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Abstract

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POLANYI' S RULE FOR PROTON TRANSITIONS AND THE HYDROGEN BOND

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The relation between the change in activation energy $\Delta\mathcal{E}$ and the change in heat of reaction Δq for a series of similar reacting substances, known as Polanyi' s rule,

$$\Delta\mathcal{E} = k\Delta q, \qquad 0 < k < 1, \tag{1}$$

is observed for many reactions in which the determining stage is the transfer of a proton from one molecule to another (1):

$$\text{A\_H} + \text{B} \rightarrow \text{A\_H} \ldots \text{B} \rightarrow \text{A}^- \ldots \text{H}^+\text{B} \rightarrow \text{A}^- + \text{H}^+\text{B}.$$

Since the mass of the proton is appreciably smaller than the mass of atoms A and B, to a first approximation it may be assumed that, during the motion of the proton from one potential well to another, the distance between A and B in the complex with the hydrogen bond A_H ... B does not change. Usually the motion of the proton itself is then treated as classical. In accordance with this, Polanyi' s rule (1) is interpreted as a consequence of the fact that, in going from one substance to another, the points of the potential curve for the proton are displaced in one and the same direction along the energy axis, and in such a way that the displacement of the top of the potential barrier is smaller than the displacement of the second minimum, i.e. $\Delta U < \Delta Q$ (Fig. 1; see, for example, (2)). In an article by one of us (3) it was shown that the proportionality between ΔU and ΔQ is easily justified if, for the series of substances considered, the energy of the system A_H ... B depends only on one slightly changing parameter. However, the inequality $\Delta U < \Delta Q$ is difficult to justify purely theoretically. Moreover, as will be seen below, the facts indicate that for processes of proton transfer this inequality is not fulfilled, whereas Polanyi' s rule may turn out to be valid.

Fig. 1. Potential curves for proton transitions in the system A_H ... B for two different B

Fig. 2. Model of a double asymmetric potential well (formula (2))

Figure 1: Fig. 2. Model of a double asymmetric potential well (formula (2))

Fig. 3. Dependence of the energy levels E_0 on $\rho_0(=U_0^a)$ at $s=\text{const}$

Figure 2: Fig. 3. Dependence of the energy levels E_0 on $\rho_0(=U_0^a)$ at $s=\text{const}$

The motion of a proton from one potential well to another in reality cannot be treated classically. The energy of a proton in a double potential well is quantized, and the proton transition is, apparently, a multistage process of its stepwise excitation to one of the vibrational levels situated somewhat above the barrier, followed by "descent" into the ground state of the right-hand well. In this case the activation energy $\mathcal{E}$ (at absolute temperature $T=0$) will be equal to the distance between the zero level of the left-hand well and the indicated intermediate level. The distance between the zero levels of the two wells is the heat of reaction q (at $T=0$). To justify Polanyi' s rule it is necessary to investigate how $\mathcal{E}$ and q change for a chosen series of substances. We shall

to assume that this series is chosen so that, in the endothermic direction of the reaction, q decreases (the basicity of substance B increases).

Finding the energy levels in an asymmetric double potential well in the general case is a problem involving considerable mathematical difficulties*. We solved the corresponding one-dimensional Schrödinger equation in the quasiclassical approximation, assuming that the proton moves in a potential field $V(Z)$ having the following form** (see Fig. 2):

Fig. 2. Model of a double asymmetric potential well (formula (2))

$$\begin{aligned}
&V(Z)=\tfrac{1}{2}\mu\omega_a^2(Z+a)^2, && -\infty<Z\le -a;\\
&V(Z)=U^a\left[1-(Z/a)^2\right], && -a\le Z\le +b;\\
&V(Z)=\tfrac{1}{2}\mu\omega_b^2(Z-b)^2+Q, && +b\le Z<+\infty
\end{aligned} \tag{2}$$

$$\left(Q=U^a\left[1-(b/a)^2\right]\right).$$

Here μ is the reduced mass of the proton; U^a is the height of the potential barrier, measured from the minimum of the deeper potential well (a); the meaning of the parameters a and b is clear from Fig. 2. Instead of the independent parameters a, b, and U^a, we introduce the following dimensionless quantities: $U_0^a=U^a/\hbar\omega_a$, $\rho_0=(a/2\hbar)\sqrt{2\mu U^a}$, $s=b/a$. We also introduce the notation: $Q_0=Q/\hbar\omega_a$, $U_0^b=(U^b/\hbar\omega_a)=U_0^a-Q_0$, $E_0=E/\hbar\omega_a$ (E is the energy). The calculation was carried out under the assumption that the frequencies ω_a and ω_b are equal.

Fig. 3. Dependence of the energy levels E_0 on $\rho_0(=U_0^a)$ at $s=\text{const}$

Fig. 4

Figure 3: Fig. 4

In order to follow the change in the relative position of the energy levels as a function of the parameters ρ_0 and U_0^a, we shall vary the latter simultaneously in such a way that the equality $\rho_0 = U_0^a$ is satisfied, i.e., so that the approach of the minima of the potential curve (decrease of a) is accompanied by a simultaneous lowering of the height of the potential barrier U^a. One may expect that precisely such a situation is realized in reality, for example, in passing from weak bases to stronger ones. In what follows— Further, for brevity, we shall speak simply of the convergence of the minima. The values of the energy $E_{0,n}(\rho_0, U_0^a, s)$, obtained as a result of solving the problem, are presented graphically in Figs. 3 and 4. The values $E_{0,n}$, plotted on the ordinate axis, are counted from the deeper minimum (a). On the vertical axis are also plotted the values of the parameter $U_0^a = \rho_0$. Thus, the points of the energy curves lying in our graphs below (above) the straight line $U_0^a = \rho_0$, correspond, obviously, to such values of the parameter ρ_0 for which the calculated $E_{0,n}$ lie below (above) the top of the barrier. In Fig. 3, for $s^2 = 0.9$ and $s^2 = 0.5$, the behavior is shown of several levels selected from among those for which the deeper potential well (a) is the "parent" one (these levels belong to well (a) when the minima are separated to infinity). Figure 4 gives the curves $E_{0,n}$ for two cases: under the assumption that $U_0^b = \text{const}$, and under the assumption that $Q_0 = \text{const}$. In the calculations three parameters were varied simultaneously: ρ_0, U_0^a, and s. Numbers with a prime refer to levels for which the potential well (b) is the "parent" one.

Fig. 4. Dependence of the energy levels E_0 on $\rho_0 (= U_0^a)$

According to the usual interpretation ($^{1-3}$), for the direct process $\mathrm{A\_H} \ldots \mathrm{B} \rightarrow \mathrm{A}^- \ldots \overset{+}{\mathrm{H}}\mathrm{B}$ there is a relation between the height of the potential barrier U^a and the quantity Q:

$$\Delta U^a = k' \Delta Q. \tag{3}$$

To explain the Polanyi rule one must assume that $0 < k' < 1$. Since $U^a = U^b + Q$,

* Blinc and Hadži (^{4}) solved this problem by representing the proton wave function as a linear combination of the wave functions of two harmonic oscillators, each corresponding to the appropriate potential well.

** To construct a quasiclassical function valid near the top of the potential barrier, we used the fact that, for a barrier of parabolic form, an exact solution of the wave equation is known. For a detailed presentation of the solution method, see (^{5}).

it follows from (3) that

$$\Delta U^b = -(1 - k')\Delta Q, \tag{4}$$

i.e., as Q decreases, the barrier height for the reverse process increases. This assertion, however, is not consistent with the data on the vibrational spectra of the hydrogen bond. Indeed, according to Barrow (^{6}), in the spectra of a number of complexes A_H ... B, with a sufficiently strong base B, an additional frequency ν' appears, arising as a result of the splitting of lev—

of two potential wells, and whose intensity increases on going to stronger bases. This frequency in Fig. 4 corresponds to the transition from the ground level E of well (a) (not reproduced in the figure) to the excited primed level. According to the experimental data, ν' proves to be smaller than the "unprimed" frequency ν, and the difference $\Delta\nu = \nu - \nu'$ decreases on going to stronger bases. Within the framework of our model such a regularity is obtained only in the case when, as ρ_0 decreases, both quantities U^b and Q decrease, i.e., U^a falls more rapidly than Q. Thus, according to Fig. 4, for $U_0^b = \text{const}$, as ρ_0 decreases the primed level is lowered more rapidly than the unprimed one; moreover, at large ρ_0 (in the region of interest to us, to the right of the straight line $U_0^a = \rho_0$, i.e., below the top of the potential barrier) $\nu' > \nu$, which contradicts the experimental data. In the other limiting case, when $Q_0 = \text{const}$, the sign and course of $\Delta\nu$ obtained for each overtone in its own range of variation of ρ_0 are qualitatively consistent with these data (curves n and n'; $n - 1$ and $n' - 1$). The more rapid decrease of U^a in comparison with Q as ρ_0 decreases means that, on going to a stronger base, the shortening of the hydrogen bond affects the barrier height more strongly than it affects the position of the minimum (b), as a result of which $k' > 1$ (see (3) and (4)).

Polanyi' s rule (1) can be justified in the following way. First of all, let us note that the energy levels, as the minima approach one another, first decrease and then begin gradually to rise (Figs. 3 and 4). The lower levels behave like the higher ones, but their noticeable change begins at smaller ρ_0. As calculations have shown, the lowering of a level immediately preceding its attainment of a minimum value takes place in that region of variation of ρ_0 (for each level its own region of ρ_0) where the quantum effects of over-barrier reflection are small. The proton transfer from one well to the other occurs precisely through such a level (denote it by E_m). It is clear that, on the average, the slope of these levels in the indicated range of variation of ρ_0 will be smaller than for the lower primed levels, which reach their minimum values at smaller ρ_0 (see, for example, in Fig. 4 the levels n and $n' - 1$ in the interval $4 < \rho_0 < 6$). Therefore one may write $\partial E_m/\partial\rho_0 < \partial E_{l'}/\partial\rho_0,\ m > l'$. Since $\mathcal{E} = E_m - E\ \ $, $q = E_{l'} - E\ \ $, then $\Delta\mathcal{E} = [(\partial E_m/\partial\rho_0) - (\partial E\ \ /\partial\rho_0)]\Delta\rho_0$ and $\Delta q = [(\partial E_{l'}/\partial\rho_0) - (\partial E\ \ /\partial\rho_0)]\Delta\rho_0$. Here l' is the number of the lower level of well (b). From these equalities we find:

$$\frac{\Delta\mathcal{E}}{\Delta q} = \left(\frac{\partial E_m}{\partial\rho_0} - \frac{\partial E}{\partial\rho_0}\right) \bigg/ \left(\frac{\partial E_{l'}}{\partial\rho_0} - \frac{\partial E}{\partial\rho_0}\right) = k < 1, \tag{5}$$

where k is approximately constant. If E lies appreciably below the ground level of the right-hand well (b), then a change in the position of the latter has little effect on the position of E, i.e. $(\partial E \;/\partial\rho_0) \simeq 0$, and, consequently, $k > 0$. Under this condition formula (5) expresses Polanyi’ s rule.

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