

diameter, a , is found to be 3.22×10^{-8} , and the constant $A = a \sqrt{4\pi\epsilon^2 4N/D_0 kT} 1000$, is 0.747 at 25° . The other constants of equation (2) were evaluated by the same procedure as in part 2. The values thus obtained are: $B = 0.0864$ and $B' = 0.0503, 0.0698$ and 0.0875 for potassium, sodium and lithium chlorides, respectively.

In Fig. 2 the activity coefficients of pure acid, determined by the various methods, are plotted against molality.

Summary

1. The electromotive force of hydrochloric acid-alkali chloride cells at constant total molality has been measured.

2. Various methods of calculating the activity coefficients of hydrochloric acid in alkali chloride mixtures have been used and a comparison of the results has been given.

3. It has been shown that the linear variation of $\log \gamma$ with concentration is valid at the high concentrations used.

4. An approximate simplified method for the determination of the constants of the Hückel equation has been used with satisfactory results.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

THE ACCURATE DETERMINATION OF CYANIDE BY DISTILLATION FROM SULFURIC ACID SOLUTION

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In a certain investigation in this Laboratory it became necessary to determine accurately alkali cyanide in the presence of relatively large amounts of chloride, bromide, nitrate or sulfate by distillation from moderately strong sulfuric acid solution. A large number of methods in use for industrial, agricultural and biological analysis involve the isolation of cyanide by distillation from sulfuric acid solution. In such cases, however, the highest degree of accuracy is rarely demanded. Roe¹ discourages the practice of distilling from strong acid solution, stating that (1) at higher temperatures there is a loss of hydrocyanic acid due to hydrolysis to ammonium formate; (2) the hydrocyanic acid is evolved too rapidly to be quantitatively absorbed in the alkaline absorbing solution.

No contradiction to Roe's statement, or data on either the maximum obtainable accuracy or the possible interference of large amounts of salts could be found, hence this investigation was carried out.

Materials and Apparatus.—All salts used in this work were reagent grade. Arbitrary strength (approx. 0.19 *N*) solutions of potassium cyanide

¹ J. H. Roe, *THIS JOURNAL*, **45**, 1878-1883 (1923).

were standardized daily against 0.2000 *N* silver nitrate, by the well-known Liebig-Denigès method as modified by Kolthoff.²

In order to duplicate conditions, the volume prior to titration was adjusted to 450 cc., both in standardization and in the analysis of the distillates. Conductivity water was used throughout. Distillation was carried out in a 500-cc. Pyrex distilling flask which was fitted with a two-holed rubber stopper carrying a thermometer and a glass tube drawn to a fine capillary extending to the bottom of the flask. A very gentle flow of air through the latter prevented any bumping or back suction during distillation. The hydrocyanic acid was absorbed in a relatively simple absorption apparatus. A wide-mouthed bottle, 5.5 cm. in diameter and 20 cm. in height, was fitted with a two-holed rubber stopper carrying a small (2.5 cm. diameter) inverted, long-stem funnel, so adjusted that the mouth of the funnel was fixed about 2 cm. from the bottom of the bottle. An auxiliary absorption tube consisting of a U-shaped three-bulb calcium chloride tube (Péligot type) was fitted to the other stopper hole. The funnel stem was fitted to a 16-cm. all-glass condenser, which was in turn connected to the side tube of the distilling flask. The rubber connections were of heavy-walled suction tubing, tightly wrapped with adhesive tape to ensure a very snug fit.

The alkaline absorption solution was prepared by diluting 15 cc. of 6 *N* sodium hydroxide to approximately 200 cc. A 100-cc. pressure operated pipet (with a highly constricted tip to assure uniform delivery) was used in measuring the cyanide portions.

Procedure.—The cyanide solution was pipetted directly into the distilling flask. The absorption apparatus and condenser were then connected to the flask and weighed amounts of the salts introduced, followed by water and 6 *N* sulfuric acid in rapid succession. (Total volume about 250 cc.) The stopper was immediately inserted and the flask thoroughly agitated until the salt had dissolved. The air flow through the ebullition tube was then started and the solution distilled at a moderate rate for a period of thirteen to fifteen minutes, after boiling had commenced. (From 60 to 80 cc. of solution distilled over during this time.)

Discussion

Series (A) and (B) show that very accurate and consistent results are obtained when the rate of heating up to the distillation temperature is rapid (five minutes). When heated about one-half as rapidly (Series (C)), the results in general are from 0.1 to 0.3% low. The conditions under which low results were obtained (Series (D)) would obviously be unwarranted in an actual determination by this method. Yet the results

² Kolthoff and Furman, "Volumetric Analysis (Practical Volumetric Analysis)," John Wiley and Sons, Inc., New York, 1929, Vol. II, p. 239.

RESULTS OBTAINED UNDER VARIOUS CONDITIONS					
Salts added, g.	Error, %	Salts added, g.	Error, %	Salts added, g.	Error, %
(Series A)		(Series B)		8 NaCl	-0.30
6 NaCl	-0.02	6 NaCl	-0.11	8 NaCl	- .04
6 NaCl	.00	8 NaCl	- .02	8 NH ₄ Cl	- .19
6 NH ₄ Cl	- .02	8 NH ₄ Cl	+ .02	8 (NH ₄) ₂ SO ₄	- .08
6 KBr	.00	8 KBr	+ .02	8 (NH ₄) ₂ SO ₄	- .17
6 KBr	- .02	8 KBr	- .08	(Series D)	
10 (NH ₄) ₂ SO ₄	- .06	8 (NH ₄) ₂ SO ₄	.00	9 KBr	- .42
10 (NH ₄) ₂ SO ₄	- .15	8 NH ₄ NO ₃	- .02	8 NaCl	- .59
7 NH ₄ NO ₃	- .13	8 NH ₄ NO ₃	+ .02	8 NaCl	- .51
7 NH ₄ NO ₃	.00	(Series C)		8 (NH ₄) ₂ SO ₄	- .51
		8 NH ₄ NO ₃	- .08		
		8 NH ₄ NO ₃	- .17		

Series (A) and (B): 0.35 and 0.60 *N* excess H₂SO₄, respectively, heated to boiling in about five minutes. Series (C): 0.60 *N* excess H₂SO₄, heated to boiling in about eleven minutes. Series (D): 0.60 *N* excess H₂SO₄, heated very slowly to 95° and maintained at this temperature thirteen to fifteen minutes before distilling.

indicate that the loss due to hydrolysis should be negligible when the hydrocyanic acid is removed from solution in relatively much shorter time, as was done in Series (A) and (B).

A number of determinations were made in which the auxiliary absorbing tube was left off. In this case the inverted funnel was merely placed as usual in the open bottle. Losses ranging from 0.1 to 0.3% resulted.

Summary

1. Alkali cyanide in presence of large amounts of chloride, bromide, nitrate, or sulfate, may be determined accurately by distillation from moderately strong sulfuric acid solution, without loss due to hydrolysis or mechanical loss of hydrocyanic acid vapor.

2. The description of materials and apparatus used, procedure, and tabulated data, showing the effect of salts and of physical conditions, have been included.

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