

In the question of activity coefficients the theory here presented leads clearly a step further than the mere application of the principle of the specific interaction. Equation 28 obviously shows that the coefficients of interaction and the salting-out coefficients are correlated by an equation into which the nature of the common ion does not enter. In case an additional inquiry into this matter should prove Equation 28 to be generally valid, it would certainly contribute to the solution of the question of the mechanism of bringing about an effect of electrical interaction between ions, such as was shown in the paper referred to as necessary in order to be able to account for the peculiarities of salt solutions.

Summary

From the point of view that the individualities of salt solutions have an origin similar to that of the individual salting-out effect in the case of non-electrolytes, equations were set up to govern the osmotic and activity functions of uni-univalent salts in pure and mixed solutions.

These equations were found to be strongly supported by the most accurate experimental results including measurements of freezing-point lowerings, electromotive force and solubilities.

Ratios of activity coefficients were calculated on the ground of these equations in conjunction with the principle of the specific interaction of ions.

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THE USE OF PHTHALATE SOLUTIONS FOR HYDROGEN ELECTRODE STANDARDS

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The recent proposals to replace the calomel electrode by phthalate solutions as standard hydrogen electrodes led the present authors to investigate the reliability of such solutions.

A buffer solution of potassium hydrogen phthalate and sodium hydroxide was made up as described by Clark and Lubs.¹ Fifty cc. of 0.2 *M* potassium hydrogen phthalate solution and 45.45 cc. of 0.2 *M* sodium hydroxide were mixed and diluted to 200 cc. with conductivity water. This solution was made up to give a Sørensen value of 6.0 and when tested by indicators this value was obtained.

Using the method described by Beans and Oakes² a quantity of this solution was tested by the hydrogen electrode. Measurements were taken

¹ Clark and Lubs, *J. Biol. Chem.*, **35**, 3, 504 (1916).

² Beans and Oakes, *THIS JOURNAL*, **42**, 2116 (1920).

over a period of 48 hours. During this time there was a continued increase in the observed e.m.f. as shown in Curve 1, Fig. 1. At the end of 48.5 hours the solution, whose original Sørensen value was 6.0 had a Sørensen value of 7.01. A portion of the solution removed from the electrode chamber at the end of 48.5 hours gave a Sørensen value of 7.0 by indicators.

A second solution of approximately 0.2 M potassium hydrogen phthalate was freshly made up with conductivity water and when tested with indicators was found to have a Sørensen value of 3.9. A portion of this solution in the hydrogen electrode chamber gave the results plotted in Curve 3, Fig. 1. Here again the phthalate buffer solution continued to

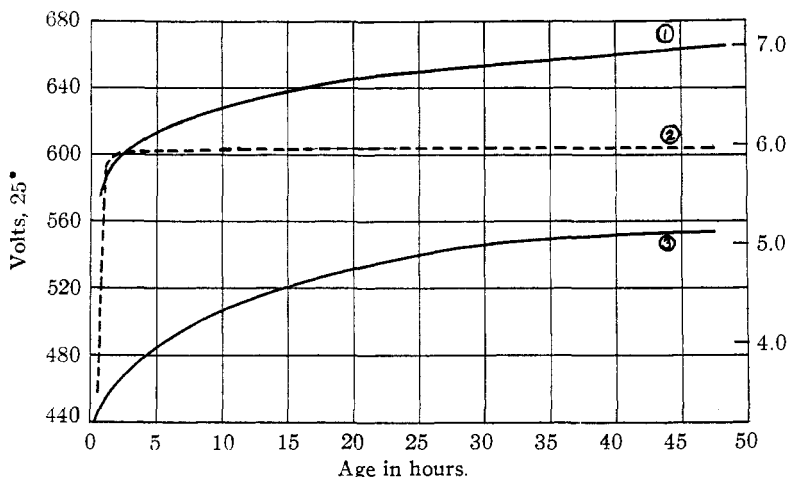


Fig. 1.—Observed e. m. f. change with the time. (1) Potassium hydrogen phthalate and sodium hydroxide. (2) Monopotassium phosphate and sodium hydroxide. (3) Potassium hydrogen phthalate.

increase steadily in voltage during the entire course of the experiment.

As a control on the equipment, method and manipulation, a solution consisting of 50 cc. of 0.2 M monopotassium phosphate and 8.70 cc. of 0.2 M sodium hydroxide diluted to 200 cc. with conductivity water was investigated. This solution was made up to give a Sørensen value of 6.0 and when tested by indicators was found to have a Sørensen value of 6.0.

Since this solution came to a constant voltage after 8 hours the actual values obtained are given in Table I and plotted in Curve 2, Fig. 1.

Time		P_H	Time		P_H
Hrs.	Min.		Hrs.	Min.	
	30	3.52	7	48	5.96
	42	4.96	30	20	5.96
1	7	5.80	47	30	5.96
4	58	5.91			

In these determinations the chain $\text{Hg} \left| \text{HgCl}, \text{KCl}(\text{Sat}) \right| \text{KCl}(\text{Sat}) \left| \text{Buffer Solution} \right| \text{H}_2$ was used in which $e_2 = e_1 -$ observed e.m.f. $e_1 = 0.5266$ volts.³ The Sørensen values were calculated according to the formula $P_{\text{H}} = \frac{-E_2}{0.05916} - \log K$. Assuming α 0.1 M HCl at $25^\circ = 0.92 K$, the equilibrium constant of $2\text{H}^+ \rightleftharpoons \text{H}_2 = 10^{-4.671}$ at 25° .

As a further check on these results, a different sample of pure phthalic anhydride was secured and solutions of the acid phthalate were tested in the manner described above with practically the same results. There was a continuous drift throughout the 48 hours of observation, the Sørensen value of the buffer increasing continuously.

The hydrogen gas was purified by passing it first through alkaline permanganate solution, through alkaline pyrogallate solution, through a cotton plug and finally saturating with water vapor at 25° . The entire cell chain was placed in a water thermostat at $25^\circ \pm 0.02^\circ$.

In preparing our solution of potassium hydrogen phthalate the phthalic acid was first carefully sublimed, then the potassium acid phthalate purified by three recrystallizations. Hendrixson,⁴ has shown that no increase in purification is effected by more than three recrystallizations. In recrystallizing, care was taken not to allow the temperature of the solution to fall below 20° .⁵ The crystals were finally dried to constant weight at 110 – 115° . Upon examination under the microscope all these crystals of acid phthalate were seen to be hexagonal plates with no needle forms present.

Conductivity water was used throughout this work. The hydrogen electrodes were of plate form freshly coated with platinum black and thoroughly cleaned. No corrections were made for changes in barometric pressure, as these corrections were too slight to affect the hydrogen-ion concentrations to an appreciable extent.

It is evident, then, that our most careful purification of these phthalate solutions failed to produce a product that gives a constant Sørensen value with the hydrogen electrode.⁶ That the difficulties encountered are most certainly due to changes in the phthalate solutions and not to the apparatus or manipulation, is shown by the constancy of the results obtained with the same equipment on phosphate solutions and the fact that indicators recorded the same differences as did the hydrogen electrode. Furthermore, the drift is too great to be accounted for by a reduction of any impurity which could be present in only the most minute quantity if at all.

³ Ostwald, *Z. physik. Chem.*, **35**, 333 (1900). Fales and Vosburgh, *THIS JOURNAL*, **40**, 1300 (1918). Fales and Mudge, *ibid.*, **42**, 2434 (1920).

⁴ Hendrixson, *THIS JOURNAL*, **42**, 724 (1920).

⁵ Dodge, *ibid.*, **42**, 1655 (1920).

⁶ Since finishing this investigation A. R. T. Merrill, *ibid.*, **43**, 2688 (1921) in her work on cystine makes the statement: "The acetic acid-sodium acetate mixtures of Walpole were used in place of the potassium hydrogen phthalate solutions recommended by Clark and Lubs as the latter gave a decided drift when determining the hydrogen-ion concentration by the electrometric method, due possibly to reduction occurring." We have had three private communications from other workers who have experienced similar difficulty with phthalate solutions.

There is, of course, a slight possibility that even a minute trace of impurity might catalyze the reduction of the phthalate. Even if this is the case, it is clear that the most careful methods of purification fail to remove this catalyst and the use of phthalates for hydrogen electrode measurements would be justified only after carefully testing them for freedom from change under continued use.

The authors are indebted to Dr. F. D. Dodge for his kindness in testing the purity of our potassium hydrogen phthalate. Dr. Dodge reported that after carefully examining the products we had purified for both the initial and check experiments, he could detect no impurities and the two samples were identical in being pure potassium hydrogen phthalate.

Summary

1. The most carefully purified phthalate solutions gave a progressive decrease in hydrogen-ion concentration when in continued contact with the hydrogen electrode.

2. This decrease in hydrogen-ion concentration is due to changes in the phthalate itself, probably a reduction reaction.

3. If impurities are responsible for the changes noted, their action must be that of catalysts in the reduction of the phthalate, as they could not possibly be present in sufficient quantity to account for the entire change by themselves.

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RHYTHMIC DEPOSITION OF PRECIPITATED VAPORS

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The phenomenon of rhythmic or periodic precipitation and allied phenomena has received considerable attention since Liesegang¹ recorded his observations of it, now referred to frequently as Liesegang's rings or phenomenon. A common illustration of this is the rhythmic precipitation of silver chromate in concentric rings, when a crystal of silver nitrate is placed upon a gelatin film containing some dichromate. The phenomenon may be of importance in geology and is of great importance in biology,² where striae so frequently encountered, may be recalled. For example the structure causing iridescence in mother-of-pearl³ may be referable to this phenomenon as well as that in various insects and beetles

¹ Liesegang, "Chemischer Vorgänge in Gallerten," Leipzig, 1898.

² Liesegang, *Naturw. Wochenschr.*, **41** (1910). Bechhold, "Die Kolloide in Biologie und Medizin," Steinkopff, Leipzig, 1920.

³ Pfund [*J. Franklin Inst.*, **183**, 453 (1917)] has recently made a study of the color and structure of mother-of-pearl, concluding that no simple periodic condition of environment can account for it. For further illustration see Bechhold, Ref. 2.