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Journal of Electroanalytical Chemistry 483 (2000) 2–6

Journal of
Electroanalytical
Chemistry

Tutorial on rate constants and reorganization energies[☆]

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Received 4 October 1999; received in revised form 10 December 1999; accepted 10 December 1999

Abstract

These lecture notes, presented as a tutorial at the Euroconference on Modern Trends in Electrochemistry of Molecular Interfaces, consist of the following sections: (i) elementary transition state theory of reaction rates; (ii) elementary ion solvation theory; (iii) elementary solvent reorganization theory; (iv) generalizations; (v) extension to the metal | liquid interface; (vi) extension to the liquid | liquid interface, and (vii) examples of references © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Electron transfer theory; Transition state theory; Free energy; Non-equilibrium dielectric polarization

1. Individual topics

1.1. Elementary transition state theory of reaction rates

We calculated the rate constant using transition state theory and the electron transfer theory given in the subsequent sections.

The kinetic energy along a 'reaction coordinate' q is $p^2/2\mu$, where $p = \mu\dot{q}$, $\dot{q}$ is $\mathrm{d}q/\mathrm{d}t$, and μ is an effective mass for motion along q. The number of 'quantum states' for motion along q in the phase space volume element $\mathrm{d}q\,\mathrm{d}p$ is $\mathrm{d}q\,\mathrm{d}p/h$. Accordingly, the probability of the reacting system being in $(q, q + \mathrm{d}q)$ and $(p, p + \mathrm{d}p)$, $P\,\mathrm{d}q\,\mathrm{d}p$, is

$$P\,\mathrm{d}q\,\mathrm{d}p = \frac{\mathrm{e}^{-G(q^{\dagger})/kT}\,\mathrm{e}^{-p^2/2\mu kT}}{\mathrm{e}^{-G_{\mathrm{r}}/kT}}\,\frac{\mathrm{d}q\,\mathrm{d}p}{h} \tag{1}$$

where G_{r} is the Gibbs energy of the reactants plus environment, for all coordinates. $G_{\mathrm{r}}(q^{\dagger})$ is the Gibbs energy at $q^{\dagger}$ associated with all coordinates except q. (It does contain the potential energy at q, but not the kinetic energy $p^2/2\mu$ for motion along q.) The probability/length along q, i.e. the probability density, at $q^{\dagger}$, equals the above divided by $\mathrm{d}q$.

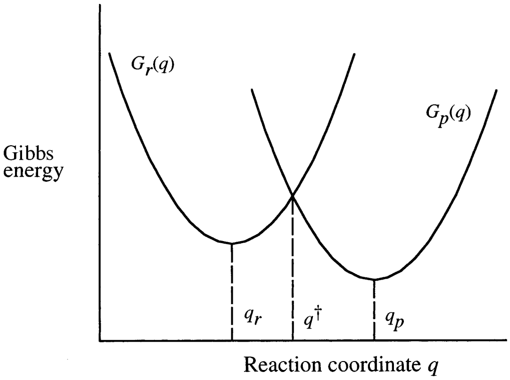

Fig. 1. Gibbs energy curves of reactants plus environment, $G_{\mathrm{r}}(q)$, and products plus environment, $G_{\mathrm{p}}(q)$, versus the reaction coordinate q.

To obtain k_{rate} we calculated the total reactive probability flux by multiplying this linear density $P\,\mathrm{d}p$ by the velocity $\dot{q}$ and integrating over all p from 0 to ∞. (Only positive ps at $q = q^{\dagger}$ led to the products.) We have

$$k_{\mathrm{rate}} = \mathrm{e}^{-\Delta G^{\dagger}/kT}\int_0^{\infty}\mathrm{e}^{-p^2/2\mu kT}\,\dot{q}\,\mathrm{d}p/h \tag{2}$$

where

$$\Delta G^{\dagger} = G_{\mathrm{r}}(q^{\dagger}) - G_{\mathrm{r}} \tag{3}$$

But

$$\dot{q}\,\mathrm{d}p = (p/\mu)\,\mathrm{d}p = \mathrm{d}(p^2/2\mu) \tag{4}$$

so

[☆] Paper presented at the Euroconference on Modern Trends in Electrochemistry of Molecular Interfaces, Finland, 28 August–3 September, 1999.

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0022-0728/00/$ - see front matter
PII: S0022-0728(00)00011-5

$$k_{\mathrm{rate}} = \frac{kT}{h}\,\mathrm{e}^{-\Delta G^{\dagger}/kT} \tag{5}$$

Example: suppose that the reaction is intramolecular or that it is bimolecular but where the two reactants are 'fixed' in position. Then on writing G_{r} as the sum of the value $G_{\mathrm{r}}(q_{\mathrm{r}})$ at the minimum of the $G_{\mathrm{r}}(q)$ curve in Fig. 1 given later and the contribution from the vibration about q_{r} on the G_{r} curve, expressible in terms of a vibrational partition function kT/hv, where v is the vibration frequency at q_{r} for 'vibration' along q (v is related to $\partial^2 G_{\mathrm{r}}/\partial q^2$ at $q^{\dagger}$) we have

$$\mathrm{e}^{-G_{\mathrm{r}}/kT} = \frac{kT}{hv}\,\mathrm{e}^{-G_{\mathrm{r}}(q_{\mathrm{r}})/kT} \tag{6}$$

Note that $G_{\mathrm{r}}(q^{\dagger})$ and $G_{\mathrm{r}}(q_{\mathrm{r}})$ have the same number of coordinates, one less than the total number of coordinates.

If we denote by G^* the difference

$$\Delta G^* \equiv G_{\mathrm{r}}(q^{\dagger}) - G_{\mathrm{r}}(q_{\mathrm{r}}) \tag{7}$$

we thus find

$$k_{\mathrm{rate}} \sim v\,\mathrm{e}^{-G^*/kT} \tag{8}$$

for this case. Typically $v \sim 10^{13}\ \mathrm{s}^{-1}$.

Remarks: (1) Wigner's deep insight (1938), not usually discussed in elementary books on reaction rate theory, into the basic assumption underlying classical transition state (TS) theory, involves no recrossing of the TS 'hypersurface' by trajectories as a condition for the validity of TS theory.

(2) We have not discussed, above, the nature of the reaction coordinate q. An appropriate choice includes contributions from all relevant spatial coordinates and can be defined globally. It is described briefly later.

1.2. Elementary ion solvation theory (Born, 1920)

The solvation Gibbs energy of an ion, ΔG_{solv}, equals the reversible work to transfer the ion from vacuum to the solvent. To calculate it using Born's model of almost 80 years ago, the ion is treated as a charged sphere of radius a and of charge e, embedded in the solvent, which is treated as a dielectric continuum. Continuum treatments have been very commonly used for various properties, such as ion solvation, diffusion constants, dielectric relaxation, the Goüy–Chapman model of charge distribution, and capillary waves at interfaces. Of course, continuum treatments are only approximate descriptions of the actual molecular systems.

Let us charge the ion in this continuum solvent of static dielectric constant ε_{s}. The electrostatic potential due to the ion and the surrounding solvent, at any point at a distance r from the center of the ion, is $e/\varepsilon_{\mathrm{s}} r$, where e is the charge of the ion. The work to change an ionic charge λe to $(\lambda + \mathrm{d}\lambda)e$, where λ goes from 0 to 1, is $(\lambda e/\varepsilon_{\mathrm{s}} a)$ $(e\,\mathrm{d}\lambda)$, since the electrostatic potential on the sphere is $\lambda e/\varepsilon_{\mathrm{s}} a$. (This expression is valid regardless of whether the charge is at the center of the sphere or whether it resides on the surface of the sphere.) Integration over λ, yields $e^2/2\varepsilon_{\mathrm{s}} a$. Now, subtract the corresponding electrostatic work for charging the ion in a vacuum, $e^2/2a$. So,

$$G_{\mathrm{solv}} = -\frac{e^2}{2a}\left(1 - \frac{1}{\varepsilon_{\mathrm{s}}}\right) \quad \text{(Born)} \tag{9}$$

1.3. Elementary 'reorganization' theory

Recall first a now common Gibbs energy plot:

We omit for the moment the argument that leads from multidimensional (thousands of coordinates) potential energy surfaces to Gibbs energy G versus q curves, q being the reaction coordinate. At the intersection in Fig. 1, q is denoted by $q^{\dagger}$, and the electron transfer occurs at $q^{\dagger}$. (It satisfies thereby both energy conservation and the Franck–Condon principle.)

On reaching $q^{\dagger}$ the system has experienced a major fluctuation of its various coordinates. In contrast, at q_{r}, the distribution of coordinates of the solvent, and hence its dielectric polarization function $\mathbf{P}(\mathbf{r})$ at each point $\mathbf{r}$, is in equilibrium with the charges in the reactants' system. At q_{p} the system's $\mathbf{P}(\mathbf{r})$ is in equilibrium, instead, with the charges in the products' system. At $q^{\dagger}$ it is in equilibrium with neither, i.e. $q^{\dagger}$ is associated with a substantial fluctuation of coordinates of the entire system from their equilibrium distribution at q_{r} or at q_{p}, and hence with a fluctuation of $\mathbf{P}(\mathbf{r})$ from the value of the function when $q = q_{\mathrm{r}}$ or when $q = q_{\mathrm{p}}$.

Let us calculate the Gibbs energy when the system (reactants plus environment) is around q_{r}, and also when the system, consisting of products and environment, is around q_{p}. Then we calculate the Gibbs energy change required to reach $q^{\dagger}$ from q_{r} on the $G_{\mathrm{r}}(q)$ curve in Fig. 1, as well as that to reach $q^{\dagger}$ from q_{p} on the $G_{\mathrm{p}}(q)$ curve. We then use these two quantities, plus a minimization procedure described below, to calculate the Gibbs energy barrier to the reaction, $G_{\mathrm{r}}(q^{\dagger}) - G_{\mathrm{r}}(q_{\mathrm{r}})$ in Fig. 1.

Consider two reactants fixed in position, a distance R between their centers, in a solvent free from other electrolytes. Their Gibbs energy G_{r} (considering only solvation Gibbs energy plus the sum $\varepsilon_1^{\mathrm{el}} + \varepsilon_2^{\mathrm{el}}$ of the electronic energies of reactants) is

$$G_{\mathrm{r}} = \varepsilon_1^{\mathrm{el}} + \varepsilon_2^{\mathrm{el}} - \frac{e_1^2}{2a_1}\left(1 - \frac{1}{\varepsilon_{\mathrm{s}}}\right) - \frac{e_2^2}{2a_2}\left(1 - \frac{1}{\varepsilon_{\mathrm{s}}}\right) + \frac{e_1 e_2}{\varepsilon_{\mathrm{s}} R'} \tag{10}$$

after including the coulombic interaction of the reactants $e_1 e_2/\varepsilon_{\mathrm{s}} R$. For the products G_{p} we add a p symbol to the $\varepsilon^{\mathrm{el}}$s and to the es. For brevity of presentation, we have omitted any contribution to G_{r}, G_{p} and $G(q^{\dagger})$ arising from changes in the vibrational coordinates of the reactants.

We now calculate the change in Gibbs energy required to form a system at any other q, i.e. other than the qs corresponding to $q_{\rm r}$ and $q_{\rm p}$, on curves $G_{\rm r}(q)$ and $G_{\rm p}(q)$ in Fig. 1. As indicated above, the dielectric polarization function $\mathbf{P}(\mathbf{r})$ for a system at $q_{\rm r}$ is the equilibrium one for the reactants and environment and at $q_{\rm p}$ it is the equilibrium one for the products and environment. Elsewhere in this figure, for example at $q^{\dagger}$, $\mathbf{P}(\mathbf{r})$ is a non-equilibrium dielectric polarization at each $\mathbf{r}$. We know from thermodynamics that a Gibbs energy change can be calculated from the reversible work done along a path that forms that state. That statement applies even if the state is a non-equilibrium one in terms of its macroscopic properties, such as the dielectric polarization function $\mathbf{P}(\mathbf{r})$ at each point $\mathbf{r}$ in the system. The secret to calculating it is to find a reversible path!

To do so we employ a two-stage charging process along the following reversible path, which forms the above non-equilibrium state. Let us suppose that at any point on curve $G_{\rm r}(q)$ the distribution of nuclear coordinates of the solvent is that in equilibrium with some hypothetical charges $e_{{\rm o},1}$ for reactant 1 and $e_{{\rm o},2}$ for reactant 2. What is the solvation Gibbs energy of this hypothetical system? We consider initially the case where the ions are far apart ($R=\infty$) and examine one ion. We first calculate the reversible work to charge the ion to the above hypothetical charge.

(I) Charge the ion from 0 to a hypothetical charge $e_{\rm o}$. From our previous result we have

$$\text{Work done} = -e_{\rm o}^2/2\varepsilon_{\rm s}\,a \tag{11}$$

(II) Holding the solvent nuclear coordinates fixed, but allowing the electronic polarization of solvent to adapt, we change the charge from $e_{\rm o}$ to e, so that in this reversible charging step we have

$$e_{\lambda} = e_{\rm o} + \lambda(e - e_{\rm o}),\ \lambda \text{ goes from 0 to 1} \tag{12}$$

The electrostatic potential at any point distant r from the center of the ion is

$$\phi_{\lambda}^{\rm II} = \frac{e_{\rm o}}{\varepsilon_{\rm s} r} + \frac{\lambda(e-e_{\rm o})}{\varepsilon_{\rm op} r} \tag{13}$$

since only the electronic polarization of the solvent responds to the change in charge $e_{\lambda}-e_{\rm o}$, i.e. to $\lambda(e-e_{\rm o})$, and since the corresponding dielectric constant for the change in electronic polarization is the optical dielectric constant $\varepsilon_{\rm op}$ (about 1.8 for water, whereas the static dielectric constant $\varepsilon_{\rm s}$ is about 80). The reversible work done in step II is

$$\int_{\lambda=0}^{1} \phi_{\lambda}^{\rm II}(r=a)\,{\rm d}e_{\lambda} = \frac{e_{\rm o}(e-e_{\rm o})}{\varepsilon_{\rm s}\,a} + \frac{(e-e_{\rm o})^2}{2\varepsilon_{\rm op}\,a} \tag{14}$$

Add it to the work done in step I, $e_{\rm o}^2/2\varepsilon_{\rm s}a$. Now subtracting the work to charge the actual ion in the solvent under equilibrium solvation conditions, $e^2/2\varepsilon_{\rm s}a$, the contribution to the Gibbs energy of solvation for forming this non-equilibrium dielectric polarization system, $G_{\rm solv}^{\rm noneq}$, is

$$\begin{aligned}\Delta G_{\rm solv}^{\rm noneq} &= \frac{e_{\rm o}^2}{2\varepsilon_{\rm s}\,a} + \frac{e_{\rm o}(e-e_{\rm o})}{\varepsilon_{\rm s}\,a} + \frac{(e-e_{\rm o}^2)^2}{2\varepsilon_{\rm op}\,a} - \frac{e^2}{2\varepsilon_{\rm s}\,a}\\ &= \frac{(e-e_{\rm o})^2}{2a}\left(\frac{1}{\varepsilon_{\rm op}} - \frac{1}{\varepsilon_{\rm s}}\right)\end{aligned} \tag{15}$$

Now consider two ions 1 and 2 with actual charges e_1 and e_2, but with a 'nuclear' dielectric polarization in equilibrium with hypothetical charges $e_{{\rm o},1}$ and $e_{{\rm o},2}$ and include the effect of the coulombic interaction of the ions. Instead of Eq. (15) one finds (not shown here but can be seen in a reference cited at the end)

$$\begin{aligned}\Delta G_{\rm solv}^{\rm noneq} = \Bigg[&\frac{(e_1-e_{{\rm o},1})^2}{2a_1} + \frac{(e_2-e_{{\rm o},2})^2}{2a_2}\\ &+ \frac{(e_1-e_{{\rm o},1})(e_2-e_{{\rm o},2})}{R}\Bigg]\left(\frac{1}{\varepsilon_{\rm op}} - \frac{1}{\varepsilon_{\rm s}}\right)\end{aligned} \tag{16}$$

How can we find the $e_{{\rm o},1}$ and $e_{{\rm o},2}$ corresponding to the point $q^{\dagger}$ in the Gibbs energy plot? We proceed as follows:

It can be shown that the condition that the potential energies in a multidimensional coordinate plot are equal at the transition state, which is the intersection, has as a consequence that the two Gibbs energies are also equal,

$$G_{\rm r}(q^{\dagger}) = G_{\rm p}(q^{\dagger}) \tag{17}$$

We can write, however, that

$$G_{\rm r}(q^{\dagger}) = G_{\rm r}(q_{\rm r}) + \Delta G_{\rm solv}^{\rm noneq} \tag{18a}$$

$$G_{\rm p}(q^{\dagger}) = G_{\rm p}(q_{\rm p}) + \Delta G_{\rm solv}^{\rm noneq,\,p} \tag{18b}$$

where $\Delta G_{\rm solv}^{\rm noneq,\,p}$ is the Gibbs energy required to reach $q^{\dagger}$ from $q_{\rm p}$. We note as an aside, that both $G_{\rm r}(q^{\dagger})$ and $G_{\rm r}(q_{\rm r})$ each contain the sum of electronic energies, $\varepsilon_1^{\rm el}+\varepsilon_2^{\rm el}$ (chemical energies) of the reactants, and similarly $G_{\rm p}(q^{\dagger})$ and $G_{\rm p}(q_{\rm p})$ contain those of the products, $\varepsilon_1^{\rm el,\,p}+\varepsilon_2^{\rm el,\,p}$.

Inasmuch as we have

$$G(q_{\rm p}) - G(q_{\rm r}) = \Delta G_{R'}^{\circ} \tag{19}$$

ΔG_R° being the 'standard' Gibbs energy of reaction at the separation distance R, we then have

$$\Delta G_R^{\circ} = \Delta G_{\rm solv}^{\rm noneq} - \Delta G_{\rm solv}^{\rm noneq,\,p} \tag{20}$$

We wish now to find the two unknowns $e_{{\rm o},1}$ and $e_{{\rm o},2}$.To do so we minimize $\Delta G_{\rm solv}^{\rm noneq}$, subject to the condition imposed by Eq. (17), i.e. subject to the constraint imposed by the above Eq. (20) for ΔG_R°. To perform this minimization we use the method of Lagrangian multipliers and solve for $e_{{\rm o},1}$ and $e_{{\rm o},2}$. In particular, we vary $\Delta G_{\rm solv}^{\rm noneq}$ and set $\delta\, G_{\rm solv}^{\rm noneq}=0$ (to minimize it):

$$0=\delta\ \Delta G_{\rm solv}^{\rm noneq}=\frac{\partial \Delta G_{\rm solv}^{\rm noneq}}{\partial e_{\rm o,1}}\,\delta e_{\rm o,1}+\frac{\partial G_{\rm solv}^{\rm noneq}}{\partial e_{\rm o,2}}\,\delta e_{\rm o,2} \tag{21}$$

subject to the constraint

$$\delta\ \Delta G_R^\circ=\frac{\partial[\Delta G_{\rm solv}^{\rm noneq}-\Delta G_{\rm solv}^{\rm noneq,\,p}]}{\partial e_{\rm o,1}}\,\delta e_{\rm o,1} + \frac{\partial[\Delta G_{\rm solv}^{\rm noneq}-\Delta G_{\rm solv}^{\rm noneq,\,p}]}{\partial e_{\rm o,2}}\,\delta e_{\rm o,2}=0 \tag{22}$$

However, the variations in $e_{\rm o,1}$ and $e_{\rm o,2}$ in Eq. (21) are not independent, since $e_{\rm o,1}$ and $e_{\rm o,2}$ are related via Eq. (20) for ΔG_R°. A common method to treat this problem is to introduce Lagrangian multipliers:

Multiply Eq. (22) by a constant m and add it to the Eq. (21). Using Eq. (16) and its counterpart for $\delta\ \Delta G_{\rm solv}^{\rm noneq,\,p}$ an equation of the form

$$\left[\frac{e_1-e_{\rm o,1}+m(e_1-e_1^{\rm p})}{a_1}+\frac{e_2-e_{\rm o,2}+m(e_2-e_2^{\rm p})}{R}\right]\delta\ e_{\rm o,1} + \left[\frac{(e_2-e_{\rm o,2})+m(e_2-e_2^{\rm p})}{a_2}+\frac{e_1-e_{\rm o,1}+m(e_1-e_1^{\rm p})}{R}\right]\delta\ e_{\rm o,2} \tag{23}$$

is obtained. Choose m so that the coefficient of, say, $\delta\ e_{\rm o,1}$ vanishes. That is,

$$\frac{e_1-e_{\rm o,1}+m(e_1-e_1^{\rm p})}{a_1}+\frac{e_2-e_{\rm o,2}+m(e_2-e_2^{\rm p})}{R}=0 \tag{24a}$$

Eq. (23) now becomes

$$\left[\frac{e_2-e_{\rm o,2}+m(e_2-e_2^{\rm p})}{a_2}+\frac{e_1-e_{\rm o,1}+m(e_1-e_1^{\rm p})}{R}\right]\delta e_{\rm o,2} \tag{24b}$$

But $\delta e_{\rm o,2}$ is arbitrary, so its coefficient has to be zero also. So we have

$$\frac{e_2-e_{\rm o,2}+m(e_2-e_2^{\rm p})}{a_2}+\frac{e_1-e_{\rm o,1}+m(e_1-e_1^{\rm p})}{R}=0 \tag{24c}$$

Eqs. (24a) and (24c) are two linear equations with two unknowns, $e_i-e_{{\rm o},i}+m(e_i-e_i^{\rm p})$, $i=1, 2$. Since the determinant of their coefficients does not vanish ($a_1a_2-R^2\neq 0$), it follows that each must be zero. That is

$$e_{\rm o,1}=e_1+m(e_1-e_1^{\rm p}) \tag{25a}$$

and

$$e_{\rm o,2}=e_2+m(e_2-e_2^{\rm p}) \tag{25b}$$

It then follows that

$$\Delta G_{\rm solv}^{\rm noneq^\dagger}=m^2(\Delta e)^2\lambda \tag{26a}$$

and

$$\Delta G_{\rm solv}^{\rm noneq^{\dagger'},\,p}=(m+1)^2\lambda \tag{26b}$$

where

$$\lambda=(\Delta e)^2\left(\frac{1}{2a_1}+\frac{1}{2a_2}-\frac{1}{R}\right)\left(\frac{1}{\varepsilon_{\rm op}}-\frac{1}{\varepsilon_{\rm s}}\right) \tag{27}$$

and

$$\Delta e=e_1^{\rm p}-e_1=-(e_2^{\rm p}-e_2) \tag{28}$$

From Eq. (20) for ΔG_R° and Eq. (26) we then obtain

$$-(2m+1)\lambda=G_R^\circ \tag{29}$$

and from Eqs. (26a) and (29) it finally follows that

$$\Delta G_{\rm solv}^{\rm noneq^\dagger}=\frac{\lambda}{4}(1+\Delta G_{\rm R}^\circ/\lambda)^2 \tag{30}$$

which is the desired result.

1.4. Generalizations

The following extensions of the above formulation are available in the literature.

1. Include reactants' changes in vibrational coordinates, e.g. bond lengths in each reactant.
2. Use a more general model than a pair of charged spheres for the reactants.
3. Use more compact notation that includes numerous models and stresses the linear response aspect of the theory.
4. Include quantum effects for nuclear motion, e.g. 'nuclear tunneling'.
5. Use a dielectric dispersion model for the solvent rather than just a model with two dielectric constants, $\varepsilon_{\rm s}$ and $\varepsilon_{\rm op}$.
6. Replace the dielectric continuum model by statistical mechanics.

We mentioned that the Gibbs energy versus reaction coordinate curves were obtained from the plots of the many-dimensional potential energy surfaces (plots versus thousands of coordinates). The special reaction coordinate for doing so was described, denoted here by q, in a 1960 Faraday Society Discussion article, cited as one of the references below. It is actually (or is equivalent to), at any point in the many-dimensional coordinate space, the energy difference between the potential energy of the products plus environment and that of reactants plus environment, for the entire system.

Item (3) above is an example of a common experience that a more compact notation is sometimes not only more general, but can also be simpler than the one used for a more specialized case.

1.5. Extension to a metal | liquid interface

The introduction of the 'image charge' in metal ensures that the electric potential at the metal | liquid surface is constant in the metal (Fig. 2). We have

$$\phi\ \text{(electrostatic potential)}=\frac{e}{\varepsilon_{\rm s}r}-\frac{e}{\varepsilon_{\rm s}r_{\rm i}} \tag{31}$$

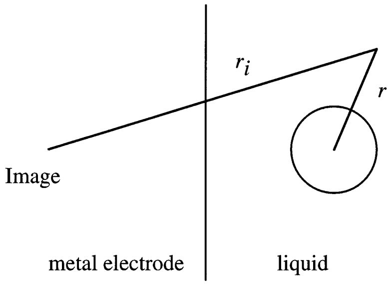

Fig. 2. An ion near a planar electrode surface, also showing its image charge.

where r and r_i are the distances to any point from the center of the ion and from its image. We again use a charging process to charge the real ion from 0 to e, and calculate the work done $\int_0^1 \phi^\lambda \mathrm{d}e_\lambda$, replacing r with a, as before, and r_2 with R. (One could include effects of other ions, e.g. electrical double layer.)

The net result of the above charging and minimization is now

$$\Delta G_R^\dagger = \frac{\lambda_{\mathrm{el}}}{4}(1 + \Delta G_R^{\mathrm{o\,el}}/\lambda_{\mathrm{el}})^2 \tag{32}$$

$$k_{\mathrm{ET}} = A e^{-\Delta G_R^\dagger/kT} \tag{33}$$

where $\Delta G^{\circ,\mathrm{el}}_R$ denotes $me(E - E_{\mathrm{o}})$, E_{o} = the 'standard' potential in the prevailing medium, calculated at the separation distance R, λ_{el} is the electrochemical λ, different somewhat from the λ in solution but related to it. A can be found using transition state theory, frequently $\sim 10^4$ cm s^{-1}.

1.6. Extension to a liquid|liquid interface

The electrostatic potential at each point is again determined by satisfying the boundary conditions at the interface:

(1) The component of the electric field parallel to the surface is continuous across the surface.

(2) The component of 'dielectric displacement' **D** perpendicular to the surface is continuous when no charge is adsorbed on the surface.

For the case of one ion in phase 1, one finds

$$\phi = \frac{e}{\varepsilon_1}\left(\frac{1}{r} - \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1}\frac{1}{r_i}\right) \tag{34}$$

where r_i denotes the distance of the field point from the image.

After extending this expression to include the charge of the other ion, and the interaction between them, one can obtain the desired electrostatic potential at any point in the system. To calculate the non-equilibrium solvation Gibbs energy, a two-stage charging process is again introduced.

Once again one obtains, after a minimization, $\Delta G_R^\dagger = \lambda/4(1 + \Delta G_R^\circ/\lambda)^2$, but now the expression for λ is more complicated. It contains a_1, a_2, ε_1, ε_2, $\varepsilon_1^{\mathrm{op}}$, $\varepsilon_2^{\mathrm{op}}$ and the positions of ions.

1.7. Examples of references

Many references are given in reviews such as

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For Sections 1.3 and 1.5

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The compact notation mentioned in Section 1.4 is given in

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A recent reference to the dielectric dispersion mentioned in Section 1.4 is

5. X. Song, R.A. Marcus, J. Chem. Phys. 99 (1993) 7768, which also contains references to the pioneering work of Ovchinnikov and Ovchinnikova (1969) and to the subsequent extensions by Dogonadze and co-workers. The Russian work is also described in J. Ulstrup, Charge Transfer in Condensed Media, Springer–Verlag, Berlin, 1979.

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