Correlation of Gas Permeability and Diffusivity with Selectivity: Orientations of the Clouds of the Data Points and the Effects of Temperature

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Supporting Information

ABSTRACT: For an extended data set for amorphous glassy polymers, the pair correlations $P_i/P_j$ fulfill with very good accuracy ($R^2$ about 0.9 or higher) where $P_i$ and $P_j$ are the permeability coefficients of the gases $M_i$ and $M_j$ in the same polymers. This allowed us to determine the orientation (medians) of the clouds of the data points on the correlations $\log P_i$ versus $\alpha_i = P_i/P_j$. It was shown that for various gas pairs the slopes of these medians are negative and increase by absolute value when the ratio of kinetic diameters of the penetrants increases. For the first time a similar analysis was carried out for pair correlations of the diffusion coefficients $D_i$ and $D_j$. On the diagrams $\log D_i$ versus $\alpha_i = D_i/D_j$ the medians show the same trend as in the diagrams for permeability coefficients. The effects of temperature on the orientation of the clouds of the data points and upper bounds (limiting lines) of the diagrams $\log P_i$ versus $\alpha_i = P_i/P_j$ were investigated using the available values of the activation energy of permeation. It was shown that for all the gas pairs the medians tend to shift down along the selectivity axis when temperature increases. Depending on a selected gas pair the slopes of the medians and upper bounds get either steeper or weaker. It was discussed that the positions and the slopes of the medians and limiting lines are sensitive to the Arrhenius parameters of gas permeation and temperature.

INTRODUCTION

The qualitative observations on trade-off between gas permeability ($P_i$) and permselectivity ($\alpha_i = P_i/P_j$), i.e., that more permeable polymers are often less permselective, were made from the very beginning of the studies of gas permeation properties of polymers, so it is difficult to recollect when and by whom this regularity was first noted. Attempts to consider quantitatively these effects were made in 1970s and 1980s. However, at that time only a limited set of the data was available, so the permeability--permselectivity correlations were drawn only for certain gas pairs (He--N$_2$ in ref 1 and H$_2$--CH$_4$ in ref 2), and no light on the reasons of such trade-off was shed. In subsequent years information on gas permeation parameters was rapidly accumulated, so several authors observed and discussed trade-off for various gas pairs and the different groups of polymers.

A great stride was made by L.M. Robeson in 1991 when he published his famous article. The achievements of this work, probably the most frequently cited in the field, were due to the fact that not only various gas combinations were considered in these correlations but also the data points for hundreds of polymers (reported in more than 300 references) were displayed. Robeson proposed a concept of upper bounds (UB), the lines in the log–log plots that limit from above the data points characteristic for various polymers. It was also shown that the slopes of UB correlated with the differences of gas kinetic diameters of penetrants, which indicated that the diffusion controlled mechanism of mass transfer governed in the considered gas–polymer systems. It should be emphasized that a fast accumulation of the data on the permeability coefficients started in the middle of the 1980s and continued later. To illustrate, Table 1 shows how the values $\alpha$(O$_2$/N$_2$), which correspond to UBs at given $P$(O$_2$), change in time.

<table>
<thead>
<tr>
<th>year</th>
<th>$\alpha$(O$_2$/N$_2$) at $P$(O$_2$) = 0.1 Barrer</th>
<th>$\alpha$(O$_2$/N$_2$) at $P$(O$_2$) = 10 Barrer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1986</td>
<td>8.4</td>
<td>5.1</td>
</tr>
<tr>
<td>1991</td>
<td>11.7</td>
<td>5.8</td>
</tr>
<tr>
<td>1996</td>
<td>13.8</td>
<td>6.2</td>
</tr>
<tr>
<td>2001</td>
<td>15.1</td>
<td>6.6</td>
</tr>
</tbody>
</table>

"The data for amorphous glassy homopolymers; the source is the database."

The accumulation of the gas permeation data of new polymers allowed L.M. Robeson to revisit UB and note that the increased number of the data points on the $P_i$ vs $\alpha_i$ diagrams made UB shift to the “upper right” parts of the diagrams, though not in the cases of all gas pairs.

The permeability--permselectivity diagrams can be characterized by two features: upper bound (UB) and the orientation of the cloud of the data points. UB shows how far the clouds of the data points are extended into the upper-right parts of the diagrams. Because of this, UB is more in demand, since it gives an idea what can be expected, in terms of the transport...
parameters, from existing and available polymeric materials. On
the other hand, it is drawn in a rather empirical way and should
be sensitive to “noise” in several randomly selected data points,
which are located in the upper part of the cloud. On the contrary,
the slope of the whole cloud of the data points is sensitive to the parameters of the whole ensemble of the data
points and thus should reflect some general behavior of
polymers as membrane materials. An examination of the
Robeson diagrams6,8 shows that these slopes vary substantially.
For example, while the range of variation of the permeability
coefficients is, e.g., $P(O_2) = 0.001–10.000$ bar and $P(H_2) =
0.1–10.000$ bar, the separation factors differ much more
significantly: $\alpha(O_2/N_2) = 1.5–15$ and $\alpha(H_2/N_2) = 2–20.000$.
This observation requires an explanation.

UB lines were predicted from rather straightforward
theoretical considerations based on the transition-state
model.9 On the other hand, it was shown10 that the concept
of free volume enables one to understand the physical
significance of the trade-off behavior and to explain the relative
positions (slopes) of the clouds of the data points on various
permeability–permselectivity diagrams.

In this paper we want to survey other aspects of these
diagrams, namely, possibilities to assess the parameters of UB
and the slopes of “the clouds” of the data points for different
gas pairs. Since permeability coefficient $P$ is the product $DS$, where $D$ is the diffusion coefficient and $S$ is the solubility
coefficient, it is of interest to examine “the analogs” of Robeson
diagrams for kinetic ($D$) and thermodynamic ($S$) components
of permeability. This problem is virtually unexplored, only
briefly mentioned in refs 6 and 11. One of the reasons for this
is obviously related to some scarcity of the data for $D$ and $S$.
However, the database on gas permeation properties of glassy
polymers7 created in 1998 by the Institute of Petrochemical
Synthesis and updated since that time is very helpful for solving
this task.

At last, the published permeability–permselectivity diagrams
are based on the data reported for ambient temperature
(mainly in the range 20–35 °C). They do not answer the
questions about what would happen with $P_i$ and $\alpha_{ij}$ (and also
$D_i$, $S_i$, and corresponding selectivities) if the gas permeation
process proceeds at elevated or reduced temperatures, and
these questions are very important from the practical viewpoint.
This subject was considered recently by Rowe et al.12 In the
present work we want to return to this point and discuss it
using the extensive transport and sorption parameters from the
database.7

## SLOPES OF PERMEABILITY VERSUS
PERMSELECTIVITY DIAGRAMS

It is known that the free volume model is applicable to the
permeability coefficients:

$$P_i = A_i \exp \frac{B_i}{V_f}$$

where parameter $B_i$ is the constant characteristic for the gas and
is a measure of molecular volume, $V_f$ is the free volume
characteristic of the polymer, and $A_i$ is the constant characteristic of the gas/polymer system. On this basis as it
was shown in ref 10 that the following equations should hold:

$$\log P_i = a + b \log P_j$$

Here the indices $i$ and $j$ correspond to gas molecules $M_i$ and $M_j$.
These linear, so-called “pair correlations” are valid for various
gas pairs, as Figure 1 demonstrates as an example. Recently,
similar correlations were considered by Robeson et al.13

![Figure 1. Correlation for hydrogen and carbon monoxide. The data points are taken from the database for amorphous glassy homopolymers at 35 °C.](image)

Combining eq 2 with the formula

$$\alpha_{ij} = \frac{P_j}{P_i}$$

leads to the equation for the medians of different clouds of the
data points on the Robeson diagrams:

$$\log \alpha_{ij} = -a - (b - 1) \log P_i$$

This equation is formally similar to the equation proposed by
Robeson6 for UB:

$$\log \alpha_{ij} = -\frac{1}{n} \log k - \frac{1}{n} \log P_i$$

(5)

However, the physical significances of the parameters of the
two equations are different.

Thus, the trade-off behavior and the form of permeability–permselectivity diagrams (the slopes of the clouds of the data
points) are direct consequences of the free volume model in
glassy polymers. Figures 2–5 present “permeability–permselectivity” diagrams for several gas pairs using the data for
amorphous glassy polymers tabulated in ref 7. These diagrams
are seemingly similar to those reported in refs 6 and 8. Some
quantitative differences are doubtless due to the fact that here
we consider only the data for glassy homopolymers, while
Robeson included in his plots the data for all described
polymers (glassy, rubbery, random copolymers). In order to
stress this difference we shall call in our cases the lines that limit
from above all the data points (shown by dashed lines in
Figures 2–5) limiting lines (LL) here and throughout the whole
paper.

It is seen that the slopes of the clouds shown in these plots
are quite different. Table 2 gives the parameters of the medians
for the gas pairs considered in Figures 2–5 and some others.
Note also that LL drawn in the empirical manner, just as it was
made in refs 6 and 8 and also presented in Table 2 differs from
the slopes of the medians for all the gas pairs considered: LL
are steeper in all the cases.
Both parameters, \((1 - b)\) and \(LL\), correlate with \((1 - d^2_i/d^2_j)\) parameters or with the ratio \(d^2_i/d^2_j\). For the UBs it was first noted by Robeson.\(^6\) The steepest orientations (medians) are observed for the gas pairs with the molecular sizes having the maximum difference (H\(_2\)/CH\(_4\) and He/N\(_2\)). More flat slopes are observed for the gas pair with close values of \(d_i\) and \(d_j\) (O\(_2\)/N\(_2\) pair). The obvious exception from such correlation (flatter slope) is observed for the CO\(_2\)/N\(_2\) pair. Here, the molecular cross sections \(d_i\) and \(d_j\) are rather close and the difference of permeability is caused mainly by great solubility coefficients of carbon dioxide. This statement is confirmed by the diagram of \(\log D(CO_2)\) versus \(\log D(CO_2)/\log D(N_2)\), as we shall see later in this article.

Thus, the medians and the orientation of the clouds (and not only LL) depend on the selected gas pair and on the role of diffusion and thermodynamic factors.

This tendency can be increased if one considers hydrocarbon gases as penetrants. In this case the common trade-off between \(\alpha_s = P_i/P_j\) and \(P_s (P_i > P_j)\) is not observed because the decisive factors are solubility coefficients of the penetrants. Such behavior is known as solubility controlled permeation, that is, when permeability coefficients are greater for penetrants with larger size or when the solubility coefficients are stronger functions of penetrant size than the diffusion coefficients. This takes place in rubbers, semicrystalline polyolefins, polyacetylenes, and even liquid films for the separation of alkanes C\(_1\)–C\(_4\) and organic vapors from permanent gases, such as air or nitrogen.\(^{11–19}\) Recently, the list of materials suitable for such a task was supplemented by several highly permeable, Si-containing addition norbornene polymers. The results for this type of permeability–permselectivity correlations are illustrated in Figures 6–8 for the pairs C\(_4\)H\(_{10}\)/CH\(_4\), C\(_3\)H\(_8\)/CH\(_4\), and C\(_2\)H\(_6\)/CH\(_4\). The data points for individual and mixed gas permeation correspond to subatmospheric or atmospheric pressure of hydrocarbons (or butane partial pressure in the runs with gas mixtures). Thus, the results for numerous siloxanes (ref 19) are obtained by extrapolation of the \(P\) values to zero pressure. The pressure (concentration) dependence of the \(P\) and \(\alpha\) values could move some points slightly but could not change the trend shown in Figures 6–8.

For all three pairs of alkanes the slopes of the correlations are positive in contrast to what is observed for the systems with diffusivity controlled permeation.\(^6\) Analysis of these figures also indicates that the larger the differences of the critical temperature \(T_c\) of the slow (methane) and faster hydrocarbons the greater are the slopes of the clouds of the data points (Table 3). This is a manifestation of the solubility controlled permeation, because the solubility coefficients increase when
the critical temperature $T_c$ and other parameters that characterize condensability of penetrants increase. This behavior has been discussed by Pinnau et al.\textsuperscript{11,16} Its reason is a low diffusivity selectivity, i.e., the slopes of the dependences of $D$ versus the size of the penetrants (critical volume, kinetic cross sections, etc.) in high free volume glassy polymers and also in rubbery materials. In the former, it is caused by unusually large free volume elements. In rubbers the size of dynamic "holes" must also be large and comparable to the size of kinetic segments. So the matrix poorly segregates molecules with different sizes. On the other hand, the slopes of the solubility coefficients versus the size ($V_c$) of polymers are more or less the same for rubbers, highly permeable and conventional glassy polymers.\textsuperscript{27} Hence, for the polymers with low diffusivity selectivity and for gas pairs with a big difference of molecular properties (e.g., methane and butane) the variation of the solubility coefficients governs the observed permselectivity.

<table>
<thead>
<tr>
<th>gas pair</th>
<th>$1 - d_1^2/d_2^2$</th>
<th>$1 - b$</th>
<th>$LL$</th>
<th>$N^a$</th>
<th>$1 - g$</th>
<th>$LL$</th>
<th>$N^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$/N$_2$</td>
<td>0.013</td>
<td>0.097</td>
<td>0.24</td>
<td>576</td>
<td>0.016</td>
<td>0.21</td>
<td>356</td>
</tr>
<tr>
<td>O$_2$/N$_2$</td>
<td>0.107</td>
<td>0.118</td>
<td>0.21</td>
<td>760</td>
<td>0.143</td>
<td>0.21</td>
<td>396</td>
</tr>
<tr>
<td>CO$_2$/CH$_4$</td>
<td>0.109</td>
<td>0.260</td>
<td>0.54</td>
<td>596</td>
<td>0.154</td>
<td>0.52</td>
<td>377</td>
</tr>
<tr>
<td>H$_2$/CH$_4$</td>
<td>1.208</td>
<td>0.707</td>
<td>0.90</td>
<td>369</td>
<td>0.952</td>
<td>1.29</td>
<td>82</td>
</tr>
<tr>
<td>He/N$_2$</td>
<td>1.917</td>
<td>0.698</td>
<td>0.95</td>
<td>361</td>
<td>0.626</td>
<td>1.43</td>
<td>80</td>
</tr>
</tbody>
</table>

$^aN$ is the number of the data points.

Figure 6. Correlation of the permselectivity $P$(C$_4$H$_{10}$)/$P$(CH$_4$) with the permeability coefficients $P$(C$_4$H$_{10}$) in Barrer: 1, polyacetylenes,$^{15,16}$ 2, norbornene polymers,$^{20-22}$ 3, polydimethylsiloxane,$^{23}$ and 4, PIM-1,$^{24}$ empty points are individual gas permeation, filled points are mixed gas permeation.

Figure 7. Correlation of the permselectivity $P$(C$_3$H$_8$)/$P$(CH$_4$) with the permeability coefficients $P$(C$_3$H$_8$) in Barrer (the experiments with individual gases): 1, polyacetylenes;$^{15,16}$ 2, norbornene polymers;$^{20-22}$ 3, siloxanes and other rubbers;$^{19,25,26}$ and 4, PIM-1.$^{24}$

Table 3. Slopes of the Diagrams Shown in Figures 6–8 and the Differences of the Critical Temperatures of Penetrants

<table>
<thead>
<tr>
<th>hydrocarbon</th>
<th>slope</th>
<th>$T_c(n) - T_c(CH_4)$, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>4$H$</em>{10}$</td>
<td>0.247</td>
<td>234</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>0.124</td>
<td>178</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>0.0268</td>
<td>114</td>
</tr>
</tbody>
</table>

the critical temperature $T_c$ and other parameters that characterize condensability of penetrants increase.

This behavior has been discussed by Pinnau et al.\textsuperscript{11,16} Its reason is a low diffusivity selectivity, i.e., the slopes of the

■ DIAGRAMS $D_1$ VERSUS $\alpha^D = D_1/D_J$ AND $S_1$ VERSUS $\alpha^S = S_1/S_J$

On the basis of the simplest form of the free volume model
\[ D_i = F_i \exp \left( -\frac{V^*_i}{V_f^*} \right) \]  

(6)

where \( V^*_i \) is the constant characteristic for the gas and is a measure of molecular volume, \( V_f^* \) is the free volume characteristic of polymer, and \( F_i \) is the constant characteristic of the gas/polymer system, it has been shown\(^{10} \) that

\[
\log D_i = f + g \log D_i
\]

(7)

Here the indices \( i \) and \( j \) correspond to gas molecules \( M_i \) and \( M_j \). Examples of these pair correlations have been reported earlier.\(^{10} \) In the same manner as it was shown above for permeability and permselectivity the following equation holds for correlations of diffusivity with diffusion selectivity:

\[
\log \alpha_{D_i} = -f - (g - 1) \log D_i
\]

(8)

Examples of such correlations are shown in Figures 9–12, and their parameters (the slopes of the medians and LL) are presented in Table 2.

Analysis of the data shown in Table 2 for diffusivity allows one to make the following conclusions.

(1) \( \text{LL} \) in all the cases are steeper than the parameters \((1 - g)\).

(2) The most negative values of \((1 - g)\) and \( \text{LL} \) are observed for the pairs with the largest differences between \( d_i \) and \( d_j \) (just as in the cases of permeability–permselectivity diagrams).

(3) The slopes of \( \text{LL}(D) \) and \( \text{LL}(P) \) are close in most of the cases.

The quantitative differences between the results obtained for \( P \) and \( D \) can be explained by different numbers of the data points \( N \) (see Table 2) available for the analysis. The data are much more numerous for \( P \), especially for \( H_2 \) and \( H_2 \); the difficulties of experimental determination of the diffusivity of these gases are well-known.

Since \( P = D S \), from the reported values of \( P \) and \( D \) it is possible to find the solubility coefficients and to draw the diagrams “\( S \) versus \( \alpha^5 \)”. This was made for several gas pairs, and Figure 13 gives an example of such a diagram for the pair \( CO_2/N_2 \). The diagrams for other gas pairs have a similar appearance. A feature of all these diagrams is a much more narrow range of the variation the solubility coefficients. It is well-known that the permeability and the diffusion coefficients vary in different polymers in the range of 5–6 decimal orders (depending of the gas) while the solubility coefficients are limited within 1–2 orders which is reflected in Figure 13. It is worth noting, however, that in all the cases the slopes of these rather spherical “clouds” are positive in contrast to most of the correlations for
temperature though rather weakly. The data for temperature for such changes. Free volume in glassy polymers depends on scarce, so it is difficult to take them into account explicitly in eq 1. The orientation of the clouds of the data points correlate with the differences between the values \(d_1^2\) and \(d_2^2\). It is not clear at what temperature the kinetic diameters of diffusing molecules are tabulated. However, a possible assumption that any changes of the permeability–permselectivity diagrams can be induced by the variations of the kinetic diameters of the penetrants should be discarded. Indeed, according to Cyvin for biatomic and multiatomic molecules the mean square amplitudes (MSA) are temperature dependent, but these dependences are very weak. Thus, for \(\text{H}_2\), MSA increases by 0.36% for the temperature variation from 0 to 1000 K, while for \(\text{N}_2\) the increase is greater though it corresponds to only 6.9%. Hence, the variation in the range 0–80 °C should result in a negligible change of \(d\) as it will be discussed later in this paper.

An analysis based on the transition state theory (TST) is more suitable for the interpretation of the temperature dependence of the parameters of the permeability–permselectivity diagrams.

Two approaches are possible for the construction of the permeability–permselectivity diagrams at different temperatures. A certain number of works on various glassy polymers reported activation energies of permeation \(E_p\) which are collected in the database. Although the majority of the works did not report the \(E_p\) values, it is possible to estimate those unknown \(E_p\) values using the correlation \(E_p \sim P(308K)\) described in ref 30. In this way, the number of the data points can be substantially increased though the accuracy of the prediction of \(P(T)\) can become poorer. Both approaches were employed in this work for calculations of \(P(T)\) and \(D(T)\). The corresponding parameters of the pair correlations are given in Tables S1 and S2 (Supporting Information).

Figure 14 presents the permeability–permselectivity diagrams for the \(\text{O}_2/\text{N}_2\) pair obtained using the total number of the \(E_p\) values (correlated and original) while Figure 15 shows similar diagrams constructed using only available experimental values of \(E_p\). It is seen that both ways of preparation of the diagrams result in similar slopes of the clouds of the data points; the slopes increase at higher temperatures, while the pre-exponential factors (free terms) decrease. A similar procedure was performed for the diagrams for other gas pairs (see Supporting Information), and it was found that the same tendency is observed independently of the used activation energies \(E_p\). Thus, a conclusion can be made that variation of temperature leads to changes in the orientation of the clouds of the data points for different gas pairs.

The parameters of the medians of the correlations on the diagrams permeability–permselectivity of different gas pairs at 0, 35, and 80 °C are given in Table 4. The values presented in it are based on only the systems where experimental activation energies have been reported. This table demonstrates that the orientation of the clouds of the data points is temperature dependent. Note that there are some discrepancies between the \((1 - b)\) parameters at 35 °C in Tables 2 and 4: in the former case the number of the data points was bigger because some of them were obtained using the correlation for \(E_p\).
It can be noted that an increase in temperature results in a shift of the clouds and, hence, the medians down along the axis of selectivity for all the gas pairs. An example of such behavior is illustrated in Figure 16. This conclusion is consistent with the results of Rowe et al.\textsuperscript{12} but was made on the basis of experimental data. Meanwhile, for various gas pairs we observe either increases in the slope of the clouds of the data point when temperature increases (most notably for O\textsubscript{2}/N\textsubscript{2} as is also evident from Figure 16) or decreases (e.g., He/N\textsubscript{2}). We shall discuss these observations later in this work together with discussion of the temperature dependence of UBs (LLs).

Figure 15. Permeability–permselectivity diagrams at 0 °C (A) and 80 °C (B) different temperatures for the O\textsubscript{2}/N\textsubscript{2} gas pair obtained using only the experimental $E_P$ values.

![Figure 15](image)

Table 4. Parameters of Equation 4 at Different Temperatures for Various Gas Pairs Estimated Using Only Experimental Values of $E_P$

<table>
<thead>
<tr>
<th>gas pairs</th>
<th>0 °C</th>
<th>35 °C</th>
<th>80 °C</th>
<th>0 °C</th>
<th>35 °C</th>
<th>80 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>O\textsubscript{2}/N\textsubscript{2}</td>
<td>0.847</td>
<td>0.771</td>
<td>0.704</td>
<td>−0.108</td>
<td>−0.124</td>
<td>−0.137</td>
</tr>
<tr>
<td>CO\textsubscript{2}/N\textsubscript{2}</td>
<td>1.654</td>
<td>1.444</td>
<td>1.224</td>
<td>−0.130</td>
<td>−0.128</td>
<td>−0.117</td>
</tr>
<tr>
<td>CO\textsubscript{2}/CH\textsubscript{4}</td>
<td>1.863</td>
<td>1.659</td>
<td>1.455</td>
<td>−0.202</td>
<td>−0.221</td>
<td>−0.234</td>
</tr>
<tr>
<td>H\textsubscript{2}/CH\textsubscript{4}</td>
<td>2.850</td>
<td>2.838</td>
<td>2.815</td>
<td>−0.679</td>
<td>−0.675</td>
<td>−0.666</td>
</tr>
<tr>
<td>He/N\textsubscript{2}</td>
<td>2.604</td>
<td>2.594</td>
<td>2.518</td>
<td>−0.661</td>
<td>−0.635</td>
<td>−0.580</td>
</tr>
</tbody>
</table>

It can be noted that an increase in temperature results in a shift of the clouds and, hence, the medians down along the axis of selectivity for all the gas pairs. An example of such behavior is illustrated in Figure 16. This conclusion is consistent with the results of Rowe et al.\textsuperscript{12} but was made on the basis of experimental data. Meanwhile, for various gas pairs we observe either increases in the slope of the clouds of the data point when temperature increases (most notably for O\textsubscript{2}/N\textsubscript{2} as is also evident from Figure 16) or decreases (e.g., He/N\textsubscript{2}). We shall discuss these observations later in this work together with discussion of the temperature dependence of UBs (LLs).

The effects of temperature on the UBs have been considered by Rowe et al.\textsuperscript{12} but these effects demand further elucidation. The following empirical approach was used here for evaluation of the temperature effects on the slopes of LLs. On every “permeability–permselectivity” diagram, two polymers were selected on the basis of the following principles: (1) their data points are located at or very close to LL or the upper bound (2008); (2) they correspond to two extreme parts of the diagrams, i.e., belong to the most and the least permeable polymers; and (3) the activation energy of permeation is available for both polymers. As the most permeable polymer, poly(trimethylsilyl propyne) (PTMSP) was chosen. Polyimides, polycarbonates, and polypyrrolone served as low permeable, highly permselecive materials. Using the reported values of the activation energy of permeation $E_P$ for different gas pairs the permeability coefficients and separation factors were calculated at different temperatures (in the range 100–500 K). In doing so it is naturally assumed that the activation energy and pre-exponential factor are temperature independent. In such a way it was possible to follow evolution of the upper bounds for different gas pairs.

Figure 16 shows how the LL lines are changed at different temperatures in the aforementioned wide range. Since the activation energies $E_P$ of PTMSP are negative, the corresponding data points in Figure 16 (and in further figures as well) are shifted to smaller values $P$ when temperature increases. For the results of Rowe et al.\textsuperscript{12} but was made on the basis of experimental data. Meanwhile, for various gas pairs we observe either increases in the slope of the clouds of the data point when temperature increases (most notably for O\textsubscript{2}/N\textsubscript{2} as is also evident from Figure 16) or decreases (e.g., He/N\textsubscript{2}). We shall discuss these observations later in this work together with discussion of the temperature dependence of UBs (LLs).

The effects of temperature on the UBs have been considered by Rowe et al.\textsuperscript{12} but these effects demand further elucidation. The following empirical approach was used here for evaluation of the temperature effects on the slopes of LLs. On every “permeability–permselectivity” diagram, two polymers were selected on the basis of the following principles: (1) their data points are located at or very close to LL or the upper bound (2008); (2) they correspond to two extreme parts of the diagrams, i.e., belong to the most and the least permeable polymers; and (3) the activation energy of permeation is available for both polymers. As the most permeable polymer, poly(trimethylsilyl propyne) (PTMSP) was chosen. Polyimides, polycarbonates, and polypyrrolone served as low permeable, highly permselecive materials. Using the reported values of the activation energy of permeation $E_P$ for different gas pairs the permeability coefficients and separation factors were calculated at different temperatures (in the range 100–500 K). In doing so it is naturally assumed that the activation energy and pre-exponential factor are temperature independent. In such a way it was possible to follow evolution of the upper bounds for different gas pairs.

Figure 16 shows how the LL lines are changed at different temperatures in the aforementioned wide range. Since the activation energies $E_P$ of PTMSP are negative, the corresponding data points in Figure 16 (and in further figures as well) are shifted to smaller values $P$ when temperature increases. For the
polymers with lower permeability the activation energies $E_P$ are positive, so the $P$ values in Figure 17 are shifted to smaller values. Therefore the sections are getting shorter when temperature increases.

It is seen that an increase in the temperature makes LL move down. The slopes of the lines are not discerned from the figure, but in fact as seen in Table 5 they increase by absolute value at higher temperatures for the pair $O_2/N_2$ for higher temperatures.

### Table 5. Slopes of LLs Calculated for Different Temperatures

<table>
<thead>
<tr>
<th>gas pair</th>
<th>100 K</th>
<th>300 K</th>
<th>500 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2/N_2$</td>
<td>−0.209</td>
<td>−0.218</td>
<td>−0.226</td>
</tr>
<tr>
<td>$CO_2/N_2$</td>
<td>−0.278</td>
<td>−0.162</td>
<td>−0.0064</td>
</tr>
<tr>
<td>$CO_2/CH_4$</td>
<td>−0.791</td>
<td>−0.566</td>
<td>−0.360</td>
</tr>
<tr>
<td>$H_2/CH_4$</td>
<td>−1.148</td>
<td>−0.976</td>
<td>−0.847</td>
</tr>
<tr>
<td>$He/N_2$</td>
<td>−1.846</td>
<td>−1.172</td>
<td>−0.829</td>
</tr>
</tbody>
</table>

Similar trends of the evolution of the LLs at different temperatures are observed for other gas pairs ($CO_2/CH_4$ and $CO_2/N_2$) as Figures 18 and 19 indicate.

The variations of the slopes for these and other gas pairs are presented in Table 5. Qualitatively the same down trends were noted by Rowe at al.\textsuperscript{12} for these gas pairs, but according to these authors the slopes are postulated independent of temperature.

Different results were obtained for the gas pairs containing the smallest molecules, $H_2$ and $He$. They are presented on Figures 20 and 21. The slopes of the lines for $H_2/CH_4$ and $He/N_2$ pairs are given in Table 5.

One may suspect that some of the results on the effect of temperature on LL can be related to random selection of the polymers and the transport parameters reported for them. So similar calculations were made for other polymers also located at or close to LL and other Arrhenius parameters. The results presented in Supporting Information show that in such cases the slopes can be different but the trends of variation of LL with temperature remain the same.
A simple analysis indicates that the variation of temperature-dependent trends of the LLs depends on the Arrhenius parameters for gas permeation. Let \( P_i \), \( P_j \) be the permeability coefficients of the gases \( i \) and \( j \) in different polymers 1 and 2. For every polymer it can be written

\[
\ln P_i = \ln P_{0i} - \frac{E_i}{RT}
\]

\[
\ln P_j = \ln P_{0j} - \frac{E_j}{RT}
\]

Hence, for the separation factors the following equations are valid:

\[
\ln \alpha_{ij} = \ln \frac{P_{0i}}{P_{0j}} - \frac{1}{RT} (E_{P_i} - E_{P_j})
\]

by combining of these formulas one obtains the following expression for the slope \( d \) of the UB (LL) and the parameter \( c \):

\[
\ln \alpha_{ij} = c + d \ln P_i
\]

For the equation of UB (or LL)

\[
\ln \alpha_{ij} = \ln P_{0i} - \ln P_{0j} - \frac{1}{RT} (E_{P_i} - E_{P_j})
\]

If we designate temperature independent terms \( \ln P_{0i} - \ln P_{0j} - (\ln P_{0i2} - \ln P_{0j2}) = A \) and \( \ln P_{0i} - \ln P_{0i2} = B \) we can obtain a simpler equation for \( d \):

\[
d = -\frac{\ln \alpha_{ij} - \ln \alpha_{i1}}{\ln P_{i2} - \ln P_{i1}} = -\frac{\ln P_{0i} - \ln P_{0j} - (\ln P_{0i2} - \ln P_{0j2}) - \frac{1}{RT} (E_{P_i} - E_{P_j})}{\ln P_{0i} - \ln P_{0i2} - \frac{1}{RT} (E_{P_i} - E_{P_j})}
\]

These expressions can be further simplified if we assume that the Arrhenius parameters obey the so-called compensation effect, i.e., linear dependence between pre-exponential factor and activation energy

\[
\ln P_0 = m + kE_p
\]

Then for the gases \( i \) and \( j \) and polymers 1 and 2 we have

\[
\ln P_{0i} - \ln P_{0j} = k(E_{P_i} - E_{P_j})
\]

\[
\ln P_{0i} - \ln P_{0j} = k(E_{P_i} - E_{P_j})
\]

By substituting these formulas into the constants \( A \) and \( B \) in eq 16 one can obtain a simpler form of the equation for \( d \):

\[
d = \frac{(E_{P_i} - E_{P_j})(RTk - 1)}{(E_{P_i} - E_{P_j})(RTk - 1) - 1}
\]

Thus, we see that the slope and the free term in eqs 14, 15, and 20 depend in a complex manner on the Arrhenius parameters and temperature. In the investigation of the effects of temperature on LL the data points that were located at LL were used. But the same should be true for other data points located within the clouds. Hence, the orientation of the clouds should also be dependent on the Arrhenius parameters.

In this regard it will be interesting to compare the data presented in Tables 4 and 5. First, when temperature increases the negative slopes of LLs are steeper (Table 5) than the slopes of the medians (Table 4). The trends of the temperature-dependent slopes in both tables are virtually the same: for the \( O_2/N_2 \) pair the increase in temperature results in steeper negative slopes, while for \( CO_2/N_2 \), \( CO_2/CH_4 \), and \( He/N_2 \) gas pairs at higher temperature the negative slopes get less steep. It is interesting that similar results were obtained on an entirely different basis in both cases: the medians were calculated using the concept of free volume while the effects of temperature on LL were analyzed using the Arrhenius equations, i.e., using the approach of the transition state theory.

It is known that at increased temperatures the size distribution of free volume becomes wider. It can be assumed that the extent of this effect will be different for polymers with larger or smaller free volume (higher or lower permeability). Therefore, the orientation of the entire cloud of points and of their LL would be different at low and high temperature limits considered in this work.

**CONCLUSIONS**

Using the data for amorphous glassy polymers the pair correlations of the type log \( P_i \) versus log \( P_j \) and log \( D_i \) versus log \( D_j \) hold where the indices \( i \) and \( j \) correspond to transport of different gases in the same polymer. These correlations are valid with great accuracy \((R^2 = 0.9 \text{ or more})\). Due to fulfillment of these correlations a possibility appears to calculate the medians (the slopes) of the correlations \( P_i \) versus \( \alpha_{ij} \) and \( D_i \) versus \( \alpha_{ij} \). It was shown that the slopes of the medians for \( P_i \) and \( D_i \) show similar trends for the same series of the gas pairs, which is an obvious consequence of the fact that the orientation of the cloud of the data points on the correlations \( P_i \) versus \( \alpha_{ij} \) is determined by the diffusion coefficients of light gases. For the gas pairs including carbon dioxide the orientation of the clouds is significantly less steep: this is related to prevailing effects of the thermodynamic component (solubility coefficient) in the permeability coefficients of \( CO_2 \). This tendency becomes dominant if one considers hydrocarbon gases (\( C_4H_{10}/CH_4 \), \( C_3H_6/CH_4 \), \( C_2H_4/CH_4 \)) as penetrants. On the corresponding diagrams \( P_i \) versus \( \alpha_{ij} \) which were considered using numerous glassy and rubbery polymers as examples, the slopes have positive values, which correlate with the difference of the critical temperatures of penetrants.

The influence of temperature on the orientations of the clouds \( P_i \) versus \( \alpha_{ij} \) and LLs was studied. While analyzing the effects of temperature two approaches were employed: (1) the consideration of the diagrams \( P_i \) versus \( \alpha_{ij} \) only for those systems where experimental \( E_p \) values are available in the database; (2) use of estimated \( E_p \) values found via empirical
formulas as described in ref 30. In the former case the number of data points is naturally less numerous. However, both approaches gave qualitatively similar results. It was shown that a distinct dependence on temperature is observed for both the medians of the clouds and the LLs. These results are the consequence of the application of the concepts of free volume model and the transition state theory.

**ASSOCIATED CONTENT**

1 Supporting Information

The parameters of the pair correlations for \( P \) and \( D \), for various gas pairs, examples of the permeability–permselectivity diagrams at different temperatures, and the plots illustrating the evolution of the limiting lines are given. This information is available free of charge via the Internet at http://pubs.acs.org/.

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**Notes**

The authors declare no competing financial interest.

**REFERENCES**


■ NOTE ADDED AFTER ASAP PUBLICATION
The version of this paper that was published ASAP on January 24, 2013, had an incorrect image for Figure 12. The figure was corrected and the paper was reposted on March 4, 2013.