CAPSULES
notes and applications from Bioanalytical Systems, Inc.

April, 1998

Peak Potential Separation for the Cyclic Voltammogram of a Reversible Process

One of the commonly quoted characteristic parameters for a cyclic voltammogram is the separation of the anodic and cathodic peak potentials, ΔE_p. For a reversible process, ΔE_p is slightly less than 60 mV, and this value is independent of the scan rate. However, the value quoted for ΔE_p for a reversible system varies between 57 and 59 mV. The aim of this Capsule is to discuss the equations from which the theoretical value of ΔE_p is derived and the parameters on which ΔE_p is dependent.

Let us first consider the relationship between the peak potential (E_p) and the redox potential for a linear sweep voltammogram ***(F1)***. The redox potential used for these definitions can either be the formal potential ($E^{0'}$) or the half-wave potential ($E_{1/2}$). These potentials are related by the equation

$$E_{1/2} = E^{0'} + \frac{RT}{nF} \ln \left(\frac{D_R^{1/2}}{D_0^{1/2}} \right)$$

When the diffusion coefficients of the oxidized and reduced species (D_O and D_R respectively) are equal, $E^{0'}$ and $E_{1/2}$ are identical.

The difference between E_p and $E_{1/2}$ for a reversible reduction is given by the equation:

$$E_p - E_{1/2} = -1.11 \left(\frac{RT}{nF} \right) = -28.5 \text{ mV at } 25\ ^\circ\text{C}.$$

Note that the difference is dependent on the temperature. It increases by about 1 mV for each 10 degree increase in the temperature (also note that n = 1 was used in the calculation of this value, and is also used in subsequent calculations).

Another parameter that is characteristic for a linear sweep or cyclic voltammogram is the half-peak potential $E_{p/2}$ (this is the potential at half the peak current).

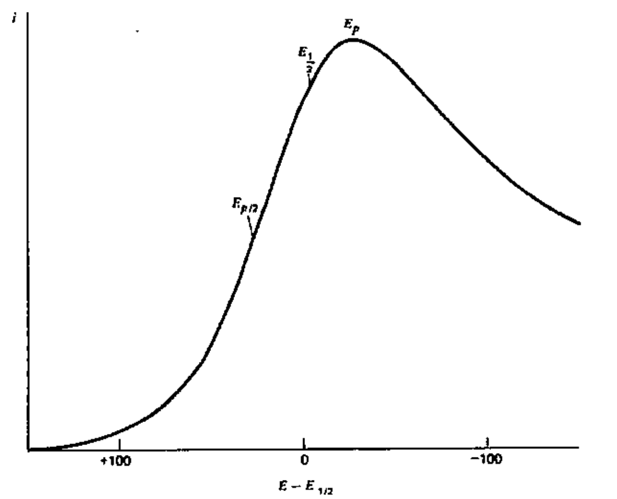

Figure 1. *Potential parameters for the linear sweep voltammogram of a reversible process.*

The difference between $E_{p/2}$ and $E_{1/2}$ for a reversible reduction is given by the equation:

$$E_{p/2} - E_{1/2} = +1.09 \left(\frac{RT}{nF} \right) = +28.0 \text{ mV at } 25\ ^\circ\text{C}.$$

Note that, while this value is similar to the value for the difference between E_p and $E_{1/2}$, it is not identical.

If the two equations above are combined, the difference between E_p and $E_{p/2}$ for a reversible process is obtained:

$$\left| E_p - E_{p/2} \right| = 2.2 \left(\frac{RT}{nF} \right) = 56.5 \text{ mV at } 25\ ^\circ\text{C}.$$

For cyclic voltammetry, it is more convenient to consider the difference between the peak potentials (ΔE_p) rather than the difference between E_p and $E_{1/2}$. Simplistically, it might be thought that this can be derived for a

BAS 2701 Kent Ave • W. Lafayette, IN 47906 • (765) 463-4527 • FAX (765) 497-1102 • bas@bioanalytical.com

reversible process by doubling the difference between E_p and $E_{1/2}$ (i.e., ΔE_p = 57 mV). However, ΔE_p is also dependent on the difference between the cathodic peak potential E_{pc} (for a reduction on the forward scan) and the switching potential E_λ, as is shown in the table below (1).

$E_{pc} - E_\lambda$ (mV)	ΔE_p(mV)
71.5	60.5
121.5	59.2
171.5	58.3
271.5	57.8
∞	57.0

As can be seen, although ΔE_p tends towards a limit of 57 mV at high values of $E_{pc} - E_\lambda$, for most experiments, ΔE_p will be 1 or 2 mV larger. Therefore, caution is required when quoting "theoretical values" for ΔE_p.

The data in the above table are based on a temperature of 25 °C. Since ΔE_p does vary with temperature, it is important to maintain a fixed temperature when quoting experimental data to a high degree of precision. If the temperature is not controlled, then this should be taken into account when quoting the experimental error.

References

1) *A.J. Bard and L.R. Faulkner, "Electrochemical Methods," Wiley, New York, 1980.*