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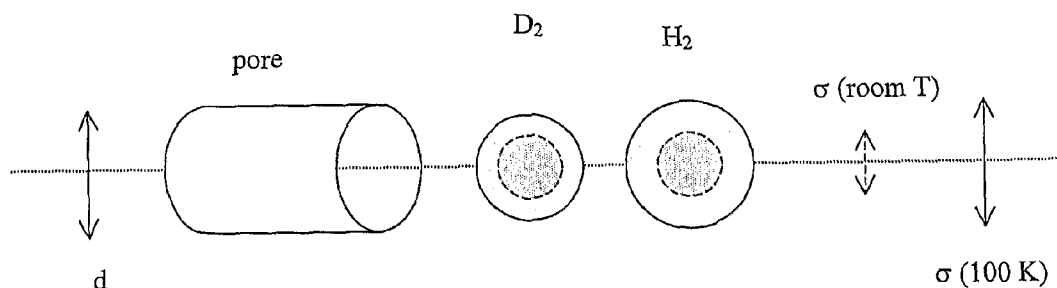
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(54) Title: ISOTOPE SEPARATION BY QUANTUM SWELLING



(57) Abstract: A method of separating H₂ and D₂, or possibly other isotopes of low molecular mass, in which a mixture of the isotopes is filtered at a temperature at which quantum swelling effects become significant. The temperature is typically in the range 10K to 100K, or preferably about 20 to 80K and most preferably about 30K. The filter system may be based on materials having a complex porous structure such as zeolite rho, or on a relatively simple material such as porous carbon. A multi-step sequence of filters may produce D₂ of over 90% purity.

ISOTOPE SEPARATION BY QUANTUM SWELLING

FIELD OF THE INVENTION

- 5 This invention relates to separation of isotopes by quantum swelling effects and in particular but not only to separation of the hydrogen isotopes H₂ and D₂.

BACKGROUND TO THE INVENTION

- 10 A range of techniques are known for separation of hydrogen isotopes, including thermal diffusion, centrifugation, laser separation, adsorption and proton exchange membranes. In general these methods are either expensive or inefficient. Microporous materials are suitable for separating many mixtures through size and shape selectivity but are generally unsuitable for hydrogen mixtures, because the hydrogen molecules (hydrogen H₂,
15 deuterium D₂, tritium T₂) ordinarily have the same size and shape, differing only in mass. The diffusivities of H₂ and D₂ differ only by a factor of $\sqrt{2}$ at room temperature for example.

- Diffusion of hydrogen molecules in microporous materials has been investigated
20 theoretically in a classical framework using energies determined by the traditional Lennard Jones potential. However, in narrow pores at low temperatures when the space available for movement of molecules becomes comparable to the de Broglie wavelength of the molecules, quantum effects can become significant. The correction to the classical potential depends inversely on temperature and molecular mass, and differences between
25 the effective size of different hydrogen isotopes or other isotopes can arise.

SUMMARY OF THE INVENTION

- It is an object of the invention to provide an alternative method for separation of hydrogen
30 isotopes at low temperatures, and also possibly other isotopes with similarly small molecular mass.

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In one aspect the invention may be said to reside in a method of separating isotopes, including: providing a fluid containing a mixture of the isotopes, preparing a filter system having a pore size at room temperature which is greater than the molecular diameters of the isotopes, cooling the mixture and the filter system to a temperature at which quantum
5 effects differentially enlarge the diameters of the isotopes and differentially effect their passage through the filter, and passing the mixture once or more through the filter system to separate the isotopes.

In one embodiment the isotopes are H_2 and D_2 , and the filter system includes zeolite rho.
10 Preferably the temperature is in the range 10K to 100K, more preferably 20 to 80K, and most preferably about 30K. The filter generally includes one or more membranes of zeolite rho. A range of other isotopes with small molecular mass such T_2 , ^3He , ^4He may be separated from various mixtures by a method of this general kind, using a range of different filter systems.

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In another aspect the invention resides in a system for implementing a method as defined above. The invention may further be said to reside in any alternative combination of features that are indicated in this specification. All equivalents of these features are deemed to be included.

20

LIST OF FIGURES

Preferred embodiments of the invention will be described with reference to the accompanying drawings, of which:

25

Figure 1 shows the Lennard-Jones potential for H_2 and D_2 at 50K,

Figure 2 shows temperature variation of the LJ size parameter σ for H_2 and D_2 ,

Figure 3 schematically indicates quantum swelling of H_2 and D_2 at low temperatures,

Figure 4 shows the structure and pore size of zeolite rho,

30

Figure 5 shows selectivity data for D_2 over H_2 ,

Figure 6 summarises data for various isotopes and temperatures, and

- 3 -

Figure 7 outlines a separation system.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

5 Referring to the drawings it will be appreciated that the invention may be implemented in various forms, and that this description is given by way of example only. The invention is described primarily in relation to separation of hydrogen isotopes using zeolite rho as a porous material, although it will be appreciated that other isotopes and materials may also be suitable. Full details of the separation system have not been given but will be known to
10 a skilled person.

Figure 1 shows Lennard Jones (LJ) potential for interactions between gaseous H_2 or D_2 and an oxygen atom in the solid phase of a microporous material. Oxygen provides the bulk of the interaction potential with a gaseous host in a zeolite. In this figure U is the potential
15 energy, k_B is the Boltzmann constant, r the distance between a gas molecule and solid atom, and σ is the distance between the gas molecule and the solid atom at the position where the potential changes from being attractive to repulsive. Both the gas molecule and solid atom are assumed spherical. The solid line is the classical potential which is identical for both H_2 and D_2 . The dashed and dotted lines respectively include their quantum
20 corrections at 50K. The different values of r at $U=0$ for example indicate that the effective size of H_2 is larger than D_2 at this temperature, an effect which is known as "quantum swelling" [1-3].

Figure 2 shows temperature variation in the effective LJ size parameter σ for H_2 and D_2
25 after the quantum correction is made. Computer simulations have determined that the critical pore size that the gas molecule can enter is roughly 0.96σ . The value of σ increases as temperature decreases with the increase being greater for H_2 than D_2 . This leads to an increasing steric hindrance which reduces the diffusivity of H_2 over D_2 through narrow pores which are about the same size as the molecules. A microporous material having
30 pores of a suitable size can therefore be effective as a filter so long as the temperature is controlled within an appropriate range.

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Figure 3 shows the effect schematically in relation to an ideal pore of diameter d , where the effective value of σ at room temperature (about 20 °C) for both H_2 than D_2 is 0.2782 nm, but swells to 0.291 nm and 0.285 nm respectively at 100 K. If d is 0.28 nm, which corresponds approximately to zeolite rho, then D_2 will pass through the pore relatively easily while H_2 will be relatively hindered. In quantum terms, the effect may be considered to arise when the uncertainty in position of the molecule, as estimated by the de Broglie wavelength λ for example, is comparable to $(d - 0.96\sigma)$ where σ is the room temperature value. A reasonable condition the effect to be economic for purposes of isotope separation is thought to be given by $\lambda/(d - 0.96\sigma) > 10$.

10

Figure 4 shows the zeolite rho cage which presents a window having a pore size of 0.543 nm measured centre to centre between oxygen atoms as indicated. After subtracting the diameter of the oxygen atom as 0.2644 nm the pore size is 0.2786 nm. At 100 K the value of σ for H_2 has increased to 0.29 nm so that 0.96σ is 0.2784 nm which approximately matches the pore size. At still lower temperatures passage of the H_2 molecule through the cage is increasingly hindered. Zeolite rho can therefore be used as a filter material in separating H_2 and D_2 although a range of other materials will also be suitable such as aluminophosphates ALPO-25, ALPO-21, aluminosilicate Bikitaite, and borosilicate RUB-24, for example. Porous carbon materials have been shown to be useful in some circumstances [4-5].

20

Figure 5 shows the variation of kinetic selectivity with temperature for H_2 and D_2 in zeolite rho determined by computer simulation. Kinetic selectivity is defined as the ratio of the transport diffusivity of D_2 to H_2 with the closed and open circles in the main figure demonstrating the difference between classical and quantum corrected calculations respectively. Their values are similarly low towards room temperature where quantum effects are negligible, and are also thought to be low at very low temperatures where both H_2 and D_2 are effectively swollen beyond the pore size and are similarly hindered. At around 10-100 K however, preferably 20-80K, and especially at around 30K, the pore size lies between the effective size of the two isotopes, so that D_2 diffuses relatively easily while H_2 does not. The inset to this figure shows the flux selectivity, defined as the product

25

30

- 5 -

of the equilibrium constant and the kinetic selectivity, and provides the flux ratio when the gas phase concentration gradient is the same for each isotope. Open triangles and closed triangles represent flux selectivity based on quantum and classical considerations respectively.

5

Figure 6 gives specific σ and λ values for various isotopes at room temperature, 100K, 65K, 40K and 30K, by way of example. It can be seen that a separation system having a suitably selected filter material could be effective in separating a range of different mixtures. A recent experiment has shown that a mixture of H_2 and D_2 can be effectively
10 filtered on porous carbon medium at around 77K [5].

Figure 7 shows a system that could be used for separation of hydrogen isotopes. It includes a filter in which a membrane module having one or more zeolite rho membranes supported on a porous ceramic such as alumina. The support would be in the form of
15 tubes, typically about 10 mm in outer diameter and coated on the inner surface with a zeolite rho layer typically about 1-30 microns thick. The tube length may be in the range of 0.5 to 2 meters, for a feedstock reservoir having a volume of 100-400 lit and pressure as high as 300 bar. The membrane separator will be kept at a low temperature, in range of 20 to 80 K. Feedstock from the reservoir flows through the tubes, and the permeate collected
20 from the shell side of the membrane in the permeate reservoir. The permeate will be richer in deuterium as only a small fraction of the hydrogen will flow through into the permeate, while essentially all the deuterium will flow through. The vacuum pump will maintain low pressure on the permeate side, and a pressure controller will control the pressure in the feed side.

25

Typically, in nature most mixtures have about 1 part of deuterium per 5000 parts of hydrogen, and the process will enhance the deuterium to hydrogen ratio by a factor of 20-30 in a single pass. The product gas pressure will be boosted after the vacuum pump to a suitable level for storage in the collection vessel. When sufficient product has been
30 collected it can be further concentrated by a factor of 20-30 by again passing through the membrane module. This process can be repeated till sufficient purity of deuterium has

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been obtained. For example, even based on a conservative estimate of concentration by a factor of 20, after four steps deuterium of 97 percent purity may be obtained, while after five steps deuterium of over 99.8 percent purity may be obtained.

- 5 Large flow rates of hydrogen are available in ammonia plants where hydrogen is an important feedstock for ammonia synthesis. Use of such a membrane device in an ammonia plant will provide an economical application of the method to concentrate and produce deuterium. In such situations the feedstock reservoir is not necessary, and the process runs on a continuous flow of hydrogen from its source.

10

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- 15 5. X Zhao, et al, "Kinetic Isotope Effect for H₂ and D₂ Quantum Molecular Sieving in Adsorption/Desorption on Porous Carbon Materials", J Phys Chem B 2006, 110, 9947-9955.

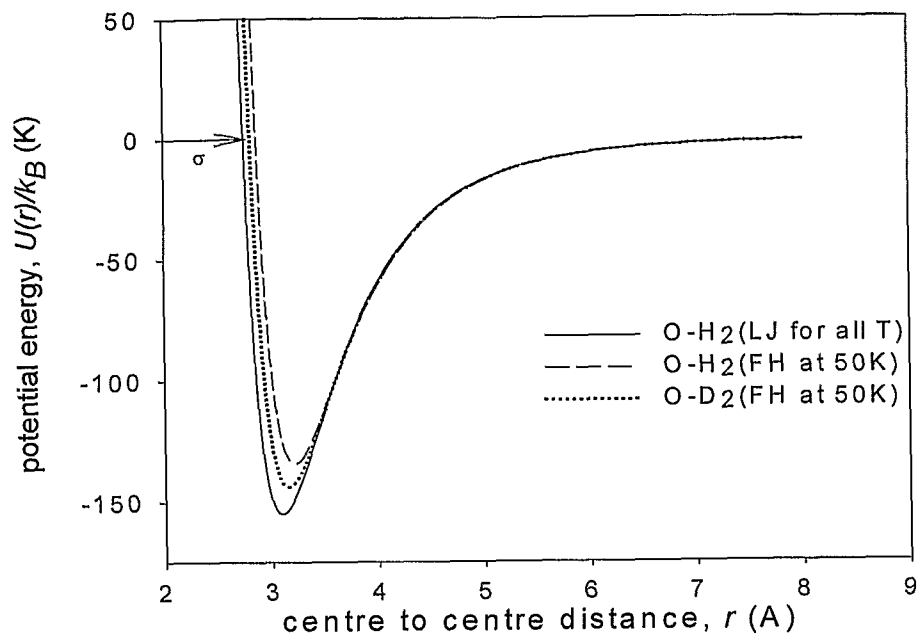
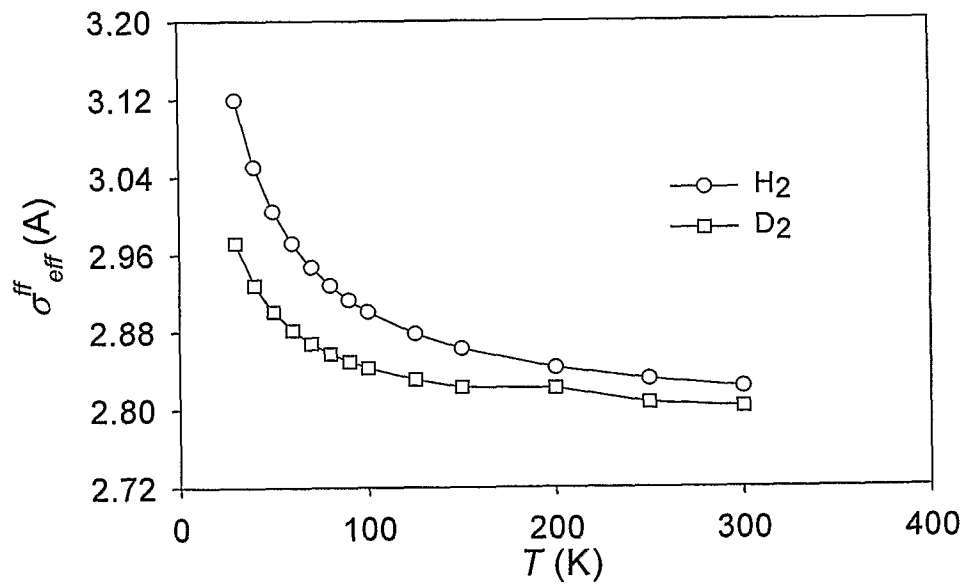
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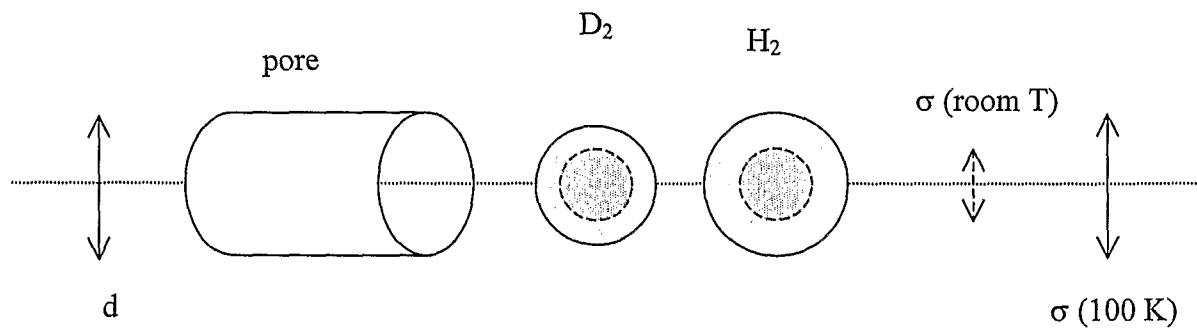
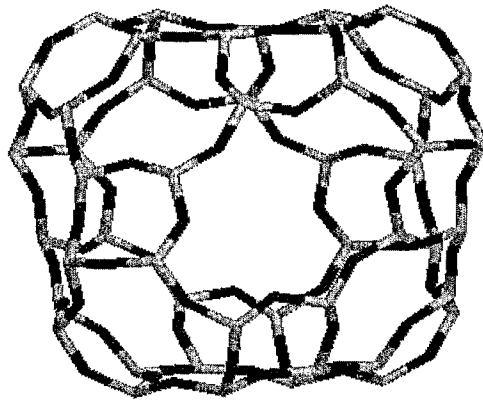
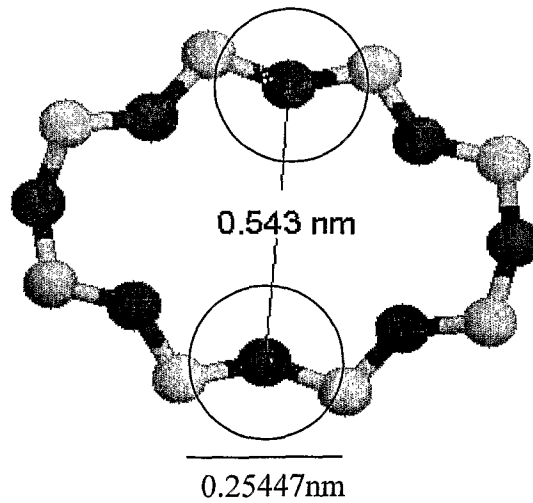
CLAIMS

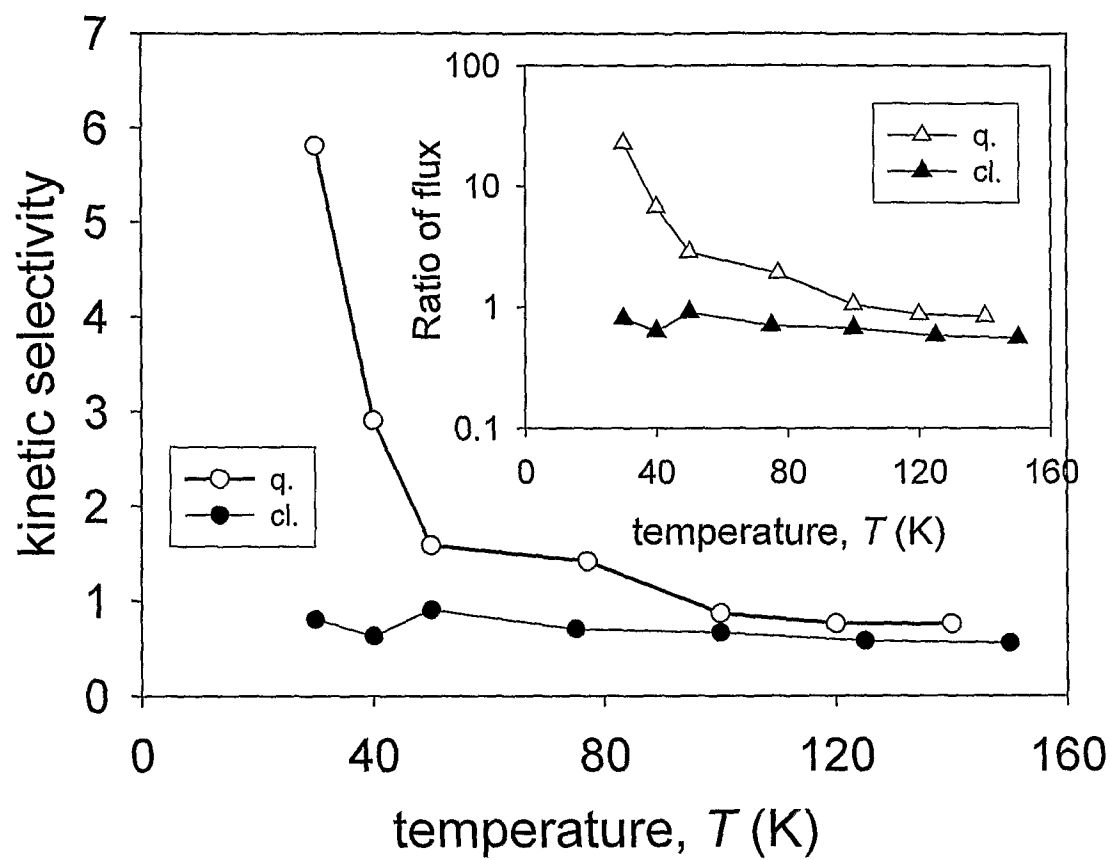
1. A method of separating isotopes, including:
providing a fluid containing a mixture of the isotopes,
5 preparing a filter system having a pore size at room temperature which is generally greater than the molecular diameters of the isotopes,
cooling the mixture and the filter system to a temperature at which quantum effects differentially enlarge the diameters of the isotopes and differentially effect their passage through the filter, and
10 passing the mixture once or more through the filter system to separate the isotopes.
2. A method according to claim 1 wherein the isotopes are H₂ and D₂, and the filter system includes zeolite rho.
- 15 3. A method according to claim 2 wherein the temperature is in the range 10K to 100K and preferably about 20 to 80K and most preferably about 30K.
4. A method according to claim 2 wherein the filter includes one or more membranes of zeolite rho.
20
5. A system for separation of the isotopes H₂ and D₂, including:
a reservoir containing a mixture of the isotopes to be separated,
a pair of collectors for respective isotopes when separated, and
a temperature controlled separator connected between the reservoir and the
25 collectors,
wherein the separator includes a filter arrangement having a pore size which differentially affects passage of the isotopes at the control temperature due to quantum swelling.

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6. A system according to claim 5 wherein the filter arrangement includes one or more membranes of zeolite rho, aluminophosphate ALPO-25, aluminophosphate ALPO-21, aluminosilicate Bikitaite, borosilicate RUB-24, or porous carbon materials.
- 5 7. A system according to claim 6 wherein the filter arrangement includes one or more membranes of zeolite rho.

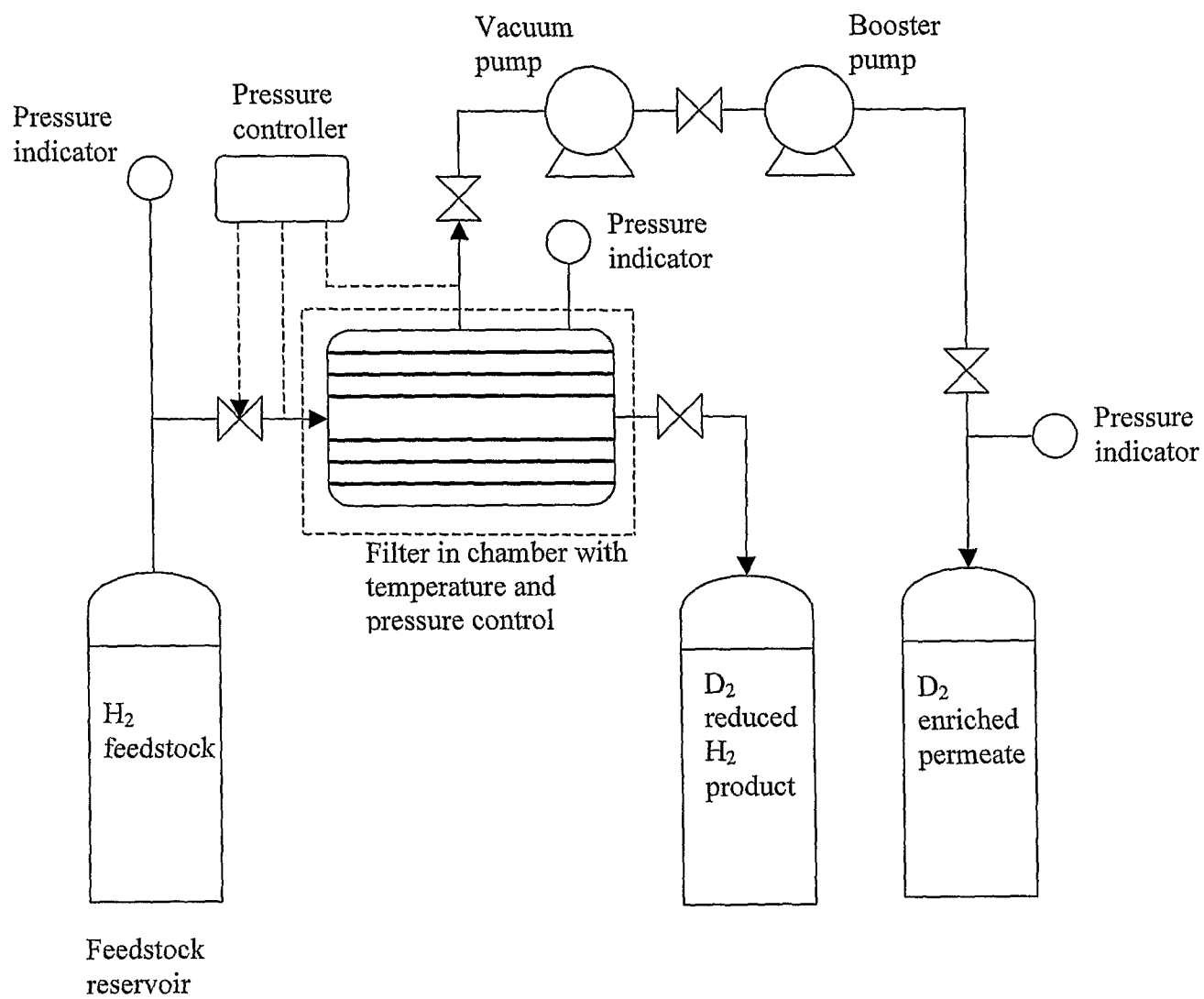
**FIGURE 1****FIGURE 2**

**FIGURE 3****FIGURE 4**

**FIGURE 5**

	H ₂	D ₂	T ₂	He ³	He ⁴
σ (room T)	0.2782	0.2782	0.2782	0.258	0.258
σ (100K)	0.2901	0.2843	0.2823	0.2667	0.2646
σ (65K)	0.2958	0.2875	0.2844	0.2710	0.2680
σ (40K)	0.3050	0.2928	0.2882	0.2781	0.2737
σ (30K)	0.3119	0.2972	0.2913	0.2836	0.2782
λ (65K)	0.1526	0.1079	0.0882	0.1247	0.1083
λ (40K)	0.1945	0.1376	0.1124	0.1590	0.1380
λ (30K)	0.2246	0.1589	0.1298	0.1836	0.1594

FIGURE 6

**FIGURE 7**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2006/000907

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

B01D 59/00 (2006.01) **B01D 15/26** (2006.01) **B01D 59/12** (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01D 59/00, 59/12, 15/26

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DWPI: B01D 59/00 or 59/02 and keywords (chill+ or cool+ or cryogenic+); B01D 15/26

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6332914 B (LEE, MYUNG W) 25 December 2001 Whole document	1-7
A	Derwent Abstract Accession No 95-028881/04, Class K05 and RU 1619492 C (AS USSR CHEM PHYS POWER PROBLEMS INST) 30 May 1994 See abstract	1-7
A	Patent Abstracts of Japan, JP 61-138519 A (HIDEO ET AL) 26 June 1986 See abstract	1-7



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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU2006/000907

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Patent Document Cited in Search Report	Patent Family Member
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RU 1619492	
JP 61138519	
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END OF ANNEX	