Isotopic Effects in the Self-diffusion Coefficient in an Equimolar Binary Mixture

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Isotopic Effects in the Self-diffusion Coefficient in an Equimolar Binary Mixture

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In the last few years molecular dynamics has become a valuable tool in calculating the thermodynamical, structural and transport behaviour of a lot of many-particle systems in different fields of science and application. First the aims and essential features of molecular dynamics (MD) are described. In the second part self-diffusion coefficients of N_2/CH_4 mixtures for isotope substituted methanes in dependence on temperature, pressure, mass and diameter are calculated. Avoiding large computational efforts the calculations are performed by a kinetic hard sphere theory fitting the hard sphere diameters by MD runs.

In den letzten Jahren wurden molekulardynamische Rechnungen zur Bestimmung thermodynamischer und Transportgrößen sowie Struktureigenschaften einer Reihe von Vielteilchensystemen auf verschiedenen Anwendungsgebieten durchgeführt. Im ersten Teil werden Ziele und wesentliche Merkmale der Molekulardynamik dargestellt. Im zweiten Teil werden Selbstdiffusionskoeffizienten in N_2/CH_4-Mischungen für isotopensubstituierte Methane in Abhängigkeit von Temperatur, Druck, Masse und Teilchengröße berechnet. Um den rechentechnischen Aufwand zu verringern, wird eine kinetische Hartkugeltheorie benutzt, wobei die Teilchendurchmesser durch MD-Rechnungen angepaßt werden.

Keywords

1. Introduction

There is an increasing interest in the theories describing gaseous and liquid states of mixtures. This is partly due to the development of the application of statistical mechanics techniques to the results of computer simulations [1].

One of the investigations in this field is to evaluate the role of particle mass and size played for the transport properties [2–8].

Starting with isotope separation (compare *G. Hertz* [9]) isotopic effects in diffusion phenomena became more and more important.

Until now no theoretical approach is able to describe diffusion processes in dense gases of particles with realistic pair interaction potentials with the accuracy needed to find isotopic effects in the diffusion coefficients.

Two ways seem to be possible to overcome this situation. The first one is to replace analytical theories by computer simulations. The second one is to try to replace the real system by a somewhat less realistic "effective" system for which a sufficient theoretical approach already exists.

Since the computer simulations for diffusion coefficients are very expensive in computer time we have combined these two possible ways.

We made some simulations to fit the parameters of an effective hard sphere (HS) system to a dense gas of Lennard-Jones (LJ) particles.

Than we used the results of the Enskog theory [10] with empirical corrections to predict the isotopic effects in the diffusion coefficients over a wide range of pressure and temperature.

Especially the mass and size dependence of the self-diffusion coefficients and of their ratios in binary mixtures is of theoretical interest because some hydrodynamic and quasihydrodynamic theories fail to express such effects readily, while other theories — like kinetic and perturbation theoretical ones — do predict their existence.

It is also of experimental interest because isotope effects may interfere with practical determinations of self-diffusion coefficients and because there are many applications in the chemical industry and in geological systems.

2. Theoretical background and results of computer simulation

In the absence of definite theories computer simulation appears to be the best way to study specific effects such as on mass and size.

The advantage of the simulation is that one can alter one parameter of a species holding all other parameters constant, so that intermingled effects can be separated.

Fig. 1 gives a survey of different experimental and theoretical methods and quantities.

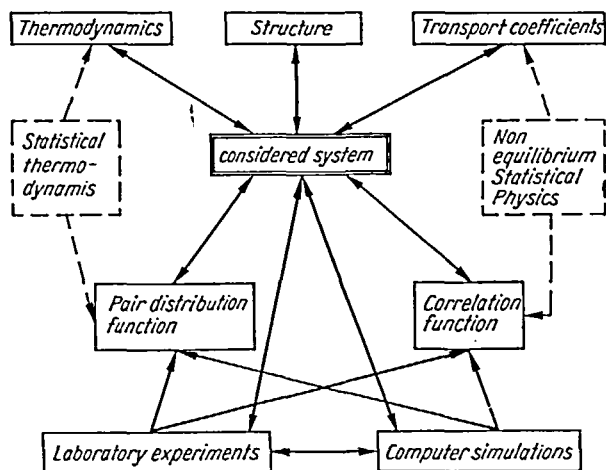Thermodynamic, structural and transport data are of interest for all systems considered.

Fig. 1. Methods to investigate many particle systems

In principle at least all data can be calculated by methods of statistical thermodynamics and nonequilibrium statistical physics using pair distribution functions and correlation functions. But of course for real complex systems there exist a lot of difficulties especially regarding the knowledge of intermolecular and intramolecular interaction and especially in the case of nonequilibrium behaviour where the theory is not yet established in all cases.

To improve the situation or to overcome the difficulties it is necessary to include experimental data from laboratory experiments. Additionally in the last decades computer simulations have come into play more and more [11]. They serve as a powerful tool to get exact thermodynamics, structural and transport data by solving equations of motion for the considered systems. In a certain sense computer simulations play a dual role: In instances where no calculations are available to interpret measurements, simulations can play the role of a theory. In other instances where no measurements are available to check the theory, it can generate the experimental data needed. In other words in the absence of real experiments the data can be used as experimental data and if exact theories are lacking they may serve to examine theoretical approximations or empirical formulas. And to say it once more, by computer simulations one can make separate and detailed estimations of the influence of all parameters which are experimentally interlinked.

Let us come to some hints concerning the theoretical background. It is the aim of this paper to treat dynamical isotope effects. First only a few remarks about the equilibrium situation. For thermodynamical isotope effects there exists a well-known theory of *Bigeleisen*, *Wolfsberg* [12] and *Galimov* [13] using partition function ratios, which gives closed formulas for all thermodynamical isotope effects.

The virial theorem

$$ P = \frac{NkT}{V} - \frac{1}{6} \frac{N^2}{V^2} \int_V r \frac{\partial u(r)}{\partial r} g(r) \, dr \tag{1} $$

forms the central relation by which the equation of state may be gained in analytic theories or computer simulations. $U(r)$ is the pair potential. $g(r)$ is the radial pair distribution function [14], which serves as another starting point for calculating thermodynamic quantities.

Now let us come to some aspects of dynamical processes and nonequilibrium behaviour.

Here the investigation of the processes must include the dynamics or kinetics.

These processes are governed by the laws of hydrodynamics, irreversible thermodynamics and the statistical theory of irreversible processes. Instead of the partition function or the radial distribution function the so-called correlation functions K are the most important quantities

$$ K(t, t') = \langle \dot{A}_1(t) \, \dot{A}_2(t') \rangle = Tr\{(\dot{A}_1(t), \dot{A}_2(t') \varrho\} \tag{2} $$

The time correlation function K is defined as the thermodynamic average (or trace) of the product of two dynamical variables $\dot{A}_t$, each of which expresses the instantaneous deviation of a fluid property from its equilibrium value at particular points in space and time t. The average is taken over the phase coordinates of all the molecules in the fluid with an equilibrium ensemble ϱ as the weighting function.

A time correlation function is therefore a function of space and time, and it describes the thermal fluctuations which occur spontaneously in the equilibrium system.

All transport coefficients can be determined by Fourier-transformations of correlation functions. As a special case the diffusion coefficient in the low frequency limit is

$$ D = \frac{1}{3} \int_0^\infty dt \, \langle \dot{r}(0) \cdot \dot{r}(t) \rangle \tag{3} $$

with $\dot{r}$ beeing the time derivative of space vector r.

The formula

$$ D = \lim_{t \to \infty} \frac{1}{6Nt} \sum_{i=1}^N \left(r(t) - r(0) \right)^2 \tag{4} $$

(N = particle number) is often used in practical calculations and we use it as well.

The starting point in calculating the physical behaviour is the determination of the mechanical state of the system under consideration by all generalized spatial coordinates q_i and all generalized momentum coordinates p_i.

— For small systems with single particles this state is given by the laws of mechanics

— In the case of macroscopic thermodynamic systems the laws of statistical physics (thermodynamics) will give the desired behaviour

— Using several hundred up to several thousand particles per system computer simulations try to represent real macroscopic systems with the help of Newtonian mechanics.

There exist two main methods of computer simulations
    molecular dynamics (MD) and
    the Monte Carlo procedure (MC).

Here we restrict ourselves to MD because it also gives the dynamical behaviour.

What does molecular dynamics mean?
Molecular dynamics describes the mechanical motion of the system by solving equations of motion such as for instance Newton's second law or the Lagrangian equations.
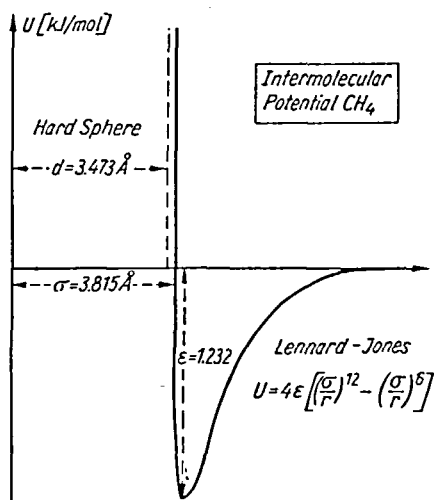
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Fig. 2. The Lennard-Jones potential

What steps are necessary?

1) Selection of the intermolecular potential
   We choose the Lennard-Jones potential (Fig. 2) or the rigid sphere potential

2) It should be noted that there exist different algorithms (*Verlet*, *Toxvaerd*, *Gear*, *Leapfrog* and so on [15, 16]).
   We use the Leapfrog algorithm.

3) After a certain time period of "thermalization" to forget the start configuration the MD run can be used for averaging the desired functions. Assuming ergodicity, that means, equality of ensemble and time averages we use the time average. To avoid surface effects so-called periodic boundary conditions are used. That means that the particular box with particles will be multiplied identically. Particles which disappear for instance to the box above come into the box from below again. So it is possible to simulate macroscopic systems.

Now let us give a short summary of results from the literature especially those due to *Jolly*, *Bearman*, *Lantelme*, *Schön* and *Hoheisel* [2—8].

I. While it is known that for diluted gases the transport coefficients are roughly proportional to the inverse of the square root of the mass of colliding particles, the many experiments now available show clearly that the diffusion isotope effect is very small for such systems. In dense systems the situation is quite different. The computer simulations confirm this observation. *Jolly* and *Bearman* fitted their MD runs to give the empirical relation

$$\ln (D/D^+) = b_0 + b_1 \ln (m_2/m_1) + b_2[\ln (m_2/m_1)]^2 \qquad (5)$$

with the masses m_i and $D^+ = 1 \cdot 10^{-9}$ m²s⁻¹.

The b_i are empirical coefficients, which in general depend on the details of molecular parameters such as size, shape and moment of inertia and on the thermodynamic states and which also obey symmetry relations.

II. It is possible to describe inverse isotope effects as well, that is, to explain situations in which heavy isotopes diffuse more rapidly than light ones. For example, b_1 could change the sign or b_2 could be sufficiently large to cancel the b_1 contribution. Some such cases are given by changing the concentration in the mixture.

III. If a tracer diffusion coefficient is introduced to denote the self-diffusion coefficient D_T of a solute T of mass m_T at infinite dilution in a solvent S of mass m_S, the empirical

equation is written for small mass variations.

$$D_T = D_S(m_T/m_S)^{b_1} = D_S(m_1/m_2)^{-0.056}$$

$$\approx D_S - (0.056\ D_S/m_S)\ \Delta m . \qquad (6)$$

IV. It is shown that the isotope effects of D are less sensitive to the change of parameters used in the calculation than the diffusion coefficients themselves.

Especially the isotope effect is practically insensitive to a change of the particle number of the system in the range of 108 to 864 [17]. But it is necessary to have long runs [5]. Therefore it is justified for us to use 108 particles in our runs only but a large number of time steps (up to 100000, compare Tab. 1, which shows all data used in our MD runs).

108 particles, cubic box,
periodic boundary conditions
concentrations: $x_1 = x_2 = 0.5$
box length (different cases): e.g. 27 Å
time increment: $t = 10^{-14}$ s (integration step width)
length of MD runs: 40000 ... 100000 time steps
(standard 70000)

Tab. 1. Data used for our computer simulations

b. 1. Particle parameters (standard values)

	CH₄	CD₄	N₂
σ[Å]	3·817	3·802	3·698
ε[kJ/mol]	1·232	1·221	0·79
m[g/mol]	16·0	20·0	28·0

3. Hard sphere theory

3.1. Used relation

Because of the large computational time we additionally used a kinetic theory for hard spheres on the Enskog level (due to *Easteal* and *Woolf* [6] to get not only simple results but curves over ranges of different parameters such as temperature T, pressure P, masses m_i, potential parameters σ_i and particle number N_i. This theory yields

$$(D_1)_2 = (3kT/16\pi) \{\varrho_1 g_{11}(d_1)\ d_1^2(kTm_1/4\pi)^{1/2} +$$

$$+ (\varrho_2/16)\ g_{12}(d_{12})\ d_{12}^2[kTm_1m_2/2\pi(m_1 + m_2)]^{1/2}\}^{-1} \qquad (7)$$

$d_{12} = (d_1 + d_2)/2$

$d_i \qquad$ hard sphere diameter

$\varrho_i = N_i/V$

$V \qquad$ Volume

$k \qquad$ Boltzmann's constant

$(D_1)_2 \qquad$ self-diffusion coefficient of sort 1 in mixture with sort 2

$g_{ij}(d_{ij}) \qquad$ pair distribution function at the point of contact

Of course the Enskog theory is not correct at high densities and not even in the case of dense gases. But with suitably chosen effective particle parameters it is well suited to fit MD data.

3.2. Selection of an effective hard sphere diameter

It is of course impossible even in the monocomponent case to find an effective hard sphere (HS) diameter d which depends only on the particle sort and the temperature for a given LJ system. The cause of the density dependence of d lies mainly in the attractive part of the LJ potential the influence of which depends strongly on the density.

In [18, 19] d is chosen by comparing pressure measurements of a real monocomponent system with the pressure of a hard sphere system of the same temperature, number density and particle masses. d is defined as the HS diameter which yields the correct pressure. This is a rather crude method of finding d and in other studies more refined but also more complicated methods have often been used.

A comparable simple method is also described in [20] for methane. Comparing the density of methane at the freezing point with that of randomly packed hard spheres d is chosen in a simple manner. In [21] two methods are proposed. A very simple but poor method is to choose a diameter

$$a = (4\pi\varrho/3)^{1/3}.$$ (8)

A better one is to use the Stokes-Einstein relation to put

$$d = kT/(2 \cdot \pi \cdot \eta \cdot D)$$ (9)

but this requires the knowledge of D and η.

For the so-called soft core potential which contains only a twelfth power repulsive part without attractive forces the Barker/Henderson radius or the WCA-effective diameter which both arise from perturbation theories [14] of the equilibrium equation of state are sometimes used to calculate transport properties. In [22] it is argued that the so-called Verlet/Weis diameter d

$$\left(\frac{d}{\sigma}\right) = \frac{0.3837 + 1.068/T^*}{0.4293 + 1/T^*}, \qquad T^* = \frac{kT}{\varepsilon}$$ (10)

which is chosen from WCA theory [23] gives a good effective HS system to determine the viscosity of LJ particles. But it is well known that particle diameters estimated by viscosity measurements are too large to represent other properties of the system [24] well.

Using MD calculation we found the d values of Verlet/Weis too large to yield effective hard sphere diameters for the description of self-diffusion in dense gases.

In [25] the effective diameter is determined by comparing the dynamical structure factor $S(k)$ of the real system with that of a hard-sphere system.

Unfortunately the $S(k)$ of the real system is not available in many cases.

All those methods have one common disadvantage. The effective diameter used to describe, for instance, diffusion is calculated from other properties of the system. It is therefore not at all clear whether it really yields a good description of diffusion.

Thus there remains one method, which is used in [26]. The effective HS diameter for the description of diffusion is determined by comparing diffusion measurements with MD simulation results. But what is the use of such an effective HS system if the diffusion coefficient is already known? For example, the calculated diameter can also be used in mixtures or in the presence of boundaries, caves, and so on.

In our case we assume that the effective HS system yields the same changes of the self-diffusion coefficients as the real system does after small changes in particle diameters or masses. So the small isotopic effects may be detected which are very difficult to examine by measurements or computer simulations.

Fortunately computer simulations show that the diffusion properties are nearly unaffected by isotopic changes in the attractive potential part of LJ-systems which cannot be represented in the HS model [27].

The expectation value of the relative kinetic energy of colliding particles is $2 \cdot kT$. It is greater than the mean

relative kinetic energy of a randomly chosen pair of particles because fast moving particles collide more often.

The shortest distance reached in a central collision of two LJ particles with this relative kinetic energy is

$$\tilde{d} = \sigma \cdot \left(\frac{1}{2} + \frac{1}{2}\sqrt{1 + \frac{2kT}{\varepsilon}}\right)^{-1/6}$$ (11)

Of course most collisions occurring in the system are no central ones. But $\tilde{d}$ seems to be also a convenient rough approximation to d for diffusion.

3.3. Corrections to the Enskog theory

In the Enskog theory only static correlations in configuration space (i. e. the radial pair correlation function) are taken into account. All dynamic effects are neglected completely. Moreover, since the traditional Enskog theory [10] includes contradictions with respect to the Onsager relations, a revised Enskog theory has been introduced [28].

But this theory yields very complicated expressions for the transport coefficients and it doesn't take into account dynamical effects either. So for practical purposes it seems to be reasonable to use the expressions of the traditional Enskog theory and to introduce empirical corrections concerning the transport coefficients in order to fit them to computer simulation results. Fig. 3 shows such a correction factor of the self-diffusion coefficient for a monocomponent hard sphere fluid as a function of the packing fraction. The temperature dependence is negligible. The main part of the curve has been taken from [21, 29]. In [19] the decrease of the self-diffusion coefficient to almost zero at high densities was examined. For dilute gases the correction factor must be equal to unity. So the dashed parts of the curve have been introduced empirically.

Finally let us give a short interpretation of the density dependence of the correction. It has been well known since the famous Molecular Dynamics calculations of *Alder/Wainwright* [30] that for long times the velocity autocorrelation function decreases very slowly compared with the predictions of the Enskog theory. This so-called "long time tail" is due to repeated collisions of pairs of molecules and leads to an increase of the self-diffusion coefficient of dense gases. If
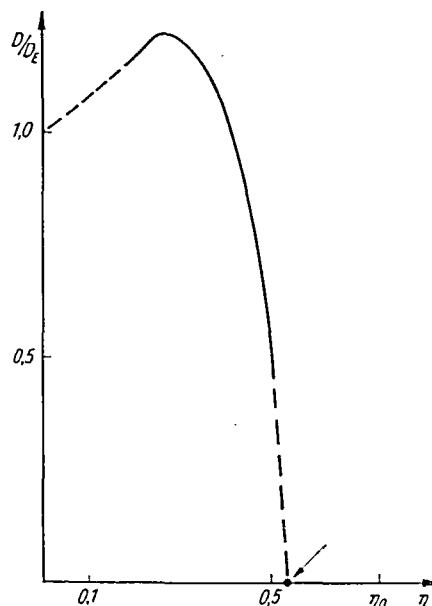

Fig. 3. Correction factor of the self-diffusion coefficient

the density of the fluid is nearly that of a solid, each particle is closely surrounded by its neighbours which form a kind of cage making diffusion nearly impossible.

The correction shown in the figure is given in the mono-component case as a function only of the density. In mixtures it becomes a rather complicated function of all particle parameters and the concentrations as well. Since it must be fitted from simulation results no closed expression is available. So we restricted ourselves to introducing only the correction of the corresponding monocomponent case for mixtures as well. This will be a very good approximation if the particle parameters in the mixture differ only slightly. But even in all other cases we hope to cover a great part of the effect in this way and in any case to improve the Enskog values of the self-diffusion coefficients.

4. Results

The changes ΔD of the self-diffusion coefficients of mixtures of nitrogen and isotope substituted methanes ($\Delta m \neq 0$) are
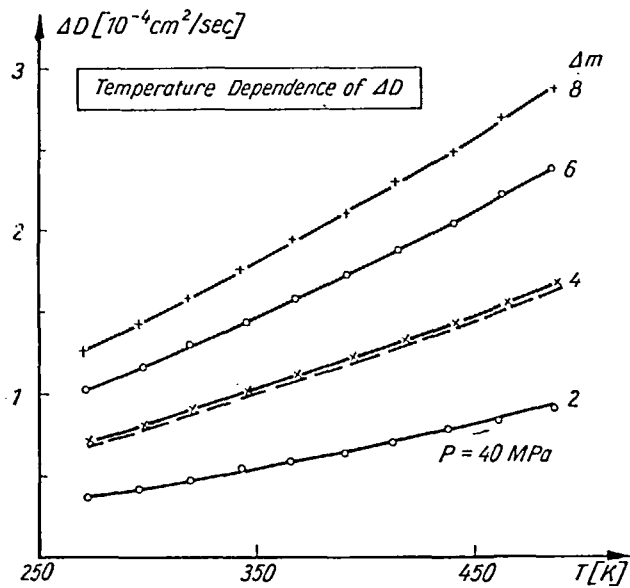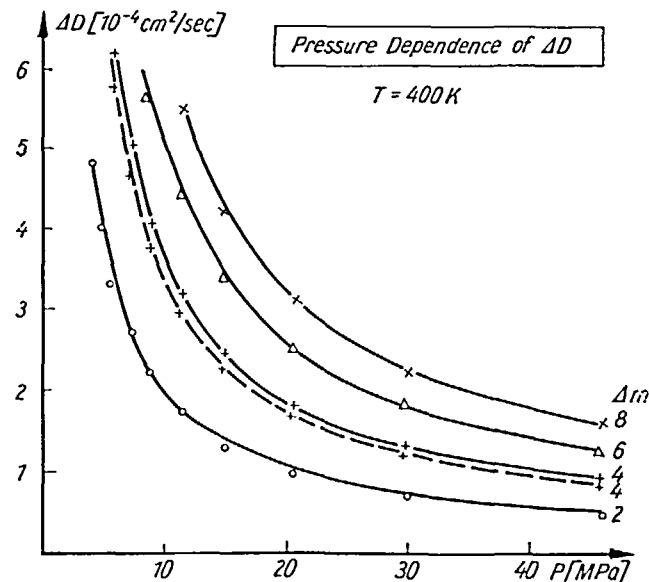

Fig. 4. Temperature dependence of ΔD

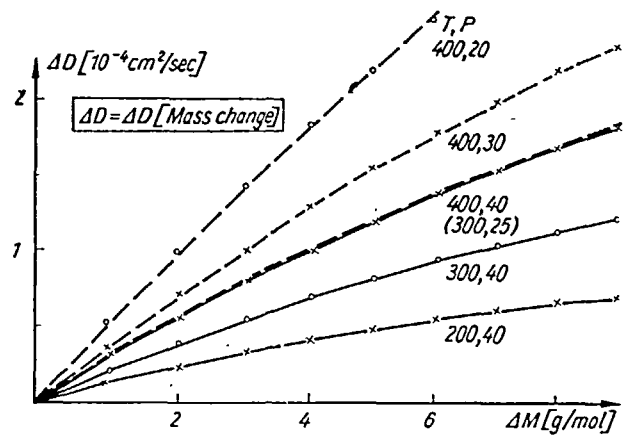Fig. 5. Pressure dependence of ΔD

Fig. 6. Mass dependence of ΔD

calculated from equation (7) because up to now for isotope effects MD calculations are not exact enough.

The results are given in dependence on temperature T (Fig. 4), pressure p (Fig. 5) and mass m (Fig. 6 — dashed curve for $T = 400$ K —) in the following figures, where ΔD represents the difference of $(D_1)_2$ for the mixture nitrogen/methan and $(D_1)_2$ for the mixture nitrogen/methane with mass change Δm.

The effective diameter d used is determined by adjusting self-diffusion coefficients $(D_1)_2$ from MD runs (Tab. 2) to the results of eq. (7). Although it depends on the temperature T too here its value for $T = 400$ K is used as a first approximation.

Tab. 2. Data from MD runs used to fit HS diameters. $T^+ = 1$ K, $p^+ = 1$ MPa and $D^+ = 10^{-3}$ cm²/s. So we found from (7) $d_1 = 3.55 \cdot 10^{-10}$ m, $d_2 = 3.47 \cdot 10^{-10}$ m.

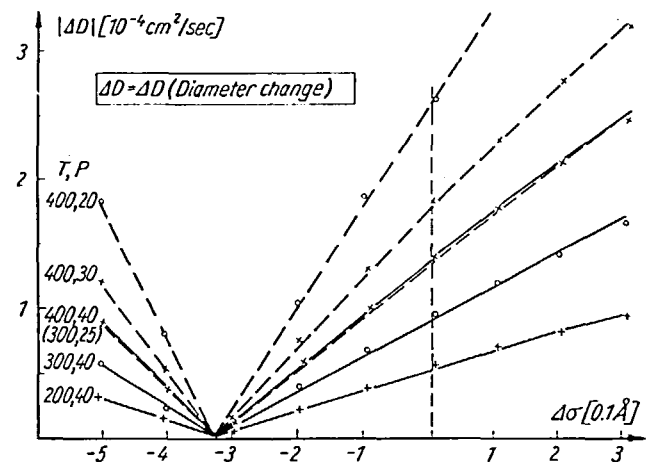| MD-run	T/T^+	p/p^+	$(D_1)_2/D^+$	$(D_2)_1/D^+$
I	397·5	37·6	1·01	0·94
II	400·7	37·9	1·10	0·89
III	399·5	37·7	1·11	0·94

Fig. 7. Diameter dependence of ΔD

To determine the complete isotope effect the contribution of the change of the diameter d by isotope substitution must be included. The dashed curves in Figs. 4 and 5 show the tendency of this influence (d is substituted by 0·996 d). For $\Delta m = 4$ Fig. 7 shows this influence over a fictive range of $\Delta \sigma = \sigma(CD_4) - \sigma(CH_4)$. For technical reasons the absolute values of ΔD are drawn and therefore the sign of ΔD in the

range of $\Delta\sigma < - 0.32$ Å is changed. Figs. 6 and 7 show that the isotope effects for $T = 400$ K, $P = 40$ MPa are practical the same as for $T = 300$ K, $p = 25$ MPa.

Further MD investigations [27] will discuss these effects in more detail.

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Deuterium in Pectolite: Kinetic and Synthetic Studies*)

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It is known, that pectolite exhibits the lowest deuterium content among all the hydrominerals. This is due to pecularities of its structure. In present work the kinetics of extraction of crystallic water from pectolite and from muscovite is examined. In the first case preferently "heavy" water (i.e. enriched in its deuterium content) is expelled from the mineral and in the second case — "light" water. An activation energy of 60 kcal/mole may be attributed to dehydratation of both the minerals. Experiments show, that delta D in synthetic pectolites does not depend on the isotopic composition of surrounding water.

Es ist bekannt, daß die Pektolithe von allen wasserhaltigen Mineralien den geringsten D-Gehalt haben. Dies kann auf eine Besonderheit ihrer Struktur zurückgeführt werden. In der vorgelegten Arbeit wird die Kinetik der Extraktion von Kristallwasser aus Pektolithen und aus Muskoviten verfolgt. Im ersten Fall wird bevorzugt „schweres" Wasser ausgeschieden, während im zweiten Fall das „leichte" Wasser bevorzugt wird. Die Aktivierungsenergie von 60 kcal/Mol deutet auf eine Dehydratation in beiden Fällen hin. Die Versuche zeigen, daß die D-Werte in synthetisierten Pektolithen nicht von der isotopen Zusammensetzung des umgebenden Wassers abhängen.

Keywords

Kuroda et al. [1] have found that pectolite exhibits the lowest D/H values of all terrestrial minerals. These values for hydrominerals, which are in paragenetic equilibrium with pectolite, are not anomalous. The authors mentioned suggest that the explanation lies in the size of the O—H—O bridge in the structure of pectolite.

Our studies [2] reaffirmed the low D/H values for Siberian pectolites. It is a common view, that isotopes of elements differ by masses of their nuclei, whereas their electron envelopes are identical. Usual gravitational forces are neglected in atomic theory. Thus there remains a single parameter: the radius of a nucleus. *Preston* suggests [3] that the nucleus of deuterium is rather "loose" and its dimensions correspond to particles composed of tens of nucleones.

In this connection two problems deserve attention: (a) what kind of kinetics controls the excretion of deuterium from pectolites? and (b) what sort of behaviour has a pectolite synthesized with water of unusual isotopic composition? A synthesizing procedure was described by *Clark* and *Bunn* [4].

In Fig. 1 curves of isotopic composition of water extracted from muscovite and pectolite as a function of time at two constant temperatures are given. Along the ordinate axis the δD values are plotted as obtained by eq. (4). In all the cases the isotopic composition of water, extracted during a certain time interval, was determined. The preceding portion of water was carefully removed from the measuring system. Thus, the quantities measured were proportional to the extraction rate.

For an interpretation of experiments we involve the phenomenological first order reaction kinetics. The quantity

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