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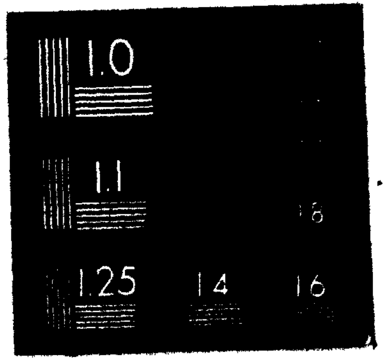

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THERMOCHEMICAL MEASUREMENT OF THE LIGAND FIELD SPLITTING ENERGIES FOR HEXAAMMINE AND HEXAAQUO COMPLEXES OF SOME TRANSITION METAL(II) IONS

A thesis
submitted in partial fulfilment of the requirements
for the Degree of Doctor of Philosophy
at Dalhousie University

by

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March, 1972

DALHOUSIE UNIVERSITY

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Author **Badri bin Muhammad.**

Title **Thermochemical measurement of the ligand field splitting energies for hexaammine and hexaaquo complexes of some transition metal(II) ions.**

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ABSTRACT

Various low-energy and high-energy modifications for ammines of some transition metal sulphates have been prepared. Their energy differences, obtained from the heat of solution measurements, have given substantial verification for the validity of the thermochemical method recently proposed for measurement of ligand field splitting energy.

Hydrates of $CoCl_2$ and $NiCl_2$ have been studied to show that the method is also applicable to salts other than the sulphates. In order to illustrate the sensitivity of the technique, the value of 10Dq for the complex $[Fe(H_2O)_6]^{2+}$ in the double salt $Fe(H_2O)_6SO_4.(NH_4)_2SO_4$ has been estimated. This was found to be comparable to the value obtained by the spectroscopic method.

IR and reflectance spectroscopy have been used to illustrate possible differences in the nature of the bonding in the two modifications of salt hydrates. From the information thus obtained, a possible theoretical explanation of the correlation between the difference in heats of solution and the ligand field splitting energy has been presented.

SYMBOLS AND ABBREVIATIONS

TGA	thermogravimetric analysis
DTA	differential thermal analysis
Z	nuclear charge
Z_{eff}	effective nuclear charge
e	electronic charge
μ	dipole moment
$\mathring{A}$	Angstrom unit
ΔG^{o}	standard free energy change
ΔH^{o}	standard enthalpy change
ΔH_{s}	heat of solution
σ	surface free energy
Q_{DB}	heat of transition
$10Dq$, Δ_{o}	ligand field splitting energy
ν	absorption maximum
B	Racah parameter
α	polarizibility
U	lattice energy
C	covalent energy
E	stabilization energy
N	Avogadro's number
A	Madelung constant
n	constant related to compressibility
r_{k}	radius of cation
r_{a}	radius of anion
K	stability constant
pK	stability constant index
M	molar concentration
μV	microvolt
mV	millivolt
$m\mu$	millimicron
D	bond dissociation energy
$\propto$	proportional to

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INTRODUCTION

1. Hydrates

Transition metal complexes have long been known to have a number of physical and chemical properties which distinguish them from other metal ions. Even though the more general valence bond (VB) theory and the molecular orbital (MO) theory have been applied to describe the nature of bonding in these complexes, the ligand field theory (LFT) has been widely used, due to its relative simplicity.

In several ways the ligand field theory resembles the crystal field theory, developed by Bethe (1), where the bonding in the complexes is regarded as completely ionic. One of the differences is the requirement by the ligand field theory that some degree of covalent bonding must exist in these complexes, and in some cases, such as $Fe(CO)_5$, π-bonding has to be considered too, in order to account for the greater metal-carbon bond energy of M-C=O compared to the metal-carbon bond energy of $M\text{-}CH_3$ (2,3).

Thus for a simple complex, such as $[M(H_2O)_6]^{2+}$, the energy for each metal-ligand bond could be estimated by applying classical electrostatic theory to the interaction between the positive charge on the metal ion, Ze, and the dipole moment of water, μ, at a distance R. This energy is about 50 kcal./mole

(4) for each metal-ligand bond, which is considerably smaller than any usual covalent or ionic bond energy. Owing to the relative weakness of the bonds in the complexes, they could easily be broken and consequently many reactions involving metal-ligand bonds have been studied, both in the solid state and in solution.

Considerable attention has been given to the question of the nature of these complexes. In particular, attempts have been made to decide the number of water molecules coordinated to a particular ion. Bockris (5), who reviewed the older experimental data on the aquo-complexes concluded that the number of water molecules bonded to each metal ion is variable depending on the cation. This variation could be understood in terms of a simple model where the electrostatic influence of the cation on the neighbouring water molecules would vary according to the sizes and charges of the ions. The nearest water molecules would be more affected and the influence would be weaker for the more distant ones. In this model, the nearest water molecules which make up the inner-coordination sphere are thought to be more specific in number than those which make up the outer or secondary-sphere.

Isotopic fractionation experiments on the aquo-complexes (6,7) have given support to the idea of definiteness of the coordination number of a hydrated metal ion though this may not necessarily be true for the larger cations such as Cs^+. In fact it has been found that for the hydrated Cr^{3+} and Al^{3+} the coordination number is six. Similarly, recent investigations using experiments on small-angle scattering of X-rays have indicated that a coordination number of six is also true for the hydrated Co^{2+} and Ni^{2+} ions (8-10).

However, it has been generally accepted for a long time that most of the hydrated cations have the general formula $[M(H_2O)_6]^{n+}$, and, furthermore, all six water molecules in such species are equivalent (11,12). In this state, the six water molecules are octahedrally arranged around the cation and they are commonly known as ligands.

In solution, the importance of these ligands is obviously to stabilize the cation by reducing the concentration of the charge density on the metal ion. In crystalline solids, however, the presence of ligands is sometimes necessary to stabilize the crystals as a whole. For example, in $Fe(H_2O)_6SiF_6$, the six water molecules are coordinated to the Fe^{2+} ion to form a larger cationic species, and thereby would increase the SiF_6^{2-} - SiF_6^{2-} distances, resulting in reduction of the repulsive interaction. The Fe^{2+} alone is too small to give a stable SiF_6^{2-} - SiF_6^{2-} interionic distance and therefore no anhydrous $FeSiF_6$ is known to exist (13).

In most crystalline solids, however, the six water molecules may not be octahedrally arranged around the metal ion because the presence of the anions may induce further interaction

(14) such as hydrogen bonding. Thus some of the bonds might be less strong than others in complexed species.

In addition to the ligands, another type of water molecule may also be present in a crystalline hydrate. These molecules may be bonded differently and serve a different purpose other than stabilizing the cation or the crystal as a whole. Such water is commonly known as "anionic" water, "lattice" water or "structural" water. This anionic water is sometimes regarded as filling the spaces in the lattice due to the nature of packing (15) or in some cases it might act as a bridge between two lattice layers (16). The strength of the bonds holding such water molecules to the lattice constituents varies from one solid to another. It is considered to be slightly greater than the energy of a metal-ligand bond, though some authors believe it to be smaller (17,18).

In the pentahydrate of copper(II) sulphate, for example, it has been demonstrated by X-ray analysis that four of the five water molecules are coordinated to the copper ion at a distance of about 1.98 Å (19) while the other one is hydrogen bonded to the sulphate ion and two of the ligands; hence it has been known as anionic water, as shown (20) in Fig. 1. Similarly, the heptahydrate of nickel(II) sulphate has been shown to have octahedral entities of $[Ni(H_2O)_6]^{2+}$ with the H_2O-Ni bond length varying from 1.96 Å to 2.08 Å (21) while the other water molecule is hydrogen bonded to the sulphate ion and to two of the ligands.

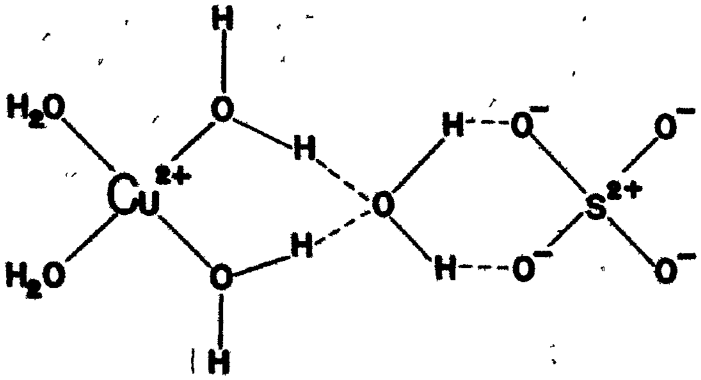
Figure 1

Hydrogen bonding in the hydrates of Copper Sulphate

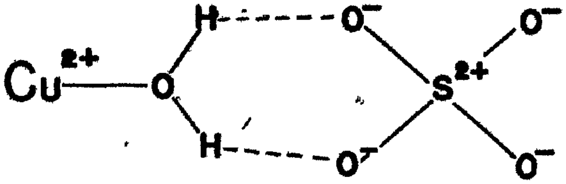
a pentahydrate

b monohydrate

a



b



A slightly different situation is found in the alums, such as the potash alum, $KAl(SO_4)_2 \cdot 12H_2O$. Crystal structure analysis has shown that each of the metal ions, K^+ and Al^{3+}, is surrounded by six water molecules in an octahedral fashion with a H_2O-K bond length of 2.94 Å and a H_2O-Al bond length of 1.94 Å (22). Because of the relatively longer bond length of H_2O-K compared to other metal-water bond lengths, the water molecules around the potassium ion in the alum are considered to be lattice water (23).

The variation in the bond lengths and the types of bonding given above for the water molecules in the hydrated salts indicate differences in their bond energies. Thus, not all of them are equivalent; some of them would be weaker than others and hence would be more sensitive to reaction. For example, in thermal dissociation, the anionic water in the pentahydrate of copper sulphate would be evolved at a much higher temperature than the other four water molecules (24-26). This, however, does not necessarily mean that in all cases the anionic water is more strongly bonded than the ligands. For example, the heptahydrate of nickel(II) sulphate is known to lose its anionic water easily to form the hexahydrate in which all six water molecules are coordinated to the metal ion (27,28). It is also thought that the non-coordinated water molecules in potash alum are evolved at a lower temperature than the water molecules which are ligands (17,18).

Thus, in the process of thermal dissociation of a salt, the reaction

$$MX.aH_2O_{(s)} \longrightarrow MX_{(s)} + aH_2O_{(g)} \qquad [1]$$

would go to completion after passing through a number of stages involving formation of various stable intermediate hydrates. Some of these intermediate hydrates may be stable over a wide range of temperature depending on the strength of the remaining metal-ligand bonds. Since the early part of this century extensive investigations (29) have been done in this field to determine the number of stable hydrates that could exist for each salt. For this purpose the modern techniques of differential thermal analysis (DTA) and thermogravimetric analysis (TGA) have been most helpful. The number of stable intermediate hydrates varies from one salt to another but most chemists have now agreed to the number for each. However, there are still a few uncertainties (30-32) especially when the existence is only transitory (33).

If a salt hydrate is heated slowly, the process of thermal dissociation is analogous to boiling, where the dissociation pressure of the salt becomes equal to atmospheric pressure. Therefore the number of intermediate hydrates that could be observed in the course of dehydration would depend on the external pressure of the chamber containing the salt (34,35). Under atmospheric pressure, for example, the heptahydrate of magnesium sulphate would give the anhydrous salt after passing through several stages, as follows (33,36)

$$MgSO_4{\cdot}7H_2O_{(s)} \rightarrow MgSO_4{\cdot}6H_2O_{(s)} + H_2O_{(l)} \quad \text{at } 55\text{–}56^{\circ}C$$

$$MgSO_4{\cdot}6H_2O_{(s)} \rightarrow MgSO_4{\cdot}5H_2O_{(s)} + H_2O_{(l)} \quad \text{at } 85\text{–}95^{\circ}C$$

$$2H_2O_{(l)} \rightarrow 2H_2O_{(g)} \quad \text{at } 105\text{–}10^{\circ}C$$

$$MgSO_4{\cdot}5H_2O_{(s)} \rightarrow MgSO_4{\cdot}3H_2O_{(s)} + 2H_2O_{(g)} \quad \text{at } 120\text{–}25^{\circ}C$$

$$MgSO_4{\cdot}3H_2O_{(s)} \rightarrow MgSO_4{\cdot}2H_2O_{(s)} + H_2O_{(g)} \quad \text{at } 135\text{–}45^{\circ}C$$

$$MgSO_4{\cdot}2H_2O_{(s)} \rightarrow MgSO_4{\cdot}H_2O_{(s)} + H_2O_{(g)} \quad \text{at } 145\text{–}95^{\circ}C$$

$$\text{and } MgSO_4{\cdot}H_2O_{(s)} \rightarrow MgSO_{4\,(s)} + H_2O_{(g)} \quad \text{at } 320\text{–}40^{\circ}C$$

If dehydration was done by using the DTA technique, each of the reactions above would give an endotherm indicating the absorption of heat. Under reduced pressure the dissociation temperature would be lowered; consequently each of the endotherms on the DTA chart would be shifted to a lower temperature. The shift might be so large that the endotherms would overlap each other. For example, at a pressure of 24 Torr, only two endotherms at 45°C and 90°C were observed by Rassonskaya (37) in the thermogram for $MgSO_4{\cdot}7H_2O$.

It is probable that the endotherm at 45°C indicates dissociation of the heptahydrate to the pentahydrate followed by the dissociation of the pentahydrate to the monohydrate at 90°C.

Closer examination of the solid phase during the decomposition process for each of the hydrates of magnesium sulphate would reveal two processes taking place:

(i) the elimination of water from the lattice, and

(ii) a change in the lattice structure from that of the parent hydrate to that characteristic of the product.

When thermal dissociation is done by applying a differential heating technique, there is a possibility that the second process would not occur immediately following the first (35). One reason for this is that not enough energy is transferred to the reaction centre to start the nucleation of the stable product. Because of this, a metastable solid phase may appear and its subsequent rearrangement to form the stable one may take place only on further heating. Ordinarily most salts form their lower hydrates in stable form fairly easily. This is the reason for the occurrence of stages in the course of dehydration to the anhydrous salts.

If the crystal lattice of the parent hydrate remains intact after evolution of water it is expected that this would also be the lattice of the product. Not very many salts have thus far been found to show this behaviour but the dehydration of $CaSO_4.(0.5H_2O)$ may be cited as an example. The water-soluble anhydrous $CaSO_4$ obtained by heating the hemihydrate in air at 170-90°C would absorb water vapour easily to re-form the hemihydrate (38). The X-ray diffraction pattern for this anhydrous salt is very similar to that for the hemihydrate. Thus it has been concluded that the lattice structures are similar also. If the anhydrous salt were further heated, it would become insoluble in water and would not absorb water easily when left in air. The density of the salt would increase with the temperature of heating, until at about 380°C it would become virtually constant. The X-ray diffraction pattern would now be different from that of the hemihydrate and hence the lattice structure would not be the same as that of the hemihydrate. Thus it appears that the process of evolution of water molecules from the crystalline hemihydrate would not be accompanied by lattice rearrangement, and this lattice would remain intact and stable. The formation of the new lattice - that of the anhydrous salt, would only be possible if enough energy were supplied to initiate the process. In doing so the lattice would contract giving the observed increase in density of the salt.

In spite of the fact that the crystallization of the metastable intermediate phase to form the more stable final phase requires a relatively high temperature of heating, the process itself is exothermic. Normally this process occurs immediately following the evolution of water from the lattice and therefore the heat effect is obscured by the endothermic effect of the latter. If the two processes were separated, their individual heat effects could be observed on DTA, and this has been shown to be the case for the dehydration of $MgSO_4 \cdot 7H_2O$ at a pressure of 24 Torr. Following the endotherms at 45°C and 90°C, an exotherm occurred at 280°C on further heating (38).

Investigation of the product of dehydration of $MgSO_4 \cdot 7H_2O$ at a pressure lower than 24 Torr has also been made (39-41). Experiments performed at a pressure lower than that at which the minimum rate of dehydration occurred, e.g., 4 Torr at 40°C, yielded products which did not diffract X-rays coherently. The products were quite stable and characteristic lines of the monohydrate (kieserite) were only observed in their X-ray diffraction patterns when the salts were heated at about 130°C for two days (39). Products of a similar nature were also obtained for hydrates of several metal sulphates (42,43) and manganese oxalate dihydrate (44), when the ligands were removed under vacuum.

These experimental results suggest that the metastable phase which appears to be normal for the case of $CaSO_4$ may not be necessarily so for other salts. It seems likely that the loss of water ligands, from the pentahydrate of copper sulphate for example, is accompanied by lattice collapse to form the metastable phase. This phase would lack adequate lattice order to diffract X-rays coherently and might remain stable over a period of time. Thus the question arises whether the water present in either the hemihydrate or the dihydrate of calcium sulphate is actually ligand water or lattice water. Crystal structure analysis of the dihydrate shows that the H_2O-Ca distance is 2.44 Å (15), however this does not necessarily mean that the water molecules are ligands. The fact that the lattice does not collapse in the case of $CaSO_4$ would strongly indicate that the water molecules simply fill vacant spaces in the lattice. Removal of these water molecules from the lattice would seem only to create holes, and since there would be no subsequent rearrangement of the remaining lattice constituents, rehydration to give the original hydrate could occur fairly easily.

Similar discussion would appear also to apply to the products of dehydration of $UO_2^{2+}C_2O_4^{2-}\cdot 2H_2O$, $ThF_4\cdot 3H_2O$ and $UF_4\cdot 3H_2O$. It has been observed that the lower hydrates of these salts have similar X-ray patterns to those of the parent hydrates (45-47). $ThF_4\cdot(2.5-3)H_2O$, prepared from an aqueous solution of Th^{4+} in 40% HF would yield $ThF_4\cdot(0.5-2)H_2O$ on standing in the mother liquor for two days. Both thorium salts gave $ThF_4\cdot(0.5)H_2O$ when heated at 250°C under vacuum, but $ThF_4\cdot(2.5-3)H_2O$ would not form $ThF_4\cdot(0.5-2)H_2O$ when heated in an oven (48). Since their X-ray diffraction patterns were similar, all the hydrates of ThF_4 have been regarded to have similar lattices. The anhydrous salt obtained by heating HF and ThO_2 at 450°C, however, gave a product which showed a different X-ray pattern. This salt did not react with water to form any of the higher hydrates (49).

2. Metastable phases

The possibility of formation of metastable phases is now widely accepted. Sixty years ago it was only a working hypothesis proposed by Partington (50) to describe the sequence in the dehydration process. Partington regarded a crystal as composed of molecular aggregates of the anhydrous salt and the attached water oscillating about fixed points in a definite space lattice. If the kinetic energy of one of these aggregates exceeded a finite amount, the components would part and a molecule of water would be ejected from the space lattice. This would disrupt that portion of the lattice adjacent to the centre of the disturbance. This lattice would break down and the molecules of solid lower hydrate or anhydride would fall together into an amorphous aggregate which would rearrange only slowly to give a stable new space lattice, that of the normal crystalline form.

However, evidence from the dehydration kinetics of copper(II) sulphate pentahydrate led Rae (51) to conclude that the lower hydrates formed were microcrystalline, instead of amorphous as suggested by Partington. According to Frost et al.(52) the formation of microcrystalline lower hydrates was possible in that as dehydration proceeded from nucleated points on the crystal surface, contraction occurred resulting in capillary formation. The regions between these capillaries would be closely packed with a disordered assembly of microcrytals. Thus crystals of macrosizes could not be formed as a result of the discontinuity due to these capillaries.

While there is no conclusive support in favour of either mechanism, it has been generally accepted that the formation of the amorphous or microcrystalline forms is really an important concept which may explain a number of observations. When the true nature is uncertain the word metastable has often been used to describe the state. While the earlier mechanism is viewed as a more plausible explanation for the hydrates of metal sulphates, some authors have thought that certain results could be more readily explained by assuming that the metastable intermediate products are microcrystalline.

Studies of the kinetics of dehydration have provided better understanding of the dehydration process. Ordinarily, the interpretation of kinetic data is quite difficult because of the possibility that the water evolved might be re-sorbed. To avoid this complication, Garner and Tanner (53) carried out their kinetic study of the dehydration of $CuSO_4 \cdot 5H_2O$ under vacuum. They pointed out that the thickness of the product layer on the surface of undecomposed salt did not appreciably retard the rate of dehydration under vacuum. This would imply that the product is very porous to water vapour. There might, however, be pressure due to water vapour between a reaction interface and the crystal surface. This could hinder the escape of water vapour. The experiments of Garner and Tanner were apparently carried out under conditions of dynamic equilibrium, where the rate of production of water vapour equals the rate of its removal. It would follow that the lower the pressure, the greater would be the rate of dehydration. However, Topley and Smith (54) and Volmer and Seydel (55), who independantly investigated the rate of dehydration of $MnC_2O_4 \cdot 2H_2O$ at various pressures of water vapour, found that this was not strictly true. The relation obtained is reproduced in Fig. 2. With increasing pressure the rate was found to decrease to a minimum at about 0.1 Torr at which point it rose to a maximum at about 1 Torr before gradually decreasing again as the pressure approached the equilibrium vapour pressure of the hydrate.

Although Topley and Smith made an attempt to explain this phenomenon, the explanation offered by Volmer and Seydel is now generally accepted. According to them, under vacuum, water molecules could leave the surface of the salt without hindrance. The product would likely be amorphous and would have a higher free energy of formation than the normal crystalline salt due to an additional strain energy. This additional strain energy could originate from the difference in molecular volume in the solid reactant and product.

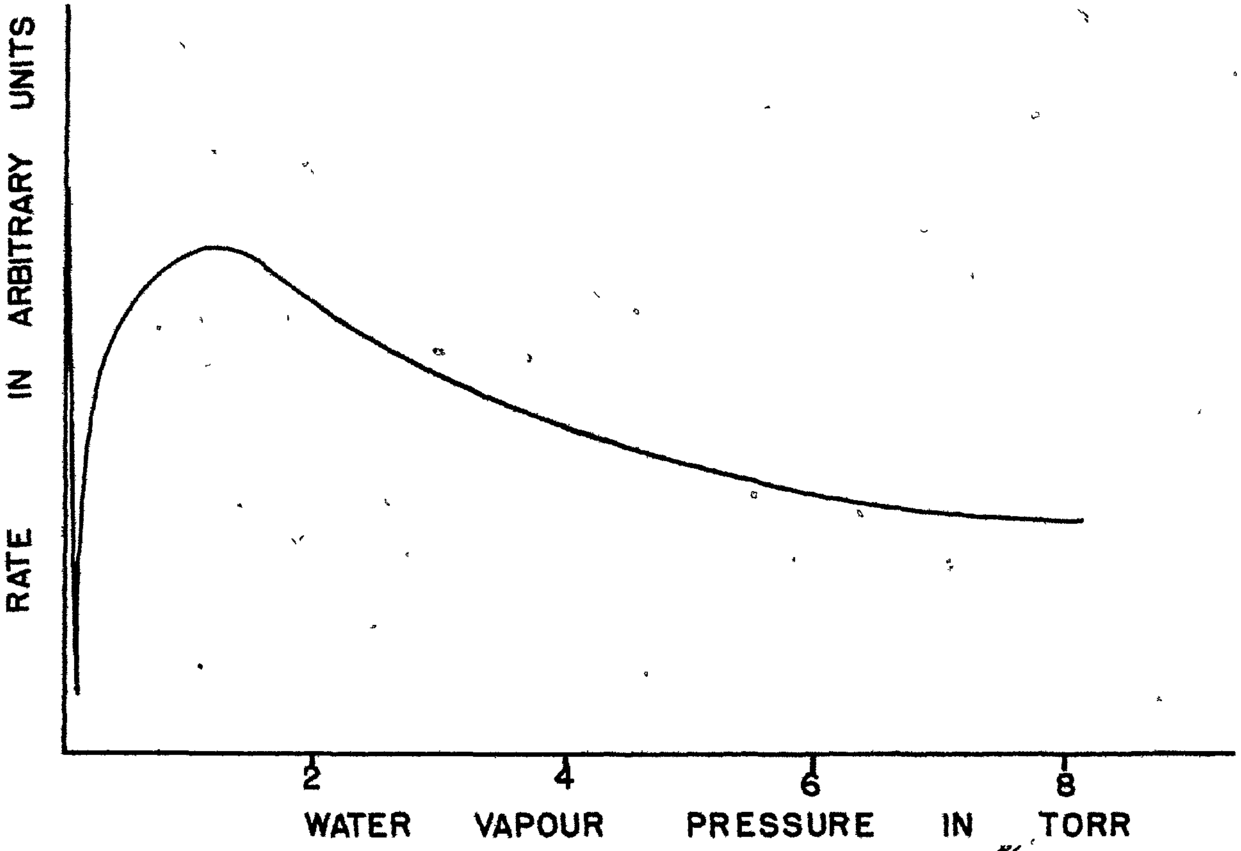
For a reaction like

$$A_{(s)} \longrightarrow B_{(s)} + C_{(g)}$$

the molecular volume of the product, B, is in general smaller than the molecular volume of the reactant, A (56). Because a

Figure 2

Topley - Smith effect



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solid phase cannot readily accomodate this volume change by viscous flow, a strain is set up in both phases. Therefore in the expression for the free energy of formation of a reaction nucleus, the energy term due to this must be included, i.e.,

$$\Delta G^* = a\sigma i^{2/3} + b\, i\, (\Delta G + E) \qquad (1)$$

where σ is the surface free energy, i is the number of molecules in the nucleus, ΔG is the chemical free energy change for the overall reaction, E is the strain energy, a and b are constants (57). If product B is amorphous, the strain energy could be spread out through the entire crystal. In a normal crystalline product this strain energy would be released upon crystallization. This seems to explain why the rate of dehydration decreased to a minimum as the pressure of water vapour increased.

At higher pressure, recrystallization would occur; thus the product would shrink and cracks would form. This would facilitate the subsequent release of water vapour and hence release the strain energy, to increase the rate. The product would then be crystalline and would have a lower free energy. Further decrease in rate would be due to approach of the equilibrium vapour pressure.

Several experiments on dehydration of salts under vacuum have been done since then especially by Frost and coworkers at Queen's University. Some of the salts did not show the rate-pressure relation as above which has been generally known as the "Topley-Smith" effect.

With the exception of the cases mentioned for the hydrates of $CaSO_4$, ThF_4, $UO_2C_2O_4$ and UF_4, most hydrates of other metal salts yield products of vacuum dehydration which do not diffract X-rays coherently. It appears that for the four examples given above, there is strong covalent bonding in the lattices of the higher hydrates to form rigid crystalline networks. The removal of water molecules from such lattices would not be accompanied by lattice relaxation. The spaces formerly occupied by water molecules would not be filled by the remaining lattice constituents and therefore rehydration of the product would be facilitated. If, as a result of lattice rearrangement, these spaces were filled, the packing would be tighter and this would hinder the ease of rehydration.

For other salts also, such as $CuSO_4$, the removal of water would not result in lattice rearrangement, but because the crystalline network is less rigid, the lattice would probably collapse into an amorphous aggregate. On the basis of the experimental results on the relation between the rate of dehydration and the pressure of water vapour, it appears that the chaotic aggregation of the lattice constituents of the product would, in the presence of water vapour, rearrange to form a solid crystalline network. The influence of water vapour on the process of rearrangement seems to be similar to the effect of heating, in that both would increase the mobility of the lattice constituents to rearrange and form the normal crystalline salt. If the pressure of the water vapour increased the more extensive would be the crystallization of the product phase to the point that at atmospheric pressure the product of dehydration of a salt would be completely crystalline.

3. Properties of the Products of Vacuum Dehydration.

It has been mentioned that the products of vacuum dehydration lack lattice order which results in the failure of the salts to diffract X-rays coherently. In a normal crystalline material, the lattice is composed of a periodic arrangement of unit cells in three dimensions. This periodic arrangement is responsible for the ability of a crystal to diffract X-rays coherently. For the anhydride of $UO_2C_2O_4$, however, it appears that the skeletal lattice of the trihydrate remains intact on vacuum dehydration and thus the principal diffraction lines due to UO_2^{2+} and $C_2O_4^{2-}$ can be observed.

Without such periodic arrangement of the lattice constituents, a solid is said to have no short range order. This term is often used to describe the structures of glasses and liquids, since these substances also do not diffract X-rays. However, short range order alone is insufficient to determine whether a material can give a regular X-ray pattern. This short range order must continue to a finite extent to give long range order before X-rays can be diffracted coherently. Microcrystals for example, do not diffract X-rays because they do not have long range order. A microcrystal is made up of a number of unit cells, the sum of which does not exceed the limit of 100 Å in thickness. According to Azaroff (58) this is the size limit for a microcrystal to be able to diffract X-rays. Thus it is possible that a product of vacuum dehydration may be in form of microcrystals and not composed of amorphous aggregates as described above.

It is understood that such a structure would be very unstable, so that in time and under appropriate conditions it would revert to the normal crystalline form. However, for some very stable products of vacuum dehydration of certain salts, microcrystalline structure would be unlikely. At least for $NiSO_4$, the structure of the product may resemble glass. Since glasses do not diffract X-rays coherently, they are thought to lack crystallinity. This has led to the view that glasses are viscous, supercooled liquids. A pictorial representation in two dimensions of the bonding in a glass is shown in Fig. 3b. Silicon atoms are bonded to other silicon atoms by oxygen to form cyclic units of different sizes in which no regular order occurs. This is in contrast to the regular cyclic units of a crystalline material containing the same chemical species, Fig. 3a. If the product of vacuum dehydration of $NiSO_4$ has a structure very similar to that shown in Fig. 3b, reversion to the normal crystalline form might be possible if the bonds were broken and the mobility of the Ni^{2+} and SO_4^{2-} ions were increased. Likewise glasses have a tendency to become crystalline

Figure 3

Atomic arrangement in glasses and crystals

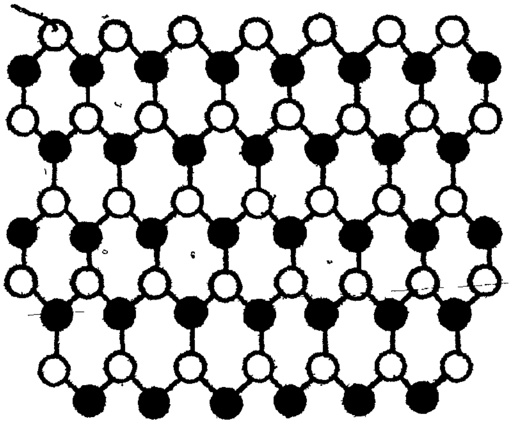
a crystalline material

b glass

● silicon

○ oxygen

a



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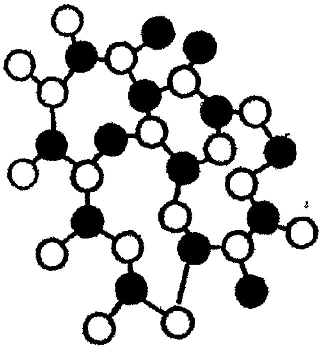


after standing for a long time (59). Crystals may separate when aged glasses are heated (60).

In a compound containing highly symmetrical anions, such as sulphate ions, glass formation could be achieved if the anions were subjected to asymetrical forces strong enough to distort the bonds (61). In the products of vacuum dehydration of sulphate salts such forces could very well be present to give the proposed random distribution of ions. If so, heating and cooling would be expected to cause migration of the ions and ligands. Changes in coordination symmetry of the cation would cause changes in the colour of the sample. This has been observed to occur in glasses containing cobalt and nickel cations (61).

The lack of lattice order may also cause the product of vacuum dehydration of a salt to have a higher heat capacity and a higher entropy than the normal crystalline material. Giauque and Archibald (62) found that MgO, prepared by heating $Mg(OH)_2$ at 300-350°C under vacuum, has a heat capacity of about 1.998 cal./deg.-mole at 100°K. This value is higher than the heat capacity for the normal crystalline MgO, prepared by crystallization from the melt (63), which was found to be 1.894 cal./deg.-mole at 100°K. Similarly, Frost <u>et al</u>. (52) measured the heat capacity for both the normal crystalline $MgSO_4 \cdot H_2O$ and corresponding salt obtained by vacuum dehydration of the heptahydrate. Using the extrapolation technique introduced by Kelley et al. (64) to calculate the heat capacity at lower temperatures, the entropy for both forms was evaluated by graphical integration. The monohydrate obtained by vacuum dehydration of the heptahydrate was found to have an entropy about 2.8 e.u. higher than that of the normal crystalline salt.

Frost <u>et al</u>. (52) discussed the difference in the heat capacity in terms of bond strength of the solid. It appeared that in a disordered lattice, the average bond strength between the chemical species would be weaker than that expected for a normal crystalline lattice. Consequently, the average frequency of thermal vibration would be lower, resulting in a higher heat capacity. Alternatively, if the products of vacuum dehydration were microcrystalline, the greater surface density and the lower vibrational frequency at the surface could also account for the observed properties. Quinn, Missen and Frost (65) found that the product of vacuum dehydration of $MgSO_4 \cdot 7H_2O$ has a larger surface area than the normal crystalline salt, as measured by the method of Brunauer, Emmett and Teller (66). From their results, they suggested that the product of vacuum dehydration was interspersed with capillaries having width from 11 Å to 20 Å. Thus it appears that as dehydration proceeds from the nucleated points on the crystal surfaces, contraction occurs resulting in the formation of these capillaries.

The process of reversion of the product of vacuum dehydration to its normal crystalline form is normally accompanied by evolution of heat as observed in the differential thermal analysis for $MgSO_4 \cdot 7H_2O$ (38). This exothermal effect indicates that the product of vacuum dehydration of a salt has a higher energy content than the normal crystalline salt; thus it shall be termed "high-energy" modification. Therefore it has higher heat of hydration and higher heat of solution. Measurements have been made by various authors (40,67-69) and the energy difference has been the most important single criterion for distinguishing the high-energy form from the normal crystalline form.

A microcrystalline salt should have the extra energy content mostly in the form of surface energy. Sodium chloride, for example, has a surface energy of about 155 ergs $cm.^{-2}$ on the (100) face (70). The surface area of the high-energy modification of $CoCl_2$ was found to be about 39.5 $m^2 gm.^{-1}$ (65). If these values are considered to be typical for the salts investigated, a rough approximation for the surface energy would be about 6×10^7 ergs $gm.^{-1}$ or 1.4 cal. $gm.^{-1}$. This surface energy seems to be enough to account for the excess energy of $CoCl_2$ (67) but it is much too small to account for the case of $MgSO_4$, for example.

Thus it appears that the high-energy modification of a hydrate could be approximately regarded to have a disordered lattice. Such a form could conceivably possess a large entropy and this would decrease when the solid reverts to its normal crystalline form with evolution of heat. It is obvious that the amount of heat given off would be proportional to the amount of high-energy modification present in a sample. Thus Frost, Moon and Tompkins (68) investigated the quantity of the high-energy modification that could be present in samples dehydrated at various pressures of water vapour. From their results it is obvious that the fraction of the high-energy form present in a sample is determined by the pressure of water vapour during dehydration.

Jamieson et al. (71,72) carried out vacuum dehydration experiments at low pressures in the presence of various desiccants. The heats of solution of the products were measured and plotted as a function of percent water left in the salts. The heat of solution graph for the hydrates of cobalt(II) sulphate is reproduced in Fig. 4 as an example. The heats of solution for the normal crystalline hydrates which were prepared by heating the heptahydrate in an oven fell on the lines AB and BC where A is the heat of solution for the anhydrous salt, B is the heat of solution for the monohydrate and C is that for the heptahydrate. The line BC has the equation

$$y_{BC} = 114.7 - 2.80x.$$

The high-energy modifications of lower hydrates prepared by vacuum dehydration of the heptahydrate have their heats of solution falling on the line CDE with the equation

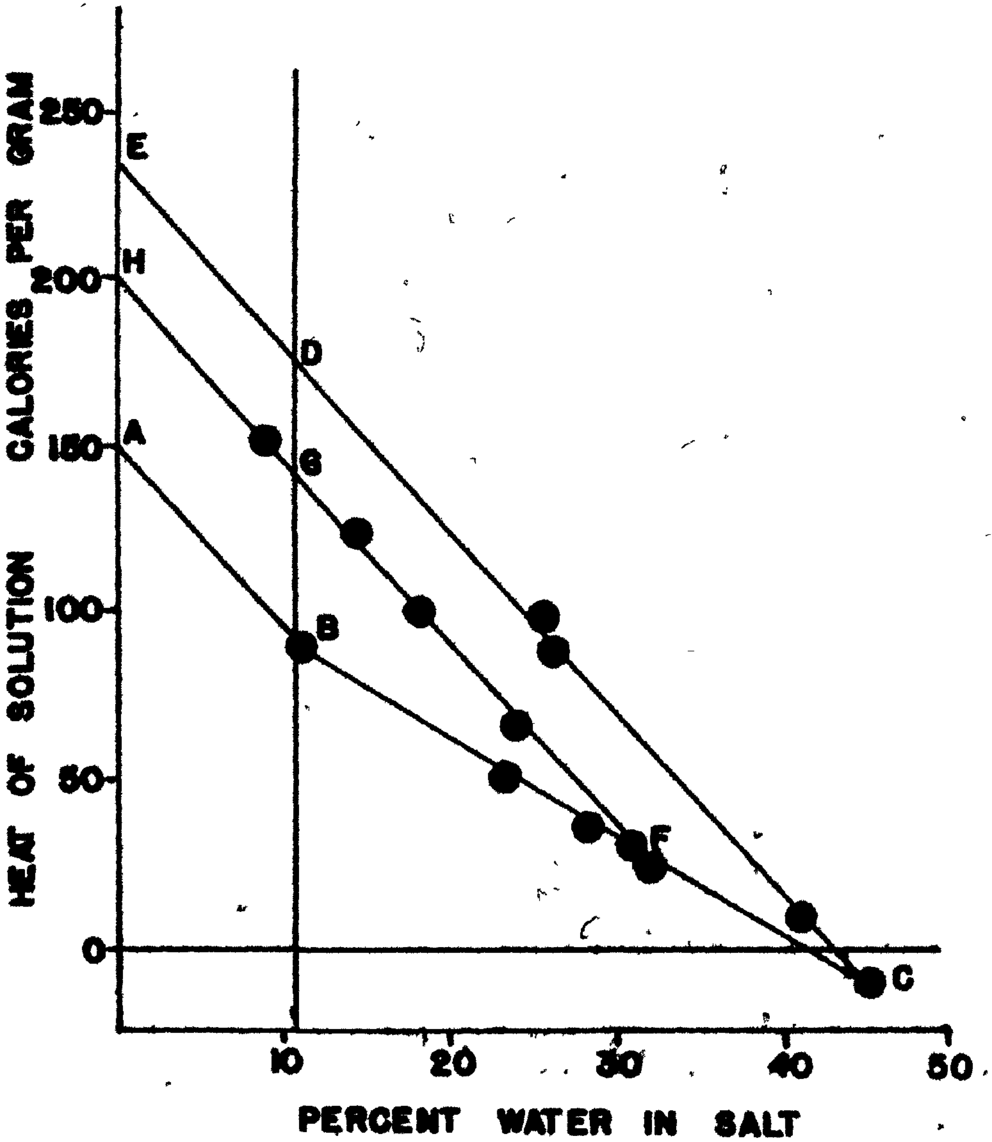
$$y_{CDE} = 200 - 5.52x.$$

The maximum heat difference between the two forms, Q_{DB}, has been calculated for each salt investigated. For the hydrates of cobalt(II) sulphate, Q_{DB} was estimated to be about 70 cal./gm.

The significance of the quantity Q_{DB} became apparent when it was later realized to be proportional to the ligand field

Figure 4

Heats of solution for the hydrates of cobalt sulphate


HEAT OF SOLUTION CALORIES PER GRAM
250
200
150
100
50
0
E
H
A
D
G
B
F
C
10
20
30
40
50
PERCENT WATER IN SALT

splitting energy. For example, when the values of Q_{DB} for the salts investigated were expressed as kcal./mole of heptahydrate they were identical with the ligand field splitting energies of the hexaaquo cations, as found by the spectroscopic method. This discovery has initiated the present study on the ammine complexes of the same salts in an attempt to ascertain the usefulness and validity of the thermochemical method for measuring ligand field splitting energies.

4. Ligand field splitting energy

The ligand field splitting energy denotes the separation between two sets of degenerate d-orbitals of a metal ion in an octahedral field.

The d-orbitals of a metal ion, which would be completely degenerate for a free ion in the gas phase, would not have equal energy in the presence of an electrostatic field resulting from the arrangement of ligands around it. In an octahedral field, the five d-orbitals would split into two groups: the t_{2g} orbitals which are triply degenerate and the e_g orbitals which are doubly degenerate.

A system containing one electron, denoted by d^1 (e.g. in Ti^{3+}) would serve as the simplest example. In an octahedral field this electron would occupy one of the t_{2g} orbitals which are lower in energy than the e_g orbitals. If the electron is excited to the higher e_g orbitals, it would absorb radiation. The difference in energy between these two sets of orbitals could then be calculated from the frequency of the absorbed radiation.

For this simplest case, the energy difference is termed the ligand field splitting energy which is often abbreviated as 10Dq or Δ_o. Similarly, the ligand field splitting energy for a d^9 system could be found since the absence of one electron could be treated in the same manner as the presence of one electron (73). Fig. 5 illustrates the orbital splitting.

Cases other than d^1 and d^9 are more complex; thus the frequency of the absorbed radiation may not give the ligand field splitting energy directly. This is not surprising since some degree of interaction between the electrons would be expected in a many-electron system. For such cases, the analyses of the spectra are made with the use of group theory. Fig. 6 shows the various energy states for the $3d^n$ systems in an octahedral field. The expressions for their relative energies are given in Table 1 in terms of Dq and the electronic interaction parameter, B, which is also known as the Racah parameter. Such diagrams and tables could be used for evaluating 10Dq for an octahedral complex when the absorption maxima in its spectrum are found experimentally. Each of these maxima represents the energy separation between the ground state and one of the excited states.

As an example, the reflectance spectrum for $CoCl_2 \cdot 6H_2O$ shall be discussed. Three absorption maxima, ν_1, ν_2 and ν_3,

Figure 5

Orbital splitting for $3d^1$ in an octahedral field

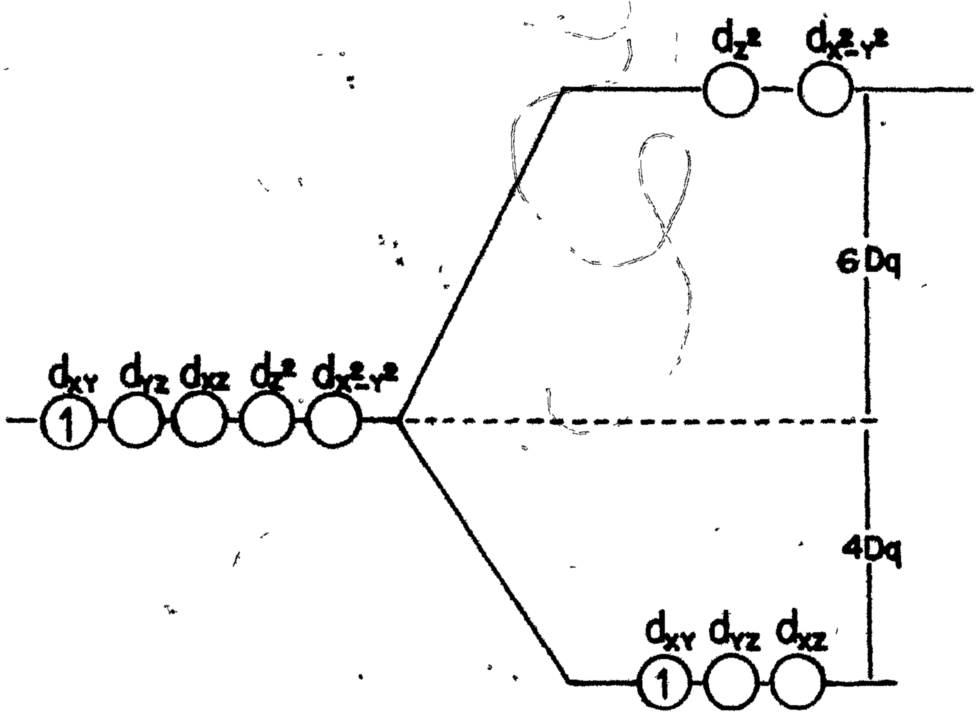

dXY dYZ dXZ dZ² dX²-Y²
1
dZ² dX²-Y²
6Dq
4Dq
dXY dYZ dXZ
1

Figure 6

Energy states for $3d^n$ in an octahedral field

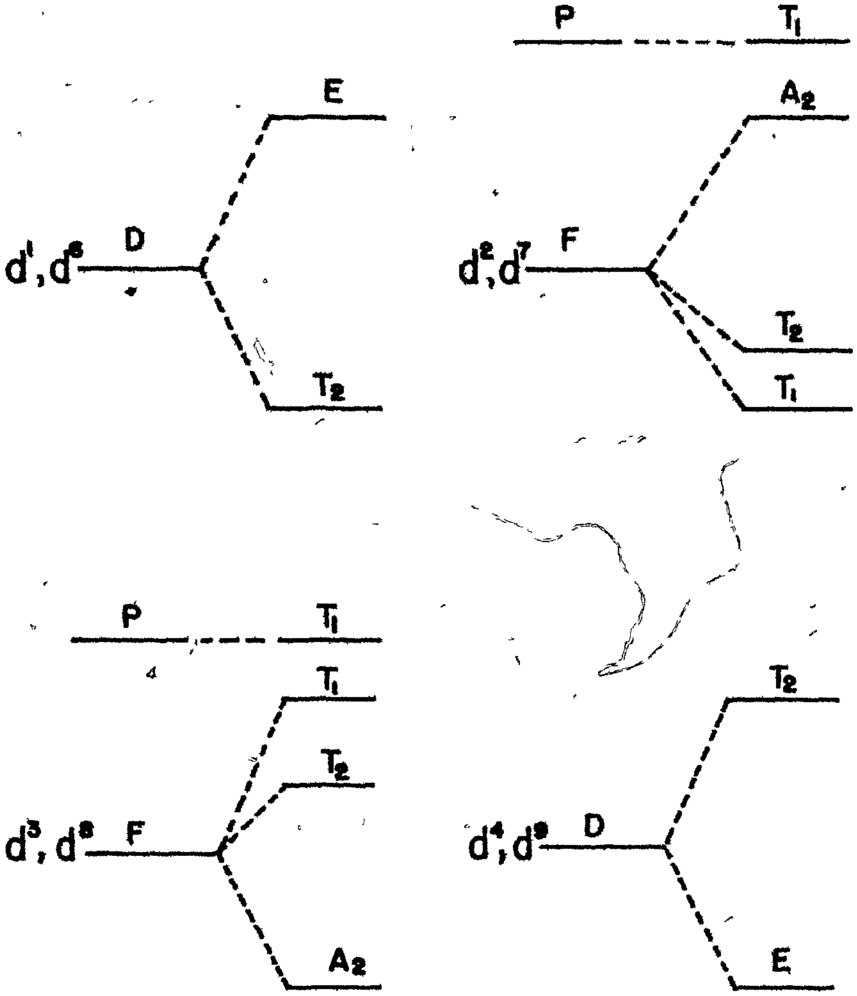

d^1, d^6
D
E
T_2
d^2, d^7
F
P
T_1
A_2
T_2
T_1
d^3, d^8
F
P
T_1
T_1
T_2
A_2
d^4, d^9
D
T_2
E

Table 1

Energy states and energy expressions for $3d^n$ systems in octahedral field

3d systems	states	energy expressions
d^1, d^6	T_2	$-4Dq$
	E	$6Dq$
d^2, d^7	T_1	$7.5B - 3Dq - \frac{1}{2}(225B^2 + 100Dq + 180DqB)^{\frac{1}{2}}$
	T_2	$2Dq$
	A_2	$12Dq$
	T_1	$7.5B - 3Dq + \frac{1}{2}(225B^2 + 100Dq + 180DqB)^{\frac{1}{2}}$
d^3, d^8	A_2	$-12Dq$
	T_2	$-2Dq$
	T_1	$7.5B + 3Dq - \frac{1}{2}(225B^2 + 100Dq + 180DqB)^{\frac{1}{2}}$
	T_1	$7.5B + 3Dq + \frac{1}{2}(225B^2 + 100Dq + 180DqB)^{\frac{1}{2}}$
d^4, d^9	E	$-6Dq$
	T_2	$4Dq$

found (74) at 18,500 cm.$^{-1}$, 17,000 cm.$^{-1}$ and 8,000 cm.$^{-1}$ due to the electronic transition from the $^4T_{1g}(F)$ ground state to the $^4T_{1g}(P)$, $^4A_{2g}(F)$ and the $^4T_{2g}(F)$ states respectively. From Table 1,

$$\nu_1 = E[{}^4T_1(P)] - E[{}^4T_1(F)] = (225B + 100Dq + 180DqB)^{\frac{1}{2}}$$

$$\nu_2 - \nu_3 = E[{}^4A_2(F)] - E[{}^4T_2(F)] = 10Dq.$$

$$\therefore 10Dq = 17{,}000 - 8{,}000$$

$$= 9{,}000 \text{ cm.}^{-1}$$

$$\text{and } B = 775 \text{ cm.}^{-1}.$$

Recently a very simplified method for carrying out a theoretical calculation of the relative energy of each of the d-orbitals in any form of electrostatic field has been published (75,76). However the method is limited to d^1 and d^9 systems where the electronic repulsion is minimal.

Some expressions for calculating 10Dq in an octahedral field have been proposed. Using rigorous quantum mechanical principles, Van Vleck (73) arrived at the equations

$$10Dq = \frac{5}{3}\, eq \frac{\langle r^4 \rangle}{R^5} \text{ ergs (for point charges)} \qquad (2)$$

$$10Dq = \frac{25}{3}\, e\mu \frac{\langle r^4 \rangle}{R^6} \text{ ergs (for point dipoles)} \qquad (2a)$$

where e is the electronic charge, q is the charge on the ligand, μ is the dipole moment, R is the metal-ligand distance and $\langle r^4 \rangle$ is the average radius of the d-orbitals.

Extreme caution must be used in applying these equations because several assumptions and approximations were made in the course of their derivation. Self-evident among these is the assumption that the ligands were considered to be point charges or point dipoles. Therefore one would expect that simple insertion of the values of each term in the expressions would not give a number which would agree very well with that found experimentally.

Several suggestions for the improvement of these expressions have been made (77). The value of the dipole moment of the ligand is best considered as the total dipole moment which is the sum of the permanent dipole moment, μ_o, and the induced dipole moment, μ_i. The latter increases with the intensity of the electric field experienced by the dipole. For an octahedral complex, the expression is

$$\mu_i = \alpha \frac{\left(\frac{q}{R^2} - 2.37 \frac{\mu_o}{R^3} \right)}{\left(1 + 2.37 \frac{\alpha}{R^3} \right)} \tag{3}$$

where α is the polarizibility of the dipole. (The detailed derivation for the expression of μ_i is given in Appendix I.)

The value of R, the metal-ligand distance, could be obtained by several methods including crystal structure analysis or simple addition of the radii of the metal ion and the ligand. Of course, R may change depending on the environment of the complexed ion, but this change would not result in any considerable variation of 10Dq.

$\langle r^4 \rangle$ could be calculated by using the quantum mechanical expression for the radial wave-function of the 3d orbitals, R_{3d},

$$\langle r^4 \rangle = \int_0^\infty (R_{3d})^2 . \, r^4 . \, r^2 dr \qquad (4)$$

where
$$R_{3d} = \frac{4}{81\sqrt{30}} \left[\frac{Z_{eff}}{a} \right]^{7/2} r^2 \exp.(-Zr/3a)$$

a is the Bohr radius and $Z_{eff.}$ is the effective nuclear charge which could be estimated by using Slater's rule*.

However, even if the values of μ, R and $\langle r^4 \rangle$ are used, they still would not give the expected result. In order to avoid this, an empirical value for $\langle r^4 \rangle$ is commonly used, a substitution which results in the loss of importance of the above expression from a purely theoretical viewpoint. For that reason, Jørgensen (78) used the simple expression

$$10Dq \sim \frac{5}{3} \frac{\langle r^4 \rangle}{R^5} \text{ rydbergs} \qquad (5)$$

which is useful as a rough approximation for the value of 10Dq in complexes involving simple ligands such as water molecules or ammonia.

Until recently it seemed to be possible to estimate 10Dq

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* Detailed discussion of which is given in many standard books on quantum mechanics.

only from the observed spectra of the complex. Where spectral studies were impossible, as in the cases of d^0 and d^{10}, no values of 10Dq were available.

A discussion of 10Dq in relation to the lattice energy has been made (79). The lattice energy of a salt, such as the sulphate of a metal, MSO_4, is defined as the energy released when the gaseous ions combine to form the crystal. The reaction could be written as

$$M^{2+}_{(g)} + SO_4^{2-}{}_{(g)} \longrightarrow MSO_{4\,(s)} \qquad [3]$$

The heat of reaction, ΔH, could be calculated from a knowledge of the heats of formation of $MSO_{4\,(s)}$, $M^{2+}_{(g)}$ and $SO_4^{2-}{}_{(g)}$ (80-82). ΔH is related to the lattice energy, U, as

$$\Delta H = U + 2RT \qquad (6)$$

where T is the temperature and R is the gas constant.

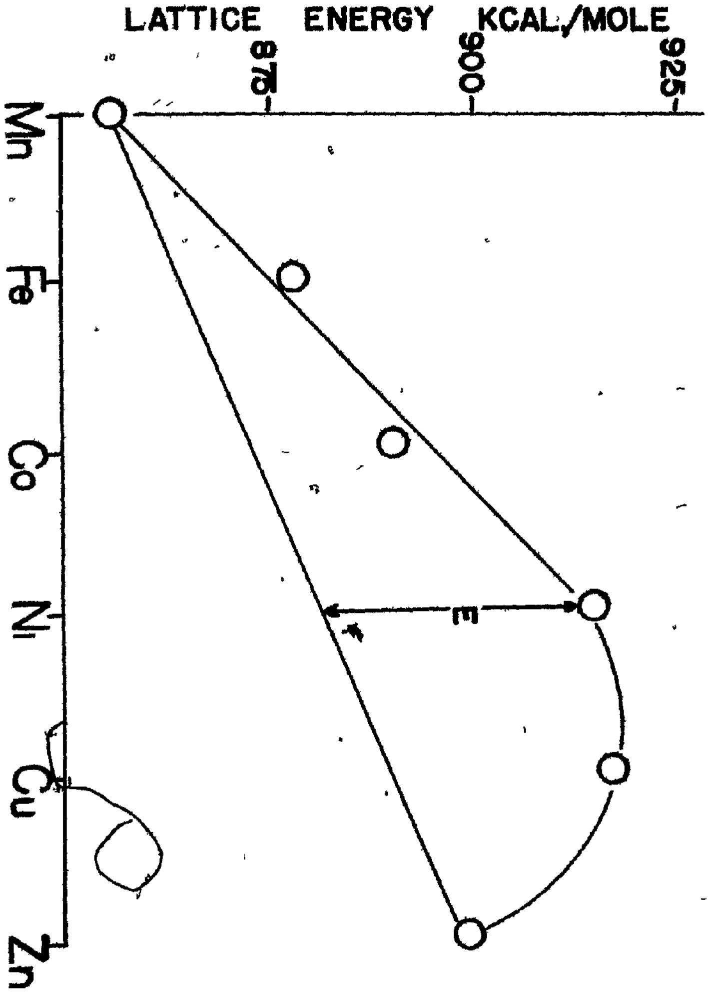
In general, the lattice energy, U, could be expressed as

$$U = U_i + C + E$$

where U_i is the energy of interaction between ions, E is the energy of crystal field stabilization and C is the energy of formation of partially covalent bonds in the crystal MSO_4 (83). Therefore, the increase in lattice energy of the series $MnSO_4$ to $ZnSO_4$ (84), Fig. 7, has been attributed to the increase in C and E. For $MnSO_4$ and $ZnSO_4$, E is zero. Therefore their lattice

Figure 7

Lattice energies for some metal sulphates


LATTICE ENERGY KCAL./MOLE
875
900
925
Mn
Fe
Co
Ni
Cu
Zn
E

A similar formula for calculating the lattice energy has also been given by Kapustinskii (89) and was later refined by Yatsimirskii (90). It is

$$U_i = 287.2 \frac{(\sum n)\, Z_k Z_a}{(r_k + r_a)} \left[1 - \frac{0.345 - 0.00870(r_k + r_a)^2}{(r_k + r_a)} \right] \quad (10)$$

where r_k and r_a are the radius of the cation and anion respectively. This formula has gained wide popularity since the values for the terms are easily obtained in the literature.

However, since both expressions for U_i are derived strictly from the electric interactions between the ions in the crystal, the lattice energy obtained in this way is therefore only the ionic part of the total lattice energy, U, of a salt. U_i is therefore expected to be less than the value obtained experimentally. For a non transition metal salt, this value is less by an amount which is termed the covalent energy, C. For a transition metal salt, this value is still less by an amount which is termed the stabilization energy, E.

Thus this method of estimating 10Dq seems to be also limited to the salts of the transition metals with $d^1 - d^4$ and $d^6 - d^9$ and therefore having some stabilization energy. It is not useful for calculating 10Dq for the manganese(II) and zinc(II) salts. In addition to that, no attempt has been made to extend the calculation for the evaluation of the lattice energy of a salt containing complex ions such as the hexaaquo or hexaammine ions of the metals.

Perhaps the main disadvantage of calculating 10Dq from the lattice energy lies in its inaccuracy. This is evident from the fact that 10Dq is of the order of 25 kcal./mole for the divalent ions of the first row of transition metals. This is a mere fraction of the total lattice energy of the salts which is of the order of 700 kcal./mole for the sulphates of these transition metals.

Thus it seems desirable to have a supplementary technique for the purpose of measuring the ligand field splitting energy without the necessity of studying the spectra. Such a technique was suggested by Jamieson _et al._ (71). Even though no theoretical principle has yet been given to justify the technique, the number of experimental results published has given substantial support to its validity. Except for the hydrates of copper(II) sulphate, all the hydrates of metal sulphates from manganese(II) to zinc(II) were found to give the maximum heat difference, Q_{DB}, in kcal./mole of heptahydrate, to be equal to the ligand field splitting energy for the hexaaquometal(II) ion. For the hydrates of copper(II) sulphate the maximum heat difference, Q_{DB}, was found to be too small to be considered as an expression of 10Dq for the hexaaquocopper(II) ion. Thus apart from investigating the ammine complexes, some time therefore has been devoted to the study of this apparent anomaly.

5. Copper sulphate

Copper(II) ion is a d^9 system where the hexaaquo and the hexaammine complexes would be expected to give simple spectra, each consisting of a single absorption maximum. However, it turns out that the spectra of copper(II) complexes are quite complicated because most of the complexes have tetragonal symmetry as shown in Fig. 8b instead of octahedral symmetry as shown in Fig. 8a (91,92).

In an octahedral field, the d-orbitals of the copper(II) ion would have their relative energy as shown in Fig. 9b. If a tetragonal distortion is applied along the z-axis by removing the two trans-ligands from the metal ion, the effect on the individual orbital is shown in Fig. 9c. The relative energy of the d_{z^2} orbital would be lowered with respect to the other orbitals. The extent of this would depend on the extent of the distortion. Fig. 9c shows the intermediate case where the ligands on the z-axis are further away than those in the xy-plane but their potential is still felt by the central copper(II) ion. If these two ligands are so far away that the complex is essentially of a square planar configuration, Fig.8c, the energy of the d_{z^2} orbital could sink well below that of the d_{xy} orbital as shown in Fig. 9d.

Hexaaquocopper(II) ion in aqueous solution is thought to have tetragonal symmetry as shown in Fig. 8b. Therefore it is expected that the absorption maxima would be seen in its spectrum due to the electronic transitions from the d_{xz} and d_{yz} orbitals to

Figure 8

Ligand symmetry around copper ion

Figure 9

Orbital splitting in ligand fields
of different symmetry

FIGURE 8

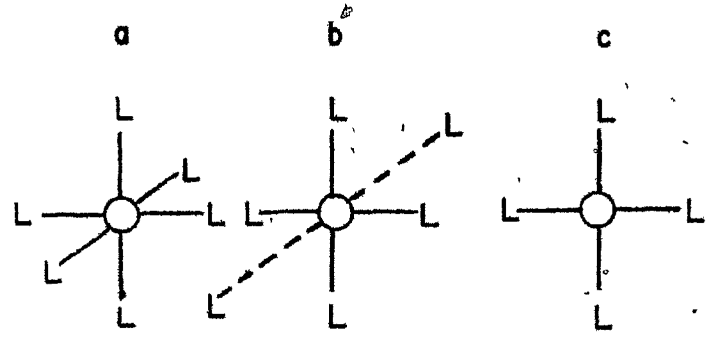
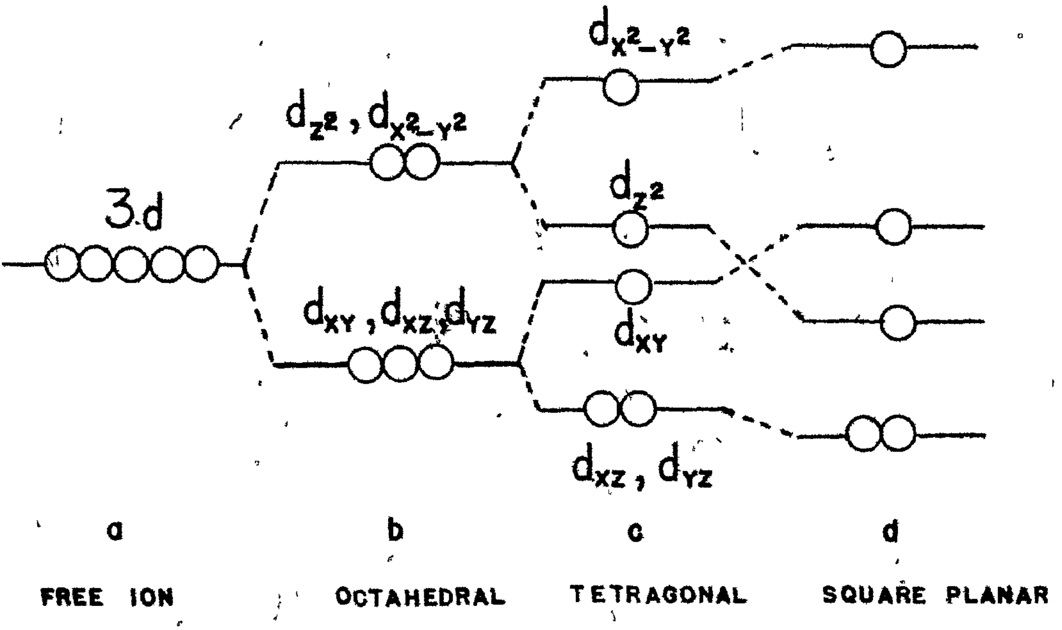


FIGURE 9



the d_{xy}, d_{z^2} and $d_{x^2-y^2}$ orbitals with increasing energy. However, since the energy separation of these orbitals is only of the order of 5×10^3 cm.$^{-1}$ and their half-width is about 3×10^3 cm.$^{-1}$, resolution of these bands is impossible (93).

Thus the problem for an investigator dealing with the spectra of copper(II) complexes is to decide which maximum denotes which electronic transition. If there is a broad band, as seen in the spectrum of hexaaquocopper(II), the investigator must first analyse it into the probable components, using a knowledge of the stereochemistry of the complex. Such a method was used by Bjerrum et al. (94) in their investigation of the aquo and ammine complexes of copper(II) ions in aqueous solution. The broad absorption band was resolved into two bands having maxima at 790 mμ and 1060 mμ for the aquo complexes. With the help of their theoretical calculation of the relative energies of these d-orbitals, they assigned the bands as due to the electronic transitions from the d_{xy} and d_{z^2} orbitals to the $d_{x^2-y^2}$ orbital. Since the third band due to the transition from the d_{xz} and d_{yz} orbitals to the $d_{x^2-y^2}$ orbital was not seen within the wavelength region of their study, it has been concluded that this would probably occur in the ultraviolet region of higher frequency. From the results of this investigation, Orgel (95) estimated the value of 10Dq for the hexaaquo and hexaammine complexes of copper(II) ions to be 12,000 cm.$^{-1}$ and 16,000 cm.$^{-1}$ respectively.

Holmes and McClure (96) investigated the reflectance spectrum of the tetraaquocopper(II) ion found in copper sulphate pentahydrate. Crystal structure analysis has shown (19) that the copper ion is surrounded by four water molecules in the xy-plane. The other coordination positions on the z-axis are filled by two oxygen atoms, each from different neighbouring sulphate ions. This gives a tetragonal symmetry. As was the case with the hexaaquo complexes in aqueous solution, the absorption band was found to be very broad. Detailed analyses have been made using polarized light with application of a Gaussian distribution curve to analyse the spectra. The broad band was found to be composed of three symmetric bands having maxima at 14,500, 13,000 and 10,500 cm.$^{-1}$ corresponding to the transitions from the d_{xz}, d_{yz} and d_{xy} to the $d_{x^2-y^2}$. The transition from d_{z^2} was assumed to be in the infrared region where it could not be detected. The value of 10Dq for this tetraaquo complex was estimated to be the same as that for $[Ni(H_2O)_6]^{2+}$ (97).

A truly octahedral arrangement of six water molecules around copper(II) ion was found in $CuSiF_6 \cdot 6H_2O$ (98). Pappalardo (98) recorded the reflectance spectrum of this salt. Two maxima obtained were attributed to spin-orbit coupling, and 10Dq deduced from this was 11.2 X 10^3 cm.$^{-1}$.

Detailed reviews of the spectroscopy of copper(II) complexes have been given (99,100). From the experiments done on the hexammines of copper(II) halides, Eliott and Hathaway (100) have assigned values ranging from 10.4 X 10^3 cm.$^{-1}$ to 10.6 X 10^3 cm.$^{-1}$

for 10Dq. From their investigation of $Cu(NH_3)_5SO_4$, they gave 10Dq of 11 X 10^3 cm.$^{-1}$. These measurements show that the values of 10Dq for copper(II) complexes are not as high as have been estimated by Jørgensen and quoted by Orgel (95) but of the order of 10 X 10^3 cm.$^{-1}$. This would be comparable to the values of 10Dq obtained for other metal complexes in the same series.

Estimation of 10Dq for copper(II) complexes by the calorimetric method in the present investigation is not intended to prove which values cited in the literature are correct. It is done to show that the anomaly mentioned for the case of the hydrates of copper(II) sulphate in the earlier part of this thesis is only apparent, and that the heat of solution line for the high-energy modification of these hydrates must be located with great care.

The heats of solution for the hydrates of copper(II) sulphate given by previous workers are reproduced in Fig. 10. The heats of solution for the normal crystalline lower hydrates have been fitted (68) to two equations:

$$y_{CF} = 75.24 - 2.276x$$

and $$y_{FB} = 82.74 - 2.562x.$$

Considering only high-energy modifications which contain less than 10.14% water (monohydrate composition), Frost, Moon and Tompkins (68) gave the equation describing them as:

$$y_{FGH} = 149.0 - 5.098x$$

which intercepts the low line BC at approximately the trihydrate

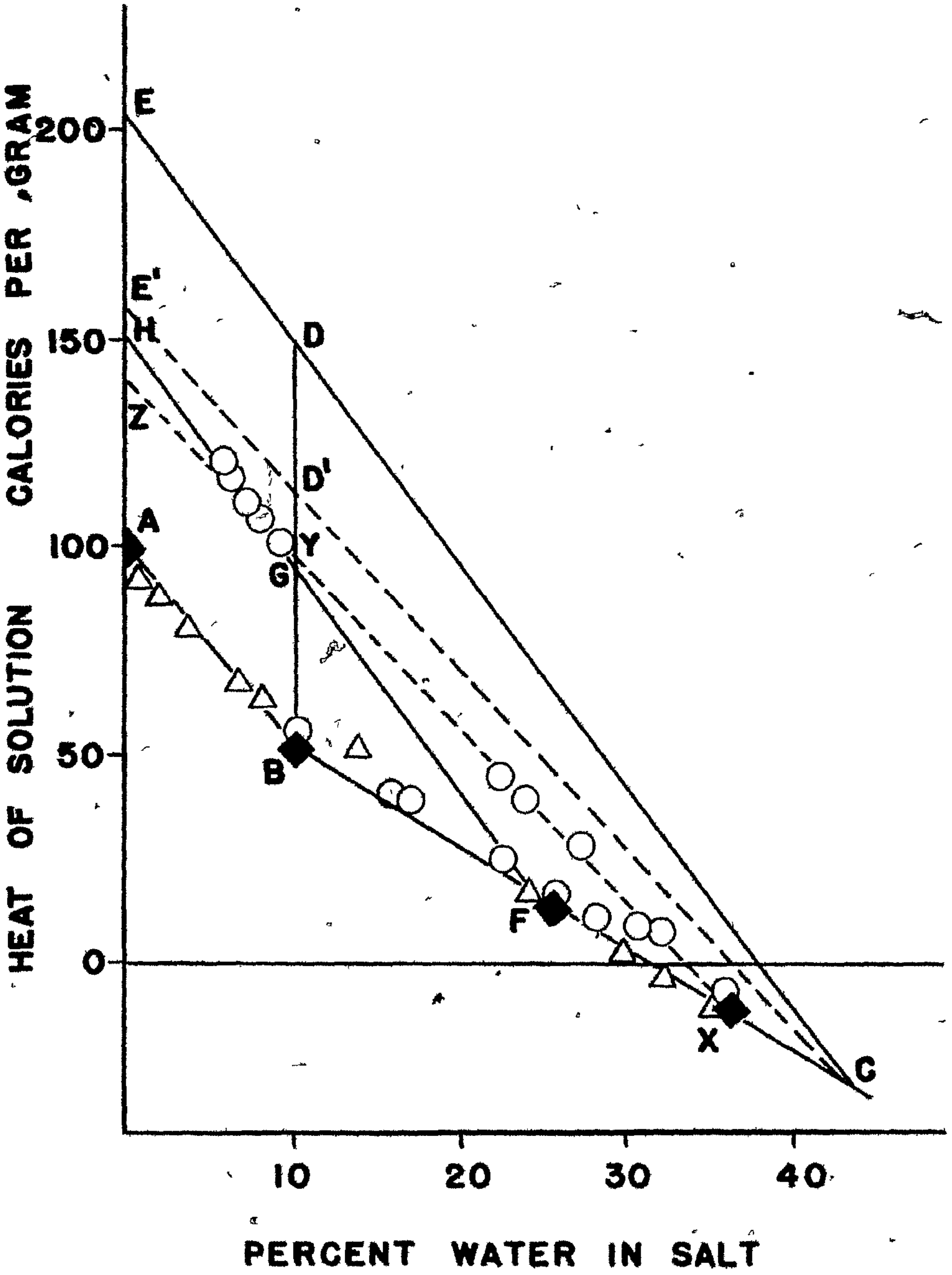
Figure 10

Heats of solution for hydrates of $CuSO_4$

○ Data from Frost, Moon and Tompkins

△ Data from Donnan and Hope

◆ Data from Bichowsky and Rossini


HEAT OF SOLUTION CALORIES PER GRAM
PERCENT WATER IN SALT
200
150
100
50
0
10
20
30
40
E
E'
H
Z
A
D
D'
Y
G
B
F
X
C

composition. If all the heats of solution for the products of vacuum dehydration were considered, the equation of the line XYZ which passes through all these points have been calculated to be

$$y_{XYZ} = 142.4 - 4.276x.$$

Within the limit of experimental error this line is parallel to AB (i.e. the line joining the heats of solution of the anhydrous salt and the monohydrate) which is in accord with what has been found for other hydrates of metal sulphates (71,72). By extrapolating y_{CF}, the heat of solution for the heptahydrate could be found and using the slope of y_{XYZ} the heat of solution for the high-energy monohydrate at point D' was estimated as 113 cal./gm. The heat of solution for the normal crystalline monohydrate is 56.87 cal./gm. and thus the heat of transition is 56.13 cal./gm. or about 17 kcal. per mole of heptahydrate. However this energy seems to be too low to be regarded as the value of 10Dq for the hexaaquocopper(II) ion which has been given as approximately 30 kcal./mole (95)

If the equation for y_{FGH} is used instead, the heat of solution for the monohydrate at point D has been estimated to be approximately 146 cal./gm. which would give the heat of transition approximately as 89 cal./gm. or 25 kcal./mole of heptahydrate. However, the line FGH is not parallel to AB, which seems unusual compared to the cases which have been studied (71,72).

It seemed, therefore, that further research was necessary so that the general applicability of the calorimetric technique for determination of 10Dq could be established.

Two alternatives are left for consideration:

(i) If the line XYZ in Fig. 10 is correctly interpreted, in order that the energy difference could be expressed as 10Dq for hexaaquo-copper(II) ion, there would have to be a monohydrate which would have a heat of solution of about 10 cal./gm. This seems to be very unlikely because it is too low by comparison with the heats of solution of the monohydrates of other metal sulphates.

(ii) On the other hand, if the line FH is accepted as correct, it must be shown that it represents the heat of solution line for the high-energy lower hydrates, with the trihydrate as starting material. Next, a lower line which represents the heats of solution for the normal crystalline hydrates must be found so that the estimation of the heat of solution at the monohydrate composition would give an energy of the order of 45 cal./gm.

The second alternative seems to be more plausible because it is possible that a small fraction of the high-energy form was present in the sample which gives the heat of solution falling on the line BC in Fig. 10; and therefore has a higher heat of solution than the pure normal crystalline form. To ensure completeness of recrystallization, the compound could be heated in a sealed tube (43), thus one would expect the product to give a lower heat of solution. Furthermore, if such a monohydrate were obtained, the heat of solution line from the monohydrate to the anhydrous form would be parallel to the line FGH.

6. The chlorides

According to the ligand field theory, the value of 10Dq for a complex should not vary a great deal from one environment to another. The minor variation observed is attributed to the difference in the secondary coordination. This has been shown to be true for many complexes, such as the ammines of copper(II) halides which have been discussed.

The values of 10Dq for hexaaquocobalt(II) complex in two different environments are 9.3×10^3 cm.$^{-1}$ in $CoCl_2.6H_2O$ crystal (74) and 9.5×10^3 cm.$^{-1}$ in $CoSO_4.7H_2O$ (96). The reason for this is that in the hexaaquo complexes, the potential experienced by the electron or electrons in the d-orbitals is almost exclusively due to the six water molecules around the metal ion since they, collectively enveloping the ion, shield it from the influence of the field set up by the anions around it.

Furthermore, the splitting of d-orbitals is completely determined by the potential and not by other properties of the ligands such as their size or shape. Thus the ligands which can set up stronger potential placed at larger distance from the metal ion may set up a potential equal to that of a weaker ligand placed at a shorter distance. This concept, therefore, implies that an octahedral field is one with equal magnitude of potential applied from the six corners of an octahedron; and this could be set up by any mixture of ligands as long as the requirement above is fulfilled.

Thus it seems natural to believe that the present calorimetric technique of estimating 10Dq would also apply to any kind of salt hydrate. Among these hydrates, the chlorides have been of interest because from the previous study (67), the heat difference between the high-energy modification and the normal crystalline monohydrate was found to be too small to be regarded as an expression for 10Dq.

From the gas absorption study (65), the high-energy monohydrate of cobalt(II) chloride has a large surface area of 35.9 $m.^2 gm.^{-1}$. The ratio of excess heat to the surface area is 0.26 $cal.m.^{-2}$ which is of the same order of magnitude as that found for MgO which is considered as microcrystalline (101,102). This ratio is smaller than the corresponding case for the high-energy monohydrate of $MgSO_4$, i.e. 5.9 $cal.m.^{-2}$, which has been viewed to have a disordered lattice (40). Therefore it has been concluded that the products of vacuum dehydration of cobalt(II) chloride hexahydrate are microcrystalline.

It has also been found that the relation between the rate of dehydration and the water vapour for the hexahydrate of cobalt(II) chloride (41) is somewhat similar to the "Topley-Smith" effect (54) found for $MnC_2O_4.2H_2O$, except for the absence of the sharp minimum at low pressure of water vapour. Instead, there is a maximum in rate at a water vapour pressure of 1 Torr at 30°C. If this maximum is equivalent to the peak which occurs at 1 Torr in the case of $MnC_2O_4.2H_2O$, one would expect the product to be microcrystalline.

The ease of formation of microcrystals for the lower hydrates of cobalt(II) chloride under vacuum is understandable. The chloride ion is spherical and smaller than the sulphate ion. It is expected that ionic mobility is greater for the chloride ion than for the sulphate ion. It is also true that the lower hydrates of the chloride have a great tendency to dissolve in their own water of crystallization. Even though water molecules could escape easily under vacuum, it seems possible that while passing through the disordered product layer they may initiate recrystallization of the latter.

With slightly different interpretation applied to the results of the study on the ammine complexes and the hydrates of copper(II) sulphate, it seems possible to give some meaning to the heats of solution measured for the hydrates of these chlorides. It will be considered that the line joining the heats of solution of the high-energy hydrates need not necessarily pass through the point representing the heat of solution of the starting material on the line BC. This procedure was adopted for the analysis of the heat of solution data for the hydrates of copper(II) sulphate and shall be used when warranted.

A point of theoretical interest is that although $CoCl_2 \cdot 6H_2O$ has six water molecules, not all of them are ligands as generally believed. Crystal structure analysis has shown that only four of these are ligand water while the other two are anionic (103, 104). The other two coordination positions are filled by the chloride ions to give a distorted octahedral field.

Such a situation has also been seen to apply to the pentahydrates of copper(II) sulphate and manganese(II) sulphate, where the axial ligands are oxygen atoms from the sulphate ions. Since the technique has been sucessfully applied to these salts, it seems possible that it would also apply to the hydrates of the chlorides.

7. Double salts

A number of hexahydrates of metal ions are found in double salts of general formula $MSO_4.(NH_4)_2SO_4.6H_2O$. All the six water molecules are ligands arranged almost octahedrally around the metal ion. Some metal-ligand bond distances are listed in Table 2. This arrangement suggests that 10Dq for the complexes in double salts should be of the same order of magnitude as those given for the corresponding complexes in the sulphates and the chlorides.

Of these, the spectrum of $[Fe(H_2O)_6]^{2+}$ has been discussed (105). The absorption spectrum of the complex in aqueous solution is virtually identical to that obtained for the complex in the sulphate salt. Two absorption maxima are at 10,400 cm.$^{-1}$ and 8,300 cm.$^{-1}$ respectively, indicating the split of the e_g orbitals. A similar spectrum has also been obtained for the complex in

Table 2

Metal-water bond distances in double salts

Metal ion	Bond distances in Å	ref.
Fe	2 at 2.14, 2 at 1.88, 2 at 1.85	106,107
Ni	2 at 2.085, 2 at 2.083	
-	2 at 2.036	108
Cu	2 at 2.22, 2 at 2.10, 2 at 1.96	109
Zn	4 at 2.07, 2 at 2.12	110

$FeSiF_6 \cdot 6H_2O$ salt with the maxima at 10,300 cm.$^{-1}$ and 8,700 cm.$^{-1}$. The split could be attributed to either the spin-orbit coupling, tetragonal distortion or the Jahn-Teller effect.

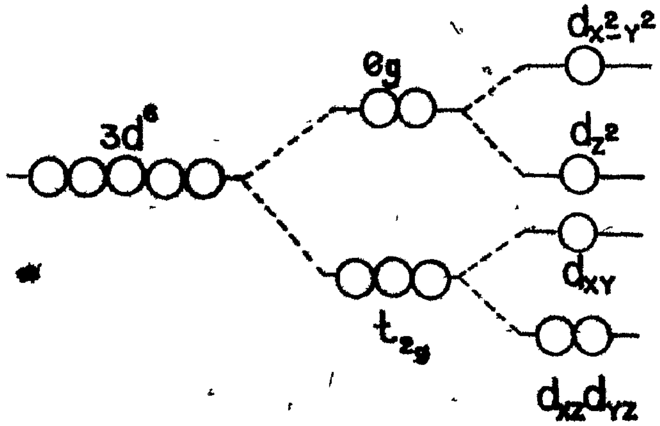
The complex in aqueous solution is expected to possess perfect octahedral symmetry. Therefore the split in the e_g orbitals cannot be due to tetragonal distortion but due to either a dynamic Jahn-Teller effect or spin orbit coupling. Cotton and Meyers (105) suggested that the spin-orbit coupling for Fe^{2+} ion is too small to account for the splitting. Therefore the effect must be due to a dynamic Jahn-Teller effect.

However, in $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, it has been shown that the iron(II) ion is located at the centre of a tetragonally distorted octahedron. Thus the energy levels of the orbitals could be arranged approximately as shown in Fig. 11. Since the transition absorption maxima are found at 10,800 cm.$^{-1}$ and 8,400 cm.$^{-1}$, the 10Dq would be approximately 9,600 cm.$^{-1}$.

It would be interesting to see whether the calorimetric technique could measure the value of 10Dq for this case. Part of the present investigation shall be devoted to the estimation of 10Dq for the complex $[Fe(H_2O)_6]^{2+}$ in the salt $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$.

Figure 11

Orbital splitting of $3d^6$ system in octahedral and tetragonal ligand fields


$d_{x^2-y^2}$
e_g
$3d^6$
d_{z^2}
d_{xy}
t_{2g}
$d_{xz}d_{yz}$

8. Spectroscopy

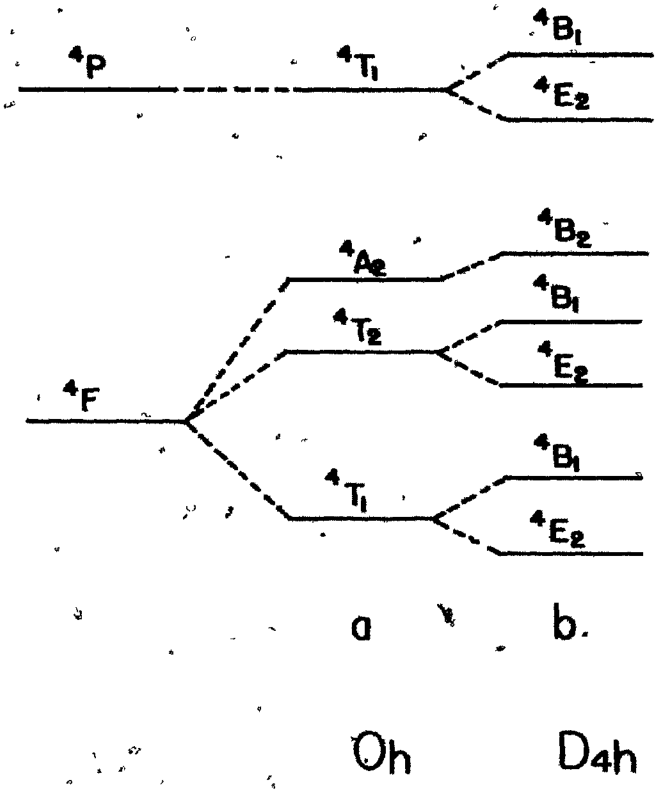
It has been observed that the two different modifications of salt hydrates differ quite a great deal in their colours. The high-energy monohydrate of cobalt(II) sulphate, for example, is deep violet while the lower-energy modification is rosy. The yellow colour of the monohydrate of nickel(II) sulphate turns green when this compound is heated in a sealed tube at an elevated temperature. These colours indicate differences in the energy levels of the metal ions as a consequence of the variation in the coordination around them.

For cobalt(II) salts, it has been suggested (111) that the deep violet and red colorations are due to octahedral coordination while the blue colour may be due to tetrahedral coordination around the cobalt(II) ion. Since neither modification of the monohydrate of cobalt(II) sulphate shows any blue coloration, it seems possible to conclude that neither involves tetrahedral coordination. Therefore, the difference between the two modifications must be sought in the nature of the arrangement of the oxygen atoms around it.

The energy levels of cobalt(II) ion shall be considered as an example, Fig. 12. In the free ion, the electronic ground state of the high-spin cobalt(II) ion is ^4F and the excited state of the same multiplicity is ^4P. In an octahedral field, the ^4F state would split into $^4A_{2g}$, $^4T_{2g}$ and $^4T_{1g}$ in order of decreasing

Figure 12

Energy states of cobalt(II) ion in octahedral and tetragonal fields

^4P
$^4T_1$
$^4B_1$
$^4E_2$
^4F
$^4A_2$
$^4B_2$
$^4T_2$
$^4B_1$
$^4E_2$
$^4T_1$
$^4B_1$
$^4E_2$
a
b.
Oh
D4h

energy, while the ^4P would give $^4T_{1g}$ state. In a field of lower symmetry, such as D_{4h}, all states with the exception of $^4A_{2g}$, would split further, as shown in Fig. 12b. The spectrum of the salt would show several maxima, the number of which is primarily determined by the number of the excited states having the same multiplicity.

If water molecules of the hexaaquo complex of cobalt(II) were removed, the symmetry around the cobalt ion would change, and thus the absorption maxima in its spectrum would be shifted. This change would depend on the effect of removal of these water molecules on the lattice environment of the cobalt(II) ion. In this investigation two possible cases have been studied; with and without rearrangement of the sulphate ions around the metal ions.

With rearrangement of the sulphate ions to form the normal crystalline hydrate, the octahedral field around the metal ion would be distorted because it is expected that the potential set up by $(O\text{-}SO_3)^{2-}$ would be weaker than that due to H_2O. If the symmetry of the resulting field is assumed to be D_{4h}, as shown in Fig. 12b, the absorption maxima would split, one of which would be on the higher energy side of the original peak. As more water molecules are removed from the coordination sphere, the symmetry would again approach that of the octahedral symmetry of the anhydrous salt because then the sulphate ions around it would determine the symmetry. The extent of the splitting of the maxima in the spectra of these complexes would depend on the extent of the distortion; if the distortion is large, the maxima would be resolvable, otherwise they would overlap.

For the cases when rearrangement of the sulphate ions is not extensive, which results in the formation of microcrystalline lower hydrates, the short range order of the ions would be present and would be the same as that of the macrocrystals. The symmetry of the field around the metal ion would be the same as that described for the normal crystalline hydrates. Therefore the spectrum of such a salt would be the same except for the broadening of the maxima due to lower symmetry around the cobalt(II) ions on the surface. This is so because, in the microcrystals, the number of such species on the surface would be considerable in relation to the number of fully coordinated species in the bulk.

If the product is amorphous, the sulphate ions do not rearrange to form another crystal lattice, the symmetry of the potential field around the metal ion is less definite. When the percent of water left in the salt is high, the symmetry of the field around the complex is determined by the number of water molecules attached to it. As more of these water molecules are removed, the symmetry would be less definite until the monohydrate (or anhydrous) stage is reached where they are totally stripped of water and the ions would fall into complete chaos. Such an arrangement of ions would give a spectrum with no definite maxima, but a broad band covering the whole range of possible absorption maxima which arise from these different symmetries.

In all cases, however, the maximum due to the electronic transition from the ground state to the $^4T_{1g}(P)$ state would be quite distinct because it lies somewhere around 19,000 cm.$^{-1}$. The variation in 10Dq and in the symmetry of the field would not affect the position and the intensity of this band a great deal.

9. Infrared spectroscopy

The dehydration process for the hydrates of transition metal sulphates goes to completion after passing through various stages of intermediate integral hydrates. It has been suggested that to a certain degree the water molecules present in the parent hydrates are non-equivalent. In all instances, the monohydrate is formed as the last stage before dehydration proceeds to give the anhydrous salt. It has been generally accepted that the last water to go, which is contained in the monohydrate, is anionic water: a water molecule which is strongly bonded to the sulphate ion by hydrogen bonding. Even in the case of the hexahydrate of nickel(II) sulphate where crystal analysis has shown that all six water molecules are coordinated to the nickel ion, the last water to leave at a temperature of about 290°C is believed to be anionic. How this last water, which is initially coordinated to the nickel ion, becomes anionic is not yet fully understood.

Under vacuum, however, the dehydration proceeds at a faster rate from the onset of the experiment. Some salts form the anhydrides without passing through any intermediate stage, as shown in Fig. 13. It appears that when dehydration is done under vacuum the water molecules leaving the salt are nonselective. At a lower pressure, such as 0.3 Torr, both types of bonded H_2O, coordinated or anionic, have equal chance of leaving the salt. Thus, statistically, in $CoSO_4 \cdot 7H_2O$, the dehydration would be six to one in favour of the coordinated water over that of the anionic water. If this is true, then in the high-energy monohydrate, some of the water would be anionic and some would be coordinated. Unfortunately, there is no easy way to show that this is true.

In the preliminary study of the infrared absorption spectra for the products of vacuum dehydration of the heptahydrate of cobalt(II) sulphate, it was found that the spectrum of the salt shows almost all the features of the parent heptahydrate as shown in Fig. 14. The absorption bands at 3200 cm.$^{-1}$, 1650 cm.$^{-1}$ and 1100 cm.$^{-1}$ have been assigned to the O-H stretching, H_2O deformation and $O-SO_3$ stretching respectively (112). The band at 1650 cm.$^{-1}$ suggests that the remaining water molecules in the high-energy monohydrate are coordinated to the metal ions because this band is also present in the spectrum of the heptahydrate but absent in the spectrum of the crystalline monohydrate.

In the recent measurement of the magnetic susceptibility of the high-energy hydrates of $MnSO_4$, $FeSO_4$ and $CoSO_4$ (113) it was found that these salts have higher magnetic susceptibility than their corresponding low-energy modifications. It was proposed that

Figure 13a

Vacuum TGA

1 $MnSO_4 \cdot 5H_2O$

2 $FeSO_4 \cdot 7H_2O$

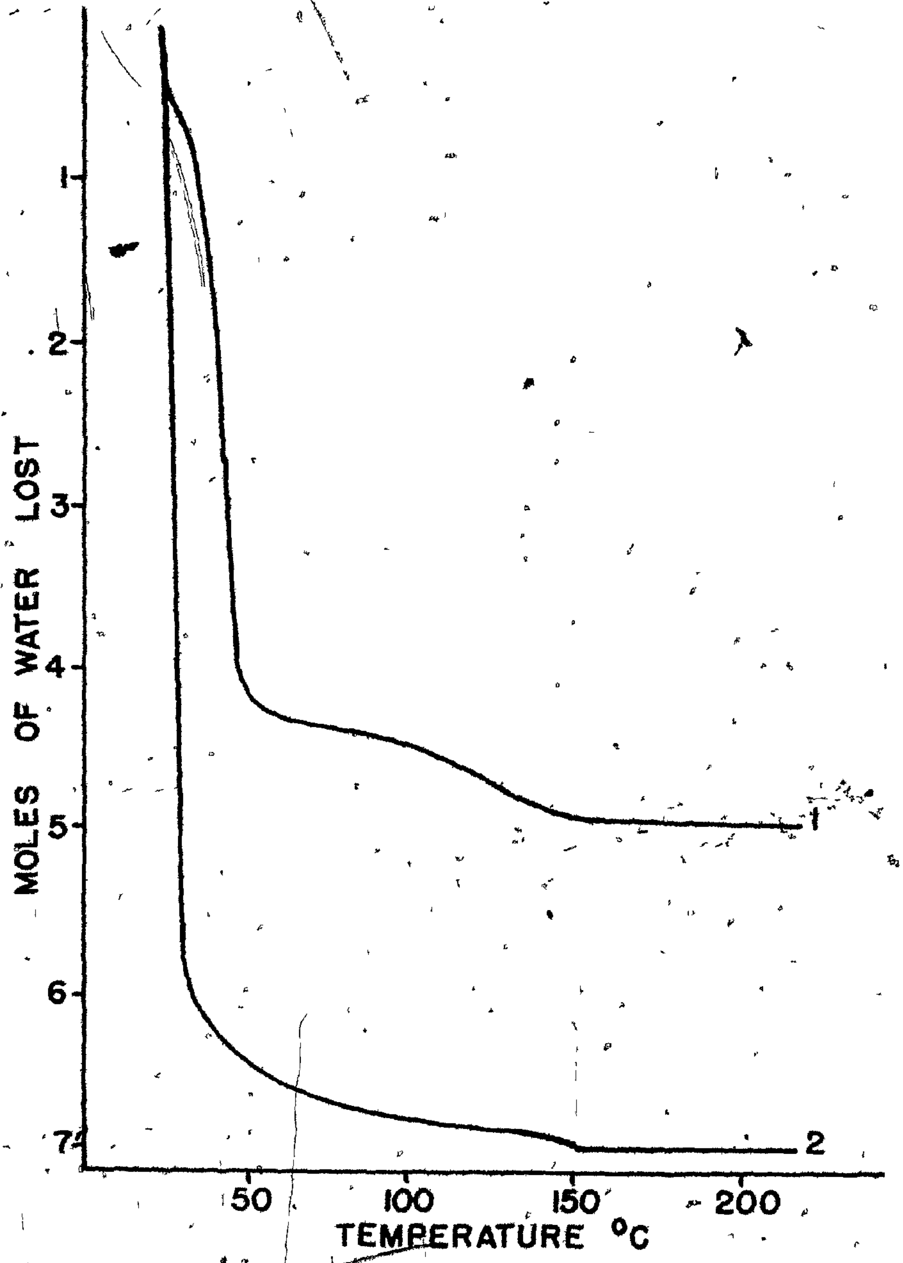
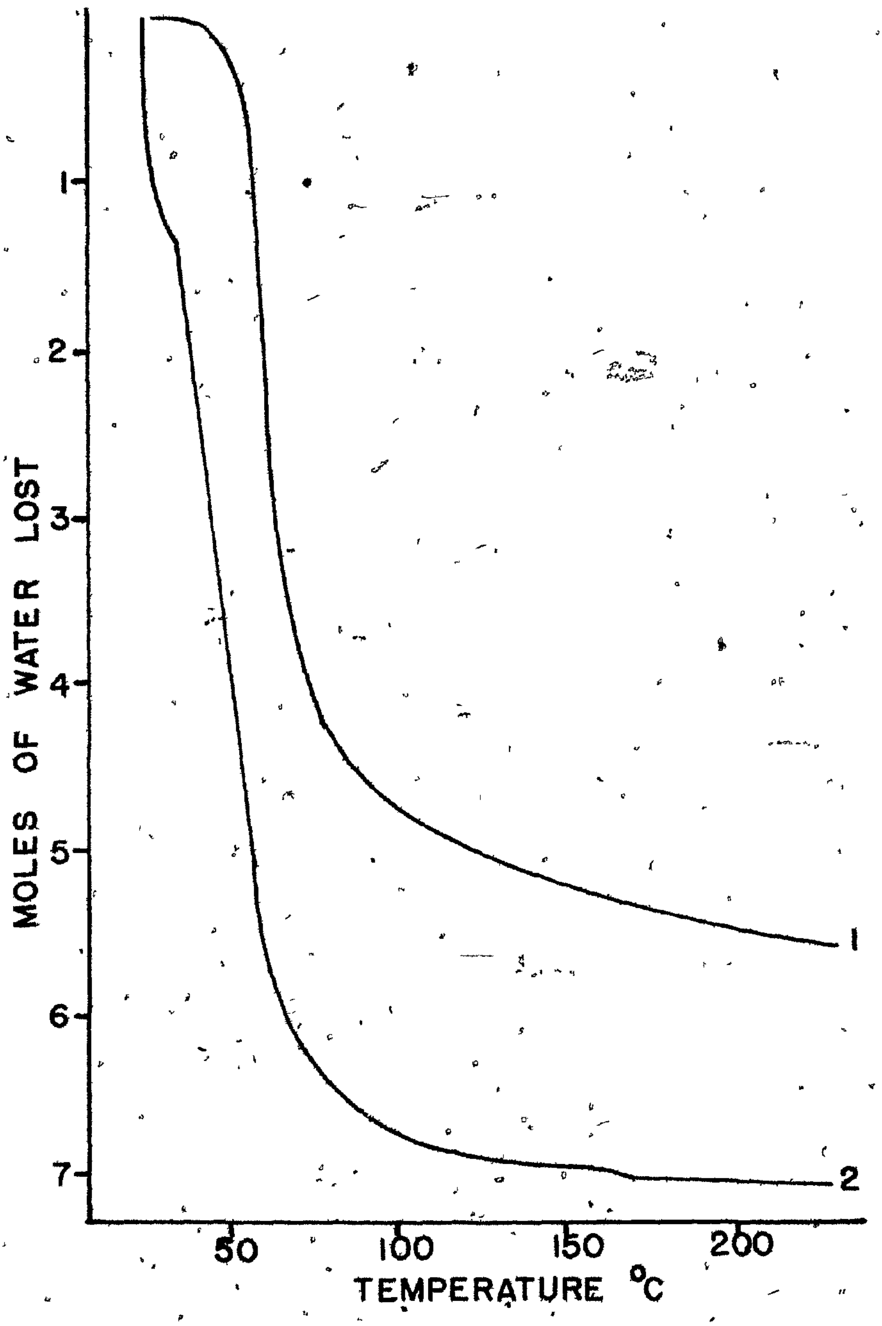

MOLES OF WATER LOST
1
2
3
4
5
6
7
TEMPERATURE °C
50
100
150
200
1
2

Figure 13b

Vacuum TGA

1 $CoSO_4 \cdot 7H_2O$

2 $NiSO_4 \cdot 6H_2O$


MOLES OF WATER LOST
1
2
3
4
5
6
7
50
100
150
200
TEMPERATURE °C
1
2

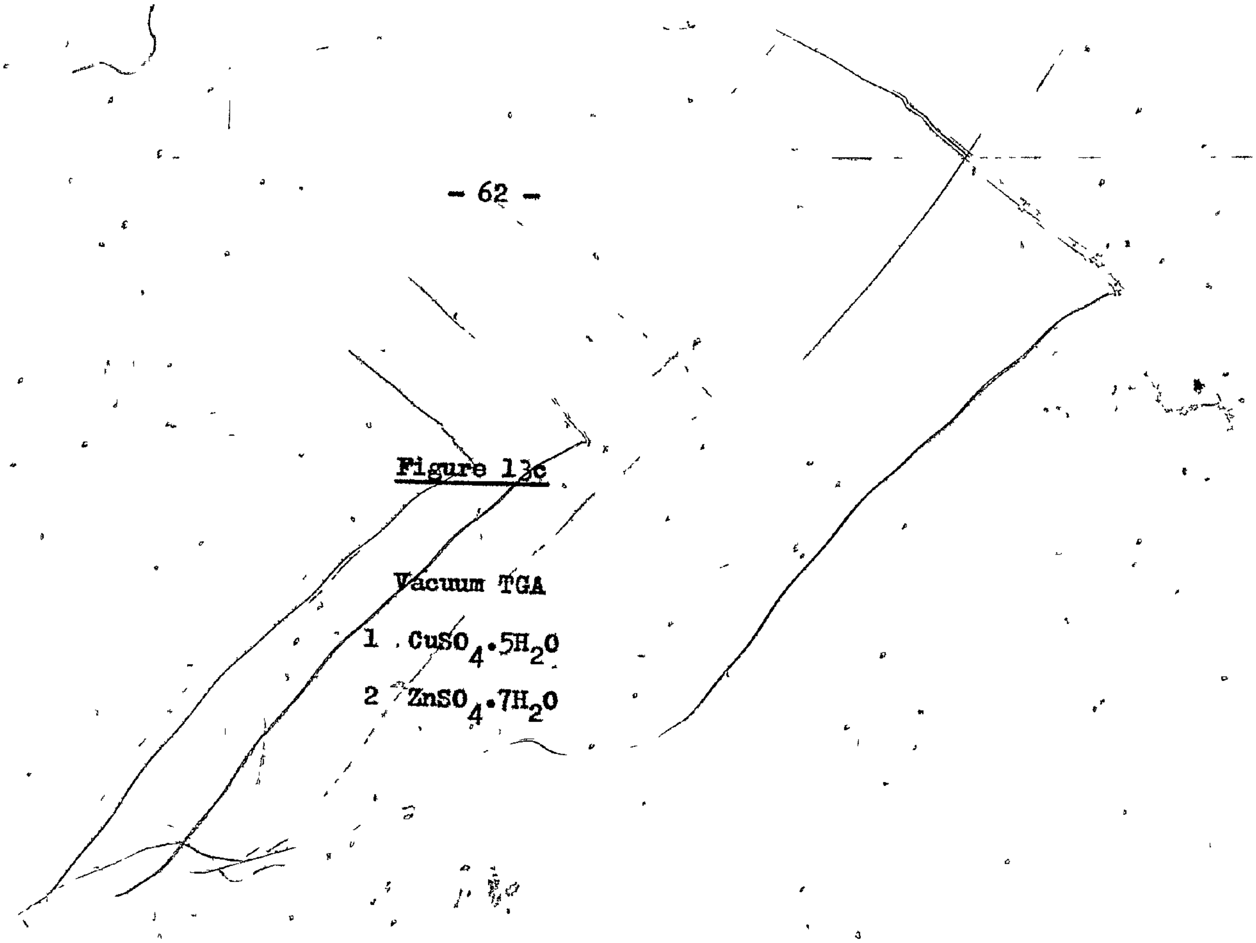


Figure 13c

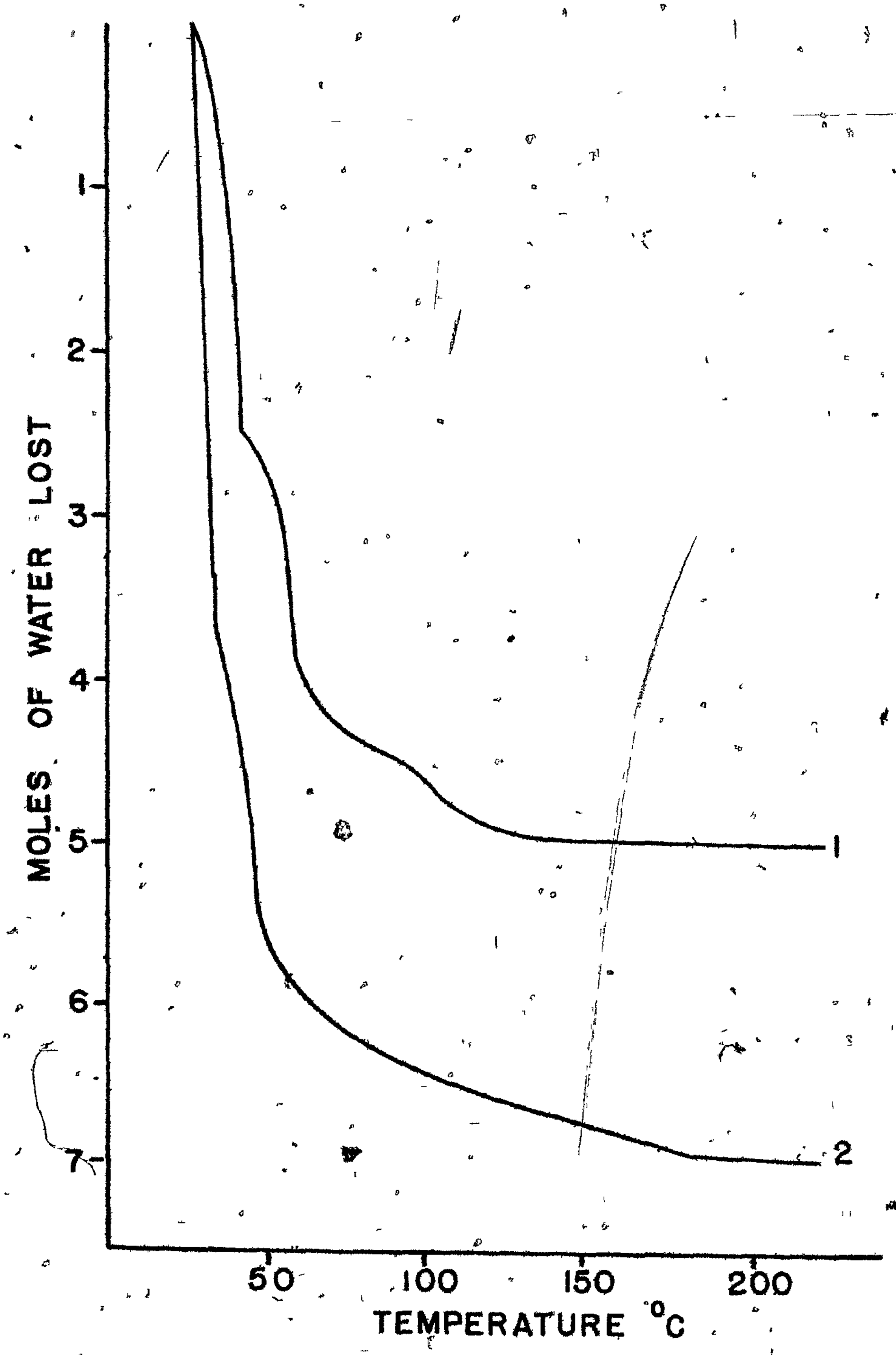
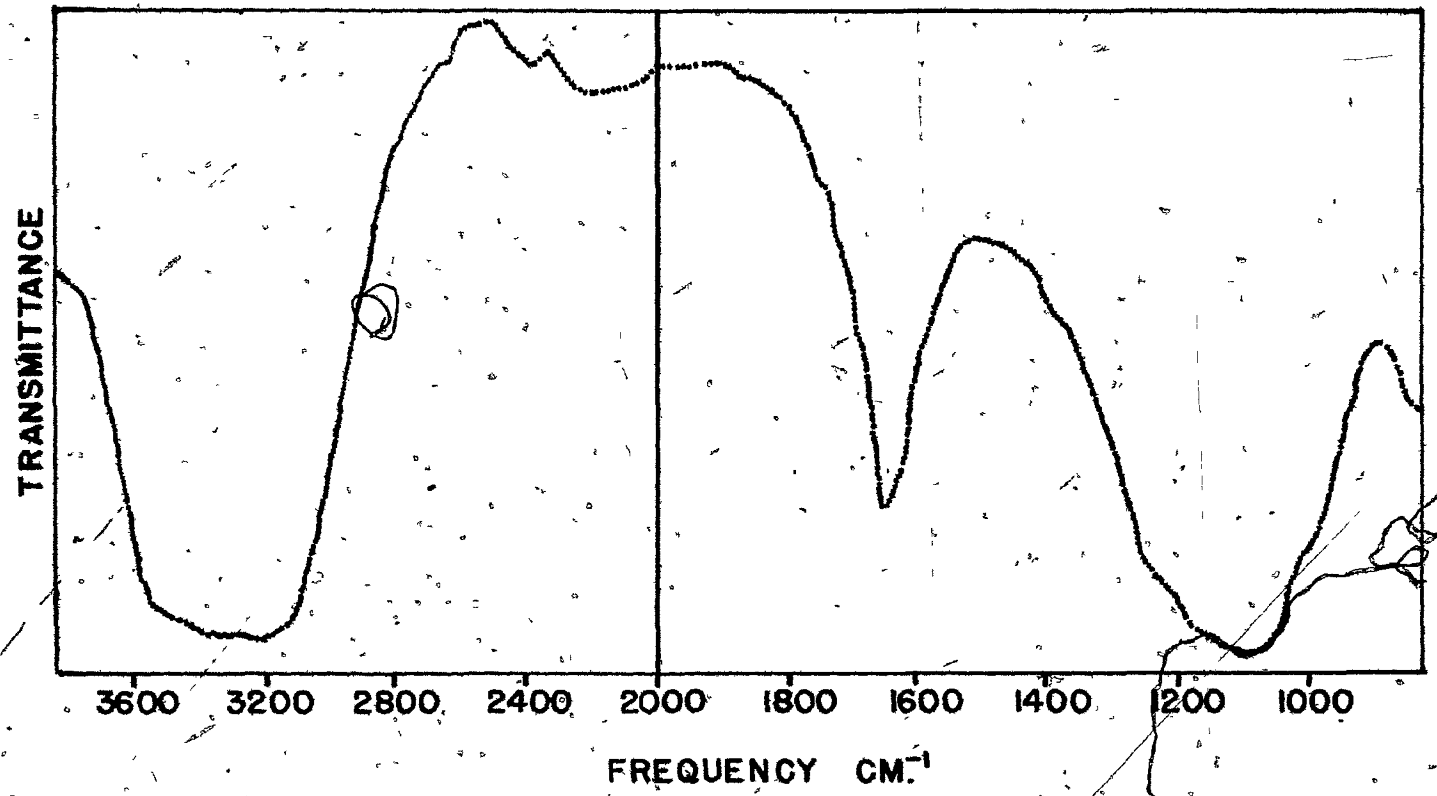

MOLES OF WATER LOST
1
2
3
4
5
6
7
50
100
150
200
TEMPERATURE °C
1
2

Figure 14

Infrared spectrum of the high-energy monohydrate of cobalt(II) sulphate


TRANSMITTANCE
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
FREQUENCY CM.$^{-1}$

[redacted]

the increase in symmetry of the ligand field around the metal ion would be enough to account for the difference. For the symmetry to increase, the first mole of water to leave the salt under vacuum must be the anionic water. The presence of anionic water in the salt would be expected to distort the octahedral arrangement of the six water molecules around the metal ion. Furthermore, as has been discussed, removal of any of the water molecules coordinated to the metal ion is out of question because this would lead to a lowering of the symmetry.

10. Heat of solution

The equations describing the solution process of a salt are

$$MSO_4 \cdot xH_2O + (6-x)H_2O \longrightarrow MSO_4 \cdot 6H_2O \qquad [4a]$$

$$MSO_4 \cdot 6H_2O + \text{solvent} \longrightarrow MSO_4 \cdot 6H_2O_{(\text{solvated})} \qquad [4b]$$

Equation [4a] represents rearrangement of the molecules due to the attractive forces between aquo ligands and solid. Equation [4b] represents the solvent effect when the solid changes phase during the mixing with the solvent.

The process represented by [4b] could be pictured as the solid "melting" into the solvent, so that the normal heat effect is essentially the heat of fusion of the solid (114). When the heat absorbed differs markedly from the heat of melting of the solid, it indicates that there must be a certain interaction between the dissolving molecules and the molecules of the solvent. This is a very common phenomenon in aqueous solution.

In the absence of such interaction, the heat of solution of a solid would be expected to equal the heat of melting of the solid at that temperature. Such a case is termed the "ideal solution". Since there is no special solute-solvent interaction, the heat of solution would be independent of the final concentration of the solution; i.e., no heat of dilution. This condition is not obtained when an electrolyte is dissolved in water since hydration of the metal ions and anions must certainly take place.

For non-transition metal ions, such as Mg^{2+} and Zn^{2+}, the heat of solution could be described by the simple electrostatic theory. For transition metal ions, however, the reaction represented by equation [4a] would introduce an effect called stabilization energy.

According to Werner (115), the coordination positions about a given central ion cannot remain unfilled. It has been demonstrated that in $Co(NH_3)_6Cl_3$, the three chlorine atoms are ionic and the hexaamminecobalt(III) ion is tripositive (116). However, if one of the ammonia molecules is removed from the coordination sphere of cobalt(III), one of the chloride ions would fill the vacant position to form $[Co(NH_3)_5Cl]Cl_2$ where the negative charge on the chloride ion has neutralized one positive charge on cobalt.

Similarly in crystals, such as $FeCl_2 \cdot 4H_2O$, when the four molecules of water are removed, the chloride ions would migrate into the coordination positions left vacant by the former to complete the coordination number of six. In $FeCl_2 \cdot 4H_2O$, the four water molecules are arranged around the Fe^{2+} ion at the four corners of a square at a distance of 2.09 Å while the two chloride ions are each occupying the positions above and below Fe^{2+} ion at a distance of 2.59 Å (117). Removal of two water molecules, for example, would leave two positions vacant in the square, but the adjacent chloride ions in the crystal lattice would move in to fill these two positions in $FeCl_2 \cdot 2H_2O$ where the H_2O-Fe distance is 2.07 Å and the Fe-Cl distance is 2.49 Å (118).

Thus, the removal of ligands from a complex ion in crystals must bring about a filling of the empty coordination positions and therefore subsequent rehydration must involve the displacement of the anions from the coordination sphere. Consequently the net effect would be due to the differences in the stabilization energy and bond energy of the two species.

The particular solute-solvent interaction is therefore determined by the nature of the solvated species. It is important in the present investigation to maintain uniformity of the solvated species; a fact which is quite certain to hold for the solution of aquo complexes. Furthermore, such solute-solvent interaction would depend on the final concentration of the solution and it would seem to be desirable, when possible, to include values of heat of dilution in the calculated values of heat of solution.

The heat of dilution for copper sulphate has been measured experimentally (119) and has been used in the present investigation. No such data are available for the other salts. However, the quantity of primary interest in this investigation is the difference in the heat of solution of two modifications of monohydrate (or monoammine), and it seems that their heats of dilution would cancel one another. Any small error which might be caused by these quanties could be minimized by dissolving approximately the same weight of salt in a constant volume of solvent.

In a thermodynamic study, the heat of solution is especially useful in the calculation of relative heats of formation for salt hydrates. This is mainly because of the fact that the heat of solution varies linearly with the percent water content of the salt (120). Donnan and Hope (120) have shown that the heat of solution of the mixtures of hydrates between two stable integral hydrates must fall on a straight line.

Let the average composition of the salt be $MSO_4 \cdot xH_2O$. Thus

$$MSO_4 \cdot xH_2O = p(MSO_4 \cdot mH_2O) + q(MSO_4 \cdot nH_2O)$$

where $p + q = 1$ and $mp + nq = x$. Therefore,

$$p = \frac{(x - n)}{(m - n)} , \quad q = \frac{(m - x)}{(m - n)}$$

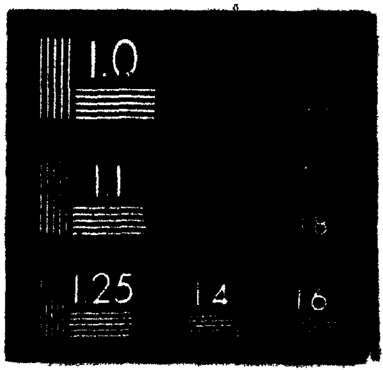
Let the heat of solution of hydrate m be a and that of hydrate n be b. Therefore the total heat of solution, y, of $MSO_4 \cdot xH_2O$ is

$$y = a\frac{(x - n)}{(m - n)} + b\frac{(m - x)}{(m - n)}$$

The plot of y as a function of x for each pair of successive hydrates will determine a particular straight line, so that the result will be a series of straight lines intersecting at the values of x corresponding to the successive hydrate.

It should not be taken as a rule, however, that a change in the slope is necessary to indicate the existence of integral hydrates. The relation given above does not require this condition: it merely indicates the possibility of its occurrence. Therefore, it is not surprising that even in the case of the hydrates of copper sulphate there is really no inflection observed on the heat of solution line of normal crystalline hydrates to indicate the existence of the trihydrate.

2 OF/DE **4**



11. Ammine complexes

In contrast to the aquo complexes no detailed account of deammoniation of ammine complexes can be presented because little work has yet been done. This is especially true for deammoniation under vacuum. This would seem to be a result of the difficulty of obtaining a stable integral high ammine such as the hexaammine.

Even though several workers (121-126) have indicated the possibility of preparing the hexaammines of metal sulphates, such compounds are not stable at ordinary temperature in air. They must be kept under ammonia atmosphere at a very low temperature. The hexaammines of manganese(II) and zinc(II) sulphate, for example, are stable only at -78°C (121) and -35°C (122), respectively.

Ephraim (123) has shown which various integral ammines occur in the course of deammoniation to the anhydrous salt. The results of his investigation are reproduced in Table 3. Recent investigations (124-126) have confirmed the existence of some of these intermediate integral ammines.

While the higher ammines are very unstable as compared to their corresponding hydrates, the lower ammines are very stable. No sufficient explanation can yet be given for this. However, according to Grinberg (129) a compound such as $M(NH_3)_6X$ is stable

Table 3

Stable integral ammines of metal sulphates

Sulphate of	Integral ammines*						
	6	5	4	3	2	1	$\frac{1}{2}$
Mn	+	+	−	−	+	−	+
Fe	+	−	+	+	+	+	−
Co	+	−	+	+	+	−	+
Ni	+	−	+	−	+	+	−
Cu	−	+	+	−	+	+	−
Zn	−	+	+	+	+	+	+

* + indicates stability, − indicate instability

only if the molecular volume of X is greater than that of SO_4^{2-} anion (r = 2.30 Å). This is because a smaller anion has a higher tendency towards coordination with the central ions.

The higher stability of the lower ammines may be explained by the fact that ammonia, being a slightly stronger ligand than water, would form a stronger bond with the central metal ion. It could also be that the total hydrogen bond energy in the ammine complexes contributes significantly to this stability. For the purpose of comparison, the temperatures of decomposition of the monohydrates and the monoammines are given in Table 4.

As is the case with the aquo complexes, much has been published (93,94,100) on spectral studies of the ammine complexes of these metal ions. Most investigations have been concerned with the hexaammines of the cations in solution, where they are known to be more stable than in the solid phase. Reflectance studies on d-d transitions have been done on some of the complexes (93) but due to their instability, analysis has been quite difficult and even doubtful. A knowledge of the stereochemistry of these complexes is helpful for proper interpretation of the absorption bands.

Since ammonia was chosen as ligand because of its relative simplicity, one would expect that most of its behaviour under vacuum deammoniation and thermal dissociation would be closely similar to that of the aquo complexes. Therefore the process

Table 4

Decomposition temperatures for monohydrates and monoammines of metal sulphates

Sulphate of	Decomposition temp., in °C		ref.
	monohydrates	monoammines	
Mn	173*	313	123
Fe	376*	400	126
Co	239*	340	124
Ni	290*	380	125
Cu	168*	380	127
Zn	188*	380*	

* From Jamieson's unpublished data.

of vacuum deammoniation was carried on at a pressure of 0.05 Torr or less to ensure that the rate of deammoniation would be high and that the energy difference would be maximized.

For the purpose of preparing the highest possible high-energy modification a suitable desiccant for all hydrates and ammines has not yet been found. One desiccant may be suitable for cobalt sulphate but not for copper sulphate. In any case, most of the difficulty in the present investigation has been in obtaining the low-energy forms of various lower ammines, for, as will be explained later, many of the complexes obtained have been found to give heats of solution falling on the high line corresponding to the high-energy modification.

EXPERIMENTAL

1. Preparation of ammine complexes

The dissociation of a complex ion, MA_n, in solution may be represented by the equation

$$MA_n \longrightarrow MA_{n-1} + A$$

(where the charges are ommited for simplicity). The equilibrium constant for the process,

$$K_n = \frac{[MA_{n-1}][A]}{[MA_n]}$$

is called the instability constant of the complex ion MA_n. The stability constant, for the reverse reaction, is given by the reciprocal of the instability constant. Table 5 gives the successive stability constant indices, pK, (130) for some ammine complexes in aqueous solution. It is evident that the hexaammines of these metal ions cannot be crystallized from aqueous solution. Even for the nickel(II) ion, for which the pK of the hexaammine is positive, the crystals obtained from aqueous solution have been found to be of composition $NiSO_4 \cdot 4NH_3 \cdot 2H_2O$ (131).

Crystallizing the salt from concentrated ammonia solution is also doubtful because the crystals obtained this way for the case of copper sulphate have been shown to be of composition $Cu(NH_3)_4SO_4 \cdot H_2O$ (16). The water molecules in this salt are anionic

Table 5

Stability constant indices for some ammine complexes in aqueous solution

	Metal ions			
	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
pK_1	2.11	2.79	4.15	2.37
pK_2	1.63	2.24	3.50	2.44
pK_3	1.05	1.73	2.89	2.50
pK_4	0.76	1.19	2.13	2.15
pK_5	0.18	0.75	− 0.52	−
pK_6	− 0.62	0.03	−	−

and only evolved at 145°C (132,133), at which temperature some of the coordinated ammonia may be driven out.

Thus all the ammine complexes prepared for the present investigation were obtained from the reaction of dry ammonia gas with the anhydrous salts of the metal sulphates (134-137).

Suitable temperatures for the preparation of the anhydrous salts of the metal sulphates from the higher hydrates were determined from experiments in thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Thus $CoSO_4$ was obtained by heating $CoSO_4 \cdot 7H_2O$ (J.T.Baker analyzed reagent) in an oven at 270°C for three days; anhydrous $NiSO_4$ was similarly obtained from $NiSO_4 \cdot 6H_2O$ of Fisher certified reagent grade at a temperature of 350°C; anhydrous $MnSO_4$ was obtained from $MnSO_4 \cdot H_2O$ (Merck & Co. Ltd.) at 265°C; $ZnSO_4$ was prepared by dehydration of $ZnSO_4 \cdot 7H_2O$ of J.T.Baker analyzed reagent grade at 250°C; and $CuSO_4$ was prepared at 250°C from $CuSO_4 \cdot 5H_2O$ supplied by Fisher Scientific Co. The anhydraous salt of $FeSO_4$ from Fisher Scientific Co. was found to contain some water which was removed by heating the salt under vacuum at 170°C. Except for $FeSO_4$, completeness of dehydration was checked by the loss in weight, which agreed well with the calculated value within 0.1%.

The anhydrous salts obtained were finely powdered and about 4 gm. of each were taken for reaction with anhydrous ammonia gas (supplied by Matheson of Canada Ltd.). The salt was placed in a reaction tube, A, Fig. 15, and connected to a vacuum line with thick rubber tubing, R. The system was initially evacuated by opening the stop-cocks D and C. When evacuation was complete, stop-cock D was closed and ammonia was led in for the reaction through stop-cock B. The pressure of ammonia was kept at one atmosphere for about two days. In each case during the initial stage of reaction there was evolution of heat accompanied by an increase in volume of the solid. Reaction was speeded up by cooling the reaction tube in liquid nitrogen or in a bath of dry ice and acetone. The composition of the product was determined from both the gain in weight and gravimetric analysis. As has been reported (124,138,139) most of the hexaammines of these salts were unstable. Gravimetric sulphate analyses were necessary since these compounds were used as starting materials for the preparation of lower ammines. This was done by dissolving about 0.4 gm. of the salt in about 20 ml. of 1M HCl. The sulphate was precipitated by adding an excess of concentrated solution of $BaCl_2$. The mixture was boiled for several minutes and about 0.5 ml. of concentrated HNO_3 was added to dissolve any $BaSO_3$ present. The mixture was later cooled and the precipitate of $BaSO_4$ was collected and washed. It was dried in an oven at 110°C and weighed. The weight of metal sulphate in the ammine salt was calculated from the weight of $BaSO_4$ obtained. Thus the weight of ammonia could be obtained from the difference. The results are listed in Table 6.

Figure 15

Apparatus for the preparation of ammines

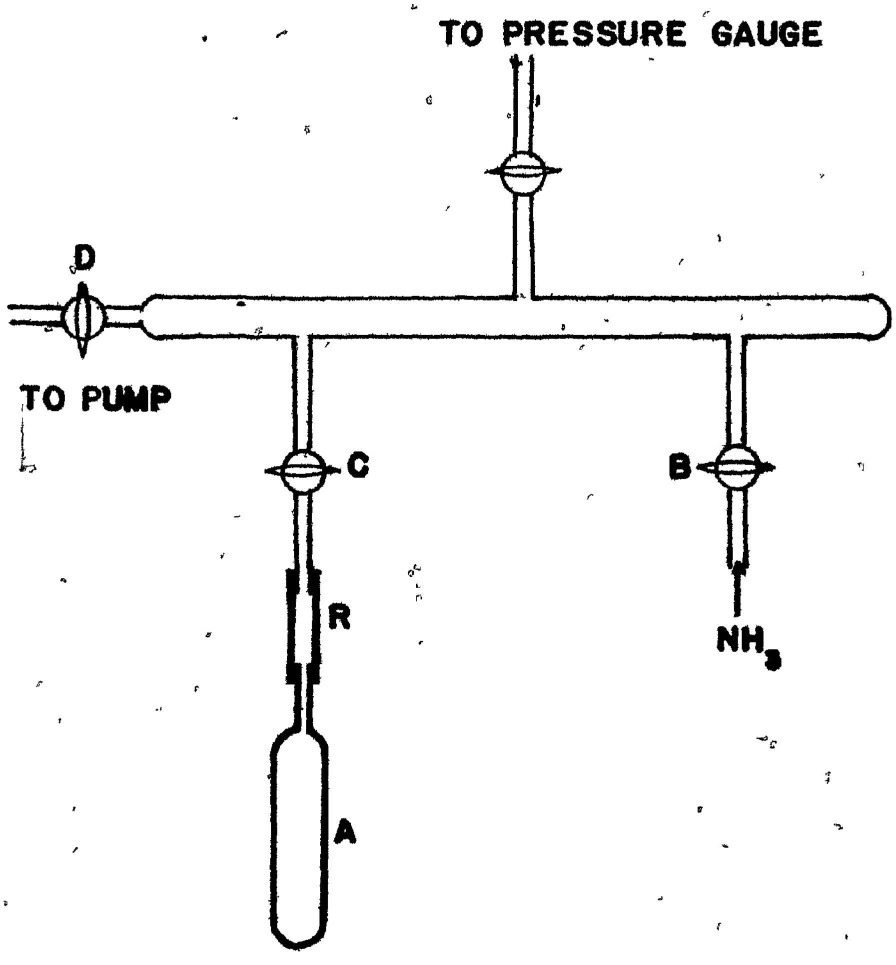

TO PRESSURE GAUGE
D
TO PUMP
C
B
R
NH_3
A

Table 6

Percent ammonia found by gravimetric sulphate analysis

Sulphate of	Percent ammonia
Mn	35.62
Fe	39.65
Co	38.30
Ni	39.61
Cu	29.57
Zn	29.76

Some of the hexaamine of cobalt(II) sulphate was also prepared, essentially as described by Wendlandt and Smith (125), by passing dry ammonia gas through a suspension of the free salt in absolute ethanol. Samples prepared in this way and by direct reaction of anhydrous ammonia gas on the free salt were subjected to thermal analysis at a heating rate of about 0.12 deg./min. and were found to be virtually identical, Fig. 16.

A sample of $NiSO_4 \cdot 6NH_3$, which was prepared by the method of Werner (140), has been shown to be essentially identical to both the hexaammine prepared by the reaction of dry ammonia gas with the anhydrous salt and that reported by George and Wendlandt (126), although the colors of the salts were different, due presumably to different particle sizes.

The ammines of the sulphates of cobalt(II), nickel(II), copper(II) and zinc(II) were stored in tightly closed bottles and kept in a desiccator under an ammonia atmosphere. The ammines of the sulphates of manganese(II) and iron(II) had to be kept in sealed tubes because traces of water vapour and oxygen from the air turned the compounds brown, probably due to oxydation or hydrolysis.

Deammoniation of the salts was done under vacuum or in an oven at various temperatures previously determined (124-128,141, 142) after which the glass tubes containing the samples were sealed to prevent water vapour in the air from reacting with the lower ammines.

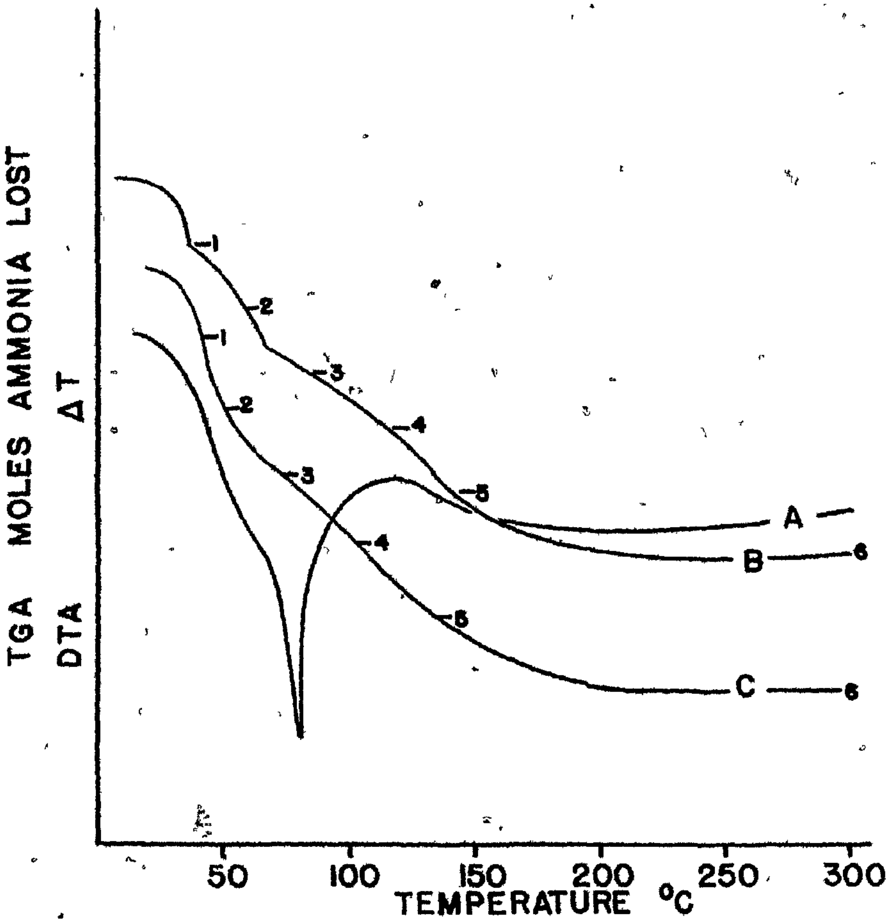
Figure 16

TGA and DTA for ammines of cobalt(II) sulphate

A DTA for $CoSO_4.6NH_3$ prepared by the reaction of ammonia gas on the free salt.

B TGA for $CoSO_4.6NH_3$ prepared as above.

C TGA for $CoSO_4.6NH_3$ prepared by the reaction of ammonia gas on the free salt in methanol.


TGA MOLES AMMONIA LOST
DTA ΔT
A
B
C
1
2
3
4
5
6
50
100
150
200
250
300
TEMPERATURE °C

Deammoniation under vacuum was done in an apparatus () similar to that used for the preparation of the ammines. The glass tube containing the sample was placed horizontally and connected to the vacuum line by a piece of rubber tubing. This arrangement was necessary to prevent the fluffy solid from being carried away by the evolved ammonia from the salt. In addition to that, this would expose more surface area for faster deammoniation which was done at about 5×10^{-3} Torr.

After partial loss of ammonia, some samples were heated in sealed tubes at different temperatures for various time intervals. They are denoted as "sealed" in tables of heat of solution. Heating the sample in a sealed tube was found necessary for the preparation of low-energy ammines because, in some cases, heating in an oven did not result in the formation of low-energy modifications of the lower ammines.

In order to establish points near C on the line BC in the heat of solution graphs, several attempts were made to obtain compounds with more ammonia molecules coordinated. This was done by sealing the reaction tube at an ammonia pressure of one atmosphere and performing the heat of solution measurement immediately. The results are recorded in tables of heat of solution as having been made by "direct preparation".

2. Hydrates of copper(II) sulphate

$CuSO_4 \cdot 5H_2O$ of Baker analyzed reagent grade was used for the preparation of the lower hydrates of copper(II) sulphate. Thermogravimetric analysis showed that the water content of the salt was in good agreement with the theoretical value. The sample was ground slightly before dehydration. The methods of dehydration were similar to those described for the hydrates of other metal sulphates (71,72).

Several authors have suggested that the formation of a product layer on the crystal surface may hinder the ease of escape of the evolved water molecules (134-135). It is possible that, during vacuum dehydration, such water molecules within the product layer may initiate crystallization of the product itself. Therefore, some small crystals of pentahydrate of copper(II) sulphate were also prepared (145). These were obtained by adding absolute ethanol slowly to a concentrated solution of copper sulphate in distilled water. The small crystals formed were collected and dried over a stream of air at room temperature.

It has been observed that the reaction of ammonia with the anhydrous metal sulphate gave finely powdered ammine complexes. If such a powdery product could also be obtained from the reaction of water vapour with anhydrous copper(II) sulphate, it would help to prevent crystallization of the product during dehydration under vacuum. Thus some pentahydrate of copper(II) sulphate was prepared by exposing a sample of finely powdered anhydrous salt to water vapour. Completeness of rehydration was checked by the gain in weight, and was found to be 34.98% which was close to the pentahydrate composition, 36.08%.

It was found necessary also in the later part of this investigation to prepare some trihydrate of copper(II) sulphate. One batch of the salt was obtained by dehydrating the pentahydrate over concentrated H_2SO_4. The product with the desired composition was obtained after frequently checking the loss in weight of the sample.

Another batch of trihydrate of copper(II) sulphate was obtained by crystallizing the salt from a solution of the pentahydrate in absolute methanol (146). This was done by adding the pentahydrate slowly, while stirring, to warm methanol. When the solution was cooled, crystals of trihydrate appeared. They were collected and dried over a stream of air at room temperature. Thermogravimetric analysis showed that the composition was that of trihydrate and the mode of dehydration was similar to that found for the trihydrate obtained by dehydration of the pentahydrate over concentrated H_2SO_4, Fig. 17.

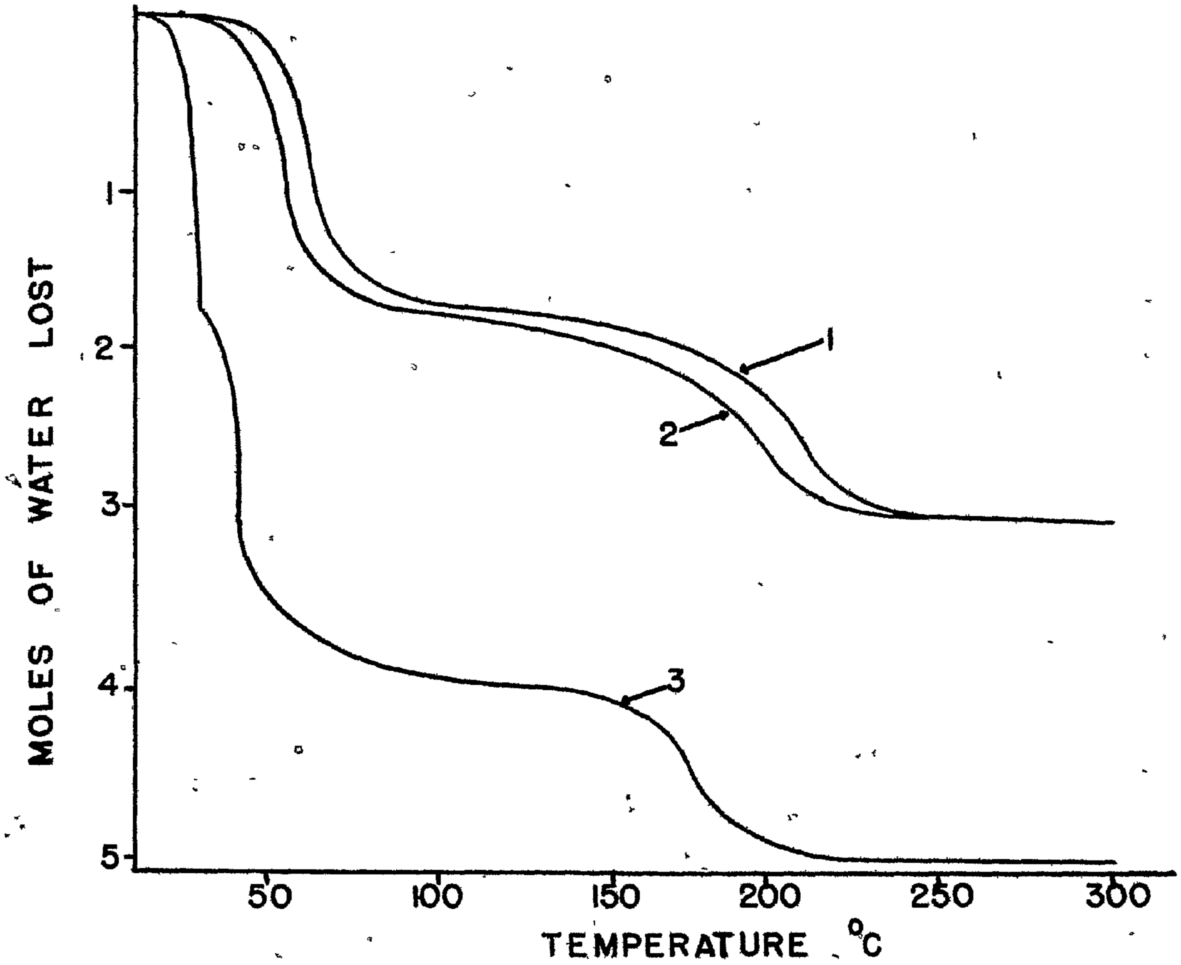
Figure 17

TGA for pentahydrate and trihydrate of $CuSO_4$

1 Trihydrate from methanol
Heating rate = 0.363°C/min.

2 Trihydrate from pentahydrate over conc. H_2SO_4
Heating rate = 0.287°C/min.

3 Pentahydrate
Heating rate = 0.355°/min.


MOLES OF WATER LOST
1
2
3
4
5
50
100
150
200
250
300
TEMPERATURE °C
1
2
3

3. The chlorides

The starting materials used for subsequent preparation of the lower hydrates of the chlorides were hexaaquocobalt(II) chloride and hexaaquonickel(II) chloride, both of Baker analyzed reagent grade. The lower hydrates were prepared by heating the slightly ground hexahydrate in an oven at various temperatures or by dehydrating the hexahydrate under vacuum at a pressure of about 1×10^{-5} Torr.

Dehydration in an oven was done by placing the salt in an open vessel to facilitate escape of the water vapour evolved. If the hexahydrate was heated in a glass tube, with one end closed, the water vapour could not escape easily and would be reabsorbed by the solid product to form a fused mass. This would form a hard crust inside the tube as more water was driven off at higher temperatures.

Vacuum dehydration was done in the presence of BaO and concentrated H_2SO_4 as desiccants. Dehydrated products obtained by using only BaO as desiccant had lower heats of solution. An activated silica gel trap was used adjacent to BaO and concentrated H_2SO_4 to enhance the attainment of a pressure of 1×10^{-5} Torr, especially at the beginning of the experiments. Vacuum dehydration at room temperature under these conditions yielded, after 24 hours, a product of about monohydrate composition, in agreement with the previous investigations (40,67).

From the decomposition temperatures of the salts, it appears that water molecules contained in these chlorides are more weakly bonded than those in sulphate hydrates. In the case of nickel salts, for example, the decomposition temperature of nickel chloride monohydrate is 160°C (147) but 290°C for the monohydrate of nickel sulphate. Similarly, under vacuum, the hexahydrate of nickel chloride dehydrates easily at room temperature to its monohydrate, whereas the hexahydrate of nickel sulphate hardly dehydrates at the same temperature.

4. Ferrous ammonium sulphate

The starting material used for subsequent preparation of the lower hydrates of ferrous ammonium sulphate was the hexahydrate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, supplied by Fisher Scientific Co. The normal crystalline lower hydrates were prepared by heating the hexahydrate in a pyrex tube through which a stream of nitrogen flowed at a pressure slightly greater than atmospheric.

Vacuum dehydration was done in a manner similar to that described for the chlorides. In the first group of experiments where the attainment of the pressure of about 1×10^{-5} Torr was slow (at the beginning of an experiment) the heats of solution of the lower hydrates fell on a lower line, FK, as shown in the heat of solution graph, Fig. 31 on page 153. Therefore an activated silica gel trap was used in conjunction with various desiccants to accelerate the attainment of a pressure of about 1 x 10^{-5} Torr. The results obtained were then satisfactory. The rate of dehydration at such a low pressure was quite fast, reaching the dihydrate stage after about 24 hours. Beyond this, dehydration proceeded very slowly.

5. The heats of solution of hydrates in aqueous ammonia

Lower hydrates of cobalt(II) sulphate were prepared in the same manner as described (71). The starting material used was $CoSO_4 \cdot 7H_2O$ of Baker analyzed reagent grade. The heats of solution were measured by dissolving the salts in 200 ml. of 3M aqueous ammonia.

6. Heat of solution measurements

The heats of solution of the ammine complexes were measured in dilute aqueous ammonia, or in hydrochloric acid when necessary, to ensure complete solubility. In pure water the ammine complexes were hydrolyzed. The ammine complexes of manganese(II) sulphate and iron(II) sulphate were dissolved in 1M hydrochloric acid solution, whereas the ammines of the sulphates of cobalt(II), nickel(II), copper(II) and zinc(II) were dissolved in 3M, 0.75M, 0.3M and 0.75M aqueous ammonia, respectively.

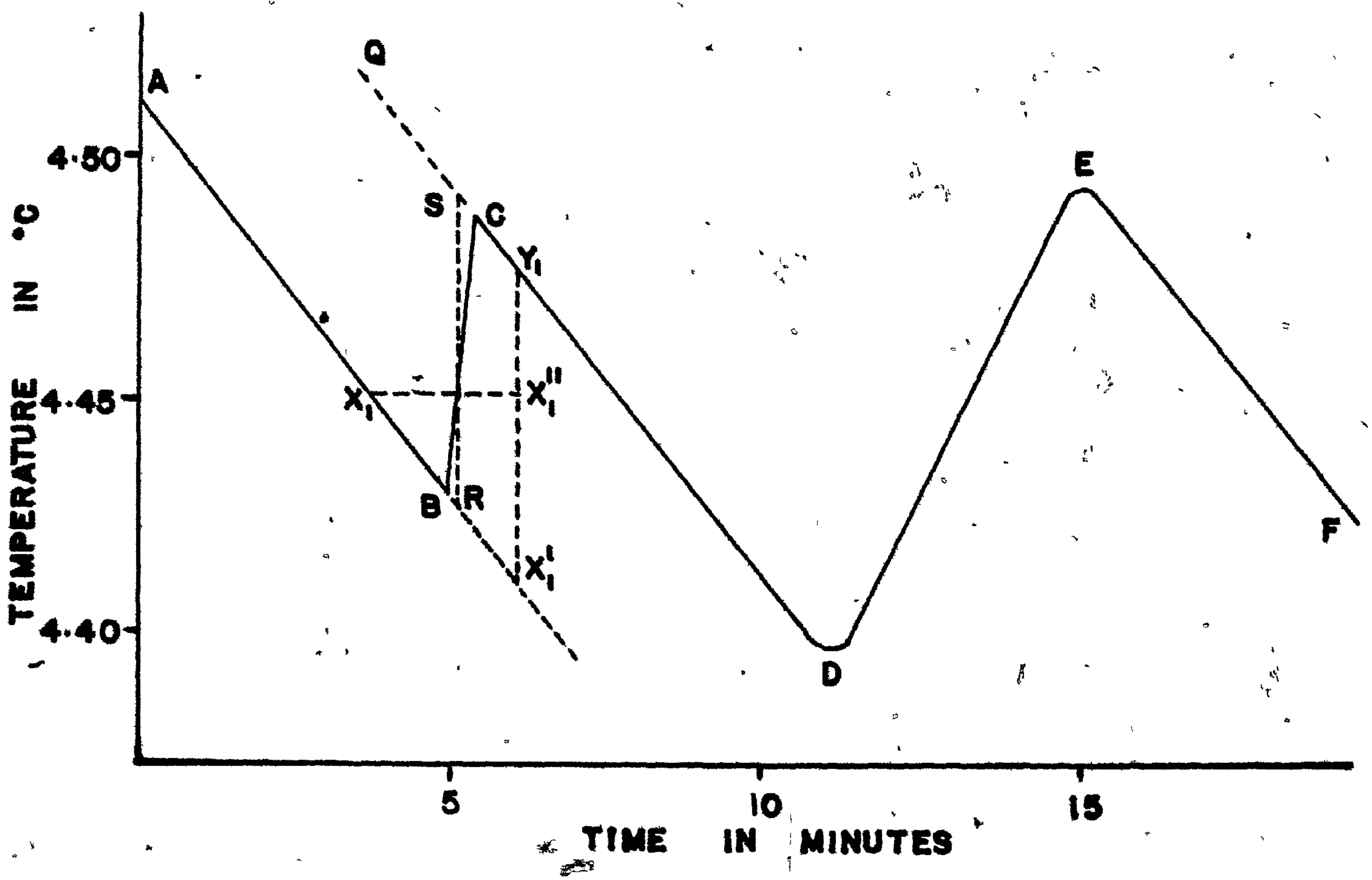
7. Calorimetry

Integral heats of solution were measured in a calorimeter consisting of a silvered Dewar flask equipped with a mechanical stirrer and a Beckmann thermometer. One litre of solvent was used in each experiment. The weight of the sample was between 0.2 and 0.3 gm. The heat capacity of the calorimeter was determined from the change in temperature caused by a known quantity of electrical energy from a heater made of chromel A wire encased in a glass tube containing distilled water as a heat conductor. An Eico low-ripple battery eliminator was used to supply rectified power. Throughout the period of heating the voltage and current were quite steady at, for example, 4.00±0.02 volts and 6.00 ±0.002 amperes. Correction of the measured current due to change in resistance of the heater due to temperature rise could have been made as shown in Appendix III, although this was unnecessary in the present experiments. Time was measured with a stop-watch to about 240±0.1 sec. Determination of the temperature change due to either the energy input or solution of the sample, which was probably the limiting factor, appeared to be accurate to ±0.002 degree. The heat capacity of the calorimeter changed slightly with the nature of the solvent. The average value for each solvent concentration is used in subsequent calculations. The minimal error in heat of solution was about ±2.1 calories.

Typical cooling and heating curves are shown in Fig. 18.

Figure 18

Heating and cooling curves in a typical heat of solution measurement


A
Q
S
C
Y₁
X₁
X₁''
B
R
X₁'
D
E
F
4·50
4·45
4·40
TEMPERATURE IN °C
5
10
15
TIME IN MINUTES

AB is the cooling curve for the solvent which was heated initially to about 29°C. When such a curve was linear, the sample was added to the solvent at B. There was a sudden temperature rise (or fall). Owing to thermal lag, the calorimeter was given about 30 seconds for stabilization until the temperature came to C when normal linear cooling was resumed. Five minutes were taken before reaching point D when the heater was switched on for four minutes. When cooling was again linear, at point E, the temperature was again recorded until point F was reached.

The temperature change due to solution of a sample was obtained by the method described in Appendix II. It was assumed that the rate of cooling along the lines AB, CD and EF was constant for the temperature range and this was found to be so most of the time. When this condition was not fulfilled, a graphic method was used to measure the temperature change such as RS in Fig. 18.

The heats of solution for the hydrates of copper(II) sulphate were measured in the same calorimeter. One litre of distilled water was used as solvent. For the hydrates of cobalt(II) chloride, nickel(II) chloride and ferrous ammonium sulphate, the heat of solution measurements were done using a new calorimetric assembly which shall be described. About 0.3 gm. of each salt was dissolved in 200 ml. of distilled water. All the salts dissolved readily. Except for copper sulphate, no heat of dilution data were available for the compound studied. Thus no attempt has been made to correct the heat of solution obtained, particularly since energy differences rather than the individual values were required for the measurement of ligand field splitting energies.

8. Construction of a calorimeter

The limitation of the calorimeter described previously was its inability to measure the temperature change accurately when the heat of solution of a salt was very small. For such cases when ΔT was less than 0.01°C, with an uncertainty of the thermometer of $\pm 0.002^{\circ}$C, the error in the heat of solution could be greater than 20%. To avoid this the new calorimeter was designed and built.

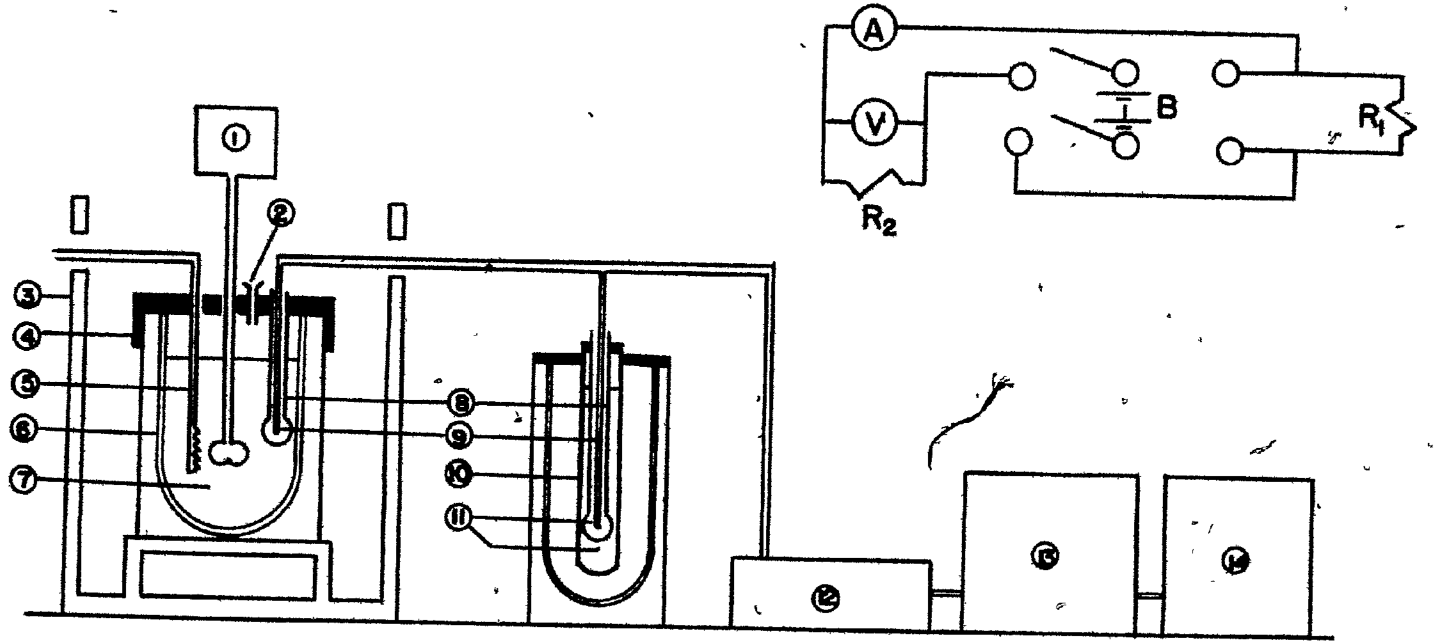
The assembly is shown schematically in Fig. 19. The essential features of this new apparatus are the same as the one previously described with the exception that the Beckmann thermometer has been replaced by a copper-constantan thermocouple to measure the voltage change due to the temperature change on solution of a sample, or due to a known quantity of electrical energy supplied by a heater. This voltage change could be recorded or read directly on a voltmeter.

The voltmeter used to register the voltage is a Hewlett-Packard 419A DC Voltmeter which has been made to be able to read a potential difference as small as 0.01 µV. It has a number of working ranges, from 3 µV to 10,000 V. Each range could be amplified to one full volt if its output is connected to a recorder. Thus if 0.1 µV is registered on the 10 µV range, the output would

Figure 19

Calorimetric assembly

1	stirrer
2	glass funnel for sample delivery
3	wooden box
4	foamed polystyrene cover
5	heater, 4.75 ohms
6	200 ml. silvered Dewar flask
7	solvent
8	pyrex tube encasing thermocouple
9	thermocouple
10	test-tube containing t-butanol
11	t-butanol
12	Cahn recorder control
13	419A DC null voltmeter
14	recorder
A	ammeter
V	voltmeter
R_1	auxiliary resistance
R_2	heater, 4.75 ohms
B	12-volt battery .


A
V
B
R1
R2
1
2
3
4
5
6
7
8
9
10
11
12
13
14

be 0.01 V, but if 0.1 μV is registered on the 3 μV range, the output would be 0.03 V.

The physical principle used in the construction of this new calorimeter is that of thermoelectric effect where it is known (148) that the e.m.f. generated by thermal effect on a thermocouple system is:

$$\text{e.m.f.} = \int_{T_1}^{T_2} \alpha . dT$$

where α is the constant for a particular pair of metals used for constructing the thermocouple and dT is the temperature differential. It is clear that the e.m.f. induced is dependant only on the temperature difference between the two junctions of the thermocouple, $T_1 - T_2$.

If the temperature of the cold junction is designated as T_1 (T_1 being constant) and that of the hot junction in the solvent as T_2, the voltage recorded is completely determined. For T_1 at 0°C, the melting point of ice, and T_2 at 22°C, room temperature, the e.m.f. would be registered as 0.868 mV. To measure this voltage on the voltmeter above, the working range would have to be of 1 mV or 3 mV. If a salt is dissolved, its heat of solution would cause a change in the temperature, T_2, of the solvent to $T_2 + \Delta T_2$, which in turn would cause a change in voltage. This is usually of the order of 10 μV. Such a change in voltage is very insignificant in the 1 mV working range.

To avoid this, the initial voltage caused by the temperature difference $T_2 - T_1$ should be very small so that a more sensitive working range could be used and consequently a change of 10 µV could be detected easily. This requirement could be obtained by placing the two junctions at approximately the same temperature.

There are two ways of doing this; one way is to bring the temperature of the reference junction to room temperature, as the solvent is, or alternatively to lower the temperature of the solvent close to that of the reference junction. The second method is difficult to put into practice but the first method could easily be implemented.

In the present investigation, the temperature of the equilibrium between

$$\text{t-butanol}_{(\text{solid})} \rightleftharpoons \text{t-butanol}_{(\text{liquid})}$$

was used as T_1 because at room temperature of about 22°C this equilibrium could easily be attained. Other compounds could be used instead but they may be more difficult to obtain and probably are more expensive.

Alternatively one could use the temperature of the vapour of a pure liquid at its boiling point as the temperature of the reference junction, T_1. The advantage of this method is that by varying the pressure above the liquid, the temperature of boiling could be varied at will to suit the temperature of the solvent. However, a more elaborate set-up would be necessary to isolate the reference junction from the temperature of the room.

The capacity of the Dewar flask used was 200 ml. instead of one litre to ensure that the voltage change was high but that it could also still house the shaft for the stirrer, the encased thermocouple, the heater and the funnel for sample delivery.

Using the optimum working range, the calorimeter could read as accurately as ±0.001 at 0.046 cal. This is exemplified by the results given in Table 7 and Fig. 20 where the number of divisions on the recorder is plotted against the number of calories supplied by the heater. The linear relation shows the accuracy one could obtain from this assembly.

9. Hydrates of cobalt(II) sulphate

Lower hydrates of cobalt(II) sulphate were prepared from the heptahydrate of Baker analyzed reagent grade by heating in an oven or *in vacuo*, as previously described (71). For a reflectance study the salt was placed in a shallow glass cup which could be fitted into the sample holder of a Unicam SP 500 reflectance attachment. The standard used was $MgCO_3$ for the whole range of the spectrometer (200- 1000 mµ).

For an infrared study, the high-energy hydrates of cobalt(II) sulphate were obtained by dehydrating the salt under vacuum in the presence of BaO as desiccant. The low-energy

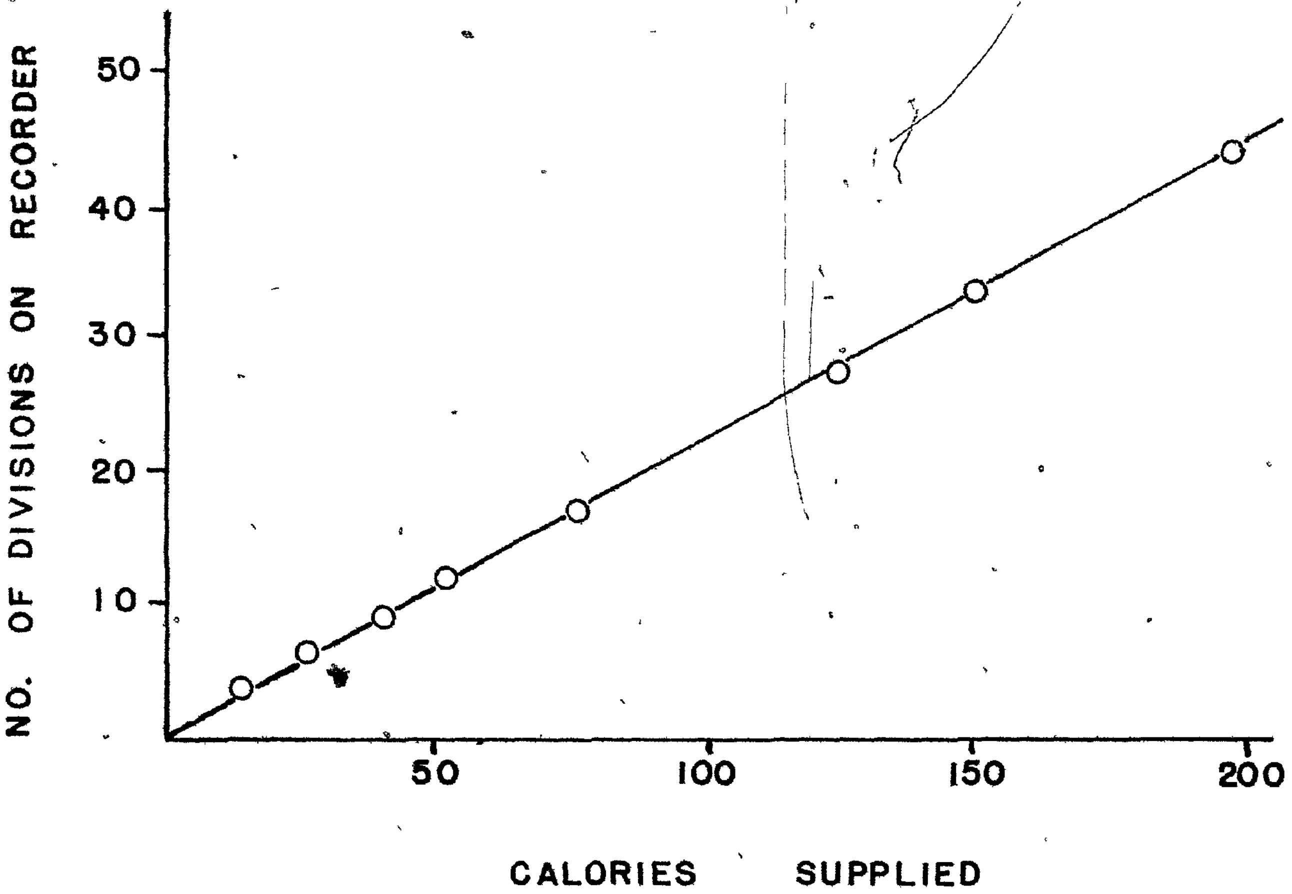
Table 7

Recorder readings as function of power supplied

Power supplied in calories	no. division on recorder
50.1	11.5
37.5	8.3
12.5	3.0
24.9	6.1
74.8	16.6
124	27.4
148	33.2
198	44.0

Figure 20

Recorder reading as a function of power supplied


NO. OF DIVISIONS ON RECORDER
50
40
30
20
10
50
100
150
200
CALORIES SUPPLIED

modifications of these hydrates were obtained by heating the heptahydrate in an oven. Each IR spectrum was obtained from a nujol mull of the salt between two sodium chloride plates, using a Unicam SP 1000 infrared spectrophotometer.

For the purpose of preparing some deuterated complex of cobalt(II) sulphate, about 4 ml. of saturated solution of the anhydrous salt in D_2O (supplied by Stohler Isotope Chemicals) was prepared at about 100°C. When the solution was cooled, crystals of the deuterated complex of cobalt(II) sulphate appeared. This complex will be referred to as salt I.

About 2 gm. of salt I were heated in an oven at 130°C for 12 hours. The product obtained, salt II, was essentially of composition $CoSO_4.D_2O$, as verified by its IR spectrum, Fig. 36 on page 165. Salt II was then exposed to water vapour at room temperature for 12 hours in a previously evacuated reaction tube, in the same way that the ammine complexes were prepared. The product obtained after rehydration, salt III, appeared to be moist - a phenomenon which seems to occur for the rehydration of $CuSO_4$ (51). It was dried over a stream of air at room temperature. The IR spectrum of salt III is shown in Fig. 37. The salt is essentially of composition $Co(H_2O)_6SO_4.H_2O$.

Salt III was divided into two portions. One portion was dehydrated under vacuum up to about the dihydrate composition (salt IV), and the other portion was dehydrated in an oven to yield salt V of composition $Co(H_2O)SO_4 \cdot D_2O$. The spectra of salts IV and V are shown in Fig. 38 and Fig. 39, respectively. From Fig. 38, salt IV appears to contain no heavy water.

RESULTS

1. Ammine complexes

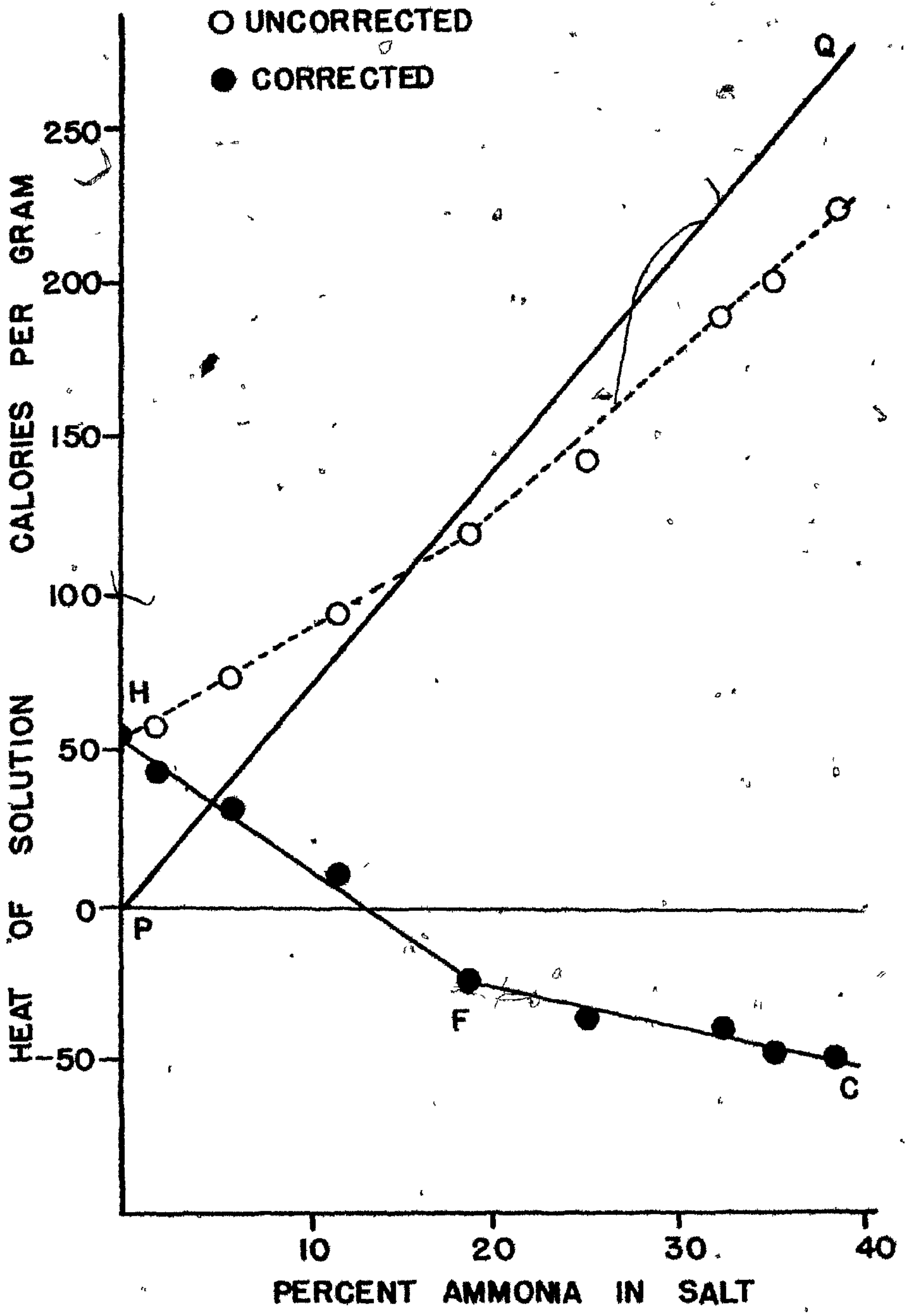
The results given in Tables 8 to 13 and Figs. 22 to 27 show that linear relations are obtained by plotting the heats of solution in cal. per gram of solute against the percentage of ammonia in the samples. The vertical lines in Figs. 22 to 27 are at the monoammine compositions. Since the heat of solution lines AB (between the free salts and the monoammines) have different slopes from the heat of solution lines BC (between the monoammines and heptaammines) it is evident that the last ammonia is bonded differently. Thus it is assumed that the monoammines are $M(SO_4.NH_3)$.

As in the case of the aquo complexes, the lines CE which represent the maximum possible heats of solution for samples which might be prepared from the heptaammines, $MSO_4.7NH_3$, which are probably $[M(NH_3)_6]^{2+}(SO_4.NH_3)^{2-}$, have been calculated and drawn through the point C for each heptaammine.

For the ammine complexes of the sulphates of manganese(II) and iron(II), the heat of solution increases with increasing ammonia content in the samples. This relation is shown in Fig. 21 by the open circles which denote the heat of solution for some ammines of manganese(II) sulphate. That the free salt has lower heat of solution than the higher ammines is

Figure 21

Heats of solution for ammines of manganese(II) sulphate
in 1M HCl



○ UNCORRECTED
● CORRECTED
HEAT OF SOLUTION CALORIES PER GRAM
250
200
150
100
50
0
-50
Q
H
P
F
C
10
20
30
40
PERCENT AMMONIA IN SALT

contradictory to the previous observations on the hydrates and the ammines of the sulphates of cobalt(II), nickel(II), copper(II) and zinc(II). For various reasons which will be clear later, it appears that all ammonia molecules in the samples were neutralized by the hydrochloric acid, with evolution of heat. This heat of neutralization is represented by the straight line PQ in Fig. 21 passing through the origin with a slope of 7.10 cal./one percent ammonia. The full circles in Fig. 21 therefore denote the differences between heats of solution obtained directly and the heats of neutralization of the ammonia content, giving the normal relations such as have been found for other systems. These corrected values are used for subsequent discussion and plotted in Fig. 22 for ammines of manganese(II) sulphate and in Fig. 23 for ammines of iron(II) sulphate.

For consistent results, it is necessary that all heat of solution samples dissolve to give the same species in aqueous solution of either ammonia or hydrochloric acid. While the hydrates would form hexaaquometal(II) ions when dissolved in water, it is not necessary that the ammines form hexaammine-metal(II) ions when dissolved in aqueous ammonia solution. The consistent results, however, suggest that it is reasonable to assume that the hexaammines were formed in solution. However, even if it were some other species such as $[M(NH_3)_x(H_2O)_{6-x}]^{2+}$, the difference in heat of solution such as Q_{DB} would be unchanged.

Manganese(II) sulphate

Using the method of least squares, the heat of solution data for the low-energy ammines of manganese(II) sulphate could be represented by the equations:

$$y_{BC} = -2.36 - 1.32x,$$
$$\text{and } y_{IK} = 52.4 - 4.17x,$$

where the line BC represents the heats of solution for the low-energy ammines obtained by heating the high ammine in an oven, and the line IK represents the heats of solution for the lower ammines similarly prepared at higher temperatures. The two lines appear to intersect at the diammine composition, I. Attempts to obtain a sample of monoammine with heat of solution falling at point B were not successful. Several sealed tube experiments were done but samples obtained this way were insoluble in 1M aqueous hydrochloric acid.

The samples obtained by vacuum deammoniation have heats of solution falling along the line FH which intersects the line BC at the tetraammine composition, F. The linear relation for the line FH, obtained by the method of least squares, is

$$y_{FH} = 90.6 - 4.15x.$$

By extrapolating the line BC in Fig. 22, the heat of solution for $Mn(NH_3)_6SO_4.NH_3$ (with 44.14% ammonia) has been estimated as -60.5 cal./gm. and that of $Mn(SO_4.NH_3)$ as -15.7

Table 8

Heats of solution for ammines of $MnSO_4$.

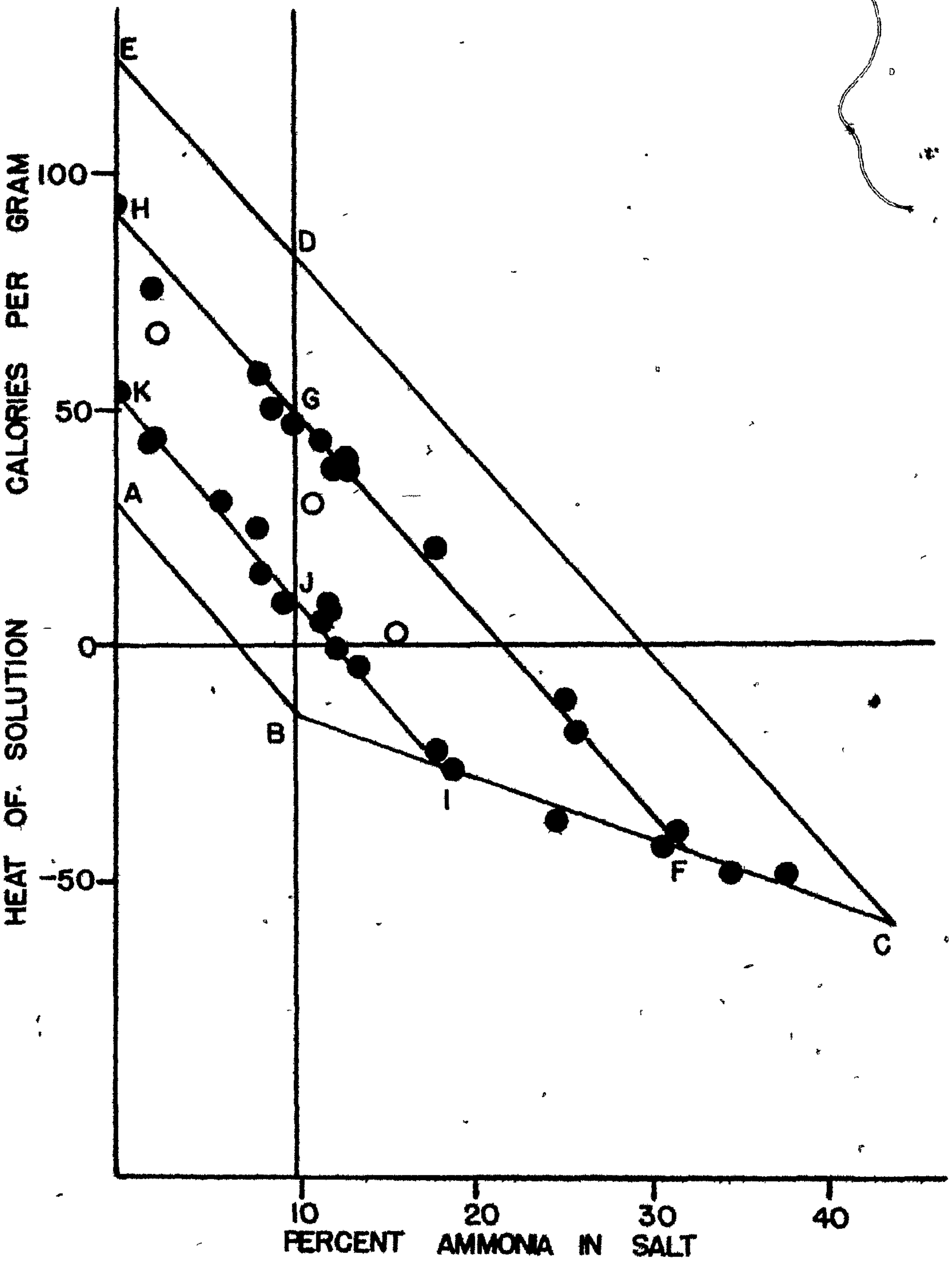
Percent ammonia	Heat of solution (cal./gm.)	Method of preparation
18.17	-24.1	heat at 75°C
19.20	-26.1	..
24.92	-38.2	..
25.28	-38.5	..
31.08	-44.9	..
32.36	-42.4	direct preparation
35.15	-50.0	..
38.31	-50.8	..
0.0	54.1	heat at 300°C
1.90	42.6	..
2.16	45.2	..
6.02	29.6	..
8.07	20.0	..
9.68	8.91	heat at 141°C
11.68	2.87	..
11.83	9.22	..
12.17	6.91	..
12.54	-1.71	..
13.83	-5.09	..

Table 8 (continued)

Percent ammonia	Heat of solution (cal./gm.)	Method of preparation
0.0	93.1	vacuum at 112°C
2.53	78.0	..
8.40	56.4	..
9.05	49.4	..
10.75	46.0	..
11.91	41.2	vacuum at room temp.
12.36	36.3	..
13.34	37.3	..
13.44	36.5	..
18.26	19.0	..
25.58	-14.9	..
26.24	-21.0	..

Figure 22

Heats of solution for ammines of $MnSO_4$


HEAT OF SOLUTION CALORIES PER GRAM
100
50
0
-50
10
20
30
40
PERCENT AMMONIA IN SALT
E
H
D
K
G
A
J
B
I
F
C
O

cal./gm. The line CDE has been drawn by using the slope of −4.15 passing through point C for $Mn(NH_3)_6SO_4 \cdot NH_3$. Thus it is possible to estimate the heat of solution for the high-energy $MnSO_4 \cdot NH_3$ at D as 80.5 cal./gm. This value gives the maximum energy of transition for the monoammine composition as 96.2 cal./gm. or 26.0 kcal./mole of heptaammine, which is equivalent to 9.10×10^3 $cm.^{-1}$.

Iron(II) sulphate

Heat of solution data for the ammines of iron(II) sulphate have been treated similarly. The linear relations are:

$$y_{BC} = -24.0 - 1.22x,$$

$$y_{IK} = 38.1 - 4.57x,$$

$$\text{and} \quad y_{FH} = 82.5 - 4.59x.$$

The lines IK and BC appear to intersect at the diammine composition, I. Salts with ammonia content lower than I could not easily be obtained. Even though they were heated in sealed tubes, their heats of solution fell on the line IK.

Extrapolation of the line BC gave the heat of solution for $Fe(NH_3)_6SO_4 \cdot NH_3$, with 43.96% ammonia, as 77.4 cal./gm. and that for $FeSO_4 \cdot NH_3$, with 10.08% ammonia, as −36.2 cal./gm. Using the slope of −4.59, the line CDE has been drawn representing the high-energy modification line with an equation

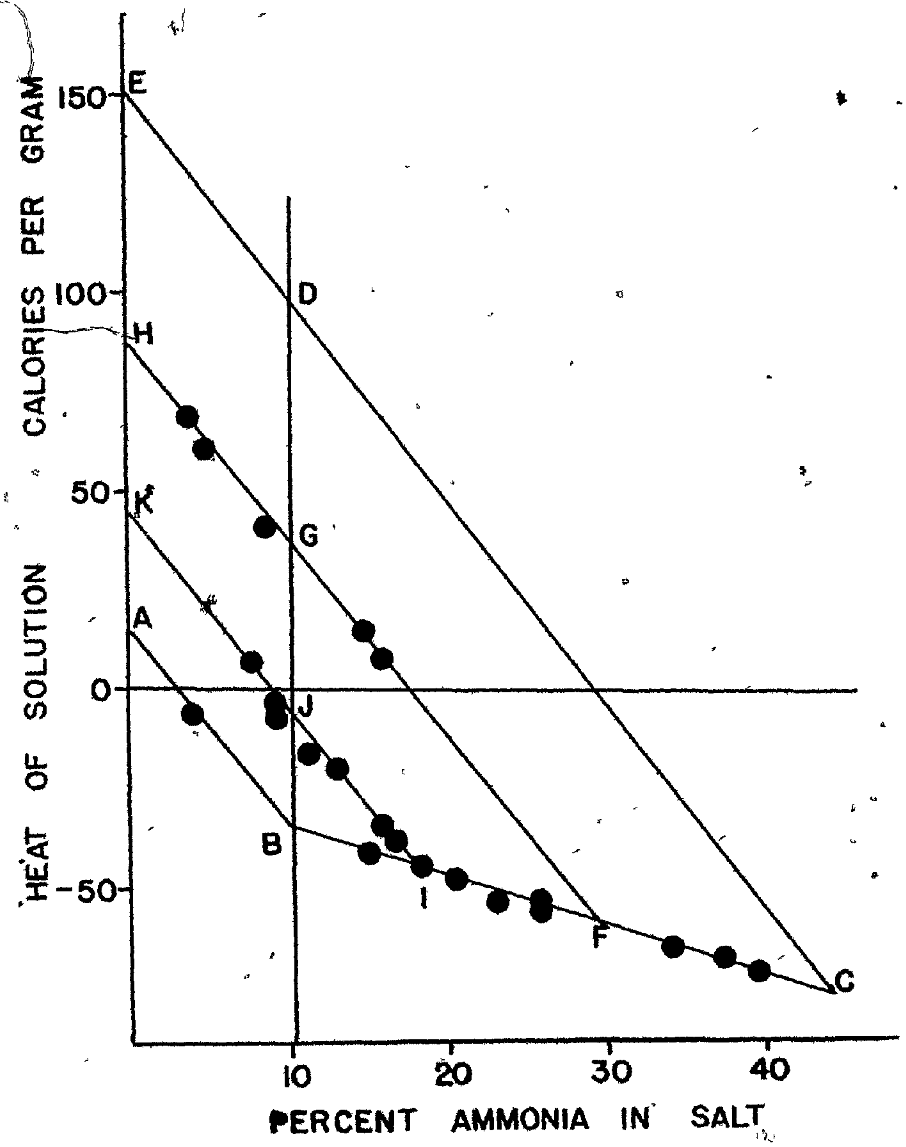
Table 9

Heats of solution for ammines of $FeSO_4$

Percent ammonia	Heat of solution (cal./gm.)	Method of preparation
15.05	-42.2	sealed at 123°C
18.31	-45.0	over H_2SO_4 at 22°C
20.46	-48.2	heat at 79°C
23.06	-54.4	..
25.80	-53.9	..
25.90	-57.3	..
34.08	-65.6	direct preparation
37.24	-68.5	..
39.66	-72.1	..
3.78	68.4	vacuum at 79°C
4.76	60.7	..
8.63	41.8	..
14.62	14.9	vacuum at 22°C
15.82	7.74	..
7.65	6.76	sealed at 123°C
9.13	- 6.30	heat at 79°C
9.20	- 3.81	sealed at 123°C
11.25	-16.6	heat at 79°C
12.97	-20.3	sealed at 123°C
15.95	-34.7	sealed at 123°C
16.77	-38.0	over H_2SO_4 at 22°C
4.01	- 6.67	sealed at 123°C

Figure 23

Heats of solution for ammines of $FeSO_4$


HEAT OF SOLUTION CALORIES PER GRAM
150
100
50
0
-50
E
D
H
G
K
A
J
B
I
F
C
10
20
30
40
PERCENT AMMONIA IN SALT

$$y_{CE} = 124 - 4.59x.$$

Using this equation, the heat of solution for the monoammine at D was found to be 78.3 cal./gm. or 31.0 kcal./mole of hepta-ammine which is equivalent to 10.9 X 10^3 cm.$^{-1}$.

Cobalt(II) sulphate

The heat of solution data for the ammines of cobalt(II) sulphate may be expressed by linear relations as:

$$y_{BC} = 167 - 5.09x,$$

$$y_{AB} = 197 - 8.26x,$$

$$\text{and } y_{FH} = 296 - 8.26x.$$

Extrapolation of the line BC gives an estimate of the heat of solution of $Co(NH_3)_6SO_4 \cdot NH_3$, with 43.38% ammonia, as -54.0 cal. per gram and that of $Co(SO_4 \cdot NH_3)$, with 9.89% ammonia, as 117 cal./gm. The line CDE with a slope equal to that of the line FH in Fig. 24, has been drawn through the point C for $Co(NH_3)_6SO_4 \cdot NH_3$. The heat of solution for the high-energy $CoSO_4 \cdot NH_3$ at point D on the line CDE is then calculated as 223 cal./gm. Therefore, the maximum energy of transition is

$$227 - 117 = 106 \text{ cal./gm.}$$

which is equivalent to 10.2 X 10^3 cm.$^{-1}$ per mole of $Co(NH_3)_6SO_4 \cdot NH_3$.

Figure 24

Heats of solution for ammines of $CoSO_4$

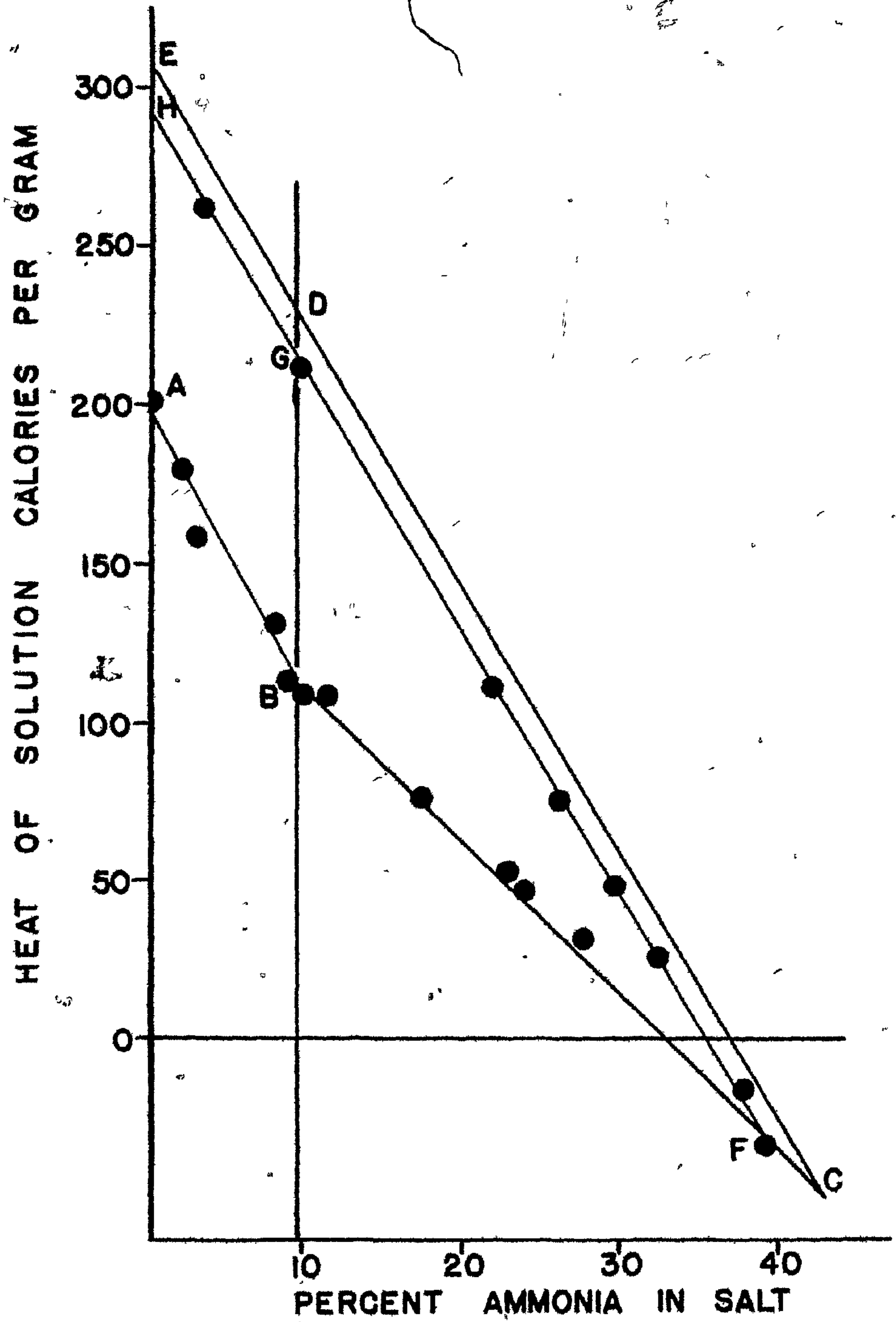

HEAT OF SOLUTION CALORIES PER GRAM
300
250
200
150
100
50
0
10
20
30
40
PERCENT AMMONIA IN SALT
E
H
D
G
A
B
F
C

Table 10

Heats of solution for ammines of $CoSO_4$

Percent ammonia	Heat of solution (cal./gm.)	Method of preparation
4.39	261	vacuum at 100°C
10.3	212	..
22.2	111	vacuum at 48°C
26.2	74.0	vacuum at room temp.
30.1	47.2	..
32.9	24.5	direct preparation
38.3	-16.8	..
10.4	110	direct preparation
12.1	108	heat at 130°C
18.1	76.4	heat at 80°C
23.2	51.1	..
24.7	46.6	heat at 40°C
28.2	18.2	heat at 140°C
39.8	-35.6	direct preparation
0.0	201	heat over 350°C
2.15	180	heat at 300°C
3.92	158	..
8.89	131	heat at 130°C
9.78	113	direct preparation

Nickel(II) sulphate

Similar linear relations for the heat of solution data for the ammines of nickel(II) sulphate are:

$$y_{BC} = 116 - 3.60x,$$

$$y_{FH} = 250 - 6.96x,$$

$$\text{and } y_{IK} = 176 - 6.98x.$$

Lower ammines of nickel(II) sulphate prepared under vacuum gave heats of solution along the line FH in Fig. 25, but samples prepared by heating in an oven gave lower heats of solution, falling between the lines IK and FH, as shown by the points marked with open circles. The line IK was obtained for the heats of solution of samples having approximately the desired percentage of ammonia which were heated in sealed tubes at elevated temperatures.

Extrapolation of the line BC gives the heat of solution of $Ni(NH_3)_6SO_4.NH_3$, with 43.15% ammonia, as -41.0 cal./gm. and that of $Ni(SO_4.NH_3)$, with 9.91% ammonia, as 79.9 cal./gm. The line CDE in Fig. 25, drawn through the point C for hexaamminenickel(II) sulphate monoammine, has been calculated using the slope of the line FH as

$$y_{CE} = 262 - 6.96x.$$

The heat of solution for the maximum possible high-energy

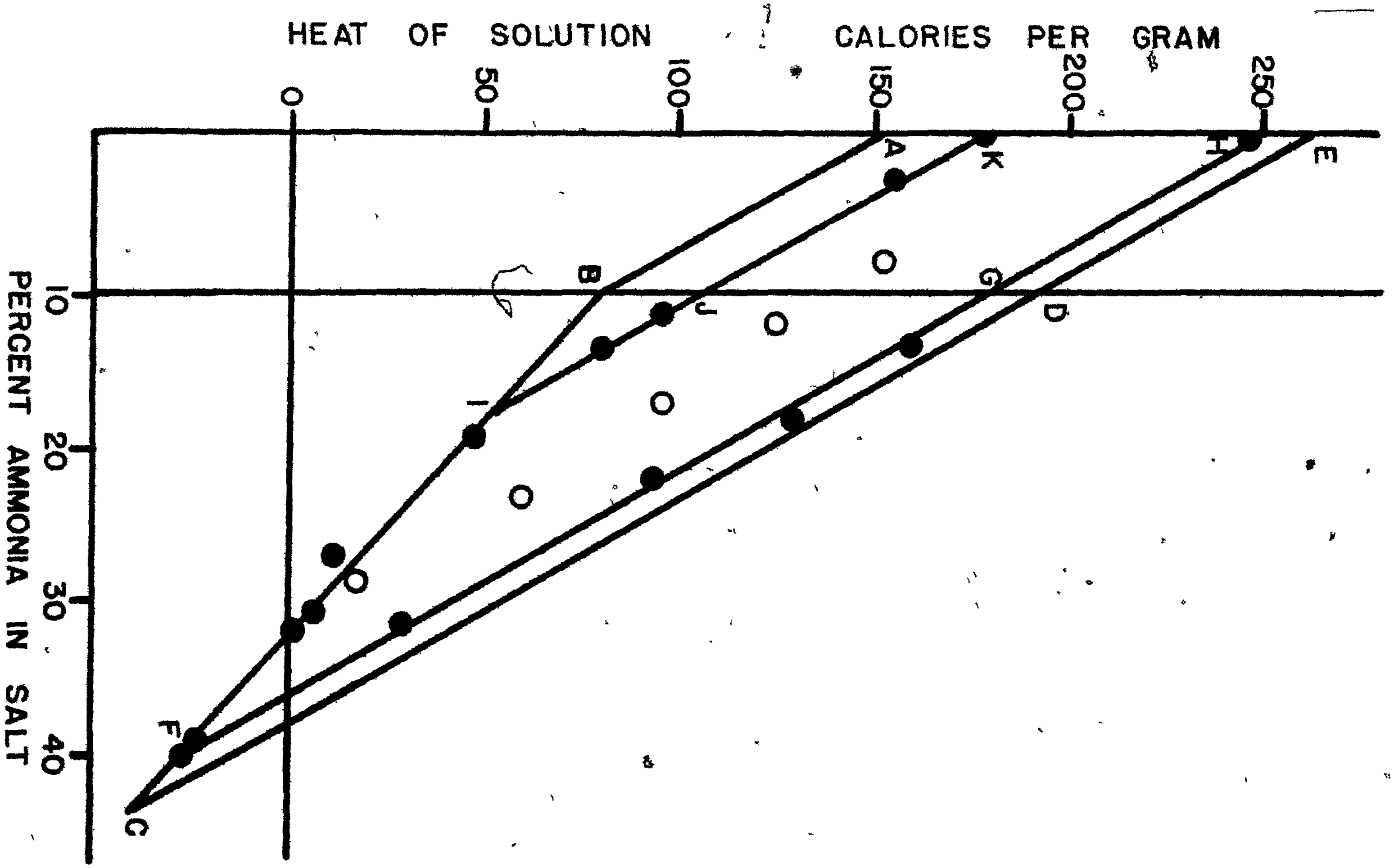
Table 11

Heats of solution for ammines of $NiSO_4$

Percent ammonia	Heat of solution (cal./gm.)	Method of preparation
0.0	246	vacuum at 130°C
12.5	160	vacuum at 100°C
18.3	129	vacuum at 70°C
22.1	93.2	vacuum at 70°C
31.4	28.3	vacuum at room temp.
39.9	-27.7	direct preparation
19.6	48.2	heat at 253°C
27.1	11.8	heat at 77°C
30.6	6.40	heat at 70°C
32.2	0.0	heat at 70°C
39.0	-23.9	direct preparation
39.9	-27.7	direct preparation
0.0	177	sealed tube 350°C
2.94	155	sealed tube at 340°C
11.6	95.8	sealed tube at 200°C
13.8	80.0	sealed tube at 200°C

Figure 25

Heats of solution for ammines of $NiSO_4$


HEAT OF SOLUTION CALORIES PER GRAM
0
50
100
150
200
250
PERCENT AMMONIA IN SALT
10
20
30
40
A
B
C
D
E
F
G
H
I
J
K

modification of $NiSO_4.NH_3$ at point D on the line CDE can then be estimated as 193 cal./gm. Thus the maximum energy of transition can be calculated as 113 cal./gm. which is equivalent to 10.8 X 10^3 $cm.^{-1}$ per mole of $NiSO_4.7NH_3$.

Copper(II) sulphate

Data for the heats of solution for ammines of copper(II) sulphate have been treated similarly. The linear relations are:

$$y_{BC} = 90.6 - 3.86x,$$

$$y_{FH} = 218 - 7.52x,$$

$$y_{IK} = 197 - 7.47x.$$

The heat of solution for the heptaammine of copper(II) sulphate which is probably hexaamminecopper(II) sulphate monoammine, $Cu(NH_3)_6SO_4.NH_3$, at point C was estimated by extrapolating the line BC, and was found to be -74.54 cal./gm., and the heat of solution of $Cu(SO_4.NH_3)$ was found to be 53.37 cal./gm. Using the slope of the line FH as -7.52, the line CDE has been drawn to pass through the point C. This line allows the estimation of the heat of solution of $CuSO_4.NH_3$ of high-energy modification as 174.7 cal./gm. Thus the heat of transition, Q_{DB}, is 121.3 cal. per gm. which is equivalent to 11.8 X 10^3 $cm.^{-1}$ per mole of heptaammine which is probably the entity which contains the $[Cu(NH_3)_6]^{2+}$ species.

Table 12

Heats of solution for ammines of $CuSO_4$

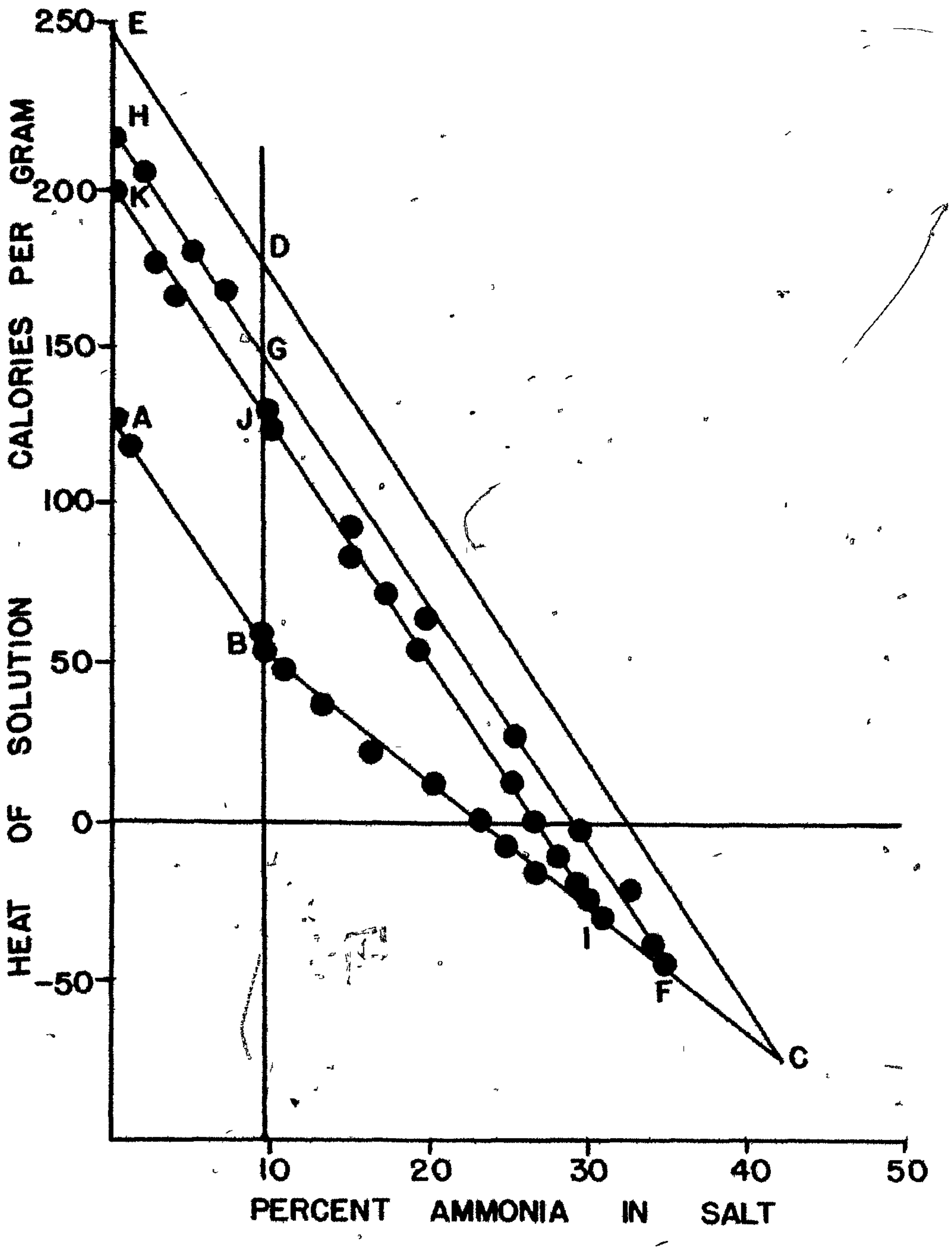
Percent ammonia	Heat of solution (cal./gm.)	Method of preparation
0.0	127	sealed tube at 240°C
1.11	118	..
1.74	119	..
9.50	58.1	..
9.74	52.6	sealed tube at 140°C
10.9	47.7	..
13.2	35.6	..
16.1	21.2	..
19.7	14.2	..
20.3	10.5	..
23.1	- 0.76	..
24.7	- 9.36	sealed tube at 100°C
25.4	-11.4	..
26.5	-17.0	..
28.2	-17.3	..
29.91	-20.5	direct preparation
30.00	-26.5	heat at 100°C
30.90	-32.3	heat at 100°C
31.10	-28.0	direct preparation
34.79	-46.5	direct preparation
0.0	199	vacuum at 240°C
2.63	176	vacuum at 100°C
3.50	170	..
3.78	169	..

Table 12 (continued)

Percent ammonia	heat of solution (cal./gm.)	Method of preparation
9.64	123	vacuum at 40°C
9.74	128	..
10.00	123	..
14.5	89.1	..
15.0	82.7	..
17.2	70.9	..
19.0	53.2	..
24.5	12.3	vacuum at room temp.
25.4	11.4	..
26.6	- 1.32	..
28.2	-15.9	..
28.7	-18.9	..
0.0	215	vacuum at 200°C
1.60	206	..
2.00	204	..
5.00	179	..
6.81	168	Vacuum at 60°C
17.6	92.2	..
19.7	63.7	vacuum at 38°C
25.2	25.8	direct preparation
29.5	- 3.79	..
32.57	-23.4	..
34.09	-40.4	..
34.35	-44.6	..
34.79	-46.5	..

Figure 26

Heats of solution for ammines of $CuSO_4$


HEAT OF SOLUTION CALORIES PER GRAM
250
200
150
100
50
0
-50
E
H
K
A
D
G
J
B
I
F
C
10
20
30
40
50
PERCENT AMMONIA IN SALT

Zinc(II) sulphate

The heats of solution for zinc(II) sulphate complexes with ammonia can be expressed as:

$$y_{AB} = 127 - 7.32x,$$

$$y_{BC} = 88.2 - 3.74x,$$

$$\text{and } y_{FH} = 201 - 7.32x.$$

As shown in Table 13, simple heating of a high ammine in an oven gave lower ammines with heats of solution falling between the lines AB and FH in Fig. 27. These points are marked with the open circles. To obtain lower ammines with heats of solution falling on the line AB, the salts with the desired compositions were heated in sealed tubes at elevated temperatures.

The heat of solution for $Zn(NH_3)_6SO_4{\cdot}NH_3$, with 42.76% ammonia, was estimated as -71.6 cal./gm. and that for $Zn(SO_4{\cdot}NH_3)$ as 52.5 cal./gm. Using the slope of the line FGH, the line CDE has been drawn having the equation

$$y_{CE} = 240 - 7.32x,$$

which gave the heat of solution for monoammine at D as 170 cal./gm. The maximum heat of transition is 117.5 cal./gm. or 32.9 kcal./mole of heptaammine which is equivalent to 11.5×10^3 cm.$^{-1}$.

Table 13

Heats of solution for ammines of $ZnSO_4$

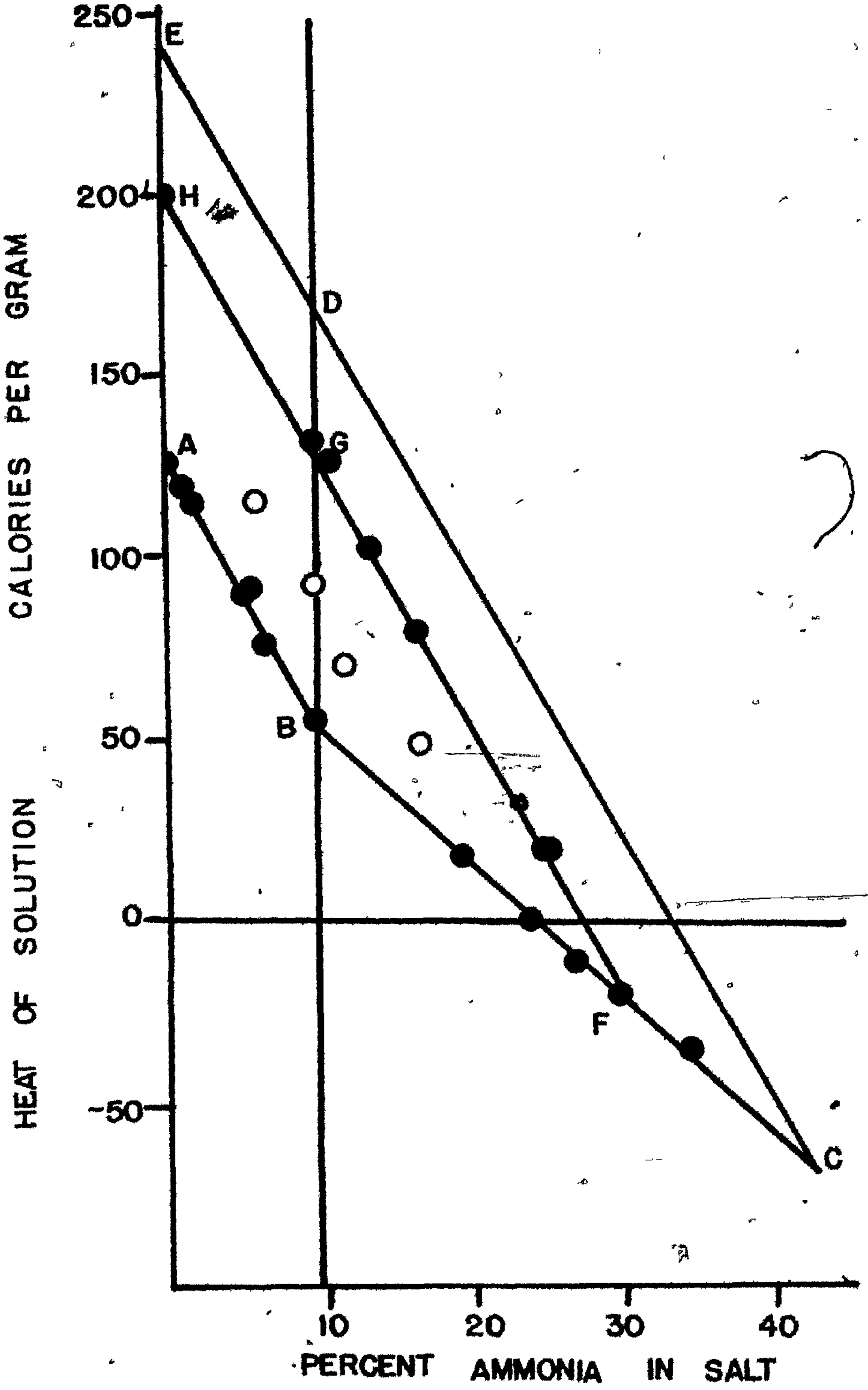
Percent ammonia	Heat of solution (cal./gm.)	Method of preparation
0.0	198	vacuum at 298°C
9.63	131	vacuum at 210°C
10.86	125	vacuum at 203°C
13.47	101	vacuum at 100°C
16.43	81.8	vacuum at 87°C
24.61	16.4	vacuum at room temp.
25.21	17.4	"
4.41	118	heat at 300°C
5.70	112	heat at 300°C
5.84	115	heat at 265°C
6.12	100	heat at 240°C
9.57	79.7	heat at 260°C
11.74	71.9	heat at 190°C
12.48	54.7	heat at 70°C
14.58	48.1	heat at 120°C
15.29	40.9	heat at 110°C
16.10	36.5	heat at 140°C
0.0	124	sealed tube 350°C
1.05	118	sealed tube 240°C
2.06	113	sealed tube 350°C
6.56	75.1	sealed tube 300°C
9.60	52.7	sealed tube 300°C
5.27	89.9	sealed tube 300°C
5.88	89.4	sealed tube 335°C

Table 13 (continued)

Percent ammonia	Heat of solution (cal./gm.)	Method of preparation
9.60	52.7	sealed tube at 200°C
19.43	15.4	sealed tube at 50°C
24.03	- 2.08	heat at 36°C
27.32	-14.4	direct preparation
29.67	-22.9	"
34.15	-38.8	"

Figure 27

Heats of solution for ammines of $ZnSO_4$


250
200
150
100
50
0
-50
E
H
D
A
G
B
F
C
10
20
30
40
PERCENT AMMONIA IN SALT
HEAT OF SOLUTION CALORIES PER GRAM

2. Copper sulphate pentahydrate

The first group of experiments with the hydrates of copper(II) sulphate was done to reproduce earlier data given by Frost, Moon and Tompkins (68). The low energy hydrates were prepared by heating the pentahydrate in an oven or by dehydrating it over concentrated H_2SO_4 in a desiccator at room temperature. The heats of solution listed in Table 14 have been corrected for the dilution effect by applying the experimental results obtained by Lang *et al.* (119). The linear relation, calculated by the method of least squares, has been found to be

$$y = 82.71 - 2.57x.$$

Though the present results seem to be in close agreement with previous data, they differ in that there is no break in the slope at the trihydrate composition.

The heats of solution for the salts obtained by dehydrating the pentahydrate under vacuum are given in Table 15. Various samples were placed simultaneously at a pressure of 0.05 Torr. However, the use of this technique caused a considerable lapse of time before a pressure of 0.05 Torr was obtained, thus resulting in some samples having heats of solution well below the line XY in Fig. 10 on page 45. However, since their heats of solution seem to fall in line with the heat of solution line FH, given by Frost, Moon and Tompkins for the hydrates of high-energy modification, these heats of solution seem to further indicate the

Table 14

Heats of solution for crystalline hydrates of $CuSO_4$

Percent water	Heat of solution (cal./gm.)	Method of dehydration
9.97	57.13	heat at 160°C
10.98	56.00	heat at 53°C
14.51	45.02	over H_2SO_4
15.98	40.78	..
17.77	36.02	..
19.83	32.12	..
24.54	19.71	..
25.07	18.85	..
32.47	-0.43	..

Table 15

Hydrates of copper(II) sulphate
several samples simultaneously dehydrated under vacuum
pressure 5×10^{-2} Torr, initial pressure high

Percent water	Heat of solution (cal./gm.)	Dehydration temperature °C
4.60	122.5	87
7.33	108.8	57
11.93	84.29	43
14.17	65.76	43
17.99	50.93	54
20.37	40.40	54
21.45	33.44	22
25.21	35.46	22
26.52	24.74	22

Table 16

Hydrates of copper(II) sulphate
single sample in vacuum line, pressure 5×10^{-2} Torr

Percent water	Heat of solution (cal./gm.)	Dehydration temperature, °C
12.38	83.77	28
19.97	51.88	46
29.57	37.87	22
32.24	5.60	22

significance of the line FH. Therefore this has initiated further research to define the origin of the line FH along the line BC.

In an attempt to reproduce the line XY, the next group of experiments, therefore, was done with only single samples being dehydrated in the vacuum line. The results obtained, Table 16, have therefore indicated the reproducibility of the results obtained by Frost, Moon and Tompkins (68).

Hydrates of high-energy modification

In the previous investigations on the hydrates of metal sulphates (71,72), it was found possible to prepare samples having heats of solution which fell on a line with a slope parallel to AB, such as the line CDE for the case of hydrates of cobalt(II) sulphate, and with intercept along the line BC at C (where C is the percent of water content of the starting material). In the studies of the hydrates of copper(II) sulphate, attempts were made to define such a line which passes through the pentahydrate composition. Several experiments were done at very low pressures and in the presence of various desiccants. The results obtained are summarized in Tables 17-22. Even when fine crystals of the pentahydrate were used for dehydration under vacuum at a pressure of about 5×10^{-6} Torr, no product having the required heat of solution was obtained. Thus it appears that as yet the techniques and knowledge available are insufficient to enable the preparation of truly amorphous lower hydrates of copper(II) sulphate with heats of solution falling on a

Table 17

Hydrates of copper(II) sulphate
vacuum dehydration in the presence of BaO, p = $5X10^{-2}$ Torr

Percent water	Heat of solution (cal./gm.)	Dehydration Temperature, °C
3.30	133.1	81
5.88	110.5	81
9.28	99.72	81
18.93	57.94	43
26.95	27.40	22
30.47	12.86	22
34.19	2.94	22

Table 18

Hydrates of copper(II) sulphate
vacuum dehydration at pressure less than $5 X 10^{-4}$ Torr

Percent water	Heat of solution (cal./gm.)	Dehydration temperature, °C
8.46	100.0	81
29.75	15.33	22
30.47	10.69	22
33.21	7.33	22

Table 19

Hydrates of copper(II) sulphate
vacuum dehydration in the presence of BaO,
pressure 5X10^{-4} Torr

Percent water	Heat of solution (cal./gm.)	Dehydration temperature, °C
5.12	113.3	41
9.63	96.14	22
11.43	80.52	22
18.67	56.06	22
29.43	14.38	22
29.81	16.06	22

Table 20

Hydrates of copper(II) sulphate
vacuum dehydration in presence of BaO and silica gel trap
pressure 1X10^{-6} Torr

Percent water	Heat of solution (cal./gm.)	Dehydration temperature, °C
12.01	80.38	22
20.36	59.10	22
24.20	36.31	22

Table 21

Hydrates of copper(II) sulphate
vacuum dehydration in the presence of BaO and graphite trap
pressure 1×10^{-6} Torr

Percent water	Heat of solution (cal./gm.)	Dehydration temperature, °C
13.32	77.12	40
26.20	29.42	22
27.96	24.63	22
33.02	0.73	22

Table 22

Hydrates of copper(II) sulphate
vacuum dehydration of rehydrated copper(II) sulphate

Percent water	Heat of solution (cal./gm.)	Dehydration temperature, °C
11.18	94.04	22
13.44	74.85	22
18.34	53.74	22

line originating from the pentahydrate composition and parallel to the line AB.

The high-energy hydrates from the trihydrate

Since several experimental results, given in Table 15, have suggested that it was possible to obtain samples of lower hydrates with heats of solution falling on the line FGH, it seems necessary to investigate whether the products of vacuum dehydration of the trihydrate would have heats of solution falling on the same line. Thus the trihydrate of copper(II) sulphate was used as starting material for vacuum dehydration experiments; the heats of solution for the products are listed in Table 25. When the points are plotted on the heat of solution graph, Fig. 28, they fall on the straight line FGH.

Low-energy hydrates

It appeared then that the most important problem was to prepare samples which were completely crystalline and thus would have heats of solution slightly lower than those given by Frost, Moon and Tompkins (68). Since heating the pentahydrate in an oven or dehydrating it over concentrated H_2SO_4 could not produce the required samples, some hydrates were heated in sealed tubes at elevated temperatures. Unfortunately such a technique was found only suitable for the preparation of crystalline hydrates having percent water content of 10.14 (the monohydrate composition) or less. Attempts to apply a similar technique for preparation of the higher hydrates were not very successful due to extensive decomposition.

It was suggested that the lower hydrates prepared by dehydrating the pentahydrate of copper(II) sulphate might contain some high energy form. It is expected that in the presence of water vapour this would completely revert to its normal crystalline form. Therefore, some hydrates were prepared by exposing the anhydrous salt and the trihydrate to water vapour. However this technique gave little success as the heats of solution for the samples prepared this way did not usually give the required values, Tables 23 and 24. Thus it was found necessary to prepare a purely crystalline lower hydrate which could be used for the preparation of other lower hydrates. Such a purely crystalline hydrate was the trihydrate of copper(II) sulphate prepared by crystallizing the salt from a concentrated solution of pentahydrate in methanol. The heats of solution for the salts prepared this way fell on the line BC as shown in the heat of solution graph, Fig. 28, and in Table 26.

Tables 28–30 summarize the data selected for the purpose of calculating the best equation for the straight line through all these points. Table 28 was used to calculate the equation for the line FH. Table 29 was used to calculate the equation for the line BC and Table 30 was used to calculate the equation for the line AB.

Using the equation describing the line BC as

$$y_{BC} = 62.2 - 1.94\, x,$$

Table 23

Experiments with $CuSO_4 \cdot 3H_2O$

Percent water	Heat of solution (cal./gm.)	Method of preparation
24.85	16.64	pentahydrate over H_2SO_4
25.63	11.56	rehydration of $CuSO_4 \cdot 3H_2O$
28.07	6.51	..

Table 24

Experiments with anhydrous $CuSO_4$

Percent water	Heat of solution (cal./gm.)	Method of preparation
9.49	53.21	rehydration of $CuSO_4$
9.63	54.74	..
11.09	50.46	..
34.89	-4.82	..

Table 25

Vacuum dehydration of trihydrate

Percent water	Heat of solution (cal./gm.)	Dehydration temperature, °C
4.24	118.8	70
5.99	110.7	70
7.54	107.2	70
10.56	87.08	43
16.73	55.02	22
18.67	33.36	22
22.18	25.66	22

Table 26

Experiments with $CuSO_4 \cdot 3H_2O$ crystallized from methanol

Percent water	Heat of solution (cal./gm.)	Dehydration temperature, °C
8.94	46.85	61
10.59	45.39	61
11.51	46.11	59
11.87	38.56	59
25.30	13.38	59

Table 27

Hydrates of copper(II) sulphate in sealed tubes experiments

percent water	Heat of solution (cal./gm.)	Temperature of heating
0.0	96.58	212
0.0	95.63	246
3.69	70.04	246
8.27	49.48	246
10.14	40.1	200
15.80	37.14	90
21.23	20.06	90
22.73	17.61	90
29.88	6.20	90
32.60	-0.74	90

the heat of solution for the crystalline monohydrate has been estimated as 42.5 cal./gm.; and that of the heptahydrate as −23.6 cal./gm. The equation calculated for the line FGH is

$$y_{FH} = 144 - 5.16\ x.$$

Using the slope of the line FH as −5.16, the equation for the line CE parallel to the line FH passing through the point C on the line BC has been calculated to be

$$y_{CE} = 204 - 5.16\ x.$$

The heat of solution for the monohydrate of high-energy modification at D could then be estimated as 152 cal./gm. Therefore, the energy difference between points D and B is 109 cal./gm. or 31.3 kcal./mole of heptahydrate. Expressed in wave numbers, this energy is equivalent to 10.9×10^3 cm.$^{-1}$.

Table 28

Hydrates of copper(II) sulphate
Data for calculating the equation for y_{FH}

percent water	heat of solution (cal./gm.)	vacuum dehydration
1.11	134.1	at 81°C
3.30	133.1	81°C
4.24	118.8	70°C
4.60	122.5	87°C
5.12	113.3	41°C
5.88	110.5	81°C
5.99	110.7	70°C
7.33	108.8	57°C
8.46	100.0	70°C
9.28	99.72	81°C
9.63	96.14	22°C
10.56	87.08	43°C
11.18	94.04	22°C
11.43	80.52	22°C
11.93	84.29	43°C
12.01	80.38	22°C
12.38	83.77	28°C
13.32	77.12	40°C
13.44	74.85	22°C
14.17	65.76	43°C
16.73	55.02	22°C
17.99	50.93	54°C
20.37	40.40	54°C
21.45	33.44	22°C
22.18	25.66	22°C
24.85	16.64	22°C

Table 29

Hydrates of copper(II) sulphate

Data for calculating the equation for y_{BC}

Percent water	Heat of solution (cal./gm.)	Method of preparation
10.14	40.11	sealed at 200°C
10.59	45.39	heat at 61°C
11.87	38.56	heat at 59°C
21.23	20.06	over H_2SO_4
22.73	17.61	over H_2SO_4
25.30	13.38	-
25.63	11.56	rehydration
28.07	6.51	rehydration
29.88	6.20	over H_2SO_4
32.66	-0.74	over H_2SO_4
34.89	-4.82	rehydration
36.08	-9.03	-

Table 30

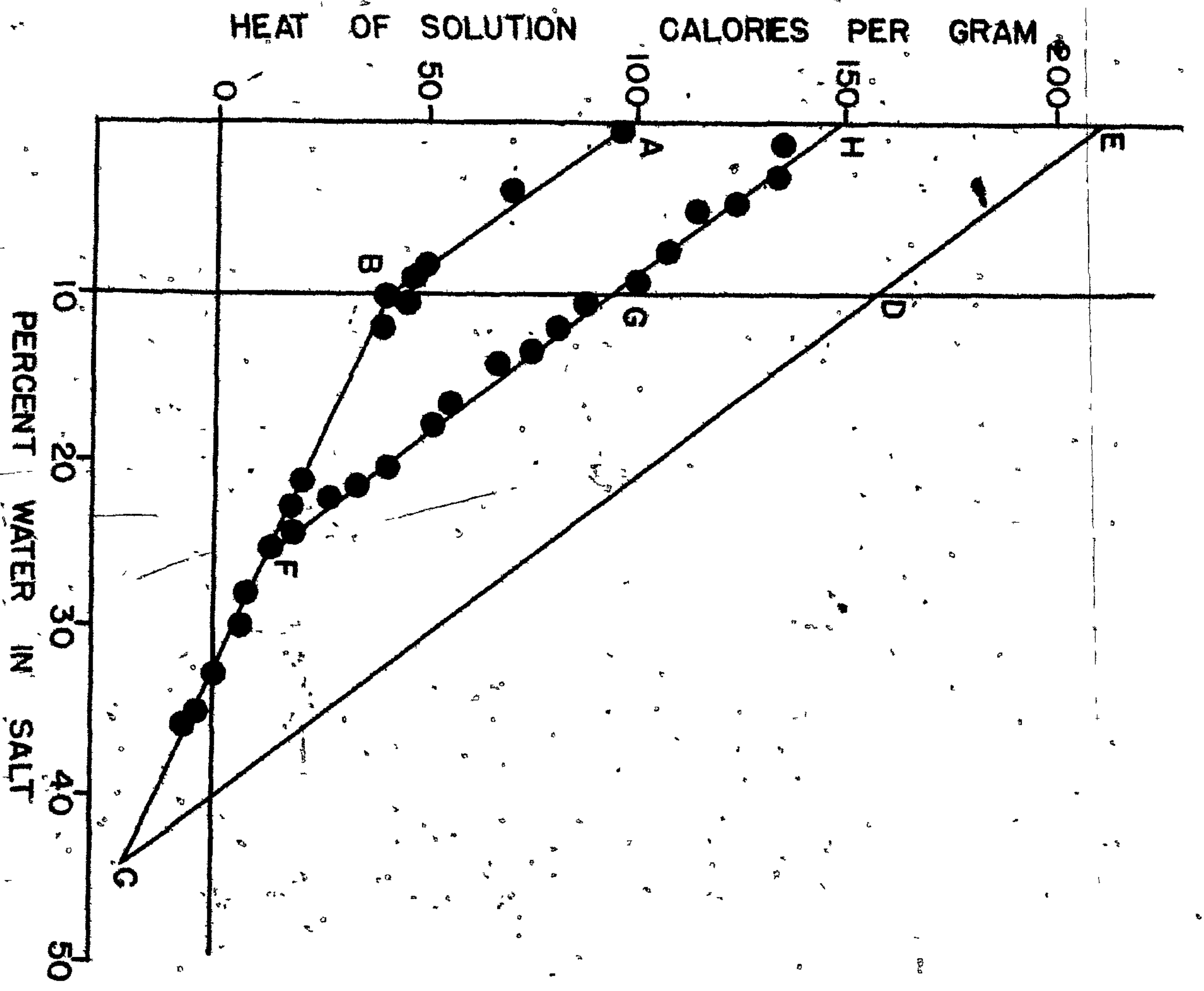
Hydrates of copper(II) sulphate

Data for calculating the equation y_{AB}

Percent water	Heat of solution (cal./gm.)	sealed at
0.0	95.63	246°C
3.69	70.04	246°C
8.27	49.49	246°C
8.94	46.85	200°C
10.14	40.11	200°C

Figure 28

Heats of solution for hydrates of $CuSO_4$


HEAT OF SOLUTION CALORIES PER GRAM
0
50
100
150
200
PERCENT WATER IN SALT
10
20
30
40
50
A
B
C
D
E
F
G
H

3. The chlorides

The heats of solution for the hydrates of cobalt(II) chloride are summarized in Table 31 and Fig. 29 and those for the hydrates of nickel(II) chloride in Table 32 and Fig. 30.

Cobalt(II) chloride

The heats of solution for the lower hydrates of cobalt chloride, prepared by heating the hexahydrate in an oven, were similar to those for the lower hydrates of the sulphate. The hydrates having composition between the hexahydrate and the monohydrate had heats of solution falling on the straight line BC with the equation

$$y = 116 - 2.72x,$$

where x is the percent of water in the salt and y is the heat of solution in cal./gm. The hydrates with composition between the monohydrate and the anhydrous salt had heats of solution falling on the straight line AB with the equation

$$y = 153 - 5.62x.$$

The heats of solution for the lower hydrates prepared under vacuum, in the presence of only BaO as desiccant, have been fitted to the straight line FGH with the equation

$$y = 201 - 5.51x.$$

By extrapolating the line BC to C, where C is the heptahydrate

Table 31

Heats of solution for hydrates of $CoCl_2$

Percent water	Heat of solution (cal./gm.)	Method of dehydration
0.36	152	heat at 160°C
1.95	140	..
4.18	128	..
7.69	110	..
7.96	110	..
8.96	102	..
11.51	87.0	..
15.67	71.8	heat at 120°C
15.82	64.4	..
21.72	58.0	heat at 75°C
30.11	36.5	..
38.40*	10.2	over $Mg(ClO_4)_2$
40.10	8.1	heat at 49°C
40.14*	5.5	over Al_2O_3
45.43	-8.3	
0.0	181	vacuum with BaO, 69°C
2.07	172	..
2.25	169	..
11.54	116	vacuum with BaO, 22°C
11.58	120	..
11.65	114	..
12.32	122	..
15.10	101	..

Table 31 (cont'd)

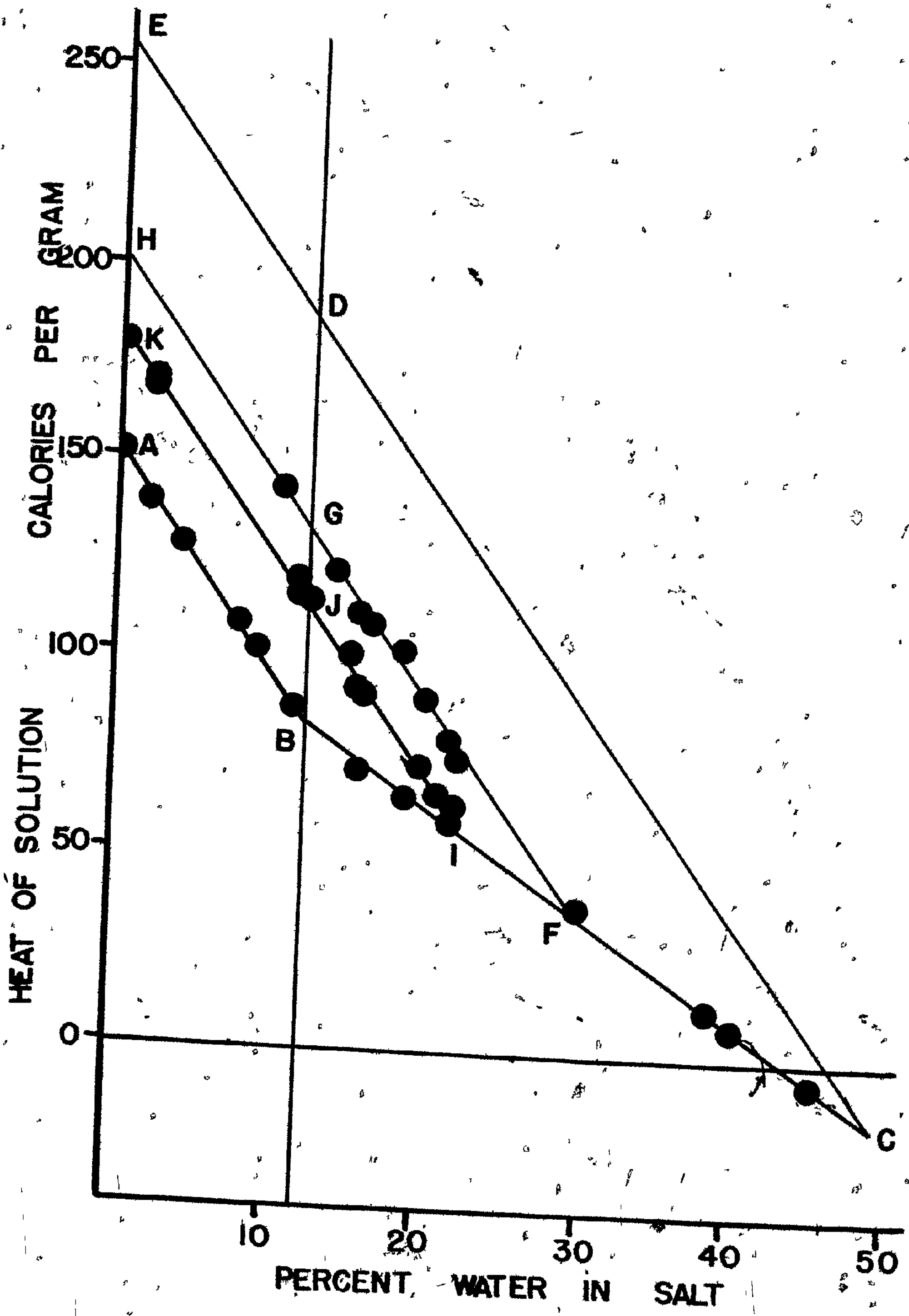
Percent water	Heat of solution (cal./gm.)	Method of preparation
15.60	92.4	vacuum with BaO, 22°C
19.79	72.3	..
20.92	65.7	..
20.93	64.9	..
22.03	62.7	..
10.34	144	vacuum at 58°C **
14.04	122	vacuum at 22°C **
15.64	112	..
16.58	110	..
18.76	102	..
19.97	89.6	..
21.68	79.8	..
22.07	75.3	..
22.71	77.8	..

* Jamieson's unpublished data

** with BaO, conc. H_2SO_4 and activated silica gel cold trap

Figure 29

Heats of solution for hydrates of $CoCl_2$


HEAT OF SOLUTION CALORIES PER GRAM
0
50
100
150
200
250
PERCENT WATER IN SALT
10
20
30
40
50
E
H
K
A
D
G
J
B
I
F
C

composition, the heat of solution for the heptahydrate has been estimated to be -18.16 cal./gm. Using the slope of -5.52, the line CDE has been drawn. The heat of solution for the highest possible modification of the monohydrate at point D was then estimated to be 187 cal./gm. Since the heat of solution for the crystalline monohydrate at point B is 82.8 cal./gm., the heat of transition, Q_{DB}, has been found to be 104.2 cal./gm. or 26.6 kcal./mole of heptahydrate which is equivalent to 9.31×10^3 cm.$^{-1}$. This value is in good agreement with the value of 10Dq found for the complex in crystals of cobalt(II) chloride hexahydrate.

Nickel(II) chloride

The heats of solution for the hydrates of nickel(II) chloride have been treated similarly. The heats of solution of the salts falling on the line BC are given by the equation

$$y = 132 - 2.96x.$$

The heats of solution for the salts prepared by vacuum dehydration of the hexahydrate in the presence of only BaO as desiccant fall on the line IJK with the equation

$$y = 202 - 5.42x.$$

By extrapolating the line BC to C, the heat of solution for the heptahydrate was estimated to be -14.2 cal./gm. and that of the normal low energy monohydrate at B was 95.5 cal./gm. The line CDE

Table 32

Heats of solution for hydrates of $NiCl_2$

Percent water	Heat of solution (cal./gm.)	Method of dehydration
3.12	145	heat at 150°C
5.07	136	..
13.88	92.0	heat at 100°C
20.61	68.4	..
35.61	26.3	..
37.10 *	22.8	Over Al_2O_5
40.77	11.7	Over H_2SO_4
45.47	- 3.53	
1.91	175	vacuum with BaO, 98°C
6.37	154	vacuum with BaO, 80°C
7.80	142	vacuum with BaO, 80°C
10.96	126	vacuum with BaO, 22°C
12.87	117	..
15.51	94.6	..
18.19	87.4	..
20.43	73.7	..
20.59	78.8	..

Table 32 (cont'd)

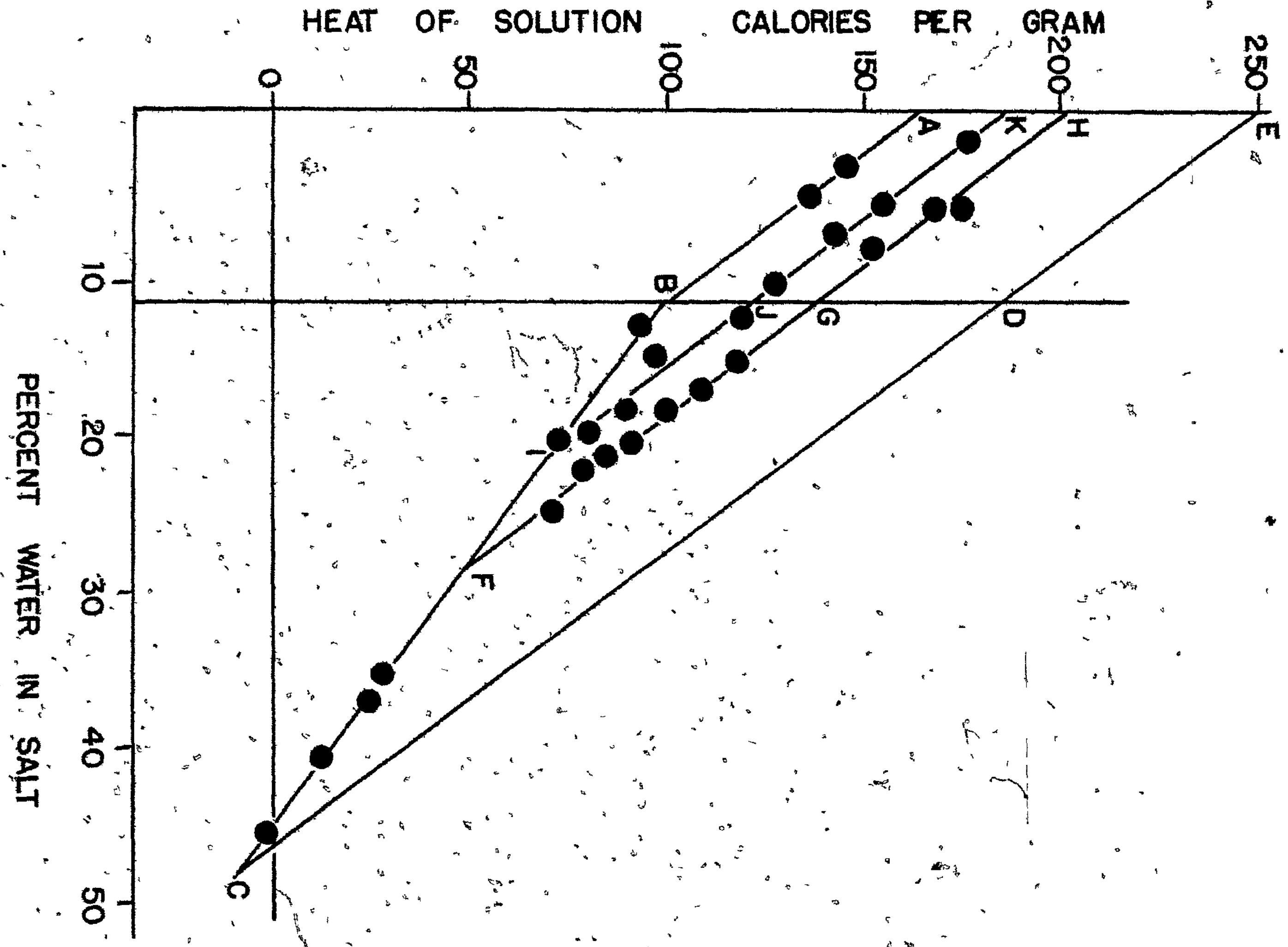
Percent water	Heat of solution (cal./gm.)	Method of dehydration
6.13	174	vacuum at 76°C **
6.17	167	••
6.74	167	••
8.67	150	vacuum at 50°C **
16.08	115	vacuum at 30°C **
17.75	107	••
18.53	99.0	••
19.03	97.0	••
20.57	88.4	vacuum at 22°C **
21.07	87.6	••
21.07	82.2	••
21.24	89.9	••
21.84	83.2	••
22.89	77.5	••
25.46	69.3	••

* Jamieson's unpublished data

** with BaO, conc. H_2SO_4 and activated silica gel cold trap

Figure 30

Heats of solution for hydrates of $NiCl_2$


HEAT OF SOLUTION CALORIES PER GRAM
0
50
100
150
200
250
PERCENT WATER IN SALT
10
20
30
40
50
A
K
H
E
B
J
G
D
I
F
C

[redacted]

has been drawn to pass through point C with the slope of -5.42. The heat of solution for the highest possible modification of the monohydrate at D was estimated to be 187 cal./gm. Thus the heat of transition, Q_{DB}, was found to be 91.5 cal./gm. of monohydrate or 23.4 kcal./mole of heptahydrate.

4. Ferrous ammonium sulphate

The heats of solution for the hydrates of ferrous ammonium sulphate are summarized in Table 33 and in Fig. 31. The normal crystalline salts have heats of solution falling on the lines FI and IK, where I is the dihydrate composition. Attempts to obtain the low-energy monohydrate, having heat of solution at point B, were unsuccessful. The compound decomposed when heated in a sealed tube.

Under vacuum, when the pressure was high (greater than about 1 X 10^{-4} Torr), the product of dehydration would have heat of solution falling along the line FK. When the pressure was lower than 1 X 10^{-4} Torr, the heats of solution of the product would fall on the line IJK.

The straight line equation for the line FI is

$$y_{FI} = 33.5 - 2.05x,$$

while that for the line IK is

$$y_{IK} = 64.6 - 4.72x,$$

3 OF/DE 4

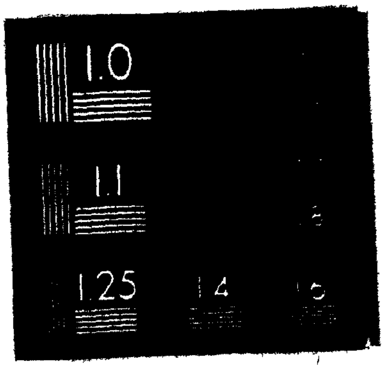


Table 33

Heats of solution for hydrates of ferrous ammonium sulphate

Percent water	Heat of Solution (cal./gm.)	Method of dehydration
9.48	67.3	vacuum at 22°C *
10.4	62.4	..
11.2	60.3	..
11.9	53.4	..
14.1	41.8	..
14.9	33.9	..
15.0	32.9	..
23.52	0.14	..
24.21	- 7.95	..
24.37	- 5.80	..
26.72	-15.45	..
27.56	-22.47	..
0.0	64.1	heat at 120°C
1.38	58.4	..
5.73	36.9	heat at 70°C
6.62	34.1	heat at 50°C
9.27	21.4	..
10.7	15.1	..
11.0	12.1	..
11.3	10.2	..

Table 33 (cont'd)

Percent water	Heat of solution (cal./gm.)	Method of dehydration
11.3	10.2	heat at 50°C
17.57	- 2.34	..
25.62	-20.00	..
27.56	-22.47	
0.76	62.6	vacuum at 22°C **
2.74	58.6	..
2.81	57.6	..
3.26	60.6	..
4.41	52.8	..
4.60	51.0	..
5.36	47.8	..
8.60	39.0	..
8.65	39.9	..
15.79	13.6	..
16.64	13.0	..
17.07	11.4	..

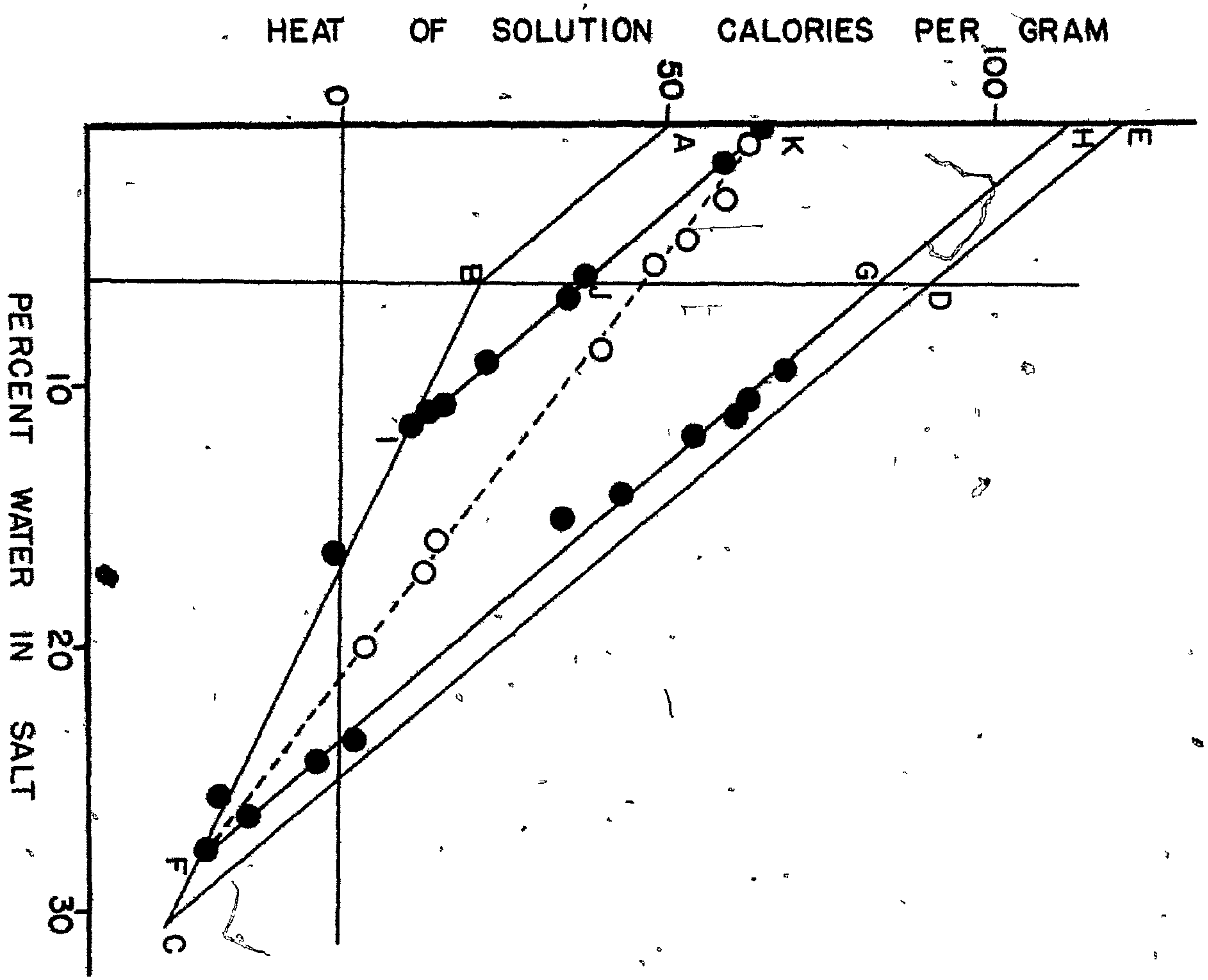
* pressure less than 1 X 10^{-4} Torr

** pressure higher than 1 X 10^{-4} Torr

Figure 31

Heats of solution for hydrates of

ferrous ammonium sulphate


HEAT OF SOLUTION CALORIES PER GRAM
0
50
100
PERCENT WATER IN SALT
10
20
30
A
B
C
D
E
F
G
H
I
J
K

and that for the line FGH is

$$Y_{FH} = 109 - 4.76x.$$

By extrapolating the line FI, the heat of solution for the monohydrate at B has been estimated to be 21.23 cal./gm. and that for the heptahydrate at C as -29.68 cal./gm. The line CDE has been drawn parallel to the line IK to pass through the point C. The heat of solution for the highest possible modification of the monohydrate at D was estimated to be 38.26 cal./gm. Thus the heat of transition is 67.03 cal./gm., which is equivalent to 9.62×10^3 $cm.^{-1}$ per mole of heptahydrate.

5. Hydrates of cobalt(II) sulphate

The heats of solution for the hydrates of cobalt(II) sulphate in 3M aqueous ammonia are listed in Table 34 and plotted in Fig. 32. The low-energy hydrates prepared by heating the heptahydrate in an oven have heats of solution falling along the line BC given by the equation

$$y_{BC} = 180.4 - 2.88x,$$

and along the line AB given by the equation

$$y_{AB} = 216.4 - 6.35x.$$

In the presence of BaO as desiccant, the products of vacuum dehydration of the heptahydrate have heats of solution

Table 34

Heats of solution for hydrates of cobalt sulphate
in 3 M aqueous ammonia

Percent water	Heat of solution (cal./gm.)	Method of dehydration
6.98	233	vacuum at 50°C *
16.15	175	vacuum at 22°C *
17.21	173	..
24.82	127	..
25.72	128	..
27.05	115	..
29.60	105	..
33.97	80.6	..
1.09	213	heat at 250°C
1.82	199	..
4.74	191	..
6.98	170	..
10.30	151	..
11.25	153	heat at 150°C
13.08	146	heat at 130°C
13.15	145	..
13.47	143	..
14.70	146	heat at 110°C
21.29	124	..
22.53	115	..
24.87	102	..
37.24	67.0	heat at 90°C
44.86	39.8	

Table 34 (cont'd)

Percent water	Heat of solution (cal./gm.)	Method of dehydration
10.9	219	vacuum at 22°C **
13.7	219	..
14.0	205	..
16.0	199	..
25.81	148	..
28.88	128	..
38.48	74.0	..
44.86	39.8	

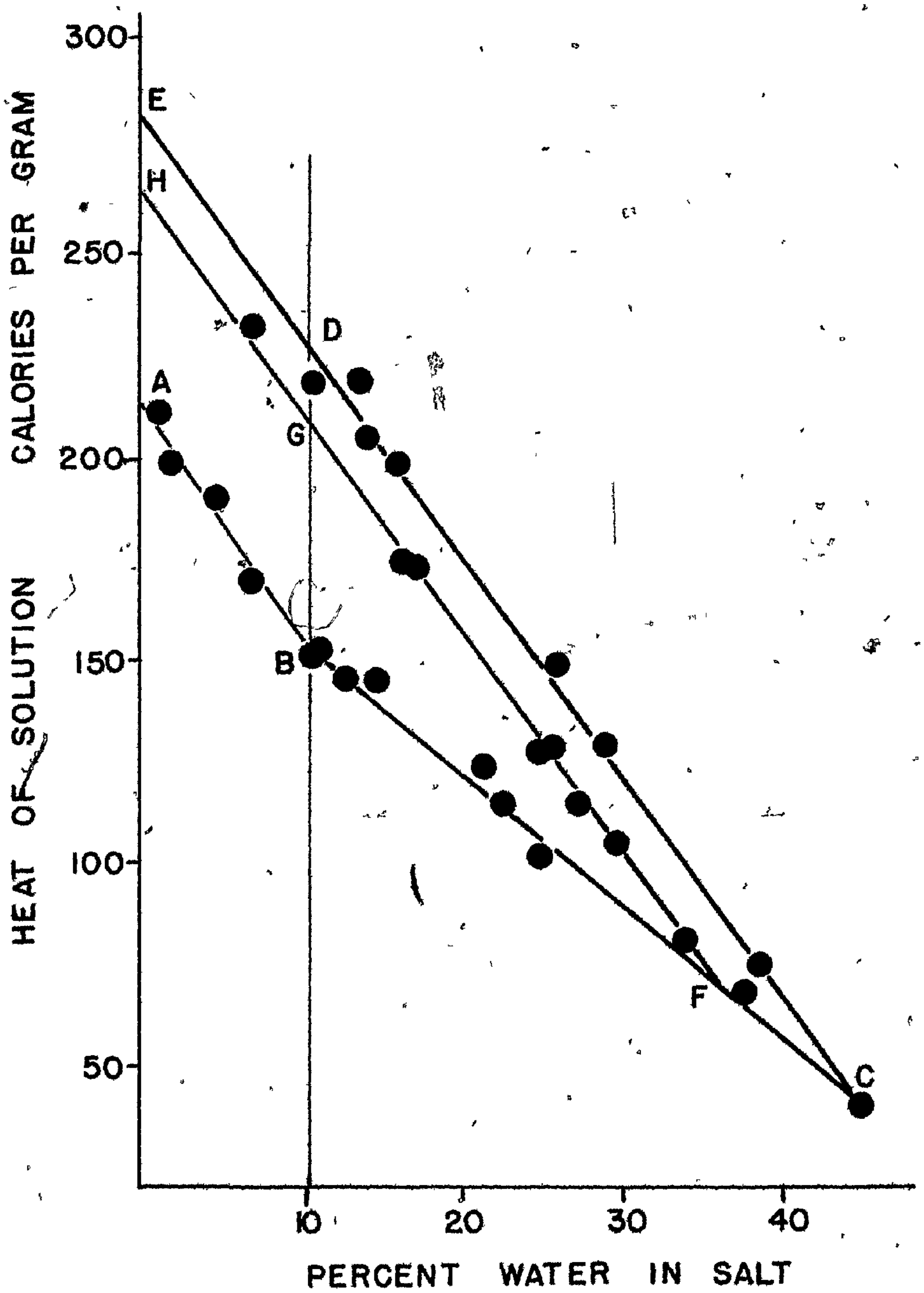
* with BaO

** with BaO and activated silica gel cold trap

Figure 32

Heats of solution for hydrates of cobalt(II) sulphate

in 3M aqueous ammonia


300
250
200
150
100
50
HEAT OF SOLUTION CALORIES PER GRAM
E
H
D
A
G
B
F
C
10
20
30
40
PERCENT WATER IN SALT

falling along the line FH with the equation

$$y_{FH} = 269.3 - 5.61x.$$

Because of the relatively high pressure at the beginning of the experiments, these salts have lower heats of solution than the corresponding hydrates prepared by using an activated silica gel cold trap in conjunction with BaO as desiccants. By using both desiccants, the products of vacuum dehydration fell on the line CDE with an equation

$$y_{CE} = 284.3 - 5.39x.$$

6. Spectroscopy

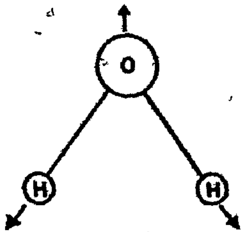
Despite considerable evidence in support of the present technique for the determination of the ligand field splitting energy, a theoretical justification is still lacking. The formation of one would appear to require more information about the nature of the electric field surrounding the metal ion, both in the normal crystalline salt and in its high-energy modification. This electric field, to a large extent, is determined by the lattice constituents immediately surrounding the metal ion although the next nearest neighbours also play an important role. In the heptahydrate, the six water molecules determine the nature of this field and in the anhydrous salt the feature is determined by the sulphate ions. In the intermediate hydrates it is certainly a mixture of these two species.

The spectroscopic experiments were done for the purpose of examining the differences between the two modifications as this would be expected to help in correlating Q_{DB} to 10Dq. The infrared spectra would be used to identify the differences in the bonding and the electronic absorption spectra would be used to postulate the type of crystal field around the metal ion.

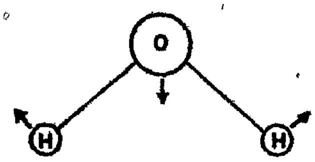
Infrared spectra

While the full spectra of the salts are reported here, only the fundamental modes of vibration of H_2O, D_2O and SO_4 shall be discussed. (The strong absorption bands at 2900 cm.$^{-1}$, 1465 cm.$^{-1}$, 1380 cm.$^{-1}$ and 700 cm.$^{-1}$ are all due to various modes of C-H vibration in nujol.)

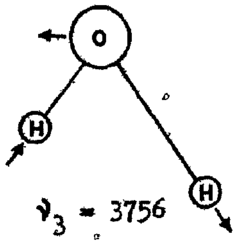
In the gas phase, a water molecule has three fundamental modes of vibration (149,150): ν_1 which is Raman active, ν_2 and ν_3 which are infrared active.



$\nu_1 = 3652$



$\nu_2 = 1595$



$\nu_3 = 3756$

When the water molecule is coordinated to a metal ion, as found in $Co(H_2O)_6SO_4.H_2O$, the O-H bonds are weakened by the decrease in electron density. This effect is shown in the decrease in the frequency of asymmetric stretching, ν_3, which occurs at 3350 cm.$^{-1}$ in the spectrum of $Co(H_2O)_6SO_4.H_2O$ (112). When the salt is heated in an oven at 130°C, all the six water molecules coordinated to Co^{2+} ion are lost. Thus in $CoSO_4.H_2O$ the last water in the salt is hydrogen bonded to the sulphate ion (151). Because it is differently bonded, ν_2 would be significantly different from the corresponding vibration of the coordinated water molecules. Thus no absorption is expected to occur at 1600 cm.$^{-1}$.

The infrared spectrum of the high energy monohydrate, Fig. 14, page 63, shows an absorption band at 1650 cm.$^{-1}$. This appears to indicate that the remaining water is coordinated to the metal ion and is not hydrogen bonded to the sulphate ion as in the monohydrate of the normal crystalline form. Thus vacuum dehydration appears to favour the removal of anionic water to ~~that of~~ the coordinated species.

In order to further investigate this point, the dehydration of the deuterated complexes of cobalt(II) was studied. The spectrum in Fig. 35 shows that in spite of the fact that the D_2O was about 95% pure, the amount of H_2O present in salt I was quite significant. The band at 3300 cm.$^{-1}$ assigned to H_2O is almost as intense as that at 2500 cm.$^{-1}$ assigned to D_2O. The extent of "contamination" actually had no effect because most of the H_2O was driven off when salt I was heated to give salt II, Fig. 36. The D_2O left appears to be hydrogen bonded to the sulphate ion together with traces of H_2O. This conclusion is supported by the absence of bands at 1650 cm.$^{-1}$ and 1250 cm.$^{-1}$ due to H_2O and D_2O deformation, respectively.

It has been assumed that rehydration of salt II to form salt III under the described conditions would not involve D_2O-H_2O exchange. The spectrum of salt III, Fig. 37, shows that this

Figure 33

Infrared spectrum of cobalt(II) sulphate heptahydrate

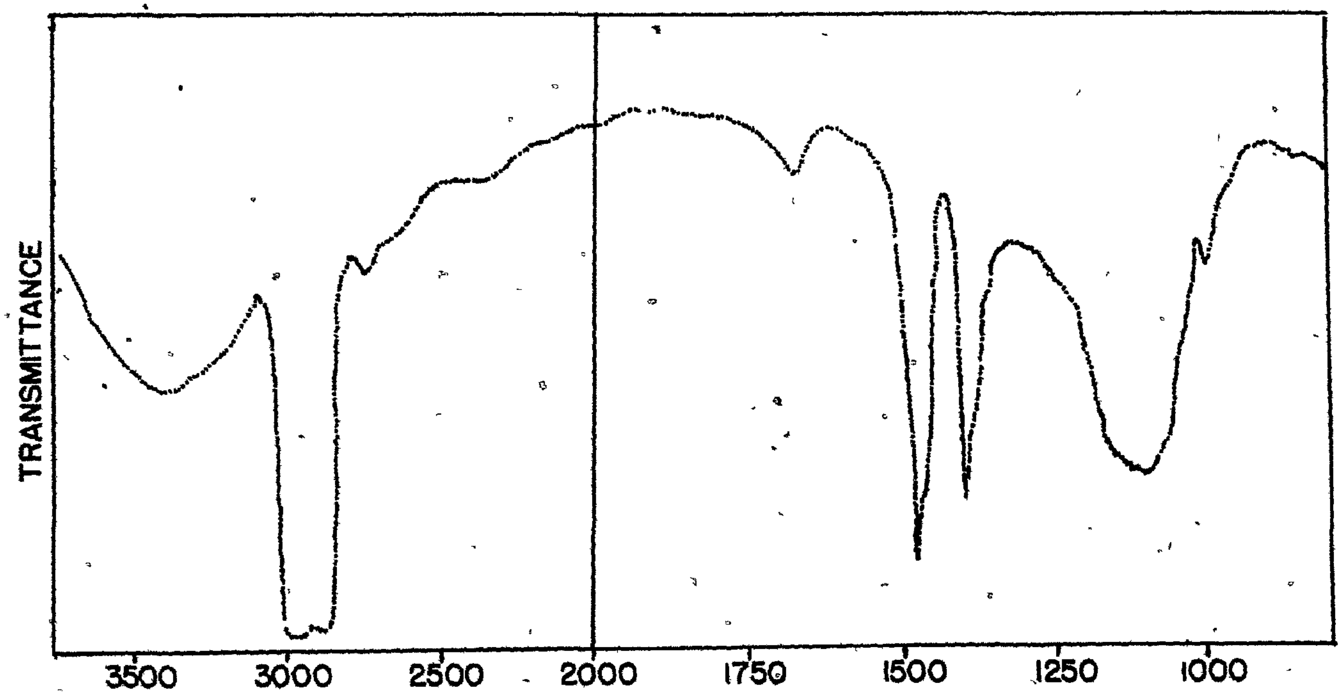

TRANSMITTANCE
3500
3000
2500
2000
1750
1500
1250
1000

Figure 34

Infrared spectrum of cobalt(II) sulphate monohydrate

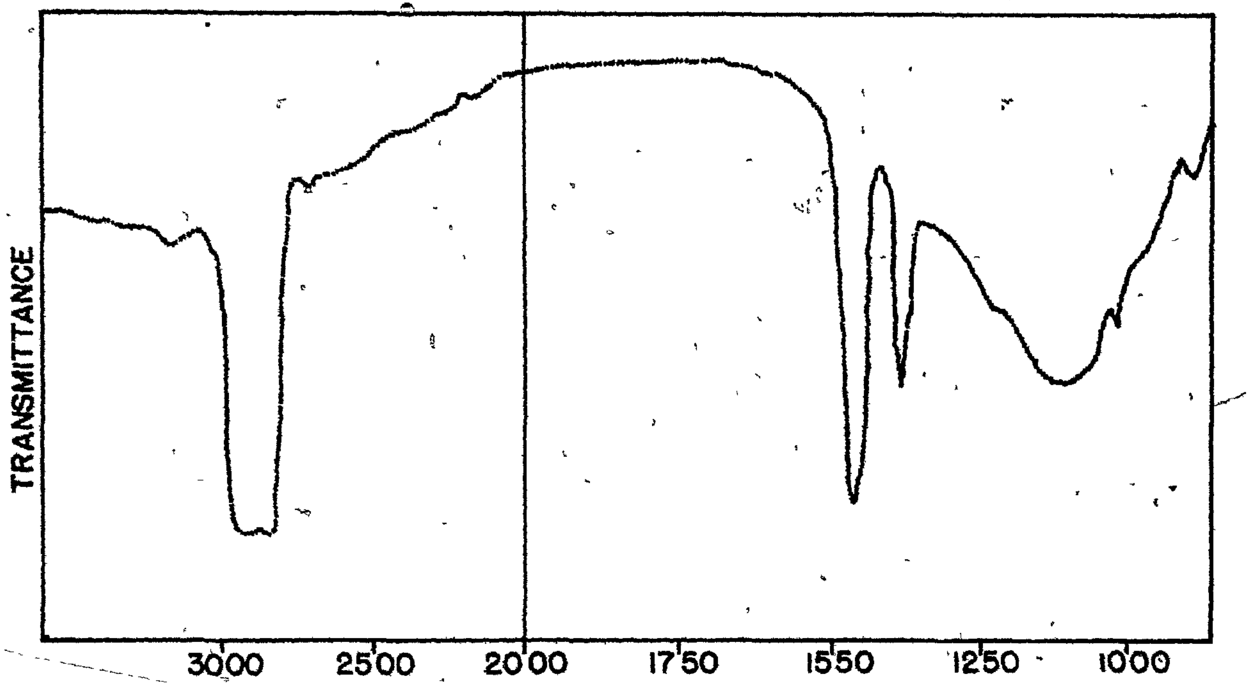

TRANSMITTANCE
3000
2500
2000
1750
1550
1250
1000

Figure 35

Infrared spectrum of deuterated cobalt(II) sulphate heptahydrate

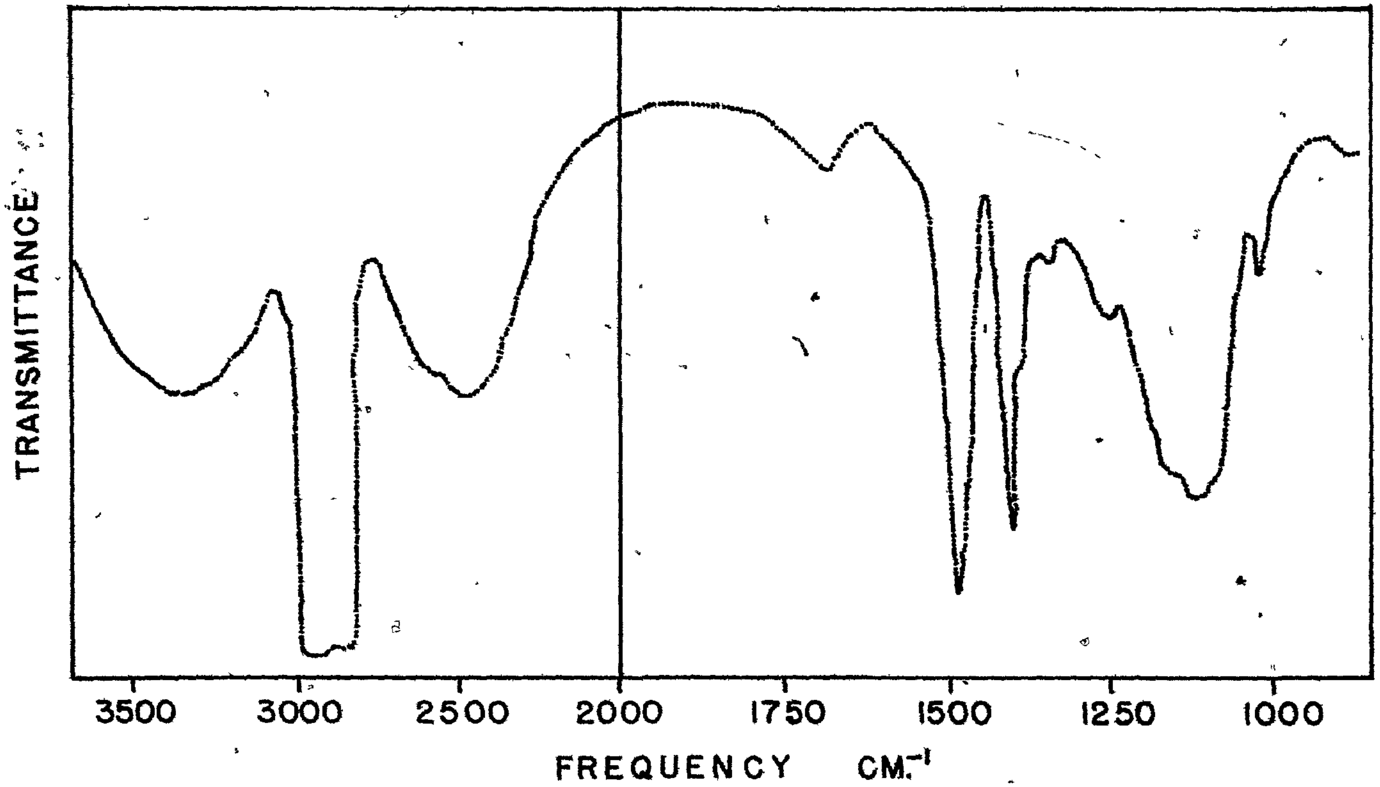

TRANSMITTANCE
3500
3000
2500
2000
1750
1500
1250
1000
FREQUENCY CM.$^{-1}$

Figure 36

Infrared spectrum of deuterated cobalt(II) sulphate monohydrate

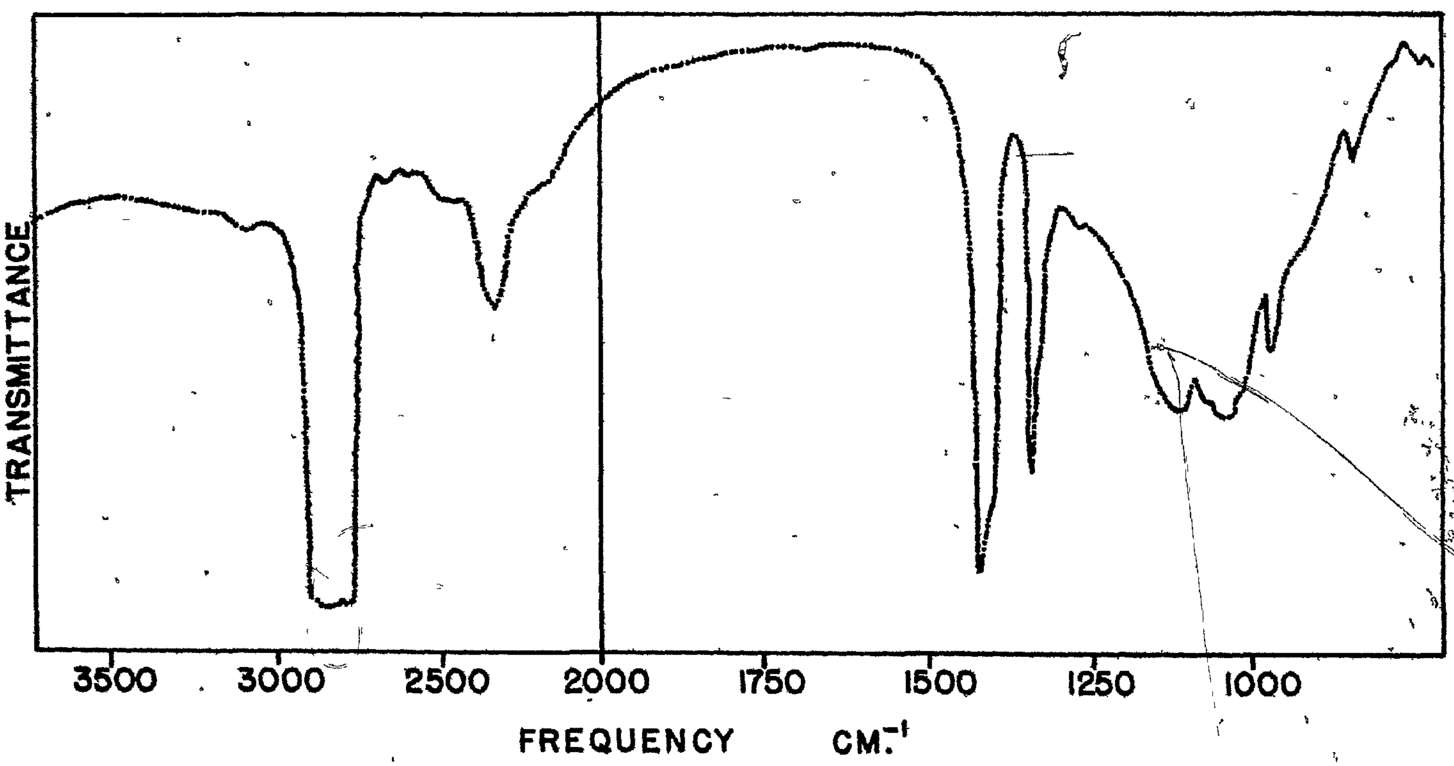
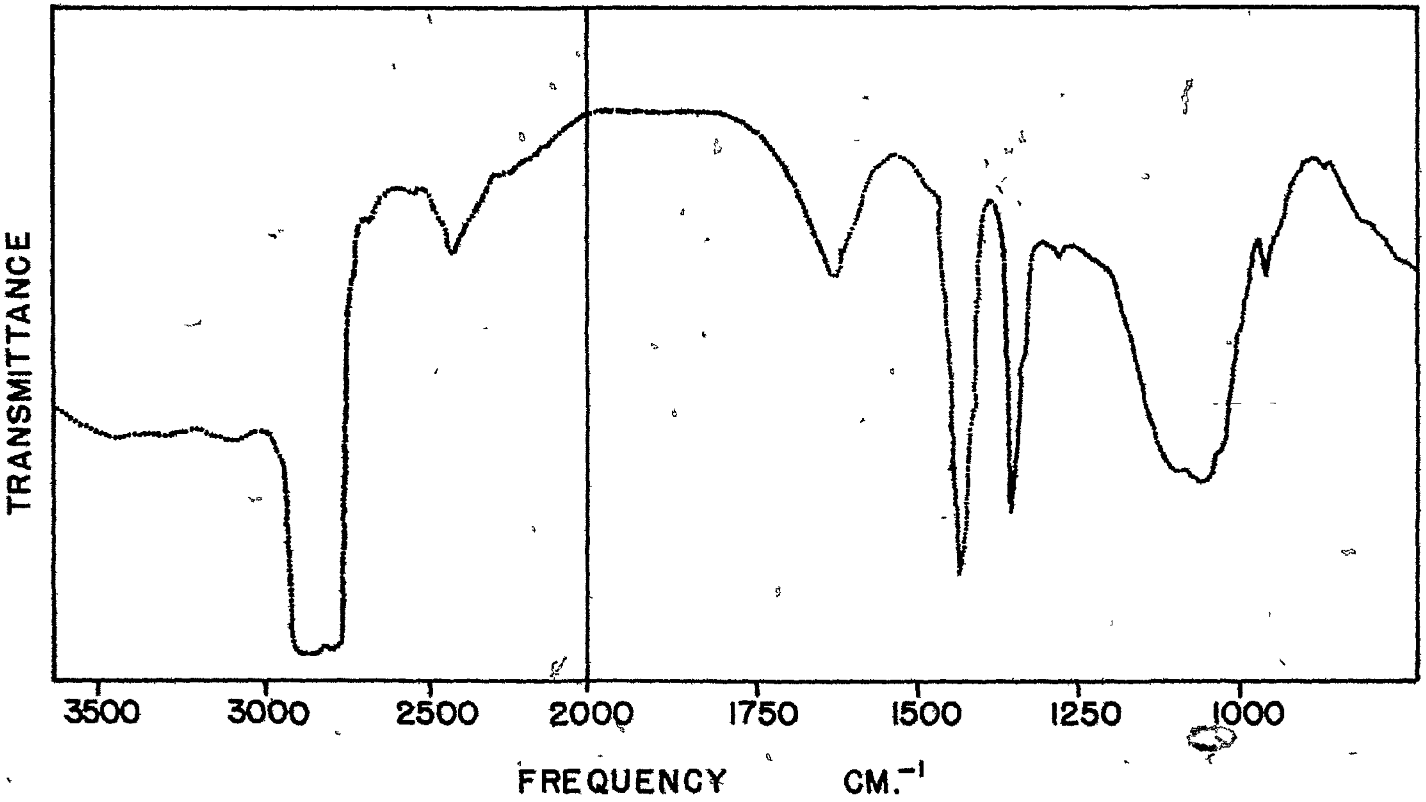

TRANSMITTANCE
3500
3000
2500
2000
1750
1500
1250
1000
FREQUENCY CM.⁻¹

Figure 37

Infrared spectrum of hexaaquocobalt(II) sulphate monodeuterate


TRANSMITTANCE
3500
3000
2500
2000
1750
1500
1250
1000
FREQUENCY CM.$^{-1}$

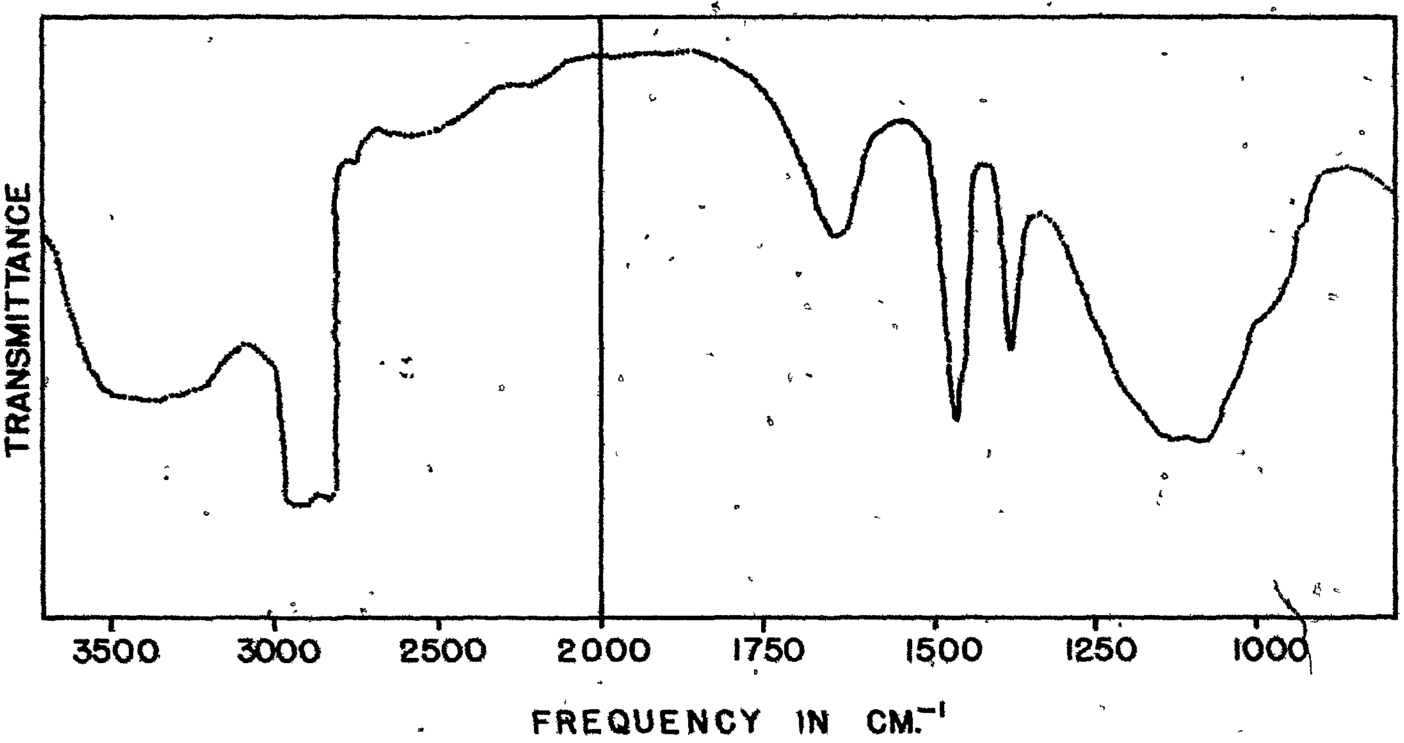
assumption is quite valid since no D_2O deformation frequency is observed at 1250 cm.$^{-1}$. Thus D_2O stays bonded to the sulphate ion with its O-D stretching frequency occuring at 2500 cm.$^{-1}$. This band persisted in the spectrum of salt V which was obtained by dehydrating salt III in an oven but disappeared in the spectrum of salt IV. On the basis of these experiments, it has been concluded that under vacuum the anionic water must be evolved prior to the coordinated water.

The weak band appearing at 980 cm.$^{-1}$ in the spectrum of $Co(H_2O)_6SO_4.H_2O$ has been assigned to the symmetric stretching of the sulphate ion. The asymmetric stretching band at about 1100 cm.$^{-1}$ is broad with several shoulders due to partial removal of the degeneracy. The extent of the splitting increases in the normal crystalline monohydrate as a result of coordination (152,153).

In the high-energy modifications of these hydrates, the absorption bands due to SO_4^{2-} become more rounded with very little splitting. This may be attributed to the loose vibration resulting from lattice chaos or perhaps to the lack of covalent bonding so that the SO_4^{2-} species exists in a purely ionic state, in which case the asymmetric stretching modes are completely degenerate and the symmetric stretching mode could not be seen because under symmetric consideration it is infrared inactive.

Figure 38

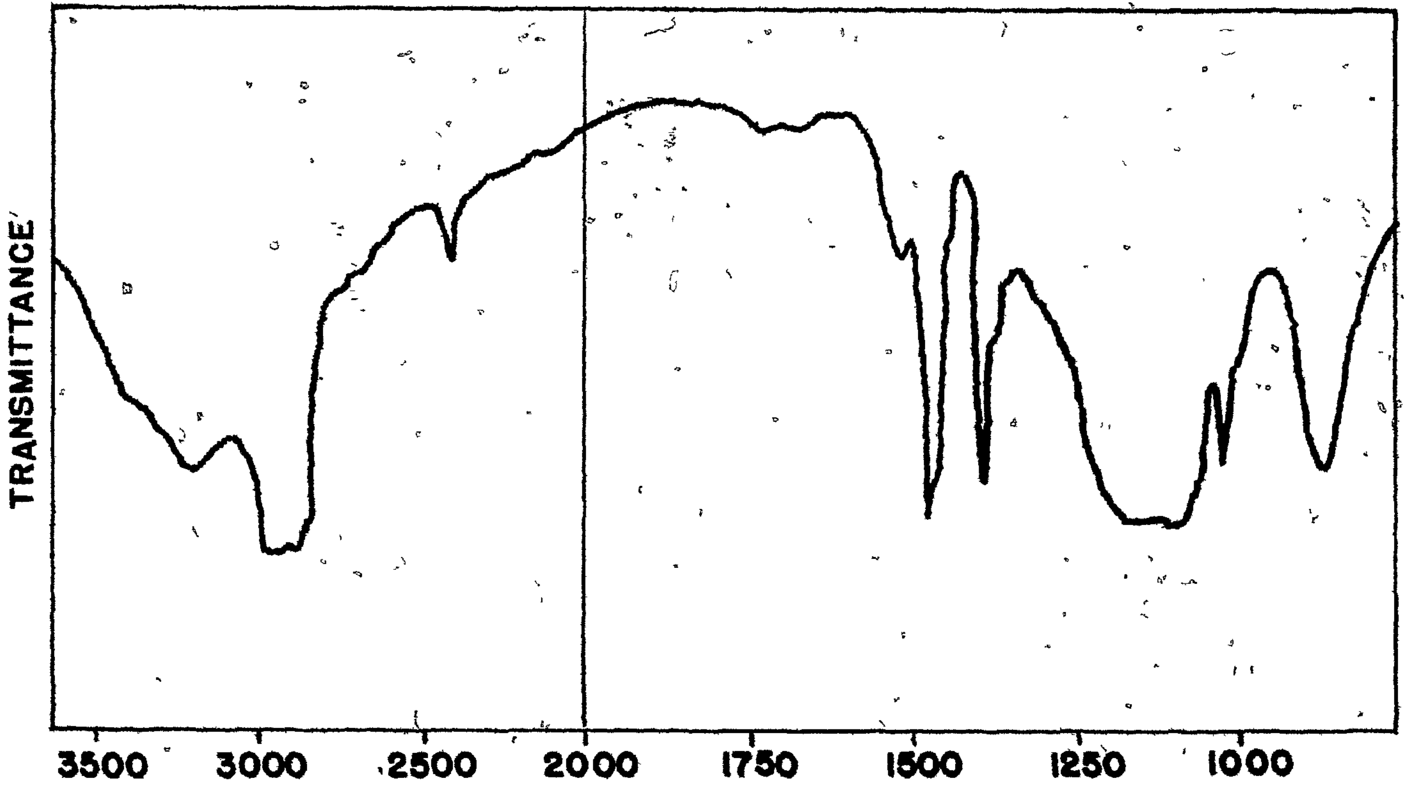
Infrared spectrum for the product of vacuum dehydration of $Co(H_2O)_6SO_4 \cdot D_2O$


TRANSMITTANCE
3500
3000
2500
2000
1750
1500
1250
1000
FREQUENCY IN CM.$^{-1}$

[redacted]

Figure 39

Infrared spectrum of the product of dehydration of $Co(H_2O)_6SO_4 \cdot D_2O$ in an oven


TRANSMITTANCE
3500
3000
2500
2000
1750
1500
1250
1000

7. Reflectance spectroscopy

The reflectance spectra of the hydrates of cobalt(II) sulphate are given in Figs. 40 and 41. The assignment of the various maxima have been made with the help of Tanabe and Sugano diagrams (154) for cobalt(II) salts and various previous investigations (74,96,155). The maximum at about 21,700 cm.$^{-1}$ in the spectrum of $Co(H_2O)_6SO_4 \cdot H_2O$ has been assigned to the electronic transition *

$$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$$

while that at about 19,400 cm.$^{-1}$ has been assigned to the electronic transition

$$^2T_{2g}, {}^2T_{1g}(G) \leftarrow {}^4T_{1g}(F)$$

The assignment of the more intense band at 19,000 cm.$^{-1}$ to the spin-forbidden transition from the ground state $^4T_{1g}(F)$ to the $^2T_{1g}$ and $^2T_{2g}$ has been made for several reasons. Strictly speaking the bands due to these transitions should be weak and sharp. However, it is possible that since the $^4T_{1g}(P)$, $^2T_{1g}(G)$ and the $^2T_{2g}(G)$ are close to each other in energy, spin-orbit coupling may occur between these states. This would result in the increase in the absorption intensity and broadening of the spin doublet bands. The close lying of the doublet states in energy results in the appearance of only a single band which represents the sum of the absorptions of both states, thus giving a considerable intensity of the absorption

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* This is a somewhat debatable assignment. See p. 871 of Cotton and Wilkinson (ref.11).

Figure 40

Reflectance spectra of crystalline hydrates of cobalt(II) sulphate

1 $CoSO_4{\cdot}7H_2O$

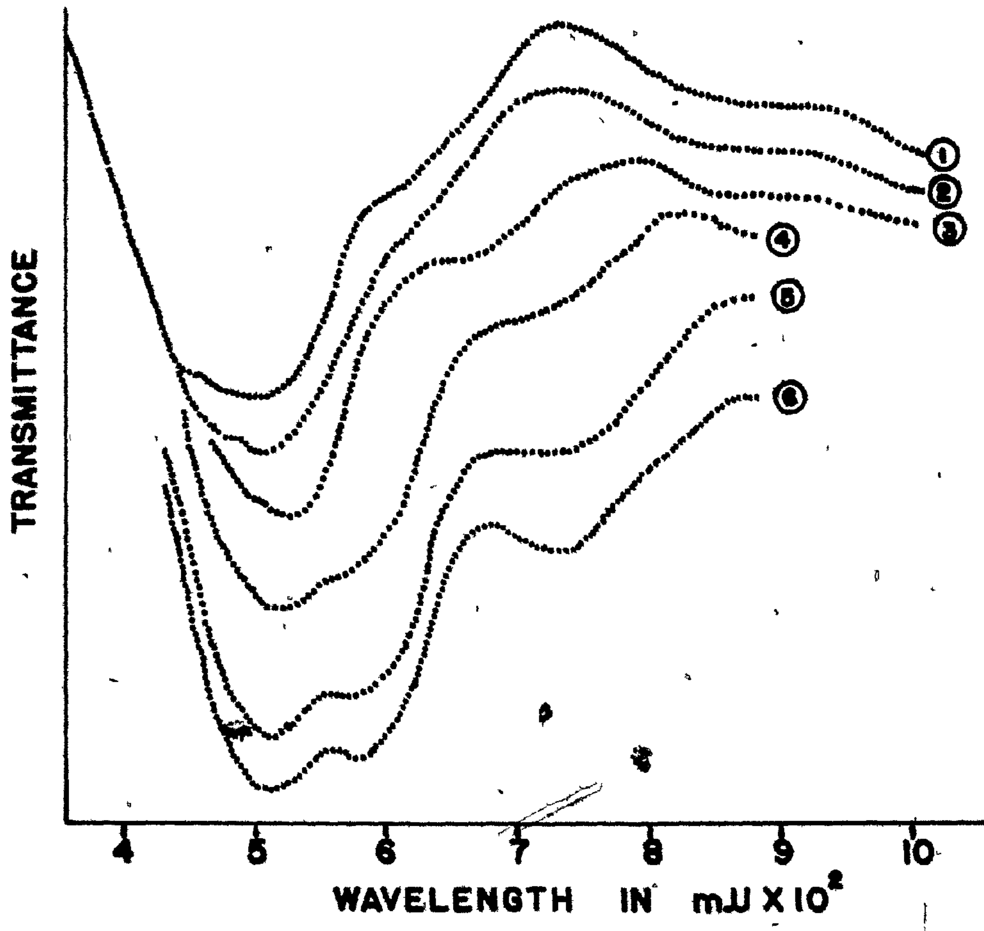
2 $CoSO_4{\cdot}6H_2O$

3 $CoSO_4{\cdot}4H_2O$

4 $CoSO_4{\cdot}H_2O$

5 $CoSO_4{\cdot}\frac{1}{2}H_2O$

6 $CoSO_4$


TRANSMITTANCE
WAVELENGTH IN mµ X 10²
4
5
6
7
8
9
10
①
②
③
④
⑤
⑥

compared to the spin allowed transition band due to the quartet $^4T_{1g}(P)$ state.

It should be noted that the most intense band at 19,000 cm.$^{-1}$ remained constant in the spectra of the salts, from the heptahydrate to the anhydrous salt of cobalt(II) sulphate. If this band were due to the electronic transition to the $^4T_{1g}(P)$ state, it would move toward the lower energy region as the ligand field decreases from the heptahydrate to the anhydrous salt. Instead, the absorption band at 21,700 cm.$^{-1}$ is the one that seems to be shifted to the lower energy region as the ligand field becomes weaker. Thus the peaks at 21,700 cm.$^{-1}$ in the spectrum of the heptahydrate and at 17,000 cm.$^{-1}$ in the spectrum of the anhydrous salt have been assigned to the electronic transition from the ground state to the $^4T_{1g}(P)$ state.

Referring to the Tanabe-Sugano diagram (154), it is obvious that the $^2T_{1g}(G)$ and the $^2T_{2g}(G)$ states remain virtually constant with respect to the changes in the strength of the ligand field. Therefore the transitions to these states remain constant at 19,000 cm.$^{-1}$ despite changes in composition of the hydrates of cobalt(II) sulphate.

The electronic transition from the ground state to the $^4T_{2g}(F)$ is not seen in the region of investigation since it is near 8100 cm.$^{-1}$ (96). The transition to the $^4A_{1g}(F)$ state occurs just below the $^4T_{2g}(P)$ state and thus appears only as a shoulder at about 16,000 cm.$^{-1}$, on the intense absorption curve at 19,000 cm.$^{-1}$.

As the salt gradually lost its water, the maxima shifted to the lower energy region until the spectrum of the anhydrous salt was obtained. The free salt shows the electronic transitions as follows:

$^2T_{2g}$, $^2T_{1g}(G)$ ← $^4T_{1g}(F)$ at 19,000 cm.$^{-1}$

$^4T_{1g}(P)$ ← at 17,000 cm.$^{-1}$

and $^4A_{1g}(F)$ ← at 13,800 cm.$^{-1}$.

The products of vacuum dehydration of cobalt(II) sulphate gave entirely different spectra, Fig. 41. The absorption maxima at about 20,000 cm.$^{-1}$ have broadened into just a single band with little, if any, shoulder. The various maxima seen in the lower energy region in the spectra of the low-energy salts are not seen in the spectra of the high-energy salts because it seems that the absorption occurs within the entire region from 16,000 cm.$^{-1}$ to 10,000 cm.$^{-1}$; except for a little hump at about 12,500 cm.$^{-1}$ which is probably due to the electronic transition from the ground state to the $^4A_{1g}$ state.

Thus the electronic absorption spectra of the normal crystalline hydrates of cobalt(II) sulphate do not show the expected increase in the energy of transition as the symmetry of the ligand field decreases from O_h to D_{4h}. A gradual decrease is observed, instead, as the percent of water content decreases, suggesting that the potential around the metal ion also decreases. While it is true that a tetragonal field in $Co(H_2O)_4SO_4{\cdot}H_2O$ must result in the increase in the energy of transition, this could only be so if the remaining ligands exert the same potential as in the heptahydrate. Thus it appears that when the sulphate ions rearrange to fill the coordination positions left vacant by the water molecules, this would be accompanied by lattice contraction. This would bring the oxygen atoms from the sulphate ions closer to the protons on the water molecules and hence increase the hydrogen bonding. This hydrogen bonding would result in a shift of electron probability from the sulphate ion to the water molecule; the net effect of which is to depolarize the dipole moment and thus transform it into a weaker ligand. Consequently, it would exert a weaker potential on the metal ion and therefore the split in the d-orbitals would be smaller.

From the lack of splitting of the band corresponding to the transition to $^4T_{1g}(P)$ state, it appears that the extent of depolarization is appreciable, so much so that the potentials due to water molecules and sulphate ions would be almost equal. If this were true, then the potential field must be approximately octahedral throughout the dehydration process.

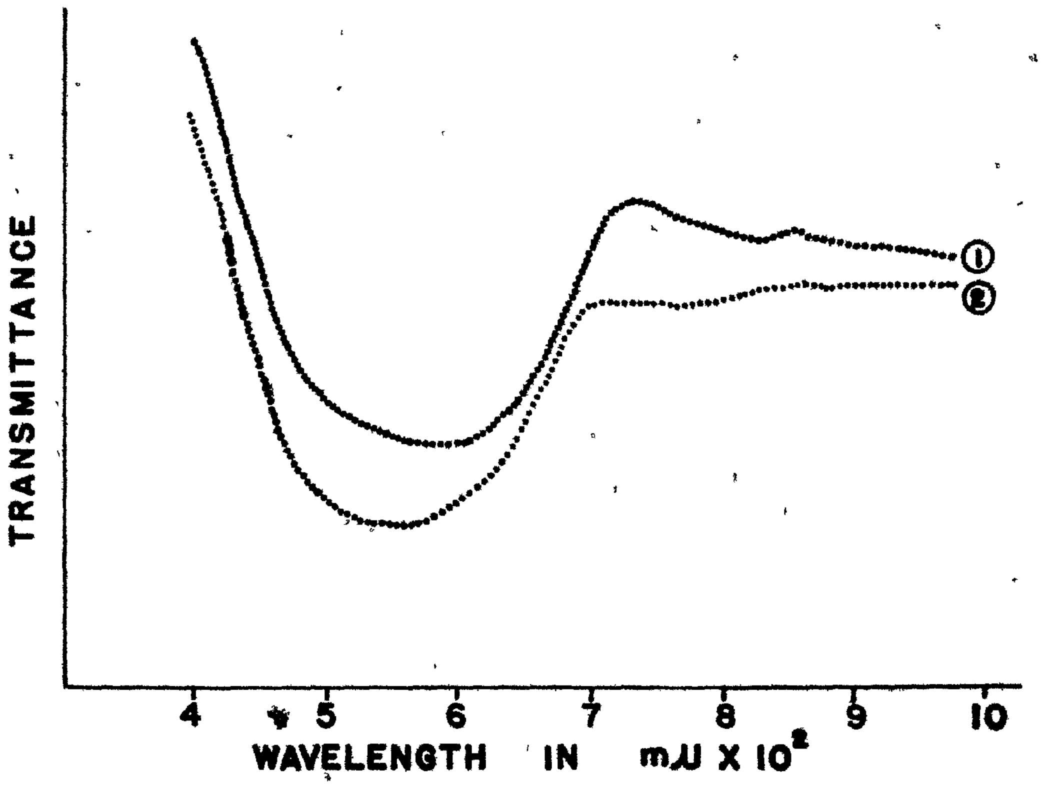
The spectra of the high-energy hydrates show all the features expected. The absorption due to the electronic transition to the $^4T_{1g}(P)$ state is quite broad. This could be attributed to

Figure 41

Reflectance spectra of high-energy hydrates of cobalt(II) sulphate

1 9.86% water left in salt

2 19.01% water left in salt


TRANSMITTANCE
①
②
4
5
6
7
8
9
10
WAVELENGTH IN mμ X 10²

the fact that the high-energy hydrate is loosely packed, resulting in the relaxation of the metal-ligand bonds. Since the mechanism of transition is vibronic in nature, the absorption band would be broadened.

However, the reason for the broadening of the band could also be attributed to the presence of all possible symmetries of the field, as a result of lattice chaos. Since each metal ion is in a different field symmetry, it is expected that the splitting of the d-orbitals would be different. Some transitions would be higher and some would be lower. This is evident from the fact that the tail of the $^4T_{1g}(P)$ band on the longer wavelength side does not go to zero but is broad right to the end of the range of the investigation (10,000 cm.$^{-1}$). The only distinct feature, seen at about 13,000 cm.$^{-1}$, is a hump which is probably due to the transition to the $^4A_{1g}(F)$ state. No exact assignment could be made without further evidence.

X-ray diffraction and electron microscope studies

Parthasarathy (113) has examined some normal crystalline hydrates as well as their high-energy modifications with a polarizing microscope. Most of the lower hydrates showed some sign of crystallinity. Four extinction positions were observed in one complete rotation of the microscope stage. However, no conclusive evidence for the presence or absence of crystallinity could be obtained for the samples prepared under vacuum.

In an attempt to search further for the evidence of crystallinity in the high-energy modifications, three different hydrates of nickel(II) sulphate were examined by both the electron microscope and X-ray diffraction experiments. Salt I, containing 16.04% water, was prepared by heating $Ni(H_2O)_6SO_4$ in an oven at 145°C. The heat of solution for this salt fell on the line IJK in the heat of solution graph for the nickel sulphate system (72). Salt II, containing 14.09% water, was prepared by heating the hexahydrate under vacuum at 59°C. The heat of solution for this salt fell on the line FGH in the heat of solution graph. Salt III was prepared by heating a sample containing 14.59% water for 12 hours in a sealed tube at a temperature of 200°C. This salt was found to be insoluble in water.

The different diffraction properties between salt I and salt II are shown by the presence of a few lines in Plate I but not in Plate II. Thus it may be inferred that the products of vacuum dehydration are amorphous or microcrystalline. As seen in Plate III the crystallinity of the salt increases when it is heated in a sealed tube at an elevated temperature. It is seen that there are many more lines in Plate III than in Plate I.

The difference between salt I and salt II is less clear when seen by an electron microscope. This is illustrated by Plates IV and V for salt I, and Plates VI and VII. There appears to be no sign of crystallinity at all in the two salts, which is in great contrast to salt III as shown in Plates VIII, IX and X. Plate VIII shows that the crystallization of the product of dehydration is partially complete at that temperature. This is evident from the smoothness of the surface of the solid on the upper left side of Plate VIII. This is in great contrast to the roughness of the adjacent surface on the right side, where it is seen that minute crystals are formed. Under much higher magnification these minute crystals show sharp edges, indicating a high degree of crystallinity.

Even though the present results give only slight information regarding the differences between several salts mentioned above, it is hoped that these experiments may give some indication to any interested reader about what to expect, if he is interested in investigating this subject further from this angle.

X-ray diffraction patterns for some hydrates of $NiSO_4$

Plate I: Product of dehydration of $Ni(H_2O)_6SO_4$ in an oven at 145°C - 16.04% water.

Plate II: Product of vacuum dehydration of $Ni(H_2O)_6SO_4$ - 14.09% water.

Plate III: Hydrate of $NiSO_4$ with 14.59% water heated in sealed tube at 200°C.

Plate I

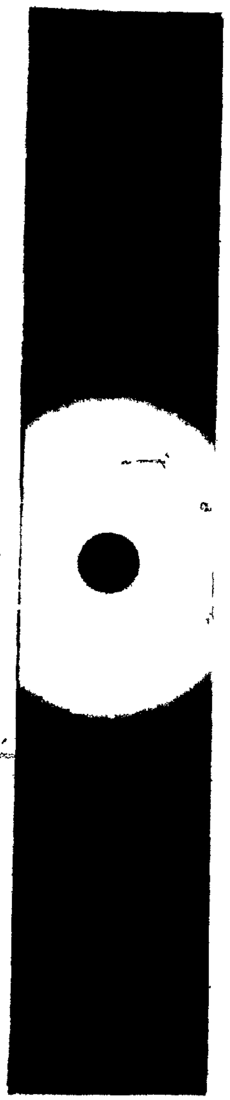


Plate II

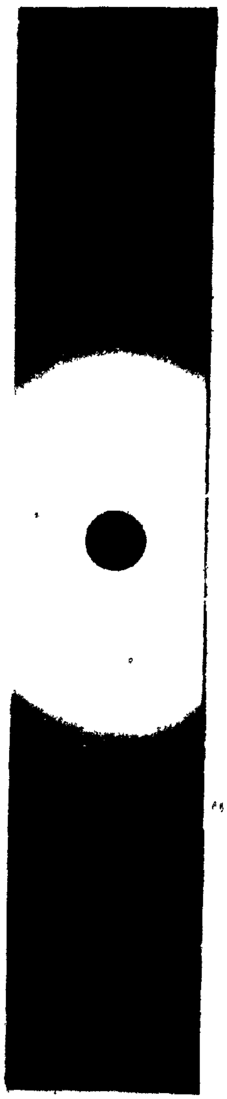
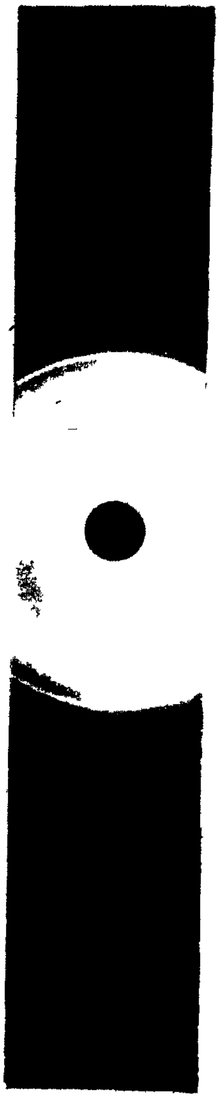


Plate III



Scanning electron microscope

Plate IV: Product of dehydration of $Ni(H_2O)_6SO_4$ in an oven at 145°C - 16.04% water.
Magnification: X 225

Scanning electron microscope

Plate V: Product of dehydration of $Ni(H_2O)_6SO_4$ in an oven at 145°C - 16.04% water. Magnification: X 7500.

Scanning electron microscope

Plate VI: Product of vacuum dehydration of
$Ni(H_2O)_6SO_4$ - 14.09% water.
Magnification: X 750

Scanning electron microscope

Plate VII: Product of vacuum dehydration of
$Ni(H_2O)_6SO_4$ - 14.09% water
Magnification: X 7500.

Scanning electron microscope

Plate VIII: Hydrate of $NiSO_4$ with 14.59% water
heated in sealed tube at 200°C.
Magnification: X 225.

Scanning electron microscope

Plate IX: Hydrate of $NiSO_4$ with 14.59% water heated in sealed tube at 200°C. Magnification: X 2250.

Scanning electron microscope

Plate X: Hydrate of $NiSO_4$ with 14.59% water
heated in sealed tube at 200°C.
Magnification: X 7500.

DISCUSSION

1. Heat of solution

The heats of solution now obtained for the ammine complexes show much similarity to the results for the aquo complexes given by Jamieson et al. (71). For each salt, the heat of solution line for the high-energy ammines is always parallel to the line AB (from the anhydrous salt to the monoammine) just as the heat of solution line for the high-energy hydrates was always parallel to AB (from the anhydrous salt to the monohydrate). In all cases, the heats of solution for the normal crystalline salts fall on the lower lines BC and AB, where C is the heat of solution for the heptaammine.

In each case, the products of vacuum deammoniation of the ammines of $NiSO_4$, $CoSO_4$ and $CuSO_4$ have heats of solution along a line which intersects the line BC at the hexaammine compositions for $CoSO_4$ and $NiSO_4$, and the pentaammine composition for $CuSO_4$. Hence these three salts resemble the hydrates of $MnSO_4$, $FeSO_4$, $CoSO_4$, $NiSO_4$ and $ZnSO_4$ (71,72). These hydrates, especially those of the sulphates of iron(II), cobalt(II) and zinc(II) could be regarded as "ideal" since the heats of solution for the low-energy and the high-energy monohydrates at B and D were experimentally measurable quantities, and hence the heat of transition, Q_{DB}, for each system was directly obtained from the experimental results. The products of vacuum dehydration for the hydrates of $MnSO_4$

and $NiSO_4$, however, have heat of solution lines intersecting the low lines BC at the pentahydrate and the hexahydrate compositions respectively; hence the heat of solution for the high-energy monohydrate at D was not obtained experimentally but was located by extrapolation. Similarly, the products of vacuum deammoniation for each of the ammines of $CoSO_4$, $NiSO_4$ and $CuSO_4$ have heats of solution on a line FGH which intersects the line BC at the composition of the starting material.

The heat of solution results for the ammines of $MnSO_4$, $FeSO_4$ and $ZnSO_4$, as well as the hydrates of $CoCl_2$ and $NiCl_2$, also resemble those for the hydrates of $MnSO_4$, $FeSO_4$, $CoSO_4$, $NiSO_4$ and $ZnSO_4$. The high-energy modifications of these salts do not, however, have heats of solution on a line which intersects the low line BC at the composition of the starting material. Instead, the high-energy modifications for each system have heats of solution on an intermediate line, and thus have been regarded as "less ideal" in this investigation. It has been assumed that each line CDE or each intermediate line must be parallel to the line AB since each of these lines represents the heats of solution for a series of successive dehydration or deammoniation products which do not undergo lattice rearrangement. It is certainly desirable, when possible, to establish points D on lines CDE by experiment, instead of extrapolating data for lower lines.

Such extrapolation might not even be valid if, as is the case for copper(II) sulphate, the experimental lines which apparently correspond to AB and BC were higher than the actual lines for the normal crystalline lower hydrates. Thus the heats of solution for the lower hydrates obtained by heating copper(II) sulphate pentahydrate in an oven suggest that some fraction of the high-energy form is present due to incomplete crystallization of the salt to its most stable form. It appears that the process of crystallization of the metastable phase is complete only by heating the salt in sealed tubes at elevated temperatures. If such sealed tube experiments were not done, the heat of solution estimated for the normal crystalline monohydrate would be higher and consequently the heat of transition Q_{DB} would be too low.

Furthermore, it should be recalled that the establishment of the line FGH for the $CuSO_4$ system was the main factor which led to the search for a sample of crystalline monohydrate which has a heat of solution at point B in Fig. 28. Thus vacuum dehydration or deammoniation experiments are very important in the present calorimetric technique for the estimation of the heat of transition, Q_{DB}.

The inability as yet to obtain an ideal heat of solution line for the ammines of $MnSO_4$, $FeSO_4$ and $ZnSO_4$ is attributed to instability of the hexaammines of these salts. Note that the starting materials for the preparation of lower ammines of these metal sulphates were approximately of the tetraammine composition even though higher ammine compositions which were close to the hexaammine could be obtained. Because of the instability of each hexaammine, the initial pressure of deammoniation under vacuum was high. It has been shown that the higher ~~the~~ pressure of dehydration, the lower was the fraction of high-energy hydrate present in the products (68). It is assumed that this is also true for the ammine systems.

However, it is difficult to say that high pressure was the only cause of this because the results obtained for the vacuum dehydration experiments of $CuSO_4 \cdot 5H_2O$ suggested that some other factors which are still unknown might be involved. For this salt, vacuum dehydration, even at a pressure of 1 X 10^{-6} Torr, failed to give a sample with heat of solution on a high-line originating from the pentahydrate composition.

One could propose that in the case of the ammines an additional factor might have been the extreme instability of the hexaammine lattice due to steric hindrance of ammonia molecules as ligands in a solid sulphate. Ammonia is a bigger molecule than water with a molecular volume of 11.5 $Å^3$ compared to 11.0 $Å^3$ for water. Such steric hindrance may cause two molecules of ammonia to be held more loosely than the other four and thus as soon as they are given off the lattice would automatically assume the structure of the tetraammine with all four remaining ammonia molecules held strongly. Probably the position of the sulphate ion is not very different in the tetraammine than in the hexaammine, so that rearrangement could occur without difficulty.

The lability of aquo and ammine ligands cannot be compared with the situation in solution where it is known that ammonia molecules are bonded more strongly to give a higher ligand field splitting energy. In a solid sulphate, the presence of the sulphate ion has to be taken into account too, since further steric hindrance could be involved. This is true if one compares the instabilities of the hexaammines of metal sulphates with the hexaammines of metal chlorides, since the chloride ion has a smaller ionic volume than the sulphate ion.

The intermediate points denoted by open circles in the heat of solution graphs can now be accounted for. The heat of solution graph for the ammines of nickel(II) sulphate shall be considered as an example. It has been stated earlier that the line IJK indicates removal of ammonia from the coordination sphere without subsequent rearrangement of the lattices of the products, and the line BC is the heat of solution line for those samples which have rearranged to form the normal crystalline lower ammines. Consider the hexaammine at point I. When two molecules of ammonia are removed from the coordination sphere, if rearrangement occurs the product takes the form of the tetraammine. Subsequent removal of ammonia from the tetraammine would, of course, give the product according to the following general rule: with rearrangement the heat of solution would fall on the line BC, but without rearrangement it would fall on a line parallel to IJK, which seems to have been approximated by the open circles. These open circles, therefore, represent the high-energy modification line corresponding to the tetraammine as starting material and indicate the existence of a relatively stable intermediate phase with respect to rearrangement. This stability is aquired by virtue of the immobility of either the sulphate ion or ammonia in the lattice to rearrange to give the normal crystalline form. Rearrangement of a hexaammine lattice to a tetraammine lattice occurs probably because the lattice volume of a hexaammine is large enough for freer movement of the coordinating species such as the ammonia molecules or the sulphate ions. It would seem that the tetraammine lattice would be more compact and therefore free movement would not be possible, resulting in no rearrangement under ordinary conditions. However, to a slight extent this restriction might be removed if the compound was heated so that the lattice would expand and the entities would gain some kinetic energy; thus rearrangement was possible under sealed tube conditions. Furthermore, to achieve this, sealing was necessary to ensure that the ammonia released would not escape, possibly allowing the formation of lower ammines.

If such steric hindrance is a result of compactness of a lattice, one could predict that the smaller the cation the more difficult it is to obtain the lower line BC in going from Mn^{2+} to Cu^{2+}, a fact which has been observed in this laboratory.

It seems likely that the rearrangement is entirely due to the sulphate ions. This seems to be so because, from the heat of solution graphs, no matter where a high-energy line originates along the line BC, the energy required to break each metal-ligand bond is the same for any ammonia content. Furthermore, as one moves down from one integral ammine to another integral ammine on any line, the energy required to break the metal-ligand bond is the same. This would indicate that the bond strength remains the same, no matter from which lattice the bond originated.

One particular case which we have encountered in this thesis is the dehydration of $CuSO_4 \cdot 3H_2O$ which was prepared in three different ways. As shown in Fig. 17 on page 85, the reaction

$$CuSO_4 \cdot 3H_2O \longrightarrow CuSO_4 \cdot H_2O + 2H_2O$$

occurs at almost the same temperature. This could only be so if there is no rearrangement of the water molecules coordinated to the Cu^{2+} ion. If there is rearrangement, a new geometry would be assumed by the complex and this would change the metal-ligand bond strength. Consequently, this would be reflected in the decomposition temperature and since it has been stated earlier that the slope of the heat of solution line for the high-energy modification is a measure of the metal-ligand bond energy, this change in energy would change the slope of this line also; a fact which has not been observed in this investigation.

The results obtained for the hydrates of $CoCl_2$ and $NiCl_2$ illustrate the possibility of preparing samples with higher heats of solution. Previous investigation of the hydrates of $CoCl_2$ suggested that the products of vacuum dehydration are microcrystalline (67). In view of the differences in the experimental conditions, however, it could be assumed that the products obtained in the present experiments are slightly different. Even if they were microcrystalline, it is interesting to note that the combined effect of BaO and concentrated H_2SO_4 as desiccants was to raise the energy content of the samples prepared by vacuum dehydration. This is probably due to the shortening of the time for attaining low pressure in the vacuum system. It appears that the initial rate of removal of water vapour was very important so that recrystallisation of the high-energy product into its stable form could be prevented. Once recrystallization was induced by the formation of nuclei the normal crystalline material could multiply and recrystallization could spread throughout the solid product at a very fast rate. This could be understood if the microcrystals with heats of solution falling on the line FGH were regarded to be smaller than those with heats of solution falling on the line IJK. This implies that microcrystals formed at a lower pressure are smaller than those formed at a higher pressure, and as the pressure is decreased the size of microcrystals formed decreases. Thus for samples of high-energy having heats of solution falling on the highest lines CE, there should not be even microcrystalline structure.

But for the tendency to form mixtures of a high-energy form and the starting material, one could also classify the hydrates of $FeSO_4 \cdot (NH_4)_2SO_4$ as ideal and those of $CuSO_4$ as less ideal. Frost, Moon and Tompkins (68) regarded as microcrystalline the products of vacuum dehydration of $CuSO_4 \cdot 5H_2O$ which have composition of water higher than that of the monohydrate. The heats of solution of these products (Fig. 28) which fell on the line XY, were lower than would be expected for the high-energy form. Experiments on vacuum dehydration of $Fe(H_2O)_6 \cdot (NH_4)_2SO_4$ have been helpful in understanding more about this line XY. This is because the line FK in Fig. 31 shows a similar feature to the line XY. From the relationship between the heats of solution and the compositions of the salts given by Donnan and Hope (120) it appears that the hydrates of $FeSO_4 \cdot (NH_4)_2SO_4$ which have heats of solution falling along the line FK are mixtures of the hexahydrate and the anhydrous salt. The anhydrous salt obtained by heating the hexahydrate in a nitrogen atmosphere, or prepared by vacuum dehydration at a pressure of about 1 X 10^{-3} Torr, has heat of solution at point K. This would suggest that when the salt is dehydrated at a pressure of about 1 X 10^{-3} Torr, each $[Fe(H_2O)_6]^{2+}$ would lose four water molecules to form $[Fe(H_2O)_2]^{2+}$. The normal crystalline form of this dihydrate is stable, with heat of solution at point I in Fig. 31. Under vacuum, the existence of the dihydrate appears to be only transitory. Thus further dehydration would readily give the anhydrous salt, which has heat of solution at point K.

Thus it appears that each $[Fe(H_2O)_6]^{2+}$ in the hexahydrate of ferrous ammonium sulphate after losing some water would then lose all its coordinated water molecules, irrespective of other $[Fe(H_2O)_6]^{2+}$ groups in the crystals. At any intermediate composition, the product would be likely a mixture of the hexahydrate and the free salt, with heat of solution falling along the line FK.

Similarly, it is doubtful that the products of vacuum dehydration of $CuSO_4 \cdot 5H_2O$ which have heats of solution falling along the line XY in Fig. 28 are really microcrystalline. It appears that, under vacuum, the decomposition of the pentahydrate to form the trihydrate would be accompanied by lattice rearrangement. The trihydrate stage is transitory and dehydration would proceed to the monohydrate stage with the formation of the corresponding high-energy form. Thus an intermediate product would be a mixture of the high-energy monohydrate and pentahydrate. Thus this mixture would have a heat of solution on the line XY joining the heat of solution points for the pentahydrate and the high-energy monohydrate.

Garner and Tanner (53) arrived at a similar conclusion although in a less definitive way. They dehydrated a $CuSO_4 \cdot 5H_2O$ crystal under vacuum. When dehydration was partially completed they split the crystal and found that the core of the crystal was made up of undecomposed pentahydrate. This pentahydrate was covered by a layer of dehydrated salt. Later, Kohlschutter and Nitschmann (43) carried out an X-ray diffraction study on the products of vacuum dehydration of $CuSO_4 \cdot 5H_2O$ at 20°C. The products which were of about the trihydrate composition gave X-ray diffraction patterns which showed weak pentahydrate lines. The present suggestion that the products of vacuum dehydration of $CuSO_4 \cdot 5H_2O$ are mixtures of the pentahydrate and the high-energy monohydrate is compatible with these data.

One question which arises from these studies is whether the same anhydrous salt was prepared from the higher hydrates and the higher ammines. It has been observed that the colour of anhydrous nickel sulphate prepared from its hydrate is much brighter than the anhydride prepared from its higher ammine. Similarly, when the hydrates of nickel sulphate with heats of solution falling on the line IJK were heated in sealed tubes, the colour of the salts gradually turned from yellow to green. It has been proposed that, under such treatment, the sulphate ion would rearrange to form a normal crystalline salt, but, as has been observed (71), the products are insoluble in water. The obvious conclusion would appear to be that rearrangement of the sulphate ions also involves formation of covalent bonding between SO_4^{2-} and M^{2+}. As the covalency of the bond increases, the less soluble the product becomes. One would, therefore, expect the anhydride which was prepared from a higher ammine to be different from that prepared from a higher hydrate because the temperature required for the preparations is higher for the ammines than for the hydrates, as shown in Table 4 on page 72.

This has been observed in the cases of cobalt(II) sulphate and zinc(II) sulphate. In aqueous ammonia, the heat of solution of anhydrous $CoSO_4$ prepared by heating the higher ammine was found to be 197 cal./gm. while that prepared from the higher hydrate was 216 cal./gm. Similarly, the heat of solution of $ZnSO_4$ prepared from the higher hydrate was 163.7 cal./gm.* and that from the higher ammine was 127 cal./gm. Thus for consistency in the present investigation, all of the anhydrides of metal sulphates used for heat of solution measurements have been prepared from the higher ammines.

From these studies one might conclude that the nature of the lower hydrates and ammines is determined by the extent of the rearrangement of the sulphate ions. In a salt of high-energy modification, the sulphate ions are bonded to the metal ions purely by ionic bonds, while in a normal crystalline salt the bonds are partially covalent. The extent of this covalency would be determined by the nature of displaced ligands.

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* This value was obtained by dissolving the anhydrous zinc(II) sulphate, prepared by heating the heptahydrate in an oven at 200°C, in 0.75 M aqueous ammonia.

2. Ligand field splitting energy

The ligand field splitting energies now obtained for the hexaammines of nickel(II) and cobalt(II) are in close agreement with the original values of Jørgensen (95,156-158) just as the maximum differences in heat of solution between the high-energy and normal crystalline hydrates of several metal sulphates have previously been shown to be equivalent to the spectroscopically measured ligand field splitting energies for several hexaaquo cations. Thus there appears to be further verification that the present technique, at least in principle, could be used to give quantitative measurements of the ligand field splitting energies for octahedral complexes.

Unfortunately no spectroscopic values have been given for the ligand field splitting energies of the hexaammines of manganese(II), iron(II) and zinc(II) and therefore such values cannot be quoted here for comparison. In aqueous ammonia the ammines of manganese(II) and iron(II) are hydrolyzed to their hydroxides which precipitate as black solids. In one molar aqueous hydrochloric acid these salts dissolve readily. This could be due to marked lability of ammonia ligands which would allow reactions such as

$$[M(NH_3)_6]^{2+} + 6L \longrightarrow [ML_6]^{2+} + 6NH_3 \qquad [5]$$

where L could be either H_2O or Cl^- in solution. The ammonia released could then undergo hydrolysis

$$NH_3 + H_2O \rightleftharpoons NH_4OH \longrightarrow NH_4^+ + OH^- \qquad [6]$$

The occurrence of reaction [6] depletes the concentration of ammonia in solution, producing the inactive NH_4^+. Thus the equilibrium of reaction [5] would be displaced to the right. The OH^- could then react with the metal complex, $[ML_6]^{2+}$ to form the black hydroxide observed,

$$[ML_6]^{2+} + 2OH^- \longrightarrow M(OH)_2 + 6L \qquad [7]$$

In the presence of excess hydrogen ion, ammonia removed would react directly according to equation [8]

$$NH_3 + H^+ \rightleftharpoons NH_4^+ \qquad [8]$$

The dissociation constant of NH_4^+ is of the order of 10^{-10}. Therefore no OH^- would be present and the net reaction can be written as

$$[M(NH_3)_6]^{2+} + 6H^+ + 6L \longrightarrow [ML_6]^{2+} + 6NH_4^+ \qquad [9]$$

From the heat of solution data, e.g. Fig. 21 for the ammines of manganese(II) sulphate, it is apparent that all the ammonia ligands in the heat of solution samples have been replaced by water molecules or chloride ions, and therefore it is necessary to subtract the heat of neutralization of ammonia from the heat of solution of every sample except (?) the anhydrous salt. The quantity to be subtracted, 710 cal./gm. of ammonia content, is obtained from thermochemical data (80,81) for the equation

$$NH_{3(aq)} + HCl_{(aq)} \rightarrow NH_4Cl_{(aq)} \qquad [10]$$

where $\Delta H^o = \Delta H_f^o \, NH_4Cl_{(aq)} - \Delta H_f^o \, NH_{3(aq)} - \Delta H_f^o \, HCl_{(aq)}$

$= - 71.13 + 19.35 + 39.687 = 12.09$ kcal./mole

$= 710.1$ cal./gm.

It is probably because of this that no attempt has been made to measure ligand field splitting energies spectroscopically for ammines of manganese(II) and iron(II), since the hexaammines (or any lower ammines) do not exist in aqueous solution. It is, of course, impossible to measure the ligand field splitting energies for zinc(II) complexes spectroscopically since all the 3d orbitals are filled so that no absorption spectra due to the d-d transition could be observed.

However the values obtained both by the present calorimetric method and the spectroscopic method for other complexes of the metal ions may be used for the purpose of comparison. From the spectrochemical series it is known that the ligand field splitting energies due to H_2O, NH_3 and ethylenediamine (en) are in the order

$$H_2O < NH_3 < en.$$

The values (71,95,157,159,160) for those ligands and various cations under consideration are reproduced in Table 35 and Fig. 42 together with the values found for the hexaammines of manganese(II), iron(II) and zinc(II). It seems that they all are of the same order of

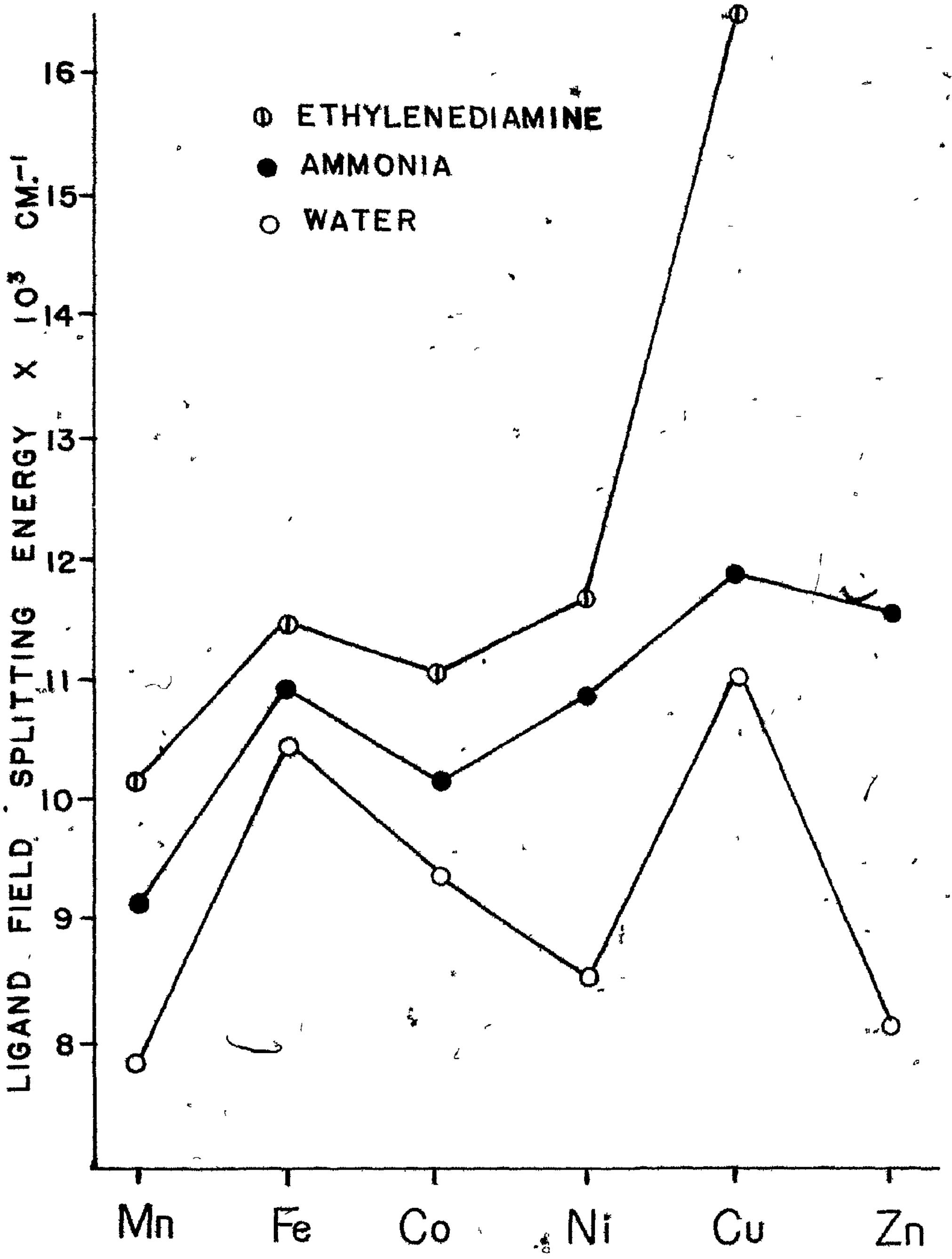
Table 35

Ligand field splitting energy in octahedral field, 10Dq

cation ligand	$10Dq \times 10^3$ cm.$^{-1}$		
	H_2O	NH_3	en.
Mn^{2+}	7.80	9.10	10.1
Fe^{2+}	10.4	10.9	11.4
Co^{2+}	9.30	10.1	11.0
Ni^{2+}	8.50	10.8	11.6
Cu^{2+}	12.6	15.1	16.4
Zn^{2+}	8.30	11.5	-

Figure 42

Ligand field splitting energies for some metal complexes


ⴲ ETHYLENEDIAMINE
● AMMONIA
○ WATER
LIGAND FIELD SPLITTING ENERGY X 10^3 CM.$^{-1}$
16
15
14
13
12
11
10
9
8
Mn
Fe
Co
Ni
Cu
Zn

magnitude; thus giving confidence in the present method. For various reasons discussed above, it is unfortunate that no ligand field splitting energy for the trisethylenediamine zinc(II) has yet been given. However, the ligand field splitting energy obtained for hexaaquozinc(II) (72) appears to suggest that the present assignment of 10Dq for hexaamminezinc(II) is correct.

The ligand field splitting energy obtained for $[Co(H_2O)_6]^{2+}$ in $CoCl_2 \cdot 6H_2O$ which has been found to be 9.3×10^3 cm.$^{-1}$ is in good agreement with that found by the spectroscopic method (74). This value is smaller than the corresponding value obtained for the same complex in the sulphate. The 10Dq for $[Ni(H_2O)_6]^{2+}$ cation in the chloride has not been quoted in the literature but the value of 23.4 kcal./mole obtained in this investigation is comparable to 24.0 kcal./mole obtained by Jamieson et al. (71) for the complex in the sulphate salt. Thus it is obvious that the present technique is as sensitive as, if not more than, the spectroscopic method for estimating 10Dq for the simple complexes studied.

These unrelated methods for estimating 10Dq, namely the spectroscopic method and the present calorimetric method, have shown that the ligand field splitting energy for a metal complex differs from one environment to another. It seems possible to conclude that the difference is due to the variation in the metal-ligand bond distance, since 10Dq is inversely proportional to the fifthpower of the metal-ligand bond distance, R, (73). An increase in R should decrease 10Dq. However from crystal structure analyses it has been shown in most cases that the difference in metal-ligand bond distance is quite small. As an example, in $NiSO_4 \cdot 6H_2O$ the H_2O-Ni bond length is between 2.02 Å and 2.04 Å (27) whereas in $NiCl_2 \cdot 6H_2O$, it is 2.10 Å (161). In view of the slight variation of metal-ligand bond length, the difference in 10Dq cannot be due to this, especially when the difference is as large as that observed for cobalt(II) complexes. It is more likely that the variation in 10Dq is due to differences in the secondary coordination sphere (74). The similarities of the ligand field splitting energies for the hexaaquo complexes in the sulphate salts to those of the corresponding species in aqueous solution is probably due to the similarity of the secondary coordination involving oxygen from the neighbouring sulphate ions in the sulphate salts or oxygen from water molecules in aqueous solution (94). For the chlorides, on the other hand, the secondary coordination sphere is made up of chloride ions and therefore only a slight difference is expected.

Great care is necessary when one compares the values of 10Dq for all these complexes. In aqueous solution various complexes of a number of metal ions in different salts have been found to have the same value of 10Dq. Such is not necessarily true for crystals. Thus the ligand field splitting energy now measured for $[Cu(H_2O)_6]^{2+}$ is not necessarily a better value than that quoted in the literature (95) for the same ion in solution.

The $[Fe(H_2O)_6]^{2+}$ ion is probably the best example to further illustrate this point. The H_2O-Fe bond distances in $Fe(H_2O)_6SO_4 \cdot H_2O$ vary from 2.068 Å to 2.144 Å (162) while in $Fe(H_2O)_6SO_4 \cdot (NH_4)_2SO_4$ they vary from 1.85 Å to 2.14 Å (107). On the average the H_2O-Fe bond distance in the double salt is shorter; consequently it is expected that 10Dq would be higher. Although the ligand field in the double salt is tetragonal, it is possible to estimate the ligand field splitting energy, 10Dq, for an octahedral field from the appropriate correlation diagram (shown in Fig. 11, p. 54). The value thus obtained (about 9.6×10^3 cm.$^{-1}$) is lower than the value for the $[Fe(H_2O)_6]^{2+}$ ion in $FeSO_4 \cdot 7H_2O$ or in solution. This is probably because NH_4^+ ions in the double salt, by virtue of their positivity, render the secondary coordination sphere less negative and thus decrease the ligand field splitting energy to more than compensate for the expected increase due to shorter metal-ligand bond distances.

3. Ligand field splitting energy from the lattice energy

The equation which relates the heat of solution of the monohydrate to that of the heptahydrate is

$$MSO_4 \cdot H_2O \;+\; 6H_2O \;\longrightarrow\; MSO_4 \cdot 7H_2O$$

where the enthalpy of reaction, ΔH, is the difference between the heats of solution of the two salts,

$$\Delta H = \Delta H_{solution}(\text{monohydrate}) - \Delta H_{solution}(\text{heptahydrate})$$
$$= \Delta H_s(1) - \Delta H_s(7).$$

It appears that ΔH is a measure of only the energy of bonding for the six water molecules in the heptahydrate. This would seem to be true if the lattice arrangement of the monohydrate is similar to that of the heptahydrate. However, addition of water molecules to crystalline lower hydrates involves lattice rearrangement and therefore ΔH must include the enthalpy of this rearrangement.

Consider the reactions when various salts dissolve in water:

a) heptahydrate

$$MSO_4 \cdot 7H_2O + aq. \longrightarrow [M(H_2O)_6]^{2+}_{(aq)} + [SO_4 \cdot H_2O]^{2-}_{(aq)} \; ; \Delta H_s(7)$$

b) tetrahydrate

$$\left.\begin{array}{l} MSO_4 \cdot 4H_2O + 3H_2O \longrightarrow MSO_4 \cdot 7H_2O \\ MSO_4 \cdot 7H_2O + aq. \longrightarrow [M(H_2O)_6]^{2+}_{(aq)} + [SO_4 \cdot H_2O]^{2-}_{(aq)} \end{array}\right\} \Delta H_s(4)$$

c) monohydrate

$$\left.\begin{array}{l} MSO_4 \cdot H_2O + 6H_2O \longrightarrow MSO_4 \cdot 7H_2O \\ MSO_4 \cdot 7H_2O + aq. \longrightarrow [M(H_2O)_6]^{2+}_{(aq)} + [SO_4 \cdot H_2O]^{2-}_{(aq)} \end{array}\right\} \Delta H_s(1)$$

$\Delta H_s(7)$ involves only the breaking of the lattice into its ions, $[M(H_2O)_6]^{2+}_{(aq)}$ and $[SO_4 \cdot H_2O]^{2-}_{(aq)}$. $\Delta H_s(1)$ and $\Delta H_s(4)$, however, involve:

i) the energy of breaking of $M^{2+}-SO_4^{2-}$ bonds, $D(M-SO_4)$,

ii) the energy of formation of H_2O-M^{2+} bonds, $D(M-OH_2)$,

iii) the energy of formation of $[M(H_2O)_6]^{2+}-SO_4^{2-}$ bonds, $D(MOH_2-SO_4)$,

iv) the difference in crystal field stabilization energies, $E_{H_2O}-E_{SO_4^{2-}} = \Delta E$, and

v) the heat of solution of the heptahydrate, $\Delta H_s(7)$.

Similar effect are seen in both cases except for the fact that the number of $M-SO_4$ bonds broken and H_2O-M bonds formed would be six for the monohydrate and three for the tetrahydrate, i.e.

$$\Delta H_s(4) = 3D(M-SO_4) + \Delta E_4 + \Delta H_s(7) - 3D(M-OH_2) - 3D(MOH_2-SO_4)$$

$$\Delta H_s(1) = 6D(M-SO_4) + \Delta E_1 + \Delta H_s(7) - 6D(M-OH_2) - 6D(MOH_2-SO_4).$$

Therefore, $\Delta H = 6D(M-SO_4) - 6D(M-OH_2) - 6D(MOH_2-SO_4) + \Delta E_1$ where ΔE_1 is the extra crystal field stabilization energy of the hexaaquo complex over that of the sulphato complex by virtue of its stronger ligand field.

The values of $-\Delta H$ for all metal sulphates studied are given in Table 36 and Fig. 43. It is known that for the high spin manganese(II) and zinc(II) salts, the values of ΔE is zero. Therefore for these two salts

$$\Delta H = 6D(M-SO_4) - 6D(M-OH_2) - 6D(MOH_2-SO_4)$$

only. If it is assumed that $D(M-OH_2)$ and $D(MOH_2-SO_4)$ vary linearly with the atomic number of these metal ions, as represented

Table 36

Heats of reaction, ΔH, and differences in stabilization energies, ΔE

Sulphate	ΔH (kcal./mole)	ΔE (kcal./mole)
Mn	8.08	0
Fe	12.25	3.15
Co	17.84	7.69
Ni	19.86	8.66
Cu	14.27	2.02
Zn	13.35	0

by the dotted line in Fig. 43, it is apparent that

$$\Delta E = \Delta H + 6D(M\text{-}OH_2) - 6D(M\text{-}SO_4).$$

Some values of ΔE estimated in this way are listed in Table 36. Thus it seems possible to calculate ΔE for a hexaaquo complex and consequently 10Dq, if the values of 10Dq for sulphato complexes are known, or vice-versa.

The values of 10Dq for sulphato complexes may be found either by

i) calculating from a knowledge of their lattice energies, or

ii) from spectroscopic measurements.

At the present time very few if any spectral data are available for anhydrous or free salts of metal sulphates. Therefore the following discussion is restricted to the evaluation of 10Dq from the lattice energies of the salts.

<u>Lattice energy of an anhydrous metal sulphate</u>

The experimental lattice energy of a salt may be calculated from known thermodynamic data for the reaction

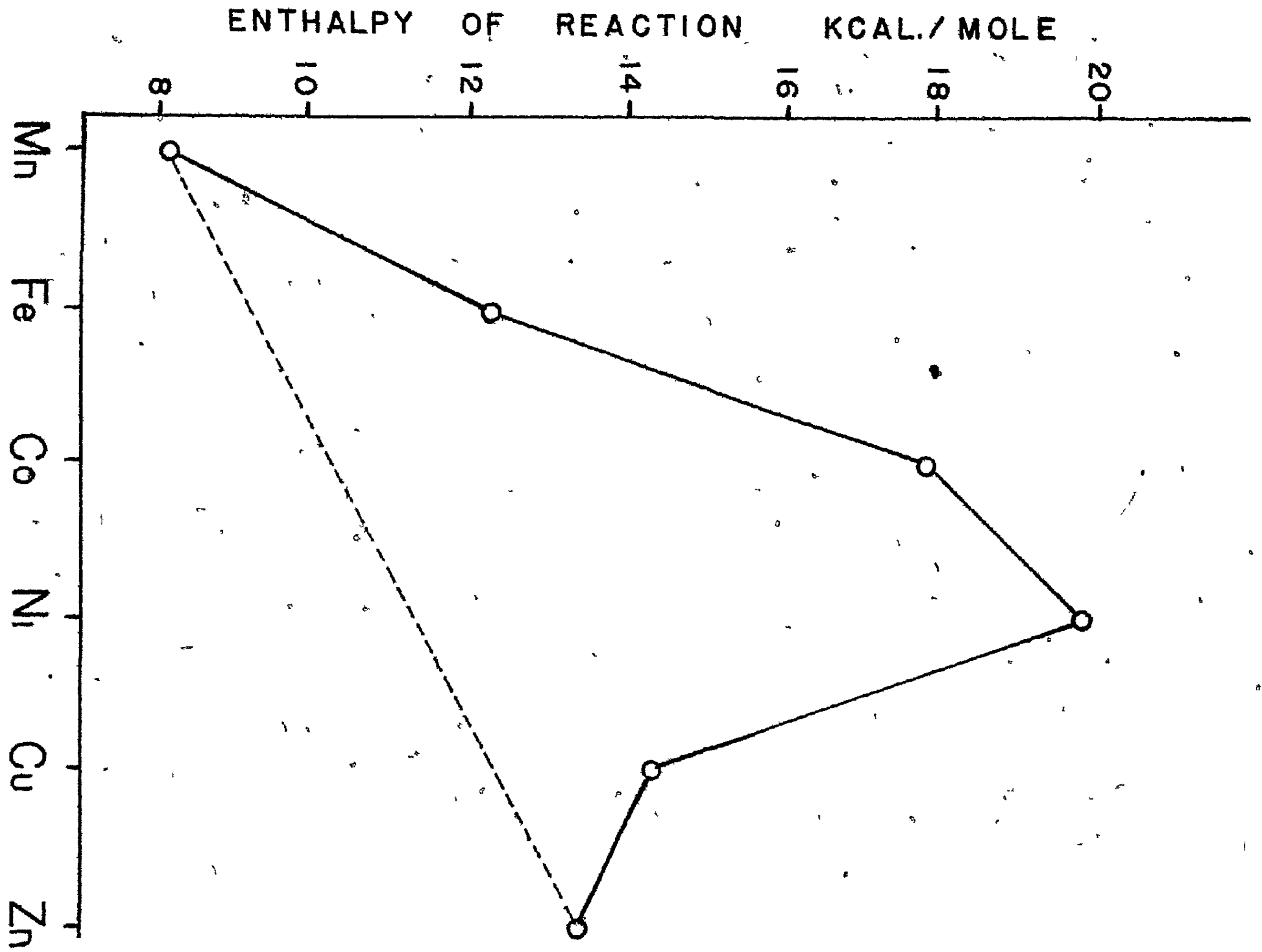
$$M^{2+}_{(g)} + SO^{2-}_{4\,(g)} \longrightarrow MSO_{4\,(s)} \qquad ; \Delta H,$$

where $\Delta H = U + 2RT$

$$= -\Delta H^{o}_{f}\, M^{2+}_{(g)} - \Delta H^{o}_{f}\, SO^{2-}_{4\,(g)} + \Delta H^{o}_{f}\, MSO_{4\,(s)}.$$

<u>Figure 43</u>

Enthalpy of reaction for hydrates of metal sulphates


ENTHALPY OF REACTION KCAL./MOLE
8
10
12
14
16
18
20
Mn
Fe
Co
Ni
Cu
Zn

Heats of formation of various species have been collected from several sources and are given in Table 37. The lattice energies calculated are listed in Table 38 and plotted in Fig. 44.

Semi-empirical values of the lattice energies, U_i, have been calculated using the expression of Kapustinskii and Yatsimirskii (89,90).

$$U_i = 287.2 \left(\sum n\right)\frac{Z_k Z_a}{(r_k + r_a)}\left[1 - \frac{0.345}{(r_k + r_a)} + 0.00870\,(r_k + r_a)\right]$$

According to Kapustinskii (163) r_a for sulphate ion is 2.30 Å. Values of r_k from various sources are listed in Table 37 and Fig. 45. The value of U_i thus calculated for a salt is always smaller (83) than U obtained experimentally from a Born-Haber cycle. This is because U_i by nature of its derivation is only an estimate of the ionic energy term of the lattice energy; covalency and crystal field stabilization energy terms have not been included. Thus, if they are considered

$$U = U_i + C + E.$$

It is known that for manganese(II) and zinc(II) complexes the value of E is zero. Therefore for these two metal salts,

$$U = U_i + C.$$

Assuming that the energy due to covalency is linear from manganese to zinc, the line joining these two metal ions could be used to

Table 37

Heats of formation of $M^{2+}_{(g)}$ and MSO_4 (s)
(in kcal./mole).

	$\Delta H_f\ M^{2+}_{(g)}$		$-\Delta H_f\ MSO_4$ (s)	
	a*	b*	a*	b*
Mn	601.45	601.65	251.3	254.2
Fe	650.7	658.9	221.3	220.5
Co	687.7	681.2	216.7	207.5
Ni	700.8	701.4	216.0	213.0
Cu	730.1	732.3	184.7	186.6
Zn	664.9	664.7	233.4	233.9

a* from ref. 82
b* from ref. 79

Table 38

Experimental lattice energies, in kcal./mole

	a*	b*	c*	d*
Mn	695.75	698.65	695.75	698.65
Fe	715.0	714.2	723.2	722.4
Co	747.4	738.2	740.9	731.7
Ni	759.8	756.8	760.4	757.4
Cu	757.8	759.7	760.0	761.9
Zn	741.3	741.8	741.1	741.6

* a these values are taken from ref. 82,
b these values are calculated from ref. 82 and 71
c these values are calculated from ref. 82 and 79
d these values are calculated from ref. 79 and 71.

Figure 44

Experimental lattice energies for some metal sulphates

□ calculated from ref. 82 and 71

◇ calculated from ref. 82 and 79

○ calculated from ref. 79 and 71

● taken from ref. 82.

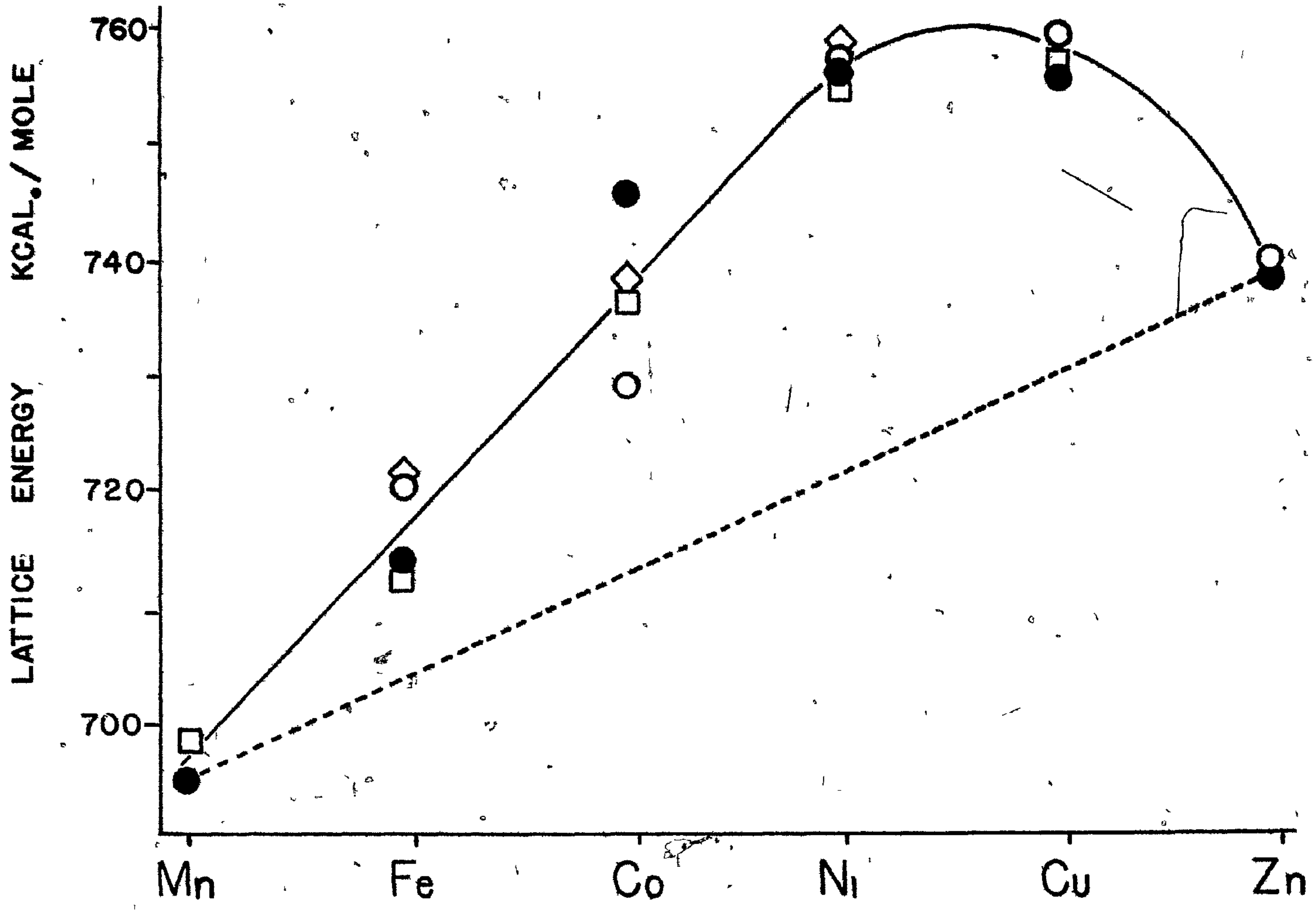

LATTICE ENERGY KCAL./ MOLE
760
740
720
700
Mn
Fe
Co
Ni
Cu
Zn

Table 39

Radii of some metal ions
(in Å)

Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	ref.
0.91	0.83	0.82	0.78	0.72	0.83	79
0.80	0.76	0.70	0.68	0.92	0.69	11
0.80	0.75	0.72	0.69	–	0.74	164
0.80	0.74	0.72	0.69	0.72	0.74	82

Table 40

Lattice energies of MSO_4 in kcal./mole
(calculated from Kapustinskii equation)

Mn	Fe	Co	Ni	Cu	Zn	ref.
658.8	673.1	675.0	682.4	693.9	673.1	79
678.7	686.2	697.8	701.7	657.1	699.8	11
678.7	688.1	693.9	699.8	-	690.0	164
678.7	690.0	693.9	699.8	693.9	690.0	82

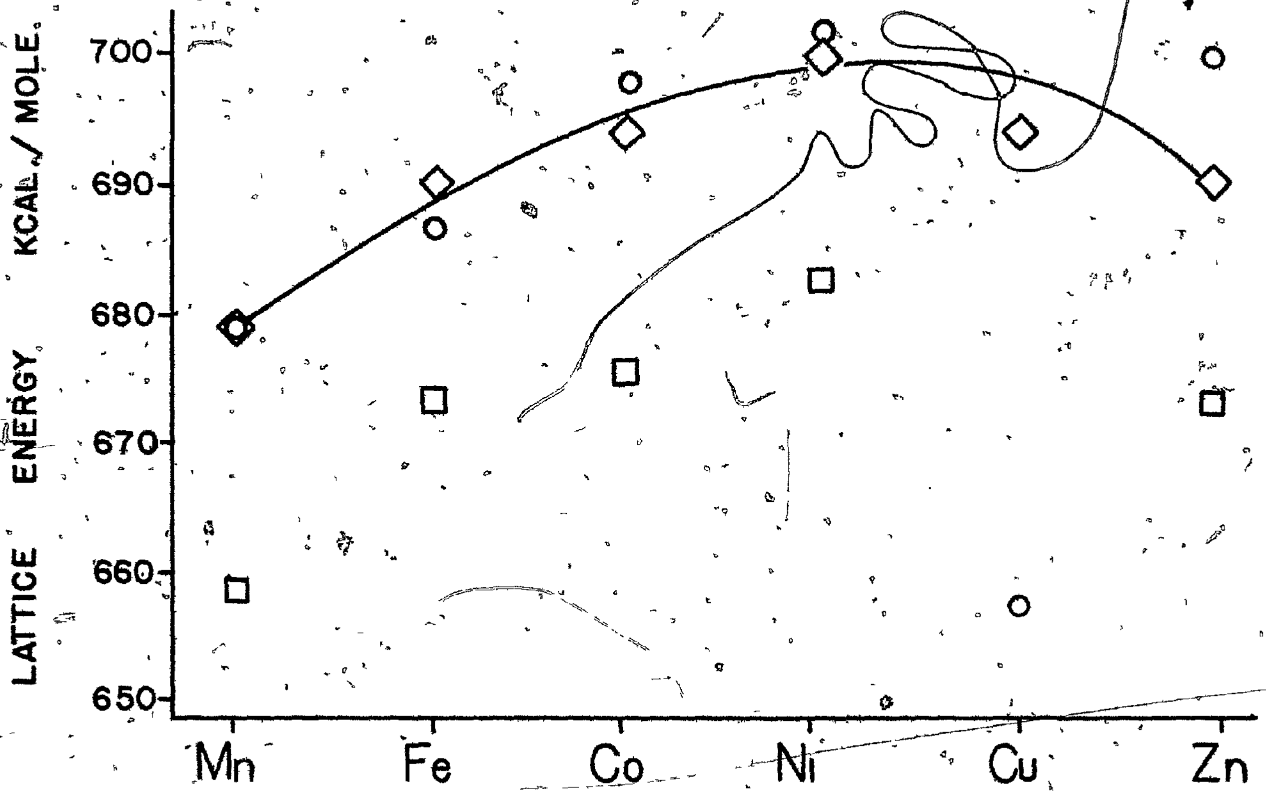
Figure 45

Ionic lattice energies for some metal sulphates

□ from ref. 79

◇ from ref. 164

○ from ref. 11


LATTICE ENERGY KCAL./ MOLE.
700
690
680
670
660
650
Mn
Fe
Co
Ni
Cu
Zn

[redacted]

estimate C for other metal sulphates. Thus knowing U, U_i and C, the value of E could be found for each salt; such values are given in Table 41. This table may be used to obtain crystal field stabilization energies of the aquo complexes, and consequently values of 10Dq. The results of calculation are shown in Table 41 and seem to agree reasonably well with the values obtained by other methods.

Table 41

Stabilization energies of metal complexes in an octahedral field

Metal ion	E (in Dq)	E_{SO_4} (in kcal.)	$E_{SO_4} - E_{H_2O}$ (in kcal.)	E_{H_2O} (in kcal.)	$10Dq_{H_2O}$ (in kcal.)
Mn^{2+}	0	0	0	0	–
Fe^{2+}	4	8.92	3.15	12.07	30.2
Co^{2+}	8	14.0	7.69	21.69	27.1
Ni^{2+}	12	20.36	8.66	29.02	24.17
Cu^{2+}	6	16.66	2.02	18.68	31.23
Zn^{2+}	0	0	0	0	–

4. Origin of Q_{DB}.

It is obvious now that for any particular salt Q_{DB} is a constant quantity which depend on the ligands removed. For consistent results both the high-energy and the low energy forms of the salt must dissolve to give the same solvated species.

When the hexahydrate of a metal sulphate dissolves in water, the heat of solution of the salt may be identified with the energy required to break the lattice into its ionic components plus their solvation energies. For example, $Co(H_2O)_6SO_4 \cdot H_2O$ would dissolve in water to form the hexaaquocobalt(II) ion and sulphate monohydrate ion, i.e.,

$$Co(H_2O)_6SO_4 \cdot H_2O \longrightarrow [Co(H_2O)_6]^{2+}_{(solvated)} + SO_4^{2-} \cdot H_2O_{(solvated)} \; ; \quad \Delta H_s(7)$$

Similarly, the solution of the monohydrate would be

$$CoSO_4 \cdot H_2O + 6H_2O \longrightarrow Co(H_2O)_6SO_4 \cdot H_2O \longrightarrow$$
$$[Co(H_2O)_6]^{2+}_{(solvated)} + SO_4^{2-} \cdot H_2O_{(solvated)} \quad ; \Delta H_s(1)$$

As discussed earlier, the heat of solution for the heptahydrate could be considered in terms of bond energies as the energy of interaction between the complex and the sulphate ion:

$$\Delta H_s(7) = 6\,D(MOH_2\text{-}SO_4),$$

and that of the monohydrate as

$$\Delta H_s(1) = \sum \text{energies of the bonds broken} - \sum \text{energies of the bonds formed} + \Delta E_1{}^{*}.$$

$$\text{i.e., } \Delta H_s(1) = 6D(M-SO_4) + 6D(MOH_2-SO_4) - 6D(M-OH_2) - 6D(MOH_2-SO_4) + E_{H_2O} - E_{SO_4}.$$

$$\therefore \Delta H_s(1) - \Delta H_s(7) = 6D(M-SO_4) - 6D(M-OH_2) - 6D(MOH_2-SO_4) + \Delta E_1$$

Similarly, in aqueous ammonia, the heats of solution of the salts would be represented by

$$Co(H_2O)_6SO_4\cdot H_2O + 7NH_3 \longrightarrow Co(NH_3)_6SO_4\cdot NH_3 + 7H_2O \longrightarrow$$

$$[Co(NH_3)_6]^{2+}_{(solvated)} + SO_4^{2-}\cdot NH_{3(solvated)} \;;\; \Delta H'_s(7)$$

and

$$CoSO_4\cdot H_2O + 7NH_3 \longrightarrow Co(NH_3)_6SO_4\cdot NH_3 + H_2O \longrightarrow$$

$$[Co(NH_3)_6]^{2+}_{(solvated)} + SO_4^{2-}\cdot NH_{3(solvated)} \;;\; \Delta H'_s(1)$$

where
$$\Delta H'_s(7) = 6D(M-OH_2) + D(SO_4-H_2O) + 6D(MNH_3-SO_4) + 6D(MOH_2-SO_4) - 6D(M-NH_3) - D(SO_4-NH_3) - 6D(MNH_3-SO_4) + E_{NH_3} - E_{H_2O}$$

and

$$\Delta H'_s(1) = 6D(M-SO_4) + D(SO_4-H_2O) + 6D(MNH_3-SO_4) - 6D(M-NH_3) - D(SO_4-NH_3) - 6D(MNH_3-SO_4) + E_{NH_3} - E_{SO_4}$$

$$\therefore \Delta H'_s(1) - \Delta H'_s(7) = 6D(M-SO_4) - 6D(M-OH_2) - 6D(MOH_2-SO_4) + \Delta E_1$$

---

*ΔE is the difference in stabilization energies (see page 208).

Thus in both cases $\Delta H_s(1) - \Delta H_s(7)$ is the same and consequently the slope of the line BC is the same. Jamieson et al. (71) gave the heat of solution line BC for the hydrate of cobalt(II) sulphate as:

$$y_{BC} = 114.7 - 2.80x,$$

and the results obtained in the present investigation for the heats of solution of the salts in aqueous ammonia gives

$$y'_{BC} = 180.4 - 2.88x.$$

The corresponding expression for the heat of solution difference for the high-energy modification of the monohydrate and the heptahydrate is:

$$\Delta H_s(1^*) - \Delta H_s(7) = 6D^*(M\text{-}SO_4) + 6D(M\text{-}OH_2) - 6D(MOH_2\text{-}SO_4)$$

where $D^*(M\text{-}SO_4)$ is the metal-sulphate bond energy in the high-energy hydrates. In the present infrared study of the salts, it has been concluded that the metal-sulphate ion bond in the high-energy salts is completely ionic, whereas in the normal crystalline salts it is partially covalent. Thus the relation

$$\Delta H_s(1^*) - \Delta H_s(1) = \left[\Delta H_s(1^*) - \Delta H_s(7)\right] - \left[\Delta H_s(1) - \Delta H_s(7)\right]$$

$$= 6D^*(M\text{-}SO_4) - 6D(M\text{-}SO_4)$$

$$= Q_{DB},$$

is obtained, where δ_{DB} appears to be only the energy of the covalency of the six metal-ligand bonds.

However, it has also been concluded that the increase in the covalency of each $M-SO_4$ bond was due to the inherent property of the crystal field to maintain its octahedral symmetry around the metal ion. On this basis it seems possible that the energy of covalency was gained by the crystal to compensate the loss of potential energy due to the removal of water around the metal ion, i.e.,

energy of covalency $\propto$ potential due to the water.

In a hydrate of a metal sulphate, the interaction between the sulphate ion and the complex is coulombic as well as covalent, i.e., through hydrogen bonding between the oxygen atoms on the sulphate ion and the protons on the ligands. When a ligand water is removed, the interaction between the metal ion and the sulphate ion is purely coulombic. As cystallization occurs, the normal crystalline material is formed. During this process, heat is evolved due to an increase in the covalency of the bonding between the sulphate ion and the metal ion. If crystallization does not occur, however, no heat is given off and the excess energy, which otherwise would be evolved when covalency in the bonding increased, would increase as more ligand water is removed from the lattice.

Thus the difference in the lattice energy between the high-energy modification and its normal crystalline form lies mainly in the energy of covalency. The energy of ionic interaction in the high-energy hydrate seems to remain constant because the loss in the energy of metal-water interaction as a result of the removal of water molecules would be compensated by the gain in metal-sulphate interaction energy which is the result of lattice relaxation. This loss and gain in ionic interaction energy would preserve the total ionic lattice energy of the original salt, the heptahydrate. If this is so, one could calculate this energy by using several expressions mentioned in an earlier section and compare the results obtained with the heat of solution data.

The lattice energy of $Ni(H_2O)_6SO_4$ is made up of ionic interaction between the metal ion and water dipoles, U_{MOH_2}, the metal ion and the sulphate ion, U_{MSO_4}, the stabilization energy due to ligand water, E_{H_2O}, and a covalent energy term, C. i.e.,

$$U_{Ni(H_2O)_6SO_4} = U_{MOH_2} + U_{MSO_4} + E_{H_2O} + C.$$

The lattice energy of the high-energy anhydrous nickel(II) sulphate would then be

$$U_{NiSO_4^*} = U_{MOH_2} + U_{MSO_4} + E_{H_2O}$$

$U_{NiSO_4^*}$ could be calculated by using simple electrostatic theory if it is assumed that, in the hexahydrate of nickel(II) sulphate, the ionic species are $[Ni(H_2O)_6]^{2+}$ ions surrounded by SO_4^{2-} ions (27,28) as shown schematically in Fig. 46. The radius of $[Ni(H_2O)_6]^{2+}$ would then become equal to the sum of the ionic radius of nickel(II) ion, 0.69 Å (82,164), and the diameter of water molecule, 2.76 Å (82). The radius of sulphate ion is 2.30 Å (163). Therefore the ionic component of the lattice energy of $Ni(H_2O)_6SO_4$ due to $[Ni(H_2O)_6]^{2+}$ and SO_4^{2-} interaction could be calculated by using the Kapustinskii equation as 395.6 kcal./mole.

The overall ionic interaction energy due to the nickel ion and water molecules could be calculated by considering both the attraction energy due to Ni^{2+} and H_2O, and dipole - dipole repulsion energy due to the water molecules. The energy of attraction is given by

$$U_a = -6 \frac{Ze\mu}{r^2}$$

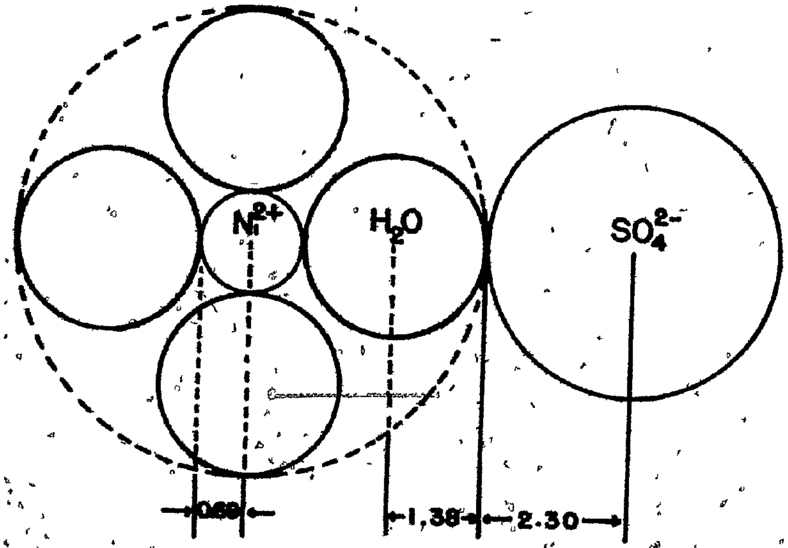
where Ze is the electronic charge on the metal ion, 9.60×10^{-10} esu, μ is the dipole moment of water, 1.87×10^{-18} esu-cm., and r is the metal-water distance. (There are six water molecules around each nickel ion, therefore the multiplication by 6).

The energy due to dipole - dipole repulsion could be calculated by using the expression given by Garrick (165) and Hirschfelder et al. (166):

$$U_r = \sum_{k=1}^{15} \frac{\mu^2}{s_k^2} (1 + \cos.^2 \theta_k),$$

Figure 46

Schematic diagram for $[Ni(H_2O)_6]^{2+}SO_4^{2-}$


Ni^{2+}
H_2O
SO_4^{2-}
0.69
1.38
2.30

where s_k is the distance between the dipole under consideration and the $k^{th.}$ dipole, θ is their angle of alignment. For an octahedral arrangement of dipoles around a metal ion, U_r becomes

$$U_r = 7.115 \frac{\mu^2}{r^3}$$

Therefore the overall energy is

$$U_a + U_r = 7.115 \frac{\mu^2}{r^3} - 6 \frac{Ze\mu}{r^2}$$

For $r = 2.07$ Å, $U_a + U_r = 321.3$ kcal./mole

$= U_{NOH_2}$

The stabilization energy of the hexaaquonickel(II) ion in the sulphate salt is 12Dq. Given 10Dq for the complex is 24.0 kcal./mole,

$$E_{H_2O} = 28.8 \text{ kcal./mole.}$$

Therefore the total ionic energy, $U_{NiSO_4^*}$, is

$$U_{NiSO_4^*}\Big| = 359.6 + 321.3 + 28.8$$
$$= 745.7 \text{ kcal./mole.}$$

The lattice energy for the anhydrous nickel sulphate at A on the heat of solution graph (71) has been calculated earlier as 757.1 kcal./mole. Therefore, on the basis of this calculation, the heat of transition from K to A is 757.1 - 745.7 = 11.4 kcal./mole or 73.7 cal./gm. of the anhydrous salt.

From the heat of solution measurements for the hydrates of nickel sulphate (71), it is known that the heat of transition from K to A is equal to that from J to B. The heat of solution for the high-energy monohydrate obtained experimentally, at J, has been estimated to be 160.9 cal./gm., and the heat of solution for the monohydrate at B was 84.94 cal./gm. Therefore the heat of transition, Q_{JB}, which is equal to Q_{KA}, is 75.96 cal./gm. This energy is almost equal to the difference in the lattice energies calculated above.

Thus it may be concluded that the difference in the energies of the two modifications of the hydrates is the result of the lack of covalent energy in the bonding of the high-energy hydrates. This energy is released when the formation of the covalent bond is favourable.

Since this energy is proportional to the potential energy of water in the salt, it appears possible that this energy is also proportional to 10Dq. Recall that Van Vleck (73) expressed 10Dq as

$$10Dq = \frac{25}{3} \frac{e\mu\langle r^4\rangle}{R^6}$$

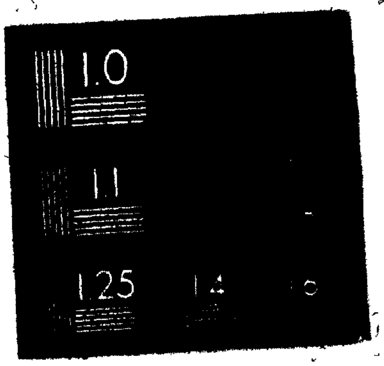
If the right-hand side of the expression is multiplied and divided by Z, the charge on the metal ion, the expression becomes

$$10Dq \doteq -\left[\frac{Ze\mu}{R^2}\right]\frac{25}{3}\,\frac{\langle r^4\rangle}{ZR^4}$$

The quantity in the paranthesis is the potential energy of interaction between the central ion and the ligand at a distance R. For a given ion, $\langle r^4\rangle$ is constant. Therefore 10Dq is proportional to the interaction potential and consequently also proportional to the heat of transition Q_{DB}.

While this thesis was in preparation, a recent book by S. T. Ashcroft and C. T. Mortimer entitled "Thermochemistry of Transition Metal Complexes", Academic Press, London and New York. 1970. appeared in the MacDonald Library. Some of the work with aquo complexes, which indicated the possibility of a thermochemical method for measuring ligand field splitting energies, and led to the work of this thesis, was quoted in this book, p.p. 351-355.

4 OF/DE 4



Appendix I

Theoretical Calculation of 10Dq

The expression given by Van Vleck (73) for calculating the value of 10Dq for an octahedral complex is

$$10Dq = \frac{25}{3} \frac{e\mu \langle r^4 \rangle}{R^6}.$$

In order to use this expression the value of μ, $\langle r^4 \rangle$ and R have to be found.

1. Evaluation of $\langle r^4 \rangle$

The quantum mechanical expression for $\langle r^4 \rangle$ is

$$\langle r^4 \rangle = \int_0^\infty (R_{3d})^2 . r^4 . r^2 \, dr,$$

where R_{3d} is the radial wavefunction of 3d-orbitals. This is given as

$$R_{3d} = \frac{4}{81\sqrt{30}} \left[\frac{Z_{eff}}{a}\right]^{7/2} . r^2 \exp\left[\frac{-Z_{eff}.r}{3a}\right]$$

where a is the Bohr radius (a=0.529Å) and Z_{eff} is the effective charge of the nucleus on the d-electron.

$$\therefore \langle r^4 \rangle = \frac{16}{81^2 . 30} \left[\frac{Z_{eff}}{a}\right]^7 \int_0^\infty r^{10} . \exp\left[\frac{-2Z_{eff}\, r}{3a}\right] .dr$$

Using the mathematical identity

$$\int_0^\infty x^n \exp(-ax).\,dx = \frac{n!}{a^{n+1}}$$

$$\therefore \int_0^\infty r^{10}\exp(-2Z_{eff}\,r/3a).\,dr = (3a/2Z_{eff})^{11}.\,10!$$

$$\therefore \left\langle r^4 \right\rangle = \frac{16}{81^2.\,30}\left[\frac{Z_{eff}}{a}\right]^7 (3a/2Z_{eff})^{11}.\,10!$$

which after simplifying gives

$$\left\langle r^4 \right\rangle = 9\,(3^2/2^7)\,(a/Z_{eff})^4$$

$$= 2000 \times 10^{-32}/(Z_{eff})^4 \ \text{cm.}^4$$

The value of Z_{eff} could be estimated by applying Slater's rule. For Fe^{2+}, Z_{eff} is 6.21.

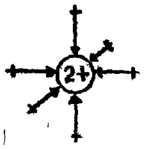
$$\therefore \left\langle r^4 \right\rangle = 2000 \times 10^{-32}/(6.21)^4$$

$$= 1.345 \times 10^{-32} \ \text{cm.}^4.$$

2. Evaluation of total dipole moment, μ.

To calculate μ it is necessary to find the value of the induced dipole moment of the ligands. Classical electrostatic theory could be used and the derivation for a general case has been given (165). Here the special case on the octahedral arrangement shall be presented.

Considering a collection of dipoles around a positive ion



it is evident that the ion dipoles and dipole-dipole interactions determine the value of dipole induced. The dipole-dipole interaction potential, V, is given by

$$V = \sum_{k=1}^{k=n} \frac{\mu}{s_k^2} \cdot \cos. \theta_k$$

where s_k is the distance of $k^{th.}$ dipole from the dipole under consideration and θ_k is the angle of alignment. Therefore the electric field, E_d, due to this interaction at the dipole under consideration is

$$E_d = \frac{dV}{dR} = \frac{d}{dR}\left[\sum_{k=1}^{k=n} \frac{\mu}{s_k^2} \cdot \cos.\theta_k\right]$$

$$= -\sum_{k=1}^{k=n} \frac{u}{s_k^3} \cdot (1 + \cos.^2\theta_k).$$

The electric field, E_i, due to a positive ion is

$$E_i = \frac{Ze}{R^2}$$

$$\therefore \text{ total field, } E, = E_i + E_d$$

$$= \frac{Ze}{R^2} - \sum_{k=1}^{n} \frac{\mu}{s_k^3} (1 + \cos.^2 \theta_k)$$

For six dipoles arranged octahedrally, $n = 5$, $s_1 = s_2 = s_3 = s_4 = R\sqrt{2}$ $\theta_1 = \theta_2 = \theta_3 = \theta_4 = \pi/4$, $s_5 = 2R$, $\theta_5 = 0$.

$$\therefore E = \frac{Ze}{R^2} - \frac{4\mu}{R^3\sqrt{8}} (1 + \cos.^2 \frac{\pi}{4}) - \frac{\mu}{8R^3} (1 + \cos.^2 \theta)$$

$$= \frac{Ze}{R^2} - \frac{2.37\,\mu}{R^3}$$

Since induced dipole moment, μ_i, is proportional to the field intensity, therefore

$$\mu_i = \alpha E$$

where α is the polarizibility of the dipole.

$$\therefore \mu_i = \alpha \left(\frac{Ze}{R^2} - \frac{2.37\,\mu}{R^3} \right)$$

But $\mu = \mu_i + \mu_o$, where μ_o is the permanent dipole moment of the ligand. After simplifying,

$$\mu_i = \frac{\alpha \left(\frac{Ze}{R^2} - \frac{2.37\,\mu_o}{R^3} \right)}{1 - \frac{2.37\alpha}{R^3}}$$

Therefore, to calculate μ_1, the values of α, μ_0, and R have to be known. For water molecules and ammonia, they are listed in Table A(1). Substituting those values, μ_1 and subsequently could be found.

$$\mu_{NH_3} = 3.948 \text{ debye units, and}$$

$$\mu_{H_2O} = 3.645 \text{ debye units.}$$

3. Evaluation of 10Dq

To calculate 10Dq then, all values are inserted in the expression

$$10Dq = (25/3)\ e\mu \frac{\langle r^4 \rangle}{R^6}$$

For the complex hexaaquoiron(II)

$$10Dq = (25/3)\ \frac{4.8 \times 10^{-10} \times 3.645 \times 10^{-18} \times 1.345 \times 10^{-32}}{(2.14)^6 \times 10^{-48}}$$

$$= 2.041 \times 10^{-12} \text{ ergs or } 10.2 \times 10^3 \text{ cm.}^{-1}.$$

which is about 0.4×10^3 cm.$^{-1}$ less than the experimental value of 10.4×10^3 cm.$^{-1}$.

For hexaammineiron(II)

$$10Dq = 10.5 \times 10^3 \text{ cm.}^{-1}$$

which is about 0.4×10^3 cm.$^{-1}$ less than the experimental value of 10.9×10^3cm.$^{-1}$.

If instead, the value of $\langle r^4 \rangle$ is considered as constant for a particular ion, such as Fe^{2+}, in the presence of any ligand and taking the experimental value of 10Dq for the hexaaquoiron(II) as a reference, one could calculate the value of 10Dq for any similar complex of the metal ion. For example:

$$\frac{10Dq_{NH_3}}{10Dq_{H_2O}} = \frac{\mu_{NH_3} \cdot R^6_{H_2O}}{\mu_{H_2O} \cdot R^6_{NH_3}}$$

$$= 1.0243$$

$$\therefore 10Dq_{NH_3} = 1.0243 \times 10.4 \times 10^3 \text{ cm.}^{-1}$$

$$= 10.7 \times 10^3 \text{ cm.}^{-1}.$$

which is 0.2×10^3 cm.$^{-1}$ smaller than the experimental value obtained in this investigation.

Table A(1)

Some Physical Constants for H_2O and NH_3

	H_2O	NH_3
permanent dipole moment	1.85	1.40
radius	1.38	1.40
polarizibility	1.48	2.26

Appendix II

Sample experiment - Ammines of $FeSO_4$.

1. Preparation of ammine

1. weight of reaction tube + $FeSO_4$	11.1750 gm.
2. weight of tube	9.1732 gm.
∴ weight of $FeSO_4$	2.0018 gm.

$FeSO_4$ was reacted with anhydrous ammonia gas at room temperature (22°C) at a pressure of 1 atmosphere.

3. weight of tube after reaction	12.4908 gm.
∴ weight of product	3.3176 gm.
∴ weight of ammonia in product	1.3158 gm.

∴ % ammonia = 39.66

∴ molecular formula is $FeSO_4 \cdot (5.86)NH_3$

2. Sulphate analysis

1. weight of beaker + salt	25.0300 gm.
2. weight of beaker	24.7937 gm.
∴ weight of salt	0.2363 gm.

The salt was dissolved in 50 ml. of 1M aqueous HCl and 1 ml. of concentrated HNO_3 was added. $BaSO_4$ was precipitated by adding a concentrated solution of $BaCl_2$. The precipitate was collected in a sintered glass funnel.

3. weight of glass funnel + $BaSO_4$	16.7506 gm.

4. weight of sintered glass funnel 16.5315 gm.

∴ weight of $BaSO_4$ 0.2191 gm.

molecular weight of $BaSO_4$ is 233.43 gm.

∴ no. moles of $BaSO_4$ collected is 9.386×10^{-4}

∴ no. moles of $FeSO_4$ in original salt is 9.386×10^{-4}

molecular weight of $FeSO_4$ is 151.93 gm.

∴ weight of $FeSO_4$ in original salt is 0.1426 gm.

∴ weight of ammonia in original salt is 0.0937 gm.

∴ % ammonia = 39.65 (theoretical 39.66%)

3. <u>Deammoniation of salt</u>

1. weight of glass tube + sample 8.3925 gm.
2. weight of glass tube 8.1776 gm.

∴ weight of sample 0.2149 gm.

weight of ammonia in sample 0.0852 gm.

Deammoniation under vacuum at 79°C for 12 hours at a pressure of 1×10^{-3} Torr.

3. weight of glass tube + product 8.3124 gm.

∴ weight of product 0.1348 gm.

∴ weight of ammonia lost 0.0801 gm.

∴ weight of ammonia left 0.0051 gm.

∴ % ammonia in product 3.78.

4. Heat of solution measurement

1. weight of tube + sample	6.1915 gm.
2. weight of tube + sample left	6.0567 gm.
∴ weight of sample used	0.1348 gm.

solvent: 1 litre of 1M HCl at 29°C.

Time	Temp.	Time	Temp.	Time	Temp.	Time	Temp.
0.	3.999	6.5	3.921	12.0	-	17.5	3.898
0.5	3.991	7.0	3.914	.		18.0	3.891
1.0	3.984	7.5	3.908	.		18.5	3.884
1.5	3.977	8.0	3.900	.		19.0	3.879
2.0	3.970	8.5	3.892	.		19.5	3.871
2.5	3.963	9.0	3.886	.		20.0	3.865
3.0	3.957	9.5	3.880	15.0	heat off	20.5	3.858
3.5	3.950	10.0	3.871	.		21.0	3.850
4.0	3.943	10.5	3.864	16.0	3.918		
4.5	3.938	11.0	3.858	16.5	3.911		
5.0	3.930	heat on		17.0	3.904		
sample in		voltage: 4.02 V current: 580 mA.					
6.0	3.928	11.5	-				

rate of cooling from 0' to 11' = 0.0139 deg./min.

from 6' to 21' = 0.0138 deg./min.

5. Calculation

In Fig. 18 on page 90, the lines BP and CQ were extrapolated from the lines AB and DC respectively. To calculate the temperature change such as RS ($=\Delta T^{o}C$), the following steps were performed:

1. The slope of the line AB was found from the relation

$$dT = S.dt,$$

where dT is a small change in temperature, S is the slope, a constant, and dt is a small change in time. By integrating

$$\int_{T_A}^{T_B} dT = \int_{t_A}^{t_B} S.dt = S\int_{t_A}^{t_B} dt$$

$$\therefore T_B - T_A = S\,(t_B - t_A)$$

$$\therefore S = (T_B - T_A)/(t_B - t_A)$$

where T_A is the temperature at point A, and T_B at B, and t_A is the time at point A, and t_B at B.

2. T_1 was deduced between $X_1Y_1 = (Y_1 - X_1'')$

3. Since AP is parallel to QD,

$$\begin{aligned} \Delta T = SR &= Y_1X_1' \\ &= (Y_1 - X_1'') + (X_1'' - X_1') \\ \text{but } (X_1'' - X_1') &= (X_1 - X_1'').S \\ &= t_1S \end{aligned}$$

where $t_1 = (X_1 - X_1'')$ = time elapsed from X_1 to Y_1.

4. Therefore,

$$\Delta T = (Y_1 - X_1'') + (X_1 - X_1'').t$$
$$= \Delta T_1 + S.t_1.$$

By calculating ΔT for as many pairs of points as possible, X_1Y_1, X_2Y_2, X_3Y_3,.....X_nY_n, the average value of ΔT was found. The same procedure was followed for calculating the temperature difference between D and E for the determination of the heat capacity of the calorimeter. Knowing the weight of the sample, the heat of solution, ΔH_s, could be found from the relation

$$\Delta H_s = \frac{\Delta T \times C}{w}$$

where C is the heat capacity of the calorimeter and w is the weight of the sample dissolved.

For this example for the heat of solution of an ammine of $FeSO_4$, the average of ΔT_1 was 0.071 for the lines AB and CD, and 0.011 for the lines CD and EF in the time interval t_1 between 5 and 10 minutes. Using the rate of cooling, S, for the lines AB and CD as 0.0139°C/min., t_1S is found to be 0.834°C. Therefore ΔT is 0.0124°C. Similar treatment on the lines CD and EF gives the heat capacity of the calorimeter as 1035 cal./°C. Therefore the heat of solution is

$$\Delta H_s = \frac{\Delta T \times C}{w} = \frac{0.0124 \times 1035}{0.1348}$$
$$= 95.2 \text{ cal./gm.}$$

Since the salt contains about 3.78% ammonia, the heat of neutralization has to be subtracted from this. It is 26.86 cal. Therefore the corrected heat of solution for the salt is 68.3 cal. per gram.

Appendix III.

Average Current Input during the Heating Period.

The current was found to be nearly constant and could be represented by

$$I = A + Bt + Ct^2$$

Suppose at time t_1 the current was I_1 and, at time t_2, I_2.

Let t_3 be the total time of energy input.

$$\text{i.e. } t_1 + t_2 = t_3$$

$$I_{av.} = (I_1 + I_2)/2$$

$$\therefore I_{av.} \cdot t_3 = \int_0^{t_3} I.dt = At_3 + \frac{B}{2} t_3^2 + \frac{C}{3} t_3^3.$$

$$\therefore I_{av.} = A + \frac{B}{2} t_3 + \frac{C}{3} t_3^2 .$$

$$\therefore \frac{I_1 + I_2}{2} = \frac{1}{2}(A + Bt_1 + Ct_1^2) + (A + Bt_2 + Ct_2^2)$$

$$= A + \frac{B}{2}(t_1 + t_2) + \frac{C}{2}(t_1^2 + t_2^2)$$

$$= A + \frac{B}{2} t_3 + \frac{C}{3} t_3 .$$

$$\therefore \frac{t_3^2}{3} = \frac{1}{2}(t_1^2 + t_2^2) = \frac{1}{2}(t_3^2 - 2t_3t_2 + 2t_2^2)$$

$$\therefore 6t_2^2 - 6t_3t_2 + t_3^2 = 0$$

$$\therefore t_2 = t_3(1 \pm /\tfrac{1}{3})\tfrac{1}{2} = 0.79t_3.$$

and $t_1 = 0.21t_3$

Therefore the values of current at 0.79 and 0.21 of the total time were noted and their average value was taken for further calculation.

Appendix IV

Key values for generating thermocouple tables.

For a copper-constantan thermocouple, the following values could be used.

Temp., °F	Voltage, V
-50	-1.6540
0	-0.6695
50	0.3890
100	1.5170

Example: to find V corresponding to 72°F.

T_o $\quad V_o = -0.6695$ mV.
T_1 $\quad V_1 = 0.3890$ mV.
T_2 $\quad V_2 = 1.5170$ mV.

$$V_{72^{\circ}F} = \frac{(T-T_1)}{(T_o-T_1)} \cdot \frac{(T-T_2)}{(T_o-T_2)} \cdot V_o + \frac{(T-T_o)}{(T_1-T_o)} \cdot \frac{(T-T_2)}{(T_1-T_2)} \cdot V_1$$

$$+ \frac{(T-T_o)}{(T_2-T_o)} \cdot \frac{(T-T_1)}{(T_2-T_1)} \cdot V_2$$

$$= \frac{(72-50)\ (72-100)}{(0-50)\ (0-100)} \cdot (-0.6695) + \frac{(72-0)\ (72-100)}{(50-0)\ (50-100)} \cdot$$

$$(0.3890) + \frac{(72-0)\ (72-50)}{(100-0)\ (100-50)} \cdot (1.5170)$$

$$= 0.8768 \text{ mV.}$$

Appendix V

Estimation of errors

Standard deviations σ, which give estimates of the probable errors due to addition, subtraction, multiplication and division of various measurements may be calculated using standard formulae.*

For

$$R = A + B + C$$

the standard deviation in the value of R, σ_R, is given by the formula

$$(\sigma_R)^2 = (\sigma_A)^2 + (\sigma_B)^2 + (\sigma_C)^2$$

where σ_A, σ_B and σ_C are the standard deviations in A, B and C respectively. For

$$R = A \times \frac{B}{C}$$

σ_R is given by the formula

$$\left(\frac{\sigma_R}{R}\right)^2 = \left(\frac{\sigma_A}{A}\right)^2 + \left(\frac{\sigma_B}{B}\right)^2 + \left(\frac{\sigma_C}{C}\right)^2$$

Thus the standard deviations associated with the present investigation may be estimated. For the example given in Appendix II, for the uncertainty in the weight of the salt of ± 0.0001 gm.,

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* H. A. Laitinen, Chemical Analysis, McGraw-Hill, New York. 1960. p. 544.

the composition of the starting material is 39.66 ± 0.01%.

The heat capacity of the calorimeter has been estimated to be accurate to 1.05×10^3 cal./°C. With the uncertainty of the Beckmann thermometer of about 0.002 °C, the individual heat of solution appears to be accurate to ± 2.1 cal. (cf. p. 89).

For the purpose of estimating errors in Q_{DB}, the heat of solution data for the ammines of nickel(II) sulphate and the hydrates of nickel(II) chloride shall be considered. The former illustrate possible errors in the heats of solution measurements obtained from the simple calorimeter described on page 89 and the latter from the new calorimetric assembly (p. 92).

For a collection of data, x_i, y_i, an equation of the form of

$$y = mx + b$$

has been obtained by applying the method of least squares *

$$\text{where} \qquad m = \frac{n\sum x_i y_i - (\sum x_i)(\sum y_i)}{n\sum x_i^2 - (\sum x_i)^2}$$

$$\text{and} \qquad b = \frac{\sum y_i - m\sum x_i}{n}$$

The sum of the squares of the deviations, $\sum d_i^2$, has been calculated. The standard deviation in the slope, σ_m, and the standard deviation in the intercept, σ_b, have been estimated by using the formulae **

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* T. B. Crumpler and J. H. Yoe, Chemical Computions and Errors, Wiley, New York. 1949. p. 217.

** H. D. Young, Statistical Treatment of Experimental Data, McGraw-Hill, New York. 1962. p. 122.

$$\sigma_m^2 = \frac{\sum d_i^2}{n\sum x_i^2 - (\sum x_i)^2}$$

$$\sigma_b^2 = \frac{(\sum d_i^2 /n)(\sum x_i^2)}{n\sum x_i^2 - (\sum x_i)^2}$$

For ammines of Nickel(II) sulphate, the equations are

$$y_{BC} = (116 \pm 5) - (3.60 \pm 0.17)x$$

$$y_{FH} = (250 \pm 3) - (6.96 \pm 0.12)x$$

The heat of solution for the monoammine at B is

$$(116 \pm 5) - (35.7 \pm 1.7)$$
$$= (80 \pm 5) \text{ cal./gm.}$$

The heat of solution for the heptaammine at C is

$$(116 \pm 5) - (157 \pm 7)$$
$$= (-41 \pm 9) \text{ cal./gm.}$$

Using the slope of the line FH, the equation for the line CE has been calculated as

$$y_{CE} = (193 \pm 10) - (6.96 \pm 0.12)x.$$

The heat of solution of the monoammine at D is therefore (193 ± 10) cal./gm.

$$\therefore \quad Q_{DB} = (193 \pm 10) - (80 \pm 5)$$
$$= (113 \pm 12) \text{ cal./gm.}$$

or 31 ± 3 kcal./ mole of heptaammine.

For the hydrates of nickel(II) chloride

$$y_{BC} = (132 \pm 2) - (2.96 \pm 0.04)x$$

$$y_{FH} = (202 \pm 1) - (5.42 \pm 0.08)x.$$

The heat of solution for the monohydrate at B is

$$(132 \pm 2) - (36.1 \pm 0.4) = 96 \pm 2 \text{ cal./gm.}$$

The heat of solution for the heptahydrate at C is

$$(132 \pm 2) - (146 \pm 2) = -14 \pm 2 \text{ cal./gm.}$$

Using the slope of the line FH, the equation for the line CE has been calculated to be

$$y_{CE} = (253 \pm 2) - (5.42 \pm 0.08)x.$$

Therefore the heat of solution for the monohydrate at D is

$$(253 \pm 2) - (66 \pm 2) = 187 \pm 3 \text{ cal./gm.}$$

$$\begin{aligned} \therefore Q_{DB} &= (187 \pm 3) - (96 \pm 2) \\ &= 91 \pm 3 \text{ cal./gm. or } 23 \pm 1 \text{ kcal./ mole of heptahydrate.} \end{aligned}$$

This accuracy is obviously better than that in the spectroscopic technique for estimating 10Dq since most spectra for transition metal complexes are quite broad, so that the absorption maxima cannot be assigned to any great accuracy.

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