Temperature and solvent (solute) polarizability in electron transfer reactions

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Bell-shaped Arrhenius law in electron transfer

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Polarizability of the donor-acceptor complex and Q-model of electron transfer

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How rates and spectra are affected by the solvent polarizability?

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Nyquist and all what followed ...

Nyquist theorem (1928): \( \langle \delta A^2 \rangle \propto k_B T \)

Fluctuation-dissipation theorem (Kubo):

\[
\langle \delta A^2 \rangle = k_B T \chi(\infty)
\]

Nyquist theorem

Marcus theory (1956):

\[
P(X) \propto e^{-\frac{(X-X_0)^2}{2\sigma^2}}
\]

\[
\sigma^2 = \langle \delta X^2 \rangle \propto T
\]

\[
P(0) \propto e^{-\beta \Delta F_{FDT}}
\]

Arrhenius
Reorganization energy

\[ \langle \delta X^2 \rangle = 2k_B T \]

macroscopic variable

Violation of FDT:

\[ \langle \delta M^2 \rangle \]

\[ \langle \delta \rho^2 \rangle \]
Microscopic properties

= 

Ability to design
Back to molecules

enthalpic entropic

\[ \lambda = \lambda_p + \frac{\sigma_d^2}{2k_B T} \]

dipolar reorientations positional (density) fluctuations

\[ \lambda = a + \frac{b}{T} \]

hyperbolic temperature law

DVM, MP’93
generally non-Arrhenius

\[ k \propto e^{-\beta \Delta G^\dagger (T)} \]

\[ \Delta G^\dagger (T) = \frac{(\lambda(T) + \Delta G_0(T))^2}{4\lambda(T)} \]

\[ \Delta G_0 = a' + b'/T \]
ET in MTHF

dielectric continuum

gust, Moore, Moore

dielectric continuum

top of Marcus inverted parabola

\[ \lambda(T^*) + \Delta G_0(T^*) = 0 \]
Marcus bell-shaped law in the Arrhenius coordinates

\[ \ln(\kappa_{ET}) \]

\[ \ln(\kappa_{IET}) \]

\[ G_{a} = 0 \]

\[ -\Delta G_{0} \]

\[ 1/T \]

\[ \ln[k_{R} \times s] \]

\[ 1000/T \ (K^{-1}) \]

Exp. (R)  
Theory (R)
Miller’s charge-shift complexes

Closs+Miller, Science’88
Negative activation enthalpy

ClQSB

QSB

Exp.  Q-model  Marcus

1000/T (K$^{-1}$)

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Driving force vs $T$

$$k_{ET} = \frac{2\pi}{\hbar} V^2 e^{-S} \sum_{m \geq 0} \frac{S_m}{m!} P_G(-m\hbar \omega_v)$$

$$P_G(X) = \left[2\pi \sigma_X^2\right]^{-1/2} e^{-\frac{(X-X_0)^2}{2\sigma_X^2}}$$

**generic Gaussian (Marcus) model**

$$P_Q(X) = \beta A \sqrt{\frac{\lambda \alpha^3}{|X - X^*|}} e^{-\beta(\alpha|X - X^*| + \alpha^2 \lambda)}$$

$$I_1(2\beta \sqrt{\alpha^3 \lambda|X - X^*|})$$

**non-Gaussian, Q-model (JCP’00)**
Gaussian model is inconsistent with experimental driving force
Possible scenario

\[
\alpha_f \gg \alpha_i
\]

\[
\Delta E(q) = \Delta E_0 + aq + bq^2
\]

non-Gaussian

\[
b \propto \Delta \alpha
\]
Q-model

\[ 2\lambda^{St} = \lambda \frac{\alpha(1 + 2\alpha)}{(1 + \alpha)^2} \xrightarrow{\alpha \to \infty} 2\lambda \]

non-Gaussian parameter

Maximum of the inverted parabola:

\[ -\Delta G_0^{\text{max}} \simeq (\lambda + \lambda_v) \]

\[ -\Delta G_0^{\text{max}} \simeq (\lambda + \lambda_v) \frac{\alpha}{1 + \alpha} \quad \alpha \to 0 \quad 0 \]

\[ \lambda = \lambda^{St} \quad \text{(Marcus)} \]

Marcus

Q-model
Energy gap law

\[ \alpha \approx 1 \]

Miller complexes

Maximum rate can be achieved at a much smaller driving force! (requires polarizable donor-acceptor complexes)
Solvent polarizability

\[ \lambda \propto c_0 \]

\[ c_0 = \epsilon^{-1}_\infty - \epsilon^{-1}_s \]

Pekar factor

Non-polar solvents (CCl4):

\[ \epsilon_\infty \approx \epsilon_s, \quad c_0 \to 0 \]

Polar solvents:

\[ \lambda(\epsilon_\infty = 2) \approx \frac{1}{2} \lambda(\epsilon_\infty = 1) \]

potential issue for force-field simulations
Reformulating Marcus functional

Marcus theory (1956):

\[ F[\mathbf{P}] = \frac{1}{2\chi^L} \mathbf{P} \ast \mathbf{P} - \mathbf{E}_0 \ast \mathbf{P} \quad \chi^L = (4\pi)^{-1} c_0 \]

\[ F_n = -\lambda = \frac{c_0}{8\pi} \mathbf{E}_0 \ast \mathbf{E}_0 \]

Microscopic functional:

\[ E[\tilde{\mathbf{P}}_n] = F_e + \frac{1}{2} \sum_{\gamma, \mathbf{k}} \frac{|\tilde{\mathbf{P}}_{\gamma n}|^2}{\chi_{nn}(k)} - \sum_{\gamma, \mathbf{k}} q^\gamma(k) \tilde{\mathbf{F}}_0^\gamma \cdot \tilde{\mathbf{P}}_n^\gamma \]

k-dependent polarization field

k-dependent susceptibility function
Microscopic susceptibilities

One can produce “microscopically motivated” continuum:

\[ \kappa \rightarrow 0 \]
Have Pekar and Marcus looked at the right continuum?

- NO
- There are multiple continua
- Different continua converge to numerically similar results
- The convergence is very slow and is not reached for typical conditions
Susceptibilities from simulations

\[ k \rightarrow 0 \text{ limit} \]

polarizable water

\[ \chi^L = (4\pi)^{-1} c_0 \]

![Graph showing susceptibility vs. \( \varepsilon_\infty \)]

\[ \chi^L_m = \frac{\varepsilon_s - 1}{4\pi \varepsilon_s} \left( \frac{\varepsilon_\infty + 2}{3\varepsilon_\infty} \right)^2 \]

Multiple continua can be produced from microscopic models
\[ \lambda \text{ at } k \neq 0 \]

Dependence on the refractive index predicted by the Pekar factor is too strong. Not supported by microscopic calculations.

\[ \lambda(\varepsilon_{\infty}) \text{ is nearly flat} \]
Lippert-McRae equation (1957)

\[ \hbar \Delta \omega \propto [g(\epsilon) - g(\epsilon_{\infty})] \]

\[ g(\epsilon) = \frac{\epsilon - 1}{2\epsilon + 1} \]

k=0 limit of microscopic theories:

\[ \hbar \Delta \omega \propto g(\epsilon_{\infty}, \epsilon) \]

\[ g(\epsilon_{\infty}, \epsilon) = \frac{\epsilon_{\infty}^2 + 2}{3} \left( \frac{\epsilon_{\infty} + 2}{3\epsilon_{\infty}} \right)^2 \frac{(\epsilon - 1)(\epsilon - \epsilon_{\infty})}{2\epsilon^2 - \epsilon\epsilon_{\infty} - \epsilon_{\infty}} \]

Weaker dependence of the line shift on the refractive index!
ET in nonpolar liquids

\[ X^{\text{ind}} = -\left(\alpha/2\right) \sum_k \left[ \mathbf{E}_{2k}^2 - \mathbf{E}_{1k}^2 \right] \]

\[ \sigma_X^2 = \langle (\delta X^{\text{ind}})^2 \rangle = 2k_B T \lambda^{\text{ind}} \]

\[ \lambda^{\text{ind}} = \beta \left( \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \right)^2 g^{\text{ind}} \]

\[ \beta = (k_B T)^{-1} \]

\( \epsilon_\infty \approx \epsilon_s, \ c_0 \to 0 \)

violation of the Nyquist (FDT) theorem
(microscopic-length of fluctuations)

\( \lambda^{\text{ind}} \approx 0.2 - 0.3 \ eV \ \text{CCl}_4 \)
Conclusions

Hyperbolic temperature dependence of the reorganization energy: non-Arrhenius, bell-shaped kinetic law

Non-Gaussian statistic of the energy gap can lead to dramatic improvements of the efficiency of solar energy conversion (energy-gap law)

Dependence on the refractive index is incorrect in classical model for both the reaction rates and spectral shifts

$$\Delta \omega \propto g(\epsilon_{\infty}, \epsilon)$$
Temperature calculations

\[ \lambda(T^*) + \Delta G_0(T^*) = 0 \]

dielectric continuum