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Revisiting the experimental and theoretical upper bounds of light pure gas selectivity–permeability for polymeric membranes[☆]

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ABSTRACT

Robeson [L.M. Robeson, J. Membr. Sci. 62 (1991) 165–185] described “upper bounds” correlating the pure gas selectivity with the permeability of the faster gas, P_A . The exponential dependence of the selectivity–permeability trade off, $-1/n$, according to the relationship $\alpha_{A/B} = P_A/P_B = k_{-1/n} P_A^{1/n}$, was shown to be a function of the difference in the kinetic diameter of the gas pairs, $\Delta_{A/B} = d_B - d_A$. Robeson recently revisited the upper bounds [L.M. Robeson, J. Membr. Sci. Available online 22 April 2008], adding two new gas pairs, CO_2/N_2 and N_2/CH_4 and, with only minor changes to the slopes of the upper bounds, confirmed the relationship between $-1/n$ and $\Delta_{A/B}$. Significant changes were reported for the front factor k . Freeman [B.D. Freeman, *Macromolecules*, 32(1999) 375–380] developed a theoretical model which describes these upper bounds as a function of a reduced kinetic diameter, $\lambda_{A/B} = (d_B/d_A)^2 - 1$ and $\alpha_{A/B} = \beta_{A/B} P_A^{-\lambda_{A/B}}$. The theoretical model opened the possibility of setting upper bounds for gas pairs for which experimental upper bounds were not reported. Despite quantitative predictions of both $-1/n$ and $k^{-1/n}$ (or $\beta_{A/B}$) calculated values of $\alpha_{A/B}$ compared poorly with Robeson’s upper bounds for many of the gas pairs. This work revisits Robeson’s findings as well as those of Freeman and seeks to improve the predictive accuracy of Freeman’s model. Robeson had noted that the low precision of many of the kinetic gas diameters could have contributed to the scatter in his correlation of $-1/n$ and $\Delta_{A/B}$. Considering this hypothesis, the gas diameters were re-estimated using the Error in the Variable Method (EVM) with the regression criterion based on the predicted selectivity at three permeabilities compared to Robeson’s upper bounds. Very small changes to the gas diameters, typically $<0.09 \text{ \AA}$, made a significant improvement in the overall accuracy of the predicted selectivity and the correlation of $\lambda_{A/B} = -1/n$. Freeman’s f value, a constant in the E_D correlation as a function of the gas collision diameter, was revised from 12,600 to 16,909 cal mol^{-1} (52.7 to 70.7 KJ mol^{-1}). Recent predictions of the theoretical upper bound are reviewed and corrections proposed based on Freeman’s model and parameters for the gas pairs: N_2/CH_4 and CO_2/N_2 .

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1. Introduction

Robeson [1,2] made the important discovery of a strong correlation of the selectivity of pure, light gas pairs in polymeric membranes with the permeability of the faster permeating gas. The selectivity of a gas pair is $\alpha_{A/B} = P_A/P_B$ where P_i is the permeability of a pure gas across a dense polymer film defined by volumetric flux per unit driving force for a given thickness. The collection of numerous experimental data showed an upper bound, well defined by a straight line on a log–log plot of $\alpha_{A/B}$ as a function of P_A . The slope of the upper bound, $-1/n$, was shown to be linearly correlated with the difference of kinetic diameter of the gases [3], $\Delta_{A/B} = d_B - d_A$,

where $\alpha_{A/B} = k^{-1/n} P_A^{1/n}$. While this manuscript was under review, Robeson [4] revisited the upper bounds and confirmed the correlation of $-1/n$ with $\Delta_{A/B}$. In addition, two highly relevant gas pairs, N_2/CH_4 and CO_2/N_2 were included in his analysis. Overall, the greatest changes regarded revising the front factor k . Robeson attributed this to the significantly higher selectivities for many gas pairs with perfluorinated polymers.

Freeman [5] made a significant advance by theoretically predicting $-1/n$ and $k^{-1/n}$ where he derived the expression

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

beginning from the definition of permeability of gas A as the product of the gas diffusivity and solubility in the polymer, $P_A = D_A S_A$. The derivation of Freeman’s expression is presented in the theoretical section.

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A major advantage of Freeman's formulation was that it allowed one to define upper bounds for any gas pairs, or to corroborate an existing gas pair, for example, the two important gas pairs, CO₂/N₂ [6–10] for greenhouse gas mitigation or N₂/CH₄ [10], for which Robeson [4] has recently assigned upper bounds. Furthermore, having a mechanistic model gives one insight for improving polymer selectivity/permeability. As will be seen in the theoretical development, the contributions of solubility to overall performance can be singled out. Likewise, the contributions of diffusivity can be considered in terms of more basic parameters which relate to inter-polymer chain spacing, polymer chain stiffness and the activation energy of diffusion. This has been already suggested by Freeman [5] and further elucidation is beyond the scope of this work.

A major difference between Freeman's work and Robeson's findings was the definition of the exponential dependence of the selectivity on P_A , hence forth termed "the slope". Freeman's exponent was defined as $\lambda_{A/B} = (d_B/d_A)^2 - 1$ or the reduced kinetic diameter. This definition of the exponent was the result of the assumed mathematical form of the dependency of the activation energy of diffusion, E_{D_A} , on the gas diameter.

Absolute predictions of $\alpha_{A/B}$ for many of the gas pairs were not satisfactory. The Error in the Variable Method (EVM) [11–14] or Error In the Variable (EIV) method was used to estimate a new set of gas diameters for improved correlation of $\lambda_{A/B}$ with Robeson's slopes. In addition, an alternative criterion for estimating the parameter f , the intercept of E_{D_A} vs. d_{gas}^2 plots, was used to yield greatly improved overall estimates of the upper bounds for the 13 gas pairs identified by Robeson [1,2,4]. Comparisons of theoretical upper bounds by others have been made for N₂/CH₄ and CO₂/N₂ using Freeman's parameters and those estimated in this work by EVM. Comparison of the correlation of the upper bound slopes with $\lambda_{A/B}$ or $\Delta_{A/B}$ is inevitable, but is not the purpose of this work. The primary goal is to improve the predictive accuracy of Freeman's theoretical model.

2. Theory

2.1. Diffusivity

Freeman's theoretical prediction of $\alpha_{A/B}$ from correlations of the diffusivity and solubility are briefly summarized here as it will be heavily referred to in the current work.

Beginning with the definitions of $P_A = D_A S_A$ and $\alpha_{A/B} = P_A/P_B$ the selectivity can be expressed as

$$\alpha_{A/B} = \frac{D_A S_A}{D_B S_B} \quad (2)$$

The diffusivity of a gas in a polymer is an activated process where

$$\ln D_A = \ln D_{0A} - \frac{E_{D_A}}{RT} = a \frac{E_{D_A}}{RT} - b - \frac{E_{D_A}}{RT} \quad (3)$$

D_{0A} is a front factor and is also correlated with E_{D_A} by an Arrhenius type relationship. Freeman used the value of 0.64 for a from Barrer and Skirrow [15] and b values of 9.210 and 11.513 for rubbery and glassy polymers, respectively, were based on Krevelen's [16] presentation of log–log plots of D_0 vs. E_D . The value of a from Krevelen's plots would be 0.686 at 298 K and 0.709 at 308 K. While reasonably close to the Barrer and Skirrow value, the changes in final predictions of the selectivity can be very large.

2.2. Activation energy of diffusivity

Conveniently, E_{D_A} can be expressed as a function of the gas diameter, eventually giving rise to the slope of the log–log plot of $\alpha_{A/B}$ vs.

P_A . The activated components of the diffusion process in Brandt's [17] model are

$$E_{D_A} = E_i + E_b + f'RT \quad (4)$$

where E_i , the *inter* molecular term, is the energy required to cause a volume change in the polymer to allow the passage of a gas molecule. The volume change contains a "correction term" for the pre-existing volume in the polymer. The free volume per unit length of the polymer is ϕ , the square root of which is a measure of the "linear distance perpendicular to the chain", i.e. $\phi^{1/2}/2$ (a value of 0.9 Å is used in the calculations later [18]). For gas diameters less than $\phi^{1/2}/2$, logically, the activation energy for diffusive flow is zero. The *intra* molecular contribution, E_b , represents the strain energy of moving two polymer molecules apart. E_i and E_b are defined below, along with approximate solutions where $s \gg d - \phi^{1/2}/2$ and $d \gg \phi^{1/2}/2$.

$$E_i = \frac{1}{2} (d - \phi^{1/2}/2)^2 \left[\left(\frac{s}{d - \phi^{1/2}/2} \right)^2 - 1 \right]^{1/2} d_{\text{poly}} N P_i \approx \frac{1}{2} s^2 \times (d - \phi^{1/2}/2) d_{\text{poly}} N P_i \approx \frac{1}{2} s^2 d d_{\text{poly}} N P_i \quad (5)$$

$$E_b = 36 \frac{V_0 z}{f'} \left[\left(\frac{s}{d - \phi^{1/2}/2} \right)^2 - 1 \right]^{-1} \approx 36 \frac{V_0 z}{f' s^2} \left(\frac{d - \phi^{1/2}}{2} \right)^2 \approx 36 \frac{V_0 z}{f' s^2} d^2 \quad (6)$$

and

$$f' = \frac{2sz}{\lambda} \quad (7)$$

where d is the gas molecule diameter, $f = 16$ [17] represents the number of degrees of freedom involved in a particular motion, s (13 Å [18]) is the segment length of the polymer which sweeps out the required volume change and λ is the length of one backbone chain bond. The proportionality constant, $z \approx 1$, [17] hence f' also represents the number of backbone chain bonds involved in the diffusion process. P_i is the internal pressure of the polymer (3250 cal mol⁻¹ [17]), N is Avogadro's number, d_{poly} the chain thickness of the polymer, and V_0 (2750 cal mol⁻¹ [17]) is the potential energy hindering rotation. The thermal energy stored in f degrees of freedom is fRT and is not part of the activation energy of diffusion but part of the total energy.

Rubbery polymers are expected to have larger contributions from E_i while glassy polymers would be dominated by E_b [19]. Michaels [18] estimated that E_i was at least one order of magnitude larger than E_b for polyethylene. Using the values in the parenthesis above, E_i/E_b ranged from 20.3 to 10.1 for gas diameters of 2.55 and 4.00 Å, respectively, with the total increasing from 2200 to 4200 cal mol⁻¹.

Brandt postulated that the predicted value of 5.8 kcal/mol for ethane diffusing through polyethylene underestimated the experimental value of 13,300 cal mol⁻¹ primarily because the internal pressure, P_i , was low. In order for the activation energy of a glassy polymer to be dominated by E_b and hence correlate with the square of the gas diameter, V_0 would have to increase by at least two orders of magnitude, with no change in P_i . Most likely P_i would also increase for glassy/stiffer backbone polymers.

From this discussion it is clear that the dependence of E_{D_A} on the gas diameter can be represented by a number of different functionalities. Freeman used the form

$$E_{D_A} = cd^2 - f \quad (8)$$

which, when used with Eq. (3), yields

$$\ln D_A = -cd^2 \frac{(1-a)}{RT} + f \frac{(1-a)}{RT} + b \quad (9)$$

where d is the gas diameter and c and f are the slope and intercept from a plot of E_{D_A} as a function of the square of the gas diameter. In some cases, such as Haraya's [20] work on polyimide, the intercept was a strong function of the gas diameters used, primarily as a result of the value for CO_2 . Using kinetic diameters, an intercept of $2400 \text{ cal mol}^{-1}$ was obtained, while using collision diameters [16] this value increased to 7400 kcal/mol . It must be noted that the correlation coefficient was very low, <0.5 for this data set with either type of gas diameter. There was no data for H_2 and He due to the short lag times, which would have been the most important for determining the value of the intercept. A positive intercept is inconsistent with the theoretical models above.

The choice of gas diameters has been a point of contention for correlating E_{D_A} data. The collision diameter has generally been accepted as the best source while gas permeation data, and Robeson's plots, are best correlated by kinetic diameters. It is remarkable that Freeman's theoretical model accurately predicts the exponential dependence of $\alpha_{A/B}$ on P_A .

2.3. Gas solubility

The solubility of gases in polymers is well correlated with the Lennard-Jones temperature, ε/k , where ε is the depth of the intermolecular potential energy function and k is the Boltzman constant. Michaels [18] used the correlation:

$$\ln S_A = M + N \left(\frac{\varepsilon}{k} \right) \quad (10)$$

where N , 0.023 K^{-1} , is common for all polymers (0.023 K^{-1}) and M is $-9.844 \text{ (cm}^3 \text{ (STP) cm}^{-3} \text{ cmHg}^{-1})$ for glassy polymers and $-8.923 \text{ (cm}^3 \text{ (STP) cm}^{-3} \text{ cmHg}^{-1})$ for rubbery polymers [16].

2.4. Theoretical & experimental upper bounds

Using Eq. (2) and substituting for the ratio of the diffusivities:

$$\ln \alpha_{A/B} = c \frac{(1-a)}{RT} (d_B^2 - d_A^2) + \ln \frac{S_A}{S_B} \quad (11)$$

The permeability of the faster gas is introduced using

$$\ln P_A = -cd_A^2 \frac{(1-a)}{RT} + f \frac{(1-a)}{RT} + b + \ln S_A \quad (12)$$

Eqs. (11) and (12) are combined to give

$$\begin{aligned} \ln \alpha_{A/B} &= - \left[\left(\frac{d_B}{d_A} \right)^2 - 1 \right] \ln P_A + \ln \frac{S_A}{S_B} - \left[\left(\frac{d_B}{d_A} \right)^2 - 1 \right] \\ &\quad \times \left(b - f \frac{(1-a)}{RT} - \ln S_A \right) = -\lambda_{A/B} \ln P_A + \ln \frac{S_A}{S_B} - \lambda_{A/B} \\ &\quad \times \left(b - f \frac{(1-a)}{RT} - \ln S_A \right) \end{aligned} \quad (13)$$

$$\begin{aligned} \alpha_{A/B} &= P_A^{-\lambda_{A/B}} \exp \left[\ln \frac{S_A}{S_B} + \lambda_{A/B} \ln S_A - \lambda_{A/B} \left(b - f \frac{(1-a)}{RT} \right) \right] \\ &= P_A^{-\lambda_{A/B}} \frac{S_A}{S_B} S_A^{\lambda_{A/B}} \exp \left[-\lambda_{A/B} \left(b - f \frac{(1-a)}{RT} \right) \right] = \beta_{A/B} P_A^{-\lambda_{A/B}} \end{aligned}$$

where the solubility and their ratios are essentially constant and so a \ln - \ln plot of selectivity as a function of the permeability of gas A has a slope of $-\left((d_B/d_A)^2 - 1 \right) = -\lambda_{A/B}$. Freeman noted that $\lambda_{A/B}$ was

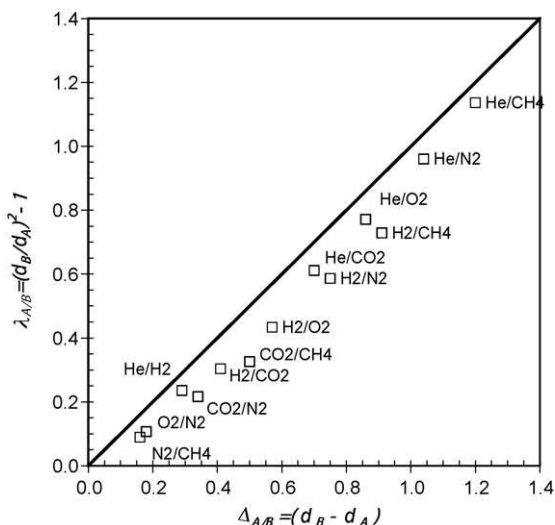


Fig. 1. Comparison of $\lambda_{A/B}$ and $\Delta_{A/B}$ using kinetic diameters according to Breck. Gas pairs CO_2/N_2 , N_2/CH_4 and CO_2/CH_4 are also included.

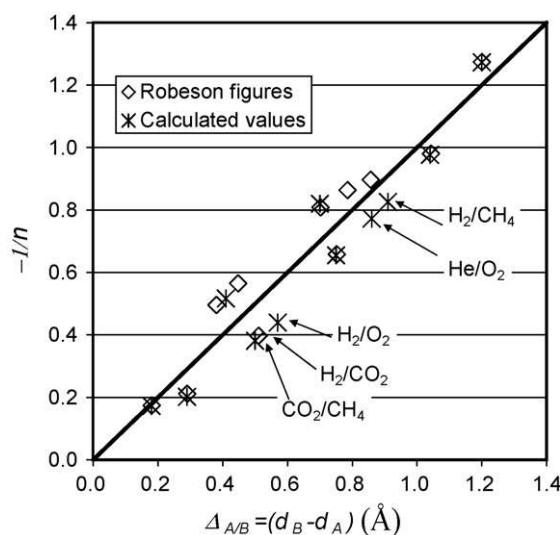


Fig. 2. Comparison of $-1/n$ vs. $\Delta_{A/B}$ from Robeson's figures [1,2] and calculated values of $\Delta_{A/B}$ and tabulated values of $-1/n$.

proportional to Robeson's observation of the slope of the upper bound $\Delta_{A/B} = d_B - d_A$:

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

where the factor $(d_B + d_A)/d_A^2$ is relatively constant compared to the difference of the gas diameters. Freeman thereby found a theoretical basis for Robeson's observed upper bound slopes being correlated with $\Delta_{A/B}$. While C is relatively constant compared to $d_B - d_A$ there is a systematic relationship between $\Delta_{A/B}$ and $\Delta_{A/B}$ as seen in Fig. 1¹.

Robeson's original findings [1,2] are plotted in Fig. 2, where open diamonds represent values from figures in the references. The star

¹ The kinetic diameters used in this work are those given by Breck, not those of Freeman [5] as there appears to be a typesetting error in the later reference (He, H_2 and CH_4). Freeman's calculated values were reproduced for $\lambda_{A/B}$ and $\beta_{A/B}$, it is clear he used the correct values.

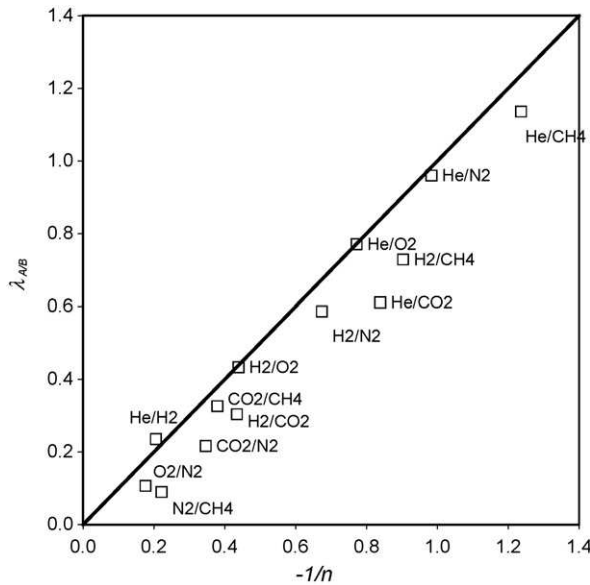


Fig. 3. Comparison of $\lambda_{A/B} = (d_B/d_A)^2 - 1$ as a function of Robeson's experimental $-1/n$ values.

symbols represent calculated values from tabulated values of n and the kinetic gas diameters. It appears that the $x - y$ co-ordinates were inverted for five gas pairs². What appeared to be a random distribution of data about the $-1/n = d_B - d_A$ line now shows a systematic deviation from $y = x$, in a fashion similar to that seen in Fig. 1, with the exception of two gas pairs. In Robeson's most recent publication, the data are shown correctly.

Robeson [4] suggested that the non-zero intercept of $-1/n$ vs. $\Delta_{A/B}$ could be attributed to a uniform error in all the zeolite gas diameter data with respect to what they should be in polymer diffusion data. This hypothesis was examined by two approaches. In the first, by attempting to determine a value for this bias in the gas diameters by setting the average value of the residuals of $-1/n$ vs. $\Delta_{A/B}$ to zero by applying a correction to all the gas diameters. The resultant line is $y = 0.8471x + 0.0958$, $r^2 = 0.9502$ and the current estimates of the gas diameters would have to be reduced by 0.327 nm. Clearly this is not a suitable method as the slope is grossly in error and the bias on the gas diameters is quite large. In a second approach, the estimate of the bias is taken such that the intercept of the $-1/n$ vs. $\Delta_{A/B}$ plot is zero, this method yields a correction of 16 nm and a slope of 9.0, obviously not plausible. An alternative hypothesis is that there is an individual bias for each gas diameter, the estimation of which is ideally suitable for the EVM.

The similarity between Figs. 1 and 2 immediately suggests an improved correlation of $-1/n$ with $\Delta_{A/B}$ (Fig. 3). The greatest deviations are for the gas pairs H_2/CO_2 , He/CO_2 and He/CH_4 . Not surprisingly, these gas pairs include a gas for which the kinetic diameter is only available to one significant digit. This had been identified as a potential source for the scatter by Robeson [1,2,4]. The impact of this on the correlation of $-1/n$ with $\Delta_{A/B}$ is discussed in Section 3.2 when EVM estimates for the gas diameters are determined.

Freeman's theoretical model also yields a quantitative estimate³ of the selectivity or upper bound as a function of P_A :

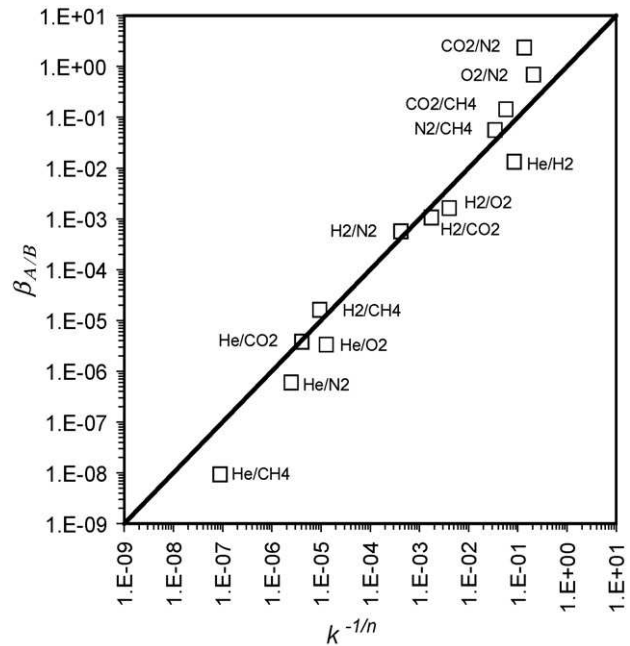


Fig. 4. Comparison of Robeson's experimental $k^{-1/n}$ and Freeman's analogous term, $\beta_{A/B}$. New estimate of $f = 14,154$ cal/mol.

$$k^{-1/n} = \beta_{A/B} = N \left(\frac{\varepsilon_A}{k} - \frac{\varepsilon_B}{k} \right) \exp \left[M + N \left(\frac{\varepsilon_A}{k} \right) \right] \times \exp \left[-\lambda \left(b - f \frac{(1-a)}{RT} \right) \right] \quad (15)$$

these values are reported in Fig. 4, our calculated values for $\beta_{A/B}$ match Freeman's plotted values within 6%. We also reproduced the selectivity-permeability plots of Favre [21] for the O_2/N_2 , CO_2/N_2 and CO_2/CH_4 gas pairs. Freeman's estimate of 12,600 cal/mol was used for f and a temperature of 298 K. We obtained a reasonably close value of 12,898 cal mol⁻¹ when minimizing the sum of squares of residuals function:

$$SSR = \sum_1^{11} (\log(\beta_{A/B}) - \log(k^{-1/n}))^2 \quad (16)$$

for the 11 gas pairs. When using the Robeson [4] upper bounds and all 13 gas pairs, the value of f was revised to 14,154 cal mol⁻¹.

3. Results and discussion

3.1. $\alpha_{A/B}$ vs. P_A predictions

Freeman's model has the great benefit of quantitatively predicting the upper bound for which an experimental bound has not been reported. Before predicting bounds for "new" gas pairs, the ability to predict the upper bound for the 13 "classic" gas pairs should be confirmed. The reasonable approximation of $-1/n$ and $\beta_{A/B}$ suggests that one should obtain a useable estimate of $\alpha_{A/B}$ for other gas pairs. However, predicting the gas pairs for which the upper bound is most accurately estimated is not straightforward. The accuracy of $\beta_{A/B}$ and $\lambda_{A/B}$ must be taken into account simultaneously. In some cases either $\beta_{A/B}$ or $\lambda_{A/B}$ can be a poor predictor of the relevant Robeson parameter but a very good estimate of the upper bound can be had. For example, Fig. 5 shows the upper bounds for two gas pairs according to Robeson and Freeman's model. The predictions for CO_2/CH_4 are exceptionally good. In this case $\lambda_{A/B}$ was a good predictor of $-1/n$ while $\beta_{A/B}$ was a relatively poor predictor of $k^{-1/n}$. Predictions of $\alpha_{A/B}$ for He/CH_4 are more than one order

² The authors have used Robeson's tabulated values for $-1/n$ and k and have reproduced the graphed upper bounds in all the figures. The open diamonds in Fig. 2 were taken from Robeson's figures using calipers.

³ The exponential function on the solubility term for gas A is missing in Eq. (16) in Freeman [5], Eq. (12) in the same reference is correct.

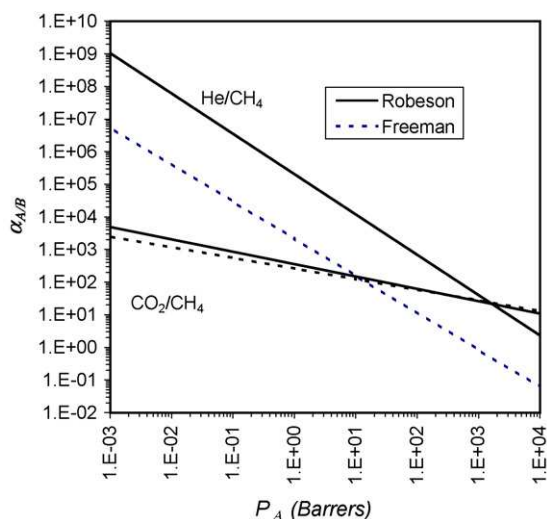


Fig. 5. Comparison of upper bounds for pure gas selectivity according to Robeson's experimental observations and Freeman's theoretical predictions.

of magnitude lower than Robeson's upper bound. In this case $\beta_{A/B}$ was an excellent predictor of $k^{-1/n}$ while $\lambda_{A/B}$ was a poor predictor of $-1/n$.

An over estimation of the selectivity could be considered acceptable, simply indicating that the "best possible" films at a given permeability have not been produced yet. An under estimation of the upper bound is less desirable, as the reason for having an upper bound is lost. This issue will be discussed again in Section 3.2.

In general, Freeman's model under predicts $\alpha_{A/B}$ for most gas pairs. When $-1/n$ differs even slightly from $\lambda_{A/B}$, the relative error is a function of P_A (Fig. 5). Freeman used one adjustable parameter in his model, f , representing the y -intercept when the activation energy of diffusion is plotted as a function of the gas diameter. His updated value of $14,154 \text{ cal mol}^{-1}$ was obtained by optimizing the value of $\beta_{A/B}$ in comparison to Robeson's $k^{-1/n}$ values.

The value of the constant a in Eq. (3) is set at 0.64 as per Freeman. The alternative value of $a = 0.686$, according to Krevelen, yields a value of $f = 16,229 \text{ cal mol}^{-1}$ but will leave predicted values of $\beta_{A/B}$ unchanged. The relationship between a and f is determined by $f(1-a)/RT$ in Eq. (13). For the remainder of this work, the value of a is 0.64.

An alternative strategy to optimize the value of f is to minimize the sum of squares of residuals of the error of the theoretical and observed selectivity of the upper bounds. Using this criterion an estimate of $f = 18,757 \text{ cal mol}^{-1}$ was obtained. This reduced the selectivity based SSR from 38.57 to 18.34 and tripled the SSR based on $\beta_{A/B}$ compared to $k^{-1/n}$ in Fig. 4. The interaction between $\lambda_{A/B}$ and $\beta_{A/B}$ suggests that a modification of f alone would be inadequate to improve the theoretical prediction of the upper bounds. Further consideration should be given to the gas diameters used for estimating $\lambda_{A/B}$ and this will be discussed in the next section.

3.2. EVM estimates of d_k

EVM was applied to the present problem, considering only the gas diameters and the parameter f . Normally EVM would be applied simultaneously to both the model parameters (dependent variables) and the independent variables. In the present case Robeson's estimates of $-1/n$ and $k^{-1/n}$ are taken to be exact, fully realizing that there can be a change in both of these parameters as there has been in the recent revision of the upper bounds [4].

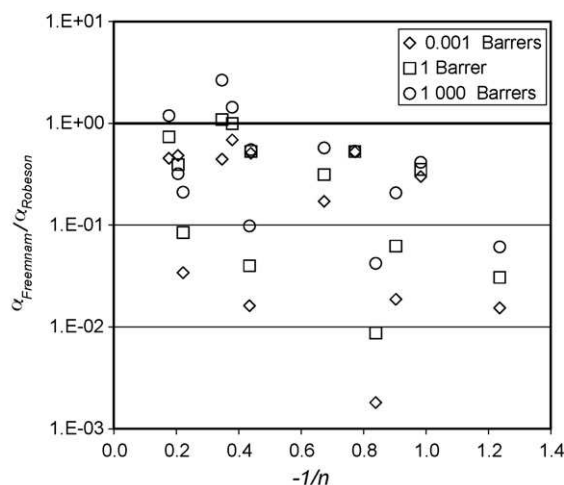


Fig. 6. Freeman's predicted selectivity normalized by Robeson's selectivity as a function of P_A and $-1/n$ using Breck's diameters and $f = 14,154 \text{ cal mol}^{-1}$.

The solution was obtained in two manners. The first was a simultaneous optimization of the gas diameters and f based on the sum of squares of residuals of the logarithm of the ratio of the predicted and observed selectivity, SSR_α . Eq. (17), at three permeabilities (1000, 1 and 0.001 Barrers, 1 Barrer = $10^{-10} \text{ cm}^3 \text{ (STP) cm cm}^{-1} \text{ s}^{-1} \text{ cmHg}^{-1}$). Three permeability values were used in order to account for changes in the accuracy of the predicted selectivity when the slope of the upper bounds, $-1/n$, did not match $\lambda_{A/B}$. This regression essentially tries to make the data points in Fig. 6 approach $y = 1$.

No constraints were placed on either f or the gas diameters. The sum of squares of residuals of reference diameters for the six gases and the current estimates was also used as a regression criterion which was added to the three previous criteria.

$$SSR_\alpha = \sum_{i=1}^{13_gaspairs} \left(\sum_{P1}^{P3} (\log(\alpha_{A/B_Robeson}) - \log(\alpha_{A/B_Freeman})) \right)^2 + \sum_{i=1}^6 (d_{ki_Breck} - d_{ki_current})^2 \quad (17)$$

$$SSR_\lambda = \sum_{i=1}^{13_gaspairs} (\lambda_{A/B} + 1/n)^2 + \sum_{i=1}^6 (d_{ki_Breck} - d_{ki_current})^2$$

$$SSR_\beta = \sum_{i=1}^{13_gaspairs} (\log \beta_{A/B} - \log k^{-1/n})^2 + \sum_{i=1}^6 (d_{ki_Breck} - d_{ki_current})^2$$

This served as a constraint on the gas diameter estimates, ensuring that solutions remained relatively close to the accepted values defined by Breck [3]. Very small changes in all the gas diameters, Table 1, were required to generate significant improvements to $\lambda_{A/B}$ and $\alpha_{A/B}$.

The solution was also obtained in a sequential manner, which served to ensure a global minimum for SSR_α was obtained. First, the gas diameters were optimized such that SSR_λ was minimized, such that $\lambda_{A/B} = -1/n$ in Fig. 3. Second, f was optimized in order to minimize SSR_β such that $\beta_{A/B} = k^{-1/n}$ in Fig. 4. Finally, both f and the gas diameters were re-estimated simultaneously using the current values for the gas diameters and f while minimizing SSR_α . The same solutions were obtained when the gas diameters and f were optimized simultaneously with Breck's values as the initial guesses. The SSR_λ was reduced to almost half its initial value, while SSR_β almost doubled.

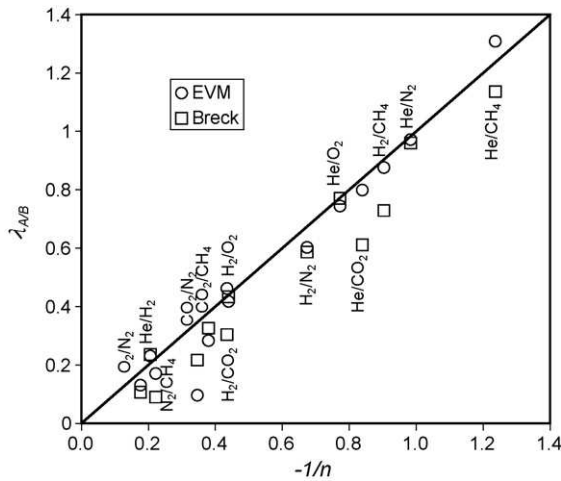


Fig. 7. Comparison of $\lambda_{A/B}$ as a function of the experimental $-1/n$ from Robeson, using Breck's literature values for the kinetic diameter and EVM estimates.

The overall improvement in accuracy of the predicted selectivity is noted by the reduction of SSR_{α} in Table 1. Significantly lower values for SSR_{λ} and SSR_{β} were obtained when these criteria were minimized individually, but priority was given to SSR_{α} .

The changes in gas diameters were random (i.e. increasing or decreasing) and all were less than 0.09 \AA or less than 4%, with the exception of CO_2 . The estimate of CO_2 increased from 3.3 to 3.427 \AA , which remains a minor correction. The improvement in correlation of $\lambda_{A/B}$ with $-1/n$ is notable using the EVM estimates (Fig. 7). The correlation of $\beta_{A/B}$ with $k^{-1/n}$ in Fig. 8, did not improve, as SSR_{β} increased.

Ultimately, it is $\alpha_{A/B}$ as a function of P_A that is of greatest importance. Hence using a criterion based on this, SSR_{α} , Eq. (16), is used with the EVM. The overall improvement in predicting the selectivity can be seen by comparing Figs. 6 and 9 where the scatter is greatly decreased (note the log-scale change).

One could argue for a different criterion to be used with the EVM. If upper bounds are truly upper limits, then a regression criterion which forces all predicted $\alpha_{A/B}$ to be greater than the observed $\alpha_{A/B}$ could be postulated. This may lead to grossly overestimating the upper bounds for some gas pairs. This type of criterion would also violate a primary assumption of linear least squares regression: that the dependent variable(s), $\alpha_{A/B}$, $\lambda_{A/B}$ and $\beta_{A/B}$ are randomly, normally distributed about true value(s). Further-

Table 1
Summary of literature kinetic gas diameters and f and EVM estimates of these parameters and the absolute/relative changes

Criterion	Nominal values		Solution	
SSR_{α}	38.5529		6.07372	
SSR_{λ}	0.16050		0.09197	
SSR_{β}	3.84163		6.46498	
Gas	Diameter (\AA)	Diameter (\AA)	Change (\AA)	% Change
He	2.6	2.55488	-0.04512	-1.74%
H_2	2.89	2.83406	-0.05594	-1.94%
CO_2	3.3	3.42667	0.12667	3.84%
O_2	3.46	3.37414	-0.08586	-2.48%
N_2	3.64	3.58760	-0.05240	-1.44%
CH_4	3.8	3.88178	0.08178	2.15%
$f(\text{cal mol}^{-1})$	14,154	16,909	2755	19.46%

Note that the SSR_{λ} for the EVM estimates does not include the second term in Eq. (17) in order to denote a true comparison to the SSR_{λ} for the Breck diameters where this term would be zero.

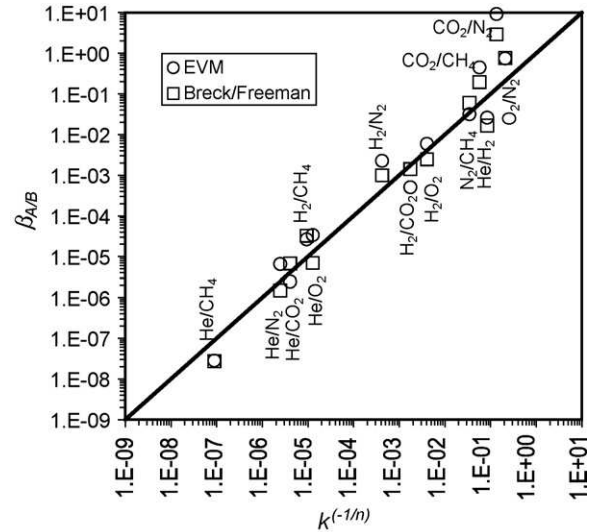


Fig. 8. Comparison of $\beta_{A/B}$ as a function of $k^{-1/n}$ from Robeson [4], using EVM estimates of the gas diameters and $f = 16,909 \text{ cal mol}^{-1}$ compared to the Breck gas diameters and Freeman's updated (Robeson 2008 data and including CO_2/N_2 and N_2/CH_4 gas pairs) estimate of $f = 14,154 \text{ cal mol}^{-1}$.

more, all the literature correlations for solubility and diffusivity have already been determined using least squares regression. Imposing a different error distribution on the selectivity, by making all the theoretical predicted upper bounds greater than or equal to the Robeson upper bounds, is not in agreement with this approach. Nonetheless one should be aware of the nature of the predicted upper bound for a given gas pair and expect that some will be below, and some will be above, Robeson's upper bounds.

3.3. Literature kinetic gas diameters

Robeson [1] commented on the lack of precision of the kinetic diameter estimates and their potential impact on the scatter of his $-1/n$ vs. $\Delta_{A/B}$ correlation. Of particular concern were gas pairs with similar diameters such as O_2/N_2 or CO_2/CH_4 or for which the gas diameters are reported to only

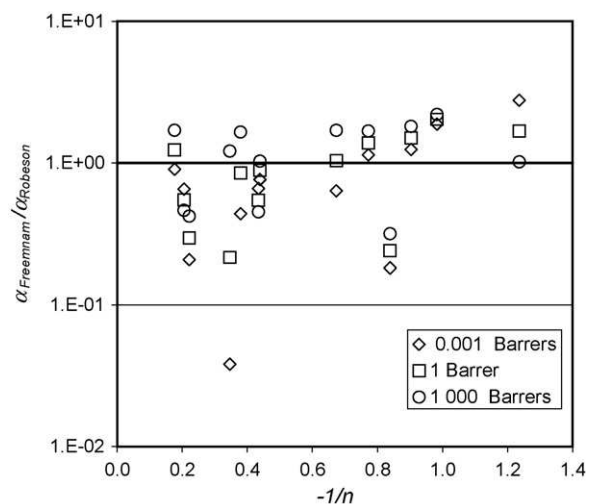


Fig. 9. Freeman's predicted selectivity normalized by Robeson's selectivity as a function of P_A and $-1/n$ using EVM estimates of the kinetic gas diameters from Table 1 and $f = 16,909 \text{ cal mol}^{-1}$.

one decimal point. The series of kinetic gas diameters summarized by Breck are culled from different techniques, which could also lead to discrepancies when trying to correlate $-1/n$ with either $\lambda_{A/B}$ or $\Delta_{A/B}$. Koros et al. [22] reported on the use of kinetic diameters, as reported by Breck based on adsorption in zeolites, as being relevant to gas diffusion in polymeric membranes. The collision diameters as presented by Krevelen yield a negative $\lambda_{A/B}$ for gas pairs such as CO_2/CH_4 , CO_2/N_2 and N_2/CH_4 .

There may be some questions regarding the accuracy of the kinetic diameters for CO_2 and CH_4 . Both of these are reported to only 2 significant digits. The Lennard–Jones (6–12) potential gives $\sigma = 4.05 \text{ \AA}$ and 3.64 \AA for CO_2 and N_2 , respectively. These can be based on viscosity measurements or 2nd virial coefficients [23]. Based on the adsorptive behaviour of CO_2 and N_2 in a zeolite, Breck used the minimum Pauling dimension (width) of 3.7 \AA for σ , from which the kinetic diameter of $3.7/2^{(1/6)} = 3.296 \text{ \AA}$ is obtained. The Pauling dimension for CO_2 also agrees with the value Kihara [24] obtained (3.7 \AA) for his spherocylindrical L–J potential model. Now the kinetic diameter for CO_2 is based on the minimum Pauling diameter, but the N_2 minimum Pauling dimension has a length of 3.0 \AA which would still make it smaller than CO_2 .

The collision diameter for N_2 reported by Krevelen is 3.80 \AA , while Hirschfelder et al. [23] reported a range from 3.681 to 3.749 \AA . Breck used Kihara's value for N_2 of 4.09 \AA for r_{min} giving a kinetic diameter of 3.64 \AA . Breck also used Kihara's value for H_2 , both of these based on his spheroidal L–J potential model, rather than the spherocylindrical L–J potential from which CO_2 may have been based.

Krevelen correlated E_{D_A} with the collision diameter. The collision diameter and kinetic diameters match very well for the majority of gases (Fig. 10). Differences between the two references are small, literally of the same scale as changes determined by EVM. The major deviations are for NH_3 , CO_2 , propane and benzene. CO_2 is the only gas of concern in this work and the two values cannot be reconciled with respect to the slopes of upper bounds and the correlation of E_{D_A} . The E_{D_A} correlations clearly need the collision diameter while the slopes of the upper bounds need the kinetic diameter. This is not consistent with the kinetic diameters used to evaluate $\lambda_{A/B}$ and this could have contributed to the poor corre-

lation of $\lambda_{A/B}$ with $-1/n$ in Fig. 3 for H_2/CO_2 and He/CO_2 . Indeed, the correlation of $\lambda_{A/B}$ with $-1/n$ in Fig. 7 using the EVM estimates for the kinetic diameters is greatly improved as the CO_2 diameter moves closer to the collision diameter.

Nonetheless, Freeman's model was remarkable in predicting the key parameters of Robeson's observations; $-1/n$ via $\lambda_{A/B}$ and $k^{-1/n}$ via $\beta_{A/B}$. Prediction of the selectivity, as well as the aforementioned parameters was greatly improved using EVM, and a different minimization criterion. These discussions on the literature values of the kinetic gas diameter certainly allow for some inaccuracy. The very small changes in the gas diameters noted in Table 1 are reasonable in light of this.

3.4. Lennard–Jones temperatures

The Leonard–Jones temperatures used to estimate the solubility of the gases are those reported by Krevelen. There are some discrepancies in the values used for the kinetic/collision diameters and the L–J temperature. The two parameters are linked as part of the solution of the L–J potential function and as such, one can strongly argue that the gas diameter and the L–J temperature should not be taken from separate sources.

Krevelen reports ε/k for H_2 as 60 K with a collision diameter of 2.83 \AA while Breck uses Kihara's diameter of 2.89 \AA which is coupled with $\varepsilon/k = 32.4 \text{ K}$. Hirschfelder's diameter for H_2 is 2.928 with $\varepsilon/k = 37$.

In the case of N_2 , Krevelen's $\varepsilon/k = 71$ while Kihara's value is 101 K and Hirschfelder's values are $\sim 95 \text{ K}$. Trying to use any of these alternate estimates of ε/k gave mixed results in terms of estimating either $\beta_{A/B}$ or the overall accuracy of the upper bound predictions.

3.5. Comparison of literature upper bounds for CO_2/N_2 , N_2/CH_4 and CO_2/CH_4

Recently Cecopieri-Gomez [10] revised the CO_2/CH_4 upper bounds and proposed CO_2/N_2 and N_2/CH_4 upper bounds comparing Freeman's predictions with available experimental results. Favre [21] also used Freeman's model in a study on CO_2/N_2 and CO_2/CH_4 separations in industrial applications. These three gas pairs are examined in detail particularly in view of the predicted upper bounds using Freeman's model, prior to Robeson's recently reported upper bounds.

3.5.1. CO_2/N_2

Previous presentations of CO_2/N_2 upper bounds were made by Shida [6,7], Hu [8], Khan [9] and Dai [25]. At the time there was no upper bound for this gas pair defined by Robeson. This upper bound was generated by using a slope of -0.34 as would have been predicted by $(d_{\text{N}_2} - d_{\text{CO}_2}) = 0.34$ and the most extreme point from Park and Paul [26] as described by Dai et al. [25]. Only the Khan upper bound is shown for clarity as the Dai upper bound is essentially co-linear. Several of the films of Shida, Hu and Khan were identified as being above the upper bound. Their data and upper bound are shown in Fig. 11, the slope of -0.30 approximates the value expected using $-\Delta_{A/B} = 0.34$. The theoretical upper bound used by these authors is well below the upper bound estimated by Cecopieri-Gomez and us using Freeman's model.

There are significant differences between Cecopieri-Gomez's [10] upper bound and that predicted in this work using Freeman's model with the Breck gas diameters and $f = 12,600 \text{ cal mol}^{-1}$, both in terms of the slope and intercept. Cecopieri-Gomez's tabulated value for $\log(\beta_{A/B})$, or the "origin ordinate" was given as 2.52 . This corresponds to the log of the selectivity at 1 Barrer, however in their Fig. 2, this was plotted as $\log(\beta_{A/B})$ at 0.1 Barrers. Cecopieri-Gomez

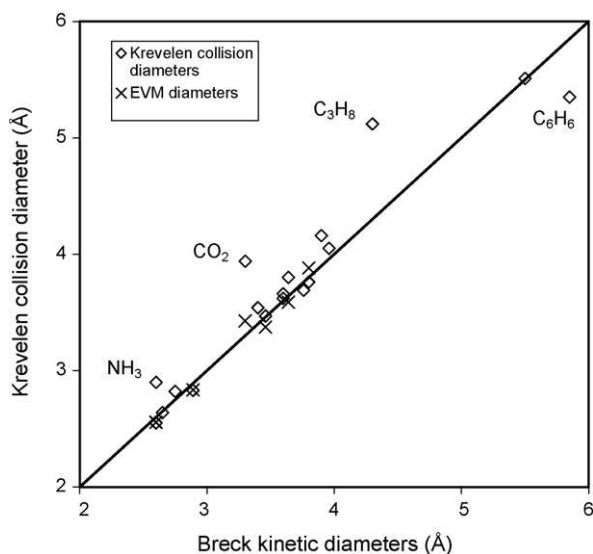


Fig. 10. Comparison of Krevelen's summary of collision diameters and Breck's summary of kinetic diameters. EVM diameters shown for comparison.

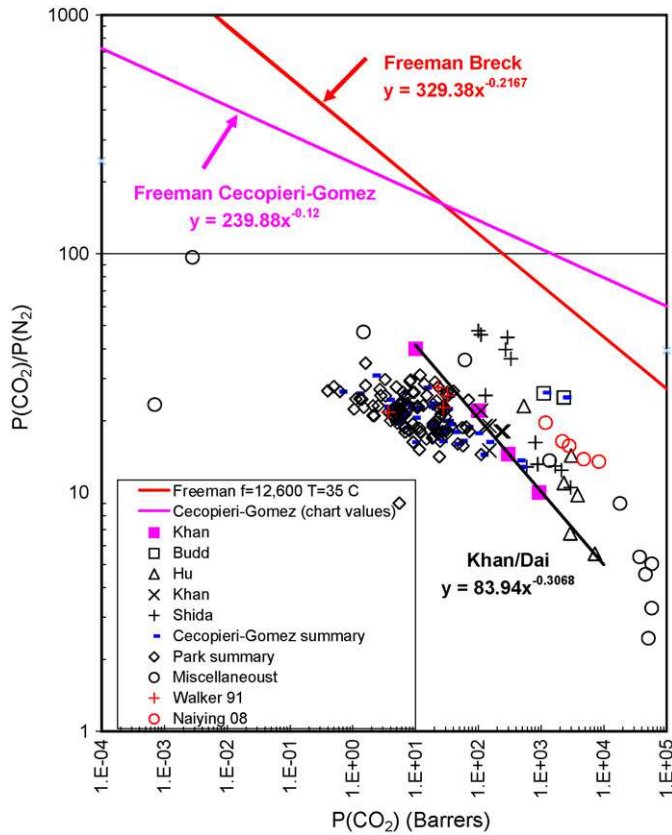


Fig. 11. Comparison of CO_2/N_2 theoretical upper bounds prior to Robeson [4].

et al. correctly reported the slope, or $-\Delta_{A/B}$ (their Table 5), as -0.217 , but from their Fig. 2 the slope was approximately -0.12 . Our upper bound matches that of Favre [21].

Robeson's current [4] data set for CO_2/N_2 and his upper bound are shown in Fig. 12. Also shown in this figure are the theoretical upper bounds from Freeman's model for two cases, the red line represents Freeman's model using the Breck diameters and an updated value for $f = 14,154 \text{ cal mol}^{-1}$ and the blue line is Freeman's model using the EVM estimates for the gas diameters. Freeman's model with the Breck diameters predicts a similar value for the pre-exponential constant (426.3) compared to Robeson's value (392.5). The slopes are also somewhat different at -0.217 for $\lambda_{A/B}$ using the Breck diameters and -0.346 for $\Delta_{A/B}$.

The EVM methodology yielded improvements in the match between $\Delta_{A/B}$ and $-1/n$, Fig. 7 for all gas pairs except CO_2/N_2 and CO_2/CH_4 . In all other cases, where the deviation from $\lambda_{A/B} = -1/n$ was significant and the improved correlation was obvious. The upper bound using Freeman's model and EVM are shown in blue, with a slope of -0.0961 . This is dramatically different from Robeson's well defined upper bound.

3.5.2. N_2/CH_4

Robeson's experimental data and N_2/CH_4 upper bound are shown in Fig. 13, along with several other theoretical upper bounds. Cecopieri-Gomez's calculated upper bound using Freeman's model is shown in pink, their slope (-0.13036 tabulated, -0.11 from their Fig. 3) confirms their use of the erroneous Freeman diameters for estimating $\lambda_{A/B}$. Using the Breck kinetic diameters one would predict a slope of -0.0898 . Their predicted selectivity at $\log(P_{\text{N}_2}) = -2$ is given as $\log(\alpha_{A/B}) = 1.39$ or $\alpha_{A/B} = 24.5$. This value could not be reproduced in this work, the largest value for $\alpha_{A/B}$ at 0.01 Barrers, using any combination $\lambda_{A/B}$ or $\Delta_{A/B}$, with Breck's or

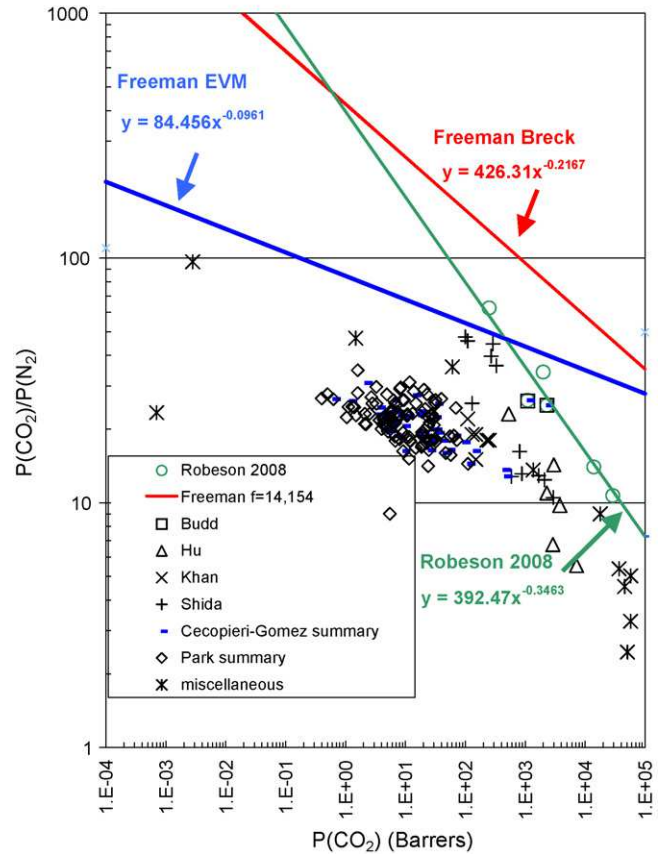


Fig. 12. Comparison of Robeson's [4] CO_2/N_2 upper bounds with predicted upper bounds according to (1) Freeman/Breck using $f = 14,154 \text{ cal mol}^{-1}$ and (2) Freeman using EVM.

Freeman's diameters, is 5.6. Using Freeman's diameters and $\lambda_{A/B}$, we calculated a selectivity of 1.22 at 0.01 Barrers, close to Cecopieri-Gomez's logarithm for $\log(\alpha_{A/B})$. For comparison purposes we show Freeman's upper bound, in red, predicted with the Breck diameters and $f = 12,600 \text{ cal mol}^{-1}$, which also corresponds to the values calculated by Favre [21]. The up-dated upper bound for the Freeman/Breck model using the 13 gas pairs and upper bounds of Robeson [4] is not shown for clarity but is just above the 1999 predictions. Both significantly under-predict the literature data.

The theoretical upper bound using Freeman's model with the new value for f and the EVM estimates of the gas diameters, predicts a slope of -0.171 . The EVM slope is a much better match than the Breck diameters (-0.090) and reasonably close to Robeson's slope of -0.221 . Freeman's EVM predictions of the selectivity are much better than with the Breck diameters, although they are still somewhat below actual experimental upper bound.

3.5.3. CO_2/CH_4

Cecopieri-Gomez et al. [10] modified Robeson's upper bound for the CO_2/CH_4 gas pair to include Budd's [27] data on PIMs. They also compared this to Freeman's prediction suggesting there was a good match between their new upper bound and that of Freeman.

Cecopieri-Gomez's predicted upper bound using Freeman's model (pink line in Fig. 14) was generated by using the erroneously reported gas diameters in [5] with $\lambda_{A/B} = -0.375$. Our predictions using the Breck diameters are shown for comparison purposes in red where $\lambda_{A/B} = -0.326$. Using Robeson's updated upper bounds and Freeman's new f as determined in this work ($14,154 \text{ cal mol}^{-1}$) left the slope unchanged but the pre-

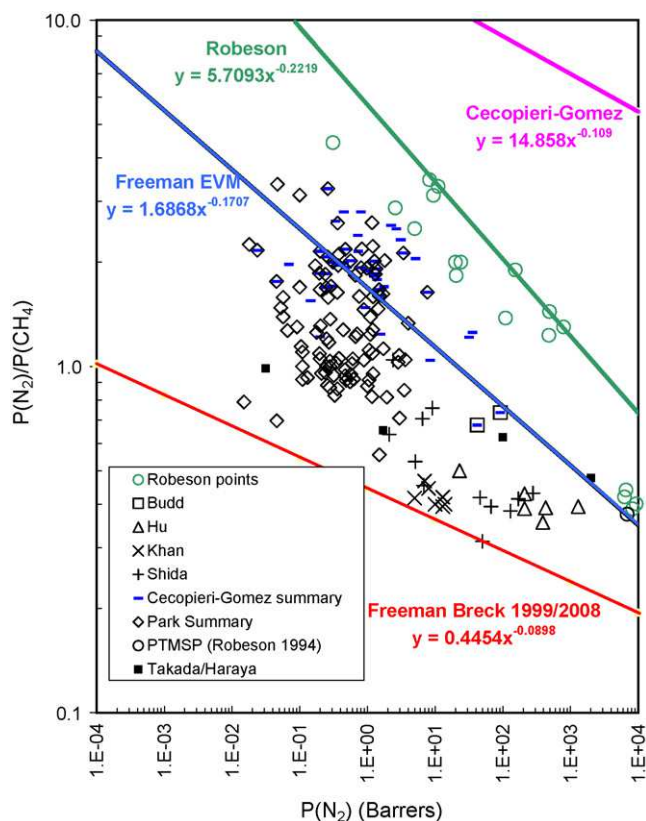


Fig. 13. N_2/CH_4 selectivity as a function of nitrogen permeability, experimental data and theoretical/experimental upper bounds as noted.

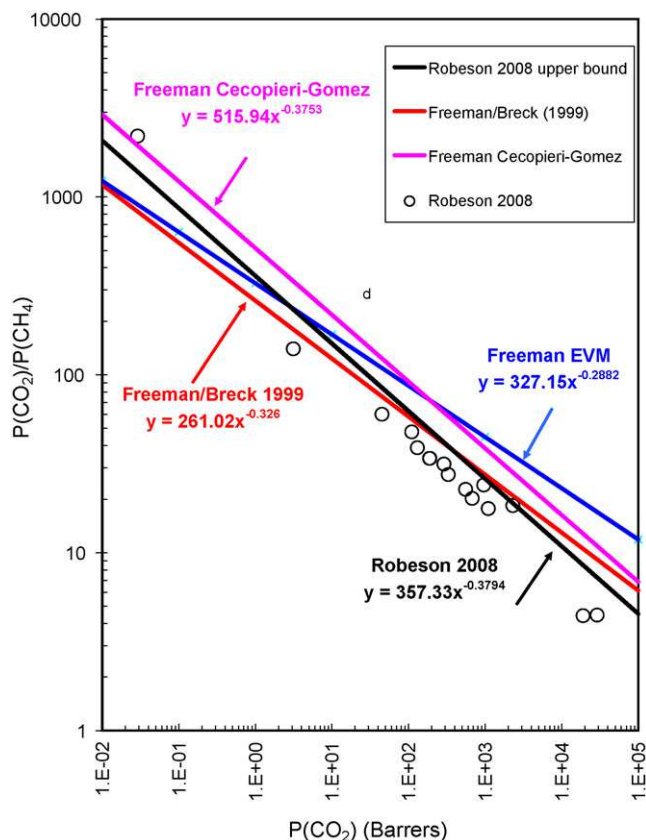


Fig. 14. Comparison of experimental data and upper bounds, and theoretical upper bounds for CO_2/CH_4 .

exponential constant increased from 261 to 355 (not shown for clarity).

Robeson left the slope of the upper bound virtually unchanged at -0.379 . Using the Breck diameters, the slope predicted by $\lambda_{A/B}$ is -0.326 agreeing reasonably well with Robeson's new slope. The EVM prediction of the upper bound's slope is -0.288 , a poorer prediction of $-1/n$ than the Breck diameters. For this gas pair, even $\Delta_{A/B} = 0.5$ is a poor predictor of $-1/n$.

4. Conclusions

Significant improvements of the quantitative prediction of the experimental upper bounds via Freeman's theoretical model were demonstrated using the Error in the Variable Method which allows for reasonable changes to the kinetic gas diameters of Breck [3]. The greatest change was associated with CO_2 , from 3.3 to 3.427 Å, an increase of less than 4%. Other gas diameters changed by less than 2.5%, and this change is typical of the differences between collision diameters and kinetic diameters for most gases in the literature.

It was observed that small changes in the gas diameters improved correlation of Robeson's slopes with Freeman's reduced kinetic diameters, $\lambda_{A/B} = (d_B/d_A)^2 - 1$. The parameter f , indicative of the activation energy for diffusion for a gas of zero diameter, was re-estimated from 14,154 to 16,909 cal mol $^{-1}$ (59.2 to 70.7 KJ mol $^{-1}$).

Theoretical predictions of the upper bounds for N_2/CH_4 , CO_2/N_2 and CO_2/CH_4 were compared to other literature values and errors were identified. The upper bound slope for the CO_2/N_2 gas pair predicted by the EVM based $\lambda_{A/B}$ slopes of Freeman's model (-0.096) was significantly different from Breck based $\lambda_{A/B}$ slope (-0.217) and Robeson's slope (-0.346). The EVM slope for CO_2/CH_4 was marginally poorer (-0.288) compared to the Breck/ $\lambda_{A/B}$ slope (-0.326) and Robeson's experimental slope of (-0.379). The N_2/CH_4 slope based on $\lambda_{A/B}$ improved from -0.090 (Breck) to -0.171 (EVM) compared to Robeson's upper bound slope of -0.222 .

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⁴ Freeman's original estimate of 12,600 cal mol $^{-1}$ was based on Robeson's 1991 and 1999 upper bounds. The value of 14,154 cal mol $^{-1}$ is based on Robeson's 2008 upper bounds by regression of $\beta_{A/B}$ on $k^{-1/n}$.

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