tions increase will be a matter of considerable interest and importance. Another important test of the limiting law which must eventually be carried out is the diffusion of a trace ion in a salt solution whose ions are chemically different from the trace ion.

Summary

1. The Onsager equation for the diffusion coefficient of an ion at very low concentration in a salt solution of relatively high concentration has been adapted to the phenomenon of self-diffusion.

2. The limiting law of the theory has been derived and compared with experimental values of the self-diffusion of radioactive sodium ion and radioactive iodide ion in sodium iodide solutions, and of radioactive silver ion in silver nitrate solutions. The agreement between the theoretical predictions and experimental results is not exact but is reasonably satisfactory.

NEW HAVEN, CONN. RECEIVED JUNE 16, 1950

[CONTRIBUTION FROM DIVISION OF ANALYTICAL CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Electrokinetics of Hydrogen Evolution.[1,2] II. Deuterium Overvoltage on Mercury

BY B. POST AND C. F. HISKEY

In a previous paper[3] measurements of hydrogen overvoltage on mercury cathodes were reported for a wide range of current densities and temperatures. Comparable measurements of deuterium overvoltage (*i.e.*, overvoltage in solutions of DCl in 99.8% D_2O) are described in this paper. From these measurements the value of the electrolytic separation factor of the hydrogen isotopes may be estimated and compared with the available experimental data.[4] It appears that these overvoltage and separation factor data enable us to exclude from consideration one mechanism which has been proposed as an explanation of hydrogen overvoltage.

Experimental

With the few exceptions to be noted below the apparatus and procedures employed in this investigation were identical with those described in ref. 3.

The use of deuterium and deuterium compounds necessitated the introduction of some minor changes in procedure. Dilution of the heavy water by light water had to be prevented. All equipment was dried carefully before use, and rinsed once by distilling several ml. of heavy water through the system. This water was then removed before the deuterium oxide which was to be used in the experiments was introduced.

Solutions of deuterium chloride in deuterium oxide were used as electrolytes. These were prepared by distilling heavy water onto anhydrous aluminum chloride and bubbling the evolved gas through the heavy water. This solution was subsequently distilled into the cathode compartment of the overvoltage cell.

In all runs the deuterium chloride concentration was 0.1 *M*. The acidity of the electrolyte solutions was determined by measuring the potential difference between a platinum black reference electrode in the cell and an external calomel electrode, as described in the previous paper.

Deuterium, purified in the gas train used for the hydrogen in the previous investigation, was used to flush the solutions and the overvoltage cells free of oxygen. All solutions were saturated with deuterium before use. The platinum black reference electrode within the cell served as a reversible deuterium electrode; overvoltages were measured between it and the working mercury cathode. Experiments were made in duplicate in two cells differing only in cathode area (3.80 and 5.47 sq. cm.). About 50 ml. of deuterium oxide was used in each cell.

Results

Measurements were made at 4° (D_2O freezes at 3.8°), 11°, 20° and 10° intervals to 70°. Results of these measurements are listed in Table I.

TABLE I

DEUTERIUM OVERVOLTAGE ON MERCURY CATHODES

(0.1 *M* DCl)

Overvoltage (η) given in millivolts

i,	T, °C.							
amp./sq. cm.	4.0	11.0	20.0	30.0	40.0	50.0	60.0	70.0
1.0×10^{-6}	830	800	752	..	..	..	..	..
1.6×10^{-6}	850	824	780	..	..	..	..	..
2.5×10^{-6}	877	850	810	750	720	..	..	..
4.0×10^{-6}	902	873	842	790	750	710	..	..
6.3×10^{-6}	925	899	867	828	772	747	708	660
1.0×10^{-5}	949	919	890	850	810	770	738	706
1.6×10^{-5}	970	942	910	880	837	800	765	730
2.5×10^{-5}	990	969	932	900	860	829	792	762
4.0×10^{-5}	1012	995	958	927	880	850	822	788
6.3×10^{-5}	1039	1019	983	950	910	880	850	820
1.0×10^{-4}	1062	1040	1009	972	935	901	876	843
1.6×10^{-4}	1082	1063	1032	1000	960	931	902	870
2.5×10^{-4}	1109	1082	1052	1024	983	957	924	900
4.0×10^{-4}	1130	1110	1080	1050	1010	985	953	930
6.3×10^{-4}	1150	1132	1107	1074	1033	1009	984	957
1.0×10^{-3}	1175	1157	1128	1098	1060	1037	1008	982
1.6×10^{-3}	1200	1181	1150	1128	1087	1060	1038	1010
2.5×10^{-3}	1221	1204	1173	..	1110	..	1061	1040
4.0×10^{-3}	..	1230	1200	..	..	..	..	1070
6.3×10^{-3}	..	..	..	..	..	..	..	1100

Measurements made at current densities in excess of 10^{-5} amp./sq. cm. were reproducible to ±3 to 4 mv. in successive runs in one cell, and to ±6 mv. in separate cells using different batches of electrolyte and mercury.

As in the hydrogen investigation, it was found that measurements made at current densities less than 10^{-5} amp./cm.^{2}, above 20°, were generally unstable and showed marked deviations from a linear log i *vs.* η relation. In other regions investigated the relation between log i and η is linear.

Calculations of slopes of log i *vs.* η, and estimates of reproducibility are based on measurements made at current densities in excess of 10^{-5} amp./cm.^{2}.

Discussion of Experimental Results

Over the temperature and current density ranges investigated, deuterium overvoltages were from 50

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[1] This research was supported in part by a grant from the Office of Naval Research. That assistance is gratefully acknowledged.

[2] Some of this material was read before a meeting of the Metropolitan and Long Island Sections of the American Chemical Society, February, 1950, Brooklyn, N. Y.

[3] B. Post and C. F. Hiskey, THIS JOURNAL, **72**, 4203 (1950).

[4] See list of references in: A. H. Kimball, H. C. Urey and I. Kirschenbaum, "Bibliography of Research on Heavy Hydrogen Compounds," McGraw-Hill Book Co., New York, N. Y., 1949, pp. 285-286.

to 70 mv. higher than comparable hydrogen overvoltage values. Thus, for 20°, the Tafel relation of the two cases are given as

$$\eta_{D_2} = 1485 + 119 \log i$$
$$\eta_{H_2} = 1416 + 116 \log i$$

Slopes of the plots of deuterium overvoltage *vs.* logarithm of current density were slightly, but consistently, higher than comparable hydrogen slopes. The causes of these differences, which are beyond the range of experimental error, are not clear.

The values of the slopes (b) are given by $b = RT/\alpha F$. The variation of b and α with temperature is shown in Table II where it can be seen that the values of α range from 0.48 to 0.50; over the same temperature range, α, for hydrogen, varied from 0.50 to 0.54.

Table II

Variation of b and α with Temperature

b = slope of η *vs.* log i; $\alpha = (2.403\ RT)/bF$

T, °C.	b	α
4.0	113	0.48
11.0	116	.48
20.0	119	.49
30.0	123	.49
40.0	126	.49
50.0	130	.49
60.0	133	.50
70.0	137	.50

The relation between current density (i) and overvoltage (η) is generally written as

$$i = ce^{-(\Delta H - \alpha F\eta)/RT} \qquad \text{(I)}$$

where i = current density, ΔH is the activation energy of the slow step responsible for the overvoltage, and the other terms have their usual significance.

In Fig. 1, log i is plotted against $1/T$ for fixed values of η. Values of ΔH are computed from the slopes of these lines using Equation (I).

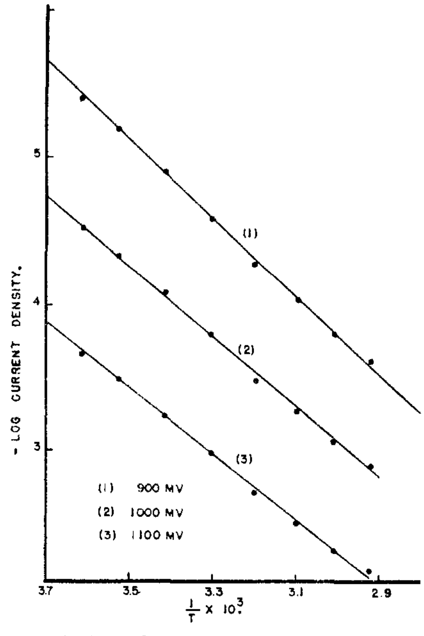

Fig. 1.—Variation of current density with temperature.

	1100 mv.	1000 mv.	900 mv.
Slope	−2.22	−2.40	−2.66
ΔH, kcal./g. ion	22.4	22.3	22.7

The mean value of α, 0.49, was used in these calculations.

Equation I may be rewritten to yield an alternative expression for ΔH

$$\Delta H = \alpha F\left[\eta - T\left(\frac{\partial \eta}{\partial T}\right)_i\right] \qquad \text{(II)}$$

$(\partial\eta/\partial T)_i$ = −2.93 mv./degree at 10^{-5} amp./sq. cm.; −3.32 mv./degree at 10^{-4} amp./sq. cm.; and −3.69 mv./degree at 10^{-5} amp./sq. cm. A mean value of $[\eta - T(\partial\eta/\partial T)_i]$ based on these values, and allowing for the uncertainty in the determination of $(\partial\eta/\partial T)_i$, is 1990 ± 30 mv., from which we have $\Delta H = 22.5 \pm 0.3$ kcal./g. ion.

It is evident from (I) that extrapolation of the lines representing the plots of overvoltage *vs.* logarithm of current density at various temperatures leads to their intersection at the potential where $\Delta H = \alpha F\eta$. This potential, ($\eta_{\text{intersection}}$), equals $[\eta - T(\partial\eta/\partial T)_i]$. The extrapolation is shown in Fig. 2. At $i = 2 \times 10^4$ amp./sq. cm., all values of η fall in the range 1990 ± 15 mv. (at this current density, where $\Delta H = \alpha F\eta$, $i = c$).

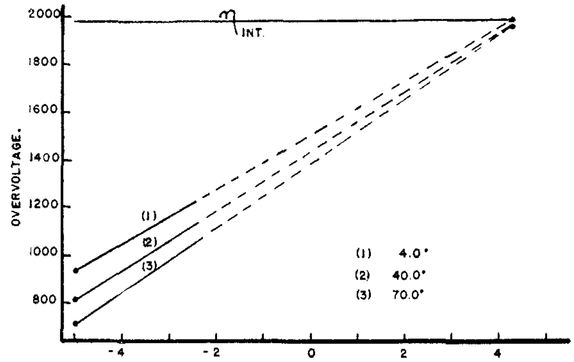

Fig. 2.—Extrapolation of log i *vs.* η for different temperatures.

The data in Table I may be summarized using a modified form of Tafel's equation

$$\eta = 1990 + \frac{RT}{F}\log\frac{i}{c} = 1990 + \frac{RT}{0.49F}\log\frac{i}{2 \times 10^4} \qquad \text{(III)}$$

The comparable equation for hydrogen overvoltage is

$$\eta = 1880 + \frac{RT}{0.50F}\log\frac{i}{1 \times 10^4} \qquad \text{(IV)}$$

Results of Other Workers

Measurements of deuterium overvoltage, using a dropping mercury electrode, have been reported by Heyrovsky,[5] Mueller[6] and Novak.[7] The relations of their results to those obtained at stationary mercury electrodes have already been treated by Jofa and colleagues.[8] It may be noted that in all

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[5] J. Heyrovsky, *Collection Czechoslov. Chem. Commun.*, **9**, 273 (1937); *ibid.*, **9**, 345 (1937); *Chem. Revs.*, **24**, 125 (1939); *Trans. Faraday Soc.*, **84**, 257 (1928).

[6] O. H. Mueller and J. Heyrovsky, *Collection Czechoslov. Chem. Commun.*, **7**, 281 (1935).

[7] J. Novak, *ibid.*, **9**, 207 (1937).

[8] N. Jofa, A. Kolychev and L. Shtifman, *Acta Physicochimica, U. R. S. S.*, **12**, 231 (1940).

these instances the overvoltage in heavy water at room temperature was found to be from 50 to 87 mv. greater than in ordinary water. Thus, for very carefully purified solutions of 0.2 N H_2SO_4 in 99.6% D_2O, Novak[7] found deuterium overvoltage to be 87 mv. greater than hydrogen overvoltage at 20°, and 71 mv. greater at 60°.

Only one investigation of deuterium overvoltage at a stationary mercury electrode has been reported. In a brief note, Bowden and Kenyon[9] described preliminary measurements of deuterium overvoltage over mercury. They reported that, at 25°, and at a current density of 10^{-4} amp./sq. cm., the overvoltage in a solution of 0.2 N H_2SO_4 in 98% D_2O equalled 980 mv.[10] The slope of the log i $vs.$ η line was reported to be 0.120. Comparable values in this study (using 99.8% D_2O compared with the 98% D_2O used by Bowden) are: η = 990 mv., and slope = 0.121, at $i = 10^{-4}$ amp./sq. cm. and 25°.

Bowden and Kenyon also measured overvoltage in ordinary water and reported that deuterium overvoltage exceeds hydrogen overvoltage by 130 mv. at 25°. Our investigations indicate that the difference ranges only from 50 to 70 mv., and that at 25° and $i = 10^{-4}$ amp./sq. cm., the difference is very close to 60 mv.; *i.e.*, Bowden and Kenyon's values of hydrogen overvoltage appear to be too low by about 80 mv. The recent work of Jofa and coworkers,[11] who measured hydrogen overvoltage on mercury over wide ranges of current densities and temperatures, also indicates that Bowden and Kenyon's values are too low by 70 to 80 mv. Bockris[12] has compiled additional evidence to bear out this point.

Overvoltage and Isotope Separation

As is well known, in the electrolysis of mixtures of light and heavy water, the gas liberated at the cathode contains a greater proportion of hydrogen than does the solution. The latter is thereby enriched in deuterium. The separation is usually expressed as the ratio of the proportions of hydrogen and deuterium in the gas to those in the liquid, *viz.*: $S = ((H/D)\text{ gas}/(H/D)\text{ liquid})$. Where exchange between the liberated gas and the liquid does not occur, the separation should reflect the difference between deuterium and hydrogen overvoltage. Hirota and Horiuti[13] have shown that such exchange does not occur to any appreciable extent at a mercury electrode.

Grew[14] and Drucker[15] have shown that reversible hydrogen and deuterium electrodes differ in potential by less than 4 mv. Hydrogen and deuterium overvoltages are therefore compared directly, no allowance being made for this small potential difference, which is less than the experimental error of our investigations. Values of hydrogen and deuterium overvoltage at 4° and 70° are shown in Fig. 3.

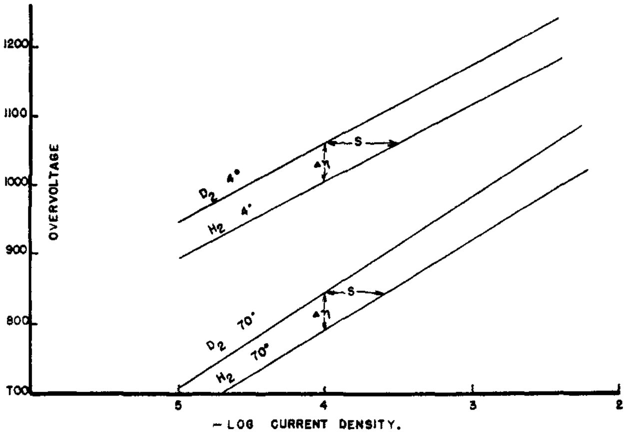

Fig. 3.—Hydrogen and deuterium overvoltage and the separation factor.

The ratio of the current passing in ordinary water to that in pure heavy water at any one overpotential and temperature is the computed separation. Thus, at 20° and η = 1000 mv. the computed separation factor is 3.1.

Separation factors, at mercury cathodes, have been determined directly by Horiuti and Okamoto[16] and Walton and Wolfenden[17] who electrolyzed acidified solutions of heavy water and analyzed the evolved gases. The former used 6% D_2O in 1 N H_2SO_4 solutions as electrolytes; the latter used 30 to 50% D_2O in solutions 0.5 N in HCl and KCl.

Horiuti and Okamoto reported a separation factor of 3.1 at room temperature (current density not specified); Walton and Wolfenden reported a mean separation factor of 3.3 ± 0.2 at 15° at current densities from 0.5 to 1.0×10^{-3} amp./sq. cm.

Bowden and Kenyon[9] reported a 130 mv. difference between hydrogen and deuterium overvoltage; this leads to a computed separation factor of 13.5. Walton and Wolfenden[17] attempted to reconcile these results with their separation data by assuming that the rate determining step in the discharge process involves two atoms. If this is the case, the evolution of HD molecules will require less energy than will the evolution of deuterium; *i.e.*, the difference between H_2 and HD overvoltage will be only about half as great as the difference between H_2 and D_2 overvoltage. Where, as in the separation experiments, the evolved gases were composed mostly of H_2 and HD, this leads to a computed separation factor of approximately $\sqrt{13.5}$ or 3.7.

Considerations of this sort led Walton and Wolfenden to reject as inapplicable to mercury electrodes, theories of hydrogen overvoltage, such as those of Gurney[18] and Erdey-Gruz and Volmer,[19] which postulated that only one atom is concerned in the rate determining step. The application of these theories to Bowden and Kenyon's data,

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(9) F. P. Bowden and H. F. Kenyon, *Nature*, **135**, 105 (1935).

(10) These results were published in graphical form only; the value given is based on a visual estimate and may be in error by as much as 10 mv.

(11) (a) Z. A. Jofa and K. P. Mikulin, *J. Phys. Chem., U. S. S. R.*, **18**, 137 (1944); (b) Z. A. Jofa and V. Stepanova, *ibid.*, **19**, 125 (1945).

(12) J. O'M. Bockris, *Chem. Revs.*, **43**, 525 (1948).

(13) K. Hirota and J. Horiuti, *Sci. Papers Inst. Phys. Chem. Research, Tokyo*, **30**, 151 (1936).

(14) Quoted by Bowden and Kenyon, ref. (9).

(15) C. Drucker, *Trans. Faraday Soc.*, **33**, 660 (1937).

(16) J. Horiuti and G. Okamoto, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, **28**, 231 (1936).

(17) H. F. Walton and J. H. Wolfenden, *Trans. Faraday Soc.*, **34**, 436 (1938).

(18) R. W. Gurney, *Proc. Roy. Soc. (London)*, **A134**, 137 (1931).

(19) T. Erdey-Gruz and Volmer, *Z. physik. Chem.*, **150**, 203 (1930).

would lead to separation factors of 13.5 in place of the observed values of 3.1 and 3.3.

From the overvoltage data presented in this paper, separation factors of 3.0 to 3.2 are computed (Fig. 3). As has been pointed out, computed separation factors are based on the relative amounts of pure H_2 and D_2 evolved at fixed overpotentials. The good agreement between these computed values and the experimental values for cases where H_2 and HD were evolved, indicates that the separation factor is independent of the molecular form in which the hydrogen and deuterium atoms are evolved.

These findings are incompatible with theories of hydrogen overvoltage which postulate as the slow step of the discharge process the combination of two or more entities on the electrode. These overvoltage and separation data can be interpreted only in terms of theories which postulate that only one particle is involved in the discharge process.

Summary

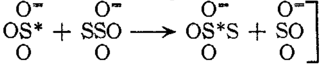
Measurements of deuterium overvoltage on mercury cathodes at current densities from 10^{-6} to over 10^{-3} amp./sq. cm. and at temperatures from 4 to 70° are reported in this paper. These have been compared with previously reported measurements of hydrogen overvoltage made under similar conditions.[1] From these data, electrolytic separation factors for hydrogen and deuterium have been computed which agree very well with experimental separation data. These overvoltage and separation data appear to preclude the possibility that the slow step of the hydrogen discharge process, at mercury cathodes, involves more than one ion or atom.

BROOKLYN 2, N. Y. RECEIVED JUNE 16, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Kinetics of the Exchange of Sulfur between Thiosulfate and Sulfite[1]

BY DONALD P. AMES[2] AND JOHN E. WILLARD

Voge[3] has reported a measurable rate at 100° for the exchange of sulfur between thiosulfate and sulfite. We have investigated the kinetics of this reaction  $\left[\underset{O}{\overset{O^=}{OS^*}} + \underset{O}{\overset{O^=}{SSO}} \longrightarrow \underset{O}{\overset{O^=}{OS^*S}} + \underset{O}{\overset{O^=}{SO}}\right]$ because it appears to be sufficiently simple so that its study offers opportunity of obtaining useful information regarding reactions between ions of similar charge.

Experimental

Radioactive Sulfur.—Elemental sulfur containing S^{35} produced by neutron bombardment[4] was heated at 100° for 10 hours[5] to convert amorphous sulfur ($S\mu$) into the soluble $S\lambda$ form. It was then dissolved in toluene, the solution was centrifuged, and sulfur was crystallized from the supernatant. Absorption curves taken on the radiations from this material agreed with those in the literature.[6]

Radioactive Sulfite.—Radioactive sulfur dioxide was prepared by burning 10-mg. samples of radioactive sulfur by careful heating in a stream of oxygen. With the excess oxygen serving as carrier, the sulfur dioxide produced was bubbled through toluene to remove any unreacted sulfur and then absorbed in a solution of sodium hydroxide (*ca.* $3M$ Merck reagent grade). The caustic scrubber consisted of a conical centrifuge tube with a two-hole stopper fitted with an inlet tube and a 6 mm. i.d., two-foot long, Vigreux column, the lower end of which extended to the bottom of the cone which contained 3 ml. of the caustic solution. The incoming gas stream forced the solution to rise in the Vigreux column and wet its surfaces.

The alkaline sulfite solutions were shown to be stable to air oxidation by periodic titrations with iodine which showed no significant change in sulfite concentration over periods of two weeks or more.

Radioactive Thiosulfate.—Radioactive thiosulfate was made by exchange of radiosulfite in aqueous solution with thiosulfate at elevated temperatures under the conditions reported in detail as the main subject of this paper. It was also made by treating elemental sulfur with sulfite in alkaline solutions.[7] Excess sulfur was removed by extraction with toluene and the thiosulfate and remaining sulfite were separated either by precipitation of the latter as strontium sulfite[8] or of the former as triethylenediaminenickel thiosulfate.[9] Depending on whether radiosulfur or radiosulfite is used in this synthesis, the thiosulfate can be tagged on either the outer or inner sulfur atom, whereas in the former synthesis it is tagged on the central sulfur atom.

Separation of the Two Sulfur Atoms of Thiosulfate.—When it was desired to determine the specific activity of the outer or inner sulfur atoms of a given sample of thiosulfate, a portion of the solution (or of the triethylenediaminenickel thiosulfate) from which sulfite and free sulfur had been removed, was frozen in a 25-ml. flask with the aid of liquid air and a few ml. of concd. hydrochloric acid was added. The flask containing the frozen reactants was then attached by a ground-glass joint to a gas absorption train, and was thermostated at 90° for 15 min. Under these conditions[10] the thiosulfate is decomposed quantitatively to sulfur dioxide and sulfur. With the aid of a stream of nitrogen the sulfur dioxide was carried into a Vigreux column absorption trap (described above) where it was absorbed by a solution of sodium hydroxide and oxidized by addition of sodium peroxide. Barium sulfate was then precipitated with excess barium chloride and prepared for counting.

The elemental sulfur produced by the acidification of the thiosulfate solution was extracted from its aqueous suspension with toluene. The toluene extract was evaporated to dryness and the sulfur residue was oxidized to sulfate by heating for four hours at 90° with fuming nitric acid. The nitric acid was decomposed by evaporation in the presence of hydrochloric acid, and barium chloride was added to precipitate barium sulfate for counting. This barium sulfate represented the outer sulfur of the thiosulfate whereas the barium sulfate produced from the sulfur dioxide fraction represented the central sulfur. In order to avoid the necessity for quantitative recovery in the chemical preparation of samples for counting, the specific activity of each barium

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(1) Presented, in part, before the Division of Physical and Inorganic Chemistry at the Sept., 1949, Meeting of the American Chemical Society at Atlantic City, N. J.

(2) Los Alamos Scientific Laboratory, Los Alamos, N. M.

(3) Voge, THIS JOURNAL, **61**, 1032 (1939).

(4) U. S. Atomic Energy Commission Isotopes Catalogue, Aug. 11, 1949, Item No. 75, procured from the Oak Ridge National Laboratory.

(5) Cooley, Yost and McMillan, THIS JOURNAL, **61**, 2970 (1939).

(6) See for example: (a) Solomon, Gould and Anfinsen, *Phys. Rev.*, **72**, 1097 (1947); (b) Yaffe and Justus, *Can. J. Research*, **26B**, 734 (1948).

(7) Watson and Rajagopalan, *J. Indian Inst. Sci.*, **8A**, 275 (1925).

(8) (a) Ephraim, "Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1947, p. 551; (b) Autenrieth and Windaus, *Z. anal. Chem.*, **37**, 290 (1898).

(9) Spacu and Spacu, *ibid.*, **89**, 192 (1932).

(10) (a) Bassett and Durrant, *J. Chem. Soc.*, 1416 (1927); (b) Friend, "Textbook of Inorganic Chemistry," Charles Griffin Co., London, 1931, Vol. VII, Part II, p. 30.