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Short communication

Experimental study of hydrogen, carbon dioxide and nitrogen permeation through a microporous silica membrane

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Abstract

The transport of hydrogen, carbon dioxide and nitrogen through a microporous tubular silica membrane has been investigated between 20 and 200°C and 3–9 bar upstream pressure. Pure compounds permeabilities decrease from H_2 to N_2 and do not show a strong dependence upon upstream pressure. Temperature variation could be described by an Arrhenius law with low apparent activation energies (3.5, 3.7 and 3.4 kJ mol^{-1}, respectively, for hydrogen, carbon dioxide and nitrogen). The ideal separation selectivity computed from these results leads to values around 3.5 and 3 for H_2/CO_2 and CO_2/N_2 separation independent of temperature. These values are significantly smaller than those expected from a strict Knudsen mechanism (4.7 and 3.7, respectively). A viscous contribution, resulting for instance from a too large pore size distribution of the active silica layer, possibly accounts for the experimental results obtained.

Keywords: Permeability; Silica; Membrane; Carbon dioxide; Hydrogen

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1. Introduction

The use of microporous inorganic membranes for gas separation applications has received increased interest in recent years. In fact, compared to polymeric membranes, mineral membranes with defect free active layers have a good stability towards high temperature conditions or corrosive atmospheres [1]. These characteristics could lead to innovative applications such as hydrogen separation in coal gasification plants, membrane reactors or hot gaseous effluents treatment (e.g. nitrogen/carbon dioxide separation performed on fumes). The mineral active layers most commonly proposed include zeolites, carbon molecular sieves and silica materials [2–4]. The latter have been shown recently to develop promising properties both in terms of permeability and selectivity, particularly towards H_2/CO_2 separation, as illustrated in Fig. 1.

Most studies reported on silica membranes deal with flat samples, given the relatively simpler preparation procedure with this type of shape. For gas separation applications however, a tubular or hollow fiber design would be more appropriate in order to enhance module packing factor [3]. To obtain this objective, the preparation protocol, which is currently used for flat samples (dip coating, drying, calcinating [5]) has to be adapted to a tubular geometry. This works intends to report early results obtained with a novel tubular microporous silica membrane consisting of a thin silica active layer on top of two mesoporous γ-alumina layers and an α-alumina support (providing mechanical strength). Active layer integrity, one of the major challenge for flat ceramic membranes [5], has been tentatively checked based on the transport analysis of hydrogen, carbon dioxide and nitrogen. The influence of temperature and upstream pressure on permeability has been studied as a way to achieve that purpose. Experimental results will be compared to a strict Knudsen or molecular sieving behavior, which are expected to hold in a defect free microporous silica membrane [5].

2. Materials and methods

The membrane is an AKP-30 tubular membrane prepared at the Laboratory of Inorganic Materials Science of the

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Nomenclature

a	asymptote slope
A	sample surface area
D	diffusion coefficient
E_A	apparent activation energy of permeation
L	active layer thickness
P	pressure
R	ideal gas constant
t	time
T	temperature
V	downstream cell volume
$\wp$	permeability

Subscripts

0	upstream chamber
L	downstream chamber

University of Twente (NL) [11]. Membrane length is 0.15 m, internal diameter 17×10^{-3} m, with an α-alumina support (thickness 2×10^{-3} m, mean pore diameter around 140×10^{-9} m) shown in Fig. 2, two γ-alumina layers (mean pore diameter around 3×10^{-9} m) and two silica layers (approximate thickness 50×10^{-9} m). The mean pore Kelvin diameter was estimated around 0.5×10^{-9} m based on permporometry experiments (oxygen permeance determination under various cyclohexane partial pressures [11]).

Pure gases permeability measurements were assessed based on monitoring pressure increase in a closed permeate side volume [10]. The overall set-up is shown in Fig. 3. Oven temperature can be set between 20 and 200°C; pressure can be increased and fixed up to 9 bar on the upstream side.

At time zero, a pure gas compound is introduced in the upper chamber and the response to this impulse is

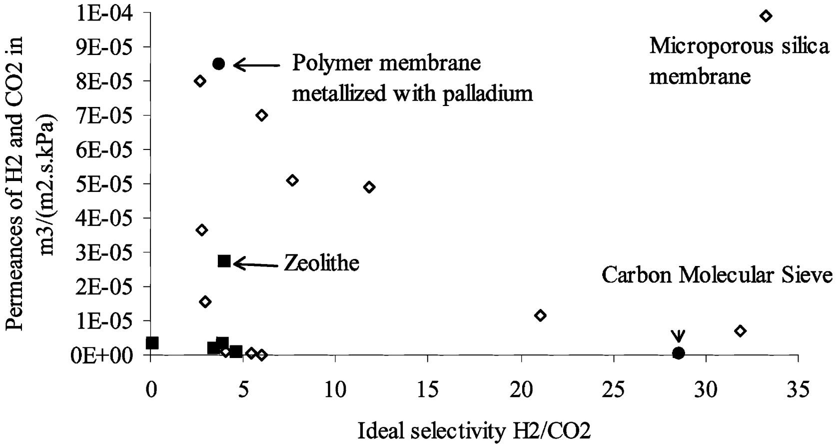

Fig. 1. Hydrogen permeability vs. H_2/CO_2 selectivity for a series of mineral membrane material candidates already reported in the literature.

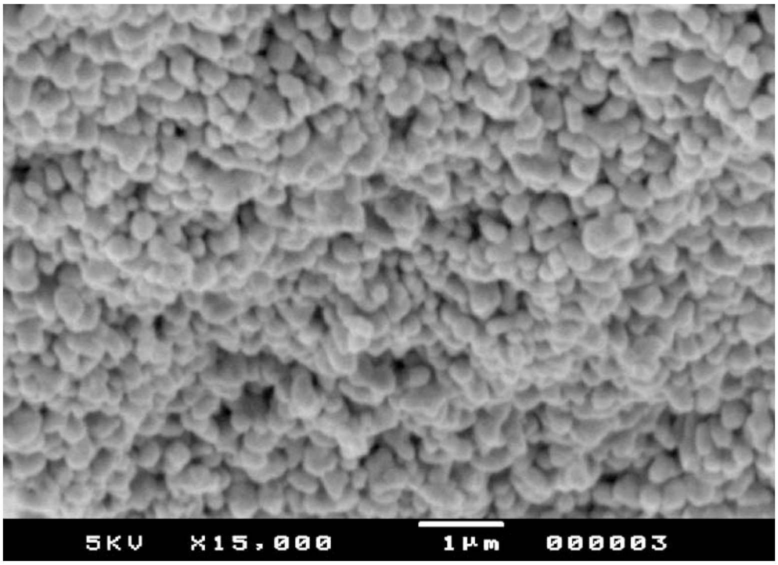

Fig. 2. Scanning electron microscopy of the alumina porous support of the silica tubular membrane investigated in this work.

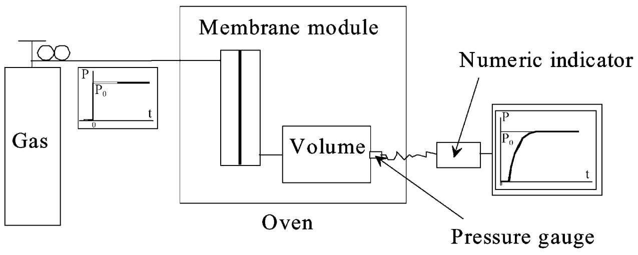

Fig. 3. Schematics of the set-up used for permeability measurement.

monitored in the downstream compartment by an active strain gauge (Edwards ASG NW16 2000 mbar). The electric signal ranging from 0 to 10 V is sent to a digital display (Edwards ADD). Analogical data monitoring (pressure versus time) is achieved thanks to a Personal Computer, before for data treatment.

Pure gas permeability through the membrane can be determined based on the method usually referred as the time-lag [6] which gives the following expression for the initial pressure slope:

$$P_L(t) = A\frac{RT\wp P_0}{VL}\left[t - \frac{L^2}{6D}\right] \qquad (1)$$

where A and L are the membrane characteristics, V the downstream chamber volume and (P_0, T) the operating parameters which are fixed for a given experiment. Thus, pure gas permeability can be determined from the slope of downstream pressure (P_L) versus time (t). Preliminary studies showed a reproducibility in the range of 1% according to the protocol described above.

3. Results

The influence of pressure and temperature on hydrogen, carbon dioxide and nitrogen permeabilities is shown in Figs. 4–6, respectively. Hydrogen permeability is systematically higher than nitrogen permeability, which in turn is always greater than carbon dioxide permeability. The fact that nitrogen permeates faster than carbon dioxide is striking and does not reflect the kinetic diameter (2.9, 3.3 and 3.6 Å, respectively for hydrogen, carbon dioxide and nitrogen), usually reported to account for the relative permeability ranking of gases in silica membranes [5] when a molecular sieving mechanism prevail. A strict Knudsen transport mechanism could possibly be proposed at this stage; in fact, Knudsen permeabilities rank theoretically based on the inverse of the square root of the gas molecular weights, that is $H_2 > N_2 > CO_2$ [1]. Nevertheless, the permeability values are significantly higher than those reported for flat silica membranes under similar operating conditions. For instance, hydrogen permeance is around 5×10^{-7} mol m^{-2} Pa^{-1} s^{-1} at 200°C for flat membranes prepared under similar conditions [11]. Thus, the existence of a strict Knudsen flow is questionable.

Generally speaking, pressure has a moderate to negligible influence on permeability values (Figs. 4–6). The tendency of hydrogen permeability to decrease with upstream pressure at low temperature is particularly unusual and has been reported only under specific conditions (such as the transport of a highly adsorbable compound through a microporous material under high temperature conditions [7]). When temperature exceeds 160°C, pressure has almost no influence on permeability, giving support again to a

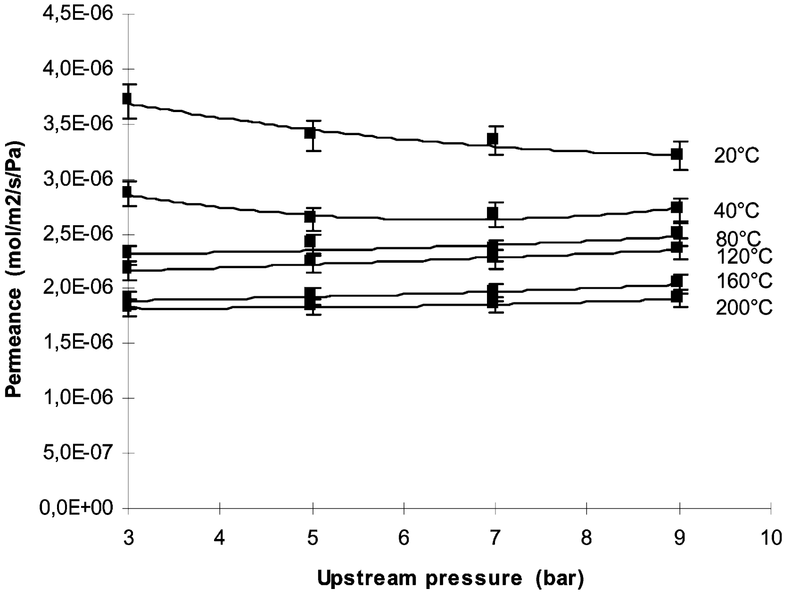

Fig. 4. Experimental hydrogen permeability values through AKP-30 tubular microporous silica membrane at 20, 40, 80, 120, 160 and 200°C, with an upstream pressure ranging from 3 to 9 bar.

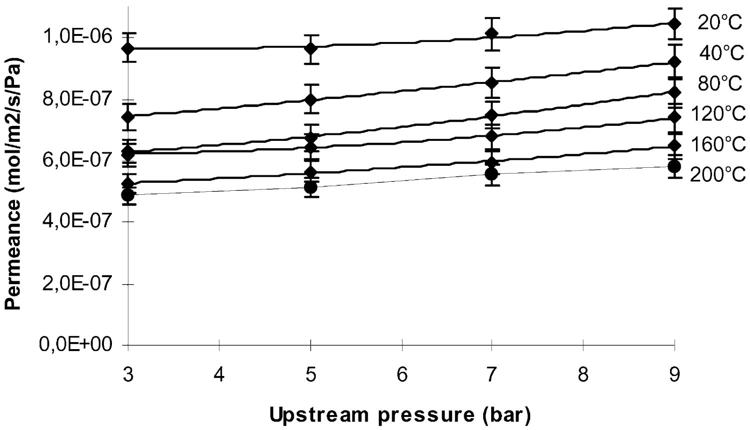

Fig. 5. Experimental carbon dioxide permeability values through AKP-30 tubular microporous silica membrane at 20, 40, 80, 120, 160 and 200°C, with an upstream pressure ranging from 3 to 9 bar.

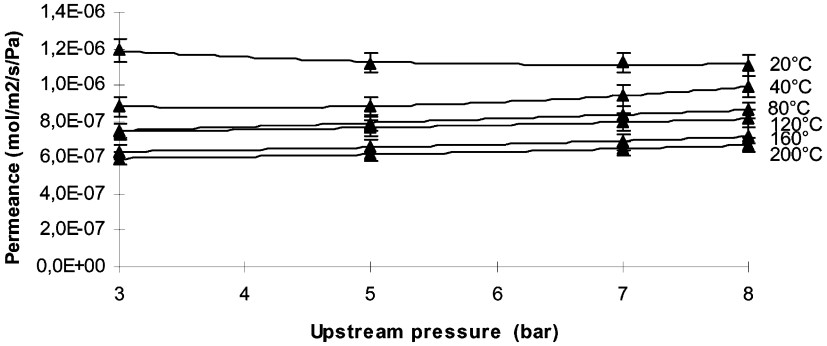

Fig. 6. Experimental nitrogen permeability values through AKP-30 tubular microporous silica membrane at 20, 40, 80, 120, 160 and 200°C, with an upstream pressure ranging from 3 to 9 bar.

Knudsen type mechanism [1]. In contrast, a strong viscous flow contribution, characteristic of the presence of defects in the active layer, would lead to a continuously increasing permeability with upstream pressure; such an event can be postulated to be essentially non-existent at this stage.

Similarly to numerous studies on gas transport in mineral membranes, temperature influence is best described based on an Arrhenius type expression

$$\wp = \wp^0 \exp\left(-\frac{E_A}{RT}\right) \qquad (2)$$

The pre-exponential term and the apparent permeation activation energy computed from experimental results are summarized in Table 1. The increase of permeability with increasing temperature leads to negative activation energies. This remains compatible with several transport mechanisms (such as viscous, Knudsen or surface flow [1,8]), except from molecular sieving mechanism. In fact, a theoretical negative apparent activation energy, very similar for each gas ($E_A = -0.5RT$) can be computed for a strict Knudsen mechanism. Based on this, the examination of the

Table 1
Experimental Arrhenius parameters for carbon dioxide, hydrogen and nitrogen permeability through AKP-30 tubular microporous silica membrane

	CO_2	H_2	N_2
$\wp^0$ (mol m^{-2} Pa^{-1} s^{-1})	7.3×10^{-7}	2.1×10^{-7}	2.6×10^{-7}
E_A (J mol^{-1})	−3706	−3522	−3412

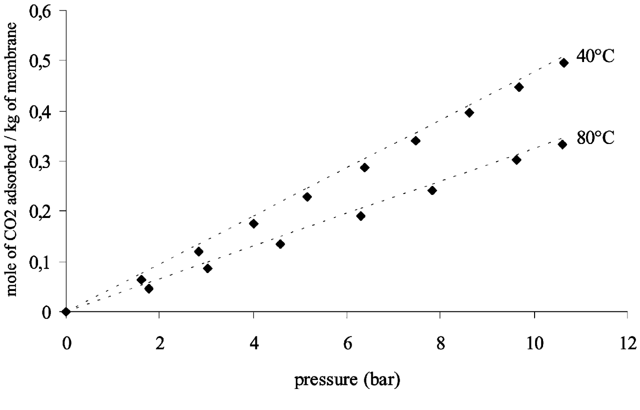

Fig. 7. Adsorption isotherms of carbon dioxide on a raw membrane material sample (i.e. active layer + alumina support) at 40 and 80°C.

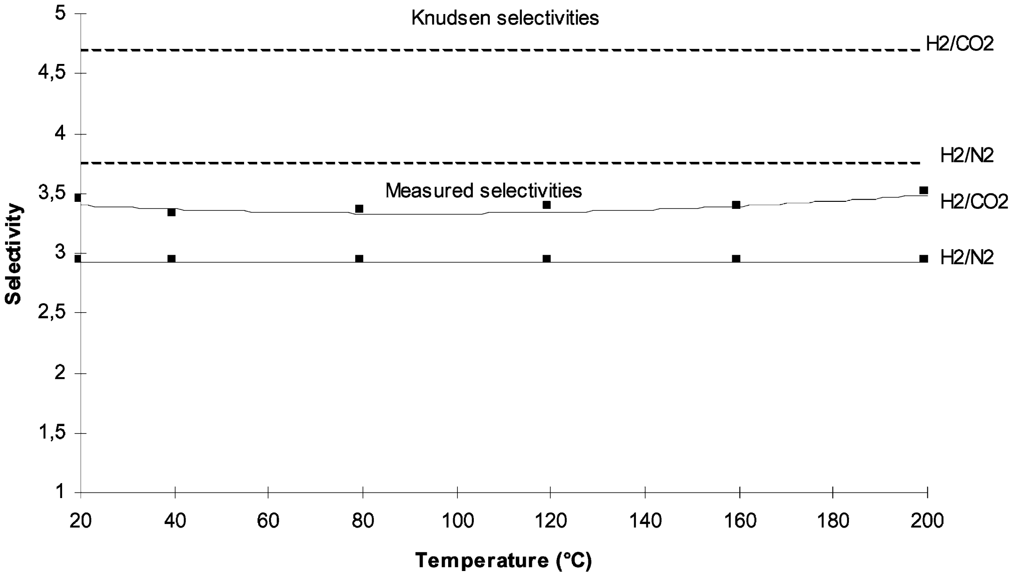

Fig. 8. Comparison between theoretical Knudsen selectivities (dashed lines) and experimental selectivities computed from pure compound permeability (squares) towards H_2/CO_2 and H_2/N_2 mixtures at different operating temperatures.

experimental values listed in Table 1 suggest that while Knudsen diffusion might not be the principal transport mechanism, it is likely to be significant. The apparent molecular weight dependence of the permeability gives another argument in favor of this hypothesis.

The possible complication resulting from a significant adsorption contribution, such as those classically observed for easily condensable gases, have been investigated based for carbon dioxide by adsorption isotherm determination (Fig. 7). The linear isotherms obtained suggest a minor effect on permeability behavior. Furthermore, the low amount of adsorbed species as well as the equivalent adsorption energy of activation can hardly account for a significant surface flow contribution.

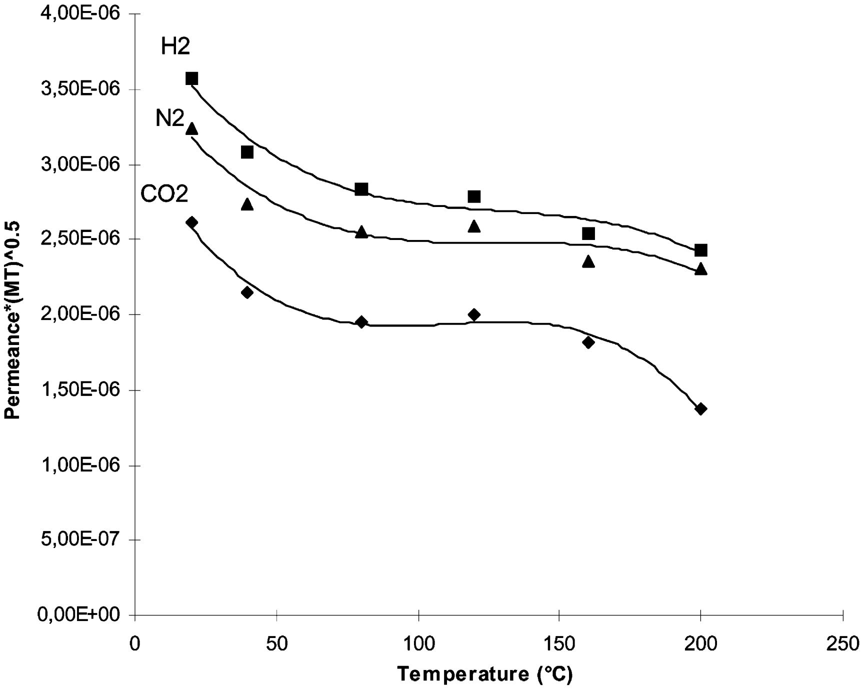

Fig. 9. Tentative correlation chart of a strict Knudsen flow mechanism for the experimental results obtained (the three lines should be superposed under this hypothesis).

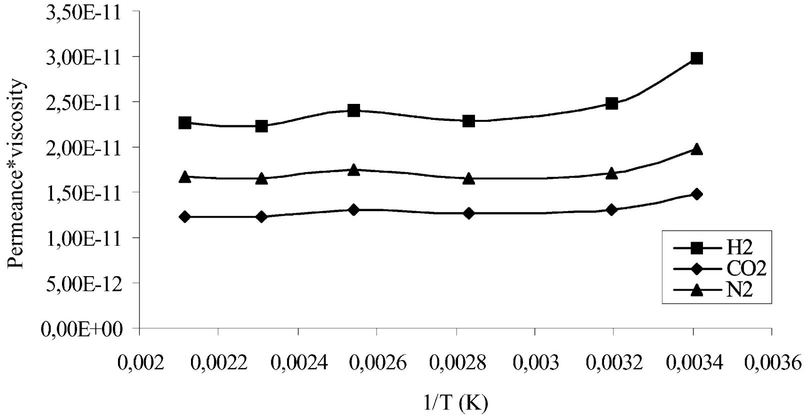

Fig. 10. Tentative correlation chart of a strict viscous flow mechanism for the experimental results obtained (the three lines should be superposed under this hypothesis).

Based on the pure compounds permeabilities, ideal separation selectivities can be computed and are shown in Fig. 5 for two model binary mixtures: H_2/CO_2 and H_2/N_2. A quasi-constancy versus temperature is obtained, the values being lower than those classically reported for similar materials (3–3.5 compared to 7.5–94 already reported for a flat silica membrane [5]). In particular, the computed selectivities are far below the theoretical Knudsen one.

Surface flow as well as molecular sieving being unable to describe the experimental results, the validity of a Knudsen flow hypothesis has been examined based on the theoretical constancy of the product $\wp\sqrt{MT}$. It can be seen in Fig. 8, that such a mechanism can hardly be proposed as the sole explanation. A strict viscous flow, leading to a non-selective material do not either fit the results (Figs. 9 and 10).

It can be stated at this stage that the membrane seems to act as a mesoporous rather than a strict microporous material with Knudsen or molecular sieving properties. Thus, the transport properties obtained would correspond more likely to a transition flow, which occurs when viscous flow and Knudsen diffusion both play a role [1,9]. An alternative explanation could be also proposed, based on a so-called viscous slip behavior [12]. According to this, hydrogen permeability could decrease of approximately 20%, while viscous flow effects would remain negligible.

4. Conclusion

The objective of this work was to explore the gas transport properties of a novel tubular silica membrane. Three gases have been selected in order to investigate the dependency of temperature and pressure upon pure compound permeability. Based on the experimental results obtained, a molecular sieving mechanism can be clearly eliminated since permeabilities do not rank according to the kinetic gas diameter and decrease with temperature. While a Knudsen flow appears to be consistent with the quasi-independency of permeability upon pressure at high temperature, the low activation energies as well as low ideal selectivities that are computed are hardly compatible with a strict Knudsen behavior. A transition flow, based on a combination of Knudsen and viscous flow can most likely be proposed in order to account for the rather high permeability and low selectivity of the material investigated in this work. Further improvements in membrane preparation have to be achieved if a defect free tubular silica membrane, exhibiting strict Knudsen or molecular sieving properties is aimed. From an application point of view such as H_2/CO_2 separation in a coal gasification power plant, the increased permeability of the tubular membrane (comparatively to flat membrane performances) is interesting. Selectivity compares however poorly on the same basis. A two-fold selectivity increase would be needed so that the reported tubular silica membrane could candidate among existing membrane materials for this separation. To that respect, the separation of hydrogen from larger molecules such as hydrocarbons could be more favorable with the membrane investigated in this work.

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