and a series of new measurements on sixteen alloys, differing widely in type, is presented. It is shown that the greatest departure from simple additivity occurs in solid solutions of metals differing greatly in chemical type and that this departure is negative in every case under observation.

4. The basic importance of compressibility as a criterion of lattice rigidity in the study of the mechanical properties of metals and alloys, especially hardness, is emphasized, and the results of the compressibility measurements are correlated with the known mechanical properties and are interpreted to be in harmony with the slip-resistance theory of hardness. Measurements on quenched and annealed carbon steels are interpreted to indicate that the quenching hardness in these steels is not caused by an increase in the cohesive forces.

[Contribution from the Wolcott Gibbs Memorial Laboratory and the Metallurgical Laboratories of Harvard University]

INTERNAL PRESSURES IN METALLIC SOLID SOLUTIONS

By Robert Franklin Mehl[1]

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The importance of compressibility in the study of chemical affinity in metallic solid solutions and intermetallic compounds has recently been emphasized, and it has been shown that from compressibility data interesting conclusions may be drawn concerning the metallurgical behavior of alloys.[2]

The problem of the attraction between unlike atoms in solid solutions may be attacked in a different way, namely, by the use of the concept of internal pressure. T. W. Richards,[3] and others,[4] have emphasized the importance of internal pressures among the factors which determine the existence and behavior of solids. Richards has correlated the conception with his equation of state for solids.[5,3a]

The quantity π_0, the internal pressure, was first calculated by the equation

$$\pi_0 = \frac{R}{V_A \alpha_s} \tag{1}$$

where V_A is the atomic volume, α_s the coefficient of cubic thermal expansion and R the gas constant. Richards recently modified this equation,[6] and now regards (1) as only an approximation. The new equation is

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[1] National Research Fellow.

[2] Mehl and Mair, This Journal, **50**, 55 (1928).

[3] The most recent treatment of internal pressures is given by (a) Richards, This Journal, **48**, 3063 (1926). The first of his many papers on this subject appeared in 1901; (b) *Proc. Amer. Acad. Arts Sci.*, **37**, 1 (1901).

[4] Traube, *Z. anorg. Chem.*, **34**, 413 (1903); Benedicks, *ibid.*, **47**, 455 (1905); Hildebrand, "Solubility," Chemical Catalog Co., New York, **1924**, pp. 69, 185.

[5] Richards, This Journal, **46**, 1419 (1924).

[6] Ref. 3 a, p. 3067.

$$\pi_0 = \frac{n'}{n' - m} \cdot \frac{R}{V_A\, \alpha_s} \qquad (2)$$

n' and m are exponents in an abbreviated form of Richards's equation of state: $p + \pi_0\, (V_0/V)^m = (\pi_p + P_\Theta)(V_0/V)^{n'}$, in which p is the external pressure, π_0 the intrinsic cohesive pressure, π_p the intrinsic distending pressure and P_Θ the thermal pressure. Using Equation (2) a series of values has been calculated for most of the cubic metals.

The simple structure of terminal solid solutions of cubic metals (of the simple substitutional type) immediately suggests that Equation (1) or (2) could be applied to estimate the chemical affinity between metals in the state of solid solution in terms of pressure, a step in the direction of evaluating this affinity in energy units. The data required are the mean atomic volume compressibilities and the coefficients of thermal expansion only, but it is necessary that the data for the pure component metals be known with an accuracy comparable with that for the alloys and also that these data refer to alloys of high purity. These two requirements appear to eliminate most of the current data on thermal expansion[7] with the exception of those on the copper-zinc system,[8] but the application of the internal pressure equation to this system is somewhat uncertain because zinc is not normally cubic. Richards prefers to limit the application of this form of his equation to cubic metals.

The recent work of C. H. Johansson,[9] however, on the thermal expansion of binary alloys of a series of cubic metals, is well adapted to the present purpose, especially since the crystal structure of each of the six systems investigated had been determined by x-ray diffraction studies which therefore give the necessary data on the mean atomic volumes.

Johansson measured the linear expansion of alloys in the systems: silver-palladium, copper-nickel, copper-gold, gold-palladium, copper-palladium and silver–gold. The coefficients at 35° are used in the calculation of the internal pressure. The datum desired is the increase in internal pressure over the rule of mixtures value for each composition. The atomic percentage composition of each alloy is required in order to calculate the mean atomic volume (which is a linear function of atomic composition when simple additivity is assumed), and the volume percentage composition in order to calculate the rule of mixtures coefficient of expansion. The cubic coefficient is obtained from the linear merely by multiplying by three; n' and m for each composition are calculated from the volume composition, since they are exponents of volume quantities. The rule of mixtures value for the internal pressure is calculated using Equation (2) and the rule of mixtures values for α_s and V_A; the "actual" internal pressure is calculated using Johansson's data (multiplied by three) and

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[7] Given in International Critical Tables, Vol. II, pp. 459–464.

[8] Hindert, Bureau of Standards, Scientific Paper, No. 410, 1922.

[9] Johansson, *Ann. Physik,* **76,** 445 (1925).

the rule of mixtures value for V_A, corrected where necessary. The results of these calculations, as applied to several among the many compositions in each system investigated by Johansson, are given in Table I.

TABLE I

RESULTS OF CALCULATIONS

System Silver-Palladium (Compositions Refer to Palladium)

Atomic %	Volume %	$\alpha \times 10^6$ at 35°	3α	Mean atomic volume	3α R. of M.	$\frac{n'}{n'-m}$	π_0 R. of M. kilomegabars	π_0 "actual" kilomegabars	Increase	% Increase
0	0	19.05	57.15	10.28	57.2	1.42	199	199	..	0
8.9	7.8	17.9	53.7	10.16	55.5	1.42	206	214	8	3.9
30.6	27.6	15.5	46.5	9.85	51.3	1.42	230	254	24	10.4
50.9	47.3	14.0	42.0	9.57	47.0	1.42	259	290	31	12.0
65.7	62.4	12.55	37.65	9.37	43.8	1.42	284	330	46	16.2
86.4	84.6	12.55	37.65	9.08	39.0	1.42	332	341	9	2.7
100.0	100.0	11.9	35.7	8.89[a]	35.7	1.42	368	368	..	0
System Copper-Nickel (Compositions Refer to Nickel)										
0	0	16.9	50.7	7.12	50.7	1.55	352	352	..	0
9.8	9.1	16.0	48.0	7.07	49.6	1.55	363	357	12	3.3
30.1	28.5	15.2	45.6	6.96	47.4	1.55	386	401	15	3.9
50.1	48.2	14.4	43.2	6.86	45.1	1.55	411	429	18	4.4
69.6	67.9	13.95	41.85	6.75	42.8	1.55	440	450	10	2.3
94.8	94.4	13.05	39.15	6.62	39.7	1.55	484	491	7	1.4
100.0	100.0	(13.0)	39.0	6.59[b]	39.0	1.55	495	495	..	0
System Copper-Gold (Compositions Refer to Gold)										
0	0	16.9	50.7	7.12	50.7	1.55	352	352	..	0
20.9	27.5	15.6	46.8	7.77	48.6	1.44	314	326	12	3.8
30.0	38.0	15.15	45.45	8.05	47.9	1.40	298	315	17	5.7
45.0	54.0	15.0	45.0	8.52	46.7	1.36	281	292	11	3.9
69.2	76.3	14.8	44.4	9.26	45.0	1.32	260	264	4	1.5
83.8	88.1	14.55	43.65	9.72	44.1	1.30	249	252	3	1.2
100.0	100.0	14.4	43.2	10.22[c]	43.2	1.28	238	238	..	0
System Gold-Palladium (Compositions Refer to Palladium)										
0	0	14.4	43.2	10.22	43.2	1.28	238	238	..	0
18.6	16.6	13.0	39.0	9.99	43.0	1.30	254	274	20	7.8
40.1	36.8	12.2	36.4	9.73	40.4	1.32	276	306	30	10.9
49.8	46.3	11.9	35.7	9.60	39.7	1.33	286	319	33	11.5
61.1	57.7	11.9	35.7	9.45	38.9	1.35	302	328	26	8.6
74.7	72.0	11.9	35.7	9.26	37.8	1.37	322	341	19	5.9
100.0	100.0	11.9	35.7	8.89[d]	35.7	1.42	368	368	..	0
System Copper-Palladium (Compositions Refer to Palladium)										
0	0	16.9	50.7	7.12	50.7	1.55	352	352	..	0
19.4	23.1	14.95	44.85	7.46	47.2	1.53	357	375	18	5.0
36.4	41.7	13.6	40.8	7.76	44.5	1.49	355	386	31	8.7
49.8	55.3	12.85	38.55	8.00	42.5	1.47	356	392	36	9.9
59.3	64.5	12.45	37.35	8.17	41.0	1.46	358	393	35	9.8
78.4	81.9	12.05	36.15	8.51	38.4	1.44	362	385	23	6.4
100.0	100.0	11.9	35.7	8.89[e]	35.7	1.42	368	368	..	0

TABLE I (*Concluded*)

System Silver-Gold (Compositions Refer to Gold)

Atomic %	Volume %	$\alpha \times 10^6$ at 35°	3α	Mean atomic volume	3α R. of M.	$\frac{n'}{n' - m}$	π_0 R. of M. kilomega-bars	π_0 "actual" kilo-megabars	In-crease	% In-crease
0	0	19.0	57.0	10.28	57.0	1.42	199	199	..	0
30.0	30.0	17.35	52.05	10.23	52.9	1.37	207	211	4	1.9
50.0	50.0	16.5	49.5	10.23	50.1	1.34	214	217	3	1.4
70.0	70.0	15.6	46.8	10.23	47.3	1.33	221	224	3	1.3
100.0	100.0	14.4	43.2	10.22[f]	43.2	1.28	238	238	..	0

[a] McKeehan, *Phys. Rev.*, **20,** 428 (1922), found the lattice constants in this series of alloys to be very closely given by the rule of mixtures.

[b] Lange, *Ann. Physik,* **76,** 476 (1925), found the lattice constants to be given within the possible experimental error by the rule of mixtures.

[c] The x-ray data on the crystal structure of this system are conflicting, as pointed out in a previous paper (ref. 2). It seems advisable to assume a simple additivity as best representative of the available data.

[d] Holgersson and Sedstrom, *Ann. Physik,* **75,** 154 (1924), found the lattice constant in this series to deviate from the rule of mixtures value at the greatest by 0.6%, falling slightly below it. This variation is probably within the limit of accuracy of the measurements of the coefficient of thermal expansion and no correction need be made for it.

[e] Holgersson and Sedstrom, *Ann. Physik,* **75,** 160 (1924), give values for the lattice constant which vary slightly above and below the rule of mixtures values. In general the intermediate compositions give values for *a* somewhat too low, but the irregularity of these values probably indicates a close adherence to the rule of mixtures. One alloy (45.5 atomic % palladium) gave evidence of the cesium chloride structure, rather than the face-centered cubic.

[f] Irregular results have been obtained for the lattice constants in this series by McKeehan, *Phys. Rev.*, **20,** 428 (1922), who found *a* to depart from the rule of mixtures 1% at the maximum. On the other hand, Weiss, *Proc. Roy. Soc.* (*London*), **108,** 643 (1925), found a strictly linear relation. Simple additivity of the atomic volume is assumed in the above calculations.

Copper and nickel are very similar chemically and have atomic volumes that are not greatly different, and the same is true of gold and silver. Accordingly there is little increase in π_0 over the rule of mixtures value (4 and 2%, respectively, at the maximum). Copper and gold are also very similar chemically, though the tendency to form compounds which they manifest in the solid state is reflected in the somewhat greater increase in π_0, though the difference in atomic volumes may also be contributory. The greatest increase in π_0 comes in the system silver-palladium (16%), elements adjacent in the periodic table. Then in order come gold-palladium (12%) and copper-palladium (10%).

It is to be noted that the increase in π_0 is apparently independent of the relative values for the component metals and independent of the difference in the lattice constants (and therefore the atomic volumes) of the component metals. With respect to the lattice constants, copper and gold differ by 0.468 Å. and give a $\Delta\pi_{\text{max.}}$ value of 6%, whereas nickel and copper differ by 0.098 Å. and give a $\Delta\pi_{\text{max.}}$ value of 4%, and silver and palladium differ by 0.220 Å. and give a $\Delta\pi_{\text{max.}}$ value of 16%.[10]

The results are especially interesting in connection with the mechanical properties of solid solutions. Internal pressures are closely parallel to hardness for the pure metals and may be taken as an index of the lattice rigidity factor in hardness as distinguished from those factors which induce hardness by reason of lattice dissymmetry.[2] The percentage increase in internal pressure in a series of solid solutions may be compared with the percentage increase in hardness, and the magnitudes of these should give an analysis of the "chemical" and the "physical" factors in determining the hardness of solid solutions.[11]

High-grade hardness data are not available for all of the systems investigated by Johansson, but for the systems copper-nickel, silver-gold and gold-copper excellent data on the scratch hardness have been published by Kurnakov and Zemczuzny.[12]

Fig. 1 gives the percentage increase in π_0 and in the scratch hardness, plotted against volume percentage composition for the system silver-gold. At the maximum these are, respectively, 2 and 104%. If, therefore, the internal pressure and hardness be taken as directly proportional for the pure metals, it may be concluded that the hardest alloy in this series owes only about one-fiftieth of its hardness to the attraction between the unlike atoms.

A similar calculation for the copper-nickel system gives an increase of 4% in the internal pressures as compared to 63% in the hardness so that the "chemical hardness" in this system is 7% of the total hardness. In the copper-gold system these values are 6 and 100%, respectively, yielding a "chemical hardness" of 6% of the total.

The slip-resistance theory of hardness (in which hardness is defined as resistance to slip along atomic planes) recognizes two basic factors causing hardness in solid solutions.[13] These are (1) the attraction between unlike atoms and (2) crystalline dissymmetry caused by the warping of the atom planes with the introduction of the foreign atom. The calculations here presented are an attempt to evaluate the relative magnitudes of these two factors. In the nature of the case such an evaluation can only be semi-

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[10] The lattice constants for these metals are taken from Davey, *Phys. Rev.*, **25**, 753 (1925).

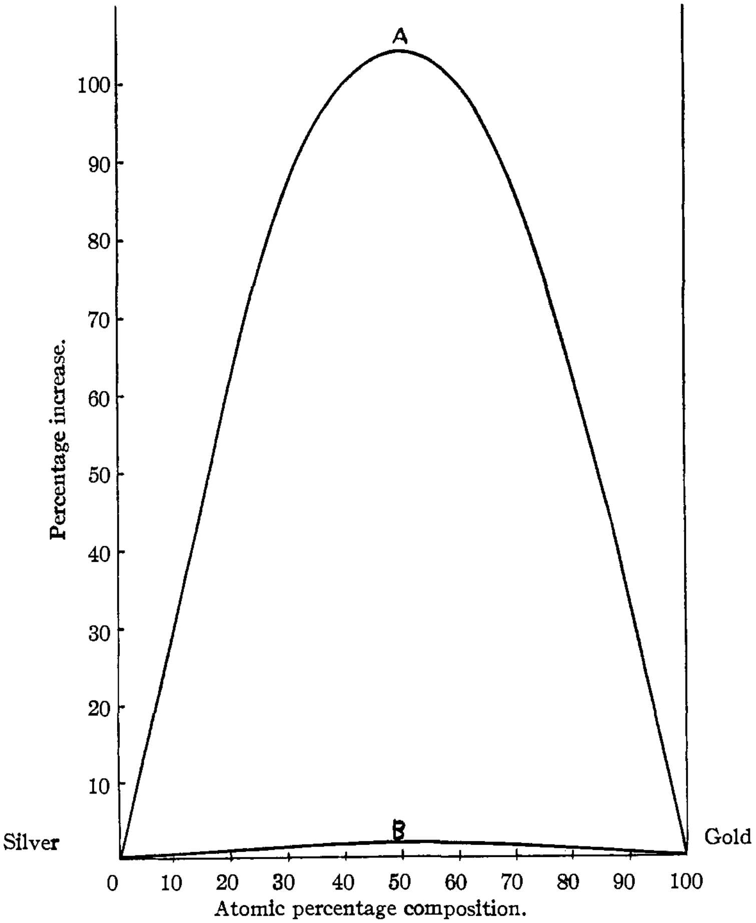
[11] Cold-work, which is very powerful in hardening metals and alloys, appears to have little or no effect upon the coefficient of thermal expansion [Jubitz, *Z. tech. Physik*, **7**, 522 (1926)], and therefore upon the internal pressure calculated therefrom. This emphasizes the fact that internal pressures are concerned only with purely cohesive forces and are not affected by lattice distortion or grain-size differences. It has already been pointed out (ref. 2) that compressibility is similarly unaffected by cold-work.

[12] Kurnakov and Zemczuzny, *Z. anorg. Chem.*, **54**, 164 (1907); **60**, 16 (1908).

[13] Jeffries and Archer, *Chem. Met. Eng.*, **24**, 1057 (1921).

quantitative, so that the percentages given must be regarded only as approximations.

Norbury[14] made measurements of hardness on a series of α-solid solutions of copper, and concluded that the hardening power of a solute atom is proportional to the difference in atomic volumes of the solute and the solvent. Rosenhain[15] has concluded that the hardness of solid solutions is largely caused by the lattice distortion introduced by the difference in size of the solvent and solute atoms. It is clear from the foregoing that Norbury's conclusion concerning the α-solid solutions of copper cannot be applied to the system silver-gold, nor perhaps to nickel-copper,



Curve A, hardness; Curve B, internal pressure.

Fig. 1.

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[14] Norbury, *Trans. Faraday Soc.*, **19**, 586 (1923–1924).

[15] Rosenhain, *Chem. Met. Eng.*, **28**, 442 (1923).

for though the atomic volumes are nearly identical in each metal pair (10.28 and 10.22, and 7.12 and 6.59, respectively), the hardness reaches a maximum increase of 100.4% in the first and 63% in the second. The conclusion seems inescapable that the hardness in these solid solutions is not caused simply by the difference in sizes of the unlike atoms. In fact, if it be assumed that the internal pressures calculated in Table I apply to each separate atom it is clear that the atomic volumes of the atoms in solid solution cannot be the same as in the elementary state. In the silver-gold system, with increasing percentage of gold, the internal pressure increases from 199 kilomegabars for pure silver to 238 kilomegabars for pure gold, an increase of 39 kilomegabars. Obviously a pressure increase of such a magnitude would diminish the volume of the silver atom very appreciably. Conversely, in an alloy rich in silver, the gold atom, subjected to a smaller internal pressure than in the pure state, would increase in volume. This variation in volume would produce a slip-resistance not indicated by the relative atomic volumes of the metals in the pure state. It is not possible to calculate this volume change from the compressibilities of the pure metals, for even if the extrapolation to these high pressures and the approximation of the expansibility of the atom under an internal pressure decrease, be admitted, it must be remembered that because of the chemical attraction between the unlike atoms in the solid solution each atom is very probably partially ionized, and that the ordinary compressibility coefficients are not applicable to the metal atom in this state. It is a significant fact, however, that the lattices of these solid solutions possess a high degree of symmetry, as shown by the sharpness of the reflection spectra obtained with x-rays. Whatever the volume changes suffered by the atoms, their symmetrical lattice positions must be accounted for, and the net volume change must be in accord with the observed small deviations from the rule of mixtures values for the densities.

As applied to non-cubic metals, the internal pressures calculated from the coefficient of linear expansion and the mean atomic volume may be taken to represent an *average* pressure around the periphery of the atom,[16] and accepting this extension of the foregoing argument, some interesting analogies can be drawn for the α-copper-zinc solid solutions.

Reference has already been made to coefficients of expansion for copper and the α-brasses.[8] There appears to be no satisfactory measurement for the coefficient of volume expansion for zinc at a comparable temperature but the linear coefficients determined by Bridgman[17] parallel and perpendicular to the hexagonal axis may be combined into a volume coefficient,

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[16] Richards, publication in press in *J. chim. phys.* See also THIS JOURNAL, **47,** 732 (1925).

[17] Bridgman, *Proc. Am. Acad. Arts. Sci.,* **60,** 305 (1925).

namely, 82.6×10^{-6}.[18] Table II gives the results of these calculations, using Equation (1). All coefficients of thermal expansion are calculated to 20°.

TABLE II

RESULTS OF CALCULATIONS

Weight % of copper	Atomic % of copper	$\alpha \times 10^6$	$3\alpha \times 10^6$	Mean atomic vol., calcd.	Mean atomic vol., obs.	3α R. of M.	π_0 R. of M., kilomeg.	π_0 "actual," kilomeg.	Increase	% Increase
100.0	100.0	16.26	48.7	7.12	7.12	48.7	237[a]	237	..	..
90.3	88.1	17.02	51.1	7.32	7.24	52.7	213	222	9	4.2
80.0	76.3	17.23	51.7	7.52	7.36	56.7	193	216	23	11.9
75.3	70.9	17.59	52.8	7.61	7.44	58.6	184	209	25	13.6
70.3	65.4	17.77	53.3	7.71	7.51	60.4	176	205	29	16.5
0.0	0.0	...	82.6	9.16	9.16	82.6	109	109	..	..

[a] This value for copper differs from that given in Table I since the coefficient $n'/(n' - m)$ has been dropped. This coefficient is unknown for zinc, but its elimination can have only a very slight effect upon the figures in the last column.

This increase in internal pressure runs closely parallel with the related properties, as shown by Table III.

TABLE III

Weight % of copper	% Decrease in specific volume[a]	% Decrease in compressibility	% Increase in internal pressure
100.0	..	..	..
90.0	1.05	13	4.2
80.0	1.71	21	11.9
70.0	2.49	26	16.5
63.0	2.95	30	20.0

[a] The figures in the second column have been calculated from those cited by Jeffries and Archer, *Chem. Met. Eng.*, **29**, 925 (1923). Those in the third column are approximated from the values determined by the author in collaboration with B. J. Mair (ref. 2). Each column refers to the percentage change from the rule of mixture value.

A fifth column, giving the percentage increase in hardness, could be appended to this table, but this had not been done because of the disagreement among the various investigators concerning the hardness of the α-brasses.[19] However, the greater hardness of the α-brasses is clearly influenced by the chemical attraction between unlike atoms and the resultant denser packing, as illustrated by the last three columns in Table III. The probable effect

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[18] Bridgman's linear coefficients are, respectively, 57.4×10^{-6} and 12.6×10^{-6}. The volume coefficient is therefore $2\ (12.6 \times 10^{-6}) + 57.4 \times 10^{-6}$.

[19] Harris, *J. Inst. Metals*, **28**, 327 (1922), reported in International Critical Tables, Volume II, p. 555, finds that the Brinell numbers for α-brass with 90, 80 and 70 percentage copper by weight are identical, namely, 45, whereas that for the 66% copper alloy is 48. Taking 40 as the Brinell number for pure copper and 39 for zinc, this is an increase over the rule of mixtures value of only 20%. Jeffries and Archer, *Chem. Met. Eng.*, **29**, 967 (1923), state that the Brinell number rises from 35 for pure copper to 55 for a 70–30 brass, an increase over the rule of mixtures value of approximately 53%.

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

BY DON M. YOST AND ROBERT J. WHITE

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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).