II) coordination polymer of dithio-oxamide, Cu(I) thiocyanate, a heat treated Cu(I) thiocyanate thiourea complex and copper metal. Keeping the oxidation state of metal same, Terentev et al[103], established that an increase in copper concentration by about 5% leads to a decrease in resistivity by an order of magnitude. This dependance was taken to indicate that d-electrons of the copper participate in the conduction mechanism.

No definite conclusion in regards to the electrical conductivity can be drawn in these complexes with respect to the concentration of Nb present, but the electrical conductivity has been found to be changing with the presence substituent groups at different positions in the benzene ring (Tables 3.20 to 3.22). It is observed that complexes having substituent at para position in the ligands have more conductivity than in the case of substituent at ortho position .

The Seebeck coefficient (α) measurements in these complexes showed that D-o-TDTB, P-o-TTB and P-pTTB complexes are n-type (negative α) semiconductor and DPDTB, DPTB, D-p-TDTB, p-o TDTB and P-p TDTB complexes to be p-type (positive α) semiconductor (Table 3.33).

3.43 Semiconducting properties of Benzimidazole and Acridine Complexes

The electrical conductivity (σ) at different temperatures of these complexes are given in tables 3.28 and 3.29 and the plots of logarithm of electrical conductivity against reciprocal of temperature in ^{o}K are given in Figs. 3.49 and 3.50. The band gaps, Eg, for the conduction process were also calculated using equation (3).

From the results reported in Table 3.34, it is seen that band gap of benzimidazole complex is 1.24 eV while that of acridine complex is 1.53 eV. Aftergut and Brown[104] reported the band gap 1.9 eV of benzimidazole, which on complex formation reduced to 1.24 eV. Similarly the band gap 1.85 eV of acridine as reported by Kleinermann and McGlynn[105], decreased to 1.53 eV on complex formation. It is also in agreement with the observation of Labes et al[98]. It has been observed by many investigators[100-109] that the introduction of a metal group into an organic polymer generally enhances its conductivity, which further confirms our observation.

Seebeck coefficient (α) measurements (Table 3.34) show that both these complexes are n-type, i.e., conduction is mainly through electrons.

$NbCl_5$ also formed a light yellow coloured complex with imidazol but it was so hygroscopic that we could not proceed with any study except that it contained nitrogen and niobium in it.

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LIST OF PUBLICATIONS

1. Thiocyanation reaction and spectroscopic studies on some copper (II) 1,3-diketonates.
   Chemical Era, 11(3), 35 (1975).

2. Thiocyanation reaction and spectroscopic studies on some chromium (III), 1,3-diketonates.
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3. Studies on the formation and semiconducting properties of lithium and potassium niobates.
   (Accepted in Journal of Indian Chemical Society).

4. Studies on the formation and semiconducting properties of alkaline earth niobates.
   (Communicated to J. Inorg. Nucl. Chem.)

5. Complexes of niobium pentachloride with N-Aryl N'-2(4,5,6-monosubstituted pyridyl) thioureas and their semiconducting properties.
   To be
   (Communicated to the Electrochemical Society of India).

6. Complexes of niobium pentachloride with 1,5-disubstituted 2,4-dithiobiurets and 1,5-disubstituted 2-thiobiurets and their semiconducting properties.
   To be
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