and the Commonwealth Fund for a Fellowship to one of us (G. C. H.).

Summary

Electron diffraction measurements on arsenious oxide, phosphorus trioxide and hexamethylenetetramine show that the molecules consist of four phosphorus or nitrogen atoms in positions (vvv) $(\bar{v}\bar{v}v)$ $(\bar{v}v\bar{v})$ and $(v\bar{v}\bar{v})$ and six oxygen atoms or methylene groups in the positions $(\pm u00)$ $(0\pm u0)$ and $(00\pm u)$. In phosphorus pentoxide there are four additional oxygen atoms in the positions (www) $(\bar{w}\bar{w}w)$ $(\bar{w}w\bar{w})$ and $(w\bar{w}\bar{w})$.

The interatomic distances and angles are: for As_4O_6, As–O = 1.80 ± 0.02 Å., O–As–O = 100 ± 1.5°, As–O–As = 126 ± 3°, for P_4O_6, P–O = 1.65 ± 0.02 Å., O–P–O = 99 ± 1°, P–O–P = 127.5 ± 1°, for $N_4(CH_2)_6$, C–N = 1.47 ± 0.02 Å., C–N–C = N–C–N = 109.5°, for P_4O_{10}, P–O = 1.62 ± 0.02 Å., P–O′ = 1.39 ± 0.02 Å., O–P–O = 101.5 ± 1°, P–O–P = 123.5 ± 1° and O–P–O′ = 116.5 ± 1°.

The shortening of the bond distances in As_4O_6, P_4O_6 and P_4O_{10} below the theoretical single-bond values is attributed to single-bond double-bond resonance. It is concluded that the abnormally low value of 1.39 Å. for the P–O′ bond in P_4O_{10} is due to the polar character of the bond.

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The Properties of Osmium Tetroxide in Carbon Tetrachloride Solutions. The Thermodynamic Constants of Osmium Tetroxide[1]

BY LEROY H. ANDERSON AND DON M. YOST

Introduction

Osmium tetroxide is known to be moderately soluble in water and very soluble in carbon tetrachloride. Von Wartenberg[2] determined the solubility to be 6.47 g. per 100 g. of water, and about 250 g. per 100 g. of carbon tetrachloride, at 20°. The distribution ratio of osmium tetroxide between carbon tetrachloride and water was determined by Yost and White[3] for dilute solutions to be 13 when the concentrations are expressed in moles per liter of both solvents. Distribution ratios were determined independently, and at about the same time, by Tschugajeff and Lukashuk[4] with essentially the same results. These authors also made solubility determinations in water but the result, 6.23 g. per 100 g. of water at 25°, does not seem to be consistent with that of Von Wartenberg.

The distribution ratio calculated from solubilities is much higher than that found in the experiments on dilute solutions. This fact indicated that either the concentrated solutions in carbon tetrachloride were exhibiting some abnormal behavior, or that in the distribution experiments water possibly was associated with the tetroxide in carbon tetrachloride layer, thus forming a different solute. In order to settle this point, distribution experiments were made with solutions whose concentrations varied from very dilute to saturation, the solubilities of osmium tetroxide in both water and carbon tetrachloride were redetermined, and the vapor pressures of carbon tetrachloride above solutions of osmium tetroxide in it were measured for the range of concentrations up to saturation.

Preparation of Materials and Experimental Methods

Osmium Tetroxide.—Osmium metal freed from ruthenium was heated to 300–400° in a glass tube in a stream of dried oxygen. The vapors of osmium tetroxide (b. p. 130°) were condensed in the distribution vessel or capsules by means of a solid carbon dioxide–alcohol bath.

All other chemicals used were of the best grade obtainable. The carbon tetrachloride was further purified by fractional distillation.

Analytical Methods.—Osmium tetroxide is frequently determined iodimetrically,[4,5] but the colored tetravalent osmium solutions hide the end-point in all but rather dilute solutions, and atmospheric oxygen affects the results. After some experimentation the following procedure was

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[1] Presented at the Second Annual Symposium of the Division of Physical and Inorganic Chemistry on the Less Familiar Elements, Cleveland, Ohio, December 27, 28 and 29, 1937.

[2] Von Wartenberg, *Ann. Chem.*, **440**, 97 (1924); **441**, 318 (1925); Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936, p. 82.

[3] Yost and White, THIS JOURNAL, **50**, 81 (1928).

[4] Tschugajeff and Lukashuk, *Z. anorg. Chem.*, **172**, 223 (1928).

[5] For other methods see Crowell, THIS JOURNAL, **54**, 1324 (1932).

adopted: the weighed sample of osmium tetroxide solution was placed in a glass-stoppered flask containing 25 cc. of an acidified (0.35 *N* in hydrochloric acid) potassium iodide solution that had been saturated previously with carbon dioxide. After about thirty minutes of gentle shaking in the dark, the resulting solution was diluted to 200 cc. with distilled water saturated with carbon dioxide, and was then titrated with standard thiosulfate with starch as an indicator. Although this method can be made to give reproducible results, it cannot be said to be highly satisfactory, and, except for the dilute solutions, was replaced by a gravimetric method in which metallic osmium was weighed.

In the gravimetric method 0.1 to 0.3 g. of hydrazine hydrochloride was dissolved in 10 cc. of 3 *N* hydrochloric acid contained in a glass-stoppered flask. After warming this solution to 55–65°, the weighed sample of osmium tetroxide solution was introduced, and the resulting mixture was digested over a water-bath for an hour. This mixture was transferred to a weighed, glazed Rose crucible, and evaporated to dryness on a hot-plate. A stream of hydrogen was started through the crucible and the latter heated over a Bunsen burner for twenty to thirty minutes. The stream of hydrogen was continued until the crucible had cooled to room temperature, and then the hydrogen remaining was displaced with carbon dioxide. This last precaution is necessary to avoid the rapid combustion of hydrogen in the presence of the finely divided metallic osmium when the crucible cover is removed.

The Distribution and Solubility Experiments.—The distribution experiments were carried out in a 20-cc. cylindrical all-glass vessel equipped with two 1-mm. diameter tubes which extended into the carbon tetrachloride and aqueous layers, respectively. A little air pressure served to force samples of either layer out through the 1-mm. tubes and into a weighing bottle or capsule. The distribution vessel itself was fastened to a mechanical shaker operating in a thermostat so that equilibrium was certainly attained in all experiments. At no time did the tetroxide solutions come in contact with oxidizable substances.

In some of the distribution experiments, and in all of the solubility determinations, small, weighed, evacuated capsules equipped with long narrow outlet tubes were used for sampling. The outlet tubes were bent at right angles near their tips, and the short tips could be broken easily under the solution. The fragment of glass broken off was recovered and weighed.

The solubility experiments were carried out in a 10-cc. glass-stoppered tube that was shaken in the thermostat at 25° for twenty-four hour periods. Solubility equilibrium was approached from both directions.

The Vapor Pressure Experiments.—The apparatus used for the vapor pressure measurements consisted of a 20-cc. cylindrical glass container equipped with an all glass "click" gage and with side-arms which held easily breakable Capsules of osmium tetroxide and carbon tetrachloride. The capsules were broken when desired by means of glass enclosed, magnetically operated iron plungers. To attain more conveniently the higher dilutions, a separate calibrated carbon tetrachloride container was connected through a stopcock and a long (20 cm.) 0.5-mm. glass capillary tube to the solution container. The carbon tetrachloride was distilled into the solution container by cooling the latter with liquid air. In order to make sure that the solution was homogeneous at all times a stirrer consisting of a glass enclosed piece of soft iron was placed in the solution container and caused to move up and down by means of an external solenoid. The osmium tetroxide could at no time come in contact with any substance other than glass. Its low partial vapor pressure and the slow diffusion through the long capillary tube prevented appreciable loss of osmium tetroxide by reaction with the stopcock grease. The whole apparatus was highly evacuated and then closed off from the pumps. From time to time the contents of the system were condensed with liquid air and pressure measurements made to assure that no air had leaked into the apparatus.

Results of the Experiments

In Table I are presented the results of the distribution experiments made at 25°. All concentrations are expressed in mole fractions.

TABLE I

RESULTS OF THE DISTRIBUTION EXPERIMENTS AT 25°

Formula mole fraction OsO_4 in water layer, N_w	Formula mole fraction OsO_4 in CCl_4 layer, N_c	Distribution ratio $R = N_c/N_w$
0.0001464	0.01204	82.2
.000405	.0320	79.0[a]
.000582	.0424	72.9
.000614	.0498	81.2[a]
.000653	.0530	81.2[a]
.000715	.0582	81.4[a]
.00135	.109	80.7
.00137	.117	85.4[a]
.00189	.1563	82.7[a]
.00196	.175	89.3[a]
.00234	.22	94[a]
.002715	.2564	94.5
.00381	.426	112.0
.00423	.520	123
.00459	.6065	132.2
.00470	.598	127.3
.00507[s]	.693[s]	136.5[s]

Solubility OsO_4 in 100 g. water at 25° = 7.24 ± 0.01 g.
Solubility OsO_4 in 100 g. CCl_4 at 25° = 375 ± 17 g.

[a] Iodimetric determinations. All others were gravimetric. [s] From solubility measurements.

The experimental error of 17 g. or 4.5% in the solubility in carbon tetrachloride arises from the fact that the solutions are very concentrated, that they have a tendency to supersaturate, and that the solubility appears to have a large temperature coefficient. The result given here is the mean of four determinations which seemed free of criticism.

In the first and second columns of the table are given the formula mole fractions of tetroxide in the aqueous and carbon tetrachloride layers, respectively, that is, the mole fractions calculated from the results of analyses on the assumption that OsO_4 is present as such. Most of the ratios are the average of two or more values obtained for the same distribution experiment. At low concentrations the error in the gravimetric method of analysis is high due to the small amount of osmium weighed. At high concentrations the volumetric method of analysis is worthless due to the errors in taking small samples of the carbon tetrachloride phase or to the errors described above.

The distribution ratio, $R = N_c/N_w$, increases slowly at first and then more rapidly with concentration. It is also evident that the ratio at the high concentrations is approaching the last value in the table which was calculated from the solubility measurements. It would appear, therefore, that the carbon tetrachloride layer contains no water associated with the osmium tetroxide.

In order to establish still more definitely that the non-ideality of the carbon tetrachloride solution is independent of the presence of water, vapor pressure measurements were made on solutions of osmium tetroxide in dry carbon tetrachloride. The results are presented in Table II. The total vapor pressures observed were corrected for the small partial pressures of osmium tetroxide on the assumption that the laws of perfect solutions were valid. For such small corrections this assumption is justified. The last column of the table contains vapor pressures calculated on the basis of an assumption to be discussed below.

TABLE II

THE PARTIAL VAPOR PRESSURE OF CARBON TETRACHLORIDE ABOVE ITS SOLUTIONS OF OSMIUM TETROXIDE AT 25°

Formula mole fraction OsO_4, N_c	Partial vapor of CCl_4 in cm. P	Vapor pressure calcd. from Raoult's law concn. = N_c	Vapor pressure calcd. from Raoult's law but assuming $4OsO_4 = (OsO_4)_4$
0.000	11.46	11.46	11.46
.0402	11.02	11.00	11.00
.081	10.56	10.55	10.55
.1105	10.05	10.20	10.20
.395	7.86	6.92	7.72
.5982	6.19	4.61	5.97
.693	5.39	3.52	5.17

It is clear from column three of the table that the vapor pressures calculated from Raoult's equation and the formula mole fractions in column one are not equal to the observed pressures, that is, the solutions are not ideal. Now it is known from electron diffraction experiments[6] and the Raman spectrum[7] that the osmium tetroxide molecule is highly symmetrical, the four oxygen atoms being at the corners of a tetrahedron with the osmium atom at the center. Carbon tetrachloride has the same symmetrical structure. In spite of this high symmetry, mixtures of the two substances do not form ideal solutions.

The results of equilibrium experiments on non-ideal binary solutions may be treated quantitatively in either of two ways. (1) By the application of the thermodynamically exact Gibbs-Duhem equation and the definition of fugacity, the fugacities of the components may be calculated for any concentration. The results of such calculations are useful and necessary for the calculation of thermodynamic quantities. (2) The assumption may be made that Raoult's equation is the expression of a law and that deviations from it are to be interpreted as indicating the formation of ions, compounds or polymers. This orthodox way of treating experimental results, especially results obtained with concentrated solutions of the kind presented here, has been criticized[8] for several reasons, one of which is that it sometimes requires the assumption of polymers in the case of inert substances such as the noble gases.

If the results of the present distribution experiments are assumed to indicate the formation of an $(OsO_4)_n$ polymer in the carbon tetrachloride solutions, it is not difficult to show that they are in accord with the assumption that the following rapid reversible reaction takes place.

$$4OsO_4 = (OsO_4)_4$$

$$K = (OsO_4)_4/(OsO_4)^4 = 6.3$$

To evaluate the equilibrium constant the limiting value of $R = 78$ for infinitely dilute solutions was determined graphically.

The vapor pressure measurements are in quantitative agreement with the assumption of this polymerization as can be seen by comparing the second and last columns of Table II.

This analysis of the results is not, however, unique, it being possible to obtain equally satisfactory agreement with the distribution and vapor pressure experiments by assuming equilibria involving a series of polymers. This would still be true if a very high degree of accuracy were feasible. Such behavior is characteristic of this method of treatment.

If the osmium tetroxide is present in carbon

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(6) L. O. Brockway, *Rev. Modern Phys.*, **8**, 260 (1936).

(7) Langseth and Quiller, *Z. physik. Chem.*, **B27**, 79 (1934).

(8) Hildebrand, "Solubility," Reinhold Publishing Corp., New York, N. Y., Second Edition, 1936. See also this author and others for a general discussion on liquids and solutions, *Trans. Faraday Soc.*, **33**, 1-279 (1937).

tetrachloride solutions as an equilibrium mixture of polymers, the nature of the bonds or interaction becomes of interest. One type of bond could be assumed to consist of an oxygen atom shared by two osmium atoms. This would imply that the normal oxygen–osmium–oxygen bond angle is distorted to make way for the shared oxygen. A less conventional but perhaps more rational picture of the assumed association of tetroxide molecules is provided by London's dispersion effect.[9] This effect gives rise to an additive interaction energy of attraction between molecules, even though the molecules themselves possess no average dipole (or multipole) moment. The additive property makes the interaction energy between any two molecules of a cluster practically independent of the number of molecules in the cluster. Accordingly, when only this type of interaction obtains there is no effect of saturation, and clusters of two, three and more molecules are conceivable. If the clusters can be regarded as polymers in equilibrium with each other then it is proper to treat the deviations from Raoult's equation of the type shown by osmium tetroxide in carbon tetrachloride as indicating polymer formation, providing, of course, that the clusters are, on the average, sufficiently far apart so that their interaction with each other is small.

It is possible that the interactions between the assumed clusters are of the same order of magnitude as those between the molecules in the clusters. In that event the calculation of equilibrium constants for assumed polymer formation in concentrated solutions of the type reported here provides no more than a convenient empirical method for expressing the properties of the solutions.

The shape and size of the osmium tetroxide molecule were determined by Brockway[6] from electron diffraction experiments. Langseth and Quiller[7] photographed the Raman spectrum. From these results the standard entropy of osmium tetroxide gas may be calculated. The heat of formation and the vapor pressures of the tetroxide were measured by von Wartenberg.[2] The entropy of metallic osmium was calculated by Lewis and Gibson,[10] and that of oxygen has been determined by Giauque and Johnston.[11] This information taken together permits the calculation of the free energies of formation of both gaseous and solid osmium tetroxide. The necessary data and the results of the calculations are presented in Table III.

TABLE III

THE THERMODYNAMIC CONSTANTS OF OSMIUM TETROXIDE

Interatomic distance Os— O = 1.66 ± 0.05

Symmetry number σ = 12

Raman frequencies in cm.$^{-1}$ and their degeneracies (in parentheses)

$\omega_1(1)$	$\omega_2(2)$	$\omega_3(3)$	$\omega_4(3)$
971	568	1187	688

Standard entropies at 25° and one atmosphere in cal./deg.

OsO_4(g), 65.65 Os(s), 7.8 ± 0.5 O_2(g), 49.03

Solubility in water = 0.0284 mole/kg. water at 25°

Free energies and heat contents.

$Os(s) + 2O_2(g) = OsO_4(s)$

$\Delta F^\circ_{298} = -70{,}900$ cal. $\Delta H = -93{,}600$ cal.

$OsO_4(s) = OsO_4(g)$

$\Delta F^\circ_{298} = 2{,}800$ cal. $\Delta H = 13{,}500$ cal.

$Os(s) + 2O_2(g) = OsO_4(g)$

$\Delta F^\circ_{298} = -28{,}000$ cal. $\Delta H = -80{,}100$ cal.

$Os(s) + 2O_2(g) = OsO_4(aq)$

$\Delta F^\circ_{298} = -68{,}788$ cal.

The stability of osmium tetroxide is shown by the large negative value of ΔF°_{298}. The observation made by von Wartenberg that the tetroxide does not decompose at 1500° may be shown by an easy calculation to be consistent with the above free energy and heat content values.

The free energy values might also be combined with the results of Kirschman and Crowell[12] to obtain the free energies of some of the reduced forms of osmium in aqueous solutions.

Summary

The distribution ratios of osmium tetroxide between carbon tetrachloride and water have been measured at 25° for the whole range of concentrations up to saturation and found to vary from $R = N(\text{in } CCl_4)/N(\text{in } H_2O) = 78$ to $R = 136$. The results of solubility measurements are in agreement with the ratio at high concentrations.

The vapor pressures of dry carbon tetrachloride above its solutions of osmium tetroxide were measured at 25° and over the range of concentrations up to saturation. The results do not accord with Raoult's equation.

Electron diffraction, spectroscopic and thermal data are used to evaluate the free energies of gaseous, solid and aqueous osmium tetroxide.

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(9) London, *Trans. Faraday Soc.* **33**, 8 (1937).

(10) Lewis and Gibson, THIS JOURNAL, **39**, 2554 (1917).

(11) Giauque and Johnston, *ibid.*, **51**, 2300 (1929).

(12) Kirschman and Crowell, *ibid.*, **55**, 488 (1933).