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SUPEREXCHANGE COUPLING IN HEXAHALOSALTS OF ELEMENTS IN THE THIRD TRANSITION SERIES

By

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PREFACE

Magnetic measurements have been used extensively by chemists for the elucidation of molecular structure, determination of the valency of atoms and the stereochemistry of complexes and characterization of bond type. Amongst the substances studied, compounds of transition elements have been the subject of most investigation because of the greater wealth of information obtained from them.

The behavior of first transition series compounds, simple as well as complex, is quite well understood on the basis of our present knowledge. The experimental results in the vast number of compounds studied agree with those predicted theoretically. In the case of the second and third transition series elements, however, the susceptibility values are anomalously low. These anomalies serve to indicate our ignorance of the behavior of these atoms. In order that magnetic measurements may be used reliably for the purposes mentioned above, the discrepancies between experiment and theory have to be accounted for.

In recent years, attempts have been made to explain some of these anomalies, in terms of crystal field splitting, spin-orbit and spin-spin or superexchange coupling through intermediate diamagnetic ions. In many compounds the paramagnetic sites are very close to one another and in such cases interactions between adjacent paramagnetic ions are possible. In order to avoid this difficulty, it is advisable to study magnetically dilute systems. Such a system can be obtained by dissolving the compound in either a liquid solvent or an isomorphous diamagnetic salt. Of these two techniques, the latter only is suitable for a complete temperature study

of the magnetic susceptibility.

The present thesis describes one such attempt and is concerned with the measurements of the effective moments of Ir (IV), Os (IV) and Re (IV) at increasingly high dilutions. The salts used were usually hexachloro complexes and they were diluted with isomorphous diamagnetic hexachloroplatinum (IV) salt. Measurements were also made on hexabroosmate (IV) diluted with hexabromoplatinate (IV). These solid solutions were studied over a temperature range from 90°K to 302°K.

In this thesis the introduction is divided into two parts; the first part deals with the theories of magnetism which are used in later discussions and the second part is concerned with the background and development of the problem under consideration.

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ABSTRACT

Theories of magnetism with special reference to Ligand field and Kotani's theory are discussed. An investigation of the applicability of Kotani's theory to the complexes of heavy transition elements is described.

Magnetic susceptibilities of potassium chloroplatinate, potassium chloroiridate, potassium chloroosmate, potassium bromoosmate, potassium chlororhenate and potassium hydroxy-pentachlorotungstate were measured over a temperature range 90°K to 300°K. It is shown that the complexes, with the exception of potassium chlororhenate, do not obey the Curie-Weiss law.

Measurements have been carried out on the paramagnetic salts diluted with isomorphous diamagnetic potassium chloroplatinate and potassium bromoplatinate over a temperature range 90°K to 300°K. It is shown that the magnetic moments of the paramagnetic ions increase as their concentration in the solid solutions decreases. This shows that there is a considerable interaction between paramagnetic ions in crystals of the pure substances and that this interaction is decreased by the inclusion of diamagnetic ions in the crystals, giving a higher value for the magnetic moment.

Although pure substances do not follow Kotani's theory, on dissolution in an isomorphous diamagnetic salt there is a trend towards normal behavior and at infinite dilution of the paramagnetic ion normal behavior is attained. Thus it has been shown that there is appreciable orbital contribution to the magnetic moment of Ir (IV) ion and that a value of the right order of magnitude for the coupling constant could be calculated from the magnetic susceptibility measurements for ions with d_{ϵ}^{4} configuration.

INTRODUCTION

A) Theories of Magnetism

All substances possess magnetic properties in some degree and exhibit one or more of five different types of behavior: diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism and ferrimagnetism. Diamagnetism is a universal property; paramagnetism is usually shown by many ions of transition series elements, by molecules possessing an odd number of electrons or by molecules having unpaired electrons and by most metals. Ferromagnetism, ferrimagnetism and antiferromagnetism are special cases of paramagnetism. The major difference is that these three are group effects whereas paramagnetism is an atomic or molecular effect. Paramagnetism, whenever present, is generally so much larger than the diamagnetism that it overshadows the latter but in order to obtain the correct value for the paramagnetism the underlying diamagnetism has to be corrected for. Quantitatively, magnetic behavior can be expressed by defining a term κ, which can be set equal to the ratio of the intensity of magnetization I to the strength of the applied field H:

$$\kappa = I/H$$

The quantity κ is known as "volume susceptibility". For most practical work "gram susceptibility" denoted by χ is used. These two are related by the expression

$\chi = \kappa/\rho$ where ρ is the density of the substance.

For diamagnetic substances χ is -ve and is independent of field strength and temperature. For paramagnetic substances χ is +ve and of

somewhat larger magnitude and is independent of field strength but normally varies inversely with temperature. For ferromagnetic substances χ is +ve and of much larger magnitude being dependent on field strength and temperature in a complex manner.

Classical Theory of Paramagnetism

Paramagnetism arises due to the permanent magnetic moment of an atom. An atom will have a permanent magnetic moment if it has an odd number of electrons or if there are some unpaired electrons.

Langevin (1905)[1,2], considered each molecule as a small magnet, which under the influence of the applied field tends to be oriented in the direction of the field. This tendency, however, is opposed by a disorienting effect due to thermal energy. By considering these two effects, he derived the expression

$$\chi_M = \frac{N \mu^2}{3 k T} \qquad (1)$$

where χ_M is molar susceptibility,

N is Avogadro's number,

μ is the permanent magnetic moment,

k is the Boltzmann constant and

T is the absolute temperature.

According to expression (1) the paramagnetic susceptibility varies inversely with absolute temperature. This generalization is known as Curie's law and was discovered before Langevin derived the expression (1). However, it is found that many substances do not obey Currie's law: $\chi = \frac{C}{T}$, rather they follow the Curie-Weiss law: $\chi = \frac{C}{(T-\theta)}$ where C is known as the Curie constant and θ is the Weiss constant. The significance of these constants will be seen later.

Classical Theory of Diamagnetism

Langevin (1905)[1,2], showed that by applying an external magnetic field to a system of electrons moving about a relatively heavy nucleus, a precession of the electronic orbit occurs (Larmor precession) and this induces a magnetic field in a direction opposite to that of the applied field. This leads to the diamagnetism.

Although the simple Langevin theory explains many experimental phenomena, such as the difference between the temperature effects in paramagnetism and diamagnetism, its incompleteness was pointed out by Miss van Leeuwen[3], and it was necessary to obtain the help of quantum mechanics to obtain more accurate expressions. Thus Van Vleck[4] derived analogous expressions for paramagnetic and diamagnetic susceptibilities.

For the paramagnetic case he obtained

$$\chi_M = N\bar{\bar{\mu}}^2/3kT + N\alpha \qquad (2)$$

where $\bar{\bar{\mu}}^2$ is the square of the low-frequency part of the magnetic moment vector, averaged over time, this average being itself averaged over the various normal states approximately weighted according to the Boltzmann factor. $N\alpha$ is the combined temperature independent contribution of high-frequency elements of the paramagnetic moment and the diamagnetic part.

Before considering the application of Van Vleck's equation to the experimentally determinable quantities, it is worthwhile to review some of the principles in quantum theory which find use in equations to be used in connection with the calculations of the magnetic moment.

Quantum Theory

In order to account for the behavior of an electron emitting light in the presence of a magnetic field, four quantum numbers are required,

these are

1) The total quantum number n with values

1, 2, 3, ------- n.

2) The orbital angular momentum quantum number l, having integral values from 0 to (n-1).

3) The spin momentum quantum number m_s, representing the projection of spin vector on the direction of the magnetic field, having values $\pm$ 1/2.

4) The orbital momentum quantum number representing the projection of vector on the direction of magnetic field, which may take values l, l -1, ------ 0, -(l-1), -l.

In an atom with more than one electron, the way in which the quantum numbers are attributed to different electrons is governed by the Pauli Principle which states that no two electrons in the same system can have the same set of values of all the four quantum numbers.

The magnetic moment of an atom in general consists of two parts, viz. the "orbital" and "spin" portions. The magnetic moment due to a rotating electron is given by $\frac{\sqrt{l(l+1)}\ e \cdot h}{4\pi mc}$

l is the orbital angular quantum no.

h is Planck's constant

e is the charge on the electron

m is the mass of the electron

c is the velocity of light.

The magnetic moment with l equal to unity is a fundamental quantity known as the Bohr magneton.

In most cases we are dealing with atoms which have more than one electron and the magnetic moment of the atom will depend on the way the

angular and spin momenta combine or couple together to form the resultant angular momentum of the atom.

The most common mode of coupling is the so-called "Russell-Saunders" Coupling, in which it is assumed that all the orbital angular momenta of different electrons combine to form a quantized resultant L and the spin momenta combine to give a quantized resultant S. Further these L and S combine to form a resultant J, which is the total angular momentum of the electron system of the atom. The energy associated with the atom will depend on the value of J. Thus, there are different energy levels possible in an atom and to find out the "ground" state Hund's rules are used. These rules are:

1) S has the highest value consistant with the Pauli principle.

2) The value of L is then maximum.

3) J = L-S when the shell is less than half-filled and J = L+S when the shell is more than half-filled.

J can have half-integral or integral values depending on S. There are 2S + 1 ways in which L and S may combine if $L > S$, but 2L + 1 ways in which L and S may combine if $L < S$, The energy associated with the atom depends on the value of J, hence the value of 2S + 1 or 2L + 1 gives the multiplicity of energy levels.

The energy separation between the outermost components of a multiplet is known as the "overall width". The multiplets are said to be wide or narrow depending on whether the energy separation between successive levels is very large or very small with respect to kT.

In "Russell-Saunders" coupling, it is assumed that the interaction between the spin and orbital momenta of an electron is not strong,

however, if this interaction is strong enough, the spins no longer form a resultant S, or the orbital angular momenta a resultant L. Instead the l_i and s_i of an individual electron form a resultant $j_i = l_i \pm 1/2$. The various j vectors combine to form the resultant J. This is known as "j-j coupling". Although Russell-Saunders coupling is most common, j-j coupling is likely to be realized in heavy atoms such as those of the third transition series, because of their high effective nuclear charge. These types are two extreme forms of coupling and it is quite likely that in certain cases an intermediate type can exist. Attempts have been made to account for the anomalous magnetic behavior of the ions of the third transion series on the assumption that an intermediate type of coupling exists in these ions.[16]

On application of the magnetic field H, the ground state will be split into (2J + 1) levels, the separation between them being g β H, where 'g' is known as the Landé splitting factor, which is given by the expression:

$$g = 1 + \frac{J\,(J+1) + S\,(S+1) - L\,(L+1)}{2J\,(J+1)}$$

This factor was introduced by Landé empirically to account for the anomalous Zeeman effect, and was given a theoretical basis in wave mechanics.

In applying Van Vleck's equation to calculate the magnetic moment of an atom, there are three different cases to be considered.

Writing Van Vleck's equation

$$\chi_M = \left(N\,\mu^2/3\,kT\right) + N\,\bar{a} \quad \text{-------} \qquad (2)$$

in terms of the Bohr magneton β gives

$$\chi_M = N\left(\frac{\beta^2\,\mu_B^2}{3\,kT} + \bar{a}\right) \quad \text{-------} \qquad (3)$$

where μ_B is the low frequency part of the magnetic moment expressed in

Bohr magnetons.

The three cases are:

a) Multiplet Intervals Small Compared to kT.

High frequency elements of the paramagnetic moments will be absent and the diamagnetic part may be neglected. Since the multiplet intervals are small compared to kT the atoms will reside in a variety of different energy levels and it is reasonable to assume that the coupling between L and S will be small and that their vectors will precess about H independently. This gives

$$\chi_M = \frac{N\beta^2}{3kT}\left[4S(S+1) + L(L+1)\right] \quad \text{------} \quad (4)$$

In many transition series compounds the coupling between L and S is so small that the orbital contribution to the magnetic moment may be quenched by the effect of the crystal field, leaving the spin component free, and in such cases the paramagnetic part of the susceptibility is given by

$$\chi_M = \frac{N\beta^2}{3kT}\left[4S(S+1)\right] \quad \text{-------} \quad (5)$$

This is the so-called "spin-only" formula, which is most commonly used in calculating the magnetic moment of transition metal ions.

In certain cases, especially among the heavier elements, the coupling between L and S may be quite large, and then the orbital moment is not completely quenched, correspondingly the magnetic susceptibility lies between

$$\frac{N\beta^2}{3kT}\left[4S(S+1) + L(L+1)\right] \text{ and}$$

$$\frac{N\beta^2}{3kT}\left[4S(S+1)\right], \text{ depending on the extent of coupling.}$$

b) Multiplet Intervals Large Compared to kT.

In this case all the atoms will be in their lowest state and the expression pertaining is

$$\chi_M = \frac{N g^2 \beta^2 J (J+1)}{3 kT} + N \alpha \qquad (6)$$

where J is the vector sum of L and S

g = Landé factor

β = Bohr magneton

This expression is very satisfactory for rare earth ions.

c) Multiplet Intervals Comparable to kT.

The lower energy components of the multiplet will be populated to a significant extent, decreasing upwards. The calculations involve the summation of the atoms with the different values of J, considering the Boltzmann distribution of particles.

From the expressions (5) and (6) given above it is obvious that in cases where the multiplet intervals are large or small compared to kT, the susceptibility will depend inversely on the temperature, except for the relatively small temperature independent high frequency elements. But when the multiplet intervals are comparable to kT, striking departures from the Curie law are observed.

The Weiss Constant.[18] Its origin and significance.

Weiss extended Langevin's theory by considering the mutual interaction of the molecular magnetic fields and deduced the expression

$$\chi = \frac{C}{T - \theta}$$

where θ is a constant known as the Weiss constant.

Although θ originated with the molecular field its present day significance is not restricted to this concept. It can be considered to arise from three different causes. First, it may be due to exchange forces between paramagnetic atoms or ions. Second, it may be due to distortion effects involving orbital angular momentum when the multiplet intervals are neither very large nor very small as compared to kT. Third, θ may appear as the effect of a nonhomogeneous electric field produced by neighbouring ions or oriented solvent molecules upon the orbital moment of the electrons. Experimentally θ may be determined from the intercept of a plot of $1/\chi$ against absolute temperature, if such a plot is linear.

The temperature independent paramagnetism and antiferromagnetism were mentioned earlier. These will now be considered briefly.

Temperature Independent Paramagnetism

This may be considered as arising from contribution to the magnetism from atoms in energy states which are separated from the ground state by an energy ($h\nu$) which is large compared to kT (Van Vleck's high frequency elements). It is convenient to picture the effect as arising from an unbalanced orbital contribution. In many compounds this effect is quite appreciable.

Antiferromagnetism

In certain substances, χ first increases with increasing temperature reaching a maximum at a particular point, known as the Néel temperature, and then it steadily decreases as in normal paramagnetic substances. This effect arises as a result of exchange interaction between two sublattices of which one has all the electron spins parallel but in an opposite

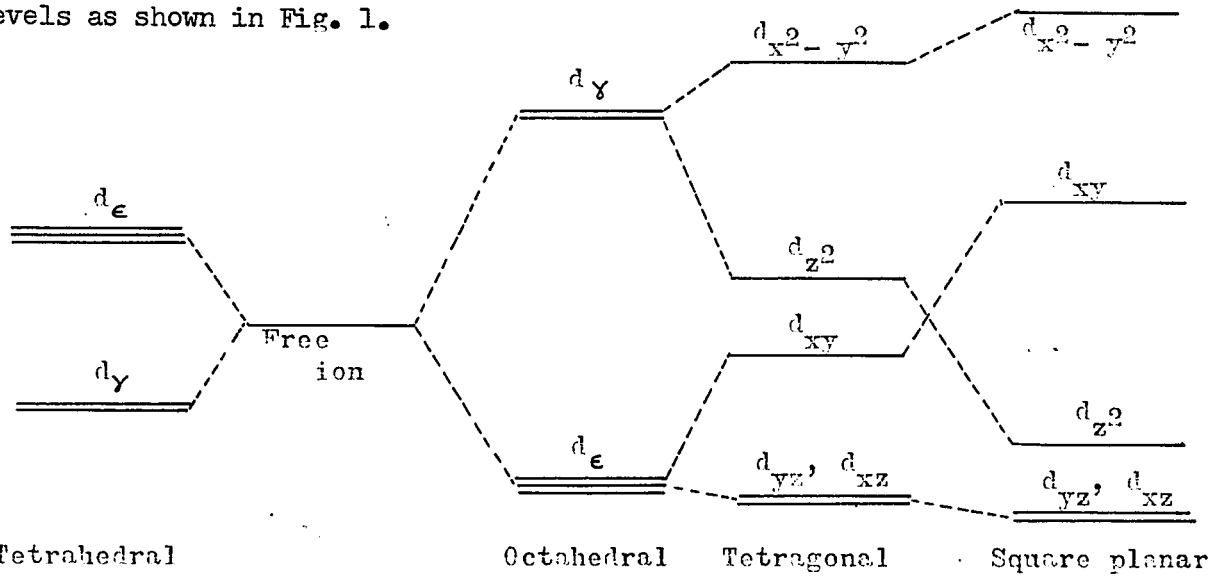
direction to the concerted spins of the other sublattice. This interaction can take place between nearest paramagnetic neighbours and probably between next nearest neighbours in a crystal. In some cases the interaction between nearest neighbours takes place through intervening diamagnetic ions and such a process in termed as superexchange.

It is known that transition metal ions often show a large decrease in magnetic moment when coordinated with certain ligands. An explanation for this was first given by Pauling in terms of covalent bond formation leading to pairing of electrons. Later Van Vleck explained the low values in terms of Ligand-field theory and this theory is so commonly used in explaining the magnetic behavior of transition metal ions, the brief discussion following will not be out of place.

Ligand Field Theory

This was developed in the early thirties by Bethe, Van Vleck and others. The main features of this theory are as follows.

1) When a transition metal ion is surrounded by ligands, the degeneracy of the five d-orbitals is removed and they are split into different energy levels as shown in Fig. 1.



In the case of an octahedral complex the lower level consists of a set of three orbitals, known as d_ϵ and the upper set consists of two orbitals, d_γ.

2) In certain cases, especially among the third transition metal ions, 10 Dq the energy separation between the d_ϵ and d_γ orbitals is quite large and the d_ϵ orbitals are completely filled before the filling up of the d_γ orbitals can take place. This accounts for "low-spin" complexes of elements in the third transition series.

On the basis of this, an important contribution was made by Kotani who was able to account for certain anomalous behaviour of the compounds of heavy elements.

The theory of Kotani[5]

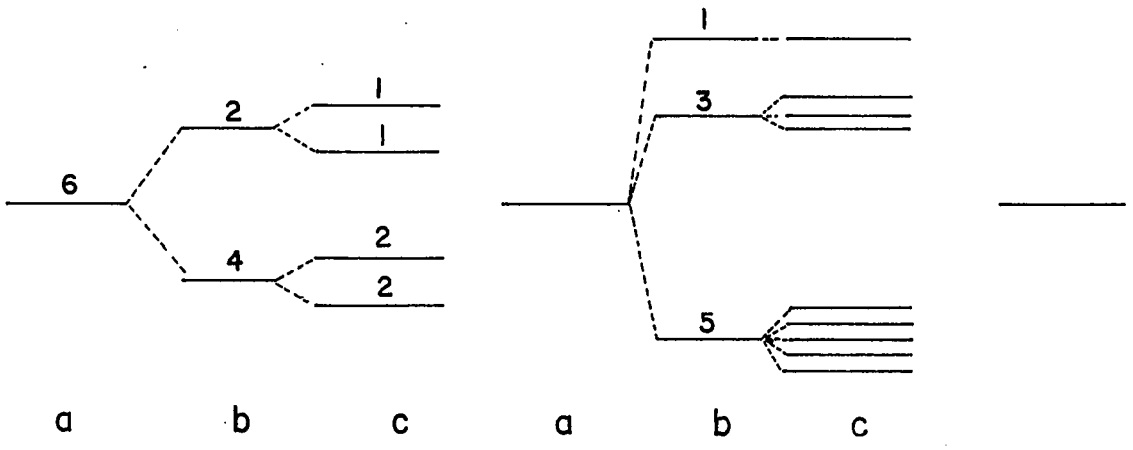
Essentially this theory takes account of spin-orbit coupling. In his calculations Kotani assumed that,

(i) there is a large crystal field splitting, due to 6 symmetrically placed ligands, so that the d_γ orbital lies sufficiently high above the d_ϵ set, and hence the central ion has the configuration $d_\epsilon^{\,n}$ only,

(ii) there is no exchange interaction between paramagnetic ions in the substance and we have effectively a "one ion problem".

He considered the various configurations ($d_\epsilon^{\,n}$) for different values of n, namely $1 \ll n \ll 5$. In each case the ground level of the free ion is degenerate, but due to the spin-orbit coupling interaction and the magnetic field the degeneracy is removed and various energy levels are formed. The splitting due to spin-orbit interaction and magnetic field, for various configurations can be pictured as shown in Fig. 2.

Fig. (2)



Upright for d_ϵ^1 Upright for d_ϵ^2 d_ϵ^3

Invert for d_ϵ^5 Invert for d_ϵ^4

(a) degenerate ground level.

(b) Splitting due to spin-orbit interaction.

(c) Splitting due to magnetic field.

The molar susceptibility is given by the expression:

$$\chi_{mol} = L \frac{\sum_{n,m} \left\{ \frac{(E_{nm}^{(1)})^2}{kT} - 2E_{nm}^{(2)} \right\} e^{-\frac{E_n^{(0)}}{kT}}}{\sum_n g_n e^{-\frac{E_n^{(0)}}{kT}}} \qquad (7)$$

where $E_n^{(0)}$ refers to the energy levels in the absence of a magnetic field, and $E_{nm}^{(1)}$ and $E_{nm}^{(2)}$ denote coefficients of 1st and 2nd order Zeeman displacements of levels respectively, defined by the relation

$$E_{nm} = E_n^{(0)} + E_{nm}^{(1)}H + E_{nm}^{(2)}H^2 + \text{-----}$$

Kotani substituted the energy values of the levels shown in Fig. 2

in the expression (7) for molar susceptibility and derived an expression for the variation of magnetic moment with the temperature in terms of the spin-orbit coupling constant A and the Boltzmann constant k, for various configurations d_ϵ^n.

The results can be represented graphically as shown in Figure 3.

The main conclusions drawn from these calculations are:

(i) for the first transition series where the value of A is of the order of kT, the moments fall on the right hand side of the graph roughly where expected on the basis of the spin-only value for the "spin-paired" complexes.

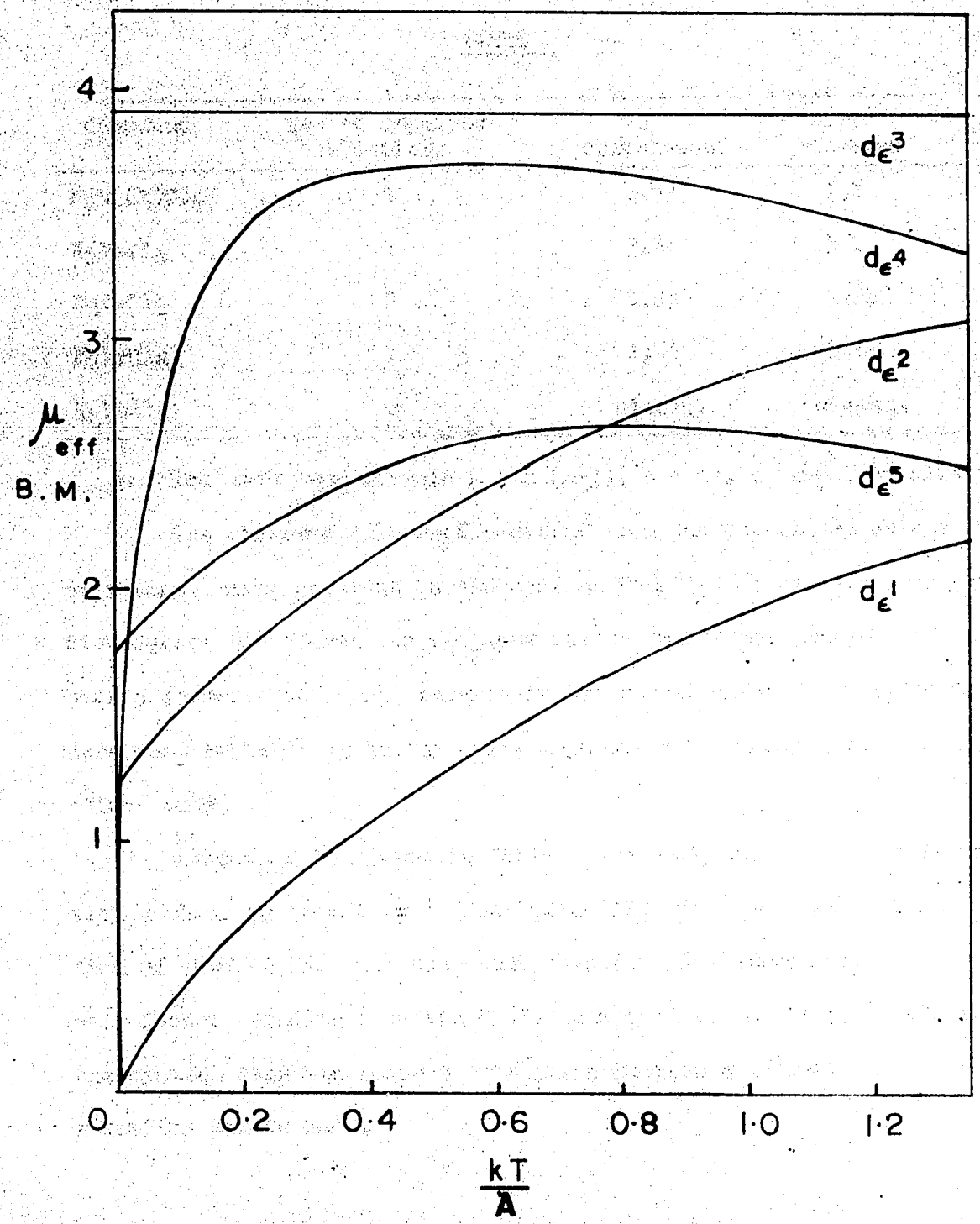
(ii) For the second and third transition series, A is quite large and a temperature dependence of the magnetic moment is observed.

For various cases the behavior expected from the theory is as follows. In cases of d_ϵ^1 and d_ϵ^4, μ_{eff} tends to zero as the temperature approaches zero. In cases of d_ϵ^2 and d_ϵ^5, however, μ_{eff} tends to the finite values 1.22 and 1.73 respectively as the temperature approaches 0°K. At high temperatures μ_{eff} approaches 2.24 in both cases d_ϵ^1 and d_ϵ^5, while it approaches 3.16 in cases d_ϵ^2 and d_ϵ^4. How far these expectations are borne out by experimental results will be shown later.

The Background and the Development of the Problem

The magnetic properties of complex compounds of the second and third transition series are being investigated by a number of workers in order to throw some light on the anomalous behavior which substances containing heavy atoms exhibit. The first thing that strikes one about the magnetic properties of these compounds is the fact that they are of "low spin" type. This is explained readily by the ligand field and molecular orbital theories. However, values of the magnetic moments obtained -

Fig. (3). Plots of μ_{eff} as a function of $\frac{kT}{A}$ (Kotani's theory)



experimentally are lower than those calculated using the spin-only formula. In Table I are given some of the reported values for chlorocomplex of quadrivalent elements of third transition series, the measurements having being made at 294-298°K.

TABLE I

Compound	No. of unpaired electrons	μ calculated	μ_{eff} observed	Ref.
$K_2W(OH)Cl_5$	2	2.83	1.8	6
K_2ReCl_6	3	3.87	3.2	7
K_2OsCl_6	2	2.83	1.44	7
K_2IrCl_6	1	1.73	1.65	7
K_2PtCl_6	0	diamag.	diamag.	

μ calculated from formula $\mu = n(n+2)$, n = no. of unpaired electrons.

The observed values of μ differ from the calculated values, the difference being greatest in the case of K_2OsCl_6. A satisfactory explanation cannot be offered for such low values unless measurements are made over a temperature range, because it has become apparent recently that care must be taken in interpreting magnetic data obtained at room temperature only.

Compounds mentioned in Table I are examples of d_ϵ^n configurations with n changing from 2 to 6 from $K_2W(OH)Cl_5$ to K_2PtCl_6. With the exception of $K_2W(OH)Cl_5$, all compounds have the same structure, so that the only factor changing from the W (IV) compound to the Pt (IV) compound is the central atom and hence a comparison between different d_ϵ^n configurations can be made.

d_ϵ^6. The d_ϵ orbitals can accomodate 6 electrons and in K_2PtCl_6 the d_ϵ set is completely filled thus leading to the observed diamagnetism of K_2PtCl_6.

d_ϵ^5. K_2IrCl_6 is an example of d_ϵ^5 configuration. The observed magnetic moment is lower than the spin-only formula. Measurements over a broad temperature range were first carried out by Norman and Morrow[8]. Susceptibilities were determined at temperatures ranging from 78°K to 300°K. Their results are given in TABLE II.

TABLE II

Temp. °K	$\chi_M \times 10^6$	μ	$\mu_{eff.}$
298	1131 ± 8	1.73	1.64
273	1257 ± 22	1.76	1.66
231	1468 ± 3	1.76	1.65
226	1495 ± 0	1.76	1.64
195	1723 ± 15	1.78	1.64
91	2969 ± 9	1.72	1.47
78	3277 ± 13	1.71	1.43

Values of $1/\chi_M$ were plotted against the absolute temperature and it was observed that there was a slight deviation from linearity at low temperatures and that the Curie-Weiss law was followed approximately. From the plot the Weiss constant was found to be 34°K and the values of μ reported in Table II were calculated using the expression:

$$\mu = 2.84\left[\chi_M (T + \theta)\right]^{1/2}$$

The value of μ obtained in this way seems to be roughly constant. But on the other hand, if μ_{eff} is calculated using the expression

$$\mu_{eff} = 2.84 \left[\chi_M \times T\right]^{1/2}$$

the values given in the table are obtained and the value decreases with decreasing temperature. If the values of μ_{eff} are plotted against temperature, the points lie on a smooth curve which seems to tend toward a constant value of 1.65 at higher temperatures and at low temperatures the value of μ_{eff} tends to a value which is much lower than 1.73. This behavior is unlike that expected for the d_ϵ^5 configuration according to Kotani's theory. We must, however, recall that the theory is applicable only to complexes in which there is no interaction between paramagnetic ions. The fact that K_2IrCl_6 does not follow Kotani's theory leads us to believe that there is some sort of interaction between Ir atoms in K_2IrCl_6.

From the low value of the magnetic moment and the sign of the Weiss constant Norman and Morrow suggested that antiferromagnetic interaction may be present in K_2IrCl_6.

Earlier Griffiths and Owen[9] reported paramagnetic resonance experiments on iridium atoms present in low concentration in ammonium chloroplatinate. The paramagnetic resonance spectrum exhibited a complex hyperfine structure due to not only the iridium nucleus but also to the nuclei of the six chlorine atoms surrounding each iridium atom. From the hyperfine structure and the low values of the g-factor it was deduced that there is appreciable charge transfer between the central iridium ion and the surrounding chlorines, the electron responsible for paramagnetism spending 70% of its time about the iridium atom and 30% about the chlorine atoms.

Such a charge transfer would facilitate an exchange interaction between the $IrCl_6^=$ units and furthermore the distance between Ir-Ir in the crystals of pure K_2IrCl_6 is compatible with the idea of such exchange. Griffiths, Owen, Park and Partridge[10] investigated the paramagnetic resonance spectrum of adjacent iridium ions in chloroplatinate crystals and determined the exchange interactions between them. From the sign (+ve) of this interaction they concluded that there should be an antiparallel alignment of the spins. The susceptibility measurements at low temperatures carried out by Cooke, Lazenby, McKin, Owen and Wolf[11] revealed an antiferromagnetic transition in the region of liquid helium temperature thus supporting the idea of exchange interaction. These workers measured susceptibilities at 90°K and 298°K also. Their results will be discussed later.

An interesting observation about the hexahaloiridium (IV) salts is, that as the size of the halogen atom increases the distance Ir-Ir increases thereby causing a reduction in the interaction between neighbouring ions and giving a higher magnetic moment viz.,

Cs_2IrF_6	μ_{eff} = 1.42 B.M.[12]
K_2IrCl_6	μ_{eff} = 1.65 B.M.[7]
$(NH_4)_2IrBr_6$	μ_{eff} = 1.77 B.M.[8]

This observation suggests that if by some means we can reduce the interaction between the paramagnetic ions and try to attain a situation in which the mutual interaction is negligible, we should essentially have an isolated ion which would exhibit its normal paramagnetic behavior. One such attempt was that of Sloth and Garner[13]. They determined the magnetic

susceptibility of pure Na_2IrCl_6 and of an aqueous solution of this salt. The magnetic moment of the pure salt was 1.58 B.M. and that of a 0.609 M solution was 1.75 B.M. Since a temperature study of the system could not be made and the system was not studied at increasing dilutions it is not possible to draw any conclusions from this work, but it is obvious that by dissolution the interaction between ions was decreased.

It was therefore thought profitable to investigate the magnetic properties of K_2IrCl_6 diluted with isomorphous diamagnetic K_2PtCl_6 at increasing dilutions and at various temperatures.

$d_\epsilon{}^4$. In the case of K_2OsCl_6, the magnetic moment at room temperature (1.44 B.M.) is much lower than the spin-only value of 2.83 for two unpaired electrons and this value decreases with decreasing temperature. Os (IV) is an example of the $d_\epsilon{}^4$ configuration for which the spin-orbit coupling constant A is large with respect to kT. Consequently, according to Kotani's theory the magnetic susceptibility should be independent of the temperature. Syrkin and Belova[14] observed that the susceptibility of K_2OsCl_6 is indeed independent of temperature from 77° to 292°K. Similar behavior was observed for $(NH_4)_2$ Cs Br_6 by Johansen and Lindberg[15].

Nyholm and co-workers[16] have collected the data on various Os (IV) compounds, which are reproduced in Table III.

The measurements enclosed in parenthesis are those in which the extrapolation to zero temperature was somewhat unreliable, as the susceptibility was varying appreciably at the lowest temperatures of measurements.

The values of A shown in Table III have been derived by extrapolating the susceptibility to zero temperature, when according to Kotani's theory $\chi_M = \frac{24\ N\ \beta^2}{A}$.

TABLE III

Compound	μ_{eff} 300°K	$\chi_M \times 10^6$ extrapolated to zero temp.	A (cm^{-1})
K_2OsF_6	1.30 B.M.	715	8,800
K_2OsCl_6	1.50 B.M.	941	6,700
K_2OsBr_6	1.20 B.M.	609	10,300
K_2OsI_6	1.38 B.M.	(870)	(7,200)
Cs_2OsF_6	1.48 B.M.	950	6,600
Cs_2OsCl_6	1.66 B.M.	1220	5,200
Cs_2OsBr_6	1.74 B.M.	(1450)	(4,300)
Cs_2OsI_6	1.62 B.M.	1180	5,300

The values of A thus obtained are greater than the expected value of ~ 2000 cm^{-1} by a factor of three or four. In order to account for these high values Nyholm and co-workers considered one of Kotani's assumptions invalid; namely that the spin-orbit interaction is much smaller than the interelectronic repulsion. They assumed that there exists an equivalent of j-j coupling within d_ϵ set. On this assumption the susceptibility at zero temperature is given by

$$\chi_M = \left(\frac{16}{3}\right) N\beta^2/A$$

Accordingly the values of A derived are smaller by a factor of 9/2 compared to those given in Table III. However, this involves the difficulty that j-j coupling may also exist in the d_ϵ^3 configuration and it is consequently difficult to explain the spin-only moment in these

compounds. They further remark that the presence of antiferromagnetism seems unlikely and that there should be a variation in the observed susceptibilities of different haloosmates on account of the different degrees of delocalization of electrons on the central atom, with consequent change in the effective value of A. This effect should change regularly with increasing atomic number of the halogen involved. However, the distribution of the measured values of susceptibility given in Table III is random. It may be noted, however, that the moments for the caesium salts are higher than the corresponding potassium salts. This observation leads us to believe that there is an interaction between neighbouring osmium atoms through intervening diamagnetic ions and, that this superexchange coupling decreases as the distance between the osmium atoms increases. It is evident that isomorphous dilution experiments on potassium chloroosmate should decide this question. The author believes that such experiments make possible an accurate determination of the value of the spin-orbit coupling constant for Os (IV) in $OsCl_6^{=}$.

d_ϵ^3. As they provide an example of the d_ϵ^3 configuration of a third transition period element, halorhenates have been investigated fairly extensively. Kotani's theory predicts a temperature independent magnetic moment of 3.87 B.M. for these compounds but the values obtained are lower than this as shown in Table IV.[16]

TABLE IV

Complex	Solution	μ_{eff} 300°K	θ	μ
K_2ReF_6	-	3.32	40°K	3.50
	aqueous	3.25	-	-
K_2ReCl_6	-	3.25	86°K	3.70
	aq., dil. HCl	3.50	-	-
K_2ReBr_6	-	3.19	105°K	3.70
	aq. HBr	3.6	-	-
K_2ReI_6	-	3.32	100°K	3.70

The high value of θ as well as the increase in the magnetic moment on dissolution of the complex, with the exception of the fluoro-compound suggests that there is antiferromagnetic interaction in these compounds. Further evidence for exchange interaction is obtained from paramagnetic resonance studies in which it was observed that a pure sample of K_2ReCl_6 showed no resonance absorption, but in crystals diluted with K_2PtCl_6, six isotropic equally spaced broad lines appeared with a centre of gravity at $g = 1.8$.

In the table the value of μ is calculated using the expression $\mu = 2.84\sqrt{\chi_{Re}(T + \theta)}$. It is seen that even after the allowance for θ is made the value of magnetic moment is lower than the spin-only value of 3.87 B.M.

Penney and Schlapp[17] have developed a theory to explain values of the magnetic moment which are less than the spin-only values for d_ϵ^3 configurations. According to their theory

$$\mu_{observed} = \mu_{spin\text{-}only}\left(1 - \frac{4A}{30\,Dq}\right) \text{-------} \quad (8)$$

Nyholm and co-workers[16] applied this expression to the halorhenates to estimate the spin-orbit coupling constant A. They arrived at a value of about 1800 cm^{-1}, which is of the correct order of magnitude for ions of the third transition series.

d_ϵ^2. For d_ϵ^2 case, Kotani's theory predicts a temperature dependent magnetic moment, with a range of values between 1.22 and 3.16 for very low and high temperatures, respectively. It appears that no example of d_ϵ^2 configuration has been investigated to verify this. In the third transition series, the complex $K_2W(OH)Cl_5$ is an example of d_ϵ^2 and since a temperature study of this compound has not been reported, the author measured the magnetic susceptibilities at three temperatures from 90°K to 300°K. It should be noted that the ligand field in this compound cannot be strictly cubic so that Kotani's theory cannot be expected to apply precisely. Experimental difficulties in preparing mixed crystals containing this substance precluded an investigation of the effect of isomorphous dilution.

EXPERIMENTAL

Magnetic Measurements

The Gouy method was used for determination of magnetic susceptibilities. The basic principles involved in this method are as follows.

If a cylindrical sample is suspended between the poles of a magnet as shown in Fig. 4, the sample is subjected to a non-uniform magnetic field and there is therefore a force acting on the sample. This force is given by

$$f = \frac{1}{2} \chi H^2 A \quad \text{-------} \quad (9)$$

where χ is volume susceptibility,

H is field strength,

A is the area of cross section.

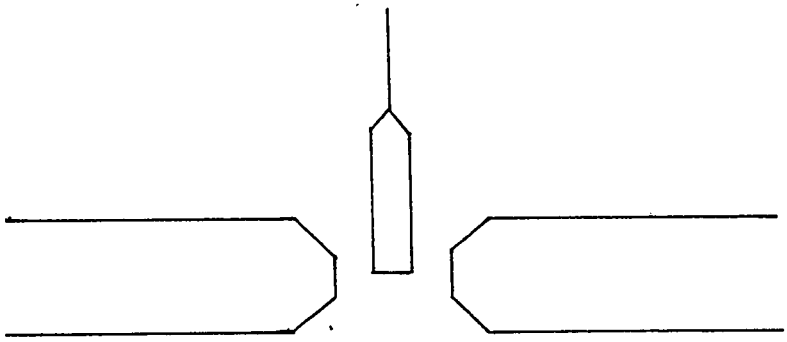


Fig. 4

The above equation holds if the atmosphere surrounding the sample has negligible susceptibility and the field is negligible at the outer end of the sample. If the sample is suspended in air the equation to be used has the form

$$f = \frac{1}{2} (\chi - \chi_o) H^2 A$$

where χ_o is the susceptibility of air.

A precise determination of K_o is difficult since it varies with the atmospheric conditions. A 3 degree change in temperature or a 1% change in barometric pressure will cause a 1% change in K_o. In order to avoid this source of error the sample tube is evacuated. If the pole pieces have a truncated conical shape and the sample is sufficiently long the condition of zero field at the outer end of the sample can be achieved and equation (9) may be used. The force on the sample due to the magnetic field is usually measured by suspending the sample from one arm of a micro-balance. If ΔW is the apparent change in the weight of the sample upon application of the magnetic field, then

$$f = g\Delta W = \frac{1}{2} K H^2 A \quad \text{where } g \text{ is the gravitational constant}$$

$$\text{or} \qquad = \frac{2 \cdot g \cdot \Delta W}{H^2 A}$$

This gives the volume susceptibility K, and in order to obtain gram susceptibility, we use the equation

$$= \frac{2 \cdot g \cdot l \cdot \Delta W}{H^2 m} \quad \text{-------} \qquad (10)$$

where l is the length of the sample column and m is the mass of the sample.

The susceptibilities of various samples were calculated using equation (10) and gram susceptibilities of the paramagnetic ions in the solid solutions where calculated using Wiedemann's additivity law,

$$\chi = \chi_1 m_1 + \chi_2 m_2$$

where χ is the experimentally determined susceptibility and χ_1, χ_2, m_1 and m_2 are the susceptibilities and mole fractions of two components, respectively.

Description of the Magnetic Balance

An Ainsworth projection type microbalance was used for measuring the force on the sample due to the magnetic field. The balance was not damped and the weighings were carried out by the method of swings. The sensitivity of the balance was checked before making measurements at different temperatures. The sample was suspended from the left hand pan of the balance between the pole pieces by means of a stirrup, a turnbuckle and a quartz fibre. By means of the turnbuckle the position of the sample could be adjusted so that the lower end was exactly in the middle of the pole pieces where the field intensity is a maximum.

The electromagnet possessed truncated pole pieces, the gap between these being 1.9 cms. The electromagnet was mounted on an adjustable table that could be moved in two horizontal directions at right angles to one another. Measurements were made at four different field strengths obtained by using currents of 2.5, 5.0, 7.5 and 10.0 amps. The currents were drawn from a set of lead accumulators, adjusted by a rheostat and were measured by a Bach-Simpson Ltd., Model 9 ammeter which provided an accuracy of $\pm$0.5%.

The sample was contained in a pyrex glass tube, the diameter of which was chosen as small as possible, so that the field at a particular height would be uniform, as required by the theory of the Gouy method. The diameter of the sample tube in the present work was outer diameter = 3 mm; inner diameter = 1.5 mm.

In order to fill the sample tube, it was sealed to another tube with a larger diameter and having a ground glass joint at the other end. The tube was charged with the sample and evacuated. The sample tube was

sealed and a hook made at the upper end. In suspending the tube from the quartz fibre care was taken to ensure that the sample was vertical. By means of the turnbuckle the lower end of the sample was adjusted to be in the middle of pole pieces, vertically. The magnet was aligned so that the sample tube was in the middle of the pole pieces, horizontally and laterally. The sample tube, quartz fibre and the turnbuckle were enclosed in a glass jacket so that no portion of the system from pan to the sample was subject to air currents.

Correction for the empty tube

Since glass is diamagnetic, it is necessary to determine the change in weight, a decrease in this case, which occurred when the field was applied to the empty sample tube. For these measurements, at different temperatures and different field strengths, the tube was evacuated, sealed and suspended between the pole pieces as described.

The corrections for the tube used in subsequent measurements are given in Table V.

TABLE V

Current	Temperature			
	298-302°K	224°K	195°K	90°K
2.5 amp.	-0.050 mg.	-0.050 mg.	-0.050 mg.	-0.055 mg.
5.0 amp.	-0.193 mg.	-0.196 mg.	-0.196 mg.	-0.220 mg.
7.5 amp.	-0.417 mg.	-0.415 mg.	-0.415 mg.	-0.490 mg.
10.0 amp.	-0.626 mg.	-0.612 mg.	-0.612 mg.	-0.744 mg.

The temperatures were measured with a copper-constantan thermocouple.

Calibration of field Strength

Magnetic balances are usually calibrated with the aid of substances of known susceptibility. In the present work hydrated ferrous ammonium sulphate (Mohr's salt) was used as standard substance. Its gram susceptibility is given by [18]

$$\chi = 9500 \times 10^{-6} / (T + 1) \text{ -------} \qquad (11)$$

where T is the absolute temperature at which the measurements are made.

Chemically pure Mohr's salt was recrystallized from water and used in the present work. The sample was dried, finely powdered and unfformly packed in the tube by tapping. The measurements were made at 25°C and the value of H^2 in expression (10) was calculated knowing χ from expression (11). In order that expression (10) could be used, it is necessary that the field at the outer end of the sample be zero. It was found that if the length of the sample column is more than 6 cms. there is negligible field acting on the outer end. The average values of three determinations are given in Table VI. Different measurements agreed within 1%.

TABLE VI

Current	Field Strength
2.5 amp.	1475 gauss.
5.0 amp.	2942 gauss.
7.5 amp.	4325 gauss.
10.0 amp.	5320 gauss.

Magnetic measurements of different samples

The measurements were carried out at different temperatures by the procedure described above for the calibration. The gram susceptibility was calculated from expression (10) and the molar susceptibility for pure compounds was calculated in turn by multiplying the gram susceptibility by the molecular weight.

The magnetic moments were calculated using the equation

$$\mu_{eff} = 2.84\sqrt{\chi_M * T}$$

or $$\mu = 2.84\sqrt{\chi_M (T + \theta)}$$

Low temperature measurements

For low temperature work, the lower end of the jacket was immersed in a coolant contained in a Dewar flask specially constructed so as to fit between the pole pieces[18].

Measurements were made at various temperatures: room temperature, 224°K, 195°K and 90°K. During the measurements, it was noticed that a considerable amount of moisture condensed on the sample tube and the weight of the sample tube steadily increased. In order to obtain the correct value for the change in the weight when the field was applied, the rest point of the balance was determined between every reading and the change in weight was obtained from the mean of two rest points.

Precision and Accuracy of magnetic measurements

In order to determine the standard deviation in magnetic measurements, ten measurements were carried out on a sample of recrystalised Mohr's salt at room temperature and a magnetic field generated by 5.0 amp.

current. The apparent change in the weight on application of the magnetic field was determined in each case. The summary of the results is given below.

Average of ten measurements	3.761 mg.
Average deviation	0.123
Standard deviation	0.0167

Further measurements were carried out with different alignments of the sample tube with respect to the pole pieces, to determine the errors due to improper positioning. The results of these measurements are given below.

	ΔW
Correct position	3.761 mg.
Sample tube 1 mm. higher	3.737 mg.
Sample tube 1 mm. lower	3.747 mg.
Sample tube 1 mm. to left	3.869 mg.
Sample tube 1 mm. to right	3.836 mg.
Sample tube 1 mm. in front	3.754 mg.

From the above figures it is seen that an error of less than 1% is introduced if the position of the sample is 1 mm. higher or lower than or 1 mm. in front of the correct position but the error amounts to 2.3% if the sample is 1 mm. closer to one of the pole pieces than when in the correct position. Since the sample could be suspended in the correct position within 0.5 mm. in each direction, the errors due to incorrect positioning were less than 1%.

The length of the column could be measured to a tenth of a millimeter and since the lengths were usually 6.5 to 7.5 cms, this error would be about 0.1%.

Preparations of Samples

Potassium chloroplatinate K_2PtCl_6

A stock solution of chloroplatinic acid was prepared as follows. Pure platinum metal supplied by Johnson, Matthey and Mallory Ltd. was dissolved in minimum amount of aqua regia and the solution evaporated to dryness on a steam bath. The resulting residue was treated three times with concentrated hydrochloric acid and evaporated each time to dryness. The final residue was dissolved in 0.1 N HCl. The potassium salt was prepared from this by concentrating some of the solution in an evaporating dish and cooling in an ice bath. An excess of cold and filtered saturated solution of reagent grade potassium chloride was then added to the solution. The resulting yellow precipitate of potassium chloroplatinate was separated by filtering through a porous crucible. The product was washed with distilled water and dried in an oven at 120°C. Results of analysis: Platinum calculated 40.12%, found 40.12%.

Bromoplatinic acid

This was prepared from the stock solution of chloroplatinic acid by evaporating the latter 3 times with redistilled hydrobromic acid. This was used in the preparation of a solid solution of potassium bromoplatinate and potassium bromoosmate.

Potassium chloroiridate

A stock solution of sodium chloroiridate was prepared by a method described by Beamish and Hill[19]. Iridium sponge supplied by Johnson, Matthey and Mallory Ltd. was mixed with ten times its weight of reagent grade sodium chloride. This was evenly spread in a porcelain boat. The

boat and its contents were placed in a quartz ignition tube. Cylinder chlorine dried by bubbling it through concentrated sulphuric acid and passing it over a freshly exposed surface of phosphorus pentoxide was passed through the ignition tube. Chlorine and associated vapours issuing from the other end of the ignition tube were led through a train of absorbing solutions, usually 6N hydrochloric acid. The tube and its contents were heated to 700°C for 8 hours, during which time the iridium was converted to chloroiridate. The contents of the boat were dissolved in 0.1 N HCl. No insoluble residue was left in the boat. The ignition tube was washed with 0.1 N hydrochloric acid. The solutions were combined and filtered through a sintered glass crucible and stored as a stock solution. The potassium salt was prepared from this as follows.

The solution was concentrated and chlorine was passed through it in order to oxidise any Ir (III) that might have formed during evaporation to Ir (IV). The concentrated solution was cooled in an ice-bath. An excess of cold, saturated and filtered solution of reagent grade potassium chloride was added to the concentrated solution of sodium chloroiridate whereupon a dark brown precipitate of potassium chloroiridate was formed. This was separated on a filtering crucible, washed with distilled water and dried in an oven at 120°C. The dried product was dissolved in 0.1 N HCl and recrystallized; chlorine being passed through the solution to prevent reduction. Results of analysis: Iridium, calculated 39.77%; found 39.51%.

Potassium chloroosmate

A stock solution of chloroosmic acid was prepared according to

the procedure of Gilchrist[20] from osmium supplied by Johnson, Matthey and Mallory Ltd. Osmium metal was heated in a porcelain boat in an ignition tube and the tetroxide formed was condensed in a trap using dry ice and alcohol mixture. A suction pump was used to draw the tetroxide into the trap. When all the metal had been consumed, the condensed tetroxide was transferred to a flask using 6 N hydrochloric acid. The hydrochloric acid solution was heated under reflux for 3 hours with a little ethyl alcohol. The complete conversion of tetroxide to chloroosmate (IV) was indicated by the transparent red colour of the solution. Potassium chloroosmate was prepared from this stock solution by a method similar to the ane used for potassium chloroplatinate. Results of analysis: Osmium, calculated 39.54%; found 39.12%.

Potassium bromoosmate

A stock solution of bromoosmic acid was prepared by a method similar to that used for chloroosmic acid. In this preparation hydrobromic acid was used instead of hydrochloric acid. The potassium salt was prepared from the free acid by adding a cold saturated solution of reagent grade potassium bromide.

Potassium chlororhenate

This was prepared from rhenium sponge supplied by Johnson, Matthey and Mallory Ltd. The metal was mixed with a 10% excess of the theoretical amount of reagent grade potassium chloride and the mixture spread evenly in a porcelain boat. The boat was contained in an ignition tube. The mixture was first heated in nitrogen to drive off the moisture. A current of dry chlorine was then passed through the ignition tube and the tube was

heated to 500°C. Greenish yellow potassium chlororhenate was formed in the boat and some sublimate of rhenium chlorides condensed on the walls of the tube. The salt was twice recrystalized from 5% hydrochloric acid. Results of analysis: rhenium, calculated 39.05%; found 37.25%.

Potassium hydroxypenta chlorotungstate. $K_2W(OH)Cl_5$

This was prepared by the method described by Olsson[21] as follows. Five grammes of tungstic acid were gradually added to a solution of 3 g. of potassium carbonate until all was dissolved. The solution was filtered through glass wool and diluted to 10 ml. It was then added to 150 ml. of hot concentrated hydrochloric acid through which HCl gas was kept bubbling. The solution of tungstic acid was added slowly with stirring and waiting between each addition for the solution to become clear. The solution was cooled rapidly and the precipitated tungstic acid separated by filtering through glass wool. The tungsten in the solution so obtained was reduced to the quadrivalent state with granulated tin. 10 g. of pure tin were placed in an Erlenmayer flask through which a continuous stream of nitrogen was passed. Filtered tungstic acid solution was quickly added to the tin and the flask stoppered. The reduction of W (VI) began immediately as was observed by the colour change from colourless to blue and then to violet. At this point the reduction was stopped by pouring the solution into another flask filled with nitrogen. HCl gas was then bubbled through this solution for 4-5 hours. The solution was then placed in an ice bath for 3-4 hours, whereupon a dark green powder separated. This was separated on a filtering crucible in a nitrogen atmosphere, washed successively with alcohol and ether and dried in nitrogen. The green crystals are stable

in the atmosphere and give a red solution in water which is readily oxidized. Results of analysis: tungsten, calculated 40.28%; found 40.01%.

Preparation of solid-solutions of complexes

The complexes used in forming solid solutions, namely potassium chloroplatinate, potassium chloroiridate, potassium chlorosmate, potassium chlororhenate, potassium bromoplatinate and potassium bromoosmate are all isomorphous. They crystalize with an antifluorite type structure and the values of their lattice constants do not differ appreciably one from another. X-ray diffraction patterns for the paramagnetic complexes and the diamagnetic diluent displayed no noticeable differences in the line spacings, so that X-ray patterns could not be used for establishing the homogeneity of the solid solutions. However, the lattice constants and the ionic radii of the central atom of the complex ion given in Table VII show that the conditions are ideal for forming solid solutions. Later the magnetic measurements showed that solid solutions were indeed obtained.

TABLE VII

Compound	Lattice Constant	Central Atom	Ionic Radii	Ref.
K_2PtCl_6	9.730	Pt^{4+}	0.48 A°	22
K_2IrCl_6	-	Ir^{4+}	-	-
K_2OsCl_6	9.729	Os^{4+}	0.56 A°	23
K_2ReCl_6	9.861	Re^{4+}	0.56 A°	24
K_2PtBr_6	10.35	Pt^{4+}	0.48 A°	25
K_2OsBr_6	10.30	Os^{4+}	0.56 A°	23

There appear to be no published data for K_2IrCl_6. Of the above

mentioned compounds K_2PtCl_6 and K_2PtBr_6 are diamagnetic and hence K_2PtCl_6 served as solvent for diluting the paramagnetic compounds K_2IrCl_6, K_2OsCl_6 and K_2ReCl_6, respectively. K_2PtBr_6 was used as diluent for K_2OsBr_6.

The solid solutions in present work could not be prepared by the method of fusing the component salts in different proportions as these salts decompose before they melt. Consequently, the method of co-precipitation had to be used.

Solid solution of chloroplatinate and chloroiridate

Although the precipitation of potassium chloroplatinate by adding a saturated solution of potassium chloride to chloroplatinic acid is essentially quantitative, it is not so in case of chloroiridic acid. On account of this fact, solid solutions of definite compositions could not be prepared by measuring aliquot amounts of the respective stock solutions. Rather, the composition had to be established by subsequent analysis of the mixed crystals. In order to obtain a series of solid solutions with a range of concentrations, stock solutions of chloroplatinic acid and chloroiridic acids were mixed in different proportions. The solution was then concentrated by evaporation. Chlorine gas was bubbled through to prevent reduction of Ir (IV) to Ir (III). An excess of cold, saturated and filtered solution of reagent grade potassium chloride was then added with constant stirring. The product formed was immediately separated by filtering through a porous crucible, washed with distilled water, sucked dry with the water pump and then dried in an oven at 120°C.

Solid solutions of chloroosmate and chloroplatinate

These were prepared in the same manner as that used for chloropla-

tinate and chloroiridate except that chlorine was not passed through the solution.

Solid solution of bromoosmate and bromoplatinate

This was prepared in the same way except that the bromocomplexes and potassium bromide were used instead of chlorocomplexes and potassium chloride.

Solid solutions of chlororhenate and chloroplatinate

Since it was not convenient to make a stock solution of chlororhenic acid pure potassium chlororhenate was used. A portion of this salt was dissolved in minimum of 10% hydrochloric acid and the solution was cooled in an ice bath. A few ml. of chloroplatinic acid and a saturated solution of reagent grade potassium chloride were also cooled in an ice bath. The three solutions were then mixed quickly with constant stirring. The product formed was separated on a filtering crucible washed with distilled water, sucked dry by means of a water pump and dried in an oven at 120°C.

ANALYSES

All the products except solid solutions containing rhenium were analysed by standard methods. Compounds were analysed to determine their purity and the solid solutions to determine their composition.

Determination of Platinum

In K_2PtCl_6. This was determined by a method given by Beamish and co-workers[26]. A weighed sample was dissolved in a minimum amount of water in an unetched beaker. 3 g. of sodium acetate and 12 drops of formic acid were then added. The solution was digested at 90-95°C for 12 hours. Chloroplatinate was reduced to platinum metal. The solution was then filtered through a number 42 Whatman filter paper, the precipitate was washed with hot distilled water until the filtrate showed the absence of chloride. The precipitate was ignited at 800°C in a muffle furnace, cooled in a desiccator containing a cotton pad soaked with a saturated solution of calcium nitrate to maintain constant humidity. The precipitate was weighed under conditions approaching 50% relative humidity. For this a small beaker containing a saturated solution of calcium nitrate was always kept in the balance case. The balance used for weighings was a Sartorius-Werke projected scale balance. Weighings were carried out using crucibles as tare weights.

A blank was determined for the analysis and was subtracted from the final weight.

In case of solid solution, the composition was established by analysing the paramagnetic ion. It was only in the case of Pt-Ir solid solutions that the analysis for platinum in the filtrates from the

iridium analysis could be done without undue difficulty. This was carried out on a few samples to verify the composition.

The filtrates from iridium analysis were evaporated to dryness three times with concentrated hydrochloric acid and platinum was precipitated from this residue by reduction with formic acid as described above.

Determination of Iridium

In K_2IrCl_6. This was carried out by igniting a weighed quantity of the sample in a muffle furnace at 700°C, leaching out the potassium chloride formed with distilled water and again igniting in an ignition tube through which a current of hydrogen was passed. The pure metal formed in this way was cooled in hydrogen and then in nitrogen. The crucible was weighed under conditions of constant humidity.

Ir in solid solutions

A modification of Gilchrist's method described by Beamish and Hill[22] was employed. In this method, Ir was precipitated hydrolytically by adding 10% sodium bicarbonate solution until a pH of 6 was reached. The precipitate was weighed as iridium metal after ignition in hydrogen.

Platinum was determined in the filtrate as described. The results of the analysis of various solid solutions are given in Table X.

TABLE X

Composition of Solid Solutions K_2 (Pt,Ir) Cl_6

No.	Wt.% Ir (1)	(2)	Wt.% K_2IrCl_6 Average	Atom % Ir	Atom % Pt
1*	24.92	25.29	63.11	63.25	36.75
2	21.17	21.18	53.25	53.39	46.61
3	14.03	13.73	34.90	35.02	64.98
4	8.05	7.93	20.08	20.17	79.83
5	4.96	5.02	12.54	12.60	87.40

Determination of Osmium

In K_2OsCl_6. A weighed quantity of sample was ignited in a current of hydrogen at 600°C. Potassium chloride formed by decomposition was leached out with water and the residue again ignited in hydrogen at 600°C. The osmium metal thus obtained was converted to the volatile tetroxide by ignition in a muffle furnace at 700°C and finally the crucible was once more heated in hydrogen. No visible residue was left in the crucible.

Os in solid solutions

Osmium was separated by distillation of the tetroxide. The distilling apparatus was similar to that used by Westland and Beamish[27]. A weighed amount of sample was fumed with perchloric acid and the tetroxide was collected in 48% hydrobromic acid. Osmium was determined gravimetrically in this solution with 2-phenylbenzothiazole[28]. The precipitate was washed with 2 N hydrochloric acid[29]. The precipitate was ignited to osmium metal in hydrogen and finally volatilized as tetroxide.

The results for different samples are given in Tables XI and XII.

TABLE XI

Composition of Solid Solutions $K_2(Os,Pt)Cl_6$

No.	Wt. % Os (1)	Wt. % Os (2)	Wt. % K_2OsCl_6 Average	Atom % Os	Atom % Pt
1	26.65	26.54	67.28	67.51	32.49
2	19.76	19.86	50.10	50.34	49.66
3	13.32	13.01	33.32	33.55	66.45
4	7.42	7.39	18.74	18.89	81.11
5	3.08	3.13	7.87	7.94	92.06

TABLE XII

Composition of Solid Solution K_2 (Os,Pt) Br_6

No.	Wt. % Os	Wt. % K_2OsBr_6	Atom % Os	Atom % Pt
1	2.63	10.34	10.40	89.60

Determination of rhenium

There is no recorded method for the separation of rhenium from platinum; consequently it was necessary to establish a special procedure for the analysis of the mixed crystals containing rhenium. Nitron has been used as a precipitant for rhenium, but it was found that platinum is coprecipitated almost quantitatively. It was therefore decided to separate platinum from the solution by reduction to metal and to estimate rhenium in the filtrate by precipitation with nitron. Solutions containing known amounts of rhenium and platinum were prepared as follows for the preliminary investigations.

An aliquot amount of chloroplatinic acid was evaporated to dryness, taken up in water and filtered. A weighed quantity of potassium chlororhenate (IV) was added to the filtered solution. About 200 mgs. of sodium acetate and 2 drops of 3% hydrogen peroxide were added and the solution heated to 80° to 95°C. 15 drops of 90% formic acid were added to the hot solution whereupon a precipitate was formed immediately. The precipitate coagulated overnight at 80-95°C and was separated by filtering through a number 42 Whatman filterpaper. The filtrate was acidified with 2N sulphuric acid, heated to about 80°C and rhenium precipitated by adding 2 ml. of freshly prepared 5% nitron acetate solution. The precipitate was

allowed to stand for two hours at 0°C after which it was filtered through a porous crucible, washed with 0.3% aqueous solution of nitron acetate, dried for 2-3 hours at 110°C and weighed. The results of different analyses are given in Table VIII.

TABLE VIII

Sample No.	Pt taken	Re taken	Re recovered	% Error
1	74 mg.	22.4 mg.	21.2 mg.	- 5.3
2	74 mg.	8.48 mg.	7.70 mg.	-21.0
3	24 mg.	18.40 mg.	19.60 mg.	+ 6.5
4	24 mg.	13.15 mg.	12.17 mg.	- 7.5
5	24 mg.	8.11 mg.	5.57 mg.	-31.3

The results provide no promise that the process could be made quantitative. It was considered advisable to develop a method which does not depend upon the reduction of platinum in aqueous solution. The volatility of rhenium oxides and oxyhalides offers a method for separating the element from platinum since upon heating, the compounds of the latter decompose to form platinum metal. The apparatus shown in Fig. 5 was used for the volatilization of rhenium. It consisted of a bubbling tower (A) containing concentrated sulphuric acid, a quartz ignition tube (B) and two receivers (C) and (D).

Preliminary investigations were carried out on samples of pure potassium chlororhenate and on mixtures containing varying amounts of potassium chloroplatinate and potassium chlororhenate.

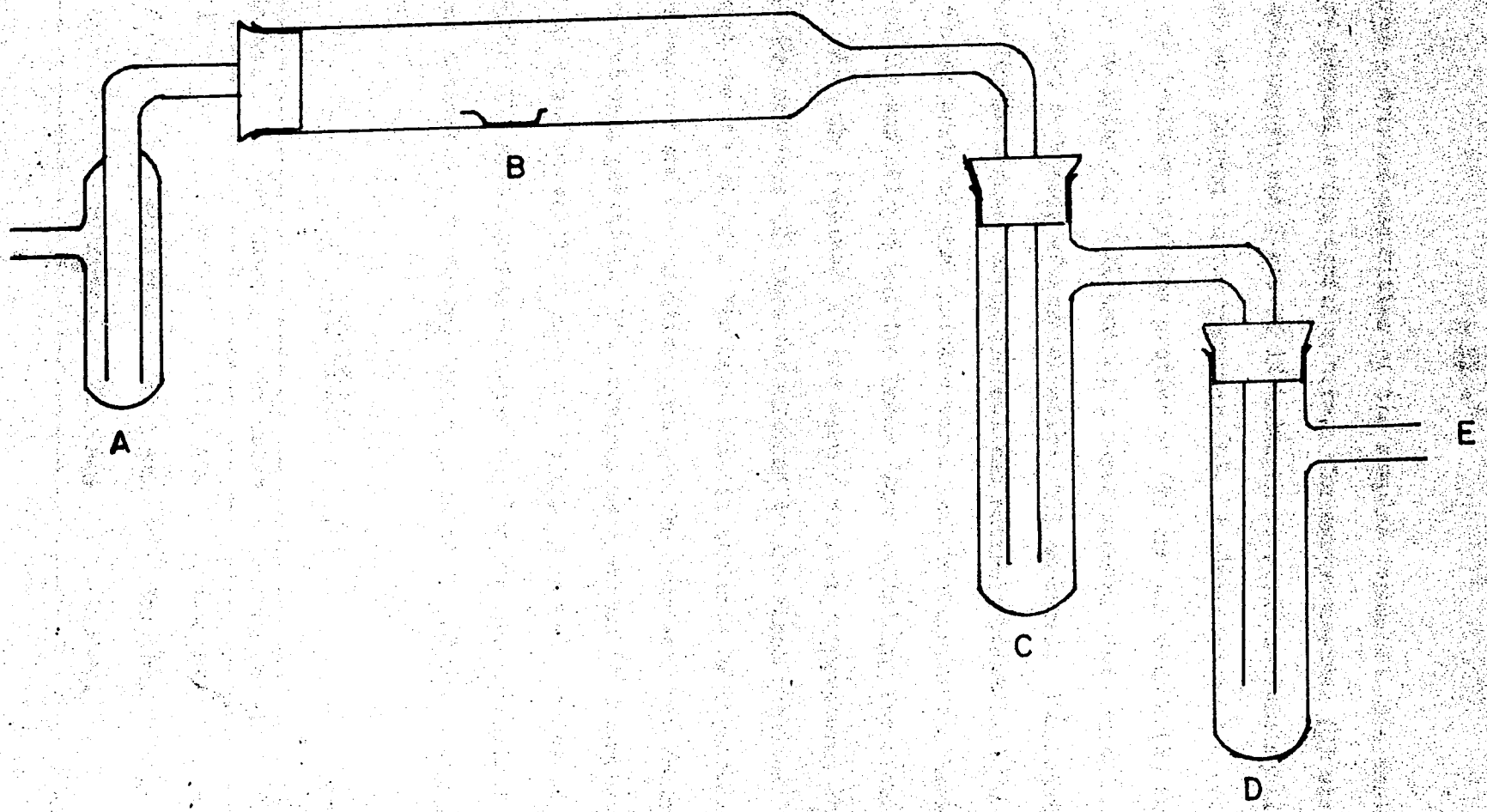


Fig. (5). Diagram of apparatus used for determination of Rhenium

Procedure: - Weighed quantities of the samples contained in a small alumina boat were placed in the ignition tube. The empty receiver (C) was cooled with liquid oxygen and 7 ml. of 1% hydrogen peroxide containing 0.1% sodium hydroxide were placed in the receiver (D). A slow stream of air was drawn through the train by applying suction at (E) and the combustion tube was heated by applying the full heat of a Meker burner. The contents of the boat at first darkened, afterwhich molten KCl appeared. The heating was continued for 30 minutes after the KCl had entirely volatilized and condensed on cooler parts of the ignition tube. After removing the heat, the stream of air was stopped and the Dewar flask containing the liquid oxygen removed. When the receiver (C) had warmed to room temperature, the contents of the receiver (D) were transferred to the first receiver by gently blowing at the outlet (E). The boat and its contents of crystalline platinum were removed and the ignition tube and the receivers rinsed with dilute alkaline hydrogen peroxide. The rinsings were warmed to decompose most of the peroxide and neutralised with 2 N H_2SO_4. A one ml. excess of acid was then added. The solution was filtered and the rhenium determined with nitron as described previously. The results of 3 analyses are given in Table IX.

TABLE IX

Sample No.	Pt taken	Re taken	Re recovered	Error
1	-	11.3 mg.	11.5 mg.	- 0.8%
2	80.2 mg.	17.1 mg.	16.5 mg.	- 3.5%
3	80.2 mg.	22.3 mg.	22.1 mg.	- 0.9%

Although the results show that this is not a very accurate method for the analysis it was adopted for the subsequent analysis of the solid solution of chlororhenate and chloroplatinate, because the accuracy was adequate for the purpose of calculating the magnetic susceptibility of rhenium in the solid solution.

The result of the analysis of the solid solution is given in Table XIII.

TABLE XIII

No.	Wt. % Re		Wt. % K_2ReCl_6	Atom % Re	Atom % Pt
1	6.54	6.80	17.10	17.03	82.97

Determination of tungsten

$K_2W(OH)Cl_5$[30]

A known weight of the compound was dissolved in water and the solution acidified with hydrochloric acid. Chlorine water was added until the colour of the solution changed from red to yellow, due to formation of tungstic acid. The solution was then evaporated to dryness, slurried with water and the residue transferred to a number 42 Whatman filter paper. The filtrate from this operation was evaporated to dryness, after adding a little chlorine water and whatever residue was formed was transferred to the filter paper with 7% HCl. The filter paper was ignited in a crucible at 750-800°C and the residue weighed as tungstic oxide, under conditions of constant humidity.

Determination of oxidation state of tungsten

The tungsten sample was titrated with potassium permanganate, and since the aqueous solution of the compound is easily oxidized by air, it was necessary to carry out the process in an atmosphere of carbon dioxide. A weighed amount of sample was placed in a clean dry flask. The flask was stoppered with a rubber bung having four holes. Two of these were used as inlet and outlet for carbon dioxide. A thistle funnel with a stopcock was inserted through a third hole and the tip of the burette was inserted through the fourth. Carbon dioxide was allowed to flow through the flask for some time, afterwhich water was added from the thistle funnel. The solution was agitated by means of a magnetic stirrer. The solution was titrated against standardized 0.01 N $KMnO_4$. At first the solution was pink and as titrant was added it became colourless. The end point was marked by a persistant pink colour, when all tungsten was oxidized to W (VI). The change in oxidation state was calculated from the equivalents of permanganate used to oxidize one gram atom of tungsten. The results of two analyses are given below.

1) Equivalents of $KMnO_4$ consumed = .000127

Moles of compound taken = .000055

No. of electrons transferred = $\frac{.00013}{.000055}$ = 2.3

2) Equivalents of $KMnO_4$ consumed = .00013

Moles of compound taken = .000073

No. of electrons transferred = $\frac{.00013}{.000073}$ = 1.8

The average of these two gives the number of electrons transferred as 2.0, and since the final oxidation state is six, the oxidation state of the tungsten in the compound was four.

RESULTS AND DISCUSSION

The results of analyses of the various solid solutions are included in Tables X to XIII. Data from the magnetic measurements on the compounds and solid solutions are given in Tables XIV, XV, XVII, XIX and XX.

TABLE XIV

Results of magnetic measurements on pure compounds

Compound	Temp.	Field Strength	Δ W	χ_g	$\chi_M \times 10^6$	μ_{eff}
K_2PtCl_6	298°K	1	-0.025 mg.			
		2	-0.088 "			
		3	-0.204 "	-0.431	209.5	
		4	-0.269 "			
	224°K	1	-0.020 "			
		2	-0.041 "	-0.419	203.7	
		3	-0.163 "			
		4	-0.270 "			
	90°K	1	-0.055 "			
		2	-0.061 "	-0.511	248.4	
		3	-0.241 "			
		4	-0.392 "			
K_2IrCl_6	298°K	1	+0.129 mg.			
		2	0.501 "	2.146	1246	1.72
		3	1.073 "			
		4	1.614 "			
	224°K	1	0.180 "			
		2	0.688 "	2.961	1634	1.71
		3	1.473 "			
		4	2.220 "			
	90°K	1	0.293 "			
		2	1.284 "	5.406	2860	1.44
		3	2.792 "			
		4	4.249 "			

TABLE XIV (continued)

Compound	Temp.	Field Strength	Δ W	χ_g	$\chi_M \times 10^6$	μ_{eff}
K_2OsCl_6	298°K	1	0.065 mg.			
		2	0.253 "	1.344	857.7	1.44
		3	0.570 "			
		4	0.858 "			
	195°K	1	0.064 "			
		2	0.264 "	1.349	860.1	1.16
		3	0.568 "			
		4	0.844 "			
	90°K	1	0.070 "			
		2	0.275 "	1.349	860.1	0.79
		3	0.588 "			
		4	0.863 "			
K_2OsBr_6	300°K	1	0.074 mg.			
		2	0.300 "	.963	991	1.55
		3	0.637 "			
		4	0.951 "			
	195°K	1	0.069 "			
		2	0.297 "	.943	981	1.24
		3	0.637 "			
		4	0.938 "			
	90°K	1	0.075 "			
		2	0.282 "	.952	982	0.84
		3	0.650 "			
		4	0.951 "			
K_2ReCl_6	298°K	1	0.592 mg.			
		2	2.331 "	8.881	4449	3.26
		3	5.097 "			
		4	7.609 "			
	195°K	1	0.808 "			
		2	3.235 "	12.23	6050	3.07
		3	6.978 "			
		4	10.475 "			
	90°K	1	1.296 "			
		2	5.105 "	19.54	9537	2.62
		3	11.209 "			
		4	16.759 "			

TABLE XIV (continued)

Compound	Temp.	Field Strength	Δ W	χ_g	$\chi_M \times 10^6$	μ_{eff}
$K_2W(OH)Cl_5$	298°K	1	0.199 mg.	4.88	2516	2.45
		2	0.810 "			
		3	1.688 "			
		4	2.552 "			
	224°K	1	0.234 "	5.77	2922	2.29
		2	0.946 "			
		3	1.984 "			
		4	3.000 "			
	90°K	1	0.401 "	9.97	4837	1.87
		2	1.579 "			
		3	3.471 "			
		4	5.271 "			

ΔW is the apparent change in weight of the substance when the magnetic field was applied. This has been corrected for the diamagnetism of the empty glass container. For each of the samples the quantity $\frac{\Delta W}{H^2}$ at a given temperature was independent of the field strength showing that the quantity of ferromagnetic impurity in the sample was negligible, consequently the value χ_g or χ_{exp} was calculated from the mean value of $\frac{\Delta W}{H^2}$ for the four values of field strength. The values of χ_M are reported after correcting for the diamagnetism of the ions including the underlying diamagnetism of the paramagnetic ion.

The results will be discussed separately for each electron configuration.

d_ϵ^5 Ir (IV)

The results marked with an asterisk in Tables X and XV are for the sample through which chlorine was not bubbled when the solid solution was prepared. In Fig. 9 and 10 the results are marked with an asterisk

so as to show that a low value of magnetic moment was obtained, probably due to the presence of some Ir (III) ions in the solid solutions. Figures 6, 7 and 8 show the plots of $1/\chi_M$ against temperature for pure K_2IrCl_6 and the various solid solutions. It is seen that slight deviations from linearity are observed. If, however, the best straight line is drawn through the points for pure K_2IrCl_6 a value of θ equal to 62°K is obtained. The value thus obtained differs from the value (34°K) obtained by Norman and Morrow[8] who also observed the deviation from a linear plot. However, the author's data agree well with those of Cooke et al[11]. These workers fitted their results at two temperatures to the expression

$$\chi = \frac{C}{T + \theta} + \alpha_p + \alpha_d \qquad (12)$$

where χ is the measured susceptibility

C is the Curie constant

α_p is the temperature-independent paramagnetism

α_d is the diamagnetic susceptibility,

T and θ have their usual significance and they obtained the value of α_p equal to 0.30 and θ equal to 33.5°K, assuming C as 0.301 c.m.u./mole.

Agreement between the θ value obtained by the two sets of workers is good but their approaches are quite different. Cooke and others make an assumption that the Curie-Weiss law is exactly obeyed and that there is a large temperature-independent paramagnetism, whereas Norman and Morrow do not assume any temperature-independent paramagnetism and they pointed out that the Curie-Weiss law was followed approximately.

When the author's results at 90°K and 298°K were fitted to the

Fig. (6). Plot of $1/\chi_m$ against temp. for K_2IrCl_6

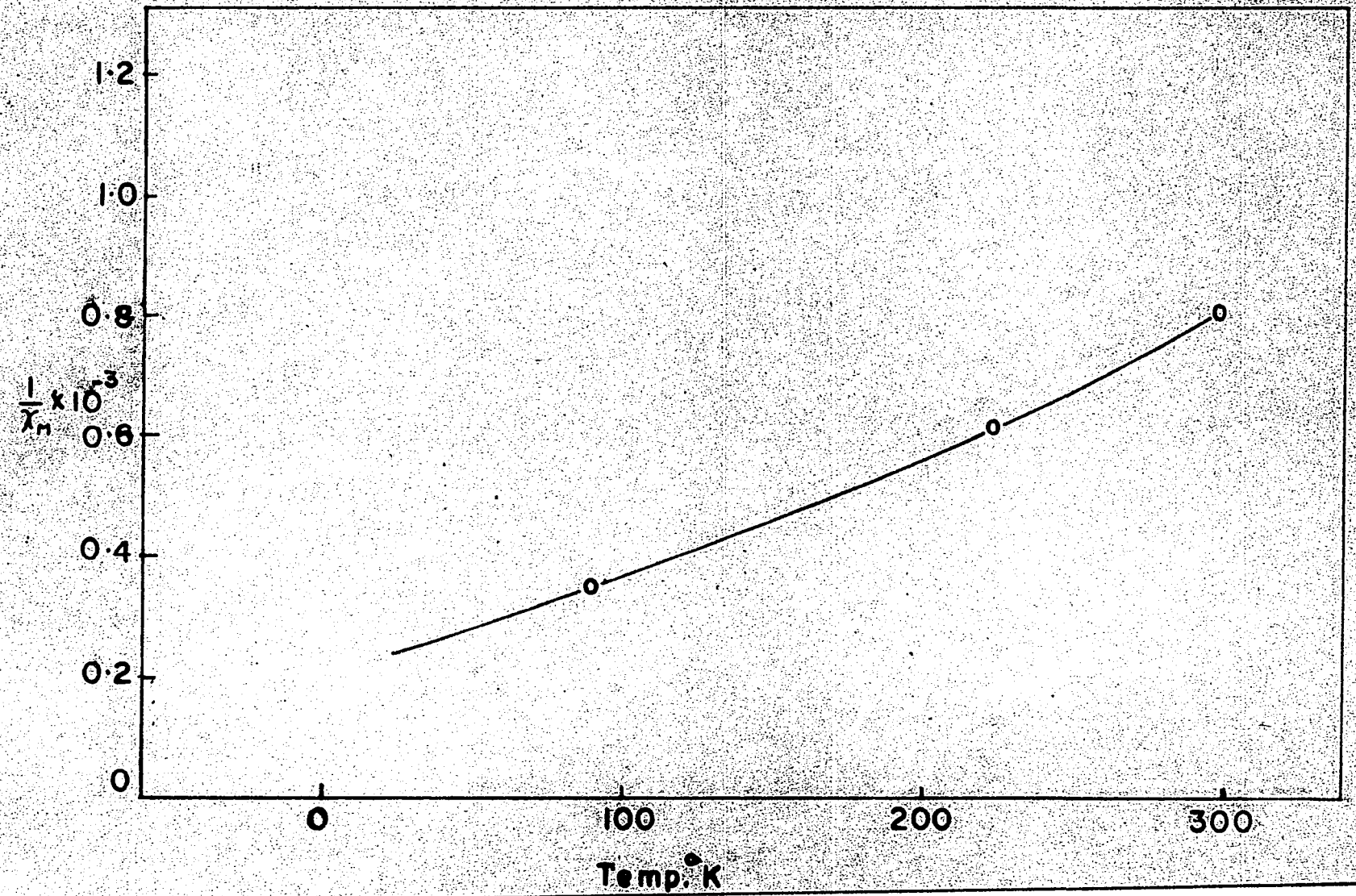


Fig. (7). Plot of $1/\chi_m$ against temp. for $K_2(Pt, Ir)Cl_6$ Prod. 3

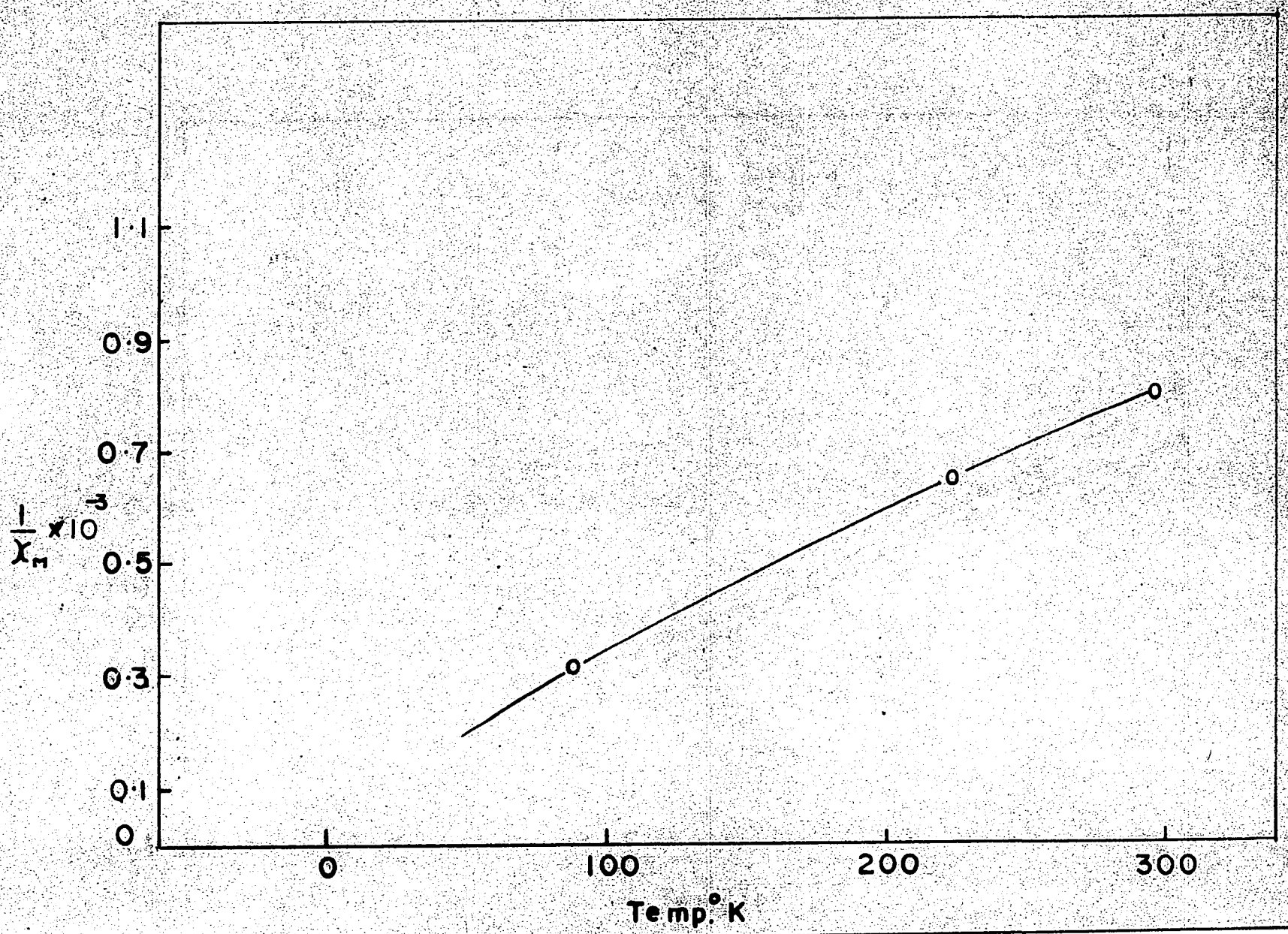
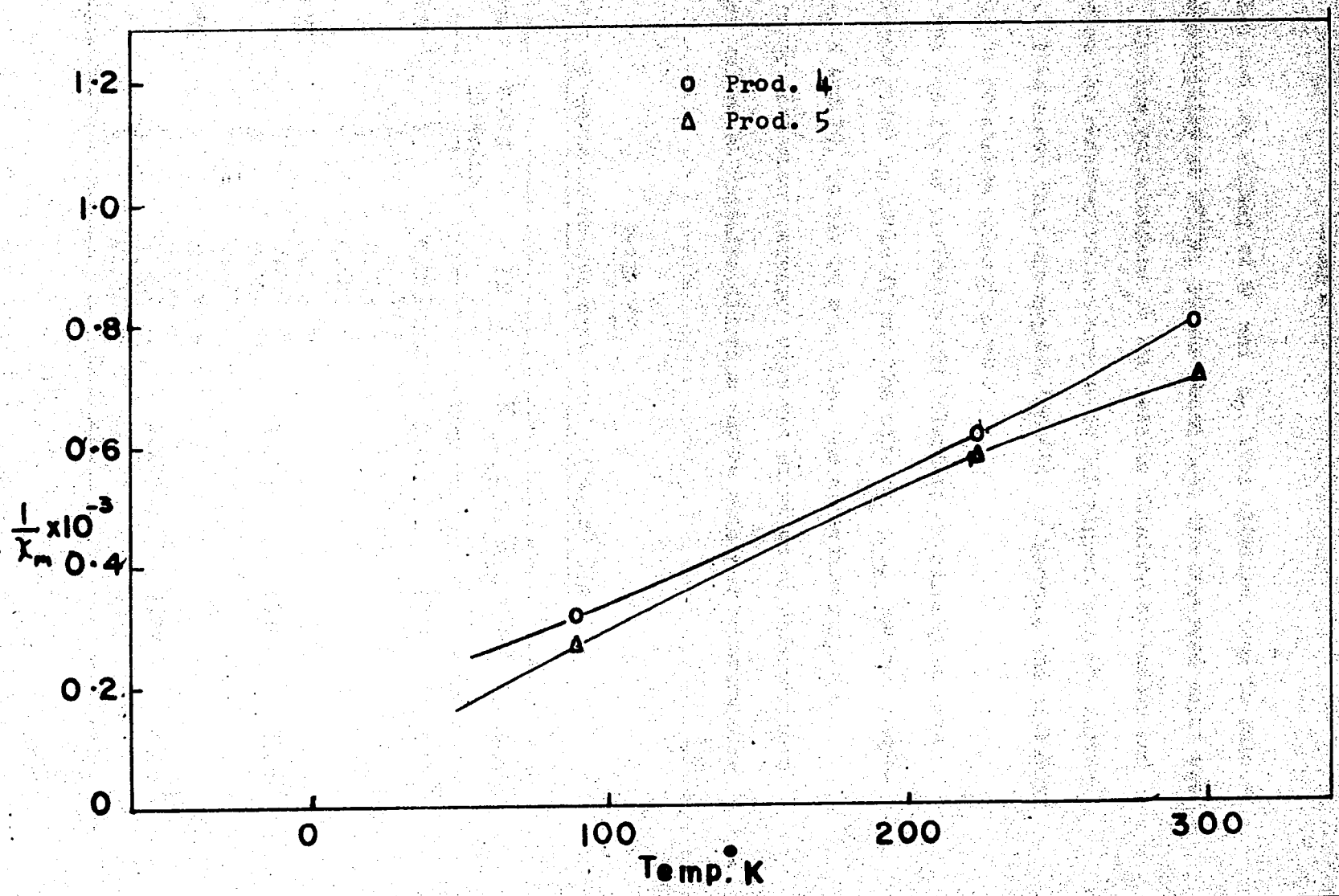


Fig. (8). Plots of $1/\chi_m$ against temp. for $K_2(Pt, Ir)Cl_6$



expression (12) and the values of θ and α_p thus obtained used to calculate the susceptibility at 224°K, it was found that the observed value was 8.5% higher. Similar calculations on the results obtained by Norman and Morrow show that the observed values are up to 10% higher than the calculated values. This shows that the expression (12) is inexact and probably does not apply to potassium chloroiridate.

From the results of various solid solutions of chloroplatinate and chloroiridate given in Table XV and the plot of μ_{eff} against composition in Fig. 9 and 10, it may be seen that the effective magnetic moments of the Ir (IV) atom increase with the dilution of chloroiridate ions and their values at infinite dilution may be obtained by extrapolation.

TABLE XV

Results of Magnetic Measurements on K_2 (Pt,Ir) Cl_6

Prod. No.	Temp.	Field Strength	ΔW	χ_{exp}	$\chi_{Ir} \times 10^6$	μ_{eff}
1	298°K	1	0.045 mg.	0.921	1037	1.57*
		2	0.163 "			
		3	0.343 "			
		4	0.524 "			
	224°K	1	0.056 "			
		2	0.237 "	1.324	1337	1.55*
		3	0.497 "			
		4	0.772 "			
	90°K	1	0.121 "			
		2	0.507 "			
		3	1.081 "	2.850	2577	1.36*
		4	1.654 "			

TABLE XV (continued)

Prod. No.	Temp.	Field Strength	ΔW	χ_{exp}	$\chi_{Ir} \times 10^6$	μ_{eff}
2	298°K	1	0.035 mg.	0.876	1188	1.68
		2	0.138 mg.			
		3	0.285 mg.			
		4	0.430 mg.			
	224°K	1	0.049 "	1.25_6	1522	1.65
		2	0.198 "			
		3	0.411 "			
		4	0.625 "			
	90°K	1	0.100 "	2.70_2	2918	1.45
		2	0.417 "			
		3	0.911 "			
		4	1.380 "			
3	298°K	1	0.025 mg.	0.463	1241	1.72
		2	0.078 "			
		3	0.161 "			
		4	0.250 "			
	224°K	1	0.032 "	0.700	1552	1.67
		2	0.126 "			
		3	0.250 "			
		4	0.393 "			
	90°K	1	0.085 "	1.80_8	3214	1.52
		2	0.324 "			
		3	0.656 "			
		4	1.021 "			
4	298°K	1	0.003 mg.	0.090	1255	1.73
		2	0.021 "			
		3	0.049 "			
		4	0.081 "			
	224°K	1	0.016 "	0.258	1631	1.71
		2	0.062 "			
		3	0.116 "			
		4	0.185 "			
	90°K	1	0.043 "	0.832	3232	1.53
		2	0.178 "			
		3	0.406 "			
		4	0.672 "			

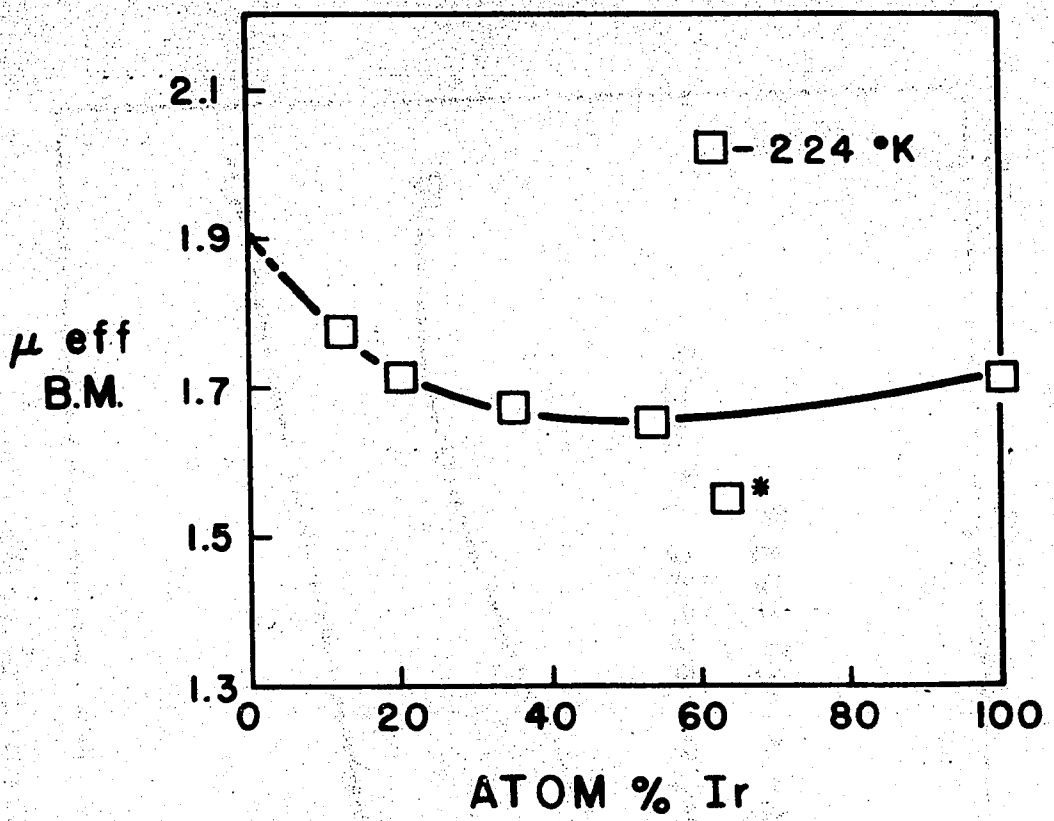
TABLE XV (continued)

Prod. No.	Temp.	Field Strength	Δ W	χ_{g} exp	$\chi_{Ir} \times 10^{6}$	μ_{eff}
5	298°K	1	-0.006 mg.			
		2	-0.016 "	-0.064	1416	1.84
		3	-0.023 "			
		4	-0.033 "			
	224°K	1	0.005 "			
		2	0.006 "	0.034	1745	1.77
		3	0.006 "			
		4	0.007 "			
	90°K	1	0.026 "			
		2	0.115 "	0.459	3739	1.64
		3	0.157 "			
		4	0.300 "			

In the above Table field strengths 1, 2, 3 and 4 correspond to 1475, 2940, 4325 and 5320 gauss, respectively.

Plots of μ_{eff} against composition for $K_2(Ir, Pt)Cl_6$

Fig. (9)



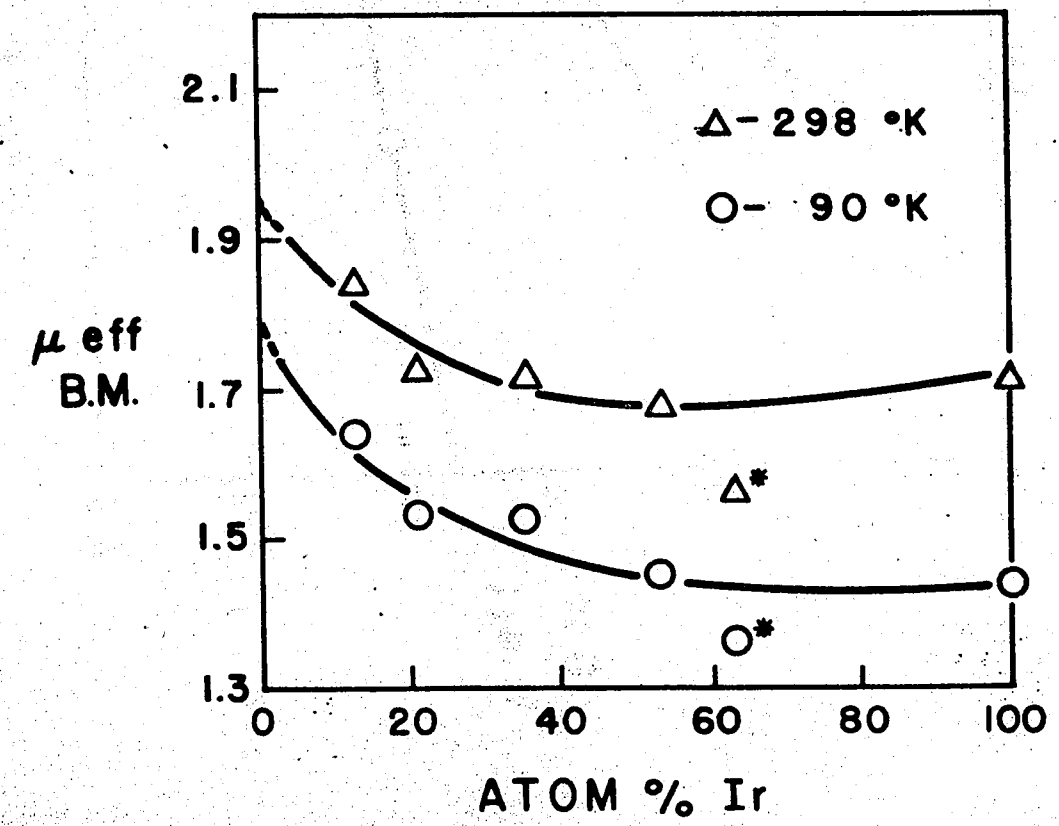


Fig. (10)

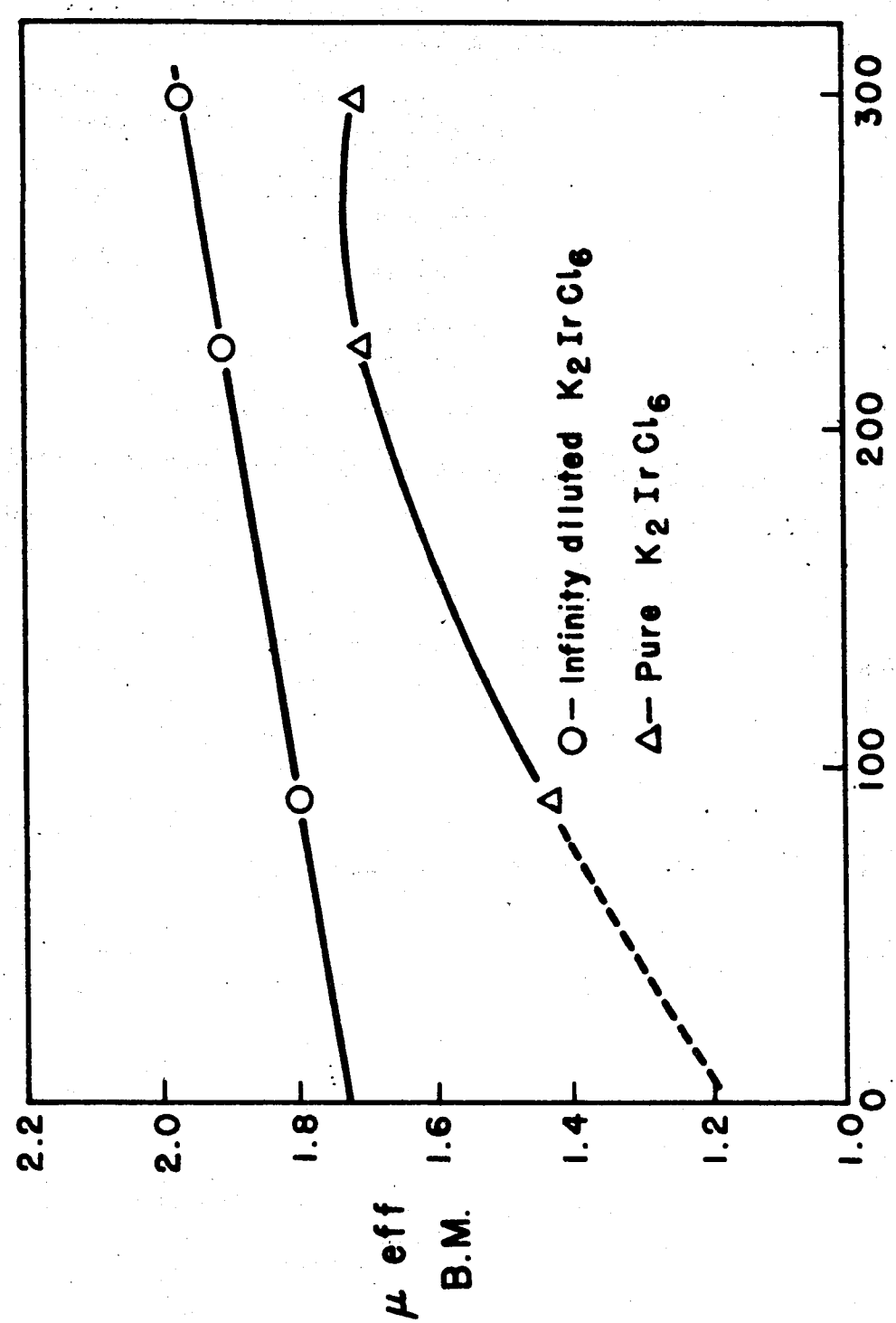


Fig. (11). Plots of $\mu_{eff.}$ against Temperature for Pure K_2IrCl_6 and infinitely diluted K_2IRCl_6.

The extrapolated values of magnetic moment are given in Table XVI and are plotted against temperature in Fig. 11.

TABLE XVI

Temp. °K	μ_{eff} at infinite dilution	χ_M at infinite dilution
298	197 B.M.	1.63×10^{-3}
224	1.91 B.M.	2.04×10^{-3}
90	1.80 B.M.	4.50×10^{-3}

Fig. 12 gives the variation of the magnetic moment with temperature as expected by Kotani's theory for ions with large spin-orbit coupling constants.

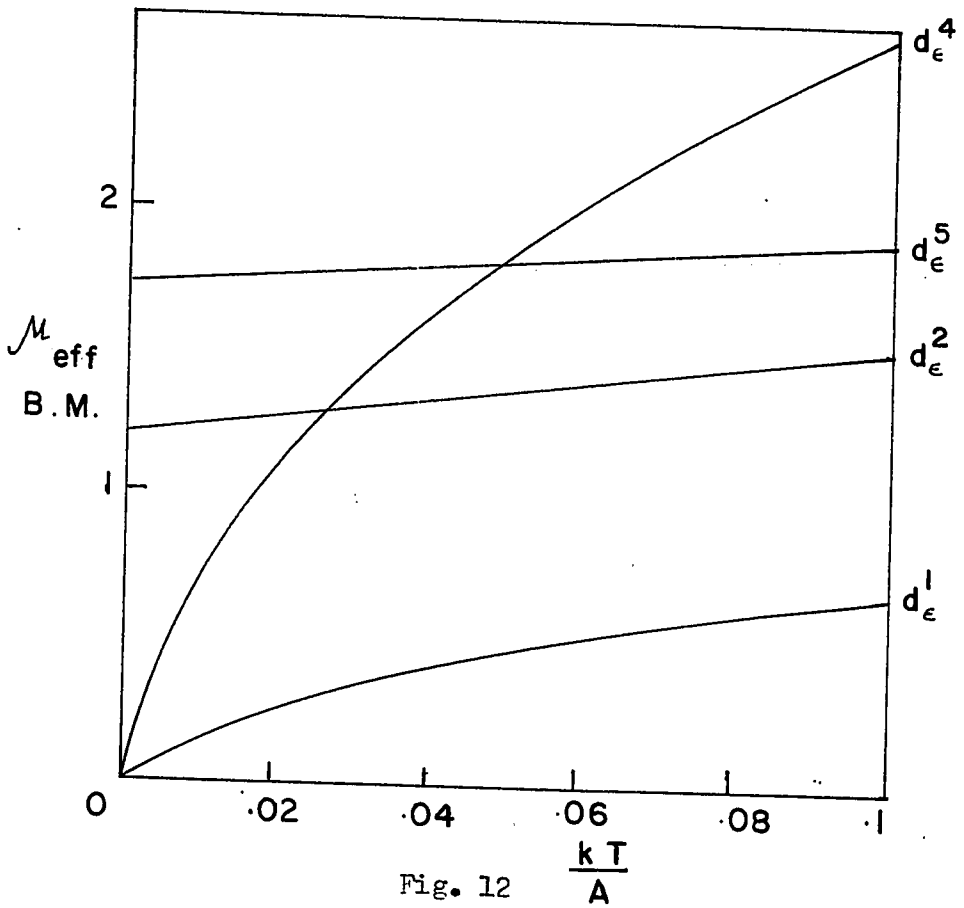


Fig. 12

By comparison with other ions in the third transition series, a value of the order to 2000 cm^{-1} is expected for the spin-orbit coupling constant for Ir (IV), consequently, the temperature dependence shown in Fig. 12 for d_ϵ^5 is expected. This predicts a straight line approaching 1.73 B.M. at 0°K and about 2.0 B.M. at room temperature. Fig. 11 shows that pure K_2IrCl_6 does not behave in the way predicted by Kotani's theory, whereas the expected behavior is realized for an infinitely dilute solid solution of potassium chloroiridate. The good agreement between theory and experiment may be fortuitous because the extrapolated values cannot be expected to be precise; however, the result clearly shows that by dilution of chloroiridate ions, the interaction between neighbouring ions is reduced and an effectively isolated ion is obtained, which behaves as expected by Kotani's theory.

It may be seen from the plot of μ_{eff} against temperature that the Curie-Weiss law is not obeyed by magnetically dilute potassium chloroiridate.

The fact that the magnetic moment of chloroiridate ion at infinite dilution at room temperature is 1.97 B.M. shows that there is appreciable contribution from the orbital motion of electrons in the Ir (IV) ion. In pure chloroiridate, however, due to exchange interaction a lower value is obtained.

This shows that Cooke and co-workers are not justified in calculating C, the Curie constant from the expression

$$C = \frac{N g^2 \beta^2 s (s + 1)}{3 k} \qquad (13)$$

where N is the Avogadro's number,

g is the Landé splitting factor,

β is the Bohr magneton and

s is the resultant spin quantum number,

because the expression assumes a spin-only moment for the ion.

d_ϵ^4 Os (IV)

Kotani's theory predicts a temperature-independent paramagnetism for the d_ϵ^4 configuration. It may be seen from Table III that this is true not only for the pure compounds of Os (IV) such as K_2OsCl_6, K_2OsBr_6, $(NH_4)_2OsBr_6$, K_2OsF_6, Cs_2OsF_6, Cs_2OsCl_6 and of Ru (IV) and Ir (V)[16] but is also true, within the limits of experimental error for the solid solutions of chloroosmate and chloroplatinate.

It was pointed out in the introduction that the values of the susceptibilities of various halo-complexes of osmium should increase with the atomic number of halogen, but the values given in Table III do not appear to support this. Apparently, however, the value reported for K_2OsBr_6 by Nyholm and co-workers[16] is in error. Johanson and Lindeberg[15] reported a value 980 x 10^{-6} e.m.u. for $(NH_4)_2$ Os Br_6 and since K_2OsBr_6 does not differ magnetically from $(NH_4)_2$ $OsBr_6$ a similar value for K_2OsBr_6 may be expected. In the present investigation the value 986 ($\pm$ 5) x 10^{-6} was obtained over a temperature range 90° to 300°K. Assuming this to be a correct value it appears that as the atomic size of the halogen increases the value of the magnetic moment increases except in the case of the hexaiodo complex. It may also be seen from Table XVII that as the concentration of chloroosmate ion decreases the magnetic moment increases.

TABLE XVII

Results of Magnetic Measurements on $K_2(Pt,Os)Cl_6$

Prod. No.	Temp.	Field Strength	Δ W	χ_{exp}	$\chi_{Os} \times 10^6$	μ_{eff}
1	301°K	1	0.038 mg.	0.865	928.8	1.50
		2	0.157 "			
		3	0.341 "			
		4	0.511 "			
	195°K	1	0.038 "			
		2	0.156 "	0.865	920.1	1.20
		3	0.349 "			
		4	0.503 "			
	90°K	1	0.032 "			
		2	0.156 "	0.836	899.4	0.80
		3	0.340 "			
		4	0.502 "			
2	302°K	1	0.029 mg.			
		2	0.118 "	0.550	944.0	1.51
		3	0.239 "			
		4	0.358 "			
	195°K	1	0.027 "			
		2	0.115 "	0.563	944.9	1.21
		3	0.240 "			
		4	0.357 "			
	90°K	1	0.028 "			
		2	0.107 "	0.550	932.4	0.82
		3	0.242 "			
		4	0.346 "			
3	300°K	1	0.011 mg.			
		2	0.049 "	0.263	1003	1.56
		3	0.105 "			
		4	0.160 "			
	195°K	1	0.010 "			
		2	0.059 "	0.254	973.5	1.23
		3	0.110 "			
		4	0.135 "			
	90°K	1	0.015 "			
		2	0.052 "	0.296	1034	0.86
		3	0.114 "			
		4	0.160 "			

TABLE XVII (continued)

Prod. No.	Temp.	Field Strength	Δ W	χ_{exp}	$\chi_{Os} \times 10^6$	μ_{eff}
4	302°K	1	0.006 mg.			
		2	0.009 "	0.056	1252	1.74
		3	0.017 "			
		4	0.019 "			
	195°K	1	0.003 "			
		2	0.012 "	0.056	1220	1.38
		3	0.018 "			
		4	0.020 "			
	90°K	1	0.006 "			
		2	0.006 "	0.034	1301	0.97
		3	0.005 "			
		4	0.011 "			
5	301°K	1	-0.009 mg.			
		2	-0.026 "	-0.175	1567	1.94
		3	-0.058 "			
		4	-0.099 "			
	195°K	1	-0.010 "			
		2	-0.017 "	-0.159	1592	1.58
		3	-0.054 "			
		4	-0.094 "			
	90°K	1	-0.004 "			
		2	-0.043 "	-0.202	1894	1.17
		3	-0.070 "			
		4	-0.113 "			

In the above Table field strengths 1, 2, 3 and 4 correspond to 1475, 2940, 4325 and 5320 gauss, respectively.

These results may be interpreted as follows. In halo-complexes, as the size of the halogen atom increases, the distance between neighbouring osmium ions increases, diminishing the interaction between paramagnetic ions. In solid solutions platinum atoms take the place of some of the osmium atoms. The superexchange between neighbouring atoms is no longer possible and the magnetic moment increases. The values of the magnetic

moment at different temperatures of various solid solutions are plotted against concentration in Fig. 13. From this figure the values at infinite dilution of chloroosmate may be obtained by extrapolation. The extrapolated values of magnetic moment and the values of susceptibility calculated from these are given in Table XVIII. It is seen that those values are also independent of temperature.

TABLE XVIII

Temperature	μ_{eff} infinite dilution	O_s infinite dilution
298°K	2.13 B.M.	1.90×10^{-3}
195°K	1.76 B.M.	1.94×10^{-3}
90°K	1.38 B.M.	1.92×10^{-3}

According to Kotani's theory the value of the spin-orbit coupling constant may be calculated by using the expression

$$\chi_M = \frac{24\ N\ \beta^2}{A} \quad \text{-------} \quad (14)$$

where χ_M is the susceptibility at 0°K. A value of 3240 cm^{-1} is thus obtained using the extrapolated susceptibility values. This is of the order of magnitude expected for atoms of the third transition series.

Nyholm and co-workers obtained a range of values between 5000 and 10,000 cm^{-1} by fitting their results given in Table III to expression (14) and they admit that the values are greater than expected by a factor of three or four.

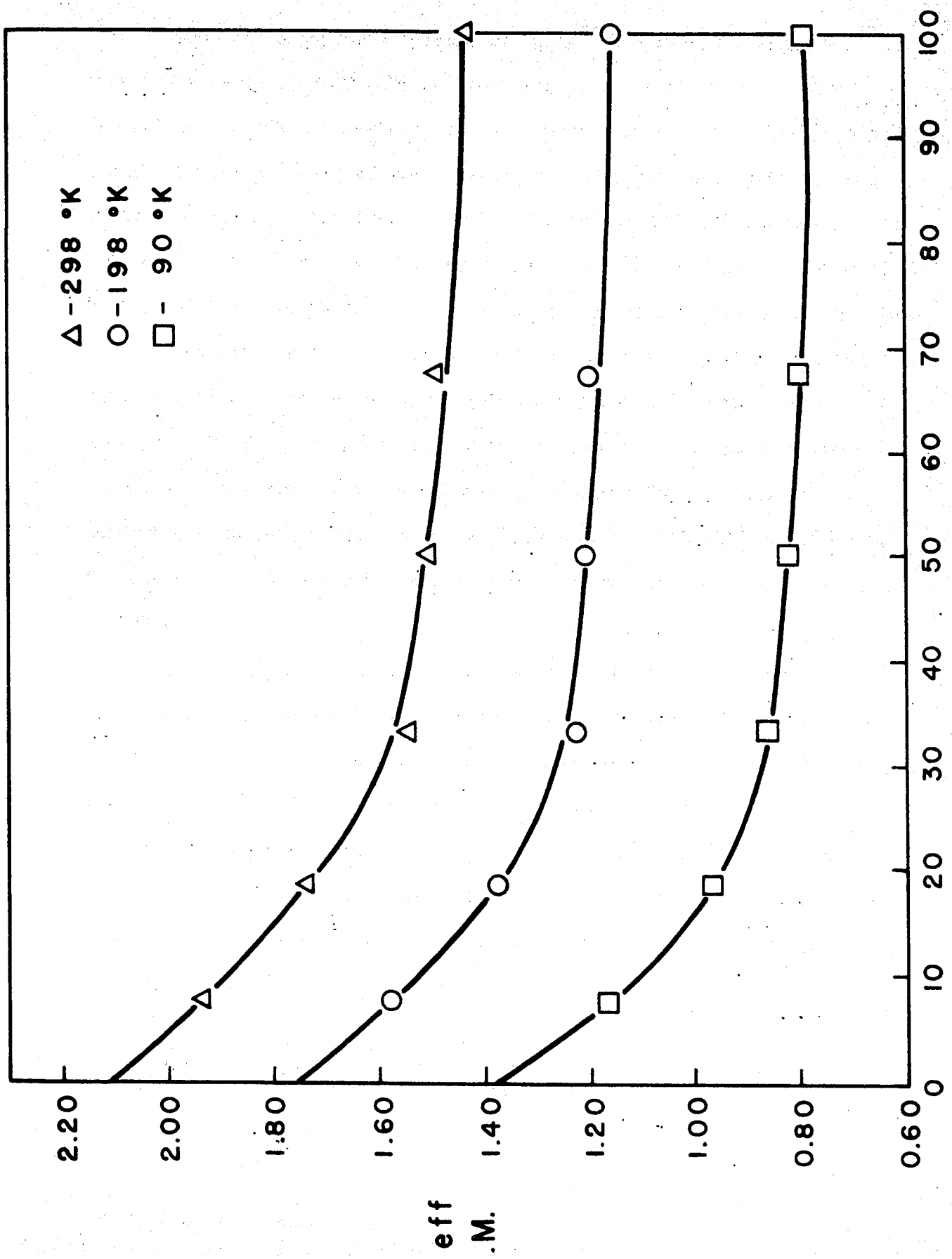


Fig. (13). Plots of μ_{eff} against composition for $K_2(Pt, Os)Cl_6$

From the absorption spectra of $OsCl_6^{2-}$ and $OsBr_6^{2-}$, Jorgenson[31] obtained a value of 3600 cm^{-1} for the spin-orbit coupling constant of Os (IV) in complexes. Any such value obtained for A pertains only to the ion in its environments of ligand atoms and must be expected to be some 20 to 40% less than the free ion value[32]. Griffith[33] estimated a value of 4500 cm^{-1} for the free Os (IV) atom. The value obtained by the author for Os (IV) atom in the $OsCl_6^{=}$ complex - is in good agreement with these values.

With this value of spin-orbit coupling constant, the variation of magnetic moment with temperature could be represented by the curve for the configuration d_ϵ^4 given in Fig. 12. This requires that at room temperature a value of about 2.0 B.M. should be obtained for Os (IV). In pure compounds, however, values as low as 1.44 B.M. for K_2OsCl_6 and 1.55 B.M. for K_2OsBr_6 are obtained because of superexchange between neighbouring osmium atoms.

It is still a matter of speculation as to how effective the bromine atom is in transmitting a superexchange coupling. The author's measurements on the solid solutions of bromoosmate and bromoplatinate, reported in Table XIX show that the magnetic moment of osmium in solid solution is greater than in pure K_2OsBr_6. It may, therefore, be concluded that bromine atoms can also transmit spin coupling and that superexchange is partly responsible for the low value of the magnetic moment in bromoosmate.

TABLE XIX

Solid solution of K_2OsBr_6 and K_2PtBr_6

Prod. No.	Temp.	Field Strength	Δ W	χ_{exp}	$\chi_{Os} \times 10^6$	μ_{eff}
1	302°K	1	-0.011 mg.			
		2	-0.036 "	-0.142	1587.	1.96
		3	-0.111 "			
		4	-0.135 "			
	195°K	1	-0.012 "			
		2	-0.041 "	-0.156	1486.	1.52
		3	-0.108 "			
		4	-0.171 "			
	90°K	1	-0.011 "			
		2	-0.056 "	-0.179	1319.	0.97
		3	-0.115 "			
		4	-0.193 "			

d_ϵ^3 Re (IV)

For the d_ϵ^3 case, Kotani's theory predicts a temperature independent magnetic moment of 3.87 B.M. The plot of μ_{eff} against $\frac{kT}{A}$ is a straight line parallel to the $\frac{kT}{A}$ axis. This implies that regardless of the spin-orbit coupling constant A, the value of μ_{eff} should be 3.87 B.M. at all temperatures. Any deviations from this could be due to causes such as exchange interactions or distortions of the cubic field. It is unlikely that there would be any distortions of the crystaline field due to the six octahedrally placed chlorine atoms around the rhenium atom, so the most likely explanation for the low values of μ_{eff} in chlororhenates is the occurance of antiferromagnetic interactions.

The values of the magnetic susceptibility of pure K_2ReCl_6 are given in Table XIV and the plot of $1/\chi_M$ against absolute temperature is

given in Fig. 14. It is seen that pure K_2ReCl_6 follows the Curie-Weiss law exactly with a θ value of 90°K. The results obtained agree with those of Klemm and Steinberg[34]. If the magnetic moment is calculated taking the value of θ into account, the values of magnetic moment given in Table XXI are obtained. These values are lower than the spin-only values of 3.87 B.M. The data obtained from the solid solution of chlororhenate and chloroplatinate are given in Table XX and the reciprocal of the susceptibility is plotted against temperature in Fig. 14.

TABLE XX

Solid Solution of K_2ReCl_6 and K_2PtCl_6

Prod. No.	Temp.	Field Strength	Δ W	χ_{exp}	Re x 10^6	μ_{eff}
1	298°K	1	+0.086 mg.			
		2	0.339 "	1.530	5478	3.62
		3	0.752 "			
		4	1.111 "			
	195°K	1	0.134 "			
		2	0.546 "	2.413	7915	3.52
		3	1.174 "			
		4	1.719 "			
	90°K	1	0.281 "			
		2	1.099 "	4.968	15300	3.34
		3	2.438 "			
		4	3.599 "			

It is seen that the solid solution also obeys the Curie-Weiss law exactly and a value of θ equal to 26°K is obtained. When the magnetic moments are calculated using the Curie-Weiss expression, the values given in Table XXI are obtained.

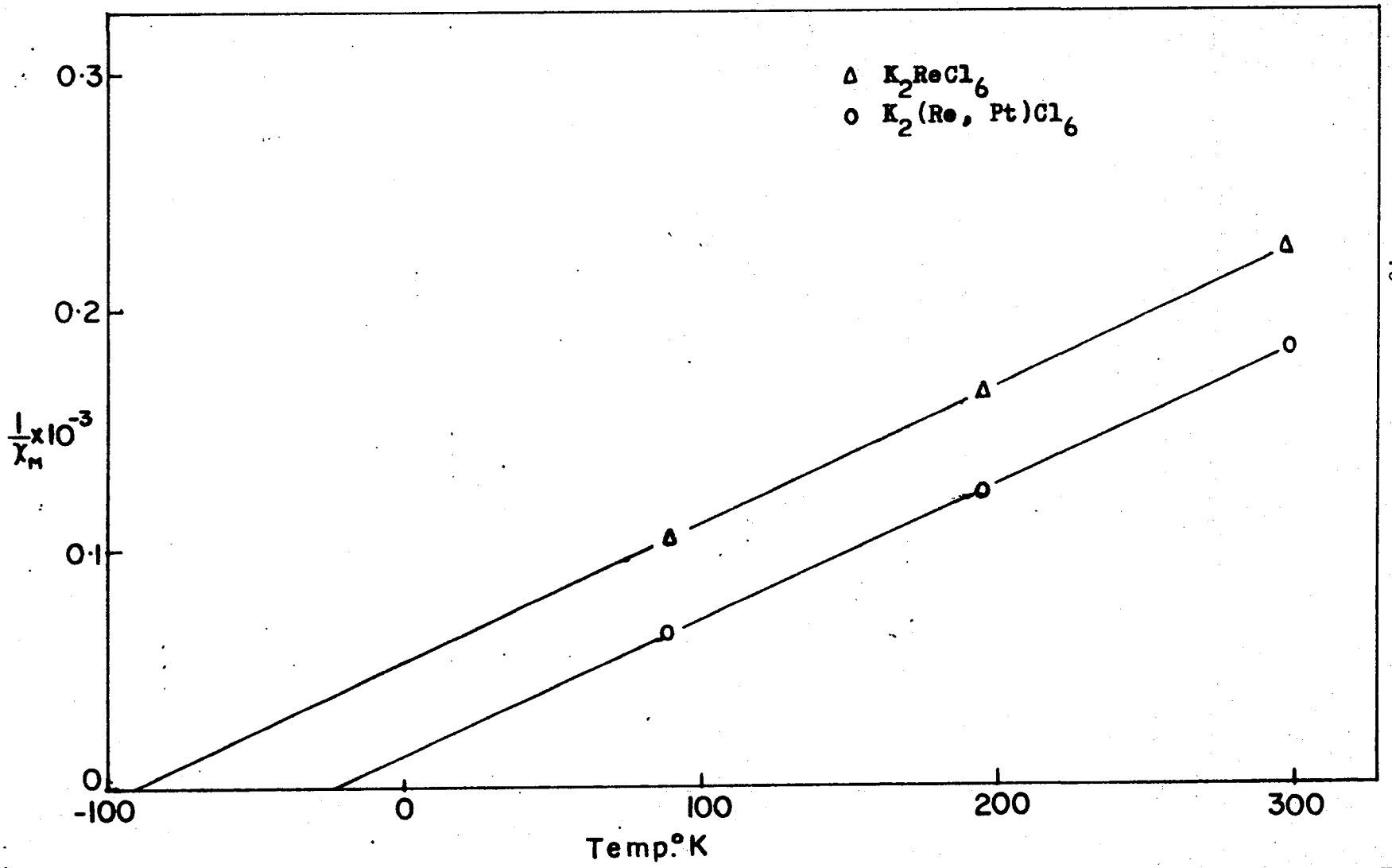
TABLE XXI

Temperature	μ for pure K_2ReCl_6	μ for $K_2(Re,Pt)Cl_6$
298°K	3.72	3.77
195°K	3.72	3.74
90°K	3.71	3.77

In the above tables, field strengths 1, 2, 3 and 4 refer to 1475, 2940, 4325 and 5320 gauss, respectively.

The measurements made on the solid solution of chlororhenate and chloroplatinate suggest that the magnetic moment has increased upon dissolution of the chlororhenate ion. However, further measurements on solid solutions with a range of concentrations are necessary to establish this fact. If the conclusion drawn is correct and Penney and Schlapp's[17] theory is applied to these results it would mean that the spin-orbit coupling constant for rhenium in the pure chlororhenate is different from that in solid solution, which is not likely. The cause for the low values of magnetic moments of chlororhenate is therefore the exchange interaction between the neighbouring ions and not the spin-orbit coupling. Since the measurements were made on one solid solution only this point cannot be considered as proved, but it is suggested that if solid solutions with a range of concentration were studied and the value at infinite dilution obtained, a temperature independent magnetic moment of 3.87 B.M. might be obtained.

Fig. (14). Plots of $1/\chi_m$ against temp. for K_2ReCl_6 and $K_2(Re, Pt)Cl_6$



d_ϵ^2 $K_2W(OH)Cl_5$

The values of susceptibility at three temperatures are given in Table XIV and their reciprocals are plotted against temperature in Fig. 15. It is observed that the compound does not obey the Curie-Weiss law. The effective magnetic moments are plotted against temperature in Fig. 16. For the d_ϵ^2 configuration Kotani's theory predicts a curve Fig. (3) approaching 1.22 B.M. at high temperatures. However, Kotani's theory may not be applicable quantitatively to $K_2W(OH)Cl_5$ because the six ligands are not identical as assumed in Kotani's theory. The author's results at any rate show a temperature dependence of the magnetid moment as predicted by Kotani's calculations for the d_ϵ^2 configuration.

Fig. (15). Plot of $1/\chi_m$ against temperature for $K_2W(OH)Cl_5$

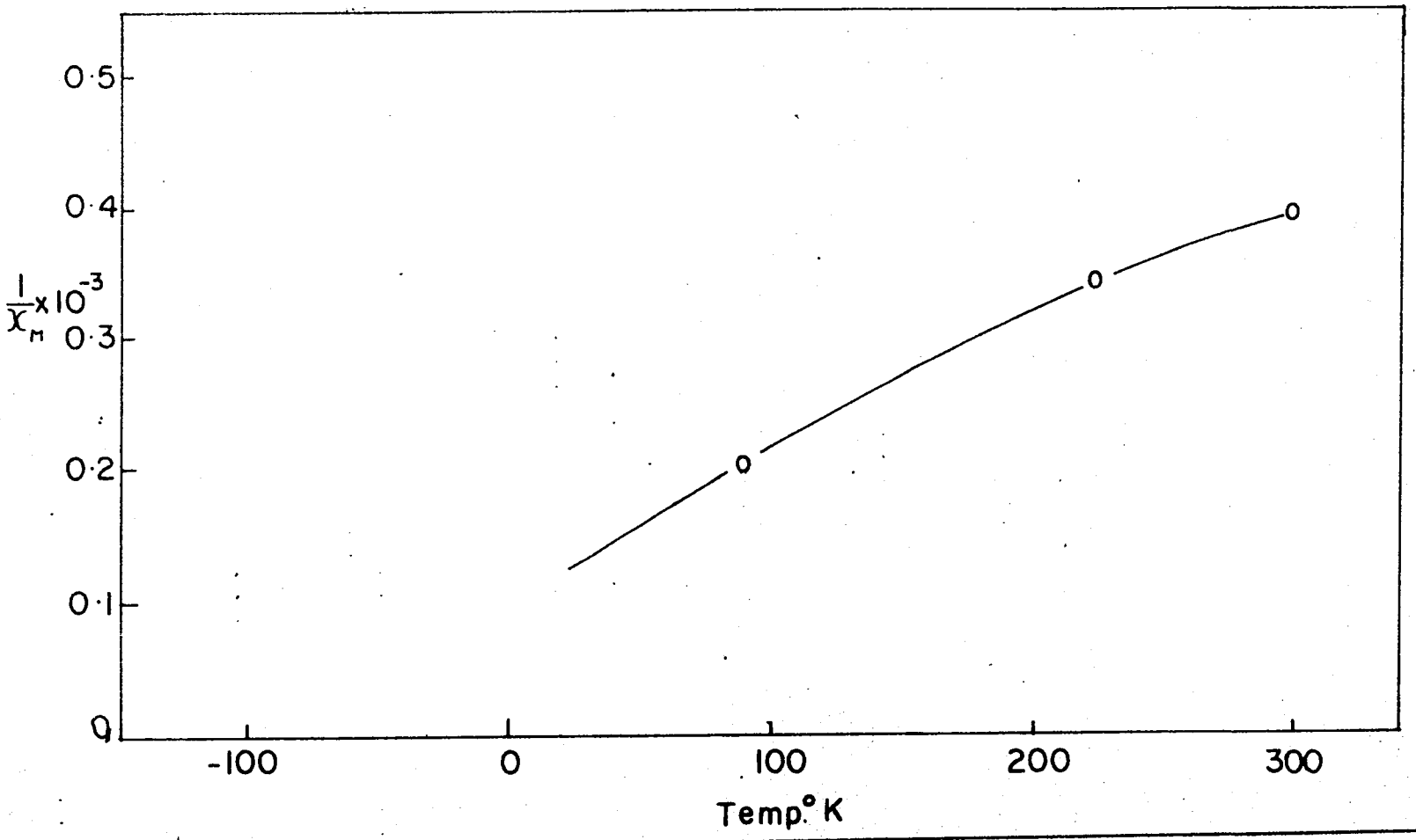
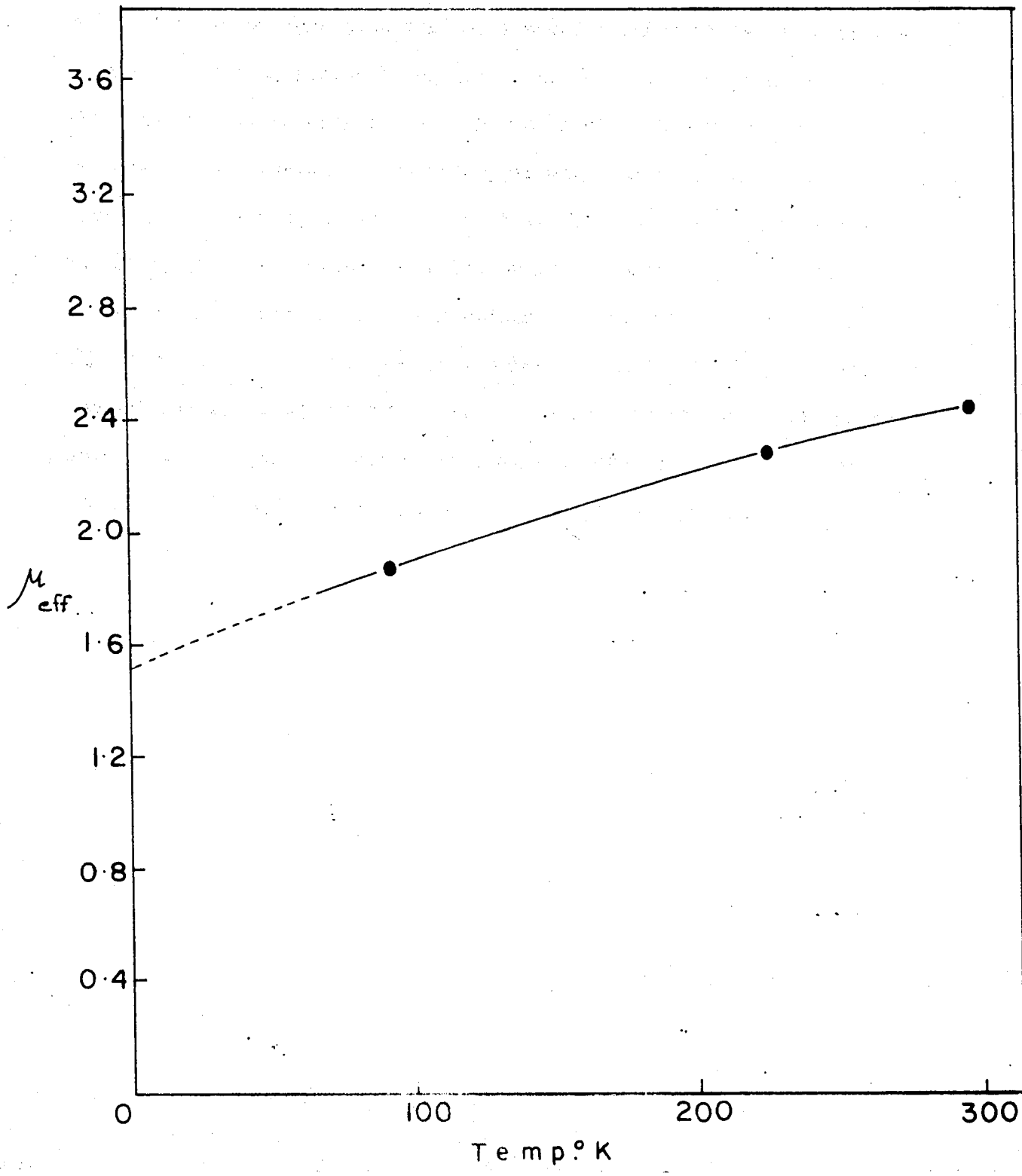


Fig. (16). Plot of μ_{eff} against temperature for $K_2W(OH)Cl_5$



CONCLUSIONS

Certain conclusions may be drawn from the present investigations. It may be said conclusively that in some of the paramagnetic halo-complexes of the third transition series, a superexchange mechanism operates through the intervening halogen atoms and it is partly because of this that the pure substances show anomalous magnetic behavior. The ions can be made to show "normal" behavior by isomorphous dilution with a diamagnetic compound serving as an host lattice. Thus it has been seen that there is an appreciable orbital contribution to the magnetic moment of Ir (IV) and that antiferromagnetic interactions are present in chloroiridate, chloroosmate, bromoosmate and chlororhenate complexes which accounts for the low values of magnetic moments in the pure substances. It has been shown that spin-orbit coupling constants of the right order of magnitude are obtained from the measurements on the dilute crystals.

SUGGESTIONS FOR FURTHER WORK

In the present investigation the author has worked with the ions in the quadrivalent state, but similar work on ions in other valence states as well as on complexes with other halogens as ligands might be successfully carried out and should give much helpful information. Thus the work on the bromoosmate and bromoplatinate could be carried out at other concentrations and it could be seen whether the temperature dependence of magnetic susceptibility as observed in the present investigation is observed at other concentrations as well. Investigations on the solid solutions of chlcrorhenate and chloroplatinate are being carried out at present in this laboratory. If similar work is carried out on fluoro- and bromorhenates perhaps it will be possible to account for the inverse trend of antiferromagnetic interactions in halorhenates. Complexes of ruthenium and rhodium could be studied in a similar manner and their behavior compared with the ions in the third transition series.

CLAIMS TO ORIGINAL RESEARCH

1. Magnetic susceptibility measurements at different temperatures for $K_2W(OH)Cl_5$ have been carried out.
2. Establishing the oxidation state of tungsten in the compound $K_2W(OH)Cl_5$ by oxidation with $KMnO_4$.
3. Magnetic measurements were carried out on solid solutions of
   a) Chloroplatinate and chloroiridate,
   b) Chloroplatinate and chloroosmate,
   c) Chloroplatinate and chlororhenate,
   d) Bromoplatinate and bromoosmate.
4. Calculation of the spin-orbit coupling constant of the right order of magnitude for O_s (IV) in complex $OsCl_6^{2-}$.
5. A method for separation of platinum from rhenium was attempted.

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