what the reagent is, nor whether it is hot or cold. Apparently the more liquid used in the first washing, the greater the amount of reducing substance removed; but only a small amount of reagent is needed to remove most of the material.

When the titration is made in the cold and 0.1 *N* permanganate is used, there is practically no significant effect on the titration as ordinarily carried out, but when 0.02 or 0.01 *N* permanganate is used, and especially when the titration is carried out hot, the error may become relatively great.

Washing the filter paper previous to use is a great aid in avoiding excessive consumption of permanganate. In fact, our work indicates that if the filter is given a preparatory washing with 25 cc. of the reagent, filtration and titration can be carried out, even at 70–80°, without error on this account. Even comparatively long exposure of paper, or titration in the presence of the paper, is not ordinarily objectionable.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

A STUDY OF SOME RARE EARTH COMPOUNDS.

BY A. J. GRANT AND C. JAMES.

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von Welsbach has shown that the double oxalates of the rare earths and ammonia may be used for the separation of the rare earths, and that these compounds are better suited for the purpose than the similar potassium salts. These facts brought to the minds of the authors the possibility of using the derivatives of some of the amines with perhaps even better results. This paper describes the work carried out by the authors along this line together with the examination of a few new salts.

It was decided to study roughly the solubilities of several suitable rare earth oxalates in solutions of oxalates of methylamine, ethylamine and triethylamine. Methylamine was prepared from acetamide in the usual manner. However, the preparation of the latter upon a large scale did not appear to be a simple matter at first, for the use of sealed glass tubes was too slow and expensive. A trial with an iron mercury bottle soon showed that this type of apparatus could not be employed since the iron was badly attacked. The method recommended by Schulze in which one molecule of ammonium thiocyanate was heated with two and one-half molecules of glacial acetic acid at the boiling point for four days gave a good yield. In this case the crude product appeared to contain impurities which were hard to remove, and, in addition, unpleasant gases and vapors were evolved during the process.

The authors found that the best method for the production of acetamide was to pass a large amount of dry ammonia into glacial acetic acid until the boiling liquid smelt of the gas. The whole was then heated with a long air condenser for about thirty hours. After every five or six hours the liquid was treated with dry ammonia. When the time had elapsed, the mass was fractionally distilled with the result that an excellent yield of very good acetamide was obtained.

Butyramide was easily prepared in a similar manner.

Ethylamine was prepared by the action of alcoholic ammonia upon ethyl bromide. The operation was carried out in a mercury bottle heated in a pail of boiling water. The various amines were separated by ethyl oxalate. A considerable amount of the primary amine, and a fair quantity of the tertiary compound were formed.

The amines were then neutralized by the careful addition of oxalic acid and evaporated to crystallization.

The relative solubilities of the oxalates of neodymium, gadolinium, dysprosium, thulium, yttrium and ytterbium in the amine oxalates were roughly determined. A 20% solution of the amine oxalate was used in each case, and in the triethylamine series the solubility of lanthanum oxalate was examined. The lanthanum oxalate caked somewhat and the sides of the bottle were covered with fine white crystals.

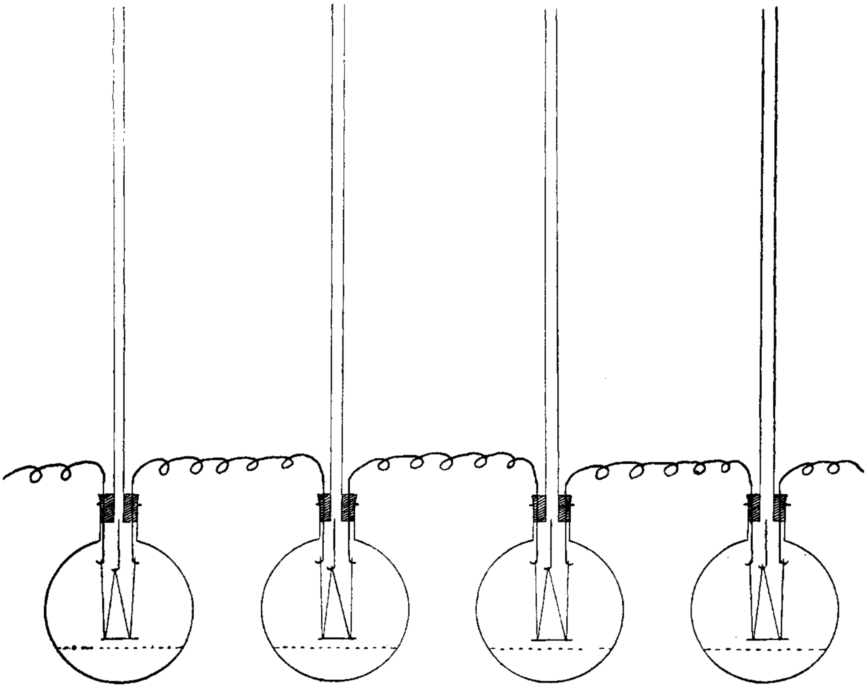
The results are given in the table below.

Element.	G. R_2O_3 per 100 cc. methylamine oxalate.	G. R_2O_3 per 100 cc. ethylamine oxalate.	G. R_2O_3 per 100 cc. triethylamine oxalate.
Lanthanum	...	...	0.032
Neodymium	0.027	0.107	0.065
Gadolinium	0.069	0.360	0.883
Dysprosium	0.276	1.787	1.432
Yttrium	0.877	1.653	1.006
Thulium	4.082	5.728	1.340
Ytterbium	5.242	5.858	2.048

The above results seemed to indicate that there was no great variation in the series of solubilities, and, owing to the high cost of these reagents, no more work was done with them.

Diphenylsulfonates.—Since the diphenylsulfonic acids are said to be strong acids and since some are said to resemble sulfuric acid so much that it is hard to differentiate between them by their reactions, it seemed advisable to examine these bodies.

Here again the writers encountered great difficulty in the preparation of diphenyl. Many of the old methods, such as the passing of benzene vapor through a red-hot tube, bromobenzene and sodium, diazo reaction, and anhydrous stannic chloride and benzene through a red-hot tube were tried. Of the methods listed, the simplest and cheapest appeared to be the first. This method was examined at great length by using an electrically heated tube with an elaborate system of return pipes and condenser, etc. Even though the temperature was varied the tube soon became stopped up. This was probably due to the fact that the temperature was too high in all cases. Even when an iron tube was worked at a lower temperature in a combustion furnace, poor yields were obtained. Owing to the fact that a previous worker had described the preparation involving the use of a carbon or metallic filament taken from an incandescent lamp, it seemed highly probable that a larger filament of nichrome ribbon would cause a more rapid formation of diphenyl. In order to prove whether or not this might be the case, a series of three liter flasks were fitted with good cork stoppers. The nichrome ribbon was supported by means of three nickel wires passing through the corks. Two of these wires were used to carry the current. The filament was large enough to reach from the base of the neck to just below the surface of the 150 cc. of benzene contained in the flask. In addition to the above fittings, each cork stopper was bored and the lower end of a condenser tube inserted. In order to commence the operation each flask was heated by means of a Bunsen burner until all air had been driven from the flask; as soon as this point had been reached the current from the alternating lighting circuit was turned on and the burners quickly turned out. The heat from the filament kept the benzene boiling excellently. In order to make the operation successful, it is necessary that the temperature of the filament be not too high, for otherwise the benzene will be carbonized and the filament will suddenly glow and break.



Using four flasks as described above, and keeping the ribbon at a dull red, diphenyl was obtained in large quantities. As soon as the current was turned on, the diphenyl was observed running down the sides of the flask, and after the operation had been continued for five or seven hours the contents of the flasks solidified upon cooling. The accompanying figure will give a clearer view of the arrangement of the flasks and ribbon.

The diphenyl monosulfonic acid was first prepared by heating about equal weights of diphenyl and sulfuric acid on the water bath for twelve hours. Under these conditions the monosulfonic acid should be the principle product. The sulfonated material was diluted with water and treated with a saturated solution of cupric chloride. The difficultly soluble copper salt of the monosulfonic acid then separated. The crude salt was recrystallized two or three times, dissolved in hot water and the copper thrown out as copper sulfide by hydrogen sulfide. The clear filtrate was evaporated.

Since neodymium oxide did not easily dissolve in the sulfonic acid, a slightly acid solution of the sodium salt was prepared and added to a solution of neodymium chloride. The precipitated salt was dissolved in a large amount of water and allowed to crystallize. The compound formed a mass of light pink crystals, only slightly soluble in water.

The per cent. of neodymium oxide found was 17.67, while the salt containing six molecules of water of crystallization contains 17.68% neodymium oxide according to theory.

Neodymium Ferricyanide, $NdFeC_6N_6.4H_2O$.—When a solution of potassium ferricyanide is added to a dilute solution of neodymium chloride no precipitate is formed. However, when a strong solution of both reagents is used or when the former mixture is evaporated considerably, a highly crystalline precipitate of the ferricyanide of neodymium is thrown down.

This compound was prepared by adding a hot solution of potassium ferricyanide to a boiling solution of neodymium chloride. The precipitate was separated upon a Büchner funnel and washed with warm water. The salt possessed a rich brick color with an orange tint, and was slightly soluble in water. An analysis showed that the salt contained 39.24% neodymium oxide which coincides with the theoretical amount required by the formula given above.

Lanthanum Ferricyanide, $LaFeC_6N_6.4H_2O$.—This salt was obtained in a similar manner to the neodymium compound outlined above. It did not possess quite such a rich color, and was a little more soluble in water. Analysis showed a water content which was practically in agreement with the four molecules of the neodymium compound.

Yttrium Ferricyanide.—This substance is very much less soluble in water than the compounds described above. It is precipitated from dilute aqueous solutions as a fine powder by adding potassium ferrocyanide to a solution of an yttrium salt. Since the ferricyanides of erbium, thulium and ytterbium are still less soluble than the yttrium compound, this process can be employed for the purification of yttrium material. The fractionation is very rapid. This was proved in a very simple manner. Yttrium oxide containing erbium was dissolved in hydrochloric acid, the solution was made neutral and brought to a boil. No special type of apparatus was used, the solution being heated in a beaker and precipitated by adding a solution of the ferricyanide. The precipitate was treated with sodium hydroxide, filtered, washed, dissolved in hydrochloric acid and precipitated with oxalic acid. The oxalate was ignited, dissolved in hydrochloric acid and reprecipitated as the oxalate. The equivalent was then determined in the usual manner.

The filtrate from Fraction 1 was again treated with more potassium ferricyanide and the precipitate removed and treated similarly to Fraction 1. In all five fractions were obtained in this manner.

No. of fraction.	Atomic weight.
1	104.90
2	99.99
3	96.65
4	94.80
5	93.00

In conclusion, the writers would like to point out that the yttrium earth ferricyanides are much less soluble than heretofore believed. This method for the purification is perhaps the most rapid known, for the above fractionation was not carried out under very favorable conditions. This work is being continued.

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THE ARSENATES OF LEAD.

[THIRD PAPER.]

BASIC ARSENATES.

BY C. C. MCDONNELL AND C. M. SMITH.

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There is very little published work concerning the basic arsenates of lead. It was observed by Graham as early as 1833[1] that when trisodium arsenate was added in excess to a solution of acetate of lead the resulting precipitate contained an excess of base. He apparently did not recognize this as a basic arsenate and did not investigate the reaction further. It is only comparatively recently that any definite knowledge has been gained in this direction. Two basic arsenates have been previously recorded and these, together with a third produced by us, are here described.

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[1] *Phil. Trans. Roy. Soc.*, 133, 266 (1833).