Thermochimica Acta, 13 (1975) 105–108

Note

Thermodynamic behaviour of silver–silver iodate and silver–silver bromate electrodes in formamide at 25°C

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(Received 10 April 1975)

In previous communications[1,2], we reported the standard potentials of the $Ag(s)/AgIO_3(s)/IO_3^-$ and $Ag(s)/AgBrO_3(s)/BrO_3^-$ electrodes in formamide at 25, 30 and 35°C from the solubility measurements of silver iodate and silver bromate in this solvent at these temperatures. With a view to have an independent check on the values of the standard potentials of these electrodes, the cell:

$$\mathrm{Hg,\ Hg_2Cl_2,\ KCl(saturated)\ \|\ KXO_3(m),\ AgXO_3,\ Ag} \qquad \text{(A)}$$

where XO_3^- stands for IO_3^- or BrO_3^-, has been studied in formamide at 25°C. The values for the standard potentials of these electrodes obtained from the study of cell (A) are in good agreement with the values obtained from the study of an independent cell:

$$\mathrm{Ag,\ AgCl,\ KCl(m)\ \|\ KXO_3(m),\ AgXO_3,\ Ag} \qquad \text{(B)}$$

From the standard potentials of these electrodes, the standard free energy change (ΔG^0) for the corresponding electrode process has been evaluated at 25°C.

EXPERIMENTAL

Silver iodate and silver bromate were the same samples used in the previous studies[1,2]. Potassium chloride, potassium iodate and potassium bromate (BDH, AnalaRs) were dried above 100°C for 2 h and kept in a vacuum desiccator over calcium chloride until required. Formamide (Riedel, pure) was further purified as described earlier[3].

Silver–silver iodate and silver–silver bromate electrodes were prepared by the method similar to that of the silver–silver acetate electrode[4]. The silver electrodes were freshly made for each run a few hours before the cells were prepared. The electrodes made by the thermal method from silver oxide, were immersed in potassium iodate or potassium bromate solution saturated with the corresponding silver salt and surrounded by excess solid.

Calomel electrodes were made as described by Hills and Ives[5]. Triple-distilled and vacuum-dried mercury and a very fine sample of calomel (BDH, AnalaR) were used. Other procedures such as purification of nitrogen, preparation of silver–silver chloride electrodes were similar to those described elsewhere[6].

Potassium salt solutions were prepared by dissolving appropriate weighed amounts of potassium salt in known weights of formamide. Saturated solutions of potassium chloride in formamide for the salt bridge were prepared as usual. All transfers and rinsing involving salt solution in formamide were carried out in a dry box.

The cell vessels for cell (A) are of the type recommended by Prasad and Jena[7], and cell (B) is of the type recommended by Cann and Mueller[8]. The half cells in both the cells (A) and (B) are connected by salt bridges having stop-cock arrangements. The e.m.f. measurements were made using a Leeds & Northrup K-2 potentiometer, a d.c. Leeds & Northrup galvanometer (Cat. No. 2430) and a Cambridge Wastern cell D-402-A. All measurements were made in an air thermostat maintained at 25±0.05°C.

The cells (A) and (B) were set up in the similar manner as described earlier[4,9,10], and were then transferred to the air thermostat. Purified nitrogen was bubbled through each cell compartment for 15–30 min. All outlets from the cell compartments were fitted with calcium chloride guard tubes during the passage of the gas.

The e.m.f. of the cell (A) was found to vary with time in the manner similar to that of the hydrogen–calomel cell[10], whereas in the case of cell (B), the variation of e.m.f. was almost similar to that of the cells consisting of the silver–silver acetate[4], silver–silver chloride[6] and silver–silver oxalate[9] electrodes. The e.m.f. of cell (A) was consequently measured at intervals of 1 h upto 15 h and then the values obtained were extrapolated to zero time[4,6,10] to yield the true e.m.f. of the cell, corresponding to zero decomposition of the solvent. Similar extrapolation of the e.m.f. values measured upto 8 h was made for getting the true e.m.f. of cell (B).

RESULTS AND DISCUSSION

The summaries of e.m.f. data obtained from cells (A) and (B) are given in Tables 1 and 2 as functions of KXO_3 molality. The standard potential, $E°$, of the $Ag(s)/AgXO_3(s)/XO_3^-$ electrode was found by the usual method[9,10] of extrapolation of the auxiliary function, E' given by

$$E' = E + E_{ref} + \frac{2.3026RT}{F}\log m = E° - \frac{2.3026RT}{F}\log \gamma \qquad (1)$$

to $m = 0$, where m and γ are the molalities and the activity coefficients of XO_3^-. Using the value, 0.2880 V as the $E°$ of the $Hg/Hg_2Cl_2/KCl$(saturated) electrode[11] and the value 0.1986 V as that of the $Ag/AgCl/Cl^-$ electrode[6] in formamide at 25°C, the middle term of equation (1) was calculated for every molality. By plotting these calculated values against the corresponding molalities, and extrapolating to $m = 0$. by the method of least squares, the $E°$ values of the $Ag(s)/AgXO_3(s)/XO_3^-$ electrodes have been obtained.

TABLE 1

SUMMARY OF e.m.f. DATA FOR CELL (A) IN FORMAMIDE AT 25°C

$m \times 10^4$ (mol kg^{-1})	E (V)	E' (V)
	$XO_3^- \equiv IO_3^-$	
1.725	0.1995	0.2649
2.638	0.1880	0.2643
3.528	0.1775	0.2612
4.890	0.1656	0.2578
6.387	0.1520	0.2510
8.487	0.1402	0.2465
9.831	0.1336	0.2438
	$XO_3^- \equiv BrO_3^-$	
6.32	0.3954	0.4942
9.38	0.3862	0.4951
11.35	0.3781	0.4919
14.03	0.3702	0.4894
18.92	0.3639	0.4908
21.10	0.3568	0.4865
26.38	0.3489	0.4843

TABLE 2

SUMMARY OF e.m.f. DATA FOR CELL (B) IN FORMAMIDE AT 25°C

$m \times 10^4$ (mol kg^{-1})	E (V)	E' (V)
	$XO_3^- \equiv IO_3^-$	
1.220	0.2990	0.2661
2.528	0.2789	0.2647
4.612	0.2610	0.2623
5.140	0.2590	0.2631
5.981	0.2520	0.2600
6.839	0.2498	0.2611
	$XO_3^- \equiv BrO_3^-$	
4.38	0.4930	0.4929
8.32	0.4748	0.4911
10.03	0.4670	0.4882
14.83	0.4538	0.4851
18.90	0.4459	0.4833
20.12	0.4408	0.4799

The $E°$ values of the $Ag(s)/AgIO_3(s)/IO_3^-$ electrode obtained from cells (A) and (B) were found to be 0.2700 V and 0.2673 V, respectively, and are in good agreement with the value, 0.2711 V reported earlier from the solubility measurements[1].

The $E°$ values of the $Ag(s)/AgBrO_3(s)/BrO_3^-$ electrode were found to be 0.4933 V and 0.4963 V, respectively, obtained from the study of cells (A) and (B).

These values are somewhat inferior to the value, 0.4997 V as the standard potential of this electrode at 25 °C determined from the solubility measurements[2] in formamide. The agreement between the E° values obtained from three independent procedures for these electrodes is found to be much better in the case of the silver–silver iodate electrode than in the case of the silver–silver bromate electrode and this might be due to the lower solubility of silver iodate in comparison with silver bromate in formamide.

From the standard potential of the $Ag(s)/AgXO_3(s)/XO_3^-$ electrode at 25 °C, the standard free energy change, ΔG° of the process, $AgXO_3(s) \rightarrow Ag^+(\text{solvated}) + XO_3^-(\text{solvated})$ is found to be −26050 J and −47580 J, for the $Ag(s)/AgIO_3(s)/IO_3^-$ and $Ag(s)/AgBrO_3(s)/BrO_3^-$ electrodes, respectively.

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