

## A Model for the Prediction of Electron-transfer Rates in the Highly Exergonic Region, applied to the Reaction between Solvated Electrons and Arenes in Tetrahydrofuran

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Anharmonic oscillator perturbations to the classical model of outer-sphere electron-transfer reactions are examined and used to fit rate constant data in the exergonic Marcus-invented region. Oscillator energy functions of the type  $G(x) = ax^2(1 + bx^2)$  and  $G(x) = ax^2(1 + bx^2 + cx^4)$  are used. Here  $x$  is the reaction co-ordinate for electron transfer which has the value zero at the origin of the donor and unity at the origin of the acceptor. The function  $G(x) = ax^2[1 + bx^2/\sqrt{(c^2 - x^2)}]$ , where  $a$ ,  $b$ , and  $c$  are constants, an oscillator with variable anharmonicity term, very successfully reproduces the data for reaction between solvated electrons and arenes in tetrahydrofuran. Such a model will be useful in constructing the energy surface for single-electron-transfer reactions.

The classical model of outer-sphere electron-transfer reactions developed by Marcus,<sup>1</sup> Hush,<sup>2</sup> Sutin,<sup>3</sup> and others is very successful in rationalizing rates where the driving force is not too large. It is a potentially useful tool in the construction of an energy surface for electron-transfer reactions. This construction will form a part of the complete energy surface for single-electron transfer (SET) reactions where electron transfer is followed by fast unimolecular bond cleavage.<sup>4</sup> An important drawback from such applications is that the classical model does not successfully predict the rate of electron transfer for strongly exergonic reactions. We demonstrate that by modifying the shape of the energy well which contains the electron to be transferred, this classical model can be extended to give satisfactory predictions of reaction rates in this exergonic region as well as in the region where  $\Delta G^\circ \approx 0$ . The utility of the classical model for the construction of SET reaction profiles is thereby enhanced.

In the classical model, outer-sphere electron-transfer reactions are considered subject to an activation energy due to solvent reorganization and bond reorganization processes, and to occur when the particles are at the van der Waals collision distance apart. Solvent dipole fluctuations and bond vibrations are treated as harmonic oscillators. Weak interaction between the donor and acceptor potential energy surfaces is considered. The activation free energy for electron transfer with a free energy difference  $\Delta G^\circ$ , corrected for any electrostatic work involved in bringing the particles together, is given by the Marcus equation (1).<sup>1</sup> Here,  $a$  is the total reorganization energy due to solvent

$$\Delta G^\ddagger = (a/4)(1 + \Delta G^\circ/a)^2 \quad (1)$$

and bond reorganization. The rate constant for bimolecular electron transfer ( $k_{\text{act}}$ ) is given by equation (2) where  $Z$  is the

$$k_{\text{act}} = \kappa Z \exp(-\Delta G^\ddagger/RT) \quad (2)$$

bimolecular collision rate and  $\kappa$  is unity for adiabatic electron transfer. Theory is concerned with predicting the reorganization energy term for a given reaction.

We are concerned in this paper with electron-transfer processes involving arenes and arene radical-ions. It is known for these reactions that solvent fluctuations are the major contributor to the reorganization energy term.<sup>5</sup> This energy term is usually considered to be the same for various arene and arene radical-ion partners. A prediction of the Marcus theory is

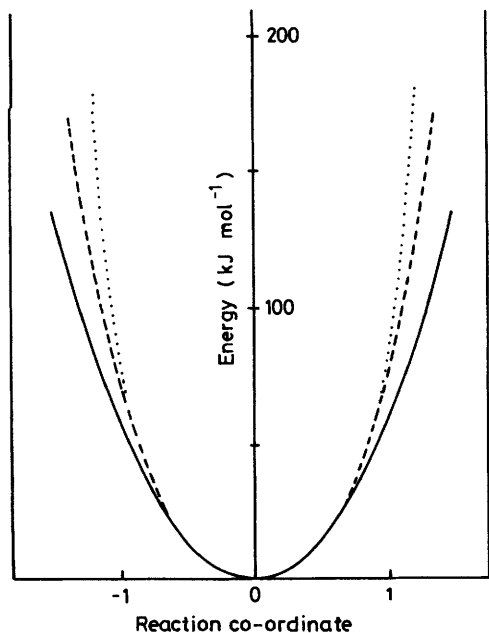
that the reaction rate decreases with increasing driving force in the region of highly exergonic electron-transfer reactions. Such an inverted region has been difficult to demonstrate experimentally because reaction rates in the region of interest are faster than the rate for bimolecular diffusion in most solvents. The following relevant data come from three different laboratories.

Scandola<sup>6</sup> has shown that electron-transfer occurs with diffusion control, even for highly exergonic reactions in acetonitrile, where an inverted region is predicted. Millar<sup>7</sup> circumvented the diffusion control problem by measuring the rate of electron-transfer between an arene radical-anion and an arene, both attached to the same steroid framework. An inverted region was demonstrated but the  $\log k_{\text{act}}$  versus  $\Delta E^\circ$  curve is not parabolic as predicted from the Marcus equation. Salmon<sup>8</sup> examined the rate of reaction between the solvated electron and arenes in tetrahydrofuran, where the bimolecular diffusion rate is large enough to reveal that the reaction rate enters an inverted region. The dependence of reaction rate on driving force was not that predicted by the Marcus equation. Solvent reorganization is the principal process contributing to the reorganization energy term for this process.

In order to improve agreement between theory and experiment, workers have extended the classical model to include electron transfer when particles are further than the van der Waals collision distance apart.<sup>9</sup> A quantum-mechanical model has also been proposed and this predicts relationships between reaction rate and driving force that are more similar to those found by experiment.<sup>10</sup> Some of the results<sup>7</sup> discussed in this paper have previously been interpreted using the quantum-mechanical model.

Rate constants for the photo-induced charge-separation and dark charge-recombination between porphyrin and quinone molecules attached to a rigid frame have also been obtained.<sup>11</sup> An inverted region, similar to that found by Millar, was observed. For such charge-separated to neutral-state reactions, the vibrational frequency of the solvent mode in the two states is expected to be different. The reactions are not covered by the discussion here which relates only to electron transfer with no overall change in the charge attached to the reacting pair. A theoretical discussion of charge-separation reactions has been made.<sup>12</sup>

*Modified Potential Energy Functions.*—Our aim is to produce a scheme that will be of assistance in constructing a reaction



**Figure 1.** Shapes of energy functions: — parabolic,  $G(x) = ax^2$ ; --- anharmonic parabola,  $G(x) = ax^2(1 + bx^2)$  with  $b = 0.4$ ; ..... function  $G(x) = ax^2[1 + bx^2/\sqrt{c^2 - x^2}]$  with  $b = 0.4$  and  $c^2 = 1.65$ . For the three cases,  $a$  was obtained by taking  $G(x, 0.5) = 15 \text{ kJ mol}^{-1}$

profile for SET processes. Define the reaction co-ordinate  $x$  for the electron-transfer step as zero at the minimum of the electron donor well and unity at the minimum of the electron acceptor well. There is only weak interaction, with no preferred direction, between the donor and acceptor functions during electron transfer. In consequence, the individual energy functions must be even-symmetrical. Expansion of the energy function as a Taylor series therefore has the form (3). The term  $G(0)$  is zero by convention.

$$G(x) = G(0) + (d^2G/dx^2)_{x=0} \cdot x^2/2! + (d^4G/dx^4)_{x=0} \cdot x^4/4! + (d^6G/dx^6)_{x=0} \cdot x^6/6! + \dots \quad (3)$$

(a) *Successive approximations to the Taylor series.* (i) The parabolic equation (4) is a first approximation to this expansion

$$G(x) = ax^2 \quad (4)$$

and the Marcus equation for  $\Delta G^\ddagger$  is derived from this.

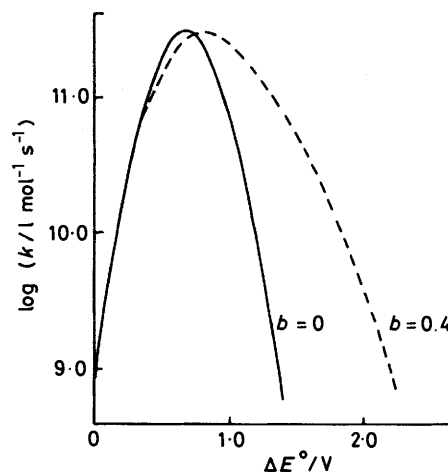
(ii) A second approximation is the function (5) where  $a$  and  $b$

$$G(x) = ax^2(1 + bx^2) \quad (5)$$

are constants to be determined. It is the simplest anharmonic oscillator model for solvent fluctuations. The anharmonicity constant,  $b$ , must be positive to reduce the discrepancy between Marcus predictions and experiment for rate constants in the exergonic region. Related anharmonic and parabolic potential energy functions are compared in Figure 1.

For convenience in the calculation of predicted electron-transfer rate constants based on this energy function, energy and driving force are scaled by writing  $y = G(x)/a$  and  $y_0 = \Delta G^\circ/a$ , respectively. The two overlapping wells between which electron transfer occurs are now described by equations (6) and (7). At

$$y = x^2(1 + bx^2) \quad (6)$$



**Figure 2.** Electron-transfer rate constant versus driving force curves obtained using the function  $G(x) = ax^2(1 + bx^2)$  with  $\Delta G^\ddagger(0) = 15 \text{ kJ mol}^{-1}$  and  $Z = 3.0 \times 10^{11} \text{ l mol}^{-1}$

$$y - y_0 = (x - 1)^2[1 + b(x - 1)^2] \quad (7)$$

the point of intersection of these two curves we have equation (8). Solution of equation (8) gives the value of  $x$  at this point of

$$x^3 - (3/2)x^2 + [(2b + 1)/2b]x - (b + y_0 + 1)/4b = 0 \quad (8)$$

intersection. There is only weak interaction between the energy wells so substitution of this value into equation (5) gives  $\Delta G^\ddagger$  for the process. Then  $k_{\text{act}}$  is found using expression (9).

$$k_{\text{act}} = Z \exp(-\Delta G^\ddagger/RT) \quad (9)$$

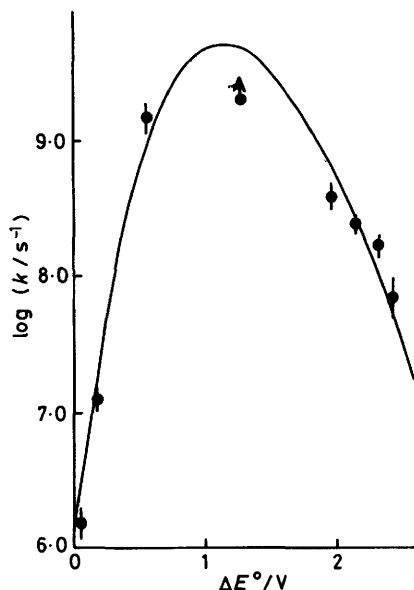
This procedure was used to derive  $\log k_{\text{act}}$  versus  $\Delta E^\circ$  data for Figure 2. Following usual practice in the electrochemical literature, the value of  $a$  is defined through the free energy of activation,  $\Delta G^\ddagger(0)$ , for the symmetrical self-exchange reaction where  $\Delta G^\circ = 0$  and  $x = 0.5$ . Typical values of  $Z = 3 \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$  and  $\Delta G^\ddagger(0) = 15 \text{ kJ mol}^{-1}$  were selected. The constant  $b$  was given an arbitrary value for each curve in Figure 2 and then the corresponding value of  $a$  could be obtained.

To obtain the data for one curve, a range of values of  $\Delta E^\circ (= -\Delta G^\circ/F)$  were selected and the corresponding values of  $\log k_{\text{act}}$  computed as follows. The value of  $y_0$  was obtained and equation (8) was then solved for  $x$  using Cardan's method<sup>13</sup> to find the one real root. The value of  $y$  in equation (5) corresponding to this value of  $x$  is  $\Delta G^\ddagger/a$ . Hence the value of  $\Delta G^\ddagger$ , and from this  $\log k_{\text{act}}$ , can be obtained.

Inspection of a range of curves, from which only two are selected in Figure 2, suggested that we could model the rate data for electron transfer between groups attached to a steroid framework.<sup>5</sup> There are three adjustable parameters,  $\Delta G^\ddagger(0)$ ,  $b$ , and  $Z$ . This reaction is unimolecular so  $Z$  is a frequency factor.

Systematic variations of the parameters was carried out and a best fit of computed curves to experimental data obtained after visual inspection. The principal effect of a change in a parameter is as follows. Adjustment of  $Z$  changes the ordinate at the curve maximum. Adjustment of  $\Delta G^\ddagger(0)$  changes the abscissa at the curve maximum and the relative position of this maximum with respect to where the curve crosses the vertical axis. Raising the value of  $b$  enhances the deviation from the parabolic relationship for large values of  $\Delta E^\circ$ .

The best fit with experimental data is shown in Figure 3 using  $\Delta G^\ddagger(0) = 21 \pm 1 \text{ kJ mol}^{-1}$ ,  $b = 0.35 \pm 0.02$ ,  $Z = (5.4 \pm 0.5) \times$



**Figure 3.** Rate constants for electron transfer between an arene radical-anion and an arene, both attached to a steroid skeleton, under driving force  $\Delta E^\circ$ , from ref. 7. The curve is computed using function (5) with  $\Delta G^\ddagger(0) = 21.0 \text{ kJ mol}^{-1}$ ,  $b = 0.35$ ,  $Z = 5.4 \times 10^9 \text{ s}^{-1}$

$10^9 \text{ s}^{-1}$ . Alteration of these values over the range indicated is necessary to produce a noticeable change in the shape of the calculated curve. The value adopted for  $\Delta G^\ddagger(0)$  from the calculations is larger than that for related bimolecular electron-transfer processes where the average value<sup>14</sup> is *ca.*  $15 \text{ kJ mol}^{-1}$ . Such a result is expected since the reacting arenes are held apart by more than the sum of their van der Waals radii. The fit is as good as that achieved using the quantum mechanical treatment which also required a choice of three parameters.<sup>7</sup>

(iii) Equation (5) cannot model the reaction between solvated electrons and arenes in a satisfactory manner because the observed rate profile<sup>8</sup> shows a much shallower dip in the exergonic region than in Figure 3. Therefore, a third approximation to the energy well was used to model these results, taking function (10) where  $a$ ,  $b$ , and  $c$  are constants to be determined.

$$G(x) = ax^2(1 + bx^2 + cx^4) \quad (10)$$

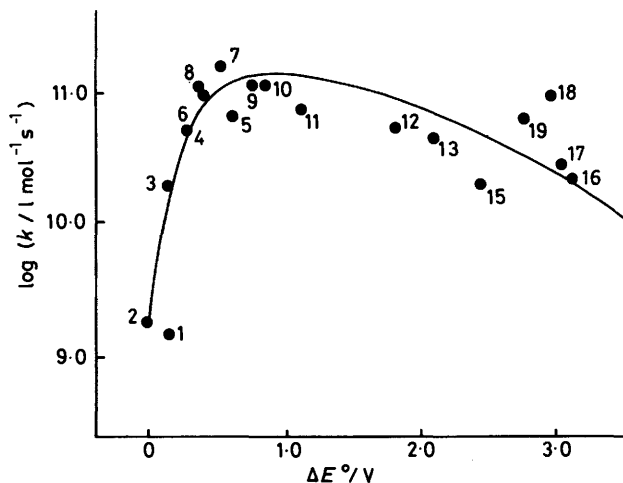
The value of  $x$  at the point of intersection of this donor well with an acceptor well defined by expression (11) is given by the

$$G(x) - \Delta G^\circ = a(x-1)^2 [1 + b(x-1)^2 + c(x-1)^4] \quad (11)$$

real root of an equation of the fifth degree in  $x$ . In order to obtain electron-transfer rate constants, energy and driving force were scaled as in the previous example by substituting  $y = G(x)/a$  and  $y_0 = \Delta G^\circ/a$ . A range of values for  $\Delta E^\circ$  was selected and converted to the corresponding values of  $y_0$ . The fifth-degree equation in  $x$  was then solved using the Newton-Raphson method<sup>15</sup> and  $\Delta G^\ddagger(x)$  obtained for each point by substituting this value of  $x$  into equation (10). A value for  $k_{\text{act}}$  at each point was calculated as before and then corrected for bimolecular diffusion (rate constant  $k_{\text{diff}}$ ) to give the electron-transfer rate constant  $k_t$  by using equation (12).

$$1/k_t = 1/k_{\text{act}} + 1/k_{\text{diff}} \quad (12)$$

There are five parameters  $\Delta G^\ddagger(0)$ ,  $b$ ,  $c$ ,  $Z$ , and  $k_{\text{diff}}$ , which can



**Figure 4.** Rate constants for solvated electron attachment to arenes in tetrahydrofuran under driving force  $\Delta E^\circ$  from ref. 8. The curve is computed using function (10) with  $\Delta G^\ddagger(0) = 13 \text{ kJ mol}^{-1}$ ,  $b = 0.5$ ,  $c = 0.5$ ,  $Z = 2.51 \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $k_{\text{diff}} = 2.92 \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $E^\circ$  for solvated electron  $-2.94 \text{ V versus s.c.e.}$  Substrates are: (1) 2,4,6-trimethylpyridine; (2) phenol; (3) 4-aminobenzonitrile; (4) pyridine; (5) pyrimidine; (6)  $\alpha$ -methylstyrene; (7) benzonitrile; (8) biphenyl; (9) stilbene; (10) pyrene; (11) 9,10-diphenylanthracene; (12) nitrobenzene; (13) *m*-dinitrobenzene; (15) benzoquinone; (16) tetracyanoethene; (17) galvinoxyl; (18) tetrachloro-1,4-benzoquinone; (19) 2,2'-diphenyl-1-picrylhydrazyl

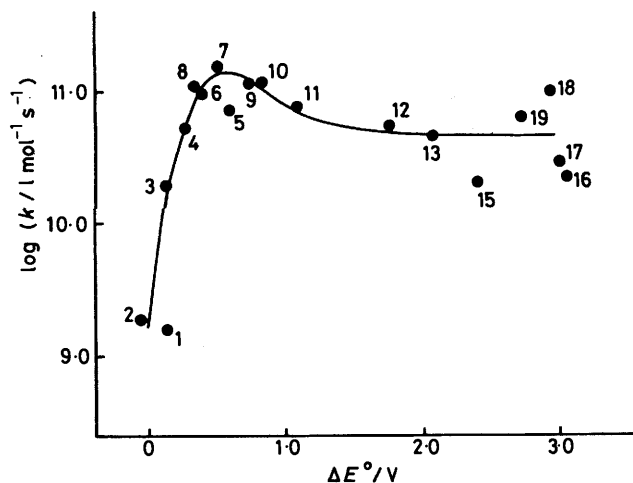
be adjusted to obtain a fit between the computed curve for  $\log k_t$  versus  $\Delta E^\circ$  and the experimental data. The principal effect of a change in a parameter value is as follows. Adjustment of  $Z$  and  $k_{\text{diff}}$  changes the ordinate at the curve maximum and the shape of the curve in this region. Adjustment of  $\Delta G^\ddagger(0)$  changes the abscissa at the curve maximum and the shape of the curve at the lower left. Adjustment of  $b$  and  $c$  changes the shape of the right-hand section of the curve.

Computed graphs of  $\log k_t$  versus  $\Delta E^\circ$  were compared with the experimental values of  $\log k_t$  versus  $E_{\frac{1}{2}}$  for the electron acceptor and shifted along the potential axis to achieve the best fit. The shift gives  $E^\circ$  [versus saturated calomel electrode (s.c.e.) reference electrode] for the solvated electron in the solvent for  $E_{\frac{1}{2}}$  measurements. It is necessary to assume that  $\Delta E^\circ$  for any solvated electron, electron acceptor pair is the same in tetrahydrofuran as in the solvent for  $E_{\frac{1}{2}}$  measurements. For related compounds this assumption is valid.<sup>16</sup>

Systematic variation of the parameters then gave the best fit shown in Figure 4. The total of six adjustable parameters have values  $\Delta G^\ddagger(0) 13 \pm 1 \text{ kJ mol}^{-1}$ ,  $b = 0.10 \pm 0.05$ ,  $c = 0.50 \pm 0.05$ ,  $Z = (2.9 \pm 0.1) \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $k_{\text{diff}} = (2.5 \pm 0.1) \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$  and in the solvent for  $E_{\frac{1}{2}}$  measurements (solvated electron)  $= -2.94 \pm 0.05 \text{ V versus s.c.e.}$  Alteration of these values over the range indicated is required to produce a noticeable change in the calculated curve.

Function (10) is moderately successful in predicting the trend of results for reaction between solvated electrons and arenes.<sup>8</sup> A shallow inverted region in the rate constant versus driving force relationship is predicted. The energy function described in the next paragraph reproduces this rate constant data with much greater success.

The rate measurements of Scandola<sup>6</sup> for electron transfer between species in acetonitrile show an extended range of diffusion control in the exergonic region. When  $k_{\text{diff}}$  is given the value of  $1.5 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$  to be expected in acetonitrile, then such an extended range of diffusion control is predicted and this model can successfully reproduce the experimental rate profile.



**Figure 5.** Rate constants for solvated electron attachment to arenes in tetrahydrofuran under driving force  $\Delta E^\circ$  from ref. 8. The curve is computed using the function (13) with  $\Delta G^\ddagger(0) = 13 \text{ kJ mol}^{-1}$ ,  $b = 0.10$ ,  $c^2 = 1.65$ ,  $Z = 2.92 \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $k_{\text{diff.}} = 2.51 \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $E^\circ$  for solvated electron =  $-2.94 \text{ V versus s.c.e.}$  Substrates identified in Figure 4

(b) *A new energy function.* An alternative energy function that can be used to predict the results for reaction between the solvated electron and arenes suggests itself because the rate constants measured in the most exergonic regions in Figure 4 seem distributed about a plateau. The terms of the Taylor series beyond the first can be approximated by some suitable function and equation (13) appeared convenient. This empirical approach to our problem is exactly that used by Morse<sup>17</sup> when he proposed the energy function for the bond stretching. Its justification is that the experimental data can be reproduced. Expression (13) is compared in Figure 1 with the simple harmonic oscillator.

$$G(x) = ax^2[1 + bx^2/\sqrt{(c^2 - x^2)}] \quad (13)$$

This function is parabolic for small values of  $x$ . As  $x$  approaches the value of  $c$  then  $\Delta G(x)$  approaches infinity. When  $\Delta G^\circ$  is large and negative for electron transfer between two centres, the activation energy for the process becomes independent of  $\Delta G^\circ$  and approaches the value of  $G(x)$  when  $x = (1 - c)$ .

We proceeded to compute data for  $\log k_t$  versus  $\Delta E^\circ$  for electron transfer between two energy wells exactly as in section (a) (iii). The Newton-Raphson method was used to find the value of  $x$  at the point of intersection of the donor and acceptor wells. The value of  $G(x)$  at this point is  $\Delta G^\ddagger$  for the electron-transfer process. A value for  $k_{\text{act}}$  was obtained from  $\Delta G^\ddagger$  and corrected for bimolecular diffusion.

There are five parameters  $\Delta G^\ddagger(0)$ ,  $b$ ,  $c$ ,  $Z$ , and  $k_{\text{diff.}}$  that can be adjusted to obtain a fit between the computed curve for  $\log k_t$  versus  $\Delta E^\circ$  and the experimental data<sup>8</sup> for reaction between solvated electrons and arenes in tetrahydrofuran. With the exception of  $c$ , adjustment of the parameters changes the shape of the curve as discussed in section (a) (iii). Adjustment of  $c$  changes the ordinate at the plateau level. At this plateau,  $\Delta G^\ddagger = G(c - 1)$  given by equation (13).

As before under section (a) (iii), the computed curves of  $\log k_t$  versus  $\Delta E^\circ$  were shifted along the potential axis to achieve the best fit with the experimental results for  $\log k_t$  versus  $E_{\frac{1}{2}}$  for the electron acceptor. The amount of shift corresponds to  $E^\circ$  versus s.c.e. for the solvated electron.

The fit with experimental data is shown in Figure 5 where  $\Delta G^\ddagger(0) = 13 \pm 1 \text{ kJ mol}^{-1}$ ,  $b = 0.1 \pm 0.05$ ,  $c^2 = 1.65 \pm 0.10$ ,  $Z = (2.9 \pm 0.1) \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $k_{\text{diff.}} = (2.5 \pm 0.1) \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$ , and  $E^\circ$  (solvated electron) =  $-2.94 \pm 0.05 \text{ V versus s.c.e.}$  The fit with experimental data shown in Figure 5 is very good up to the region where the driving force  $\Delta E^\circ = 2.0 \text{ V}$ . Point 5 due to pyrimidine does not follow the general trend of results and we have no explanation for this. The calculated line fits the average trend of results in the region  $E^\circ > 2.0 \text{ V}$  but these results show much more scatter than the previous ones.

When  $k_{\text{diff.}}$  is given a value of  $1.5 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$  expected in acetonitrile, then the rate measurements of Scandola<sup>6</sup> can also be reproduced.

(c) *Further investigations.* The essential requirements for an alternative energy function are that it should be parabolic for small values of the parameter  $x$  and become steeper than a parabola for large values of  $x$ . Other functions can probably be found that will reproduce the experimental data for  $\log k_t$  as a function of  $\Delta E^\circ$ .

We have also used function (14) which is similar in form to

$$G(x) = ax^2[1 + b/(c^2 - x^2)] \quad (14)$$

equation (13). Beginning with equation (14), we can generate  $\log k_t$  versus  $\Delta E^\circ$  curves which are almost indistinguishable from those obtained using equation (13). Figure 5 is reproduced, within the limits of experimental errors, when we use the following constants,  $\Delta G^\ddagger(0) = 13 \pm 1 \text{ kJ mol}^{-1}$ ,  $b = 0.25 \pm 0.05$ ,  $c^2 = 1.65 \pm 0.10$ ,  $Z = (2.9 \pm 0.1) \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $k_{\text{diff.}} = (2.5 \pm 0.1) \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$ , and  $E^\circ$  (solvated electron) =  $-2.94 \pm 0.05 \text{ V versus s.c.e.}$

We prefer function (13) however because this is easily seen as an anharmonic expression with a variable anharmonicity constant.

*Conclusions.*—A reaction co-ordinate,  $x$ , is defined for the electron-transfer process between two species. It is given the value zero at the minimum of the donor energy function and unity at the minimum of the acceptor energy function. These energy functions are even symmetrical functions of  $x$  and are expressed as a Taylor expansion in  $x^n$  where  $n$  is even. Truncation of the series at  $x^2$  gives the classical harmonic oscillator model for electron transfer which operates well outside the strongly exergonic region. Truncation of the series at  $x^4$  gives an energy function which can be used to fit the rate data for electron transfer between groups attached to a rigid steroidal framework. Truncation of the series at  $x^6$  allows a moderately good fit for the rate data from reactions between the solvated electrons and arenes. This latter rate data are however better reproduced using the energy function (13).

These successive approximations are a convenient mathematical operation for modelling a complex situation and the coefficients of  $x^4$  and higher terms have no physical significance. The coefficient of  $x^2$  is the Marcus reorganization energy.

The advantage of this approach is that the coefficients of the expression (13) which models the bimolecular electron-transfer reaction can be applied to other situations. The energy function can then be used to construct reaction co-ordinate diagrams for the reversible electron-transfer part of a multistep SET reaction.

Deviations between predictions of electron-transfer rate based on the Marcus equation with those based on expression (13) become important when  $\Delta E^\circ > 0.5 \text{ V}$ . Expression (13) reproduces electron-transfer rate data for reaction between solvated electrons and arenes until  $\Delta E^\circ > 2.0 \text{ V}$ .

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