The Normal Weston Cadmium Cell

F. E. Smith

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X. *The Normal Weston Cadmium Cell.*

By F. E. Smith, *A.R.C.Sc.*
(From the National Physical Laboratory.)

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[Plate 5.]

The experimental investigations described in this communication had as their primary object the improvement of the Clark and Weston Cadmium Cells as standards of electromotive force.

The older investigations of Rayleigh,[*] Kahle,[†] and Glazebrook and Skinner[‡] proved the Clark cell to be very trustworthy, and only within the last few years has any serious attempt been made to displace it from the premier position in which it was placed in 1894. In 1892 Weston[§] introduced the cell bearing his name. This cell contains a solution of cadmium sulphate instead of zinc sulphate, as in the Clark, and an alloy of cadmium and mercury forms the negative pole. As originally specified, the solution was saturated at 4° C., and no crystals of cadmium sulphate were inserted in the cell; under normal conditions there was therefore no change in the concentration for small variations in temperature. When the solution is saturated at all temperatures, *i.e.*, when solid cadmium sulphate is always present in the cell, the name "Cadmium Cell" has been frequently assigned to it in order to distinguish it from the original form. In this communication the latter cell is the type experimented with, and since it is referred to as the Weston Cadmium Cell in the reports of the International Conference the same name has been adopted by the author.

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[*] Lord Rayleigh, 'Phil. Trans.,' 175, p. 412, 1884, and 176, p. 781, 1886.

[†] K. Kahle, 'Zeitsch. f. Instrumentenk.,' 12, p. 117, 1892, and 13, p. 293, 1893.

[‡] R. T. Glazebrook and S. Skinner, 'Phil. Trans.,' 183, p. 567, 1892.

[§] Weston, 'The Electrician,' vol. 30, p. 741, 1892.

Lord RAYLEIGH[*] was the first to point out that the quality of the mercurous sulphate used as the depolariser in Clark cells was a cause of variation in E.M.F.; and Mr. SWINBURNE[†] arrived at the same conclusion in 1891. Later JAEGER and LINDECK[‡] attributed similar variations in the Weston cadmium cell to the same salt.

In 1902 some experiments at the National Physical Laboratory[§] plainly indicated that the mercurous sulphate might produce variations in the E.M.F. as great as 0·002 volt, or 1 part in 700 of the voltage of the Clark cell. A new specification of the mode of manufacture of the depolariser was thought to be desirable, and experiments were immediately made with this end in view.

Almost simultaneously CARHART and HULETT,[||] at the University of Michigan, and WOLFF,[¶] at the National Bureau of Standards, Washington, attacked the same problem, and a little later H. v. STEINWEHR,[**] at the Physikalisch-Technische Reichsanstalt, made a special study of the change of E.M.F. produced by varying the size of the crystals of the depolariser. While it must be admitted that the chemistry of the standard cell is still incomplete, an analysis of results shows that different observers can set up cells of almost identical E.M.F., and that their constancy is many times that of the standards used ten years ago.

PREPARATION OF THE MATERIALS.

Mercury.

In all our work the commercial mercury was cleaned with dilute nitric acid, washed with distilled water, and distilled twice *in vacuo.*

The Depolariser.

At the National Physical Laboratory the mercurous sulphate has been prepared in four ways: (1) Electrolytically; (2) by chemical precipitation, mercurous nitrate being added to sulphuric acid; (3) by the re-crystallisation of purchased samples of mercurous sulphate from strong sulphuric acid; and (4) by the action of fuming sulphuric acid on mercury.

The first of these methods was developed in 1904 by CARHART and HULETT[||] and also independently by WOLFF.[¶] The mercurous sulphate is formed at a mercury

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[*] Lord RAYLEIGH, 'Phil. Trans.,' 175, p. 412, 1884, and 176, p. 781, 1886.

[†] J. SWINBURNE, 'British Association Report,' Section A, 1891.

[‡] W. JAEGER and ST. LINDECK, 'Zeitschr. f. Instrumentenk.,' 21, p. 33, 1901.

[§] F. E. SMITH, 'British Association Report,' Section A, 1904.

[||] H. S. CARHART and G. A. HULETT, 'Amer. Electrochem. Soc. Trans.,' 6, pp. 109–126, 1904.

[¶] F. A. WOLFF, 'Amer. Electrochem. Soc. Trans.,' pp. 49–58, April 7, 1904.

[**] H. v. STEINWEHR, 'Zeitschr. f. Instrumentenk.,' 25, pp. 205–208, July, 1905; also 'Zeitschr. f. Elektrochem.,' pp. 578–581, 1906.

anode in dilute sulphuric acid, the latter, in the experiments made at the National Physical Laboratory, consisting of 1 volume of strong sulphuric acid (density 1·84) to 5 volumes of water; its strength was, therefore, about 3·0 molecular. The anode surface was kept well exposed by a glass stirrer, and the current density was from 1 to 5 amperes per 100 sq. centims. of anode surface. In the second method purchased protonitrate of mercury was sometimes used, but more often it was made from mercury and nitric acid. About 15 cub. centims. of concentrated nitric acid was added to 100 grammes of mercury, and when the action was over, or nearly over, the resulting solution was added to 200 cub. centims. of dilute nitric acid (1 of acid to 40 of water). The acid solution of mercurous nitrate thus formed was run as a very fine stream from the narrow orifice of a pipette into 1000 cub. centims. of hot dilute sulphuric acid (1 to 3), the liquid being well stirred during the mixing. Mercurous sulphate was precipitated. It was washed two or three times by decantation with dilute sulphuric acid (1 to 6) and filtered. The third method of manufacture is more costly. A purchased sample of the salt is heated with concentrated sulphuric acid to a temperature of about 150° C. and the hot clear acid carefully poured into dilute sulphuric acid (1 to 6), when precipitation of pure mercurous sulphate results. The fourth method, as originally employed, is troublesome. Fuming sulphuric acid is added to pure distilled mercury and stirred well until the action between the two is practically at an end. Mercurous sulphate is thus formed in the cold and appears in the crystalline form after a few minutes. Equally satisfactory results are obtained, however, if sufficient mercury is placed in a crystallising dish to cover the base and the fuming sulphuric acid added to a depth of 2 or 3 millims. The dish is covered with a clock glass and placed in a dark room for one or two weeks.

In all the methods of production the resulting mercurous sulphate was washed two or three times by decantation with dilute sulphuric acid (1 to 6) and afterwards introduced into a Buchener funnel for the removal of the acid as completely as possible by exhaustion with a filter pump. The sides of the funnel were washed down with neutral saturated cadmium sulphate solution and the salt washed 5 or 6 times with more of the same solution. About 5 cub. centims. was needed for each washing. In a few instances the sulphate was straightway employed for the manufacture of the depolarising paste, but in the majority of cases it was transferred together with a little of the cadmium sulphate solution to a small stock bottle. After a week or ten days the solution was always slightly acid to congo red paper and the mercurous sulphate was therefore washed once more before using.

In much of the earlier work absolute alcohol which had been specially distilled was employed for washing the mercurous sulphate, and the salt was stored in contact with more of the same liquid. We cannot, however, recommend this procedure, as we believe slight hydrolysis results, owing to the absorption of moisture by the alcohol.

Cadmium Amalgam.

The amalgam has been prepared in two ways, (1) by depositing cadmium electrolytically in a weighed quantity of pure mercury, the electrolyte being an acid solution of cadmium sulphate, (2) by heating together pure cadmium and mercury, the resulting mass being washed with dilute sulphuric acid to remove the surface dross. The amalgams used have been one part of cadmium to seven parts of mercury ($12\frac{1}{2}$ per cent.) or one part of cadmium to nine parts of mercury (10 per cent.). We have employed amalgams of other concentrations, but not in the cells discussed in this paper. The investigations of DEARLOVE,* KERP and BOETTGER,† BIJL,‡ PUSCHIN,§ and JAEGER‖ have shown that attention must be paid to the percentage of cadmium in the amalgam. It appears probable that in an amalgam containing between 6 and 14 per cent. of cadmium, there is at normal temperatures a solid and a liquid phase, of which the former is an isomorphous mixture of mercury and cadmium. The E.M.F. of the amalgam towards a cadmium sulphate solution does not depend on the relative amounts of the two phases, and on adding cadmium to the amalgam no change in E.M.F. occurs therefore until the liquid phase disappears. Similarly, if cadmium is extracted from the mixture the E.M.F. is constant until the solid phase disappears. A rise in temperature increases the liquid and diminishes the solid phase: for any particular amalgam there are, therefore, limits of temperature between which the two phases are always present. JAEGER has shown that for all amalgams in which the two phases exist the E.M.F. towards a cadmium sulphate solution is constant for a given temperature. DEARLOVE first proposed a $12\frac{1}{2}$ per cent. amalgam; this is satisfactory at all ordinary temperatures and has been generally employed.

The Cadmium Sulphate.

We have usually ground the purchased crystals and made a saturated or nearly saturated solution by agitation and warmth. This was filtered to clear and placed in crystallising dishes to slowly evaporate. The resulting crystals were well washed several times with water and the final solution tested for acidity with congo red paper.

A saturated solution of cadmium sulphate yields crystals of the composition $CdSO_4\frac{8}{3}H_2O$ at all temperatures up to 74° C., when $CdSO_4H_2O$ separates instead. KOHNSTAMM and COHEN¶ believed that they had discovered a transition point at

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* A. DEARLOVE, 'The Electrician,' vol. 31, p. 645, 1893.

† KERP and BOETTGER, 'Zeitschr. f. anorgan. Chem.,' 25, p. 1, 1900.

‡ BIJL, 'Zeitschr. f. Phys. Chem.,' 41, p. 641, 1900.

§ PUSCHIN, 'Zeitschr. f. Phys. Chem.,' 34, p. 621, 1901.

‖ W. JAEGER, 'WIED. Ann.,' 65, p. 106, 1898; 'Zeitschr. f. Instrumentenk.,' 20, p. 317, 1900.

¶ T. KOHNSTAMM and E. COHEN, 'WIED. Ann.,' 65, p. 344, 1898.

about 17° C., but the irregularities were afterwards traced by COHEN* to a transition which the 14·3 per cent. amalgam which was used undergoes at 23° C. The solution has also been investigated by H. v. STEINWEHR,† who failed to confirm any transition point at about 17° C. Cadmium sulphate is very soluble and increases very little in solubility over the ordinary range of temperature. As purchased, the crystals are generally acid, and in all cases it appears necessary to purify by recrystallisation.

Setting up of the Cell.

We have employed the Rayleigh H form of cell in nearly all our work. A platinum wire was fused into the lower end of each limb, and the parts of the wire inside the vessel were amalgamated by passing an electric current from a platinum anode through an acid solution of mercurous nitrate to each of the wires in turn. The vessel was washed out twice with dilute nitric acid, and several times with distilled water; it was dried in an oven. A small pipette was used for the introduction of the amalgam, and a small thistle funnel for the insertion of the mercurous sulphate paste and cadmium sulphate crystals. The main stock of amalgam was flooded with very dilute sulphuric acid, and melted over a water bath; a little was then introduced into one of the limbs of the H vessel. After the amalgam had solidified the limb containing it was washed out several times with distilled water, care being taken not to wet the interior of the other limb. A little distilled water was then added, and the amalgam again melted by immersing the H vessel in hot water; after solidification it was washed once more. Into the other limb of the vessel sufficient mercury was added to cover the amalgamated platinum wire and then the mercurous sulphate paste was introduced. The paste consisted of mercurous sulphate mixed with about one-fourth its volume of powdered recrystallised cadmium sulphate, and about one tenth its volume of pure mercury. (The latter was not added when the mercurous sulphate was prepared electrolytically or by means of fuming sulphuric acid.) To this mixture sufficient saturated cadmium sulphate solution was added, so that when well mixed the whole formed a thin paste. After the introduction of some of this paste into the limb containing the mercury, powdered crystals of cadmium sulphate were added to the contents of each limb, and after an interval of one hour sufficient saturated cadmium sulphate solution was inserted to fill the vessel to the top of the cross-connecting-tube. The cells were hermetically sealed with the aid of a blow-pipe. For the comparison of their electromotive forces the cells were immersed in paraffin oil and were maintained at an approximately constant temperature of 17° C. The comparisons were made by means

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* E. COHEN, 'Zeitschr. f. Phys. Chem.,' 34, p. 621, 1901. W. JAEGER and ST. LINDECK, 'Ann. d. Physik (4),' 3, p. 366, 1900; also 'Zeitschr. f. Phys. Chem.,' 35, p. 98, 1900.

† H. v. STEINWEHR, 'Ann. d. Physik, pp. 1046–1052, 1902.

of a high-resistance (15,000 ohms) potentiometer made by O. WOLFF, of Berlin, and a Broca galvanometer of 1000 ohms resistance made in the workshops of the National Physical Laboratory. It was quite easy to read to one hundred-thousandth of a volt, and, if necessary, one-tenth of this could be estimated with considerable accuracy.

When testing samples of mercurous sulphate we have often used a four-limb vessel similar to two Rayleigh H-form vessels crossed. Cadmium amalgam was placed in one limb, and in the other three mercury and the depolarisers were inserted. The electrolyte was a saturated solution of cadmium sulphate.

Unit of Electromotive Force.

In a recent communication to the Royal Society, Professor AYRTON, Mr. MATHER, and the author* have given the E.M.F. of some of the cells included in Table I. in terms of the ampere (10^{-1} C.G.S.) and the international ohm. While it must be admitted that this E.M.F. is possibly different from the true E.M.F. in volts (10^{-8} C.G.S.) by 2 or perhaps 3 parts in 10,000, it is probably the most accurate value known, and has the further advantage of being the mean of values the observations of which extended over 19 months. A further deduction is that the E.M.F. of most of the cells under observation did not change in this period by more than 0·00001 volt. We have therefore given the E.M.F. of cells in Table I. in terms of the ampere (10^{-1} C.G.S.) and the international ohm.

It is impossible to give all the observations over the period 1904–1907; those given are at approximately equal intervals of time. In cases where considerable changes in the E.M.F. have resulted, more extensive observations are given in subsequent tables. The values for the period May, 1904, to October, 1905, have been deduced from intercomparisons of cells, as no value in terms of the ampere and international ohm could be assigned until the later date.

Table I. gives the results of the observations on 60 cells. Since 1904 more than 200 cells have been set up, and a few of those which seem to be most valuable from the point of view of results obtained are included in the table. For the 60 cells in Table I., 16 samples of mercurous sulphate have been used, 6 of cadmium amalgam and 5 of cadmium sulphate. In some cases the mercurous sulphate was washed with alcohol; the letter A is then inserted in column 5 of the table. The approximate depth of the paste is given in column 6, and the numbers in column 7 indicate the range of the dimensions of the mercurous sulphate crystals in thousandths of a millimetre. Particulars of the cadmium amalgam are given in columns 8 and 9; E indicates that the amalgam was prepared by the electro-deposition of cadmium, and F by the fusion of cadmium and mercury. The mercurous sulphate was usually prepared two weeks in advance of its use as a depolariser in a cell.

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* W. E. AYRTON, T. MATHER, and F. E. SMITH, "On a New Current Weigher," 'Phil. Trans.,' 1907.

TABLE I.

Cell.	Date of manufacture.	Depolariser.					Cadmium amalgam.		Electromotive force at 17° C.							Mean E.M.F., June, 1907.
		Method of preparation.	Number of preparation.	Washing.	Depth in millimetres.	Size of crystals in microns.	Composition.	Preparation.	One month after preparation.	Dec., 1904.	June, 1905.	Dec., 1905.	June, 1906.	Dec., 1906.	June, 1907.	
							per cent.									
CH 10	Oct., 1904	II.	3	—	6	—	10	E	1·01830	30	31	30	27	29	28	28
,, 11	,, ,,	,,	3	—	7	—	10	,,	30	29	28	28	26	28	27	
,, 16	,, ,,	,,	3	—	7	—	10	,,	31	31	30	30	28	28	29	
,, 25	,, ,,	,,	4	A	7	—	10	,,	33	32	32	31	30	30	31	30
,, 26	,, ,,	,,	4	,,	7	—	10	,,	31	30	30	32	31	31	30	
,, 27	,, ,,	,,	4	,,	6	—	10	F	32	32	32	32	30	31	30	
,, 12	,, ,,	,,	4	,,	6	—	10	,,	31	30	29	29	30	29	29	
E 51	Nov., ,,	I.	5	,,	6	—	10	E	30	31	30	32	29	28	28	28
,, 52	,, ,,	,,	5	,,	10	—	10	,,	31	30	29	30	31	32	30	
,, 53	,, ,,	,,	5	,,	8	—	10	,,	32	33	32	31	30	30	30	
,, 05	,, ,,	,,	5	—	8	—	12½	,,	30	31	27	29	28	28	28	
,, L5	,, ,,	,,	5	—	7	—	12½	,,	30	29	27	26	27	26	26	
,, 62	Feb., 1905	,,	6	—	10	5 to 15	10	,,	34	—	34	34	33	33	33	28
,, 63	,, ,,	,,	6	—	6	,,	10	,,	33	—	33	33	32	31	32	
,, 66	,, ,,	,,	6	—	11	,,	10	,,	33	—	32	33	32	31	32	
,, 67	Mar., 1905	,,	7	—	5	—	10	,,	36	—	30	30	26	34	20	
,, 68	,, ,,	,,	7	—	7	—	10	,,	30	—	29	28	28	27	28	
,, 69	,, ,,	,,	7	—	6	—	10	,,	30	—	29	28	25	24	24	
,, 70	,, ,,	,,	7	—	6	—	10	,,	31	—	29	28	28	26	26	
N 23	Sept., ,,	IV.	2	A	15	5 to 20	12½	,,	22	—	—	29	31	31	32	31
,, 24	,, ,,	,,	2	,,	18	,,	12½	,,	23	—	—	30	31	32	32	
,, 25	,, ,,	,,	2	,,	13	,,	12½	F	17	—	—	32	32	31	31	
,, 26	,, ,,	,,	2	,,	10	,,	12½	,,	22	—	—	31	30	32	31	
,, 17	,, ,,	,,	2	,,	10	,,	12½	,,	33	—	—	32	31	30	31	
HA 1	April, 1906	II.	8	—	5	5 to 30	12½	E	32	—	—	—	31	30	30	30_5
,, 2	,, ,,	,,	8	—	5	,,	12½	,,	32	—	—	—	31	30	30	
,, 3	,, ,,	,,	8	—	5	,,	12½	,,	33	—	—	—	32	32	32	
,, 4	,, ,,	,,	8	—	5	,,	12½	,,	32	—	—	—	33	32	31	
,, 5	,, ,,	,,	8	—	6	,,	12½	F	34	—	—	—	31	30	30	
,, 6	,, ,,	,,	8	—	7	,,	12½	,,	31	—	—	—	30	29	30	

TABLE I. (continued).

Cell.	Date of manufacture.	Depolariser.					Cadmium amalgam.		Electromotive force at 17° C.							Mean E.M.F., June, 1907.
		Method of preparation.	Number of preparation.	Washing.	Depth in millimetres.	Size of crystals in microns.	Composition.	Preparation.	One month after preparation.	Dec., 1904.	June, 1905.	Dec., 1905.	June, 1906.	Dec., 1906.	June, 1907.	
							per cent.									
B 41	Mar., 1906	II.	6	—	6	5 to 30	10	E	1·01832	—	—	—	30	29	30	29
,, 42	,, ,,	,,	6	—	6	,,	10	,,	30	—	—	—	28	29	29	
,, 43	,, ,,	,,	6	—	7	,,	10	,,	29	—	—	—	29	29	30	
,, 149	,, ,,	,,	6	—	7	,,	10	,,	30	—	—	—	29	28	29	
,, 151	,, ,,	,,	7	—	7	,,	10	,,	29	—	—	—	28	28	27	
R 1	,, ,,	III.	4	—	5	—	10	,,	33	—	—	—	32	32	32	32
,, 2	,, ,,	,,	4	—	6	—	10	,,	33	—	—	—	33	32	32	
,, 3	,, ,,	,,	4	—	6	—	10	,,	34	—	—	—	33	31	32	
E 80	,, ,,	I.	8	—	6	3 to 15	10	,,	30	—	—	—	28	29	28	28_5
,, 81	,, ,,	,,	8	—	6	,,	10	,,	30	—	—	—	30	29	28	
,, 82	,, ,,	,,	8	—	7	,,	10	,,	31	—	—	—	30	31	29	
,, 83	,, ,,	,,	8	—	6	,,	10	,,	30	—	—	—	28	27	28	
HA 7	Nov., 1906	II.	12	—	6	5 to 30	$12\frac{1}{2}$	F	31	—	—	—	—	31	29	30
,, 8	,, ,,	,,	12	—	5	,,	$12\frac{1}{2}$	,,	30	—	—	—	—	30	30	
,, 9	,, ,,	,,	12	—	7	,,	$12\frac{1}{2}$	,,	33	—	—	—	—	30	31	
,, 10	,, ,,	,,	12	—	7	,,	$12\frac{1}{2}$	,,	32	—	—	—	—	28	30	
P 410	Mar., 1907	,,	14	—	5	,,	$12\frac{1}{2}$	,,	31	—	—	—	—	—	30	30
,, 411	,, ,,	,,	14	—	5	,,	$12\frac{1}{2}$	,,	31	—	—	—	—	—	29	
,, 413	April, 1907	,,	14	—	5	,,	$12\frac{1}{2}$	E	31	—	—	—	—	—	30	
,, 414	,, ,,	,,	14	—	11	,,	$12\frac{1}{2}$	,,	32	—	—	—	—	—	30	
AB 1	Jan., 1905	IV.	3	—	8	—	$12\frac{1}{2}$	,,	23	—	22	22	21	21	21	—
,, 2	,, ,,	,,	3	—	7	—	$12\frac{1}{2}$	,,	21	—	20	20	19	19	19	—
D 1	,, ,,	I.	4	—	—	5	10	,,	28	—	26	22	17	07	05	—
,, 2	,, ,,	,,	4	—	—	6	10	,,	26	—	22	17	10	10	09	—
,, 3	,, ,,	,,	4	—	—	6	10	,,	25	—	17	15	12	07	05	—
,, 4	,, ,,	IV.	3	—	—	6	10	,,	31	—	30	26	25	23	23	—
,, 5	,, ,,	,,	3	—	—	5	10	,,	32	—	30	26	22	20	20	—
M 6	Feb., 1906	,,	6	—	—	7	10	,,	30	—	—	—	28	25	18	—
,, 7	,, ,,	,,	6	—	—	6	10	,,	30	—	—	—	30	27	14	—
,, 8	,, ,,	,,	6	—	—	6	10	,,	32	—	—	—	31	22	10	—

Discussion of the Results.

Effect of Various Amalgams.

The E.M.F.'s of the cells set up with amalgams prepared at different times agree under otherwise equal conditions within 1 part in 100,000. The amalgam prepared by the electrodeposition of cadmium in mercury is perhaps preferable for the cells of standardising institutions, but our observations do not show any certain difference between it and that prepared by the fusion of cadmium and mercury, when the latter amalgam is freed from dross.

Effect of the Cadmium Sulphate.

We have obtained our cadmium sulphate from various sources, but after one crystallisation and thorough washing of the crystals with water no certain difference in the behaviour of the solutions has been detected.

Effect of the Depolariser.

The mean value of the cells set up with the electrolytic mercurous sulphate is 1·01828 volts; that of the cells containing the salt prepared by chemical precipitation (Method II.) is 1·01830 volts; when mercurous sulphate was employed which had been precipitated from hot strong sulphuric acid, 1·01832 volts is the mean; and the salt prepared with fuming sulphuric acid gives 1·01831 volts.

We conclude that the mode of manufacture of the mercurous sulphate is immaterial, provided that certain conditions are observed, and our guiding principle in the manufacture of the salt and the preparation of the paste is to prevent hydrolysis by keeping the salt in contact with dilute sulphuric acid (1 to 6), or with saturated cadmium sulphate solution. This is in accordance with HULETT's investigations.

CARHART and HULETT* have examined Weston cadmium cells containing electrolytic and chemically prepared sulphate (Method II.), and conclude that there is no appreciable difference in E.M.F. Later, HULETT† constructed two other cells containing the chemical sulphate, and found them about 0·00015 volt higher than cells containing the electrolytic salt. He concludes that the electrolytic sulphate is the most reliable preparation. Dr. F. A. WOLFF and C. E. WATERS‡ have examined many more specimens, and conclude that the four methods dealt with in this communication give practically identical results. They have also examined samples of mercurous sulphate prepared by the action of sulphuric acid containing a small percentage of nitric acid on mercury (Lunge reaction); by the reduction of mercuric sulphate by mercury, and by digesting commercially pure samples of mercurous

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* H. S. CARHART and G. A. HULETT, 'Amer. Electrochem. Soc. Trans.,' 6, pp. 109–126, 1904.

† G. A. HULETT, 'Phys. Rev.,' 22, pp. 321–338, June, 1906.

‡ F. A. WOLFF and C. E. WATERS, 'Electrical World,' 49, pp. 100, 101, January 12, 1907.

sulphate with sulphuric acid. The last method gave the largest difference, but this was of the order of 5 parts in 100,000 only.

Mr. J. A. SADD, A.C.G.I., a student demonstrator of the Central Technical College, has constructed some cadmium cells in accordance with a specification published by the author[*] in 1905. These cells contain mercurous sulphate prepared electrolytically, and were forwarded to the National Physical Laboratory for comparison with our standards. There are ten cells in all, and their values at 17° C. are as follows :—

1·01832 volts.	1·01839 volts.
34	39
35	40
37	42
38	43

Mr. H. TINSLEY, of Beckenham, Kent, has also prepared some cadmium cells in accordance with the specification mentioned above. In this case the depolariser was prepared with mercurous sulphate precipitated by adding mercurous nitrate to sulphuric acid (Method II.). Most of Mr. TINSLEY'S cells are also greater in E.M.F. than the N.P.L. standards, the difference being about 1 part in 10,000.

In May, 1907, 12 cadmium cells prepared by Dr. F. A. WOLFF of the National Bureau of Standards, Washington, were brought to England by Dr. BURGESS, and a direct comparison between the cells of the two institutions was thus rendered possible. Cells which were believed to nearly represent the normal cell were chosen to compare with those from Washington, and the following differences were observed :—

TABLE II.

National Bureau of Standards cadmium cells.		National Physical Laboratory cadmium cells.	
Cell.	E.M.F. of cell minus mean E.M.F. of all microvolts.	Cell.	E.M.F. of cell minus mean E.M.F. of all microvolts.
WP 8	+ 1	P 52	+2
,, 9	− 7	,, 53	−1
,, 10	0	,, 54	−1
W 19	+ 1	,, 55	−1
,, 105	−11	,, 210	+2
,, 181	0	C 12	−2
,, 182	0	,, 17	+3
,, 183	+ 2	,, 19	0
,, 184	+ 1	,, 117	−1
,, 185	+ 6	H 26	+2
,, 186	− 1	,, 28	+4
,, 187	+ 4	,, 29	−2

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[*] F. E. SMITH, 'British Association Report,' Section A, 1905

The mean E.M.F. of the 12 "National Bureau of Standards" cells is less than the mean E.M.F. of the 12 N.P.L. cells by 3 microvolts.

P 52, P 53, P 54, and P 55 were set up in November, 1906,
C 12, C 17, C 19, and C 117 ,, ,, June ,,
H 26, H 28, and H 29 ,, ,, February, 1907,
P 210 ,, ,, March ,,

The mean E.M.F. of the 12 N.P.L. cells is not quite the mean of all the N.P.L. cadmium cells, which are believed to be normal; the latter cells have the higher mean by about 2 parts in 100,000.

Eleven of the twelve cadmium cells from Washington contain electrolytic mercurous sulphate; the twelfth, W 105, contains mercurous sulphate prepared by the Lunge reaction. The depth of the pastes in these cells is about 1·5 centims. The twelve cells of the National Physical Laboratory contain mercurous sulphate prepared chemically (Method II.), and the depth of the paste is about 0·5 centim. The nett result of these comparisons with other observers is that mercurous sulphate of sufficiently uniform properties can be prepared in several ways, provided that certain conditions are observed. The possibility of an approximately constant size of mercurous sulphate crystal resulting from all the methods must not, however, be overlooked, and as the size of the crystal has not been stipulated by us, it is necessary to examine the evidence on this point.

H. v. STEINWEHR* was the first to call attention to the part played by the size of the crystal, and our method of investigation is very similar to that employed by him.

Effect of the Size of the Crystals of Mercurous Sulphate.

Twenty samples of mercurous sulphate have been examined under the microscope, and in twelve cases microphotographs have been taken, the magnification being 250. Of these, eleven are reproduced on Plate 5. It will be seen from these microphotographs that not only do the crystals vary considerably in size, but that each method of preparation produces its own particular type of crystal. The electrolytic method, as employed by us, gives small crystals, somewhat imperfect in shape, and varying in size from 2 to 8 microns (0·002 to 0·008 millim.). The crystals resulting from the chemical precipitation method are very much rounded, like pebbles; they have the appearance of being formed from perfect crystals, the edges of which have been rounded by the solvent action of the hot dilute sulphuric acid. The uniformity in the size of the crystals is more marked in the samples produced by this method than in the specimens made in any other way tried by us. The size of most of the crystals in figs. 2 to 4 varies from 5 to 30 microns. The mercurous sulphate produced

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* H. v. STEINWEHR, 'Zeitschr. f. Instrumentenk.,' 25, pp. 205–208, July, 1905.

by the action of fuming sulphuric acid on mercury is evidently in the form of large crystals, but most of these appear to get broken in the washing processes, with the result that the size of the grain is considerably diminished. Figs. 9 and 10 show these fragments of crystals, which vary in size from 5 to 25 microns.

We have not taken any microphotographs of crystals produced by Method III., as this method is only of interest as an independent means of obtaining mercurous sulphate; it is far too troublesome to be generally employed. We have, however, prepared some very large crystals by a method suggested by H. v. STEINWEHR.* A dilute acid solution of mercurous nitrate was allowed to flow very slowly indeed from a burette into dilute sulphuric acid (1 to 4) heated to 100° C. over a water-bath. Small crystals of mercurous sulphate were at first formed, which grew, however, in the slightly super-saturated solution of mercurous sulphate until many of them attained a length of a few millimetres. The crystals were washed with dilute sulphuric acid (1 to 6) and the finer particles were removed by agitation with the acid and rapid decantation. The resulting product was undoubtedly of large grain, and there were numerous particles present of the size shown in fig. 5. The length of this crystal is about 400 microns.

In September, 1906, three cells were set up which contained these large crystals of mercurous sulphate as a depolariser. Table III. gives the results of observations on these cells from October, 1906, to May, 1907.

TABLE III.

Cell.	1906.			1907.				
	October.	November.	December.	January.	February.	March.	April.	May.
S 1	1·01843	42	42	40	41	41	40	39
S 2	36	35	35	34	35	34	34	35
S 3	40	38	39	38	40	38	39	38

The cells are not in very good agreement and the mean E.M.F. is about 8 in 100,000 higher than the E.M.F. of the normal cells in Table I. Recently we have set up more cells with a second sample of large-grained mercurous sulphate, and they also have E.M.F.'s higher than 1·01830 volts. In order that there should be no doubt about the size of the crystals in S 1, S 2, and S 3, they were unsealed in June, 1907, the pastes washed with dilute sulphuric acid to remove the cadmium sulphate crystals and the residue examined microscopically. It was apparent that during the preparation of the depolarising paste and its insertion in the cell many of the large crystals

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* H. v. STEINWEHR, 'Zeitschr. f. Instrumentenk.,' 25, pp. 205–208, July, 1905; also 'Zeitschr. f. Electrochem.,' pp. 578–581, 1906.

were broken, with the result that the mean size of the crystals was diminished, but the fragments were still much larger than the crystals prepared by any of the other methods. Figs. 1 and 8 (Plate 5) are microphotographs of some of the crystals of mercurous sulphate after their removal from the cells S 1, S 2, and S 3. It was observed that in all cases there was a small number of comparatively small crystals, or fragments of crystals, associated with the large ones, but we found this unavoidable. In one instance we took very great pains to eliminate small particles, and succeeded in doing so to a considerable extent, but subsequent examination of the crystals after the manufacture of the depolarising paste and its insertion in a cell showed that their size had been appreciably reduced.

Table IV. enables a comparison to be made between cells set up with crystals of various sizes.

TABLE IV.

Cells.	Mercurous sulphate.	Size of most of the crystals in microns.	Mean E.M.F.
E 62, &c.	Electrolytic I.	5 to 15	1·01828
E 80, ,,	,, I.	3 ,, 15	28_5
HA 1, ,,	Chemical II.	5 ,, 30	30_5
B 41, ,,	,, II.	5 ,, 30	29
HA 7, ,,	,, II.	5 ,, 30	30
P 410, ,,	,, II.	5 ,, 30	30
N 23, ,,	Fuming acid IV.	5 ,, 20	31
S 1, S 2, S 3	STEINWEHR'S method	about 10 per cent., 20 ,, 30 ,, 60 ,, 40 ,, 100 about 20 per cent., greater than 100	37

The higher E.M.F. of the cells S 1, S 2, S 3 is probably due to slight impurities in the mercurous sulphate, and not to the large size of the crystals. During the preparation of these crystals the sulphuric acid was not stirred, and the only agitation of the liquid was that produced by the mixing and by convection currents. It is possible for slight hydrolysis to result under such circumstances, and also possible for mercurous nitrate to be imprisoned in some of the large crystals which are formed. The latter appears to be not improbable in our case.

If we exclude from Table IV. those cells set up with the very large crystals, we have as the limits of the dimensions of the others 3 to 30 microns, and we conclude that if the size of the crystals be within these limits they will have very nearly the same solubility and practically give the same E.M.F. in a standard cell.

This conclusion is not in accordance with observations made by STEINWEHR, who first called attention to the possible effect of the size of the crystals, and claims that it is a principal cause of the variations observed in standard cells. Lord KELVIN has shown that the saturation pressure of small drops of water is greater than that of large drops; similarly the solubility of small particles is greater than that of large ones, and therefore the saturated solution will show a greater E.M.F. than the saturated solution of the large crystals. With fluctuating temperatures the tendency is for the small crystals to disappear and the mean size of the crystals to increase; this lowers the concentration and with it the E.M.F. It is only for *very* small crystals that the change in solubility is appreciable, and at present it is not possible to calculate the change in E.M.F. produced by the variation in size.

STEINWEHR[*] examined several samples of purchased mercurous sulphate; two such salts from KAHLBAUM and MERCK respectively gave a difference in E.M.F. of 5 parts in 10,000, and it was found that the dimensions of the crystals of the salt K giving the higher E.M.F. were of the order of 1 micron, while the crystalline structure could be seen in a number of particles of the other salt (M). The crystals of M were about 10 to 20 microns long. By grinding the M salt the difference was reduced to 1 or 2 parts in 10,000. Very large crystals were prepared by a method very similar to that afterwards used by ourselves (p. 404), and the E.M.F. of a cell containing these very large crystals was lower than that of a cell containing the K salt by 0·7 to 0·8 millivolt. By grinding some of the large crystals and setting up a cell with the small particles as a depolariser the E.M.F. was increased by 0·6 millivolt, and was therefore comparable with the K cell.

We also have set up cells with KAHLBAUM'S mercurous sulphate which was washed with water and is therefore hydrolysed. The E.M.F. of these cells is at present 1·0186 volts and is constant; indeed, from the point of view of constancy of E.M.F., these cells are as good as any of those dealt with in Table I.; fig. 11 (Plate 5) is a microphotograph of the salt used. The average size of the crystals is from 2 to 10 microns. The salt from KAHLBAUM, used by STEINWEHR, was smaller than this, the particles being from 1 to 2 microns in length at the most. The difference of 0·3 millivolt found by us between cells set up with KAHLBAUM'S salt and those set up with mercurous sulphate prepared by ourselves appears to be due not to a difference in size of grain, but to the hydrolysis of the former salt.

HULETT[†] has also measured the size of mercurous sulphate crystals prepared electrolytically and found the particles to vary in length from 2 microns to 130 microns, but has found no difference in the E.M.F. of cells set up with these crystals.

It is, of course, always possible that in an occasional preparation a very large number of exceedingly fine crystals may be produced, and in such a case the change of E.M.F. described by STEINWEHR will result, but unless there are numerous small crystals in *all* of our preparations—and this is highly improbable—the large crystals of mercurous sulphate which are sufficiently soluble to act as an efficient depolariser cannot give an E.M.F. appreciably lower than those which are from 5 to 30 microns

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[*] H. v. STEINWEHR, 'Zeitschr. f. Instrumentenk.,' 25, pp. 205–208, July, 1905; also 'Zeitschr. f. Elektrochem.,' pp. 578–581, 1906.

[†] G. A. HULETT, 'Phys. Rev.,' 22, pp. 321–338, June, 1906.

in length. The question is an interesting one, and we hope to extend our investigation, but at present there appears to be no necessity to stipulate the size of the crystals. We would, however, draw attention to the uniformity of the size of the crystals of the chemically precipitated salt, and as Method II. is the easiest of any of the methods of preparation used by us, we strongly recommend it, or one founded on it, as a standard method of preparation.

Constancy of the Cell.

The results recorded in Table I. indicate remarkable constancy of most of the cells. Eighty per cent. of the first fifty cells have apparently varied by not more than 2 parts in 100,000 since the first month of their preparation. Of the remainder, four have varied from 3 to 5 parts, one 6 parts and one 16 parts in 100,000. There are four others which belong to the N group of cells; these were low at first, but rose to the normal value 3 months after preparation. Further remarks on these four cells appear on p. 410. The last eight cells in Table I. are anomalous. In 12 months the three M cells have fallen 10, 16 and 21 parts in 100,000 respectively, and the five D cells have values about 30 parts in 100,000 lower than the normal. Of the approximately constant cells, twelve have been set up for 2½ years, twenty-three for more than 18 months, and thirty-six for more than 12 months. It is important to note that the comparatively new cells, *i.e.*, those set up in March and April, 1907, are practically identical in E.M.F. with the cells set up in 1904.

Of the abnormal cells it is noteworthy that, with the exception of E 67, they belong to three groups and that the change in them has been practically continuous from the time of their construction. The cells were prepared in a manner apparently the same as that of the normal cells, and we are unable to offer a complete explanation of their remarkable behaviour. Examination of the solutions shows that they are not appreciably acid, and tests on the amalgams indicate that they give the same E.M.F. as those used in the new cells. The depolarisers are, however, at fault. This we have proved by connecting one of the cells with a new cell by means of a syphon and measuring the E.M.F. between the negative pole of the new cell and the positive pole of the abnormal cell. The same low E.M.F. was recorded. Something may have happened during the preparation of the depolarisers for these abnormal cells, but we are not aware of any departure from our usual proceeding.

There is, however, another indication that the depolarisers have changed, and we wish to draw particular attention to this, as it may lead to the discovery of the cause of the disturbance. In nearly all of the cells which have fallen by as much as 0·0002 volt many of the small crystals of cadmium sulphate have changed in colour, and in some cases the colour of the depolariser has also changed. The cadmium sulphate crystals in these cells of low E.M.F. are of a yellowish-brown tint and the mercurous sulphate in places is slightly yellow, or, in a few instances, green. This change has also been noted in cells set up with some samples of purchased mercurous sulphate, but these cells are high in E.M.F. and approximately constant. In the normal cadmium cells the appearance of the mercurous sulphate is the same as when freshly prepared. An interesting question is whether the change in colour of the paste is the result of association with the other ingredients of the standard cell or not, and whether a charging or discharging current produces or accelerates the change. The first part of this question may be answered so far as association with the cadmium amalgam is concerned, for we have kept many samples of the paste together with saturated cadmium sulphate solution and mercury in stock bottles. In two of these pastes green patches have appeared and the dimensions of the patches are slowly increasing. The change is therefore independent of the presence of free cadmium or cadmium amalgam. The probable acceleration of the change due to a charging or discharging current is discussed on pp. 413–415.

A number of anomalous cells were closely examined in order to detect any other peculiarities besides that of the coloration of the depolariser and crystals of cadmium sulphate. In one of the cells a small bubble of air was imprisoned between the glass and the paste, and the paste in contact with the bubble and to a depth of 1 millim. from it was of a yellow tint, the remaining portion of the depolariser being normal in colour. From these colour observations it appears probable that the change is of the nature of a hydrolysis, but at present we have no reason to think that all the pastes will, with time, similarly change, and that, as suggested by HULETT,[*] the cathode leg of the cadmium cell is a system in unstable equilibrium. Instead we are inclined to believe that something abnormal occurred in the preparation of the pastes.

Two cells which were low in E.M.F. by 0·0001 volt, but very constant, were opened, and the solution in them was found to be very slightly acid. We regard this as an indication of insufficient washing of the mercurous sulphate. Cell No. 2 was employed in a potentiometer circuit during the estimation of current in absolute measure by the Ayrton-Jones Balance. It was used from October, 1905, to June, 1907, and could not have fallen by more than 1 part in 100,000 during this period. Its low initial E.M.F. is probably due to the presence of acid.

HULETT concludes that many of his cells have fallen 11 parts in 100,000 in a little over two years, but that Clark cells have remained constant. In 1904 the author pointed out that some cadmium cells made in 1902 had apparently fallen 0·00007 volt; these, however, were prepared in the old way with purchased mercurous sulphate washed with water, and since 1904 there is every reason to believe that they have remained constant.

Drs. K. E. GUTHE and C. L. v. ENDE[†] record the following results:—Three cadmium cells were prepared by them on Nov. 2, 1906; by the 17th of the same month each had fallen about 50 microvolts below the normal value; by Dec. 13, 1906,

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[*] G. A. HULETT, 'Phys. Rev.,' 23, pp. 166–183, August, 1906.

[†] K. E. GUTHE and C. L. v. ENDE, 'Phys. Rev.,' 24, pp. 214–221, February, 1907.

the mean fall was 100 microvolts, and there was evidence that they were still falling. These three cells contained pastes prepared by Dr. GUTHE. On Nov. 10, 1906, four other cadmium cells were prepared, and contained mercurous sulphate supplied by Dr. HULETT. By Jan. 19, 1907, the mean fall of these cells was 0·00049 volt; on the same date their average E.M.F. was about 0·00023 volt lower than that of the three cells previously considered.

Dr. GUTHE also gives the values of some Clark and cadmium cells set up with electrolytic and chemically prepared pastes by Professors CARHART and HULETT. The Clark cells appear to have remained constant since their construction in 1904, but some of the cadmium cells have fallen by 3 to 4 parts in 10,000. In some cases more than half of this change took place during the first year.

The results obtained at the National Physical Laboratory are, on the whole, decidedly in favour of the constancy of the cell, and tend to show that the fall in E.M.F. of certain N.P.L. cells is due to the mercurous sulphate in them being somewhat abnormal when they were set up. An investigation of the pastes of abnormal cells appears to be desirable, and may possibly lead to some explanation of the want of constancy which the foregoing statement shows has been noted by some observers.

E.M.F. of freshly prepared Cells.

When mercurous sulphate is freshly prepared and apparently free from acid, if cells are set up with it as a depolariser on the same day as that of the precipitation they do not usually take up their normal value immediately. They are sometimes high at first, but fall rapidly in E.M.F., sometimes attaining their normal value within a few hundred thousandths of a volt in a few hours, but more often an interval of several days is required. An example of this is afforded in the case of B 151. This was completed at 2.15 P.M. on the same day as the depolariser was manufactured; it was inserted in a constant temperature bath, and observations of the E.M.F. were immediately made. At the same time another cell, B 149, was completed; in this the depolariser was mercurous sulphate which had been prepared three weeks previously and had since remained in contact with saturated cadmium sulphate solution. This cell attained its normal value almost immediately.

TABLE V.

Cell.	Day of preparation, March 7th, 1906.									March 8th.	March 9th.
	2.20 P.M.	2.33.	2.37.	2.45.	3.0.	3.10.	3.30.	4.0.	5.0.		
B 151	1·01861	56	55	53	51	50	49	48	47	39	36
B 149	1·01837	36	36	35	34	34	34	33	33	32	32

"Ageing" of Cells.

Lord RAYLEIGH observed that the electromotive force of Clark cells when originally set up was invariably high, and in some cases the fall in E.M.F. in a few weeks was 0·02 volt. This fall in E.M.F. immediately after manufacture has been confirmed by numerous observers, and in consequence Clark cells were supposed to require "ageing." The same is true of Weston cadmium cells if set up with pastes prepared similarly to those used by Lord RAYLEIGH, but such extreme changes as 2 per cent. have not come under the author's notice. The mercurous sulphate prepared by any of the four methods described in this communication does not require "ageing," or to a very small extent only.

Washing with Alcohol.

The group of cells, of which N 23 to N 26 are types, were abnormal in their behaviour. The E.M.F. was at first 3 parts in 10,000 low, but gradually increased until it was normal, and since then it has remained approximately constant. The mercurous sulphate for these cells was washed with absolute alcohol to free the salt from acid, but no attempt was made to remove the alcohol by further washing the sulphate with saturated cadmium sulphate solution. The salt was removed from the filter and immediately made into paste. Table VI. gives the observations from the date of preparation, September 20, 1905, to January 1, 1906; Cell N 17 contains mercurous sulphate from the same sample, but which was freed from alcohol before making up the paste.

TABLE VI.

Cell.	Sept. 20, 1905.	Sept. 30.	Oct. 10.	Oct. 20.	Oct. 30.	Nov. 10.	Nov. 20.	Nov. 30.	Dec. 20.	Jan. 1, 1906.
N 23	1·01800	06	11	19	22	23	25	27	29	32
„ 24	03	10	14	18	23	25	27	28	30	33
„ 25	00	04	08	12	17	21	24	26	32	32
„ 26	10	13	16	19	22	25	28	29	31	32
„ 17	37	35	33	33	33	32	33	32	32	32

GUTHE and v. ENDE* prepared some mercurous sulphate which was not thoroughly free from alcohol and found the E.M.F. of some Clark cells 0·00040 volt lower than normal when set up with this, and there was *no* appreciable change in the course of time. Their observations extended over three months.

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* K. E. GUTHE and C. L. v. ENDE, 'Phys. Rev.,' 24, pp. 214–221, February, 1907.

The Temperature Coefficient and "Lag."

In experimental work involving the use of the Clark cell, temperature corrections have invariably to be introduced owing to the high value of the temperature coefficient. This is the most serious objection to its use. The temperature coefficient of the cadmium cell is much smaller and has been determined by Jaeger and Kahle, who give the following equation connecting temperature and E.M.F.:

$$E_t = 1{\cdot}0186 - 0{\cdot}000038\,(t-20) - 0{\cdot}00000065\,(t-20)^2.$$

At the National Physical Laboratory six cells were chosen and their temperatures were varied very slowly from 10° C. to 30° C. The maximum rate of change of temperature was 1° C. per hour, and before making an observation at any particular temperature the oil bath in which the cells were immersed was kept at that temperature for at least an hour, a toluene thermostat capable of maintaining a constant temperature to 0°·01 C. being employed. The cycle of temperature was repeated three times. The agreement between the cells was excellent, and the mean values of the E.M.F.'s were taken to obtain the temperature coefficient by the method of least squares. The resulting temperature formula is

$$E_t = E_{17} - 0{\cdot}000034_5\,(t-17) - 0{\cdot}00000066\,(t-17)^2.$$

This is in very good agreement with Jaeger and Kahle's formula. The changes in E.M.F. from 10° C. to 15° C., 10° C. to 20° C., and 10° C. to 30° C., as deduced from the two formulæ, are given below.

° C.	Jaeger and Kahle.	N.P.L.
10 to 15	$0{\cdot}00015_1$ volt.	$0{\cdot}00014_3$ volt.
10 ,, 20	$0{\cdot}00032_5$,,	$0{\cdot}00031_8$,,
10 ,, 30	$0{\cdot}00077_0$,,	$0{\cdot}00076_8$,,

The lag of E.M.F. with respect to temperature changes was shown by Ayrton and Cooper[*] to be much greater in the Board of Trade tube form of cell than in the **H** form. They concluded that there is a "simple lag," which may be removed by a comparatively short interval of constant temperature, and a "semi-permanent lag," which requires many hours of steady temperature for its complete removal. We have made similar observations on the Weston cadmium cell and find evidence of the same lag in it. The effect is, however, very small when the temperature changes are slow and the range of temperature only a few degrees, as in the experiments of Ayrton and Cooper on the Clark cell. When the range of temperature is about 15° C. and the change of temperature very rapid, a difference in E.M.F. of about 30 microvolts is often observed after the normal temperature of the cell has been restored for 4 or

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[*] Ayrton and Cooper, 'Roy. Soc. Proc.,' 59, p. 368, 1896.

5 hours. Much, however, depends on the construction of the cell. An extreme case is illustrated in fig. 12. Here a cell was maintained at a temperature of 55° C. for 12 hours and was then plunged into a bath of paraffin oil at 17° C. The oil was stirred, and observations of the E.M.F. were frequently made. At 11.20 A.M. (see fig. 12) the cell was at a temperature of 55° C. and was then immersed in the oil at 17° C. Twenty minutes afterwards the E.M.F. was normal to 1 part in 4000; after a total interval of 40 minutes it was right to 1 in 10,000, and after 1 hour to about 7 parts in 100,000. Fourteen days elapsed, however, before the cell was within 2 parts in 100,000.

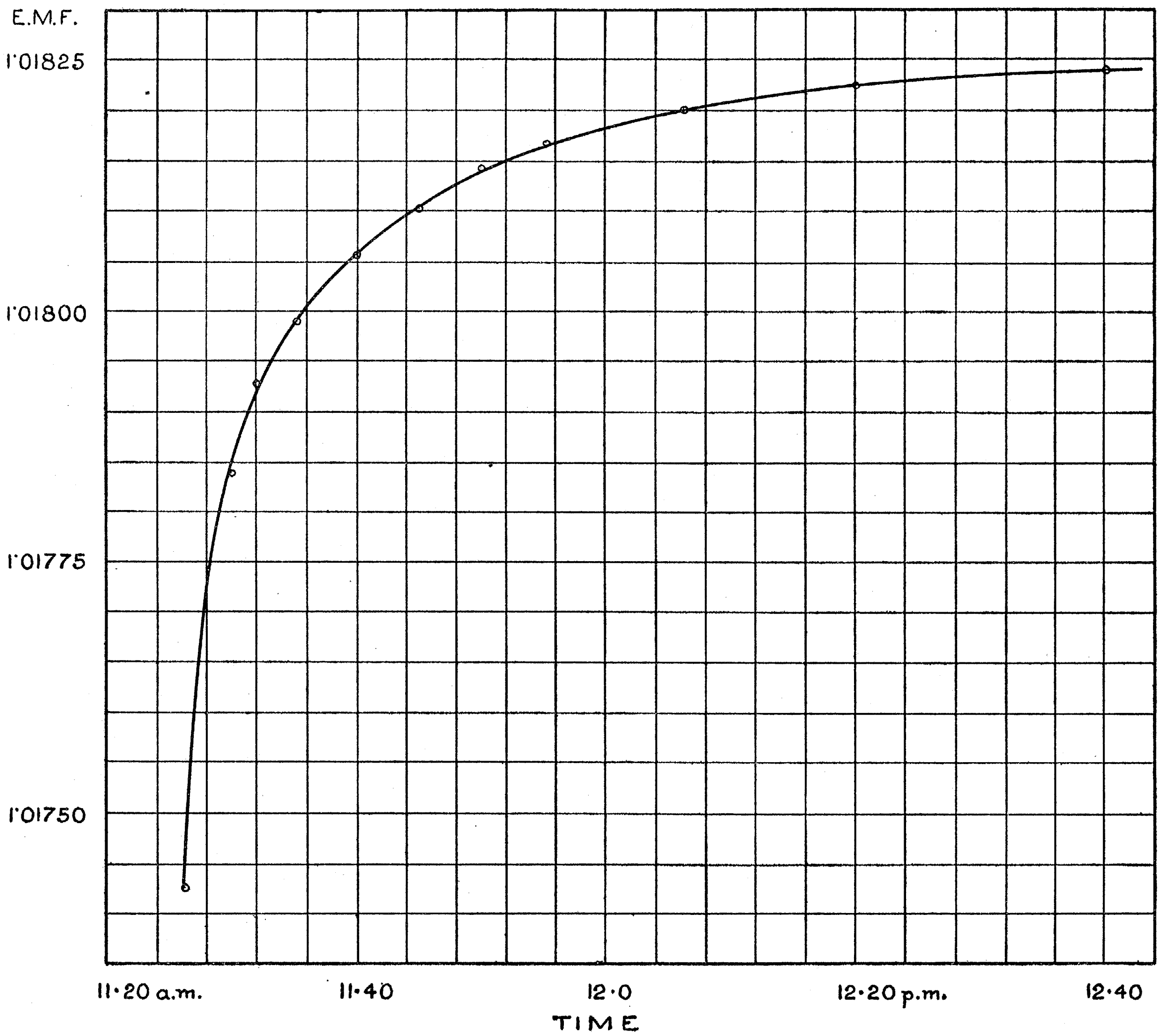

Fig. 12. Recovery curve of cell suddenly cooled from 55° C. to 17° C.

Recovery after Short-circuiting.

In order to test the recuperative power of the Weston cadmium cell, one of the cells was short-circuited for 1 minute, another for 5 minutes, a third for 5 hours, and a fourth for 5 days. The recovery of the first two cells is illustrated in figs. 13 and 14. It will be observed that the cell which was short-circuited for 1 minute was right within a ten-thousandth of a volt 1 minute afterwards, but 40 minutes were occupied in its recovery to 1 part in 100,000. The cell which was short-circuited for 5 minutes was nearly 1 in 1000 low 1 minute afterwards; at the end of the second minute it was 1 in 2000 low, and after 5 minutes it had recovered within 1 in 5000; about 1½ hours were required for its complete recovery. The restoration of the E.M.F. of the third cell was much slower; 1 minute after the circuit was opened its E.M.F. was about 0·1 volt, which value it appeared to retain for 3 minutes. The E.M.F. then changed suddenly from 0·1 to 0·85 volt, and at the end of 4 minutes its voltage was 0·9. The recovery was then more gradual. Ten minutes after breaking the circuit the E.M.F. was 0·0061 volt below normal, 20 minutes afterwards 0·0028 volt low, and 5 hours afterwards it was low by 0·00040. It recovered within 1 in 10,000 in 24 hours, but 3 weeks were occupied in its complete recovery. The cell which was short-circuited for 5 days had an E.M.F. less than 0·05 volt 5 minutes after breaking the circuit, and its E.M.F. did not rise above 0·08 volt for

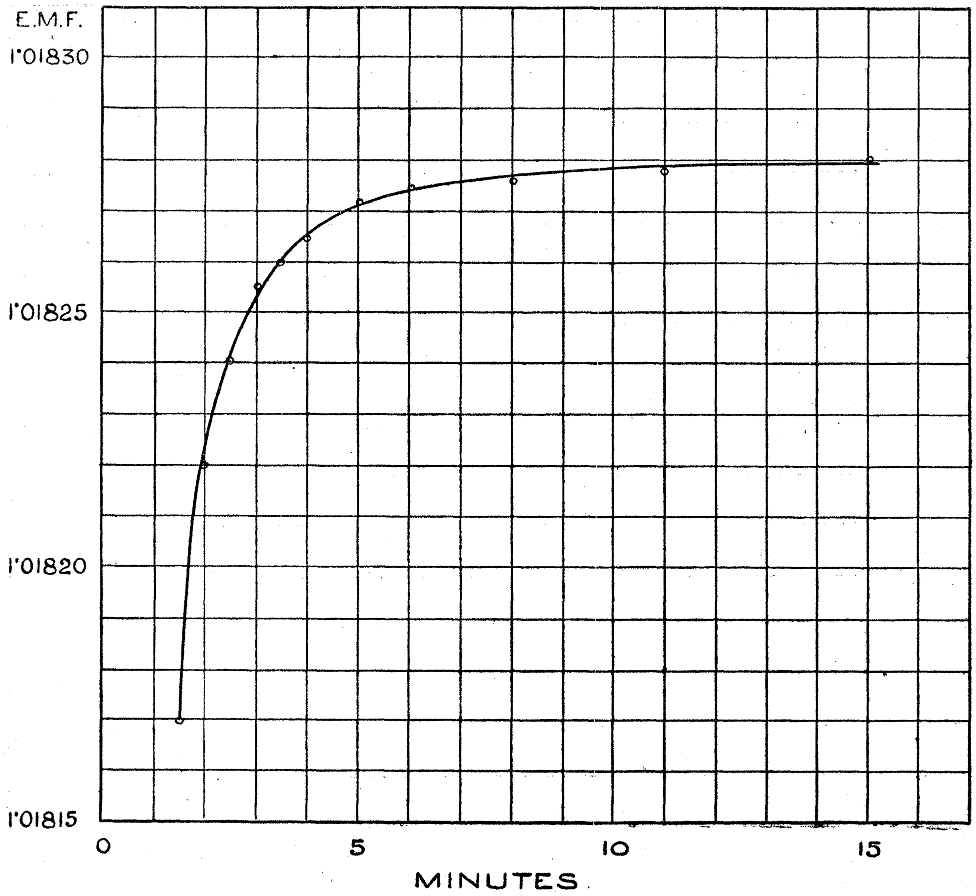

Fig. 13. Recovery curve of cell short-circuited for 1 minute.

more than 6 hours. Twenty-four hours afterwards, however, its E.M.F. was normal within 2 parts in 10,000, and it completely recovered within 6 weeks.

In 1884 Lord Rayleigh made some experiments on the polarisation of Clark cells and conclusively showed that the effect of short-circuiting for a few minutes rapidly passed away.

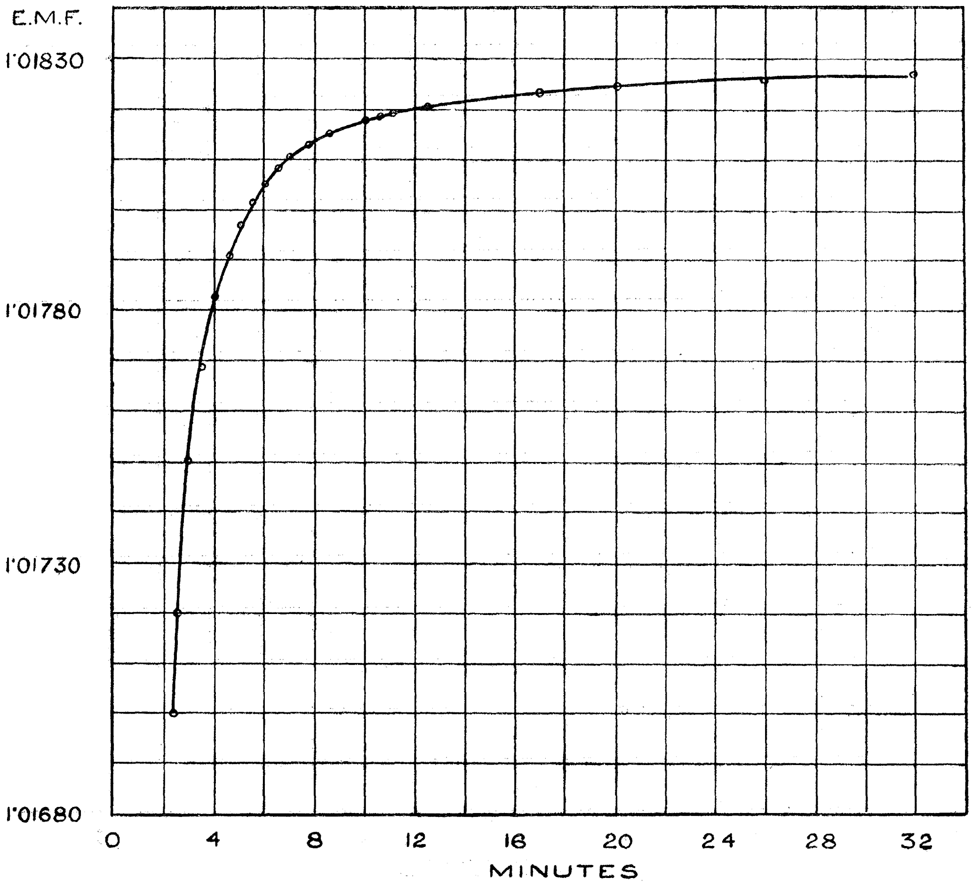

Fig. 14. Recovery curve of cell short-circuited for 5 minutes.

Recovery curves for the Clark cell have been published by Fisher,* for a large type of cadmium cell by Tinsley,* and for the Calomel or Hibbert cell by Hibbert.* An analysis of such curves leaves little doubt that short-circuiting is only temporarily injurious.

Charging the Cell.

In practice, a standard cell is usually placed in a circuit in which a very small current alternates in direction. These small charging and discharging currents can have no immediate serious effect on the cell, as is amply proved by many cadmium cells in use at the National Physical Laboratory which are frequently checked in the

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* W. C. Fisher, "The Potentiometer and its Adjuncts," 'Electrician' Series; W. Hibbert, 'The Electrician,' vol. 37, p. 32, 1896; H. Tinsley, 'The Electrician,' vol. 47, p. 991, 1901.

Electrical Standards Department. That a small current may be taken *from* the cell without any permanent effect is proved from the observations when cells have been short-circuited, but the effect of a comparatively large charging current may be more serious. Lord RAYLEIGH attempted to manufacture a Clark cell by the formation of electrolytic mercurous sulphate inside an **H** vessel, the anode being mercury, the electrolyte zinc sulphate, and the cathode an amalgam of zinc. The cells so formed were not constant, and their E.M.F.'s were low. In 1904 we attempted in a similar way to produce cadmium cells, but it was evident that normal mercurous sulphate was not formed, as the resulting salt was highly coloured; it was sometimes yellow, but more often green. The fact that the depolariser in some of our anomalous cells has, after a long period, turned a yellowish-green suggested to us that its formation might be accelerated by small charging currents. The constancy of other cells subject to the same treatment is certainly against such a view, but a slight difference in the original composition of the depolarisers might account for the more rapid change. To test this point, we placed a normal cell in circuit with, but in opposition to, two Leclanché cells for 18 hours. At the end of that time a green compound had formed between the mercury electrode and the glass, but the depolariser appeared to be unchanged. There is little doubt, however, but that some of the green salt was present over the whole surface of the mercury. The E.M.F. of this cell was at first very high, but in 4 weeks it gradually fell to 1·01833 volts. The observations which we have so far made do not enable us to say whether any further fall is probable, but it is evident that the small charging currents to which a cell is subjected in a potentiometer circuit do not seriously affect its E.M.F.

Portability of the Cell.

Many of the cells made at the National Physical Laboratory are portable, and may be sent through the post. In these cells the two limbs of the **H** vessel are constricted at points about 1½ centims. from their lower ends, and when making up the cell, cadmium sulphate crystals are added until the upper surface of a crystalline layer is on a level with the narrowest part of the tube in which the crystals are placed. Cadmium sulphate solution is then added and the cells are exposed in a warm room for a week or more before sealing. Some of the liquid evaporates, and many of the fine crystals are loosely cemented together. This crystalline plug keeps the contents in their proper places and enables the cell to be inverted.

Conclusions.

(1) The electromotive force of the Weston cadmium cell is the same whether it contains electrolytic mercurous sulphate, chemically prepared sulphate, the salt as precipitated by the dilution of hot strong sulphuric acid in which mercurous sulphate is dissolved, or that resulting from the action of fuming sulphuric acid on mercury.

(2) The size of the crystals of mercurous sulphate prepared by the first two and the last of the above methods usually varies from 5 microns to 15 microns, and we have found no electromotive difference between a saturated solution of these crystals in a cadmium sulphate solution and a saturated solution of very large mercurous sulphate crystals in the same solvent.

(3) The simplest method of preparing mercurous sulphate is by chemical precipitation, and the product is more uniform than that of any other method so far examined.

(4) The electromotive force is the same whether the cadmium amalgam is prepared by the electro-deposition of cadmium in mercury, or by the fusion of cadmium and mercury. At normal working temperatures either a 10 or a 12½ per cent. amalgam may be used.

(5) The electromotive force is probably constant over long periods of time, but the cells should be compared with those of a standardising institution every 12 months; failing this, they should be compared with freshly set up cells.

(6) The change of E.M.F. with temperature may be calculated from JAEGER and KAHLE'S equation or from that obtained at the National Physical Laboratory. As the former has been used for so many years, we suggest its universal adoption.

(7) The small charging and discharging currents to which a cell is subjected in a potentiometer circuit do not seriously affect the value of the electromotive force.

We desire to express our thanks to the Committee of the British Association for grants of money for the purchase of materials; to Dr. GLAZEBROOK for much advice concerning the construction of the cells, and to Mr. J. A. SADD, of the Central Technical College, and Mr. TINSLEY, for constructing standard cells to compare with ours.

APPENDIX.

Added December 4, 1907.

ON THE COMPARISON OF THE ELECTROMOTIVE FORCES OF WESTON CADMIUM CELLS PREPARED AT WASHINGTON, AT PARIS, AT BERLIN, AND AT TEDDINGTON.

Dr. BURGESS of the National Bureau of Standards, Washington, journeyed to Paris and Berlin after his visit to Teddington, and very kindly took with him a number of cadmium cells from the National Physical Laboratory in addition to others from Washington. Dr. F. A. WOLFF has forwarded us a report on the measurements of the cells in Paris, from which we make the following abstracts.

Eight of the American cells and eight of the English cells were compared at the Laboratoire Central d'Électricité under conditions which allowed of an approximation to 1 part in 100,000. The maximum deviation of the eight American cells from their mean was found to be 0·00002 volt, and the difference between this mean and the mean of the Weston cadmium cells of the Laboratoire Central was of the order of 0·00001 volt. The maximum deviation of the eight English cells was about 0·00003 volt, and their mean E.M.F. differed from the E.M.F. of the French cells by about 0·00001 volt. A second set of comparisons, made at Paris in August, confirmed the first measurements on the American cells.

Dr. Burgess left four English cells at the Laboratoire Central, and M. Janet, the Director of the Laboratory, has compared these with the French cells, with the following results.

TABLE VII.

Cell No.	Approximate difference from mean in microvolts.				
	June, 1907.	July, 1907.	October, 1907.	November 20, 1907.	November 30, 1907.
P 52	+10	+ 1	+ 5	− 4	+ 1
P 210	−10	− 4	−10	+ 1	+ 1
H 28	0	+ 1	−10	−19	−24
C 17	−10	+ 1	+15	+ 1	− 9
K 14	—	—	—	+11	+18
K 13	—	—	—	+ 6	+14
K 12	—	—	—	+ 6	+ 1
Mean E.M.F. of English cells − mean E.M.F. of French cells	+10	+24	+10	+14	+ 9

The cells K 12, K 13, K 14, were set up at the National Physical Laboratory on October 2, 1907, and Mr. Agar Baugh kindly took them to M. Janet. The cells H 26, H 28, and H 29 (see p. 402) were set up with pastes which may be very slightly acid.

Eight of the American cells and eight of the English cells were compared at Berlin, June 20 and June 21, while two American cells and four English cells remain at the Reichsanstalt and have been intercompared from June 20 to September 30, 1907. The following statements are extracted from a formal report by Messrs. Jaeger and Lindeck.

The results of the tests of the Weston cells brought over from America and England are given in Table VIII. Since only the cells 183 and 184 from America, and H 29, P 55, C 117, and C 12 from England, have been left in Charlottenburg, the mean (indicated by A) of these six cells is taken as the basis of values given in Table VIII.

TABLE VIII.

Weston cells—America.			Weston cells—England.		
Cell No.	Difference from A in microvolts.		Cell No.	Difference from A in microvolts.	
	June 20.	June 21.		June 20.	June 21.
19	− 3	− 7	H 26	− 3	− 7
105	− 13	− 18	C 19	+ 12	+ 5
P 8	− 8	− 8	P 53	+ 2	+ 1
P 9	− 8	− 13	P 54	+ 2	+ 1
P 10	− 8	− 13	P 55	+ 2	+ 2
183	+ 7	− 3	C 12	+ 2	+ 4
184	− 3	− 3	C 117	+ 2	+ 7
187	− 3	− 3	H 29	− 8	− 6
Mean. . . .	− 5	− 8	Mean. . . .	+ 1	+ 1

It will be seen that the American and English cells agree very well among each other. In the first series of measurements: Mean E.M.F. of English cells − Mean E.M.F. of American cells = +0·000006 volt, and in the second series of measurements the difference is +0·000009 volt. Two cells which Mr. RAYNER of the National Physical Laboratory kindly took from Teddington to the Reichsanstalt, in September, show equally good agreement.

The German cells mentioned in Table IX. (the series are designated by P, O, and M) were prepared in March, 1907, with three different samples of mercurous sulphate made by the von Steinwehr precipitation method. During the first few months after their preparation these cells showed on the average a decrease in E.M.F. of about 1 part in 10,000, and the E.M.F. had not attained a state of constancy at the commencement of the measurements in question. Drs. JAEGER and LINDECK suggest that the cause of this alteration lies in the fact that the three samples of mercurous sulphate were washed out with dilute sulphuric acid in course of preparation. The relative agreement in the individual groups is, however, very good. In the P group there are eight cells and the difference between any one cell and the mean has at no time exceeded 2 parts in 100,000; in the O group there are six cells, and in the M group six cells, and the corresponding differences for these groups are about 1 and 1·7 parts in 100,000, respectively. Intercomparisons were made with the older cells (1899) of the Reichsanstalt, which were taken as constant during the period June 20 to September 30, 1907.

TABLE IX.

Mean E.M.F. of the Single Groups – the mean E.M.F. of the American, German (September 9, 1907), and English Cells.

Group.	Differences in microvolts.				
	June 20, 1907.	June 21, 1907.	July 11, 1907.	September 28, 1907.	September 30, 1907.
A. (2 American and 4 English)	−15	−10	−13	−21	−12
B. (8 German P cells) . . .	+25	+30	+20	−12	− 6
C. (6 ,, O ,,) . . .	+54	+57	+48	—	+21
D. (6 ,, M ,,) . . .	+67	+71	+54	—	+14
Mean German P, O, M cells	+49	+53	+41	—	+10

As will be seen from the above table, the cells from America and England have remained constant during the period June 20 to September 30; the German cells of Groups P, O, M, have, however, decreased 4 parts in 100,000. Drs. JAEGER and LINDECK think that it is not improbable that the alteration will continue, but owing to the slightness of the change this can only be tested after long periods.

It would seem, as the result of the last measurements on September 30, that the differences between the various cells compared were, at that time, only a few parts in 100,000. By making use of the average value of the cells P, O, M, obtained at this time, and taking into consideration the data given in Dr. WOLFF's report (and part of that given on p. 403 of this communication), Drs. JAEGER and LINDECK give the following differences for the cells of the different countries, the figures being rounded off to the hundred-thousandth part :—

$$\left.\begin{array}{l}\text{E.M.F. of English cells}\\ \quad\text{(Mean of more than 100 cells)}\end{array}\right\} - \left\{\begin{array}{l}\text{E.M.F. of American cells}\\ \quad\text{(Mean of 12 cells)}\end{array}\right\} = +1\times10^{-5} \text{ volt,}$$

$$\left.\begin{array}{l}\text{E.M.F. of German cells}\\ \quad\text{(Mean of P, O, M cells)}\end{array}\right\} - \text{E.M.F. of English cells} = \pm0\times10^{-5} \text{ ,,}$$

$$\text{E.M.F. of German cells} - \text{E.M.F. of American cells} = +1\times10^{-5} \text{ ,,}$$

As the French cells are also in good agreement with the American and English cells, considerable advance would appear to have been made with the standard cell question.

The English cells, H 26, C 19, P 53, and P 54, were received at Washington on August 22. On the same date C 19 was about 40 microvolts higher than its companion cells, but on August 27 a comparison led to the results given in

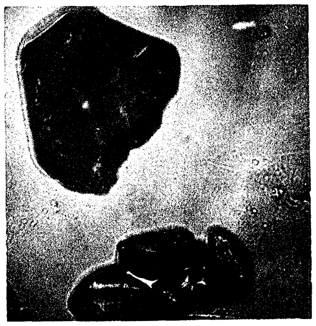
Table X. Dr. WOLFF has also forwarded the results of comparisons made by him on P 8, P 9, P 10, and 187 (American), of PCN 4 and PCN 6 (French), and O 1 and O 2 (German). Unfortunately, the depolariser in the German cells was disturbed in transit, and the results obtained are not, therefore, given in Table X.

TABLE X.

August 27, 1907. E.M.F. of Cell—Mean E.M.F. of the American, French, and English Cells.

American	P 8 $-\ 2 \times 10^{-6}$ volt P 9 $-\ 5 \times 10^{-6}$ „ P 10 $-\ 5 \times 10^{-6}$ „ 187 $+\ 5 \times 10^{-6}$ „	Mean $= -2 \times 10^{-6}$ volt
French	PCN 4 $+ 16 \times 10^{-6}$ „ PCN 6 $- 18 \times 10^{-6}$ „	Mean $= -1 \times 10^{-6}$ „
English	H 26 $-\ 5 \times 10^{-6}$ „ C 19 $+\ 5 \times 10^{-6}$ „ P 53 $+\ 4 \times 10^{-6}$ „ P 54 $+\ 5 \times 10^{-6}$ „	Mean $= +2 \times 10^{-6}$ „

We heartily thank the various gentlemen who have assisted in these comparisons.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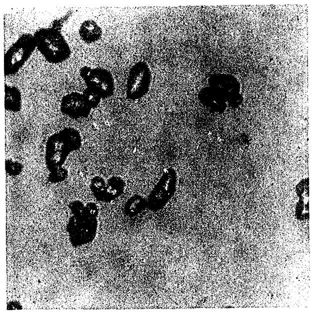
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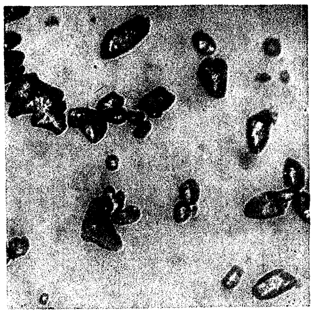
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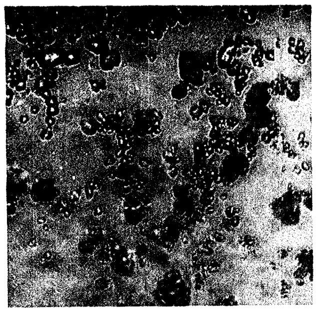
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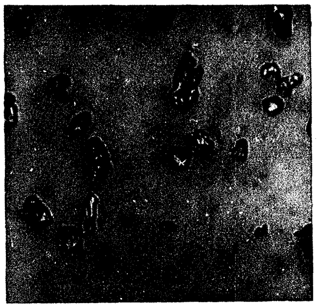
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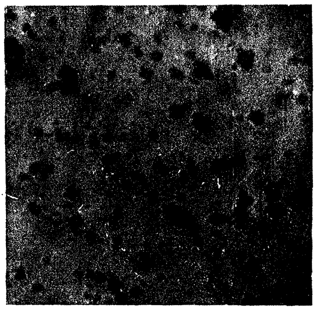
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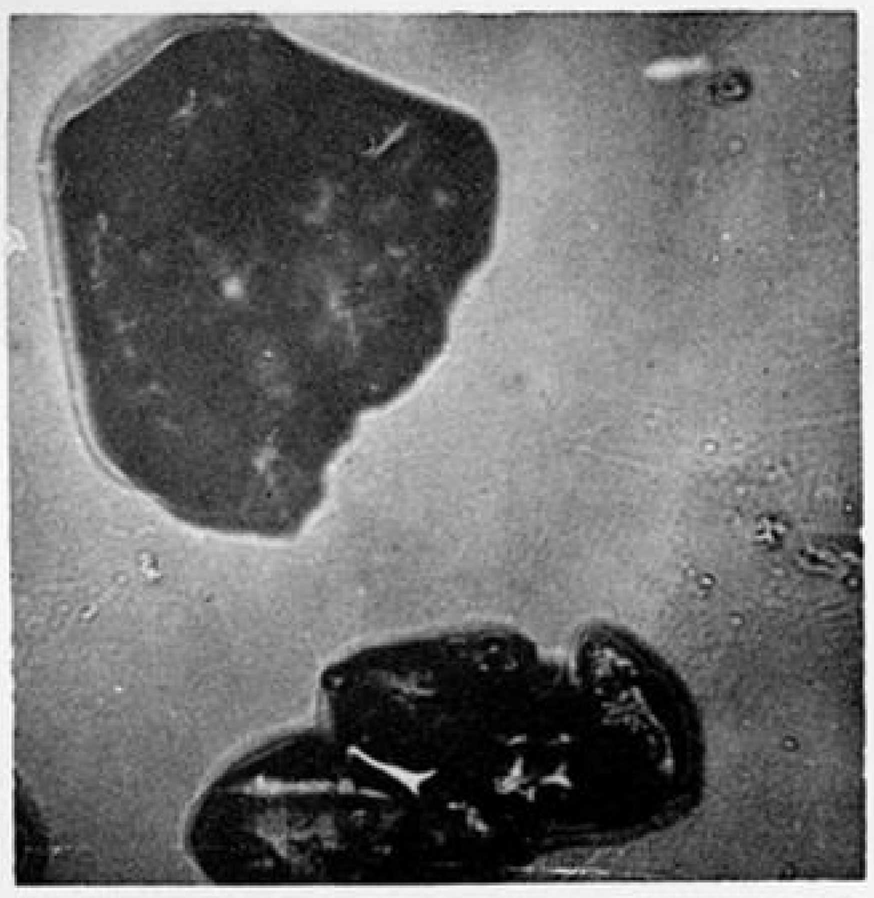
MICROPHOTOGRAPHS OF CRYSTALS OF MERCUROUS SULPHATE. Magnification = 250.

Figs. 1, 5, 8.	Steinwehr's method of preparation.
,, 2, 3, 4.	Chemical method of preparation.
,, 6, 7.	Electrolytic method of preparation.
,, 9, 10.	Fuming sulphuric acid method of preparation.
,, 11.	Purchased from Kahlbaum.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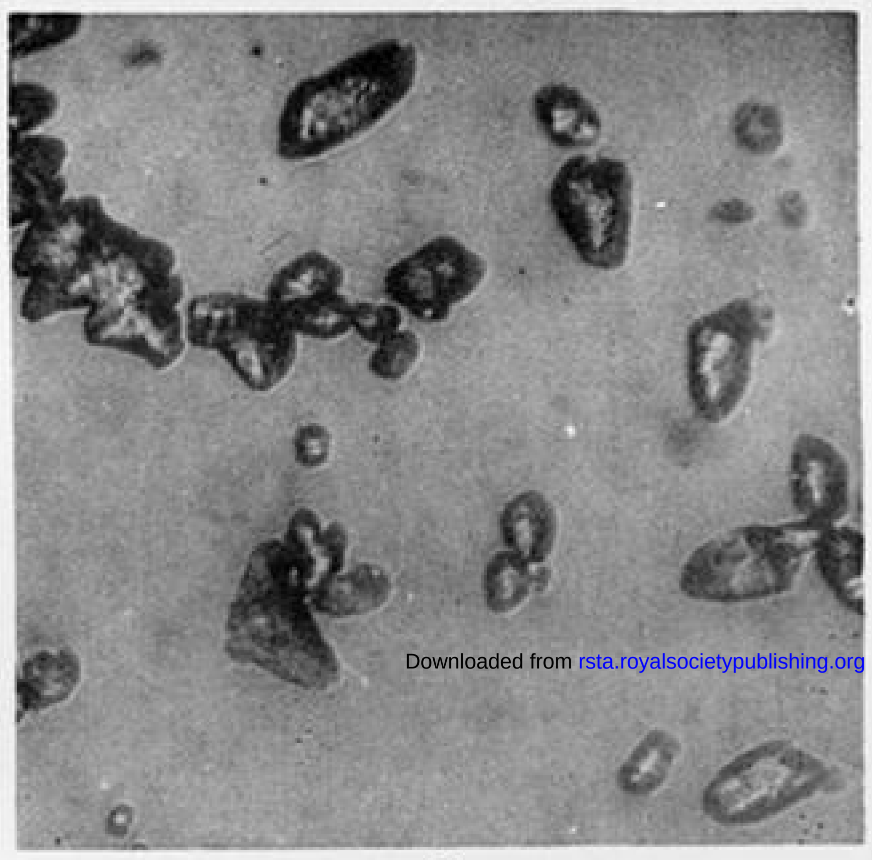
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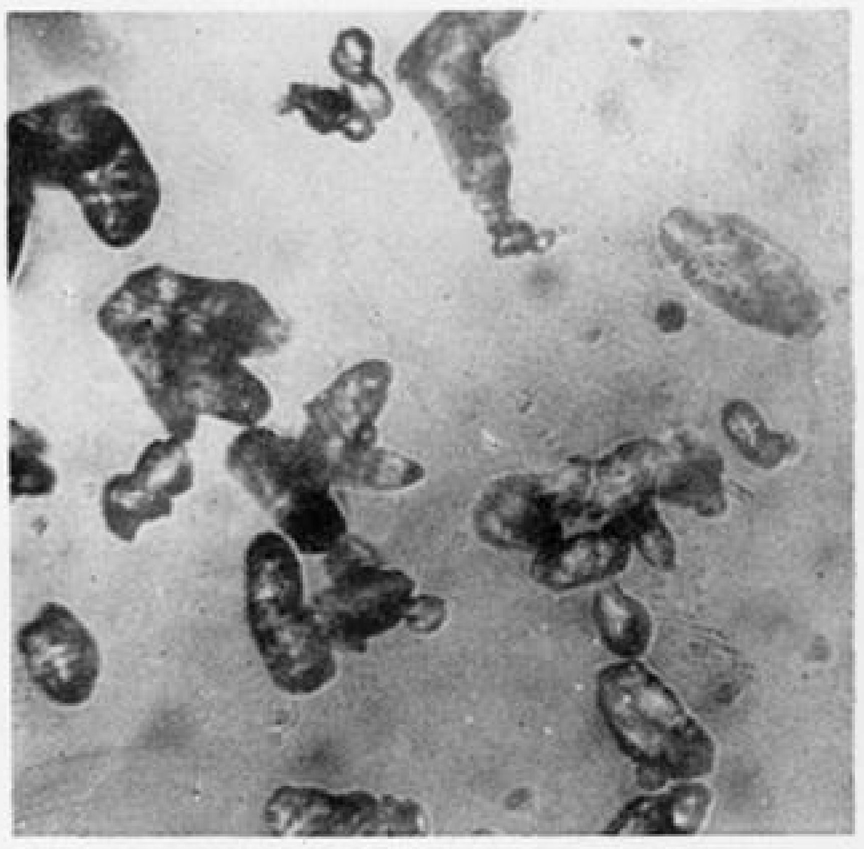
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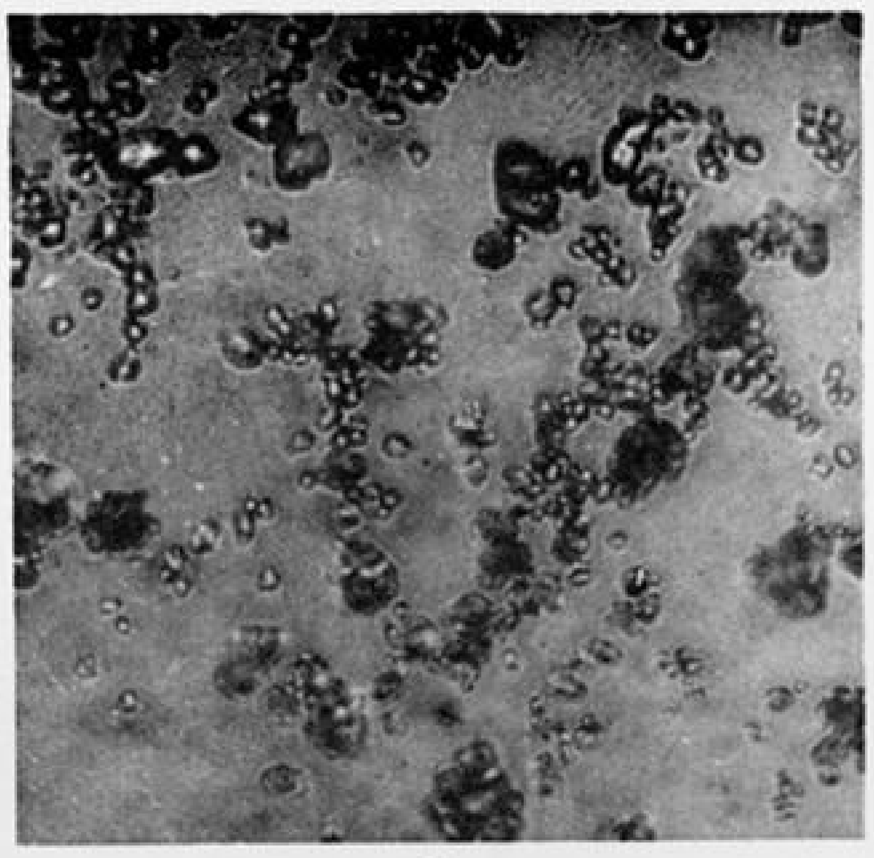
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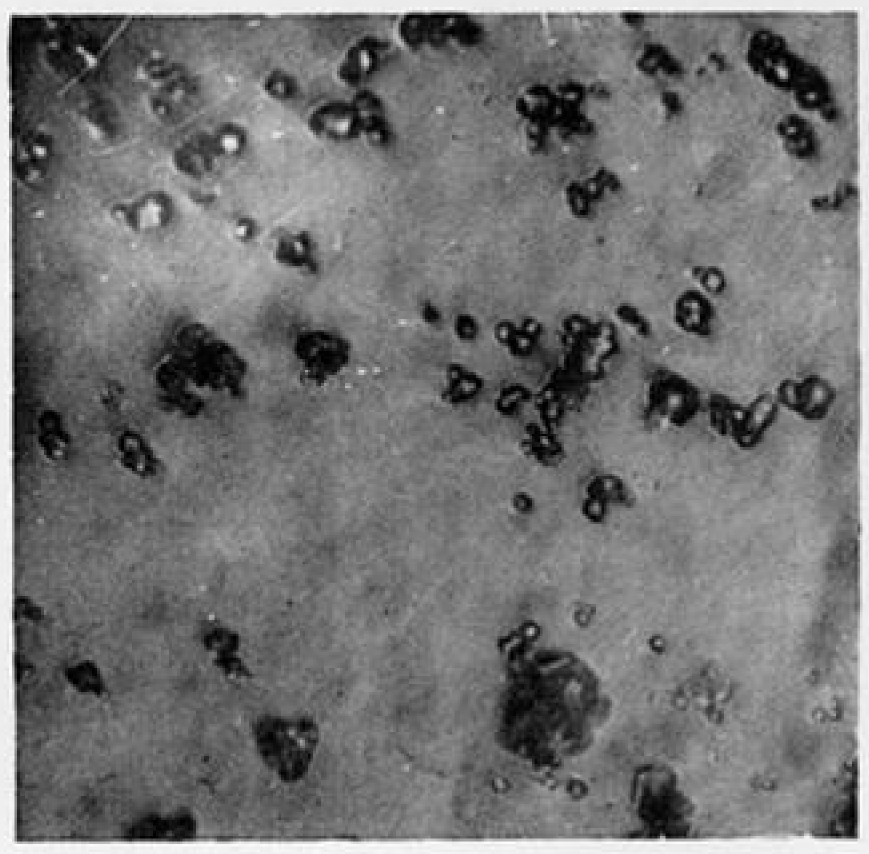
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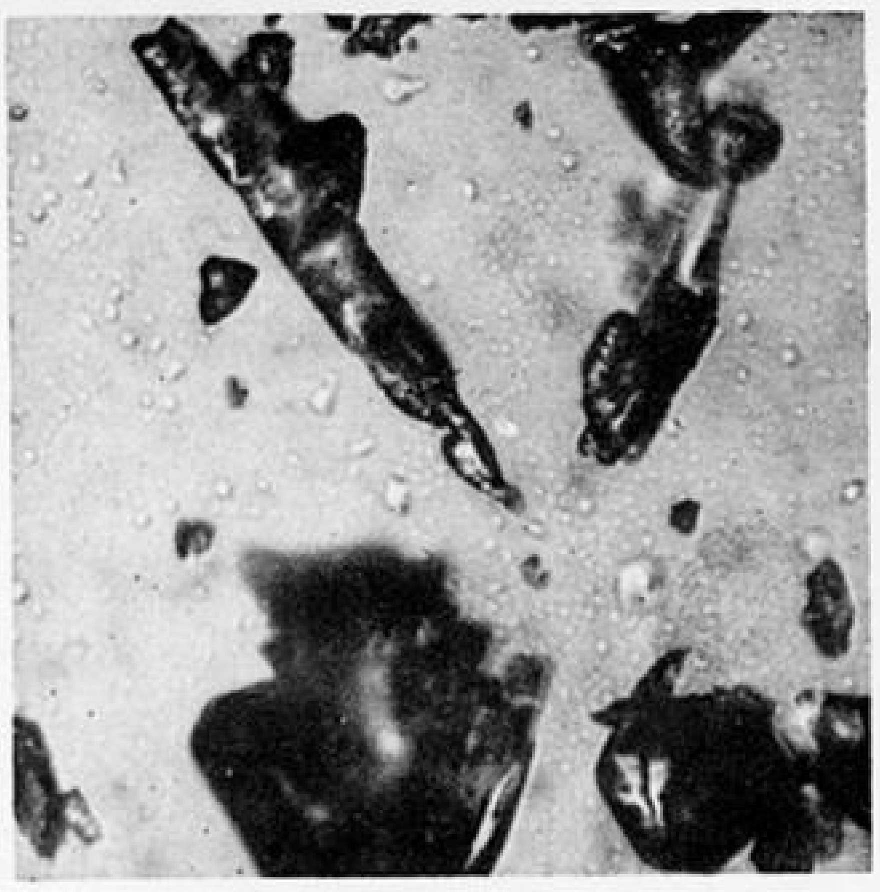
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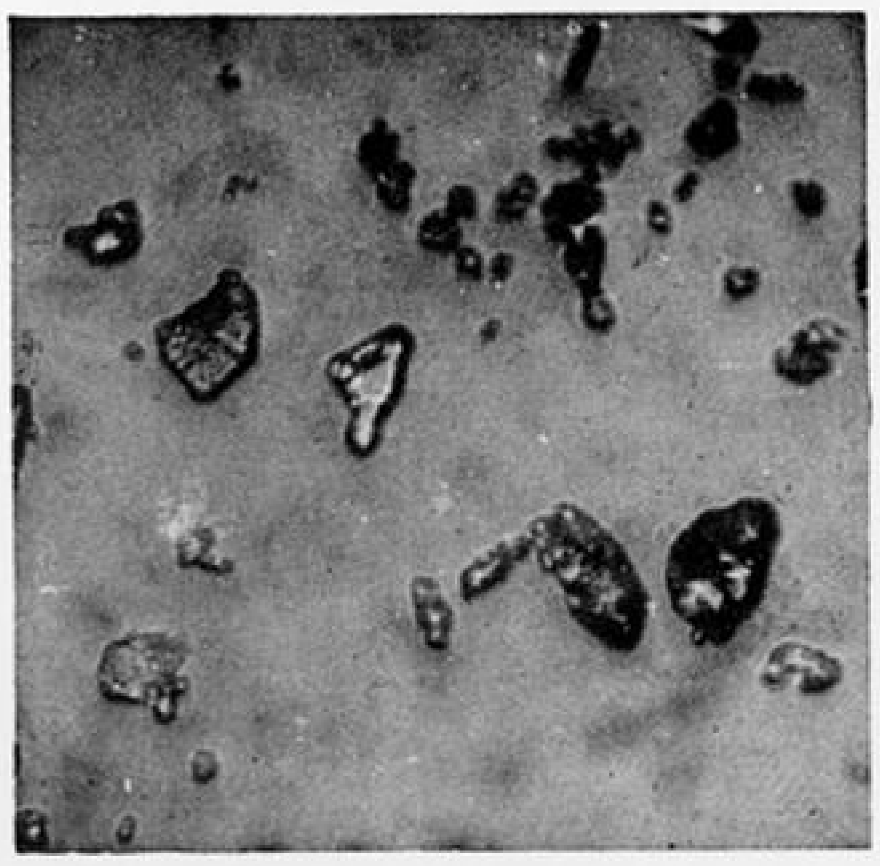
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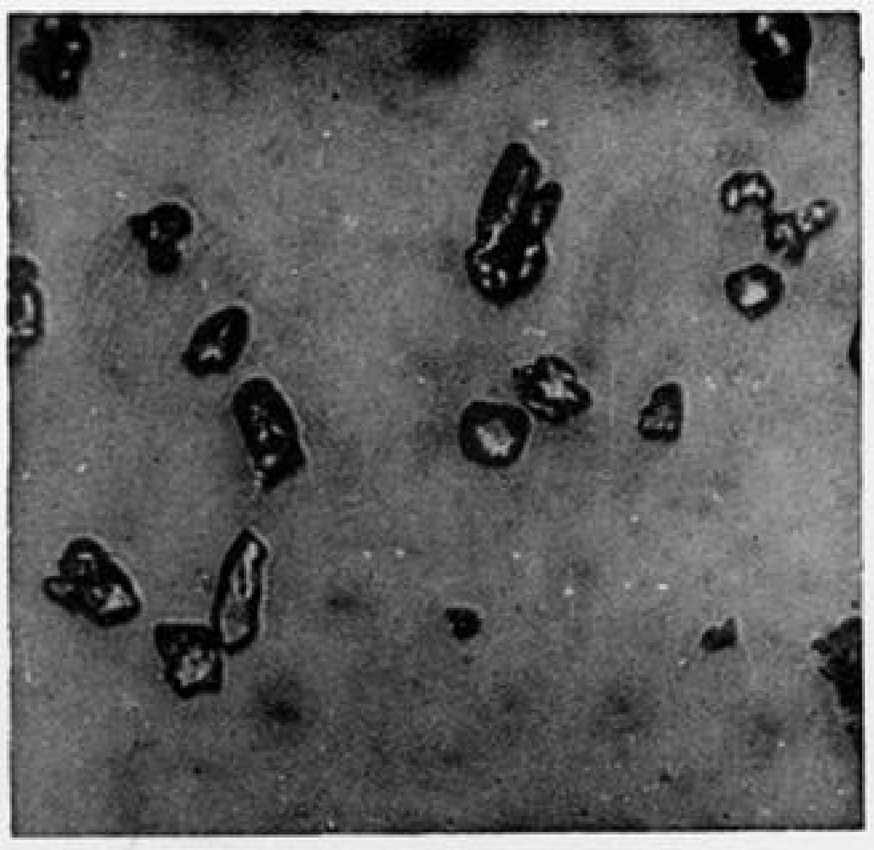
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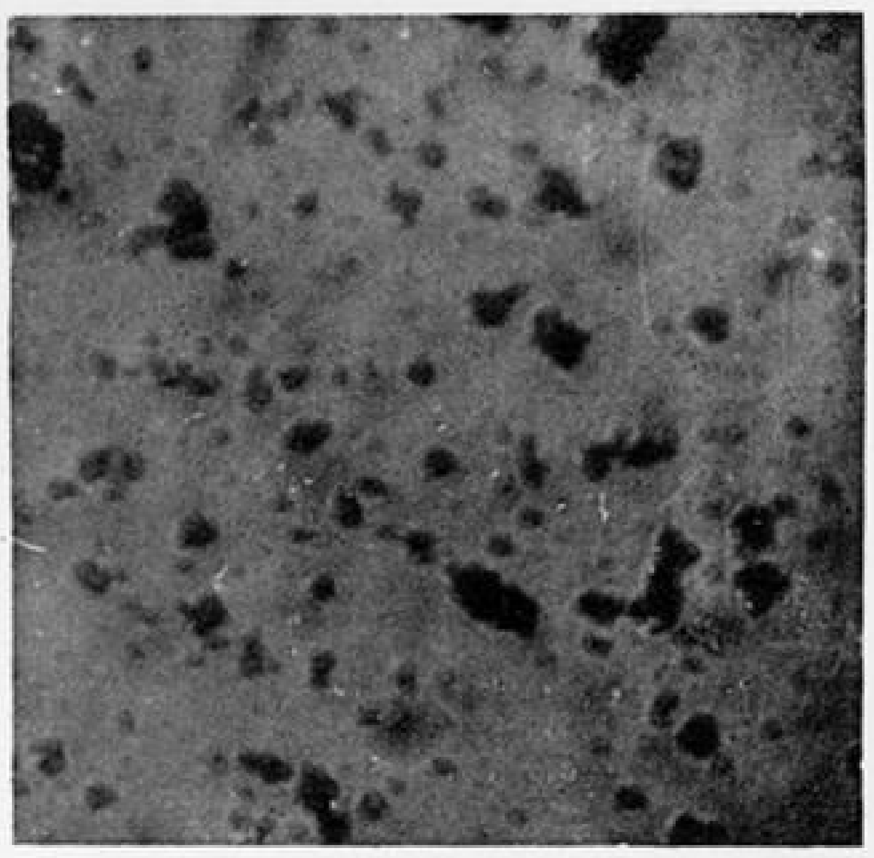
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