

Det Kgl. Danske Videnskabernes Selskab.  
Mathematisk-fysiske Meddelelser **XII**, 10.

---

STUDIES  
IN MAGNETOCHEMISTRY

PART I.  
COMPLEX RHODIUM COMPOUNDS

BY

J. A. CHRISTIANSEN AND R. W. ASMUSSEN



KØBENHAVN  
LEVIN & MUNKSGAARD  
EJNAR MUNKSGAARD

1934

Printed in Denmark.  
Bianco Lunos Bogtrykkeri A/S.

It is the intention in this series of papers to investigate the magnetism of complex compounds, using in part the collection of substances left by S. M. JØRGENSEN in this laboratory and partly compounds prepared by ourselves. The magnetic properties of these complex salts are in several cases rather peculiar and it is probable that a systematic survey of their magnetism will give information regarding the type of bonds and in some cases, according to the theory of PAULING<sup>1</sup>, supply us with means to draw conclusions relating to the spatial arrangement of the coordinated groups. We shall, however, for the present confine ourselves to study complex compounds of nickel and the platinum metals, since a material which covers cobalt and chromium compounds has already been furnished by R. ROSENBOHM<sup>2</sup> and complex iron salts have been studied by L. WELO<sup>3</sup>.

Magnetic measurements of simple salts of the elements of the first transition series show that the magnetic moments found are in good agreement with those calculated by means of the expression  $\mu = \sqrt{4S(S+1)}$ \*; here S is the spin quantum number for the term of the ion in question. This formula is a modification, suggested by BOSE<sup>4</sup>

<sup>1</sup> LINUS PAULING, J. Am. Ch. Soc. **53**, 1391. 1931.

<sup>2</sup> R. ROSENBOHM, Z. physikal. Ch. **93**, 693. 1919.

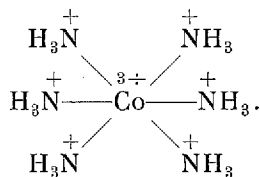
<sup>3</sup> L. WELO, Phil. Mag. **VII**, **6**, 481. 1928.

<sup>4</sup> D. M. BOSE, Zeits. für Phys. **43**, 864. 1927.

\*  $\mu$  is the magnetic moment in Bohr units.

of the van Vleck equation  $\mu = \sqrt{L(L+1) + 4S(S+1)}$  and seems to indicate that the orbital magnetic moment is eliminated — in some cases only in part — by the perturbing effects of the surrounding ions or molecules of the solvent.

The theory of the magnetic properties of the complex compounds has been treated by several authors, i. g. — BOSE<sup>1</sup> and L. PAULING<sup>2</sup> to whom we refer. As the theory has not yet been fully developed we have felt the need of some empirical means of classification. For this reason we have adopted a procedure originally proposed by G. N. LEWIS and later on extensively used by LANGMUIR, SIDGWICK and others. Let us as an example consider the ion  $[\text{Co}(\text{NH}_3)_6]^{3+}$  in which the valencies between Co and  $\text{NH}_3$  from chemical evidence seem to be qualitatively of the same nature as for instance in carbon compounds. If we write the compound  $(\text{NH}_3)_6\overset{3+}{\text{Co}}$ , the central ion will have  $Z = 27 - 3 = 24$  electrons surrounding it. But in this case the  $\text{NH}_3$ 's are chemically saturated and the nature of the bonds remains obscure. If, however, as proposed by LEWIS, we subtract one electron from each of the six  $\text{NH}_3$  and add them to the central ion, we get six unsaturated derivatives —  $\text{NH}_3^+$  of the  $\text{NH}_4^+$ -ion and in the same time a central ion containing  $Z = 24 + 6 = 30$  electrons. The constitution then becomes:



Here the central ion has the "effective atomic number"  $Z = 30$  and the valency  $v = 6$ . We now propose to use

<sup>1</sup> D. M. BOSE, Zeits. für Phys. **35**, 219. 1925.

<sup>2</sup> L. PAULING l. c.

the number  $n = Z + v$  as a number of classification, in our example  $n = 36$ . The usefulness of this method of classification of magnetic data appears in the first place from the fact that, in all cases hitherto investigated, the ion in consideration is diamagnetic when  $n$  is equal to the atomic number of the nearest inert gas.

We have now collected data from the literature on magnetic moments of complex compounds. From these we have in table 1 calculated  $S$  by means of the Bose equation. The  $S$  values given are thus to be considered as empirical constants.  $D$  is the difference between the atomic number of the inert gas and  $n$ .

Table 1.

$n = 33$ $D = 3$	$S$
1. $K_3Cr(CN)_6$	$3.03 \cdot \frac{1}{2}$
2. $Cr(NH_3)_6J_3$	$2.73 \cdot \frac{1}{2}$
3. $\left[ Cr \begin{array}{c} Cl_2 \\ (NH_3)_4 \end{array} \right] J$	$2.93 \cdot \frac{1}{2}$
$n = 34$ $D = 2$	
4. $K_4Cr(CN)_6 \cdot 2H_2O$	$2.44 \cdot \frac{1}{2}$
5. $K_3Mn(CN)_6$	$2.73 \cdot \frac{1}{2}$
6. $Ni(NH_3)_4SO_4$	$1.6 \cdot \frac{1}{2}$
7. $K_2Ni(CN)_4$	0
$n = 35$ $D = 1$	
8. $K_4Mn(CN)_6 \cdot 3H_2O$	$1.23 \cdot \frac{1}{2}$
9. $K_3Fe(CN)_6$	$1.23 \cdot \frac{1}{2}$
10. $Na_3FeF_6$	$4.98 \cdot \frac{1}{2}$
11. $(NH_4)_2 \left[ Fe \begin{array}{c} F_5 \\ H_2O \end{array} \right]$	$5.05 \cdot \frac{1}{2}$
12. $[Cu(NH_3)_4](NO_3)_2$	$1.1 \cdot \frac{1}{2}$

	$n = 36 \quad D = 0$	S
13.	$K_4 Fe(CN)_6$	0
14.	$Na_3 \left[ Fe \begin{array}{c} NH_3 \\ (CN)_5 \end{array} \right]$	0
15.	$Na_4 \left[ Fe \begin{array}{c} NO_2 \\ (CN)_5 \end{array} \right]$	0
16.	$[Co(NH_3)_6] Cl_3$	0
17.	$\left[ Co \begin{array}{c} (NH_3)_5 \\ NO_2 \end{array} \right] S_2O_6 \cdot H_2O$	0
18.	$K_3 Co(CN)_6$	0
	$n = 38 \quad D = \div 2$	
19.	$Ni(NH_3)_6 Br_2$	$2.2 \cdot \frac{1}{2}$
	$n = 54 \quad D = 0$	
20.	$K_4 Mo(CN)_8$	0
21.	$Rh(NH_3)_6 Cl_3$	0
	$n = 84 \quad D = 2$	
22.	$[Pt(NH_3)_4] SO_4$	0
	$n = 86 \quad D = 0$	
23.	$K_4 W(CN)_8$	0
24.	$\left[ Jr \begin{array}{c} (NH_3)_5 \\ NO_2 \end{array} \right] Cl_2$	0
25.	$\left[ Pt \begin{array}{c} (NH_3)_4 \\ Cl_2 \end{array} \right] Cl_2$	0

## Literature to the table:

W. BILTZ, Z. anorg. u. allg. Ch. **170**, 129. 1928. Numbers 1, 5, 7, 9, 13, 18, 20 and 23.

ROSENBOHM, l. c. 2, 3, 6, 12, 16, 17, 19, 22, 24 and 25.

WELO, l. c. 10, 11, 14 and 15.

RHAY and BHAR, J. Ind. Chem. Soc. **5**, 497. 1928 cited in the Tables Annuelles **VIII. 2**, 390. 1931. Substances number: 4 and 8.

This work: 21.

The table shows that, as a whole, a rule may be obtained, which is nearly that proposed by BOSE<sup>1</sup>. The rule is that the number  $D$  multiplied by  $\frac{1}{2}$  gives the empirically determined  $S$ . The rule is by no means exact. We wish especially to point out the enormous deviation of the iron-fluorides.

Furthermore we call attention to the fact that the experimental results of this work prove that the magnetism of the rhodium complexes are in conformity to the rule mentioned above, that when  $D = 0$ , the substance is diamagnetic.

### Chemical Part.

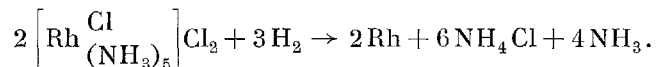
The collection of complex rhodium compounds left by S. M. JØRGENSEN at this laboratory covers about fifty salts, all of which have been prepared by S. M. JØRGENSEN in the years 1882—91. In a series of papers entitled "Beiträge zur Chemie der Rhodiumammoniakverbindungen"<sup>2</sup> S. M. JØRGENSEN has given a detailed account of their preparation and chemical properties. We confine ourselves to pointing out one fact, which is important for the present work in view of the magnetic purity of the substances here measured, namely: — The rhodium metal was cleansed through chloropentamminerhodium chloride, which salt it is easy to obtain in a high degree of purity (S. M. JØRGENSEN used this compound in determining the atomic weight of rhodium); many other complex rhodium compounds were prepared using this compound as a mother-substance. Thirty salts were selected, the crystals of which were well-formed and judging by appearances might be

<sup>1</sup> D. M. BOSE, Zeits. für Phys. **35**, 219. 1925.

<sup>2</sup> I—V J. pr. Ch. **27**, 433. 1883. VI—VIII J. pr. Ch. **34**, 394. 1885. IX J. pr. Ch. **44**, 48. 1891.

supposed to have preserved their composition. However, ten compounds could not be measured because the amount of the substance after having been pulverized turned out to be too small for filling the glass tube. One more compound was omitted because the analysis shewed that the composition differed considerably from that given by its formula. It is interesting to note that so many of these complex salts have preserved their original composition in the fifty years elapsed since their preparation.

The quantitative analysis of the compounds comprises estimations of rhodium, the halogen elements, water and nitrate. The analysis was in most cases performed as a microanalysis. The rhodium compounds here investigated leave after reduction in hydrogen rhodium metal; the process may be represented by the following reaction, taking purpureo-rhodium chloride as an example:



It is possible to estimate in one and the same quantity of substance rhodium and halogen utilizing the wellknown method of Pregl in organic analysis of substances which contain halogen. The substance is weighed out into a porcelain boat and placed in the combustion tube. The pearls of the tube are moistened with a solution of sodium sulphite. A thoroughly purified current of hydrogen is slowly passed through the combustion tube, which finally is heated very cautiously. After cooling, the boat is weighed and the tube washed out. The washing water is evaporated until the volume is 25 cc, and the halogen estimated by Volhard's method. — Blind tests gave no halogen. — Estimations of ammonia gave too low values probably because the ammonia is decomposed in the presence of rhodium.



## The Results of Analysis.

## Chloro-purpureo-compounds.

$\left[ \text{Rh} \begin{smallmatrix} \text{Cl} \\ (\text{NH}_3)_5 \end{smallmatrix} \right] \text{Cl}_2$	Mol. = 294.44	Dried in the air
Substance: 9.905 mg	Rh: 3.641 mg	
— : 9.665 -	- : 3.379 -	0.985 cc 0,1 n AgNO <sub>3</sub>
S. M. J.: 34.99 % Rh	36.09 % Cl	
34.95 —		
35.00 —		
R. W. A.: 34.94 —	35.66 —	
34.96 —		
Calc.: 34.95 —	36.13 —	

$\left[ \text{Rh} \begin{smallmatrix} \text{Cl} \\ (\text{NH}_3)_5 \end{smallmatrix} \right] (\text{NO}_3)_2$	Mol. = 347.55	Dried at 100°
Substance: 9.736 mg	Rh: 2.873 mg	cc. AgNO <sub>3</sub> = 0.272
S. M. J.: 29.89 % Rh	10.09 % Cl	
R. W. A.: 29.51 —	9.91 —	
Calc.: 29.64 —	10.20 —	

$\left[ \text{Rh} \begin{smallmatrix} \text{Cl} \\ (\text{NH}_3)_5 \end{smallmatrix} \right] \text{CO}_3 \cdot \text{H}_2\text{O}$	Mol. = 301.55	Dried at 100°
Substance: 9.674 mg	Rh: 3.277 mg	cc AgNO <sub>3</sub> = 0.319
S. M. J.: 34.00 % Rh		
R. W. A.: 33.87 —	11.68 % Cl	
Calc.: 34.13 —	11.76 —	

$\left[ \text{Rh} \begin{smallmatrix} \text{Cl} \\ (\text{NH}_3)_5 \end{smallmatrix} \right] \text{SO}_4 \cdot \frac{3}{4} \text{H}_2\text{SO}_4$	Mol. 393.15	Dried at 90°
Substance: 9.350 mg	Rh: 2.444 mg	cc AgNO <sub>3</sub> = 0.237
S. M. J.: 26.29 % Rh	8.96 % Cl	
R. W. A.: 26.15 —	8.97 —	
Calc.: 26.18 —	9.03 —	

**Bromo-purpureo-compounds.**

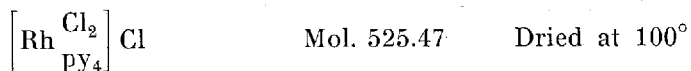
$\left[ \text{Rh} \begin{smallmatrix} \text{Br} \\ (\text{NH}_3)_5 \end{smallmatrix} \right] \text{Br}_2$	Mol. 427.82	Dried at 100°
Substance: 9.554 mg	Rh: 2.307 mg	cc AgNO <sub>3</sub> = 6.631
S. M. J.: 24.08 % Rh	56.00 % Br	
24.14 —		
24.19 —		
R. W. A.: 24.14 —	55.47 —	
Calc.: 24.05 —	56.04 —	

$\left[ \text{Rh} \begin{smallmatrix} \text{Br} \\ (\text{NH}_3)_5 \end{smallmatrix} \right] (\text{NO}_3)_2$	Mol. 392.00	Dried at 100°
Substance: 9.826 mg	Rh: 2.583 mg	cc AgNO <sub>3</sub> = 0.248
S. M. J.: No estimation	20.47 % Br	
R. W. A.: 26.28 % Rh	20.20 —	
Calc.: 26.25 —	20.39 —	

**Jodo-purpureo-compounds.**

$\left[ \text{Rh} \begin{smallmatrix} \text{J} \\ (\text{NH}_3)_5 \end{smallmatrix} \right] \text{J}_2$	Mol. 568.33	Dried at 100°
Substance: 9.476 mg	Rh: 1.709 mg	cc AgNO <sub>3</sub> = 0.495
S. M. J.: 18.22 % Rh	66.82 % J	
R. W. A.: 18.04 —	66.25 —	
Calc.: 18.10 —	66.94 —	

$\left[ \text{Rh} \begin{smallmatrix} \text{J} \\ (\text{NH}_3)_5 \end{smallmatrix} \right] (\text{NO}_3)_2$	Mol. 439.01	Dried at 100°
Substance: 8.649 mg	Rh: 2.035 mg	cc AgNO <sub>3</sub> = 0.194
S. M. J.: No estimation	28.82 % J	
R. W. A.: 23.52 % Rh	28.53 —	
Calc.: 23.44 —	28.91 —	

**Compounds containing Pyridine.**

It was found necessary to carry out a combustion in a current of air before the reduction in hydrogen. This is probably the reason for the rather bad chloride-estimations.

Substance: 7.583 mg    Rh: 1.481 mg    cc AgNO<sub>3</sub> = 0.389

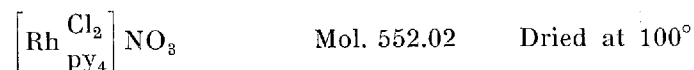
S. M. J.: 19.50 % Rh      20.22 % Cl

19.57 —

19.53 —

R. W. A.: 19.52 —      18.18 —

Calc.: 19.59 —      20.24 —



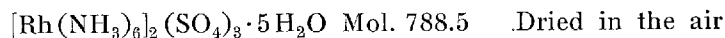
Substance: 8.790 mg    Rh: 1.641 mg    cc AgNO<sub>3</sub> = 0.286

S. M. J.: 18.73 % Rh      12.71 % Cl

18.74 —

R. W. A.: 18.67 —      11.55 —

Calc.: 18.64 —      12.85 —

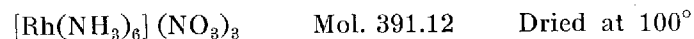
**Luteo-compounds.**

Substance: 9.686 mg    Rh: 2.459 mg

S. M. J.: 26.19 % Rh

R. W. A.: 26.31 —

Calc.: 26.10 —



As it turned out that this substance explodes when heated in the hydrogen current, we carried out the analysis

in the following way: — The substance was weighed out and repeatedly evaporated with HCl; this process converts the salt completely into luteorhodium chloride, which is dried at 100° and weighed. Finally the luteocompound is reduced in hydrogen.

Substance: 0.2139 g luteochloride: 0.1696 g Rh: 0.0563 g  
 S.M.J.: 26.38 % Rh 47.43 % NO<sub>3</sub>  
 R.W.A.: 26.32 — 47.50 —  
 Calc.: 26.31 — 47.56 —

#### Xantho-compounds.

$\left[ \text{Rh} \begin{array}{c} \text{NO}_2 \\ (\text{NH}_3)_5 \end{array} \right] \text{C}_2\text{O}_4$  Mol. 322.08 Dried at 100°

Substance: 6.483 mg Rh: 2.050 mg

S.M.J.: 31.66 % Rh

R.W.A.: 31.61 —

Calc.: 31.95 —

$\left[ \text{Rh} \begin{array}{c} \text{NO}_2 \\ (\text{NH}_3)_5 \end{array} \right] \text{S}_2\text{O}_6 \cdot \text{H}_2\text{O}$  Mol. 412.22 Dried over H<sub>2</sub>SO<sub>4</sub>

Water was estimated by heating at 100°.

Substance: 9.107 mg anhydride: 8.825 mg Rh: 2.313 mg

S.M.J.: 24.96 % Rh 4.40 % H<sub>2</sub>O

R.W.A.: 25.40 — 3.09 —

Calc.: 24.96 — 4.37 —

It is evident that the hydrate has lost water of crystallisation. If we calculate our rhodium analysis to the anhydride we get for  $\left[ \text{Rh} \begin{array}{c} \text{NO}_2 \\ (\text{NH}_3)_5 \end{array} \right] \text{S}_2\text{O}_6$ .

Found: 26.20 % Rh. Calc.: 26.11 % Rh.



sured is placed in a tube of glass which dips into the magnetic field between the pole-pieces of a magnet as

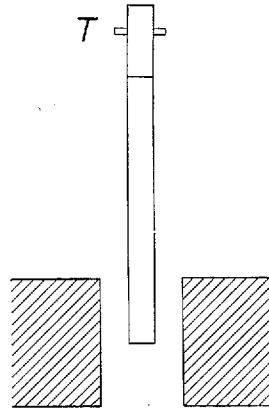


Fig. 1.

shown in Fig. 1. The pull is then measured by weighing. The pull  $F$  is given by:

$$F = \frac{1}{2} A (\kappa_1 - \kappa_2) (H_0^2 - H_1^2)$$

in which equation the meaning of the letters is:

$H_1$  = the field at the upper end of the column of substance

$H_0$  = - - - lower - - - - -

$\kappa_1$  = the volume susceptibility of the substance

$\kappa_2$  = - - - - - air

$l$  = the length of the column

$A$  = the area (cross-sectional) of the column.

We re-write the above expression in the form:

$$\kappa_1 = \kappa_2 + \frac{2F}{A(H_0^2 - H_1^2)}$$

If the weight of the substance is  $p$ , then its density will be  $d = \frac{P}{l \cdot A}$  and we calculate the mass susceptibility of the substance measured:

$$\chi = \frac{z_1}{d} = \frac{z_2 \cdot l \cdot A}{p} + \frac{2 \cdot l}{H_0^2 - H_1^2} \cdot \frac{F}{p}$$

Taking the volume susceptibility of the atmosphere equal to  $0,03 \cdot 10^{-6}$  we get:

$$10^6 \cdot \chi = \frac{0,03 \cdot l \cdot A}{p} + k \cdot \frac{F}{p}$$

$l \cdot A$  is determined by weighing out the tube with water;  $p$  and  $F$  are determined by the process of weighing. The apparatus-constant  $k$  is calculated by means of the results obtained when measurements are carried out with standard-substances of carefully determined susceptibilities.

---

The arrangement of the apparatus is shown in Fig. 2. The balance is a Kuhlmann microbalance (Ultrawaage) with mechanical damping. The balance allows in ordinary analytical weighings an accuracy of 0,0005 mg and it is possible to estimate 0,0003 mg. However, the preciseness of the "magnetical" weighings is only 0,005 mg. The reason is probably to be sought in the suspension mechanism of the tube. The form of this tube is shown in Fig. 1, the taps  $T$  allow the tube to be placed vertically in the field by means of the cardanical suspension-arrangement shown in Fig. 3.  $S_1 L_1 S_2$  is a ring of brass,  $S_1$  and  $S_2$  are two holes into which the stirrup (brass also) fits.  $L_1$  and  $L_2$  are two U-shaped indentations into which the taps  $T$  of

the tube fits. The stirrup is suspended by a 0,1 mm transformer wire from the arm of the balance. All connections are links of copper. The tube is let down into the gap between the pole-pieces through the brass-tube M; the iris diaphragm

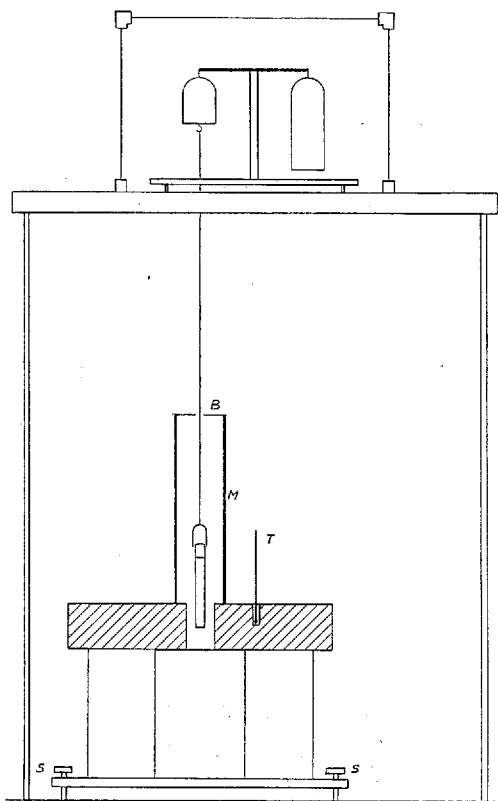


Fig. 2.

B (from an ordinary camera shutter) is then nearly closed. The gap between the pole-pieces is filled out with a copper-block ( $1,5 \times 5 \times 5$  cm) which has a vertical boring for the tube and a horizontal one closed with glasswindows for the observer to ensure that the lower end of the tube is in the



right position in the field. Furthermore, the whole apparatus is placed in a room of mill-board. Panes of glass allow the room to be illuminated from the outside. A piece of pitchblende is placed in the room and also in the balance case in order to eliminate possible electric charges. The pole-pieces were earthed. The screws S (in Fig. 2) allow us to give the magnet such a position that the axis of the brass-tube coincides with the suspension-wire. With regard to the position of the glass-tube in the field we mention that the lower end of the tube is placed 1 mm above the lower horizontal tangent-plane of the above mentioned horizontal, circular boring. However, the measurements have shown that a 1—2 mm's displacement from this position does not influence the results; neither does a  $180^\circ$  rotation about the vertical axis.

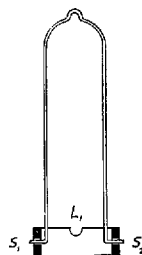


Fig. 3.

The current through the electromagnet is 180 milliamps and is kept constant by means of a variable resistance. Variations in the current are easily observed when watching the swings of the balance through the telescope. In the case of diamagnetic substances which give pulls of the order of 0,3 mg, a variation of  $\pm 1$  milliamp is of no significance. However, variations of this order considerably influence the pull when a paramagnetic substance is measured. The thermometer (T Fig. 2) in the pole-piece did not indicate any increase in the temperature during a measurement.

The mode of procedure in carrying out an experiment is described in the sequel. The glass-tube is cleansed by boiling it with dilute nitric acid, then washed with distilled water and dried by heating in a vacuum. The tube is

finally placed in the suspension arrangement and let down into the gap between the pole-pieces and left for 15 minutes. It is then weighed, the current turned on and weighed again. This process is repeated once more and the resulting pulls averaged. This blank experiment gives the "own pull" of the tube, which is very constant<sup>1</sup>. The finely pulverized substance is placed in the tube. This must be carried out very carefully. The substance is rammed into the tube by means of a glassrod which fits in the tube. Each portion of substance should give a height of 2 mm. The tube is packed until the length of the column corresponds to the calibration mark (72 mm) and is then left in the apparatus for 20 minutes. The tube is then weighed, the current switched on and weighed again. This process is carried out 3 times. The pulls are averaged and the susceptibility calculated. The tube is filled once more with the same substance and the experiment repeated. We quote as an example the observations for Bromo-purpureorhodium nitrate.

Empty tube:	3.153800	3.153796
+ field:	3.153765	3.153759
own pull	÷ 0.035 mg	÷ 0.037 mg
mean	÷ 0.036 mg	

1. Packing                      Temperature 18°,0

Current-Milliamps .....	180.0	180.0	180.0
Tube + substance gr .....	4.212565	4.212560	4.212560
+ field .....	2197	2194	2190
Force mg .....	÷ 0.368	÷ 0.366	÷ 0.370

Mean: ÷ 0.368 mg     $F = \div 0.332 \text{ mg}$      $p = 1.058764 \text{ g}$

Calculation gives  $\chi = \div 0.336 \cdot 10^{-6}$ .

<sup>1</sup> Some preliminary experiments were undertaken with different samples of glass in order to find out which kind of glass gives the smallest pull. It came out that specimens of R<sup>III</sup> were best for our pur-

## 2. Packing Temperature 18° 0

Current-Milliamps .....	179.0	180.0	180.0
Tube + substance gr .....	4.291665	4.291660	4.291662
+ field gr .....	1285	1285	1280
Force mg .....	÷ 0.380	÷ 0.375	÷ 0.382

Mean: ÷ 0.379 mg    F = ÷ 0.347 mg    p = 1.137864 g

$$\chi = \div 0.324 \cdot 10^{-6}$$

Mean value of  $\chi = \div \frac{1}{2} (0.336 + 0.324) \cdot 10^{-6} = \div 0.33 \cdot 10^{-6}$ .

The susceptibilities have been calculated from the equation given above:

$$10^6 \chi = \frac{0,03 \cdot l \cdot A}{p} + k \cdot \frac{F}{p}$$

The tube used in the experiment just stated had  $l \cdot A = 0,832$  cc. This figure emerges as the result of several calibrations, using mercury and water as standard substances. F is given in milligrams and p in grams. k is determined experimentally using as a standard substance  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  for which:

$$\chi_{17^{\circ},3} = 32,57 \cdot 10^{-6} \text{ and } \theta = \div 1 \text{ (Weiss-correction).}^1$$

The susceptibility for this substance is then known at any temperature wanted. It is important that k is a constant and this depends upon how constant  $H_0$  and  $H_1$  are as  $k = \frac{2 \cdot l}{H_0^2 - H_1^2} \cdot H_0$  (between the pole-pieces) is a constant but  $H_1$  decreases outwards. If, however, we use a column of substance sufficiently long  $H_1$  will be negligible compared to  $H_0$ . The sufficient length is determined experimentally.

pose. Later on a sample of glass of unknown origin which had a very small "own pull" was used. We mention that 59<sup>III</sup>, 16<sup>IV</sup> and pyrexglass are diamagnetic and R<sup>III</sup> glass paramagnetic.

<sup>1</sup> JACKSON, Phil. Trans. 1924, A. 224, 1.

The standard substance is filled into the tube and for each portion the pull is measured. The packing is continued until the column is so long that the pull is constant.

Length of column mm	pull mg
7.0	0.003
16.5	0.145
27.5	3.82
41.5	13.81
49.0	14.62
57.0	14.96
65.0	15.04
68.5	15.07
72.0	15.07
78.0	15.07

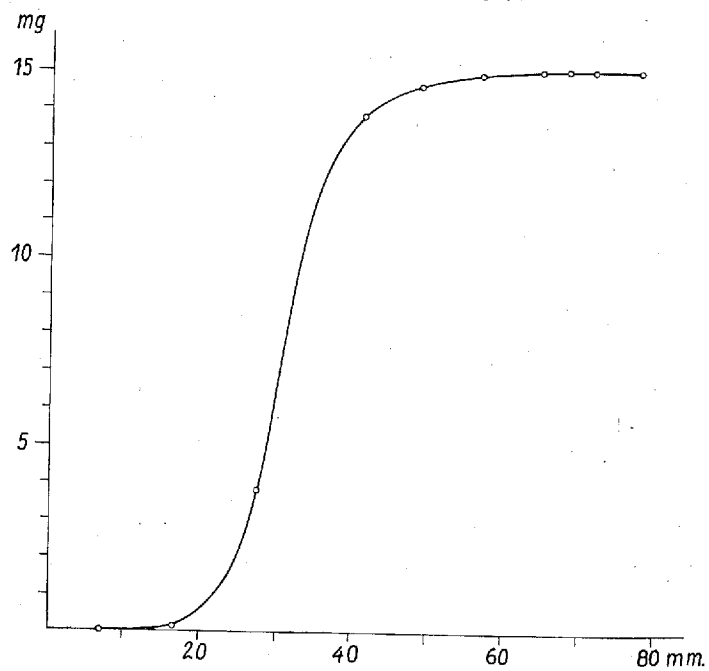


Fig. 4.

The result is shown in the plot Fig. 4. The pull is seen to be constant for lengths exceeding 65 mm. We have used 72 mm as the length of the column of substance for all tubes. Using the same  $l$ , we obtain the same value for  $k$  by different tubes. The value of  $k$  has been determined several times during the work as a control for the constancy of the field.  $k$  has been measured, using different tubes and different degrees of packing of the substance in the tube. The standard substance has been recrystallized twice of water containing sulphuric acid. The analysis gave the theoretical composition.

Values of  $k$ .

Tube 1	1.154	before recrystallization
	1.147	
	1.145	
	1.142	
Tube 2	1.137	
	1.136	
	1.138	

The difference in the values for these two tubes is a consequence of the uncertainty in fixing the calibration mark at 72 mm.  $k$  determinations using redistilled water as a standard-substance in the same tubes gave respectively 1.145 and 1.137. The  $k$  values show the reproducibility of the measurements. We point out that the absolute length of the tube does not influence the results; the measurements are relative.

The results of our measurements are given in the table. We give the calculated susceptibilities and their mean. The susceptibilities are mass susceptibilities according to the

usual custom. (International Critical Tables and Landolt-Börnstein's Tables). The uncertainty is in most cases 4 %.

	Temperature	$\div \chi \cdot 10^6$	$\div \chi \cdot 10^6$ mean	
$\left[ \text{Rh} \begin{array}{c} \text{Cl} \\ (\text{NH}_3)_5 \end{array} \right] \text{Cl}_2$	18°,0	0.443 0.436	0.440	
$\left[ \text{Rh} \begin{array}{c} \text{Cl} \\ (\text{NH}_3)_5 \end{array} \right] (\text{NO}_3)_2$	17°,5	0.316	0.316	
$\left[ \text{Rh} \begin{array}{c} \text{Cl} \\ (\text{NH}_3)_5 \end{array} \right] \text{CO}_3, \text{H}_2\text{O}$	18°,5	0.439 0.442	0.441	
$\left[ \text{Rh} \begin{array}{c} \text{Cl} \\ (\text{NH}_3)_5 \end{array} \right] \text{SO}_4, \frac{3}{4} \text{H}_2\text{SO}_4$	19°,5	0.405 0.397	0.401	
$\left[ \text{Rh} \begin{array}{c} \text{Br} \\ (\text{NH}_3)_5 \end{array} \right] \text{Br}_2$	18°,0	0.336 0.324	0.330	
$\left[ \text{Rh} \begin{array}{c} \text{Br} \\ (\text{NH}_3)_5 \end{array} \right] (\text{NO}_3)_2$	19°,0	0.352 0.309 0.265	} 1	
$\left[ \text{Rh} \begin{array}{c} \text{J} \\ (\text{NH}_3)_5 \end{array} \right] \text{J}_2$	19°,5	0.338 0.347		0.343
$\left[ \text{Rh} \begin{array}{c} \text{J} \\ (\text{NH}_3)_5 \end{array} \right] (\text{NO}_3)_2$	19°,8	0.377 0.387		0.382
$\left[ \text{Rh} \begin{array}{c} \text{NO}_2 \\ (\text{NH}_3)_5 \end{array} \right] \text{C}_2\text{O}_4$	18°,5	0.251 0.244	0.248	
$\left[ \text{Rh} \begin{array}{c} \text{NO}_2 \\ (\text{NH}_3)_5 \end{array} \right] \text{S}_2\text{O}_6 \cdot \text{H}_2\text{O}$	18°,5	0.333 0.337	0.335	

<sup>1</sup> The preparation contained some darker spots. The analysis of the substance gave the composition stated. The reason for the variation is not a finer and finer pulverization, because the effect did not occur with other substances.

	Temperature	$\div \chi \cdot 10^6$	$\div \chi \cdot 10^6$ mean
$\left[ \text{Rh} \begin{array}{c} \text{NO}_2 \\ (\text{NH}_3)_5 \end{array} \right] (\text{NO}_3)_2$	17°,9	0.323	0.318
		0.314	
$\left[ \text{Rh} \begin{array}{c} \text{Cl}_2 \\ \text{PY}_4 \end{array} \right] \text{Cl}$	19°,0	0.509	0.503
		0.497	
$\left[ \text{Rh} \begin{array}{c} \text{Cl}_2 \\ \text{PY}_4 \end{array} \right] \text{NO}_3$	18°,5	0.340	0.341
		0.342	
$\left[ \text{Rh} \begin{array}{c} \text{H}_2\text{O} \\ (\text{NH}_3)_5 \end{array} \right] \begin{array}{c} \text{NO}_3 \\ \text{PtCl}_6 \end{array}, \text{H}_2\text{O}$	19°,5	0.407	0.424
		0.441	
$\left[ \text{Rh} \begin{array}{c} \text{H}_2\text{O} \\ (\text{NH}_3)_5 \end{array} \right] \text{Co}(\text{CN})_6$	19°,5	0.132	0.139
		0.146	
$[\text{Rh}(\text{NH}_3)_6]_2(\text{SO}_4)_3 \cdot 5 \text{H}_2\text{O}$	19°,5	0.402	0.404
		0.406	
$[\text{Rh}(\text{NH}_3)_6](\text{NO}_3)_3$	20°,0	0.352	0.364
		0.376	

All the measurements in this paper have been carried out by R. W. ASMUSSEN.

We desire to thank the Carlsberg Fund for a grant which made possible this work and a work published earlier (R. W. ASMUSSEN: Ueber die Konstitution der Peroxylaminsulfosäure *Z. anorg. u. allg. Ch.* **212**, 317, 1933).

Chemical Dept. A  
of the Royal Technical College,  
Copenhagen.

