ACETONE.

$$\gamma = chs + s^2 = (1.022 \times 27.75 \times 0.7998) + 0.64 = 23.32 \text{ dynes at } 16.8^\circ.$$

$$(1.022 \times 24.22 \times 0.7656) + 0.59 = 19.55 \text{ dynes at } 46.4^\circ.$$

$$\gamma(Mv)^{\frac{2}{3}} = (58/0.7998)^{\frac{2}{3}} \times 23.32 = 406.1 \text{ ergs at } 16.8^\circ.$$

$$(58/0.7656)^{\frac{2}{3}} \times 19.55 = 351.6 \text{ `` `` } 46.4^\circ.$$

$$\frac{d[\gamma(Mv)^{\frac{2}{3}}]}{dt} = \frac{406.1 - 351.6}{46.4 - 16.8} = \frac{44.5}{29.6} = 1.840.$$

The smallness of this constant indicates association in acetone. To determine the amount of association, we multiply the molecular mass M, by a factor x, which represents the average number of simple molecules that have coalesced to form a complex molecule. The calculation is as follows :

$$\left(\frac{2.121}{1.840}\right)^{\frac{3}{2}} = 1.25 \text{ between } 16.8^\circ \text{ and } 46.4^\circ.$$

the average molecular mass throughout this range of temperature is accordingly 1.25 × 58 = 73.

The apparatus described above was made by Walmsly, Fuller & Co., of Chicago, and has proven satisfactory in every detail. The makers inform me that they are ready to furnish the apparatus provided with a micrometer screw divided according to the metric as well as the English system.

ON THE REACTION BETWEEN CARBON TETRACHLORIDE AND THE OXIDES OF NIOBIUM AND TANTALUM.

BY M. DELAFONTAINE AND C. E. LINEBARGER.

Received April 20, 1896.

EUG. DEMARCAY[1] states that if the vapor of carbon tetrachloride be passed over the oxide of niobium or of tantalum heated below redness, the metallic oxides are converted into chlorides. "Dans le cas de l'acide niobique, la reaction se produit déja, bien qu' avec lenteur à la temperature de la naphthalene bouillante (280°) et avec une extréme rapidité à 440°."[2]

Now the chlorides of these rare elements enter into reaction

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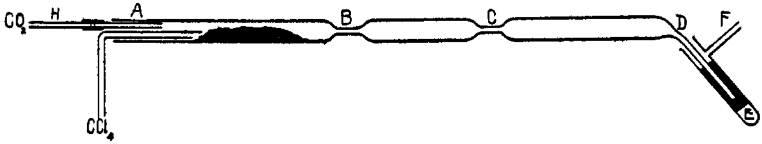
[1] *Compt. Rend.*, 104, 111, *1887*.

[2] *Loc. cit.*

very readily, and may serve as the starting points for numerous syntheses. Demarcay's statements led us to believe that the reaction in question would furnish a rapid method of obtaining these chlorides in quantity with comparative ease. On making use of the method, however, we found that the reaction does not take place in just the way indicated by Demarcay. We will first communicate our results obtained with niobic acid.

We used niobic pentoxide obtained from recrystallized potassium oxyfluosalt resulting from treatments of samarskite. The salt was decomposed in the usual way by sulphuric acid, boiled with water, and the residue ignited at strong red heat to expel the last traces of sulphuric acid.



The oxide was placed in one end of a piece of hard glass tubing, constricted in several places (Fig. 1), and the tube was heated in the vicinity of the oxide in a combustion furnace to 300°–400°. When the vapor of carbon tetrachloride was passed over the heated oxide, a reaction occurred immediately, and a yellowish white sublimate condensed in the cooler parts of the tube. If the oxide employed was quite pure, almost the totality of it could be converted into the volatile product. By careful application of heat it was possible to drive the sublimed substance into the further portions of the tube; it was then seen that the sublimate could be separated into two main portions, a more volatile one of a yellow color, and a less volatile one of a nearly white color. The properties of the yellow product were those of the pentachloride of niobium, while the properties of the whitish portion agreed with those of the oxychloride of niobium. By far the larger portion of the product of the reaction consisted of the oxychloride. The action of carbon tetrachloride on niobic acid seems to yield principally the oxychloride of niobium as the solid product; of the gaseous products formed, phosgene seemed to predominate.

It was thought that possibly the presence of even a slight amount of air might exercise an oxidizing influence upon the pentachloride at the moment of its formation, converting it into the oxychloride. We accordingly carried out the same experiment in an atmosphere of carbon dioxide, but could not see that the proportion of the pentachloride was at all increased.

Again it was considered that the relative amount of the pentachloride might be made greater by allowing the reaction to take place in an atmosphere of chlorine, but even under such conditions the principal product was found to be the oxychloride.

We conceive then that the main reaction of carbon tetrachloride and niobic pentoxide may be represented by the equation

$$3CCl_4 + Nb_2O_5 = 2NbO.Cl_3 + 3COCl_2,$$

which illustrates again the tendency that niobium has to enter into combination as *niobyl.*

We have prepared a considerable quantity of niobyl chloride according to the above reaction, and, after numerous experiments, have adopted the following method of conducting the operation:

A tube of the shape indicated in the figure is prepared and filled with niobic pentoxide between *A* and *B*. As the chlorine compounds of niobium are quite voluminous, care has to be taken not to employ too much of the oxide; we found that for a tube of about two cm. bore and having a length of about forty cm. between *A* and *B*, ten to fifteen grams could be taken. The tube is placed in a combustion furnace and the portion in the vicinity of the oxide heated to about 400°. A current of dry carbon dioxide is now passed through the tube to dry it thoroughly and expel the air. The constrictions at *B* and *C* are heated nearly to redness to prevent their becoming stopped up, and carbon tetrachloride is gently distilled over upon the niobium compound. It is advisible to discontinue the current of carbonic acid by pinching the delivery tube together at *H*, since often the pressure of the tube becomes sufficient to throw the acid out of the generator. In the early stages of the operation, there occurs a transportation of substance in such a fine state of division that it is carried clear through the tube; in order to prevent its entering the wash bottle containing sulphuric acid, and connected at *F*, a little glass wool or asbestos fiber is packed around the end of the tube in *E*. When *B C* becomes nearly filled with the products of the reaction, it is heated to a temperature just sufficient to volatilize the pentachloride, which may then be driven over into *C D*, leaving almost pure oxychloride in *B C*. When the reaction is at an end, no more carbon tetrachloride is passed into the tube, but the current of carbon dioxide is again sent through it in order to aid in the separation of the pentachloride from the oxychloride of niobium. Any carbon tetrachloride that may have condensed in *C D* is driven over into *E*, and *B C* and *C D* are so heated that the pentachloride passes through the constriction *C* and condenses just in front of *D*. While it is possible to drive almost all of the pentachloride out of *B C* and thus to obtain almost pure oxychloride, there is always a not inconsiderable portion of the latter compound that finds its way into *C D*.

In several experiments we found that a small quantity of an orange-colored sublimate collected at the further end of *C D*, which circumstance proves that this substance is more volatile than the pentachloride of niobium. H. Rose[1] also observed the formation of such a colored product when he was engaged in the investigation of chlorine on an intimate mixture of charcoal and tantalic acid. He found that if the acid employed contained "nur die geringste Spur von Wolframsäure, so zeigt sich bei der Darstellung des Chlorids eine sehr kleine Menge von einem rothem Chloride, das etwas flüchtiger als das Tantalchlorid ist." The compound is probably the oxytetrachloride of tungsten, its formation being due to a slight contamination of our niobic acid with a tungsten compound.

When we passed the vapor of tetrachloride over tantalic acid, no reaction took place at a lower temperature than 400°, when a small amount of volatile substance was formed, which soon ceased, however. Even on heating to a temperature high enough to cause the Bohemian glass tube to soften, we did not obtain any more of the sublimable product. The tantalic oxid turned yellow and assumed a pasty condition. It is probable that the

[1] *Ann. chem. phys.*, *Pogg.*, 99, 75, *1856*.

sublimed substance consisted of the chlorine compounds of niobium, since it is quite possible that our tantalic oxid was not entirely free from an admixture of niobic oxid. This behavior suggests a method of purification of tantalic acid containing a little niobic acid; we will not lay much stress on this, however, until we have done more work on the subject.

The readiness with which niobium oxychloride was formed in all our experiments contrasting with the comparatively small quantity of the pentachloride obtained illustrates once again the great inclination niobium has to enter into combination not as an individual element, but in the form of the radical *niobyl*. The action of sulphur and chlorine on NbO, investigated by Delafontaine, the numerous series of oxyfluo-salts prepared by Marignac, and the decomposition of niobyl chloride by magnesium are other facts of the same import. In this respect the analogy of niobium and vanadium is very striking, but it is almost entirely lacking in niobium and tantalum.

THE CHEMICAL NATURE OF DIASTASE.[1]

SECOND PAPER.

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received May 15, 1896.

In a former paper, by one of us,[2] the results of some attempts to isolate diastase have been detailed. This work has been continued, but as yet no preparations of diastase have been realized more active than those there described. The results given in the former paper, however, have been confirmed, and details of the process for obtaining highly active diastase have been determined more exactly.

Here follows a concise account of this later work so far as it is worth placing on record.

Fifteen kilograms of fine ground malt were treated with thirty liters of five per cent. sodium chloride brine, and after standing some time, with frequent stirring, the extract was pressed out and filtered, yielding sixteen liters of clear filtrate. The meal residue was again treated with fifteen liters of five per cent. brine

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[1] From the Report of the Connecticut Agricultural Experiment Station for 1895.

[2] Eighteenth Annual Report of this Station, pp. 192-207; *J. Am. Chem. Soc.*, 17, 587-603.