Short Communications

Charge and outer Helmholtz potential for a mercury electrode in aqueous NaF at 25°

The accompanying tables were compiled to facilitate the application of the theory of the electrical double layer to the study of electrode kinetics[1,2]. They were obtained by numerical interpolation and extrapolation from the data of GRAHAME[3] on the mercury–aqueous NaF interface at 25°, using a digital computor. The surface charge density q and the potential ψ of the outer Helmholtz plane *vs.* the solution are listed in Table 1 as a function of electrode potential (*vs.* S.C.E.) for various concentrations of NaF. ψ was calculated from the equation[2]

$$\psi = \left(\frac{2\ RT}{ZF}\right) \sinh^{-1} \left(\frac{\pi q^2}{2\varepsilon\ kTc}\right)^{\frac{1}{2}} \tag{1}$$

of the Gouy-Chapman theory with the assumption of no specific adsorption of sodium or fluoride ions. To enable the reader to assess the accuracy of the calculation, Grahame's reported data for 0.001 M NaF are given in Table 2 for comparison with the values calculated by extrapolation from his data for 0.01 M NaF. This was the least favourable extrapolation undertaken.

METHOD OF CALCULATION

A. Extrapolation

From Grahame's data for E *vs.* q at concentration c_1, a new table of potentials E' was calculated for concentration c_2 at the same values of q, by assuming that the change in E was the same as the change in ψ and calculating the change in ψ from eqn. (1). This is in accordance with Grahame's rule that the potential drop across the inner Helmholtz layer depends only on the surface charge[3]. Then q' was calculated at equal increments of potential by quartic Lagrangian inverse interpolation in the table of E' *vs.* q. The potential ψ was finally calculated from q' using eqn. (1)

B. Interpolation

This was similar to the extrapolation, but potentials E' were calculated from data at both higher and lower concentrations and a linearly weighted average taken. A quartic Lagrangian interpolation was used to obtain values of E at a common value of q for both higher and lower concentrations.

TABLE 1A

CALCULATED FROM DATA AT 0.01 M, E AND ψ IN VOLTS, q IN $\mu C/cm^2$

E vs. S.C.E.	0.00100 M		0.00150 M		0.00200 M		0.00300 M		0.00500 M		0.00750 M		0.0100 M	
	q	ψ	q	ψ	q	ψ	q	ψ	q	ψ	q	ψ	q	ψ
−1.850	−21.99	-0.245_9	−22.19	-0.235_9	−22.34	-0.228_3	−22.54	-0.218_9	−22.80	-0.205_8	−23.01	-0.195_0	−23.16	-0.188_8
−1.750	−20.13	-0.240_7	−20.32	-0.230_8	−20.45	-0.223_8	−20.64	-0.213_8	−20.88	-0.201_9	−21.08	-0.191_4	−21.22	-0.184_9
−1.650	−18.36	-0.236_0	−18.54	-0.226_1	−18.67	-0.219_1	−18.85	-0.209_2	−19.08	-0.196_7	−19.26	-0.186_8	−19.40	-0.179_7
−1.550	−16.65	-0.231_0	−16.83	-0.221_1	−16.95	-0.214_1	−17.13	-0.204_9	−17.35	-0.191_8	−17.53	-0.181_0	−17.66	-0.174_0
−1.450	−15.02	-0.225_7	−15.18	-0.215_0	−15.30	-0.208_0	−15.47	-0.199_0	−15.68	-0.186_0	−15.85	-0.176_8	−15.98	-0.169_8
−1.350	−13.43	-0.220_0	−13.60	-0.210_2	−13.71	-0.203_2	−13.88	-0.193_5	−14.08	-0.181_1	−14.25	-0.171_9	−14.37	-0.164_4
−1.250	−11.88	-0.213_7	−12.04	-0.204_0	−12.16	-0.197_1	−12.32	-0.187_9	−12.52	-0.175_1	−12.68	-0.165_3	−12.80	-0.158_4
−1.150	−10.29	-0.206_9	−10.46	-0.196_7	−10.58	-0.189_9	−10.74	-0.180_9	−10.95	-0.168_2	−11.12	-0.158_6	−11.24	-0.151_8
−1.050	− 8.70	-0.197_7	− 8.87	-0.188_3	− 8.98	-0.181_6	− 9.15	-0.172_1	− 9.36	-0.160_2	− 9.52	-0.150_7	− 9.64	-0.144_0
−0.950	− 7.05	-0.186_0	− 7.23	-0.177_8	− 7.35	-0.171_9	− 7.52	-0.162_1	− 7.74	-0.150_5	− 7.91	-0.141_3	− 8.04	-0.134_7
−0.850	− 5.29	-0.172_2	− 5.48	-0.163_6	− 5.61	-0.157_6	− 5.80	-0.148_8	− 6.03	-0.137_7	− 6.21	-0.128_9	− 6.34	-0.122_7
−0.750	− 3.46	-0.150_4	− 3.65	-0.142_8	− 3.78	-0.137_9	− 3.97	-0.129_5	− 4.21	-0.119_6	− 4.40	-0.111_0	− 4.54	-0.105_0
−0.650	− 1.74	-0.115_7	− 1.90	-0.109_0	− 2.01	-0.105_7	− 2.18	-0.099_6	− 2.40	-0.091_7	− 2.57	-0.085_3	− 2.70	-0.080_7
−0.550	− 0.61	-0.066_0	− 0.67	-0.060_0	− 0.71	-0.057_5	− 0.78	-0.053_1	− 0.89	-0.047_0	− 0.98	-0.044_0	− 1.05	-0.041_9
−0.450	0.10	0.014_1	0.13	0.015_4	0.16	0.015_8	0.20	0.015_8	0.24	0.015_1	0.28	0.014_1	0.31	0.013_4
−0.350	1.05	0.090_8	1.17	0.086_4	1.26	0.083_1	1.40	0.078_2	1.58	0.072_0	1.73	0.066_0	1.84	0.063_3
−0.250	2.65	0.136_0	2.85	0.130_3	3.00	0.125_0	3.21	0.118_7	3.48	0.110_0	3.70	0.103_0	3.86	0.097_0
−0.150	4.82	0.167_4	5.07	0.159_6	5.24	0.154_0	5.49	0.146_0	5.81	0.135_9	6.06	0.127_8	6.25	0.122_0
−0.050	7.28	0.188_5	7.54	0.180_0	7.73	0.173_0	8.00	0.165_2	8.34	0.154_9	8.60	0.145_6	8.80	0.139_3
0.050	9.88	0.204_2	10.16	0.195_2	10.35	0.188_8	10.63	0.179_8	10.99	0.168_4	11.27	0.159_9	11.48	0.152_0
0.150	12.62	0.216_8	12.92	0.207_0	13.13	0.201_0	13.43	0.191_8	13.82	0.180_1	14.12	0.170_9	14.35	0.164_9
0.250	15.61	0.227_7	15.94	0.218_4	16.18	0.211_7	16.52	0.202_4	16.96	0.190_0	17.31	0.181_3	17.57	0.174_7

TABLE 1B

CALCULATED FROM DATA AT 0.01 *M* AND AT 0.1 *M*, *E* AND ψ IN VOLTS, *q* IN μC/cm^2

E vs. S.C.E.	0.0150 *M*		0.0200 *M*		0.0300 *M*		0.0500 *M*		0.0750 *M*		0.100 *M*	
	q	ψ	*q*	ψ	*q*	ψ	*q*	ψ	*q*	ψ	*q*	ψ
−1.850	−23.37	−0.178$_0$	−23.52	−0.171$_0$	−23.74	−0.162$_0$	−24.01	−0.149$_5$	−24.24	−0.139$_0$	−24.42	−0.132$_7$
−1.750	−21.41	−0.174$_4$	−21.55	−0.167$_4$	−21.76	−0.157$_5$	−22.02	−0.145$_1$	−22.23	−0.135$_2$	−22.39	−0.128$_3$
−1.650	−19.58	−0.169$_8$	−19.72	−0.162$_8$	−19.91	−0.152$_9$	−20.15	−0.140$_5$	−20.35	−0.130$_7$	−20.50	−0.123$_6$
−1.550	−17.83	−0.165$_1$	−17.96	−0.158$_1$	−18.14	−0.148$_2$	−18.37	−0.135$_8$	−18.56	−0.126$_1$	−18.70	−0.119$_2$
−1.450	−16.15	−0.160$_0$	−16.27	−0.153$_0$	−16.44	−0.143$_2$	−16.67	−0.130$_0$	−16.84	−0.121$_2$	−16.98	−0.114$_3$
−1.350	−14.53	−0.154$_0$	−14.65	−0.147$_0$	−14.81	−0.137$_0$	−15.03	−0.125$_6$	−15.20	−0.116$_0$	−15.32	−0.109$_2$
−1.250	−12.96	−0.148$_7$	−13.07	−0.141$_8$	−13.23	−0.132$_2$	−13.44	−0.120$_0$	−13.60	−0.110$_4$	−13.72	−0.103$_7$
−1.150	−11.40	−0.142$_2$	−11.51	−0.135$_4$	−11.67	−0.125$_8$	−11.87	−0.113$_8$	−12.03	−0.104$_3$	−12.14	−0.097$_6$
−1.050	− 9.80	−0.134$_5$	− 9.92	−0.127$_8$	−10.08	−0.118$_4$	−10.28	−0.106$_6$	−10.44	−0.097$_3$	−10.56	−0.090$_8$
−0.950	− 8.20	−0.125$_5$	− 8.32	−0.118$_0$	− 8.48	−0.109$_7$	− 8.68	−0.098$_2$	− 8.83	−0.089$_2$	− 8.94	−0.082$_0$
−0.850	− 6.51	−0.113$_0$	− 6.63	−0.107$_6$	− 6.80	−0.098$_8$	− 7.00	−0.087$_8$	− 7.16	−0.079$_2$	− 7.26	−0.073$_1$
−0.750	− 4.72	−0.097$_8$	− 4.84	−0.092$_1$	− 5.01	−0.084$_0$	− 5.22	−0.073$_0$	− 5.37	−0.066$_1$	− 5.47	−0.060$_8$
−0.650	− 2.86	−0.074$_0$	− 2.98	−0.069$_3$	− 3.14	−0.062$_7$	− 3.32	−0.054$_4$	− 3.46	−0.048$_0$	− 3.55	−0.043$_7$
−0.550	− 1.15	−0.037$_7$	− 1.22	−0.035$_1$	− 1.32	−0.031$_4$	− 1.43	−0.026$_8$	− 1.51	−0.023$_4$	− 1.56	−0.021$_0$
−0.450	0.34	0.012$_3$	0.37	0.011$_3$	0.40	0.010$_1$	0.44	0.008$_6$	0.47	0.007$_5$	0.49	0.006$_7$
−0.350	1.99	0.058$_1$	2.10	0.054$_4$	2.26	0.049$_2$	2.44	0.042$_8$	2.58	0.037$_8$	2.68	0.034$_4$
−0.250	4.08	0.090$_8$	4.24	0.085$_7$	4.46	0.078$_5$	4.73	0.069$_5$	4.94	0.062$_5$	5.08	0.057$_5$
−0.150	6.50	0.113$_8$	6.68	0.107$_0$	6.93	0.099$_7$	7.24	0.089$_4$	7.48	0.081$_2$	7.66	0.075$_6$
−0.050	9.06	0.130$_5$	9.25	0.124$_3$	9.52	0.115$_5$	9.86	0.104$_5$	10.12	0.095$_8$	10.31	0.089$_7$
0.050	11.76	0.143$_8$	11.97	0.137$_3$	12.26	0.128$_3$	12.63	0.116$_0$	12.94	0.107$_0$	13.18	0.101$_7$
0.150	14.66	0.155$_0$	14.90	0.148$_5$	15.23	0.139$_3$	15.67	0.127$_8$	16.05	0.118$_7$	16.20	0.112$_0$

TABLE 1C

CALCULATED FROM DATA AT 0.1 M, 0.66 M AND 0.916 M, E AND ψ IN VOLTS, q IN $\mu C/cm^2$

E vs. S.C.E.	0.150 M		0.200 M		0.300 M		0.500 M		0.750 M		E vs. S.C.E.	1.00 M	
	q	ψ	q	ψ	q	ψ	q	ψ	q	ψ		q	ψ
−1.750	−22.59	-0.118_5	−22.73	-0.111_0	−22.94	-0.102_0	−23.22	-0.090_0	−23.45	-0.080_8	−1.850	−25.70	-0.078_4
−1.650	−20.69	-0.114_1	−20.82	-0.107_2	−21.01	-0.097_0	−21.26	-0.085_8	−21.47	-0.076_7	−1.750	−23.60	-0.074_4
−1.550	−18.87	-0.109_5	−19.00	-0.102_7	−19.18	-0.093_2	−19.40	-0.081_5	−19.60	-0.072_5	−1.650	−21.63	-0.070_6
−1.450	−17.15	-0.104_7	−17.26	-0.097_0	−17.43	-0.088_5	−17.64	-0.077_0	−17.82	-0.068_2	−1.550	−19.76	-0.066_4
−1.350	−15.48	-0.099_0	−15.59	-0.092_0	−15.75	-0.083_7	−15.94	-0.072_3	−16.12	-0.063_8	−1.450	−17.99	-0.062_3
−1.250	−13.87	-0.094_3	−13.97	-0.087_7	−14.12	-0.078_5	−14.29	-0.067_4	−14.46	-0.059_1	−1.350	−16.29	-0.058_1
−1.150	−12.28	-0.088_4	−12.39	-0.081_0	−12.52	-0.073_0	−12.68	-0.062_2	−12.84	-0.054_2	−1.250	−14.62	-0.053_7
−1.050	−10.70	-0.081_8	−10.80	-0.075_5	−10.94	-0.066_0	−11.09	-0.056_5	−11.24	-0.049_0	−1.150	−13.00	-0.049_1
−0.950	− 9.09	-0.074_2	− 9.19	-0.068_1	− 9.32	-0.060_0	− 9.47	-0.050_2	− 9.62	-0.043_3	−1.050	−11.40	-0.044_2
−0.850	− 7.41	-0.065_0	− 7.51	-0.059_4	− 7.64	-0.051_0	− 7.79	-0.043_0	− 7.93	-0.036_8	−0.950	− 9.78	-0.039_0
−0.750	− 5.62	-0.053_4	− 5.72	-0.048_5	− 5.85	-0.042_0	− 6.00	-0.034_5	− 6.12	-0.029_3	−0.850	− 8.08	-0.033_0
−0.650	− 3.68	-0.038_1	− 3.77	-0.034_3	− 3.89	-0.029_5	− 4.02	-0.024_0	− 4.13	-0.020_3	−0.750	− 6.24	-0.026_1
−0.550	− 1.63	-0.018_1	− 1.69	-0.016_2	− 1.75	-0.013_8	− 1.83	-0.011_2	− 1.89	-0.009_5	−0.650	− 4.21	-0.018_1
−0.450	0.51	0.005_7	0.52	0.005_1	0.53	0.004_3	0.54	0.003_3	0.54	0.002_7	−0.550	− 1.95	-0.008_5
−0.350	2.80	0.030_0	2.89	0.027_0	3.00	0.023_2	3.10	0.018_8	3.18	0.015_8	−0.450	0.56	0.002_4
−0.250	5.28	0.050_0	5.41	0.046_4	5.59	0.040_4	5.78	0.033_4	5.93	0.028_5	−0.350	3.26	0.014_1
−0.150	7.89	0.067_8	8.05	0.062_3	8.26	0.055_0	8.50	0.046_2	8.70	0.039_0	−0.250	6.05	0.025_4
−0.050	10.57	0.081_2	10.75	0.075_3	11.00	0.067_1	11.29	0.057_3	11.55	0.050_1	−0.150	8.88	0.035_9
0.050	13.48	0.092_0	13.69	0.086_7	13.97	0.078_0	14.28	0.067_4	14.56	0.059_4	−0.050	11.78	0.045_4
											0.050	14.92	0.054_8
											0.150	20.29	0.067_6

TABLE 2

DATA GIVEN BY GRAHAME[3] FOR 0.001 *M* NaF

E (*vs.* S.C.E.)	*q* ($\mu C/cm^2$)
—1.75	—20.12
—1.65	—18.34
—1.55	—16.64
—1.45	—15.00
—1.35	—13.43
—1.25	—11.88
—1.15	—10.32
—1.05	— 8.72
—0.95	— 7.05
—0.85	— 5.15
—0.75	— 3.48
—0.65	— 1.81
—0.55	— 0.54
—0.45	+ 0.14
—0.35	+ 1.05

ACKNOWLEDGEMENT

The compilation of these tables was undertaken at the suggestion of Professor LUCIEN GIERST, Université Libre de Bruxelles.

SUMMARY

Tables of double layer potentials were calculated from literature data.

Department of Chemistry,
Harvard University,
Cambridge 38, Mass. (U.S.A.)

C. D. RUSSELL

1 L. GIERST, *Transactions of the Symposium on Electrode Processes, Philadelphia, 1959*, Ed. E. YEAGER, John Wiley & Sons, Inc., New York, 1961, p. 109.
2 R. PARSONS, *Advances in Electrochemistry and Electrochemical Engineering*, Vol. I, Ed. P. DELAHAY, Interscience Publishers, Inc., New York, 1961, p. 1.
3 D. C. GRAHAME, *J. Am. Chem. Soc.*, 76 (1954) 4821.

Received August 7th, 1963

J. Electroanal. Chem., 6 (1963) 486–490

The current–potential equation for linear-sweep voltammetry

The theory of voltammetry with linearly changing potential ("linear-sweep polarography") for a reversible redox-system has been treated by ŠEVČIK[1] and RANDLES[2]. ŠEVČIK solved the diffusion equation for linear diffusion by using the Laplace transformation; RANDLES used a numerical method.

Their results can be summarized in the following current–potential equation:

$$i = \frac{n^{\frac{3}{2}} F^{\frac{3}{2}}}{R^{\frac{1}{2}} T^{\frac{1}{2}}} A C^0 v^{\frac{1}{2}} \left(\sqrt{D_0} + \frac{\sqrt{D_R}}{\theta}\right) \cdot P\left(\frac{nF}{RT} \cdot vt\right) \tag{1}$$