

Rehm–Weller equation

Empirical correlation found between the observed second-order rate constant, k_q , for an intermolecular electron-transfer reaction and the Gibbs energy of the photoinduced electron transfer process within the encounter complex ($\Delta_{\text{ET}}G^0$):

$$k_q = \frac{k_d}{1 + \frac{k_d}{K_d Z} \left[\exp\left(\frac{\Delta G^\ddagger}{RT}\right) + \exp\left(\frac{\Delta_{\text{ET}}G^0}{RT}\right) \right]}$$

with k_d and k_{-d} the rate constant for the formation and separation, respectively, of the encounter (precursor) complex, $K_d = k_d/k_{-d}$, Z the universal collision frequency factor, R the gas constant, T the absolute temperature and ΔG^\ddagger the activation Gibbs energy of the forward electron transfer reaction.

Note:

In the original formulation of this equation the value $\frac{k_d}{K_d Z} = 0.25$ in acetonitrile was used.

Source:

PAC, 2007, 79, 293 (*Glossary of terms used in photochemistry, 3rd edition (IUPAC Recommendations 2006)*) on page 413