

# The Reversible Reduction Potential of the Proton in Water and in Non-aqueous Solvents

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Parker, V. D., 1992. The Reversible Reduction Potential of the Proton in Water and in Non-aqueous Solvents. – Acta Chem. Scand. 46: 692–694.

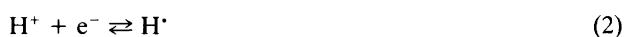
Dedicated to Professor Lars Skattebøl on the occasion of his 65th birthday.

The normal hydrogen electrode (NHE) has long been the standard reference for electrode reactions. The hydronium ion in its standard state, activity of unity in water at 298.15 K, is in equilibrium with dihydrogen gas in its standard state, 1 atmosphere pressure at 298.15 K. The NHE half-reaction is (1) which is assigned a standard free-energy



change, and hence electrode potential of 0. While the NHE serves to anchor the electrode potential scale for all other redox couples it is not commonly used as a reference electrode.

In recent years thermochemical cycles, in which electrode potentials are used to give reliable estimates of experimentally inaccessible quantities, have been applied extensively.<sup>1</sup> Often, as exemplified by determination of C–H,<sup>2</sup> C–C<sup>3</sup> or Metal–H<sup>4</sup> bond dissociation energies ( $E_{\text{bd}}$ ), the thermochemical cycles include the energy differences in heterolysis and homolysis of bonds. The electrode potentials that appear in these cycles are for electron transfer reactions in the absence of accompanying chemical reactions. The proton reduction potential of interest in these applications is eqn. (2). In this paper we derive the revers-



ible electrode potentials for eqn. (2) in water and other common electrochemical solvents.

The reversible electrode potential for reaction (2) in water can be related to the NHE reaction (1) by the thermochemical cycle illustrated in Scheme 1. The free energy of formation of the hydrogen atom ( $\Delta G_f$ ) is equal to 48.58 kcal mol<sup>-1</sup>.<sup>5</sup> However, the free energy of solvation of the hydrogen atom [ $\Delta G_{\text{solv}}(\text{H}^\cdot)$ ] is experimentally inaccessible. In the following section arguments are presented to justify taking the free energy of solvation of helium [ $\Delta G_{\text{solv}}(\text{He})_{\text{aq}}$ ] to be very nearly equal to that expected for  $\Delta G_{\text{solv}}(\text{H}^\cdot)_{\text{aq}}$ .

|  | Free energy  |
|--|--|
| $\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons 1/2 \text{H}_2(\text{gas})$ | 0  |
| $1/2 \text{H}_2(\text{gas}) \rightleftharpoons \text{H}^\cdot(\text{gas})$         | $\Delta G_f(\text{H}^\cdot)$   |
| $\text{H}^\cdot(\text{gas}) \rightleftharpoons \text{H}^\cdot(\text{aq})$          | $\Delta G_{\text{solv}}(\text{H}^\cdot)_{\text{aq}}$   |
| <hr/>  |  |
| $\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{H}^\cdot(\text{aq})$  | $\Delta G_{\text{solv}}(\text{H}^\cdot)_{\text{aq}} + \Delta G_f(\text{H}^\cdot)_{\text{gas}}$ |

Scheme 1.

The reversible potential for the reduction of the proton in water. The free energy of solvation of a gas in liquid solution is given by eqn. (3) where  $X_{\text{gas}}$  is the mole fraction of

$$\Delta G_{\text{solv}}(\text{gas}) = -RT \ln X_{\text{gas}} \quad (3)$$

the gas in solution under 1 atm gas pressure. Enthalpies and entropies of solvation of the rare gases in water, derived<sup>6</sup> from the temperature dependence of the Henry's law constant, were used to calculate  $\Delta G_{\text{solv}}(\text{gas})$  at 25°C which are listed in Table 1 along with the van der Waals radii. It is evident that  $\Delta G_{\text{solv}}(\text{gas})$  are correlated to the van der Waals radii ( $R$ ). Linear correlation results in eqn. (4), the correlation coefficient being equal to 0.99. Use of eqn. (4) to calculate  $\Delta G_{\text{solv}}$  results in an average deviation of  $\pm 0.05$

$$\Delta G_{\text{solv}}(\text{calc}) = 8.66 - 0.0128 R \quad (4)$$

kcal mol<sup>-1</sup> from the experimental value. The van der Waals radius of the hydrogen atom is 120 pm which results in  $\Delta G_{\text{solv}}(\text{calc})$  of  $7.12 \pm 0.05$  kcal mol<sup>-1</sup> in aqueous solution.

Having a reliable estimate of  $\Delta G_{\text{solv}}(\text{H}^\cdot)_{\text{aq}}$ , the reversible electrode potential  $\{E_{\text{rev}}[(\text{H}^+)_{\text{aq}}/(\text{H}^\cdot)_{\text{aq}}]\}$  for eqn. (2) can be calculated to be equal to  $-2.42$  V vs. NHE. An uncertainty of 0.01 V in  $E_{\text{rev}}[(\text{H}^+)_{\text{aq}}/(\text{H}^\cdot)_{\text{aq}}]$  corresponds to  $\pm 0.23$  kcal mol<sup>-1</sup> in  $\Delta G_{\text{solv}}(\text{H}^\cdot)$  which is well out of the range implied in the previous paragraph. Thus, assuming  $\Delta G_{\text{solv}}(\text{H}^\cdot)$  to be equal to  $\Delta G_{\text{solv}}(\text{He})$  results in  $E_{\text{rev}}[(\text{H}^+)_{\text{aq}}/(\text{H}^\cdot)_{\text{aq}}]$  equal to  $-2.42$  V vs. NHE.

Table 1. Free energies of solvation in water and van der Waals radii of rare gases.

| Element | $\Delta G_{\text{solv}}(\text{gas})^a$ | Radius <sup>b</sup> | $\Delta G_{\text{solv}}(\text{calc})^c$ |
|---------|--|---------------------|---|
| Helium  | 7.07                                   | 122                 | 7.10 (-0.03)                            |
| Neon    | 6.67                                   | 160                 | 6.61 (+0.06)                            |
| Argon   | 6.25                                   | 191                 | 6.22 (+0.03)                            |
| Krypton | 6.07                                   | 198                 | 6.13 (-0.06)                            |

<sup>a</sup>Free energy of solvation of the gas at 298.15 K at 1 atm gas pressure expressed in kcal mol<sup>-1</sup>. Calculated from  $\Delta H$  and  $\Delta S$  data in Ref. 6. <sup>b</sup>van der Waals radii ( $R$ ) in pm from Ref. 9.

<sup>c</sup>Calculated from linear correlation equation [ $\Delta G_{\text{solv}}(\text{calc}) = 8.66 - 0.0128 R$ ], correlation coefficient equal 0.99. The numbers in parentheses are the differences between the experimental and calculated values.

*Thermochemical relationship between  $E_{\text{rev}}[(\text{H}^+)_{\text{aq}}]$  and bond dissociation energies.* The difference in free energies of heterolytic and homolytic bond dissociation above the double line in Scheme 2 is directly related to the electrode

|                                 |  | Free energy  |
|---------------------------------|--|--|
| H-A                             | $\rightleftharpoons \text{H}^+ + \text{A}^-$ | $\Delta G_{\text{het}}(\text{H-A})$                                |
| H <sup>•</sup> + A <sup>•</sup> | $\rightleftharpoons \text{H-A}$              | $-\Delta G_{\text{hom}}(\text{H-A})$                               |
| <hr/>                           |  |  |
| H <sup>•</sup> + A <sup>•</sup> | $\rightleftharpoons \text{H}^+ + \text{A}^-$ | $-F\Delta E_{\text{rev}}(\text{A}^{\bullet} - \text{H}^{\bullet})$ |

Scheme 2.

potential difference below the double line.<sup>1</sup> Thus,  $\Delta G_{\text{het}}(\text{H-A}) - \Delta G_{\text{hom}}(\text{H-A})$  can be determined directly from the difference in reduction potentials of A<sup>•</sup> and H<sup>•</sup>. Since an abundance of  $\Delta G_{\text{het}}(\text{H-A})$  data (equal to  $+RTpK_{\text{a}}$ ) exist, the most important application of Scheme 2 is for the determination of  $\Delta G_{\text{hom}}(\text{H-A})$ . The gas-phase bond dissociation energy [ $E_{\text{bd}}(\text{H-A})$ ] can be obtained from the relationship in eqn. (5). The last two terms in (5) are most

$$E_{\text{bd}}(\text{H-A}) = \Delta G_{\text{hom}}(\text{H-A}) - \Delta G_{\text{solv}}(\text{H}^{\bullet}) + TS_{\text{f}}^{\circ}(\text{H}^{\bullet}) - \Delta G_{\text{solv}}(\text{A}^{\bullet} - \text{H-A}) + TS_{\text{f}}^{\circ}(\text{A}^{\bullet} - \text{H-A}) \quad (5)$$

often neglected in similar equations on the basis that the quantities for A<sup>•</sup> and H-A cancel. It is interesting to note that  $E_{\text{bd}}(\text{H-A})$  is independent of  $\Delta G_{\text{solv}}(\text{H}^{\bullet})$  since this term appears with a positive sign in  $\Delta G_{\text{hom}}(\text{H-A})$  and a negative sign in eqn. (5).

*The reduction potential of the proton in non-aqueous solvents.* In a previous section it was shown that  $\Delta G_{\text{solv}}(\text{gas})$  in water are directly dependent upon the van der Waals radii of the atoms and that  $\Delta G_{\text{solv}}(\text{H}^{\bullet})$  is closely approximated by the corresponding term for helium. The relationship between  $E_{\text{rev}}[(\text{H}^+)_{\text{aq}}/(\text{H}^{\bullet})_{\text{aq}}]$  in a second solvent (S) to that in water is illustrated in Scheme 3. The free energies of trans-

Table 2. Reversible reduction potentials of the proton in various solvents.<sup>a</sup>

| Solvent      | $\Delta G_{\text{tr}}^{\text{aq} \rightarrow \text{S}}(\text{H}^+)^b$ | $\Delta \Delta G_{\text{solv}}^{\text{S} \rightarrow \text{aq}}(\text{H}^{\bullet})^c$ | $E^{\circ}/\text{vs. NHE}$ |
|--------------|---|--|----------------------------|
| Water        | —   | —  | -2.42                      |
| Acetonitrile | +11.1   | -1.4   | -1.88                      |
| DMSO         | -4.5  | -0.8   | -2.58                      |

<sup>a</sup>At 298.15 K, assuming  $\Delta \Delta G_{\text{solv}}^{\text{S} \rightarrow \text{aq}}(\text{H}^{\bullet})^c$  equal to that for hydrogen. <sup>b</sup>Free energy of transfer of the proton from water to the solvent from Ref. 10. <sup>c</sup>The difference in free energy of solvation of the hydrogen atom between the solvent and water, taken to be equal to that for the hydrogen molecule.

|                                      |  | Free energy   |
|--------------------------------------|--|---|
| H <sup>•</sup> (aq) + e <sup>-</sup> | $\rightleftharpoons \text{H}^{\bullet}(\text{aq})$ | $-FE_{\text{rev}}[(\text{H}^+)_{\text{aq}}/(\text{H}^{\bullet})_{\text{aq}}]$       |
| H <sup>•</sup> (aq)                  | $\rightleftharpoons \text{H}^{\bullet}(\text{S})$  | $\Delta \Delta G_{\text{solv}}(\text{H}^{\bullet})$                                 |
| H <sup>•</sup> (S)                   | $\rightleftharpoons \text{H}^{\bullet}(\text{aq})$ | $-\Delta \Delta G_{\text{tr}}^{\text{aq} \rightarrow \text{S}}(\text{H}^{\bullet})$ |
| <hr/>                                |  |   |
| H <sup>•</sup> (S) + e <sup>-</sup>  | $\rightleftharpoons \text{H}^{\bullet}(\text{S})$  | $-FE_{\text{rev}}[(\text{H}^+)_{\text{S}}/(\text{H}^{\bullet})_{\text{S}}]$         |

Scheme 3.

fer of the proton from water to a number of solvents [ $\Delta G_{\text{tr}}^{\text{aq} \rightarrow \text{S}}(\text{H}^+)$ ] are known<sup>7</sup> and Scheme 3 can be used to determine  $E_{\text{rev}}[(\text{H}^+)_{\text{S}}/(\text{H}^{\bullet})_{\text{S}}]$  providing that  $\Delta \Delta G_{\text{solv}}(\text{H}^{\bullet})$ , the difference in solvation energies of H<sup>•</sup> in solvent S and in water, can be estimated.

The free energy of solvation of H<sub>2</sub> in water is equal to 6.5 kcal mol<sup>-1</sup> at 298 K and values have been reported<sup>8</sup> in acetonitrile (5.1 kcal mol<sup>-1</sup>) and in dimethyl sulfoxide (5.7 kcal mol<sup>-1</sup>). Assuming that  $\Delta \Delta G_{\text{solv}}(\text{H}^{\bullet})$  is equal to that for the hydrogen molecule results in  $\Delta G_{\text{solv}}(\text{H}^{\bullet})$  equal to 5.7 and 6.3 kcal mol<sup>-1</sup> in acetonitrile and dimethyl sulfoxide, respectively. Application of Scheme 3, using the data summarized in Table 2., then results in  $E_{\text{rev}}(\text{H}^+)_{\text{S}}$  equal to -1.88 V (acetonitrile) and -2.58 V (dimethyl sulfoxide).

*Conclusions.* Considering the potential of the NHE as a measure of the oxidizing power of the proton is misleading. The reversible reduction potentials (Table 2) clearly show why the proton is not a common oxidant in water or in aprotic solvents.

*Acknowledgements.* This research was supported by the National Science Foundation (CHE-9106618). This support is gratefully acknowledged.

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Received January 10, 1992.