Ultra Violet and Visible Spectra of Some Divalent Transition Cupferrone Complexes

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(Z. Naturforsch. **29 a**, 719—724 [1974]; received December 8, 1973)

The UV and visible absorption spectra of the ammonium salt of cupferrone and manganese, cobalt, nickel, copper and zinc divalent cupferrate complexes are investigated. The absorption bands observed are given and assigned on the basis of ligand field theory.

In the UV absorption spectrum of the cupferrone metal complexes a characteristic shift in the maxima and minima appears. The effect of solvent on this shift was investigated.

The spectra of transition-metal complexes are of interest since the presence of d electrons produces new and complicated problems. It is necessary to identify and assign the absorption bands as far as possible before a correct identification of the transition-metal ion transitions in these complexes can be made.

Cupferrone (Nitrosophenyl hydroxylamine) is a well known chelating agent with useful application for selective separation of a number of radioactive elements. Precipitation behaviour as well as extraction parameters of cupferrone are well established [1, 2]. The IR absorption spectrum and the assignment of the different absorption bands detected of the ammonium salt of cupferrone and some divalent transition metal cupferrone complexes are reported [3–5]. Very recently Yoshimura et al. [6], studied the UV and IR spectra of cupferrone and neocupferrone and they assigned the different absorption bands detected.

The present contribution is aimed to investigate the UV and visible spectra of the ammonium salt of cupferrone and some divalent transition cupferrate complexes.

Experimental

All chemicals used were A.R. grade, B.D.H. Label. The ammonium salt of cupferrone was obtained from "Renal" finomvegyszergyar, Budapest, Hungary. The different cupferrate complexes were prepared by a method described elsewhere [1, 5]. Elemental chemical analysis [5] (gravimetric and microanalysis) for the metal complexes prepared gave a chemical composition of ML_2, where M stands for the metal (Mn, Co, Ni, Cu and Zn) and L for the ligand $[C_6H_5O_2N_2]$.

The UV and visible measurements were carried out using a PYE Unicam SP 800, UV recording spectrophotometer.

Results and Discussion

The UV and visible spectra of the ammonium salt of cupferrone and its metal complexes with divalent manganese, cobalt, nickel, copper and zinc in different solvents: methyl, ethyl, isopropyl alcohols and dioxan are given in Figures 1 – 5. In Tables 1 and 2, the wavelength and molar extinction coefficients of the absorption maxima observed for the different complexes are tabulated. The obtained UV spectrum of ammonium cupferrone is characterized by four absorption bands. In this respect two absorption bands were observed for different solvents at 223 nm and 282 nm which are more or less similar to that previously reported [5, 6]. The intense band around 223 nm shows a weak solvent effect. A band shift of 14 nm, however, was observed in the case of dioxan. The absorption band at 282 nm remains constant for different solvents; only in the case of dioxan a blue shift of 27 nm was obtained. Since the nitroso group is a strong electron acceptor, while the hydroxyl group as well the phenyl ring are electron donors, these bands are considered to be essentially charge transfer bands [6]. The band at 223 nm could be satisfactorily assigned to the $A_{1g} \rightarrow B_{1u}$ transition of the benzene ring, while the band at 282 nm was assigned to the $A_{1g} \rightarrow B_{2u}$ transition of the benzene ring. Moreover, beside these two bands a shoulder appears at 305 nm for solutions in methyl, ethyl and isopropyl alcohol, which moved to shorter wavelengths with increasing solvent polarity and disappears in the case of dioxan. Further, it was ob-

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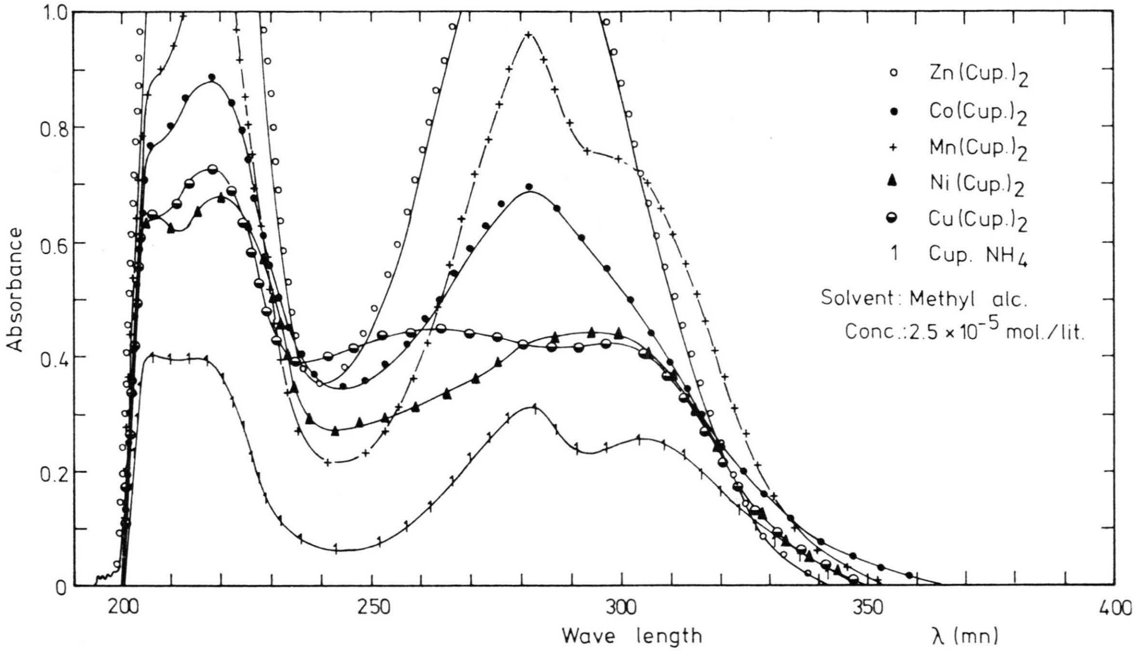

Fig. 1. UV spectra of ammonium cupferrone and its metal complexes in methyl alcohol.

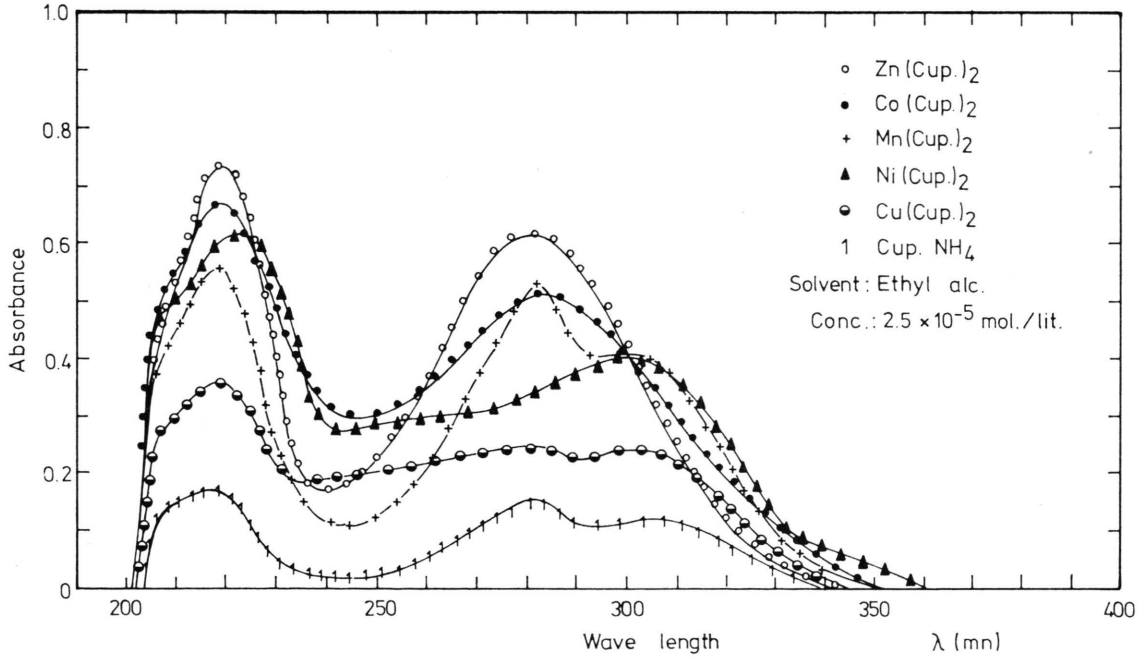

Fig. 2. UV spectra of ammonium cupferrone and its metal complexes in ethyl alcohol.

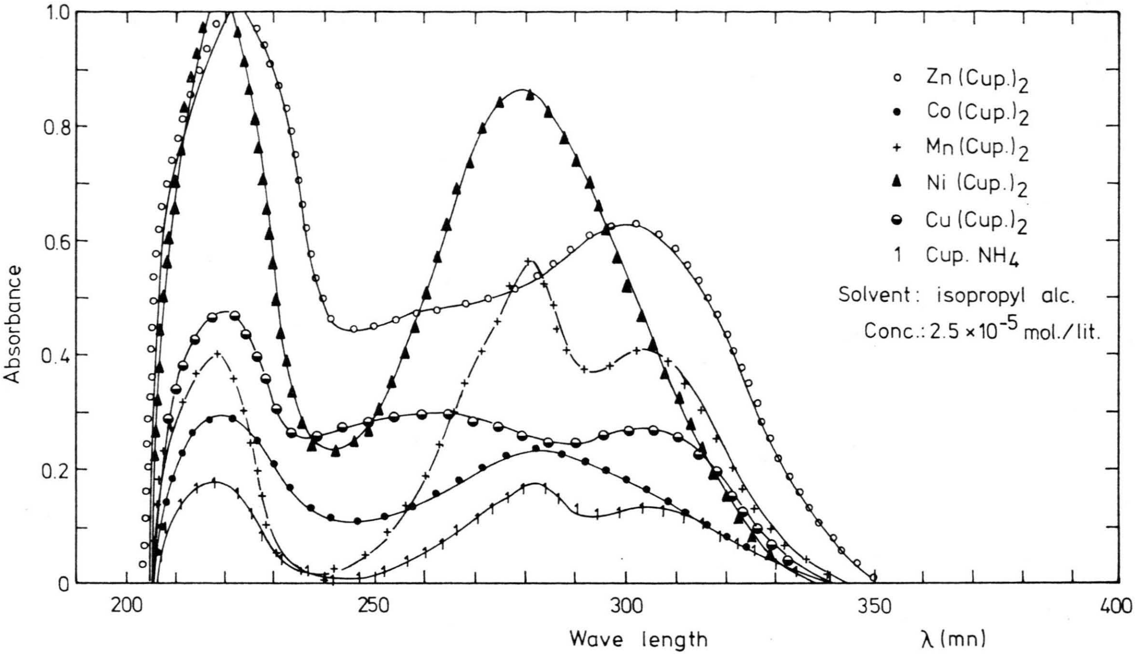

Fig. 3. UV spectra of ammonium cupferrone and its metal complexes in isopropyl alcohol.

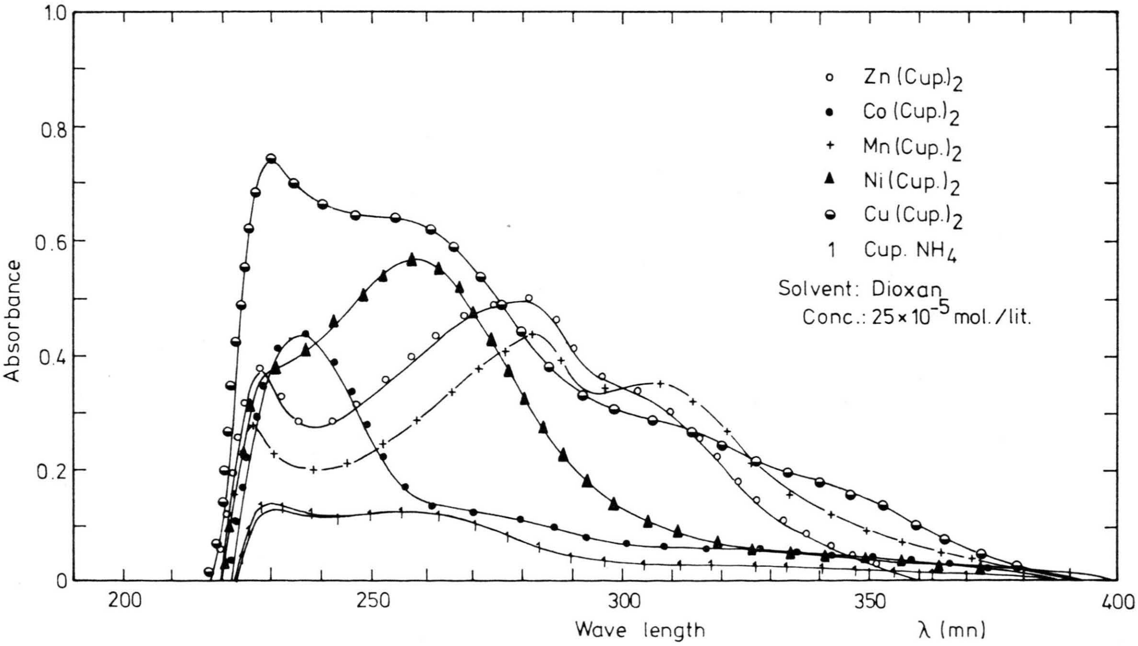

Fig. 4. UV spectra of ammonium cupferrone and its metal complexes in dioxan.

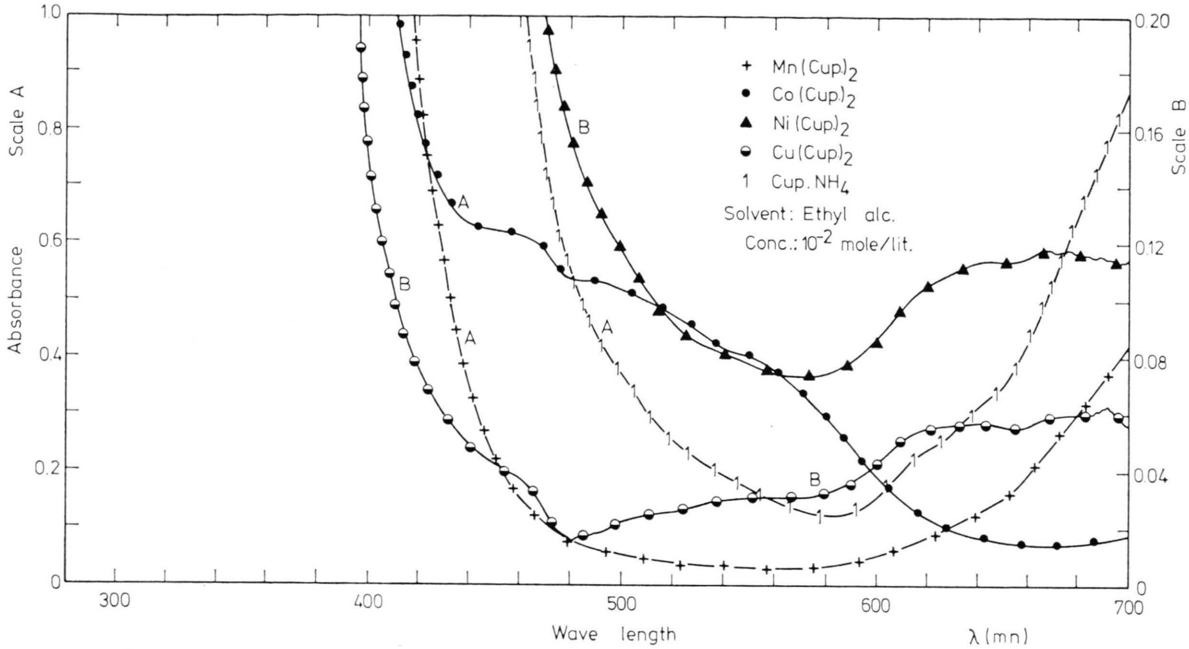

Fig. 5. Visible spectra of ammonium cupferrone and its metal complexes in ethyl alcohol.

Table 1. The molar extinction coefficient and the wave lengths of the absorption maxima for some divalent transition complexes in the ultraviolet region. (sh = shoulder, b = broad).

Complex	Methyl alc. λ_{max} (nm)	$\varepsilon \cdot 10^{-3}$	Ethyl alc. λ_{max} (nm)	$\varepsilon \cdot 10^{-3}$	Isopropyl alc. λ_{max} (nm)	$\varepsilon \cdot 10^{-3}$	Dioxan λ_{max} (nm)	$\varepsilon \cdot 10^{-3}$
NH_4 Cup.	206	16.0						
	216	15.8	218	7.0	218	8.6	230	5.8
	282	12.72	282	6.4	282	8.0	255	5.2
	305	10.4	307 (b)	4.8	307	6.2		
Mn $(Cup)_2$	207 (sh)	26.0						
Electron	218	high	219	22.4	219	17.6	222	11.0
Configuration	281	38.6	282	21.2	282	23.6	282	17.6
d^5	302 (sh)	29.6	302 (sh)	16.4	305	16.6	306	14.0
Co $(Cup)_2$	207 (sh)	31.0						
d^7	218	33.4	220	24.8	220	13.6	235	17.6
	282	27.6	207	22.4	282	10.4		
Zn $(Cup)_2$	207 (sh)						229	14.0
d^{10}	218	64.5	220	29.4	220	63.0	280	19.8
	282	42.0	282	24.8	281	45.0	305 (sh)	12.8
Ni $(Cup)_2$	282	20.4						
d^8	220	27.2	223	24.8	223	47.5	229 (sh)	14.8
	295 (b)	18.0	301 (b)	16.0	302 (b)	25.2	257	22.8
Cu $(Cup)_2$	207	26.0						
d^9	218	29.2	220	14.6	220	20.6	230	30.0
	261 (b)	18.0	282 (b)	10.0	262	12.0	255 (sh)	25.6
	300 (b)	17.2	305 (b)	9.6	305	11.2	312	10.7

served that in the case of methyl alcohol a band was developed at 206 nm ($\varepsilon = 16.0 \times 10^3$), which fades in other solvents; this band could be attributed to the effect of the strong interaction between cupferrone and the polar solvent on the charge transfer bands (could be $'A_{1g} \rightarrow {'E_{2u}}$ transition).

Table 2. The molar extinction coefficient and the wave lengths of the absorption maxima for different metal complexes in ethanol solution in the visible region.

Complex	λ_{max} (nm)	ε
Co(Cup)$_2$ d^7	460	62
	490	54
	550 (sh)	40
Ni(Cup)$_2$ d^8	643 (sh)	11.68
	666	11.9
Cu(Cup)$_2$ d^9	620	5.4
	643 (sh)	5.8
	666 (sh)	6.0
	692	6.4

The UV absorption spectra of Mn, Co and Zn cupferrate complexes recorded in the present work are similar to that of ammonium cupferrone. However, a slight shift of the observed bands is found for the metal complexes. Such behaviour could be explained on the premises that by replacing the ammonium group by relatively stronger electron acceptor metal cations, electrons will be shifted from benzene ring through the oxygen ligand. Thus, with a removal of negative charge (electrons) from the benzene ring, the energy required to remove an electron to higher orbitals will increase with a subsequent decrease in position of the band wavelength.

Manganese cupferrate: IR measurements reported[6] suggest a tetrahedral structure for the cupferrate complexes investigated. Following Tanabe and Sugano[7, 8], the crystal field in tetrahedral manganese complexes does not become strong enough to force a change of the ground state from the $^6A_1(S)$ level to the $^2T_2(^2I)$ level. Therefore the spectrum of manganese complexes can be identified[7] as follows:

The three absorption bands observed at 218 nm, 281 nm, and 302 nm could be satisfactorily ascribed to the transitions[7]: $^6A_1(S) \rightarrow {}^4T_2(F)$, expected at 217.4 nm, $^6A_1(S) \rightarrow {}^4A_2(F)$, expected at 282 nm and $^6A_1(S) \rightarrow {}^4T_1(P)$, expected at 308.6 nm. The transition $^6A_1(S) \rightarrow {}^4T_1(F)$ (264 nm) was not observed, however a shoulder appeared at 207 nm for the solution in methyl alcohol and could be considered as a charge-transfer band sensitive to solvent polarity.

Cobalt cupferrate: Related to the UV and visible spectra of cobalt cupferrate, three intense bands were observed in UV region at 207 nm, 218 nm and 282 nm and three weak bands in the visible at 460 nm, 490 nm and 550 nm. For the solution in dioxan only one band was observed in UV region at 235 nm ($\varepsilon = 17.6 \times 10^3$). These bands could be satisfactorily interpreted on the basis of the ligand field theory for tetrahedral cobalt complexes[8, 9] which predicts the following transitions of the quartet and doublet states of Co^{2+} in the visible region;

$^4A_2(F) \rightarrow {}^4T_1(P)$ at 550 nm, $^4A_2(F) \rightarrow {}^2T_1(G)$ at 490 nm and $^4A_2(F) \rightarrow {}^2T_2(G)$ at 440 nm.

The absorption bands observed in the ultra violet region could be ascribed to the splitting of other doublet levels of Co^{2+} (^2F, ^2H and ^2D levels). Some possible transitions are $^4A_2 \rightarrow {}^2A_2(F)$ and $^4A_2 \rightarrow {}^2A_1(F)$.

The absorption bands observed in the spectrum of zinc cupferrate 207 nm, 220 nm, 280 nm and 305 nm are most likely to be charge-transfer bands.

Referring to the UV and visible spectra of nickel and copper cupferrate complexes it is clear that the $A_{1g} \rightarrow B_{1u}$ transition band of the benzene ring is also shifted, nevertheless the other parts of the spectra are completely changed.

Nickel cupferrate: three absorption bands in the ultraviolet at 207 nm, 220 nm and 295 nm and two bands in the visible at 643 nm and 666 nm were observed. Liehr et al.[10] discussed the spectra of tetrahedral nickel complexes and predicted the following transitions for the triplet states of Ni^{2+} ions,

$^3T_1(F) \rightarrow {}^3T_2(F)$ at 641 nm, $^3T_1(F) \rightarrow {}^3T_1(P)$ at 625 nm and $^3T_1(F) \rightarrow {}^3A_2(F)$ at 530.7 nm.

Other absorption bands in the UV region could be assigned to the transitions arising from the splitting of the ^1G level of the Ni^{2+} ion.

Copper cupferrate: four intense bands in the UV at 207 nm, 218 nm, 261 nm and 300 nm and four weak bands in the visible at 620 nm, 643 nm, 666 nm and 692 nm were observed. Ligand field theory suggests only one transition between the doublet states of the Cu^{2+} ion in a tetrahedral field, $^2T_2(D) \rightarrow {}^2E(D)$ at about 6000 cm^{-1}, in the near IR region. In tetrahedral complexes the approximation of distinguishing between ligand field transitions in the d shell of the central ion and charge transfer transitions between the ligands and the ion largely breaks down[11]. Since both copper and nickel are very strong electron acceptors, the new UV absorption bands observed in their complexes could be assigned as a charge transfer bands related to the metal bonding.

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Polaron Conduction and Optical Absorption of Amorphous Selenium Films

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(Z. Naturforsch. **29 a**, 724–727 [1974]; received December 19, 1973)

The temperature dependence of electrical conductivity in amorphous selenium films is investigated. The experimental results show a polaronic conduction in the states near the Fermi level, in agreement with Mott's model. Optical absorption measurements show the rate at which the valence band states fall off with energy into the energy gap.

The mechanism of electronic conduction in amorphous materials is not yet understood. Because of the disordered lattice structure, the energy band structure cannot be as readily derived for these materials as it has been for periodic lattices. Nevertheless, it is believed that valence and conduction bands do exist for the amorphous structure, but a true band gap of forbidden energies between the valence and conduction bands probably does not exist. Instead, energy states at the band edges may smear or tail into a pseudo-gap. Within this pseudo-gap the states are localized, and outside the pseudo-gap, in the valence and conduction bands, the hole and electron states are nonlocalized as in the valence and conduction bands of crystalline semiconductors [1, 2]. Electronic conductivity could take place by hopping of carriers in the localized states. In order to identify the mechanism of conduction for amorphous selenium, we have conducted measurements of the temperature dependence of conductivity on various amorphous selenium films.

Electrical Conductivity

Amorphous selenium films were prepared by thermal evaporation of spectral pure selenium in a vacuum of $\sim 10^{-5}$ torr at an evaporation rate of 15 Å per second from a tantalum boat onto quartz plates. The samples were provided with silver electrodes. The so-formed contacts are not blocking. Measurements were made for two different voltages applied to the sample: 1500 and 2000 volt using a stabilized high voltage power supply. The current which flowed through the sample was measured by a Vibrating Reed Electrometer sensitive to detect currents as low as 10^{-15} A. Figure 1 shows the dependence of the current intensity (plotted on log scale) on the reciprocal temperature at different applied voltages. Sample thickness of 1553 Å and 6550 Å (determined by interferometric methods [3] were used. The 2000 V curve shows a change of slope around 240 K. For temperatures above 240 K, the slope of the straight line is independent of the applied voltage and gives an activation energy about 0.43 eV, whereas for temperatures below 240 K the activation energy is strongly influenced by the applied voltage. The presence of more than one activation energy was observed on As_2Se_3 samples [4]. Rossiter and Warfield [5] reported a change in the mobility activation energy with temperature, in amorphous selenium. Several activation energies in the conductivity of amorphous silicon layers were observed [6] and interpreted as a result of the hopping process. Moreover, the existance of a critical tem-