

## NOTES

**Historical Note on the Equilibrium between Methanol and its Decomposition Products.**—In a recent paper<sup>1</sup> Messrs. B. S. Lacy, R. G. Dunning and H. H. Storch state that my determinations of the equilibrium constants of the reactions



and



were carried out later than 1922.

May I be allowed to state that the work contained in my paper<sup>2</sup> published in 1926 on Reaction 1 was carried out during the spring of 1917 by myself, and the work on Reaction 2 during the spring of 1918 by Mr. Arne Olsen and myself.

I may perhaps add that my equations are expressions of the concentration constants and thus may be easily transformed into equations for the pressure constants without recalculation of the single experimental values and finally that Lacy and co-workers have included in their Fig. 1 my experiments Nos. 16 and 17, which as stated in my paper, ought not to be included on account of obvious loss in activity of the catalyst.

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RECEIVED APRIL 23, 1930  
PUBLISHED AUGUST 5, 1930

**A Note on the Preparation of Silver-Free Copper.**—The preparation of standard solutions for the estimation of small amounts of silver in copper spectrographically requires silver-free copper. A number of commercial samples of copper were tested and all contained silver. Even one obtained from England which the vendors stated was apparently silver-free gave a spectrogram which showed distinct silver lines. It was therefore deemed advisable to experiment on the separation of the last spectrographic traces of silver from copper. The following procedure successfully accomplished this result.

Commercial copper sulfate was recrystallized three times and a spectrogram made from it showed only a small amount of silver (about 0.004% was found later). Four hundred grams of this recrystallized sulfate was made up to two liters with 5% nitric acid, the solution divided into eleven portions and electrolyzed for one hour between platinum electrodes with a current of 0.05 ampere at seven volts. The electrodes were removed from the solution, washed, and the small deposit was dissolved in nitric acid. The clean electrodes were put back into the solutions and the electrolysis con-

<sup>1</sup> Lacy, Dunning and Storch, *THIS JOURNAL*, **52**, 926 (1930).

<sup>2</sup> Christiansen, *J. Chem. Soc.*, 413 (1926).

tinued for sixteen hours, after which the deposits were dissolved as before. In this manner seven fractions were made. Each of these fractions was evaporated to dryness and ignited to convert the copper nitrate to oxide. The weight of copper oxide obtained in each of the fractions together with the current strength and the duration of electrolysis is shown in the table. The estimated silver content of the copper in each fraction is shown in the last column. The residue was obtained by evaporating the whole two liters of solution from which the copper had been deposited to dryness and igniting.

TABLE I  
EXPERIMENTAL DATA

No.	CuO, g.	Time, hours	Current, amp.	Silver, %
1	1.5	1	0.05	0.125
2	8	16	.05	.008
3	4	8	.05	.0005
4	9	17	.05	.0002
5	12	23	.05	none
6	66	24	.2	none
7	24	9	.2	none
Residue	1.5	..	..	.015

Copper oxide from fraction six was reduced in a silica tube by means of hydrogen, the copper was melted in a silica crucible in an induction furnace and drawn into a bar from which electrodes were cut. An arc spectrogram of these copper electrodes showed no trace of the silver line at 3281. Copper itself gives a faint line which might be confused with the silver line at 3383. The most persistent silver line is at 3281. The presence of as little as 0.0002% silver in copper can be detected by means of this line when the solution method of comparison is employed.

The silver was estimated by comparing the intensity of this line in a spectrogram given by a measured amount of the unknown with its intensity in spectrograms of measured amounts of solutions of known silver content. The amount used in each case was one-tenth of a cubic centimeter of solution containing 10% of copper. This was placed in a hollowed graphite electrode, dried in an oven at 110° and then arced for three minutes using a current of ten amperes at 50 volts. This is the well-known method described by C. C. Nitchie [“Quantitative Analysis with the Spectrograph,” *Ind. Eng. Chem., Anal. Ed.*, 1, 1 (1929)].

CONTRIBUTION FROM THE  
MICHIGAN COLLEGE OF MINING AND TECHNOLOGY  
HOUGHTON, MICHIGAN  
RECEIVED MAY 19, 1930  
PUBLISHED AUGUST 5, 1930

BART PARK