



The upper bound revisited

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ABSTRACT

The empirical upper bound relationship for membrane separation of gases initially published in 1991 has been reviewed with the myriad of data now presently available. The upper bound correlation follows the relationship $P_i = k\alpha_{ij}^n$, where P_i is the permeability of the fast gas, α_{ij} (P_i/P_j) is the separation factor, k is referred to as the “front factor” and n is the slope of the log–log plot of the noted relationship. Below this line on a plot of $\log \alpha_{ij}$ versus $\log P_i$, virtually all the experimental data points exist. In spite of the intense investigation resulting in a much larger dataset than the original correlation, the upper bound position has had only minor shifts in position for many gas pairs. Where more significant shifts are observed, they are almost exclusively due to data now in the literature on a series of perfluorinated polymers and involve many of the gas pairs comprising He. The shift observed is primarily due to a change in the front factor, k , whereas the slope of the resultant upper bound relationship remains similar to the prior data correlations. This indicates a different solubility selectivity relationship for perfluorinated polymers compared to hydrocarbon/aromatic polymers as has been noted in the literature. Two additional upper bound relationships are included in this analysis; CO₂/N₂ and N₂/CH₄. In addition to the perfluorinated polymers resulting in significant upper bound shifts, minor shifts were observed primarily due to polymers exhibiting rigid, glassy structures including ladder-type polymers. The upper bound correlation can be used to qualitatively determine where the permeability process changes from solution-diffusion to Knudsen diffusion.

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1. Introduction

The separation of gas mixtures employing polymeric membranes has been commercially utilized since the late 1970s. While the ability to separate gas mixtures was recognized much earlier, the commercial reality generated a significant amount of academic and industrial research activity. Membrane separation offers the advantage of low energy cost but has a high initial capital expense relative to the more established gas separation processes (e.g. adsorption and cryogenic distillation). With the increased cost of energy, membrane separation is reemerging as an economic option for various gas separations. Another area of emerging importance could be the recapture of CO₂ from industrial processes for reuse or sequestration, and the key separation (CO₂/N₂) for this area is included in the upper bound analysis. The key parameters for gas separation are the permeability of a specific component of the gas mixture and the separation factor. It was recognized that these are trade-off parameters as the separation factor generally decreases

with increasing permeability of the more permeable gas component. This trade-off relationship was shown to be related to an upper bound relationship where the log of the separation factor versus the log of the higher permeability gas yielded a limit for achieving the desired result of a high separation factor combined with a high permeability [1,2] for polymeric membranes. The upper bound relationship was shown to be valid for a multitude of gas pairs including O₂/N₂, CO₂/CH₄, H₂/N₂, He/N₂, H₂/CH₄, He/CH₄, He/H₂, H₂/CO₂ and He/CO₂. The upper bound relationship is expressed by $P_i = k\alpha_{ij}^n$, where P_i is the permeability of the more permeable gas, α is the separation factor (P_i/P_j) and n is the slope of the log–log limit. It was observed that $-1/n$ versus Δd_{ji} (where Δd_{ji} is the difference between the gas molecular diameters ($d_j - d_i$)) yielded a linear relationship. This observation revealed that the diffusion coefficient governed the upper bound limits. Group contribution methods were noted to predict both permeability and separation factors for aromatic polymers and demonstrated the structure–property relationships to optimize membrane separation [3–5].

The empirical upper bound relationship was shown to be theoretically predicted by Freeman [6] yielding good agreement with the experimental data previously compiled. The value of $-1/n$ was shown to be predicted by activation energy theory to be related to

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the gas molecular diameters by:

$$\frac{-1}{n} = \left(\frac{d_j}{d_i} \right)^2 - 1 = \left[\frac{d_j + d_i}{d_i^2} \right] (d_j - d_i) \quad (1)$$

As the term in the square brackets is reasonably constant, the value of $-1/n$ can be approximated by $(d_j - d_i)$ as demonstrated by the empirical relationship. The value of k was predicted by Freeman to be expressed by:

$$k^{-1/n} = \frac{S_i}{S_j} S_i^{-1/n} \exp \left\{ \frac{1}{n} \left[b - f \left(\frac{1-a}{RT} \right) \right] \right\} \quad (2)$$

where S_i and S_j are the solubility constants, a has a universal value of 0.64, b has a value of 9.2 for rubbery polymers and 11.5 for glassy polymers and f is a constant dependant upon the polymer and chosen to be 12,600 cal/mol to provide the best fit of the upper bound data. The value of k is referred to as the front factor for the upper bound relationship.

The data utilized for the initial upper bound relationship was from studies listing permeability data on various polymers with limited emphasis on membrane separation. Since the publication of the upper bound concept, a significant number of studies have been directed towards achieving and exceeding the upper bound for various gas pairs. The published data on membrane separation since 1991 now well exceeds the data utilized in the initial correlation and thus provides an excellent comparison of the validity of the upper bound concept and progress towards optimizing the structure/property relationships. This paper will tabulate the data since the initial publication and compare these results versus the original empirical upper bound data. As would be expected, the increased emphasis on membrane separation and the improved structure/property understanding from experimental studies and group contribution approaches has resulted in a number of observations equal to and exceeding the original upper bound. The comment in the original paper [1] "As further structure/property optimization of polymers based on solution/diffusion transport occurs, the upper bound relationship should shift slightly higher. The slope of the line would, however, be expected to remain reasonably constant." will be shown to be correct. The upper bound relationship is based on homogeneous polymer films and several approaches involving heterogeneous membranes have been demonstrated to easily exceed the upper bound. Surface modification is one method that clearly exceeds the upper bound limits as would be expected from the series resistance model as noted in an earlier paper [2]. UV surface modification [7], ion beam surface carbonization [8] and surface fluorination [9,10] are among the viable surface modifications yielding such behavior. Another approach initially proposed by Koros and co-workers [11] is typically referred to as a mixed matrix approach where selective molecular sieving structures are incorporated into a polymeric membrane. The mixed matrix approach has been reported in many studies [12–14] with results exceeding upper bound behavior. Another approach involving carbon molecular sieving membranes produced by carbonization of aromatic polymer membranes [15,16] also yields permselective properties well above the upper bound relationships. Molecular sieve membranes with well-defined uniform pore structure would, in essence, be considered to be the true upper bound limit for polymeric membranes. A recent paper on a novel approach to molecular sieving type structures [17] employed a solid-state thermal transformation of a polyimide to a benzoxazole-phenylene structure in the main chain yielding a material with remarkable CO₂/CH₄ separation. The thermal transformation yielded insoluble and infusible polymers with molecular sieving pore dimensions. Achievement of such molecular sieving structures in solution (or melt) processable polymeric

membranes is presently not possible and the upper bound correlation is an empirical relationship demonstrating the state-of-the-art for approaching true molecular sieving structures. Heterogeneous membranes, surface modified membranes and molecular sieve membranes are not considered in the same class of polymeric materials employed for establishing the upper bound correlation. It should be noted that several of the polymers comprising points on or near the present empirical upper bound have structural characteristics (e.g. ladder-type polymers) that start approach molecular sieving type structures.

The initial publication on the upper bound allowed for a determination of the state-of-the-art limits for polymeric gas membrane separation. With a specific goal in focus, a large number of studies have resulted with the objective to find polymeric structures which exceeded the empirical upper bound limits. While only modest increases have been observed with some of the gas pairs, there have been gas pairs where important shifts have occurred as discussed in the following data review. The major surprise involves the unique characteristics of a series of perfluorinated commercial polymers relative to He based gas pairs. The importance of ladder-type rigid polymers was at least partly recognized earlier and several examples of these polymers have allowed shifts in the upper bound.

2. Upper bound relationships

The protocol chosen for data selection involved a similar procedure as noted in the original paper [1]. Data were chosen where the polymer data were utilized from the same study with the same experimental film preparation conditions. Generally these involve soluble (or melt) processable polymers. While the vast majority of the data in the literature appears correct, there are situations where errors have been observed. These can include experimental errors, manuscript errors ("typos"), and insufficient significant figures in the permeability value(s). In several cases, the potential where such data errors or insufficient significant figures may be present are pointed out for the cases where the data comprise upper bound properties. In a few cases, data were not included where it has been noted by other studies in the literature to not be either correct or not reproducible. One of the specific polymers where extremely large variations have been reported include polyaniline variants. The overall literature is fortunately consistent in the permeability-separation factor data for polyaniline variants and these data were included. The number of papers where the data were obtained approached 300 thus inclusion of all the references is not presented except in the cases where the specific data points were in the range of or comprise the present upper bound. The specific polymeric structures of interest are not presented but rather the designation of the polymer class and relevant description. The interested reader should refer to the references noted for actual structure. Thermal transformation of polymers to yield molecular sieving structures is considered outside this analysis. These procedures will yield separation characteristics well above the upper bound correlation but also yield insoluble and infusible polymeric materials. It is noted that the "upper bound" line is determined empirically ("by eye") as in the original reference [1] with sufficient data to establish a realistic bound over several decades of permeability.

3. O₂/N₂ upper bound relationship

The O₂/N₂ separation remains the most studied gas pair with more data existing in the literature than any of the other pairs. The myriad of data points shows an intensity just below the original

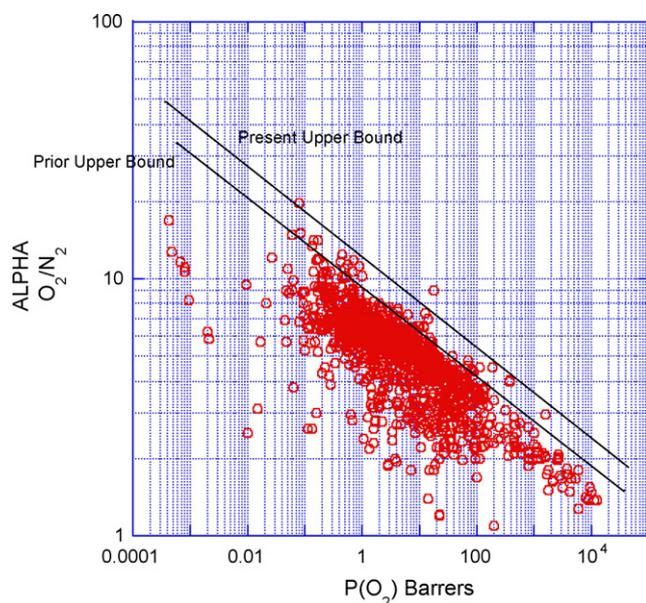


Fig. 1. Upper bound correlation for O₂/N₂ separation.

upper bound with a few data points emerging above allowing for a new upper bound relationship (Fig. 1). The key points defining the new upper bound are tabulated in Table 1. The position of the one data point above the present upper bound ($P(O_2) = 18$ barrers; $\alpha(O_2/N_2) = 9.0$) is questioned as only one significant figure was noted for nitrogen permeability. Two data points (PIM-1 and PIM-7) are worth noting as these are based on ladder polymeric structures (PIM = polymers of intrinsic microporosity) thus approaching the molecular sieving type structures necessary to yield high separation capabilities. Several polyimide variants also comprise points near on the upper bound.

4. CO₂/CH₄ upper bound relationship

The second most investigated gas pair for membrane separation is CO₂/CH₄. The myriad of data points since 1991 confirm the importance of this gas pair (Fig. 2). The ladder polymers (PIM-1 and PIM-7) noted above for O₂/N₂ separation also show good CO₂/CH₄ separation capabilities (Table 2). A series of rigid (also ladder-like) polymer variants has been recently published which exhibit

Table 1

Experimental data points close to the present empirical upper bound for O₂/N₂ separation

Polymer	$P(O_2)$ barrers	$\alpha(O_2/N_2)$	Reference
Polyimide (BPDA-ODA)	0.079	19.8	[18]
Polyimide (BTDA-ODA)	0.170	14.2	[18]
Polyetherimide (3d: cyclohexyl substituted indan unit in main chain)	0.90	11.2	[19,20]
Polypyrrolone (6FDA/PMDA (25/75)-TAB)	1.01	10.3	[21]
Sulfonated brominated PPO (60% DBr; 32.9% DSul.)	12.6	7.4	[22]
Sulfonated brominated PPO (60% DBr; 20.2% DSul.) (D = degree of)	14.0	7.0	[22]
Polyimide (BADBSBF-BTDA)	18.0	9.0	[23]
Poly[1-phenyl-2- <i>p</i> -(trimethylsilyl)phenylacetylene]	1550	2.98	[24]
PIM-1	370	4.0	[25]
PIM-7	190	4.5	[25]

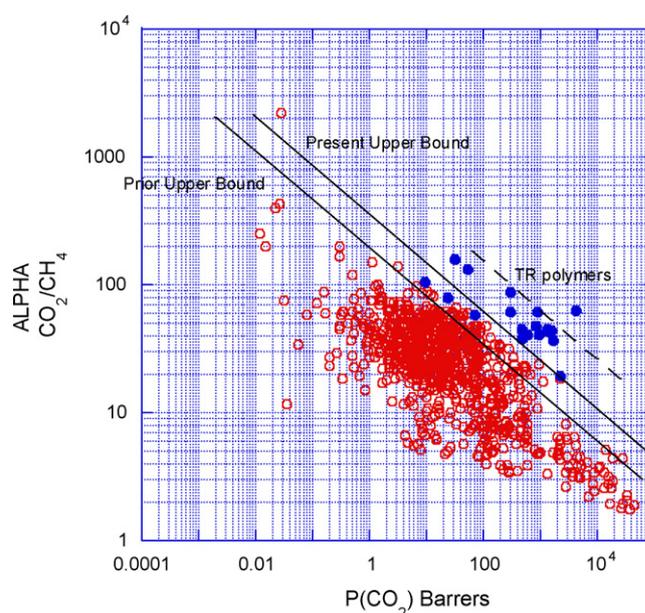


Fig. 2. Upper bound correlation for CO₂/CH₄ separation (TR, thermally rearranged; data from Ref. [17]).

even improved separation characteristics [17]. These polymers (TR (thermally rearranged)) comprising benzoxazole-phenylene or benzothiazole-phenylene structures in the main chain have been shown to exhibit exceptional CO₂/CH₄ separation capabilities. While these polymers are unique, they are considered in the class of molecular sieving materials produced by thermal reactions yielding insoluble, infusible materials. The present upper bound is determined without these data with the data on these polymers (closed circles) included for comparison. These polymers are truly unique and the analysis of structure [17] shows molecular sieving type pore dimensions with separation properties outside of the soluble (or melt) processible polymers comprising the upper bound correlations. It should be noted at high partial pressures (>5 atm) the CO₂ solubility may be in the range of film plasticization and thus the pure component separation values may be different than that actually observed for the CO₂ gas mixtures (CO₂/CH₄; CO₂/N₂; H₂/CO₂; He/CO₂) noted in this paper. This is less of a problem for the gases with lower boiling and critical temperatures.

Table 2

Experimental data points close to the present empirical upper bound for CO₂/CH₄ separation

Polymer	$P(CO_2)$	$\alpha(CO_2/CH_4)$	Reference
PVSH doped polyaniline	0.029	2200	[26]
Polypyrrole 6FDA/PMDA (25/75)-TAB	3.13	140	[21]
Polyimide TADATO/DSDA (1/1)-DDBT	45	60	[27]
Poly(diphenyl acetylene) 3a	110	47.8	[28]
Polyimide 6FDA-TMPDA/DAT (1:1)	130.2	38.9	[29]
Polyimide 6FDA-TMPDA/DAT (3:1)	187.6	33.9	[29]
Polyimide PI-5	190	33.9	[30]
Poly(diphenyl acetylene) 3e	290	31.5	[28]
Poly(diphenyl acetylene) 3f	330	27.5	[28]
Polyimide 6FDA-TMPDA	555.7	22.7	[29]
Polyimide 6FDA-durene	677.8	20.18	[31]
6FDA-based polyimide (8)	958	24	[32]
PIM-7	1,100	17.7	[25]
PIM-1	2,300	18.4	[25]
PTMSP	19,000	4.42	[33]
PTMSP	29,000	4.46	[33]

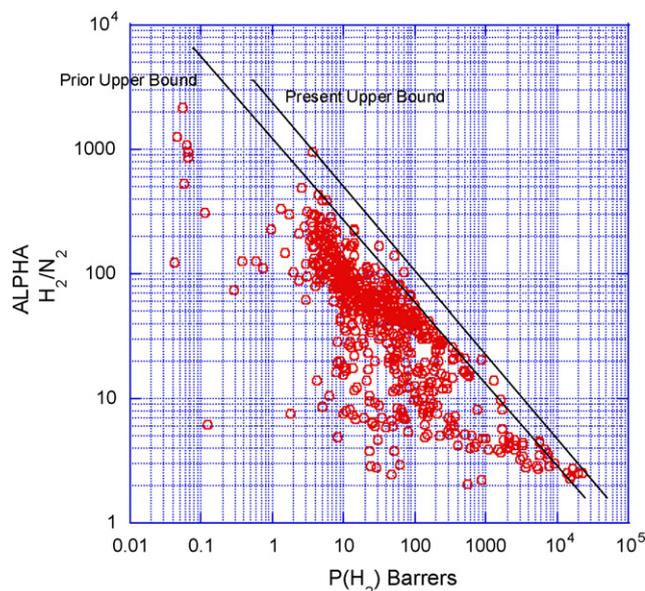


Fig. 3. Upper bound correlation for H₂/N₂ separation.

5. H₂/N₂ upper bound relationship

The H₂/N₂ upper bound relationship is shown in Fig. 3 with the key data points listed in Table 3. Although a large amount of data has been generated since 1991, a very minor shift in the upper bound relationship is noted. Again the ladder polymers, PIM-1 and PIM-7 comprise points on the upper bound as with the two gas pairs noted above. The other polymers include polyimide variants at the low permeability end with poly(trimethylsilylpropyne) data points at the high permeability end of the upper bound.

6. H₂/CH₄ upper bound relationship

The upper bound relationship for H₂/CH₄ is illustrated in Fig. 4 with the key data points tabulated in Table 4. As with H₂/N₂, only a modest shift in the upper bound position has been observed with a significant amount of data points just above the original upper bound. Polyimide variants comprise several of the upper bound positions at the low permeability end with poly(trimethylsilylpropyne) and variants at the high permeability end of the upper bound. Two perfluorinated polymers also have positions near the present upper bound and these polymers will be noted in a number of gas pair separations to be discussed in further sections of this paper.

Table 3

Experimental data points close to the present empirical upper bound for H₂/N₂ separation

Polymer	$P(\text{H}_2)$	$\alpha(\text{H}_2/\text{N}_2)$	Reference
Polybenzoxazinone imide (PBOI-2-Cu ⁺)	3.7	960	[34]
Polyimide (1,1-6FDA-DIA)	31.4	165	[35]
Polyimide (NTDA-BAPHFDS(H))	52	141	[36]
Poly(amide-imide) (3a)	72	103	[37]
PIM-7	860	20.5	[25]
PIM-1	1,300	14.1	[25]
Poly(trimethylsilylpropyne-co-phenylpropyne) (95/5)	20,400	2.5	[38]
Poly(trimethylsilylpropyne)	23,200	2.5	[38]

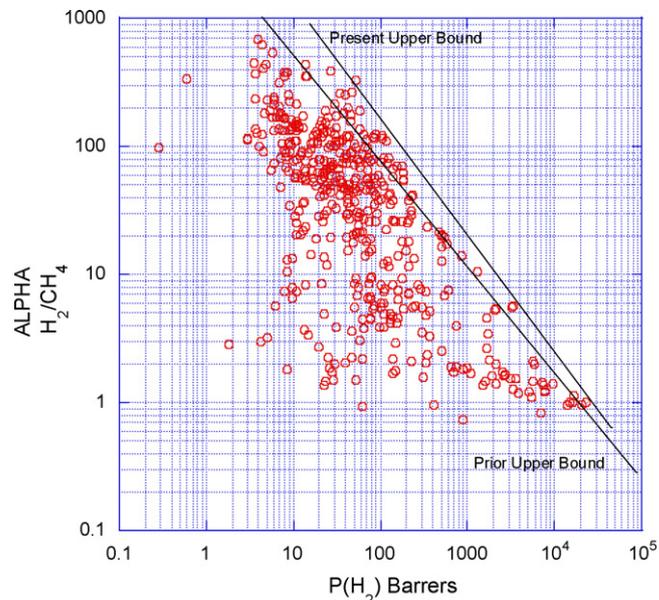


Fig. 4. Upper bound correlation for H₂/CH₄ separation.

Table 4

Experimental data points close to the present empirical upper bound for H₂/CH₄ separation

Polymer	$P(\text{H}_2)$	$\alpha(\text{H}_2/\text{CH}_4)$	Reference
Sulfonated polyimide (DAPHFDS(H))	52	325	[36]
Polyimide (6FDA-mMPD)	106	121	[39]
Polyimide (6FDA-DDBT)	156	78.8	[27]
Hyflon [®] AD60X	187	61.7	[40]
Teflon AF-2400	3,300	5.5	[41]
Poly(trimethylsilylpropyne)	17,000	1.13	[42]
Poly(trimethylsilylpropyne-co-phenylpropyne) (95/5)	20,400	0.953	[38]
Poly(trimethylsilylpropyne)	23,200	0.995	[38]

7. He/N₂ upper bound relationship

The upper bound relationship for He/N₂ separation is shown in Fig. 5 with the relevant data points listed in Table 5. The upper bound shift since 1991 is very minor in spite of the much larger dataset available presently. Polypyrrolone and polyimide variants offer data setting the position of the upper bound at lower permeability with poly(trimethylsilylpropyne) data near the higher permeability section of the upper bound. The fluorinated polymer (Hyflon[®] AD) offers good separation at intermediate permeability values.

Table 5

Experimental data points close to the present empirical upper bound for He/N₂ separation

Polymer	$P(\text{He})$	$\alpha(\text{He}/\text{N}_2)$	Reference
Polypyrrolone (6FDA/PMDA (10/90)-TAB)	22.5	622	[21]
Polypyrrolone (6FDA/PMDA (25/75)-TAB)	35.7	364	[21]
Polypyrrolone (6FDA-TAB)	166	64.4	[21]
Polyimide (6FDA-6FpDA:DABA (2:1))	142	65	[43,44]
Polyarylate (TMHFBA I/T)	182	64.8	[45]
Hyflon [®] AD	405	48.8	[40,46]
Hyflon [®] AD60X	476	50.3	[40]
Poly(trimethylsilylpropyne)	6500	0.97	[47]
Poly(trimethylsilylpropyne)	6500	1.03	[42]

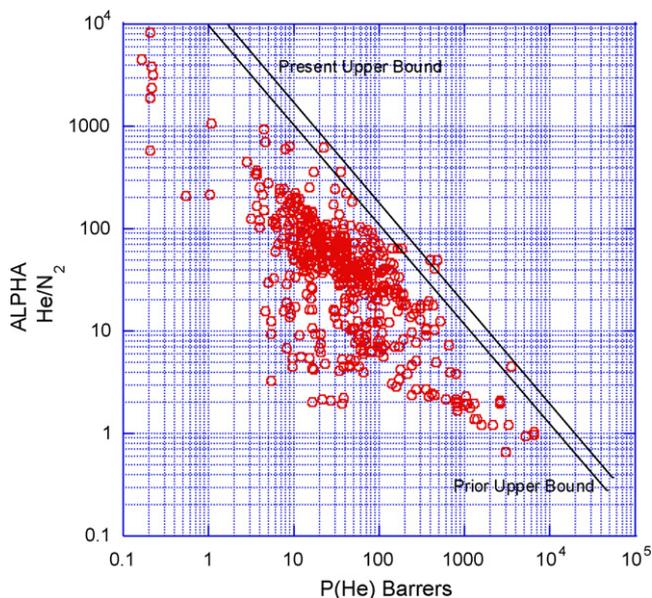


Fig. 5. Upper bound correlation for He/N₂ separation.

8. He/CH₄ upper bound relationship

The upper bound data for He/CH₄ separation is illustrated in Fig. 6 with the key data points tabulated in Table 6. Polypyrrolone data comprise the upper bound positions at the lower permeability range with poly(trimethylsilylpropyne) data at the upper end of the permeability. The intermediate data points of interest are all fluorinated polymers as will be noted in many of the separations involving He. A reasonable shift in the front factor has occurred with virtually no change in slope with the present data compared with the earlier upper bound data.

9. He/H₂ upper bound relationship

The upper bound data for He/H₂ is shown in Fig. 7 with the important data points tabulated in Table 7. A major change has

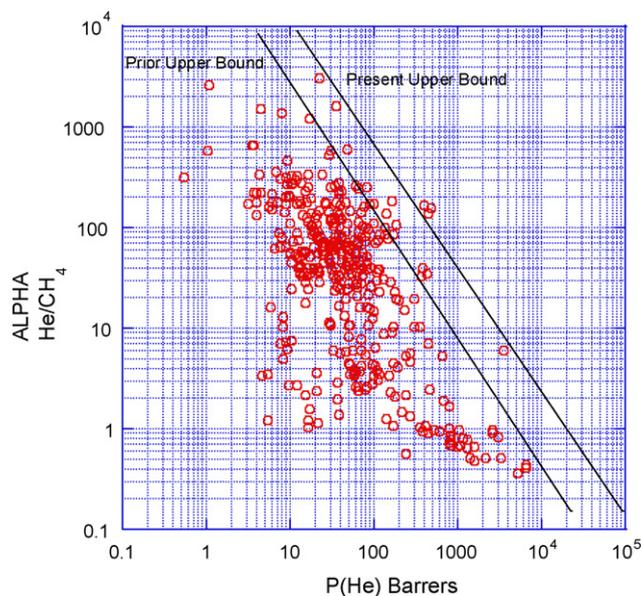


Fig. 6. Upper bound correlation for He/CH₄ separation.

Table 6

Experimental data points close to the present empirical upper bound for He/CH₄ separation

Polymer	$P(\text{He})$	$\alpha(\text{He}/\text{CH}_4)$	Reference
Polypyrrolone (6FDA/PMDA (10/90)-TAB)	22.5	3041	[21]
Polypyrrolone (6FDA/PMDA (25/75)-TAB)	35.7	1594	[21]
Polypyrrolone (6FDA-TAB)	166	184	[21]
Hyflon AD60X (solution cast)	369	32.9	[46]
Hyflon AD60X (melt pressed)	405	167	[40]
Hyflon AD60X (melt pressed)	405	169	[46]
Hyflon AD60X (solution cast)	455	136	[40]
Hyflon AD60X (solution cast)	476	157	[40]
Teflon AF-2400	3600	6.0	[41]
Poly(trimethylsilylpropyne)	6500	0.406	[47]
Poly(trimethylsilylpropyne)	6500	0.433	[42]

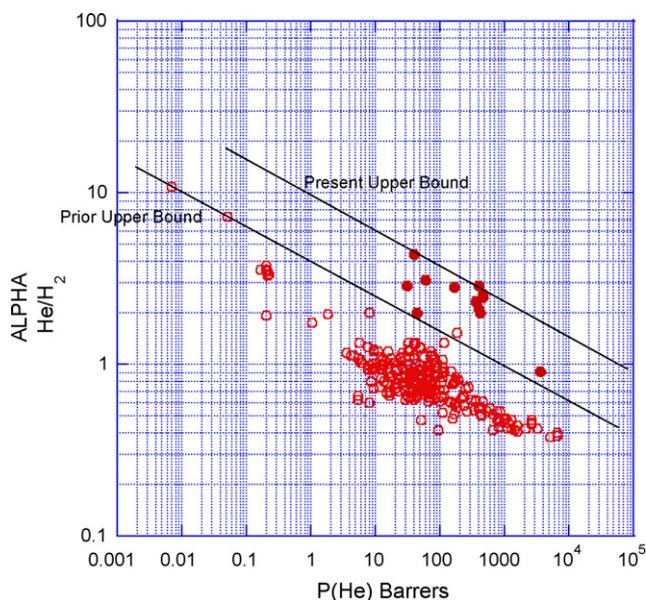


Fig. 7. Upper bound correlation for He/H₂ separation (solid circles are for perfluorinated polymers).

occurred since the prior upper bound position was noted. This is exclusively due to the appearance of data involving perfluorinated polymers such as those listed in Table 7. Without these data, the upper bound would have virtually remained unchanged. It is of interest to note that one of the data points (Nafion[®] 117) was noted in the earlier reference but was a singular data point well above the data existing at that time and not considered to be an upper bound position as sufficient data did not exist to allow correlation over several decades of permeability. With the present data,

Table 7

Experimental data points close to the present empirical upper bound for He/H₂ separation

Polymer	$P(\text{He})$	$\alpha(\text{He}/\text{H}_2)$	Reference
Viton [®] E60 fluoroelastomer	30.5	2.87	[48]
Nafion [®] 117	40.9	4.39	[49]
Viton [®] GF fluoroelastomer	43.9	2.01	[48]
Cytop [™]	170	2.8	[50]
Fluorinated polynorborene	185	1.52	[51]
Hyflon [®] AD60X (solution cast)	369	2.34	[46]
Hyflon [®] AD60	390	2.1	[50]
Hyflon [®] AD60X (melt pressed)	405	2.89	[40,46]
Hyflon [®] AD80	430	2.0	[50]
Hyflon [®] AD60X (solution cast)	455	2.45	[40]
Hyflon [®] AD60X (solution cast)	476	2.55	[40]
Teflon [®] AF-2400	3600	1.06	[41]

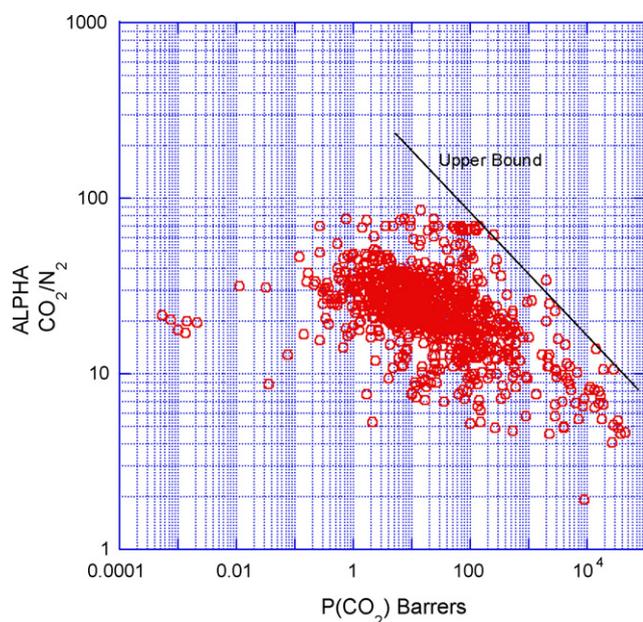


Fig. 8. Upper bound correlation for CO₂/N₂ separation.

it is obvious that particular data point comprises an upper bound position. While the front factor has moved significantly, the slope does not appear to have changed although sufficient data does not exist to clearly confirm that observation. As the slope remains constant but the front factor has shifted significantly, it appears that the perfluorinated polymers may exhibit a unique He/H₂ solubility relationship relative to hydrocarbon polymers.

10. CO₂/N₂ upper bound relationship

In an earlier reference [2] it was noted that a clear correlation of CO₂/N₂ did not exist with the data plotted according to the upper bound protocol. Now it appears that sufficient data exists to show a correlation as shown in Fig. 8 with key data points listed in Table 8. Several of the important data points include the PIM-1 and PIM-7 noted above for several other gas pairs. It has been noted in the literature that polymers containing poly(ethylene oxide) units have interesting CO₂/N₂ separation properties [52,53] and two of the polymers noted have similar units in their structure. Poly(trimethylgermylpropyne) and poly(trimethylsilylpropyne) offer upper bound properties at the higher permeability end of the data.

11. N₂/CH₄ upper bound relationship

The N₂/CH₄ separation characteristics were not correlated in the previous papers [1,2] although several more recent references have noted an upper bound relationship [50,56]. Plotting the available

Table 8
Experimental data points close to the present empirical upper bound for CO₂/N₂ separation

Polymer	$P(\text{CO}_2)$	$\alpha(\text{CO}_2/\text{N}_2)$	Reference
Poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene]	250	62.5	[54]
PIM-7	1,100	26.2	[25]
Modified poly(dimethylsiloxane)	2,000	34.2	[55]
PIM-1	2,300	25	[25]
Poly(trimethylgermylpropyne)	14,000	14	[33]
Poly(trimethylsilylpropyne)	29,000	10.7	[33]

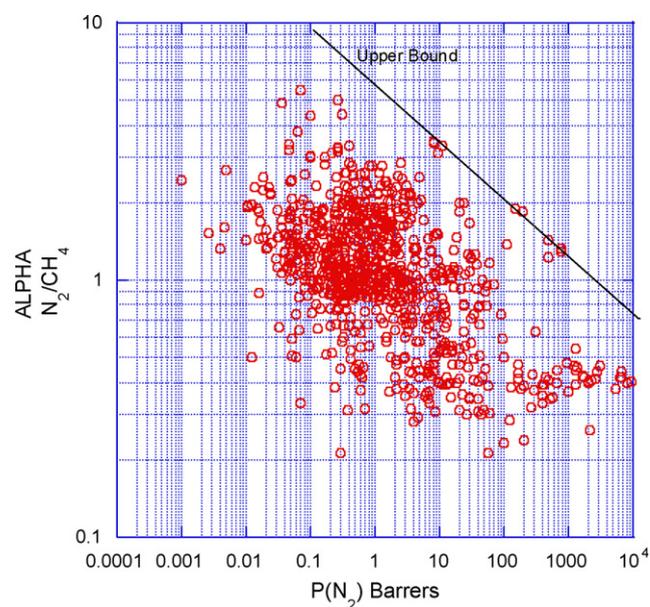


Fig. 9. Upper bound correlation for N₂/CH₄ separation.

data, an upper bound relationship is observed (Fig. 9) with important data points listed in Table 9. Most of the data points on or very near the upper bound are in the perfluorinated polymer family which are also noted for a number of the gas pairs in this paper which involve He. One data point ($P(\text{N}_2)=153$; $\alpha(\text{N}_2/\text{CH}_4)=1.9$) involving poly(trimethylsilylpropyne-co-phenylpropyne) (60/40) appears out of line with the rest of the copolymers in the reference cited as all the other copolymers and homopolymers exhibited $\alpha(\text{N}_2/\text{CH}_4)$ values less than 1.0. The CH₄ permeability was listed as 80.2 barrers where it would be more realistic to be 180.2 barrers to be consistent with the copolymer data trend. Without the fluorinated polymer data, another upper bound with a similar slope could be envisioned with data points listed in Table 9 which would be in the range of the value noted in the figure.

Table 9

Experimental data points close to the present empirical upper bound for N₂/CH₄ separation

Polymer	$P(\text{N}_2)$	$\alpha(\text{N}_2/\text{CH}_4)$	Reference
Polyimide (6FDA-mPDA)	0.31	4.43	[57]
Poly(pyrrolone)(6FDA-TAB)	2.58	2.87	[21,58]
Cytop™	5	2.5	[50]
Hyflon® AD60X (melt pressed)	8.3	3.46	[40,46]
Hyflon® AD60X (solution cast)	9.46	3.12	[40]
Hyflon® AD60X (solution cast)	11.1	3.31	[40]
Hyflon® AD	20	2.0	[50]
Hyflon® AD60X (solution cast)	20.5	1.83	[46]
Hyflon® AD80X	24	2.0	[50]
Teflon® AF-1600	110	1.38	[50]
Poly(trimethylsilylpropyne-co-phenylpropyne) (60/40)	153	1.9	[38]
Teflon AF 2400	480	1.23	[50,59]
Teflon AF 2400 (melt pressed)	490	1.44	[59]
Teflon AF 2400	790	1.30	[41]
Poly(trimethylsilylpropyne)	6300	0.42	[42]
Poly(trimethylsilylpropyne)	6600	0.44	[60]
Poly(trimethylsilylpropyne-co-phenylpropyne) (95/5)	8300	0.388	[38]
Poly(trimethylsilylpropyne)	9350	0.401	[38]

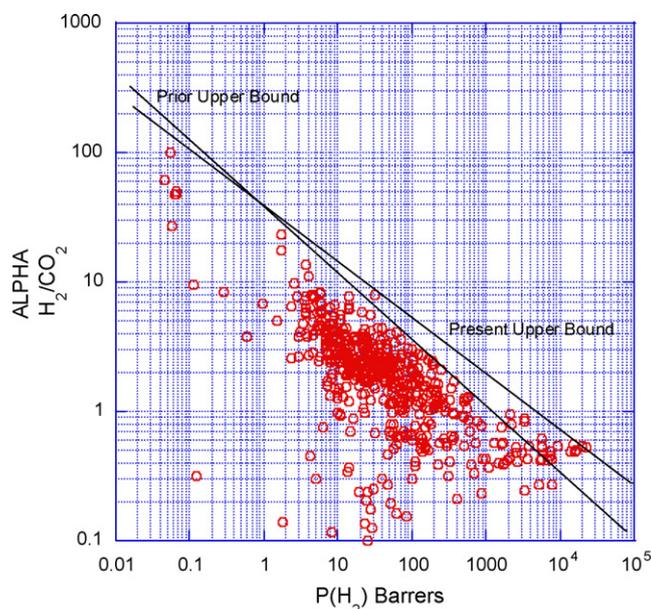


Fig. 10. Upper bound correlation for H₂/CO₂ separation.

12. H₂/CO₂ upper bound relationship

The earlier upper bound relationship for H₂/CO₂ was published in Ref. [2]. The data compiled in this study are illustrated in Fig. 10 with key data points listed in Table 10. A limited shift in the upper bound relationship is noted, primarily a slight slope change resulting from a number of poly(trimethylsilylpropyne) data points at the higher permeability end of the relationship. The limited number of data points at the lower permeability area of the dataset may have skewed the slope versus the original correlation [2].

13. He/CO₂ upper bound relationship

The initial He/CO₂ upper bound relationship was from Ref. [2]. The present data are illustrated in Fig. 11 with important data positions tabulated in Table 11. A shift in position has been observed primarily due to the perfluorinated polymer data now in the literature. These polymers have generally resulted in front factor shifts for all gas pairs comprising He. Without these data only a very small change in the upper bound position would be observed.

14. Upper bound analysis

The key variables of the upper bound curves from the upper bound relationships ($P_i = k\alpha_{ij}^n$) are tabulated in Table 12 for the present upper bound data versus the prior upper bound data.

Table 10

Experimental data points close to the present empirical upper bound for H₂/CO₂ separation

Polymer	P(H ₂)	α (H ₂ /CO ₂)	Reference
Liquid crystalline polyester (HBA/HNA 30/70)	0.0545	100.9	[61]
Polyaniline (redoped)	1.753	23.1	[62]
Polyimide(1,1-6FDA-DIA)	31.4	8.05	[35]
Poly(trimethylsilylpropyne)	13,900	0.495	[63]
Poly(trimethylsilylpropyne)	16,200	0.489	[47]
Poly(trimethylsilylpropyne-co-phenylpropyne)	20,400	0.538	[38]
Poly(trimethylsilylpropyne)	23,300	0.53	[38]

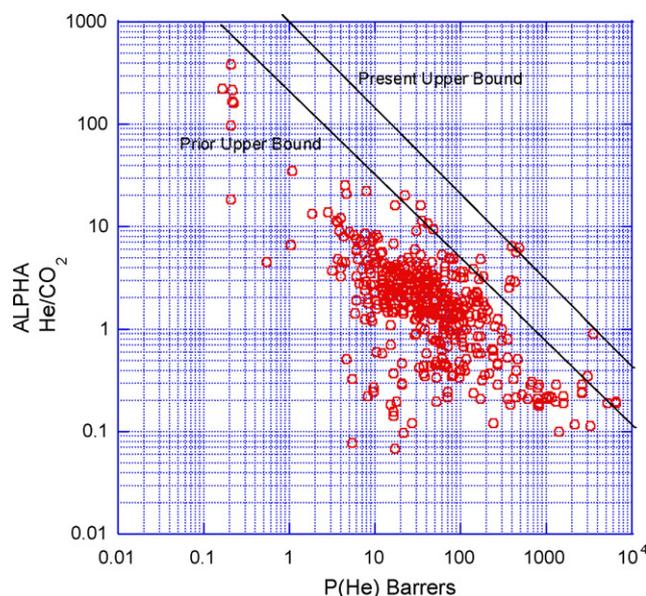


Fig. 11. Upper bound correlation for He/CO₂ separation.

The slope of the upper bound, n , has been previously shown to be a linear relationship of $-1/n$ versus $d_j - d_i$. The gas diameter chosen was the Lennard-Jones kinetic diameter reported by Breck [65]. The present data versus prior data from Table 12 are illustrated in Fig. 12a and b. Overall, very minor differences are observed with the present data showing a very slightly better fit and also intercepting the 0, 0 position on the x -, y -axis for Fig. 12a. As predicted by theory, the slope of this relationship is almost one. In both data sets, the poorest fit is with the He/CH₄ upper bound slope. As only two significant figures are present diameters for these gases from the noted reference, modest variation could be attributed to this situation. In Fig. 12b, $-1/n$ is plotted versus $(d_j/d_i)^2 - 1$ as predicted from theory. The present data shows a slightly better fit than the prior data in both plots (higher R values). The data fit is slightly better in Fig. 12b than with $d_j - d_i$ although the line does not pass through the 0,0 x -, y -axis position. This suggests that the values of the gas kinetic diameters are not exact but that the difference between the gas diameters is exact. This indicates that the kinetic diameter values determined from zeolite data may uniformly be off relative to polymer diffusion.

The upper bound will not extend indefinitely as the permeability of the fast gas increases. The permeability process will change from solution-diffusion to Knudsen diffusion separation as the pore size increases. The diffusion separation contribution to the separation factor will change from molecular sieving to Knudsen diffusion.

Table 11

Experimental data points close to the present empirical upper bound for He/CO₂ separation

Polymer	P(He)	α (He/CO ₂)	Reference
Polypyrrolone (6FDA/PMDA (10/90)-TAB)	22.5	20.3	[21]
Polyimide (6FDA-durene) (crosslinked)	34.4	16.1	[64]
Cytop™	170	4.86	[50]
Hyflon® AD (solution cast)	369	2.54	[46]
Hyflon® AD60	390	3.0	[50]
Hyflon® AD80	430	2.87	[50]
Hyflon® AD60X (melt pressed)	405	6.43	[40,46]
Hyflon® AD60X (solution cast)	455	5.67	[40]
Hyflon® AD60X (solution cast)	476	6.18	[40]
Teflon® AF-2400	3650	0.923	[41]
Poly(trimethylsilylpropyne)	5250	0.187	[63]
Poly(trimethylsilylpropyne)	6500	0.196	[47]

Table 12
Tabulation of the values of the front factor k and the upper bound slope n

Gas pair	k (barrers)	n
Prior upper bound data (1,2)		
O ₂ /N ₂	389,224	-5.800
CO ₂ /CH ₄	1,073,700	-2.6264
H ₂ /N ₂	52,918	-1.5275
H ₂ /CH ₄	18,500	-1.2112
He/N ₂	12,500	-1.0242
He/CH ₄	5,002	-0.7857
He/H ₂	960	-4.9535
CO ₂ /N ₂	NA	NA
N ₂ /CH ₄	NA	NA
H ₂ /CO ₂	1200	-1.9363
He/CO ₂	705	-1.220
H ₂ /O ₂	35,760	-2.277
He/O ₂	4,600	-1.295
Present upper bound data		
O ₂ /N ₂	1,396,000	-5.666
CO ₂ /CH ₄	5,369,140	-2.636
H ₂ /N ₂	97,650	-1.4841
H ₂ /CH ₄	27,200	-1.107
He/N ₂	19,890	-1.017
He/CH ₄	19,800	-0.809
He/H ₂	59,910	-4.864
CO ₂ /N ₂	30,967,000	-2.888
N ₂ /CH ₄	2,570	-4.507
H ₂ /CO ₂	4,515	-2.302
He/CO ₂	3,760	-1.192
H ₂ /O ₂	NA	NA
He/O ₂	NA	NA

The upper bound relationship is specifically a diffusion-dominated relationship as D_i/D_j decreases with permeability whereas the solubility selectivity ($k_s = S_i/S_j$) is considered invariant with permeability. The Knudsen diffusion selectivity will vary inversely with the square root of the molecular weight of the gas; thus,

$$\frac{D_i}{D_j} = \sqrt{\frac{M_j}{M_i}} \quad (3)$$

The position on the upper bound where $D_i/D_j = (M_j/M_i)^{1/2}$ will be where $\alpha_{ij} = k_s D_i/D_j = k_s (M_j/M_i)^{1/2}$. The selectivity separation factor, k_s , can be estimated by several relationships as noted by Freeman [6,66]:

$$\ln S_i = a + 0.016T_c \text{ thus } \ln \left(\frac{S_i}{S_j} \right) = 0.016(T_{ci} - T_{cj}) \quad (4)$$

where T_c is the critical temperature of the gas and

$$\ln S_i = b + 0.023(\varepsilon_i/k) \text{ thus } \ln(S_i/S_j) = 0.023[(\varepsilon_i/k) - (\varepsilon_j/k)] \quad (5)$$

where ε/k is the Lennard-Jones temperature. In essence, the analysis is simply determining the permeability value on the upper bound curve where the D_i/D_j value is equal to that predicted for Knudsen diffusion. Note that the Knudsen diffusion solubility selectivity is unity and thus the value of α_{ij} is the ratio of the diffusion coefficients. The transition from solution-diffusion to Knudsen diffusion is where the value of D_i/D_j for solution-diffusion is the same as predicted for Knudsen diffusion. However, the upper bound analysis for solution-diffusion has a contribution of solubility selectivity which must be taken into account in order to directly compare the D_i/D_j values from the respective separation processes.

The transition from solution-diffusion to Knudsen diffusion should occur at similar effective pore diameters for the various gas pairs with some variation based on the specific gas diameters. At equivalent pore diameter, there will be some variation in the permeability value of the fast gas. However, at large pore diameter, the permeability values are in reasonable proximity of each other as noted for PTMSP where variation in permeability range from 6500 barrers for He to 33,000 barrers for CO₂ [47]. This is at least a consequence that the solubility selectivities are the reverse of the diffusion selectivities for the gas pairs shown except in the case of O₂/N₂ and CO₂/CH₄. The above analysis was employed to determine the permeability value of the fast gas where the diffusion selectivity decreases to the value predicted by the Knudsen relationship. The values shown in Tables 13a and 13b show that the critical temperature prediction of the solubility selectivity allows for tighter range in permeability where Knudsen diffusion values are observed than the Lennard-Jones temperature predictions. This agreement is believed to be due to the better prediction of solubility selectivity relative to the upper bound data. The very approximate values of the solubility selectivities obtained using these values can lead to significant variation in the predicted permeability where Knudsen diffusion begins. It should also be noted that surface diffusion can occur between solution-diffusion and Knudsen diffusion at intermediate pore diameters for the more condensable gases and may be relevant for CO₂ based separations at lower temperature and higher pressures.

These results show that the most permeable of polymeric membranes, PTMSP, is close to the pore diameter where molecular sieving selectivity will transition to Knudsen diffusion selectivity. The pore diameter of PTMSP is in the range of 0.9–1.2 nm [67,68].

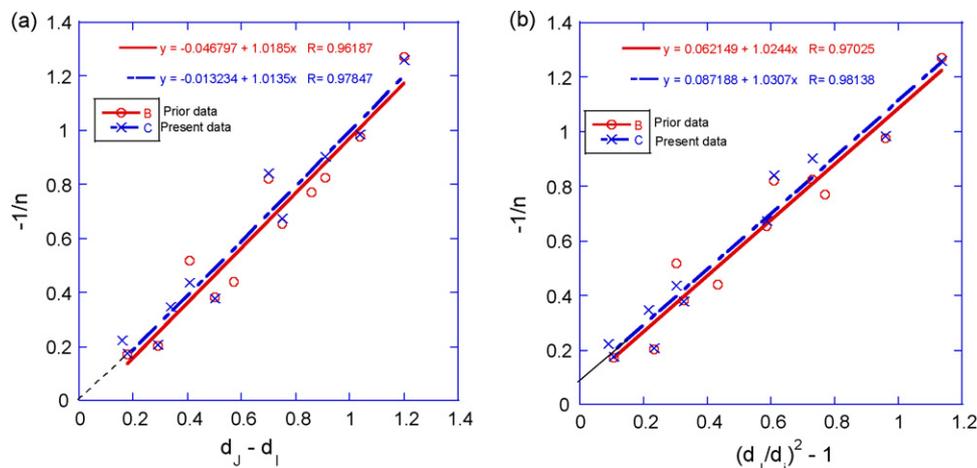


Fig. 12. (a and b) Correlation of the upper bound slope with gas diameter data on the specific gas pairs.

Table 13aTransition permeability to Knudsen diffusion using critical temperature to calculate k_s

Gas pair	$S_i/S_j = k_s$	$(M_j/M_i)^{1/2}$	$k_s(D_i/D_j) = k_s(M_j/M_i)^{1/2}$	$P_i(\text{barrers})$
O ₂ /N ₂	1.575	0.9354	1.473	156,500
H ₂ /N ₂	0.225	3.742	0.842	126,130
H ₂ /CH ₄	0.0803	2.828	0.227	140,400
He/N ₂	0.144	2.646	0.381	53,070
He/CH ₄	0.0515	2.0	0.103	124,620
He/H ₂	0.641	0.707	0.453	2,817,000
He/H ₂ (prior data)	0.641	0.707	0.453	48,510
CO ₂ /CH ₄	6.151	0.603	3.709	169,520
N ₂ /CH ₄	0.357	0.756	0.270	939,300
CO ₂ /N ₂	17.24	0.7977	13.75	15,980
He/CO ₂	0.00837	3.3166	0.02776	269,440
H ₂ /CO ₂	0.01306	4.6904	0.06123	2,799,000
H ₂ /CO ₂ (prior data)	0.01306	4.6904	0.06123	267,900

The transition range from solution-diffusion to Knudsen diffusion is expected to begin in this range as molecular sieving separation is generally considered to be within 2–3 molecular kinetic diameters and transition to Knudsen diffusion above that value. The addition of nanoscale fumed silica to poly(4-methyl-2-pentyne) (PMP) [69] and PTMSP [70] has been shown to yield increased free volume and gas permeability. With PTMSP, it was noted that this increase in free volume results in diffusion coefficient and selectivity data suggesting a transition from solution-diffusion to Knudsen diffusion.

The high permeability value for the onset of Knudsen diffusion of the present He/H₂ data relative to the prior data is a consequence of the perfluorinated polymers significantly increasing the front factor. This indicates these polymers may have unique selectivity separation for specific gas pairs (particularly those based on He). They are also the major data points setting the upper bound for N₂/CH₄ with the same observation of higher onset permeability than the other gas pairs. The H₂/CO₂ upper bound curve for the prior data has a better agreement with this analysis than the present data. In spite of the variation in the data, it is apparent that the upper bound relationship allows for a reasonable prediction of the transition from solution-diffusion to Knudsen diffusion.

15. Discussion of results

In many cases, the empirical upper bound relationship based on data available in 1991 has not significantly changed even though emphasis has been placed on structural modifications designed to improve the separation capabilities. Of the potential gas pairs

Table 13bTransition permeability to Knudsen diffusion using Lennard-Jones temperature to calculate k_s

Gas pair	$S_i/S_j = k_s$	$(M_j/M_i)^{1/2}$	$k_s(D_i/D_j) = k_s(M_j/M_i)^{1/2}$	$P_i(\text{barrers})$
O ₂ /N ₂	2.289	0.9354	2.1409	18,700
H ₂ /N ₂	0.7765	3.742	2.9057	20,050
H ₂ /CH ₄	0.129	2.828	0.365	83,000
He/N ₂	0.2470	2.646	0.6535	30,655
He/CH ₄	0.0411	2.0	0.0822	149,470
He/H ₂	0.318	0.707	0.2249	85,050,000
He/H ₂ (prior data)	0.318	0.707	0.2249	1,556,600
CO ₂ /CH ₄	2.881	0.603	1.737	1,252,000
N ₂ /CH ₄	0.166	0.756	0.1257	29,460,000
CO ₂ /N ₂	17.32	0.7977	13.82	15,750
He/CO ₂	0.01426	3.3166	0.0473	142,800
H ₂ /CO ₂	0.0448	4.6904	0.2102	163,600
H ₂ /CO ₂ (prior data)	0.0448	4.6904	0.2102	24,590

P_i for Tables 13a and b represents the permeability on the upper bound curve where the solution-diffusion D_i/D_j value is equal to that predicted for Knudsen diffusion.

comprising He, H₂, O₂, N₂, CO₂ and CH₄, two additional pairs have been added to those already noted in prior papers [1,2], namely, CO₂/N₂ and N₂/CH₄ both of which could have relevance in commercial applications. A previous attempt to correlate a CO₂/N₂ upper bound relationship was not successful but with the myriad of data presently available an upper bound correlation appears to exist. N₂/CH₄ separation data were correlated as several papers have discussed the upper bound relationship in presentation of their data.

The slope of the upper bound as predicted in the initial paper [1] has not significantly changed for the gas pairs presented. In several cases, the “front factor” k has shown more than just minor increases.

The major changes that are observed for specific gas pairs are detailed as follows. The major shift observed involves the shift in the “front factor” for the He/H₂ upper bound. The data points comprising the upper bound and many close to the upper bound are from perfluorinated aliphatic polymers including Nafion® (tetrafluoroethylene-sulfonated perfluoroether copolymer), perfluorinated elastomers (e.g. Viton®), Teflon® AF series (copolymers of tetrafluoroethylene and 2,2-bisfluoromethyl-4,5-difluoro-1,3-dioxole), Hyflon® AD series (copolymers of tetrafluoroethylene and 2,2,4-trifluoro-5 trifluoromethoxy-1,3 dioxole) and Cytop™ (perfluoro(4-vinyl-1-butene)). Without the inclusion of these data, the He/H₂ upper bound would be virtually unchanged. The data from these perfluorinated aliphatic polymers also comprise the majority of data points on or near the upper bound for several other gas pairs (N₂/CH₄; He/CO₂; He/CH₄). The addition of data for these fluorinated polymers results in the major change in observed membrane separation upper bound properties since the initial publication. Without these data, the upper bound shifts for all the various gas pairs previously published would have been quite minor. This difference appears primarily related to differences in the front factor, k . This indicates that the solubility selectivity, k_s , is different for the perfluorinated polymers than typical hydrocarbon based polymers. This has been shown to be the case from the value of the slope N in the expression below:

$$\log S = M + N(T_b) \quad (6)$$

where T_b is the gas boiling temperature. For hydrocarbon polymers the values of N are reasonably constant; whereas for the perfluorinated polymers noted above, the values of N are also reasonably constant but different from the hydrocarbon polymers [50].

The perfluorinated polymers offer unique membrane separation characteristics for the gas pairs noted with performance above the myriad of polymer structures outside of this family. The perfluorinated polymers noted above are all commercial variants. Perhaps even improved results could be achieved with a detailed structure property study involving additional fluorinated monomers.

A recent publication [17] involving a rigid ladder-like polymer has provided a series of data points above the original upper bound for CO₂/CH₄ yielding the appearance of a similar slope but a major shift in the front factor. These data were not included in the present upper bound analysis as these polymers are insoluble and infusible with structural characteristics similar to molecular sieving systems such as carbon molecule sieves. A modest shift in the CO₂/CH₄ upper bound curve has occurred primarily due to several data points on a ladder polymer [25].

A number of publications in the literature have noted surface modification can lead to better than “upper bound” performance as would be expected from the series resistance model. The upper bound relationship is based on homogeneous films and thus surface modified systems are not comparable. However, a situation does exist for thin films of glassy polymers where aging results in significant permeability decrease often with selectivity increase [71,72]. This is the result of free volume diffusing out of the film surface resulting in densification and thus decreasing permeability.

While this should not be a problem for thick films (within the time scale of film preparation and testing) from which almost all of the data utilized in the upper bound correlation are based, it could be relevant for the dense layer thickness employed for commercial membrane separation films (range of 100 nm).

16. Conclusions

A review of the permeability data since 1991 when the initial upper bound relationship was proposed has been conducted to determine the shift in the upper bound position for various gas pairs chosen from combination of He, H₂, O₂, N₂, CO₂ and CH₄. The results show only modest shifts from the 1991 upper bound correlation for O₂/N₂, H₂/N₂, H₂/CH₄, CO₂/CH₄ and He/N₂. From the 1994 correlations of H₂/CO₂ and He/CO₂, H₂/CO₂ shows only a minor change. Significant shifts in the position of the upper bound line were observed for He/CH₄, He/CO₂ and He/H₂. The shifts in the upper bound for He/CO₂, He/CO₂ and He/H₂ were due to aliphatic fluorocarbon polymers for which very limited data existed in 1991. The fluorinated polymers noted are commercial systems including Nafion[®], Hyflon[®], Viton[®], Cytop[™] and Teflon[®] AF variants. These polymers exhibit an uncharacteristic higher He permeability relative to the other gas components of the pairs noted. The slope of the upper bound relationship remained reasonably constant even when shifts in the position were observed as predicted in the initial upper bound reference. Without the data on these perfluorinated polymers, the upper bound shifts for all the gas pairs would be minor. From the comparison of the data intercept with the expected Knudsen diffusion transition, it is suggested that the solubility relationship for He/H₂ may be different in the perfluorinated polymers than the other polymers comprising the data.

Two new upper bound correlations, CO₂/N₂ and N₂/CH₄ were presented and the N₂/CH₄ upper bound data points were comprised of the perfluorinated polymers noted above. While it was expected that ladder-type rigid polymers had the potential of upper bound characteristics due to molecular sieving type structures, the unique characteristics of the perfluorinated polymers noted was unexpected. The importance of rigid glassy polymers (polyimides, polypyrrolones) has been well-recognized as well as the potential of ladder-type polymers. The number of ladder-type polymers experimentally evaluated to date is relatively few thus further synthesis/permeability characterization should allow even more promising systems relative to membrane separation.

Analysis of the upper bound lines allows a qualitative prediction on the onset of Knudsen diffusion. This analysis indicates that poly(trimethylsilylpropyne) is within the range of this transition from solution-diffusion to Knudsen diffusion separation.

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