

# Basis of Permeability/Selectivity Tradeoff Relations in Polymeric Gas Separation Membranes

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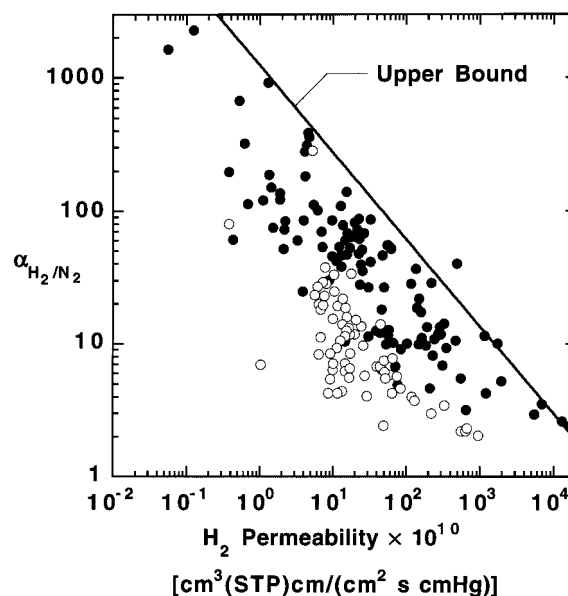
**ABSTRACT:** Gas separation properties of polymer membrane materials follow distinct tradeoff relations: more permeable polymers are generally less selective and vice versa. Robeson<sup>1</sup> identified the best combinations of permeability and selectivity for important binary gas pairs (O<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/CH<sub>4</sub>, H<sub>2</sub>/N<sub>2</sub>, etc.) and represented these permeability/selectivity combinations empirically as  $\alpha_{A/B} = \beta_{A/B} P_A^{-\lambda_{A/B}}$ , where  $P_A$  and  $P_B$  are the permeability coefficients of the more permeable and less permeable gases, respectively,  $\alpha_{A/B}$  is selectivity ( $=P_A/P_B$ ), and  $\lambda_{A/B}$  and  $\beta_{A/B}$  are empirical parameters. This report provides a fundamental theory for this observation. In the theory,  $\lambda_{A/B}$  depends only on gas size.  $\beta_{A/B}$  depends on  $\lambda_{A/B}$ , gas condensability, and one adjustable parameter.

## Introduction and Background

Polymer membranes are used commercially to separate air, to remove carbon dioxide from natural gas, and to remove hydrogen from mixtures with nitrogen or hydrocarbons in petrochemical processing applications.<sup>2</sup> For a given pair of gases (e.g., O<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/CH<sub>4</sub>, H<sub>2</sub>/N<sub>2</sub>, etc.), the fundamental parameters characterizing membrane separation performance are the permeability coefficient,  $P_A$ , and the selectivity,  $\alpha_{A/B}$ . The permeability coefficient is the product of gas flux and membrane thickness divided by the pressure difference across the membrane. Gas selectivity is the ratio of permeability coefficients of two gases ( $\alpha_{A/B} = P_A/P_B$ ), where  $P_A$  is the permeability of the more permeable gas and  $P_B$  is the permeability of the less permeable gas in the binary gas pair.

Polymers with both high permeability and selectivity are desirable. Higher permeability decreases the amount of membrane area required to treat a given amount of gas, thereby decreasing the capital cost of membrane units. Higher selectivity results in higher purity product gas. Over the past 25 years, the gas separation properties of many polymers have been measured, and a substantial research effort in industrial, government, and university research laboratories has resulted in polymers that are both more permeable and more selective than first generation materials.<sup>3</sup>

A rather general tradeoff relation has been recognized between permeability and selectivity: Polymers that are more permeable are generally less selective and vice versa.<sup>1,3</sup> On the basis of an exhaustive literature survey, Robeson<sup>1,4</sup> quantified this notion by graphing the available data as shown in Figure 1, which presents hydrogen permeability coefficients and H<sub>2</sub>/N<sub>2</sub> separation factors for many polymers. Materials with the best performance would be in the upper right-hand corner of this figure. However, materials with permeability/selectivity combinations above and to the right of the line drawn in this figure are exceptionally rare. This line defines the so-called "upper bound" combinations



**Figure 1.** Relationship between hydrogen permeability and H<sub>2</sub>/N<sub>2</sub> selectivity for rubbery (○) and glassy (●) polymers and the empirical upper bound relation.<sup>1</sup>

of permeability and selectivity of known polymer membrane materials for this particular gas pair. Lines such as the one shown in Figure 1 were constructed on an empirical basis for many gas pairs using published permeability and selectivity data. The upper bound performance characteristics were best described by the following equation:<sup>1</sup>

$$\alpha_{A/B} = \beta_{A/B} P_A^{-\lambda_{A/B}} \quad (1)$$

which indicates that as the permeability of an upper bound polymer to gas A,  $P_A$ , increases, selectivity of the polymer for gas A over gas B,  $\alpha_{A/B}$ , decreases. Robeson reports values for  $\lambda_{A/B}$  and  $\beta_{A/B}$  for many common gas pairs.<sup>1,4</sup>

The reason for this tradeoff has been widely discussed, but no theoretical justification of the form of eq 1 or fundamental predictions of  $\lambda_{A/B}$  and  $\beta_{A/B}$  have been offered. Robeson noted an excellent empirical correlation

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between  $\lambda_{A/B}$  and the difference between the kinetic diameters of the penetrant molecules,  $d_B - d_A$ .<sup>1</sup> The theory presented in this article gives excellent predictions of  $\lambda_{A/B}$  with no adjustable parameters and suggests that the slope of the upper bound is a natural consequence of the strong size-sieving nature of the stiff chain glassy polymeric materials whose properties generally define the upper bound. Moreover, the theory provides good estimates of  $\beta_{A/B}$  with only one adjustable parameter. The theory is developed for amorphous polymers and does not account for the influence of penetrant concentration on permeation properties.

## Theory

As Sir Thomas Graham proposed,<sup>5</sup> the transport of gases in dense, nonporous polymers obeys a solution diffusion mechanism. Under the driving force of a pressure difference across a membrane, penetrant molecules dissolve in the upstream (or high pressure) face of a membrane, diffuse across the membrane, and desorb from the downstream (or low pressure) face of the membrane. Diffusion is the rate-controlling step in penetrant permeation. The rate-controlling process in diffusion is the creation of gaps in the polymer matrix sufficiently large to accommodate penetrant molecules by thermally stimulated, random local segmental polymer dynamics.<sup>3,6</sup> Based on this mechanism, the permeability coefficient of a polymer to gas A can be written as

$$P_A = S_A D_A \quad (2)$$

where  $S_A$  is the solubility coefficient and  $D_A$  is the diffusion coefficient of gas A.

The selectivity of a polymer for gas A over gas B,  $\alpha_{A/B}$ , is given by

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{S_A}{S_B} \frac{D_A}{D_B} \quad (3)$$

The diffusion of small molecules is an activated process, and at temperatures away from thermal transitions in the polymer (e.g., glass transition, melting, etc.), the Arrhenius equation is obeyed:<sup>7</sup>

$$D_A = D_{0A} \exp\left(-\frac{E_{DA}}{RT}\right) \quad (4)$$

where  $D_{0A}$  is a front factor,  $E_{DA}$  is the activation energy for diffusion,  $R$  is the gas constant, and  $T$  is the absolute temperature. Barrer<sup>8</sup> and Van Amerongen<sup>9</sup> observed a simple correlation between the front factor and activation energy:

$$\ln D_{0A} = a \frac{E_{DA}}{RT} - b \quad (5)$$

where  $a$  and  $b$  are independent of gas type. Additionally,  $a$  is independent of polymer type and has a universal value of 0.64.<sup>10</sup>  $b$  has a value of  $-\ln(10^{-4} \text{ cm}^2/\text{s}) = 9.2$  for rubbery polymers and  $-\ln(10^{-5} \text{ cm}^2/\text{s}) = 11.5$  for glassy polymers.<sup>11</sup> Equation 5 is often referred to as a "linear free energy" relation. Similar relations between

front factors and activation energies are observed for viscosity of organic liquids, molten salts, and metals<sup>12</sup> and for first-order chemical reaction kinetics,<sup>13</sup> which are also activated processes described by the Arrhenius equation.

Two explanations have been proposed to justify eq 5. First, Barrer noted that eq 5 may be the result of a rather simple "compensation effect".<sup>10</sup> The range of  $\ln D_A$  in eq 4 is always small relative to that of  $E_{DA}/RT$ .<sup>10</sup> Therefore, to a first approximation in many cases,  $\ln D_A$  is almost constant over the ranges of temperature typically explored. The parameters  $E_{DA}$  and  $D_{0A}$  in eq 4 are determined by curve fitting the data to this equation. Any uncertainty in the value of  $E_{DA}$  (determined from the curve fit) that acts to increase the apparent  $E_{DA}$  is compensated for by an increase in the apparent value of  $D_{0A}$  and vice versa. Similar arguments have been advanced to account for the relationship between front factors and activation energies for viscosity.<sup>14</sup> On this basis, eq 5 is simply a mathematical artifact.

Second, within the framework of the Eyring's activated state theory,  $\ln D_{0A}$  is proportional to the entropy change of activation.<sup>15</sup> In this context, eq 5 indicates that activation entropy is directly proportional to activation energy. A linear free energy relation in chemical kinetics is interpreted to mean that the reaction mechanism is similar among a related series of reactions.<sup>13</sup> By analogy, the mechanism of small molecule diffusion in polymers is taken to be similar among a variety of polymers when eq 5 is obeyed. However, mechanistic differences may exist between glassy and rubbery polymers since  $b$  is substantially higher for glassy polymers than for rubbery polymers. At a fixed activation energy and assuming the penetrant jump length is not strongly different in rubbery and glassy polymers, the activation entropy is an order of magnitude lower in glassy polymers than in rubbery polymers.<sup>16</sup> Interestingly, the polymers that define the upper bound relation in Figure 1 and in related plots for other light gas pairs are stiff-chain, amorphous glassy polymers.<sup>1</sup>

On the basis of continuum mechanics models for the creation of holes or vacancies in materials, Lawson<sup>16</sup> and Keyes<sup>17</sup> suggested that the ratio of activation entropy to activation energy should be approximately 4 times the thermal expansion coefficient, which has been observed in some cases for diffusion of small molecules in polymers. Alternatively, according to Barrer's "zone" theory of diffusion, a penetrant executes a diffusion jump in an activated region (or zone) comprising segments of polymer molecules near the diffusing penetrant molecule. The size of the activated zone determines both  $E_{DA}$  and activation entropy or, equivalently,  $\ln D_{0A}$ .<sup>8</sup> The larger the size of the activated zone required for diffusion, the higher is the energy,  $E_{DA}$ , required to create it and the larger is the entropy change associated with the creation of the activated state.

In addition to eq 5, the theory requires a relation between activation energy and penetrant size. Van Krevelen reports that activation energy of diffusion correlates best with the square of penetrant diameter for a wide range of polymers and does not provide separate correlations for rubbery and glassy polymers.<sup>11</sup> Meares found that the activation energy of gas diffusion coefficients in poly(vinyl acetate) increased linearly with penetrant collision diameter squared both above and below the glass transition temperature.<sup>18</sup> Meares

developed a qualitative macroscopic explanation of these results based on the notion that the activation energy is proportional to the volume of the activated state, which is proportional to the product of penetrant diameter squared and penetrant jump length.<sup>18</sup> Other more recent models, such as Brandt's model, also provide support for the notion that activation energy depends on the penetrant diameter squared for stiff-chain glassy polymers such as those that define the upper bound relations.<sup>19</sup> In glassy polymers, activation energy vs penetrant diameter squared plots usually extrapolate to activation energies of zero for finite sized penetrants.<sup>6,20</sup> Brandt's model ascribes this observation to the existence of a finite interchain separation in the nonactivated or equilibrium state.<sup>19</sup> Therefore, the effect of penetrant size on activation energy is modeled as follows:

$$E_{D_A} = cd_A^2 - f \quad (6)$$

where  $c$  and  $f$  are constants which depend on the polymer, and  $d_A$  is the penetrant diameter. For light gases, the kinetic diameter, which characterizes the smallest zeolite window through which a penetrant molecule can fit,<sup>21</sup> is the most appropriate measure of penetrant size for transport property correlations.<sup>6,11</sup> Therefore, in this work,  $d_A$  is taken to be the kinetic diameter of the penetrant. Van Krevelen reports  $c$  values from 250 for extremely flexible poly(dimethylsiloxane) to approximately 1100 cal/(mol Å<sup>2</sup>) for stiff-chain, glassy poly(vinyl chloride).<sup>11</sup> Polymers that have high diffusivity selectivity should have high values of  $c$ . In this regard, for a high-performance glassy polyimide (synthesized from 3,3',4,4'-biphenyltetracarboxylic dianhydride and 4,4'-diaminodiphenyl ether), the value of  $c$  may be as high as 2400 cal/(mol Å<sup>2</sup>).<sup>22</sup> The value of  $f$  ranges from 0 for rubbery polymers and low-performance glassy polymers to approximately 14 000 cal/mol for the polyimide prepared by Haraya et al.<sup>22</sup> The ratio  $\sqrt{f/c}$  is a crude measure of the average distance between polymer chains. For the polyimide just described,  $\sqrt{f/c}$  is 2.5 Å.

Equation 6 should apply to polymers with interchain spacings on the order of or smaller than the size of the penetrant molecules so that thermally activated motion of polymer chain segments controls penetrant diffusion. The theory is not expected to be valid if the interchain spacings are significantly larger than the size of the penetrant molecules because, in this case, the rate-limiting step for penetrant diffusion would not necessarily be controlled by polymer chain motion. The theory is restricted to light gas molecules, such as He, H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, and the like, where gas kinetic diameter provides a good measure of penetrant size as it relates to transport properties. For larger penetrants (e.g.,  $d_A > 4.4$  Å for poly(vinyl acetate)<sup>20</sup>) the activation energy versus penetrant diameter squared relation becomes concave to the penetrant size axis. Moreover, for larger penetrants, kinetic diameter is not a good estimate of penetrant size important for transport properties.<sup>23</sup> In these cases, eq 6 is not strictly obeyed, and the theory will not be valid.

Combining eqs 4, 5, and 6 gives the following expression for the diffusion coefficient:

$$\ln D_A = -\left(\frac{1-a}{RT}\right)cd_A^2 + f\left(\frac{1-a}{RT}\right) - b \quad (7)$$

Thus, within the scope of this theory, the logarithm of gas diffusivity decreases in proportion to penetrant diameter squared. This scaling of diffusion coefficient with penetrant size is consistent with the empirical correlations of Van Krevelen<sup>11</sup> and Teplyakov and Meares.<sup>24</sup> Based on eqs 2 and 7, the permeability coefficient is

$$\ln P_A = -\left(\frac{1-a}{RT}\right)cd_A^2 + f\left(\frac{1-a}{RT}\right) - b + \ln S_A \quad (8)$$

and selectivity is

$$\ln \alpha_{A/B} = \ln(S_A/S_B) + \ln(D_A/D_B) = \ln(S_A/S_B) + \left(\frac{1-a}{RT}\right)c(d_B^2 - d_A^2) \quad (9)$$

Combining eqs 8 and 9 yields

$$\ln \alpha_{A/B} = -\left[\left(\frac{d_B}{d_A}\right)^2 - 1\right] \ln P_A + \left\{ \ln\left(\frac{S_A}{S_B}\right) - \left[\left(\frac{d_B}{d_A}\right)^2 - 1\right] \times \left(b - f\left(\frac{1-a}{RT}\right) - \ln S_A\right) \right\} \quad (10)$$

Equation 10 is the primary result of this theory and can be used to gauge selectivity changes as one explores various polymers with different permeability coefficients. This equation is based on the four hypotheses embodied in eqs 2, 4, 5, and 6.

For a wide range of polymers, solubility and selectivity change much less than either selectivity or permeability coefficients.<sup>1</sup> Therefore, for a particular gas pair and a fixed value of the parameter  $f$ , the term in curly brackets in eq 10 changes little from one polymer to another. In this case, the logarithm of selectivity should decrease linearly as the logarithm of permeability increases, consistent with the empirical upper bound line in Figure 1. Equation 10 has the same mathematical form as the empirical relation reported by Robeson if  $\lambda_{A/B}$  and  $\beta_{A/B}$  in eq 1 are identified as follows:

$$\lambda_{A/B} = (d_B/d_A)^2 - 1 \quad (11)$$

and

$$\beta_{A/B} = \frac{S_A}{S_B} \exp\left\{-\lambda_{A/B}\left[b - f\left(\frac{1-a}{RT}\right)\right]\right\} \quad (12)$$

Using kinetic diameters for  $d_A$  and  $d_B$  in eq 11, the slopes of the  $\ln \alpha_{A/B}$  vs  $\ln P_A$  plots were calculated and compared with the empirically determined slopes from Robeson<sup>1,4</sup> in Figure 2. The kinetic diameters used for this calculation are given in Table 1. In general, the agreement between the calculated and observed slopes is strikingly good given the approximate nature of the slopes and the fact that the predictions are based on a theory with no adjustable parameters.

Robeson observed an excellent empirical correlation of  $\lambda_{A/B}$  with the difference between the kinetic diameters (in angstroms) of the gas molecules:<sup>1</sup>

$$\lambda_{A/B} = d_B - d_A \quad (13)$$

If the expression for  $\lambda_{A/B}$  in eq 11 is rewritten as follows



$$\left(\frac{d_B}{d_A}\right)^2 - 1 = \left[\frac{d_B + d_A}{d_A^2}\right](d_B - d_A) \quad (14)$$

then eq 13 will provide as good a correlation for  $\lambda_{A/B}$  as eq 11 if the term in square brackets is constant. For the penetrant pairs in Figure 2, the term in square brackets is approximately 0.8 and exhibits little variation. For example, the lowest value of the term in square brackets is 0.60 for  $O_2/N_2$ , and the highest value is 0.95 for  $He/N_2$ . In contrast,  $\lambda_{A/B}$  values for these gas pairs vary by more than a factor of 7. Thus, the good agreement that Robeson observed using eq 13 is consistent with theory since the term in square brackets in eq 14 varies little among the gas pairs considered.

To estimate  $\beta_{A/B}$ , solubility and solubility selectivity values for different gases are required. Additionally, the parameter  $f$  is not prescribed by this treatment and is treated as an adjustable parameter. Like gas dissolution in liquids, penetrant dissolution in polymers is regarded as a two step thermodynamic process: (1) condensation of the gaseous penetrant to a liquidlike density and (2) mixing of the pure compressed penetrant with the polymer segments.<sup>6</sup> The first step is governed by penetrant condensability, and the second depends on polymer-penetrant interactions. For light gas penetrants that do not undergo specific interactions with the polymer, the first effect is often dominant, and as a result, penetrant solubility in polymers typically scales with convenient measures of penetrant condensability, such as penetrant boiling point, critical temperature, or Lennard-Jones temperature,  $\epsilon/k$ .<sup>6</sup> For the latter,  $k$  is Boltzmann's constant, and  $\epsilon$  is the potential energy well depth parameter in the Lennard-Jones potential energy function. A model of penetrant solubility in polymers, developed from classical thermodynamics, gives the following relation between penetrant Lennard-Jones temperature and gas solubility in amorphous polymers where strong specific polymer-penetrant interactions (e.g., hydrogen bonding) are not important.<sup>24,25</sup>

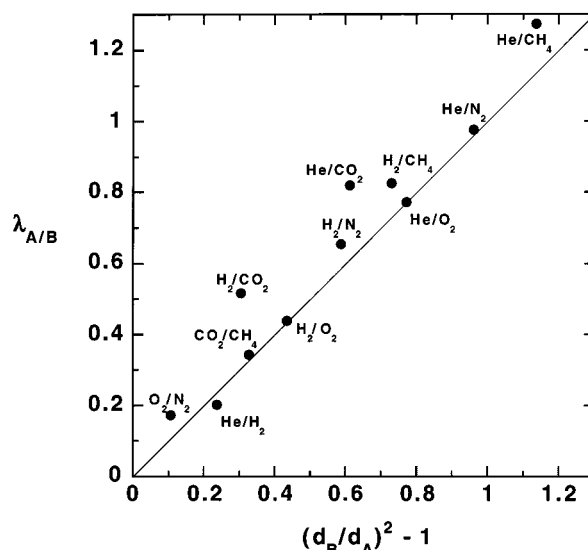
$$\ln S_A = M + N(\epsilon_A/k) \quad (15)$$

where  $M$  and  $N$  are parameters. For a variety of liquids, rubbery polymers, and glassy polymers,  $N$  is  $0.023 \text{ K}^{-1}$ .<sup>6,11</sup>  $M$  is sensitive to polymer-penetrant interactions and, consequently, varies somewhat from polymer to polymer. However, for simplicity,  $M$  is constrained to a constant value. Accordingly, Van Krevelen recommends a value of  $-9.84$  (with solubility in units of  $\text{cm}^3 \text{ (STP)}/(\text{cm}^3 \text{ cmHg})$ ).<sup>11</sup> Equation 15 can be used to calculate solubility selectivity:  $\ln(S_A/S_B) = N(\epsilon_A/k - \epsilon_B/k)$ . As the parameter  $N$  has the same value for many materials, predictions of solubility selectivity should be more accurate than predictions of solubility.

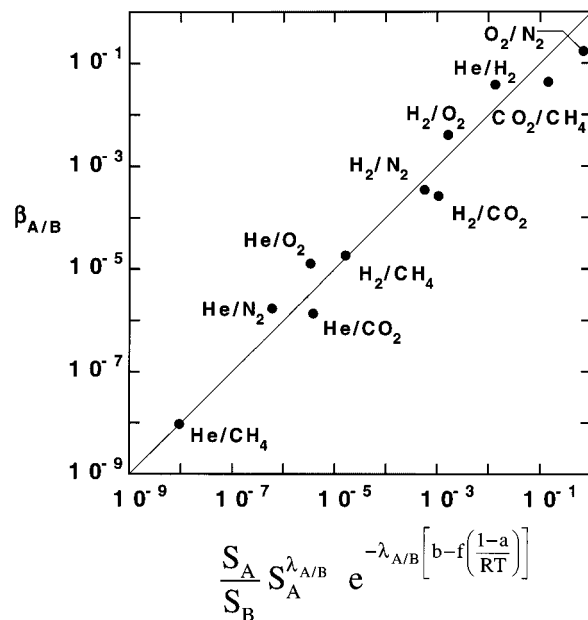
Equation 15 was used in eq 12 to estimate  $\beta_{A/B}$  as shown below:

$$\beta_{A/B} = N \left( \frac{\epsilon_A}{k} - \frac{\epsilon_B}{k} \right) \left( M + N \frac{\epsilon_A}{k} \right)^{\lambda_{A/B}} \times \exp \left\{ -\lambda_{A/B} \left[ b - f \left( \frac{1-a}{RT} \right) \right] \right\} \quad (16)$$

These values are compared in Figure 3 with the  $\beta_{A/B}$  values reported by Robeson. The Lennard-Jones temperatures are recorded in Table 1. Equation 16 contains one adjustable parameter,  $f$ . For simplicity, this



**Figure 2.** Comparison of slopes of  $\ln \alpha_{A/B}$  vs  $\ln P_A$  plots,  $\lambda_{A/B}$ , reported by Robeson<sup>1,4</sup> with theoretical prediction (solid line). Gas pairs are listed as A/B (i.e.,  $O_2/N_2$  implies that  $O_2 = A$  and  $N_2 = B$ ).  $d_A$  and  $d_B$  are the kinetic diameters of penetrants A and B, respectively, taken from the tabulation by Breck.<sup>21</sup>



**Figure 3.** Comparison of front factors of  $\ln \alpha_{A/B}$  vs  $\ln P_A$  plots,  $\beta_{A/B}$ , reported by Robeson<sup>1,4</sup> with theoretical prediction (solid line). The best fit of the data to the theory is obtained with the parameter  $f$  set to  $12\,600 \text{ cal/mol}$ . The units of  $\beta_{A/B}$  are  $[\text{cm}^3 \text{ (STP) cm}/(\text{cm}^2 \text{ s cmHg})]^{\lambda_{A/B}}$ .

**Table 1. Penetrant Size and Condensability Parameters**

penetrant	kinetic diam (Å) <sup>21</sup>	$\epsilon/k$ (K) <sup>11</sup>	penetrant	kinetic diam (Å) <sup>21</sup>	$\epsilon/k$ (K) <sup>11</sup>
He	2.69	10.2	$O_2$	3.46	107
$H_2$	2.8	60	$N_2$	3.64	71
$CO_2$	3.3	195	$CH_4$	3.87	149

parameter was constrained to be a constant for all gas pairs, and its value was determined by a least-squares minimization procedure assuming that the experiment temperature,  $T$ , was 298 K. If some of the data were determined at other temperatures, then the value of  $f$  would be adjusted accordingly. The best value of  $f$  was approximately  $12\,600 \text{ cal/mol}$ .

The agreement of the theory with Robeson's values is impressive considering that only one adjustable parameter is used to describe the upper bound permeability/selectivity behavior of these 11 gas pairs. However, for some gas pairs, there are significant deviations between the calculated front factors and those reported by Robeson. The assumption that  $M$  and  $f$  are constant for all polymers that might lie on the upper bound for all of these gas pairs is clearly a strong approximation which could be relaxed if one were interested in predictions related to specific gas pair/polymer combinations. Also, the upper bound lines were drawn somewhat subjectively, and some disagreement with the theory is not surprising.

### Implications and Conclusions

Equation 10 can be written as

$$\ln \alpha_{A/B} = -\lambda_{A/B} \ln D_A + \left\{ \ln \left( \frac{S_A}{S_B} \right) - \lambda_{A/B} \left( b - f \left( \frac{1-a}{RT} \right) \right) \right\} \quad (17)$$

This form of eq 10 highlights the impact of changes in penetrant diffusion coefficients from polymer to polymer on the upper bound selectivity. The solubility selectivity term in eq 17 should change little from polymer to polymer, and the term  $\lambda_{A/B}b$  is a constant for a given gas pair and a given polymer class (i.e., rubbery or glassy). This result, that diffusivity should play a more important role than solubility in determining upper bound selectivity values, is consistent with the conclusions of Robeson.<sup>1</sup> The theory also provides a rationale for the following heuristic that has emerged as a result of many years of systematic experimental structure/property studies:<sup>3,6</sup> for these light gas pairs, the most productive route discovered to improve permeability/selectivity properties is to modify polymer chemical structure to increase polymer backbone stiffness (i.e., increase  $c$ , which increases  $\alpha_{A/B}$  (cf. eq 9)) while simultaneously disrupting interchain packing to increase  $f$ , thereby increasing diffusivity and, in turn, permeability (cf. eq 8).

Based on the agreement of the theory with the experimental data for many gas pairs, the fundamental characteristics of polymers with outstanding gas separation properties for one pair of gases are shared by polymers having excellent separation properties for other gas pairs. Indeed, Robeson noted that some high glass transition temperature, rigid backbone, amorphous polymers with relatively large interchain spacings (i.e., high fractional free volume) lie on or near the upper bound lines for many gas pairs.<sup>1</sup> Of course, the vast majority of polymers do not lie on the upper bound lines. Rubbery polymers generally sieve penetrants weakly based on size, so the parameter  $c$  in eq 6 is low or the activation energy is proportional to only the first power of penetrant diameter. Both of these characteristics move polymers away from the upper bound lines. Additionally, if interchain spacing is low,  $f$  will be lower, thereby decreasing diffusion coefficients (cf. eq 7) and, in turn, permeability coefficients.

Within the scope of this simple theory, there is no influence of polymer structure on the slope of the upper bound or tradeoff curves,  $\lambda_{A/B}$ , as this parameter depends only on penetrant size ratio. If this is true, then the slopes of the upper bound lines are unlikely to change with further polymer development efforts. In

contrast,  $\beta_{A/B}$  contains variables that can be systematically tuned by rational polymer structure manipulation to simultaneously improve permeability and selectivity characteristics. In this regard, the most fruitful pathway for development of higher performance polymeric membranes for the separations discussed in this paper is to systematically increase  $\beta_{A/B}$ , either through solubility selectivity enhancement and/or increases in chain stiffness (i.e., increasing  $c$ ), while simultaneously increasing interchain spacing (i.e., fractional free volume), to increase selectivity while maintaining or increasing permeability. Increasing interchain separation to increase permeability without sacrificing selectivity should only be effective as long as the interchain separation is not so large that penetrant diffusion coefficients are no longer governed by thermally stimulated polymer segmental motions. Materials that are beyond this limit may already exist. Poly(1-trimethylsilyl-1-propyne), the most permeable polymer known and the polymer which has the highest free volume of all hydrocarbon-based polymers, also has the lowest selectivities for permanent gases (e.g.,  $O_2/N_2$ ) of all polymers and exhibits many permeation characteristics similar to those of microporous materials.<sup>26-28</sup>

Simply increasing polymer backbone stiffness (to the extent that this increases  $c$  in eqs 7 and 9) results in increased selectivity but lower diffusivity and, therefore, permeability. So backbone stiffness increases should be coupled with increases in interchain separation to achieve both higher permeability and higher selectivity. These simple considerations suggest that simultaneous chain stiffness and interchain separation increases can be used to systematically improve separation performance until the interchain separation becomes large enough that the polymer segmental motion no longer governs penetrant diffusion. As indicated above, unless significant enhancement in solubility selectivity could be achieved, this limit would represent the asymptotic end point in the performance of polymeric membranes whose separation properties are dictated by the hypotheses embodied in eqs 2, 4, 5, and 6. To achieve still higher selectivity/permeability combinations, materials that do not obey these simple rules would be required.

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