

The final result is not affected either by the excess of reagent or the longer time of treatment.

The material was heated to various temperatures, cooled and oxidized by hypochlorite. The results are given in Table VI.

TABLE VI

Heated, min.	Temp., °C.	Active O/Ni	Active O/Ni for pure NiO
180	300	0.0507	0.100
90	370	.0420	.066
180	370	.0417	.066
90	570	.0172	.020
90	900	.0172	.006

At lower temperatures the oxide surface is partially covered by alumina, judging from the lower active oxygen values. However at 900° the growth of crystals and hence the decrease in surface area is quite evidently prevented, thus illustrating the role of a promoter in preventing the sintering of a catalyst at high temperature.

**Acknowledgment.**—The authors wish to thank Dr. E. F. Burton and Professor H. J. C. Ireton of the Department of Physics of the University of Toronto for their kind aid and facilities for the x-ray work.

### Summary

1. Nickel oxide is composed of very small crystals when prepared at lower temperatures from the hydroxide.

2. By treating the nickel oxide with cold sodium hypochlorite solution, the surface takes up oxygen in an "active" condition which can be determined later by iodimetry. No separate phase of higher oxide is formed and, assuming a monomolecular layer, the particle size of the oxide can be calculated.

3. The x-ray determination of particle size makes it appear likely that after oxidation by hypochlorite there is one atom of active oxygen to each atom of nickel on the surface.

4. The particle size increases with increasing temperatures of preparation according to the equation  $\log D = kT + C$  where  $D$  is the diameter of crystal,  $T$  the temperature, and  $k$  and  $C$  are constants.

5. The possible structure of the adsorbed water film on nickel oxide has been given.

6. The presence of aluminum oxide in nickel oxide retards sintering at high temperatures.

TORONTO, ONTARIO

RECEIVED OCTOBER 14, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND PLANT LABORATORIES, URAL INSTITUTE OF FERROUS METALS]

## New Oxidation-Reduction Indicators. I. Phenylanthranilic Acid (*o*-Diphenylamine Carbonic Acid)

By W. S. SYROKOMSKY AND V. V. STIEPIN

After studies made by Walden<sup>1</sup> and his co-workers on the indicator properties of nitro- and amino-derivatives of diphenylamine, A. V. Kirsanov,<sup>2</sup> suggested as possible indicators carboxylic derivatives of diphenylamine the ortho, meta and para diphenylamine carbonic acids.

The first of these compounds was prepared by A. V. Kirsanov and V. M. Cherkasov<sup>3</sup> according to Ullmann.<sup>4</sup> These two investigators conducted some preliminary qualitative experiments with this compound as an indicator. The other two derivatives have never been prepared, but are now in the course of preparation for investigation. The molar oxidation potential of *o*-diphenyl-

amine carbonic (phenylanthranilic) acid was determined by us, using the method described by Walden, Hammett and Chapman.<sup>5</sup> The results gave a value of 1.08 volts, referred to the hydrogen electrode (the mean from eight well-checked titration curves). Such a high oxidation potential is quite unexpected in the diphenylamine series of indicators, and places it in an exceptional position in this series.

A stock solution of indicator was used (0.005 *M* solution of the sodium salt of phenylanthranilic acid, prepared by dissolving the acid in an equivalent quantity of sodium carbonate).

From 3 to 5 drops are satisfactory for most titrations. As might be expected from the value of the oxidation potential, the indicator works quite

(1) Walden, Hammett and Edmonds, *THIS JOURNAL*, **56**, 350 (1934).

(2) Laboratory of Organic Chemistry, Ural Geological Trust.

(3) Kirsanov and Cherkasov, *Bull. soc. chim.* (in press).

(4) Ullmann, *Ann.*, **355**, 312 (1907).

(5) Walden, Hammett and Chapman, *THIS JOURNAL*, **55**, 2649 (1933).

well with ceric sulfate and permanganate at low acidities in a sulfuric acid medium. With dichromate, without ferrous iron, the acidity must be not less than 2 *N*; a trace of ferrous iron exerts a catalytic effect, promoting oxidation by the dichromate at a lower acidity. Vanadates require still higher acidity, from 4 to 6 *N*. The change of color is from colorless to pink, without intermediate changes (with vanadates, to pink-violet). The resulting colored oxidation products are stable, and fully reversible, but fading takes place after several hours. Back titration of the oxidant with a reduction solution (ferrous iron) is quite permissible, and with direct titrations gives very concordant results.

The indicator correction was determined by titrating the solutions of ferrous iron with dichromate and with ceric sulfate, both with the indicator and potentiometrically. Table I shows the negligible indicator error.

TABLE I  
INDICATOR ERROR OF PHENYLANTHRANILIC ACID

	Indicator method	Potentiometric method
Normality of Fe <sup>++</sup> soln.	0.07166	0.07167
Normality of ceric sulfate soln.	.02839	.02835 <sup>a</sup>

<sup>a</sup> Normality was determined against sodium oxalate.

The oxidation potential of the new indicator, as might be predicted, is sufficient for the determination of iron without necessitating the use of phosphoric acid, as is the case with other indicators of the diphenylamine series. Determination of iron in a standard sample of iron ore gave figures which checked very closely with the certificate value—without using phosphoric acid.

The determination of vanadium in a titanium-magnetite ore, in pig iron, in steel and in vanadium slags obtained from the melting down of titanomagnetite pig iron, conducted according

to a modified method of Lang and Kurtz,<sup>6</sup> gave very concordant data as compared with the results obtained by the standard gravimetric and methods of Walden, Hammett and Edmonds.<sup>7</sup> Phenylanthranilic acid may be especially recommended in titrations with ceric sulfate, as with this oxidant extremely sharp changes of color, and negligible indicator errors, prevail.

### Conclusions

1. The indicator properties of a new oxidation-reduction indicator were studied. The indicator phenylanthranilic acid gives sharp, reversible color changes from colorless to pink or to pink-violet with the normal oxidants used in volumetric analysis. It is more stable in the presence of an excess of oxidant than diphenylamine and its derivatives.

2. The value of the normal oxidation potential was determined and found to be +1.08 volt, referred to the hydrogen electrode. In this value, the indicator may be compared with phenanthroline (+1.14 volts).

3. The indicator error, as determined by potentiometric methods, was found to be negligible.

4. The new indicator may be used successfully in all standard oxidation volumetric procedures such as titrations with dichromate, ceric sulfate and permanganate, and is especially advantageous in the determination of ferrous iron (as its use obviates the need for phosphoric acid), and in titrations with ceric sulfate.

5. The new indicator is cheap, and may be prepared easily in most laboratories of organic chemistry, in contradistinction to *o*-phenanthroline, the preparation of which is difficult and costly.

SVERDLOVSK, U. S. S. R. RECEIVED JANUARY 30, 1936

(6) Lang and Kurtz, *Z. anal. Chem.*, **88**, 288 (1931).

(7) Walden, Hammett and Edmonds, *THIS JOURNAL*, **56**, 57 (1934).