PARAMETERS OF THE HOPPING MODEL FOR SURFACE DIFFUSIVITY OF GAS ON SOLID

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To describe the so-called surface diffusivity of gas molecules on a solid surface at low coverage, many investigators\(^9\text{-}^{15,20}\) have focused their attention on the hopping model. In this model, two important parameters, i.e., the temperature-independent term in the Arrhenius equation of activated diffusion and the ratio of the activation energy of surface diffusion to the heat of adsorption, are included.

In this study, a large number of data of surface diffusivity reported in the literature were correlated to investigate the parameters.

1. Representation of Surface Diffusivity

Based on the hopping model, the authors\(^13\) have derived an expression for the surface diffusivity as follows.

\[
D_{so} = \frac{D_{iso}}{v_s} \left( \frac{\tau_o}{K \sqrt{2\pi M}} \right)^a = \frac{D_{iso}}{v_s} \left( \frac{\tau_o}{K \sqrt{2\pi M}} \right)^a
\]

(1)

where

\[
D_{iso} = (m\lambda_o)^2/2\tau_{do}
\]

(2)

and

\[
a = \frac{\Delta E}{Q}
\]

(4)

\(\gamma_s\) refers to the surface roughness factor.\(^11\)

Though Eq. (1) was obtained by assuming Henry’s law\(^13\) for the adsorption equilibrium, it will satisfy the case of the non-linear equilibrium condition by introducing the adsorption equilibrium coefficient \(K\) expressed as the ratio of surface concentration to gas-phase concentration.

2. Estimation of Parameters

2.1 \(D_{so}\) and \(a\) at low surface coverage

The surface diffusivities were plotted against \((\tau_o/K)\cdot\sqrt{RT/2\pi M}\) in the range of \(\theta<0.1\) as shown in Fig. 1. \(\tau_o\) were calculated from Lindeman’s formula.\(^6\)

The values of \(D_{so}\) and \(a\) can be determined from Fig. 1 and are summarized in Table 1. From these, it is found that \(D_{so}\) and \(a\) do not depend on adsorbate, but only on adsorbent.

\(D_{so}\) for graphitized carbon having a homogeneous surface is extremely larger than those for the other solids having a heterogeneous surface. However, this may not be explained in terms of surface homogeneity because \(D_{so}\) for the carbon used by Ponzi et al.,\(^16\) which has a heterogeneous surface, exhibits the same magnitude as that for the graphitized carbon.

2.2 Hopping distance of adsorbed molecules

On the assumption that \(\gamma_s\) is equal to \(\tau_{do}\), \((m\lambda_o)^2/\gamma_s\) were obtained as shown in Table 1. From these, it is found that \(m\lambda_o\) is about 5\(\AA\) for the solids except for graphitized carbon and molybdenum sulfide, by letting \(\gamma_s = 1.0\). This seems to be plausible as the lattice spacing of the solids. In this case \(m\lambda_o\) becomes unity. Similarly, one can obtain \((m\lambda_o)^2\) as about 25\(\AA^2\) for the graphitized carbon. This may correspond to a hopping covering about five or more lattice spacings.

Since there is no method to evaluate \(m\), \(D_{so}\) must be determined experimentally. Fortunately, once the value of \(D_{so}\) for a solid is obtained, it may be used effectively for any other systems that include this solid.

2.3 Surface coverage dependencies of \(a\) and \(D_{so}\)

From the relations between \((\tau_o/K)\cdot\sqrt{RT/2\pi M}\) and \(v_D D_{so}\) for every 0.1 increment of \(\theta\), the dependencies of \(a\) and \(D_{so}\) on \(\theta\) were investigated. The results are shown in Figs. 2 and 3. The obvious increases in \(a\) in the range of \(\theta>0.4\) may be due to the increases in \(\Delta E\) with increasing surface concentration. Though \(a\) seems to decrease slightly with increasing \(\theta\) in the range of \(\theta<0.4\), it may be regarded as almost constant in this region for the evaluation of the surface diffusivities.

According to Higashi et al.,\(^10\) \(D_{so}\) may be expressed by

\[
D_{so} = \frac{1}{1-\theta} D_{so}^a
\]

(5)

where \(D_{so}^a\) is defined as \(D_{so}\) at \(\theta=0\) and can be obtained by extrapolation of \(D_{so}\). From Fig. 3, it is
found that for the cases of Vycor glass and carbon black, \( D_{so} \) is well expressed by Eq. (5) in the range of \( \theta < 0.4 \). For graphitized carbon, however, \( D_{so} \) deviates extremely from the equation; the curve shows a minimum value near \( \theta = 0.25 \) as shown by the solid line. The effect of \( \theta \) on \( D_{so} \) for the graphitized carbon can be explained in terms of \( m \) varying with \( \theta \).

Though \( \gamma_s \) has been assumed to be unity in this paper, a similar result can be obtained even if \( \gamma_s \) is assumed to be 2.0. A still larger value of \( \gamma_s \) is inappropriate because \( m \) becomes so large as to be impractical. This means that \( v_s \) may be roughly evaluated to be about ten or less. This agrees with the result of Barrer et al.\(^4\).

### 3. Estimation of Surface Diffusivity

From Eqs. (1) and (5), \( D_{se} \) in the range of \( \theta < 0.4 \) is expressed as follows.

\[
D_{se} = \frac{1}{\nu_s (1-\theta)} D_{so} \left[ \frac{\tau_0}{K} \frac{RT}{\sqrt{2\pi M}} \right]^a
\]  

### Table 1. Parameters obtained from Fig. 1

<table>
<thead>
<tr>
<th>Solids</th>
<th>( D_{so} ) [cm(^2)/s]</th>
<th>( a )</th>
<th>( (m_s \nu_s)^2/\gamma_s \times 10^{16} ) [cm(^2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphitized carbon</td>
<td>0.67</td>
<td>0.53</td>
<td>670</td>
</tr>
<tr>
<td>Vycor glass</td>
<td>0.016</td>
<td>0.54</td>
<td>31</td>
</tr>
<tr>
<td>Silica gel</td>
<td>0.015</td>
<td>0.61</td>
<td>29</td>
</tr>
<tr>
<td>Alumina</td>
<td>0.025</td>
<td>0.35</td>
<td>37</td>
</tr>
<tr>
<td>Silica-alumina</td>
<td>0.015</td>
<td>0.59</td>
<td>26</td>
</tr>
<tr>
<td>Molybdenum sulfide</td>
<td>0.028</td>
<td>0.57</td>
<td>112</td>
</tr>
<tr>
<td>Carbon black</td>
<td>0.034</td>
<td>0.56</td>
<td>34</td>
</tr>
</tbody>
</table>

Fig. 1. Correlations of surface diffusivities for \( \theta < 0.1 \).

Fig. 2. Dependency of \( a \) on surface coverage.

Fig. 3. Dependency of \( D_{se} \) on surface coverage.
$D^*$ can be regarded as approximately equal to $D_{so}$ in the range of $\theta < 0.1$. Furthermore, $D^*$ and $\alpha$ may be intrinsically determined for each solid. $v_g$ may be also determined experimentally or empirically.

However, one should notice that there are solids for which the surface coverage term in Eq. (6) is not suitable, though such solids are considered to be rare.

### Nomenclature

- $a$ = ratio of $AE$ to $Q$ ([-])
- $D_{so}$ = effective surface diffusivity ($[cm^2/s]$)
- $D_{se}$ = parameter in Eq. (3) ($[cm^2/s]$)
- $D_{tso}$ = parameter in Eq. (2) ($[cm^2/s]$)
- $D^*$ = $D_{so}$ at $\theta = 0$ ($[cm^2/s]$)
- $AE$ = activation energy of surface diffusion ($[J/mol]$)
- $K$ = adsorption equilibrium coefficient ($[cm]$)
- $M$ = molar mass ($[g/mol]$)
- $m$ = hopping distance in units of lattice spacings ([-])
- $Q$ = heat of adsorption ($[J/mol]$)
- $R$ = gas constant ($[J/(K\cdot mol)]$)
- $T$ = temperature ($[K]$)

- $\gamma_s$ = surface roughness factor ([-])
- $\theta$ = surface coverage ([-])
- $\lambda_s$ = mean length of lattice spacings ($[cm]$)
- $v_g$ = tortuosity factor for gas-phase diffusion ([-])
- $v_s$ = tortuosity factor for surface diffusion ([-])
- $\tau$ = mean adsorption life of molecules ($[s]$)
- $\tau_s$ = parameter defined by $\tau = \tau_s \exp(Q/RT)$ ($[s]$)
- $\tau_d$ = mean resting time of molecules at adsorption site ($[s]$)
- $\tau_{so}$ = parameter defined by $\tau_s = \tau_{so} \exp(AE/RT)$ ($[s]$)

### Literature Cited