Standard E.m.f. of the Hydrogen-Mercurous Bromide Cell from 5 to 45°C

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The cell H_2 , $Pt | HBr(aq) | Hg_2Br_2 | Hg$ has been found to behave similarly to the hydrogencalomel cell, but increased difficulties are encountered because of the more ready disproportionation of the mercurous halide. E.m.f. of the cell have been measured at 5 deg. intervals between 5 and 45°C for hydrobromic acid solutions between 0.005 and 0.2 molal, and have been used to obtain the first direct determinations of standard e.m.f.s. Thermodynamic functions of the cell reaction have been evaluated as have activity coefficients of aqueous HBr.

The present paper is concerned with a study of hydrogen-mercurous bromide cell, which had not hitherto been adequately investigated. The mercury-mercurous bromide electrode has, however, received much attention ¹⁻⁸ and both of the cells

 $H_{2},Pt \mid HBr(aq) \mid Hg_{2}Br_{2} \mid Hg$ (A)

$Ag | AgBr | KBr(aq) | Hg_2Br_2 | Hg$ (B)

have been studied over narrow ranges of electrolyte concentrations and temperatures. The standard electrode potential of the mercury-mercurous bromide electrode has not, however, been determined directly, but only by use of existing values of mean molal ionic activity coefficients of hydrobromic acid in aqueous solution (cell A), or of the standard potential of the silver-silver bromide electrode (cell B). The most reliable values for these quantities come from two investigations of the cell

$$H_2, Pt \mid HBr(aq) \mid AgBr \mid Ag$$
(C)

first, by Harned, Keston and Donelson⁹ and recently by Hetzer, Robinson and Bates.¹⁰ Agreement between the various E° values so obtained for the mercurymercurous bromide is poor, and since all of the existing studies had been made with the classical mercury-mercurous salt paste technique, it was evident that this electrode system was ready for development.

Finely divided mercurous bromide was found to form a characteristic "skin" upon mercury when shaken with it in the dry state, and so resembles calomel in forming some special association with the mercury surface, characterized by strong adhesion.¹¹ A little of this grey skin, conveyed on a mercury globule to the surface of a clean, dry mercury pool, immediately spreads over the whole available surface and forms the basis of a highly reproducible electrode. Precautions are necessary to exclude oxygen and to prevent seepage of solution between the mercury and the walls of the containing vessel; silicone treatment of the vessel is effective for the latter purpose.

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Mercuric mercury more readily forms anionic complexes ¹² with bromide than with chloride ion. This favours the disproportionation of mercurous bromide in presence of mercury and aqueous hydrobromic acid, so that its "solubility" rises rather rapidly with increasing acid concentration. Because of this, the limit of concentration of hydrobromic acid for satisfactory operation of the mercurymercurous bromide electrode is about 0.2 molal, considerably lower than the corresponding limit for the calomel electrode (>1 m). This electrode also shows the same equilibration characteristics as the calomel electrode. When the deoxygenated solution is introduced to the oxygen-free cell containing the dry electrode components, there is an initial rapid rise in e.m.f. followed by a slow approach to the final equilibrium value. Consequently, protracted experiments are unavoidable if measurements over a temperature range are not to be adversely affected, and absence of any temperature-hysteresis effects in experiments leading to acceptable results must be ensured. Nevertheless, it has been found possible to measure e.m.f.s of cell A, with reproducibility not worse than $\pm 40 \,\mu V$ for hydrobromic acid solution from 0.005 to 0.2 molal over the temperature range 5-45°C.

EXPERIMENTAL

The apparatus and technique were identical to those described in the preceding paper. Mercurous bromide was prepared by adding a dilute, aqueous solution of hydrobromic acid dropwise to a rapidly stirred, slightly acidic solution of mercurous nitrate, standing over mercury. The suspension was stirred for 24 h, washed by decantation with dilute hydrobromic acid, and finally with water. It was then filtered, washed again, dried and stored over phosphoric oxide in vacuum. The mercurous bromide was protected from light during preparation and storage, but its reported photosensitivity ⁸ was never observed.

The hydrobromic acid was prepared by Booth's method.¹³ It was twice fractionally distilled with rejection of large head and tail fractions, to give constant-boiling acid, which was used to prepare three stock solutions. These solutions were stored in silica vessels in the dark under an atmosphere of nitrogen. They were analyzed by differential potentiometric weight titration against Specpure silver, fused in hydrogen, as primary standard. Cell solutions were prepared by weight dilution of one of the stock solutions, immediately before use.

RESULTS AND DISCUSSION

THE STANDARD ELECTRODE POTENTIAL

E.m.f. values for the hydrogen-mercurous bromide cell, corrected to 760 mm pressure of hydrogen, are collected in table 1; each result is the mean of readings from two independent pairs of electrodes, which rarely differed by more than 20 μ V.

TABLE 1.—E.I.I. OF THE CELL H ₂ , Pt HBI(ad) Hg ₂ BI ₂ Hg FROM 3 TO 4	1) Hg ₂ Br ₂ Hg from 5 to 45°C	HBr	, Pt	H_{2}	CELL	THE	OF	.—E.m.f.	TABLE 1
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molality	ty absolute volts × 10 ⁵ at °C temperatures								
$\times 10^{2}$	5	10	15	20	25	30	35	40	45
0.5064	39782	40244	40669	41082	41464	41842	42222	42589	42956
0 ·7546	37940	38351	38749	39129	39494	39842	40177	40513	40847
1.0140	36572	36957	37329	37682	38022	38349	38657	38959	
2.001	33453	33786	34103	34401	34685	34953	35208	35453	35687
3.007	31602	31901	32186	32452	32708	32952	33169	33385	33581
4.962	29331	29592	29836	30068	30280	30478	30659	30827	30986
7.088	27718	27952	28167	28373	28554	28724	28879	29014	29142
8.940	26652	26857	27055	27242	27407	27560	27685	27816	27932
9.829	26230	26427	26616	26792	26958	27092	27225	27337	
l8·470	23312	23451	23592	23734	23830	23927	24000	24064	24128

HYDROGEN-MERCUROUS BROMIDE CELL

As in the preceding paper, two types of extrapolation were used. Using the limited form of the activity coefficient relationship, 4 Å was found to be the most satisfactory common value of a_i and the E° values reported elsewhere ¹⁴ were evaluated on that basis. Using the extended form of the relationship, a different set of minimizing a_i values was found, all close to 4.5 Å from 5 to 35° C but rising to 5.10 and 6.35 Å at 40 and 45° C respectively. Because it is unlikely to increase with temperature, a common, constant, minimum value of 4.5 Å was adopted. Any unusual temperature effects should therefore be reflected in the values of β . The values of E° and β obtained are listed in table 2. In table 3 the new E° values are compared with those recorded in the literature.

TABLE 2.—STANDARD	e.m.f. (OF THE	HYDROGI	EN-MERCUROUS	BROMIDE	CELL	FROM	5 то	o 45°C	Ξ,
			VOLTS, a	$a_i = 4.5 \text{ Å}$						

temp. °C	E_m°	probable error in E°, mV	β	probable error in β
5	0.14100	0.02	0 ·1742	0.0006
10	0.14084	0.04	0.1753	0.0016
15	0.14048	0.03	0 ·1849	0.0009
20	0.13993	0.04	0 ·1769	0.0012
25	0.13923	0.03	0 ·1798	0.0009
30	0.13839	0.03	0·1804	0.0009
35	0.13741	0.03	0 ·1858	0.0009
40	0.13636	0.04	0 ·1933	0.0012
45	0·13524	0.02	0 ∙1999	0.0012

TABLE 3.—CONSENSUS OF E° VALUES OF THE HYDROGEN-MERCUROUS BROMIDE CELL, VOLTS

temp. °C	present work	Dakin ⁷ and Ewing	Larson ⁶	Gerke ⁴ and Geddes	Ishikawa ⁵ and Ueda
5	0.14100	_			
10	0.14084	—		—	
15	0 ·14048	0·1407 8	_	<u> </u>	
20	0.13993	0.14009	0.14001		
25	0.13923	0·13925	0·1389*	0.1385*	0.1395*
			0·13970	0.1396	
30	0.13839	0 ·13823		<u> </u>	
35	0 ·13741	0 ·13707			
40	0·13636				
45	0.13524				

* calculated on the basis of activity coefficients determined by Harned, Keston and Donelson.9

The comparison is satisfactory; however, whilst the agreement with Dakin and Ewing's results ⁷ is good at 25°C, there is substantial disagreement about the variation of E° with temperature. This is reflected in the disagreement between the existing thermodynamic functions for the cell reaction and the values derived from this work. The new E° data have been fitted, by method of least squares, to a cubic equation in $(t-25^{\circ}C)$, i.e.,

$$E^{\circ}_{Hg_{2}Br_{2}} = 0.13923 - 1.5612 \times 10^{-4} (t - 25) -2.7688 \times 10^{-6} (t - 25)^{2} + 3.0227 \times 10^{-8} (t - 25)^{3} (5 \le t \le 45^{\circ} \text{C})$$
(1)

The mean deviation of the observed E° values from the equation was 0.01 mV. Eqn. (1) was used to calculate the thermodynamic functions of the cell reaction

which are compared with previous values in table 4. The results have also been combined with those of Hetzer, Robinson and Bates ¹⁰ for cell C, in order to obtain standard e.m.f. of the cell

Ag | AgBr | HBr(aq) | Hg₂Br₂ | Hg,
$$\Delta E^{\circ} = E^{\circ}_{Hg_2Br_2} - E^{\circ}_{AgBr_3}$$

which were fitted by the equation

$$\Delta E^{\circ} = 0.05965 + 3.515 \times 10^{-4} t - 8.678 \times 10^{-7} t^2 + 1.522 \times 10^{-8} t^3, \tag{2}$$

the standard deviation being 0.02 mV. This equation was used to derive thermodynamic functions of the cell reaction $Ag + \frac{1}{2}Hg_2Br_2 = Hg + AgBr$, which are shown in table 5, together with the literature data.

TABLE 4.—THERMODYNAMIC FUNCTIONS OF THE STANDARD CELL REACTION

 $\frac{1}{2}H_2 + \frac{1}{2}Hg_2Br_2 = Hg + HBr(aq)$ at 25°C.

function	value from eqn. (2)	literature value 15
ΔG^0 , cal	- 3211	-3217
ΔS^0 , cal deg. ⁻¹	-3.60	-3.27
ΔH^0 , cal	-4251	-4190
ΔC_{p0} , cal deg. ⁻¹	- 38.1	

TABLE 5.—THERMODYNAMIC FUNCTIONS OF THE CELL REACTION

function	value from eqn. (3)	literature value				
ΔG^0 , cal	-1571	$-1033^{15};$	- 1569 6			
ΔS^0 , cal deg. ⁻¹	7.76	8.44 15;	9.65 6			
ΔH^0 , cal	743	930 15				
ΔC_p^0 , cal deg. ⁻¹	0.01	2.5 *				

* using the value of $C_{pHg_2Br_2}$ given in table 6.

It is possible, from the data of table 4, to re-evaluate the standard thermodynamic functions of mercurous bromide, in terms of the corresponding values for the bromide ion currently accepted. The results are shown in table 6 and compared with existing data.

TABLE 6.—STANDARD THERMODYNAMIC PROPERTIES OF MERCUROUS BROMIDE AT 25°C

property	Br- (aq)	Hg ₂ Br ₂ (new)	Hg2Br2 (old)
ΔG^0 , cal mole ⁻¹	24.574	- 42.726	-42.714
ΔH^0 , cal mole ⁻¹	-28·9 00	-49.224	- 49.420
S^0 , cal deg. ⁻¹ mole ⁻¹	19.29	51.98	50 ·9
C_p^0 , cal deg. ⁻¹ mole ⁻¹	- 30.7	+21.2	

THE ACTIVITY COEFFICIENTS OF aq. HBr

 γ_{\pm} values for aq. HBr, evaluated at rounded molalities, using a constant a_i value of 4.5 Å and β values from table 2, are given in table 7 where they are compared with those obtained from the silver chloride cell. The agreement is good except at the highest temperatures and concentrations and here the derived \bar{L}_2 values show anomalous trends (cf. table 8). These uncertainties became more apparent with successive differentiations and it was not considered worth while attempting to evaluate \bar{J}_2 for HBr from these measurements.

72.5

63·0

 $22 \cdot 3$

0.05

0.07

0.10

TABLE 7.---MEAN MOLAL ACTIVITY COEFFICIENTS OF HYDROBROMIC ACID IN AQUEOUS SOLUTION $\gamma_{\pm} \times 10^4$

m	5	10	15	20	temp. °C 25	30	35	40	45
0.001	9665	9662	9659	9657	9654	9651	9649	9645	9642
(H and O)	(967)	(967)	(967)	(966)	(966)	(966)	(965)	(964)	(964)
0.002	9539	9535	9532	9528	9524	9520	9516	9512	9508
0.005	9310	9306	9301	9294	9289	9283	9277	9271	9265
0.01	90 83	90 76	9071	9062	9055	9047	9040	9033	9025
(H and O)	(910)	(909)	(908)	(907)	(906)	(906)	(905)	(904)	(904)
(H. R and B)			• •		(906)	• •			. ,
0.02	881 0	8801	8796	8783	8774	8764	8755	8747	8739
0.05	8407	8389	8387	8366	8355	8343	8333	8326	8316
(H, R and B)					(838)				
0.07	8251	8239	8239	8214	8203	8190	818 0	8174	8165
0·10	8105	8116	8095	8065	8054	8040	8030	8027	8020
(H and O)	(812)	(811)	(808)	(807)	(805)	(804)	(802)	(800)	(797)
(H, R and B)	. ,		. ,	• •	(808)			• •	
0.20	7907	7894	7911	7863	7853	7837	7834	7839	784 0
TABLE 8	Relativ	'E PARTIAL	ENTHAI	LPIES OF	AQUEOUS	HYDROBRO	MIC ACID	, cal mo	le ⁻¹
m	10	15		20	temp. °C 25	30	35		40
0.001	17.8	18.4	1	9.3	20.5	21.8	23.5	25	5.5
0.002	23.6	25.9		28· 0	29.9	31.3	32.4	33	3.2
0.005	35.8	39.1	4	2.0	44.6	46.6	48·2	49	9.3
0.01	43.4	53.3	5	5.9	60 ·1	62.4	62.9	61	1.3
0.02	59.3	68.1	7	4.6	78.7	79.7	77.6	71	1.9

SUMMARY OF THE E.M.F. MEASUREMENTS

91.6

100.4

124.9

74·0

77.8

95.3

These cells are not yet as satisfactory in performance as was originally hoped, their defects being associated with the complicated equilibration reactions attending anion-reversible electrodes based on mercury. The full significance of these complications is not yet clear, but it seems that the high exchange currents associated with reversible electrodes are not necessarily a feature of the final interfacial equilibrium of these heterogeneous systems.¹⁶ The point has been made previously¹¹ that a finite exchange current cannot be supported by the metal ion concentration of anion-reversible electrode of the second kind. The high degree of reversibility which is observed in the early stages of the electrode life is a special feature of a particular modification of the solid in the interphase which is evidently unstable. The decline in reversibility accompanying the progressive equilibration means that useful measurements can only properly be made after some optimum time. These difficulties are not apparent in the e.m.f. measurements unless they are specifically looked for, and possibly the silver halide electrodes are likewise sensitive.

103.0

114.3

150.3

107.9

119.0

155.4

104.7

112.3

136.9

93.3

94.1

77.8

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