

point found to be  $43.1^{\circ}$ ; the compound  $\text{AgClO}_4 \cdot \text{C}_6\text{H}_6$  has also been isolated and its transition point found to be  $145^{\circ}$ .

4. The ternary system, silver perchlorate-water-benzene is marked by the possession of 6 realizable invariant equilibria, and a large number of monovariant equilibria, affording at least one example of every type of equilibrium theoretically possible for a ternary system containing volatile components.

5. The ternary eutectic representing 3 solid phases, solution and vapor is at  $-58.4^{\circ}$ ; the eutectic of highest temperature is at  $42.1^{\circ}$ . The course of the 24 monovariant equilibria originating at these 2 quintuple points and the 4 intermediate quintuple points has been studied.

6. Isothermal diagrams have been constructed to show the various equilibria existing at temperatures between  $-58.4^{\circ}$  and  $+145^{\circ}$ .

7. Between  $5.24^{\circ}$  and  $22.4^{\circ}$ , 3 coexistent liquid phases can be prepared in stable equilibrium with each other and their vapor. The occurrence of two separate fields of unsaturated solution is explained as due to the intersection of the solubility curve of silver perchlorate with the binodal curve representing the limited solubility of benzene and water. The occurrence of a third field is explained as due to the existence, between  $-2.7^{\circ}$  and  $+30^{\circ}$  (approximately), of an additional closed binodal curve, which does not extend to any one of the 2-component axes at any temperature. It appears to be the first demonstrated case of a closed binodal curve.

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## A SIMPLE METHOD OF ELECTROMETRIC TITRATION IN ACIDIMETRY AND ALKALIMETRY

BY PAUL FRANCIS SHARP WITH F. H. MACDOUGALL

Received November 29, 1921

The object of the investigation reported in this paper was to find a number of constant and reproducible electrodes which would be electromotively equivalent to hydrogen electrodes dipping in solutions of various known concentrations of hydrogen ion. The usefulness of such electrodes will be at once apparent. If, for example, it becomes necessary to titrate an unknown acid solution to an end-point which shall be a definite hydrogen-ion concentration, the half-cell containing a hydrogen electrode and the unknown solution is connected with one of our electrodes and alkali is run into the unknown solution until a galvanometer indicates a zero e.m.f. The method is applicable especially to all cases in which the titration is carried to a definite hydrogen-ion concentration, or more generally to all cases in which the correct potential difference at the electrode in the solution at the end of the titration is known in advance.

After we had practically completed our investigation, we found that Pinkhof<sup>1</sup> had constructed various cadmium electrodes with the same purpose in mind. His electrodes cover the range of hydrogen-ion concentrations from  $10^{-6}$  to  $10^{-10}$ . His results are reproduced in Table I. He used electrodes which were 11-13% cadmium amalgam.

TABLE I  
EXPERIMENTS OF PINKHOF

Composition of electrode solution		Potential against 0.1 N KCl calomel electrode	Equivalent to a hydrogen electrode in a solution of hydrogen-ion concentration
Salt	N		
Cd(NO <sub>3</sub> ) <sub>2</sub> .....	1.3	0.696	$10^{-8}$
CdCl <sub>2</sub> .....	0.1	0.754	$10^{-7}$
CdI <sub>2</sub> .....	0.1	0.812	$10^{-8}$
KI.....	0.21		
CdI <sub>2</sub> .....	0.01	0.870	$10^{-9}$
KI.....	0.6		
CdI <sub>2</sub> .....	0.01	0.929	$10^{-10}$
KI.....	1.05		

After investigating a large number of electrodes, we also found that the cadmium electrodes were the ones best adapted for the range  $10^{-6}$  to  $10^{-10}$ . As our measurements were made with apparently greater accuracy, and as, in addition, we found suitable lead electrodes for the range of  $10^{-4}$  to  $10^{-6}$ , we feel that it would be desirable to make our results available.

The reference electrode used in standardizing our half-cells was the N potassium chloride calomel electrode recommended by Lewis, Brighton, and Sebastian,<sup>2</sup> who give 0.2828 volt at 25° as the e.m.f. of the combination: H<sub>2</sub>(1 atm.), H<sup>+</sup>(M) || KCl(0.1 M), KCl(M), HgCl, Hg.

The results given in Table II are the average of all of a number of determinations, the comparisons being made against at least 4 different calomel cells. None of the determinations differed from the averages given in the table by more than 0.0002 volt. All measurements were made with cells immersed in a water-bath kept at a temperature of 25° ± 0.01°.

The mercury used in this work was purified by spraying it several times into dil. nitric acid and then distilling it under reduced pressure. The amalgams were 12 to 12.5% of lead or cadmium. They were prepared by heating the weighed materials until solution was complete and then filtering the liquid while hot through a filter paper with a pinhole in it. The calomel for the reference electrodes was prepared by electrolysis of approximately 2 N hydrochloric acid, using a rotating mercury anode and a small platinum wire cathode.<sup>3</sup>

<sup>1</sup> Pinkhof, *Chem. Weekblad*, **16**, 1168 (1919).

<sup>2</sup> Lewis, Brighton, and Sebastian, *THIS JOURNAL*, **39**, 2245 (1917).

<sup>3</sup> Lipscomb and Hulett, *ibid.*, **38**, 20 (1916). Hulett, *Phys. Rev.*, **22**, 47 (1906). Wolf and Waters, *Bur. Standards Reprint No. 70* (1907).

Calomel prepared by this method was compared with calomel obtained by precipitation, but no differences greater than 0.0002 volt were detected in cells using the two kinds of calomel.

The potassium chloride was of c.p. grade and was recrystallized several times, although no difference was detected between the cells made with the recrystallized material and those made with the c.p. salt. Lead iodide was prepared from c.p. lead acetate and potassium iodide and washed by decantation. Two different samples of cadmium sulfate and 3 different samples of potassium iodide, all of c.p. grade, were compared and found to give identical results within the limits of the experimental errors.

All salts used were dried at 500° for several hours and preserved in tightly stoppered bottles.

To simplify the preparation of the electrode solutions, Col. 1 of Table II gives the number of cubic centimeters of stock solutions of 0.5 *N* cadmium sulfate and 2.0 *N* potassium iodide which on dilution to a total volume of 100 cc. will give an electrode solution of the proper concentration.

As several of the common proteins have their iso-electric point near a hydrogen-ion concentration of  $10^{-4.7}$ , an electrode was constructed corresponding to this concentration.

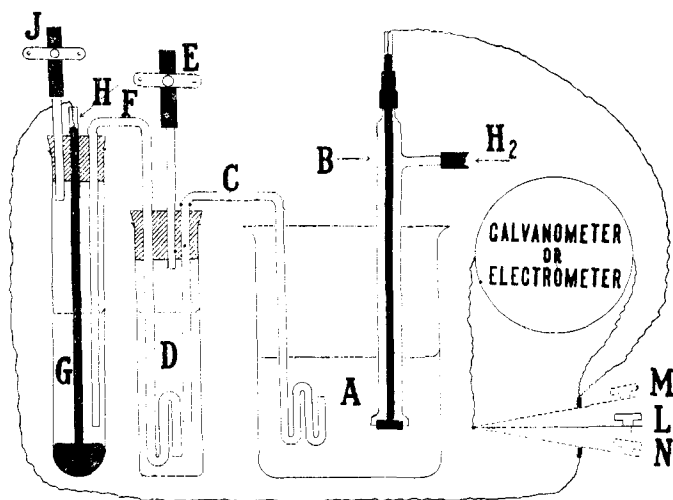
TABLE II  
EXPERIMENTAL DATA

Electrode solution Dilute quantities given to total volume of 100 cc.		Potential against normal calomel electrode	Calculated potential of hydrogen electrode in solutions of indicated hydrogen-ion concentration	
12-12.5% Lead amalgam and lead iodide				
Cc.	<i>N</i>	Salt		
0.52	2	KI	0.5195	0.5194 $10^{-4}$
2.90	2	KI	0.5609	0.5608 $10^{-4.7}$
6.14	2	KI	0.5786	0.5786 $10^{-5}$
67.50	2	KI	0.6378	0.6377 $10^{-6}$
12-12.5% Cadmium amalgam				
100.00	0.5	CdSO <sub>4</sub>	0.6967	0.6968 $10^{-7}$
0.20	2.0	KI		
10.00	0.5	CdSO <sub>4</sub>	0.7560	0.7560 $10^{-8}$
10.14	2.0	KI		
100.00	0.5	CdSO <sub>4</sub>	0.8150	0.8151 $10^{-9}$
26.40	2.0	KI		
2.00	0.5	CdSO <sub>4</sub>	0.8742	0.8743 $10^{-10}$
48.70	2.0	KI		

### Experimental Arrangements

The apparatus and method of use are indicated in Fig. 1. It may be sufficient to state that B is a dipping hydrogen electrode of the Hildebrand<sup>4</sup> type. Siphon C and Vessel D contain saturated potassium chloride. The liquid to be titrated is placed in the beaker A. Siphon F and vessel G contain the electrode solution. Through mercury in the glass

<sup>4</sup> Hildebrand, THIS JOURNAL, 35, 847 (1913).



tube H, connection is made by means of a platinum wire with the lead or cadmium amalgam at the bottom of the electrode vessel G.

### Summary

Employing electrodes of lead amalgam and of cadmium amalgam, the authors have prepared a series of half-cells which are electromotively equivalent to hydrogen electrodes in contact with solutions in which the hydrogen-ion concentrations are, respectively,  $10^{-4}$ ,  $10^{-4.7}$ ,  $10^{-5}$ ,  $10^{-6}$ ,  $10^{-7}$ ,  $10^{-8}$ ,  $10^{-9}$ ,  $10^{-10}$ .

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

## MEASUREMENT OF SOLUBILITY BY FLOATING EQUILIBRIUM. THE SOLUBILITY OF LEAD ACETATE

BY MERLE L. DUNDON AND W. E. HENDERSON

Received December 5, 1921

### Introduction

It has been shown by Richards and Shipley<sup>1</sup> that a small glass float of suitable size and shape, completely immersed in a liquid, is sensitive to very small changes in the density of that liquid. They have applied this principle to the quantitative analysis of solutions and to the calibration of thermometers.

Lamb and Lee<sup>2</sup> have by a slightly different procedure measured the density of various solutions with an accuracy of one part in the seventh

<sup>1</sup> Richards and Shipley, *THIS JOURNAL*, **34**, 599 (1912); **36**, 1 (1914).

<sup>2</sup> Lamb and Lee, *ibid.*, **35**, 1666 (1913).