upon the zinc atom of this denser packing on the copper lattice has been discussed in a previous publication.[2]

Summary

1. It is pointed out that the chemical attraction between unlike atoms in metallic solid solutions of the simple substitutional type should manifest itself by increased internal pressures.
2. The average internal pressures in a series of binary systems of cubic metals have been calculated and it has been shown that the increase in internal pressure is positive and that it may amount to as much as 46 kilomegabars (in the silver-palladium system).
3. The results of the calculations of internal pressure have been applied in an analysis of the factors controlling hardness in solid solutions and it has been shown that the increased cohesive forces account for only a small fraction of the total hardness increase.
4. Similar calculations have been applied to the copper-zinc system, with limiting assumptions, and various properties affected by the increase in internal pressure have been correlated.

[Contribution from Gates Chemical Laboratory, California Institute of Technology, No. 155]

THE ACID-FORMING PROPERTIES OF OSMIUM TETROXIDE

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Received October 8, 1927 Published January 5, 1928

Introduction

There has been difference of opinion as to whether osmium tetroxide, OsO_4, is an acid anhydride. Ephraim[1] concludes that the oxide probably does not form an acid from the supposed facts that its solubility in solutions of strong bases is the same as in water, that it does not react with them to form salts and that the concentration of hydroxide ion does not change when the tetroxide is dissolved in alkaline solutions. He did not regard as conclusive the evidence afforded by the results of Tschugaeff,[2] who prepared substances of the type $OsO_4.CsOH$ and $OsO_4.2KOH$. Since then Krauss and Wilkins[3] have also prepared unstable substances such as $OsO_4.2CsOH$. Hofmann[4] measured the electrical conductivity of osmium tetroxide solutions and found it to be very small; thus, with 1 g. dissolved in 100 cc. of water the specific conductivity was found to be 10.9×10^{-6}, while that of the water used was 5×10^{-6}. He concludes that solutions of the

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[1] F. Ephraim, "Inorganic Chemistry," English translation by P. C. L. Thorne, Gurney and Jackson, London, **1926**, p. 376.

[2] Tschugaeff, *Compt. rend.*, **167**, 162 (1918).

[3] Krauss and Wilkins, *Z. anorg. allgem. Chem.*, **145**, 151 (1925).

[4] Hofmann, Ehrhart and Schneider, *Ber.*, **46**, 1657 (1913).

tetroxide are neutral and not acid. The qualitative experiments of von Wartenberg[5] constitute good evidence that the substance is an acid anhydride. He found that, while it could be almost completely extracted from its solutions in water by a few shakings with carbon tetrachloride, it could in turn be extracted almost completely from the carbon tetrachloride by four treatments with a 25% solution of sodium hydroxide. Finally, Professor W. C. Bray has pointed out to us that, inasmuch as the solutions of the tetroxide in water are nearly colorless while those in alkaline solutions are orange-yellow, a new substance must have been formed, which is probably an anion of the acid[6] H_2OsO_5.

This article describes an investigation of the distribution-ratios of osmium tetroxide between carbon tetrachloride and water and sodium hydroxide solutions, from which an ionization constant of perperosmic acid H_2OsO_5 has been calculated. Experiments with potassium chlorate solutions were also made to determine by an independent method whether or not osmium tetroxide forms a complex with chlorate ion; for Hofmann[4] found that the solubility of potassium chlorate is greater in solutions of the tetroxide than in water, and from these results concluded that a complex exists.

We wish to express here our appreciation of the helpful suggestions made by Professor A. A. Noyes. The investigation was aided on the financial side from a grant made to him by the Carnegie Institution of Washington.

Experimental Procedure

The water and carbon tetrachloride used in the experiments were freed from oxidizable impurities by well-known methods.

To a definite volume of the stock solution of osmium tetroxide in well-cleaned, glass-stoppered tubes definite volumes of water or solutions were added in amounts sufficient to make the total volume 25.00 cc. To this 25.00 cc. of carbon tetrachloride was added, the glass stoppers were inserted, the tubes placed in a thermostat at 25°, and shaken vigorously at frequent intervals. It was found that equilibrium was easily attained.

The method of analysis used was substantially that described by Krauss

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[5] Von Wartenberg, *Ann.*, **440**, 97 (1924).

[6] The naming of this acid offers special difficulty. It is highly desirable that the analogous acids of the elements manganese, iron, ruthenium and osmium have corresponding names. The acids H_2MnO_4, H_2FeO_4, H_2RuO_4, H_2OsO_4 are universally called manganic, ferric, ruthenic and osmic acids; and there exists an acid $HRuO_4$ which, in analogy with permanganic acid, is called perruthenic acid. This excludes the use of this name for the acid H_2RuO_5 (corresponding to RuO_4); and if the name perosmic acid be used, as it often is, for H_2OsO_5, it will introduce an inconsistency in the nomenclature of the related acids. A new type of name is therefore needed for the two acids of the elements with valence eight, and Professor A. A. Noyes has suggested to us that the most suggestive names would be derived by doubling the prefix *per*, thus designating H_2RuO_5 and H_2OsO_5 as perperruthenic and perperosmic acids.

and Wilkins.[3] It consisted in pipetting definite volumes of each liquid phase into 50 cc. of 2 *N* hydrochloric acid containing 2 g. of potassium iodide in stoppered flasks and titrating the liberated iodine with standard thiosulfate. Carbon tetrachloride was added to the mixtures in which it was not already present. It was necessary to extract the tetroxide from the chlorate solutions with carbon tetrachloride and analyze the extracts, since chloric acid reacts with iodide. The main objection to this method of analysis is the difficulty of determining the end-point in the dark green solutions of reduced osmium, especially when very dilute thiosulfate is used. The concentrations of thiosulfate varied from 0.00249 *N* to 0.0259 *N*, depending on the amount of osmium present in the sample analyzed.

Results of the Distribution Experiments

Table I contains the results. The distribution-ratios r are calculated directly from the concentrations by the expression $r = c_{CCl_4}/c_{Aq}$.

TABLE I

RESULTS OF THE DISTRIBUTION EXPERIMENTS AT 25°

Number	Millimoles of OsO_4 per liter in		Aqueous layer	Distribution-ratio r
	CCl_4 layer	Aqueous layer		
1	6.40	0.532	Water	12.0
2	6.47	.545	Water	11.9
3	6.51	.541	Water	12.0
4	6.53	.532	Water	12.3
5	6.86	.558	Water	12.3
6	13.0	1.03	Water	12.7
7	13.1	1.02	Water	12.8
8	5.08	2.35	NaOH, 0.0587 *N*	2.16
9	5.09	2.36	NaOH, 0.0587 *N*	2.16
10	5.92	1.54	NaOH, 0.0277 *N*	3.84
11	5.92	1.54	NaOH, 0.0277 *N*	3.84
12	6.83	0.634	$KClO_3$, 0.2000 *N*	10.8
13	6.83	.632	$KClO_3$, 0.2000 *N*	10.7

The values of the distribution ratio between the tetrachloride and water show a slight increase with the concentration of the tetroxide, which is probably to be ascribed to error in the analyses of the more dilute solutions.

The Ionization Constant of Perperosmic Acid

We may assume that osmium tetroxide unites with water to form an acid which ionizes according to the equation $H_2OsO_5 = H^+ + HOsO_5^-$, and that correspondingly the reaction with hydroxide is $H_2OsO_5 + OH^- = HOsO_5^- + H_2O$. It is obvious then by the mass-action law, if K_w and K_A are the ionization constant of water and acid, respectively, that

$$\frac{(H^+)\ (HOsO_5^-)}{(H_2OsO_5)} = \frac{K_w(HOsO_5^-)}{(OH^-)\ (H_2OsO_5)} = K_A \qquad (1)$$

Now the quotient of the distribution ratio r_s for the alkaline solution and that, r_w, for water is evidently

$$\frac{r_s}{r_w} = \frac{(\mathrm{H_2OsO_5})}{(\mathrm{H_2OsO_5}) + (\mathrm{HOsO_5^-})} \text{ whence follows } \frac{(\mathrm{HOsO_5^-})}{(\mathrm{H_2OsO_5})} = \frac{r_w - r_s}{r_s}. \quad (2)$$

Combining this with Equation (1) we get

$$K_A = \frac{K_w(r_w - r_s)}{(\mathrm{OH^-})r_s} \quad (3)$$

The value of r_w is taken as 12.3, the average of experiments 1–7.

The values of K_A calculated with $K_w = 10^{-14}$ and r_s as given by experiments 8–9 and 10–11 are 8.0×10^{-13} and 7.9×10^{-13}, respectively. The agreement is very satisfactory.

This acid has therefore a constant even smaller than that of $\mathrm{HCO_3^-}$ (6×10^{-11}) and is one such that its salt $\mathrm{NaHOsO_5}$ would be about 30% hydrolyzed in a 0.1 *M* solution. In view of the extreme weakness of the acid, it is not surprising that the tetroxide has not heretofore been proved to be an acid anhydride.

The results of experiments 12 and 13 show that a complex between osmium tetroxide and chlorate ion is probably formed, although it is not a very stable one.

Summary

The distribution ratio of osmium tetroxide between carbon tetrachloride and water has been found to have an average value of 12.3 when the concentrations are expressed in quantities per unit volume. The ratio is found to be much less when the aqueous phase consists of 0.0277–0.0587*N* sodium hydroxide, showing that much of the tetroxide is converted into a salt by the alkali. From the results, the ionization constant is calculated to be 8.0×10^{-13} for the first hydrogen of the acid $\mathrm{H_2OsO_5}$, which it is proposed to call perperosmic acid.

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