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

---

[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).

open and two samples of salt removed. The samples were leached with water, or dilute ammonia when zinc chloride was present. The salt dissolved in the water and the cadmium metal that had been dissolved in the salt precipitated as a fine powder. The cadmium precipitate was filtered off, dissolved in nitric acid and determined polarographically. The solution was titrated for chloride. From these two determinations and the initial ratio of salts, the composition of the final salt was calculated.

Materials.—Anhydrous manganous chloride was obtained from the A. D. Mackay Co., New York. Anhydrous cerium chloride was supplied by Dr. F. H. Spedding of Iowa State College. The anhydrous chlorides of calcium, cadmium and zinc were prepared by heating the hydrates *in vacuo*. Anhydrous magnesium chloride was made by heating the hydrate with ammonium chloride *in vacuo*. The ammonium salt sublimed off and left a product containing one mole % magnesium oxide. The potassium chloride was dried by heating *in vacuo*.

Results

The results obtained are shown in Figs. 1 and 2. Three determinations of the solubility of cadmium in its chloride gave 13, 14 and 15 mole % cadmium in the final mixture. The spread of these values gives an indication of the reproducibility of the results. Heymann, *et al.*,[4] found 15 mole % cadmium in its chloride after equilibration at 690°.

The solubility of the metal in mixtures of its chloride with three chlorides of different anion to cation ratio is given in Fig. 1. The salts used for that study were the chlorides of electropositive metals whose cation radii were similar to that of cadmium. From the figure it may be seen that the addition of any of those salts to the cadmium chloride reduced the solubility of the metal. Potassium chloride was the most effective; cerium chloride was the least effective and calcium chloride was intermediate in its effect in reducing the solubility. The effectiveness of the added salts in decreasing the solubility is inversely related to the anion to cation ratio. That is, the smaller the anion to cation ratio the more effective the salt in reducing the solubility of the cadmium.

Figure 2 shows a comparison of the solubility in mixtures of cadmium chloride with several divalent chlorides. The salts were chosen to give a wide range in electropositiveness of the element of the cation. From the standard free energies of formation given in Table I it may be seen that there is a marked drop in electropositiveness from calcium to magnesium to manganese to zinc. The chlorides of these metals diminish the solubility of cadmium in relation to their electropositiveness, except for zinc chloride. Thus calcium chloride is the most effective, manganous the least and magnesium chloride intermediate in reducing the solubility.

In its effect on the solubility of the cadmium, zinc chloride was between those of calcium chloride and magnesium chloride. It was expected from the correlation with free energy of formation that zinc chloride would be less effective than manganous chloride. This exception may have been due to the reduction of the zinc chloride by cadmium,[5] or it may indicate that the solubility should be compared with some more subtle property than the free energy.

Discussion

The data so far obtained on the solubilities of metals in their fused chlorides can be summarized as follows: (1) For the metals of group II of the Periodic Table the solubility of the metals in their chlorides increases as the cation radius increases.[2] (2) The solubility increases as the ratio of number of anions to cations increases (shown in the case of K, Sr, Ce).[3] (3) The solubility is decreased (for Cd in $CdCl_2$) on the addition of the chloride of an electropositive metal; the smaller the anion to cation ratio of the added salt, the more the solubility is decreased. (4) On the addition of chlorides (divalent chlorides to cadmium chloride) the solubility is decreased, and the more electropositive the metal of the added chloride, the greater the decrease in the solubility.

These results are all in accord with a concept of metal in salt solutions suggested to the author by Dr. David Harker. According to that suggestion the chloride ions of the molten salt are arranged approximately in a close-packed structure. The chloride ions are packed in that way and determine the general structure of the system because they are the larger ions. The positive ions are situated in the octahedral holes left among the chloride ions.[6] The cations of the dissolved metal go into any such unoccupied holes.

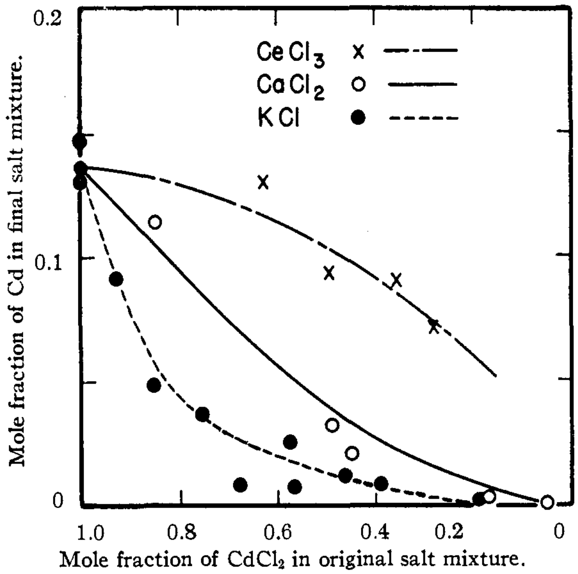

Fig. 1.—The solubility of cadmium in mixtures of cadmium chloride with the chlorides of mono-, di- and trivalent electropositive metals at 740°.

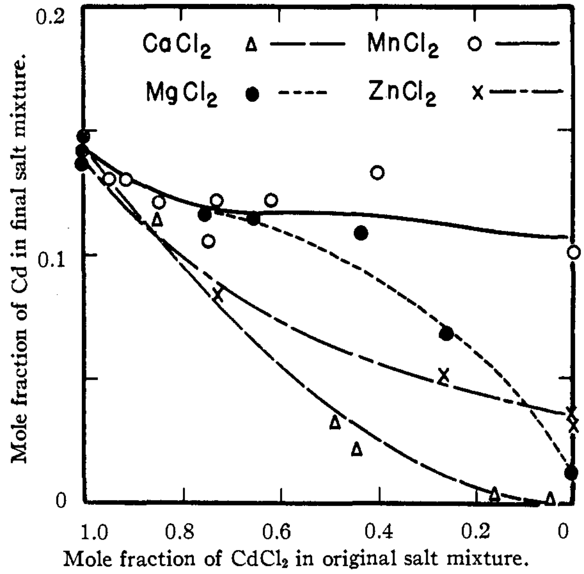

Fig. 2.—The solubility of cadmium in mixtures of cadmium chloride with several divalent chlorides at 740°.

---

[4] E. Heymann, R. J. L. Martin and M. F. R. Mulcahy, *J. Phys. Chem.*, **47**, 473 (1943).

[5] The zinc chloride was found to be reduced by the cadmium. A sample that initially contained only zinc chloride in the salt phase was found to contain 10 mole % cadmium chloride after equilibration.

[6] For a more detailed explanation of this point see: A. F. Wells, "Structural Inorganic Chemistry," Oxford Press, London, 1945. p. 278.

In a 1–1 salt there are as many cations as holes and so in the pure salt the holes are all filled. In a 2–1 or a 3–1 salt, one-half and two-thirds of the holes are empty. Therefore, the greater solubility of metal in a salt of large anion to cation ratio (item 2 above) is plausible since the concentration of holes in the salt depends upon the anion to cation ratio. The larger the cation the further the anions surrounding the hole are separated. Thus the metals with larger cations are more soluble (items 1 and 3 above).

The electrons transferred to the salt by the dissolved metal are in bands or zones of energy states belonging to the salt system as a whole. As the salt of a more electropositive metal is added the energy levels would be raised, making it more difficult for an electron from the metal to be transferred to the salt and in effect reducing the solubility of the metal (item 4 above).

The experimental facts seem to fit in with the picture suggested. A more detailed investigation of the correlation of solubility with electropositiveness of added salt should be made.

Acknowledgment.—This research was supported by the Office of Naval Research. The author is indebted to Mr. Manual Kanter for determining the effect of calcium chloride on the solubility.

CHICAGO 16, ILLINOIS RECEIVED AUGUST 14, 1951

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

The Reaction of Cerium with Oxygen

BY DANIEL CUBICCIOTTI[1]

The oxidation of cerium has been found to obey the parabolic law from 30 to 125°. Above 125° the reaction started parabolically but subsequently became linear. The parabolic portion became shorter as the temperature was increased. Cerium was the most rapidly oxidizing metal yet studied. The energy of activation of the parabolic reaction was the smallest yet observed.

The oxidations of certain metals,[2] namely, thorium, uranium and aluminum have been found to obey the parabolic law at low temperatures and the linear law at higher temperatures. Loriers[3] has reported that cerium oxidizes linearly at 300°. Since the ratio of molal volumes of oxide to metal is greater than unity, it would be expected that cerium would oxidize parabolically.[4] Thus the author supposed that the oxidation of cerium also undergoes the parabolic–linear transition. The present study shows that that supposition was correct.

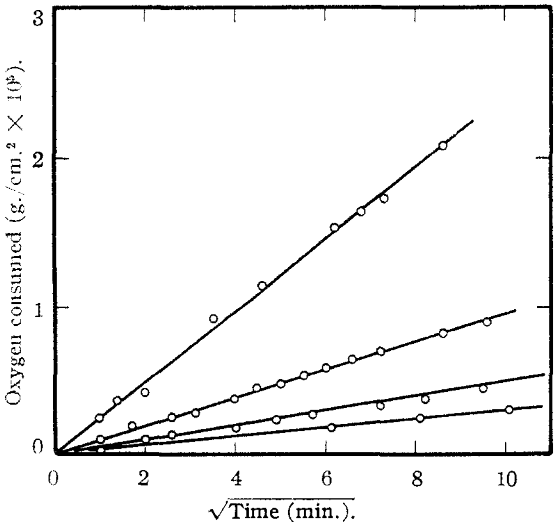

Fig. 1.—Parabolic plot of the oxidation of cerium at 30, 44, 68 and 125°.

Experimental

The method and apparatus were the same as those used for uranium.[2] Cerium metal was obtained from the A. D. Mackay Co., New York. It was stated to contain 92.6% cerium, 1.1% iron and the balance other rare earth metals. Two rectangular blocks each about 2.5 × 1 × 0.5 cm. were cut from the ingot obtained. These were abraded until the surface was free of pockets and salt inclusions. Immediately before each oxidation the surface was abraded with 400 emery cloth and washed with carbon tetrachloride. For each oxidation 120 minutes of preheating was allowed before the oxygen was admitted and the oxidation started. To clean the surface for the oxidation made at 30° the block was chilled so that it was always well below room temperature. This treatment probably only reduced the thickness of oxide initially present, and the oxidation of the clean metal may be more rapid than that observed.

Results

From 30 to 125° the oxidations were quite parabolic over a 100-minute interval. Figure 1 shows the type of data obtained in that temperature range on a parabolic plot.

Above 125° the oxidation started as a parabola but after a time became linear. This change may be seen in Fig. 2 where a linear plot of the higher temperature data is given. It may be seen that as the temperatures of the oxidations were increased the duration of the parabolic portion decreased. This effect in the cerium oxidation is more evident than in the case of uranium or thorium.

The rate constants obtained are shown in Fig. 3 as the logarithm of the constant *versus* reciprocal of absolute temperature. The left hand line and abscissa represent the linear oxidations and the right hand ones represent the parabolic. From the slopes of the straight lines one can calculate the energies of activation for the two reactions. For the linear reaction the value is 14 kcal. per mole while for the parabolic it is 12 kcal. per mole.

---

(1) North American Aviation, Inc., Downey, Calif.

(2) D. Cubicciotti, THIS JOURNAL, to be published.

(3) J. Loriers, *Compt. rend.*, **229**, 547 (1949).

(4) N. J. Pilling and R. E. Bedworth, *J. Inst. Metals*, **29**, 529 (1923).