urements, we consider the values given in Table II to be the best available at this time.

Summary

1. A simple and reliable procedure has been described whereby the quinhydrone electrode may be used in cells without liquid junction, employing vacuum technique.

2. The reproducibility of the quinhydrone electrode in 0.01 M hydrochloric acid solution has been carefully studied, employing the cell Pt/quinhydrone, HCl (0.01 M)/AgCl/Ag. The electromotive force of this cell has been found to be reproducible to within a tenth of a millivolt from 0 to 40°, although side reactions destroy the equilibrium after a short time at temperatures above 30°.

3. Values have been obtained from 0 to 40° for the potential of the above cell and the normal potentials of that cell and the cell, Pt/quinhydrone, HCl/H_2, with an accuracy of ± 0.1 mv. from 0 to 25° and ± 0.15 mv. from 30 to 40°.

NEW HAVEN, CONNECTICUT

RECEIVED AUGUST 19, 1933
PUBLISHED DECEMBER 14, 1933

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY, STATE COLLEGE OF WASHINGTON]

The Activity Coefficients and Transference Numbers of Potassium Iodide[1]

BY RALPH W. GELBACH

Electromotive forces of concentration cells, with and without ion transfer, have been measured at 25 ± 0.02°. The following types of cells have been measured.

(A) $KHg_x \mid KI\ m_1, AgI \mid Ag—Ag \mid AgI, KI\ m_2 \mid KHg_x$
(B) $KHg_x \mid KI\ m_1 \mid KI\ m_2 \mid KHg_x$
(C) $Ag \mid AgI, KI\ m_1 \mid KI\ m_2, AgI \mid Ag$

Materials, Apparatus and Method.—Chemically pure potassium iodide was thrice recrystallized from distilled water and dried in an air-bath at about 80°. Solutions were made from weighed portions of the salt by adding a definite quantity of conductivity water and boiling for a definite time on an electric hot plate. The hot solutions were saturated with hydrogen by permitting the gas to bubble through them for several minutes, then finally cooled to room temperature under an atmosphere of hydrogen. By standardization of operations it was easily possible to control concentrations within 0.2%.

---

(1) A portion of the data was obtained by Helen Marburger Fredell as a partial fulfilment for the Master's Degree.

The mercury used for making the amalgams was purified as previously described.[2]

The amalgam was prepared by electrolyzing a solution of chemically pure potassium hydroxide. The concentration of potassium was about 0.1%.

The apparatus was the same as used previously.[3]

The silver iodide electrodes were prepared in a manner similar to the preparation of the silver bromide electrodes.[3] These deviated among themselves by not more than 0.03 millivolt.

In Table I are given the electromotive forces of the concentration cells with and without liquid junction. The value given in each case is the mean of at least two separate sets of readings. Due to instabilities of the system the accuracy of duplication is less than desired, the maximum deviation in some cases being slightly in excess of 0.5%.

TABLE I

m_1	m_2	E_A, volt	$E_{comp.}$, volt	ΔE, mv.	E_B, volt	F_C, volt	$E_{comp.}$, volt	ΔE, mv.
0.002	0.020	0.11153	0.1137	2.2	0.05585	0.05552	0.05623	0.71
.005	.050	.11083	.1118	1.0	.05492	.05523	.05537	.14
.010	.050	.07622	.0777	1.5	.03800	.03671	.03821	.60
.010	.100	.10925	.1105	1.3	.05524	.05414	.05448	.34
.020	.100	.07653	.0767	0.2	.03879	.03769	.03770	.01
.020	.200	.10872	.1092	.5	.05512	.05365	.05363	− .02
.050	.500	.10817	.1082	.0	.05514	.05322	.05319	− .03
.050[a]	.500	.1087	.1082	.5				
.100[a]	1.000	.1091	.1091	.0				
.200[a]	2.000	.1125	.1125	.0				

[a] Data from Harned and Douglas.

Activity coefficients were calculated in a manner similar to that used by Scatchard.[4] In consequence of the measurements having been made on concentration cells only an arbitrary value of 2 volts was assumed for the electromotive force of the cell KHg_x/KI 0.01 m, AgI/Ag. On this basis values of E_0' have been calculated.

In very dilute solution $E_0 - E_0' = -0.05915\sqrt{m}$ which upon differentiation with respect to $\sqrt{m}$ gives a slope at zero concentration of 0.05915. By plotting the values of E_0' against $\sqrt{m}$ and extending the curve to infinite dilution so that the slope at the intercept of the zero axis was 0.05915 the value of E_0 was found to be 1.7591 volts. The activity coefficients calculated from the equation

$$E_0' = E + 0.1183 \log m = E_0 - 0.1183 \log \gamma \qquad (1)$$

are shown in column 4 of Table II.

---

(2) Pearce and Gelbach, *J. Phys. Chem.*, **29**, 1023 (1925).

(3) Gelbach and Huppke, THIS JOURNAL, **48**, 1504 (1926).

(4) Scatchard, *ibid.*, **47**, 641 (1925).

TABLE II

m	E	E_0'	γ	$\gamma_{\text{calcd.}}$	$\gamma_{\text{H\&D}}$	N_K
0.002	2.07881	1.75952	0.992	0.952		0.4983
.005	2.03461	1.76240	.938	.928		.4979
.010	2.00000	1.76340	.920	.903		.4974
.020	1.96728	1.76629	.869	.872		.4968
.050	1.92378	1.76987	.810	.820		.4954
.100	1.89075	1.77245	.772	.775	0.775	.4940
.200	1.85856	1.77587	.721	.719		.4917
.300	1.8386	1.7768	.709	.703	.715	
.500	1.81561	1.7800	.666	.674		.4878
.500[a]	1.8150	1.7796	.674	.674	.678	
1.000[a]	1.7816	1.7716	.645	.648	.649	
2.000[a]	1.7461	1.7817	.644	.651	.646?	

[a] These voltages are from "corrected" electromotive force data of Harned and Douglas, THIS JOURNAL, **48**, 3095 (1926).

The Debye–Hückel constants were evaluated by substituting in the equation

$$\log \gamma = \frac{-0.354\sqrt{2m}}{1 + N\sqrt{2m}} + P\,(2m) \tag{2}$$

values of γ at several concentrations. A graphic solution of this system of equations yielded approximate values of N and P which were used as first approximations in the equation

$$E_2 - E_1 = \frac{4.605\,RT}{F}\left[\frac{0.354\sqrt{2m_1}}{1 + N\sqrt{2m_1}} - \frac{0.354\sqrt{2m_2}}{1 + N\sqrt{2m_2}} + 2P\,(m_2 - m_1) + \log\frac{m_2}{m_1}\right] \tag{3}$$

In a manner similar to that of Jones and Dole[5] N and P were determined to be, respectively, 0.866 and 0.0182. Observed and computed electromotive forces for cells without transference are shown in columns 3 and 4 of Table I. The agreement is satisfactory in concentrations greater than 0.01 molal but at higher dilutions the deviation becomes as large as 2%, which, in all probability, is largely due to difficulties encountered with the amalgam electrodes.

The activity coefficients calculated from equation (2) which are shown in column 5 of Table II are considered to be more accurate than those determined by the extrapolation method because of the unreliability of data obtained with amalgam electrodes in dilute solution. These values also correlate much better those given by Harned and Douglas (*loc. cit.*).

Transference numbers were calculated from the equation of Jones and Dole,[5] $t = A/(1 + B\sqrt{m})$. The equation for the electromotive force, E_t, of the cell, type C, was employed for the evaluation of the constants A and B. Substituting $A = 1.4990$ and $B = 0.0106$, the computed values of E_t show very good agreement with the observed voltages. Referring to columns 8 and 9, it is to be noted that agreement here is much better

---

(5) Jones and Dole, THIS JOURNAL, **51**, 1073 (1929).

$$
\begin{aligned}
E_t = \frac{2RT}{F}\Bigg[&(1 - A)\ln\frac{m_2}{m_1} + A\ln\frac{1 + B\sqrt{m_2}}{1 + B\sqrt{m_1}} + \left[\frac{0.8152}{N} + \frac{1.153\,A}{B - N\sqrt{2}}\right] \times \\
&\left[\frac{1}{1 + N\sqrt{2m_2}} - \frac{1}{1 + N\sqrt{2m_1}}\right] + \frac{1.153\,AB}{(B - N\sqrt{2})^2}\Bigg[\ln\frac{1 + B\sqrt{m_2}}{1 + B\sqrt{m_1}} + \ln \\
&\frac{1 + N\sqrt{2m_2}}{1 + N\sqrt{2m_1}}\Bigg] + 4.6052\,P(m_2 - m_1) - \frac{9.2103\,AP}{B^2}\Bigg[B\sqrt{m_2} - B\sqrt{m_1} - \ln \\
&\frac{1 + B\sqrt{m_2}}{1 + B\sqrt{m_1}}\Bigg]\Bigg] \qquad (4)
\end{aligned}
$$

than in the case of the amalgam electrodes. Even though errors are rather large in higher dilutions, the constants are sufficiently well defined to render transference numbers accurate beyond the third decimal place as they were formerly expressed.

Summary

1. The electromotive forces of concentration cells of potassium iodide have been measured.

2. The Debye–Hückel constants have been determined for potassium iodide and the activity coefficients have been calculated.

3. Transference numbers have been accurately determined.

PULLMAN, WASHINGTON RECEIVED AUGUST 21, 1933
PUBLISHED DECEMBER 14, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

Intermediate States of Reduction of Chromic Acid[1]

BY T. R. BALL AND KEITH D. CRANE

Weinland and his co-workers[2] have prepared several double salts of pentavalent chromium oxychloride, $CrOCl_3$, with the chlorides of the alkali metals and with the hydrochlorides of organic bases.[3] Olsson[4] has repeated this work and also prepared a double fluoride of CrO_2F with potassium fluoride. A search of the literature has failed to reveal the isolation of any other pentavalent chromium compounds. However, a number of authors have postulated the intermediate formation of penta- and tetravalent chromium in the reduction of chromic acid.[5] This has

---

[1] This work was made possible by assistance to the senior author from a grant made by the Rockefeller Foundation to Washington University for research in science.

[2] Weinland, *Ber.*, **37**, 3784 (1905); Weinland and Fiederer, *ibid.*, **39**, 4042 (1906); **40**, 2090 (1907).

[3] Weinland and Beck, "Darstellung anorganischer Präparate," J. C. B. Mohr, Tübingen, 1913, p. 97.

[4] Olsson, *Arkiv. Kemi. Mineral Geol.*, **9**, No. 10, 10 (1924).

[5] Bray, *Z. physik. Chem.*, **54**, 463 (1906); Luther and Rutter, *Z. anorg. Chem.*, **54**, 1 (1907); Jablczyński, *ibid.*, **60**, 38 (1908); Mitchell, *J. Chem. Soc.*, **125**, 564 (1925); Kolthoff and Furman, "Potentiometric Titrations," John Wiley and Sons, Inc., New York, 1931, 2d ed., p. 275.