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OXIDATION-REDUCTION REACTIONS IN IONIZING SOLVENTS

GENERAL DISCUSSION

I. EXCHANGE REACTIONS AND ELECTRON TRANSFER REACTIONS INCLUDING ISOTOPIC EXCHANGE

Mr. P. J. Proll and **Dr. L. H. Sutcliffe** (*Liverpool University*) (*communicated*): Incorporation of the equilibrium, Co(II)+Co(II)⇌Co(I)+Co(III), suggested by Longuet-Higgins, in place of the dimerization equilibrium does not lead to a rate law corresponding to that observed. Several deficiencies become apparent:

(i) the order with respect to Pb(IV) would be predicted to vary whereas it was found to be unity under all conditions;

(ii) either the reaction would not go to completion or added Co(III) would retard the reaction: neither of these effects was observed;

(iii) the highest power predicted for the dependence on the concentration of cobaltous acetate would be 2 but a value as high as 2·3 was obtained. This fact led to the postulation of the dimeric form of Co(II).

Prof. R. A. Marcus (*Polytechnic Inst. of Brooklyn*) said: In his treatment of electron transfer, one of Laidler's[1] assumptions was that the reaction rate equals the rate of diffusion (as computed by Debye [2]) of the reactants towards each other under the influence of their interionic forces, multiplied by some factor which includes an electron tunnelling term. This *ad hoc* assumption is, it will be shown below, incorrect. The correct multiplicative factor will include a diffusion constant, which in Laidler's case cancels the one in his diffusion rate. The final expression does not depend on the diffusion constant, when the reaction is inefficient.

Examples where the role of diffusion in bimolecular reaction rates has been incorrectly treated in force-free cases have been discussed recently.[3] Using related arguments, we deduce here an expression applicable to systems where intermolecular forces influence the diffusion. The reaction scheme normally consists of a diffusion step (1) to form some A . . . B pair, which in turn can either diffuse apart (reverse process in step 1) or react:

$$\mathrm{A}+\mathrm{B}\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}\mathrm{A}\ .\ .\ .\ \mathrm{B}, \tag{1}$$

$$\mathrm{A}\ .\ .\ .\ \mathrm{B}\xrightarrow[k_2]{}\text{products}. \tag{2}$$

Let $c(r)$ denote the concentration of B with respect to some A at an A—B distance r. (Ref. (3) gives a precise interpretation of c.) The net flux of diffusion of B towards an A, $J(R)$, at $r = R$, must equal the reaction rate,

$$J(R) = k_2 c(R), \tag{3}$$

where $c(R)$ is the concentration of A . . . B's and R is a typical A . . . B distance. The diffusion equation to be solved is

$$J(r) = 4\pi r^2[D(\mathrm{d}c/\mathrm{d}r)+vc], \tag{4}$$

where v, the relative velocity caused by the forces, equals a velocity per unit force, u, multiplied by the force, $\mathrm{d}w/\mathrm{d}r$, $w(r)$ being the work required to bring A and B from infinity to r. D is the sum [4] of the diffusion constants of A and B. The term u is readily shown to be D/kT. (At equilibrium, $J = 0$ and $c = c_0 \exp(-w(r)/kT)$, c_0 being the value of c at $r = \infty$. Substituting these results this value of u follows at once.) One has therefore

$$J(r) = 4\pi r^2\left(D\frac{\mathrm{d}c}{\mathrm{d}r}+\frac{Dc}{kT}\frac{\mathrm{d}w}{\mathrm{d}r}\right). \tag{5}$$

[1] Laidler, *Can. J. Chem.*, 1959, **37**, 138.
[2] Debye, *Trans. Electrochem. Soc.*, 1942, **82**, 265.
[3] Collins and Kimball, *Ind. Eng. Chem.*, 1949, **41**, 2651.
[4] Smoluchowski, *Z. physik. Chem.*, 1917, **92**, 129.

In the steady-state $J(r)$ is independent of r. Solving (5) subject to boundary condition (3) and setting $c = c_0$ at $r = \infty$, we find for the overall rate constant, k, which is the flux per unit c_0, J/c_0:

$$\frac{1}{k} = \frac{\exp w(R)/kT}{k_2} + \frac{1}{4\pi D \Big/ \int_{r=R}^{\infty} \exp(w/kT)\mathrm{d}r/r^2} \qquad (6)$$

Substituting Laidler's numbers into (6), one finds that the second term in the r.h.s. is negligible. Or more simply, a comparison of the known bimolecular rate constant k with the diffusion term in (6) leads to the same conclusion. Thus, when a reaction is sufficiently inefficient, its rate constant does not depend on D.

An alternative method of deducing (6), which is perhaps somewhat more illustrative of the physical processes involved and which shows more clearly the relationship with Debye's equation for a purely diffusion-controlled reaction rate, is the following.

In (1) and (2), we can set $\mathrm{d}c_{\mathrm{A}\ldots\mathrm{B}}/\mathrm{d}t = 0$ in the steady state and obtain for the overall rate constant

$$k = k_1[k_2/(k_2+k_{-1})]. \qquad (7)$$

k_1 is the rate constant computed by Debye by integrating (5) subject to the Smoluchowski boundary condition,[1] $c = 0$ at $r = R$. (This boundary condition prevents back diffusion.) k_1 is the flux per unit c_0 and was found in this way to be [2]

$$k_1 = 4\pi D \Big/ \int_{R}^{\infty} \exp(w/kT)\mathrm{d}r/r^2. \qquad (8)$$

We see, incidentally, from (7) that k indeed equals Debye's term k_1, multiplied by some efficiency factor, but not the one assumed [3] previously.

Similarly, k_{-1} is the flux when $c(R) = 1$ and $c(\infty) = 0$. We find upon integrating (5),

$$k_{-1} = 4\pi D \exp[w(R)/kT] \Big/ \int_{R}^{\infty} \exp(w/kT)\mathrm{d}r/r^2. \qquad (9)$$

Combining (7), (8) and (9), (6) is once again obtained.

In (6), incidentally, it is convenient to define a rate constant k_e which would be the value of k if $c(R)$ always had its equilibrium (Boltzmann) value, which it does when $k_2 \ll k_{1-}$. This value of k_e, it is seen from (6) or (7), equals $k_2 \exp[-w(R)/kT]$. When k_e is very small relative to the diffusion term, we see that from (6) that $k = k_e$ and the reaction rate is " activation controlled ". When the converse is true, k equals Debye's expression $4\pi D \Big/ \int_{R}^{\infty} \exp(w/kT)\, r/r^2\mathrm{d}$, and the reaction is diffusion controlled.

Prof. E. L. King (*University of Wisconsin*) said: In the paper by Dr. Stranks, a value of the second-order rate constant for the reaction of $Co(NH_3)_n^{2+}$ and the ion-pair $Co(NH_3)_6^{3+} . Cl^-$ is presented. To obtain this from the experimental data, it is necessary to use a value of the equilibrium quotient for the reaction

$$Co(NH_3)_6^{3+} + Cl^- = Co(NH_3)_6^{3+} . Cl^-.$$

[1] Smoluchowski, *Z. physik. Chem.*, 1917, **92**, 129.
[2] Debye, *Trans. Elektrochem. Soc.*, 1942, **82**, 265.
[3] Laidler, *Can. J. Chem.*, 1959, **37**, 138.