

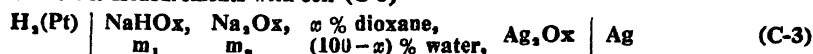
E° of $\text{Ag}/\text{Ag}_2\text{Ox}$, Ox^{2-} in Aqueous and Dioxane – Water Media at a Number of Temperatures and the Related Thermodynamic Quantities

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From e.m.f. measurements with cell (C-3)

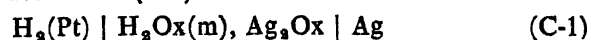


where, $x=0, 10, 20$ and 30 , E° of $\text{Ag}/\text{Ag}_2\text{Ox}$, Ox^{2-} has been measured at 288.15, 298.15, 308.15 and 318.15 K. Over the temperature range E° values in absolute volt are given by

$$\begin{aligned} &0.4818 - 8.8833 \times 10^{-4} (t-25) - 9 \times 10^{-6} (t-25)^2 - 9.167 \times 10^{-7} (t-25)^3 \text{ for } x=0, \\ &0.4793 - 3.8166 \times 10^{-4} (t-25) - 37 \times 10^{-6} (t-25)^2 - 25.833 \times 10^{-7} (t-25)^3 \text{ for } x=10, \\ &0.4610 - 1.4267 \times 10^{-4} (t-25) + 55. \times 10^{-6} (t-25)^2 - 1.833 \times 10^{-7} (t-25)^3 \text{ for } x=20, \\ &0.4353 - 1.3200 \times 10^{-4} (t-25) + 7.5 \times 10^{-6} (t-25)^2 - 1.5 \times 10^{-7} (t-25)^3 \text{ for } x=30. \end{aligned}$$

where t is the temperature ($^\circ\text{C}$). The values of the thermodynamic quantities ΔG° , ΔH° and ΔS° for the reaction $\text{Ag}_2\text{Ox}(\text{s}) + 2\text{e} = 2\text{Ag}(\text{s}) + \text{Ox}^{2-}$ have been determined for each of these solutions at the above temperatures.

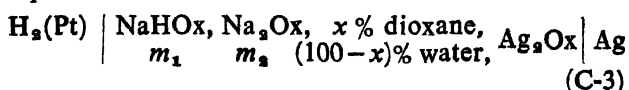
THE values of E° of $\text{Ag}/\text{Ag}_2\text{Ox}$, Ox^{2-} electrode in aqueous solution were first determined by Ferrel *et al.*¹ at 298.15, 303.15 and 308.15 K from e.m.f. values of cell (C-1).



Later on Sircar and Prasad² determined the E° value of the same electrode at 308.15 K only from cell (C-2),



assuming complete elimination of liquid junction potential. The two e.m.f. values given by the two sets of workers at 308.15 K differed by more than 3 mV. The E° values of Ag/AgOx , Ox^{2-} electrode at a number of temperatures in water – dioxane medium are not known. Hence cell (C-3) was set up to determine the E° values of $\text{Ag}/\text{Ag}_2\text{Ox}$, Ox^{2-} electrode at 288.15, 298.15, 308.15 and 318.15 K in both aqueous and dioxane – water media.



where, $x=0, 10, 20$ and 30 .

Experimental

All the chemicals were either of A.R. or G.R. grade. Water used was double-distilled. Dioxane was purified³ and invariably freshly distilled dioxane was used for preparing the solutions. NaHOx was prepared *in situ* from carbonate-free

NaOH and H_2Ox . The experimental solutions were deoxygenated by bubbling pure and presaturated N_2 slowly for 10–12 h and were allowed to enter the cell under pressure of N_2 . $\text{Ag} \mid \text{Ag}_2\text{Ox}$, Ox^{2-} electrodes were prepared by first generating a velvety coat of silver on a clean Pt helix of 3–4 turns sealed in corning glass tubing by allowing a paste of thrice-crystallised Ag_2Ox to decompose on its surface in graded stages from 373 to 773 K in a muffle furnace. Loss of Ag by sputtering was prevented by surrounding the corning glass tube holding the sealed-in Pt helix by coaxial corning glass tube (~ 1 cm dia.). Three or four helpings of a moderately thick paste of Ag_2Ox followed by heating in graded stages from 373 to 773 K gave a good velvety coat of Ag on Pt spiral. This was then evenly coated with a moderately thick paste of Ag_2Ox . The $\text{Ag} \mid \text{Ag}_2\text{Ox}$ electrode thus prepared was sealed in the cup of a B-24 interchangeable joint of corning glass. The potential of these electrodes slowly increased and only after a fortnight it gave a constant and steady value. It was further observed that the electrodes when used continuously for 6–8 h developed bias potential of several mV which disappeared when short-circuited for 24 h in a solution of 0.1 N Na_2Ox . The electrodes when used in rotation, allowing at least 48 h of rest and equilibration in H_2Ox solution, worked satisfactorily and had bias potential of less than 0.02 mV. So duplicate all-glass H-shaped cells, one limb containing $\text{Ag}/\text{Ag}_2\text{Ox}$ electrode and the other containing hydrogen electrode, were used. The hydrogen purification assembly, thermostat, potentiometer and galvanometer assembly were as descri-

bed earlier⁴. All weights were corrected for buoyancy. The concentration of dioxane was in weight percent and that of electrolytes in mol kg^{-1} correct to a micromol kg^{-1} . The cells gave steady e.m.f. values for at least 1.5 h. after attaining the requisite temperature and agreed with duplicate within 0.02 mV. The reported e.m.f. values are all corrected for barometric pressure, vapour pressure and bubbler depth and are the mean of the e.m.f. values of the duplicate cells.

Results and Discussion

Ignoring charges for the sake of neatness the e.m.f. of cell (C-3) is given by equation (1),

$$E = E^\circ - \frac{2.3026 RT}{2F} \log m_{\text{H}}^2 \cdot m_{\text{Ox}} \cdot \gamma_{\text{H}}^2 \cdot \gamma_{\text{Ox}} \quad (1)$$

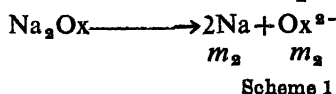
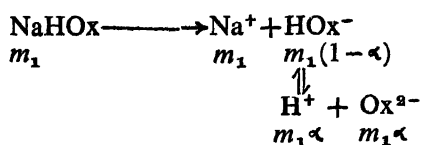
Modified Davies equation for activity coefficient of electrolytes has been found to be valid both in aqueous⁵ as well as dioxane-water mixed solvent of at least upto 30% (w/w) dioxane content⁶ upto an ionic strength of *ca.* 0.1 mol kg^{-1} . So on rearranging equation (1) we get equation (2),

$$E + \frac{k}{2} \cdot \log m_{\text{H}}^2 \cdot m_{\text{Ox}} - \frac{3kA \sqrt{\mu}}{1 + \sqrt{\mu}} = E^\circ - \frac{k}{2} \beta \mu \quad (2)$$

where, $k = 2.3026 \frac{RT}{F}$, $\beta = 2\beta_{\text{H}} + \beta_{\text{Ox}}$, $E^\circ = E_{\text{Ag}/\text{Ag}_2\text{Ox}, \text{Ox}^{2-}}^\circ$ and A is Debye-Hückel constant for the respective solvents in $\text{mol}^{-1/2} \text{kg}^{1/2}$, whose values were obtained from literature⁷.

The ionic equilibria in solutions of cell (C-3) may be represented in Scheme 1, giving the ionic strength (μ) of the cell solution by equation (3),

$$\mu = m_1 + 3m_2 + 2m_1\alpha \quad (3)$$



The second step dissociation constant K_2 of oxalic acid is given by equation (4),

$$\log K_2 = \log \frac{m_{\text{H}} \cdot m_{\text{Ox}}}{m_{\text{HOx}}} - \frac{4A \sqrt{\mu}}{1 + \sqrt{\mu}} + \beta_2 \mu \quad (4)$$

The values of K_2 and β_2 had been reported from this laboratory earlier^{8,9}. Starting with $\mu \approx m_1 + 3m_2$, using known values of K_2 , β_2 and using equations (3) and (4), by a process of iteration we get constant values of α , m_{H} , m_{Ox} and m_{HOx} at different temperatures for different solvent compositions. Table 1 shows these values for 30% dioxane solution at 298.15 K. For brevity, the values for other temperatures and other solvent compositions have not been shown.

The values of left-hand-side of equation (2) denoted as Y for each of the solutions at each of the temperatures were plotted against μ . These plots (some of which are shown in Fig. 1) were all linear. The divergence of the points from the straight lines was mostly within 0.1 mV but in a

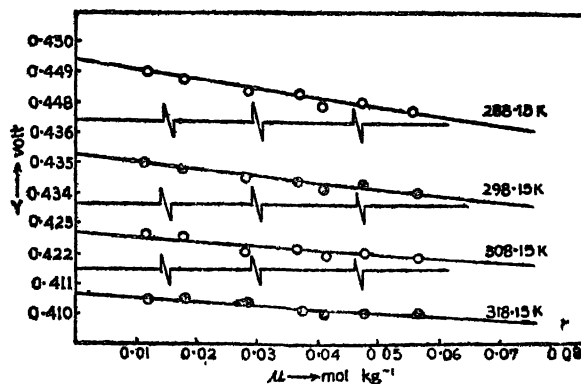


Fig. 1. Plots Y of equation (2) vs μ for 30% (w/w) dioxane.

few case was within 0.2 mV. The intercepts of the plots at $\mu = 0$ gave the values of $E^\circ (= E_m^\circ)$ and the slopes the values of β . The linearity of the plots shows that the values of β remain reasonably constant over the range of ionic strength for each of the solutions at each of the temperatures considered. Values of β so obtained are shown in Table 2.

TABLE 1—E.M.F., IONIC STRENGTH AND MOLALITY OF IONIC SPECIES IN SOLUTIONS OF CELL (C-3)*

Dioxane - Water = 30% (w/w), Temp. = 298.15 K

$m_1 =$ NaHOx	$m_2 =$ Na ₂ Ox	E abs. V	m_{H}	m_{Ox}	μ	Y^{**}
0.002 980	0.002 979	0.813 10	0.000 014 8	0.002 998	0.011 946	0.495 047
0.004 647	0.004 646	0.806 52	0.000 016 9	0.004 663	0.018 619	0.494 819
0.007 243	0.007 242	0.799 75	0.000 020 6	0.007 263	0.029 010	0.494 509
0.008 662	0.008 661	0.797 10	0.000 022 5	0.008 683	0.034 690	0.494 472
0.010 307	0.010 305	0.794 48	0.000 024 5	0.010 329	0.041 271	0.494 260
0.011 866	0.011 864	0.792 64	0.000 026 8	0.011 890	0.047 511	0.494 330
0.014 012	0.014 010	0.790 07	0.000 028 7	0.014 039	0.056 099	0.494 008

*All concentrations and ionic strengths in mol kg^{-1} . ** $Y = E + \frac{k}{2} \log m_{\text{H}}^2 \cdot m_{\text{Ox}} - \frac{3kA \sqrt{\mu}}{1 + \sqrt{\mu}}$

TABLE 2—VALUES OF STANDARD ELECTRODE POTENTIAL OF SILVER—SILVER OXALATE ELECTRODE IN MOLAL, MOL-FRACTIONAL AND MOLAR SCALES*

Dioxane wt. %	Temp. K	β kg mol ⁻¹	$E_{Ag/Ag_2Ox, Ox^{2-}}^{\circ}$ (abs. V)		
			E_m°	E_N°	E_c°
0	288.15	5.812	0.490 7	0.291 2	0.490 7
	298.15	7.472	0.481 8	0.275 4	0.481 6
	308.15	7.327	0.471 1	0.257 8	0.470 8
	318.15	3.458	0.458 1	0.232 9	0.452 5
10	288.15	1.735	0.482 0	0.286 7	0.482 6
	298.15	1.995	0.479 3	0.277 2	0.479 6
	308.15	2.458	0.469 2	0.260 3	0.469 3
	318.15	2.186	0.436 2	0.220 5	0.436 2
20	288.15	7.981	0.476 0	0.285 1	0.476 9
	298.15	5.671	0.461 0	0.263 5	0.461 7
	308.15	4.580	0.447 1	0.243 0	0.447 6
	318.15	3.802	0.433 2	0.222 5	0.433 4
30	288.15	1.084	0.449 4	0.263 5	0.450 8
	298.15	0.740	0.435 3	0.242 9	0.436 4
	308.15	0.528	0.422 7	0.223 9	0.423 5
	318.15	0.444	0.410 7	0.205 4	0.411 3

*Maximum standard error in β is 0.003 (only at 288.15 K for 10% dioxane it is 0.007) and that in E_m° is 0.0002.

From the experimental E_m° values, the values of E_c° (standard electrode potential on molarity scale) and E_N° (standard electrode potential on mol-fractional scale) have been calculated using equations (5) and (6), respectively.

$$E_c^{\circ} = E_m^{\circ} + 2k \log (d_o / \text{gm cm}^{-3}) \quad (5)$$

$$E_N^{\circ} = E_m^{\circ} - 2k \log (\text{kg mol}^{-1} / M_{xy}) \quad (6)$$

where, d_o is density of solvent at the particular temperature and M_{xy} the mean molar mass defined by equation (7),

$$\frac{100}{M_{xy}} = \frac{x}{M_x} + \frac{(100-x)}{M_y} \quad (7)$$

where, x is the weight percent of dioxane of molar mass M_x and M_y the molar mass of water.

The values of E_m° , E_c° and E_N° so found are given in Table 2.

The values of E_m° for each of the solutions are given accurately by an equation of the form,

$$E_m^{\circ} = E_{25}^{\circ} + a(t-25) + b(t-25)^2 + c(t-25)^3 \quad (8)$$

where, t is temperature ($^{\circ}\text{C}$) and values of a , b , c are as shown in Table 3.

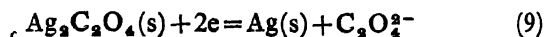
TABLE 3—VALUES OF a , b AND c IN EQUATION (8)

x wt. %	$-a$ $\times 10^{-4} \text{V deg}^{-1}$	b $\times 10^{-6} \text{V deg}^{-2}$	$-c$ $\times 10^{-7} \text{V deg}^{-3}$
0	8.883 3	-9.0	9.167
10	9.816 6	-37.0	25.833
20	14.266 7	5.5	1.833
30	13.200 0	7.5	1.500

The plots of E_N° and E_m° against $1/D$ (D =dielectric constant of the medium) (Born plot), E_c° against $\log \phi_w$ (ϕ_w =volume fraction of water in the medium), E_N° against $\log N_w$ (N_w =mol fraction of water in

the medium) (Feakins and French plot¹⁰), and $E_N^{\circ} - k \log N_w$ against $1/D$ are all similar and curvilinear. They are however not shown here.

For the reaction taking place at the $\text{Ag}/\text{Ag}_2\text{Ox}$, Ox^{2-} electrode shown by equation (9), the various thermodynamic quantities ΔG° , ΔH° and ΔS° for each of the solutions considered have been obtained using equation (8) and the well-known thermodynamic relations.



These values are shown in Table 4. It is seen from Table 4 that ΔG° value slowly increases both with increase in temperature and increase in the content of dioxane in the solvent. However ΔG° values remain negative all along. This means that the cell reaction as shown in equation (9) is facilitated all along more so at lower temperature and lower concentration of dioxane.

TABLE 4—THERMODYNAMIC FUNCTIONS FOR THE REACTION, $\text{Ag}_2\text{C}_2\text{O}_4(\text{s}) + 2\text{e} = 2\text{Ag}(\text{s}) + \text{C}_2\text{O}_4^{2-}$

Dioxane wt. %	Temp. K	$-\Delta G^{\circ}$ kJ mol ⁻¹	$-\Delta S^{\circ}$ JK ⁻¹ mol ⁻¹	$-\Delta H^{\circ}$ kJ mol ⁻¹
0	288.15	94.69 \pm 0.04	189.8 \pm 0.1	149.4 \pm 0.2
	298.15	92.95 \pm 0.04	171.4 \pm 0.1	144.1 \pm 0.2
	308.15	90.91 \pm 0.04	259.2 \pm 0.1	170.8 \pm 0.2
	318.15	87.44 \pm 0.04	298.8 \pm 0.2	182.5 \pm 0.2
10	288.15	93.01 \pm 0.00	80.4 \pm 0.01	116.2 \pm 0.04
	298.15	92.49 \pm 0.00	73.7 \pm 0.01	114.5 \pm 0.04
	308.15	90.54 \pm 0.01	366.0 \pm 0.1	203.3 \pm 0.1
	318.15	84.18 \pm 0.06	957.5 \pm 0.8	388.8 \pm 0.6
20	288.15	91.86 \pm 0.09	307.2 \pm 0.4	180.4 \pm 0.4
	298.15	89.96 \pm 0.00	275.3 \pm 0.05	171.0 \pm 0.06
	308.15	86.28 \pm 0.00	264.7 \pm 0.04	167.8 \pm 0.05
	318.15	83.60 \pm 0.00	275.3 \pm 0.04	171.2 \pm 0.06
30	288.15	86.72 \pm 0.06	292.4 \pm 0.2	171.0 \pm 0.3
	298.15	84.00 \pm 0.04	254.7 \pm 0.2	160.0 \pm 0.2
	308.15	81.57 \pm 0.02	234.5 \pm 0.09	153.8 \pm 0.1
	318.15	79.25 \pm 0.02	231.6 \pm 0.09	152.9 \pm 0.1

In aqueous solution, the ΔS° value first increases with the increase in temperature indicating probably a predominant kinetic effect. Around 303 K this trend is reversed and ΔS° value continues to decrease with the increase in temperature. A change in the structure of water around 303 K has been reported¹¹. The decrease in ΔS° values above this temperature is a consequence probably of more water molecules being immobilised by the ions, i.e. an expansion of region-A and a shrinkage of region-B of Frank and Wen model¹². Addition of a small amount of dioxane (10%) in the solvent is seen to have no effect on this trend. Dioxane is known to break the three-dimensional structure of water^{13,14}. Probably the availability of larger number of free molecules of water in the presence of larger amount of dioxane facilitates both the coordination of water molecules with dioxane and immobilisation of water molecules by ions. With sustained increase in the dioxane content this trend seems to be arrested around 20% content of dioxane. A similar behaviour regarding the change

of ΔH° values for the entire range of solvent mixture (0–30%) has been noted. It is however difficult to comment more precisely on the variation pattern of ΔS° or ΔH° in the absence of more detailed information on solvent structure.

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