The magnetic susceptibilities of the anhydrous and hydrated sulphates and double sulphates of the magnetic metals: with a note on the increased susceptibility produced by heating cobalt salts

1934 Proc. Phys. Soc. 46 872

(http://iopscience.iop.org/0959-5309/46/6/314)

538.214 : 546.7–8 : 546.56–8

THE MAGNETIC SUSCEPTIBILITIES OF THE ANHYDROUS AND HYDRATED SULPHATES AND DOUBLE SULPHATES OF THE MAGNETIC METALS: WITH A NOTE ON THE INCREASED SUSCEPTIBILITY PRODUCED BY HEATING COBALT SALTS

By E. F. HERROUN, F.I.C.

Received April 22, 1934.

ABSTRACT. It has been recognized for many years that the molecular susceptibility of many salts, particularly sulphates, is greater in the hydrated than in the anhydrous condition. Measurements of susceptibility for anhydrous and hydrated single and double salts have shown that the increase is not a specific property of water but that when potassium or ammonium sulphate is substituted for the "water of constitution" there is an increase in molecular susceptibility. With the sulphates of iron, cobalt and nickel this increase is greater than that due to a molecule of water. With manganese sulphate the difference is small but in the same direction, but with copper sulphate a molecule of water increases the susceptibility to a greater extent than a molecule of potassium or ammonium sulphate.

Note relating to the increase in susceptibility of cobalt salts after being strongly heated. The effects observed by A. Serres and by A. Chatillon have been examined and an increase in susceptibility after heating has been found, but in certain salts this is complicated by the fact that hydrolysis or oxidation occurs with the production of basic salts or oxychlorides which also cause an increase in susceptibility. Cobalt pyrophosphate appears to be stable when heated in air to 600° C. and exhibits an increase in susceptibility free from complications.

§ 1. INTRODUCTION

When Wiedemann about 70 years ago put forward his additive law, he quite clearly recognized that chemical changes may entirely alter the magnetic properties of substances. He was the first to mention* that a magnetic compound could be produced from two diamagnetic elements, copper and bromine. He also specially drew attention to the fact that the atomic magnetism of hydrated oxides and salts is, in general, greater than that of the corresponding anhydrous substances.

He stated that the magnetic properties of cobalt and nickel cyanides disappear when these bodies are dissolved in potassium cyanide, and concluded that this would not have happened if they had merely formed double salts.

---

* *Comptes Rendus.* **67**, 833 (1868) from *Monatsberichte d. König. Preuss. Akad.* July 1868.

Mlle E. Feytis* appears to have been the first investigator to measure in modern units the susceptibilities of hydrated and anhydrous copper sulphate and came to the conclusion that the molecule of water of constitution increased the susceptibility, while the four additional molecules in $CuSO_4.5H_2O$ were merely additive and behaved diamagnetically. F. W. Gray and W. M. Birse† came to a similar conclusion in regard to copper sulphate, saying that the first molecule of water increased susceptibility by 11·5 per cent, while the further addition had no marked effect.

As Graham had shown about a century ago that in salts of that kind the water of constitution could be replaced by the neutral sulphate of an alkali metal, it appeared of interest to determine whether, for example, when potassium sulphate is left in combination with a sulphate of one of the magnetic metals the susceptibility is that of the anhydrous salt or whether it is increased in a manner analogous to the effect of water of constitution.

§ 2. APPARATUS

Two modified forms of the Curie balance have been employed; the first and older balance had a thin phosphor-bronze suspension 15 cm. in length, and the observation was made by directly reading the number of degrees turned through by the torsion head in order to pull the specimen out of the gap between the poles of the fixed magnet. It was furnished with two permanent magnets of different strengths and an electro-magnet, any of which might be used, and in this way it covered a very wide range of susceptibility when the field was varied. But the rotation was difficult to read much more closely than to half a degree, so that with small deflections the accuracy was not very great.

Instead of this direct-reading instrument a reflecting one has been employed somewhat like the Curie-Cheneveau‡ balance but with a differently shaped magnet which is caused to slide along brass rails by means of a long brass screw having 20 threads to the inch. The arrangement used by Cheneveau, in which the magnet is moved in an arc concentric with the suspension of the radial arm, has not been followed. I freely admit that this arrangement has the great advantage of keeping the specimen in the centre of the gap even when large deflections are used, but the method of rotating the magnet by means of an arm or yoke with tiller lines or reins as described by Cheneveau did not seem to possess the requisite mechanical exactitude or delicacy. The application of gearing that would be free from back-lash and at the same time not excessively slow presents a difficulty, but not an insuperable one. This principle seems to possess great advantages and if the present instrument were reconstructed a circular motion would be adopted.

The drawback due to the relative shift of the specimen along the y-axis with the rectilinear motion of the magnet along the x-axis is partly met in the present instrument by the wide pole-gap (16 mm.) relative to the diameter of the specimen tubes (8 mm.) and by the small angular displacement of the balance arm, which is not more than 6° on either side of the zero position and frequently much less.

* *Comptes Rendus*, **153**, 668–71 (1911).

† *J. Chem. Soc.* **105**, 2707 (1914).

‡ *Proc. Phys. Soc.* **22**, 343–59 (1910).

In the instrument described by E. Wilson[*] the straight-screw method was used, but in that case an electromagnet was employed: where a battery of large accumulators is available and the current can be regulated by large resistance frames, such as are met with in an electrical engineering laboratory, the variation in the resistance of the copper coil of the magnet due to heating may become negligible; but even then the current has to be very accurately read, for its value must be squared since the pull varies as H^2. Also the change in the reluctance of the iron core and pole-pieces for different excitations must be taken into account by plotting a calibration curve for H. Thus the constancy of a permanent magnet as used in the Curie-Cheneveau balance has much to recommend it.

The magnet used in the present instrument was last magnetized 12 years ago, so it may be considered to have reached a steady state. Its poles are 5 cm. deep, slightly coned, and the flat opposed faces are 12·5 mm. wide and 16 mm. apart. The strength of field in the centre of the pole-gap was measured and found to be 530 c.g.s. units; actually in the position in which the pull on the specimen is a maximum, the value of H is somewhat less than 500, but for comparative purposes the field-strength may be taken to be about 500 units.

Thin-walled soda-glass tubing of external diameter 8 mm. was used for containing the specimens throughout all these measurements. The glass was found to be diamagnetic, with a very small negative susceptibility of approximately $-\ 0{\cdot}06 \times 10^{-6}$, a value so small that when the strong suspension was used no deflection could be read and with the weak suspension the double deflection was only 3 mm. on a scale at a distance of 1 metre. These suspensions were of phosphor-bronze strip 0·85 mm. wide and the weaker one gave 6·8 times the sensitivity of the strong one.

So long as the quantity of substance occupied from 2 to 4 cm. of the length of the tube the force was found to be proportional to the mass, but any length greater than 4 cm. showed a slight diminution due to the fringing of the magnetic field near the top and bottom of the magnet poles. It will be seen that with a substance occupying 4 cm. there was 0·5 cm. between the top and bottom of the specimen and the limits of the magnet poles, 5 cm. deep.

§ 3. SOURCES OF ERROR

The most common source of error in the use of magnetic balances of this type appears to lie in the use of specimens or containers of different diameter: as $H_y . dH_y/dx$ has a maximum over a very narrow belt on each side of the magnet poles, any appreciable increase in diameter must necessarily cause some part of the section of the specimen to lie in a part of the field which is farther from the zone of maximum force, with the result that lower readings for susceptibility with larger diameters are inevitable. Any substance with a susceptibility so great that it materially alters the distribution of the lines in the field is obviously unsuitable for measurement with this form of instrument. The scale, which was divided into millimetres, was bent into a curve of radius 1 m. and situated 1 m. away from the mirror attached to the

---

[*] *Proc. R. S.* A, 96, 429–55 (1918).

bar carrying the specimen. The mirror was concave of focal length 1 m., and a collimating lens was used in front of the narrow slit. The position of the edge of the image could easily be read to 0·5 mm., or even more closely, but the deflections on repetition were rarely more constant than to 1 mm. though they could be relied upon to that extent.

On a deflection of 300 mm., the error would not be greater than 1 in 300. The results for the mass susceptibility are therefore usually given to only 3 significant figures, but when a mean of several readings has been taken a second place of decimals is sometimes given though without any claim to great accuracy. When the weak suspension is used the results are shifted nearly 10-fold but the fourth figure, when given, is still doubtful.

The arm carrying the specimen was of aluminium and counterpoise weights were arranged so that they could slide along the arm on the side opposite the specimen. This arm was fully 2 cm. above the magnets when the strong suspension was used and 3 cm. when the weak one was used: no deflection due to the arm alone was observed.

There was however a small possible error worth recording, due to the fact that when not in use the magnet had a soft-iron armature placed across its poles; when this had been in position for a day or more, on its removal the instrument gave with a standard specimen a slightly greater deflection than normal, but after about half an hour the deflection was found to have recovered its usual value after which it remained constant for many hours. Even an aged magnet may have its magnetic flux temporarily increased by the use of an armature.

§ 4. SPECIMENS AND RESULTS

The salts used were of a high degree of purity, generally recrystallised, and nearly all the double salts were specially prepared for this research. The water of hydration was checked by weighing before and after dehydration. The latter process, in certain cases, was carried out in a current of dried carbon dioxide to prevent oxidation and in certain cases in a vacuum to prevent access of oxygen and also to remove the water vapour as quickly as possible. Details are given later.

All the salts of manganese, iron and cobalt and many of those of nickel and chromium were measured with the strong suspension, but some of the latter and all the copper salts were measured with the weak suspension to obtain the necessary sensitivity.

The susceptibility employed as a standard does not depend on the selection of some particular salt, but partly upon the absolute constant for the instrument found by my old friend and colleague the late Prof. Ernest Wilson in the paper already referred to. It also depends upon tests carried out with this and another instrument* devised by him. Various specimens were measured by both of us, in my case with a reflecting magnetometer and also with the balance first mentioned in this paper. In this way an average constant and standard of susceptibility were arrived at.

---

* *Proc. R. S.* A, 98, 274–84 (1920).

As one of the chief objects of the present inquiry was to examine the paramagnetic effect, if any, of intrinsically diamagnetic salts as compared with water, no allowance has been made for the negative susceptibility of any of the constituents, and the results are calculated for columns 4 and 5 of the table as if only the active constituent had any magnetic effect. By "active constituent" is meant the molecular proportion in a given salt of the sulphate of the magnetic metal concerned.

χ_M The product of the molecular weight and mass susceptibility χ_M has been given to four significant figures, but here again no reliance can be placed on the last numeral: in the case of ferric and chromic salts, half the molecular weight has been taken to bring them into line for comparison with the divalent salts.

The results are given in table 1 and special remarks will be found under the headings of the different metals. The general conclusions are then stated and the remarks concerning the anomalous results obtained from heated cobalt salts are given in a separate note.

No magneton numbers have been tabulated since Δ, in the Curie-Weiss equation, $\chi_M (T + \Delta) = C$, is commonly unknown and is probably positive in some and negative in others of the salts examined. An approximation to the magneton number may, however, be obtained either by the equation used by S. Meyer*, or by a modification which may be more simply written and easily remembered, viz: Weiss magneton number $= 240 . \sqrt{\chi_M}$, where the latter figure is expressed in c.g.s. units as in column 5 of table 1.

§ 5. REMARKS ON TABLE 1

Iron. Ferrous sulphate heptahydrate, and ferrous potassium and ferrous ammonium sulphates were dehydrated in a current of dried carbon dioxide to avoid oxidation; in this way white anhydrous salts were obtained. It is not possible to dehydrate ferric ammonium sulphate (iron alum) as it decomposes before dehydration.

It will be seen from column 4 of table 1 that ferrous sulphate has the highest value for its susceptibility in the form of ferrous ammonium sulphate, and next to it comes ferrous potassium sulphate both hydrated and anhydrous.

Anhydrous ferric sulphate has the low value of $57{\cdot}4 \times 10^{-6}$ rising to $75{\cdot}45 \times 10^{-6}$ in the form of iron alum. Magnetic dilution has evidently a great effect in both ferrous and ferric salts, and with the former both potassium and ammonium sulphate cause a greater increase in susceptibility than several molecules of water.

Manganese. In the sulphates of this metal the value of χ_M is increased only slightly by one molecule either of water or potassium sulphate, the maximum being reached with the greatest magnetic dilution in $MnSO_4 . 5H_2O$ or in $MnSO_4 . K_2SO_4 . 4H_2O$.

As manganese sulphate can be safely dehydrated by heating in air to about 300° C. its constancy renders it useful as a standard of reference, for when sealed in a glass tube it must remain unaltered indefinitely.

---

* *Phys. Z.* **26**, 51–4 (1925).

Table 1

Formula	Temperature (°C.)	χ for salt (10^{-6} units)	χ for active constituent (10^{-6} units)	χ_M (c.g.s. units)
Iron salts				
$FeSO_4$	18·2	66·4	66·4	0·01008
$FeSO_4.H_2O$	18	64·6	72·3	0·01097
$FeSO_4.7H_2O$	17	42·4	77·6	0·01178
$FeSO_4.(NH_4)_2SO_4.6H_2O$	17	32·3	83·4	0·01266
$FeSO_4.(NH_4)_2SO_4$	18	42·8	80·0	0·01215
$FeSO_4.K_2SO_4.6H_2O$	17	28·2	80·6	0·01224
$FeSO_4.K_2SO_4$	18	37·3	80·05	0·01216
$Fe_2(SO_4)_3$	21	57·4	57·4	0·01145 for $\frac{1}{2}M$
$Fe_2(SO_4)_3.6H_2O$	19·4	58·0	67·3	0·01346 „
$Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$	21·5	31·3	75·45	0·01509 „
Manganese salts				
$MnSO_4$	17·2	92·7	92·7	0·01399
$MnSO_4.H_2O$	18	83·4	93·35	0·01409
$MnSO_4.4H_2O$	19·4	66·8	98·7	0·01490
$MnSO_4.5H_2O$	17·2	62·6	99·7	0·01506
$MnSO_4.K_2SO_4.4H_2O$	17	38·0	100·0	0·01510
$MnSO_4.K_2SO_4$	18	43·6	93·9	0·01418
Cobalt salts				
$CoSO_4$ (heated in vac.)	18·5	61·6	61·6	0·009537
$CoSO_4.H_2O$	17·5	56·7	63·3	0·009812
$CoSO_4.7H_2O$	17·2	35·9	65·1	0·01009
$CoSO_4.(NH_4)_2SO_4.6H_2O$	19	26·2	66·8	0·01035
$CoSO_4.(NH_4)_2SO_4$	20	34·9	64·7	0·01002
$CoSO_4.K_2SO_4.6H_2O$	18	24·6	69·4	0·01076
$CoSO_4.K_2SO_4$	19	32·5	69·0	0·01070
ditto after 600° C.	20	34·3	72·87	0·01129
Nickel salts				
$NiSO_4$	20	26·4	26·4	0·004085
$NiSO_4.H_2O$	20·2	24·3	27·13	0·004198
$NiSO_4.6H_2O$	20·2	16·7	28·4	0·004389
$NiSO_4.7H_2O$	19	16·10	29·22	0·004520
$NiSO_4.K_2SO_4.6H_2O$	22	10·1	28·52	0·004413
$NiSO_4.K_2SO_4$	22	14·25	30·30	0·004688
$NiSO_4.(NH_4)_2SO_4.6H_2O$	28·5	11·25	28·71	0·004442
$NiSO_4.(NH_4)_2SO_4$	17	16·25	30·19	0·004661
Chromium salts				
$Cr_2(SO_4)_3.5H_2O$	18	24·5	30·2	0·005910 for $\frac{1}{2}M$
$Cr_2(SO_4)_3.8H_2O$	18	22·1	30·2	0·005927 „
$Cr_2(SO_4)_3.K_2SO_4.24H_2O$	18·5	12·8	32·6	0·006390 „
$Cr_2(SO_4)_3.K_2SO_4.6H_2O$	17	18·5	31·8	0·006241 „
$Cr_2(SO_4)_3.K_2SO_4$	17·5	22·1	31·95	0·006261 „
$Cr_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$	22	13·25	32·3	0·006335 „
$Cr_2(SO_4)_3.(NH_4)_2SO_4$	20	23·3	31·15	0·006110 „
Copper salts				
$CuSO_4$	18·5	8·79	8·79	0·001397
$CuSO_4.H_2O$	18·5	8·91	9·92	0·001577
$CuSO_4.5H_2O$	18	6·13	9·62	0·001530
$CuSO_4.K_2SO_4.6H_2O$	18	3·26	9·05	0·001439
$CuSO_4.K_2SO_4$	18·5	4·69	9·83	0·001563
$CuSO_4.(NH_4)_2SO_4.6H_2O$	18	3·61	9·06	0·001441
$CuSO_4.(NH_4)_2SO_4$	17	4·56	8·37	0·001330

Cobalt. The value given for anhydrous cobalt sulphate was obtained from the salt after dehydration at 300° C. in a vacuum: further heating in a vacuum to 400° only increased its value of χ to $62{\cdot}2 \times 10^{-6}$. The effect of heating in air to above 600° will be considered in the note on cobalt salts.

With cobalt sulphate as with iron the higher susceptibilities are exhibited by the cobalt potassium and cobalt ammonium sulphates, the effect of potassium sulphate on the anhydrous salt being distinctly greater than that due to a molecule of water of constitution, $69{\cdot}0 \times 10^{-6}$ to $63{\cdot}3 \times 10^{-6}$.

Nickel. Nickel sulphate showed a rather smaller alteration in susceptibility but, like cobalt sulphate, showed the highest values for susceptibility when in combination with potassium or ammonium sulphate. It is unlike copper sulphate in that a single molecule of water is not sufficient to develop its full susceptibility and it requires at least $7H_2O$ to do so, whereas in the anhydrous state one molecule of potassium or ammonium sulphate will give a maximum susceptibility.

The most usual form of nickel-sulphate crystals appears to be $NiSO_4.6H_2O$. The heptahydrate was specially crystallized at a low temperature. As the hexahydrate is dimorphous, crystallizing in both square prismatic and monoclinic forms, it cannot always be easily distinguished from the rhombic heptahydrate. Some confusion may result unless the water of hydration is carefully determined.

Chromium. It appears to be very difficult to obtain anhydrous chromic sulphate, methods given in the text-books having failed to give satisfactory results. It is useless to attempt to dehydrate the hydrated salt as it loses SO_3, and a basic salt or ultimately chromic oxide results. But the double salts can be dehydrated by careful heating. Chrome alums show the highest value of susceptibility for chromium sulphate, which to a great extent is maintained in the anhydrous state. While potassium chrome alum forms a definite hydrate with $6H_2O$, ammonium chrome alum seems to be unstable at that degree of hydration.

On the whole, chromium salts show an even smaller variation than nickel sulphate under varying combinations.

Copper. Copper sulphate has been included in this examination, because although not a salt of a magnetic metal, it was one of the earliest in which the effect of hydration was studied. As the susceptibility is low the changes naturally are small, and in the case of normal copper-sulphate crystals the apparent susceptibility would be appreciably raised if the negative value of the four molecules of water of crystallization were taken into account. This modification has not been introduced into table 1 in order to maintain consistency with the results for other salts in which the diamagnetic effects of water or of potassium sulphate is of far less importance.

The highest susceptibility is given by the monohydrate, and this confirms the general results obtained by Feytis and by Gray and Birse to which reference has already been made. In the case of copper sulphate the influence of potassium and ammonium sulphates in increasing susceptibility is less than that of a single molecule of water.

Water. After measurement of the susceptibilities of copper salts with the weak suspension, a determination of the constant for water was attempted as a check on the instrument and the standard of reference. After correction for the repulsion of the diamagnetic glass tube a value of $-0{\cdot}730 \times 10^{-6}$ was found at a temperature of 18° C. This is not put forward in any way as a fresh determination for water but merely as a check on calibration: even in this respect it is not of much use as the coefficient for water has been so variously estimated, from the $-0{\cdot}689 \times 10^{-6}$ found by Jäger and S. Meyer up to $-0{\cdot}79 \times 10^{-6}$ obtained by Koenigsberger and by Curie and Cheneveau. P. Sève* in his report to the Congrès International d'Électricité in 1932 adopts the value found by Piccard and Devard of

$$-0{\cdot}71993 \times 10^{-6},$$

or as a round figure $-0{\cdot}72 \times 10^{-6}$, as being accurate to 1 in 1000.

§ 6. CONCLUSIONS

It will be seen on reference to table 1 that when potassium sulphate is substituted for the water of constitution in the sulphates of iron, cobalt and nickel, there is a distinct increase in the susceptibility of the active constituent (column 4) and of the molecular susceptibility (column 5) which frequently persists and shows its effect in the fully hydrated double salts. This effect is very small but in the same direction in the case of manganese, but with copper sulphate a single molecule of water is more effective in increasing susceptibility than a molecule of either potassium or ammonium sulphate; in fact the latter, in the anhydrous salt, appears to act as a diamagnetic substance.

§ 7. A NOTE ON THE INCREASE IN SUSCEPTIBILITY PRODUCED BY HEATING COBALT SALTS

All values of susceptibility given in what follows are in 10^{-6} c.g.s. units.

In 1925 A. Serres† discovered that cobalt sulphate after having been dehydrated at a low red heat gave a susceptibility which indicated that it had 26 magnetons instead of the 25 previously assigned to it. In the following year A. Chatillon‡ published the results of experiments on cobalt chloride and referred also to cobalt sulphate. He found 26 magnetons in the case of anhydrous cobalt chloride and in a later paper§ reviews the whole subject and states that cobalt chloride in solution has been found with 22, 23, 24 and 25 magnetons and in the anhydrous state with 26.

Chemical knowledge of the ease with which most chlorides from that of magnesium upwards are hydrolyzed or oxidized would lead one to expect some such change on heating their hydrates especially in air. It was found that when cobalt chloride was dehydrated by gradual heating in air to 130° it gave a value of 90·75 for χ, but when it was heated in air to 200°–230° values ranging from 101 to 105 were consistently obtained. These high values if referred to cobalt chloride alone would give it nearly 28 magnetons; but it was found in all cases in which this chloride showed exceptionally high susceptibility that when it was dissolved in water oxychloride was always deposited on standing, the amount of it being variable.

---

* *Science Abs.* **35**, 5249 (1932).

† *Comptes Rendus*, **181**, 714–15 (1925).

‡ *Comptes Rendus*, **182**, 765 (1926).

§ *Annales de Phys.* **9**, 187–260 (1928).

Dehydration in a vacuum produced by a mercury pump was then tried in order to exclude oxygen and to facilitate the removal of the water: this yielded an anhydrous chloride that although it had been heated to 230° gave a value of 91·2 for χ.

As it is well known that the addition of ammonium chloride to magnesium chloride prevents the hydrolysis of the latter salt on concentration and drying, the double salt $CoCl_2.2NH_4Cl$ was prepared and after evaporation to dryness and heating in air to 130° the double salt gave a value 40·2 for χ corresponding to 73·5 for its contained cobalt chloride. Evidently the anhydrous cobalt chloride shows no specially high susceptibility in combination with ammonium chloride. The latter salt was then expelled by heating to 350° in a vacuum and after being cooled the residual cobalt chloride showed a susceptibility of 92·5. On solution in water it gave hardly a trace of oxychloride.

It must therefore be concluded that the value of χ for anhydrous cobalt chloride practically free from oxychloride is about 91 or 92, which justifies Chatillon's number of 26 magnetons. But in cases in which oxychloride is produced the susceptibility may evidently become considerably greater.

Nickel chloride furnishes confirmatory evidence, for when dehydrated in air at 200° it gave a value of 49·2 for χ, but when the dehydration was carried out in a current of dried carbon dioxide the value obtained was 37·5. The former figure would give a magneton number of over 19 while the latter would give only a little over the accepted value of 16: but even in this case the susceptibility of the anhydrous chloride is somewhat greater than for the same salt in solution.

It was found that although cobalt sulphate is fairly stable it slowly loses SO_3 when heated in air to temperatures above 600° and a basic sulphate is formed. This is rendered evident on solution of the salt after it has been strongly heated. When dehydrated in air at above 300° it yielded values of χ ranging from 63·2 to 66·2, but after dehydration in a good vacuum with a drying-tube attached the value of 61·6 given in table 2 was obtained. This figure was raised to 62·2 after further heating to over 400° *in vacuo*.

After this salt, previously dried at 300°, had been heated to a low red heat in air, values ranging from 75·6 to 83·5 were obtained for χ. As it appeared doubtful to what extent this increase in susceptibility might be due to the production of a basic sulphate, salts of a more fixed acid were examined.

Cobalt orthophosphate, $CO_3(PO_4)_2$, and pyrophosphate, $CO_2P_2O_7$, were prepared and dehydrated at 300° and their susceptibilities were determined. At this stage the former gave a value 76·6 for χ which for one third of the molecular weight gives $\chi_M = 0{\cdot}009370$; and after it had been heated to a little above 600° the value of χ_M was found to be raised to 0·01008. But after being heated this salt became somewhat darker in colour, a fact which suggests the production of a small amount of cobalt oxide, as if at the high temperature some of the orthophosphate had been converted into pyrophosphate and cobalt oxide.

Cobalt pyrophosphate however was quite stable at temperatures considerably above 600° and became a lighter blue in colour: after dehydration at 300° its value for χ was 67·3 but after it had been heated to 630° this value was raised to 81·4 which gives, for half the molecular weight, χ_M = 0·01188 c.g.s. unit, a value equivalent to 26 Weiss magnetons or rather more.

Table 2

Formula	Maximum temperature attained (°C.)	Conditions	Temperature of measurement (°C.)	χ (10^{-6} units)	χ_M (c.g.s. units)
$CoCl_2$	130	In air	17·5	90·75	0·01178
"	230	In air	18–22	101–105	0·01684 (mean)
"	230	*In vacuo*	18·5	91·2	0·01184
$CoCl_2.2NH_4Cl$	130	In air	17	40·2	0·009523
$CoCl_2$ from above	350	*In vacuo*	18	92·5	0·01201
$CoSO_4$	300	In air	17–20	63·2–66·2	0·010305 (mean)
"	300	*In vacuo*	18	61·6	0·009549
"	450	*In vacuo*	18	62·2	0·009642
"	630	In air	17·8	83·5	0·01294
$Co_3(PO_4)_2$	300	In air	18	76·6	0·009370
"	600	In air	18	82·4	0·01008
$Co_2P_2O_7$	300	In air	18·5	67·3	0·009826
"	630	In air	18·5	81·4	0·01188
$NiCl_2$	200	In air	20	49·2	0·006376
"	200	In dry CO_2	18	37·5	0·004857

In some of these cobalt salts therefore there appears to be a true increase in susceptibility after they have been raised to a high temperature and in others there is also a spurious effect due to the production of oxychloride or basic salts, and it is very difficult to distinguish in some cases between these effects.