Absolute Potentials of the Standard Hydrogen Electrode, Reference Electrodes and Aqueous Redox Couples of Elements of Gps. I -VIII

- Collected work dedicated to the pioneers, Volta, Davy and Faraday

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Abstract: Electrochemical potentials are conventionally referred to that of the standard hydrogen electrode (SHE) arbitrarily as zero, in the absence of the knowledge of the latter. More than two centuries after Volta, the author demonstrated for the first time, a new simple linear relation between the gaseous ionization potentials (I) and the aqueous standard redox potentials using existing data for the elements of various Groups in the Periodic Table. All these straight lines (except for Gp. VII) converged to one point at I = 0, yielding the absolute potential of SHE as 4.20 (+/- 0.03)V. For halogens (Gp. VII), the value was found to be 2.87 (+/-0.01) V. This enabled converting the existing standard potential data into absolute potentials. Since the gaseous ionization potentials are inversely proportional to the Bohr radius, an extension of the idea to absolute aqueous redox potentials enabled estimating the radii of redox components in solution and correlating them with their covalent radii.

Keywords: Absolute potential scale; Standard hydrogen electrode; Aqueous redox potentials; Reference electrodes; radii of redox components.

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Introduction

A nice account of the historical beginnings of electricity from Volta, Davy and Faraday can be found in the book, 'Chemistry is Electric' [1]. Chemical electricity involves redox processes which are conveniently studied electrochemically. To understand the physical electrochemistry of redox equilibria, a definitive knowledge of absolute electrode potential is essential.

In electrochemical literature and standard books [2,3], aqueous redox potentials are conventionally referred to that of the standard hydrogen electrode (SHE) as zero, in the absence of the knowledge of the absolute value. To quote from [2]: "*any chemical reaction involves only the difference in potentials between two couples, the absolute values are unnecessary. For this reason, the procedure has come into general use of choosing the potential of some one couple as an arbitrary zero and using this as a reference couple for potentials of all other couples. The reference couple so chosen is the hydrogen gas- hydrogen ion couple,* $H_2 = 2H^+ + 2e^-$, $E^o = 0$."

The arbitrary value, $E^o = 0 = (RT/F)\ln K_{dis} = 0.05916 \ln K_{dis}$, [2], where R is the gas constant, T is the absolute temperature and F is the Faraday constant and K_{dis} is the dissociation constant. At 25 °C, T = 298.16, (RT/F) = 0.05916 V, and $E^o = 0$ and it implies $K_{dis} = 1$.

There have been theoretical attempts to arrive at the absolute potential, E^o_{abs} (SHE) of SHE, see e.g., [4,5] and for a recent experimental approach, see [6]. The theoretical value 4.44 (+/- 0.02) V was obtained by Trasatti [4] earlier and the experimental value, 4.2 (+/-0.4) V was obtained by Donald et al [6]. By correlating the gaseous ionization potentials with the aqueous standard redox potentials, the author [7,8] obtained the value E^o_{abs} (SHE) = 4.20 (+/-0.02) V, close to that in [6].

2. Correlation of gaseous ionization potentials (I) with standard aqueous redox potentials (E^o) gives E^o_{abs} (SHE), E^o_{abs} for redox couples, and other interesting results [7-14].

For earlier work by the author relating ionization potentials and aqueous redox potentials, see [9,10]. Further researches showed *for the first time* the simple linear relations between ionization potentials and standard aqueous redox potentials [7,8]. All the straight lines (except for Gp. VII) converged to one point at I = 0, yielding the absolute potential E^o_{abs} (SHE) = 4.20 (+/- 0.03)V. For halogens (Gp. VII), the value was found to be 2.87 (+/-0.01) V.

Thus, by knowing the absolute value of SHE, the existing standard aqueous redox potentials could be converted to absolute potentials, $E^o_{abs} = E^o - E^o_{abs}$ (SHE), for the elements of the Periodic Table. Similarly, the standard potentials of reference electrodes could be tabulated on the absolute scale. See [7-12] for all the results and [12 d] for Tables in power point. Note, therefore that E^o_{abs} (SHE) = 4.20 = 0.059 ln K_{diss} and K_{diss} is not unity! Similarly for other redox couples, $E^o_{abs} = (RT/F)\ln K_{dis}$.

In [11], aqueous redox potentials are shown to be inversely proportional to the respective Bohr radius. The radii of redox components from absolute redox potentials have been correlated with covalent and aqueous ionic radii in [13].

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