ART. X.—*On Complex Inorganic Acids.* From a letter of Dr. WOLCOTT GIBBS to one of the Editors, dated Cambridge, June 14th, 1877.

YOU will doubtless remember that about twelve years since Marignac described three acids which he obtained by boiling silicic hydrate, $Si(OH)_4$, with an acid alkaline tungstate, and which he called respectively silico-tungstic, tungsto-silicic and silico-deci-tungstic acid. The two first mentioned are isomeric or metameric, and are represented by the formulas:

$$12WO_3 . SiO_2 . 4OH_2, \text{ or } W_{12}O_{34}Si(OH)_8,$$

while the third has the formula

$$10WO_3 . SiO_2 . 4OH_2 \text{ or } W_{10}O_{28}Si(OH)_8.$$

It occurred to me that these results might be generalized in various ways, and I have in fact obtained some very interesting new series of acids of the same or similar types. Platinic hydrate $Pt(OH)_4$ boiled with an acid sodic tungstate yields two isomeric or metameric sodium salts which have the formula:

$$10WO_3 . PtO_2 . 4ONa_2 + 25 \text{ aq.}$$

One of these gives magnificent olive-green crystals; the other equally fine honey-yellow prisms with a very strong adamantine luster. They are readily soluble in water and give flocky or sub-crystalline precipitates with solutions of the heavy metals and of the higher alkaloids. The corresponding potassium and ammonium salts have respectively the formulas:

$$10WO_3 . PtO_2 . 4OK_2 + 9 \text{ aq. and } 10WO_3 . PtO_2 . 4OAm_2 + 12 \text{ aq.}$$

but both belong to the yellow series. I have not yet obtained the 12-atom series corresponding to Marignac's silico-tungstates. The platino-deci-tungstates dissolve tungstic hydrate, $W(OH)_6$, on boiling, but the hydrate separates again on cooling without change. Acid molybdate of sodium also dissolves platinic hydrate giving a deep olive-green solution which appears red in thick layers. The only salt of this series yet studied crystallizes in amber-colored tabular plates which have the formula:

$$10MoO_3 . PtO_2 . 4ONa_2 + 29 \text{ aq.}$$

They are very soluble and give sub-crystalline precipitates with many metallic solutions. I think I have also obtained the corresponding metameric series, but of this more in due time. The acids corresponding to the salts above briefly described are crystalline and may be obtained from the respective barium salts by sulphuric or from the silver salts by chlorhydric acid. Nearly all the salts of both series effloresce strongly and the alkaline salts have a very distinct acid reaction, so that the limit of the basicity is certainly higher than eight. I am endeavoring to generalize these results still farther by replacing platinic hydrate by other hydrates of the same type, as for instance by those of the other metals of the platinum group and by $Zr(OH)_4$ $Ti(OH)_4$, $Sn(OH)_4$, &c., but though I have in many cases indications of the formation of new complex acids I have nothing definite at present. Silico-molybdic acid appears however to be formed by boiling acid sodic molybdate with $Si(OH)_4$ when colorless or very pale yellow crystals are formed.

Nearly five years since Scheibler discovered two phospho-tungstic acids which, according to his analyses contained, respectively, six and twenty molecules of tungstic oxide, WO_3 to one of P_2O_5. As he has published nothing whatever upon the subject since, I have thought that I could fairly enter upon the same field and have begun the study of the 20-molecule series. I have already established some very important facts with respect to the compounds of this series, and have further generalized my own results to a most unusual extent.

According to my analyses, phospho-tungstic acid has the formula

$$20WO_3 . P_2O_5 . 8OH_2 \text{ or } W_{20}O_{57}P_2(OH)_{16}$$

independently of water of crystallization. I have obtained salts of this series having respectively the formulas:

$$20WO_3 . P_2O_5 . 0Na_2 . 7OH_2 + 16 \text{ aq.}$$
$$20WO_3 . P_2O_5 . 2BaO . 6OH_2 + 18 \text{ aq.}$$
$$20WO_3 . P_2O_5 . 6BaO . 2OH_2 + 44 \text{ aq.}$$
$$20WO_3 . P_2O_5 . 7OK_2 . OH_2 + 27 \text{ aq.}$$
$$20WO_3 . P_2O_5 . 8OK_2 + 18 \text{ aq.}$$

All these salts have an acid reaction except the 8-molecule potassium salt, and I consider this—provisionally at least—as determining the limit of the basicity of the acid. This is important as showing that it is not phosphoric oxide, P_2O_5, which alone is saturated. Debray considered the corresponding phospho-molybdic acid as 6-basic, but written with the newer atomic weights it would of course be regarded as 12-basic, if his view were correct. He describes however a 7-atom silver salt which I should write

$$20MoO_3 . P_2O_5 . 7OAg_2 . OH_2 + 24 \text{ aq.}$$

and which is clearly the analogue of my potash salt above mentioned. All or nearly all the phospho-tungstates effloresce quickly in dry air. I regard the formulas above given as well ascertained excepting possibly that of the very acid sodium salt which heads the list. The analyses of these salts as well as of the platinum series are difficult, and the ready efflorescence is another obstacle to very precise work. All but the first mentioned sodium salt are colorless; the 7 and 8-atom potassium salts are splendid, and there is at least one ammonium salt which is precipitated as a very heavy snow-white crystalline powder. I have not used Scheibler's method of preparing these compounds, but obtain the acid sodium salt by mixing normal sodic tungstate and hydro-disodic phosphate, $WO_4Na_2 + 2$ ag. and $PO_4Na_2H + 12$ ag., in the proportion of 20 molecules of the former to 2 of the latter and adding NO_3H until the very alkaline liquid becomes acid. I have had much success in generalizing these results. The corresponding arsenio-tungstic acid and its salts are easily obtained, and I have more or less distinct indications of vanadio-tungstic and antimonio-tungstic acids. It may prove that there are also niobio-tungstic and tantalo-tungstic acids, and experiment will soon decide this point. But generalization is also possible in other ways. Thus I find that when in my process oxyfluo-tungstate of sodium, $WO_2F_4Na_2$, is substituted for the normal tungstate, splendid crystalline salts are formed with both arsenates and phosphates. In place of normal sodic arsenate the oxyfluo-arsenate may be employed and new acids result both with normal tungstate and oxyfluo-tungstate of sodium. The same statements are probably true with respect to molybdic compounds, only the resulting salts are not always well defined. You see that in this way the number of new acids is very great and that I have a heavy task before me. It is of course too soon to speculate on the theoretical structure of the new acids. I have given the simplest possible formulas in all cases, but it may be that those of the platino-tungstic and platino-molybdic acids must be doubled. In this case their analogy to the phospho-tungstates, &c., will be more easily seen, as we shall have for the sodium salts for instance,

$$20WO_3 . Pt_2O_4 . 8ONa_2, \text{ and } 20\,WO_3 . P_2O_5 . 8ONa_2,$$

meantime I have as yet seen no satisfactory reason for the change. I am disposed to think that the well known and very singular $\frac{3}{7}$ tungstates and molybdates, $3ONa_2 . 7WO_3$ and $3ONa_2 . 7MoO_3$, should be multiplied by 3 and written

$20WO_3 . WO_3 . 9ONa_2$, and $20MoO_3 . MoO_3 . 9ONa_2$.

They will then fall naturally into the 20-atom series. It seems also possible that the curious salt of Wöhler usually written $WO_4Na_2 + W_2O_5$ may be represented by such a formula as $16WO_3 . 4WO_2 . 7ONa_2$ or $W_{20} . W . O_{49}(ONa)_{14}$. I shall devote myself to these compounds until I have exhausted the subject as far as possible, and meantime anticipate many new results.