Abnormal Decomposition Potentials Reconsidered—A Corrected Treatment

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In a recent paper (*1*), an attempt is made to explain "abnormal decomposition potentials" of aqueous solutions of halogen acids (HX, X = Cl, Br, I) in terms of the importance of the reactions of halogens (X_2) with water to form hypohalites (XO^-). The authors were concerned that the decomposition potentials are smaller than the difference in the standard potentials ($\Delta E°$) (in ref *1* called ε_r, the reversible emf) of the halogen (X_2, X^-) and hydrogen (H^+, H_2) couples. We discuss here (i) why the concept of "decomposition potential" is imprecise and is not discussed in modern books on electrochemistry, (ii) how one can understand why such decomposition potentials are smaller than $\Delta E°$, and (iii) why the halogen–water reaction is not relevant to a description of the electrochemistry of halogen acids under most conditions.

Current–Potential Curves and the Concept of "Decomposition Potential"

In older texts on physical chemistry and electrochemistry, a "decomposition voltage" (ε_d) for the electrolysis of a solution was defined as "the point at which steady electrolysis *commences*" (*2*) (italics added). In other words, when two electrodes are immersed in a given solution—for example, a solution of HX—and an increasing voltage is applied between them, the voltage at which a steady-state current *starts* was defined as ε_d. It was generally appreciated that the point corresponding to ε_d "cannot be defined precisely" and "is now believed not to have any exact theoretical significance" (*2*). This lack of precision and theoretical significance is the reason why the concept is not deemed to be useful in modern electrochemistry, where detailed calculation of current–potential (i–E) relations under a variety of conditions is now routine.

Consider an idealized i–E curve for a 1 M solution of HX at electrodes (e.g., Pt) where the half-reactions, the oxidation of X^- and the reduction of H^+, occur without appreciable kinetic problems; that is, in the absence of overpotentials. Moreover, we assume the absence of solution resistance effects. (As Liang et al. [*1*] point out, overpotentials and resistive effects would increase ε_d and hence are not relevant to their "abnormally small" decomposition potentials.) As is standard in electrochemical practice (*3*), one can determine the behavior of the whole cell by considering the anodic and cathodic half-reactions separately, usually as measured in a three-electrode cell with a separate reference electrode, and then combining these to get the behavior of both anode and cathode at the same time. The half reactions of relevance here are:

$$X_2 + 2e = 2X^-; \qquad E°(X_2, X^-) \qquad (1)$$

$$2H^+ + 2e = H_2 \qquad E° = 0.00 \text{ V vs NHE} \qquad (2)$$
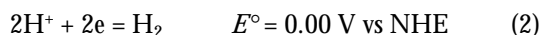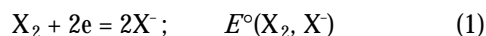
where $E°$ (X_2, X^-) (V vs NHE) for Cl, Br, and I are 1.358 for $Cl_2(g)$ and slightly higher for $Cl_2(aq)$, 1.087 $Br_2(aq)$, and 0.536 for I_3^- (*4*). These values are very close to those quoted for the reversible emf's, indicated as ε_r in ref *1*. The i–E curves, assuming Nernstian (i.e., thermodynamically reversible) half-reactions can be calculated from the expression (*3*)

$$E = E° - \frac{RT}{nF} \ln \frac{m_O}{m_R} + \frac{RT}{nF} \ln \left(\frac{i_{l,c} - i}{i - i_{l,a}} \right) \qquad (3)$$

or, rewritten in terms of the current

$$i = \frac{i_{l,a} Z + i_{l,c}}{1 + Z} \qquad (4a)$$

$$Z = \exp\left[(nF/RT)(E - E_{1/2}) \right] \qquad (4b)$$

$$E_{1/2} = E° - \frac{RT}{nF} \ln \frac{m_O}{m_R} \qquad (4c)$$

where $i_{l,c}$ and $i_{l,a}$ are the mass transfer limiting currents (A), given by

$$i_{l,c} = nFAC_O m_O \qquad (5)$$

$$i_{l,a} = nFAC_R m_R \qquad (6)$$

where n is the number of electrons transferred in the half-reactions, A is the electrode area (cm^2), F is the Faraday (96,485 C/eq), C_O and C_R are the concentrations of oxidized and reduced forms in the half-reaction in bulk solution (mol/cm^3), and m_O and m_R are mass transfer coefficients (cm/s); m_O and m_R can often be calculated from other more fundamental parameters, but are often of the order of 10^{-3} cm/s. Thus one can calculate the complete current–potential curve for each half-reaction and can combine these to yield the curve relevant for the cell. Such a curve for a 1 M HBr solution is given in Figure 1, assuming that Br_2 (or Br_3^-) and H_2 are initially absent from the solution and all m values are 10^{-3} cm/s. For simplicity we also assume the products of the reaction are totally soluble; taking account of the evolution of gaseous H_2 at about 1 atm pressure and production of liquid Br_2 would affect the shape of the resulting i–E curve, but not the principles being discussed. Indicated on the figure is also the "decomposition potential" for the solution, assuming that the point where steady-state current "starts" is where the current is 1% of the limiting current. Under these conditions the "decomposition potential" is 0.12 V smaller than the difference in $E°$ values; that is, $\varepsilon_d = 0.97$ V vs $\varepsilon_r = 1.09$ V. If the onset of current is taken at 0.1% of the limiting current,
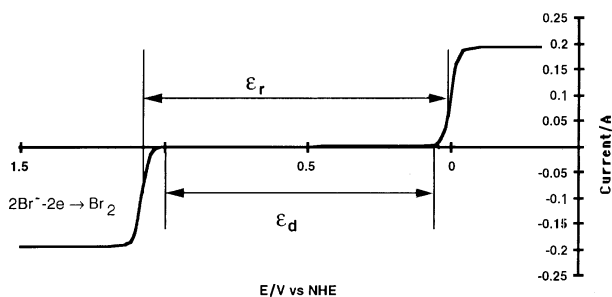
Figure 1. Idealized current–potential curve for a 1 M HBr solution. The calculation assumes $m_O = m_R = 10^{-3}$ cm/s for both half-reactions, solubility of all reactants and products, the initial absence of Br_2 and H_2, and a 1-cm^2 electrode.

then ε_d is 0.18 V smaller than ε_r. In general, under the assumed conditions, the "onset potential" precedes the half-wave potential at 25 °C by the amount $(0.05916/n) \log[(1 - x)/x]$, where x is the arbitrary choice of fraction of the limiting current selected (0.01 and 0.001 in the above example).

What is clear is that ε_d is not a well-defined quantity and it is of little real relevance under conditions when a complete current–potential curve can be defined. However, the presumed "abnormality" in $\varepsilon_d < \varepsilon_r$ does not exist; it is the natural consequence of the shape of the i–E curve.

For the sake of completeness we should mention that the actual situation, even considering the halogen acids as Nernstian systems, is more complicated, since questions of the solubility of the halogens, the formation of species like X_3^-, the pressure of H_2, and the relative magnitudes of the m values of the different species all enter into a more exact calculation. However, these considerations, while they would change the actual location and height of the i–E curves, would not change the basic concepts outlined above. Moreover, in any real electrochemical system kinetic limitations on the rate of electron transfer and resistive drop in the solution would have to be taken into account.

The Relevancy of Disproportionation Reactions in the Electrochemistry of Halogen Acids

Liang et al. (*1*) try to explain the electrochemistry of halogen acids in terms of the reactions of the halogens with water (i.e., the disproportionation of the halogen):

$$X_2 + H_2O \rightleftharpoons H^+ + X^- + HXO \quad K_d = [H^+][X^-][HXO]/[X_2] \quad (7)$$
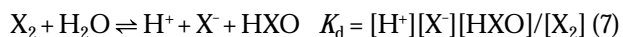
and take this into account simply by adding the free energy of this reaction to that of the cell reaction defined by eqs 1 and 2. It is well known that coupled chemical reactions can affect the electrochemistry of a half-reaction in general, and that a

reaction of the product of a half-reaction, like that implied in eq 7, can shift the i–E curve for oxidation of a halogen to less positive potentials. However, the importance of such a coupled reaction to the actual electrochemistry depends upon the extent to which it occurs under the conditions of the experiment (and, in most cases, on the rate of the coupled reaction). Even if one assumes reaction 7 is so fast that the equilibrium is established rapidly, the extent of this reaction in solutions of halogen *acids* is unimportant. From the equilibrium constant expression for eq 7,

$$[HXO]/[X_2] = K_d/[H^+][X^-] \quad (8)$$

For the values of K_d quoted in ref *1* for the different halogens, the ratios $[XO^-]/[X_2]$ are 4.2×10^{-4}, 7.2×10^{-9}, and 2.0×10^{-13} for X = Cl, Br, and I, respectively, for 1 M solutions of the halogen acids. It would, in principle, make some contribution for Cl in a 0.1 M solution (although kinetic considerations would be important here), but would be negligible for Br and I at this concentration—and at lower concentrations as well. Note that, if the solution conditions (i.e., concentration and solution pH) were not of importance, as assumed in ref *1*, one might equally try to add in the free energies of other reactions of halogens, such as the formation of halate,

$$3X_2 + 3H_2O \rightleftharpoons 6H^+ + 5X^- + XO_3^- \quad (9)$$
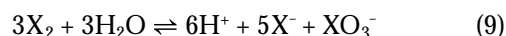
to the halogen half-reaction. Thus the disproportionation reaction is really of little consequence in defining the electrochemical behavior of halogen acids.

Conclusion

The "decomposition potential" concept, as discussed in ref *1*, is archaic and of little relevancy in modern electrochemistry. Complete current–potential curves can be calculated and they show why the current starts to flow before the standard potentials are attained. The occurrence of disproportionation reactions is not needed to explain this phenomenon, which is the natural consequence of the i–E behavior. In fact, such reactions are of little importance in understanding the redox chemistry of halogen acids at concentrations at or above levels of 10^{-3} M.

Literature Cited

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