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INTRODUCTION

A study of the literature on the magnetic properties of beryllium shows that very little work has been done on the compounds of beryllium; and, in consequence, the recorded data is very sparse. The theoretical work of Angus and Farquerson on the susceptibilities of beryllium compounds suggested the existing values given in the International Critical Tables were inaccurate, and redetermination therefore necessary.

The experimental work of Sugden² on silver compounds, Spencer and Hollens³ on cadmium compounds, and Trew⁴ on thallium compounds has shown that a systematic study of the compounds of any metal is useful in finding the atomic susceptibility of the metal.

The present thesis is an account of the experiments performed to determine the atomic susceptibility of beryllium; but the values for the molecular susceptibilities of the compounds measured do not allow of the deduction of a satisfactory figure for this quantity directly. The unsatisfactory nature of the results for beryllium may be due to:-

- (i) the peculiar position of the element at the head of its group in the Periodic Table

- (ii) the smallness of the ion
 (iii) the tendency of beryllium to
 form basic salts

and further

- (iv) the value for beryllium being a

small one, the accumulation of errors in measurement and the value of the other atoms present in the salt (δ) will all be included in the beryllium value - and so the probability is that the experimental result will be wildly inaccurate.

ANALYSIS

The method of analysis is due to Moore and Seliger. A weighed quantity of the oxide was heated with concentrated sulphuric acid until it was dissolved. The solution was cooled and about 100cc distilled water added and the solution neutralized with ammonia. 40 grams ammonium acetate, 30 grams ammonium nitrate, and 5 grams ammonium phosphate dissolved in the least amount of water were added and the solution brought to the boil. The precipitate was dissolved in 5 per cent nitric acid (about 90cc). Ammonia was added drop by drop until the precipitation of beryllium phosphate was complete.

PREPARATION AND ANALYSIS OF COMPOUNDS

Beryllium Oxide

The oxide was prepared by the method described by Parsons and Bernes.⁵

A solution of beryllium nitrate was heated with ammonia. The precipitated hydroxide was filtered on a Buchner and washed as rapidly as possible with hot water, to prevent the formation of carbonate. The precipitate was transferred to a crucible and heated in an electric furnace for three days, and cooled in a desiccator over caustic soda. Further heat then caused no further loss in weight.

Analysis

The method of analysis is due to Moser and Suiger.⁶ A weighed quantity of the oxide was heated with concentrated sulphuric acid until it was dissolved. The solution was cooled and about 100cc distilled water added and the solution neutralised with ammonia. 40 grammes ammonium acetate, 20 grms ammonium nitrate, and 5grms ammonium phosphate dissolved in the least amount of water were added and the solution brought to the boil. The precipitate was dissolved in 5 per cent nitric acid (about 90cc). Ammonia was added drop by drop until the precipitation of beryllium phosphate was complete.

After standing overnight, the precipitate was filtered into an alundem crucible and washed with 5 per cent ammonium nitrate. After drying, it was heated to redness in a nickel crucible until pure white, when it was all converted to the pyrophosphate.

1.... Weight of beryllium oxide = 0.2041 grm
 Weight of pyrophosphate = 0.7782 grm
%beryllium = 35.84

2.... Weight of beryllium oxide = 0.2656 grm
 Weight of pyrophosphate = 1.0141 grm
%beryllium = 35.85

Be-O requires Be 36.05 per cent

Be(OH)₂ BERYLLIUM HYDROXIDE

The hydroxide precipitated by ammonia from solutions of soluble beryllium salts is not of constant composition and has not the composition corresponding to the formula Be(OH)₂ as stated by Attenberg.⁷

The pure compound was prepared by the method of von Bemmelen⁸ as follows:-

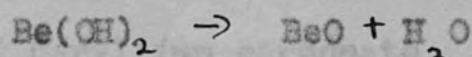
Beryllium hydroxide was precipitated from beryllium sulphate solution by addition of potassium hydroxide solution and dissolved in excess. The solution was then diluted about ten times to two litres and boiled for about an hour. A fine white crystalline precipitate was produced and filtered hot out of contact with

carbon dioxide and washed well with hot water. The boiling was repeated and more hydroxide was thrown down and filtered off. It was thought necessary to remove the hydroxide quickly owing to the rapidity with which it absorbed carbon dioxide. The boiling was repeated about four or five times, a further, though smaller yield, being obtained each time. The hydroxide was dried in a desiccator over caustic soda.

It was shown by the flame test to be free from potassium compounds.

ANALYSIS

Two analyses were made; one by the pyrophosphate method and the other by heating to convert to oxide.



1... Pyrophosphate Method

Weight of hydroxide = 0.2118 gm

Weight of pyrophosphate

= 0.4824 gm

% beryllium = 21.38

$\text{Be}(\text{OH})_2$ requires Be 20.96 per cent

2... Beryllium Oxide Method

(a) Weight of beryllium hydroxide = 0.3842 gm

Weight of beryllium oxide = 0.2262 gm

% beryllium oxide = 58.88

Beryllium oxide method

(b) Weight of beryllium hydroxide	= 0.33394 gm
Weight of beryllium oxide	= 0.1996
<u>% beryllium oxide</u>	<u>= 58.83</u>

$\text{Be}(\text{OH})_2$ requires 58.13 per cent BeO

BERYLLIUM CARBONATE BeCO_3

The specimen used was supplied The British Drug Houses, Ltd., and was analysed and found pure by the pyrophosphate method.

Analysis of beryllium carbonate

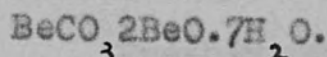
1 Weight of beryllium carbonate	= 0.4812 grm
Weight of pyrophosphate	= 0.6696 grm
<u>% beryllium</u>	<u>= 13.07</u>

2 Weight of carbonate	= 0.4427 grm
Weight of pyrophosphate	= 0.6162 grm
<u>% beryllium</u>	<u>= 13.07</u>

BeCO_3 requires Be 13.07 per cent

BASIC BERYLLIUM CARBONATE $\text{BeCO}_3 \cdot 2\text{BeO} \cdot 7\text{H}_2\text{O}$

The 'beryllium carbonate' supplied by Harrington's proved to be basic. It was, unlike the carbonate, insoluble in ammonium carbonate and had a low beryllium content which after gently drying the salt was found to be constant for a large number of specimens, and to correspond to the compound



This hydrated salt has not previously been described. A similar anhydrous salt, $2\text{BeO} \cdot \text{BeCO}_3$ was prepared by Meyer who measured the susceptibility.

Analysis was made by pyrophosphate method;

1.....	Weight of basic beryllium carbonate	0.3428 gm
	Weight of beryllium pyrophosphate	0.4068 gm
	<u>% beryllium</u>	<u>11.15</u>
2.....	Weight of basic beryllium carbonate	0.3510 gm
	Weight of beryllium pyrophosphate	0.4134 gm
	<u>% beryllium</u>	<u>11.07</u>

$\text{BeCO}_3 \cdot 2\text{BeO} \cdot 7\text{H}_2\text{O}$ requires Be 11.04%

BERYLLIUM BASIC SULPHITE $2\text{BeSO}_3 \cdot \text{BeO} \cdot 7\text{H}_2\text{O}$

The salt was prepared by the method described by Kriss and Moraht⁹ for the preparation of the normal sulphite.

Although Kriss and Moraht state that the normal sulphite can be prepared by this method, repeated attempts with suitable variation of quantities failed to yield the normal salt.

Freshly precipitated beryllium hydroxide was dissolved in alcohol saturated with SO_2 . The solution was evaporated in vacuo over caustic soda and concentrated sulphuric acid. The salt separated out as a white powder, which was rapidly filtered and dried in vacuo over soda and sulphuric acid.

It is stated by Attenberg¹⁰ that if water is present the salt is basic. Experiment proved that this is true, for it is impossible to get freshly precipitated hydroxide dry.

Analysis was made by the pyrophosphate method.

ANALYSIS OF BASIC BERYLLIUM SULPHITE

1 Weight of basic beryllium sulphite = 0.3569 gm

Weight of beryllium pyrophosphate = 0.3076 gm

% beryllium = 8.225 gm

2 Weight of basic beryllium sulphite = 0.3218 gm

Weight of beryllium pyrophosphate = 0.2816 gm

% beryllium = 8.218 gm

$2\text{BeSO}_4 \cdot \text{BeO} \cdot 7\text{H}_2\text{O}$ requires Be 8.295 %

BERYLLIUM CHROMATE TETRAHYDRATE $\text{BeCrO}_4 \cdot 4\text{H}_2\text{O}$

The chromate was prepared by the method described by Glassman (11), which consists in dissolving carbonate or basic carbonate in chromic acid.

The chromic acid used was a saturated solution diluted with an equal quantity of water.

A quantity of carbonate was treated with a slight excess of this acid. The solution was concentrated and yellow crystals formed on cooling. These were recrystallised from water or dilute chromic acid. On heating to 120°C water was given off and a salmon pink solid remained. On further heating a green and white residue remained.- presumably chromium sesquioxide and

beryllium oxide. Addition of alcohol dissolved part of the residue leaving white crystals, the solution being at first yellow and afterwards turning green.

Action of alcohol decomposed the crystals. To the crystals was added 2 - 3 times their own volume of alcohol - a pale green solution being formed and a white residue left. Chromic acid of the same strength as before was added, violent reaction taking place with the production of sparks and much heat. When a considerable quantity of chromic acid had been added a pale green precipitate began to form. This was dissolved in a very small quantity of water - being very soluble in both alcohol and water - and a dark green solution was obtained. Addition of chromic acid was continued until all the white crystals had dissolved. On slight concentration a crop of pale blue crystals were produced. These were soluble in alcohol and water.

Evaporation of the solution on the water bath to a small volume and addition of a little alcohol brought out a crop of green crystals.

These yellow crystals were found to be contaminated with sulphate, so that probably the part insoluble in alcohol consisted entirely of sulphate.

The pure chromate - prepared from chromic acid entirely free from sulphate was very difficult to crystallise, only coming out when the solution was very considerably evaporated. The crystals are very small and brownish orange in colour. They are stable in a desiccator, unlike the mixed sulphate and chromate crystals which on keeping in a desiccator appear to separate in definite white crystals (BeSO_4) and red conglomerates of (Be-CrO_4).

On heating the pure chromate, water was lost and the residue was a dark coloured powder.

Estimation of the water content was made by heating to constant weight at 120°C

Analysis

Weight of hydrated beryllium chromate = 0.3835 gm

Weight after heat = 0.2429 gm

% water = 35.19

Beryllium sulphate. This was recrystallised twice from water and dried at 120°C . $\text{BeCrO}_4 \cdot 4\text{H}_2\text{O}$ requires 36.55% H_2O at this temperature. The salt tends to form supersaturated solutions. Small tetrahedral crystals are formed by cooling the solution in ice and inoculating with a small crystal.

BERYLLIUM PERCHLORATE $\text{Be}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$

The salt was prepared by dissolving beryllium carbonate in perchloric acid. The solution was evaporated and cooled in ice. On stirring, a large mass of small transparent needleshaped crystals separated out. These were filtered on a Buchner and dried in the air.

Analysis was made by the pyrophosphate method.

Analysis

Weight of beryllium perchlorate = 0.3894

Weight of beryllium pyrophosphate = 0.0908

% beryllium = 3.251

$\text{Be}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ requires 3.22%

BERYLLIUM SULPHATE TETRAHYDRATE $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$

The specimen was British Drug Houses'

beryllium sulphate. This was recrystallised twice from water and dried on a porous tile at room temperature. The salt tends to form supersaturated solutions. Small tetrahedral crystals are formed by cooling the solution in ice and innoculating with a small crystal.

If exposed to dry air or heat the salt loses water and disintegrates with formation of lower hydrates.

Analysis

A weighed quantity of the salt was dissolved in water and brought to the boil. Boiling barium chloride solution was added drop by drop until no more precipitate formed. The precipitated barium sulphate was filtered off as rapidly as possible on a sintered glass crucible, washed with boiling water, dried and weighed.

1	Weight of beryllium sulphate	=0.3538 gms
	Weight of barium sulphate	=0.4742 gms
	<u>% sulphate</u>	<u>=55.16</u>

2	Weight of beryllium sulphate	=0.3555 gms
	Weight of barium sulphate	=0.4766 gms
	<u>% sulphate</u>	<u>=55.16</u>

BeSO₄ requires $54.24\frac{1}{2}$ sulphate

ANHYDROUS BERYLLIUM SULPHATE

The recrystallised hydrated salt was heated in a platinum dish at 200°C until no further change in weight occurred.

The white powder which resulted was very hygroscopic but it did not deliquesce. - it was sparingly soluble in water.

ANALYSIS

A weighed quantity of the salt was dissolved in hot water and the boiling solution heated with barium chloride solution until no more barium sulphate precipitated. The sulphate was filtered on a centred glass crucible, dried, and weighed.

1 Weight of beryllium sulphate = 0.3612 grm
 Weight of barium sulphate = 0.5)
 = 0.8086 grm
% sulphate = 92.13

2 Weight of beryllium sulphate = 0.4172 grm
 Weight of barium sulphate = 0.9324 grm
% sulphate = 91.98

BeSO_4 requires Be 91.40%

BERYLLIUM CHLORATE $\text{Be}(\text{ClO}_3)_2 \cdot 9 \text{H}_2\text{O}$

The salt was prepared by dissolving beryllium carbonate in chloric acid (density 1.17) until no more would dissolve. The solution was carefully evaporated on a water bath ^{to $\frac{2}{3}$ its volume}. The solution at this stage was apparently stable. On cooling, very small crystals of the chlorate were formed which were filtered off and dried over calcium chloride. On further evaporation of the mother liquor it exploded, despite the fact that care had been taken to prevent organic dust entering the solution.

The crystals are very small, deliquescent, and appear to melt on pressing. The salt is unstable to heat and decomposed to a canary yellow liquid which smelt of chlorine dioxide at room temperature on a hot day.

Analysis of the water of crystallisation was attempted by exposing to a vacuum. It was found, however, that water and chlorine dioxide were given off at the same time, and, presumably, a residue of oxide. The process is fairly rapid at first but gradually slows down taking months to complete. The

water and chlorine dioxide are absorbed by sodium hydroxide and concentrated sulphuric acid. The solid matter swells considerably, the final residue being a bulky friable mass. However after a year in vacuum, the salt still smelt of chlorine dioxide and was not entirely decomposed.

Analysis was made by the pyrophosphate method, and was attempted without success by dehydration.

ANALYSIS

Pyrophosphate method

1 Weight of beryllium chlorate = 0.5249 gms

Weight of beryllium pyrophosphate = 0.1478 gms

% beryllium = 2.66

2 Weight of beryllium chlorate = 0.5338 gms

Weight of beryllium pyrophosphate = 0.1522 gms

% beryllium = 2.64

$\frac{6\text{Be}(\text{ClO}_6)9\text{H}_2\text{O}}{3 \quad 2}$ requires Be = 2.66 %

ANALYSIS BY DEHYDRATION

Weight of beryllium chlorate = 1.0566 gms

Weight after one year in vacuum = 0.3360 gms

% loss in weight = 68.14

$\text{Be}(\text{ClO})_3 \cdot 9\text{H}_2\text{O}$ requires loss in weight 93.5 %
3 2 2

BERYLLIUM IODATE HEXAHYDRATE $\text{Be}(\text{IO}_3)_2 \cdot 6\text{H}_2\text{O}$

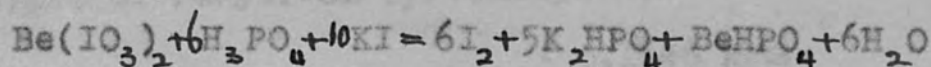
The specimen used was provided by Professor Spencer. It is a light soft mass of flaky crystals pale pink in colour.

On heating, water and iodine are driven off, so that any estimation of the water content was impossible.

ANALYSIS

The salt was analysed volumetrically by estimation of the iodate ion. A known weight of the salt was dissolved in water containing a little phosphoric acid in a standard flask.

25cc portions of this solution were titrated against standardised thiosulphate solution. To each portion 20 cc 2 N phosphoric acid was added and excess KI. The liberated iodine was titrated with thiosulphate solution, starch paste being used as indicator



Strength of thiosulphate solution 0.9982N

Volume of beryllium iodate solution. 25cc

Average volume sodium thiosulphate

solution = 36.83cc

Strength of beryllium iodate solution

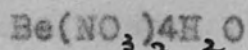
$$= \frac{36.83}{25} \times 0.9982\text{N}$$

$$= 0.5719 \text{ gm BeIO}_3 \cdot 6\text{H}_2\text{O per } 100\text{cc}$$

Weight actually taken 0.5744 gm

Salt 99.57% pure

BERYLLIUM NITRATE TETRAHYDRATE



The specimen used was from Harrington's, recrystallised twice from concentrated nitric acid. Transparent deliquescent crystals formed on vigorously stirring ~~stirring~~ the saturated solution cooled in freezing mixture. The crystals were filtered on a Buchner and dried on a porous tile over calcium chloride. The salt is extremely deliquescent.

Analysis

Analysis was made by the pyrophosphate method

1 Weight of beryllium nitrate = 0.3332 gm

Weight of beryllium pyrophosphate

= 0.1646 gm

% beryllium = 4.59

2 Weight of nitrate = 0.3956 gm

Weight of beryllium pyrophosphate

= 0.1832 gm

% beryllium = 4.35

$\text{Be}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ requires Be 44%

BERYLLIUM AMMONIUM FLUORIDE $\text{BeF}_2\text{NH}_4\text{F}$

Weight The salt was prepared by the method of
J.C.G. de Marignac. (12) $\text{BeF}_2\text{NH}_4\text{F}$

A weighed quantity of basic beryllium carbonate was dissolved by heating with hydrofluoric acid in a platinum dish. When all reaction was finished, an equivalent amount of ammonium fluoride was added.

The solution was evaporated slightly and allowed to crystallise. The supernatant liquid was poured off and the crystals dried at the pump. These were recrystallised from water but a supersaturated solution was easily formed.

ANALYSIS.

In attempting analysis by the pyrophosphate method it appeared that the fluoride ion interfered with proper precipitation.

A weighed quantity of the salt was heated in a platinum crucible with concentrated sulphuric acid. The beryllium was converted to the sulphate and hydrofluoric acid and ammonia driven off.

The sulphate was dissolved in water and analysed in the usual way.

$\text{BeF}_2\text{NH}_4\text{F} \cdot \text{H}_2\text{O}$ requires Be 5.42 %

ANALYSIS

Weight of beryllium ammonium fluoride = 0.3562 gm

Weight of beryllium pyrophosphate = 0.2828 gm

% beryllium

7.450

BeF₂NH₄F requires Be 7.453 %

BERYLLIUM SODIUM FLUORIDE BeFNaFH₂O

This salt was prepared in the same way as the ammonium salt, by adding an equivalent quantity of sodium fluoride in place of ammonium fluoride. The salt described in the literature is anhydrous but as crystallised from water and dried in a desiccator the salt was the monohydrate. This was confirmed by an estimation of the water.

Analysis

Analysis was made by the pyrophosphate method, first converting to the sulphate as before.

1 Weight of sodium beryllium fluoride = 0.5416 gm

Weight of beryllium pyrophosphate = 0.4878 gm

% beryllium

8.458

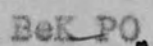
BeF₂NaF·H₂O requires Be 8.43 %

DEHYDRATION

The salt was heated in a platinum crucible in an oven; gently at first, and then more strongly until constant weight was obtained

1	Weight of sodium beryllium fluoride	= 0.2930 gms
	Weight after heating	= 0.2448 gms
	Loss of weight	= 0.0492 gms
	<u>% Loss of weight</u>	<u>= 16.79</u>

$\text{BeF}_2 \cdot \text{NaF} \cdot \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 16.62\%$

BERYLLIUM POTASSIUM PHOSPHATE

A solution of beryllium phosphate prepared by dissolving beryllium carbonate in phosphoric acid was neutralised with caustic potash solution. A crystalline precipitate of beryllium potassium phosphate was thrown down. This was filtered on a Buchner and dried on a porous tile in a warm place.

ANALYSIS

1 Analysis was made by the pyrophosphate method.

	Weight of beryllium potassium phosphate	= 0.3107 gms
	Weight of beryllium pyrophosphate	= 0.2092 gms
	<u>% beryllium</u>	<u>= 6.32 gms</u>

BeK_2PO_4 requires $\text{Be} = 6.30\%$

BERYLLIUM POTASSIUM PHOSPHATE

A solution of beryllium phosphate prepared by dissolving beryllium carbonate in phosphoric acid was neutralised with caustic potash solution. A crystalline precipitate of beryllium potassium phosphate was thrown down. This was filtered on a Buchner and dried on a porous tile in a warm place.

ANALYSIS

- 1 Analysis was made by the pyrophosphate method.
- 1 Weight of beryllium potassium phosphate = 0.3107 gms
 Weight of beryllium pyrophosphate = 0.2092 gms
% beryllium = 6.32
- 2 Weight of beryllium potassium phosphate = 0.4210 gms
 Weight of beryllium pyrophosphate = 0.2804 gms
% beryllium = 6.25

BeKPO requires Be 6.30%

BERYLLIUM SODIUM PHOSPHATE BeNaPO₄

The sodium beryllium salt was prepared in the same way as the potassium double salt - by neutralising a solution of beryllium hydrogen phosphate with sodium hydroxide.

The microcrystalline precipitate of beryllium sodium phosphate was filtered on a Buchner, washed free

from sodium hydroxide and dried on a porous tile in a warm place.

ANALYSIS

Analysis was made by the pyrophosphate method.

1 Weight of sodium beryllium phosphate = 0.6504 gms

Weight of beryllium pyrophosphate = 0.4866 gm

% beryllium = 7.025

2 Weight of sodium beryllium phosphate = 0.5596 gms

Weight of beryllium pyrophosphate = 0.4172 gms

% beryllium = 0.7000

BeNaPO_4 requires Be 7.099 %.

BERYLLIUM PYROPHOSPHATE $\text{Be}_2\text{P}_2\text{O}_7$

The salt was prepared as in the analysis of beryllium salts by heating beryllium ammonium phosphate.

A weighed quantity of this salt was heated in an electric furnace until there was no further change in weight. It was then assumed to be completely changed to the pyrophosphate.

$\text{Be}_2\text{P}_2\text{O}_7$ requires Be 7.387%

BERYLLIUM AMMONIUM PHOSPHATE $\text{Be}_4(\text{NH}_4)_4\text{P}_2\text{O}_7$

The salt was prepared as in the analysis of beryllium salts by the pyrophosphate method.

A solution of dibasic ammonium phosphate was added to a solution of an equivalent amount of beryllium nitrate. Ammonia was added to a white flocculent precipitate of beryllium ammonium phosphate was formed. This was filtered on a Buchner, washed with hot water until free from ammonia and dried on a porous tile in a warm place. It again is a very hard mass which was

ANALYSIS

Analysis was made by the pyrophosphate method.

1. Weight of beryllium ammonium phosphate = 0.3587 gms

Weight of beryllium pyrophosphate = 0.3058 gms

three times % beryllium = 7.388

2. Weight of beryllium ammonium phosphate = 0.4571 gms

Weight of beryllium pyrophosphate = 0.3592 gms

three times % beryllium = 7.378

For some time and then the phosphate separated out as

as $\text{Be}_4(\text{NH}_4)_4\text{P}_2\text{O}_7$ requires Be 7.387% ^{4 4} related to a soft

mass. On cooling and overnight this mass

became hard and crystalline. By adding the carbonate

slowly suspended in water, formation of phosphate

BERYLLIUM HYDROGEN PHOSPHATE BeHPO_4

Many attempts to make beryllium phosphates have been described, and none proved successful.

It was found that if beryllium carbonate is dissolved in an equivalent quantity of phosphoric acid, a glassy mass of phosphate forms round the carbonate and prevents the solution of this. This glassy mass was insoluble in water. On heating it became soft but did not appreciably dissolve. On cooling it set again to a very hard mass which was soluble in any acid.

An attempt was made with more dilute solution to prepare the phosphate. About 20 gms of syrupy phosphoric acid (density 1.75) were dissolved in about three litres of distilled water. The solution was raised to the boiling point and beryllium carbonate mixed to a very thin paste with water was slowly added, stirring all the time. The carbonate dissolved for some time and then the phosphate separated out as a flocculant precipitate which coagulated to a soft mass. On cooling and leaving overnight this mass became hard and crystalline. By adding the carbonate slowly suspended in water, formation of phosphate

round the carbonate is practically prevented.

The phosphate which separates is beryllium hydrogen phosphate. It seems impossible to make the normal phosphate this way.

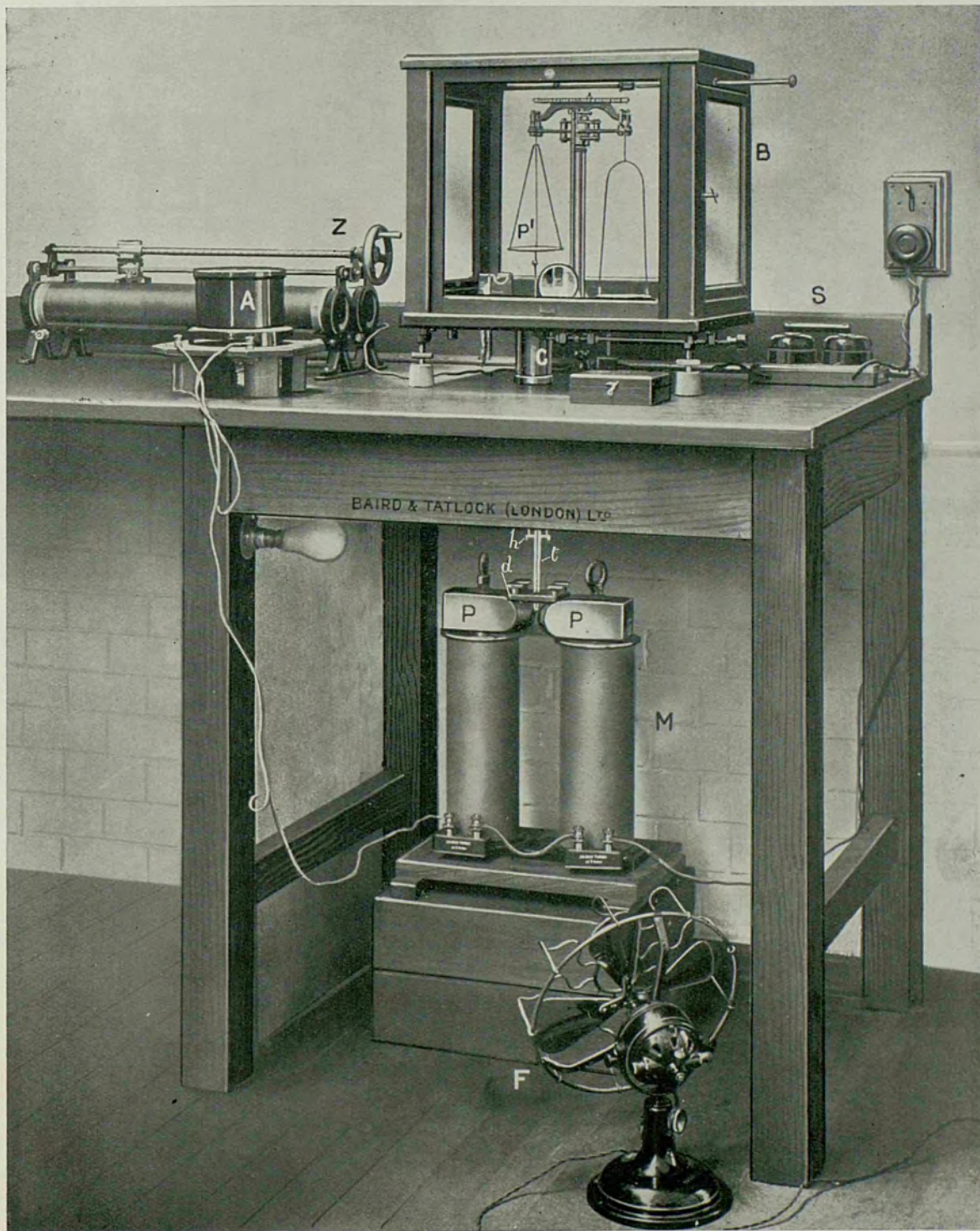
ANALYSIS

Analysis was made by the pyrophosphate method.

1 Weight of beryllium hydrophosphate = 0.4106 gms
 Weight of beryllium pyrophosphate = 0.3742 gms
 % beryllium = 8.56

2 Weight of beryllium hydrogen phosphate = 0.3162 gms
 Weight of beryllium pyrophosphate = 0.2890 gms
 % beryllium = 8.58

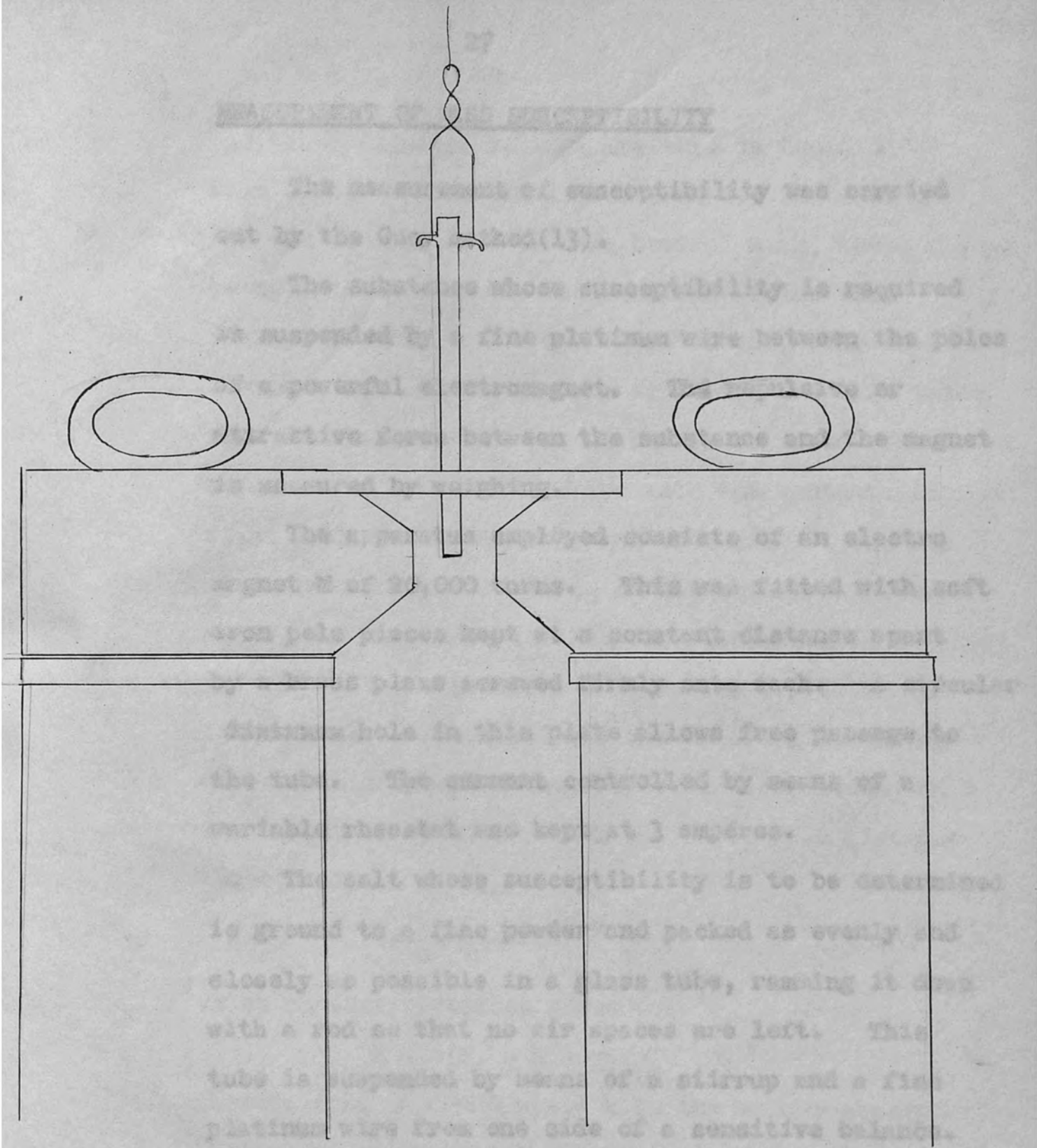
BeHPO_4 requires Be 8.58%



MEASUREMENT OF SUSCEPTIBILITY

The measurement of susceptibility was carried out by the method (13).

The substance whose susceptibility is required is suspended by a fine platinum wire from the poles of a powerful electromagnet.



The salt whose susceptibility is to be determined is ground to a fine powder and packed as evenly and closely as possible in a glass tube, ramming it down with a rod so that no air spaces are left. This tube is suspended by means of a stirrup and a fine platinum wire from one side of a sensitive balance. On this side the scale pan is replaced by a light aluminum support with a hook. The length of the suspension is adjusted so that the bottom of the tube is in the centre of the pole pieces.

DIAGRAM OF APPARATUS

MEASUREMENT OF MASS SUSCEPTIBILITY

The measurement of susceptibility was carried out by the Guoy method(13).

The substance whose susceptibility is required is suspended by a fine platinum wire between the poles of a powerful electromagnet. The repulsive or attractive force between the substance and the magnet is measured by weighing.

The apparatus employed consists of an electro magnet M of 20,000 turns. This was fitted with soft iron pole pieces kept at a constant distance apart by a brass plate screwed firmly onto each. A circular ~~disk~~ hole in this plate allows free passage to the tube. The current controlled by means of a variable rheostat and kept at 3 amperes.

The salt whose susceptibility is to be determined is ground to a fine powder and packed as evenly and closely as possible in a glass tube, ramming it down with a rod so that no air spaces are left. This tube is suspended by means of a stirrup and a fine platinum wire from one side of a sensitive balance. On this side the scale pan is replaced by a light aluminium support with a hook. The length of the suspension is adjusted so that the bottom of the tube is level with a mark at the centre of the pole pieces,

and these adjusted so that the tube is equidistant from each. The field is variable but is constant for 4mm on each side of this central mark, this being greater than the oscillations of the tube during weighing. The apparatus is very sensitive to draughts and is protected by screens; and care taken that the coils do not get so hot as to cause convection currents. The weight of the tube and contents is found with the magnet off, and then with it on, the difference giving the force on the given weight of solid, and the susceptibility is calculated as follows.

If F is the force per unit volume expressed in dynes μ_1 , the permeability of the material in medium of permeability μ_2 , A the area of cross section and l the length of cylinder, then the force F is given by the equation

$$F = \frac{A(\mu_1 - \mu_2)}{8\pi} \int_{H_2}^{H_1} H dl.$$

which an interpretation gives

$$F = A(H_1^2 - H_2^2) \frac{\mu_1 - \mu_2}{8\pi}$$

Substituting $\mu_1 = 1 + 4\pi k$ where k is the volume susceptibility of the material and k_2 that of the medium

$$F = \frac{1}{2}(k_1 - k_2) A (H_1^2 - H_2^2)$$

The cylinder is taken of such length that the upper end is in the zero field, i.e. $H_2 = 0$

$$k = \frac{2F}{AH} + k_2$$

But since $\frac{k}{d} = \chi$ & $d = \frac{W}{AL}$

$$\chi = \frac{2Fl}{WH_2} + \frac{Alk_2}{W}$$

Since measurements are made in air

$$k = -0.03 \times 10^{-6}$$

$$\chi = \frac{2Fl}{WH_2} + \frac{0.03Al}{W} \times 10^{-6}$$

Since l is constant and H_2 is also constant,

$\frac{l}{H_2}$ is a constant factor (α). Including these constant

values and the factors for the units used (F in

milligrams, W in grams, l & A in cms and square cms.)

the equation reduced to

$$\chi = \frac{\alpha F}{W} + \frac{0.03 l A}{W}$$

where

$$\alpha = \frac{2l \times 10^6 \times 981}{H_2^2 \times 1000}$$

in c.g.s. units

DETERMINATION of α 30

The balance constant α is determined by using a substance of known susceptibility.

Since the pull on the tube is not negligible, this is first determined. The pull does not alter, as shown by repeating this determination at intervals.

Having found the weight and pull of the tube the volume is found by filling to the mark with pure water and weighing, the volume being found from the density of water at that temperature.

The tube was then filled to the mark with redistilled A.R. benzene, ($\chi = .712 \times 10^{-6}$) and α found by substitution in the formula.

	$(.712 + \frac{0.30 \times 1A}{W})w$	
	$\alpha = \frac{\text{---}}{\text{---}}$	
5.77737 gms	5.77757 gms	-0.000180 gms
	F	
5.77763 gms	5.77701 gms	+0.00062 gms
5.77721 gms	5.77741 gms	-0.00020 gms
5.77722 gms	5.77741 gms	-0.00019 gms
		Mean -0.000180 gms

PULL OF THE TUBE

<u>WT. OUT OF FIELD</u>	<u>WT. IN FIELD</u>	<u>PULL</u>
4.50387 gms	4.50364 gms	-0.00023 gms
4.50394 gms	4.50370 gms	-0.00024 gms
4.50400 gms	4.50375 gms	-0.00025 gms
4.50395 gms	4.50373 gms	-0.00022 gms
4.50393 gms	4.50369 gms	-0.00024 gms
4.50385 gms	4.50360 gms	-0.00025 gms
		<u>Mean 0.00024</u>

PULL ON TUBE OF BENZENE

<u>WT. OUT OF FIELD</u>	<u>WT. IN FIELD</u>	<u>PULL</u>
5.77737gms	5.77557 gms	-0000180 gms
5.77783gms	5.77101 gms	-0.00182 gms
5.77721gms	5.77241 gms	-0.00180 gms
5.77722gms	5.77541 gms	-0.00180 gms
		<u>Mean -0.00180gms</u>

Pull due to benzene = 1.56 mgs

weight of water = 1.4432 gms

density = 0.9976 gm/cc

volume of tube = 1.446 cc

weight of benzene 1.2727

$$\alpha = \frac{(1A \times \frac{0.30}{1.273} + .712) 1.273}{F} = \frac{(\frac{1.446 \times 0.30}{1.2727} + .712) 1.273}{1.56}$$

$$= \underline{0.607}$$

The value of the susceptibility χ is then found by determining the pull on a weight of the material filling the tube when tightly packed to the same mark and substituting in the formula

$$10^6 \chi = \frac{F}{w} + \frac{0.03 \times 1A}{w}$$

In the following tables the first column contains the weight of the salt w , the second the three values of the pull determined on the packing, the third the mean pull minus the pull on the tube F . the fourth the value of χ found by substituting in the formula and the last the mean value of χ multiplied by the molecular weight giving χ_m the molecular susceptibility.

DETERMINATION OF MASS SUSCEPTIBILITY 10^6

~~BERYLLIUM HYDROXIDE Be(OH)₂~~
 BERYLLIUM OXIDE BeO

WEIGHT (Gms)	FULL (mgs)	CORRECTED FULL (mgs)	CORRECTED PULL (mgs)		
	1.10	2.78			
3.227	1.00	2.74	2.25	0.0.482	
	1.00	2.76			
		2.87			
3.410	0.90	2.90	2.35	0.479	12.11
		2.83			
1.078	0.90				
	0.94		0.69	0.428	
		2.76			
3.265	1.00	2.81	2.30	0.490	
1.212	0.90	2.85	0.74	0.408	17.81
	0.98				
	1.05				
1.280	1.06		0.82	0.421	
	1.06				
	1.03				
1.234 (1 6.9)	1.03		0.78	0.413	
	1.01				

~~10^6~~ ~~10^6~~ ~~10^6~~

BERYLLIUM HYDROXIDE $\text{Be}(\text{OH})_2$

WEIGHT (gms)	PULL (mgs)	CORRECTED PULL (mgs)	+10⁶	-10⁶
	1.10			
1.355	1.05	0.83	0.402	
	1.07			
	0.94			
1.075	0.90			
1.709	0.94	0.69	0.428	30.5
	1.01			
1.212	0.94	0.74	0.405	17.81
1.874	0.98	0.97	0.442	
	1.05			
1.280	1.06	0.82	0.421	
	1.08			
	1.03			
1.234 (1 6.9)	1.03	0.78	0.413	
	1.01			

BERYLLIUM CARBONATE BeCO_3

WEIGHT (gms)	PULL (mgs)	CORRECTED pull (mgs)	-10⁶	-10⁶
	1.47			
1.554	1.49	0.92	0.447	
	1.49			
	1.58			
1.709	1.53	0.99	0.441	30.5
	1.57			
	1.55			
1.674	1.53	0.97	0.442	
	1.54			

BASIC BERYLLIUM CARBONATE $\text{BeCO}_3 \cdot 2\text{BeO} \cdot 0.7\text{H}_2\text{O}$

WEIGHT (gms)	PULL (mgs)	CORRECTED PULL (mgs)	-10⁶	-10⁶ ₁₇
	1.90		-10⁶	-10⁶
2.081	1.97	1.42	0.496	
	1.92			
		1.16	0.513	
	2.06			
2.201	1.97			
		1.56	0.510	124.5
	2.18			
		1.16	0.509	168.1
	1.93			
2.052	2.10	1.50	0.517	
	2.00			
		1.14	0.509	
	1.97			

BASIC BERYLLIUM SULPHITE $\text{BeO}_2\text{BeSO}_3 \cdot 7\frac{1}{2}\text{H}_2\text{O}$

WEIGHT (gms)	PULL (mgs)	CORRECTED PULL (mgs)	$-10^6 \times$	$-10^6 \times$
	1.50			
1.581	1.46	1.16	0.513	
	1.49			
	1.47			
1.573	1.47	1.15	0.509	168.1
	1.47			
	1.44			
1.577	1.48	1.14	0.505	
	1.47			

BERYLLIUM CHROMATE TETRAHYDRATE $\text{BeCrO}_4 \cdot 4\text{H}_2\text{O}$

WEIGHT (grs)	PULL (mgs)	CORRECTED PULL (mgs)	$-10^6 \times$	$-10^6 \times$
	1.09			
1.678 (1 6.3)	1.14 1.1 1	0.79	0.332	
	1.12			
1.701 (1 6.5)	1.11 1.12	0.80	0.332	63.2
	1.08			
1.656 (1 6.3)	1.02 1.04	0.76	0.330	

BERYLLIUM SULPHATE TETRAHYDRATE $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$

WEIGHT (gms)	PULL (mgs)	CORRECTED PULL (mgs)	
	3.68		
4.102	3.66	3.10	0.514
	3.63		
	3.56		
4.020	3.56	3.00	0.511
	3.57		
	3.63		
4.078	3.66	3.07	0.516
	3.63		

BERYLLIUM PERCHLORATE TETRAHYDRATE $\text{Be}(\text{ClO}_3)_2 \cdot 4\text{H}_2\text{O}$

WEIGHT (gms)	PULL (mgs)	CORRECTED PULL(mgs)	-10 ⁶ X	-10 ⁶ X
	1.58			
2.050	1.57	1.27	0.32	0.430
	1.61			
	1.75			
2.314	1.73	1.42	0.32	0.424
	1.74			120.1
	1.89			
2.471	1.83	1.55	0.32	0.432
	1.90			

ANHYDROUS BERYLLIUM SULPHATE BeSO_4

WEIGHT (gms)	PULL (mgs)	CORRECTED PULL (mgs)	-10⁶	-10⁶ _u
	2.34			
3.859	2.32	1.77	0.325	
	2.34			
	2.22			
3.811	2.25	1.72	0.322	34.05
	2.23			
	2.18			
3.729	2.12	1.63	0.325	
	2.14			

Beryllium Chlorate Monohydrate $\text{Be}(\text{ClO}_3)_2 \cdot 9\text{H}_2\text{O}$

WEIGHT (gms)	PULL (mgs)	CORRECTED PULL (mgs)	-10	-10	-10
	1.70				
2.229	1.82	1.48	0.457		
	1.90				
	1.86				
2.306	1.82	1.51	0.451		152.8
	1.82				
	1.85				
2.363	1.87	1.53	0.446		
	1.84				

BERYLLIUM IODATE HEXAHYDRATE $\text{Be}(\text{IO}_3)_2 \cdot 6\text{H}_2\text{O}$

WEIGHT (gms)	PULL (mgs)	CORRECTED PULL(mgs)	-10⁶	-10⁶
	3.82			
	2.55			
4.744	3.74	3.24	0.165	
4.301	2.49	2.01	0.328	
	3.66			
	2.53			
	3.72			
4.638	3.02	3.20	0.470	
5.404	3.12	2.52	0.322	151.8
	2.96			
	3.56			
4.504	3.00	3.08	0.488	
5.152	2.90	2.42	0.326	
	2.90			

BERYLLIUM NITRATE TETRAHYDRATE $\text{Be}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

WEIGHT (gms)	PULL (mgs)	CORRECTED PULL(mgs)	$-10^6 \chi$	$-10^6 \chi_{17}$
	3.82			
4.744	3.74	3.24	0.465	
	3.66			
	3.72			
4.638	3.72	3.20	0.470	95.94
	3.70			
	3.56			
4.504	3.58	3.08	0.468	
	3.64			

BERYLLIUM AMMONIUM FLUORIDE $\text{BeF}_2 \cdot 2\text{NH}_4\text{F}$

WEIGHT	PULL	CORRECTED	$-10^6 \chi$	$-10^6 \chi_M$
	4.13			
4.326	4.11	3.61	0.564	
	4.12			
	4.03			
4.271	4.01	3.51	0.556	55.87
	4.02			
	4.15			
4.352	4.15	3.64	0.560	
	4.14			

BERYLLIUM SODIUM FLUORIDE $\text{BeF}_2 \cdot \text{NaF} \cdot \text{H}_2\text{O}$

WEIGHT (gms)	PULL (mgs)	CORRECTED PULL (mgs)	$+10^6 \times$	$-10^6 \times$
	4.00			
5.199	3.97	3.46	0.451	
	3.97			
	3.90			
5.095	3.91	3.39	0.452	48.26
	3.90			
	3.91			
5.102	3.94	3.39	0.451	
	3.85			

BERYLLIUM CHLORIDE TETRAHYDRATE $\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$

WEIGHT (gms)	PULL (mgs)	CORRECTED PULL (mgs)	-10 ⁶ X	-10 ⁶ X ₁₇
	2.08			
1.983	2.02	1.72	0.594	
	2.01			
	2.24			
2.069	2.23	1.91	0.608	91.65
	2.22			
	2.22			
2.125	2.21	1.90	0.605	
	2.22			

BERYLLIUM SODIUM PHOSPHATE BeNaPO_4

WEIGHT (gms)	PULL (mgs)	CORRECTED PULL(mgs)	-10⁶	-10⁶ ₇
	1.51			
1.697	1.57	1.20	0.507	
	1.50			
	1.43			
1.640	1.52	1.18	0.505	63.81
	1.59			
	1.53			
1.741	1.58	1.23	0.506	
	1.58			

BERYLLIUM POTASSIUM PHOSPHATE BeKPO₄

WEIGHT (gms)	PULL (mgs)	CORRECTED PULL (mgs)	-10 ⁶ X	-10 ⁶ X _П
	1.79			
1.939	1.77	1.29	0.489	
	1.83			
	1.70			
1.850	1.75	1.21	0.484	69.00
	1.70			
	1.75			
1.939	1.78	1.24	0.473	
	1.73			

BERYLLIUM AMMONIUM PHOSPHATE BeNH_4PO_4

WEIGHT (gms)	PULL (mgs)	CORRECTED PULL (mgs)	$-10^6 \chi$	$-10^6 \chi$
	1.76			
1.593	1.70	1.21	0.562	
	1.72			
	1.86			
1.759	1.85	1.35	0.561	68.90
	1.87			
	2.01			
1.879	1.96	1.48	0.564	
	1.99			

BERYLLIUM HYDROGEN PHOSPHATE BeHPO_4

WEIGHT (gms)	PULL (mgs)	CORRECTED PULL(mgs)	-10'X	-10'X
	2.14			
3.402	2.13	1.63	0.344	
	2.14			
	2.06			
3.324	2.08	1.55	0.336	35.70
	2.05			
	2.14			
3.431	2.12	1.63	0.340	
	2.17			

BERYLLIUM PYROPHOSPHATE $\text{Be}_2\text{P}_2\text{O}_7$

WEIGHT (gms)	PULL (mgs)	CORRECTED PULL (mgs)	$-10^6 \chi$	$-10^6 \chi$
	0.90	0.443	30.50	
4.291	0.94	0.39	0.083	
	0.88	0.324	34.10	
	0.85	0.451	48.24	
	0.86	0.560	35.87	
4.329	0.86	0.35	0.076	15.20
	0.87	0.568	35.90	
	0.80	0.482	69.00	
	0.80	0.804	51.65	
	0.80	0.314	90.58	
4.239	0.88	0.34	0.079	15.20
	0.87	0.232	65.20	
		0.464	95.90	
		0.489	120.10	
		0.507	124.50	
		0.509	165.10	
		0.451	158.80	
		0.526	151.80	

TABLE 1

SUBSTANCE	At.No:	$-10^6 \chi$	$-10^6 \chi_{\text{M}}$
BeO	12	0.483	12.11
Be(OH) ₂	22	0.414	17.81
BeCO ₃	34	0.443	30.50
BeHPO ₄	52	0.340	35.70
BeSO ₄	52	0.324	34.10
BeF ₂ · NaF · H ₂ O	52	0.451	48.26
BeF ₂ · 2NH ₄ F	62	0.560	55.87
BeNH ₄ PO ₄	62	0.562	68.90
BeNaPO ₄	62	0.506	63.81
BeKPO ₄	70	0.482	69.00
BeCl ₂ · 4H ₂ O	78	0.604	91.65
BeSO ₄ · 4H ₂ O	92	0.514	90.98
Be ₂ P ₂ O ₇	94	0.079	15.20
BeCrO ₄ · 4H ₂ O	100	0.332	63.20
Be(NO ₃) ₂ · 4H ₂ O	106	0.464	95.90
Be(ClO ₃) ₂ · 4H ₂ O	142	0.429	120.10
BeCO ₃ · BeO · 7H ₂ O	125	0.507	124.50
2BeSO ₃ · BeO · 7H ₂ O	170	0.509	168.10
Be(ClO ₃) ₂ · 9H ₂ O	176	0.451	152.80
Be(IO ₃) ₂ · 6H ₂ O	218	0.326	151.80

DISCUSSION OF RESULTS

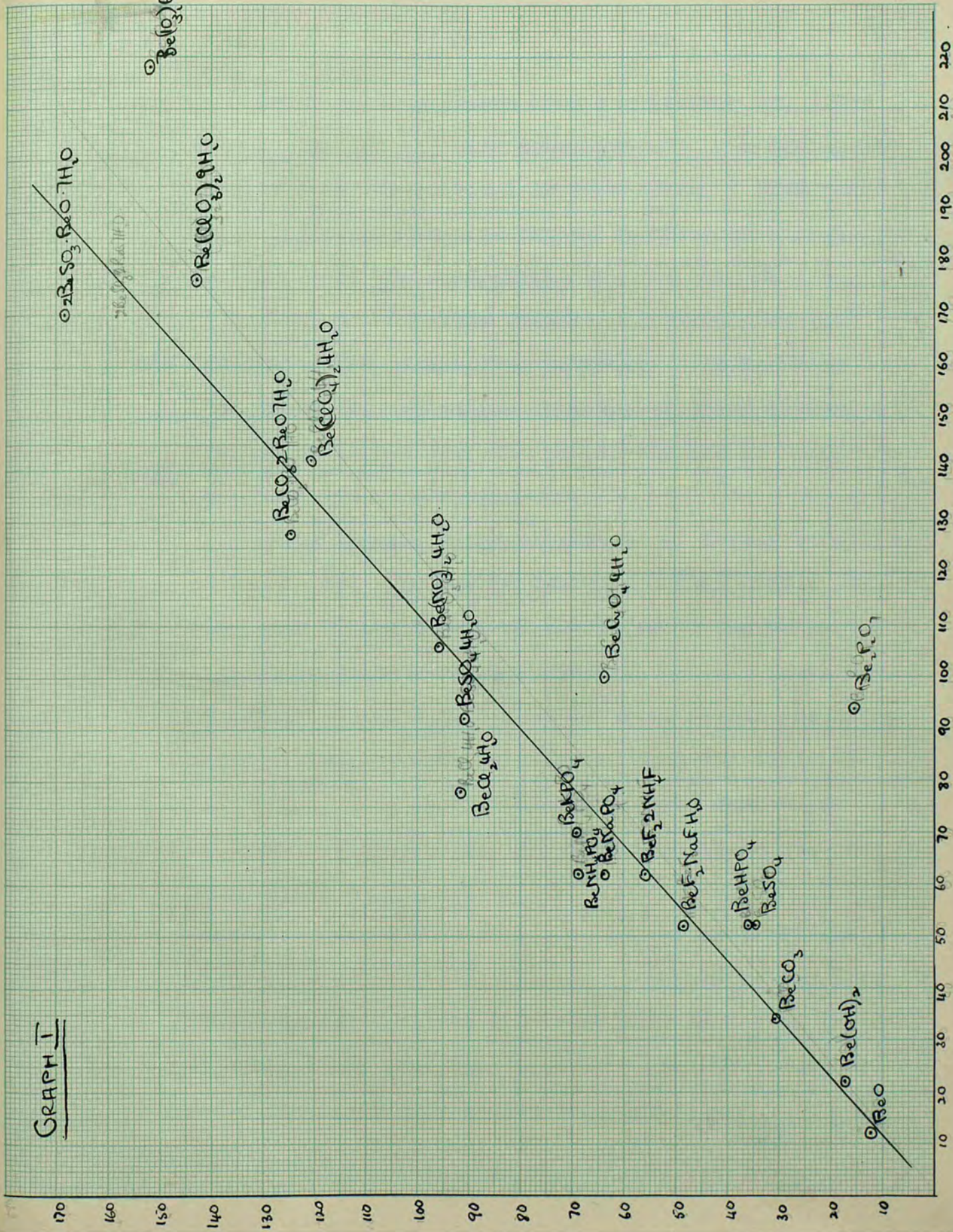
The molecular diamagnetic susceptibility of a solid polar compound may be regarded as the sum of the susceptibilities of the ions which comprise it. For a free spherical ion the susceptibility may be theoretically found from Langevin's equation:

$$\chi_n = -\frac{e^2 h^2}{6mc^2} \sum_n \bar{r}^2 = -2.83 \times 10^{10} \sum_n \bar{r}^2$$

where $\sum_n \bar{r}^2$ on the classical theory is the mean square radius summed for all the electrons in the atom or ion.

Since this equation holds only for spherical and free ions it is never in exact agreement with experimental values. In the solid salts the ions are modified by the presence of neighbouring ions of different charge and the orbits deformed to some extent, thereby altering $\sum_n \bar{r}^2$. Since the outer shell of electrons which contributes most of the susceptibility is most disturbed, the susceptibility of an ion is much less than would be supposed from Langevin's equation. The modification of the ionic radius by the co-ordination number (i.e. the number of ions of opposite sign surrounding the ion in question) decreased the interionic distance with decreasing co-ordination no: Since with divalent ions, the number of ions of opposite sign surrounding the given ion is less, a decrease of diamagnetic susceptibility is to be expected.

GRAPH I



Polar salts approach more nearly than any other ions to the ideal; with covalent compounds the agreement with the theoretical is even worse. With polar salts the susceptibility may be regarded as approximating to the sum of the susceptibilities of the two ions. With covalent compounds this is not valid, and the additivity law breaks down entirely. It has also been found that molecules of water of crystallisation frequently do not obey the additivity law if there are more than two in the molecule.

The molecular susceptibilities of twenty beryllium compounds are recorded in Table 1. They show a steady rise with rising number of electrons in the molecule. A graph of molecular susceptibility against total number of electrons shows that most of these points lie on or about a straight line, indicating that the susceptibility increases an approximately equal amount per electron, without regard for what atom it is attached to (Graph 1)

With a series of compounds of any metal if the Langevin equation is applicable it should be possible to determine the ionic susceptibility of the positive ion by subtracting from the molecular susceptibility the ionic susceptibility of the negative radical. As has

TABLE 2

COMPOUND	At: No:	10	-10	-10	-10
Monovalent anions					
Be(OH) ₂	22	0.414	17.81	15.3	-2.51
BeF ₂ 2NH ₄ F	62	0.560	55.87	49.2	-6.67
BeF ₂ NaFH ₂ O	52	0.451	48.26	37.3	-11.0
BeCl ₂ 4H ₂ O	78	0.604	91.65	92.0	+0.35
Be(NO ₃) ₂ 4H ₂ O	106	0.464	95.90	88.0	-7.9
Be(ClO ₄) ₂ 9H ₂ O	176	0.451	152.8	169.0 ^{xy}	+16.2
Be(IO ₃) ₂ 6H ₂ O	218	0.326	151.8	172.8 ^y	+21.0
Be(ClO ₄) ₂ 4H ₂ O	142	0.429	120.1	111.2 ^y	-8.8
Divalent anions					
BeO	12	0.483	12.11	4.61	-7.50
BeCO ₃	34	0.443	30.5	28.0	-2.5
BeSO ₄	52	0.324	34.1	37.0 ^x	+2.95
BeSO ₄ 4H ₂ O	92	0.514	90.98	89.0	-1.98
BeCrO ₄ 4H ₂ O	100	0.332	+63.2	19.0 ^y	-44.2
				16.8	-46.4
BeCO ₃ BeO 7H ₂ O	128	0.507	124.5	123.6	-0.9
2BeSO ₄ BeO 7H ₂ O	170	0.509	168.1	140.2	-27.9
Trivalent anions					
BeHPO ₄	52	0.340	35.7	38.4	-2.7
BeNaPO ₄	62	0.506	63.81	40.8	-23.0
BeNH ₄ PO ₄	62	0.562	68.9	47.4	-21.5
BeKPO ₄	70	0.482	69.0	53.9	-5.1
Be ₂ PO ₇	94	0.079	15.2		

already been stated, work on silver, cadmium and thallium yielded a series of results agreeing more or less closely, and from which an average might be taken.

In Table III an attempt has been made to calculate the susceptibility of the beryllium in this way. The values (δ) for the negative ion are mostly taken from The International Critical Tables; but those marked x are due to Suggen and y to Trew. As is quite obvious from the last column of Table 2, this method gives no satisfactory result for the beryllium ion. The failure to get any result for the beryllium ion may be due to the presence of large amounts of water of crystallisation and also the tendency to form basic salts which are naturally covalent. In the formation of covalent salts the orbits are increased in size and therefore a larger result would be obtained. If the molecules of water of crystallisation were attached to the positive ion, this would also have the effect of increasing the ionic radius and hence the susceptibility. If covalency or any of these other factors is present the Langevin equation cannot be applied strictly. It may also be noted that the theoretical ionic susceptibility of beryllium, since the ion is so small, would be very small, and hence any deviation from the theoretical appears a much larger percentage error than in any of the series of the compounds yet measured.

It is shown by the Langevin equation that the ionic susceptibility depends on $\sum r^2$ for the different groups of electron in each ion. This value has been calculated by Pauling, (14) Hartree, (15) and Slater (16). Pauling's value was obtained from screening constants and hence the effective nuclear charge for the different groups of electrons. The ionic susceptibility is calculated from the equation

$$\chi_A = -0.81 \times 10^{-6} \sum \frac{n^2}{Z^2} \left\{ \frac{5}{2} n^2 - \frac{31(1+l)}{2} - 1 \right\}$$

where l is the orbital quantum number. This method however involves a number of approximations. Hartree's method is one of a self consistent field for spherically symmetrical ions. In this the charge distribution satisfying the Schrödinger equation of wave mechanics is worked out. He has shown that for a number of atoms or ions the curve showing the charge per unit radial distance (in a spherical shell of unit thickness) is a function of the distance from the nucleus. Stoner (17) has calculated the diamagnetic susceptibility, using Hartree's method from the equation

$$\chi_A = -2.85 \times 10^{-6} \int_0^{\infty} r^2 \frac{dN}{dr} dr.$$

Slater's method is from space charge distribution also, using the wave function of an electron in a symmetrical form. Using this expression Brindley has calculated the susceptibility of a large number of atoms and ions, his results showing good agreement with

with experimental, particularly, however, with large values of \bar{r}^{-2}

Using Slater's rules the theoretical ionic susceptibility of the beryllium ion may be calculated. The screening constant for each electron consists of contributions from all other electrons both in the same group and in groups of lower quantum number. From this the value of the mean square radius, \bar{r}^{-2} is calculated from the equation

$$\bar{r}^{-2} = \frac{n'^2 (n' + \frac{1}{2}) (n' + 1)}{(Z - S)^2}$$

where n = effective principal quantum number

Z = atomic number

S = derived from screening constant for each electron

$(Z - S)$ = effective nuclear charge for each electron

Slater's rules are as follows:-

For s and p electrons in the same group $S = 0.35$

$S = 0.50$ when
in the 2s orbit

For s and p electron in higher groups $S = 0.00$

lower groups $S = 0.85$ where

$$n' = (n - 1)$$

$S = 1.00$ for
all
lower groups

IONS	FORMULA	Coand F.J.O.S.	W.R.A.	Exptl
Be ⁺	For the beryllium ion there are two electrons in the group Z=4	18.78	18.7	18.11
Be ²⁺	Be(OH) ²⁺	23.64	26.68	22.85
	n' = 1.0 s = 0.30			17.81
Be ²⁺		28.2	40.98	34.28
	$\sum \bar{r}^2 = \frac{2 \times 1 \times 1 \frac{1}{2} \times 2}{(4 - 0.30)^2} = \frac{6}{(3.70)^2}$			30.50
Be ²⁺	BeO	138.4	158.0	136.2
	$\sum \bar{r}^2 = 0.438$ (- this value is in atomic units)			124.80
Be ²⁺	7(OH) ²⁺			

Brindley has shown that the gram ionic susceptibility is calculated from the equation

$$10^6 \chi_{ion} = -0.790 \times \sum \bar{r}^2 \quad (\text{in atomic units})$$

By substitution

$$10^6 \chi_{Be} = -0.790 \times 0.438$$

$$-10^6 \chi_{Be} = 0.346$$

Now by the same rules consider the beryllium atom.

There are 4 electrons, 1s² where s = 0.30 n' = 1

2s² where s = 0.85 n' = 2

For 1s group as before $\sum \bar{r}^2 = 0.438$

$$\text{For } 2s \sum \bar{r}^2 = \frac{2 \times 4 \times 2 \frac{1}{2} \times 3}{(1.95)^2} = 15.79$$

$$\text{Total } \sum \bar{r}^2 = 16.23$$

$$10^6 \chi_{Be} = 0.790 \times 16.23 = 12.47$$

Now consider fully co-ordinated beryllium, having 8

electrons in the 2s group

$$\sum \bar{r}^2 = \frac{8 \times 4 \times 2 \frac{1}{2} \times 3}{(1.95)^2} = 63.60$$

$$-10^6 \chi = 50.24$$

TABLE 4 CONTINUED

IONS		FORMULA	Gaand	F.J.C.S.	W.R.A.	Exptl
Be	+0	BeO	12.94	13.5	11.6	12.11
Be	+0	Be(OH) ₂	25.54	26.65	22.85	17.81
Be	+0	BeCO ₃	38.2	40.95	34.25	30.50
Be	+0	BeCO ₃ · 3H ₂ O	152.4	159.0	136.2	124.50
2Be	+20	BeO · 7H ₂ O				
7(2H)	+0					
2Be	+2S	2BeSO ₄ · 3H ₂ O	205.61	170.01		168.8
7(H)	+0	BeO · 7H ₂ O				
Be	+S	BeSO ₄	52.14	54.36	46.6	34.1
Be	+S	BeSO ₄ · 4H ₂ O	102.54	106.96	91.66	90.98
Be	+2(N)	Be(NO ₃) ₂ · 4H ₂ O	126.56	122.07	113.07	95.9
Be	+2Cl	BeCl ₂ · 4H ₂ O	108.74	104.53	90.07	91.65
Be	+2(Cl)	Be(ClO ₄) ₂ · 4H ₂ O	153.94	160.53	137.61	120.1

TABLE 4 CONTINUED

IONS	FORMULA	Gand	F.	J.O.S.	WERRAA.	Exptl
+2 +6 -2 Be +Cr +40 +1 -2 +4(2H +0)	BeCrO ₄	107.74	111.05	95.50	63.2	
+2 +5 -2 Be +2(Cl +30) + +1 -2 9(2H +0)	Be(ClO) ₉	200.76	206.56	177.92	152.8	
+2 +5 -2 Be +2(I +30) +1 -2 6(2H +0)	Be(IO) ₆	206.90	202.91	179.69	151.8	
+2 -1 +1 Be +2F +Na -1 +1 +1 -2 +F +H +H =0	BeF ₂ NaFH ₂	41.44	42.57	37.09	48.26	
+2 -1 +1 Be +2F +2(N+4H) -1 -1 +F +F	BeF ₂ 2NH ₄ F	54.74	57.49	49.3	55.87	
+2 +1 +5 -2 Be +H +P +40	BeHPO ₄	52.44	54.61	46.89	35.7	
+2 +1 +5 -2 Be +Na +P +40	BeNaPO ₄	56.64	58.78	50.63	63.81	
+2 +1 +5 -2 Be +K +P +40	BeKPO ₄	69.14	69.01	59.95	69.0	
+2 -3 +1 +5 -2 Be +N +4H +P +40	BeNH ₄ PO ₄	74.45	78.55	76.84	68.9	
+2 +5 -2 2 Be +2P +70	Be ₂ P ₂ O ₇	92.28	96.07	82.53	15.2	

Such a value might be expected if 4 molecules of water of crystallisation were attached to the ion, or any other four groups each donating two electrons. In fact a value approaching this, -46.4 , is found in the tetrahydrated chromate.

Almost all the experimental values obtained lie between the two extremes, indicating that, although few, if any, compounds can be considered as purely polar, few are entirely co-ordinate, supporting the theories of Gray and Cruickshank for organic compounds.

Angus has calculated the susceptibilities of various atoms and ions using Slater's method but taking s and p electrons separately. Although this makes no difference in the case of the beryllium ion, with larger ions the difference is considerable.

Table 4 compares the experimental with the theoretical values, calculated by various means. The first is calculated by Gray and Farguerson from Pauling's principle, the second by Slater, and the third by Angus. In the large majority of cases the experimental value agrees more closely with Angus's value than with the others, but in all but six cases is less than Angus's value. These values are all however calculated on the basis of ionic beryllium - from the nature of the compounds this would not appear to be legitimate. It has

been suggested by Gray and Cruikshank(12) from a study of certain organic compounds that there is resonance between polar and covalent formulae for the compounds, the resultant susceptibility depending on the relative amounts of time spent by the compound in each of the two states. Since to determine the relative residual charge on the atoms present in a compound the dipole moment of the salt is required, it is impossible to apply this method for the above compounds until the dipole moments for beryllium compounds are available.

In his paper on the diamagnetic susceptibility of some beryllium compounds, Angus found that existing values for such compounds as had been measured did not agree with his calculated values. Of the compounds, the inorganic salts have been remeasured in this work. In the case of the oxide and hydrated sulphate, the new values are closer to the theoretical, as is shown in Table 3. With the hydroxide and anhydrous sulphate the present values are much less than the former and than the theoretical. The basic carbonate formerly measured had the formula $2\text{BeO} \cdot \text{BeCO}_3$ - the salt now measured is hydrated $2\text{BeO} \cdot \text{BeCO}_3 \cdot 7\text{H}_2\text{O}$. The susceptibility of this compound is much lower than would be expected by adding the equivalent of water to the unhydrated salt. This is no doubt due to the close

linkage of the water molecules in the salt. Consideration of the susceptibility indicates, however, that the constitution is more probably $\text{BeCO}_3 \cdot 2\text{Be}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$. Taking experimental values for carbonate, hydroxide and oxide and the International Critical Tables value for water, though the susceptibility is very low in either case, it is much nearer to the formula corresponding to the hydroxide

Compound	Calculated Susceptibility	Experimental Susceptibility
$\text{BeCO}_3 \cdot 2\text{BeO} \cdot 7\text{H}_2\text{O}$	145.7	124.5
$\text{BeCO}_3 \cdot 2\text{Be}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$	131.1	124.5

As calculated by Angus the susceptibility would lie between the two, but nearer the lower value, i.e. at 136.2. The chemical nature of the compound suggests that all the water is not held in the same way, since heating to 150°C will drive off part of water but some, probably held as hydroxide, cannot be driven off without completely breaking down the compound. The following table compares the present values with the I.C.T. values and those calculated by Angus.

TABLE 3

IONS		MOLECULE	CALC. (W.R.A.) I.C.T.		Exptl	
+2	-2					
Be	+ 0	Be(O	11.6	0.0	12.11	
+2	-2+	+1				
Be	+20	+2H	Be(HO)	22.85	23.1	17.81
+2	+6	-2				
Be	+S	+40	BeSO	46.64	48.3	34.05
+2	+6	-2				
Be	+S	+40	BeSO	91.66	90.3	90.98
+1	+2					
4(2H	+0-2)					
+2	+4	-2				
Be	+C	+30	BeCO	57.45	40.46	exptl-7H 0
+2	-2		2BeO			=33.5 2
2(Be	+0)				
+2	+4	-2				
Be	+C	+30	BeCO.2BeO	136.2	-	124.5
+2	-2	+1	-2 3			
2(Be	+0	+7(2H	+0-)	7H O		

(21)
 The work of Ikenmeyer on alkali Halides showed that if the graph of susceptibility against number of electrons is plotted, the values lie on a straight line. This shows that for each additional electron the susceptibility increases a certain amount.

If such a graph is plotted of all the values determined for beryllium compounds - it can be seen that all points lie on or about a straightline.

The most strikingly abnormal results are those of the chromate, pyrophosphate and iodate. All these give much lower values than would be expected. The chromate has been found in the cases of magnesium and zinc also to give lower values than then normal. In this compound the slightly diamagnetic Beryllium ion is combined with the paramagnetic ~~xxxx~~ chromate ion. The par magnetic effect is partially neutralised by the presence of the four water.molecules. In the case of the majority of hydrated compounds the susceptibility is larger than would be expected. If the water molecules are attached to the positive ion they would have the effect of increasing the effective ionic radius, and hence the susceptibility. Where abnormally low values are also found in the pyrophosphates of both magnesium and zinc.

In some cases, the agreement of the values for beryllium compounds with those of similar compounds of the neighbouring elements is striking. In the

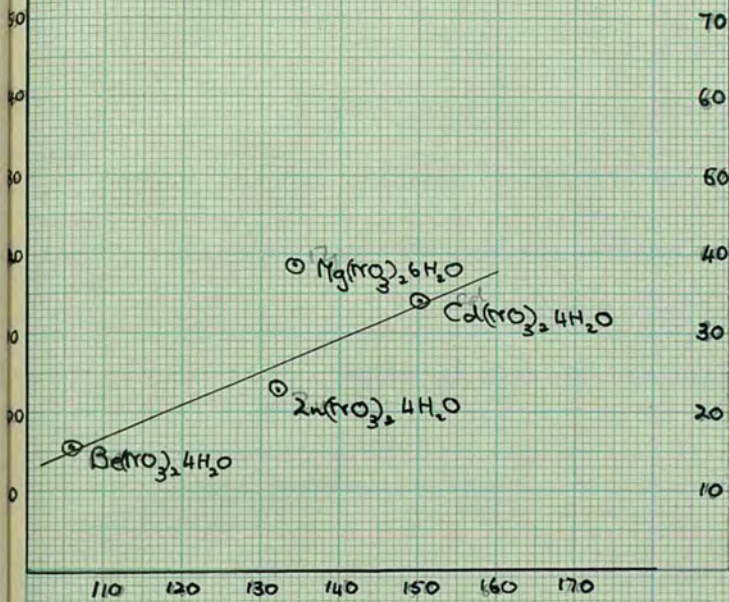
four molecules of water are present - in the chloride, nitrate, sulphate and chromate - it is possible that they are situated at the corners of a tetrahedron with the beryllium ion at the centre. The theoretical susceptibility of a fully co-ordinated beryllium ion is very much greater than that of an unco-ordinated ion. In the case of the chromate also such an arrangement would have much effect in counteracting the paramagnetism of the chromate ion. In the case of the hexahydrated iodate however the position is not the same. The susceptibility is much lower than is expected. This is found to be true also in the case of magnesium. The chemical behaviour of the iodate indicates that the water molecules are not loosely held, since heat breaks up the compound before all the water can be driven off. It is, therefore, probable that in view of this close packing the orbits of the component ions are considerably compressed, hence giving a very low value for the susceptibility.

The pyrophosphate is a completely abnormal compound, entirely covalent. The susceptibility would therefore be expected to be very high. Such extremely low values are also found in the pyrophosphates of both magnesium and zinc.

In some cases, the agreement of the value for beryllium compounds with those of similar compounds of the neighbouring elements is striking. In the

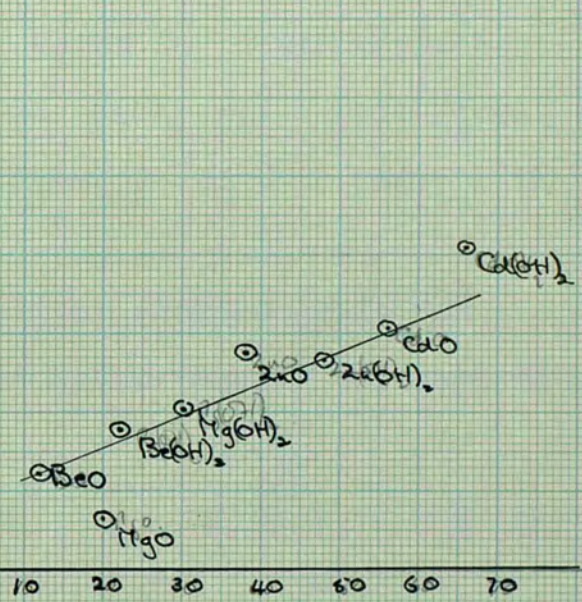
GRAPH 2

HYDRATED NITRATES OF CADMIUM,
ZINC, MAGNESIUM AND BERYLLIUM



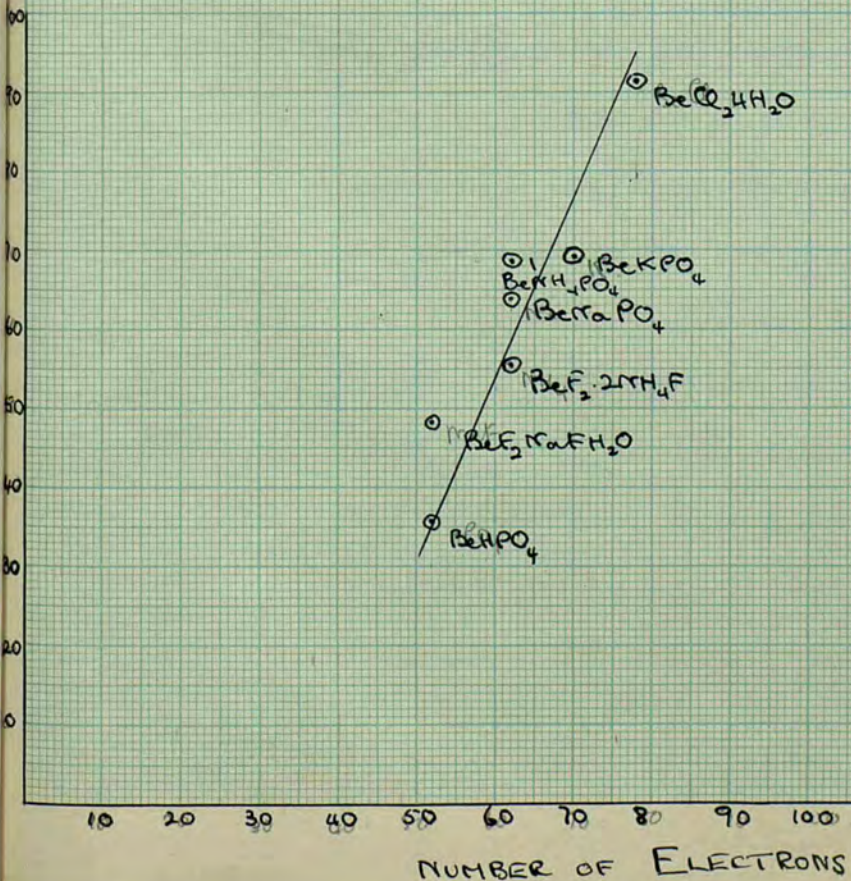
GRAPH 3

OXIDES AND HYDROXIDES OF CADMIUM,
ZINC, MAGNESIUM AND BERYLLIUM



GRAPH 4

PHOSPHATES AND COMPLEX HALIDES OF BERYLLIUM



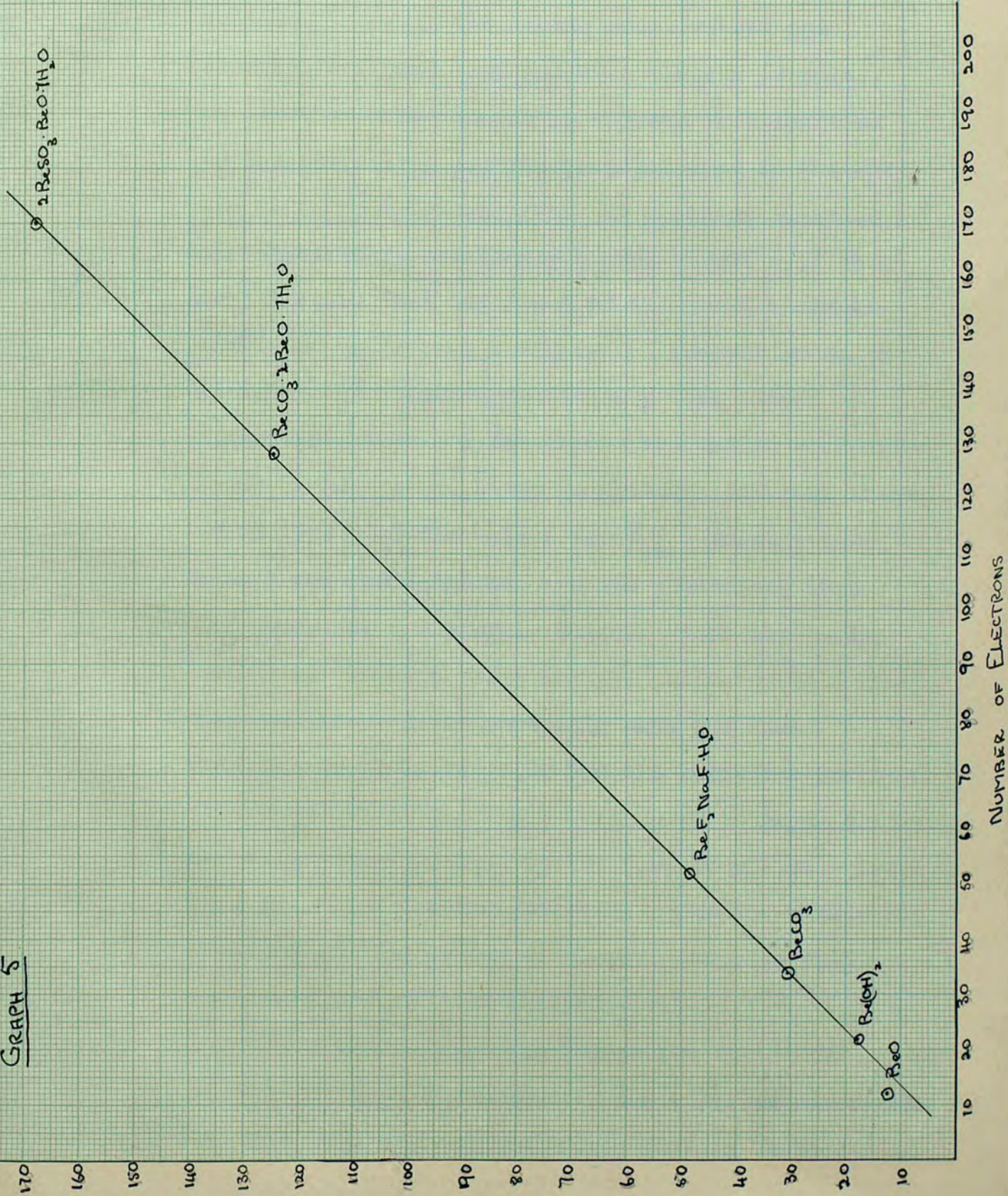
case of the tetrahydrated nitrates of beryllium, zinc and cadmium the linear relation holds almost exactly. There is no value for a tetrahydrated magnesium nitrate. The hexahydrated salt gives, as would be expected, a higher value than salts with less water (Graph 2)

Another similar set of corresponding relations is the group of oxides and hydroxides of the same metals (Graph 3)

In a study of Graph 1 it may be seen that subdivision may be made into groups having closer linear relationship. On xxx One such group comprises the phosphates and halides. The ionic susceptibility of beryllium for these compounds gives no constant value, varying in fact between $\chi_{Be} = -23.0$ for the sodium beryllium phosphate and $\chi_{Be} = -2.5$ for the beryllium hydrogen phosphate. The linear relation of these compounds is however fair, though the line has a totally different slope from that of the general line, indicating that for these compounds there is more than the usual increase of susceptibility per electron. It may be noted that all these compounds have another positive ion in addition to the beryllium hydrogen, sodium, potassium, an ammonium.

10³ M

GRAPH 5



NUMBER OF ELECTRONS

All these in their simple compounds are entirely ionised. Now if the common constituents are covalently linked, and the variable ion is polar, it might seem reasonable to suppose that increase in susceptibility per electron increase in the free ion would be different from the constant increase per electron in covalently linked atoms. If this were larger, then the slope of the graph would be increased as is here indicated. Another group of similarly constructed molecules giving linear susceptibilities are the oxide, hydroxide, carbonate, basic carbonate and basic sulphite. Although these again give variable values for χ_{Be} , these values, except for the sulphite, are low indicating that the compounds are largely polar. With the basic sulphite the high value (-27.9) indicates that the compound is at least partially covalent. Determining by Slater's method the value for coordinated beryllium with a half share in eight electrons the value comes to -25.3 units, i.e. very little less than the value for the sulphite. Similar values are obtained for the sodium beryllium phosphate (-23.0) and ammonium beryllium phosphate (-21.5)

The abnormal positive values for the ionic susceptibility are obtained in the cases of the iodate and chlorate. Since the susceptibility is so low it

may be assumed that in this case the water molecules cannot be attached to the beryllium ion since this increases the susceptibility, but must be attached in such a way that they do not contribute their full quota. The small positive value given by the anhydrous sulphate must be due to close linkage deforming and decreasing the orbits.

3 The atomic susceptibility calculated by the Darwin equation is not a constant value indicating that the equation is not applicable to these compounds due to covalency and presence of water of crystallization, etc.;

4 The theoretical susceptibility for the beryllium ion and for a fully co-ordinated beryllium atom have been calculated, and most of the values lie between these extremes.

5 Certain abnormal values are found in the greatly hydrated compounds.

6 The following compounds are not mentioned in the literature, and have now been prepared for the first time-

Beryllium sesquichloride monohydrate $BeF_2 \cdot 3/2 H_2O$

Sesqui beryllium carbonate $BeCO_3 \cdot 3H_2O$

Hydrate beryllium chlorate $Be(ClO_3)_2 \cdot 9H_2O$

SUMMARY

- 1 The susceptibilities of some twenty beryllium compounds has been measured.
- 2 The values obtained are approximately linear when plotted against M . The values fall however into two main groups, subsidiary to this general arrangement.
- 3 The atomic susceptibility calculated by the Langevin equation is not a constant value indicating that the equation is not applicable to these compounds due to covalency and presence of water of crystallisation, etc.,
- 4 The theoretical susceptibility for the beryllium ion and for a fully co-ordinated beryllium atom have been calculated, and most of the values lie between these extremes.
- 5 Certain abnormal values are found in the greatly hydrated compounds.
- 6 The following compounds are not mentioned in the literature, and have now been prepared for the first time:-

Beryllium sodium fluoride monohydrate $\text{BeF}_2 \cdot \text{NaF} \cdot \text{H}_2\text{O}$
 Basic beryllium carbonate $\text{BeCO}_3 \cdot 2\text{Be}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$
 Hydrated beryllium chlorate $\text{Be}(\text{ClO}_3)_2 \cdot 9\text{H}_2\text{O}$

New methods of preparation resulting in pure compounds
 are described for the hydrated chromate $\text{BeCrO}_4 \cdot 4\text{H}_2\text{O}$
 and beryllium hydrogen phosphate BeHPO_4

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