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Gibbs energy of photoinduced electron transfer

For photoinduced electron transfer between an acceptor (A) and a donor (D) (either one of them may be the electronically excited molecular entity) of any charge type, $z(\mathrm{A})$ and $z(\mathrm{D})$, the change in standard Gibbs energy can be approximated as (the notation is for the case of neutral species D and A)

$$\Delta_{\mathrm{ET}}G^{\mathrm{o}} = N_{\mathrm{A}}\,\{e\,[E^{\mathrm{o}}(\mathrm{D}^{+\bullet}/\mathrm{D}) - E^{\mathrm{o}}(\mathrm{A}/\mathrm{A}^{-\bullet})] + w(\mathrm{D}^{+\bullet}\mathrm{A}^{-\bullet}) - w(\mathrm{DA})\} - \Delta E_{0,0}$$

where $e = 1.602\,176\,487 \times 10^{-19}\ \mathrm{C}$ is the elementary charge, $N_{\mathrm{A}} = 6.022\,141\,79 \times 10^{23}\ \mathrm{mol}^{-1}$ is the Avogadro constant, $E^{\mathrm{o}}(\mathrm{D}^{+\bullet}/\mathrm{D})/\mathrm{V}$ is the standard electrode potential of the donor cation radical resulting from the electron transfer, $E^{\mathrm{o}}(\mathrm{A}/\mathrm{A}^{-\bullet})/\mathrm{V}$ is the standard electrode potential of the acceptor (both relative to the same reference electrode) and $\Delta E_{0,0}/\mathrm{J\ mol}^{-1}$ is the vibrational zero electronic energy of the excited partner (provided that a vibrationally equilibrated excited state at energy $E_{0,0}$ takes part in the reaction), all data referring to the same solvent.

$w(\mathrm{D}^{+\bullet}\mathrm{A}^{-\bullet})$ and $w(\mathrm{DA})$ are the electrostatic work terms that account for the effect of Coulombic attraction in the products and reactants, respectively

$$w(\mathrm{D}^{+\bullet}\mathrm{A}^{-\bullet})/\mathrm{J} = \frac{z(\mathrm{D}^{+\bullet})\,z(\mathrm{A}^{-\bullet})\,e^{2}}{4\,\pi\,\varepsilon_{0}\,\varepsilon_{\mathrm{r}}\,a}$$

$$w(\mathrm{DA})/\mathrm{J} = \frac{z(\mathrm{D})\,z(\mathrm{A})\,e^{2}}{4\,\pi\,\varepsilon_{0}\,\varepsilon_{\mathrm{r}}\,a}$$

where a is the distance of the charged species after electron transfer, ε_{r} is the relative medium static permittivity (formerly called dielectric constant), $\varepsilon_{0} \approx 8.854 \times 10^{-12}\ \mathrm{C}^{2}\ \mathrm{J}^{-1}\ \mathrm{m}^{-1}$ is the electric constant (vacuum permittivity), and $z(\mathrm{X})$ the charge of the species X.

In SI units the factor $\frac{e^{2}}{4\,\pi\,\varepsilon_{0}} = 2.307 \times 10^{-28}\ \mathrm{J\ m}$. For the case of neutral species A and D, $z(\mathrm{D}) = z(\mathrm{A}) = 0$.

Notes:

1. Several approximations are in use for the calculation of the term $w(\mathrm{D}^{+\bullet}\mathrm{A}^{-\bullet})$, depending on the nature of the species formed such as contact or solvent-separated radical ion pairs or extended and/or linked D and A molecular entities. In the latter case, the stabilization of a dipole μ in a cavity of radius ρ could be an appropriate model and

$$w(\mathrm{D}^{+\bullet}\mathrm{A}^{-\bullet}) = \frac{N_{\mathrm{A}}\,\mu^{2}}{4\,\pi\,\varepsilon_{0}\,\rho^{3}}\,\frac{\varepsilon_{\mathrm{r}} - 1}{2\,\varepsilon_{\mathrm{r}} + 1}$$

2. In the above definitions, the IUPAC recommendations for the sign and symbols of standard potentials are used. Although not complying with the IUPAC-recommended nomenclature for the standard electrode potentials, traditionally the equation has been written as:

$$\Delta_{\mathrm{ET}}G^{\mathrm{o}} = N_{\mathrm{A}} \left\{ e\,(E^{\mathrm{o}}_{\mathrm{ox}} - E^{\mathrm{o}}_{\mathrm{red}}) + \frac{[z(\mathrm{A}) - z(\mathrm{D}) - 1]\, e^2}{4\,\pi\, \varepsilon_0\, \varepsilon_{\mathrm{r}}\, a} \right\} - \Delta E_{0,0}$$

   with $E^{\mathrm{o}}_{\mathrm{ox}}$ the standard electrode potential at which the oxidation occurs, and $E^{\mathrm{o}}_{\mathrm{red}}$ the standard electrode potential at which the reduction occurs. This form of the first term within the brackets is misleading and not recommended.
3. The standard emfs of oxidation and reduction are often called, respectively, 'oxidation' and 'reduction potential'. These terms are intrinsically confusing and should be avoided altogether, because they conflate the chemical concept of reaction with the physical concept of electrical potential.
4. The equation used for the calculation of the Gibbs energy of photoinduced electron-transfer processes should not be called the *Rehm-Weller equation*.

Source:
PAC, 2007, *79*, 293 *(Glossary of terms used in photochemistry, 3rd edition (IUPAC Recommendations 2006))* on page 348