

hydrogen flow and sealing the cell produces a sudden sharp change in potential, so that this is also a very valuable criterion.

### Summary

The formation of platinum black demands the presence of some impurity, since purified chloroplatinic acid solutions give only bright electrodeposits.

Catalytic activity for the hydrogen-electrode reaction may be obtained with bright electrodeposits, or evanescently with massive platinum. The prerequisite is a freshly prepared or exposed surface.

Speed of attainment of equilibrium of hydrogen electrodes depends upon removal of oxygen, which is determined by cell design, and by catalytic properties of the electrode. Catalysis by electrodes decreases with exposure to hydrogen, is increased by oxidation, and is much less in alkaline solutions than in acid ones.

Hydrogen-electrode measurements are possible in unbuffered solutions in the neutral range, provided the electrodes are clean. This implies that the platinum has not been deposited in acid solution, that it has not been in contact with acid, and that it is in suitable physical condition.

NEW YORK, N. Y.

---

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WASHINGTON]

## THE INSTABILITY OF PHTHALATE SOLUTIONS TOWARD THE HYDROGEN ELECTRODE

BY CARL Z. DRAVES AND HERMAN V. TARTAR

RECEIVED OCTOBER 16, 1924

PUBLISHED MAY 5, 1925

A difference of opinion has appeared in the literature concerning the stability of phthalate solutions toward the hydrogen electrode. As a result, the confidence of many has been shaken in the use of the phthalate buffer solutions recommended by Clark and Lubs<sup>1</sup> as working standards of hydrogen-ion concentration for the hydrogen electrode. Because of the ease of preparation of pure standard buffer solutions of potassium hydrogen phthalate, a further investigation of this reported instability was undertaken.

Drifting potentials of the hydrogen electrode in phthalate solutions have been observed by Merrill<sup>2</sup> and by Oakes and Salisbury.<sup>3</sup> Indicators were used by the latter to prove that the phthalate buffers actually changed in hydrogen-ion concentration by an amount equivalent to more than one Sørensen unit when they were in contact with the hydrogen electrode for about 48 hours.

<sup>1</sup> (a) Clark and Lubs, *J. Biol. Chem.*, **25**, 479 (1916). (b) Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, 1923, p. 273.

<sup>2</sup> Merrill, *THIS JOURNAL*, **43**, 2690 (1921).

<sup>3</sup> Oakes and Salisbury, *ibid.*, **44**, 948 (1922).

On the other hand, Clark<sup>4</sup> found that even with different kinds of electrodes drifts of potential of less than 1 mv. were observed over a period of 24 hours, a change corresponding to less than 0.017 Sørensen unit. Data substantiating the work of Clark and indicating variations of about the same magnitude were published by Wood and Murdick.<sup>5</sup>

A review of the literature indicates that one variable factor in connection with the instability of phthalate buffer solutions which has not yet been considered is the amount of platinum black on the electrode. Willstätter and Jaquet,<sup>6</sup> have shown that free phthalic acid in glacial acetic acid is easily reduced by hydrogen in the presence of platinum black. The work presented here deals with the question whether or not potassium hydrogen phthalate in dilute aqueous solution suffers appreciable reduction in the presence of the amount of platinum black which adheres to the ordinary electrode.

### Experimental Part

The electromotive force of the following cell was measured in each case: Hg | Hg<sub>2</sub>Cl<sub>2</sub>, KCl (1.0 N) | KCl (1.0 N) | phthalate solution | H<sub>2</sub>. In the table these e.m.f. readings have been corrected to standard pressure of dry hydrogen. For the economy of space, only extreme values of the e.m.f. which show maximum variation from the mean are reported. Sørensen values were calculated from the formula,

$$P_H = \left[ \text{obs. e.m.f.} + \frac{0.05911}{2} \log \frac{760}{x} - 0.2848 \right] / 0.05911$$

The entire cell was kept in a hand-regulated air thermostat at 25 ± 0.1°. A Leeds and Northrup Type K potentiometer and a Weston cell checked against another certified by the Bureau of Standards were employed.

Commercial electrolytic hydrogen was purified by passage through alkaline pyrogallate solution, potassium permanganate and finally water at 25°.

The potassium hydrogen phthalate salt from which the buffer solutions were made was prepared according to the recommendations of Dodge,<sup>7</sup> was recrystallized thrice<sup>8</sup> above 20° and was dried to constant weight at 110–115°.

The hydrogen electrodes were all newly made from bright platinum foil, gauze and wire. The electrodes referred to in the data as "platinized lightly" were cleaned, platinized for one minute and treated as recom-

<sup>4</sup> Clark, *THIS JOURNAL*, **44**, 1072 (1922).

<sup>5</sup> Wood and Murdick, *ibid.*, **44**, 2008 (1922).

<sup>6</sup> Willstätter and Jaquet, *Ber.*, **51**, 767 (1918).

<sup>7</sup> Dodge, *J. Ind. Eng. Chem.*, **7**, 29 (1915).

<sup>8</sup> Hendrixson, *THIS JOURNAL*, **42**, 724 (1920).

<sup>9</sup> Dodge, *ibid.*, **42**, 1655 (1920).

mended by Clark.<sup>1b</sup> Those designated as "platinized heavily" were platinized with alternations of the current for at least 2 hours according to the method of Ellis.<sup>10</sup> The hydrogen electrode vessels contained about 15 cc. of solutions.

TABLE I  
E.M.F. DETERMINATIONS OF THE CELL  
Hg | Hg<sub>2</sub>Cl<sub>2</sub>, KCl (1.0 N) | KCl (1.0 N) | PHTHALATE SOLUTION | H<sub>2</sub>

Expt.	Molar concn. of KHC <sub>8</sub> H <sub>4</sub> O <sub>4</sub>	Electrode type and size (cm.)	Platinized	Time Hrs.	Corr. e.m.f.	pH
1	0.05	Foil, 0.5 × 1	Lightly		0.5198 <sup>a</sup>	3.976
				0.58	.5205	3.99
				1.00	.5199	3.98
				31.20	.5206	3.99
2	.05	Wire, 5 long	Heavily		.5198 <sup>a</sup>	3.976
				2.00	.5199	3.98
				3.00	.5205	3.99
				14.00	.5201	3.98
3	.2	Foil, 1 × 2	Heavily		.5129 <sup>b</sup>	3.86
				0.45	.5121	3.84
				4.58	.5160	3.91
				25.67	.5189	3.96
4	.05	Gauze, 2.5 × 2.5	Heavily		.5198 <sup>a</sup>	3.976
				0.20	.5038	3.70
				4.00	.5668	4.77
				24.67	.6050	5.42
				45.67	.6055	5.43
				46.67	<i>c</i>	
				46.75	.6055	5.43
				47.67	.6057	5.43
5	.2	Gauze, 3 × 12	Heavily		.5129 <sup>b</sup>	3.86
				0.45	.5105	3.82
				3.37	.5181	3.95
				74.25	.5755	
				75	<i>d</i>	
				95	.5920	
				96	<i>e</i>	
				98	.5945	
119	.6010					
123	.6013	5.35				
123	<i>f</i>					
124	.6014	5.36				

<sup>a</sup> Accepted value from Clark, Ref. 1 b, p. 274.

<sup>b</sup> Average value from data of Wood and Murdick (Ref. 5) recalculated for normal calomel electrode.

<sup>c</sup> Gauze replaced by lightly-platinized foil electrode.

<sup>d</sup> Gauze removed and replatinized.

<sup>e</sup> New foil electrode, lightly platinized; gauze left loose in cell.

<sup>f</sup> Second new foil electrode, lightly-platinized; gauze left loose in cell.

<sup>10</sup> Ellis, THIS JOURNAL, 38, 737 (1916).

The data from Expts. 1 and 2 show that with electrodes of lightly-platinized foil and heavily-platinized wire, the reduction of 0.05 *M* phthalate solution during periods of 14 and 31 hours, respectively, was at least not sufficient to affect appreciably the electromotive force of the cell. The variations of less than a millivolt in these experiments corroborate the findings of Clark<sup>4</sup> and of Wood and Murdick.<sup>5</sup> Check colorimetric determinations also showed no observable change of hydrogen-ion concentration during the progress of these experiments.<sup>11</sup>

The increasing electromotive forces of the cells used in Expts. 3 to 5 bring out decidedly the danger of using phthalate solutions with hydrogen electrodes bearing too much platinum black. That the change in potential of the hydrogen electrode was due to an actual change of hydrogen-ion concentration in each buffer was easily shown by colorimetric comparisons with indicators. These results substantiate the conclusions of Oakes and Salisbury<sup>3</sup> that the hydrogen electrode may give drifting potentials with phthalate buffers.

In Expt. 4, complete reduction as evidenced by a nearly constant electromotive force was attained after 26 hours with an especially heavily-blackened gauze in 0.05 *M* phthalate. But with the less heavily-platinized, although larger gauze electrode of Expt. 5, 120 hours was required for the complete reduction of a 0.2 *M* solution. The decrease of hydrogen-ion concentration during this process was equivalent to 1.46 Sørensen units in the former and 1.49 units in the latter solution. When complete reduction had taken place, the e.m.f. held constant for a much longer time after the hydrogen supply had been shut off.

Proof that complete reduction to the hexahydrophthalate had occurred was further established by an examination of the organic acid recovered from the solutions of Expts. 4 and 5 by acidification with hydrochloric acid. The organic acid was washed well with water but was not recrystallized. The dry acid completely melted below 192°. Careful heating produced the anhydride, an oil which was difficult to crystallize without seeding. Crystals of the anhydride melted at about 31.5°. From a study of the properties of maleinoid hexahydrophthalic acid, Baeyer<sup>12</sup> found the melting point of the acid and of the anhydride to be 192° and 32°, respectively. The anhydride of phthalic acid melts<sup>13</sup> at 130.84°.

In conclusion the writers suggest that hexahydrophthalate solutions might serve as very reliable buffers.

<sup>11</sup> The same lot of potassium hydrogen phthalate that was employed in obtaining the data here has since October been repeatedly used by one of the authors and by two graduate students in checking the potentials of several lightly-platinized foil electrodes. In every case only steady electromotive forces have been observed. (March 10, 1925.)

<sup>12</sup> Baeyer, *Ann.*, **258**, 219 (1890).

<sup>13</sup> Monroe, *J. Ind. Eng. Chem.*, **11**, 1118 (1919).

### Summary

1. The instability of phthalate buffer solutions toward the hydrogen electrode has been shown to be dependent upon the relative amount of platinum black on the electrode.

2. Complete reduction of potassium hydrogen phthalate to potassium hexahydrophthalate has been accomplished in aqueous solution, using heavily-platinized, gauze hydrogen electrodes.

3. Hexahydrophthalic acid has been recovered from the completely reduced solution.

SEATTLE, WASHINGTON

---

[CONTRIBUTION FROM THE CHEMICAL AND ZOÖLOGICAL LABORATORIES OF THE  
UNIVERSITY OF CALIFORNIA]

### THE SALT ERROR OF CRESOL RED

BY WILLIAM D. RAMAGE AND ROBERT C. MILLER

RECEIVED OCTOBER 27, 1924

PUBLISHED MAY 5, 1925

Determinations of the hydrogen-ion concentration of sea water or other saline media by colorimetric methods involve a greater or less degree of error, owing to a direct effect of the salt present on the color of the indicator. This effect is independent of the actual change in the Sørensen value ( $P_H$ ) of an unbuffered solution which occurs on the addition of salt.

The effect of the salt is usually to change the color of the indicator slightly toward the alkaline side, so that the apparent Sørensen value of the solution is somewhat greater than the actual value. With a few indicators the effect is in the opposite direction. Kolthoff<sup>1</sup> has claimed that for certain indicators the direction of the error may be reversed at stated concentrations of salt. The causes of the salt effect are obscure, and the nature and degree of the error involved have never been thoroughly investigated.

Without actual determination of the salt error, certain methods of avoiding it have been devised. In the use of standard tubes for sea water, the error is avoided by addition of experimentally determined amounts of salt to the standards. The McClendon standards have been widely used for determinations of the Sørensen value in the range of normal sea water, and Wells<sup>2</sup> has given directions for the preparation of standard tubes for use in brackish waters.

In practice, however, it has often occurred that determinations of the Sørensen values of saline solutions have been made with standards uncompensated for the salt effect. Such results are most useful only when properly corrected for amounts of salt present in the samples. The cor-

<sup>1</sup> Kolthoff, *Rec. trav. chim.*, **41**, 54 (1922).

<sup>2</sup> Wells, *THIS JOURNAL*, **42**, 2160 (1920).