Discussion and Summary

These results may be best summarized by a consideration of the behavior of Expt. 5. In this experiment a capillary of 5.33μ radius was exposed to a toluene solution whose vapor pressure was lowered to 0.082 mm. by the addition of a solute. It was found that liquid toluene condensed in this capillary, which would indicate that the vapor pressure of the toluene in the capillary was less than (21.60 − 0.082). The classical theory of capillarity, however, tells us that the vapor pressure lowering of toluene at 20° in a tube of this radius should be only 0.009 mm. of mercury. It is therefore obvious that either our experimental work is in error or the classical theory as applied to vapor pressure in capillaries is not correct.

We believe the latter to be true and are convinced that this work has been done with sufficient care to warrant such a conclusion. At this point it may be well to add that such a view does not necessarily conflict with the thermodynamic treatment of this question. Thermodynamically the problem is simply the action of a negative pressure upon the vapor pressure of a liquid. This question is rigorously handled by the well-known relationship of Gibbs. What we have shown here is that the negative pressure in the case of small capillaries may be greater than has been assumed to be the case.

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[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DEPARTMENT, THE OHIO STATE UNIVERSITY]

ZIRCONIUM. II. DETECTION OF POTASSIUM BY ZIRCONIUM SULFATE IN THE PRESENCE OF AMMONIUM IONS[1]

BY RUFUS D. REED AND JAMES R. WITHROW

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We have shown that zirconium sulfate can be used to detect potassium and that the test can be applied in the presence of sodium.[2] Ammonium ions must be eliminated prior to testing for potassium with other reagents such as sodium cobaltic nitrite, chloroplatinic acid or perchloric acid. The sensitivity of zirconium sulfate for potassium in the presence of ammonium ions was therefore investigated.

The results indicated that zirconium sulfate solution will detect 0.48 mg. of potassium in 2 cc. of reaction mixture in the presence of large amounts of ammonium sulfate. This was practically the same sensitiveness of this reagent for potassium in the absence of ammonium as in the previous work.

[1] In memory of Ira Remsen.

[2] Reed and Withrow, THIS JOURNAL, 50, 1515 (1928).

Concerning the action of alkali sulfates on zirconium sulfate, Fresenius[3] stated: "A concentrated solution of potassium sulfate rapidly produces a white precipitate of potassium zirconium sulfate. . . . Sodium sulfate and ammonium sulfate do not produce a precipitate." No reference was found indicating the effect of the presence of ammonium sulfate on the reaction between zirconium sulfate and potassium sulfate.

Experimental

In order to determine the sensitiveness of zirconium sulfate for potassium in the presence of ammonium it was necessary to prepare the following solutions.

Zirconium Sulfate Solution.—Impure zirconium sulfate was dissolved in water and the zirconium precipitated by a slight excess of sodium hydroxide. The hydroxide was washed by decantation and filtered and washed until 10 cc. of the filtrate evaporated to dryness and taken up with 2 cc. of water gave no test with sodium cobaltic nitrite. The moist zirconium hydroxide was dissolved in concentrated sulfuric acid. The somewhat dilute solution was concentrated overnight at 60° and allowed to stand for several days to reach constant composition. This solution was found to contain 0.1131 g. of zirconium sulfate and 0.0363 g. more sulfate per cc. due to excess sulfuric acid.

Potassium Sulfate Solution.—This was prepared from C. P. salt and water. Its strength was determined by evaporating a portion to dryness and igniting.

Ammonium Sulfate Solution.—The C. P. salt was dissolved in water. The solution was analyzed for ammonium by the distillation method.[4]

The solutions tested for potassium were prepared by mixing known amounts of the potassium and ammonium sulfate solutions.

Procedure

The procedure was exactly the same as given under the general procedure in the work previously published.[5] The results appear in the table.

TABLE I

SENSITIVENESS OF ZIRCONIUM SULFATE FOR POTASSIUM IN THE PRESENCE OF AMMONIUM IONS

Total volume 2 cc. $Zr(SO_4)_2$, 0.1131 g. per test

Expt.	K, g. per sample	NH_4, g. per sample	Results (time for appearance of a precipitate)
1	0.0000	0.05985	Clear and no ppt. in 5.5 hours at 0°
2	.0000	.01197	Clear and no ppt. in 5.5 hours at 0°
3	.0000	.00599	Clear and no ppt. in 3.5 hours at 0°. Tube broke
4	.02378	.02990	Ppt. in 10 min. at room temperature
5	.0158	.03990	Cloudy in 1 hour at room temp.; ppt. in 10 min. at 0°
6	.0048	.0539	Ppt. in 1 hour at 0°
7	.0024	.0569	Cloudy in 1 hour; ppt. in 1.5 hours at 0°
8	.00095	.0586	Cloudy in 1.5 hours; ppt. in 2 hours at 0°
9	.00058	.0591	Very slight ppt. in 2 hours; increased in 2.5 hours at 0°
10	.00048	.0593	Very slight ppt. in 2.5 hours; increased in 5.5 hours at 0°

[3] Fresenius, "Qualitative Chemical Analysis," C. A. Mitchell's translation of 17th edition, John Wiley and Sons, New York, **1921**, p. 182.

[4] Treadwell and Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, 6th ed., **1924**, pp. 72–73.

[5] Ref. 1, p. 1516.

Discussion

The deposits in Expts. 9 and 10 containing 0.58 mg. and 0.48 mg. of potassium were very small but could be detected by comparison with a blank.

The results indicated that zirconium sulfate will detect 0.48 mg. or more of potassium in 2 cc. of reaction mixture in the presence of large amounts of ammonium ions. This is a distinct advantage over other tests, in all of which ammonium interferes. Bray[6] found "With 1 mg. of NH_4 a precipitate formed in about 10 minutes (with sodium cobaltic nitrite); with 0.5 mg. on standing several hours." Ammonium salts also give precipitates with tartaric acid, perchloric acid and chloroplatinic acid. With perchloric acid or chloroplatinic acid the amount of potassium must be large or alcohol must be added. Zirconium sulfate will detect potassium when present to the extent mentioned in the presence or absence of ammonium ions and no alcohol is needed.

Summary

The sensitiveness of zirconium sulfate for potassium in the presence of ammonium ions was found to be 0.48 mg. or more of potassium per 2 cc. of reaction mixture. This is practically the same sensitiveness of zirconium sulfate for potassium when no other metal ions were present. This detection in the presence of ammonium is a distinct advantage over the other tests for potassium.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE THICKNESS OF ADSORBED VAPOR FILMS. II[1,2]

BY G. H. LATHAM

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There are now three outstanding theories of adsorption, namely, the unimolecular theory of Langmuir, the multimolecular theory of Polanyi and the capillary theory of Zsigmondy. Experimental data in support of each of these theories have been submitted by different investigators. In this paper we are particularly interested in the work of McHaffie and Lenher[3] and in that of Frazer, Patrick and Smith.[4] Both of these investi-

[6] Bray, THIS JOURNAL, **31**, 633 (1909).

[1] In memory of Ira Remsen.

[2] This paper has been taken from the dissertation submitted by the author to the Board of University Studies of The Johns Hopkins University as part of the requirement for the degree of Doctor of Philosophy.

[3] McHaffie and Lenher, *J. Chem. Soc.*, **127**, 1559 (1925); 1785 (1926).

[4] Frazer, Patrick and Smith, *J. Phys. Chem.*, **31**, 897 (1927).