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(54) **Title: ZEOLITE-LIKE METAL-ORGANIC FRAMEWORK MEMBRANE**

(57) **Abrégé/Abstract:**

Metal organic framework membranes can be used in gas separation applictions.

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(54) **Title**: ZEOLITE-LIKE METAL-ORGANIC FRAMEWORK MEMBRANE

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ZEOLITE-LIKE METAL-ORGANIC FRAMEWORK MEMBRANE

PRIORITY CLAIM

This application claims priority to U.S. Provisional Application No. 61/910,152, file November 29, 2013, which is incoporated by reference in its entirety.

TECHNICAL FIELD

The invention features metal-organic framework materials.

BACKGROUND

Metal-organic framework materials can be constructed to have a variety of material properties.

SUMMARY

In one aspect, a thin film membrane can include a zeolite-like metal-organic framework, wherein the thin film membrane has a selectivity for CO_2 over H_2. The thin film membrane can be anionic. The thin film membrane can have a zeolite-like structure, for example, a structure having a sodalite topology. The thin film membrane can be on a support, which can be a porous ceramic substrate, for example, a porous alumina substrate.

In another aspect, a method of separating gases can include passing a mixture of gasses through a thin film membrane comprising a zeolite-like metal-organic framework, wherein the thin film membrane has a selectivity for CO_2 over H_2.

In certain embodiments, the permeance of the thin film membrane can be higher for CO_2 than for other gases. The permeance of the thin film membrane can be higher for CO_2 than for CH_4. The thin film membrane can have a separation factor of at least 3 for CO_2 over CH_4. The permeance of the thin film membrane can be higher for CO_2 than for H_2. The thin film membrane can have a selectivity of at least 4 for CO_2 over H_2. The permeance of the thin film membrane can be higher for CO_2 than for N_2. The thin film membrane can have a separation factor of at least 6 for CO_2 over N_2. The permeance of the thin film membrane can be higher for CO_2 than for O_2. The thin film membrane can have a separation factor of at least 4 for CO_2 over O_2.

In certain embodiments, the thickness of the thin-film membrane can be between 20 and 100 μm. The thin film membrane can have a high degree of crystallinity. The zeolite-like metal-organic framework can include a linker and a metal. The metal can include a metal, such as a transition metal, group 13 metal or a lanthanide metal, for example, Indium, Yttrium, or Cadmium, or a combination thereof. The linker can include a heteroaromatic group, such as a nitrogen-containing heteroaromatic group, for example, imidazole or pyrimidine moiety.

In another aspect, a method for preparing a zeolite-like metal-organic framework membrane can include contacting a substrate with a solution mixture of carboxylic acid, an imidazole, a metal salt, and a nitric acid to form a zeolite-like metal-organic framework membrane. The method can include exchanging a cation of the ZMOF to provide a modified ZMOF.

In certain embodiments, the zeolite-like metal-organic framework membrane can be anionic. The zeolite-like metal-organic framework membrane can have a sodalite topology. The zeolite-like metal-organic framework membrane can have a selectivity for CO_2 over H_2, N_2, O_2, or CH_4. In certain embodiments, the film membrane can separate hydrocarbons by size or shape.

In certain embodiments, the method can include activating the substrate. The method can include heating the reagent while contacting with the substrate. The method can include contacting the substrate with acetonitrile after contacting with the reagent. The method can include modifying the zeolite-like metal-organic framework membrane through cation exchange with, for example, an alkali metal ion or alkaline earth metal ion, for example, Li^+, Na^+, K^+, or Mg^{2+}.

In certain embodiments, the zeolite-like metal-organic framework can include a linker and a metal. The metal can include a transition metal, group 13 metal, for example, Indium, Yttrium, or Cadmium, or a combination thereof.

Other aspects, embodiments, and features will be apparent from the following description, the drawings, and the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a crystal structure of sod-ZMOF along the six-membered window; Carbon (grey), Indium (green), Nitrogen (blue) and Oxygen (red); hydrogens were removed for clarity.

FIG. 2 shows XRD patterns of the sod-ZMOF calculated (red) and sod-ZMOF membrane (black).

FIG. 3 shows a schematic representation of the Rubotherm gravimetric-densimetric apparatus.

FIG. 4 shows a schematic representation of the Constant-volume/variable-pressure-Gas chromatography set-up

FIG. 5 shows a schematic representation of the variable-pressure-continuous permeates composition analysis technique.

FIG. 6 shows Ar adsorption isotherm of sod-ZMOF crystals at 87 K.

FIG. 7 shows SEM images of sod-ZMOF membrane supported on alumina substrate, top view (A) and cross section (B).

FIG. 8 shows an Example of the typical time lag experiment.

FIG. 9A shows a representative single gas permeation graph at 308 K showing time lag behaviour of CO_2, N_2, H_2 and C_2H_6 gases; FIG. 9B shows single gas permeability vs. Lennard Jones diameter of He, H_2, CO_2, O_2, N_2, CH_4, C_2H_4 and C_2H_6 at 308 K on sod-ZMOF membranes.

FIG. 10 shows CO_2/CH_4: 50/50 mixture permeation tested using VP-continuous permeate composition analysis technique at 308 K with 3.4 bar as a feed pressure.

FIG. 11 shows CO_2/N_2: 10/90 mixture permeation tested using VP-continuous permeate composition analysis technique at 308 with 3.4 bar as a feed pressure.

FIG. 12 shows CO_2/H_2: 30/70 mixture permeation tested using VP-continuous permeate composition analysis technique at 308 with 3.4 bar as a feed pressure.

FIG. 13 shows CO_2/H_2: 30/70 mixture permeation tested using VP-continuous permeate composition analysis technique at 268 K with 3.4 bar as a feed pressure.

FIG. 14 shows CO_2/H_2: 30/70 mixture permeation tested using VP-continuous permeate composition analysis technique at 353 K with 3.4 bar as a feed pressure.

FIGS. 15A-15B show CO_2 sorption data for sod-ZMOF: (a) fully reversible variable-temperature CO_2 isotherms and (b) Q_{st} for CO_2 calculated from the corresponding isotherms.

FIG. 16A shows adsorption of CO_2, N_2, O_2, CH_4 and H_2 at 298 K on sod-ZMOF and FIG. 16B shows IAST prediction of CO_2/N_2:10/90, CO_2/O_2:5/95, CO_2/CH_4:5/95, CO_2/H_2:30/70 mixtures adsorption selectivity (bottom).

FIG. 17A shows diffusion coefficients (D) vs. Lennard Jones diameter, and FIG. 17B shows solubility coefficients (S) (from sorption data) vs. normal boiling point as determined from CV/VP technique at 2 bar.

DETAILED DESCRIPTION

The development of CO_2 selective membrane for the CO_2 removal from different commodities such as H_2, CH_4 and O_2 is important to fulfill the growing need in CO_2 removal applications in refineries, natural gas production sites as well as in power station. So far, the reported metal organic framework membranes show low permeation selectivity to CO_2 particularly in mixture with H_2.

A defect-free zeolite-like metal organic framework (ZMOF) thin-film membrane with a pure phase sodalite topology can be fabricated using a solvothermal in-situ crystallization method on an alumina substrate, which can be porous. The absences of cracks/defects can be confirmed by the observation of time-lags during constant-volume/variable pressure permeation tests for gases. Another important feature of this ZMOF membrane is its cation exchange properties that may alter in different ways the gas adsorption and the diffusion properties, thus the possible tuning of permeance and permeselectivity of different industrially relevant gas. Depending on the physical-chemical properties, nature (organic or inorganic) and the position of the extra framework cations, ZMOF membranes can be used to target different separation application including and not limited to CO_2 capture, Olefin vs. Paraffin, light Hydrocarbon separation, n-paraffins vs. isoparaffins, cyclic-paraffin vs. aromatic, and so on. The property of the sod-ZMOF may be tuned by the substitution of different organic linkers with different dimensions and functionalities.

For both pure and mixed gas feeds, the ZMOF membrane can exhibit an adsorption-driven selectivity for carbon dioxide over relevant industrial gases, such as H_2, N_2 and CH_4, driven by adsorption. In addition, ZMOF can tackle the problem of reducing the surface modules of the membrane by using a CO_2 selective membrane. For example, to purify syngas that contains 30% of CO_2 and large fraction (70%) of H_2, ZIF-8 membrane that separate H_2 (with the large composition) selectively from CO_2 has a strict and complex requirement in terms of membrane surface. However, ZMOF membrane can permeate CO_2 faster (with the lowest fraction) than H_2 (with the highest fraction) with a selectivity of 7, thus leading to smaller module and a drastic simplification of the technology. This high selectivity of the ZMOF membrane can be appropriate for carbon dioxide capture.

A thin film membrane can include a zeolite-like metal-organic framework, and the thin film membrane has a selectivity for CO_2 over H_2. To prepare a zeolite-like metal-organic framework membrane, a substrate can contact with a carboxylic acid, an imidazole, a metal salt, and a nitric acid to form a zeolite-like metal-organic framework membrane.

ZOMFs are a class of metal-organic frameworks that are topologically isomorphic with zeolites. Zeolites have 3D framework structures built of tetrahedra linked to each other by sharing all the oxygen atoms to form regular intra-crystalline cavities and channels of molecular dimensions. A defining feature of zeolites is that their frameworks are made up of 4-coordinated atoms forming tetrahedra. These tetrahedra are linked together by their corners and make a rich variety of structures. The framework structure may contain linked cages, cavities or channels, which are big enough to allow small molecules to enter. Zeolite-like frameworks is a structure based on tetrahedral nodes.

Porous ZMOFs are a unique subset of MOFs, which are topologically related to inorganic zeolites. These anionic ZMOFs are constructed utilizing the single-metal-ion-based MBB approach that permits the generation of rigid and directional tetrahedral building units (TBUs) based on heterochelation of 6-8-coordinate single-metal ions by angular ditopic organic linkers. The linkers serve to replace the O2 bridges in traditional zeolites, while maintaining the placement of tetrahedra at similar angles (average M-L-M 145°), decorating and expanding the native zeolite-net topology. Zeolite-like metal organic frameworks have been described, for example, in U.S. Patent No. 8,415,493, which is incorporated by reference in its entirety.

Metal-organic frameworks (MOF) have shown great potential in carbon dioxide separation particularly from H_2, N_2 and CH_4 containing gases using mainly equilibrium and kinetics based adsorption technologies. See, for example, S. Xiang, Y. He, Z. Zhang, H. Wu, W. Zhou, R. Krishna, B. Chen, *Nat. Commun.* **2012**, *3*, 954; P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, *Nature* **2013**, each of which is incorporated by reference in its entirety. MOFs, in the form of microcrystalline powder materials, have found their way into many applications, like gas storage, gas separation, catalysis and drug delivery, conferred by their large cavities that can accommodate a large amount of guest molecules and small pore windows that can selectively control the passing of relatively bulky molecules. See, for example, R. J. Kuppler, D. J. Timmons, Q. R. Fang, J. R. Li, T. A. Makal, M. D. Young, D. Q. Yuan, D. Zhao, W. J. Zhuang, H. C. Zhou, *Coord. Chem. Rev.* **2009**, *253*, 3042-3066; J. R. S. Li, Julian; Zhou, Hong Cai *Chem. Rev.* **2012**, *112*, 869-932, each of which is incorporated by reference in its entirety.

The demand for integrating MOFs into various kinds of applications like gas sensing, separation and smart membranes is growing and has attracted increasing attention in the last decade. See, for example, O. Shekhah, J. Liu, R. A. Fischer, C. Woell, *Chem. Soc. Rev.* **2011**, *40*, 1081-1106; J.-R. Li, R. J. Kuppler, H.-C. Zhou, *Chem. Soc. Rev.* **2009**, *38*, 1477-1504; A. Bétard, R. A. Fischer, *Chem. Rev.* **2012**, *112*, 1055-1083; M. Shah, M. C. McCarthy, S. Sachdeva, A. K. Lee, H.-K. Jeong, *Ind. & Eng. Chem. Res.* **2012**, *51*, 2179-2199, each of which is incorporated by reference in its entirety. This is mainly due to the unique properties of MOFs over other porous materials, including permanent porosity, tunable pore windows and cage-sizes, in addition to their recently proven chemical and thermal stability. See, for example, M. Eddaoudi, H. L. Li, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 1391-1397; G. Ferey, *Chem. Soc. Rev.* **2008**, *37*, 191-214; S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem. Int. Ed.* **2004**, *43*, 2334-2375, each of which is incorporated by reference in its entirety. Nowadays, there is a strong need to develop less energy intensive CO_2 removal alternatives such as membrane-based approach, which is considered among the emerging and effective techniques for gas separation. The main advantages of this emerging technology versus conventional separation processes are lower energy cost, smaller footprint and modular design. See, for example, M. Freemantle, *Chem. Eng. News* **2005**, *83*, 3; T.-S. Chung, L. Y. Jiang, Y. Li, S. Kulprathipanja, *Prog. Poly. Sci.* **2007**, *32*, 483-507; W. Koros, G. Fleming, *J. Memb. Sci.* **1993**, *83*, 1-80, each of which is incorporated by reference in its entirety.

The use of MOFs as membranes for gas purification and separation is challenging because it depends on the fabrication of continuous MOF thin-films. Despite the intensive work in the fabrication of MOF membranes, it is still in its infancy and a great effort is needed to overcome many obstacles, like growing robust, continuous and defect-free thin films with very good attachment to the support. There have been few reports on MOF grown as thin films or used as a filler in mixed matrix membranes for gas separation.

Membranes fabricated from zeolitic imidazolate frameworks (ZIFs), a subfamily of MOFs, were reported to show good separation performance with gas permeation selectivities exceeding the limit of Knudsen mechanism behaviour. See, for example, Y. S. Li, H. Bux, A. Feldhoff, G. L. Li, W. S. Yang, J. Caro, *Adv. Mater.* **2010**, *22*, 3322-3324; H. Bux, A. Feldhoff, J. Cravillon, M. Wiebcke, Y.-S. Li, J. Caro, *Chem. Mater.* **2011**, *23*, 2262-2269, each of which is incorporated by reference in its entirety. ZIF-7, ZIF-8 and ZIF-22 membranes showed H_2/CO_2 permeation selectivity, of 13.6, 4.5 and 8.5, respectively particularly at high temperature. See, for example, Y. Li, F. Liang, H. Bux,

W. Yang, J. Caro, *J. Membr. Sci.* **2010**, *354*, 48-54; See, for example, H. Bux, A. Feldhoff, J. Cravillon, M. Wiebcke, Y.-S. Li, J. Caro, *Chem. Mater.* **2011**, *23*, 2262-2269; A. Huang, H. Bux, F. Steinbach, J. Caro, *Angew. Chem. Int. Ed.* **2010**, *49*, 4958-4961, each of which is incorporated by reference in its entirety. Molecular sieving performance with H_2/CO_2 selectivity of 7.3 was reported using ZIF-90 membrane, which was reported to undergo enhancement up to 62.3 upon post-functionalization of ZIF-90 membrane with free aldehyde groups. See, for example, A. Huang, N. Wang, C. Kong, J. Caro, *Angew. Chem. Int. Ed.* **2012**, *51*, 10551-10555, which is incorporated by reference in its entirety.

Despite the importance of post, pre-combustion capture and natural gas upgrading applications, a very limited number of studies have been reported so far on the separation of CO_2/N_2, CO_2/CH_4 and CO_2/H_2 gas systems using MOF membranes. A practical membrane for CO_2 capture from predominately H_2, N_2 and CH_4 containing gases, should exhibit a high permeance for CO_2 as compared to other gases in order to concentrate valuable commodities such as CH_4 and H_2. The separation permeselectivity in favour of CO_2 has been rarely reported with MOF membranes and was only reported on $[Cu_2(bza)_4(puz)]_n$ single-crystal MOF membrane. See, for example, S. Takamizawa, Y. Takasaki, R. Miyake, *J. Am. Chem. Soc.* **2010**, *132*, 2862-2863, which is incorporated by reference in its entirety.

A zeolite-like metal-organic framework (ZMOF) membrane can be prepared with sodalite topology (sod-ZMOF). ZMOFs represent a subset of MOFs that are topologically related to the pure inorganic zeolites and exhibit similar properties: (i) accessible extra large cavities, (ii) chemical stability, (iii) ion exchange capability that make it possible to control and tune extraframework cations for the enhancement of interaction toward specific guest molecules, and (iv) tunable inorganic and organic components that permit facile alteration of pore size and/or organic functionality. See, for example, Y. L. Liu, V. C. Kravtsov, R. Larsen, M. Eddaoudi, *Chem. Commun.* **2006**, 1488-1490, which is incorporated by reference in its entirety. Sod-ZMOF ($In(C_5N_2O_4H_2)_2(C_3N_2H_5)$) possesses a large cavity and small four and six membered windows. The four-membered window has a negligible diameter and the six membered window has a 4.1 Å diameter (FIG. 1).

A thin film membrane can include a zeolite-like metal-organic framework that includes an organic linker and a metal. The metal can include, but not limited to, Indium, Yttrium, or Cadmium. The linker can include, but is not limited to, a heteroaromatic group, such as a nitrogen-containing heteroaromatic group, for example, imidazole or pyrimidine based linkers. In one example, a thin film membrane can include $In(C_5N_2O_4H_2)_2(C_3N_2H_5)$.

The sod-ZMOF membrane can be fabricated by a modifed solvothermal reaction conditions than the corresponding synthesis methodology for single crystal growth with the main purpose to promote crystals inter-growth. See, for example, Y. L. Liu, V. C. Kravtsov, R. Larsen, M. Eddaoudi, *Chem. Commun.* **2006**, 1488-1490, which is incorporated by reference in its entirety.

A defect-free thin-film ZMOF membrane can be prepared with a sodalite topology using a solvothermal crystallization method. Crystals intergrowth can be achieved by inducing uniform nucleation in the reaction mixture and membrane continuity can be confirmed by the observed time lag behaviour for all the studied gases as well as by probing the competitive permeation of O_2 and N_2 (largely in favour of O_2). The particular anionic character of the sod-ZMOF membrane prone to interaction with the quadruple CO_2 and the small pore size (4.1 Å) make it suitable for CO_2 capture application. Sod-ZMOF membrane can show CO_2/H_2 selectivity of 5.2 and elevate selectivity of 4-6.4 and 10.5 toward CO_2 in case of CO_2/CH_4 and CO_2/N_2 mixtures, respectively. The enhancement of CO_2/H_2 selectivity to 12 at low temperature (268 K) and the drop to 2.5 at high temperature (373 K) can indicate the adsorption dominance in permeation selectivity toward CO_2 in mixture with H_2. This newly reported adsorption driven permeation behaviour in favour of CO_2 for polycrystalline MOF membranes, corroborated with analysis of diffusion and sorption behaviours via the solution-diffusion model, can be a breakthrough finding for the rational design of MOF-membrane targeting CO_2 capture and separation. Sod-ZMOF can be a suitable platform to target for fabrication of tunable MOF thin-film membranes for diverse separation applications. Sod-ZMOF crystals and membranes can be modified via cation exchange, such as Li^+, Na^+, K^+, Mg^{2+}, and so on, having diverse atomic and dimensional properties.

The cation exchanged was examined on the ZMOFs bulk material as CO_2 adsorbent, which resulted in improved CO_2 adsorption performance compared with as-prepared ZMOFs bulk material. This finding was followed by a molecular simulation study on partially and completely exchanged sod-ZMOFs membrane with Li, Na and K cations that concluded that CO_2 adsorption is favored strongly over CH_4 adsorption when a binary CO_2-CH_4 mixture is used. In light of these results, alteration of ZMOFs adsorption and diffusion properties by cation exchange will in turn alter the ZMOF membrane properties. Cation exchange by alkali-metals approach was used to modify sod-ZMOFs membrane.

MOF membrane tuned permeaselectivity properties and CO_2 affinity can be tuned via cation exchange. Notable results from the study follow. No effect on membrane continuity was observed, which was confirmed by the high O_2/N_2 selectivity and the time lag behavior in the single gas permeation. Enhancement in permeability was observed when membrane exchanged with inorganic cations (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}). It was also observed that CO_2/H_2 single gas permeation selectivity remains in favour of CO_2 after using 4-methyl imidazolium as organic cation. Moreover, inverted selectivity can be obtained with the inorganic cation (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}) exchanged membrane, even though selectivity in mixture remains in favor of CO_2 because of competition between gas mixture components. The Na^+ exchanged sod-ZMOF membrane compared with other cations exchanged membranes showed the highest CO_2/CH_4 mixture selectivity 49 at 2 bar and 308K. Even with exchanged cation the sod-ZMOF kept its sorption driven selectivity, and retained high affinity to gas molecules with higher quadrupole due to electric field generated by different cations neutralizing the framework. Cation exchanged sod-ZMOF membrane can offer two unique properties by enhancing in parallel both permeability and two key selectivities CO_2/N_2 and CO_2/CH_4 (Table 1), especially on sod-ZMOF membranes exchanged with Li^+ and Na^+ cations. The enhancement of O_2/N_2 selectivity can indicate improvement in diffusion permeation. Also, intrinsically negative charged ZMOFs may be an excellent platform to study the cation exchange approach on membrane, which can provide a new avenue for the facile tuning of membrane permeaselectivity.

Table .1

Gas Mixture	Selectivity									
	Sod-parent		Li-Sod		Na-Sod		K-Sod		Mg-Sod	
	Exp	**Ideal**	**Exp**	**Ideal**	**Exp**	**Ideal**	**Exp**	**Ideal**	**Exp**	**Ideal**
CO_2/H_2:30/70	5.2	2.5	12.2	0.4	8.7	0.4	2.8	0.5	2.5	0.5
CO_2/N_2:10/90	10.5	9.3	6.3	13.3	13.2	12.2	10.0	5.7	9	8.2
CO_2/CH_4:50/50	6.4	4.7	10.0	10.5	49.0	28.2	19.0	6	17.0	8.6

Cation exchanged ZMOF membranes had improved selectivities and permeabilities for separation for CO_2 from H_2, CH_4 and N_2 containing gases. Similar separation performance is expects for CO_2/O_2 mixtures. Moreover, by using bulky organic and inorganic cations, ZMOF can be tuned to separate linear paraffins from branched paraffins, mono-branched parrafins from di-branched paraffins, linear parrafins from cyclic paraffins and mono and dibranched paraffins from cyclic parrafins.

EXAMPLE

Preparation of ZMOF

To fabricate continuous sod-ZMOF thin film, optimization of reactions conditions was essential. Suitable conditions for the fabrication of closed-continious sod-ZMOF thin film can be obtained to to attach and inter-grow sod-ZMOF crystal on the porous/activated alumina support. This inter-growth was accomplished by a combination of solvothermal reaction scale-up, sonication and heating to induce homogeneous nucleation all over the reaction mixture. Dimethyl formamide (DMF) was exchanged afterward with low boiling point solvent (acetonitrile) and then dried under open air and room temperature conditions to avoid the formation of cracks during the solvent evaporation while drying. The powder X-ray diffraction (PXRD) pattern of the sod-ZMOF membrane (FIG. 2) shows the formation of a pure phase sod-ZMOF with a high degree of crystallinity.

Alumina substrate was polished and activated in ammonium nitrate (0.5M) solution at 85 °C for 2 hours, washed extensively and soaked in de-ionized water and dried completely at 150 °C before use. To prepare the sod-ZMOF, 4,5-Imidazoledicarboxylic acid (65 mg, 0.417 mmol), $In(NO_3)_3 \cdot 2H_2O$ (50 mg, 0.15 mmol), DMF (6.0 mL), CH_3CN (1.5 mL), imidazole (0.6 mL, 1.5 M in DMF), and HNO_3 (0.9 mL, 3.5 M in DMF) were added to a 50-mL vial. Mixture was sonicated for ~ 1 hour, until clear solution obtained, and then the substrate was added to the reaction solution. Sample was heated at 85°C for 12 hours and at 105 °C for 30 h, the resulting sample taken out from solution, washed with acetonitrile and dried and soaked in acetonitrile for 3 days with solvent refreshing to remove all DMF from the material, and then dried under open air conditions. The prepared membrane was mounted in the permeation cell and sealed with two silicone O-rings from both sides. All permeation tests were performed using constant volume/ variable pressure operation mode. After proper activation, the permeability of N_2, He, O_2, H_2 CH_4, C_2H_4, C_2H_6 and CO_2 was measured at 308 K at 2 bar upstream pressure.

Powder XRD

XRPD data were recorded on a Panalytical X'Pert Pro diffractometer at 45kV, 40mA for $Cu_{K\alpha}$(1.540) Å), with a scan speed of 0.071112 (°/s) and a step size of 0.0167113° at room temperature. Scanning electron microscope (SEM) images were taken using FEI's desktop Phenom .

Alumina substrate fabrication:

Readymade porous alumina substrates (22 mm diameter with 2 mm thickness) were purchased from Cobra Technologies BV.

Low pressure adsorption measurements

The low pressure adsorption measurement was performed on a fully automated micropore gas analyzer Autosorb-1C (Quantachrome Instruments) at relative pressures up to 1 atm. The determination of the isosteric heats of adsorption (Q_{st}) for CO_2 was estimated by applying the Clausius-Clapeyron expression using the isotherms measured at 258, 273 and 298 K. In a typical experiment, **sod**-ZMOF was activated by washing the as-synthesized crystals with DMF followed by solvent exchange in acetonitrile for 7 days. 45-60 mg of activated sample was then transferred to a 6-mm sample cell, evacuated at room temperature for 46 h (using a turbomolecular vacuum pump) and then gradually heated to 160°C/12h and cooled to room temperature

High pressure adsorption measurements

Adsorption equilibrium measurements of pure gases were performed using a Rubotherm gravimetric-densimetric apparatus (Bochum, Germany) (FIG. 3), composed mainly of a magnetic suspension balance (MSB) and a network of valves, mass flowmeters and temperature and pressure sensors. The MSB overcomes the disadvantages of other commercially available gravimetric instruments by separating the sensitive microbalance from the sample and the measuring atmosphere and is able to perform adsorption measurements across a wide pressure range, i.e. from 0 to 20 MPa. The adsorption temperature may also be controlled within the range of 77 K to 423 K. In a typical adsorption experiment, the adsorbent is precisely weighed and placed in a basket suspended by a permanent magnet through an electromagnet. The cell in which the basket is housed is then closed and vacuum or high pressure is applied. The gravimetric method allows the direct measurement of the reduced gas adsorbed amount Ω. Correction for the buoyancy effect is required to determine the excess adsorbed amount using equation 1, where $V_{adsorbent}$ and V_{ss} refer to the volume of the adsorbent and the volume of the suspension system, respectively.

These volumes are determined using the helium isotherm method by assuming that helium penetrates in all open pores of the materials without being adsorbed. The density of the gas is determined using Refprop equation of state (EOS) database and checked experimentally using a volume-calibrated titanium cylinder. By weighing this calibrated volume in the gas atmosphere, the local density of the gas is also determined. Simultaneous measurement of adsorption capacity and gas phase density as a function of pressure and temperature is therefore possible. The excess uptake is the only experimentally accessible quantity and there is no reliable experimental method to determine the absolute uptake. For this reason, only the excess amounts are considered in this work.

$$\Omega = m_{excess} - \rho_{gas}\left(V_{adsorbent} + V_{ss}\right) \qquad (1)$$

The pressure is measured using two Drucks high pressure transmitters ranging from 0.5 to 34 bar and 1 to 200 bar, respectively, and one low pressure transmitter ranging from 0 to 1 bar. Prior to each adsorption experiment, about 100 mg to 300 mg sample is outgassed 160°C at a residual pressure 10^{-4} mbar. The temperature during adsorption measurements is held constant by using a thermostated circulating fluid.

Pure Gas Permeation Measurements

A constant-volume/variable-pressure apparatus was used to determine the pure gas permeability, diffusion and sorption coefficients of the thin films via the time-lag analysis. A custom cell was used to mount the film and seal it from leaks with O-ring compression on both surfaces. Before each run, the entire system is evacuated under high vacuum at 35°C until any "leak rate" due to off-gassing is less than 1% of the rate of steady-state pressure rise for any penetrant gas. All pure gas experiments were run at 2-bar feed pressure. The downstream pressure rise during permeation was monitored with a 10 Torr MKS Baratron transduscer and the experiment was stopped after ten time-lags elapsed to ensure steady-state. The permeability of the pure gas is given by

$$P = DS = 10^{10}\left(\frac{dp_d}{dt}^{SS} - \frac{dp_d}{dt}^{LR}\right)\frac{V_d l}{(p_{up} - p_d)ART} \qquad (2)$$

where P is the permeability coefficient in Barrer (10^{-10} cm^3*(STP)* cm/(cm2 s cmHg)), dp_d/dt^{SS} is the steady-state rate of permeate pressure rise (cmHg/s) , dp_d/dt^{LR} is the downstream "leak rate" (cmHg/s), V_d is the downstream volume (cm^3), *l* is the active layer thickness (cm), p_{up} is the upstream pressure (cmHg), A is the membrane area (cm^2), R is the gas constant (0.278 cm^3 cmHg/(cm^3(STP) K)), and T is the temperature at measurement (K). The apparent diffusion coefficient D (cm^2/s) is calculated from the time-lag θ (s) as $D=l^2/6\theta$. Assuming permeation occurs via the solution-diffusion mechanism, the solubility coefficient S (cm^3(STP)/(cm^3 cmHg)), is given by S=P/D.

Mixed Gas Permeation Measurements

Constant-volume/variable-pressure-Gas chromatography technique (CV/VP)

The mixed gas permeation properties of the ZMOF thin-film on alumina support were measured at 35 °C using a setup described in literature. See, for example, H. Czichos, T. Saito, L. Smith, *Springer handbook of materials measurement methods, Vol. 978*, Springer, **2006**, which is incorporated by reference in its entirety. Feed gas mixtures of CO_2/CH_4 in molar ratios of 1:1 were run at 4bar feed pressure such that the penetrant partial pressures were comparable to those in the pure gas runs. The stage-cut, that is, the ratio of permeate flow rate to feed flow rate, was kept less than 1% such that the residue composition was essentially equal to that of the feed mixture. An Agilent 3000A Micro GC equipped with four columns and thermal conductivity detectors was calibrated for each gas pair over the composition range of interest using several calibration mixtures. A run was stopped once the permeability and permeate composition ceased to vary with time. The mixed gas permeability coefficient of gas *i* was determined by

$$P_i = 10^{10}\left(\frac{dp_d}{dt}^{SS} - \frac{dp_d}{dt}^{LR}\right)\frac{y_i V_d l}{(x_i p_{up} - y_i p_d)ART} \qquad (3)$$

where *y* and *x* are the mol fractions in the permeate and feed, respectively and the rate of pressure rise is the total rate measured for the permeate gas mixture. When the downstream pressure is negligible relative to the upstream pressure, the separation factor for a gas pair (i/j) is calculated by

$$\alpha_j^i = \frac{P_i}{P_j} = \frac{y_i / x_i}{y_j / x_j} \qquad (4)$$

Variable pressure-continuous permeate composition analysis technique using mass spectrometry (VP-continuous permeate composition analysis).

The VP-continuous permeate composition analysis technique is a sample method used to test membrane in almost close conditions to application. The permeate gas composition is monitored continuously until the occurrence of the stead state. In typical experiment for sod-ZMOF membrane, helium is supplied upstream while monitoring the gas composition in the permeate side. The helium flux during this preparation step is maintained to 5-10 cc/min until the establishment of the baseline (only presence of helium). Then, the binary gas mixture with composition a_{up}, b_{up} of interest is applied upstream with a maintained flux at 40-50 cc/min while monitoring the composition of the permeate downstream composition a_{down}, b_{down}. The system is considered in a steady state when no change in the signal of the MS is observed. The permeselectivity is calculated using the following equation (5):

$$\alpha = \frac{a_{up}/b_{up}}{a_{down}/b_{down}}$$

Gas selectivity of ZMOF

Argon adsorption studies performed on the acetonitrile-exchanged sample of sod-ZMOF show reversible Type-I isotherms representative of a microporous material (FIG. 6). The apparent BET and Langmuir specific surface area and pore volume for sod-ZMOF crystals was determined to be 474 $m^2 g^{-1}$, 590 $m^2 g^{-1}$ and 0.18 $cm^3 g^{-1}$, respectively. The narrow size of sod-ZMOF pore windows is anticipated to provide selective diffusion driving forces allowing a relatively easy passing of small molecules versus larger ones. In addition to that, its anionic character may alter the adsorption/diffusion, and also in turn permeation, properties of specific gases for gas separation applications.

The resulting sod-ZMOF thin-film membrane with a separating layer thickness of 35- 40 μm (as determined by SEM images, FIG. 7) was mounted in a custom made permeation cell and sealed from both sides with silicon O-rings for leak-tight gas permeation testing. The single gas permeation of He, H_2, CO_2, N_2, O_2, CH_4, C_2H_4 and C_2H_6 (>99.99%) was performed on the sod-ZMOF membrane using the constant-volume/variable-pressure (CV/VP) permeation technique (FIG. 4). See, for example, H. Czichos, T. Saito, L. Smith, *Springer handbook of materials measurement methods, Vol. 978*, Springer, **2006**, which is incorporated by reference in its entirety. To remove any residual guest molecules (mainly acetonitrile) additional activation was carried out in-situ by evacuation at 308 K. The membrane was considered to be fully evacuated when the downstream pressure-rise was less than 1% during the tightness test. Pure single gas permeation tests were performed by applying an upstream pressure of 2 bar. Successively, the downstream pressure rise was monitored for each single gas permeation run (He, H_2,

CO_2, N_2, O_2 CH_4, C_2H_4 and C_2H_6) using a 10 Torr transducer. The gas permeation was assumed to be at steady state when no variation was observed in the pressure rise., i.e. 7-10 times after the time-lag has elapsed (FIG. 8). Time-lag behaviour was observed for all the tested gases (FIG. 9A) indicating that the film is defect-free. The elevated O_2/N_2 selectivity of 1.7 is a further confirmation of the film's continuity. Single permeation experiments show a sharp maximum in CO_2 permeability compared to all the other tested gases (Table 1). Therefore, as shown in FIG. 9B, the sod-ZMOF membrane exhibits higher ideal selectivity for CO_2 over other gases. The obtained separation factors for CO_2 over N_2, O_2 and CH_4 were 8.7 (CO_2/N_2), 5.1 (CO_2/O_2) and 3.6 (CO_2/CH_4) (see Table 2), respectively. This selectivity toward CO_2 particularly versus H_2 is the highest reported so far using MOF-based membranes (see Table 3).

Table 1: Pure-gas permeation properties.

Gas	Lennard Jones Diameter [Å]	Normal Boiling Point [K]	Permeability [Barrer]*	Permeance [mol/(s m^2 Pa)]	Diffusivity Coeff. [cm^2/s]	Solubility Coeff. [cm^3(gas)/(cm^3(MOF) cmHg)]
He	2.55	4.2	29.4	2.0E-10	-	-
H_2	2.83	20	36.5	2.4E-10	1.8E-07	2.0E-02
N_2	3.8	77	10.8	7.3E-10	1.5E-08	7.0E-02
O_2	3.47	90	18.5	1.2E-10	2.6E-08	7.3E-02
CH_4	3.76	111	26.5	1.8E-10	1.5E-08	1.7E-01
CO_2	3.94	217	94.1	6.3E-10	2.6E-08	3.6E-01
C_2H_4	4.16	170	39.8	2.7E-10	1.3E-08	3.0E-01
C_2H_6	4.44	185	26.4	1.8E-10	8.7E-09	3.1E-01

*Barrer [=] 10^{-10}cm^3(STP) cm / (cm^2 s cmHg). Solubility coefficients were independently measured with Rubotherm apparatus from equilibrium adsorption. Permeability coefficients were independently measured from permeation experiments. Diffusion coefficients were back-calculated as D=P/S from solution-diffusion theory.

Table 2: Ideal selectivity on sod-ZMOF membrane.

Gas mixture	Ideal selectivity
CO_2/He	3.2
CO_2/H_2	2.6
CO_2/N_2	8.7
CO_2/O_2	5.1
CO_2/CH_4	3.6
H_2/N_2	3.4
H_2/O_2	2.0
H_2/CH_4	1.4
O_2/N_2	1.7

Table 3: Different MOF membranes and reported selectivities.

MOF thin film	topology	Pore size/ window size	Gas system	Selectivity	Condition	Ref.
ZIF-7	Sod		H_2/CO_2	13.6	220°C, 1 bar	[1]
ZIF-22	LTA	3/	H_2/CO_2	7.2	50°C, 0.5 bar	[2]
ZIF-90	Sod	3.5	H_2/CO_2	7.3	200°C, 1 bar	[3]
ZIF-90 post functionalized	Sod	<3.5	H_2/CO_2	62.3		[4]
ZIF-8	Sod	3.4	CO_2/CH_4	4 to 7	295K and 139.5 KPa	[5]
SIM-1	Sod	8	CO_2/N_2	1.1		[6]

See, for example, [1] Y. Li, F. Liang, H. Bux, W. Yang, J. Caro, *J. Memb. Sci.* **2010**, *354*, 48-54; [2] A. Huang, H. Bux, F. Steinbach, J. Caro, *Angew. Chem. Int. Ed.* **2010**, *49*, 4958-4961; [3] A. Huang, W. Dou, J. Caro, *J. Am. Chem. Soc.* **2010**, *132*, 15562-15564; [4] A. Huang, J. Caro, *Angew. Chem. Int. Ed.* **2011**, *50*, 4979-4982; [5] S. R. Venna, M. A. Carreon, *J. Am. Chem. Soc.* **2009**, *132*, 76-78; [6] S. Aguado, C.-H. Nicolas, V. Moizan-Baslé, C. Nieto, H. Amrouche, N. Bats, N. Audebrand, D. Farrusseng, *N. J. Chem.* **2011**, *35*, 41-44, each of which is incorporated by reference in its entirety.

In order to further confirm this selective permeation in favour of CO_2, CO_2/CH_4:50/50 and CO_2/N_2:10/90, gas-mixture permeation experiments were carried out using two permeation systems, namely state-of-the-art CV/VP-gas chromatography technique (FIG. 4) and mixture gas permeation combined with continuous gas analysis setup (FIG. 5). Both experiments revealed a selectivity toward CO_2 of 4-6.4 and 10.5 (at 3.4 bar) for the two gases systems, respectively, in good agreement with the ideal selectivity of 3.6 for CO_2/CH_4 and 8.7 for CO_2/N_2, obtained from pure-gas permeation testing at 2 bar (Table 4, FIG. 10 and FIG. 11). For the CO_2-H_2 pair gas system the CO_2 permeability was faster than H_2 with a CO_2/H_2 ideal selectivity of 2.6.

Table 4: CO_2/CH_4 mixed gas permeation results using CV/VP - gas chromatography

Binary Mixture (50:50)	Permeability CO_2 [Barrer]	Permeance CO_2 [mol/(m^2.s.Pa)]	Permeability CH_4 [Barrer]	Permeance CH_4 [mol/(m^2.s.Pa)]	Separation Factor
CO_2/CH_4 (4bar)	72.8	4.87×10^{-10}	18.4	1.23×10^{-10}	4.0

The observed reverse-selectivity, for polycrystalline MOF-based membranes, was confirmed by performing CO_2/H_2:30/70 mixture gas permeation (FIG. 12) using permeation-continuous gas analysis set-up (FIG. 5). The obtained CO_2/H_2 selectivity of 5.2 in favour of CO_2 at 308 K and 3.4 bar is likely attributed to the governance of CO_2 adsorption over H_2 in CO_2/H_2 mixture permeation. To confirm this adsorption driven behaviour, permeation test were performed at 268 and 353 K. The enhancement and contraction of CO_2/H_2 selectivity to 12 at low temperature (268 K) (FIG. 13) and 2.5 at higher temperature (353 K) (FIG. 14), respectively was another confirmation that CO_2/H_2 gas permeation is mainly governed by adsorption. In contrast to ZIFs, which are neutral, the anionic framework of the sod-ZMOFs, is mainly responsible for the reversed CO_2/H_2 selectivity. See, for example, J. F. Eubank, H. Mouttaki, A. J. Cairns, Y. Belmabkhout, L. Wojtas, R. Luebke, M. H. Alkordi, M. Eddaoudi, *J. Am. Chem. Soc.* **2011**, *133*, 14204-14207, which is incorporated by reference in its entirety. These findings are important as the economically feasible processing of shifted syngas (H_2/CO_2 mixture) require a selective membrane for the less dominant fraction which is CO_2.

In order to further confirm the selective adsorption of CO_2, the CO_2 adsorption properties of sod-ZMOF crystals were investigated at low sub-atmospheric pressure and different temperatures (FIG. 15A), in order to determine the evolution of heat of adsorption (isosteric heat Q_{st}). The CO_2 Q_{st} at low loading was found to be 29 kJ/mol (FIG. 15B) resulting mainly from the combination of interaction with the quadruple moment of CO_2 with the charged framework and the effect of pore size. The adsorption data of N_2, O_2, CH_4 and H_2 (FIG. 16A) showed a much lower adsorption uptake at room temperature as compared to CO_2. Under these conditions, it is thus expected that a high adsorption selectivity toward CO_2 will be obtained particularly vs. H_2. Accordingly, prediction of CO_2/N_2, CO_2/O_2, CO_2/CH_4 and CO_2/H_2 adsorption selectivities in gas mixtures akin to industrial gases using Ideal Adsorption Solution Theory (IAST) (see FIG. 16B) shows that the sod-ZMOF exhibits high CO_2 selectivity versus H_2 in comparison to CH_4, N_2 and O_2. See, for example, H. Chen, D. S. Sholl, *Langmuir* **2007**, *23*, 6431-6437; A. L. Myers, J. M. Prausnitz, *AIChE* **1965**, *11*, 121-127, which is incorporated by reference in its entirety. The sequence of the adsorption selectivity was $CO_2/H_2 >>> CO_2/N_2 \approx CO_2/O_2 > CO_2/CH_4$.

The single gas permeation data along with sorption data were further analyzed using the solution-diffusion model, applicable to structures with nominal pore diameter less than 10Å. See, for example, R. Baker, *Membrane technology and applications*, Wiley, **2012**, which is incorporated by reference in its entirety. In this model, gas permeability through a dense or microporous framework is the product of diffusion and solubility effects. Diffusion is characterized by a diffusion coefficient, D, which is a measure of the kinetics of gas transport through the membrane (thin film) and can be correlated well with a measure of the gas molecular size. D may be calculated from experimental permeation time-lags or back-calculated from adsorption and permeation data. Solubility is characterized by a sorption coefficient, S, which comprises the framework interactions with the gases and can be correlated well with their condensability. S may be obtained indirectly from the solution-diffusion model via knowledge of P and D, or directly from equilibrium adsorption isotherms if the material density is known.

Here, since independent measurements of both P and S using gas permeation and adsorption isotherms, respectively, were available, D was more accurately calculated as $D=P/S$. See, for example, Y. P. Yampolskii, I. Pinnau, B. D. Freeman, *Materials science of membranes for gas and vapor separation*, Wiley Online Library, **2006**, which is incorporated by reference in its entirety. FIG. 17A demonstrates that larger gas molecules experience more resistance to diffusion through the sod-ZMOF framework, causing a general decline in diffusion coefficients with size (here used as Lennard Jones diameters). See, for example, J. R. Li, R. J. Kuppler, H. C. Zhou, *Chem. Soc. Rev.* **2009**, *38*, 1477-1504, which is incorporated by reference in its entirety. As the probe molecules approach the 4.1Å pore aperture size estimated from crystal structure data, diffusion becomes more restricted. A 20-fold drop in D coefficients occurs from H_2 (2.8Å) through CO_2 to C_2H_6 (>4Å). With regards to adsorption at equilibrium, condensable gases exhibit generally stronger interactions with the medium of transport as an increase in the solubility coefficient, S, is observed with increasing boiling point in FIG. 17B. However, in the solution-diffusion model the rate-limiting step in gas permeation is typically the Fickian diffusion across the film thickness. That is, one might expect permeability coefficients to trend downwards with penetrant size like diffusion coefficients, as is often shown in the ZIF-8**.** See, for example, H. Bux, F. Liang, Y. Li, J. Cravillon, M. Wiebcke, J. Caro, *J. Am. Chem. Soc.* **2009**, *131*, 16000-16001, which is incorporated by reference in its entirety. Instead, the sod-ZMOF demonstrates adsorption-driven permeation that somewhat trends with the condensability of the gas, like the sorption coefficients that result in increase of permeability for the more condensable gases except for C_2H_6 which may be experiencing strong diffusional resistance as it is closest in size to the aperture size. The key observation, however, is that despite the restriction on the diffusion of CO_2 by the rigid and relatively small pore apertures, the affinity of sod-ZMOF to CO_2 grants it the maximum, adsorption-driven, permeability of all tested gases.

Other embodiments are within the scope of the following claims.

WHAT IS CLAIMED IS:

1. A thin film membrane comprising a zeolite-like metal-organic framework, wherein the thin film membrane has a selectivity for CO_2 over H_2.

2. The thin film membrane of claim 1, wherein the thin film membrane is anionic.

3. The thin film membrane of claim 1, wherein the thin film membrane has a zeolite-like topology.

4. The thin film membrane of claim 1, wherein the thin film membrane is on a support.

5. The thin film membrane of claim 4, wherein the support is a porous ceramic substrate.

6. The thin film membrane of claim 1, wherein the permeance of the thin film membrane is higher for CO_2 than for other gases.

7. The thin film membrane of claim 1, wherein the permeance of the thin film membrane is higher for CO_2 than for CH_4.

8. The thin film membrane of claim 1, wherein the thin film membrane has a separation factor of at least 3 for CO_2 over CH_4.

9. The thin film membrane of claim 1, wherein the permeance of the thin film membrane is higher for CO_2 than for H_2.

10. The thin film membrane of claim 1, wherein the thin film membrane has a selectivity of at least 4 for CO_2 over H_2.

11. The thin film membrane of claim 1, wherein the permeance of the thin film membrane is higher for CO_2 than for N_2.

12. The thin film membrane of claim 1, wherein the thin film membrane has a separation factor of at least 6 for CO_2 over N_2.

13. The thin film membrane of claim 1, wherein the permeance of the thin film membrane is higher for CO_2 than for O_2.

14. The thin film membrane of claim 1, wherein the thin film membrane has a separation factor of at least 4 for CO_2 over O_2.

15. The thin film membrane of claim 1, wherein the thickness of the thin-film membrane is between 20 and 100 μm.

16. The thin film membrane of claim 1, wherein the thin film membrane has a high degree of crystallinity.

17. The thin film membrane of claim 1, wherein the zeolite-like metal-organic framework includes a linker and a metal.

18. The thin film membrane of claim 17, wherein the metal includes a transition metal, group 13 metal or a lanthanide metal.

19. The thin film membrane of claim 17, wherein the linker includes a heteroaromatic group.

20. A method for preparing a zeolite-like metal-organic framework membrane comprising contacting a substrate with a solution mixture of carboxylic acid, an imidazole or a pyrimidine, a metal salt, and a nitric acid to form a zeolite-like metal-organic framework membrane.

21. The method of claim 20, wherein the zeolite-like metal-organic framework membrane is anionic.

22. The method of claim 20, wherein the zeolite-like metal-organic framework membrane has a sodalite topology.

23. The method of claim 20, wherein the zeolite-like metal-organic framework membrane has a selectivity for CO_2 over H_2.

24. The method of claim 20, further comprising activating the substrate.

25. The method of claim 20, further comprising heating the reagent while contacting with the substrate.

26. The method of claim 20, further comprising contacting the substrate with acetonitrile after contacting with the reagent.

27. The method of claim 20, further comprising modifying the zeolite-like metal-organic framework membrane through cation exchange with an alkali metal ion or alkaline earth metal ion.

28. The method of claim 20, wherein the zeolite-like metal-organic framework includes a linker and a metal.

29. The method of claim 20, wherein the metal includes a transition metal, group 13 metal or a lanthanide metal.

30. A method of separating gases comprising passing a mixture of gasses through a thin film membrane comprising a zeolite-like metal-organic framework, wherein the thin film membrane has a selectivity for CO_2 over H_2.

31. The method of claim 30, wherein the thin film membrane is anionic.

32. The method of claim 30, wherein the thin film membrane has a zeolite-like structure.

33. The method of claim 30, wherein the thin film membrane is on a support.

34. The method of claim 33, wherein the support is a porous ceramic substrate.

35. The method of claim 30, wherein the permeance of the thin film membrane is higher for CO_2 than for other gases.

36. The method of claim 30, wherein the permeance of the thin film membrane is higher for CO_2 than for CH_4.

37. The method of claim 30, wherein the thin film membrane has a separation factor of at least 3 for CO_2 over CH_4.

38. The method of claim 30, wherein the permeance of the thin film membrane is higher for CO_2 than for H_2.

39. The method of claim 30, wherein the thin film membrane has a selectivity of at least 4 for CO_2 over H_2.

40. The method of claim 30, wherein the permeance of the thin film membrane is higher for CO_2 than for N_2.

41. The method of claim 30, wherein the thin film membrane has a separation factor of at least 6 for CO_2 over N_2.

42. The method of claim 30, wherein the permeance of the thin film membrane is higher for CO2 than for O_2.

43. The method of claim 30, wherein the thin film membrane has a separation factor of at least 4 for CO_2 over O_2.

44. The method of claim 20, further comprising exchanging a cation of the ZMOF to provide a modified ZMOF.

45. The method of claim 20, wherein the film membrane separates hydrocarbons by size or shape.

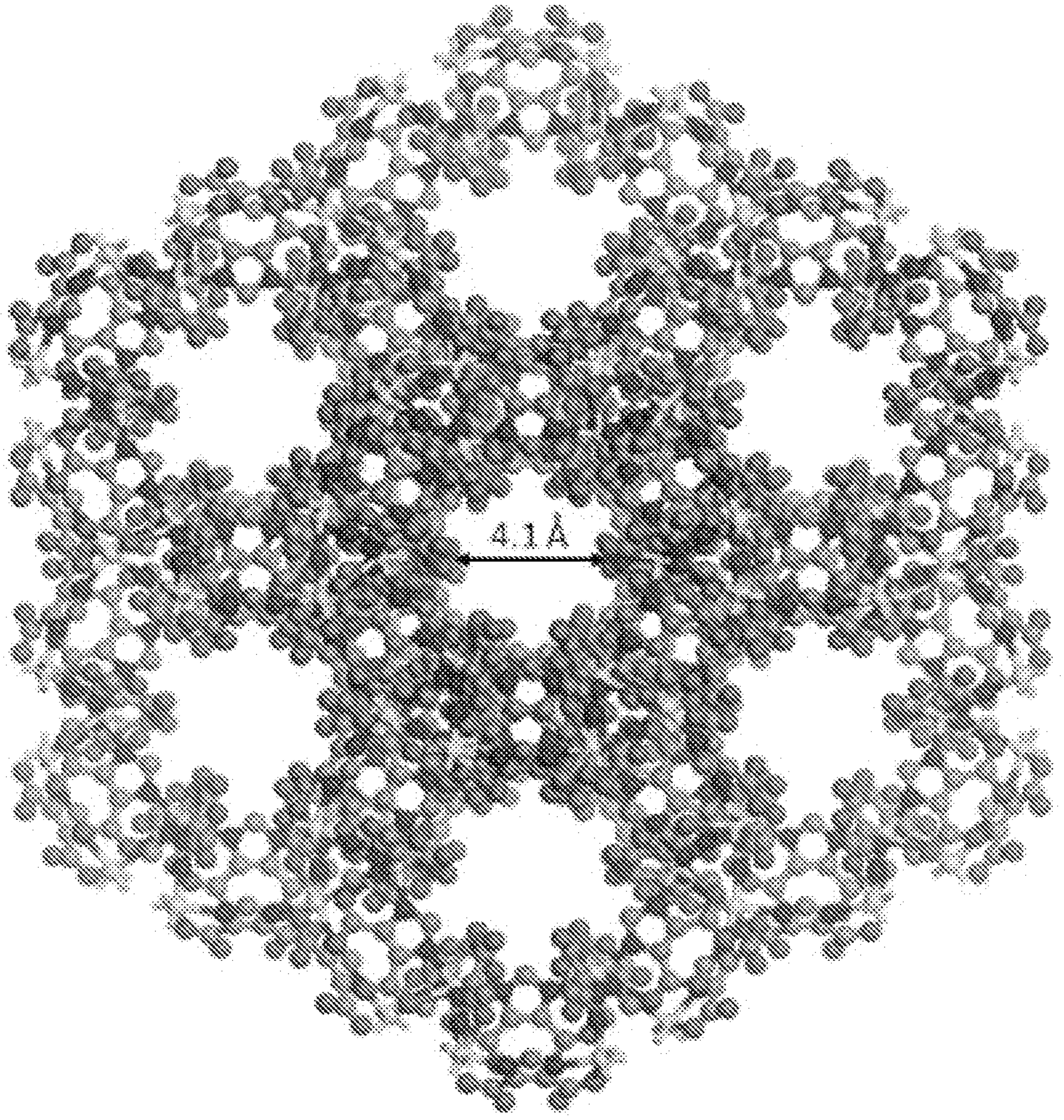


FIG. 1

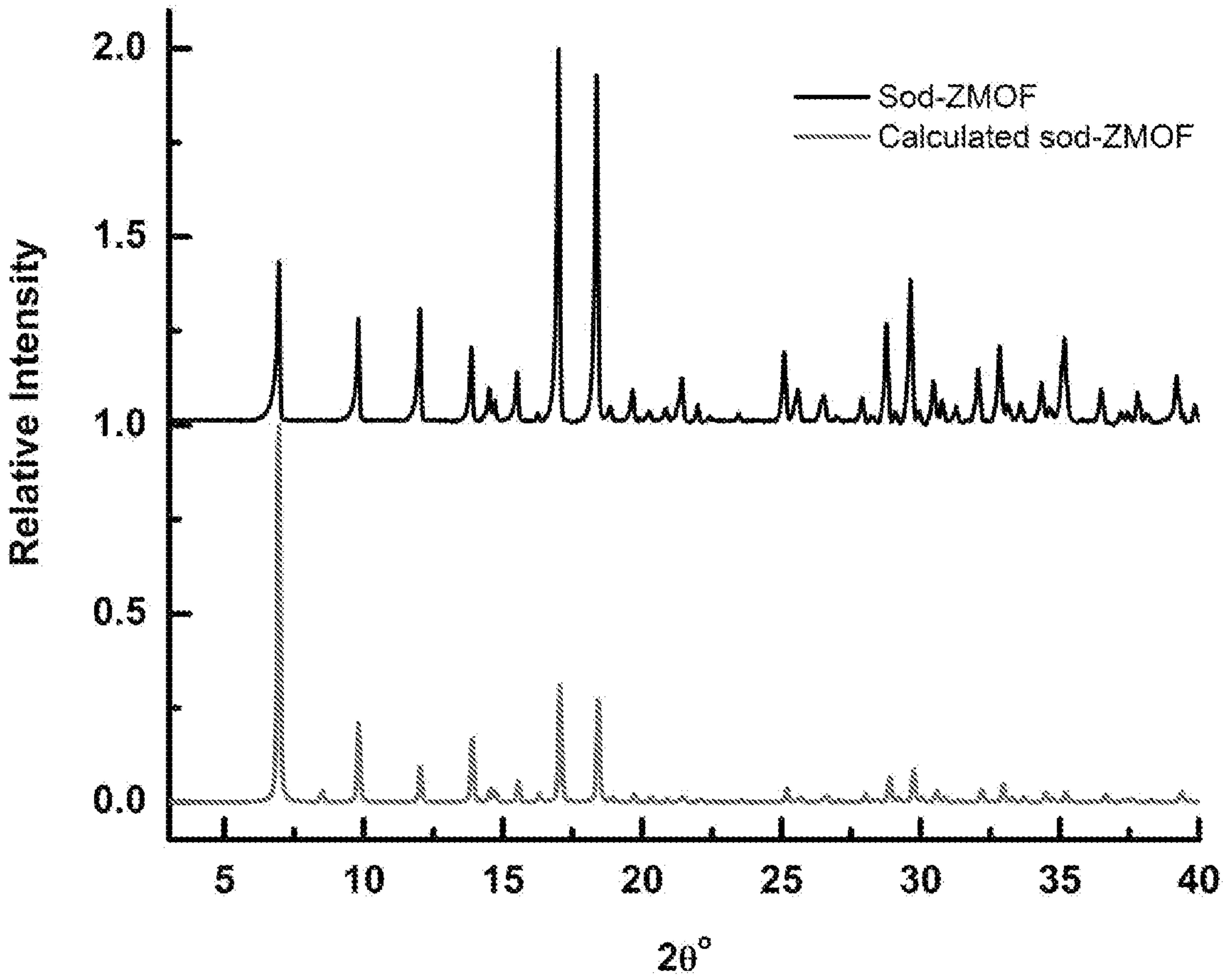

Sod-ZMOF
Calculated sod-ZMOF
Relative Intensity
2.0
1.5
1.0
0.5
0.0
5
10
15
20
25
30
35
40
2θ°

FIG. 2

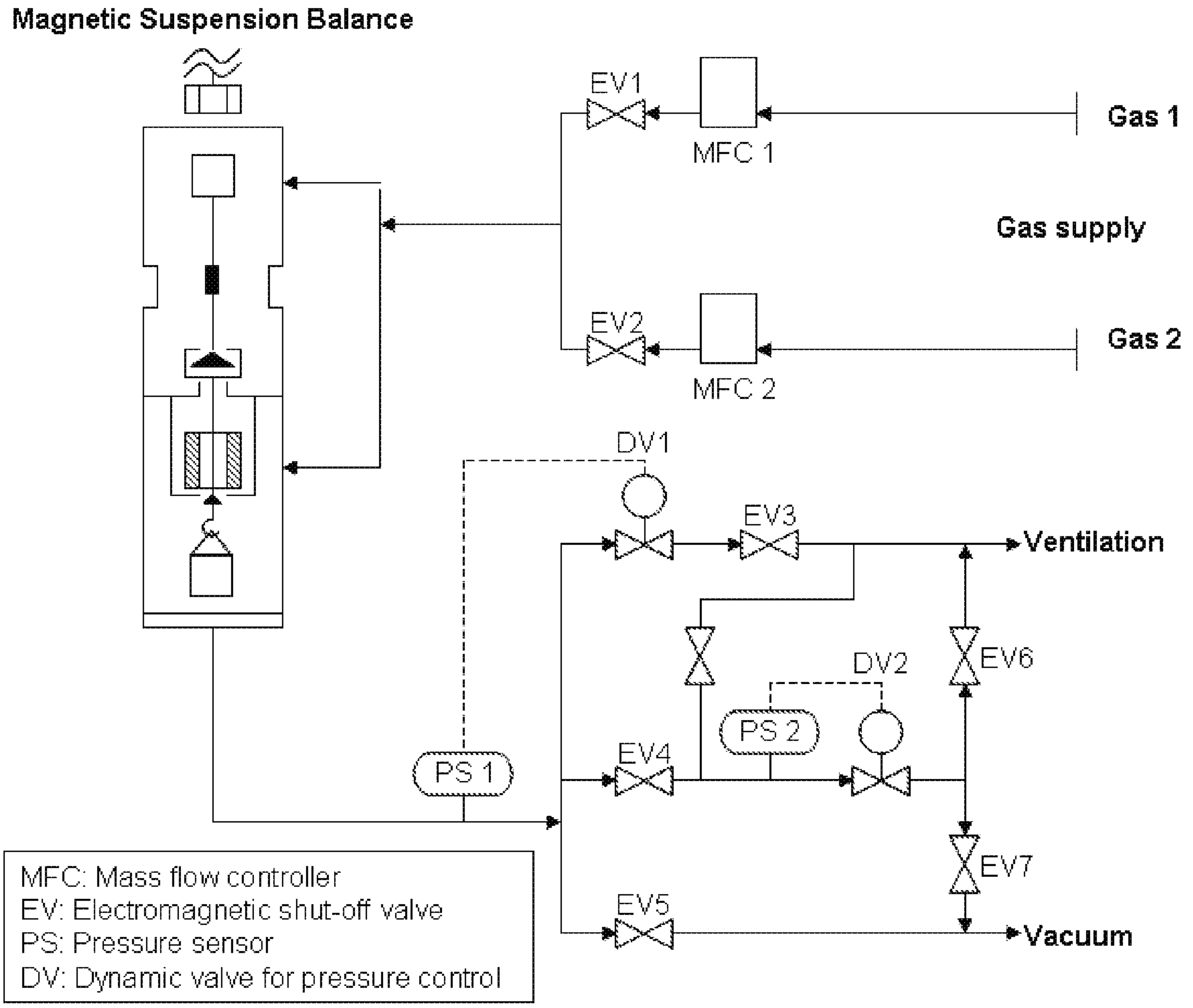

Magnetic Suspension Balance
EV1
MFC 1
Gas 1
Gas supply
EV2
MFC 2
Gas 2
DV1
EV3
Ventilation
EV6
DV2
PS 2
EV4
PS 1
EV7
EV5
Vacuum
MFC: Mass flow controller
EV: Electromagnetic shut-off valve
PS: Pressure sensor
DV: Dynamic valve for pressure control

FIG. 3

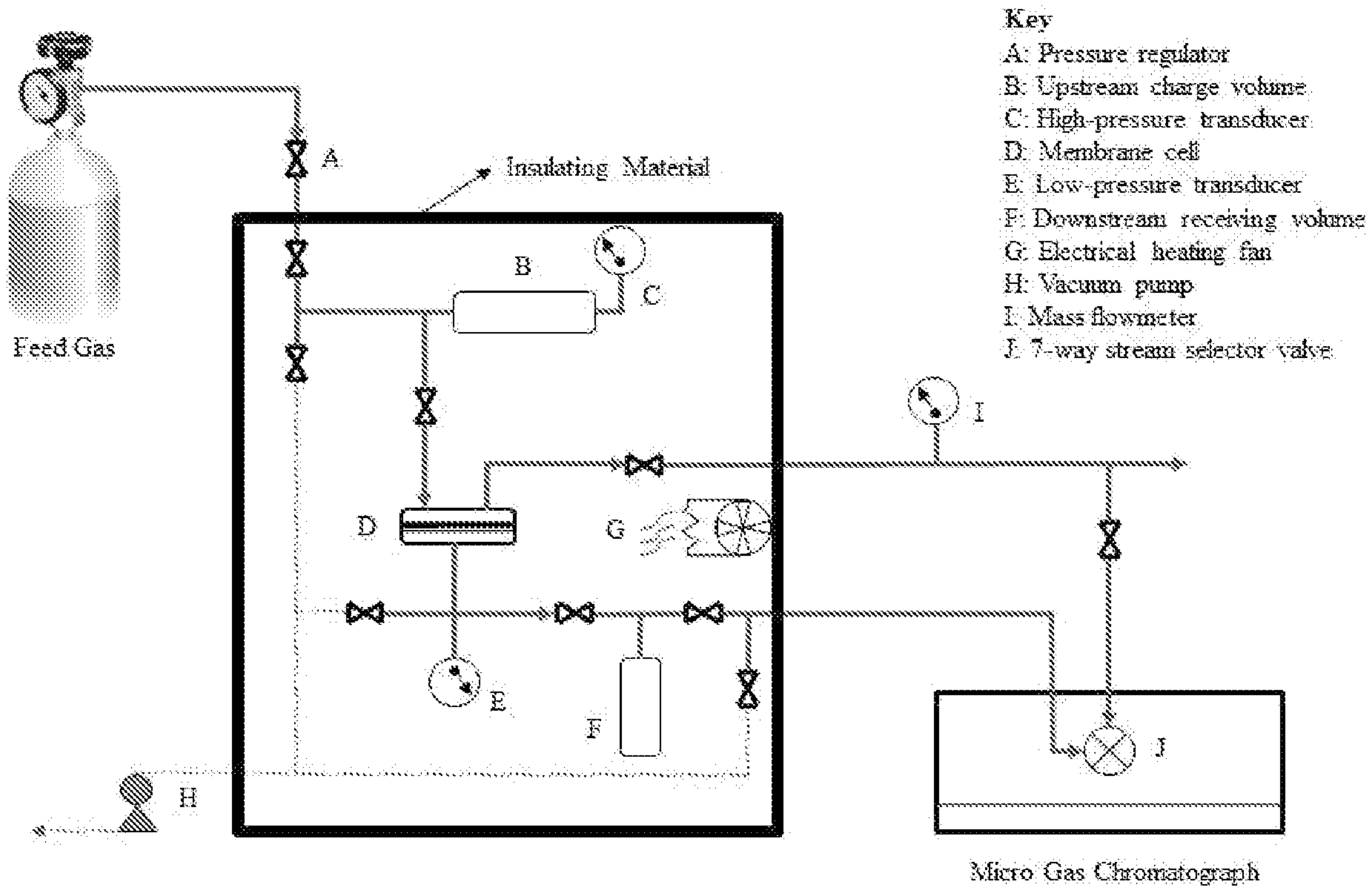

Key
A: Pressure regulator
B: Upstream charge volume
C: High-pressure transducer
D: Membrane cell
E: Low-pressure transducer
F: Downstream receiving volume
G: Electrical heating fan
H: Vacuum pump
I: Mass flowmeter
J: 7-way stream selector valve
Feed Gas
Insulating Material
A
B
C
D
E
F
G
H
I
J
Micro Gas Chromatograph

FIG. 4

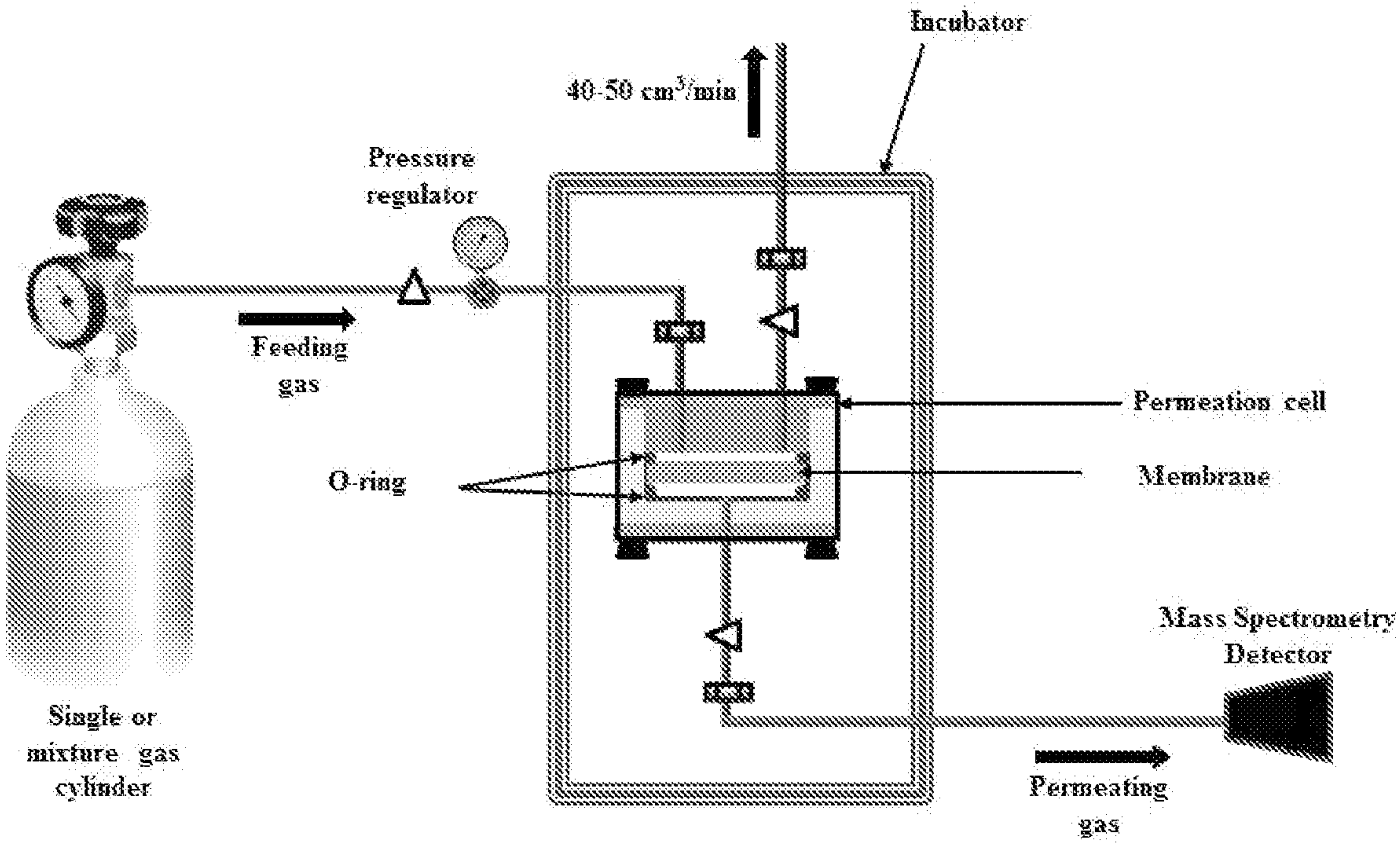

Incubator
40-50 cm^3/min
Pressure regulator
Feeding gas
Permeation cell
O-ring
Membrane
Mass Spectrometry Detector
Single or mixture gas cylinder
Permeating gas

FIG. 5

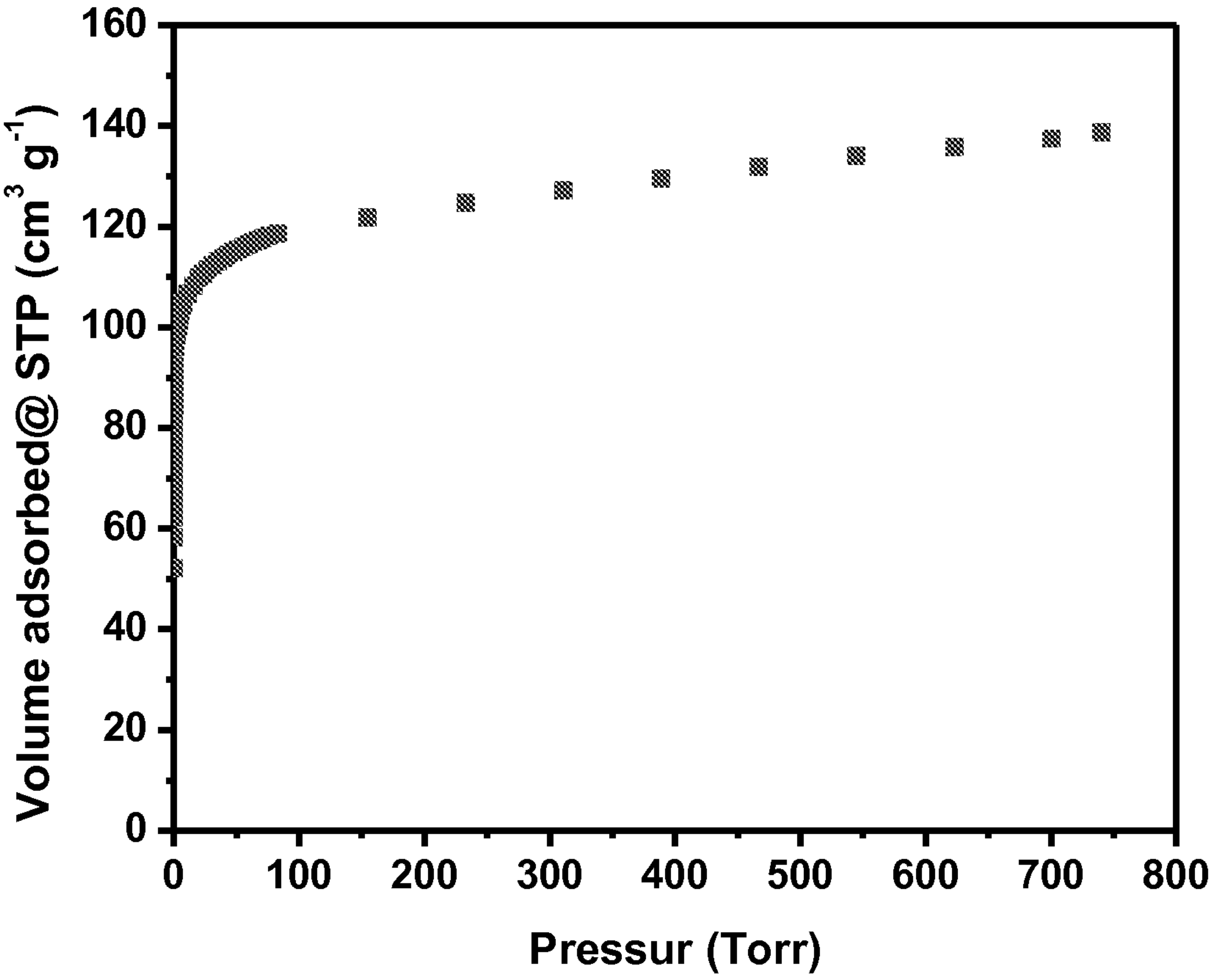

Volume adsorbed@ STP (cm^3 g^{-1})
160
140
120
100
80
60
40
20
0
0
100
200
300
400
500
600
700
800
Pressur (Torr)

FIG. 6

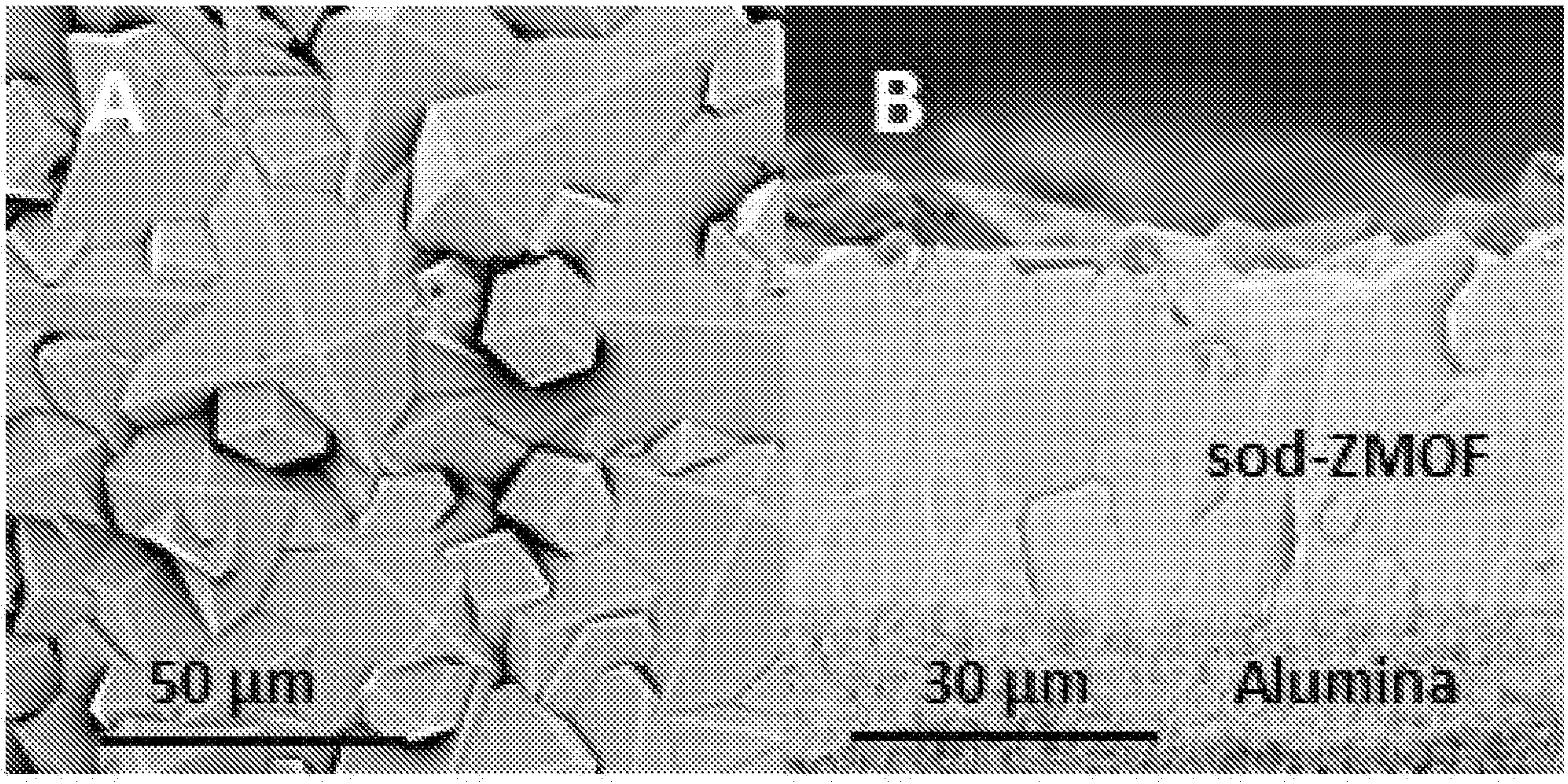


FIG. 7

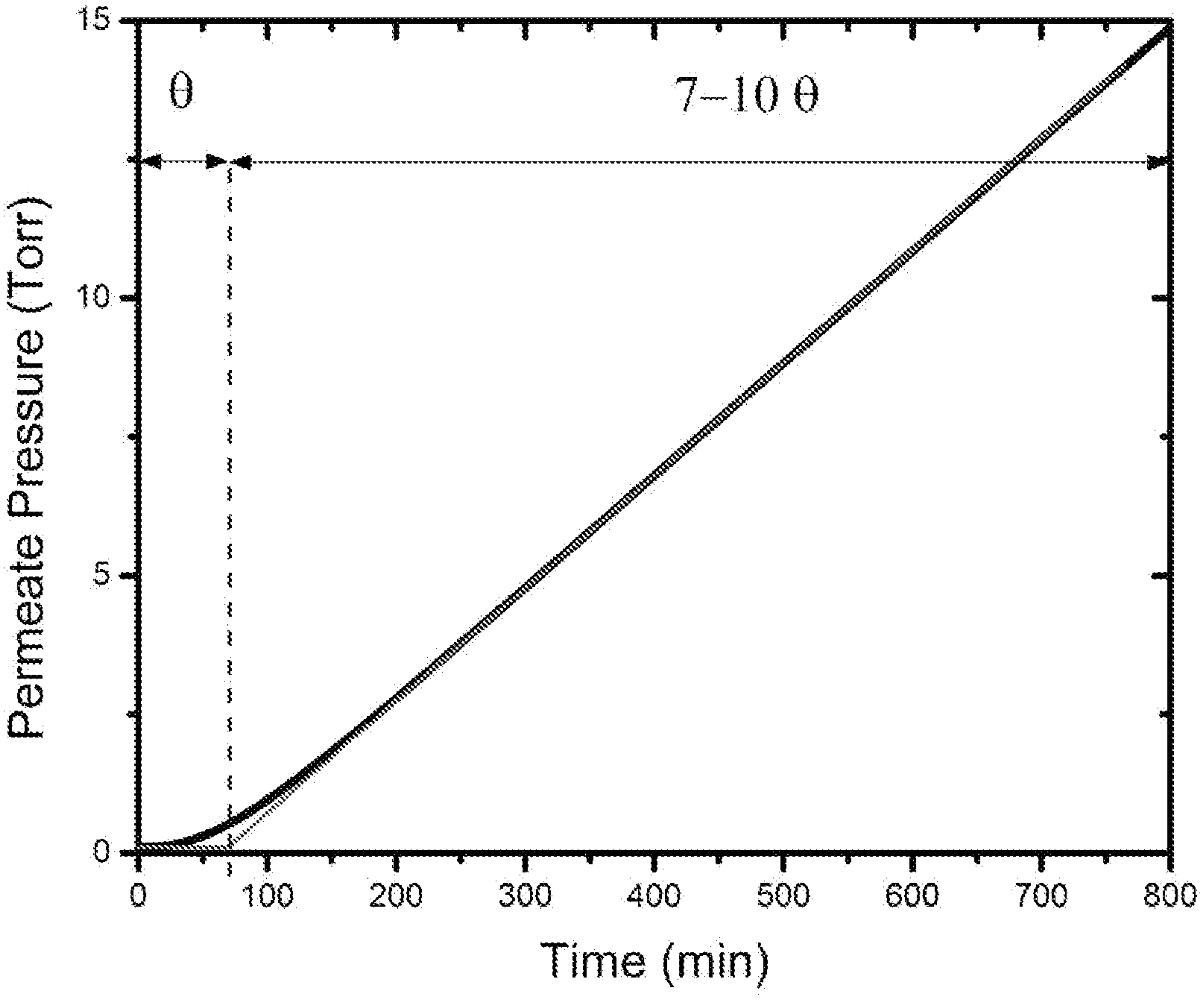

θ
7–10 θ
Permeate Pressure (Torr)
15
10
5
0
0
100
200
300
400
500
600
700
800
Time (min)

FIG. 8

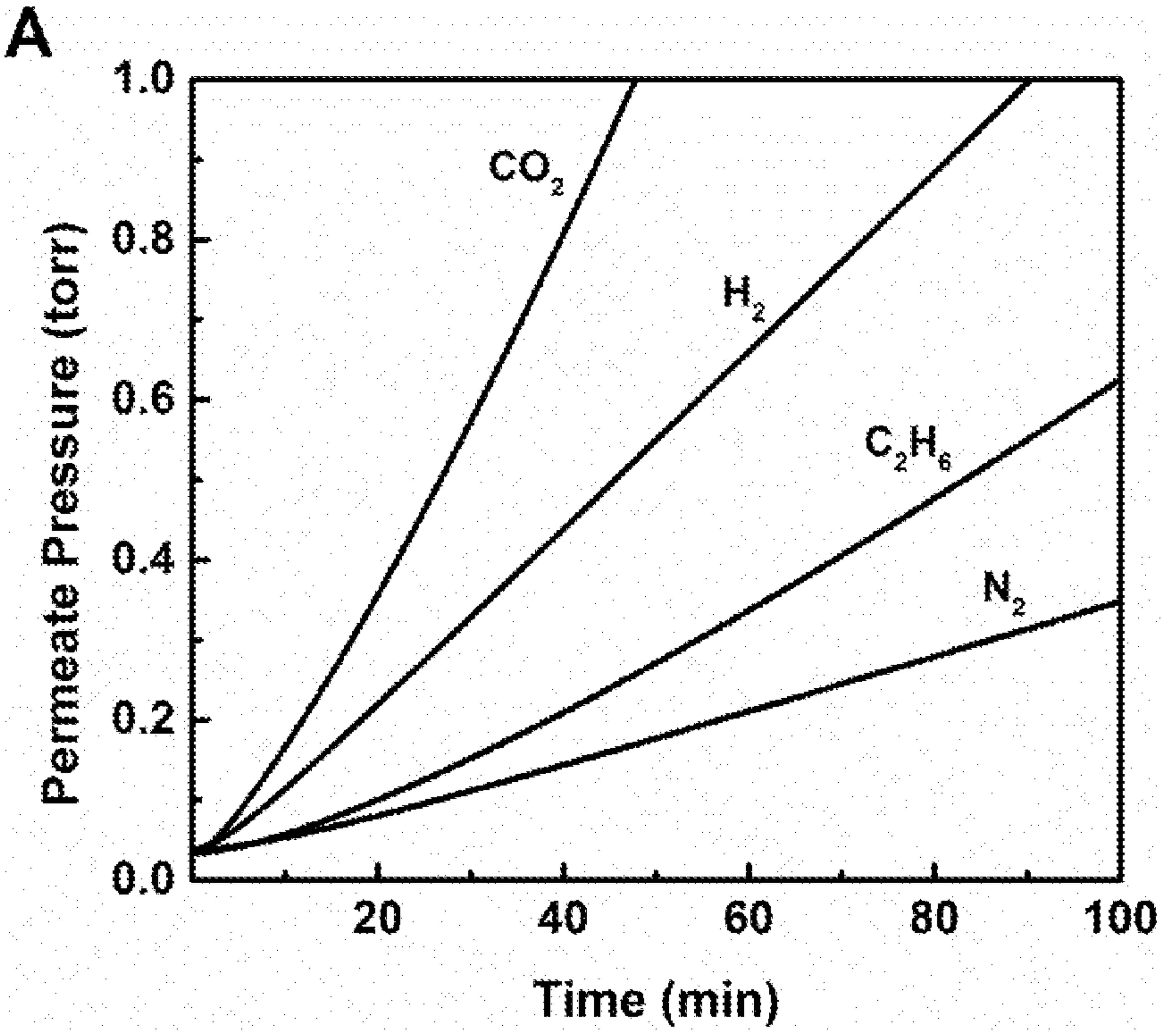

A
1.0
0.8
0.6
0.4
0.2
0.0
Permeate Pressure (torr)
CO$_2$
H$_2$
C$_2$H$_6$
N$_2$
20
40
60
80
100
Time (min)

FIG. 9A

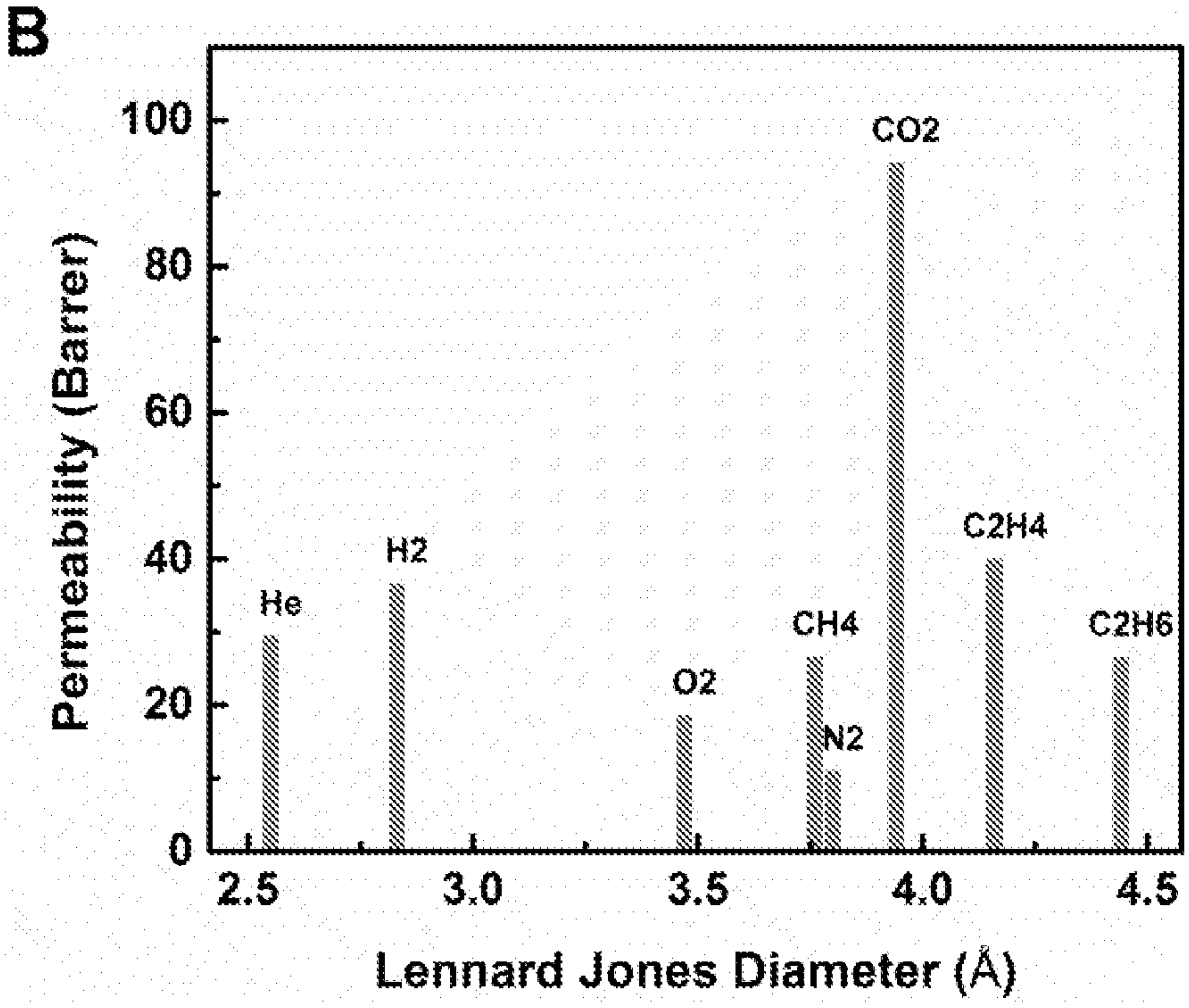

B
100
80
60
40
20
0
Permeability (Barrer)
He
H2
O2
CH4
N2
CO2
C2H4
C2H6
2.5
3.0
3.5
4.0
4.5
Lennard Jones Diameter (Å)

FIG. 9B

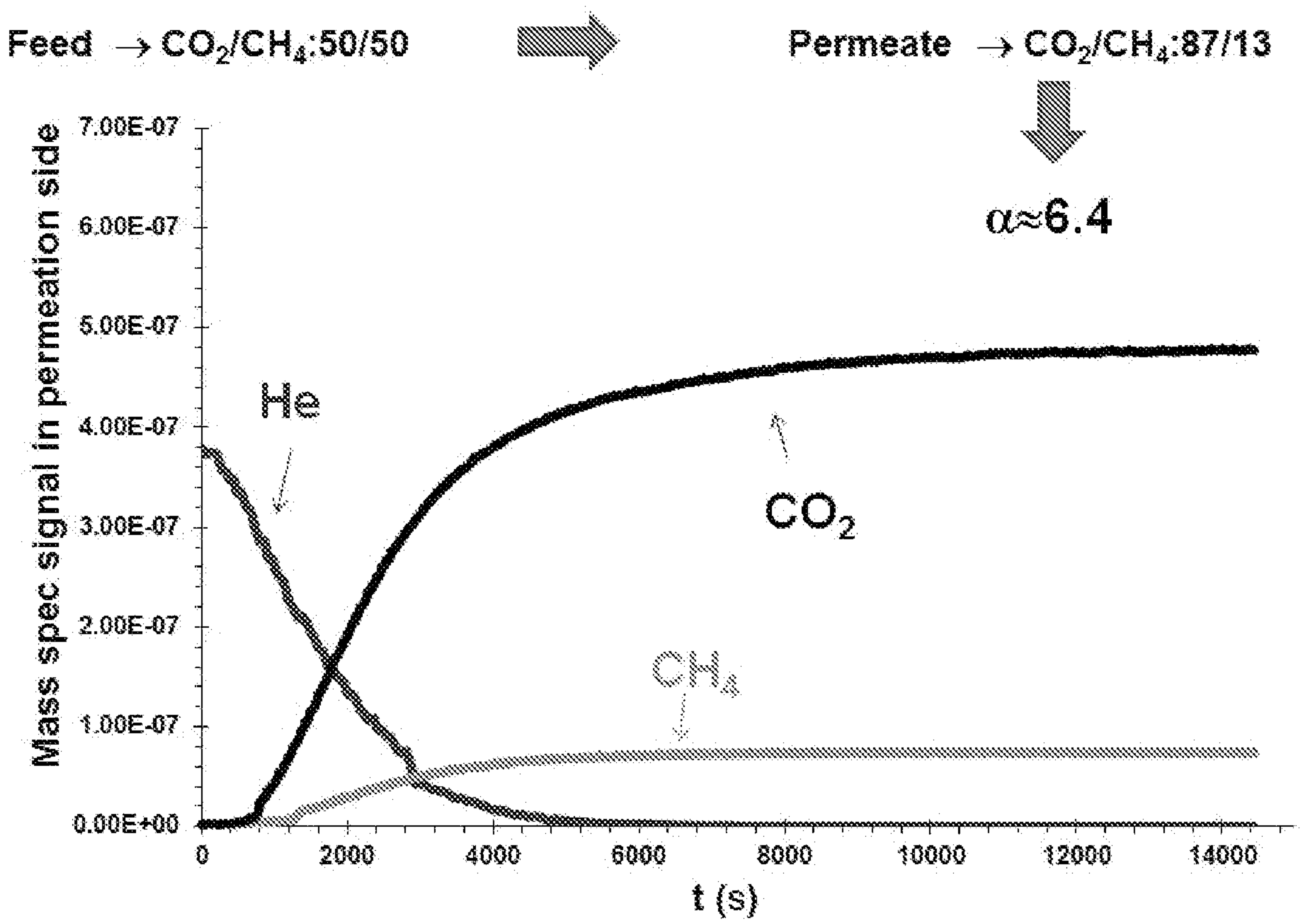

Feed → CO_2/CH_4:50/50
Permeate → CO_2/CH_4:87/13
α≈6.4
Mass spec signal in permeation side
7.00E-07
6.00E-07
5.00E-07
4.00E-07
3.00E-07
2.00E-07
1.00E-07
0.00E+00
He
CO_2
CH_4
0
2000
4000
6000
8000
10000
12000
14000
t (s)

FIG. 10

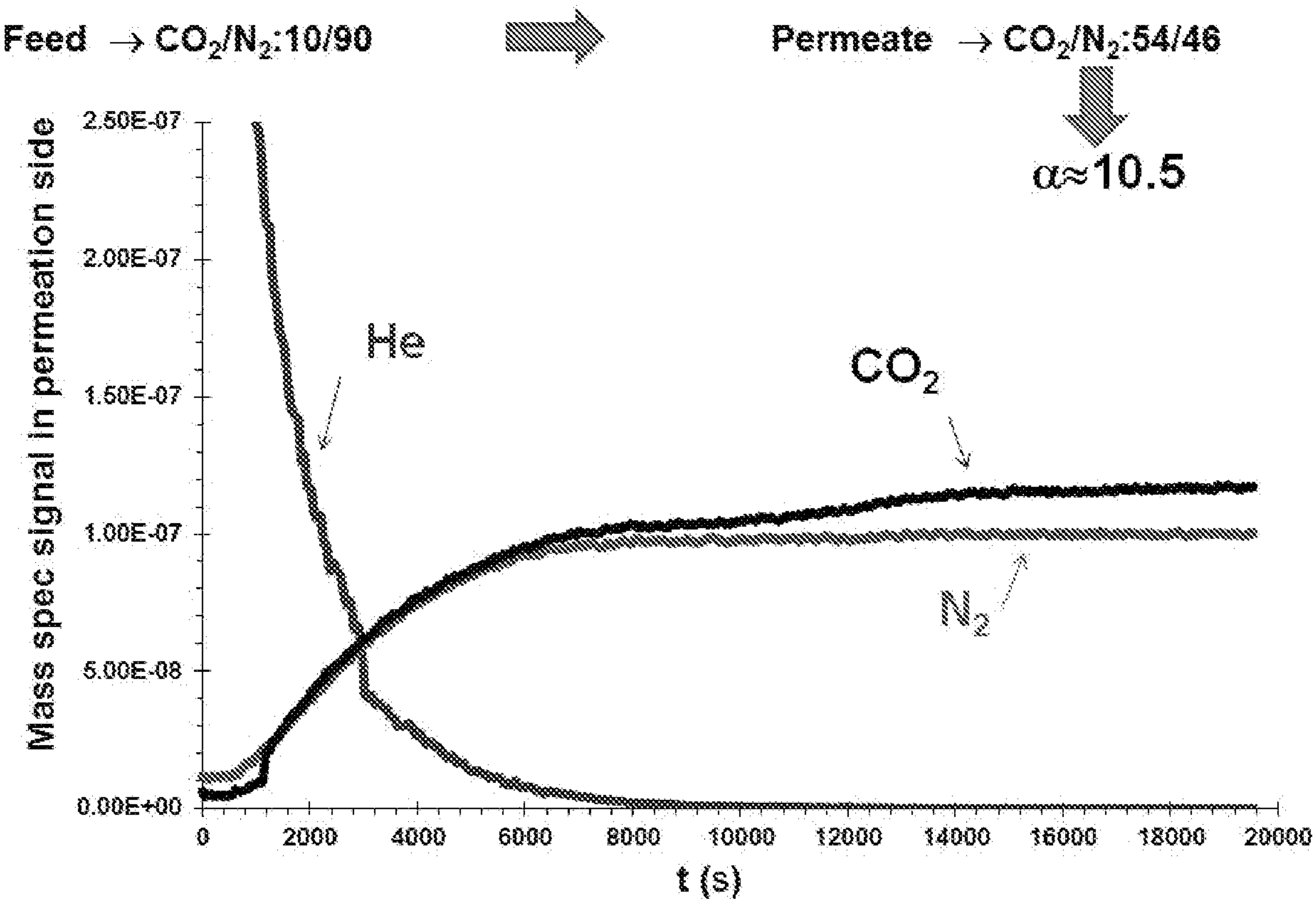

Feed → CO_2/N_2:10/90
Permeate → CO_2/N_2:54/46
α≈10.5
Mass spec signal in permeation side
2.50E-07
2.00E-07
1.50E-07
1.00E-07
5.00E-08
0.00E+00
He
CO_2
N_2
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
20000
t (s)

FIG. 11

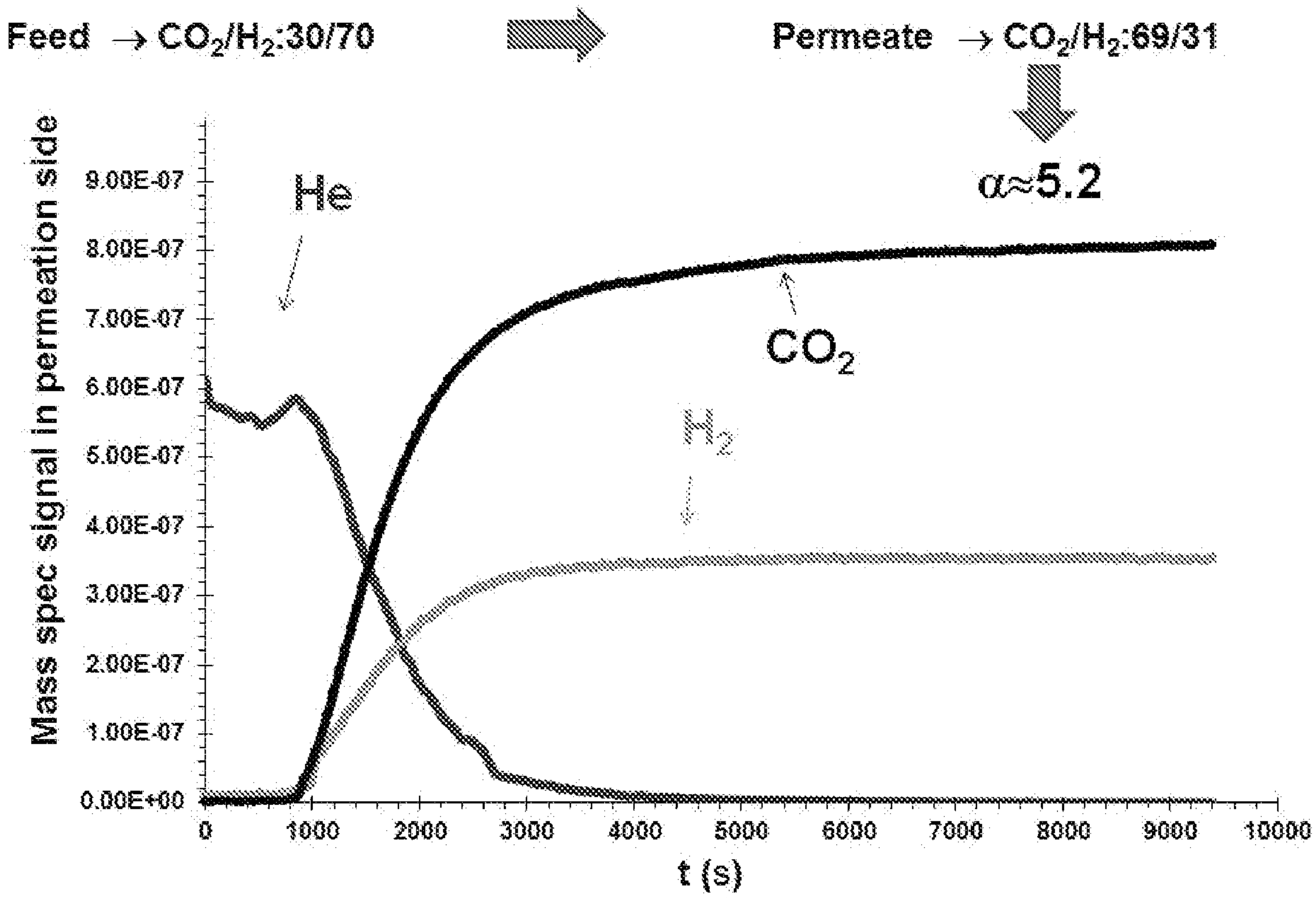

Feed → CO_2/H_2:30/70
Permeate → CO_2/H_2:69/31
α≈5.2
He
CO_2
H_2
Mass spec signal in permeation side
9.00E-07
8.00E-07
7.00E-07
6.00E-07
5.00E-07
4.00E-07
3.00E-07
2.00E-07
1.00E-07
0.00E+00
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
t (s)

FIG. 12

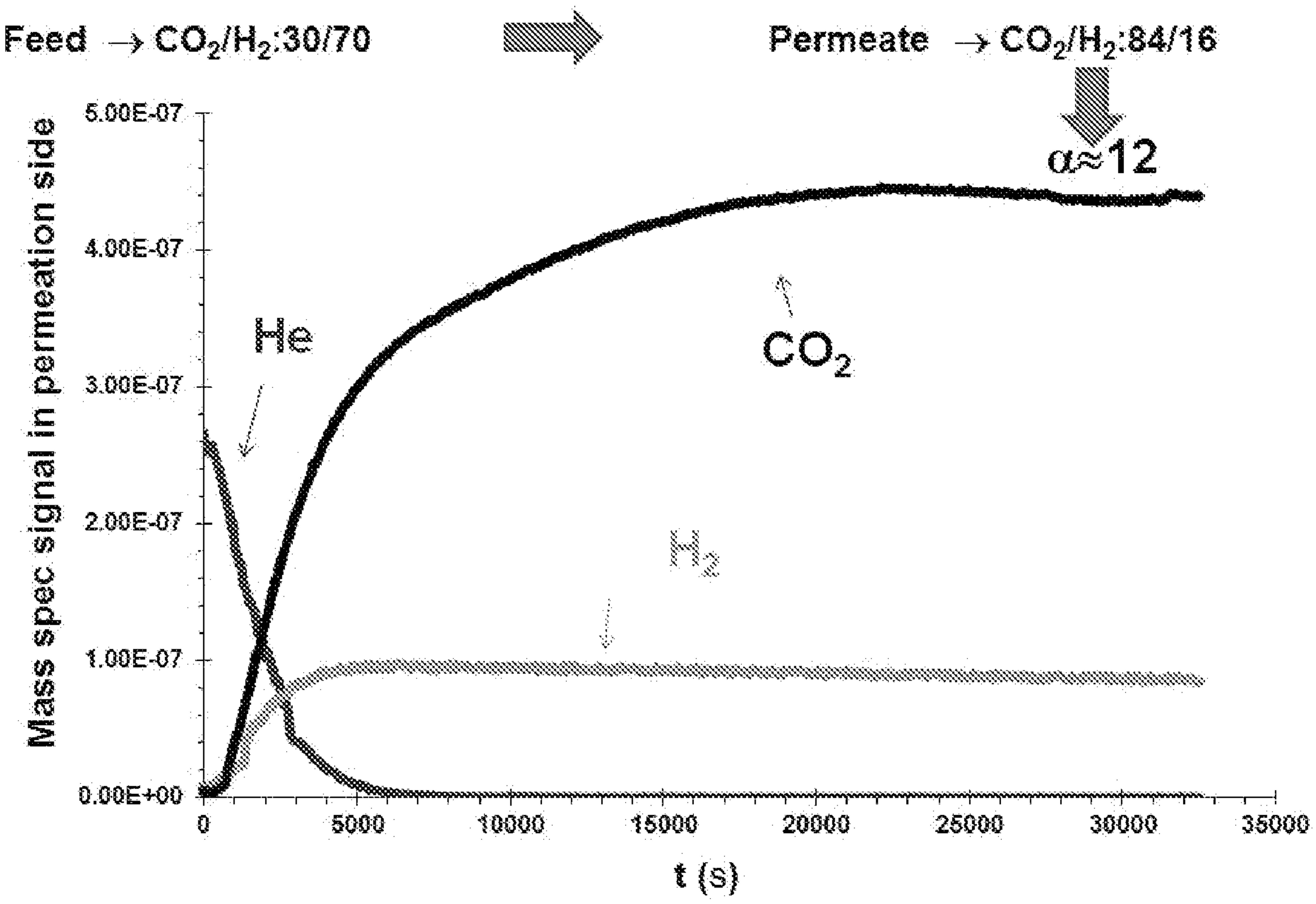
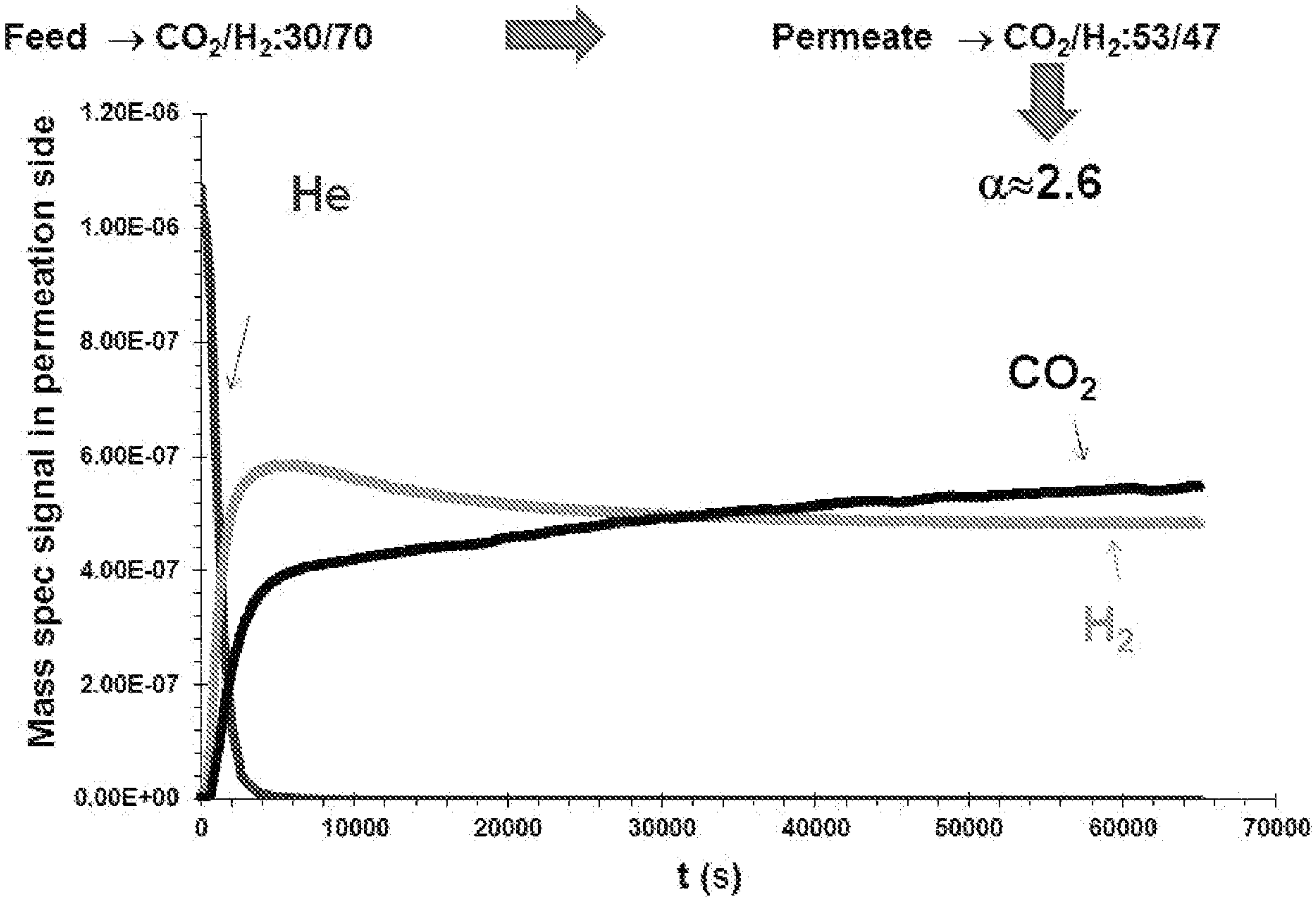

Feed → CO2/H2:30/70
Permeate → CO2/H2:84/16
α≈12
He
CO2
H2
Mass spec signal in permeation side
5.00E-07
4.00E-07
3.00E-07
2.00E-07
1.00E-07
0.00E+00
0
5000
10000
15000
20000
25000
30000
35000
t (s)

FIG. 13



Feed → CO_2/H_2:30/70
Permeate → CO_2/H_2:53/47
α≈2.6
He
CO_2
H_2
Mass spec signal in permeation side
1.20E-06
1.00E-06
8.00E-07
6.00E-07
4.00E-07
2.00E-07
0.00E+00
0
10000
20000
30000
40000
50000
60000
70000
t (s)

FIG. 14

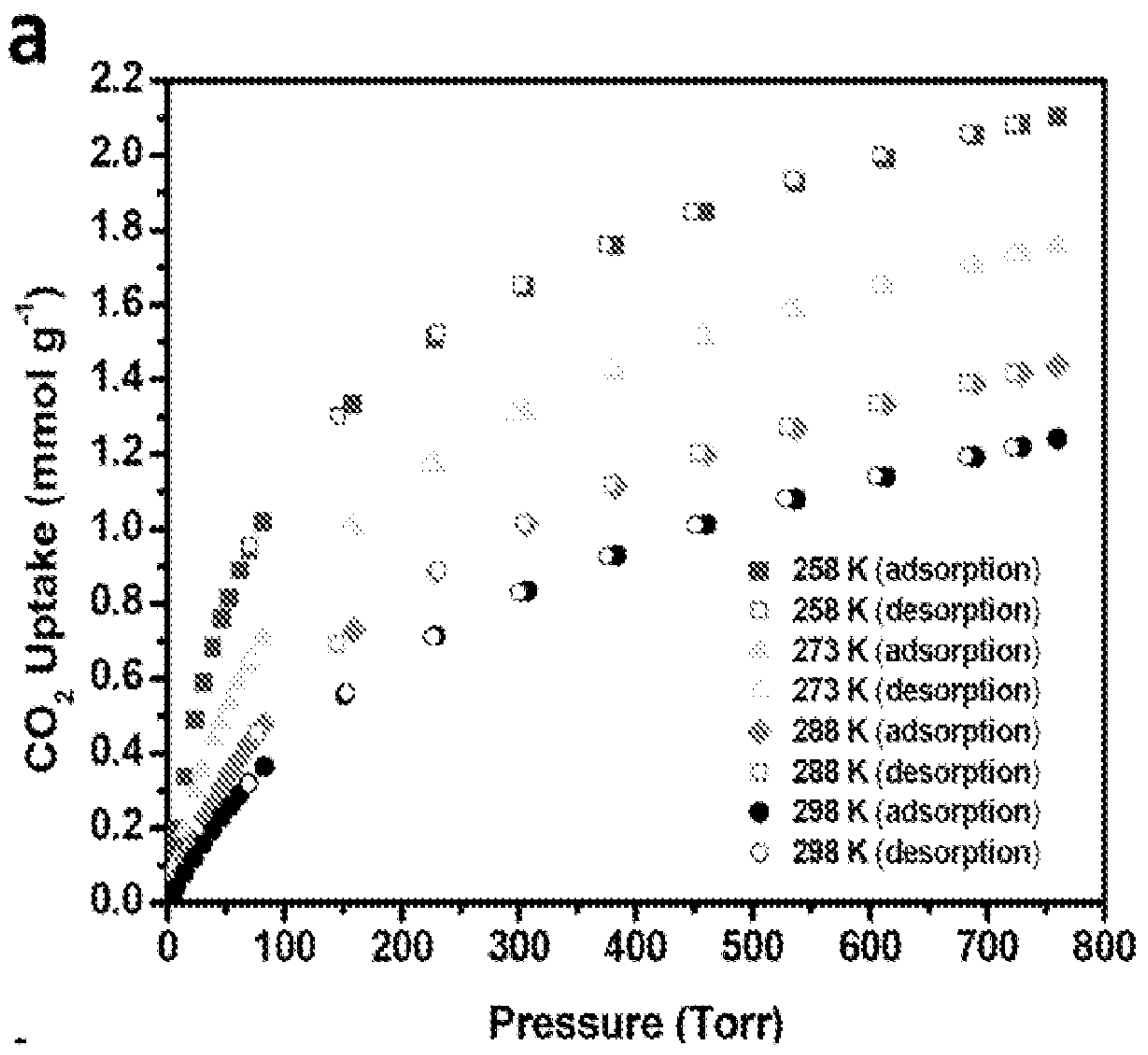


FIG. 15A

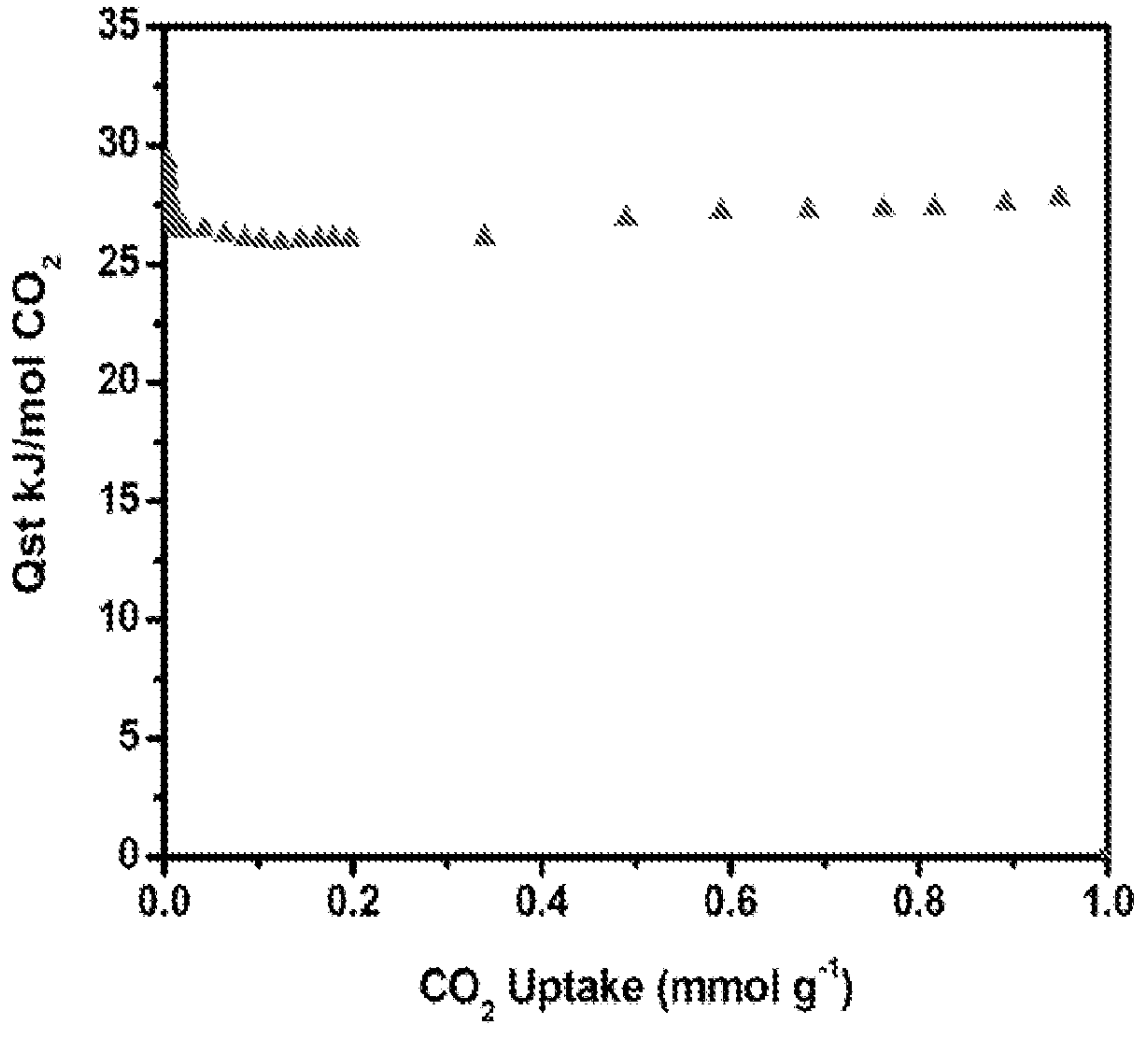


FIG. 15B

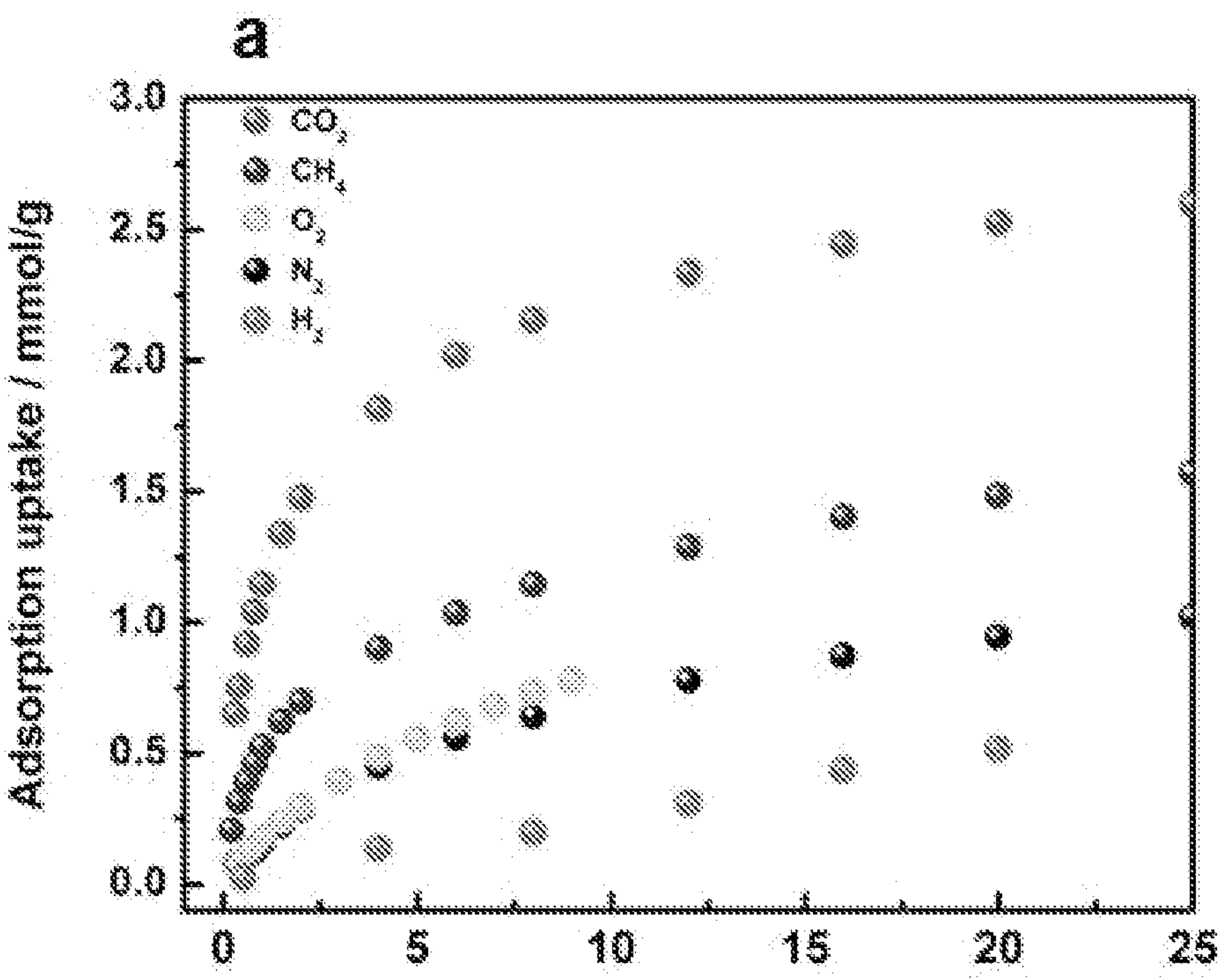


FIG. 16A

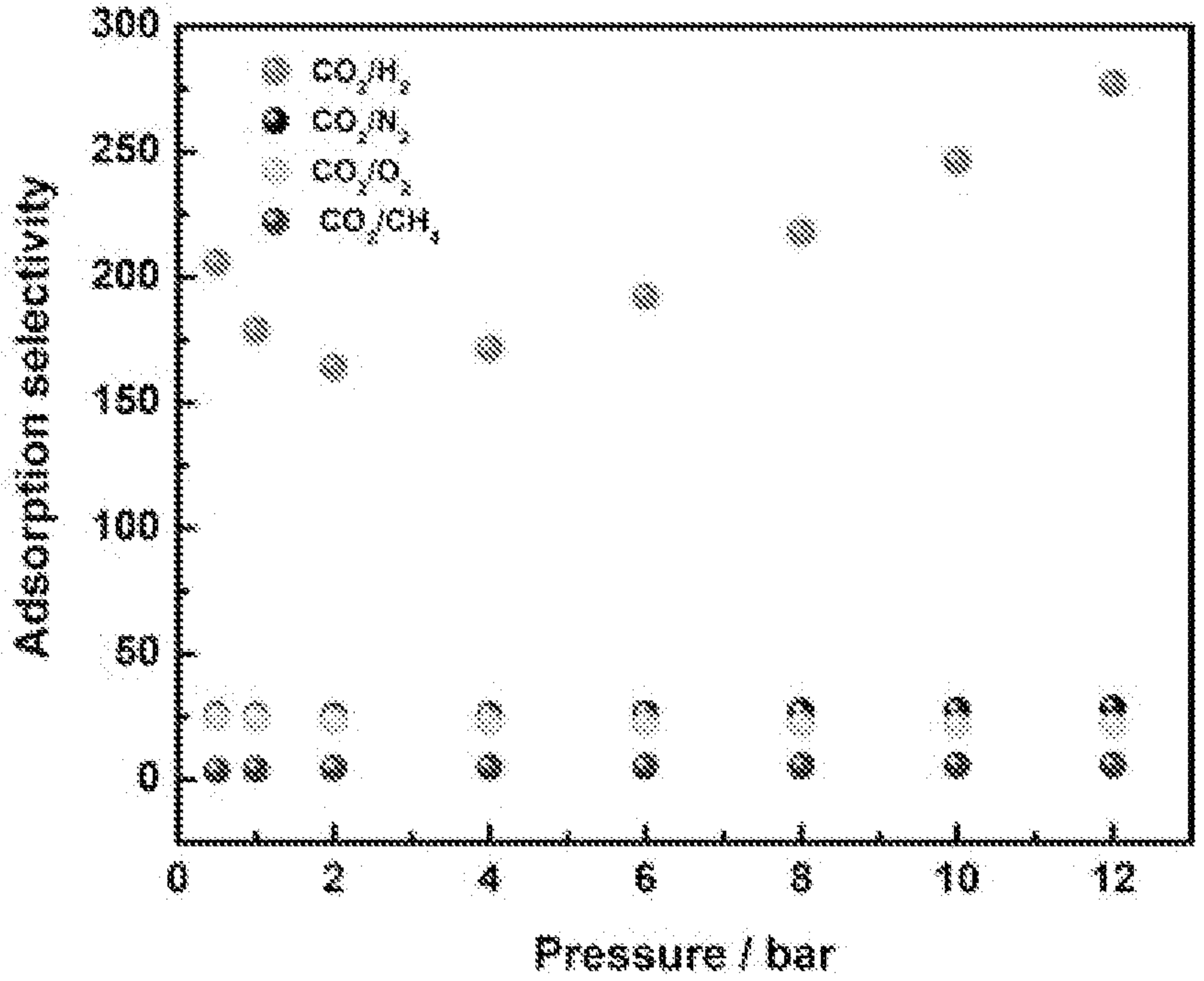


FIG. 16B

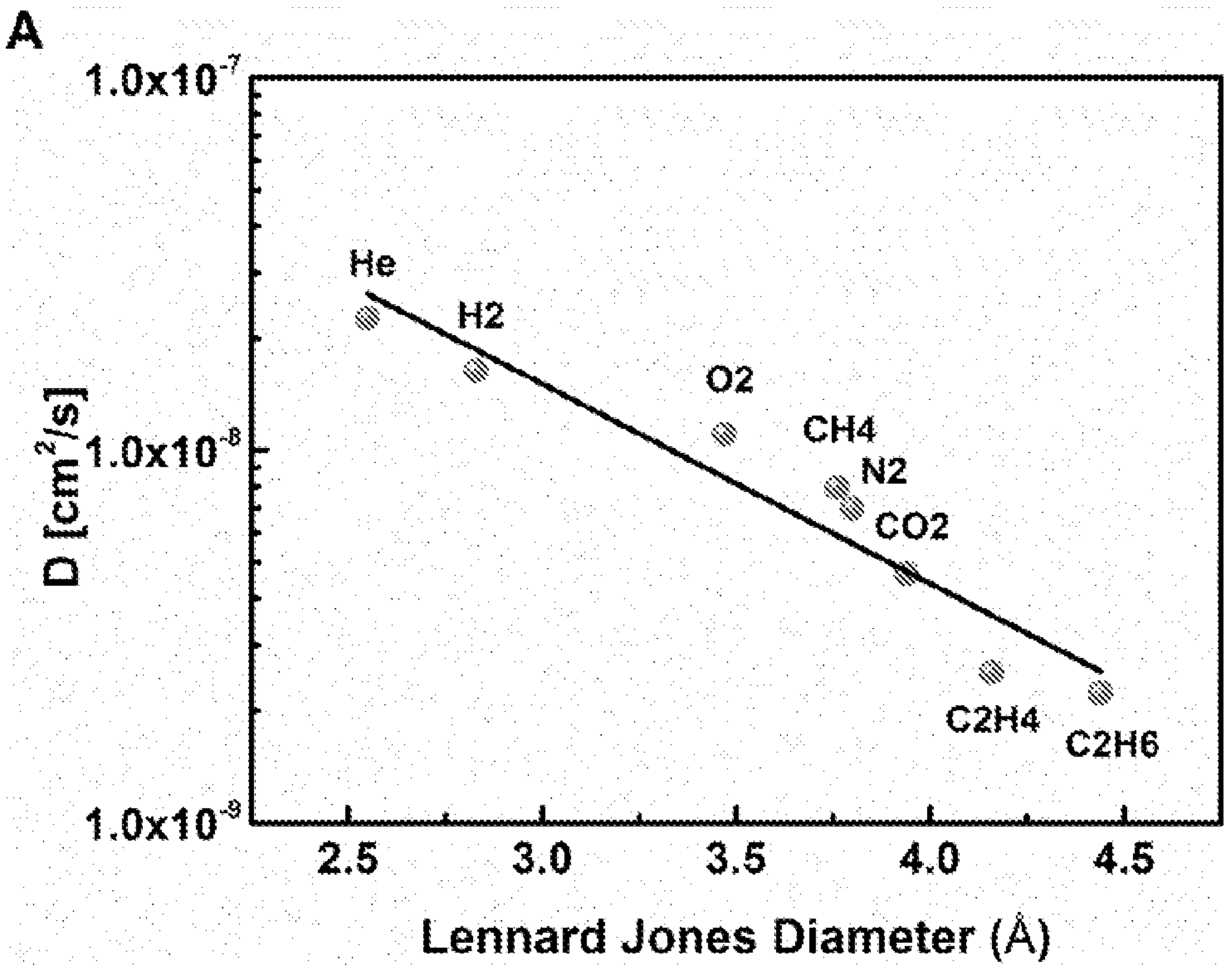


FIG. 17A

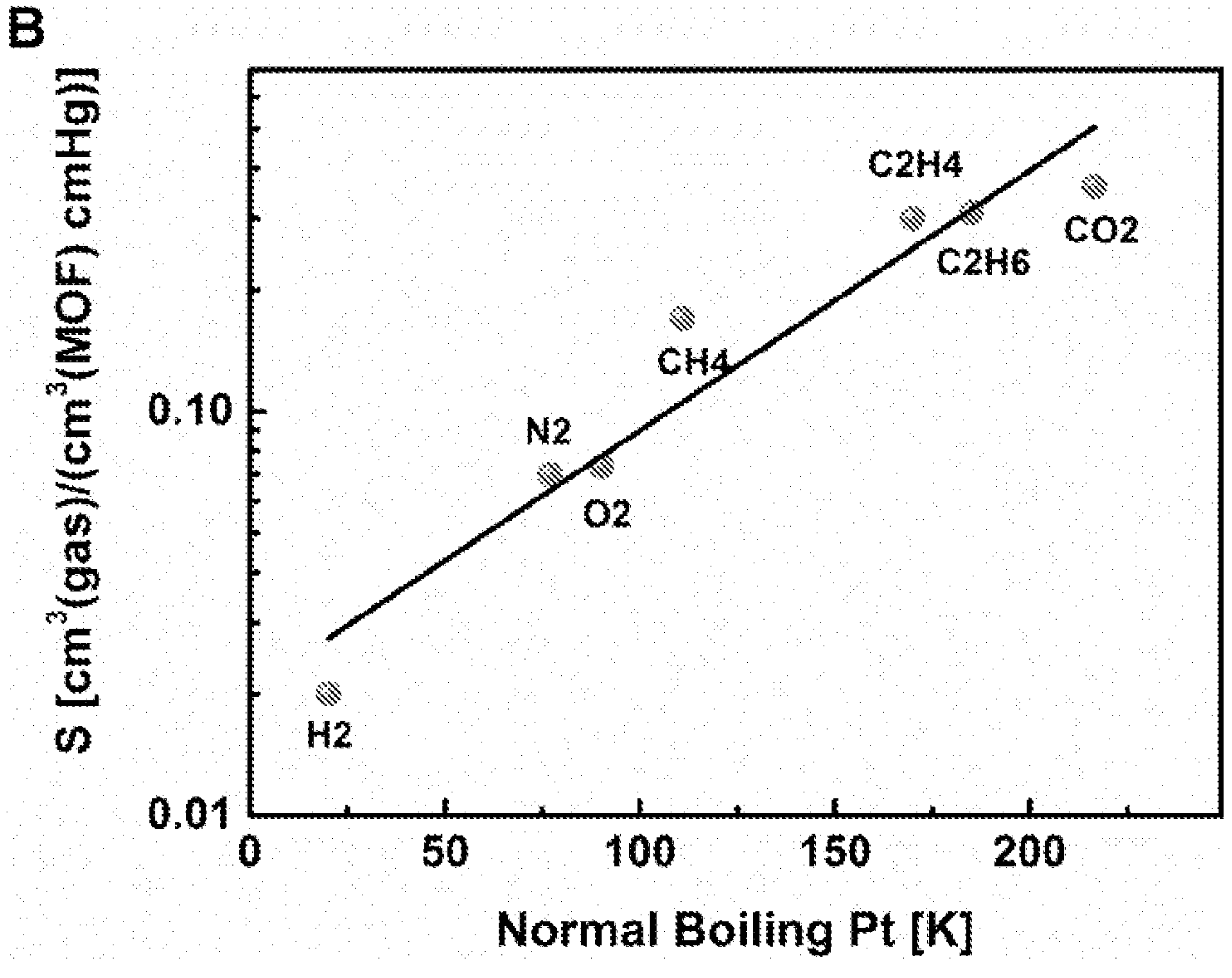


FIG. 17B