Summary.

(1) It has been shown that the supposed finite contact-angle (reputed to be the weakest point in the capillary rise method), does not exist with the liquids studied if the glass be properly cleaned and if evaporation of the liquid be prevented.

(2) The correction for the capillary rise in the wide tube calculated by Rayleigh and Laplace has been experimentally verified.

(3) A preliminary experimental curve for the capillary rise in tubes that are not wide enough to come under these mathematical equations has been obtained. This experimental curve fits smoothly between the theoretical curve for very wide tubes and the theoretical curve for very narrow tubes.

It has been shown that the method of calibrating tubes by weighing a mercury thread is not affected to an important extent by a film of air between the mercury and the glass, except perhaps in very fine capillaries. The disturbing effect of ellipticity in the cross-section of the capillary is indicated.

The difference between capillary rise in air and *in vacuo* has been determined with 6 liquids. In most cases the effect on the surface tension is less than 0.5%.

The surface tensions of water, 72.73; benzene, 28.88; toluene, 28.43; ether, 16.96; chloroform, 27.14; carbon tetrachloride, 26.77; and dimethyl aniline, 36.56, have been measured in the presence of air. Removal of air caused increases in the surface tension as follows: water, $+0.02$; benzene, $+0.14$; chloroform, $+0.10$; carbon tetrachloride, $+0.18$; ether, $+0.05$; dimethyl aniline, $+0.10$.

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THE DETERMINATION OF IRON BY THE CUPFERRON METHOD.[1]

BY G. E. F. LUNDELL.

I. Introduction.

Archibald and Fulton in a recent article[2] on the determination of iron and the separation of manganese from iron by cupferron, have made the assertions that "the cupferron precipitate of iron is slightly soluble in the acid solution in which it is precipitated" (0.001 g. of ferric oxide when 0.1373 g. of ferric oxide was precipitated in 166 cc. of solution containing 5 g. of ammonium chloride, 4 g. of cupferron, and 15 cc. of conc. hydro-

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[1] Published by permission of the Director of the Bureau of Standards.

[2] Archibald and Fulton, *Proc. trans. Roy. Soc. Can.*, **13**, III, 243–53 (1919); *J. Chem. Soc.*, **118**, 512 (1920); *C. A.*, **14**, 2454 (1920).

chloric acid or its sulfuric acid equivalent); that "the precipitate is slightly soluble in the wash water" (0.0004 g. of ferric oxide in 75 cc. of 5% hydrochloric acid followed by 25 cc. of very dilute ammonium hydroxide); and that "if corrections are applied for these solubilities, the determination of iron by this method becomes very exact" (the total corrections under the conditions cited were 0.0014 g. of ferric oxide).

These statements are so opposed to the experiences of such investigators as Baudisch,[1] Biltz and Hödtke,[2] Fresenius,[3] Nissenson,[4] Ferrari,[5] and Lundell and Knowles[6] (in two experiments only) that it was considered desirable to test the method further in order to establish the truth, so that no doubt might be cast on the results obtained in such worth while applications of the method as the separation of iron and titanium from manganese, aluminum and phosphorus, and the determination of iron in soluble organic substances.

II. Experimental.

In the experiments listed in Table I, acid solutions of ferric salts containing 0.1 g. of iron were cooled to 10°, treated with paper pulp, precipitated by a two-fold excess of cupferron, and filtered.[7] The filtrates were then treated with sulfuric acid, evaporated in platinum on the steambath, transferred to Pyrex beakers and heated with nitric acid to complete decomposition of all organic matter. The solutions were finally diluted, and iron determinations were carried out by precipitation with ammonium hydroxide in hot solution, digestion for 12 hours, filtration, treatment with sulfuric and hydrofluoric acids and weighing as Fe_2O_3. Blank determinations were carried through all operations. The cupferron precipitates obtained in Expts. 1 and 2 were washed with dil. hydrochloric acid (1:9) previously cooled to about 10° and the washings were treated as above described, with the results listed in Expts. 5 and 6.

TABLE I.—SOLUBILITY OF THE CUPFERRON PRECIPITATE OF IRON.

Expt.	Final vol. of soln. Cc.	Acid present.	% by vol.	Vol. of 10% hydrochloric acid wash used. Cc.	Fe_2O_3 found in filtrate. G.	Fe_2O_3 found in wash water. G.	Appearance of filtrate or washings.
1	300	HCl	10	None	0.0000	....	Crystal clear
2	300	HCl	20	None	0.0000	....	Crystal clear
3	200	HCl	30	None	0.0004	....	Crystal clear
4	200	H_2SO_4	20	None	0.0000	....	Crystal clear
5	300	HCl	10	275	....	0.0000	Crystal clear
6	300	HCl	20	275	....	0.0003	Slightly cloudy

[1] Baudisch, Chem.-Ztg., 33, 1298 (1909).

[2] Biltz and Hödtke, Z. anorg. Chem., 66, 426 (1910).

[3] Fresenius, Z. anal. Chem., 50, 35 (1911).

[4] Nissenson, Z. angew. Chem., 23, 969 (1911).

[5] Ferrari, Ann. chim. applicata, 4, 341 (1915).

[6] Lundell and Knowles, J. Ind. Eng. Chem., 12, 344 (1920).

[7] Through S. and S. No. 589 blue-ribbon filters.

The data indicate that the precipitation of iron by cupferron is complete in acidities of hydrochloric and sulfuric acids up to 20% by volume, and that the precipitate does not dissolve during washing with cold dil. hydrochloric acid (1:9). It is believed that the slight recovery of iron in the cloudy washings of Expt. 6 represents cupferron precipitate carried through the pores of the filter and not cupferron precipitate dissolved in the hydrochloric acid wash water. Cupferron precipitates occasionally exhibit this annoying tendency as pointed out by Lundell and Knowles[1] and the correctness of the assumption in this case is indicated by the result of Expt. 5 where the washings were crystal clear, and by the quantitative data presented in Table II.

Quantitative determinations of iron by the cupferron method are listed in Table II. Weighed portions of a ferric sulfate solution prepared by oxidation of ferrous ammonium sulfate were employed. The same titer (0.001940 g. of iron per g. of solution) was found when the solution was standardized gravimetrically with correction for silica and volumetrically by reduction with sulfur dioxide and titration with a potassium permanganate solution. In precipitations carried out in the presence of hydrochloric acid, the sulfate was first converted to the chloride by precipitation with ammonium hydroxide, filtration, washing, and solution of the precipitate in the hydrochloric acid required in the test. Double the theoretical amount of cupferron was used in all cases but one. All cupferron precipitates were ignited in platinum and treated with sulfuric acid and hydrofluoric acid before weighing.

The data presented in Table II (Expts. 1, 2, 5, 6, 7 and 8) confirm the data presented in Table I and show quite conclusively that the precipitation of iron by cupferron is complete in solutions containing as much as 20% (by volume) of hydrochloric or sulfuric acids and that the precipitate is not appreciably soluble in cold 5 or 10% (by volume) hydrochloric acid.

It is also apparent that ammonium hydroxide wash waters may cause losses; these are always indicated by the formation of cloudy or turbid filtrates. Since ammoniacal wash waters are necessary only in the rarely employed separation of iron from copper, the question of their effect is not important.

The data also demonstrate that cupferron precipitates of iron exhibit the annoying tendency of "creeping through" filters, thereby often necessitating refiltrations. Failure to observe this last precaution appears to be the simplest explanation of the "solubilities" noted by Archibald and Fulton in the determination of iron by the cupferron method.

[1] Lundell and Knowles, This JOURNAL, **42**, 1445 (1920).

TABLE II.

Determination of Iron by Precipitation with Cupferron.

Expt.	Vol. of sol. Cc.	Acid present.	% by volume.	Wash sol. used.	% by volume.	Vol. of wash water used. Cc.	Iron taken. G.	Iron found. G.	Error. G.	Remarks.
1	100	HCl	5	HCl	5	400	0.1298	0.1300	+0.0002	Filtrate and washings crystal clear.
2	400	HCl	20	HCl 10 / H$_2$O .. / NH$_4$OH 30 / H$_2$O ..	200 / 100 / 200 / 100		0.1368	0.1367	−0.0001	Trace of opalescence developed as first hydrochloric acid wash went through. Solution immediately refiltered and afterwards remained clear.
3	100	HCl	30	HCl	10	400	0.1423	0.1418	−0.0005	Filtrate and washings crystal clear.
4	400	HCl	30	HCl 10 / H$_2$O .. / NH$_4$OH 30 / H$_2$O ..	200 / 100 / 200 / 100		0.1342	0.1332	−0.0010	Filtrate and washings cloudy upon shaking. No attempt was made to recover iron.
5	100	H$_2$SO$_4$	5	HCl	10	400	0.1402	0.1402	0.0000	Filtrate became turbid at beginning of washing and refiltered at once.
6	400	H$_2$SO$_4$	5	HCl	10	..	0.1434	0.1433	−0.0001	Very faint opalescence developed during the washing of the precipitate.
7	100	H$_2$SO$_4$	20	HCl	10	300	0.1253	0.1254	+0.0001	Filtrate and washings crystal clear.
8	400	H$_2$SO$_4$	20	HCl	10	..	0.1434	0.1436	+0.0002	Filtrate and washings crystal clear.
9	400	H$_2$SO$_4$	20	HCl 10 / H$_2$O .. / NH$_4$OH 30 / H$_2$O ..	200 / 100 / 200 / 100		0.1392	{ 0.1379 / 0.0013 }	0.0000	Filtrate and washings clear until ammonium hydroxide wash. Filtrate and washings refiltered through a new paper. Washed and ignited precipitate = 0.1379 g. Recovery = 0.0013 g.
10[a]	400	H$_2$SO$_4$	20	Ditto	Ditto	Ditto	0.1388	{ 0.1377 / 0.0011 }	0.0000	Filtrate and washings turbid. Put in icebox overnight, then refiltered and washed. Washed and ignited ppt. = 0.1377 g. Recovery = 0.0011 g.

[a] Four times the theoretical cupferron requirement employed.

III. Summary.

1. The precipitation of iron by cupferron is quantitative in hydrochloric or sulfuric acid solutions containing as much as 20% by volume of either acid.

2. The cupferron precipitate of iron is not soluble in cold dil. hydrochloric acid (1:9) wash water.

3. Ammoniacal wash waters, which need be rarely employed, may cause losses. These are always indicated by the formation of turbid filtrates.

4. Crystal clear filtrates and washings are absolutely essential in accurate determinations of iron by the cupferron method.

5. Cupferron precipitates of iron occasionally exhibit the annoying tendency of creeping through the filter. Consequently when the filtrate or wash water is even opalescent the need of such corrective treatments as refiltration or digestion in the cold followed by refiltration is indicated.

WASHINGTON, D. C.

THE MOLECULAR STATE OF WATER VAPOR.

BY ALAN W. C. MENZIES.

In a recent article with the above title, Kendall[1] has directed attention to the unwarranted conclusions as to the ionization and the polymerization of water vapor drawn by Oddo[2] and by Bose[3] from the values of the vapor density of water computed from Regnault's data[4] and from the experimental values of Kornatz.[5] Because of the fundamental importance of the subject in several fields of science, and because the conclusions of Oddo and of Bose continue to be taken seriously by modern chemists,[6] certain considerations, not dealt with by Kendall, are here brought forward in regard especially to the data themselves upon which the questionable conclusions have been based; and, at the same time, the opportunity is taken to point out a notable discrepancy that requires explanation.

It may be said at the outset that, although Regnault made direct measurements of the vapor density of water, he regarded his results as abnormally high under conditions approaching saturation and suggested that this was caused either by a veritable condensation of the vapor itself, or else by a surface condensation of liquid water on the walls of the glass

[1] Kendall, THIS JOURNAL, 42, 2477 (1920).

[2] Oddo, Gazz. chim. ital., [1] 45, 319 (1915).

[3] Bose, Z. Elektrochem., 14, 269 (1908).

[4] Cf. Landolt-Börnstein-Roth, "Tabellen," 1912, p. 369.

[5] Kornatz, Inaug.-Diss., Koenigsburg, 1908.

[6] Cf. Rideal, "Ozone," 1920, p. 27; Tomkinson, Chem. News, 122, 9 (1921).