In this investigation a particular relationship between the vibration frequency and number of valence electrons is proposed for gaseous carbon monoxide species and then applied to chemisorbed species to see if the chemisorbed species follow the same relationship as the gaseous species.

The results presented in a previous investigation of the chemisorption of carbon monoxide[4] suggest that the relationship between vibration frequency and number of valence electrons is that of a right hyperbola passing through the points[5,6]: $\nu(\mathrm{CO})^+ = 2183.90$ cm.$^{-1}$ (9 valence electrons); $\nu(\mathrm{CO}) = 2143.27$ cm.$^{-1}$ (10 valence electrons); and $\nu(\mathrm{CO})^{2-} = 0$ cm.$^{-1}$ (12 valence electrons). The equation obtained by using these points is

$$[2269.96 - \nu(\mathrm{CO})][12.1182 - E(\mathrm{CO})] = 268.31 \text{ cm.}^{-1} \tag{1}$$

$\nu(\mathrm{CO})$ is the vibration frequency of the carbon–oxygen bond and $E(\mathrm{CO})$ is the number of valence electrons—a number which should be integral for gaseous species and non-integral for adsorbed species. In Table I this equation is applied to experimental data from the chemisorption of carbon monoxide on several adsorbents.

TABLE I

VIBRATION FREQUENCIES AND NUMBER OF VALENCE ELECTRONS (CALCULATED FROM EQ.1)

	"Intermedions"		"Carbonyls"	
Adsorbent	Infrared bands, cm.$^{-1}$	Number of electrons	Infrared bands, cm.$^{-1}$	Number of electrons
Copper metal[a]			2095	10.59
Copper(I) fluoride[b]			2146	9.95
Copper(II) oxide[c]	2173	9.35	2127	10.24
	2121[g]	10.32	2000	11.12
Cobalt[d]	2160	9.68	2179	9.17
	2091	10.62		
Iron oxide[e]	2127	10.24	2020	11.04
Iron	1960	11.25		
Silver[f]	2165	9.56	[h]	
	2165[g]	9.56		
	2099	10.55		

[a] A sample of copper nitrate supported on Cab-o-sil was decomposed at 450°. The oxide was reduced with hydrogen at this temperature for 12 hours. [b] Copper(I) fluoride was precipitated in a water slurry of Cab-o-sil from $CuCl_2$ and NH_4F. The precipitate was washed until free of chloride ions. The sample was heated *in situ* in the spectrometer cell to 400° and reduced with iron. [c] Cupric oxide supported on M-5 Cab-o-sil was produced by the decomposition of the nitrate at 400°, *in vacuo*. [d] The adsorbent was cobalt oxide produced by the decomposition of the nitrate supported on Cab-o-sil and reduced at 400° with purified hydrogen. [e] These data for iron and iron oxide were reported by Eischens and Pliskin.[7] [f] Supported silver nitrate was partially decomposed by heating at 250° for 15 minutes *in vacuo*. The addition of CO produced the band at 2165 cm.$^{-1}$. Hydrogen gas was next added to a total pressure of 0.5 atm. and the 2099 cm.$^{-1}$ band for chemisorbed CO then appeared. [g] These bands were determined with a grating spectrometer, others with a NaCl prism spectrometer. [h] Carbonyls may also exist on this surface but their presence was not detected.

The data in Table I seem to fall naturally into two groups which we have termed "intermedions" and "carbonyls." For both of these type structures the numbers of valence electrons as calculated from equation 1 are non-integral. With the carbonyl structures there seems to be no particular pattern to the non-integral numbers, but for the pairs of intermedions discovered on several adsorbent surfaces the differences in numbers of valence electrons correspond almost exactly to one electron and the fractional parts of the non-integral numbers are constant, *e.g.*, 0.56 for silver, 0.25 for iron, etc.

There appear to be still other differences between carbonyls and intermedions. Whereas it is probable that carbonyl structures can be present on most if not all adsorbent surfaces, it is much less certain that this is the case for intermedions. Of the adsorbent materials listed in Table I intermedions were found on all except copper metal and copper(I) fluoride, and of the various metal atoms present in these different adsorbents only copper and copper(I) atoms do not have d-orbital vacancies according to their normal electronic configurations; it is possible that d-orbital vacancies are a requirement for the formation of intermedions.

The effect of components added to metal adsorbents is to cause a shift in the absorption band of carbonyl structures in a manner that seems dependent on the electronegativity of the added component. For example, the band at 2095 cm.$^{-1}$ on copper film is shifted to 2146 cm.$^{-1}$ when fluorine is added to copper, *i.e.*, on copper(I) fluoride. Added components to metal adsorbents change the distribution of the various intermedions, but not their vibration frequencies. Again these changes seem dependent on the electronegativity of the added component. Eischens and Pliskin[7] report an infrared absorption band for carbon monoxide on iron at 1960 cm.$^{-1}$ (corresponding to an 11.25 intermedion) which was replaced by a band at 2127 cm.$^{-1}$ (corresponding to a 10.25 intermedion) upon the addition of oxygen to the system. A similar effect was noted on introducing hydrogen to the system silver–carbon monoxide (*cf.* footnote *f* in Table I).

The fractional part of the non-integral number of valence electrons associated with intermedions is thought to be a unique property of the particular metal adsorbent, *e.g.*, 0.56 for silver, 0.25 for iron, etc. It is proposed to refer to this fraction as the "polarization fraction" of the metal. Studies are now underway to relate these polarization fractions to more familiar metal properties, to provide a more theoretical interpretation of the concept of intermedions, and to apply the concepts of intermedions and polarization fractions to an interpretation of catalytic reactions.

(5) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1955, p. 522.

(6) E. K. Plyler, L. R. Blaine, and W. S. Connor, *J. Opt. Soc. Am.*, **45**, 102 (1955).

(7) R. P. Eischens and W. A. Pliskin, "Advances in Catalysis," Vol. X, Academic Press, Inc., New York, N. Y., 1958, p. 2.

MAGNETIC PROPERTIES OF $Ni_2O_3 \cdot H_2O$

By JAMES T. RICHARDSON

Humble Oil & Refining Company, Baytown, Texas

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The valence state of nickel in its higher oxides is in considerable doubt. When chlorine or bromine in alkaline solution is added to a solution of a nickel salt, the result is a black, hydrated oxide with a composition from $NiO_2 \cdot xH_2O$ to $Ni_2O_3 \cdot xH_2O$. Cairns and Ott[1] prepared and studied a compound $Ni_2O_3 \cdot 2H_2O$, which

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(1) R. W. Cairns and E. Ott, *J. Am. Chem. Soc.*, **55**, 527 (1933); **55**, 534 (1933).

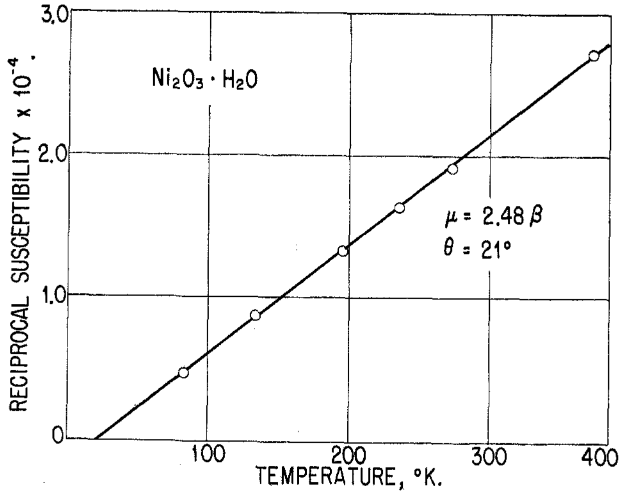

Fig. 1.—Curie–Weiss plot of $Ni_2O_3 \cdot H_2O$.

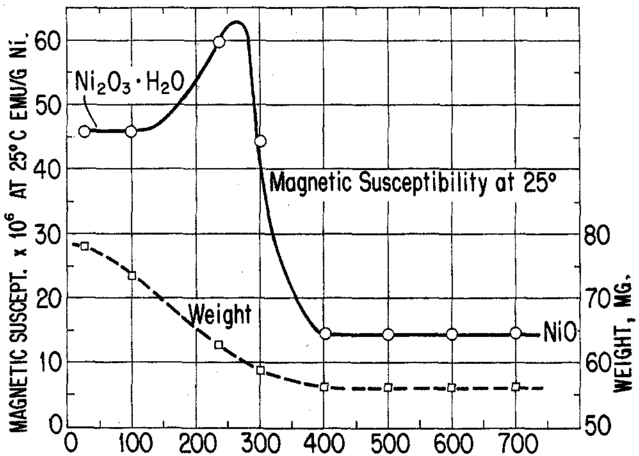

Fig. 2.—Magnetic susceptibility and weight changes for the decomposition of $Ni_2O_3 \cdot H_2O$.

decomposed on heating to $Ni_2O_3 \cdot H_2O$ and then to NiO. These authors[2] confirmed the presence of Ni^{3+} by X-ray absorption edge measurements, although Hanson and Milligan,[3] performing similar experiments, found no differences between these and NiO samples. Cairns and Ott also reported their failure to prepare anhydrous Ni_2O_3 by heating the hydrate. Recently, however, Aggarwal and Goswami[4] detected lines in electron diffraction patterns attributed to hexagonal Ni_2O_3 on the oxidized surface of nickel films. The existence of nickelic oxide is denied by Vainshtein,[5] who considers $Ni_2O_3 \cdot xH_2O$ to be a mixture of hydrated NiO and NiO_2.

In this investigation, three samples of $Ni_2O_3 \cdot xH_2O$ were prepared by adding bromine in KOH solution to solutions of nickelous chloride (a) with precipitation at 25° and air-drying, (b) with precipitation at 25° and drying at 100°, and (c) with precipitation at 100° and drying *in vacuo* at 25°. In each case chemical analyses were made for nickel (dimethylglyoxime method), "active" oxygen (Bunsen–Rupp test), and total oxygen (neutron activation analysis), with hydrogen obtained by difference. The results indicated the following compositions: (a) $Ni_2O_{3.02} \cdot 2.24H_2O$, (b) $Ni_2O_3 \cdot 1.50H_2O$, and (c) $Ni_2O_{3.05} \cdot 2.15H_2O$. X-Ray diffraction patterns of all three samples are identical and agree with sample A in ref. 1, designated by Cairns and Ott as "$Ni_2O_3 \cdot 2H_2O$." Magnetic susceptibility measurements were made from −196 to 100° on all samples, which demonstrated the same Curie–Weiss relationship shown in Fig. 1 for sample (b). The constants yield $\mu = 2.48\beta$ and $\theta = +21°$. Sample (a) was heat-treated for 24 hours at approximately 100° intervals up to 700°. Following each heat-treatment, the sample was cooled to room temperature and the magnetic susceptibility and weight measured. These data are plotted in Fig. 2. X-Ray absorption edge measurements revealed no differences between these samples and NiO. Conductivity and the Seebeck coefficient measurements show the material to be n-type, whereas NiO is p-type.

Both the room temperature susceptibility and the weight of the oxide reach a constant value when heat-treated above 400° with the susceptibility characteristic of NiO. Partial loss of H_2O occurs immediately upon heating to 100°, but with no change in the magnetic properties. Decomposition begins at about 130°, where the weight corresponds to $Ni_2O_3 \cdot 1.25H_2O$. The maximum in susceptibility between 100 and 400° is due to the presence of small particles of NiO, which exhibit enhanced superparamagnetic susceptibilities when prepared at lower temperatures.[6] This effect decreases with higher temperatures of heat-treatment and disappears above 400°.

The Curie–Weiss dependence of the susceptibility indicates the presence of one paramagnetic phase only. Chemical analysis identifies this phase as a hydrous oxide of trivalent nickel. Contrary to the findings of Cairns and Ott[1] but in agreement with Hüttig and Peter,[7] this oxide may be dehydrated below $Ni_2O_3 \cdot 2H_2O$ without changing either the structure or the magnetic properties. Decomposition to NiO occurs just before the monohydrate is reached. It, therefore, appears that, if this material is a true hydrate, it is $Ni_2O_3 \cdot H_2O$ with adsorbed water.

Trivalent nickel in a low spin state has a spin-only magnetic moment of 1.73β. The observed moment of 2.48β suggests, therefore, a low spin state with considerable unquenched orbital contribution. The positive sign of the Weiss constant is an indication of ferromagnetic coupling between the nickel atoms.

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FREE RADICALS FORMED FROM o-SUBSTITUTED NITRO COMPOUNDS[1a]

By A. J. Tench[1b] and P. Coppens[1c]

Chemistry Department, Brookhaven National Laboratory, Upton, L. I., New York

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The photochemical rearrangement of *o*-nitrobenzaldehyde to nitrobenzoic acid was discovered in 1901[2] and has been investigated by various workers (see for example ref. 3). The reaction is known to occur both in the solid state and in solution. It seemed possible that a paramagnetic species could be formed during the

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[1] (a) Research performed under the auspices of the U. S. Atomic Energy Commission; (b) Chemistry Division, Atomic Research Establishment, Harwell, Didcot, Berks, England; (c) Crystallography Department, Weizmann Institute of Science, Rehovoth, Israel.

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