Application of Equations of Electromagnetism to Chemical Relaxation Problem: Calculation of Rate Constants of Fast Reactions

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The model consists of a perturbation caused in a chemical system in equilibrium by an electric field impulse, so that the ensuing relaxation is explained by basic electromagnetic equations; the relaxation time is then compared with the one obtained by Eigen [Discuss. Faraday Soc., 17 (1954), 194]. The rate constants for a series of bimolecular reactions involving H+ or OH- ions have been calculated. These compare favourably with experimental values. Furthermore, Langevin's equation can be obtained from the expression used to calculate the rate constants.

In order to measure rate constants of the fast bimolecular reactions involving H+ or OH- ions and which are not amenable to conventional methods, Eigen et al. developed several relaxation techniques. A chemical system in equilibrium, when perturbed tends to relax to the original state. For reactions of the type A+ + B- = C, the relaxation time (\( \tau \)), is given by Eq. (1)\(^1\)\(^-\)\(^3\)

\[
\tau = \left[ K_f (C_A + C_B) + K_r \right]^{-1}
\]

where \( K_f \) and \( K_r \) are the forward and reverse rate constants and \( C_A \) and \( C_B \) are the equilibrium concentrations of species A and B, respectively.

Graphically, the system behaves as shown in Fig. 1, where \( C \) and \( \tau \) are respectively concentration and time.

Particularly, the perturbation caused by the electric field must be such that the displacement from equilibrium is relatively small and the restoration rate follows first-order kinetics. This small displacement is reflected in the exponential form of the graph shown in Fig. 1.

This exponential is described by the equation

\[
\Delta C = (\Delta C)_0 e^{-t/\tau}
\]

where \( \Delta C \) is the change of concentration, at time \( t \), of a given species from its equilibrium value and is proportional to the displacement of the degree of advancement of the reaction; \( \tau \) is the relaxation time of the system, i.e. the time needed for \( C \) to fall to \( 1/e \) of its original value, i.e. \( \Delta C = 1/e (\Delta C)_0 \).

Application of Equations of Electromagnetism

An important criterion to be fulfilled when applying the equations of electromagnetism is that the perturbation caused by the electric field must not break the medium's homogeneity and isotropy. The action of the electric field upon the charge carriers may be described by Gauss' law in differential form.

In Eq. (2), \( \mathbf{E} \) is the medium's electric field intensity and \( \rho \) is the charge density representing the change in ionic concentration due to the electric field at a point \( (x, y, z) \) and consequently giving rise to internal currents. These currents tend to disappear as the system returns to the equilibrium. The current density can be linearly related to the electric field strength by Eq. (3)\(^4\)\(^5\) where \( \mathbf{E} \) represents the medium's electric conductivity at a given temperature. Equation (3) is valid for both solids and weakly ionized solutions, under a wide range of conditions\(^8\), since \( \mathbf{E} \) is not a function of the electric field. This relation is simply Ohm's law.
The charge density, \( \rho \), can be related to the current density, \( j \), through the continuity equation, which establishes the conservation of charge (Eq. 4).

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot j = 0
\]  

From Eqs (2), (3), and (4) we obtain first-order homogeneous differential Eq. (5) involving \( \rho \) and \( t \).

\[
\frac{\partial \rho}{\partial t} + \kappa \rho = 0
\]  

The density of charge at any instant is, therefore, given by Eq. (6)

\[
\rho(x, y, z, t) = \rho_0(x, y, z) e^{-\kappa t}
\]

It is seen from Eq. (6) that the equilibrium state is approached exponentially. Since \( \kappa \) has a dimension of time and since it is the time necessary for the density of charge at any point to fall to 1/e of its original value, it may be called the relaxation time. Thus, Equations (1) and (7) may be combined to yield the final expression.

\[
[K_\rho(C_A + C_B) + K_r]^{-1} = \kappa
\]

which has been used in this investigation to calculate the rate constants.

**Langevin's Equation**

Interestingly we can obtain Langevin’s equation used to estimate the maximum rate of reactions involving ions of opposite charge, from Eq. (8).

Let us consider the ion combination reaction \( A^+ + B^- \rightarrow AB \), where the concentrations of \( A^+ \) and \( B^- \) are equal to \( x \), i.e., \( C_{A^+} = C_{B^-} = x \). Substituting these in Eq. (8) we get

\[
[2K_r(x + K_r)]^{-1} = \kappa
\]

Taking into account that, in general, \( 2K_r x >> K_r \), Eq. (9) becomes

\[
[2K_r x]^{-1} = \kappa
\]

Now expressing the conductivity in terms of the ionic conductance, we have

\[
\kappa = C_{A^+}\lambda_{A^+} + C_{B^-}\lambda_{B^-}
\]

Also taking into account that \( C_{A^+} = C_{B^-} = x \) and \( \lambda_{A^+} + \lambda_{B^-} = \Lambda \), Eq. (11) becomes

\[
\kappa = x\Lambda
\]

where \( \Lambda \) is the molar conductance having the unit \( \Omega^{-1} \text{cm}^2 \text{mol}^{-1} \). Introducing Eq. (12) in Eq. (10), we get

\[
K_r = \frac{\Lambda}{2\epsilon}
\]

Equation (13) differs from that given in the literature by a constant factor, 1000/8\( \pi \)N, where N is Avogadro’s number. It is worth noting that Eq. (11, 29) of ref. 6 is deduced from the basic equations for diffusion in accord with the Fick’s two laws.

**Results and Discussion**

In order to evaluate the forward and reverse rate constants of the reactions shown in Table 1 by Eq. (8) we need an auxiliary relation involving the ionic dissociation constant, this is expressed in Eq. (14)

\[
K_{\text{dis}} = K_r K_t^{-1}
\]

The calculations of the rate constants, given in Table 1, have been made at 25°C. The medium’s electric permittivity has been considered to be equal to that of the solvent (in this case water), since the systems treated are all relatively diluted. For a more accurate calculation it is convenient to take the medium’s electric permittivity rather than one for the solvent, since the medium’s dielectric constant must vary with ionic concentration. We must therefore remember that for each value of C in Table 2 there must correspond one value for each \( \kappa \) and \( \epsilon \) of the medium. In Table 2 are given the electric conductivities and respective molarities at 25°C that have been used in Eq. (8) to evaluate the rate constants.

**Table 1 — Comparison of the Calculated and Experimental Rate Constants for Several Reactions**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Calc.</th>
<th>Expl.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} )</td>
<td>( K_r = 3.6 \times 10^{11} )</td>
<td>( K_r = 1.4 \times 10^{11} )</td>
</tr>
<tr>
<td>( \text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3\text{OH} )</td>
<td>( K_r = 1.5 \times 10^{10} )</td>
<td>( K_r = 3.4 \times 10^{10} )</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{HCOO}^- \rightarrow \text{HCOOH} )</td>
<td>( K_r = 3.0 \times 10^{10} )</td>
<td>( K_r = 6.0 \times 10^{10} )</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{CH}_3\text{COO}^- \rightarrow \text{CH}_3\text{COOH} )</td>
<td>( K_r = 2.5 \times 10^{9} )</td>
<td>( K_r = 5 \times 10^{9} )</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{CH}_3\text{CHOHCOO}^- \rightarrow \text{CH}_3\text{CHOHCOOH} )</td>
<td>( K_r = 4.4 \times 10^{8} )</td>
<td>( K_r = 8.6 \times 10^{8} )</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{C}_6\text{H}_5\text{COO}^- \rightarrow \text{C}_6\text{H}_5\text{COOH} )</td>
<td>( K_r = 2.4 \times 10^{10} )</td>
<td>( K_r = 4.5 \times 10^{10} )</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{CCl}_3\text{COO}^- \rightarrow \text{CCl}_3\text{COOH} )</td>
<td>( K_r = 4.2 \times 10^{9} )</td>
<td>( K_r = 7.8 \times 10^{8} )</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{C}_6\text{H}_5\text{COO}^- \rightarrow \text{C}_6\text{H}_5\text{COOH} )</td>
<td>( K_r = 2.1 \times 10^{10} )</td>
<td>—</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{CH}_3\text{CHOHCOO}^- \rightarrow \text{CH}_3\text{CHOHCOOH} )</td>
<td>( K_r = 4.1 \times 10^{9} )</td>
<td>—</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{C}_6\text{H}_5\text{COO}^- \rightarrow \text{C}_6\text{H}_5\text{COOH} )</td>
<td>( K_r = 3.3 \times 10^{10} )</td>
<td>( K_r = 6 \times 10^{10} )</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{C}_6\text{H}_5\text{COO}^- \rightarrow \text{C}_6\text{H}_5\text{COOH} )</td>
<td>( K_r = 4.5 \times 10^{9} )</td>
<td>( K_r = 1 \times 10^{9} )</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{CH}_3\text{COOH} )</td>
<td>( K_r = 2.3 \times 10^{10} )</td>
<td>( K_r = 3.5 \times 10^{10} )</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{CH}_3\text{COOH} )</td>
<td>( K_r = 1.5 \times 10^{9} )</td>
<td>( K_r = 2.2 \times 10^{9} )</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{CH}_3\text{COOH} )</td>
<td>( K_r = 1.0 \times 10^{9} )</td>
<td>( K_r = 3.1 \times 10^{9} )</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{CH}_3\text{COOH} )</td>
<td>( K_r = 5.0 \times 10^{8} )</td>
<td>( K_r = 1.6 \times 10^{8} )</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{CH}_3\text{COOH} )</td>
<td>( K_r = 1.3 \times 10^{10} )</td>
<td>( K_r = 2.2 \times 10^{10} )</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{CH}_3\text{COOH} )</td>
<td>( K_r = 1.7 \times 10^{7} )</td>
<td>( K_r = 3 \times 10^{7} )</td>
</tr>
</tbody>
</table>

**Table 2 — Values of the Electric Conductivities at Different Concentrations (25°C)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>( C ) (mol/litre)</th>
<th>( \kappa ) (( \Omega^{-1} \text{cm}^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{NH}_4\text{OH}</td>
<td>0.300</td>
<td>0.5 \times 10^{-4}</td>
</tr>
<tr>
<td>\text{HCOOH}</td>
<td>0.200</td>
<td>2.4 \times 10^{-4}</td>
</tr>
<tr>
<td>\text{CH}_3\text{COOH}</td>
<td>0.250</td>
<td>0.7 \times 10^{-4}</td>
</tr>
<tr>
<td>\text{CCl}_3\text{COOH}</td>
<td>0.250</td>
<td>6.9</td>
</tr>
<tr>
<td>\text{CH}_3\text{CHOHCOOH}</td>
<td>0.110</td>
<td>1.3 \times 10^{-4}</td>
</tr>
<tr>
<td>\text{CH}_3\text{COOH}</td>
<td>0.005</td>
<td>1.9 \times 10^{-4}</td>
</tr>
<tr>
<td>( \text{C}_{(CH_3)_2}\text{NH} )</td>
<td>0.200</td>
<td>1.3 \times 10^{-4}</td>
</tr>
<tr>
<td>\text{C}_{6\text{H}_5}\text{N}</td>
<td>0.200</td>
<td>\sim 3 \times 10^{-4}</td>
</tr>
</tbody>
</table>
The results obtained using Eq. (8) have been compared with the experimental values; the units being $M^{-1}\text{sec}^{-1}$ and $\text{sec}^{-1}$ respectively for $K_r$ and $K_i$. The experimental values were taken from literature and the electric permittivity of water at $25^\circ\text{C}$ is $6.9 \times 10^{-10} \text{C}^2\text{N}^{-1}\text{m}^{-2}$ (ref. 9).

It is seen that the rate constants calculated by means of Eq. (8) are in good agreement with the experimental values. A further analysis reveals that, except water, the theoretical values are smaller than the experimental ones, differing by factor 0.5 approximately, i.e. $K_{\text{calc}} = 0.5 K_{\text{exp}}$.

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**References**