Analytic Form of the Plutonium Work Integral

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Abstract

The computer program "MACSYMA" has been used to obtain the algebraic form of the plutonium work integral. The equation is useful for estimating the minimum work which must be expended when dissolved plutonium is oxidized at constant acidity.

Discussion

Recently an integral representing the work necessary to oxidize aqueous plutonium from $N = 3.00$ to $3 < N < 6$ was presented [1]. This integral is:

$$\Delta G = -F\int(E)\mathrm{d}N \tag{1}$$

in which "F" is the Faraday constant, "E" is the potential defined by eqn. (2):

$$E = E^{\circ} + 0.05916 \log \frac{[PuO_2{}^{2+}]}{[PuO_2{}^{+}]} = 0.9164 + 0.05916 \log[M] \tag{2}$$

and N is the plutonium oxidation number defined by eqn. (3):

$$N = \frac{6M^3 + 5M^2 + 4CM + 3D}{M^3 + M^2 + CM + D} \tag{3}$$

In both eqns. (2) and (3), the letter M refers to the equilibrium ratio of hexavalent to pentavalent plutonium: $[PuO_2{}^{2+}]/[PuO_2{}^{+}]$.

An important advance in recent times is the development of a computer program* which yields the analytic form of an indefinite integral. This new program has been applied to the plutonium work integral given as eqn. (1). The result is:

$$\Delta G = -F(N)E^{\circ}_{\mathrm{VI,V}} + \frac{0.05916F}{2.30259}\left[\ln(M^3 + M^2 + CM + D) + \frac{(M^2 + 2CM + 3D)\ln(M)}{(M^3 + M^2 + CM + D)} - 3\ln(M)\right] \tag{4}$$

where the term ΔG implies that eqn. (4) is to be evaluated between the upper and lower limits of M and N. In eqns. (3) and (4) the term C represents the product $K_2[H^+]^4/K_1$, and the term D represents the product K_2C. The equilibrium constants K_1 and K_2 are defined in eqns. (5) and (6), respectively.

$$K_1 = \frac{[Pu^{3+}][PuO_2{}^{+}][H^+]^4}{[Pu^{4+}]^2} \tag{5}$$

$$K_2 = \frac{[Pu^{3+}][PuO_2{}^{2+}]}{[Pu^{4+}][PuO_2{}^{+}]} \tag{6}$$

Provided the ionic strength of the solution is at least 0.3 M, the numerical values of K_1 and K_2 appropriate for 1 M perchloric acid ($K_1 \cong (6.97)(10^{-4})$, $K_2 \cong 13.2$) are probably accurate enough for most work estimations [3], and at least illustrative for high ionic strength values. The explicit use of alpha coefficients may be avoided in eqn. (4) if the values of the constants K_1 and K_2 are corrected by the plutonium alpha coefficients [4–6]. Eqn. (4) gives ΔG per mole of plutonium.

Applied to a millimolar solution of plutonium in 10 M perchloric acid, eqn. (4) yields ΔG = 10.9 calories as the work required to oxidize pure trivalent plutonium ($M \cong 0$ and $N = 3.0$) to an equimolar mixture of the trivalent and tetravalent states ($M \cong 13.16$ and $N \cong 3.5$). This agrees with eqn. (3) of reference [1] for such a solution.

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