A STUDY OF MOLYBDENUM BLUE, ITS PROPERTIES AND COM-POSITION.—By LLOYD ALEXANDER MUNRO, B. A., Dalhousie University, Nova Scotia.

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Introduction.—Centuries before Molybdenum was recognized as an element, the name Molybdos, "heavy" had been given by the Greeks to ores of lead. Until the middle of the eighteenth century, Graphite or "Plumbago", as it was then called, and Molybdenite, were thought to be identical. Scheele, in 1778, proved that these were different minerals. In his "Treatise on Molybdena," he pointed out that one of these, Molybdenite, formed a "pecular white earth," when treated with nitric acid. "Black Lead" did not give a similar reaction. The white precipitate from Molybdenite was found to be acidic in character. Scheele named it "Acid of Molybdena" or "Molybdic Acid." The metal was isolated several years later (1790) by Hjelm. He reduced Molybdic acid by heating it with charcoal.

Molybdenum Blue is the name given to the blue coloration obtained when Molybdic Acid is reduced in acid solution. This reaction is one of the most characteristic tests for Molybdenum. In addition to this there are several other tests for the element. A common one is the precipitation of curdy mass in solution of Molybdate when not too dilute. This also gives a yellow-green color to the blow-pipe flame. It imparts a green color to the Borax bead.

Later work has brought to light other tests. The Chemical Abstracts (1913) give a paper on "Sensitive Reaction for the Detection of Molybdenum," (A.C.S. 3726). The presence of Molybdenum was shown by a blood red color obtained by KCNS in a solution of molybdate reduced by calcium chloride, or zinc and sulphuric acid. The test was not dependable when stannous chloride was used.

In 1912, Melikov published a paper (Ber. 31. 2448) on "Reaction for Detection of Molybdic Acid." The test was for

formation of a red ammonium per-molybdate similar to K₂O₂ Mo O₄ H₂ O₂.

Although the above reactions are sensitive, the standard test for Molybdenum is the formation of Molybdenum Blue. Nearly all text books on Inorganic Chemistry mention the blue as a test for Molybdenum or Tin, but few tell anything about its properties. A still smaller number assign any formula to the compound which causes coloration. Formulae suggested by these writers show little agreement.

A few extracts from well known volumes will show this clearly. The "Encylopedia Brittanica," says: "ammonium molybdate (NH₄)₁₀Mo₂₄O₁₅ with hydrochloric acid or nitric acid gives a white precipitate; with reducing agents, such as sulphurated hydrogen, sulphuric acid and zinc, stannous chloride, etc., it gives a *blue coloration*, which turns green and finally brown."

Holleman, (translated by Cooper, 1911), states:

"A very characteristic test for molybdic acid is the following: the substance is mixed with zinc and sulphuric acid. At first a blue coloration (a Molybdate of Molybdic Oxide) appears."

Kolbe also merely mentions the blue as a test. "If zinc is added to a solution of molbydic acid a blue color is first produced which becomes green and finally dark brown in color, due to reduction."

Mellor, in his very readable book on "Inorganic Chemistry," does not give any definite formula. "The molybdates," he writes, "are reduced by zinc in acid solution to one of the lower oxides, approximately Mo₂ O₃ and at the same time the color of the solution changes through various shades of violet, blue and black."

Browning of Yale, in his book "The Rarer Elements," does not suggest the formula for Molybdenum Blue.

Finally, Roscoe and Schorlemmer in their "Treatise on Chemistry," Vol. II. 1044 (1917), give the following:

"When molybdic acid is reduced in solution by sulphuretted hydrogen, sulphur dioxide, stannous chloride, nascent hydrogen, etc., a blue color is obtained, due to the formation of an oxide or oxides between the di- and the tri-oxide. The solution deposits a blue precipitate of this oxide which contains (?) water. It is termed "Molybdenum Blue."

It will be seen from the above extracts that very little is definitely known concerning the properties or composition of Molybdenum Blue. Attempts were made by various investigators to find it's formula. A number of different formulae have been brought forth. These will be briefly noted, without giving any details of the methods by which they were obtained.

The formula of lowest molecular weight is that given by Rammelsberg. He assigns to the Blue the formula $Mo_2 O_5$, = MoO_2MoO_3 . Others regard it as $Mo_3 O_8 = MoO_2.2MoO_3$.

Guichard suggests Mo₅O₁₄ 6H₂O = MoO₂ 4 MoO₃. 6H₂O. Zsigmondy says "The formula is supposed to be Mo₃O₈, 5H₂O. According to Klassen, it consist of complex derivatives of an oxide Mo₂O₅ and Molybdic acid, analogous to phosphomolybdic acid.

Since 1917, no further work has been published on the question of its composition. This research was undertaken with the object of determining the correct formula for Molybdenum Blue and to make a study of its properties.

DEMONSTRATION

A solution of ammonium molybdate was the first requisite. This was made according to the method given by Noyes. A solution of stannous chloride was also made. This was obtained by dissolving pure tin shot in concentrated hydrochloric acid and diluting it to required strength. Some metalic tin was kept in the bottom of the flask.

On attempting to obtain Molybdenum Blue by adding a portion of the SnCl₂ solution to some of the solution of ammonium molybdate, a blue coloration was first obtained. but

it soon changed to green and finally pale yellow. It was thought that this bleaching action might be due to the nitric acid in the molybdate solution. This was found to be the case. Hence neutral solutions of molybdate were used. These were made by dissolving 5 grams of the salt in 500 c c of distilled water.

Molybdenum Blue was obtained by the action of SnCl₂ in the presence of HCl, by Hydrogen sulphide from hot acid solution, nascent hydrogen, sulphur dioxide, and oxalic aicd. Quantities of the blue were obtained by stannous chloride and Dumanski's method. These were by far the most satisfactory. Dumanski dissolved 15 g of ammonium molybdate in 400 c c water. To this solution 100 c c of 3 N or 4 N. H₂SO₄ was added. The boiling solution was reduced with H₂S. Samples of the blue obtained by these two methods were dried at 40° for some hours, put in a sealed bottle and labelled according to their mode of preparation.

In the preparation of the Blue it was found that, if the amount of stannous chloride added to a constant amount of the molybdate solution, were varied, the precipitated Blue and the filtrate varied in color. It was noted that as the amount of stannous chloride was increased, the precipitated Blue became darker in color while the filtrate, instead of being blue, was green or almost colorless. By adding molybdate solution to this filtrate the blue color and further precipitate was obtained. This suggested that green was further reduction product as SnCl₂ was evidently in excess.

To prove this a few drops of hydrogen peroxide were added. A blue color was obtained. Same result was obtained with FeCl₃ as oxidizing agent. When more SnCl₂ instead of H₂O₂ was added to the green solution, a brown color appeared. When the green solution obtained with sulphur dioxide was allowed to stand exposed to the air, it became blue. This property was shown by the colorless solution obtained by reduction with Oxalic acid.



Fig. 1

A test tube containing a brown solution obtained by reduction by zinc and H₂SO₄ was treated with three drops of H₂O₂. A green color appeared in two thirds of the tube. Another drop of peroxide was then added. This gave a blue solution in the upper part of the tube. These experiments show conclusively that the green and browns are successive reduction products.

The colloidal nature of the blue was confirmed by adding an electrolyte (NaCl) to the clear filtrate. The mixture was shaken. A precipitate formed.

After allowing the solution to stand for a few hours, the precipitate was removed by filtration. The filtrate was still blue. More electrolyte was added but no further precipitate was obtained. The fact that the filtrate was blue would suggest that Molybdenum Blue exists in the crystalloidal form also.

A simple dialyzer was made by covering the mouth of a funnel tube 2" in diameter, with a membrane of sheepskin. Solutions of the Blue, the filtrates from the preparation by SnC1, and H₂S, were placed in the dialyzer and the latter kept immersed in distilled water for five days. The water was changed every twelve hours. After twelve hours dialysis, some of the water was evaporated over microscopic slides. Examination under the microscope revealed large amount of stannous chloride Slides prepared after thirty hours dialysis showed stannous chloride needles, and a little Blue. At the end of four days continuous dialysis, the water in which the dialyzer had been immersed for twelve hours, gave almost no deposit on the slide. This slight deposit consisted of tint patches of Blue with a mere trace of stannous chloride. That some Blue passes through the membrance would suggest that it might be crystalloidal as well as colloidal. The blue patches might well be aggregations of ultramicroscopic crystals.

The bleaching action of animal charcoal on solution of Molybdenum Blue was tried. The blue solution was soon bleached by the charcoal. Concerning this phonomenon Zsigmondy says: "Colloids can be completely removed from a liquid by porous bodies. As a lecture experiment the author has used the absorption of Molybdenum Blue by animal charcoal. As in other cases the absorption was quantitative and irreversible."

It was found however, that if the solution was filtered as soon as it became colorless and the filtrate treated with Sn Cl₂, a slight blue coloration was obtained. This shows that it is incorrect to assume, as Zsigmondy evidently does, that the bleaching action is wholly due to absorption. The action is also one of oxidation, although to a much smaller extent.

The oxidizing power of charcoal was shown by treating the brown solution obtained from the extreme reduction of Blue by Zinc. The supernatant liquid gradually changed to blue.

Vectoriality.—Some liquids are vectorial in character. They form "crystals" while still in the liquid, i. e., they assume definite shapes. Extensive research has been done on this property of liquids. The question as to whether, or not, colloided phases exhibit vectorial properties, has apparently not been settled to the satisfaction of all, as yet. However, men who have worked upon this problem usually support the affirmative. To quote Lincoln ("Physical Chemistry," 1920):

"Von Weimarn even believes vectoriality is manifested by gaseous substances and in addition, has presented evidence which he considers to be direct proof of the vectorality of the colloid phases. In the case of colloid iodine and certain colloid dyes, L. Pelet and Wild claim to have observed the fusion of ultra-microscopic particles which assumed definite crystalline shapes."

An attempt was made to obtain crystalline Molybdenum Blue and thus confirm the work of Von Weimarn and Pelet and Wild.

Microscopic slides were placed in shallow evaporating basin, containing filtrate from Blue prepared with SnCl₂. The solution was allowed to evaporate at room temperature. When slide became exposed it was removed and allowed to dry. It was examined under the microscope.

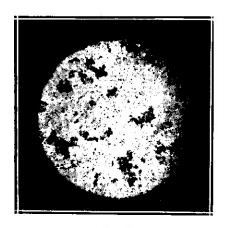


Fig. 2

The first slide showed a blue gel with little colorless crosses here and there. These little crosses were found to be incipient crystals, for, on the second slide examined, cross and square crystals, derived from these, were found side by side. The third slide (Fig. 2) showed these crystals in large numbers. In many cases the cross could be seen, forming

the diagonals of the square. This cross pattern reminded one of similar pattern found in a variety of the minerals, Andalusite, Chiastolite. The crosses in the mineral are supposed to be caused by "impurities on crystalization" (Butler). It seems more reasonable in the case of a Molybdenum compound that they are the edges of an octahedron. If this be so, they are

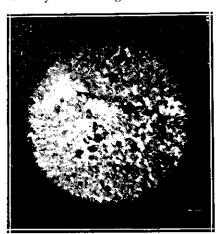


Fig. 3

molybdic oxide. A few colorless hexagonal crystals were also noticed. These were recognized as ammonium molybdate. The photograph shows these crystals, some hexagonal ones, as well as gel and amicrons.

A portion of dialyzed hydrosol was evaporated. at 18°. The deposit on slide was examined under microscope. A beautiful back ground of blue gel was seen. This gel con-

tained a few dark blue opaque particles of regular outline. They were almost cubic in shape. Fig. 3 shows the slide under low power. The hydrosol was treated with NH₄C1. Precipitate was separated from solution by filtration. The blue filtrate was allowed to evaporate over slides. Crystals were found as shown in Fig. 5 and 6. As can be readily seen, they belong to the cubic system. It will also be noticed that the corners are truncated. These little faces do not appear on crystals on slide No. 2. These crystals (No. 4) are pale blue in color. They are certainly not ammonium chloride crystals.

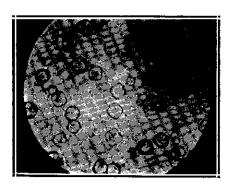


Fig. 4

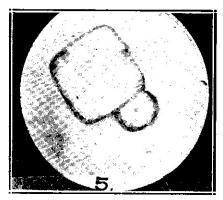


Fig. 5

They are different from either molybdic oxide or ammonium Molybdate. It is therefore probable that they are crystals of crystalloidal Blue.

Fig. 5 shows a crystal under high power. The truncated corners can be seen quite distinctly. The cross in centre appears quite plainly.

As will be noted more fully later, the hydrogel was found to be soluble in absolute alcohol.

A concentrated solution of the Alcosol was made. It was concentrated further by slow evaporation. Fig. 3 shows a section of the slide obtained. The

particles are cubes varying in color from lightblue to very dark blue, according to their thickness. The light blue ones were examined under crossed nicols. They are isotropic. A basal section of a cubic crystal would give this effect.

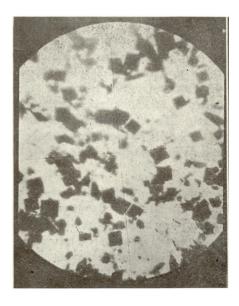


Fig. 6

The writer can see no valid reason for considering these crystals other than crystal of colloidal Molybdenum Blue. This fact would lend strength to Wiemarn's and Pelet's supposition that colloids have the property of vectorality.

Pure crystals of Stannous chloride were dissolved in absolute alcohol. A saturated solution of Ammonium Molybdate in alcohol was also prepared. Portions of the stannous chloride solution were

diluted by adding more alcohol. A few drops of this solution were added to the molybdate. A brownish precipitate was obtained. The same experiment was tried with HCl added to the molybdate solution. The same result was obtained.

The alcohol solution was treated with zinc and sulphuric acid with no apparent reaction. Sulphuretted hydrogen was passed into the solution. A colloidal solution resulted. This solution was fluorescent, giving blueish grey and red by reflected and transmitted light, respectively. After standing for some hours the solution became a fawn color and a flocculent brownish precipitate similar in color to that obtained by adding

SnCl₂, separated out. Three weeks later the solution was filtered. The precipitate formed a gel on the filter. It turned a darker brown. Lack of time prohibited further investigation. The experiments showed that Blue could not be obtained except in water solution.

The Gel.—Solubility in solvents: The hydrogel prepared by action of stannous chloride and sulphuretted hydrogen was dried. The solubility of the dried gel in various solvents was ascertained. It was found that the gel dissolved in water, absolute alcohol and methyl alcohol. No apparent solution took place when gel was shaken in ether, benzene, carbon bisulpide, acetone and chloroform. The fact that Molybdenum blue is soluble in absolute alcohol is of more importance than would, perhaps, be recognized at first glance. This will be dealt with later.

The negative character of the colloidal Blue was shown by a modification of Cohen's apparatus. It consisted of a U-tube partly filled with agar, in which sodium chloride had been dissolved. The dialyzed hydrosol was poured into each arm, the levels in each being the same. Platinum electrodes were immersed in the hydrosol. A current of 1-2 mil amperes and pressure 4 volts was passed through tube for 16 hours. At the end of that time it was found that blue solution had become colorless. The level of water in the cathode arm had risen. Solutions in each arm were tested for oxidation or reduction. The cathode arm gave negative tests. The solution from the anode tube showed oxidation, due to chlorine liberated from the electrolyte (NaC1).

A solution of the hydrosol in agar was now placed in a U-tube. Electrodes were immersed in gel. Potential was raised to 10 volts. A current of 3 milamperes was passed through tube for 16 hours. The blue migrated towards the anode. This proved that hydrosol carried a negative charge.

An experiment was undertaken to find whether the hydrosol and alcosol had the same rate of migration. Solutions of

Blue were made by dissolving equal quantities in equal volumes of water and of alcohol. These solutions were placed in tubes over agar. The tubes were connected in parallel. It was found that the migration of hydrosol was greater than that of the alcosol. Results were of little value, however, on account of the unequal diameter of the tubes. Since resistance, and therefore amount current varies with the area of cross section, and rate of migration depends on amount of current, the difference might have been partly due to difference in tubes. The resistance of the solutions was so great that the current could not be measured with mil-ammeter.

Analysis of Blue.—Samples of "hydrogel" were pulverised and dried at temperature of 105°-110°C until three weighings, taken at intervals of one hour, gave the same weight.

Apparatus.—Apparatus for reduction of an oxide was set up. It consisted of a hydrogen generator; wash bottle containing C. P. sulphuric acid; short length of hard glass tubing, small platinum boat and a U-tube containing sulphuric acid over glass beads. The platinum boat, which had been ignited, cooled in a desiccator and weighed, was partially filled

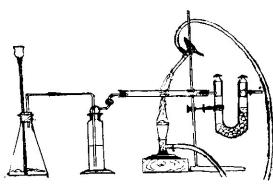


Fig. 7

with the prepar-The ed Blue. amount of Blue taken for anawas relvsis corded. The boat and Blue were placed in the hard glass tube, the apparatus connected. When a stream of hydrogen had

been passing through the apparatus for ten minutes, heat was applied to the boat. It was heated at red heat for eight hours. The boat was weighed as quickly as possible and reduction and heating continued for four hours more. At the end of that time the boat containing the residue was again weighed. The boat was allowed to cool in a stream of hydrogen. Weighing was done as rapidly as possible. It was found that the Blue lost very little or no weight during the final four hours heating. The gain in weight of the U tube served as a check.

Three determinations were made. The results agreed very well considering the possible experimental error, due to sub-limination of Molybdenum, moisture absorbed by blue during first weighing, and also variation in amount of water in hydrogel. In discussing the various formulae that have been suggested the average results obtained will be considered.

Average time	Average		Average
of reduction	Wt. of hydrogel	Wt. of residue	Loss in Wt.
12.2 hrs.	.2669 g	.1785 g	.0884 g

The residue was blueish grey. It was taken to be Molybdenum with a trace of oxide. As no further loss in weight resulted between weights at the end of eight and twelfth hours of treatment the residue could not be Mo₂O₃MoO, MoO₂, MoO₃, for these oxides are broken down below bright red heat. When the heat was increased, a metallic mirror was deposited in the tube. This would show that the residue was Molybdenum. In the following calculations it will be treated as such:

Let us consider the first formula suggested, Mo₂O₅. If this were the formula residue would weigh $\frac{\text{Mo}_2 \text{ O}_5}{\text{Mo}_2 \text{ O}_5} \times 2669 = \frac{192}{272} \times 2669 = 1884 \text{ g.}$

This is more than $5\frac{1}{2}\%$ greater than actual weight of residue. According to this formula the loss in weight would be:

$$\frac{O_5}{Mo_2 O_5} \times .2669 = \frac{80}{272} \times .2669 = .08045.$$

This is 10% smaller than experimental result. The formula ${
m Mo_2O_5}$ must therefore be considered incorrect.

Considering Guichard's formula—

 Mo_sO_{14} , $6H_2$ O it is calculated that residue should weigh Mo_s Mo_sO_{14} 6 H_2 O \times .2669 g=.1980 g. This 10% too great.

The "loss in weight" as calculated by the formula, would be correspondingly small.

The formula given in Zsigmondy's "Colloids" is Mo₃O₈, 5H₂O. This would give a residue weighing .1517 g, as calculated by

$$\frac{\text{Mo}_3}{\text{Mo}_3\text{O}_8 + 5 \text{ H}_2\text{O}} = \frac{288}{506} \times .2669 = .1517 \text{ g, or } 85.1\% \text{ of experimental value.}$$

According to this formula the weight of gas and water-vapor given off would be $\frac{O_8 \ 5 \ H_2 \ O}{Mo_3 \ O_8 \ 5 H_2 \ O} \times .2669 = \frac{218}{506} \times .2669 = 1150 \ g$, which is over 10% greater than experimental value.

The formula most generally given is Mo_3O_8 . According to this the residue would be $\frac{Mo_3}{Mo_3} \times .2669 = \frac{288}{416} \times .2669 = 1848g$

This is 3.5% greater than actual weight of residue.

Calculating the weight of oxygen given off; weight of oxygen equals $\frac{O_8}{Mo_3 O_8} \times .2669 = \frac{128}{416} \times .2669 = .0831 \text{ g.}$

which is $6\frac{1}{2}\%$ less than the "loss in weight" of sample.

From the relation of weight of residue and weight of gas given off, it was thought that the formula would be Mo₃O₈ H₂O.

Calculations were made.

Weights of residue equals-

$$\frac{\text{Mo}_3}{\text{Mo}_3 \text{ O}_8 \text{ H}_2 \text{ O}} \times .2669 = \frac{288}{434} \times .2669 = .1771 \text{ g}.$$

This agrees with experimental values within 4-5%.

The wt. of gas given off
$$\frac{O_8 H_2 O}{Mo_3 O_8 H_2 O} \times .2669 = .0898 g$$
.

This agrees within 1-1/3% of epxerimental result.

The formula Mo₃O₈2H₂ O was tried, but gave poor agreement.

From these calculations, it has been shown that the formula $\mathrm{Mo_3}$ O₈ H₂ O agrees most closely with actual weights of analysis. It should be noted also, that this formula comes the nearest to the molecular weight as determined by Dumanski. He found it to be 440. This formula $\mathrm{Mo_3}$ O₈ H₂ O gives molecular weight of 434; $\mathrm{Mo_3}$ O₈ 416 and $\mathrm{Mo_3}$ O₈ 5H₂ O = 506.

It has been found, as noted above, that the dried hydrogel is soluble in absolute alcohol. Now Zsigmondy, in his "Chemistry of Colloids," "(T. Spear, 1917)" discussing Silicic Acid Organogels, states: "The fact that water may be replaced by other substances as solvents, without any marked change in the character of the gel, points clearly, as Van Bemmelen has noted, to the assumption, that water is not there as a hydrate chemically combined, but is absorbed water that fills the spaces between the ultramicrons." He gives G. Tschermak; (Zeit. f. phys. Chemie. 53, 349-367), (1905); G. Tammann; (Zeit f. Anorg Chemie. 71, 375), (1911); as references.

It is obvious, then, that the formula for Molybdenum Blue given, in the same volume, is incorrect. If we accept the work of Bemmelen, any formula which shows one or more molecules of water of hydration must be discarded. This leaves just Mo₂O₅, or Mo₃ O₈. Of these Mo₃ O₈ is the better.

Ostwald in his "Inorganic Chemistry," says: "Between this (Mo O₂) and trioxide are the readily formed Blue compounds, the composition of which varies, and cannot be characterized with sufficient sharpness." This variation may be due to the different formula-weights of water enclosed by the ultramicrons. Certainly the formula Mo₃O₈ H₂O best expresses the

composition of the sample of Blue analyzed, but for the anhydrous gel, the formula is, no doubt, Mo₃O₈.

It would be interesting to note whether the variation in composition of the precipitated ammonium phosphomolybdates, which "seem to violate the constancy of composition test for distinguishing compounds from mixtures," could not be explained in a similar manner. Possibly the variation is due to the adsorption of water or an oxide by the ultramicrons, the amount of which varies with conditions.

The formation of Molybdenum Blue by the action of ammonium molybdate and a stannous salt is a sensitive test for tin. An attempt was made to determine the sensitiveness of the test for tin.

Stannous chloride was obtained by dissolving .2138 g of pure tin in C.P. HC1. The solution was diluted to 500 cc and 50.01 cc of this solution diluted to 500 cc. A tin bead was dropped into the resulting solution and the solution immediately titrated against an approximately 1/5% solution of Ammonium molybdate.

Average ratio
$$\frac{1 \text{ cc tin}}{60.1 \text{ cc sol. AM}}$$
Sensitivity =
$$\frac{.2138}{5000} \times \frac{1}{600} = \frac{1}{1.423.000}$$
(Some error due to $\text{SnCl}_2 \rightarrow \text{Sn Cl}_4$.)

Sensitivity of test for Molybdenum was also tried. It could not be determined with any degree of accuracy, owing to the formation of the green solution, when Sn C1₂ was in excess. This faint green color was very hard to detect.

SUMMARY OF FINDINGS OR CONFIRMATIONS

- Blue is most readily prepared by action of SnCl₂ and H₂S.
- 2. Green and brown colors are due to further reduction com-

pound. Action is reversible.

- 3. Blue only obtained in acid solution.
- 4. Negative colloid.
- 5. Exists as crystalloid also.
- Forms cubic crystals from alcohol, and transparent cubes bearing face of octahedron from blue filtrate after gel has been precipated by NH₄C1.
- 7. Insoluble in ether, chlorform, benzene, carbon bi-sulphide and acetone.
- 8. Soluble in water, absolute alcohol and methyl alcohol.
- Formula of hydrogel as obtained from analysis = Mo₃O₈,
 H₂O. Formula of Blue = Mo₃O₈.
- 10. Sensitivity of test for tin is 1 part in 1,423,000.