base, but is still unsatisfactory for indicator use. From its behavior toward mixtures of varying proportions of ferric and ferrous ions in 1 *m* sulfuric acid, its effective oxidation potential may be estimated at 0.06 below the molar ferric–ferrous potential.

2,4-Diaminodiphenylamine[9] is oxidized by ceric sulfate to a red compound which is only very slowly acted upon by excess of oxidant. An electrometric titration gave a sharp end-point at two equivalents of ceric ion to one of the diaminodiphenylamine. Two equivalents of titanous ion were likewise consumed in an electrometric reduction to a colorless solution. From these titrations (which were repeated with excellent agreement) the molar potential in 1 molar sulfuric acid referred to quinhydrone in the same solution is −0.06. An indicator with a potential in this range, stable toward strong oxidants and acids, seems not previously to have been known.

Reduction with tin and hydrochloric acid of 2,4-dinitro-4′-aminodiphenylamine and of 2,4-dinitro-4′-methoxydiphenylamine yields products with indicator properties practically identical with those of diaminodiphenylamine. The reduction product of 2,4-dinitrophenylbenzidine has indicator properties but is irreversibly oxidized by a small excess of oxidant. The products from 2,4,6-trinitrodiphenylamine and from 2,4,6,3′-tetranitrodiphenylamine show no indicator properties with ceric sulfate.

Table I

Summary of Relative Molar Oxidation Potentials in 1 *m* Sulfuric Acid against the Quinhydrone Electrode in the Same Acid

Ceric–cerous[2a]		+0.65
Vanadate–vanadyl[2b]		+ .33
Ferric–ferrous[2a]		− .01
Vanadyl–vanadous[2b]		− .33
Ferrous–phenanthroline[2a]		+ .36
Ferrous–nitrophenanthroline		+ .47
p-Nitrodiphenylamine		+ .29[a]
Diphenylamine sulfonic acid[3d]	*ca.*	+ .1[a]
Diphenylamine[6]	*ca.*	[a]
Diaminodiphenylamine		− .06

[a] These are effective, not molar potentials.

Summary

The relative oxidation potentials and indicator properties of certain derivatives of phenanthroline and diphenylamine have been investigated. Some of these are useful oxidation indicators and cover new potential ranges.

New York, N. Y. Received February 14, 1934

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[9] Prepared by reduction of the dinitro compound with tin and hydrochloric acid. The product agreed in properties with the description of Nietzki and Almenrader, *Ber.*, **28**, 2969 (1895).

[Contribution from the Department of Chemistry, Johns Hopkins University]

x-Ray Studies of the System Nickel–Oxygen–Water. III. The K-Absorption Limits of Nickel in Various Oxide-Hydrates*

By R. W. Cairns[1] and Emil Ott

Introduction

The positions of the principal absorption edges of the elements depend to an appreciable extent on the nature of the chemical bonds by which they are combined with other atoms. In the case of the lighter elements such as phosphorus, sulfur and chlorine, the magnitude of the effects is sufficient to show the influence of factors such as valence, size of surrounding atoms, crystal structure and degree of hydration. Valence changes of the absorbing element produce the largest observed displacements, causing wave length shifts of more than 20 X. U. in the case of chlorine, and a lessening effect as the atomic number of the absorber increases.

Lindsay and Voorhees[2] have measured the Fe K-absorption limits of a number of iron compounds, and have reported wave length shifts $\Delta\lambda$ for di- and trivalent iron as compared to the position of the limit for the pure element as follows

Valence state	Absorber	$\Delta\lambda$ in X. U.
II	$FeCO_3$	1.4
	$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$	1.9
II and III	Fe_3O_4	1.9
	$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O + FeCl_3 \cdot 6H_2O$	1.8
III	$FeCl_3 \cdot 6H_2O$	2.5
	Fe_2O_3	2.5

These results are quoted here in detail since we may anticipate quite comparable results for our present investigation on nickel, due to the close relationship of the two elements in question.

There has been some doubt in the past as to the valence of nickel in certain so-called oxide-hydrates. An investigation of the properties of several of these compounds was recently reported by the authors.[3] In particular, the existence of a compound having the empirical formula $Ni_2O_3 \cdot$

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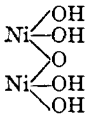
* Presented in part at the Washington Meeting of the American Chemical Society, 1933.

[1] Firestone Tire and Rubber Company Fellow, 1929–1933.

[2] Lindsay and Voorhees, *Phil. Mag.*, [7] **6**, 910 (1928).

[3] Cairns and Ott, This Journal, **55**, 527, 534 (1933).

$2H_2O$ was indicated. Consistent with observations as to its preparation, and decomposition in water and air, it was concluded that the probable structural formula was



In at least one instance[4] an investigation as to the nature of substances prepared in a manner similar to the above has led to the conclusion that such materials contain only di- and tetravalent nickel. Such a conclusion is not consistent with the above formula. Recently, LeBlanc and Möbius[5] attacked our claims on the existence of higher valent nickel (trivalent as interpreted by us) in our products. It appears thus desirable to furnish further proofs.[6]

It may be expected in view of the introductory remarks that the x-ray absorption limit of a trivalent nickel compound would differ from that of a substance containing either both di- and tetravalent nickel or divalent nickel with adsorbed oxygen only.

Experimental Part

A Seeman wedge type spectrograph (from the Seeman Laboratory) with a calcite crystal, and wedge to plate distance of 30 cm., was used in this work. The source of radiation was a Seeman metal hot-filament tube with a silver target. It was necessary to utilize a molybdenum filament, since the small amounts of tungsten thrown off from the usual filament contaminated the target and produced W L-radiation which interfered with the absorption edge measurements. The Mo filaments had a life of about ten hours, on account of rapid evaporation at operating temperatures, but this length of time was sufficient for a single exposure. The tube was operated at 20–25 milliamperes and *ca.* 30 kilovolts. Absorption screens were prepared either by rubbing the finely powdered materials into filter paper, or by mixing the powders with collodion solutions and allowing them to dry in thin films. A thin nickel foil was used to obtain the K-absorption limit of the pure element. The spectra were recorded photographically on Eastman x-ray plates, and the exposed plates were measured on a microcomparator. The second order Mo $K\alpha_2$ line was used as a reference line, and the positions of the absorption limits determined relative to it. About twenty observations were made on each plate, and at least two plates were prepared for every substance used as absorber. In addition to this, photometer curves were obtained on a Moll microphotometer, and the curves for plates to be compared were superimposed on the same paper, so that accurate comparisons could be made. Five such comparisons were made between each spectrum of an oxide-hydrate preparation and that of pure nickel. The combined data were averaged to obtain the shifts in the positions of the absorption edges of the various absorbers relative to the position of the principal edge for pure nickel.

The materials used as absorbers were prepared according to procedures previously described by us.[3] These were NiO, $Ni(OH)_2$ and preparations A and D; also mixtures of preparation A and $Ni(OH)_2$ were used as absorbing materials, for comparison purposes.

The results are compiled in the following table where $\Delta\lambda$ is the wave length shift toward shorter wave length, relative to the K-absorption limit of pure nickel. The probable error was 0.1 X. U.

	Absorbing material	O:Ni ratio	$\Delta\lambda$ in X. U.
	NiO	1.0	0.81
	$Ni(OH)_2$	1.0	1.10
	Preparation D	1.35	1.16
	Preparation A	1.5	1.82
I	1 part Prep. A 1 part $Ni(OH)_2$	1.25	1.18
II	10 parts Prep. A 1 part $Ni(OH)_2$	1.45	1.86

Discussion of Results

In no case was there any indication of a double principal edge. The results show beyond doubt that preparation A contains nickel in a valence state higher than two, contrary to the viewpoint of LeBlanc and Möbius. The questions still to be answered deal with the amounts of higher oxides present (since we are obviously not dealing with pure materials) and whether these correspond to tri- or tetravalent nickel, or both. The results obtained with preparation D and mixtures I and II show that the higher oxides must be the major constituent in order to show an absorption limit different from the one of divalent nickel compounds. This is also borne out by the results of Lindsay and Voorhees[2] on di- and trivalent iron. In that case there can be no dispute as to the valence state of the materials employed. We therefore feel justified in concluding that Sample A contains essentially higher oxide-hydrates of nickel. If this higher nickel oxide should be tetravalent, according to the analyses, the highest possible value of the ratio Ni^{IV}: Ni^{II} would be 1. Such a mixture cannot be anticipated, in view of the results obtained with iron oxides, not to show the absorption edge of divalent nickel. This however is not the case.

We thus feel further justified in considering preparation A as containing essentially trivalent

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(4) Bellucci and Clavari, *Gazz. Chim. Ital.*, **36**, 58 (1906); **37**, 409 (1907).

(5) LeBlanc and Möbius, *Z. Elektrochem.*, **39**, 753 (1933).

(6) Compare also our reply to LeBlanc and Möbius in *Z. Elektrochem.*

nickel in agreement with our previously expressed viewpoint.

Summary

The x-ray absorption limits of various nickel compounds have been studied.

It is shown that a product claimed by us previously to be essentially $Ni_2O_3 \cdot 2H_2O$ contains nickel of a valence higher than two. It is most likely trivalent nickel. This gives further support to our previous conclusions.

BALTIMORE, MD. RECEIVED FEBRUARY 17, 1934

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF THE UNIVERSITY OF WISCONSIN]

Calculations of the Activation Energies of Some Reactions between the Halogens and the Ethylene Double Bond

BY ALBERT SHERMAN[1] AND C. E. SUN

Introduction.—In a series of papers[2] Eyring and his co-workers have set forth the general methods, with relevant details, which may be used in the calculation of activation energies of chemical reactions. Applications have been made to a variety of reactions, with considerable success. In this paper further applications of the method will be made. Attention will be primarily focused upon the chemical significance of the results, rather than upon their quantum mechanical aspects, already considered in detail in the previous papers. The calculations serve as a useful tool in considering hypothetical reaction mechanisms, and in suggesting significant experiments.

Arnold and Kistiakowsky[3] studied experimentally the thermal gaseous decomposition of ethylene iodide and found that two independent mechanisms are simultaneously operative in a given temperature interval, each giving approximately equal rates, and identical final products of ethylene and iodine. This means, of course, that the respective over-all activation energies for the two mechanisms are nearly the same. One mechanism is a unimolecular decomposition, found to have an activation energy of 36.6 ± 3 kg. cal.; the other is a reaction catalyzed by iodine atoms, with an over-all activation energy of 30.2 ± 3 kg. cal. It is of interest to calculate these energies and see if one is led to the prediction of the experimental facts, since it has been emphasized that the calculations are especially useful in deciding reaction mechanisms—*i. e.*, in finding *differences* in activation energies, rather than absolute values. The calculations have also been carried out for ethylene bromide and ethylene iodide, leading to predictions yet to be checked experimentally.

Bauer and Daniels[4] studied the photobromination of cinnamic acid in carbon tetrachloride. Two mechanisms had been proposed for the reaction. Berthoud and Beraneck[5] set forth the following scheme

$$Br_2 + h\nu \longrightarrow 2Br$$
$$Br + C_6H_5{-}C{=}C{-}COOH \longrightarrow C_6H_5CBr{-}\underset{|}{C}{-}COOH$$
$$Br_2 + C_6H_5CBr{-}\underset{|}{C}{-}COOH \longrightarrow C_6H_5CBr{-}CBr{-}COOH + Br$$

Purakayastha and Ghosh[6] suggested the following mechanism

$$Br_2 + h\nu \longrightarrow 2Br$$
$$Br + Br_2 \longrightarrow Br_3$$
$$Br_3 + C_6H_5C{=}C{-}COOH \longrightarrow C_6H_5CBr{-}CBrCOOH + Br$$

Bauer and Daniels discarded Berthoud and Beraneck's mechanism because it involves atom reactions having small activation energies while the reaction was found to have a large temperature coefficient. They were unable to say much about Purakayastha and Ghosh's mechanism, however, because of the difficulty of detecting Br_3 and distinguishing it from Br. It is in just such cases as this that the quantum-mechanical calculations are particularly useful and reliable. This latter mechanism is obviously only sensible if the activation energy for the reaction of Br_3 with the double bond is less than that for Br_2 with the double bond. The respective activation energies have been calculated and are given below, together with the results of similar calculations involving I_2 and I_3, and Cl_2 and Cl_3.

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[1] National Research Council Fellow, 1933–1934.

[2] Eyring, THIS JOURNAL, **53**, 2537 (1931); Sherman and Eyring, *ibid.*, **54**, 2661 (1932); Kimball and Eyring, *ibid.*, **54**, 3876 (1932); Eyring and Kimball, *J. Chem. Physics*, **1**, 239 (1933); Taylor, Eyring and Sherman, *ibid.*, **1**, 68 (1933); Eyring, Sherman and Kimball, *ibid.*, **1**, 586 (1933); Eyring, *Chem. Rev.*, **10**, 103 (1933).

[3] Arnold and Kistiakowsky, *J. Chem. Physics*, **1**, 166 (1933).

[4] Bauer and Daniels, THIS JOURNAL, **56**, 378 (1934).

[5] Berthoud and Beraneck, *J. chim. phys.*, **24**, 213 (1927); *Helv. Chim. Acta*, **10**, 289 (1927).

[6] Purakayastha and Ghosh, *Quart. J. Indian Chem. Soc.*, **2**, 26 (1926); **4**, 409 (1927); **4**, 553 (1927).