isobutyl alcohol dissolves uranyl nitrate dihydrate with a heat evolution of 10.30 kcal./mole. In contrast, addition of acetone to tributyl phosphate reduces the heat of solution of the dihydrate in the direction of the heat of solution in acetone, to −8.72 kcal. for 25% acetone and −8.29 kcal. for 50% acetone by volume.

TABLE III

HEAT OF SOLUTION OF URANYL NITRATE DIHYDRATE IN ACETONE-ISOBUTANOL MIXTURES

Vol. % iso-BuOH	Heat of solution, kcal./mole
100	−2.58
87.5	−7.06
75	−8.84
50	−10.30
0	−6.65

The heat effects of adding water to solutions of uranyl nitrate dihydrate in the weaker bases show that at low water levels, where hexasolvate formation is minor, one should get an effect analogous to that exhibited by the acetone–alcohol mixtures. Experimental values for water–acetone mixtures (Table IV) confirm this. The −10.98 kcal. at 3.25% water represents a minimal value for the heat of solution of uranyl nitrate dihydrate in water to give undissociated uranyl nitrate tetrahydrate; the process of dissociation of the nitrates and coördination of two more molecules of water thus absorbs a net minimum of 5.6 kcal., to give the over-all value for pure water of −5.37 kcal. That the heat difference in the water case, for a lesser distance of separation of cation and anions, is 2.1 kcal. greater than for the alcohol–acetone mixtures *vs.* pure alcohol may be attributed in part to a greater binding energy for water, since the difference under discussion is the resultant of the exothermic solvent binding process, and the endothermic ion separation process. Considering this, the true value for the heat of solution to give the undissociated tetrahydrate runs ahead of the heats for the ethers, in agreement with what one would anticipate from the relative base strengths.

TABLE IV

HEAT OF SOLUTION OF URANYL NITRATE DIHYDRATE IN ACETONE-WATER MIXTURES

Vol. % H_2O	Heat of solution, kcal./mole
0.2-0.25	−6.67
0.5	−7.99
0.75	−8.68
1.25	−9.21
2.25	−9.99
3.25	−10.98
5.25	−10.26
7.75	−9.94

In view of the statements of Mathieson[13] it apparently needs to be stressed that in the absence of values for the lattice energies of the solids involved, one cannot equate solvation reaction heat values with binding energies for the molecular bases involved.

CHICAGO, ILL. RECEIVED SEPTEMBER 10, 1951

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Reduction of Nickel Oxide by Hydrogen

BY GIUSEPPE PARRAVANO

The reduction of nickel oxide by hydrogen has been studied in the range of 150–350° and initial pressures of hydrogen from 200 to 500 mm. The addition of foreign ions to nickel oxide affects both the rate and activation energy for reduction. These effects have been related to the change in the electronic properties of the oxide.

The problem of the extent to which chemical interactions involving a solid phase are affected by the energetic structure of that phase has been the subject of considerable experimental and theoretical work. These studies proceeded through different approaches, mainly centered on the elucidation of the mechanism of heterogeneous catalysis.

Theoretical advances and successful applications of the band theory of the solid state have recently led to a better understanding of the electronic properties of metallic oxides. In the field of catalysis the production of oxide semi-conductors with controlled electronic characteristics by Verwey and his school[1] discloses new possibilities, and affords a sound basis for attacking the problem of the relation between electronic states of oxides and their activity to catalyze chemical reactions.

As a preliminary study in this field, the reduction process of nickel oxide by hydrogen was investigated in order to obtain information on the effect of ionic and electronic defects in the solid phase on its reductive properties. The extensive investigations of Pease and Taylor[2] in the case of copper oxide, of Garner in the case of zinc oxide,[3] of Taylor and Starkweather[4] and Benton and Emmett[5] in the case of nickel oxide have shown that the reduction processes of metallic oxides involve several different stages. In the case of nickel oxide, after an initial auto acceleration of the reduction rate, a constant value is obtained up to relatively high conversions. The present data refer mainly to this latter stage of the reductive process and clearly show how the reaction can be greatly affected by the defective structure of the solid phase.

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(1) E. J. Verwey, P. W. Haaijman, P. C. Romeijn and G. W. Osterhout, *Philips Res. Reports*, **5**, 173 (1950).

(2) R. N. Pease and H. S. Taylor, THIS JOURNAL, **43**, 2179 (1921).

(3) W. E. Garner, *J. Chem. Soc.*, 1239 (1947).

(4) G. B. Taylor and H. W. Starkweather, THIS JOURNAL, **52**, 2314 (1930).

(5) A. F. Benton and P. H. Emmett, *ibid.*, **46**, 2728 (1924).

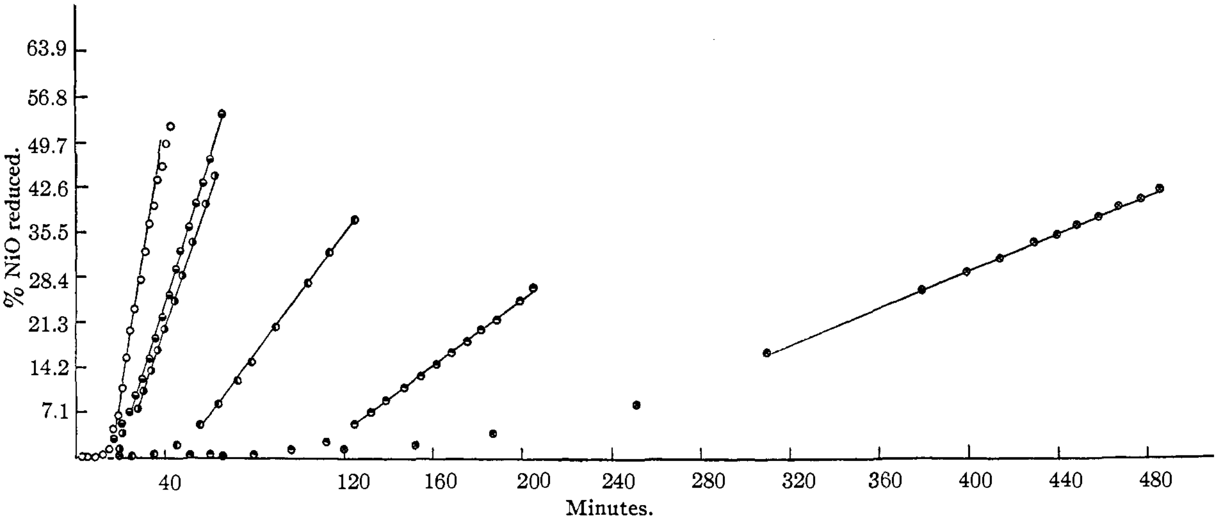

Fig. 1.—Reduction of nickel oxide by hydrogen: p_{iH_2} = 470 mm.: ⊗, t = 155°; ◓, t = 170° (NiO + 1 5 atom % Ni); ◐, t = 174°; ◑, t = 192° (NiO prepared in helium); ◓, t = 192° (NiO prepared in oxygen); ○, t = 200°.

Experimental Procedure

Preparation of Samples.—In order to obtain comparable results all oxide samples were prepared under strictly controlled conditions. C.P. nitrates were dissolved in distilled water, the solutions being standardized in the usual way. The samples containing wolfram trioxide, nickel chloride and magnesium oxide were prepared from standard solutions of ammonium wolframate, nickel chloride and magnesium oxide dissolved in nitric acid. Calculated amounts of the standard solutions, corresponding to the desired percentage of oxide impurity in the final products were added to portions of the nickel nitrate solution. The mixed solutions were evaporated overnight at 110°, decomposed slowly by heating for four hours from room temperature to 400°, fired in air at 640° for an additional three hours, and slowly cooled to room temperature. The oxide product was reduced to granular form (20–30 mesh). Pure nickel oxide samples were obtained by decomposing and firing nickel nitrate in an atmosphere of oxygen or alternatively in an atmosphere of helium. The helium was purified by being passed through a charcoal trap cooled to liquid nitrogen temperature and magnesium perchlorate.

Nickel powder was obtained by reducing nickel oxide with purified hydrogen at 300° for 24 hours at a flow rate of 3 liters per hour by cooling subsequently at room temperature in an atmosphere of purified nitrogen. The gas used in the reduction experiments was tank hydrogen purified by passing through copper heated to 400°, then calcium chloride, ascarite, phosphorus pentoxide and glass wool.

Apparatus.—Reduction rates were measured in an all glass, closed system of 392 cc. total volume. The oxide was charged (0.483 g.) in a small reactor with built in preheating coil. Hydrogen was forced to circulate through the sample by means of a two-stage alternating mercury pump driven by an electrical motor. The displacement of the pump was about 10 cc. per sec., and under these conditions reduction rates were not affected by the pumping speed. Gold foils were placed in the system in order to trap any mercury vapor which might be present. After leaving the sample, the gas passed through a trap cooled with liquid nitrogen to condense the water formed. The ensuing change in pressure was followed on a mercury manometer, and the manometer readings were taken as an indication of the extent of the reduction process. Reactor and preheating coil were kept at constant temperature by immersion in a thermostat (± 0.2°), in which silicone oil (G.E. 9981 LNTV) was circulated by means of a thermosiphon device.

Surface areas were measured by nitrogen adsorption and the results plotted according to B.E.T. theory. X-Ray data were obtained with an X-ray spectrometer using Fe radiation and Mn filter. In order to evaluate lattice distortions (if any), duplicate patterns were taken for each sample, sodium chloride being used as an internal standard. Measurements of particle size were carried out on the strongest spinel ($NiCr_2O_4$) line (2.08 Å.) using Brill's formula.

The reproducibility in the determination of the velocity constants (g. nickel oxide reduced per minute) was found to be better than 5%. The experimental error in determining the activation energies was ±0.9 kcal./mole.

Experimental Results

The data obtained for the reduction of nickel oxide at different temperatures and constant initial pressure of hydrogen (470 mm.) are presented in Fig. 1. No effect on the rate has been detected by a preliminary irradiation of nickel oxide with the full light of a mercury lamp (3 hours at room temperature). At constant temperature the rate of reduction was a linear function of the initial pressure of hydrogen in the range 200–500 mm. Similar results have been obtained in the case of a chromia containing sample (Fig. 2).

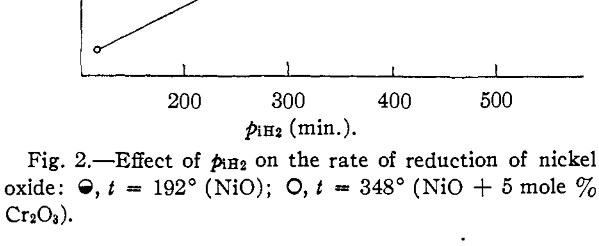

Fig. 2.—Effect of p_{iH_2} on the rate of reduction of nickel oxide: ◒, t = 192° (NiO); ○, t = 348° (NiO + 5 mole % Cr_2O_3).

The rate of reduction did not change appreciably with the use of a reducing gas of the following composition: 70.3% D_2, 6.1% HD, 23.5% H_2.

In one run (t = 192°, p_{iH_2} = 470 mm.) hydrogen was pumped off from the system as soon as the rate became constant and the sample was evacuated for 1 hour at 192°. Hydrogen was then readmitted to the system and the rate of reaction was found unchanged.

The data on the reduction of nickel oxide containing foreign ions are shown in Fig. 3 where they are plotted according to the Arrhenius equation. The calculated values for the pre-exponential factor A and the activation energy E are summarized in Table I.

It must be pointed out that the above concentrations of impurities in nickel oxide refer to over-all values of impurity

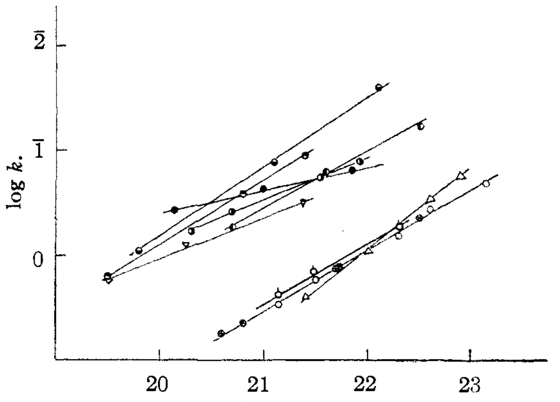

Fig. 3.—Effect of additions to nickel oxide on its rate of reduction: O, NiO fired in air or oxygen; ϕ, NiO fired in helium; ⊕, NiO + 1 mole % Al_2O_3; ⊗, NiO + 1 mole % ThO_2; Δ, NiO + 1 mole % Ag_2O; ∇, NiO + 1 mole % $NiCl_2$; ◐, NiO + 1 mole % MgO; ◑, NiO + 1 mole % Cr_2O_3; ⊖, NiO + 1 mole % Li_2O; ◒, NiO + 5 mole % Li_2O; ●, NiO + 0.5 mole % WO_3.

content. It does not imply that all the impurity is homogeneously distributed in the nickel oxide lattice. Since the purpose of the investigation was not to study in detail the effect of concentration of impurities the amount of homogeneity was not considered in the interpretation of the results.

TABLE I

REDUCTION OF NICKEL OXIDE CONTAINING FOREIGN IONS

Sample	log A g. NiO reduced per min.	E, kcal./mole	Temp. range, °C.
NiO[a]	12.69	26.4	155–200
NiO[b]	12.64	26.4	155–200
NiO + 1 mole % Ag_2O	15.60	35.2	150–200
NiO + 1 mole % Al_2O_3	12.69	25.4	172–212
NiO + 1 mole % Cr_2O_3	7.83	18.3	180–212
NiO + 5 mole % Cr_2O_3	8.00	18.9	200–350
NiO + 1 mole % Li_2O	12.20	28.2	190–240
NiO + 5 mole % Li_2O	13.18	30.5	180–240
NiO + 1 mole % MgO	10.94	24.8	170–220
NiO + 1 mole % $NiCl_2$	7.80	17.8	190–240
NiO + 1 mole % ThO_2	12.69	26.4	150–200
NiO + 0.5 mole % WO_3	3.58	9.2	185–220

[a] Heated in air or oxygen. [b] Heated in helium.

Chromia-containing samples were subjected to a more detailed study in order to investigate the effect of different chromia concentrations on the rate of reduction of nickel oxide. In Figs. 4 and 5 are shown the data obtained on nickel oxide + 15 mole % chromia at 308 and 348° and p_{iH_2} = 470 mm. Surface area, X-ray and reduction data on these samples are summarized in Table II.

TABLE II

EFFECT OF CHROMIA ON THE REDUCTION OF NICKEL OXIDE

Cr_2O_3 content in NiO mole %	Surface area, m.² g.⁻¹	log A g. NiO reduced per min.	E kcal./mole⁻¹	Temp. range, °C.	Phases present (X-ray)	Average crystallite size ($NiCr_2O_4$) A.
1	5.75[a]	7.83	18.3	180–220	NiO	...
5	8.55	8.0	18.9	200–350	NiO + increasing amount of $NiCr_2O_4$ on increasing Cr_2O_3	157
15	12.7	5.9	16.5	250–350		250
25	12.0	10.4	31.5	250–350		340

[a] Pure nickel oxide had a surface area of 2.2 m.² per g.

No lattice distortions could be detected on these samples by analysis of their X-ray diffraction spectra.

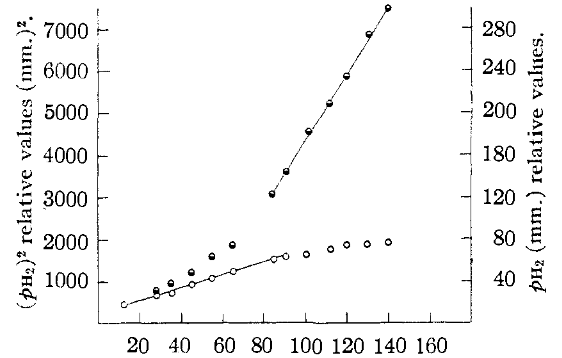

Fig. 4.—Reduction of nickel oxide containing 5 mole % chromium oxide, t = 348°, p_{iH_2} = 470 mm.: O, linear plot; ◒, parabolic plot.

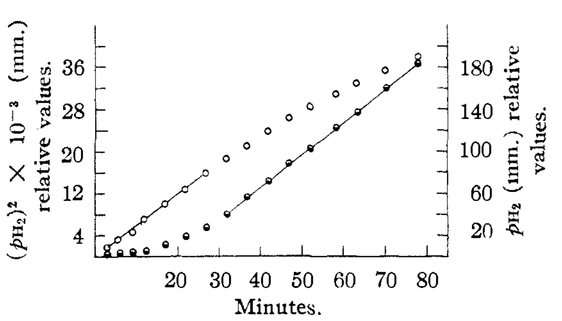

Fig. 5.—Reduction of nickel oxide containing 15 mole % chromium oxide, t = 308°, p_{iH_2} = 470 mm.: O, linear plot; ◒, parabolic plot.

Discussion

The results presented in Fig. 1 are in accord with previous work on the reduction of metallic oxides.[3,4,5] After an incubation and an induction period a linear law of reduction applies up to high conversion values. This can be explained by considering that in the present case the ratio[6] $R = V_f/V_i = 0.84$, where V_f, V_i are the specific volumes of the final product and initial reactant. If $R < 1$ a film of the product cannot be stable up to large values of conversion and fresh surface will always be present due to collapsing of the film. When, however, a metallic film is formed, the transport of matter by diffusion through this layer becomes rate determining, and the over-all process is best represented by a parabolic type of law (Figs. 4, 5).

The following steps can be envisaged as occurring during the course of the reduction process: (a) adsorption of hydrogen on the surface, (b) reaction between adsorbed hydrogen and nickel oxide with formation of water and metallic nuclei, (c) evaporation of water. Process (b) as well as the growth of the nuclei formed are accomplished by migration of nickel ions and electrons.

Wagner[7] has shown that the concentration gradient of excess zinc in zinc oxide in contact with oxygen does not vary appreciably with the oxygen pressure. If the same mechanism is operative

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(6) G. Valensi, *J. Chim. Phys.*, **47**, 489 (1950).

(7) C. Wagner, "Pittsburgh International Conference on Surface Reactions," Corrosion Publishing Co., Pittsburgh, Penna., 1948, p. 77.

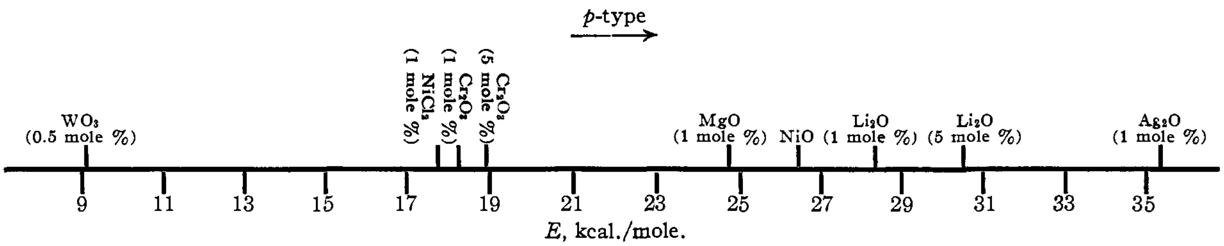

Fig. 6.—The effect of the amount of p-type character of nickel oxide on the activation energy for its reduction.

in the case of nickel oxide in the presence of hydrogen and if material diffusion or water evaporation were rate determining then the reduction rate of nickel oxide should be almost independent of hydrogen pressure. Supporting evidence in this respect is given by the fact that addition of metallic nickel produces no effect on the induction period for nickel oxide reduction in contrast to the findings of Pease and Taylor[2] for copper oxide.

Furthermore, the addition of a trivalent cation (Cr^{+3}) increases the number of cation vacancies in the nickel oxide lattice. Accordingly, the ionic conductivity will increase and likewise the diffusion rate. This is just the opposite of what it has been found. These considerations indicate that processes (b) and (c) are not, under the present experimental conditions, rate determining. Process (c) however, can become significant at low pressures, where the mechanism of reduction must be different from that occurring at higher pressures. It seems therefore that process (a), the irreversible chemisorption of hydrogen,[3] determines the rate of the reduction process.

According to this interpretation of the experimental data, it becomes clear that the initial autocatalytic rise of the rate is due to increasing surface coverage by hydrogen. This is a non-equilibrium process at any stage of the reaction.

Nickel oxide is known to be an electron defect semiconductor, containing in its lattice cationic holes ($\square(Ni^{+2})$) and an electrically equivalent number of electron holes ($\square(e^-)$). Its p-type character can be modified and controlled to a certain extent by incorporation in the lattice of suitable impurities. Recent data by Verwey[1] and Hauffe[8] have clearly shown the effect of the incorporation of foreign ions on the semi-conductivity of nickel oxide. These authors were able to demonstrate that the semi-conductivity can be increased by the introduction of monovalent cations (Li^+), while cations with higher valency than two (Cr^{+3}) have the reverse effect. An opposite behavior is to be expected as far as cationic holes are concerned. This can be seen from the following relations derived by Hauffe from the electroneutrality principle applied to the nickel oxide lattice:

$$[\square(Ni^{+2})] \times [\square(e^{-1})]^2 = \text{const. (at constant } p_{O_2} \text{ and temperature)}$$

Our significant experimental data are the following: (1) The rate of reduction is decreased by igniting the "pure" oxide in an helium atmosphere as compared to that of a sample ignited in air or oxygen. The activation energy, however, remains the same. (2) The rate is decreased in almost all cases by the addition of foreign ions. (3) The activation energy is decreased by the addition of higher valency cations (Cr^{+3}, W^{+6}) or lower valency anions (Cl^-), while it is increased by lower valency cations (Li^+, Ag^+). (4) Increasing concentrations of Li^+ decrease the rate and increase the activation energy, while increasing concentrations of Cr^{+3} (up to a certain value) have no effect upon either. (5) The addition of Mg^{+2} decreases the rate and slightly affects the activation energy. (6) Al^{+3}, Th^{+4} have no effect on either the rate or the activation energy.

Point (1) can be explained by considering that in the case of "pure" nickel oxide the rate of reduction depends on the number of positive holes only. At the surface the positive holes are destroyed by chemisorption of hydrogen. They diffuse from the bulk to the surface under a concentration gradient or space charge effect. This process is very rapid, because they can cross diffusion barriers by tunnel effect.

On the other hand the present data show that in the case of samples containing foreign ions a direct correlation between the number of positive holes in the oxides and its rate of reduction cannot be deduced. Furthermore, it must be pointed out that the present rate data are not in agreement with those of Wagner[9] and Hauffe[10] on the effect of additions of foreign ions to the rate of oxidation of nickel and zinc metals. These authors find a definite relation between the type of addition and the rate of oxidation. This disagreement emphasizes the fundamental difference between the mechanism of oxidation of nickel metal and the reduction of the oxide by hydrogen.

The values of the activation energy show a definite trend when compared to the change in p-type behavior of nickel oxide obtained by the addition of foreign ions (Fig. 6). Monovalent cations increase, while cations with a valency higher than two decrease the activation energy of the process. The reverse effect is obtained by introducing foreign anions into the nickel oxide lattice. It is believed that this fact can only be explained by assuming that the impurity centers of foreign ions interact with hydrogen surface states. No theoretical explanation is at present available for this effect. An almost continuous distribution of energy among impurity levels has been assumed by Meyer[11] and Busch[12] to explain the mechanism

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[8] K. Hauffe and A. L. Vierk, *Z. physik. Chem.*, **196**, 160 (1950); K. Hauffe, *Ann. Physik*, 6 Folge, **8**, 201 (1950).

[9] C. Wagner and K. E. Zimens, *Acta Chem. Scand.*, **1**, 547 (1948).

[10] C. Gensch and K. Hauffe, *Z. physik. Chem.*, **196**, 427 (1951).

[11] W. Meyer, *Z. Elektrochem.*, **50**, 274 (1944).

[12] G. Busch, *Helv. Phys. Acta*, **19**, 167, 189 (1945).

of semi-conductivity in different semi-conductors. It is interesting to point out that the actual position of the impurity levels in the oxide does not affect the activation energy of the reduction process. In fact, it has been found by Verwey[1] that the activation energy for semi-conductivity in lithia containing samples decreases with increasing content of lithia, while Hauffe[8] found that the activation energy for semi-conductivity is not affected by the presence of chromia.

In order that foreign ions should affect the reductive properties of nickel oxide, they have to be randomly distributed over its lattice. If a phase separation occurs, no effect is to be expected. This will be the case if the increase in energy to form a preferred grouping or a chemical compound with nickel oxide is larger than that obtained by a strictly statistical distribution of foreign ions in the nickel oxide lattice. Our results show that phase separation occurs during the addition of 1 mole % alumina and 1 mole % thoria. In the case of chromia it is known that its limiting solubility in nickel oxide is about 1 mole %.[6] This explains the similar behavior of 1 mole % and 5 mole % chromia containing samples. Higher activation energies, however, were obtained at higher chromia concentrations (25 mole %). This occurs at concentrations where sizable amounts of spinel are formed, as evidenced by X-ray analysis. At present no data are available on the electrical characteristics of nickel chromite, and therefore its effect on these properties of nickel oxide cannot be predicted.

On the basis of the present results it can be concluded that a direct correlation exists between the activation energy for reduction of nickel oxide by hydrogen and the type of addition.

The same and opposite effects can probably be predicted for other p-type and n-type oxides respectively. However, there are at present no experimental data to support these predictions.

PRINCETON, NEW JERSEY RECEIVED AUGUST 8, 1951

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ILLINOIS INSTITUTE OF TECHNOLOGY]

The Solubility of Cadmium in Mixtures of Cadmium Chloride with Other Chlorides

BY DANIEL CUBICCIOTTI[1]

The solubility of cadmium in mixtures of cadmium chloride with the chlorides of potassium, calcium, cerium, manganese, magnesium and zinc was determined at 740°. The addition of any of these salts to cadmium chloride reduced the solubility of the metal. The effectiveness of the salts in reducing the solubility is compared with the anion to cation ratio of the salt and the electropositiveness of the metal of the cation. An hypothesis as to the structure of the solutions is considered.

The solubilities of the metals of group II of the Periodic Table in their molten chlorides have been shown to increase with increasing ionic radius of the cation.[2] It has also been shown[3] that for cations of similar size the solubility of the metal increases as the ratio of the number of anions to cations in the salt increases.

The author was interested in investigating the solubility of a metal in the chlorides of other metals or in mixtures of chlorides. Such measurements may lead to a better understanding of the nature of metal in salt solutions.

It was necessary to choose a metal that was reasonably soluble in its chloride and yet one that would not reduce salts equilibrated with it. Cadmium metal has such properties. It was a simple matter to select salts that had proper anion to cation ratios. To determine whether they would be reduced by cadmium metal, their free energies of formation were compared with that of cadmium chloride. Table I gives the standard free energies of formation and the equilibrium constant for the reaction involving one mole of cadmium with the salt.

All the chlorides except that of zinc have an equilibrium constant small enough so that the possibility of reduction of the salt by cadmium may be overlooked.

TABLE I

FREE ENERGIES OF FORMATION OF SALTS AND THEIR EQUILIBRIUM CONSTANTS WITH CADMIUM

Salt	Standard free energy of formation at 1000°K., kcal. per mole[a]	Equilibrium constant for reaction $Cd + \frac{2}{n} XCl_n = CdCl_2 + \frac{2}{n} X$
$CdCl_2$	− 60.8	....
KCl	− 83.9	$10^{-23.4}$
$CaCl_2$	−158.7	$10^{-21.4}$
$CeCl_3$	−211	$10^{-16.7}$
$MgCl_2$	−115.2	$10^{-11.9}$
$MnCl_2$	− 81.0	$10^{-4.4}$
$ZnCl_2$	− 70.0	$10^{-1.9}$

[a] Data from L. Brewer, L. Bromley, P. Gilles and N. Lofgren, "National Nuclear Energy Series," Vol. IV-19B, McGraw-Hill Co., Inc., New York, N. Y., 1950, p. 76 ff.

Experimental

Method.—The solubilities were determined at 740° by equilibrating cadmium with the salt in a closed iron tube, quenching it in water, and analyzing a sample of the salt phase. An iron test-tube was made by flattening one end of a 5" × 1/2" iron tube and sealing the bottom with a spot welder. About 10 g. of cadmium and 15 g. of salt mixture, made up by weight from the components, were put in the tube in a dry-box. The top of the tube was then flattened and sealed by spot welding. The tube was heated at 740 ± 10° for one hour and then quenched in water. The pressure in the iron tube reached several atmospheres because of the air and vapors trapped within, and some of the welded joints leaked. The tubes that leaked were readily detected because water seeped in during quenching.

The tube containing the quenched sample was then cut

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[1] North American Aviation, Inc., Downey, Calif.

[2] D. Cubicciotti and C. Thurmond, THIS JOURNAL, **71**, 2149 (1949).

[3] D. Cubicciotti, *ibid.*, **71**, 4119 (1949).