

Table II gives the density differences between ordinary and heavy water for some even temperatures between the freezing point of heavy water and 50°, including a value at its density maximum and some in the neighborhood of the maximum difference. The density values of heavy water given in the third column agree with those of Stokland, Ronaess and Tronstad within ± 0.00007 g./ml. in the temperature range of their measurement.

Furthermore, the ratio of the densities of ordinary and heavy water, namely, d_{D_2O}/d_{H_2O} , also

increases by diminishing amount with increasing temperature. Since the ratio becomes 1 at 370°, it must also pass through a maximum. This maximum ratio lies, however, beyond the temperature range of this investigation.

Summary

The density of heavy water is measured with a quartz pycnometer between its freezing point and 50°. The differences between the densities of ordinary and heavy water show a maximum at 40°.

KUNMING, CHINA

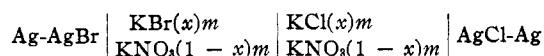
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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Elimination of Liquid Junction Potentials. III. Comparison of the Silver-Silver Chloride and Silver-Silver Bromide Electrodes at 25°

BY BENTON BROOKS OWEN AND EDWARD J. KING

As a further test of a method proposed^{1,2} for eliminating liquid junction potentials by extrapolation, the standard potentials of the silver-silver chloride and silver-silver bromide electrodes were compared by means of the cell



The electromotive force of this cell may be expressed by the equation

$$E = E^0 - k \log a_{\text{Cl}}/a_{\text{Br}} \approx E_j \quad (1)$$

where $k = 0.00019844 T$, and E_j is the unknown liquid junction potential. Keeping m constant, and varying x so that $m_{\text{Br}} = m_{\text{Cl}}$, this equation may be written

$$E = E^0 - k \log \gamma_{\text{Cl}}/\gamma_{\text{Br}} \approx E_j \quad (2)$$

In the limit, when $x = 0$, E_j must also be zero. Furthermore the term containing the activity coefficient ratio assumes thermodynamic significance under this condition, and should vary linearly with the ionic strength in dilute solutions. Consequently a value of $E_{x=0}$, obtained by extrapolation against x at constant m , differs from E^0 only by the term $[k \log \gamma_{\text{Cl}}/\gamma_{\text{Br}}]_{x=0}$ which is proportional to m . E^0 is determined by extrapolation of $E_{x=0}$ against m .

Materials and Technique.—The stock solutions of potassium chloride and nitrate were prepared from the purified salts described in the first

paper in this series.¹ The potassium bromide was some of sample B used by Owen and Foering,³ and their materials were also used in the preparation of the electrodes. The experimental procedure was similar to that outlined previously,¹ but the cells were rebuilt to eliminate the intermediate "salt bridge" of potassium nitrate. All measurements were made in duplicate. The average difference between duplicate cell readings was 0.03 m. v., and the maximum was 0.07 m. v. The electromotive forces would remain constant within these limits for a day or more.

Experimental Results and Discussion

The observed electromotive forces for $m = 0.05$ and 0.03 at 25° are plotted in Fig. 1. Each circle represents the average reading of duplicate cells. The total variation of E with x is so small that the scale of the plot is large enough to permit reading off E to 0.01 m. v. A table of data is therefore omitted. The values of $E_{x=0}$ obtained by extrapolation are 0.15128 at $m = 0.05$, and 0.15117 at $m = 0.03$. Upon the assumption that $E_{x=0}$ varies linearly^{1,2} with m , these results lead to $E^0 = 0.15100$. Since E^0 for the cell is the difference between the standard potentials of the silver-silver bromide and silver-silver chloride electrodes, it may be computed from the values obtained for these electrodes from cells without liquid junctions. The standard potential of the

(1) Owen, *THIS JOURNAL*, **60**, 2229 (1938).

(2) Owen and Brinkley, *ibid.*, **60**, 2233 (1938).

(3) Owen and Foering, *ibid.*, **58**, 1575 (1936).

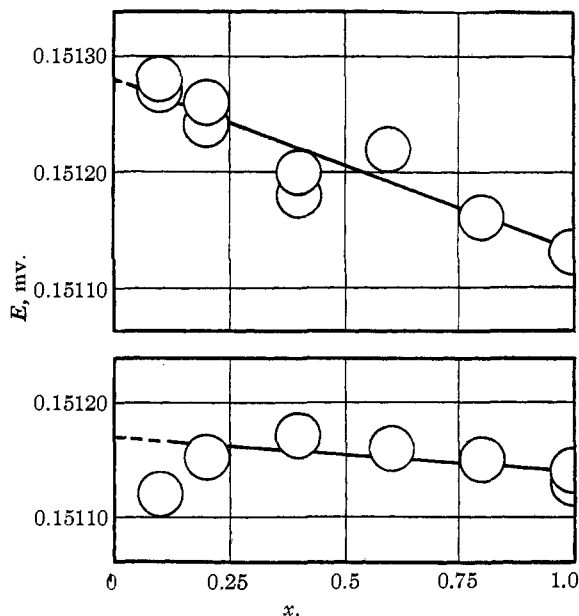


Fig. 1.—Elimination of liquid junction potentials by extrapolation of the observed electromotive forces to $x = 0$: upper plot, $m = 0.05$; lower plot, $m = 0.03$. The radii of the circles are 0.02 mv.

silver-silver chloride electrode at 25° is -0.22239 , according to equation (7) of Harned and Ehlers.⁴ The standard potential of the silver-silver bromide electrode at this temperature is given as -0.07131 by equation (5) of Harned and Donelson,⁵ and -0.07134 by equation (2) of Owen and Foering.³ These values lead to 0.15108 and 0.15105, respectively, for E^0 , in excellent agreement with the value 0.15100 obtained from the cells with liquid junctions. This indicates that liquid junction potentials can be eliminated by extrapolation, if the two electrolyte systems are highly symmetrical, and the ionic strength does not exceed 0.05.

We have not had occasion to determine whether the method is applicable to more unsymmetrical systems, such as might be encountered in studies

(4) Harned and Ehlers, *THIS JOURNAL*, **55**, 2179 (1933).

(5) Harned and Donelson, *ibid.*, **59**, 1280 (1937).

of polyvalent ions, but we have evidence that it may give unreliable results for concentrated solutions. Attempts to extend the present measurements up to $m = 0.5$ and $m = 1.0$ failed to yield useful results. The discordance between duplicate cell readings, and the variations of electromotive forces throughout the course of the measurements sometimes exceeded the total variation of E with x . Under these conditions extrapolation was impossible. Because of the large quantities involved, the salts used at these higher concentrations were from a different source than those which led to the results plotted in Fig. 1, but they were all supposedly high grade commercial samples, recrystallized once. The potassium nitrate remained clear upon addition of silver nitrate. The potassium chloride was shown to be freed from bromide by the fuchsin test.⁶ We have no satisfactory explanation of this failure at high concentrations, but record it as a warning that the method should not be used for ionic strengths above 0.05 without further investigation.

Summary

The standard potentials of the silver-silver bromide and silver-silver chloride electrodes were compared in cells with liquid junctions at 25° . The difference between these potentials was found to be 0.15100 v., in good agreement with the corresponding values 0.15108 and 0.15105 obtained from cells without liquid junctions.

Taken in conjunction with the results of the preceding studies in this series,^{1,2} this is good evidence that the method used in eliminating liquid junction potentials is fundamentally sound, but it is pointed out that experimental difficulties may be encountered if the ionic strength is too high.

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(6) Snell and Snell, "Colorimetric Methods of Analysis," Vol. I, D. Van Nostrand Co., New York, N. Y., 1936, p. 546.