

Application of Absolute Rate Theory to Intracrystalline Diffusion in Zeolites

BY JÖRG KÄRGER * AND HARRY PFEIFER

Sektion Physik der Karl-Marx-Universität, NMR-Labor,
DDR-701 Leipzig, Linnéstraße 5, German Democratic Republic

AND

REINHOLD HABERLANDT

Zentralinstitut für Isotopen- und Strahlenforschung der
Akademie der Wissenschaften der DDR, DDR-705 Leipzig,
Permoserstraße 15, German Democratic Republic

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Arguments for the applicability of absolute rate theory to molecular transport in zeolites are given. Its application to self-diffusion of methane and ethane in 5A zeolites provides satisfactory coincidence with experimental (n.m.r. pulsed field gradient technique) data in both the absolute values and the concentration dependence. A rigorous discussion of the influence of rotational barriers in the windows between adjacent supercages is presented.

In ref. (1) absolute rate theory was first applied to calculate molecular diffusion of light paraffins in 5A zeolites. The data obtained were in satisfactory agreement with the diffusion coefficients obtained experimentally by traditional uptake techniques.^{1, 2} Recent investigations using the n.m.r. pulsed field gradient technique³⁻⁵ as well as more refined uptake techniques (including the application of large laboratory synthesized zeolite crystallites)^{6, 7} have shown, however, that these uptake data for intracrystalline diffusion differ by more than four orders of magnitude from the real values (*cf.* examples in table 1). Reasons for this discrepancy have been proposed and discussed in the literature.^{5, 7-10} Noting the satisfactory agreement between the values calculated in ref. (1) on the basis of the absolute rate theory and the erroneous experimental diffusivity data, a critical reconsideration of the applicability of absolute rate theory to zeolitic diffusion seems necessary.

APPLICABILITY OF THEORY OF ABSOLUTE REACTION RATES

Though restricted to processes near equilibrium, Eyring's rate theory has found many applications in chemical reactions.¹⁴⁻¹⁶ This is mainly because it reduces kinetic problems to equilibrium problems and avoids dynamical calculations. Beyond chemical reactions other processes, *e.g.*, transport phenomena, are also treated by absolute rate theory.¹⁷

The range of applicability and validity has not yet been fixed exactly. To do this, its derivation from first principles is necessary.¹⁸ In general, Eyring's formula for absolute reaction rates is derived by assuming an equilibrium between reactants and a so-called "transition state". Thus this theory is sometimes called "transition state theory". However, the question arises whether such an "activated complex" exists at all. At least for zeolites it seems possible, considering the molecule in the

TABLE 1.—COMPARISON OF N.M.R. AND SORPTION DATA FOR INTRACRYSTALLINE SELF-DIFFUSION OF LIGHT PARAFFINS IN NaCaA ZEOLITES

system	quantity investigated	n.m.r. measurements	uptake measurements
methane/5A	pre-exponential factor $D_0/m^2 s^{-1}$ (for 2 molecules per cavity) ^a	4.5×10^{-9} ¹¹	7.2×10^{-12} ¹³
	activation energy $E/kJ mol^{-1}$ (for 2 molecules per cavity)	3.8 ¹¹	12.5 ¹³
	concentration dependence $dD(c)/dc$	> 0 ¹¹	≈ 0 ¹³
ethane/5A	pre-exponential factor $D_0/m^2 s^{-1}$ (for 1.2 molecules per cavity) ^a	10^{-9} ¹²	1.28×10^{-12} ¹³
	activation energy $E/kJ mol^{-1}$ (for 1.2 molecules per cavity)	5.8 ¹²	12.8 ¹³
	concentration dependence $dD(c)/dc$	> 0 ¹²	≈ 0 ¹³

^a Up to at least 2 molecules per cavity self-diffusion coefficients do not change significantly with increasing concentration and therefore these values are also representative of Henry's region.

supercage to be in the initial state and the molecule at the top of the intracrystalline potential wall between adjacent supercages to be in the transition state.

On the other hand, avoiding the assumption of an activated complex and assuming only Boltzmann-like distribution functions for the reactants, Ross and Mazur ¹⁹ were able to derive Eyring's formula if they introduced appropriate threshold energies. Looking at self-diffusion of molecules in zeolites one can assume that the initial Boltzmann-type velocity distribution remains unchanged. Thus absolute rate theory is appropriate to describe intracrystalline diffusion in zeolites. To obtain deeper insight, further theoretical investigations, *e.g.*, using molecular dynamical calculations, in comparison with additional experimental data are necessary. This implies complete avoidance of (equilibrium) statistical thermodynamics and consideration of intracrystalline self-diffusion as the diffusion of labelled molecules, *i.e.*, as an irreversible process, which can be handled, for example, by use of correlation functions.^{18, 20}

THE MODEL

While both self-diffusion and adsorption behaviour in X-type zeolites can be formulated in a first-order approximation by representing the energy profile in the intracrystalline space by a three-dimensional sinusoidal function,²¹ a corresponding representation of intracrystalline space in the A-type zeolite is more complicated owing to the dominant role of the windows between adjacent supercages in the diffusion processes.^{12, 22} Calculation of the self-diffusion coefficient therefore requires assumptions to be made about molecular behaviour in the supercages (initial state in Eyring's theory) as well as during passage through the windows (activated

state). According to the theory of activated jumps, the self-diffusion coefficient is given by

$$D = l^2/6\tau, \quad (1)$$

where l and τ denote, respectively, the distance between adjacent supercages and the mean lifetime in one supercage. Since molecules can leave supercages through any of the six adjacent windows, $1/\tau = 6\nu$ holds, where ν is the transition frequency from the supercage through one of the adjacent windows.

According to Eyring's formula, ν is given by

$$\nu = \kappa \frac{kT}{h} \frac{Z_{\ddagger}}{Z_A} \exp(-E_0/kT), \quad (2)$$

where Z_{\ddagger}/Z_A denotes the ratio of the partition functions in the window and in the cavity. E_0 is the corresponding energy difference which acts as activation energy. The frequency factor kT/h stems from the translational degree of freedom of the transition state in the direction of diffusion. Therefore, this degree of freedom is not included in Z_{\ddagger} . The transmission coefficient κ is an additional correction factor (of the order of one) which can be used to account for the fact that occupation of the transition state does not always lead to a diffusional jump into the neighbouring supercage. Inserting eqn (2) into eqn (1) we obtain

$$D = \left(\frac{kTl^2}{h} \right) \frac{Z_{\ddagger}}{Z_A} \exp(-E_0/kT),^* \quad (3)$$

where κ has been put equal to one for simplicity. Determination of the self-diffusion coefficient therefore requires calculation of the partition functions in the cavity as well as in the window.

Following Ruthven,¹ the cumbersome calculation of the partition function in the supercage can be avoided by applying expression (4)

$$n_A = \frac{Z_A}{z_g} \frac{p}{kT} \exp(U_0/kT) \quad (4)$$

to the adsorption isotherm, in which n_A denotes the number of sorbed molecules per supercage at pressure p .

Z_A and partition function z_g per unit volume in free gas space are reduced to a zero-respective energy level with a difference U_0 between them.

Having replaced Z_A by eqn (4) one obtains

$$D = \frac{l^2}{h} \frac{Z_{\ddagger}}{z_g} \frac{p}{n_A} \exp\left(-\frac{E_0 - U_0}{kT}\right). \quad (5)$$

For low concentrations, eqn (5) can be further simplified to give

$$D = \frac{l^2}{h} \frac{1}{K_0} \frac{Z_{\ddagger}}{z_g} \exp\left(-\frac{E_0 - U_0 + V_0}{kT}\right), \quad (6)$$

where K_0 and V_0 are, respectively, the pre-exponential factor and the activation energy of Henry's constant

$$K = n_A/p = K_0 \exp(V_0/kT). \quad (7)$$

Apart from the activation energy ($E_0 + V_0 - U_0$) of self-diffusion, the only free parameter in eqn (6) is the ratio between the partition functions in the gas phase and

* In the corresponding eqn (9) in ref. (1) an additional factor 1/6 is used. This is only correct if Z_{\ddagger} is regarded as the total partition function of all 6 windows. However, in our calculation as well as in ref. (1), Z_{\ddagger} refers to one window only.

in the window. The only assumption necessary for calculation of the diffusion coefficients in the given model refers to changes in the degrees of freedom when comparing free molecules with those in the transition state between neighbouring supercages.

In the case of a free N -atomic non-linear molecule in the gas phase, three translational and rotational degrees of freedom and, if excited at all, $(3N-6)$ vibrational degrees of freedom contribute to the partition function. Under the influence of potential in the zeolite lattice all these contributions will change. The movement through the windows between the cavities will change the degrees of freedom in the following manner. The three translational degrees of freedom will cause 2 vibrational degrees perpendicular to the axis of motion in the window and only one translational degree of freedom in the direction of motion. The three degrees of freedom of initially free rotation may yield rotational degrees more or less hindered by the window potential. For eqn (4) we have given up trying to confirm the model by comparison with adsorption properties, as it was tried for NaX zeolites in ref. (21) and by Bakaev and Smirnova for A-type zeolites in ref. (23). In contrast to the latter paper we can show, however, that the results provided by absolute rate theory for alkane diffusion in NaCaA zeolites are of more general validity than could be assumed when applying a particular potential profile.

CALCULATION AND COMPARISON WITH EXPERIMENT

We will restrict ourselves to calculation of the pre-exponential factor. Taking eqn (6), for low concentrations

$$D_0 = \frac{l^2}{h} \frac{1}{K_0} \frac{Z_{\ddagger}}{z_g} \quad (8)$$

Comparison of activation energies with theoretical values must be based on potential calculations, which are beyond the scope of this paper. Moreover, theoretical estimations of intracrystalline potentials given in the literature exhibit, in several cases, significant differences.^{1, 23-26}

The ratio of the partition functions is given by

$$\frac{Z_{\ddagger}}{z_g} = \frac{Z_{\text{int}} Z_w Z_{\text{rot}}}{Z_{g \text{ int}} z_{g \text{ trans}} Z_{g \text{ rot}}}, \quad (9)$$

where Z_{int} and $Z_{g \text{ int}}$ refer to the internal degrees of freedom, $z_{g \text{ trans}}$ to the translation, Z_w to the two-dimensional vibration in the window and Z_{rot} and $Z_{g \text{ rot}}$ to the rotation in the adsorbate and in the gas phase, respectively. They are¹⁷

$$\begin{aligned} Z_{g \text{ int}} &= \prod_{i=1}^{3N-6} \frac{\exp(-h\nu_i/2kT)}{1 - \exp(-h\nu_i/kT)}, \\ Z_w &= \frac{\exp(-h\nu_w/kT)}{[1 - \exp(-h\nu_w/kT)]^2}, \\ Z_{g \text{ rot}} &= \frac{8\pi^2(2\pi kT)^{\frac{3}{2}}}{s_j h^3} (I_A I_B I_C)^{\frac{1}{2}}, \\ z_{g \text{ trans}} &= \left(\frac{2\pi m kT}{h^2} \right)^{\frac{3}{2}}, * \end{aligned} \quad (10)$$

* In the expression for $z_{g \text{ trans}}$ and hence in the denominator of our eqn (8), in ref. (1) an additional factor e had been introduced, which in our opinion need not be indicated.

with internal vibrational frequencies ν_i of the molecule, vibration frequency ν_w of the molecule in the window, symmetry number s_j , principal moments of inertia I_A , I_B , I_C and mass m of the molecule.

Evidently, the reliability of a comparison between the calculated and experimental values depends on our knowledge of the different partition functions and especially on their ratios. At normal temperatures for diffusion experiments $Z_{g \text{ int}} = Z_{\text{int}} = 1$. An estimate of partition function Z_w for vibrations perpendicular to the window axis (= 2.28 for methane)¹ shows that this quantity is also of the order of one. Since $z_{g \text{ trans}}$ can be calculated straightforwardly, the main deficiency in our knowledge is due to ambiguity in the ratio $Z_{\text{rot}}/Z_{g \text{ rot}}$.

For spherical molecules it seems most likely that molecular rotation is barely restricted in the windows and therefore $Z_{\text{rot}}/Z_{g \text{ rot}}$ should be of the order of one. Taking calculated values of $Z_w = 2.28^1$ and $z_{g \text{ trans}} = 0.477 \times 10^{32} \text{ m}^{-3}$, of $Z_{\text{rot}}/Z_{g \text{ rot}} = Z_{\text{int}} = Z_{g \text{ int}} = 1$ and an experimental value $K_0 = 1.4 \times 10^{-8} \text{ molecules Pa}^{-1} \text{ cavity}^{-1}$ for the Henry coefficient, one obtains from eqn (8) for the self-diffusion coefficient of methane in 5A zeolites ($l = 12.3 \times 10^{-10} \text{ m}$) at $T = 250 \text{ K}$, $D_0 = 7.76 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. This value is in excellent agreement with the experimental value $D_{0 \text{ ex}} = 4.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.¹² This coincidence allows us the reasonable conclusion that the rotation of methane molecules is virtually unrestricted during passage from one supercage to the adjacent one.

By contrast, in ref. (1) molecular rotation in the windows had to be prohibited. Only with this incisive assumption and the additional factors $\frac{1}{6}$ and $1/e$ [cf. remarks concerning our eqn (3) and (10)] do theoretical values approximate the uptake data of previous investigations.

In order to consider restrictions to rotational freedom in the windows, in the first approximation the rotation in the windows can be assumed to take place in a sinusoidal potential

$$V_R = \frac{1}{2}V_{R01}(1 - \cos n_1\phi_1) + \frac{1}{2}V_{R02}(1 - \cos n_2\phi_2) + \frac{1}{2}V_{R03}(1 - \cos n_3\phi_3). \quad (11)$$

Here V_{R0i} are the maximum values of the hindering potential, ϕ_i are the angles around the rotational axis and n_i are symmetry numbers of hindered rotation. The following contribution of the hindered rotation to the partition function is obtained²⁷⁻²⁹

$$Z_{\text{rot}} = Z_{g \text{ rot}} \prod_{i=1}^3 \left[e^{-x_i} I_0(x_i) \left\{ 1 - \frac{u_i^2}{24} \frac{I_1(x_i)}{I_0(x_i)} + \frac{u_i^4}{5760} \left(7 - \frac{2}{x} \frac{I_1(x_i)}{I_0(x_i)} \right) - \frac{u_i^6}{967680} \left(32 + \left(31 + \frac{8}{x_i^2} \right) \frac{I_1(x_i)}{I_0(x_i)} \right) \right\} \right]. \quad (12)$$

x_i denotes the ratio $V_{R0i}/2kT$. $I_1(x)$ and $I_0(x)$ are the modified first- and zero-order Bessel-functions, respectively, u_i stands for the ratio $\sqrt{2\pi x_i}/Z_{g \text{ rot}}$.

As an example in fig. 1 the ratio

$$\frac{Z_{\text{rot}}}{Z_{g \text{ rot}}} = [e^{-x} I_0(x)]^r \quad (13)$$

is plotted as a function of the ratio x of potential and thermal energy, if 1, 2 or 3 rotational degrees of freedom are hindered. For simplicity it has been assumed that all potential maxima are equal ($V_{R0i} = V_{R0}$). If the difference between the theoretical and experimental results is caused by hindered rotation, the value of the correction term $Z_{\text{rot}}/Z_{g \text{ rot}}$ should be ≈ 0.6 .

Assuming that only rotation around the axis of transport is hindered ($r = 1$), we obtain $x \approx 0.7$ corresponding to a maximum value V_{R_0} of the potential energy of ca. 3.2 kJ mol⁻¹. Recalling that a difference by a factor 0.6 between the experimental and theoretical value for D_0 is not significant in comparison with the uncertainties in both the experimental data and the applied theoretical model, this value must be considered as an estimate of the order of magnitude of the influence of rotational restriction.

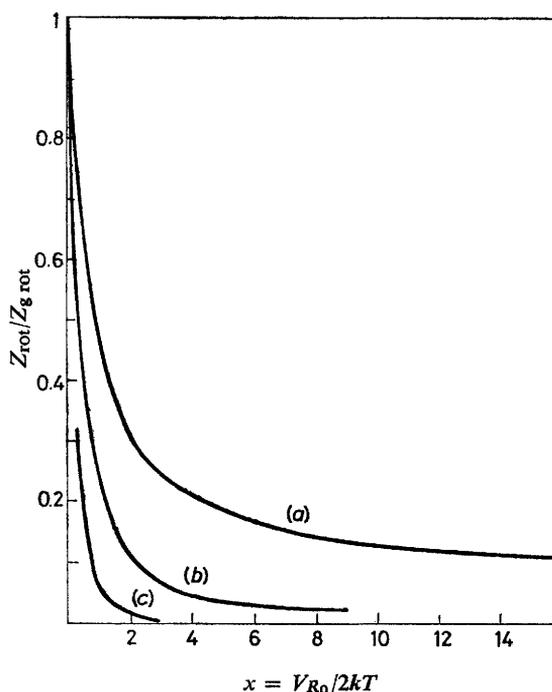


FIG. 1.— $Z_{\text{rot}}/Z_{\text{g rot}}$ as a function of $x = V_{R_0}/(2kT)$ for rotational hindrance in (a) 1, (b) 2 and (c) 3 directions.

In contrast to spherical methane molecules, self-diffusion of ethane in 5A zeolite should be more strongly influenced by potential and steric restrictions. As a first approximation we assume that the rotation of an ethane molecule in the window is restricted in such a way that the orientation of its rotational axis (C—C bond) is confined to angular deviations from the window axis $< \theta_0$.

For the rotational part of the partition function in the activated state one obtains therefore $Z_{\text{rot}} = Z_{\text{g rot}}\Omega/4\pi$, where $\Omega = 4\pi(1 - \cos \theta_0)$ represents the spherical angle of the double cone to which motion of the molecular axis is restricted. Assuming, because of lack of more detailed information, that $Z_w = 1$, one obtains with the calculated value $z_{\text{g trans}} = 1.224 \times 10^{32} \text{ m}^{-3}$ and with the experimental value $K_0 = 0.3 \times 10^{-8} \text{ molecules Pa}^{-1} \text{ cavity}^{-1}$ for $T = 250 \text{ K}$ from eqn (8)

$$D_0 = 6.25 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \Omega/4\pi. \quad (14)$$

Equating this relation to the experimental value $D_{0 \text{ ex}} = 10^{-9} \text{ m}^2 \text{ s}^{-1}$ one obtains $\Omega \approx 2$, corresponding to a reasonable value of $\theta_0 \approx 33^\circ$ for maximum angular deviation of the orientation of the molecular axis from the window axis.

In addition to prediction of absolute values, the formalism of the absolute rate theory also provides information about the concentration dependence of the self-diffusion coefficient. According to eqn (5) the concentration dependence of the self-diffusion coefficient is predominantly given by a factor $p(n_A)/n_A$. For Langmuir-type isotherms, which are typical for zeolites, $p(n_A)/n_A$ increases with increasing pressure. This is in complete accordance with the results of n.m.r. self-diffusion measurements [cf. table 1 and ref. (30)]. For higher pore filling factors, the sorption model presented here no longer holds and should be modified by choosing a transmission coefficient κ value of other than one [eqn (2)].¹⁵

Rigorous application of absolute rate theory to a simple model for paraffin migration in NaCaA zeolites reveals theoretical values which are in good agreement with the experimental results of self-diffusion. Coincidences are noted in the absolute values as well as in concentration dependences. Absolute rate theory should be regarded, therefore, as a valuable tool for the prediction of molecular transport in zeolite molecular sieves.

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