internal pressure in the hope of making possible the calculation of the absolute deviation from Raoult's law. Additional solubility data are to be obtained, and the internal pressures of metals are to be examined, so as to make possible the treatment of such quantities as the e. m. f. of amalgam concentration cells, and freezing-point diagrams.

Summary.

Various independent methods for calculating internal pressures of liquids are reviewed, and though the values they yield differ considerably, they are seen to be closely parallel. Pending a theoretical critique of the subject tables of relative internal pressures of relatively nonpolar substances are given for the sake of their practical value.

Other substances may be placed with reference to those already given by knowing their densities (as pure liquids or in solution), together with either surface tension; boiling point; the constant *a* in the van der Waals equation (which may be calculated from critical data or from the atomic values given by van Laar); the coefficient of expansion; or this last, together with the compressibility.

The use of these values is discussed in connection with predictions concerning the solubilities of solids, liquids and gases; the distillation of liquid mixtures; molecular weights and "association;" deviations from the mass law; partition coefficients; and the choice of solvent in recrystallization.

BERKELEY, CALIFORNIA.

[JOINT CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF ARIZONA AND NEW HAMPSHIRE COLLEGE.]

THE DETERMINATION OF CERIUM IN THE PRESENCE OF OTHER RARE EARTHS BY PRECIPITATION AS CERIC IODATE.

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Received May 2, 1919.

Cerous iodate and the iodates of the other rare earth elements are soluble in the presence of nitric acid, although very difficultly soluble in water. Scandium iodate is soluble in nitric acid, but less easily so than the rare earth iodates. Thorium, zirconium, and ceric iodates are almost insoluble in nitric acid provided a considerable excess of iodate ion be present.

Meyer and Speter[1] have developed a method for the separation of thorium from the rare earth compounds by precipitation as thorium iodate, from a solution strongly acid with nitric acid. It is evident that for the success of this method for thorium any cerium present must be in the trivalent form.

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[1] *Chem. Ztg.*, 34, 306 (1910).

This paper presents the results of an attempt to apply the iodate precipitation to the determination of cerium, and to its separation from the other members of the rare earth group. The hope of success was based on the fact that cerium alone of all the rare earth elements is oxidized to a higher valence by potassium bromate in nitric acid solution.

A solution of cerous nitrate was prepared from material of established purity, which in concentrated state showed no absorption bands when examined by the spectroscope.

A solution of neodymium nitrate was prepared from material of the highest purity. This solution gave no test for cerium when tested with ammonium hydroxide and hydrogen peroxide—an extremely delicate reaction.

A solution of yttrium earth nitrates was prepared from material consisting mainly of yttria, with small amounts of holmia, erbia, and dysprosia. The absence of even traces of cerium compounds in this solution was proved as in the case of the neodymium solution.

These solutions were standardized by precipitation with oxalic acid, and ignition of oxide to constant weight. The concordance obtained in the standardization of the cerous nitrate solutions by 5 portions was within two parts per thousand.

Potassium iodate was used in the form of an acid solution containing 100 g. of iodate and 333 cc. of conc. nitric acid per liter. In some instances the salt was dissolved in the smallest possible amount of dil. nitric acid, and added in this way to prevent undue increase of volume.

The washing solution contained 8 g. of potassium iodate, and 50 cc. of conc. nitric acid per liter.

Potassium bromate was usually added in solid form.

Preliminary experiments indicated that a considerable excess of iodate was necessary to make the precipitation entirely quantitative, and this accords with the experience of Meyer and Speter with thorium. By using about 10 times the theoretical amount of potassium iodate, and maintaining a rather small volume—$^1/_3$ of which was nitric acid—and then adding a little solid potassium bromate, the precipitation of ceric iodate was so complete that the filtrate gave no reaction for cerium by delicate qualitative tests.

The precipitated ceric iodate was first ignited directly, but it was evident that complete conversion to oxide was not to be obtained in this way, as considerable quantities of iodide resulted. Solution of the ceric iodate in hydrochloric acid, with the addition of a little sulfurous acid, and subsequent precipitation as oxalate was found to be feasible, but owing to the presence of mineral acid, which delays and renders less complete the oxalate precipitation, this method was not so successful as the direct treatment of the iodate precipitate with boiling oxalic acid solution. By this direct treatment the precipitate is dissolved, the ceric iodate is reduced, the liberated iodine is expelled, and the cerium is quantitatively precipitated as cerous oxalate.

To test quantitatively the completeness of the precipitation as iodate, and the suitability of the method of direct conversion to oxalate, two samples of the standard cerous nitrate solution were treated with 40 cc. of the precipitating solution. This represented 10 times the theoretical amount of iodate. About 0.5 g. of solid potassium bromate was added to the clear solution, and the resulting precipitate of ceric iodate was flocculated by gently warming. After standing until fully cold and well settled, the precipitate was filtered on a paper of close texture, and washed with the washing solution already mentioned. The precipitate, together with the filter paper, was transferred to the original beaker, 5 g. of oxalic acid and 25 cc. of water were added, and the mixture heated until the paper was well pulped, and all liberated iodine was expelled. 50 cc. of water was added, and after several hours the cerous oxalate was filtered, and ignited to oxide in the regular way, using a platinum crucible over the blast lamp to insure absence of moisture and carbon dioxide in the material to be weighed. The results were ideal, as the following figures, expressed for convenience in grams of CeO_2, will show:

CeO_2: Taken, 0.0721. Found: 0.07 1, 0.0721.

The possibility of compensating errors naturally presents itself, and it was regarded as not impossible that a slight solubility of ceric iodate might be compensated by occlusion of potassium salt with the cerous oxalate. The ignited oxides were combined, and repeatedly extracted with boiling water. The residue obtained by evaporating the solution and gently igniting, weighed 0.0003 g., showing that the amount of potassium salt occluded certainly did not exceed 0.00015 g. in each determination. Qualitative tests of the filtrates with comparative color blanks, prepared by taking 0.0002 g. of ceric oxide with ammonium hydroxide and hydrogen peroxide, showed that any cerium present was certainly less than the equivalent of 0.0002 g. of ceric oxide. Thus, if any compensation exists the amounts involved are minute.

The separation of cerium from neodymium was next attempted. By a single precipitation it was found impossible to get a complete separation of cerium and neodymium, and the amounts of cerium found were decidedly too high. By redissolving the ceric iodate, suspended in boiling water, by the gradual addition of nitric acid, as was done with thorium by Meyer and Speter,[1] and then reprecipitating by the addition of more potassium bromate and a very large excess of potassium iodate, the coprecipitated neodymium compound can be entirely eliminated. A series

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[1] *Loc. cit.*

of determinations in the presence of neodymium by the suggested method—working details will be given later—gave promising results.

Nd_2O_3 present.	CeO_2 taken.	Found.		
0.0475	0.0721	0.0716	0.0721	0.0723
0.1426	0.0721	0.0704	0.0713	
0.2852	0.0721	0.0708	0.0689*	

The results in the presence of the smaller amount of neodymium were satisfactory. With higher percentages of neodymium the results were too low. This was instructive, for in the last 4 determinations of this series it was feared that the results would be too high, and therefore the washing was somewhat extravagantly carried out, and more nitric acid was used in redissolving the first precipitate than was absolutely necessary. The figure marked with an asterisk may have been the result of some manipulative accident, but since none was definitely noted the result is included for the sake of unbiased completeness.

It is evident that the solubility of the ceric iodate is increased by the presence of an unduly large excess of nitric acid, and is decreased by a large excess of iodate ion; so in subsequent experiments the nitric acid was added cautiously until the precipitate just dissolved, and then 15 times the theoretical amount of potassium iodate was added. The washing of the iodate precipitate is best carried out by bringing the precipitate on to the filter paper, allowing it to drain, then rinsing it back into the beaker with the washing solution, and again bringing it upon the filter. The ceric iodate is voluminous, and packs tightly upon the paper. The decantation method of washing is less advisable because if requires a larger volume of wash liquid, in which the precipitate is not absolutely insoluble.

The detailed method as finally adopted may now be given, and then a table of results, together with a discussion of special cases.

To the solution containing the rare earth nitrates (any thorium having been previously removed), is added enough conc. nitric acid so that the latter shall make up $^1/_8$ of the solution. The total solution at this point should not greatly exceed 75 cc. It is also better that the amount of ceria present should not exceed about 0.15 g., since the precipitate is bulky, and the washing is rendered more difficult by the very large precipitate. About 0.5 g., very roughly estimated, of solid potassium bromate is added, and when it has dissolved, an amount of potassium iodate which is 10 to 15 times that theoretically required for the estimated ceria present is added in form of the nitric acid solution already given. This reagent is to be slowly added with constant stirring. The precipitate of ceric iodate is allowed to settle in the cold until the supernatant liquid is practically clear, and it is then filtered on a paper of close texture, such as Whatman No. 42. The precipitate is brought upon the paper pretty completely, and the beaker rinsed just once with a small amount of the washing solution already described. After draining, but not standing longer than is necessary, the precipitate is carefully rinsed from the paper back into the beaker with more of the washing solution. Any clots should be broken up with a stirring rod, and the mixture well churned. The precipitate is again brought on the same filter in the same way, and allowed to drain. It is then rinsed back into the beaker with hot water, heated to boiling, with constant stirring, and conc. nitric acid is dropped in until the precipitate is completely dissolved. Any unnecessary excess of nitric acid is to be avoided. For about 0.1 g. of ceric oxide from 20 to 25 cc. of acid will usually be required. To this solution about 0.25 g. of potassium bromate is added, and about the same amount of potassium iodate as was used in the first precipitation. This may be used in the form of the regular precipitating reagent, unless the use of this solution would make the volume unduly large, in which case the solid potassium iodate can be dissolved by heating in a small volume of 1 : 2 nitric acid, and thus added. The precipitate is allowed to settle as before, and the perfectly cold mixture is then filtered through the original paper, given one very small washing with the nitric acid-iodate washing solution, rinsed back into the beaker once more, well churned, and finally brought on to the paper and washed with 3 small portions of the washing solution. Every trace of the ceric iodate need not be removed from the beaker. The paper with the precipitate is now lifted from the funnel and dropped into the original beaker, taking care to remove any trace of ceric iodate adhering to the glass funnel, either with the upper edge of the filter paper or with a small fragment of another "ashless" filter paper. About 5-8 g. of oxalic acid crystals are now added, and then 50 cc. of water. The covered beaker is heated gently, and its contents are finally boiled until iodine vapors are no longer given off, and all sublimed iodine is vaporized from the cover glass and from the upper edges of the beaker. The cover glass and sides of the beaker are rinsed down with water, and after having stood for several hours the cerous oxalate, mixed with the pulp of the first paper, is filtered, washed with cold water, and ignited in a platinum crucible over the blast lamp. The weight of ceric oxide is obtained by deducting the weight of the two paper ashes.

In the following table are given the results of determinations carried out in the manner just outlined. Any slight deviations from the directions, and interpretations of the effects of these deviations, will be noted later.

In Nos. 1 and 2 the results are somewhat low, and this was attributed to an attempt to economize by using only 4 to 5 times the theoretical amount of potassium iodate, and working in a volume of nearly 200 cc.

In Nos. 15 to 18 the precipitates were rinsed off the paper with hot water, and allowed to stand overnight before attempting to dissolve in nitric acid. It was found impossible to dissolve completely any but No. 17 the next morning, and in all the others a certain amount of the precipitate remained as a sediment. The experiments were repeated in Nos. 19 to 22, under exactly the same conditions, but taking care to dissolve completely the ceric iodate precipitate by the prompt application of nitric acid. The results show that it is necessary to dissolve completely the first precipitate of ceric iodate to free it from admixed rare earth iodates.

No.	Nd_2O_3 present. G.	Y_2O_3, etc., present. G.	CeO_2 taken. G.	CeO_2 found. G.
1	0.2852	..	0.3605	0.3577
2	0.2852	..	0.3605	0.3575
3	..	..	0.0721	0.0719
4	..	..	0.0721	0.0717
5	..	..	0.0721	0.0718
6	..	..	0.0721	0.0722
7	0.1426	..	0.0721	0.0721
8	0.1426	..	0.0721	0.0723
9	0.4278	..	0.0721	0.0722
10	0.4278	..	0.0721	0.0717
11	0.0475	0.05	0.0721	0.0727
12	0.0475	0.05	0.0721	0.0722
13	0.1426	0.10	0.0721	0.0722
14	0.1426	0.10	0.0721	0.0723
15	0.0475	0.10	0.1442	0.1459
16	0.0475	0.10	0.1442	0.1460
17	0.1426	0.20	0.1442	0.1449
18	0.1426	0.20	0.1442	0.1468
19	0.0475	0.10	0.1442	0.1453
20	0.0475	0.10	0.1442	0.1449
21	0.1426	0.20	0.1442	0.1437
22	0.1426	0.20	0.1442	0.1444
23	0.0950	0.05	0.1442	0.1444

The filtrates from the iodate precipitations will usually show a faint suggestion of opalescence after standing a few days. The amount of ceric oxide represented in this is negligible, as the ceric iodate precipitate is voluminous, and even if pure ceric iodate it would contain only about $^1/_5$ of its weight of ceric oxide.

Summary.

A method for the determination of cerium by oxidation with potassium bromate, and precipitation with potassium iodate, followed by direct conversion of the ceric iodate to cerous oxalate has been developed.

This method has been found accurate for determining cerium in the presence of even large amounts of rare earth salts.

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