

over a wide range of conditions. At low concentrations of sulfuric acid two reactions take place simultaneously, namely, (1) $S_{(\lambda\mu)}^* + 2H_2SO_4(aq) = 2H_2O(l) + 3SO_2(g)$ and (2) $4S_{(\lambda\mu)} + 4H_2O(l) = 3H_2S(g) + H_2SO_4(aq)$. These reactions are both reversible. In the acids of higher mol fraction than 0.05, and at temperatures up to the critical point of water, Reaction 2 becomes negligible. Equilibrium pressures for Reaction 1 have been measured for acids of mol fraction ranging from 0.041 to 0.363, and at temperatures ranging from 527°A to 613°A, using a new type of apparatus. The vapor pressures of various concentrations of sulfuric acid have been measured with the same apparatus. Using these and other existent data, the free energy for the reaction $S_{(\lambda)} + 2H_2SO_4(M) = 2H_2O(g) + 3SO_2(g)$ has been calculated to be +31500 cal. at 25° and standard conditions. From these and other data the free energy of both aqueous sulfuric acid and sulfur dioxide may be calculated.

A new type of apparatus for measuring equilibrium or vapor pressures of corrosive liquids up to high pressures and temperatures has been described.

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QUANTITATIVE ANALYSIS BY CENTRIFUGE.

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Chemical investigators in the domains of biology, medicine and soil analysis have ever sought for rapid methods of experiment and analysis. In these sciences experimental deviations are so great that one must greatly increase the number of samples for analysis in order to get reliable results.¹ Speed rather than great precision is needed in such cases; one needs methods less precise than those which he would employ where the conditions more constant. Accordingly we have in text-books many rapid methods; for example, the colorimetric, the nephelometric, etc.

Curiously enough very little use is made, in such rough quantitative researches, of direct readings of the volume of the precipitate, although this is a very common method in the so-called mechanical analysis of soils. This method attains its greatest accuracy when the columns of precipitate are compressed by means of centrifugal force. In the dairy and in clinical technique the centrifuge has been much used, but it is rarely used for quantitative work in the inorganic laboratory. Nevertheless, the centrifugal method can be used with considerable accuracy. For example Hedin² succeeded in determining very satisfactorily the

¹ For example Waynicke points out that from an area as small as half an acre, one must collect over 80 samples for analysis, in order to get a moderately accurate result. (*Univ. Cal. Publ. Agr. Sci.*, 3, 1918.)

² Hedin, *Skand. Arch. f. Physiol.*, 5, (1895).

osmotic pressure of different solutions by means of plasmolyzing blood corpuscles and then reading off the compressed columns in capillary stems. The attempts which have been made to use the centrifugal method for more usual analytical purposes have never been crowned with great success, probably because of an arbitrarily chosen time for centrifuging and because the tubes employed have not been suitable for the purpose. The first experimenter who really succeeded in using this method for quantitative work was Hamburger³ who determined potassium as chloroplatinate. Since then, apparently no successful attempts to follow up this method for other purposes have been made, at least none have been found in the literature, until some years ago, however, the author succeeded in adapting Büllmann's method⁴ for potassium determinations in this manner.

The present paper shows that the centrifugal method may also be used for determining calcium and magnesium, and phosphoric, sulfuric and nitric acids. Satisfactory results in all these cases have been obtained, as will be seen. Possibly the method could also be used for other precipitates heavier than water. The details of procedure are as follows. The precipitate obtained in the usual way is shaken with the mother solution and then transferred to tubes 2.5 cm. in diameter at the top and provided with a steep funnel below leading to a capillary tube about 4 cm. long (and for compact precipitates only 1 mm. in bore).⁵ The precipitate is allowed to settle and by means of gentle shaking is, for the most part, caused to settle in the capillary stem. Many of these tubes are then centrifuged together until the precipitate in each has attained a constant height (which is usually the case in less than half an hour). The column is read with a mirror scale in order to avoid parallax in reading. These columns are reduced to the weight standard by comparison with a precipitate similarly obtained from a known weight of the substance similarly treated.

The following tables give results with different salts. In every table the first line shows the amount of the ion added expressed in milligrams. In the second line is given, for each case, the relative column height, and in the third line, that calculated under the assumption of direct proportionality. The reading limit mentioned at the right indicates the smallest amount of precipitate one is able to observe, assuming ability to read to within 0.1 mm. The agreement between the calculated and observed values is obviously very close. The results with nitric acid are especially interesting. The precipitate obtained with Busch's⁶ nitron is bulky and flocculent; wide tubes had to be used and the usual

³ Hamburger, see Ch. W. Purdy, "Practical Urine Analysis," 1895.

⁴ Büllmann, *Medd. vetenskopsakad. Nobelinst.*, 1920.

⁵ The tubes were calibrated by weighing with mercury.

⁶ Busch, *Ber.*, 38, 861 (1905).

preparation tubes were taken. Nevertheless, in spite of the rather rough instruments, the results are exceedingly good. Of course one must make sure in all cases that the tubes compared have identical diameters.

		SULFATE							
		H ₂ SO ₄ precipitated with BaCl ₂						Reading limit	
SO ₄ , mg.	15	7.5	3.75	1.65	0.98	0.33			
Vol. obs.	14.8	7.4	3.8	1.7	1.0	0.3	0.04		
Vol. calc.	15	7.5	3.8	1.7	1.0	0.3			

		NITRATE								
		HNO ₃ precipitated with nitron								
NO ₃ , mg.	8	4	4	2.64	2	1.3	1.2	0.8	0.4	0.03
Vol. obs.	10	5	5	3	2.5	1.5	1.5	1	0.7	
Vol. calc.	10	5	5	3.2	2.5	1.6	1.5	1	0.5	

		CALCIUM							
		Ca(OH) ₂ acidified and precipitated as oxalate							
Ca, mg.	1.36	0.68	0.27	0.27	0.14	0.07	0.0045		
Vol. obs.	16.0	8.0	3.2	3.2	1.6	0.8			
Vol. calc.	16.0	8.0	3.2	3.2	1.7	0.8			

		ORTHOPHOSPHATE							
		Na ₂ HPO ₄ precipitated with ammonium molybdate							
PO ₄ , mg.	0.23	0.12	0.6	0.3	0.15	0.006			
Vol. obs.	21.7	11.0	5.5	2.6	1.2				
Vol. calc.	22.0	11.0	5.5	2.7	1.3				

		MAGNESIUM							
		MgCl ₂ precipitated with NaNH ₄ HPO ₄							
Mg, mg.	3.85	2.31	1.54	0.38	0.19	0.09	0.007		
Vol. obs.	20.5	11.9	8.0	1.8	0.9	0.5			
Vol. calc.	20.0	12.0	8.0	2.0	1.0	0.5			

A more complete study of this problem, involving a larger number of precipitates, should be of great advantage for analytical chemistry, for the method is both time-saving and simple.

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