CLXXXVIII.—*The Preparation and Properties of Nickelous Oxide.*

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The physical and chemical properties of many oxides are known to depend upon the nature of the material from which these are made and upon the temperature of preparation; for instance, as this temperature is increased, the colour of ferric oxide changes from orange-red to violet and its solubility in sulphuric acid decreases (Hedvall, *Z. anorg. Chem.*, 1922, **121**, 217): also the density of alumina increases and its solubility in acids decreases (Mellor and Holdcroft, *Trans. Ceramic Soc.*, 1911, **9**, 94).

Le Blanc and Sacshe (*Z. Elektrochem.*, 1926, **32**, 58) obtained nickelous oxide of colours varying from dark grey to greyish-green by heating the basic carbonate at various temperatures from 550° to 1220°, but this alteration of colour may have been partly due to impurities which liberated iodine from acidified potassium iodide solution. Schützenberger (*Compt. rend.*, 1892, **114**, 1149), by heating nickel sulphate to red heat, prepared a greenish-yellow nickelous oxide which was insoluble in dilute acids. Benton and Emmett (*J. Amer. Chem. Soc.*, 1924, **46**, 2730) found that the reduction of nickelous oxide by hydrogen is slower the higher the temperature of preparation of the oxide.

This investigation is a systematic study of the changes in the properties of nickelous oxide when the source and the temperature of preparation are varied.

EXPERIMENTAL.

Nickelous oxide was prepared by heating to various temperatures the nitrate, the basic carbonate, and the hydroxide in air, and also the last two substances in a vacuum. The nitrate was Merck's "pure chemical" and was further purified by recrystallisation. The basic carbonate and the hydroxide were prepared in the laboratory and washed free from impurities.

The furnace used for heating consisted of a silica tube over which was wound a coil of nichrome wire. The temperatures were measured by means of an electrical pyrometer.

The nickelous oxide obtained at different temperatures was analysed by dissolving a weighed amount in hydrochloric acid and depositing nickel on a rotating platinum-gauze cathode. This method gave more accurate results than that by means of dimethylglyoxime. The analyses given below show that the oxide prepared at lower temperatures is not pure and that the impurity decreases as the temperature of preparation is raised.

NiO *from nickel nitrate heated in air.*

Temp. of preparation ...	400°	500°	800°	900°	1000°
NiO, %	99·15	99·61	99·91	100	100
Colour	Black	Grey	Greyish-green	Greenish-yellow	

NiO *from basic nickel carbonate heated in air.*

Temp. of preparation	400°	600°	700°	800°
NiO, %	95·45	98·26	98·58	98·97
Colour	Black	Grey	Greyish-green	

The oxide prepared as above liberates iodine from an acid solution of potassium iodide fairly rapidly (compare Le Blanc and Sachse, *loc. cit.*); the proportion of active oxygen, however, is small and decreases as the temperature of preparation of the oxide is raised. The oxide obtained from the carbonate contains more active oxygen than that obtained from the nitrate at the same temperature.

The oxide prepared by heating nickelous hydroxide in air is black and is less pure than that obtained in other ways; nevertheless, it liberates only a small amount of iodine at a slow rate from an acid solution of potassium iodide.

By heating basic nickel carbonate and nickelous hydroxide to 400° or 500° in a vacuum, a greenish-yellow oxide is obtained which turns black on exposure to air. This blackened oxide becomes greenish-yellow again if heated in a vacuum to 200° or if placed in an acid solution of potassium iodide, in which case iodine is liberated fairly rapidly. The greenish-yellow oxide obtained by heating the basic carbonate in a vacuum to 800°, however, does not blacken when brought in contact with air, and its purity is 100%.

The blackening described above cannot be attributed to the formation of nickelic oxide on the surface of the nickelous oxide, because this higher oxide does not become greenish when placed in an acidified solution of potassium iodide or when heated even to 500° in a vacuum. It is suggested, therefore, that the oxide adsorbs oxygen from air, forming a black adsorption complex therewith. Le Blanc and Sachse (*Z. Elektrochem.*, 1926, **32,** 204) have found from an X-ray study of the blackened oxide that it is essentially nickelous oxide with the surplus oxygen " vagabundierend " in its lattice.

Richards and Rogers (*Amer. Chem. J.*, 1893, **15**, 567) have shown that the oxides of zinc and nickel, prepared by the ignition of nitrate, occlude oxygen and other gases that are not evolved on dissolution in potassium hydroxide solution. When the oxide prepared from nickel nitrate or basic nickel carbonate at 400—800° was heated in a vacuum, the gases collected were shown to contain, not only oxygen, but also probably oxides of nitrogen or carbon dioxide and water vapour, and these are the probable impurities in nickelous oxide prepared at temperatures below 1000°. The greater activity of the oxide prepared from nitrate, towards acidified potassium iodide, may therefore be due partly to the oxides of nitrogen. Further work on the quantitative analysis of these gases is being carried out.

Physical and Chemical Properties of Nickelous Oxide.—From the foregoing it appears that the purest nickelous oxide is obtained by heating nickel nitrate to various temperatures, and such oxide has been used for the study of the variation in properties with change in the temperature of preparation.

Density. It was observed that an appreciable shrinkage of the oxide took place when it was prepared at or above 800°, and that the greenish-yellow oxide settled in water more quickly than the grey. The densities of the oxides, determined by means of a pyknometer at 28°, were as follows :

Temp. of preparation	400°	500°	700°	800°	900°	1000°
$d_{4^\circ}^{28^\circ}$	5·668	5·745	6·070	6·265	6·305	6·310

Electrical resistance. The electrical resistance was measured by an apparatus similar to that employed by Ryschkewitsch (*Z. Elektrochem.*, 1922, **28**, 289). The specific resistance was calculated from the expression $S = R\pi^2 r^4 d/M$, where R is the observed resistance of M grams of the oxide, r the radius of the tube, and d the density of the oxide.

Temp. of preparation ...	400°	600°	700°	800°	900°
Specific resistance, ohms	4,880	7,598	9,034	14,772	Very high

Solubility in sulphuric acid. The solubility of nickelous oxide was measured in 0·1*N*-sulphuric acid. The oxide (0·2 g.) was treated with the equivalent amount of acid solution, and the mixture kept at 80° and stirred for a definite time. The solution was filtered and analysed.

Temp. of preparation	400°	500°	700°	800°	900°	1000°
NiO dissolved, %	96·86	85·70	36·70	2·68	2·18	0·77

The catalytic decomposition of hydrogen peroxide. Quartaroli (*Gazzetta*, 1925, **55**, 619) has studied the decomposition of hydrogen peroxide in the presence of several oxides and has shown that most of these reactions are autocatalytic. On the other hand, according to Clarens (*Bull. Soc. chim.*, 1923, **33**, 282), the decomposition of hydrogen peroxide is a physical phenomenon and depends upon the physical properties of the catalysts. The catalytic effect of the different nickelous oxides on the decomposition of hydrogen peroxide was studied at 30°. In neutral solution the decomposition was very slow, but it was more rapid in alkaline solution. The oxide (0·2 g.) was added to 25 c.c. of a hydrogen peroxide solution (prepared by ten-fold dilution of Merck's pure 10-volume product) containing 0·25 c.c. of $0{\cdot}1N$-sodium hydroxide. 2 C.c. of this reaction mixture were titrated with $N/100$-permanganate, at intervals, and the velocity coefficient k was calculated as for a unimolecular reaction.

	Oxide prepared at			
	400°	500°	800°	1000°
Time, mins.		$N/100$-$KMnO_4$, c.c.		
0	22·0	22·0	22·0	22·0
30	17·5	18·0	20·7	21·6
60	13·4	14·3	20·2	21·2
90	9·7	10·2	19·8	20·7
120	6·7	7·6	19·3	19·6
Mean values of $k \times 10^4$	81	46	16	8

Discussion of Results.

It is evident that the density and the electrical resistance of nickelous oxide both increase, and the solubility in sulphuric acid and the catalytic activity in the decomposition of hydrogen peroxide both decrease, as the temperature of preparation is raised. A remarkable change is noticeable in the properties of the oxide prepared at and above 800°. The proportion of the oxide dissolving in sulphuric acid falls from 36·7% to 2·68% as the temperature of preparation is raised from 700° to 800°.

The changes in properties probably reach their maximum values in the oxide prepared at 1000°. The electrical conductivity and the solubility in sulphuric acid of this oxide are very small.

It appears that nickelous oxide exists in two forms: (i) the black oxide prepared at 400°, and (ii) the greenish-yellow oxide prepared at 1000°; these may be called respectively the active and the inactive variety. The inactivity may be caused by changes (i) in the size of the particles of the oxide, (ii) from the amorphous to the crystalline state, (iii) in the crystalline form, and (iv) of an intramolecular nature.

Hedvall (*loc. cit.*) has shown that the size of ferric oxide particles increases as the oxide is heated to 1000°, and the same may happen in the case of nickelous oxide. The decrease in the amount of oxygen retained by the oxide prepared at higher temperatures may, therefore, be due to this cause : it is well known that the absorptive power of a substance decreases with increase in the size of the particles.

The changes in the properties of alumina with change in the temperature of preparation were attributed by Mitscherlich (*J. pr. Chem.*, 1860, **81**, 110) to a change from the amorphous to the crystalline state; but Hedvall's *X*-ray study of nickelous oxide (*Z. anorg. Chem.*, 1922, **120**, 327) showed the oxide to have the same crystalline form before and after heating.

Berzelius (" Lehrbuch der Chemie," Dresden, I, i, 841, 1825) showed that a number of oxides, when heated to redness, undergo an internal change, attended by the evolution of heat. It has also been found by various workers that the reactivity of these oxides with sulphuric acid decreases considerably and their density increases when they are so heated. In the case of alumina these changes start at about 850° and continue up to 1500°. Probably the nickelous oxide undergoes a similar intramolecular change on heating, and this change starts at 700—800° and is nearly completed at 1000°.

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