

NICKELO-NICKELIC HYDRATE, $\text{Ni}_3\text{O}_4 \cdot 2\text{H}_2\text{O}$.

BY WILLIAM L. DUDLEY.

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IN studying the action of fused sodium dioxide on metals, I have obtained interesting crystalline compounds, some of which, at least, have never been described. Only one of them has been carefully investigated and it proves to be nickelonickelic hydrate, having the formula $\text{Ni}_3\text{O}_4 \cdot 2\text{H}_2\text{O}$.

It is prepared by fusing sodium dioxide in a nickel crucible with metallic nickel at a cherry-red heat. The action of the oxide upon the nickel proceeds with moderate rapidity, and in a few minutes scaly crystals appear floating in the fused mass. The crystals multiply steadily until, in the course of an hour, the contents of the crucible is thick with them, and comparatively little liquid remains. After cooling, the crucible is submerged in a beaker of distilled water and the undecomposed sodium dioxide together with the sodium oxide dissolves out, leaving the crystals which rapidly settle to the bottom of the liquid. The crystals should be washed several times with boiling water by decantation, and finally thrown in a filter. It is quite difficult to wash out all of the alkali, which adheres with unusual persistence. Probably the best plan to adopt is to put the crystals in a Soxhlet extraction apparatus and wash with water until no coloration is obtained with phenolphthalein. This requires about fifty hours of continuous washing. The crystals should then be dried at 110°C . and a magnet passed carefully through them to remove any particles of metallic nickel which may have eroded and not been completely acted upon.

The crystals are lustrous and almost black, with a slight brown-bronze hue. They are soft, and grind in a mortar much like graphite. The crystals seem to be hexagonal plates, but measurements of the angles have not been made. They dissolve slowly in acids, forming nickelous salts. Hydrochloric acid evolves chlorine; sulphuric and nitric acids, oxygen. They are insoluble in water and in solutions of the alkalies. The compound is not magnetic. The specific gravity is 3.4115 at 32°C .

At 130°C . the compound does not undergo decomposition, but at about 140°C . it begins to lose weight; at 240°C . the weight

remains constant. At a red heat further loss is sustained and the residue remaining is nickelous oxide. The loss from 130° C. to 240° C. is due to water driven off, and at a red heat this loss is due to the evolution of oxygen.

The compound proved to be $\text{Ni}_3\text{O}_4 \cdot 2\text{H}_2\text{O}$, as is shown by the results of the analysis :

Loss of H_2O on heating from 130° C. to 240° C. :

	Per cent.
First determination.....	13.00
Second "	13.13
Theory for $\text{Ni}_3\text{O}_4 \cdot 2\text{H}_2\text{O}$	13.06

The residue remaining after heating to 240° C. is Ni_3O_4 . On heating this residue to redness the loss of oxygen was found to be :

	Per cent.
Loss of oxygen	6.63
Theory.....	6.67

The total loss of water and oxygen obtained on heating the compound from 130° C. to redness was :

	Per cent.
First determination	18.91
Second "	18.88
Theory for $\text{Ni}_3\text{O}_4 \cdot 2\text{H}_2\text{O}$	18.86

The oxygen given off on heating to redness was determined by calcining the compound in an atmosphere of carbon dioxide and collecting in Schiff's apparatus over potassium hydroxide solution. The result gave :

	Per cent.
Oxygen	5.93
Theory for $\text{Ni}_3\text{O}_4 \cdot 2\text{H}_2\text{O}$	5.84

The nickel was determined and found to be :

	Per cent.
Nickel	63.67
Theory.....	63.72

In all of the calculations the atomic weight of nickel was taken to be 58.56 and oxygen 16.

The compound made in a nickel crucible of commerce is not perfectly pure, as the sample obtained was found to contain 0.71 per cent. of cobalt, the presence of which, however, would make no appreciable difference in the results of the analyses. No method has been found for freeing the compound from this im-

purity, and it appears at present as if the only plan would be to use a chemically pure nickel crucible in making it, for no crucible will withstand the action of fused sodium dioxide. Porcelain, iron, silver, gold and platinum crucibles are rapidly attacked.

The presence of water in this compound seems curious, but it may be due to the presence of sodium hydroxide in the sodium dioxide. Again it may be due to the water added to dissolve the soluble residue from the crystals. The first explanation seems to be the more plausible since the crystals are formed in the mass while it is fused, and they are not produced upon the addition of the water. If such is the case it would seem that the water driven off between 130° C. and 240° C. is from the breaking down of a true hydrate, rather than the expulsion of water of crystallization.

A cobalto-cobaltic hydrate, $\text{Co}_3\text{O}_4 \cdot 2\text{H}_2\text{O}$, has been described,¹ but it was obtained by exposing to moist air, Co_3O_4 , prepared by heating cobalt carbonate. Ni_3O_4 , prepared by heating nickel-nickelic hydrate to 240° C. is hygroscopic and absorbs about seven and four-tenths per cent. of water from the air at 30° C., which is completely lost at 110° C., showing that no hydrate is formed under these conditions.

The study of the action of fused sodium dioxide on the metals will be continued here, and it is hoped that some more data can be contributed soon.

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TABLE OF FACTORS.

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ATOMIC masses, based on $\text{O} = 16$, taken from an article by F. W. Clarke, this Journal, March, 1896.

	Required.	Factor.	Logarithm.
AlPO_4	Al.	0.221976	$\bar{1}.3463071$
	Al_2O_3 .	0.418489	$\bar{1}.6216835$
Sb_2O_4	Sb.	0.790067	$\bar{1}.8976643$
Sb_2S_3	Sb.	0.714570	$\bar{1}.8540446$
As_2S_3	As.	0.609522	$\bar{1}.7849890$
$\text{Mg}_2\text{As}_2\text{O}_7$	As.	0.483268	$\bar{1}.6841870$
Ag_2AsO_4	As.	0.162234	$\bar{1}.2101418$
BaSO_4	BaO.	0.657088	$\bar{1}.8176234$

¹ Genth and Gibbs: *Am. J. Sci.*, 23, 257.