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Abstract

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ON THE ROLE OF THE TUNNEL EFFECT IN CHEMICAL REACTIONS

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The theoretical study of the tunnel effect in the passage of atoms through a potential barrier ([1−6]) has recently again attracted the attention of a number of investigators ([7−13]), who point to reliable possibilities for detecting the tunnel effect experimentally. It appears important to find relations between the parameters of the barrier, the mass of the particles, and the temperature, under which the tunnel effect begins to play a noticeable role. Such a relation was first derived ([7]) for a rectangular barrier*. Recently V. I. Gol' danskii ([11]) proposed an analogous criterion for smooth barriers whose summit has a parabolic form**. This criterion, however, does not determine with sufficient accuracy the characteristic temperature T_k above which the tunnel effect may be neglected. It permits only the finding of a certain temperature $T'_k < T_k$, below which the tunnel effect undoubtedly completely determines the rate of the process—this is the region of very low temperatures ($T < T'_k$), as yet uninvestigated. Meanwhile, of special importance is the region of moderate temperatures ([10]) ($T'_k < T < T_k$), where the role of the tunnel effect is small, but nevertheless may be significant and at the same time accessible to experimental detection. Gol' danskii' s criterion is unsuitable for distinguishing the region $T < T_k$ from the region $T > T_k$ because it is derived on the basis of an approximate determination of the maximum of the integrand in the expression

$$P = \int_0^\infty W(U) w(U,T)\, dU \tag{1}$$

for the total transition probability P, where $W(U)$ is the barrier penetrability, and $w(U,T)$ is the distribution function of the energy U. However, the function $f(U) = W(U)w(U,T)$ does not always have a maximum, while the presence of a maximum is always of essential importance for the contribution of the tunnel effect to the total rate of the process***.

Therefore it is of interest to find a more exact relation that makes it possible to distinguish the region of moderate temperatures, where the tunnel effect plays a significant role, from the region of higher temperatures, where

* This relation may be written in the form

$$32\pi^2 m\delta^2(RT)^2/h^2E_0 \approx 1 \quad \text{or} \quad T_k = h\sqrt{E_0}/8\pi Rl\sqrt{2m}, \tag{a}$$

$l = \delta/2$ is the half-width of the barrier, E_0 is its height, m is the mass of the particles, and T_k is the temperature below which the rate of the process is determined predominantly by the tunnel effect.

** Gol' danskii' s relation has the form

$$T_k' = h\sqrt{E_0}/2\pi^2 Rd\sqrt{2m}, \tag{b}$$

where d is the effective half-width of the barrier (for a parabolic barrier $d = l$, for an Eckart barrier $d = l/\pi$, where l is the half-width of the barrier base).

*** For a rectangular and a parabolic barrier the function $f(U)$ has no maximum in the region $U < E_0$ (in the first case ([6,7]), on the contrary, a minimum appears), if the barrier penetrability is determined in the Wentzel-Brillouin approximation: $W(U) =$

this role for the observed rate of the process may be regarded as inessential. Such a relation can be derived for any smooth one-dimensional barrier, as was done earlier ([7]) for a rectangular barrier, by determining the ratio P'/P'', where

$$P' = \int_Q^E W(U)w(U,T)\,dU, \qquad P'' = \int_E^\infty W(U)w(U,T)\,dU \tag{2}$$

are, respectively, the total probability of passage through the barrier and over the barrier (E is the barrier height, Q is the heat effect of the process).

An expression for P'/P'' can be obtained approximately first of all for a parabolic barrier, if one uses the Wentzel–Brillouin approximation for calculating P' and the classical approximation for calculating P'' ([4,6,11,13]). Thus we find ([13])*

$$P'/P'' = P'/P^{\text{cl}} = \gamma\left(1 - e^{-(\delta-\gamma)\omega}\right)/(\delta - \gamma), \tag{3}$$

$$\gamma = E_0/RT, \qquad \delta = 2\pi^2 d\sqrt{2mE_0}/h, \qquad \omega = (E - Q)/E_0 \tag{4}$$

(E_0 is the height of the corresponding symmetric barrier for which $Q = 0$, i.e. $\omega = 1$). Usually $\gamma \gg 1$, $\delta \gg 1$, and $\gamma\omega = (E - Q)/RT \gg 1$.

For $\gamma > \delta$, if $(\gamma-\delta)\omega \gtrsim 2$, we obtain $P'/P'' = (\gamma\exp(\gamma-\delta)\omega)/(\gamma-\delta) \gg 3\gamma \gg 1$; if, conversely, $\delta > \gamma$ and $(\delta - \gamma)\omega \gtrsim 2$, then $P'/P'' = \gamma/(\delta - \gamma)$ may also be considerably greater than unity if the difference $\delta - \gamma$ is not too large. For

$\gamma \to \delta$, expansion in a series in (3) gives $P'/P'' = \gamma\omega \simeq \delta\omega \gg 1$. According to (4), the relation $\gamma \simeq \delta$ leads to Goldanskii' s criterion ([6]), which, consequently, corresponds to a significant predominance of tunneling transitions in comparison with above-barrier ones: the contribution of the tunneling effect under this condition amounts to 90-98% of the total reaction rate, corresponding to a change of $\delta\omega$ in the interval 10-50.

It may be considered that the tunneling effect begins to influence the rate of the process decisively at least when ** the condition $P'/P'' \simeq 1$ ([7]) is satisfied. This condition corresponds to the relation $\gamma \simeq \delta/2$, since, according to (3), it gives $P'/P'' = 1 - e^{-\gamma\omega} \sim 1$, because $\gamma\omega \gg 1$. With the aid of (4) and the equality $\delta = 2\gamma$ we obtain the expression

$$T_k = h\sqrt{E_0}/\pi^2 Rd\sqrt{2m} \tag{5}$$

for the temperature below which the fraction of tunneling transitions is more than 50% of the total number of particle transitions through the barrier. This temperature is twice as high as the temperature T'_k determined by Goldanskii' s relation. The correction factor to the classical reaction rate under the condition $P'/P'' = 1$ (i.e. $T = T_k$) will be $\kappa = P/P^{\text{cl}} = P/P'' = (P' + P'')/P'' = 2$.

The dependence (5) remains valid in a more rigorous derivation, based

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$$= D \exp\left[(-4\pi/h) \int \sqrt{2m(V(x) - U)}\, dx\right],$$

taking D to be constant, and taking the energy distribution function to be $w(U, T) = \varphi(T) \exp(-U/RT)$. The appearance of a maximum in the region $U < E_0$ upon applying the exact expression for $W(U)$ (where $D \to 0$ as $U \to 0$ ([6,7,9])) or of the more general expression for $w(U, T) = \varphi(T) U^n \exp(-U/RT)$ ([11]) only slightly reduces the fraction of tunneling transitions ($U < E_0$) in comparison with quasiclassical ones ($U > E_0$), but the presence of this maximum in the region $U < E_0$ is not a condition for a noticeable contribution of the tunneling effect. Only for the Eckart barrier is there a sharply expressed maximum ([3,7,8]) under all conditions, and it is undoubtedly closely connected with the contribution of the tunneling effect to the rate of particle transfer through the barrier; however, determination of the position U_m of this maximum in the Wentzel–Brillouin approximation ([11]) is very inaccurate when $U_m \to E_0$ (see the following footnote).

* For greater generality we consider an asymmetric barrier ([13]), obtained by superposing a linear potential on a symmetric parabolic barrier (the ratio P'/P'' does not depend on the direction of passage).

** One should distinguish the contribution of the tunneling effect to the actual rate from the tunneling correction to the "classical" rate of the process; the fraction of tunneling transitions may be significant ($\sim 30\%$) even when there is no noticeable difference between the actual and classical rates ([8,9]).

for a given combination of the Wigner approximations ([9,13]), which gives ([13])

$$\chi = P/P^{\text{cl}} = 1 + \pi^2\gamma^2/6\delta^2 + \gamma\left[e^{-(\delta-\gamma)/10} - e^{-(\delta-\gamma)\omega}\right]/(\delta-\gamma). \qquad (6)$$

For $\delta = 2\gamma$ we obtain $\chi = 1 + \pi^2/24 + e^{-\gamma/10} - e^{-\gamma\omega} > 1.41$ (if $\gamma\omega > 5$). A close value for χ is given by the relation obtained from (1) with the aid of a more exact expression for the barrier permeability $W(U)$ ([7,10,13]), namely ([13])

$$\chi = P/P^{\text{cl}} = (\pi\gamma/\delta)/\sin(\pi\gamma/\delta) - \gamma e^{-(\delta-\gamma)\omega}/(\delta-\gamma), \qquad (7)$$

whence, for $\delta = 2\gamma$, $\chi = \pi/2 - e^{-\gamma\omega} = 1.57$ (for $\gamma\omega > 5$). Since in the expression $\chi = P'/P^{\text{cl}} + P''/P^{\text{cl}}$ the value of P''/P^{cl} lies between 0.5 and 1 ([5]), we find that P'/P^{cl} must lie between 0.6 and 1, and P'/P'' between 0.6 and 2. It can be shown that for $\delta = 2\gamma$ the exact ratio $P'/P'' = 1$. Indeed, the exact expressions for P' and P'' can be written in the form ([13])

$$\frac{P'}{P^{\text{cl}}} = \gamma\int_0^{\omega}\frac{e^{\gamma y}\,dy}{1+e^{\delta y}}, \qquad \frac{P''}{P^{\text{cl}}} = \gamma\int_{-\infty}^{0}\frac{e^{\gamma y}\,dy}{1+e^{\delta y}}, \quad \text{where}$$

$y = (E-U)/E_0$. Setting $\delta = 2\gamma$, we obtain

$$\frac{P'}{P^{\text{cl}}} = \frac{1}{2}\gamma\int_0^{\omega}\frac{dy}{\operatorname{ch}\gamma y} = \operatorname{arctg} e^{\gamma\omega} - \frac{\pi}{4}, \qquad \frac{P''}{P^{\text{cl}}} = \frac{1}{2}\gamma\int_{-\infty}^{0}\frac{dy}{\operatorname{ch}\gamma y} = \frac{\pi}{4}. \qquad (8)$$

The values of both expressions practically coincide if $\gamma\omega > 5$ (when $\operatorname{arctg} e^{\gamma\omega} \simeq \pi/2$), so that $P'/P'' = 1$ for all chemical reactions. Thus, relation (5) is rigorously substantiated for a parabolic barrier.

It may be considered that the same relation is approximately applicable to all barriers whose tops are approximated by a parabola, if d is the half-width of the base of the parabola. It should be expected, however, that the error in determining T_k from equation (5) will nevertheless be appreciable if the base width l of the given barrier is much greater or much smaller than d. This error can be estimated by an exact calculation using the Eckart barrier as an example, where $l = \pi d$ ([11]). This barrier may be considered parabolic for all particles whose energy is above $U = 0.9E$ ([11]); however, at $T = T_k$, i.e., at $P'/P'' = 1$, a noticeable fraction of the particles can pass through the barrier considerably deeper (down to $U = 0.5E$ ([7,8])), so that the ratio δ/γ for the Eckart barrier must differ noticeably from 2.

Table 1

Eckart barrier

δ	γ	δ/γ	P'/P''	P/P^{cl}	T_k, °K	T'_k, °K	T''_k [10] (5), °K
17.3	9.65	1.79	1.1	1.6	750	418	836
52.6	31.1	1.69	1.1	1.4	373	219	440
71.5	42.5	1.68	0.96	1.3	273	162	322

This is seen from Table 1, which gives the results of calculations for three pairs of values of δ and γ for which the condition $P'/P'' \simeq 1$ is fulfilled. The values P, P', and P'' were calculated from equations (1) and (2) for $Q = 0$ by graphical integration ([3,7,8,12]). The position of the maximum U_m of the integrand in (1) in the three cases coincides with the top of the barrier: $U_m = E_0$.* δ/γ retains an almost constant value, 1.7-1.8, over very wide ranges of variation of δ ($\sim 20\div \sim 70$) and γ ($\sim 10\div \sim 40$). Hence it follows that for the Eckart barrier the more exact expression for T_k corresponds to the condition $\delta \simeq 1.75\gamma$ ($\delta = 2\gamma$ for a parabolic barrier), so that

$$T_k = \frac{7}{8} h\sqrt{E_0}/\pi R l\sqrt{2m}. \tag{9}$$

In accordance with this formula, the values of T_k in Table 1 are ~ 1.75 times larger

* According to Goldanskii ([11]), $U_m \approx E_0(\delta/\gamma)^2$. This formula gives, for the cases considered in Table 1, values of U_m 3-5 times larger than E_0. In connection with this, T'_k is considerably lower than T_k.

values of T'_k, calculated from Gol' danskii' s relation (6), and are 1.15 times smaller than the values obtained from (5) for a parabolic barrier.

It is clear that for an approximate calculation of T_k one may use relation (5) for any barriers with a parabolic summit. Comparison of expressions (5) and (9) with each other and with (a) for a rectangular barrier shows, however, how strongly T_k depends not only on the dimensions but also on the shape of the barrier. These relations may be used to determine the geometrical properties of barriers in connection with the study of the nature of the temperature dependence of process rates ([7,8,11]).

The justification given above for relations (5) and (9) makes it possible to assume that they are approximately valid for any smooth barrier, including the case when its summit is not well approximated by a parabola. As was shown for a parabolic barrier, at $T = T_k$ the relation $\chi = P/P^{cl} \simeq 1.5$ holds, and the difference $\chi - 1 \simeq 0.5$ is essentially determined by the value 0.41, which the term $\pi^2\gamma^2/6\delta^2$ takes in equation (6) at $\delta = 2\delta$ (i.e., $T = T_k$). The very same term appears in the series expansion of the first term of equation (7) ([10,13]). This, however, is nothing other than Wigner' s correction ([2]) q_w to the reaction rate.* For the Eckart barrier at $T = T_k$ (Table 1) $\chi - 1 \simeq 0.4$, with $q_w = 0.53$ (at $\delta = 1.75\gamma$). It follows from this that (5) and (9) can be derived approximately with the aid of the general expression for q_w from the relation $q_w = h^2 A/96\pi^2 m(RT)^2 \simeq 0.5$ $(A = -\partial^2 V(x_m)/\partial x^2 > 0)$, i.e., from the generalized expression

$$T_k = h\sqrt{A}/2\pi\sqrt{2m}, \qquad (10)$$

according to which T_k is determined essentially by the curvature of the potential barrier at the point of maximum. It may be assumed that this relation is applicable to any barriers of finite curvature, i.e., practically to all real barriers.

It follows from what has been said that, at the temperature determined by relations (5), (9), (10), the quantum correction to the classical reaction rate already exceeds the first approximation (ch^2). Wigner' s correction disappears at higher temperatures (see footnote** on p. 664) approximately 100° above T_k. (At $T < T_k$, higher powers of Planck' s constant begin to play a role in the series expansion of the quantum correction ([10,13]).) In this range of moderate temperatures the role of the tunnel effect can be detected experimentally by studying the influence of isotope effects on the observed values of the activation energy and of the pre-exponential factor in the commonly used expression for reaction rates ([8–10]). The temperature $T'_k \simeq T_k/2$, determined by Gol' danskii' s criterion (6), may serve to separate the region of low temperatures, where the exclusive role of the tunnel effect should be manifested by extremely low effective values of the activation energy and of the pre-exponential factor ([4,8,11]). This region is of interest for investigation.

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* Regarding the relative deviations of Wigner' s correction from the values obtained from equation (1) with the aid of the classical Boltzmann expression for $w(U, T)$, see ([8b]).

Note: Figure translations are in progress. See original paper for figures.