4. The same reaction measured in a piperidine-piperidinium ion and a phosphate buffer shows a considerable secondary salt effect, positive in the first and negative in the second case. These effects are in agreement with the theory of kinetic salt effect.

5. The reaction studied exemplifies the inadequacy of stating an ion-equilibrium constant without reference to the specific region of salt concentration to which it applies.

Copenhagen, Denmark

[Contribution from the Eppley Laboratory]

SATURATED STANDARD CELLS WITH SMALL TEMPERATURE COEFFICIENTS

By Warren C. Vosburgh

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Two kinds of Weston cells are used as standards of electromotive force, the unsaturated cell and the normal cell. The unsaturated cell has the advantage of a negligible temperature coefficient,[1] but its electromotive force is not constant over long periods of time,[2] and from a practical standpoint it is not as reproducible as the normal cell. The normal cell has the advantage of reproducibility and constancy and the disadvantage of an appreciable temperature coefficient. It has been found possible to alter the normal cell in such a way as to reduce its temperature coefficient considerably. This can be done by using for the amalgam electrode an amalgam containing tin or lead as well as cadmium.

The systems cadmium-tin-mercury and cadmium-lead-mercury have been investigated by Kremann, Prammer and Helly.[3] They found that the addition of tin or lead to a two-phase cadmium amalgam gave an amalgam that showed a constant potential difference against a solution containing cadmium ion for quantities of the added metal between 10 and 75 atomic per cent. of the whole.

Preparation of Materials

Cadmium Sulfate.—The cadmium sulfate was twice recrystallized by slow evaporation of a saturated solution at room temperature.

Mercurous Sulfate.—Mercurous sulfate 11 was used. This was a coarse-grained, electrolytic preparation which had been used in previous work.[4]

Mercury.—The mercury was passed through a column of mercurous nitrate solution in a finely divided state and then redistilled in a current of air.

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[1] Vosburgh and Eppley, This Journal, **45**, 2268 (1923).

[2] Vosburgh, *J. Optical Soc. Am.*, **11**, 59 (1925).

[3] Kremann, Prammer and Helly, *Z. anorg. allgem. Chem.*, **127**, 295 (1923).

[4] Vosburgh, This Journal, **47**, 1256 (1925).

Amalgams.—Cadmium amalgam containing 10% of cadmium was prepared by electrolysis of a solution of cadmium sulfate in redistilled water with a mercury cathode and a platinum anode.

Cadmium-lead amalgam was prepared by two different methods. Amalgam 1, used in the amalgam cells, was prepared by adding the calculated amounts of pure lead[5] to portions of the cadmium amalgam described above. Amalgam 2 was prepared by first depositing lead in a weighed amount of mercury by electrolysis of a saturated solution of specially prepared lead chloride. The resulting amalgam was weighed and cadmium was deposited in it by electrolysis of a solution of recrystallized cadmium sulfate. The concentrations were adjusted by adding portions of mercury and pure lead. Both amalgams had the same composition.

Four different cadmium-tin amalgams were made. The first was prepared by adding commercial c. p. tin to portions of the cadmium amalgam described above. The other three were prepared by electrolysis. Current was passed between an anode of commercial c. p. tin, enclosed in a coarse Alundum thimble, and a cathode of a weighed amount of mercury. The electrolyte at the start was a solution of redistilled hydrochloric acid. The tin stick was weighed occasionally as a rough check on the amount deposited. After sufficient had been deposited the amalgam was dried and weighed. Cadmium was then deposited in the amalgam in a similar manner, the anode being a stick of commercial c. p. cadmium and the electrolyte a cadmium sulfate solution. In one case, Amalgam 2, more mercury was added at the end. The weight of the completed amalgam then allowed the calculation of its composition. The composition of each amalgam in atomic per cent. and the ratio of cadmium to mercury are given in Table I.

Table I

Composition of Amalgams

Amalgam	Sn At. %	Pb At. %	Cd At. %	Hg At. %	Cd:Hg by wt.
Cd	..	..	16.5	83.5	0.111
Cd-Pb 1,2	..	10.0	14.6	75.4	.109
Cd-Sn 1	14.9	..	14.1	71.0	.111
Cd-Sn 2	13.1	..	14.3	72.6	.111
Cd-Sn 3	11.9	..	15.4	72.7	.119
Cd-Sn 4	10.7	..	15.7	73.6	.120

Cadmium-copper and cadmium-bismuth amalgams were prepared by adding the required amounts of copper and bismuth, respectively, to weighed portions of the 10% cadmium amalgam and heating. The copper was prepared by electrolysis of a solution of recrystallized copper sulfate. The bismuth was prepared by fusion of bismuth oxychloride with commercial c. p. sodium cyanide.

Preparation of the Cells

In the preparation of the cadmium-mercurous-sulfate cells the procedure described in a previous paper[4] for normal Weston cells was used, special care being taken to exclude mercuric ion. The H-vessels were the same as those used in previous work on non-portable cells.[1] The cadmium sulfate solutions were prepared by dissolving hydrated cadmium sulfate in dil. sulfuric acid solutions of known concentration.[6] These cells differed from Weston cells with slightly acid electrolytes only in that the amalgam con-

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[5] Prepared from recrystallized lead nitrate by the method of Richards and Wadsworth [This Journal, **38**, 223 (1916)].

[6] The acid concentrations in the cadmium sulfate solutions were then calculated from the data of Hulett [*Trans. Am. Electrochem. Soc.*, **14**, 77 (1908)].

tained tin or lead. The preparations of amalgam used and the acidities of the electrolytes are given in Table IIA.

In addition a few amalgam cells were prepared to compare the mixed amalgam anodes with the pure cadmium-amalgam anode. One electrode was of the pure cadmium amalgam and the other of one of the amalgams containing a third metal. The particular mixed amalgam used in each case is shown in Table IIB. The electrolyte was a saturated, slightly acid cadmium sulfate solution, and an excess of cadmium sulfate crystals was added. In the amalgam cells containing cadmium-lead amalgam a solution was used that had been evacuated to remove dissolved oxygen, and the tops of the tubes were filled with nitrogen before they were sealed. In three of the amalgam cells containing cadmium-tin amalgam an evacuated solution was used (Cell 424 being the exception) but air was left in the upper parts of the tubes when they were sealed. No effect due to the presence or absence of air was noticed.

Electromotive-Force Measurements

Electromotive-force measurements were made by means of the standard-cell potentiometer described by Eppley and Gray.[7] Normal Weston cells 1–12, described in previous papers,[4] were used as the standards, an average electromotive force of 1.018049 v. being assigned them. They were kept in an oil thermostat at 25° ± 0.02°. The measuring system was shielded as recommended by White.[8] Results were reproducible within 2 mmv., and the relative values of the cells were probably accurate to this degree. The absolute accuracy of the results depends on the electromotive force assumed for the standards, which was accurate[9] to 0.01%.

The amalgam cells, except as otherwise noted, were measured by connecting them in series with a Weston cell kept in the same thermostat, and measuring the sum of the two. It is to be noted that in the amalgam cells the pure cadmium amalgam was the positive electrode. Thus a decrease in free energy would result from the transfer of cadmium from the amalgam containing the third metal to the pure cadmium amalgam.

The cells were maintained at 25° in an oil thermostat for several months, during which time frequent measurements were made. Some of the cells with cadmium-tin-amalgam anodes had values 20 mmv. to 30 mmv. higher than the normal at the start. This was probably not due to the presence of mercuric ion, as Weston cells made with equal precautions to avoid oxidation of the mercurous sulfate did not show high initial values. On the other hand, a high initial value was shown by one of the amalgam cells with cadmium-tin amalgam as one electrode. It seems probable, therefore, that the cause lay in the amalgam. After two to four months at

[7] Eppley and Gray, *J. Optical Soc. Am.*, **6**, 859 (1922).

[8] White, This Journal, **36**, 2011 (1914).

[9] The standards agreed within 0.001% with some portable normal Weston cells checked by the Bureau of Standards. An accuracy of only 0.01%, however, was certified by the Bureau. On the basis of Weston cells made with a neutral electrolyte and assigned the value 1.01830 v. at 20° the value of the standards was about 0.001% too low.

most the cells became constant. The electromotive forces at 25° after constancy was attained, together with the details of construction, are given in Table II.

TABLE II

CONSTRUCTION AND ELECTROMOTIVE FORCES OF CELLS

A. CADMIUM-MERCUROUS-SULFATE CELLS

Cells	Amalgam	Concn. of acid Moles/liter	E.m.f. at 25° obs. v.	Corr. for acid Mmv.	E.m.f. at 25° (corr.) v.
362–363	Cd-Pb 2	0.011	1.019178	..	1.019178
418–419	Cd-Pb 2	.011	1.019184	..	1.019184
385–386	Cd-Sn 2	.011	1.019001	..	1.019001
387–388	Cd-Sn 2	.034	1.018962	39	1.019001
416–417	Cd-Sn 3	.011	1.019008	..	1.019008
443–444	Cd-Sn 3	.004	1.019021	−12	1.019009
445–446	Cd-Sn 4	.004	1.019018	−12	1.019006

B. AMALGAM CELLS, Cd(M, Hg) | $CdSO_4 \cdot {}^8/_3H_2O$, satd. | Cd(Hg)

Cells	Amalgam	E.m.f., 25° Mmv.	Cells	Amalgam	E.m.f., 25° Mmv.
335–337	Cd-Pb 1	1132	384	Cd-Sn 2	956
376–377	Cd-Sn 1	952	424	Cd-Sn 3	956

Duplicate cells did not differ by more than 5 mmv. In order to show the agreement of the different groups in Table IIA a correction for acidity was made to the electromotive forces of the cells with acid concentrations different from 0.011 mole per liter. The corrections were calculated by the equation of Obata[10] and are given in Col. 5 of the table. The electromotive forces corrected to an acid concentration of 0.011 mole per liter are given in Col. 6. Since these values agree within 10 mmv., for cells with the same kind of amalgam, it is shown that cadmium-mercurous-sulfate cells with cadmium-lead- or cadmium-tin-amalgam anodes are as reproducible as regular Weston cells.[4]

Temperature Coefficients

After equilibrium was assured at 25° the temperature of the thermostat was changed successively to 20°, 15°, 20°, 25°, 30°, 35°, 40°, 35°, 30° and 25°, and measurements were made at each temperature. The cells showed practically no hysteresis. However, the temperature was maintained constant for at least four days after a rise and for at least two weeks after a drop in temperature.[11] The temperatures were measured by means

[10] Obata, *Proc. Math. Phys. Soc. Japan*, **2**, 232 (1920). See also Ref. 4. The effect of acid on the electromotive force of a Weston cell must be due to its effect on the heat of dilution of the electrolyte and on the differential heat of solution of hydrated cadmium sulfate in the electrolyte. The presence of lead or tin in the amalgam should have no effect on the electrolyte, and Obata's equation should hold for these cells as well as for regular Weston cells.

[11] This was necessary because other different cells under investigation at the same time were slow in attaining equilibrium.

of two platinum-resistance thermometers and a mercury thermometer and were probably accurate to about 0.01°. This corresponds to about 0.5 mmv. in the electromotive force of a Weston cell and less in the electromotive force of the cells under investigation. At each temperature two or three electromotive-force measurements were made one or two days apart after the cells had become constant, and the average was taken as the value for that temperature. The two or three results seldom differed from one another by more than 2 mmv. As a sample of the results obtained the values for Cells 385 and 386 are given in Table III. In Table IV the results for all the cells are summarized.

TABLE III

ELECTROMOTIVE FORCES AT DIFFERENT TEMPERATURES

	25°	20°	15°	20°	25°	30°	35°	40°	35°	30°	25°
Cell 385, e.m.f., v.	1.019000	1.019094	1.019158	1.019093	1.019003	1.018891	1.018761	1.018624	1.018767	1.018895	1.019005
Cell 386, e.m.f., v.	1.019002	1.019096	1.019159	1.019094	1.019005	1.018894	1.018765	1.018626	1.018766	1.018896	1.019007

TABLE IV

ELECTROMOTIVE FORCES AT DIFFERENT TEMPERATURES

Cells	15° v.	20° v.	25° v.	30° v.	35° v.	40° v.
A. CADMIUM-MERCUROUS-SULFATE CELLS, CADMIUM-LEAD AMALGAM						
362–363	1.019353	1.019284	1.019180	1.019049	1.018890	1.018712
418–419	1.019363	1.019292	1.019186	1.019054	1.018893	1.018715
B. CADMIUM-MERCUROUS-SULFATE CELLS, CADMIUM-TIN AMALGAM						
385–386	1.019159	1.019094	1.019044	1.018894	1.018765	1.018625
387–388	1.019118	1.019056	1.018963	1.018852	1.018723	1.018583
416–417	1.019165	1.019102	1.019009	1.018899	1.018769	1.018629
C. AMALGAM CELLS						
	Mv.	Mv.	Mv.	Mv.	Mv.	Mv.
335–337	0.906	1.014	1.131	1.261	1.400	1.550
376–377	.708	0.822	0.953	1.101	1.267	1.455
384, 424	.711	.827	.956	1.103	1.270	1.459

It is to be noticed that Cells 385 and 386 each increased 5 mmv. during the measurements, and that the second value at 25° is about the mean of the other two. Similar, but smaller, increases took place in Cells 418, 419, 387 and 417. It is likely that the change was fairly gradual, and that the use of an average value for the electromotive force at 25° will cancel part of the error. A number of normal Weston cells increased 5 mmv. or more under the same conditions, so the change cannot be ascribed to the presence of the third metal in the amalgam.

For comparison of the temperature coefficient of these cells with that of the normal Weston cell the effect of temperature on some Weston cells was determined. Cells 353–356 which were described in a previous paper[12] were used. They were prepared with the same care that was used with the above-mentioned cells, and the electrolyte contained 0.011 mole of sulfuric acid per liter. They showed practically no hysteresis when the temperature was changed, and no permanent increase in electromotive force took place. The average electromotive force at 25° was 1.018046 v., and the differences between the values at other temperatures and this are given in Table V, Col. 2.

If the third metal in the amalgam of the cadmium-mercurous-sulfate cells has no effect other than increasing the activity of the cadmium, the electromotive force of such cells should be equal to the sum of the electromotive forces of a Weston cell and an amalgam cell with the same third metal in one of the amalgams. Thus we have Cd(Sn,Hg) | $CdSO_4.{}^8/_3H_2O$ satd. | Cd(Hg); $E_{25} = 0.000955$ v.; and Cd(Hg) | $CdSO_4.{}^8/_3H_2O$ satd. | $CdSO_4.{}^8/_3H_2O + Hg_2SO_4$ | Hg; $E_{25} = 1.018046$ v.; and as the cathode of the amalgam cell is identical with the anode of the Weston, the two cells can be combined into one, which should have an electromotive force of $1.018046 + 0.000955 = 1.019001$ v. This is in good agreement with the average value 1.019005 v. in Table II. That the same is true at other temperatures is shown in Table V. In Cols. 2 and 3 are shown the differences between the electromotive forces at the given temperatures and the electromotive force at 25° for the Weston cells and the tin amalgam cells, respectively. In Col. 4 the sums of the values in the Cols. 2 and 3 are given. In Col. 5 the differences for the cadmium-mercurous-sulfate cells with cadmium-tin-amalgam anodes are given. These are shown to be equal within the limits of error to the sums of the differences for the amalgam and Weston cells.

TABLE V

$E_t - E_{25}$

1 Temp. °C.	2 Weston Mmv.	3 Amalgam Mmv.	4 2 + 3 Mmv.	5 385, etc. Mmv.	6 4 − 5 Mmv.
15	+397	−245	+152	+155	−3
20	+222	−130	+ 92	+ 92	0
25	0	0	0	0	0
30	−258	+147	−111	−110	−1
35	−556	+314	−242	−240	−2
40	−883	+503	−380	−380	0

A similar comparison could be made in the case of the cells containing cadmium-lead amalgam, but as this would be quite like the above, and as the cadmium-lead-amalgam cells are the less practical, such a comparison is unnecessary.

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[12] Ref. 4, p. 1257.

The relation between the electromotive force of the cell with the cadmium-tin-amalgam anode and the temperature can be expressed by means of the formula[13] $E_t = E_{25} - 0.0000205\,(t - 25) - 0.00000043\,(t - 25)^2 + 0.000000008\,(t - 25)^3$. The change with temperature amounts to only 0.01% of the electromotive force for a 5° change. It is roughly two-fifths that of a Weston cell at the lower temperatures.

Cadmium-Copper and Cadmium-Bismuth Amalgam

Of the other metals which might be added to the amalgam of a Weston cell copper, bismuth and antimony were tried. Antimony did not give reproducible results. Cells were made with cadmium-copper- and cadmium-bismuth-amalgam anodes and pure cadmium-amalgam cathodes. Various amounts of the third metal were added in different cells. The electromotive forces were measured by means of a Leeds and Northrup thermocouple potentiometer, and are probably accurate to about 5 mmv. The relative accuracy should be greater than this. The results are given in Tables VI and VII.

TABLE VI

$Cd\,(Cu, Hg)\mid CdSO_4.{}^8/_3\,H_2O,\ \text{satd.}\mid Cd(Hg)$

Cu, at. %	2	5	10	15	20
E.m.f., 25°, mmv.	5	6	8	5	5
E.m.f., 35°, mmv.	10	12	12	11	12

TABLE VII

$Cu\,(Bi, Hg)\mid CdSO_4.{}^8/_3\,H_2O,\ \text{satd.}\mid Cd(Hg)$

Bi, at. %	2	5	10	15	20
E.m.f., 25°, mmv.	1710	1713	1714	1714	1698
E.m.f., 30°, mmv.	1654	2081	2080	2079	..
E.m.f., 35°, mmv.	1570	2512	2509	2507	2503

Table VI shows that the introduction of copper into a cadmium amalgam has practically no effect on the activity of the cadmium. Copper then, unlike lead or tin, does not appreciably affect the electromotive force of a Weston cell when present as an impurity in the amalgam.

Bismuth, on the other hand, has more of an effect on the activity of the cadmium than either lead or tin. Both the electromotive force and the temperature coefficient of the amalgam cells containing bismuth were considerably larger than those of the amalgam cells containing lead or tin. The constant potential range for amalgams containing a varying amount of bismuth, with cadmium and mercury present in the proportion of 1 to 9 parts by weight, is shown to be from somewhat below 5 atomic per

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[13] This formula was derived by the method of least squares from the values in Cols. 1 and 5 of Table V, the value at 40° being omitted. Electromotive forces calculated by means of it agree with the observed within 2 mmv. between 15° and 35°, and 3 mmv. at 40°.

cent. to nearly 20 atomic per cent. of bismuth. The cell with the amalgam containing 20 atomic per cent. of bismuth was slow in coming to equilibrium. If a cadmium-mercurous-sulfate cell were made with a cadmium-bismuth-amalgam anode it would have a positive temperature coefficient of about the magnitude of the negative temperature coefficient of the cell with the cadmium-tin-amalgam anode. This is shown in Table VIII. The electromotive force would be about 1.020 v. which is a little higher than usual for cells used as standard cells. It is to be noticed, however, that a cell with a cadmium-bismuth-amalgam anode and one with a cadmium-tin-amalgam anode connected in series would form a 2-v. standard with practically no temperature coefficient between 25° and 35°, at least.

Table VIII

Cells with Cadmium-bismuth- and Cadmium-tin-amalgam Anodes

1 Temp. °C.	2 Weston 350–353 v.	3 Amalgam Cd (Bi, Hg) v.	4 Sum 2–3 v.	5 Cd(Sn, Hg) 385 etc. v.	6 2 volt Std. 4–5 v.
25	1.018046	0.001714	1.019760	1.019005	2.038765
30	1.017788	.002080	1.019868	1.018895	2.038763
35	1.017490	.002509	1.019999	1.018765	2.038764

Evolution of Hydrogen from the Amalgam of Cadmium Cells

Experience with Weston cells has shown that the cadmium of the amalgam reacts slowly with the hydrogen ion of a slightly acid cadmium sulfate solution to liberate hydrogen.[14] If given off in sufficient quantity the gas may cause trouble, particularly in portable cells.[15] When the amalgam is sufficiently free from impurities, and the concentration of acid is not more than 0.04 to 0.05 mole per liter, the rate of evolution of hydrogen is negligible. However, it seems to be increased considerably by impurities in the amalgam. The question arises, then, as to what effect the presence of lead, tin or bismuth in the amalgam will have on the rate of evolution of hydrogen. To answer this question, samples of different amalgam preparations were placed in test-tubes and covered with a cadmium sulfate solution containing 1 mole of sulfuric acid per liter. About 4 cm. above the amalgam and under the surface of the solution a cork ring covered on the under side with linen cloth was placed, as in portable Weston cells, to catch the gas evolved. It was found that a cadmium-lead amalgam evolved gas slowly at room temperature, and more rapidly at an elevated temperature. A pure cadmium amalgam and a cadmium-bismuth amalgam evolved gas much more slowly, and a cadmium-tin amalgam evolved gas most slowly of all. Therefore the introduction of tin into the amalgam of an acid Weston cell should not cause any increased trouble due to evolution of hydrogen.

[14] See also Ref. 6, p. 89.

[15] See Vosburgh and Eppley, *J. Optical Soc. Am.*, **9**, 65 (1924).

Conclusions

Of the three cadmium-mercurous-sulfate cells considered above, namely, those in which tin, lead and bismuth, respectively, are present in the amalgam, the tin and bismuth cells are the more practical. They have temperature coefficients nearest zero, and the third metal in the amalgam does not increase the tendency for hydrogen to be given off at the amalgam electrode. The tin cell has an electromotive force about equal to that of many unsaturated Weston cells, and within the range of the standard-cell dials of many potentiometers. The electromotive force of the bismuth cell is above that range. Therefore the tin cell seems to be the most practical of all.

As regards constancy, the tin cell should be as satisfactory as the normal Weston cell. Dilution of the amalgam with mercury due to internal action, or withdrawal of cadmium due to current being taken from the cell, would not affect the constancy if sufficient cadmium and tin were present. Any other possible causes of a change in electromotive force should affect a similarly constructed Weston cell as well as the tin cell. Cells 385–386, the oldest of this kind, have shown no appreciable change in six months.

Summary

By substituting for the cadmium-amalgam electrode of the normal Weston cell a cadmium-tin-amalgam electrode the electromotive force was increased from 1.01805 v. to 1.01901 v. at 25°, and the temperature coefficient was decreased to about two-fifths that of the normal Weston cell. The cell thus formed was as reproducible and as nearly constant over short periods of time as the Weston cell. There is no reason to expect any greater variability over long periods of time.

A similar cell with a cadmium-lead-amalgam electrode had an electromotive force of 1.01918 v. at 25° and a higher temperature coefficient than the cell containing tin. The presence of lead in a cadmium amalgam increased the tendency for the reaction of the cadmium with hydrogen ion of the electrolyte.

In both these cells the electromotive force was equal to the sum of the electromotive forces of the Weston cell and an amalgam cell with one electrode of pure cadmium amalgam and the other a cadmium amalgam containing tin or lead.

Similar amalgam cells with bismuth in one amalgam showed that the substitution of a cadmium-bismuth amalgam for the cadmium amalgam of the Weston cell would give a cell with an electromotive force of 1.01976 v. at 25° and with a positive temperature coefficient equal to the negative temperature coefficient of the similar cell with a cadmium-tin-amalgam electrode.

Amalgam cells in which one electrode contained copper had an electro-

motive force of only about 10 mmv. and showed that the presence of copper in the amalgam of a Weston cell would not appreciably alter the electromotive force or temperature coefficient.

NEWPORT, RHODE ISLAND

[CONTRIBUTION FROM THE INSTITUTE OF THEORETICAL PHYSICS]

THE SOLUBILITIES OF THE PHOSPHATES OF ZIRCONIUM AND HAFNIUM

BY G. HEVESY AND K. KIMURA

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The unusually low solubility of zirconium phosphate in strong mineral acids insures an important role for the phosphate precipitate both in the qualitative and quantitative chemistry of zirconium. The appearance of such a precipitate in a strong acid solution containing hydrogen peroxide is the only simple qualitative reaction for zirconium. In the quantitative analysis[1] of zirconium the phosphate precipitate is no less important, especially when determining small amounts of zirconium occurring in rocks, as first proposed by Hillebrand.[2] All these conclusions have been somewhat modified by the discovery of hafnium. For example, the appearance of a precipitate in a solution of 20% sulfuric acid containing hydrogen peroxide upon the addition of sodium phosphate no longer proves with certainty the presence of zirconium, as hafnium is also precipitated under these conditions. Shortly after the discovery of hafnium, while investigating the fractional precipitation of a mixture of zirconium and hafnium by sodium phosphate from a strong acid solution, Coster and one of the present writers[3] found an accumulation of hafnium in the first precipitate, the method used being that of quantitative X-ray spectroscopy. In contrast to most of the other compounds of the two elements it was necessary to conclude from the above results that a not inappreciable difference exists between the solubilities of the phosphates of zirconium and hafnium. This result also showed that hafnium phosphate and not zirconium phosphate is the less soluble in strong mineral acids. The usefulness of the difference in the solubility of zirconium and hafnium phosphates as a method for the separation of these elements is here pointed out.[4] From the point of view of both the preparative and the analytical

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[1] Bailey [*J. Chem. Soc. Trans.*, 49, 481 (1886)] first used the phosphate in the separation and quantitative determination of zirconium. Compare also Noyes, Bray and Spear, THIS JOURNAL, **30**, 516 (1908). Biltz and Mecklenburg, *Z. angew. Chem.*, **25**, 2110 (1912).

[2] Hillebrand, *U. S. Geol. Survey Bul.*, **176**, 75 (1900).

[3] Hevesy, *Ber.*, **56**, 1503 (1923). Coster, *Chem. News*, **127**, 65 (1923).

[4] De Boer and van Arkel [*Z. anorg. Chem.*, **144**, 196 (1925)] found that zirconium and hafnium phosphates are easily soluble in hydrofluoric acid. From this fact they evolved a method for the separation of zirconium from hafnium.