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*Validation method of experimental systems  
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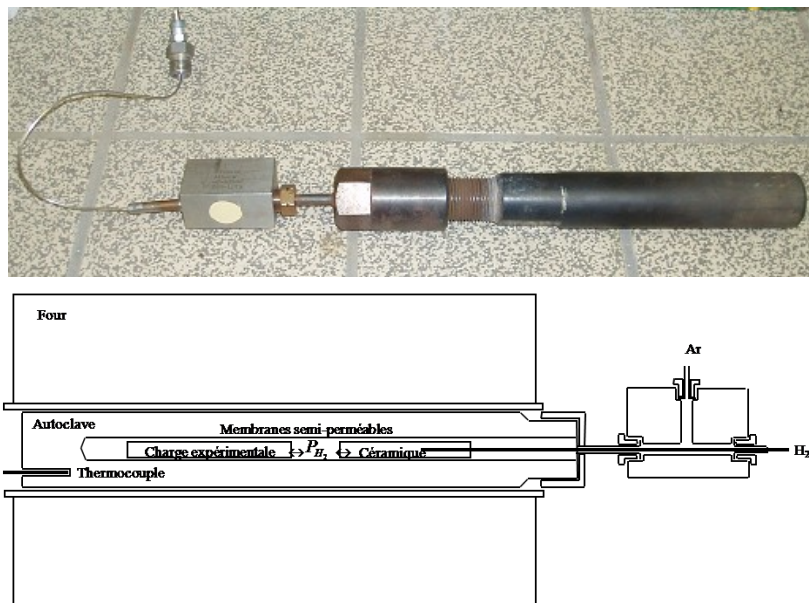
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# Hydrogen diffusion through a semi-permeable membrane Pd-Au

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Before the past nobody had calculated diffusion coefficient in a complex system with a membrane made for high temperature and high pressure experiment. The synthesis presented here explain how to determine the diffusion coefficient of hydrogen in semi-permeable membranes Information about license, EULA and contract for using these following works can be found at <https://michaelfraniatte.wordpress.com>.

# Hydrogen diffusion through a semi-permeable membrane Pd-Au: Validation method of experimental systems controlling fluids

Michael Franiatte\*

## Abstract

Hydrogen plays an important role in many high-temperature geological processes. Hydrogen-rich hydrothermal fluids venting at mid-ocean ridges have been the subject of numerous investigations over the past 10 years (e.g. Charlou et al., 2002). Hydrogen has also been considered as an alternate source of energy by petroleum industry. Consequently, understanding the behaviour of hydrogen in high temperature geological and industrial processes is of fundamental importance. Experiments on the diffusion of hydrogen gas were carried out in autoclaves at temperatures between 300°C and 600°C and total pressures up to 400 bars. The redox conditions are controlled by introducing hydrogen within the autoclave through a stainless steel tube connected to a semi-permeable membrane, both of which are held together by silver brazing. The redox conditions can be imposed by introducing hydrogen under pressure in the autoclaves. Conversely, redox conditions generated internally by reactions occurring within the autoclaves can be characterized by measuring the amount of hydrogen diffusing out of the reaction cells. In order to precisely determine the redox conditions established within these reaction cells, it is important to first characterize and calibrate the experimental system. This has been done through the determination of pressure-volume-temperature (*PVT*) relations using three different methods together with the ideal gas law, as well as the measurement of diffusion coefficients of hydrogen through a semi-permeable Pd<sub>63</sub>-Au<sub>37</sub> membrane. An appropriate generalized method to resolve *PVT* data combined with the studies made by Scientifics in the past, are in good agreement with the pressures observed, and deduced from the experimental characterization.

**Keywords:** *hydrogen, hydrothermal experiments, semi-permeable membrane, ideal gas law, diffusion coefficients, PVT properties.*

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## **1. Introduction**

Oxidation-reduction reactions relevant to geological systems have been studied for the first time by Eugster nearly half a century ago (Eugster, 1959). Different experimental techniques have been used to characterize redox conditions over a broad range of temperatures, including oxygen sensors, gas mixtures and solid buffers. The redox equilibria of oxygen sensors, gas mixtures and solid buffers have been studied by many authors (Koch-Müller and al., 1992; Scaillet and al., 1992; Beckett and Mendybaev, 1997; Berndt and al., 2002). In one experimental study, the author reviewed the kinetics and redox equilibria of redox systems which can control or measure redox equilibria (Burkhard and Ulmer, 1995). The readings observed in this study are reproducible for temperatures below 300°C. Therefore it should be important to study experimentally these systems with hydrogen line. The characterization of the experimental system is important, to know the redox conditions imposed by the hydrogen pressure. The experimental system is studied in terms of volumes, pressures and temperatures dependants. The methods used to determine the volumes of the experimental system are based on the principle of system pressure drop between two systems (the membrane system and the autoclave) considering the ideal gas law (Clapeyron, 1834). These results have allowed to determine the diffusion coefficients at 300, 400, 500 and 600°C of the semi-permeable membrane Pd-Au.

## **2. Experimental system description**

The autoclaves are inserted and heated in a cylindrical furnace. The temperature is controlled by use of a thermocouple, while the total pressure in the autoclave is externally imposed using Ar gas. An eight-valve experimental device, which can be coupled with another device, has been developed in the present work and can be used for high temperature – high pressure experimental studies of redox equilibria, involving gas mixtures or solid buffers. The experimental system consists of a membrane system part with eight valves where hydrogen and Ar (used to purify) are injected separately at a pressure below 50 bars. Ar is injected directly in the autoclave at pressure below 400 bars controlling the total pressure for an experimental capsule (semi-permeable). A schema in Fig. 1 accounts for the details. The semi-permeable membrane is an alloy of gold and palladium with 37% of gold (Au/Pd, 52/48) with broken ceramic inner. An experimental study (Pyun, 1997) shows the role of gold atoms

which restrains hydrogen diffusion. The diffusion experiments in this study were realized with Pd-Au/Pd double layers. It was demonstrate too for Pd-Au membrane up to gold 40% (Sonwane and al., 2006). Other studies show the hydrogen diffusion faster for polycrystalline gold membrane than for polycrystalline palladium membrane (Hall and al., 1976; Lau and Sun, 1972; Vasilyev and Bekrenev, 2000). Hydrogen diffusion study of the semi-permeable membrane of the hydrogen line can be compared to many hydrogen diffusion studies lead by searchers. Moreover, the choice of an alloy for the semi-permeable membrane and experimental capsule is dependant of diffusion velocity of reactions or experiments considered.

Autoclave is composed of nickel 55.26%, chromium 19%, cobalt 11%, molybdenum 10%, titanium 3.15%, aluminum 1.50%, carbon 0.09% (the reference named is PER41 alloy). Above 400°C, we have observed a hydrogen consummation by the autoclave because the equilibrium hydrogen pressure measured in the membrane system ( $P_{H_2,mb}^{eq}$ ) wasn't stable after equilibrium. Autoclave can solubilize hydrogen if there is oxide, but the mainly reason is its elements wealth used in hydrogen storage (Züttel, 2004). The diffusion coefficients determined in this study are compared to those determined experimentally by some authors (Sonwane and al., 2006; Sakamoto and al., 1982; Vasilyev and Bekrenev, 2000).

## 2.1. Volume determinations

The volumes determinations methods are realized in closed system. Ar is introduced initially at a known pressure in one of the three sections of the membrane system divided by the valves 2 to membrane, valve 2 to valve 5 and before valve 5 (Fig. 1). The last method consists of system pressure drop between the membrane system and the autoclave with hydrogen gas. The autoclave part volume can't be determining by the first method because there is no valve to recuperate Ar in a burette.

### 2.1.1. Method 1: volumes measured with a burette

Ar is discharged in a burette which was initially introduced in one of the three membrane system sections before valve 1, 2 or 5 (Fig. 2). The method to calculate the volume for one part of the membrane system considers the initial state

$$n_{Ar,spst}^0 = \frac{P_{Ar,spst}^0 \times V_{spst}}{RT} \quad (10)$$

$$n_{Ar,bur}^{eq} + n_{Ar,spst}^{eq} = n_{Ar,spst}^0 \quad (11)$$

and the final state

$$P_{Ar,bur}^{eq} = P_{Ar,spst}^{eq} \quad (12)$$

$$\frac{n_{Ar,bur}^{eq} \times RT}{V_{bur}} = \frac{n_{Ar,spst}^{eq} \times RT}{V_{spst}} \quad (13)$$

The Equations (10), (11) and (13) give

$$\begin{aligned} \frac{n_{Ar,spst}^{eq} \times RT}{V_{spst}} &= \frac{P_{Ar,spst}^0 \times V_{spst}}{V_{bur}} - \frac{n_{Ar,spst}^{eq} \times RT}{V_{bur}} \\ n_{Ar,spst}^{eq} \times \left( \frac{RT}{V_{spst}} + \frac{RT}{V_{bur}} \right) &= \frac{P_{Ar,spst}^0 \times V_{spst}}{V_{bur}} \\ P_{Ar,spst}^{eq} \times \left( 1 + \frac{V_{spst}}{V_{bur}} \right) &= \frac{P_{Ar,spst}^0 \times V_{spst}}{V_{bur}} \\ P_{Ar,spst}^{eq} + P_{Ar,spst}^{eq} \times \frac{V_{spst}}{V_{bur}} &= \frac{P_{Ar,spst}^0 \times V_{spst}}{V_{bur}} \\ P_{Ar,spst}^{eq} &= \frac{V_{spst}}{V_{bur}} (P_{Ar,spst}^0 - P_{Ar,spst}^{eq}) \\ V_{spst} &= \frac{P_{Ar,spst}^{eq} \times V_{bur}}{P_{Ar,spst}^0 - P_{Ar,spst}^{eq}} \end{aligned} \quad (14)$$

with  $P_{Ar,spst}^0$  and  $n_{Ar,spst}^0$  initial Ar pressure and mol number in one of the three membrane system parts,  $P_{Ar,spst}^{eq}$  and  $n_{Ar,spst}^{eq}$  same thinks but at equilibrium,  $P_{Ar,bur}^{eq}$  and  $n_{Ar,bur}^{eq}$ , same but for the burette, and  $V_{spst}$  and  $V_{bur}$ , are the volumes of the membrane system part studied and the burette, respectively. The results of this method are illustrated in Fig. 3 (a)-(c). The volumes ratios between the different parts of the membrane system are illustrate in Fig. 4 (a).

### 2.1.2. Method 2: ratio volumes

The method accounts of the principle system pressure drop between two systems. The equations for the ratio volume between the two systems (membrane system section and other system section) are for the initial state

$$P_{Ar,mb}^0 = \frac{n_{Ar,mb}^0 \times RT}{V_{mb}} \quad (15)$$

$$P_{Ar,sgst}^0 = \frac{n_{Ar,sgst}^0 \times RT}{V_{sgst}} \quad (16)$$

and for the final state

$$P_{Ar,sgst+mb}^{eq} = (n_{Ar,mb}^{\#} + n_{Ar,sgst}^{\#}) \times \frac{RT}{V_{sgst} + V_{mb}} \quad (17)$$

These relations give

$$\begin{aligned} P_{Ar,sgst+mb}^{eq} &= \left( \frac{P_{Ar,mb}^{\#} \times V_{mb}}{RT} + \frac{P_{Ar,sgst}^{\#} \times V_{sgst}}{RT} \right) \times \frac{RT}{V_{sgst} + V_{mb}} \\ P_{Ar,sgst+mb}^{eq} &= \frac{P_{Ar,mb}^0}{\frac{V_{sgst}}{V_{mb}} + 1} + \frac{P_{Ar,sgst}^0 \times \frac{V_{sgst}}{V_{mb}}}{\frac{V_{sgst}}{V_{mb}} + 1} \\ P_{Ar,sgst+mb}^{eq} \times \frac{V_{sgst}}{V_{mb}} + P_{Ar,sgst+mb}^{eq} &= P_{Ar,mb}^0 + P_{Ar,sgst}^0 \times \frac{V_{sgst}}{V_{mb}} \\ \frac{V_{sgst}}{V_{mb}} \times (P_{Ar,sgst+mb}^{eq} - P_{Ar,sgst}^0) &= P_{Ar,mb}^0 - P_{Ar,sgst+mb}^{eq} \\ \frac{V_{sgst}}{V_{mb}} &= \frac{P_{Ar,mb}^0 - P_{Ar,sgst+mb}^{eq}}{P_{Ar,sgst+mb}^{eq} - P_{Ar,sgst}^0} \end{aligned} \quad (18)$$

$P_{Ar,mb}^0$  corresponds to the initial Ar pressure introduced in the section closer to the membrane in the system membrane,  $P_{Ar,sgst}^0$  corresponds to the initial Ar pressure at ambient air, and  $P_{Ar,sgst+mb}^{eq}$  corresponds to the equilibrium Ar pressure. The results on ratio volumes obtained with method 2 are presented in Fig. 4 (b) showing the similarity in Fig. 4 (a) obtained with the method 1.

### 2.1.3. Calculation of membrane rate in the furnace

Two experiments were conduct with Ar initially introduced in the membrane system and the autoclave with elevation of temperatures ( $T_{amb}$ , ambient temperature to  $T_{aut}$ , autoclave temperature). The relation between the raisings pressures with the elevation of temperatures are expressed by these equations at initial state

$$P_{Ar,sgst+mb}^0 = \frac{n_{Ar,sgst+mb}^0 \times R \times T_{amb}}{V_{sgst+mb}} \quad (19)$$

at final state

$$P_{Ar, syst+mb}^{eq} = P_{Ar, aut}^{eq} = P_{Ar, int}^{eq} \quad (20)$$

$$n_{Ar, syst+mb}^0 = n_{Ar, aut}^{eq} + n_{Ar, int}^{eq} \quad (21)$$

The Equations (19) and (21) give

$$\begin{aligned} \frac{P_{Ar, syst+mb}^0 \times V_{syst+mb}}{R \times T_{amb}} = \\ \frac{P_{Ar, aut}^{eq} \times V_{aut}}{R \times T_{amb}} + \frac{P_{Ar, int}^{eq} \times V_{int}}{R \times T_{aut}} \end{aligned} \quad (22)$$

The Equations (20) and (22) give

$$\begin{aligned} \frac{P_{Ar, syst+mb}^0 \times V_{syst+mb}}{T_{amb}} = \\ P_{Ar, syst+mb}^{eq} \times \left( \frac{V_{aut}}{T_{amb}} + \frac{V_{int}}{T_{aut}} \right) \\ P_{Ar, syst+mb}^{eq} = \frac{V_{syst+mb} \times P_{Ar, syst+mb}^0}{T_{amb} \times \left( \frac{V_{aut}}{T_{amb}} + \frac{V_{int}}{T_{aut}} \right)} \end{aligned}$$

with  $x = \frac{V_{aut}}{V_{syst+mb}}$ ,  $V_{aut} = x \times V_{syst+mb}$  and  $V_{int} = (1-x) \times V_{syst+mb}$

$$\begin{aligned} P_{Ar, syst+mb}^{eq} &= \frac{P_{Ar, syst+mb}^0}{x + \frac{(1-x) \times T_{amb}}{T_{aut}}} \\ P_{Ar, syst+mb}^{eq} &= \frac{P_{Ar, syst+mb}^0 \times T_{aut}}{T_{aut} \times x + T_{amb} - T_{amb} \times x} \\ P_{Ar, syst+mb}^{eq} &= \frac{P_{Ar, syst+mb}^0 \times T_{aut}}{x \times (T_{aut} - T_{amb}) + T_{amb}} \\ x &= \frac{\frac{P_{Ar, syst+mb}^0 \times T_{aut}}{P_{Ar, syst+mb}^{eq}} - T_{amb}}{T_{aut} - T_{amb}} \end{aligned} \quad (23)$$

After the measures realized in this interpretation and the Equation (23)

- 300 to 405.6°C,  $P_{Ar, mb} = 5.38$  to 5.45 bars and  $P_{Ar, aut} = 55.1$  to 60.7 bars, so  $x_{mb} = 0.908$  and  $x_{aut} = 0.391$ .



- 403.7 to 598.6°C,  $P_{Ar,mb} = 10.67$  to 10.85 bars and  $P_{Ar,aut} = 60.7$  to 71.2 bars, so  $x_{mb} = 0.929$  and  $x_{aut} = 0.375$ .

- 300 to 598.6°C,  $P_{Ar,aut} = 55.1$  to 71.2 bars, so  $x_{aut} = 0.36$ .

The volume ratio of membrane system out of the furnace is about 90%. The volume ratio of autoclave out of the furnace is about 40%.

#### 2.1.4. Method 3: autoclave volume

The hydrogen equilibrium pressure after the hydrogen migration between the membrane system and the autoclave can be calculated. The conditions  $P$ ,  $T_{aut}$  et  $P_{H_2,mb}^0$  (hydrogen initial pressure in the membrane system) were modify to have an autoclave volume average. The calculation of hydrogen equilibrium pressure is

$$P_{H_2,mb}^{eq} = P_{H_2,aut}^{eq}$$

$$n_{H_2,mb}^0 = n_{H_2,mb}^{eq} + n_{H_2,aut}^{eq} - n_{H_2,aut}^0$$

with

$$n_{H_2,mb}^0 = \frac{P_{H_2,mb}^0 \times V_{mb}^{int}}{R \times T_{amb}} + \frac{P_{H_2,mb}^0 \times V_{mb}^{ext}}{R \times T_{aut}}$$

$$n_{H_2,mb}^{eq} = \frac{P_{H_2,mb}^{eq} \times V_{mb}^{ext}}{R \times T_{amb}} + \frac{P_{H_2,mb}^{eq} \times V_{mb}^{int}}{R \times T_{aut}}$$

$$n_{H_2,aut}^{eq} = \frac{P_{H_2,aut}^{eq} \times V_{aut}^{ext}}{R \times T_{amb}} + \frac{P_{H_2,aut}^{eq} \times V_{aut}^{int}}{R \times T_{aut}}$$

$$n_{H_2,aut}^0 = \frac{P_{H_2,aut}^0 \times V_{aut}^{ext}}{R \times T_{amb}} + \frac{P_{H_2,aut}^0 \times V_{aut}^{int}}{R \times T_{aut}}$$

so

$$P_{H_2,mb}^0 \times \left( \frac{V_{mb}^{ext}}{R \times T_{amb}} + \frac{V_{mb}^{int}}{R \times T_{aut}} \right) = P_{H_2,mb}^{eq} \times \left( \frac{V_{mb}^{ext}}{R \times T_{amb}} + \frac{V_{mb}^{int}}{R \times T_{aut}} + \frac{V_{aut}^{ext}}{R \times T_{amb}} + \frac{V_{aut}^{int}}{R \times T_{aut}} \right) - P_{H_2,aut}^0 \times \left( \frac{V_{aut}^{ext}}{R \times T_{amb}} + \frac{V_{aut}^{int}}{R \times T_{aut}} \right)$$

$$P_{H_2,mb}^{eq} = \frac{P_{H_2,mb}^0 \times \left( \frac{V_{mb}^{ext}}{T_{amb}} + \frac{V_{mb}^{int}}{T_{aut}} \right) + P_{H_2,aut}^0 \times \left( \frac{V_{aut}^{ext}}{T_{amb}} + \frac{V_{aut}^{int}}{T_{aut}} \right)}{\left( \frac{V_{mb}^{ext}}{T_{amb}} + \frac{V_{mb}^{int}}{T_{aut}} + \frac{V_{aut}^{ext}}{T_{amb}} + \frac{V_{aut}^{int}}{T_{aut}} \right)}$$

$$P_{H_2,mb}^{eq} = \frac{P_{H_2,mb}^0 \times \left( \frac{0,9}{T_{amb}} + \frac{0,1}{T_{aut}} \right) \times V_{mb} + P_{H_2,aut}^0 \times \left( \frac{0,4}{T_{amb}} + \frac{0,6}{T_{aut}} \right) \times V_{aut}}{\left( \frac{0,9}{T_{amb}} + \frac{0,1}{T_{aut}} \right) \times V_{mb} + \left( \frac{0,4}{T_{amb}} + \frac{0,6}{T_{aut}} \right) \times V_{aut}} \quad (24)$$

For the determination of autoclave volume, the Equation (24) makes appear the expression written

$$\begin{aligned} V_{mb} \times \left( P_{H_2,mb}^{eq} \times \left( \frac{0,9}{T_{amb}} + \frac{0,1}{T_{aut}} \right) - P_{H_2,mb}^0 \times \left( \frac{0,9}{T_{amb}} + \frac{0,1}{T_{aut}} \right) \right) = \\ V_{aut} \times \left( P_{H_2,aut}^0 \times \left( \frac{0,4}{T_{amb}} + \frac{0,6}{T_{aut}} \right) - P_{H_2,mb}^{eq} \times \left( \frac{0,4}{T_{amb}} + \frac{0,6}{T_{aut}} \right) \right) \\ \frac{V_{aut}}{V_{mb}} = \frac{\left( P_{H_2,mb}^{eq} \times \left( \frac{0,9}{T_{amb}} + \frac{0,1}{T_{aut}} \right) - P_{H_2,mb}^0 \times \left( \frac{0,9}{T_{amb}} + \frac{0,1}{T_{aut}} \right) \right)}{\left( P_{H_2,aut}^0 \times \left( \frac{0,4}{T_{amb}} + \frac{0,6}{T_{aut}} \right) - P_{H_2,mb}^{eq} \times \left( \frac{0,4}{T_{amb}} + \frac{0,6}{T_{aut}} \right) \right)} \end{aligned} \quad (25)$$

with a membrane system volume of 1.72 cm<sup>3</sup> determined with the method 1, the autoclave volume is 6.5 cm<sup>3</sup> (Fig. 5).

### 2.1.5. Determination of hydrogen concentration in the hydrogen line

The method 3 can be used to calculate hydrogen concentration in the entire system. The equations for the final state are

$$\begin{aligned} P_{H_2} &= P_{mb+aut}^{eq} = P_{mb}^{eq} = P_{aut}^{eq} \\ n_{mb+aut}^0 &= n_{mb}^{eq} + n_{aut}^{eq} \\ n_{mb}^{eq} &= \frac{P_{mb}^{eq} \times V_{mb}^{ext}}{R \times T_{amb}} + \frac{P_{mb}^{eq} \times V_{mb}^{int}}{R \times T_{aut}} \\ n_{aut}^{eq} &= \frac{P_{aut}^{eq} \times V_{aut}^{ext}}{R \times T_{amb}} + \frac{P_{aut}^{eq} \times V_{aut}^{int}}{R \times T_{aut}} \end{aligned}$$

so

$$n_{mb+aut}^0 = P_{H_2} \times \left( \frac{V_{mb}^{ext}}{R \times T_{amb}} + \frac{V_{mb}^{int}}{R \times T_{aut}} + \frac{V_{aut}^{ext}}{R \times T_{amb}} + \frac{V_{aut}^{int}}{R \times T_{aut}} \right)$$

$$P_{H_2} = \frac{n_{mb+cat}^0}{\left( \frac{V_{mb}^{ext}}{R \times T_{amb}} + \frac{V_{mb}^{int}}{R \times T_{cat}} + \frac{V_{cat}^{ext}}{R \times T_{amb}} + \frac{V_{cat}^{int}}{R \times T_{cat}} \right)} \quad (26)$$

## 2.2. Diffusion coefficients

The diffusion equations were recently reviewed by two authors (Dudek, 2005, 2007; Baranowski, 1992). The hydrogen flow ( $\text{mol H}_2\text{cm}^{-2}\text{s}^{-1}$ ) is determined by the equation

$$J = \left( \frac{v}{RTS} \right) \left( \frac{dp}{dt} \right)$$

$S$  corresponds at the surface of the semi-permeable membrane:  $3.272 \text{ cm}^2$  (the diameter is  $0.28 \text{ cm}$ , the width is  $3.72 \text{ cm}$ ),  $v$  corresponds to the entire volume of the experimental system. To account of temperatures heterogeneity in the hydrogen line, Equation (26) permit to determine  $J$  with

$$\frac{v}{RT} = \frac{V_{mb}^{ext}}{R \times T_{amb}} + \frac{V_{mb}^{int}}{R \times T_{cat}} + \frac{V_{cat}^{ext}}{R \times T_{amb}} + \frac{V_{cat}^{int}}{R \times T_{cat}} \quad (27)$$

$J$  was determined for a semi-permeable membrane thickness ( $0.02 \text{ cm}$ ) immaterial. It was considered a simplification of the Fick law. The equations considered are

$$J = -D(T) \text{grad}c$$

$$\text{grad}c = 1 + \frac{\partial \ln f}{\partial \ln c}$$

with  $f$  considered as  $P$ , and  $\text{grad}c$  find to be exactly 2. Fig. 6 represents a diffusion profile obtained while proceeding pressure measurements used for the determination of diffusion coefficient at  $499.8^\circ\text{C}$ .

## 2.3. Effective diffusion coefficient

The diffusion coefficient evolution,  $D(T)$ , is function of the temperature according to Arrhenius law

$$D(T) = D \times \exp\left( \frac{-Ea}{k_B \times N_A \times T} \right)$$

with the ideal gas constant, Boltzman constant and Avogadro number equals to

$$R = 8.314472 \text{ J/K/mol}$$

$$k_B = 1.3806 \cdot 10^{-23} \text{ J / K}$$

$$N_a = 6.022 \cdot 10^{23} \text{ mol}^{-1}$$

The Fig. 7 represents the result of  $D(T)$  evolution as a function of temperature for the membrane Au-Pd of hydrogen line compared to the results found in the literature [9]. The Fig. 8 shows the Arrhenius law for these membranes. The effective diffusion coefficient,  $D$  for the hydrogen line membrane Au-Pd (with 37% of gold) is  $6.8 \cdot 10^{-8} \text{ m}^2 \text{ s}^{-1}$  and activation energy is  $6406 \text{ cal mol}^{-1}$  which were determined in this study. The diffusion coefficient of a membrane in a second line, have been determined at  $350^\circ\text{C}$ . The membrane composition of the second line is about  $\text{Au}_{34}\text{-Pd}_{66}$ , and the same composition was given by a MET analysis (Fig. 9). The diffusion coefficients are in good agreement with the literature (Fig. 10). An example at  $350^\circ\text{C}$  show the determination of  $D(T)$  illustrate Fig. 11.

### 3. Method to resolve $PVT$ properties

#### 3.1. Equation of state expression

Molar fractions of constituents deduced from there concentrations in mol number for one kilogram of solvent are introduced in the Redlich-Kwong equation of state (Redlich and Kwong, 1949) modify by Soave (1972), in order to calculate the fugacity coefficient of volatile species in the fluid. The Soave-Redlich-Kwong equation of state is written

$$P = \frac{RT}{(V - b)} - \frac{a(T)}{V(V + b)} \quad (28)$$

where  $P$  is the total pressure (Pa),  $R$  is the gas constant ( $8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the absolute temperature (K), and  $V$  is the molar volume ( $\text{m}^3 \text{ mol}^{-1}$ ). The  $a(T)$  and  $b$  coefficients in Equation (28) are the attraction and repulsion parameters of the original van der Waals equation, given by

$$a_i(T) = a_i(T_c) \cdot \alpha_i(T) \quad (29)$$

and

$$b_i(T_c) = 0.08664 \frac{RT_c}{P_c} \quad (30)$$

where  $T_c$  and  $P_c$  are the critical temperature and pressure, characteristic of a pure constituent. The  $a(T_c)$  term in Equation (29) is given by

$$a_i(T_c) = 0.42747 \frac{(R \cdot T_c)^2}{P_c} / 9 \quad (31)$$

where the division by 9 come from the better results enounced by Fowler et Guggenheim (1939) adapted for a mixture and not for a perfect gases without divide by 9. The temperature-dependent  $a(T)$  term, equal to 1 at  $T_c$  and  $P_c$ , is evaluated from

$$a_i(T) = \left[ 1 + (0.48508 + 1.55171\omega - 0.15613\omega^2)(1 - \sqrt{T/T_c}) \right]^2 \quad (32)$$

where  $\omega$  is the acentric factor, characteristic of a given pure constituents. The expressions for the  $a(T)$  and  $b$  parameters for a fluid mixture are written

$$b = \sum_{i=1}^n x_i b_i(T_c) \quad (33)$$

and

$$a(T) = \sum_{i=1}^n \sum_{j=1}^n x_i x_j \sqrt{a_i(T) a_j(T)} \quad (34)$$

The molar volume is expressed in  $\text{m}^3 \text{mol}^{-1}$  by

$$V = \frac{RT}{P} z \quad (35)$$

where  $z$  is the compressibility factor. The Newton-Raphson method is used to resolve  $z$  in the equation written

$$z^3 - (1 - B)z^2 + z(A - B - B^2) - AB = 0 \quad (36)$$

$$A = \sum_{i=1}^n \sum_{j=1}^n x_i x_j \sqrt{A_i A_j} \quad (37)$$

with

and

$$B = \sum_{i=1}^n x_i B_i \quad (38)$$

with

$$A_i = 0.42747 \frac{a_i(T) P_r}{T_r^2} \quad (39)$$

and

$$B_i = 0.08664 \frac{P_r}{T_r} \quad (40)$$

with  $P_r = P / P_c$  and  $T_r = T / T_c$ , the reduced pressure and temperature.

The fugacity coefficient of the  $i$ th gas derived from the Redlich-Kwong Equation (Soave, 1972; Prausnitz et al., 1986 ; Assael et al., 1996) is expressed by

$$\ln \varphi_i = \frac{B_i}{B} (z-1) - \ln(z-B) + \frac{A}{B} \left[ \frac{B_i}{B} - \frac{2}{a(T)} \sum_{j=1}^n x_j (1-k_{ij}) \sqrt{a_i(T)a_j(T)} \right] \ln \left( 1 + \frac{B}{z} \right) \quad (41)$$

The fugacity in bar is written

$$f_i = \varphi_i \cdot x_i \cdot P \quad (42)$$

where  $P$  is in bar this time, and  $\varphi_{i,g}$  and  $x_{i,g}$  stand for the fugacity coefficient and mole fraction of the  $i$ th gas in the gas mixture, respectively.

The value of  $\varphi_{i,g}$  for  $H_2$ , given by the SRK equation of state, are show in the Fig. 12 representing in the shape of isotherms. These values are compared with the values of Shaw and Wones (1964) and Presnall (1969) determined at high pressure and high temperature as encountered in terrestrial crust.

### 3.2. Volume determination

The derivation of the Soave-Redlich-Kwong equation of state, function of  $V$ ,  $a$  and  $b$  can be used to determine the partial derived of  $\frac{\partial V}{\partial x}$  necessary for the value of the partial volumes  $V_i$  of the  $i$ th constituents in the fluid like the equations written by Rimbach and Chatterjee (1987). In this study the  $n$  constituents in the mixture is expressed by a new definition of the partial volume of the  $i$ th constituent for a mol number for gas or liquid  $n^{g,l}$  written

$$V_i^{g,l} = n^{g,l} \cdot x_i^{g,l} \left( V - \frac{1}{6 \cdot n} \frac{\partial V}{\partial x_i} \right) \quad (43)$$

because the expression in the literature couldn't be resolve for a large constituents number  $n$  written

$$V_i^{g,l} = n^{g,l} \cdot x_i^{g,l} \left( V + x_j \frac{\partial V}{\partial x_i} \right)$$

The total volume  $V^{tot}$  of the fluid is given by

$$V^{tot} = \sum V_i^l + \sum V_i^g$$

The coefficient  $-1/6n$  is demonstrated as follow. The hypothesis presented here, and named  $H_L$ , is given by the polynomial function  $L(x^m)$  written

$$L(x^n) = \sum_{m=0}^n \sigma_m \cdot x^m$$

$$L(x^n) = \frac{x \cdot L'(x^n)}{n} + L(0)$$

with

$$L(x^n) = \frac{x \cdot L(m \cdot x^{n-1})}{n} + L(0)$$

$$L(x^n) = x \cdot L(x^{n-1}) + L(0)$$

define on the interval  $[0,1]$  and derivable on the interval  $]0,1[$ . Using the existent hypothesis  $H_F$  for  $H_L$  there is a  $x$  point on the interval define by

$$L(1) - L(0) = L'(x^n)$$

$$L(x^n) + L'(x^n) = \frac{xL'(x^n)}{n} + L(1)$$

$$L(x^n) + L'(x^n) \left(1 - \frac{x}{n}\right) = L(1)$$

$$L(x^n) + L'(x^n) \left(1 - \frac{x}{n}\right) = L'(x^n) + L(0)$$

$$L(x^n) - L'(x^n) \left(\frac{x}{n}\right) = L(0)$$

The Equation (43) have  $V$  and  $\delta V$ , so

$$L(x^n) - L'(x^n) \left(\frac{x}{n}\right) = V - \frac{1}{6 \cdot n} \frac{\partial V}{\partial x_i}$$

$$\left(\frac{x}{n}\right) = \frac{1}{6 \cdot n \cdot \partial x_i}$$

with  $m=3$ , because the molar volume have this dimension, the expression would be

$$x \cdot \partial x_i = \frac{1}{2 \cdot n}$$

At  $x=0$ ,  $n=\infty$ , at  $x=1$ ,  $n=1$ , at  $x=0.5$ ,  $n=2$ . Apparently  $x$  is a function of  $1/n$ , with  $\delta x=1$  for  $x=1$  and  $\delta x=0$  for  $x=0$ , so for  $1 < n < \infty$ , it gives

$$\frac{1}{n} < x \cdot \partial x_i < 0$$

$$x \cdot \partial x_i = \frac{1}{2 \cdot n}$$

imposed

like the average between 1 and infinite for a large constituents number  $n$ , the expression of the new definition is a good approximation well demonstrate.

The factor 3 appearing in the Equations (31) and (39) with the division by 9 between the definition of  $A$  and  $a(T)$  (or the volume and the derived volume) is show by an expression compatible with the  $H_L$  hypothesis written respectively

$$L(x) = s \cdot L(x) + 1/s \cdot L'(x)$$

$$L(x) = x \cdot L'(x) + L(0)$$

with  $s=3$ , these equations combined verify

$$L(x) = L(x)$$

### 3.3. Equation of state derivation

The derived is a function of  $V$ ,  $a$  et  $b$  of Equation (28) written

$$0 = -\frac{RT}{(V-b)^2} dV + \frac{RT}{(V-b)^2} db + \frac{a\alpha dV}{(V+b)V^2} + \frac{a\alpha dV}{V(V+b)^2} + \frac{a\alpha V db}{V^2(V+b)^2} - \frac{a\alpha da}{V(V+b)} \quad (44)$$

$a$  and  $b$  is function of  $x_i$

$$0 = \left( -\frac{RT}{(V-b)^2} + \frac{a\alpha}{(V+b)V^2} + \frac{a\alpha}{V(V+b)^2} \right) dV + \left( \frac{RT}{(V-b)^2} + \frac{a\alpha}{V(V+b)^2} \right) \frac{\partial b}{\partial x_i} dx_i - \frac{a}{V(V+b)} \frac{\partial a}{\partial x_i} dx_i \quad (45)$$

writting

$$\frac{\partial V}{\partial x_i} = \frac{-\left( \frac{RT}{(V-b)^2} + \frac{a\alpha}{V(V+b)^2} \right) \frac{\partial b}{\partial x_i} + \frac{a}{V(V+b)} \frac{\partial a}{\partial x_i}}{-\frac{RT}{(V-b)^2} + \frac{a\alpha}{V^2(V+b)} + \frac{a\alpha}{V(V+b)^2}} \quad (46)$$

$$\frac{\partial V}{\partial x_i} = \frac{-(RTV^2(V+b)^2 + a\alpha(V-b)^2V) \frac{\partial b}{\partial x_i} + (V-b)^2V(V+b) \frac{\partial a\alpha}{\partial x_i}}{-RTV^2(V+b)^2 + a\alpha(V-b)^2(V+b) + a\alpha(V-b)^2V} \quad (47)$$

$$\frac{\partial V}{\partial x_i} = \frac{-(RTV^2(V+b)^2 + a\alpha(V-b)^2V) \frac{\partial b}{\partial x_i} + (V-b)V(V^2 - b^2) \frac{\partial a\alpha}{\partial x_i}}{-RTV^2(V+b)^2 + a\alpha(V-b)^2(2V+b)} \quad (48)$$

$$\frac{\partial a\alpha}{\partial x_i} = \frac{\partial}{\partial x_i} \left( \sum_{i=1}^n \sum_{j=1}^n x_i x_j (1 - k_{ij}) \sqrt{a_i(T) a_j(T)} \right) \quad (49)$$

with

$$\frac{\partial b}{\partial x_i} = \frac{\partial}{\partial x_i} \left( \sum_{i=1}^n x_i b_i(T_i) \right) \quad (50)$$

The derivation gives



$$\begin{aligned}
\frac{\partial a\alpha}{\partial x_i} &= \frac{\partial \sum_{i=1}^n \sum_{j=1}^n x_i x_j (1 - k_{ij}) \sqrt{a_i(T) a_j(T)}}{\partial x_i} \\
\frac{\partial a\alpha}{\partial x_i} &= \frac{\partial \sum_{i=1}^n \sum_{j=1}^n (x_i (1 - \sum_{k \neq i} x_k - x_i)) (1 - k_{ij}) \sqrt{a_i(T) a_j(T)}}{\partial x_i} \\
\frac{\partial a\alpha}{\partial x_i} &= \frac{\partial \sum_{i=1}^n \sum_{j=1}^n (x_i (1 - (1 - \sum_{k \neq i, j, k} x_k - x_i - x_j) - x_i)) (1 - k_{ij}) \sqrt{a_i(T) a_j(T)}}{\partial x_i} \\
\frac{\partial a\alpha}{\partial x_i} &= \frac{\partial \sum_{i=1}^n \sum_{j=1}^n (x_i (1 - (1 - (1 - \sum_{k \neq i, j, k, l} x_k - x_i - x_j - x_k) - x_i - x_j) - x_i)) (1 - k_{ij}) \sqrt{a_i(T) a_j(T)}}{\partial x_i} \\
\frac{\partial a\alpha}{\partial x_i} &= \frac{\partial \sum_{i=1}^n \sum_{j=1}^n (x_i (1 - \sum_{k \neq i, j, k, l} x_k - x_i)) (1 - k_{ij}) \sqrt{a_i(T) a_j(T)}}{\partial x_i} \\
\frac{\partial a\alpha}{\partial x_i} &= \sum_{i=1}^n \sum_{j=1}^n ((1 - x_j) - x_j) (1 - k_{ij}) \sqrt{a_i(T) a_j(T)} \\
\frac{\partial a\alpha}{\partial x_i} &= \sum_{i=1}^n \sum_{j=1}^n (1 - 2x_j) (1 - k_{ij}) \sqrt{a_i(T) a_j(T)} \\
\frac{\partial b}{\partial x_i} &= \sum_{i=1}^n b_i(T_c)
\end{aligned} \tag{51}$$

$$\frac{\partial b}{\partial x_i} = \sum_{i=1}^n b_i(T_c) \tag{52}$$

### 3.4. Molar fraction determination

The activity  $a_i$  of constituents, the molar fractions of liquid  $x_i^l$  and gas  $x_i^g$ , and the vapor fraction  $x^v$  of the fluid have been determined and applied to the H<sub>2</sub>O-CO<sub>2</sub> system (Tableau 1). The fluid pressure  $P$  corresponds to the pressure imposed when the sum of partial volume  $V_i$  of gas and liquid is equal to the volume of the experimental system when the following conditions are respected. There is a vapor fraction and a liquid fraction defining these relations

$$x^v + x^l = 1$$

$$x^g = \frac{n^g}{n^{lg}} \quad \text{and} \quad x^l = \frac{n^l}{n^{lg}}$$

$$n^{lg} = x^g n^{lg} + x^l n^{lg}$$

The fraction of  $i$  relatively to the other constituents in the liquid and gas gives

$$x_i^{lg} = \frac{n_i^g + n_i^l}{n^{lg}}$$

$$x_i^{lg} = \frac{x_i^g n^g + x_i^l n^l}{n^{lg}}$$

consequently

$$x_i^{lg} = x_i^g x^g + x_i^l (1 - x^g)$$

$$x_i^{lg} = x_i^l x^l + x_i^g (1 - x^l)$$

$$2x_i^{lg} = x_i^g x^g + x_i^l (1 - x^g) + x_i^l (1 - x^g) + x_i^g x^g$$

$$x_i^{lg} = x_i^g x^g + x_i^l (1 - x^g)$$

$$x^g = \frac{x_i^{lg} - x_i^l}{x_i^g - x_i^l} \tag{53}$$

$$x_i^g = \frac{x_i^{lg} - x_i^l (1 - x^g)}{x^g} \tag{54}$$

$$x_i^l = \frac{x_i^{lg} - x_i^g x^g}{1 - x^g} \tag{55}$$

### 3.5. Liquid and gas molar volume determinations

The liquid raise a maximum density of  $1 \text{ gcm}^{-3}$  when  $x^l = 1$ . This liquid region is a condition of low temperature and high pressure. The molar volumes of gas  $V^g$  and liquid  $V^l$  are solved with the following process as resolution. The critical pressure of the fluid is defined by

$$P_c = \sum P_c^i \cdot x_i \tag{56}$$

at  $P_c$  and  $T_c$

$$P^g = P^l = P_c = P$$

$$P^l = 2 \cdot P_c - P \tag{57}$$

Acentric factors must be modified for the liquid because the pressure has been modified. Pitzer (1955) have define the acentric factor by the interpretation of vapor pressure curves by the relation

$$\omega = -1 - \log[P_{sat}(T = 0.7 \cdot T_c) / P_c] \quad (58)$$

The value of  $\omega$  is less the number corresponding to the equation written

$$-1 - \log[P / P_c ((P_c - P) / P_c = 0.7)] - (-1 - \log[P / P_c ((2P_c - P) / P_c = 0.7)]) = -\log[0.3] + \log[1.3]$$

$$x^l = \frac{n^g}{V^{tot}}$$

At  $T$  and  $P$

(59)

$$x^c = \frac{n^c}{V^{tot}}$$

at  $T_c$  and  $P_c$

(60)

$$V^{(g)} = \frac{V^{tot}}{n^g} - M_{fluid} = \frac{(1-x^l)V^{tot}}{n^g} = \frac{x^l V^{tot}}{n^{(g)}}$$

at  $T$  and  $P$

(61)

$$V^l = \frac{(1-x^l)V^{tot}}{n^l} = \frac{x^l V^{tot}}{n^{(l)}}$$

at  $T$  and  $P^l$

(62)

$$V^l = M = \frac{x^l V^{tot}}{n^g}$$

at the standard state

(63)

with

$$n^{(g)} + n^g = n^{tot}$$

(64)

$$n^{(g)} = n^g = \frac{n^{tot}}{2}$$

consequently

(65)

with  $M_{fluid}$  resolving the molar mass of the fluid. The value of  $x^l$  at  $T$  and  $P$  or  $P^l$  can be incorporate in the two equations of state for the gas and the liquid, each phase process containing two equations of state. The relations that follow are verify, expressed in the shape

$$V^{lg} = \frac{V^{tot}}{n^{tot}} = \frac{V^{tot}}{n^g + n^{(g)}} = \frac{V^{tot}}{\frac{(1-x^l)V^{tot}}{V^{(g)}} + \frac{x^l V^{tot}}{V^l}}$$

(66)

$$n^{(g)} = \frac{V^{tot} - V^{(g)} \cdot n^g}{V^l}$$

and

imposing

$$x^v = 1 - x^l$$

If  $M_{\text{fluid}}$  is changed in the calculation, the molar volumes, at  $0^\circ\text{C}$  and  $2P_c - P$ , are inched and gives the true  $M_{\text{fluid}}$  with  $V^l$ , consequently  $T_c$  and  $P_c$  could be correlate with  $M_{\text{fluid}}$  assuming at standard state,  $V^l = M_{\text{fluid}}$  and  $V^g = 22700 \text{ cm}^3/\text{mol}$ . The following assumption is realized for temperature study corresponding to  $0 < T^\circ\text{C} < T_c$  with constituent having  $T_c > 0^\circ\text{C}$ .

#### 4. Results comparing to previous works

All the data on molar volume, reproduced by the equation applications with the Microsoft computer program named excel and visual basic macro, show good agreements with the experimental studies made by Scientifics cited. The experimental values of Presnall (1969) and the values determined by this study for temperatures between  $100$  and  $600^\circ\text{C}$  and for pressure up to  $2 \text{ kbar}$ , are less than  $3\%$  (Fig. 13). The results on a few  $PVT$  properties of pure fluid and binary mixture compared with the experimental studies find in the literature are represented in the Fig. 14-17. The properties of the fluid in the second line were study in terms of  $PVT$  properties with the equations of state resolution coupled to diffusion profile and equilibria (Fig. 18). A large difference was pointed out comparing the  $PVT$  properties of  $\text{H}_2$ - $\text{H}_2\text{O}$  evaluate in this study and the experimental properties published by Seward and Franck (1981) while pure  $\text{H}_2\text{O}$  and  $\text{H}_2$  have been determined closed to other experimental studies (see Table 2 and Fig. 19). It can be deduced from these results, that experimental measures by authors were performed differently if the study aim gases and/or liquids, and made appearing the realistic values of Kennedy (1954) on  $\text{CO}_2$  gas, and the values presented in Fig. 15 on specific volume of  $\text{CO}_2$ . The Fig. 20 gives an illustration to the method of the calculation.

For a general method to determine the mixing rule for a mixture with the knowledge of previous works made by authors and this work, it appear for a purpose that the density of the gas (i) expressed by the equation (59), mixing with another gases (i, j, ..., n) change by the law of this study writing as it follow

$$x_i^l = \frac{0.5 \cdot M_i}{V_i^{lg}} \cdot \frac{\left(1 - \sum_{j=2}^n x_j\right) \cdot \left(1 - \frac{M_i - \sum_{i=1}^n M_i \cdot x_i}{M_i}\right)}{1 + \frac{\sum_{j=2}^n V_j^{lg} \cdot x_j}{V_i^{lg}}} \quad (67)$$

## 5. Discussion on post-Lewis interpretation

In the paper of Hewitt (1977) on the equilibria of mineral buffer Ni-NiO, the hydrogen pressure diffusing through a membrane in a Shaw bomb is assimilate to the fugacity of hydrogen in the experimental capsule containing the mineral buffer and water. They said that fugacity decrease with reduced starting assemblage, although a reduced assemblage produces hydrogen. In fact, the hydrogen pressure can be inversely proportional to hydrogen fugacity, thus hydrogen pressure in membrane can't be equal to hydrogen fugacity in experimental capsule containing water. Fugacity equality Hypothesis by Lewis (1908) can't be applied to a system separate by a membrane like in a Shaw bomb. The filtered constituent fraction  $x_i$  and the total pressure  $P$  are measured in the autoclave; the hydrogen pressure is measured in the membrane  $P_i$ . The law is founded on the equality of constituent fugacities  $f_i$  on both side of the membrane, and is used to measure fugacity coefficient in the mixture ( $\varphi_i$ ). The law is written

$$(\varphi_i) = \frac{f_i}{P \cdot x_i} = \frac{P_i \cdot \varphi_i^0}{P \cdot x_i^{l+v}} \quad (68)$$

The molar fraction could correspond to  $x_i^{l+v}$ , so the Equation (56) to (58) give the expression

$$(\varphi_i) = \frac{\varphi_i^0 \cdot x_i^v}{x_i^{l+v}} = \frac{\varphi_i^{l+v}}{a_i} = \varphi_i^{0,l+v} \quad (69)$$

The study imply

$$x_i^v = \frac{P_i}{P} \quad (70)$$

Measuring  $\frac{dP}{dx}$  can't be used to determine the gas fugacity diffusing in the mixture because Equation (59) give a good accuracy to the experimental results of Bruno (1985, 1993) and Wagg et al. (1998) when considering partial pressures equality on both side of the membrane. The experimental study of Wagg et al. (1998) is in good agreement with these considerations but the studies of Bruno (1985, 1993) seem to omit the experimental total pressure (Table 3).

## 6. Conclusion

The characterization of the experimental system in term of pressure, sections volumes and their heterogeneities in temperature was performed according to the fundamental equations of advances in thermodynamics. It's important for further experiences considerations in these kinds of systems which the redox conditions should be controlled by hydrogen pressure. The methods employed to determine the volumes are correct because these volumes were used in the equations of diffusion to determine the diffusion coefficients and pressures function of temperature. The determination of diffusion coefficients which appears similar to those found by other authors allows validating the experimental system for further experiences in redox controlled system. The equations of state resolution can be applied to a few experimental systems to control the fugacity of fluid constituents.

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Table 1. Experimental data of Takenouchi and Kennedy (1964) comparing to this study on the fraction of CO<sub>2</sub> in H<sub>2</sub>O+CO<sub>2</sub> ( $X_i$ ) expressed in percent and the vapor fraction ( $X^v$ ).

P (bars)	This study			Exp. study			P (bars)	This study			Exp. study		
	X <sub>i,liq</sub>	X <sub>i,gas</sub>	X <sup>v</sup>	X <sub>i,liq</sub>	X <sub>i,gas</sub>	X <sup>v</sup>		X <sub>i,liq</sub>	X <sub>i,gas</sub>	X <sup>v</sup>	X <sub>i,liq</sub>	X <sub>i,gas</sub>	X <sup>v</sup>
350°C, 10.5%													
200	8.55	9.85	1.50	1.50	9.00	1.20	100	0.00	9.92	2.90	1.20	41.00	0.69
250	1.32	16.28	0.61	4.00	16.20	0.53	200	14.54	43.69	0.49	2.70	63.60	0.43
300	0.23	19.18	0.54	6.40	16.60	0.40	300	10.69	53.53	0.42	4.20	68.00	0.39
325	0.00	20.27	0.52	10.50	10.50	-	400	9.90	58.00	0.39	5.50	67.60	0.38
325°C, 18%													
150	3.30	9.85	2.24	1.00	10.60	1.77	500	9.85	60.58	0.37	6.40	66.00	0.38
200	21.89	18.97	1.33	2.60	24.60	0.70	600	9.66	62.84	0.36	7.40	63.60	0.38
250	3.09	27.81	0.60	4.30	32.10	0.49	700	9.42	64.88	0.35	8.40	61.30	0.39
300	1.82	31.60	0.54	6.10	34.20	0.42	800	9.18	66.70	0.34	9.40	59.30	0.39
350	0.90	34.35	0.51	8.20	33.40	0.39	900	8.97	68.31	0.33	10.40	58.00	0.39
400	0.28	36.48	0.49	11.20	28.60	0.39	1000	8.80	69.75	0.33	11.50	56.70	0.38
435	0.18	37.50	0.48	18.00	18.00	-	1100	8.65	71.04	0.32	12.50	55.50	0.38
300°C, 23.6%													
100	5.25	10.33	3.61	0.40	8.00	3.05	1200	8.52	72.21	0.32	13.20	54.80	0.38
150	0.08	12.53	1.89	1.60	29.00	0.80	1300	8.40	73.28	0.31	13.60	54.20	0.37
200	12.04	29.18	0.67	2.90	39.00	0.57	1400	8.30	74.28	0.31	14.00	54.00	0.37
250	6.92	37.14	0.55	4.10	43.40	0.50	1500	8.20	75.21	0.31	14.40	54.00	0.36
200°C, 28.8%													
300	5.72	41.09	0.51	5.40	45.40	0.46	100	37.73	6.76	0.29	1.30	71.50	0.39
350	4.85	44.03	0.48	6.80	45.60	0.43	200	27.34	31.45	0.36	2.60	82.00	0.33
400	4.53	46.05	0.46	8.40	44.80	0.42	300	7.99	61.68	0.39	3.40	82.50	0.32
450	4.48	47.51	0.44	10.40	42.20	0.42	400	7.09	65.96	0.37	4.10	81.60	0.32
500	4.39	48.82	0.43	12.70	38.00	0.43	500	7.06	68.35	0.35	4.70	80.00	0.32
550	4.27	50.02	0.42	17.00	32.00	0.44	600	6.89	70.52	0.34	5.20	78.00	0.32
575	4.20	50.59	0.42	23.60	23.60	-	700	6.68	72.46	0.34	5.60	76.00	0.33
275°C, 27%													
100	3.41	10.72	3.23	1.00	25.60	1.06	800	6.49	74.18	0.33	5.80	74.50	0.33
150	36.72	13.27	0.41	1.90	42.60	0.62	900	6.33	75.71	0.32	6.10	73.20	0.34
200	10.30	37.94	0.60	2.80	50.00	0.51	1000	6.19	77.06	0.32	6.30	72.00	0.34
250	8.06	44.24	0.52	3.80	54.00	0.46	1100	6.08	78.29	0.31	6.50	71.60	0.34
300	6.90	48.07	0.49	4.90	55.80	0.43	1200	5.98	79.40	0.31	6.70	70.60	0.35
400	5.98	52.80	0.45	7.20	55.80	0.41	1300	5.89	80.42	0.31	6.90	70.00	0.35
500	5.95	55.49	0.42	9.60	53.00	0.40	1400	5.81	81.35	0.30	7.00	69.40	0.35
600	5.75	57.79	0.41	12.00	49.60	0.40	1500	5.75	82.22	0.30	7.20	69.00	0.35
150°C, 28.8%													
700	5.49	59.86	0.40	14.40	46.00	0.40	100	31.54	22.69	0.31	1.35	88.00	0.32
800	5.20	61.73	0.39	17.50	42.00	0.39	200	27.90	30.80	0.31	2.15	91.00	0.30
885	4.97	63.16	0.38	27.00	27.00	-	300	4.97	70.49	0.36	2.60	90.00	0.30
270°C, 28.8%													
200	14.77	40.39	0.55	2.70	53.00	0.52	400	3.98	74.69	0.35	2.90	88.20	0.30
250	12.69	46.63	0.47	3.60	57.00	0.47	500	3.95	76.96	0.34	3.20	86.20	0.31
300	11.65	50.46	0.44	4.60	59.00	0.44	600	3.83	78.98	0.33	3.45	84.00	0.31
400	10.89	55.09	0.41	6.70	59.00	0.42	700	3.72	80.74	0.33	3.70	82.40	0.32
500	10.82	57.77	0.38	8.70	57.00	0.42	800	3.64	82.26	0.32	3.90	80.80	0.32
600	10.63	60.08	0.37	10.60	54.60	0.41	900	3.58	83.58	0.32	4.05	79.40	0.33
700	10.39	62.14	0.36	12.50	52.00	0.41	1000	3.54	84.74	0.31	4.20	78.00	0.33
800	10.14	63.99	0.35	14.50	49.60	0.41	1100	3.52	85.77	0.31	4.40	77.00	0.34
900	9.92	65.63	0.34	16.60	46.20	0.41	1200	3.51	86.70	0.30	4.50	76.40	0.34
1000	9.73	67.09	0.33	19.00	42.40	0.42	1300	3.51	87.53	0.30	4.60	75.80	0.34
1100	9.58	68.39	0.33	21.50	38.20	0.44	1400	3.52	88.28	0.30	4.70	75.40	0.34
1200	9.45	69.56	0.32	25.00	34.00	0.42	1500	3.53	88.96	0.30	4.80	75.20	0.34
1230	9.42	69.89	0.32	28.80	28.80	-	110°C, 28.8%						
260°C, 28.8%													
200	14.46	42.20	0.52	2.70	57.20	0.48	100	31.12	22.79	0.28	1.40	95.60	0.29
250	12.27	48.22	0.46	3.50	62.00	0.43	200	28.11	30.55	0.28	2.10	95.80	0.28
300	11.18	51.98	0.43	4.40	64.00	0.41	300	2.57	77.72	0.35	2.40	94.80	0.29
400	10.40	56.53	0.40	5.90	64.20	0.39	400	1.57	81.80	0.34	2.60	93.20	0.29
500	10.34	59.16	0.38	7.30	62.40	0.39	500	1.57	83.92	0.33	2.80	91.40	0.29
600	10.15	61.44	0.36	8.70	60.40	0.39	600	1.57	85.68	0.32	3.00	89.30	0.30
700	9.91	63.48	0.35	10.00	58.00	0.39	700	1.60	87.15	0.32	3.15	87.20	0.31
800	9.67	65.32	0.34	11.30	56.00	0.39	800	1.66	88.37	0.31	3.30	85.40	0.31
900	9.45	66.95	0.34	12.50	54.80	0.39	900	1.74	89.42	0.31	3.45	84.00	0.31
1000	9.28	68.40	0.33	13.50	53.60	0.38	1000	1.82	90.31	0.30	3.60	83.00	0.32
1100	9.12	69.69	0.32	14.50	52.40	0.38	1100	1.91	91.09	0.30	3.70	82.20	0.32
1200	8.99	70.86	0.32	15.50	51.00	0.37	1200	2.01	91.77	0.30	3.75	81.60	0.32
1300	8.88	71.94	0.32	16.00	50.40	0.37	1300	2.11	92.38	0.30	3.85	81.00	0.32
1400	8.77	72.94	0.31	16.50	50.20	0.36	1400	2.21	92.91	0.29	3.90	80.40	0.33
1500	8.67	73.86	0.31	17.50	50.00	0.35	1500	2.30	93.39	0.29	4.00	80.00	-0.05

Table 2. Interpretation of H<sub>2</sub>-H<sub>2</sub>O system *PVT* properties at critical point, between this study and the experimental study made by Seward and Franck (1981). The difference on the molar volume ( $V_M$ ) at different H<sub>2</sub> fractions ( $x_{H_2}$ ), come from the molar volume of water chosen by authors in their study (the difference is cover by the liquid and gas volume, see last column).

Seward and Franck (1981)					This Study		
$x_{H_2}$	$P_c$ (bar)	$T_c$ (°C)	$V_c$	$V_M$ (cm <sup>3</sup> mol <sup>-1</sup> )	$V_M$ (H <sub>2</sub> O)	$V_M(H_2)$	$\sum_{i=H_2}^{H_2O} (V_M^i - x_i)$
0	221.2	374.15	57.11	57.6	57.6	254.8	57.6
0.005	229	374.3	56.88	50.5	39.9	246.6	40.9
0.01	237	374.5	56.67	49.7	36.4	238.8	38.4
0.03	270	374.5	55.80	46.5	29.7	211.0	35.1
0.06	320	374.5	54.51	45.2	25.3	179.9	34.5
0.09	372	374.5	53.34	44.2	22.6	156.4	34.7
0.12	428	374.5	52.14	43.1	20.6	137.5	34.7
0.20	690	374.5	43.50	34.1	15.7	89.8	30.5
0.25	1010	375.3	37.41	27.7	12.8	65.3	25.9
0.30	1410	376.5	33.60	23.8	10.7	50.3	22.6
0.35	2020	379.0	30.97	20.1	8.8	39.0	19.3
0.38	2520	381.3	29.66	18.3	7.7	33.8	17.6
0.40	3000	383.3	-	16.9	6.9	30.4	16.3

Table 3. Analysis on the direct fugacity measurement studies of Bruno (1985, 1993) and Wagg et al. (1998). The fugacity coefficient ( $\phi_i$ ) must be equal to the pure fugacity coefficient ( $\phi_i^0$ ), because the partial pressure ( $P_i$ ) is the fraction of  $i$  ( $H_2$  or  $CO_2$ ) reporting to total pressure ( $P$ ).

	$x_i$	P (bars)	Authors		This Study		
			$P_i$	$\phi_i$	$\phi_i$	$\phi_i^0$	$P = \frac{P_i}{x_i}$
Bruno (1985)	0.8480	34.5000	30.1000	1.0400	1.0253	1.0179	35.4953
	0.8220	34.5000	29.1000	1.0330	1.0280	1.0179	35.4015
	0.7300	34.5000	27.3000	1.0280	1.0441	1.0189	37.3973
$H_2$ /Propane	0.6590	34.5000	23.3000	1.0360	1.0568	1.0179	35.3566
	0.5940	34.5000	21.5000	1.0580	1.0767	1.0183	36.1953
	0.5260	34.5000	19.6000	1.0800	1.1044	1.0188	37.2624
80°C	0.4450	34.5000	16.9000	1.1060	1.1472	1.0192	37.9775
	0.3440	34.5000	13.9000	1.1700	1.2369	1.0204	40.4070
	0.3090	34.5000	13.3000	1.2300	1.2985	1.0218	43.0421
	0.2800	34.5000	12.5000	1.2830	1.3588	1.0226	44.6429
	0.8490	34.5000	31.7000	1.1210	1.0197	1.0189	37.3380
	0.7900	34.5000	29.2000	1.1150	1.0202	1.0187	36.9620
$H_2$ /Methane	0.7640	34.5000	28.0000	1.0970	1.0205	1.0185	36.6492
	0.6520	34.5000	24.0000	1.1150	1.0229	1.0186	36.8098
	0.5360	34.5000	19.9000	1.1250	1.0265	1.0188	37.1269
80°C	0.4590	34.5000	17.5000	1.1340	1.0302	1.0193	38.1264
	0.3070	34.5000	11.9000	1.1660	1.0380	1.0196	38.7622
	0.2160	34.5000	8.8000	1.2230	1.0457	1.0206	40.7407
	0.9040	34.5000	32.9000	1.0580	1.0190	1.0169	36.3938
	0.8970	34.5000	32.3000	1.0540	1.0191	1.0168	36.0089
	0.8350	34.5000	29.6000	1.0380	1.0225	1.0165	35.4491
$H_2$ /Propane	0.7830	34.5000	28.1000	1.0470	1.0273	1.0167	35.8876
	0.7380	34.5000	26.6000	1.0470	1.0323	1.0168	36.0434
	0.6180	34.5000	22.8000	1.0770	1.0521	1.0172	36.8932
130°C	0.5450	34.5000	20.6000	1.0960	1.0697	1.0176	37.7982
	0.4720	34.5000	18.2000	1.1160	1.0920	1.0180	38.5593
	0.2650	34.5000	11.2000	1.2200	1.2040	1.0197	42.2642
Bruno and Outcalt (1993)	0.3600	33.9000	15.6000	1.2840	1.2230	1.0192	43.3333
	0.4010	33.9000	16.7000	1.2390	1.1813	1.0185	41.6459
	0.4510	33.9000	18.1000	1.1940	1.1432	1.0178	40.1330
$H_2$ /Butane 160°C	0.5980	33.9000	22.2000	1.1060	1.0729	1.0165	37.1237
	0.6210	33.9000	22.8000	1.0940	1.0654	1.0163	36.7150
Wagg et al. (1998)	0.9690	18.2235	16.6859	0.8843	0.9360	0.9359	17.2197
	0.9581	18.1545	17.2996	0.9285	0.9331	0.9329	18.0561
	0.9073	10.3563	9.3910	0.9638	0.9619	0.9612	10.3505
$CO_2$ /Isobutane 149.85°C	0.8595	11.2389	9.6875	0.9652	0.9596	0.9579	11.2711
	0.9690	19.8921	18.6855	0.9136	0.9450	0.9449	19.2832
	0.9581	19.8714	18.0511	0.8953	0.9464	0.9462	18.8405
$CO_2$ /Isobutane 74.85°C	0.9073	11.2182	10.1839	0.9690	0.9683	0.9677	11.2244
	0.8595	12.2110	10.4804	0.9661	0.9665	0.9650	12.1936

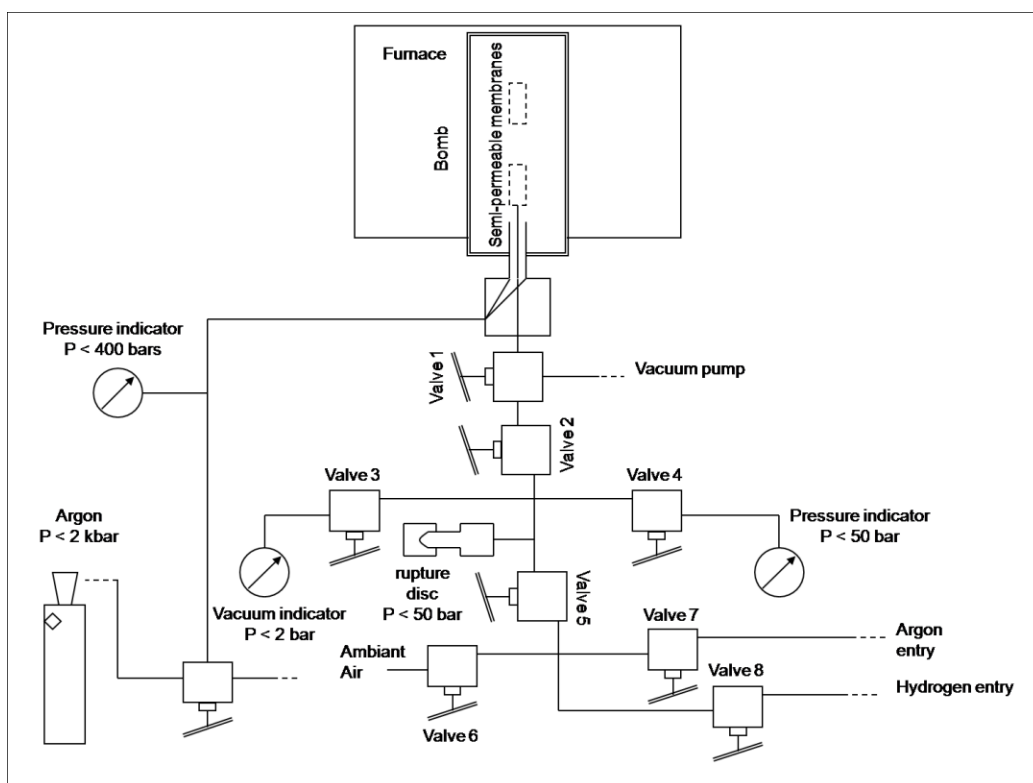


Fig. 1. Schema of the experimental system named hydrogen line.

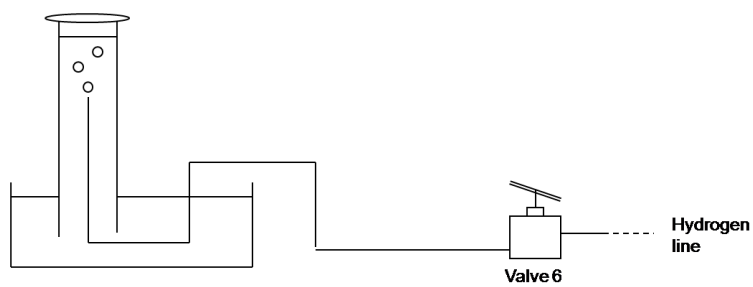


Fig. 2. Schema illustrating the measurement of Ar volume in a burette with the method 1.

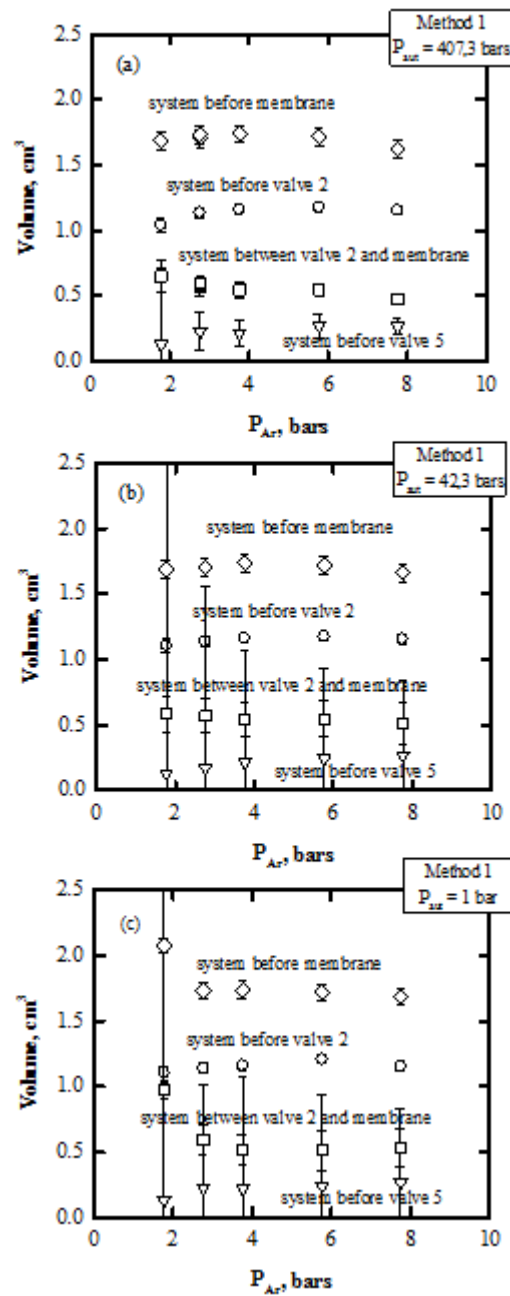


Fig. 3. Diagrams illustrating the results obtained with the method 1 on volumes of the membrane system. The inclined square points represent the volume of the system before membrane, the circle points represent the volume before valve 2, the square points are for the volume between valve 2 and the membrane, and triangle points are or the little volume before valve 5, measured at different Ar pressures ( $P_{Ar}$ ).

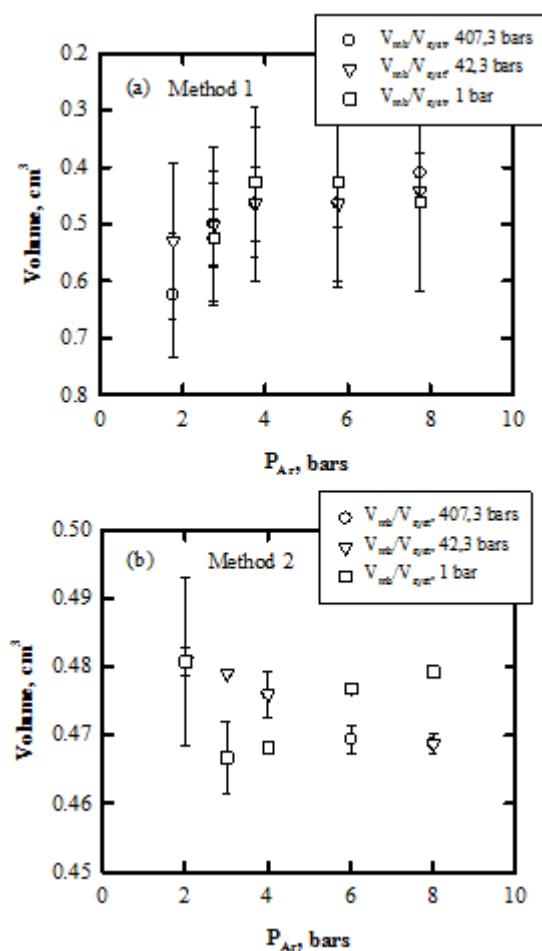


Fig. 4. Diagrams illustrating the results obtained with the methods 1 and 2 on ratio volumes of the membrane system sections. There is a similarity between the method 1, presented in (a), and method 2, in (b).

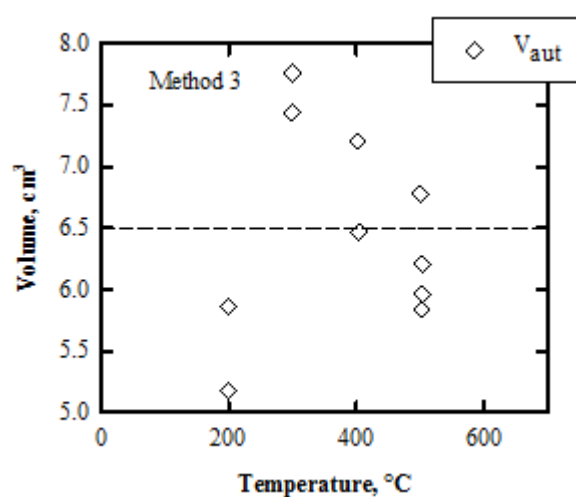


Fig. 5. Diagram illustrating the results obtained with the method 3 on ratio volumes between the autoclave and the membrane system.

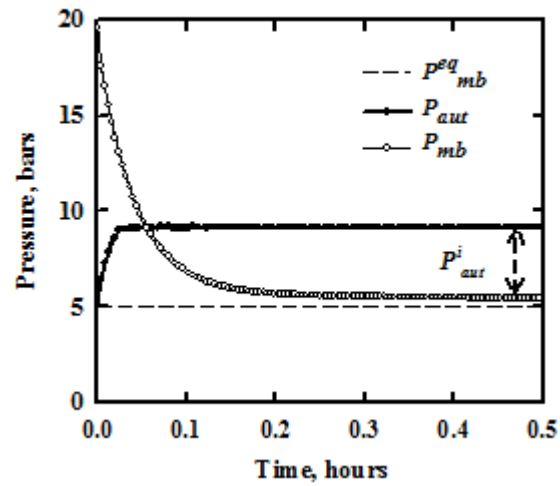


Fig. 6. Diagram illustrating the diffusion profile obtained at 499.8°C.  $P^{eq}_{mb}$  corresponds to the equilibrium pressure calculate,  $P_{aut}$  corresponds to the pressure measured in the autoclave,  $P_{mb}$  corresponds to the pressure measured in the membrane system,  $P^i_{aut}$  corresponds to initial pressure measured in the autoclave.

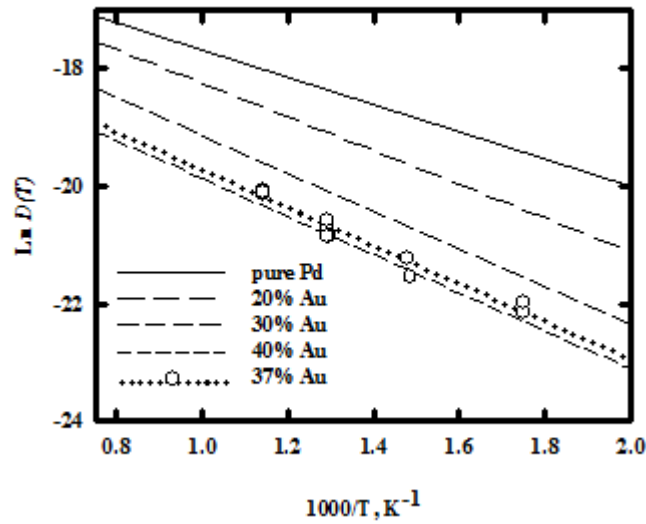


Fig. 7. Diagram illustrating the evolution of  $D(T)$  logarithm as a function of temperature reversed, for the hydrogen line membrane Au-Pd shown by the points compared to another study (Sonwane and al., 2006).



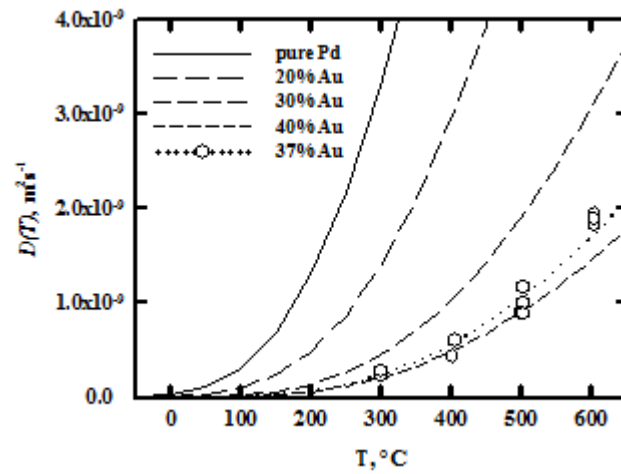
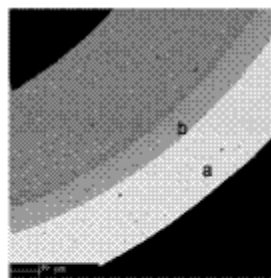


Fig. 8. Diagram representing the Arrhenius law for the hydrogen line membrane Au-Pd shown by the points compared to other study (Sonwane and al., 2006).



Atomic %	Pd	Au
Au/Pd 52/48	63.00	37.00
a	65.70	34.30
b	45.00	8.00

Fig. 9. MET photography of the second line membrane with the membrane compositions recapitulate for the two lines.

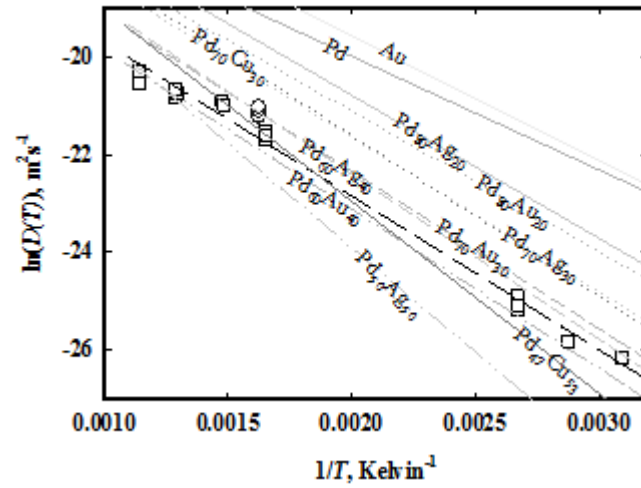


Fig. 10. Evolution of  $D(T)$  logarithm inversely function of temperature for the first line membrane Au-Pd determined in this study (long dashed lines which was fitted with the experimental data as square) compared with other studies (Sonwane and al., 2006 for Pd-Au and Pd-Ag, representing by the dashed and dotted lines, respectively ; Kamakoti et al., 2005 for Pd-Cu, in grey ; Zvesdin et Belyakov, 1968 for Au, solid lines). The coefficient of the second line membrane are representing by the circle.

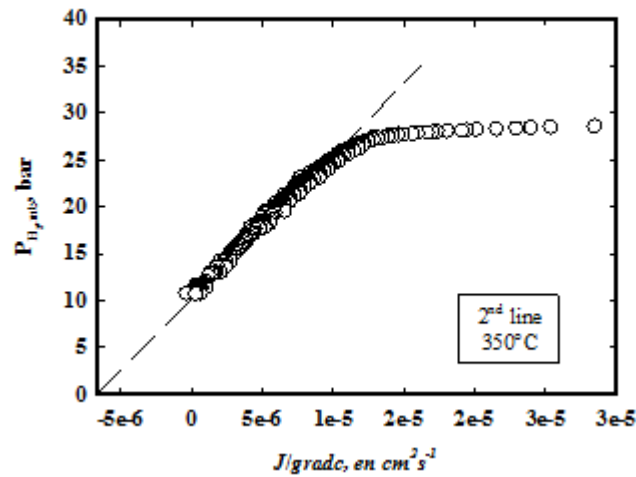


Fig. 11. Illustration of  $D(T)$  determination for the second line membrane.  $D(T)$  is determined for a pressure equal to 0. The experience temperature is 350°C.

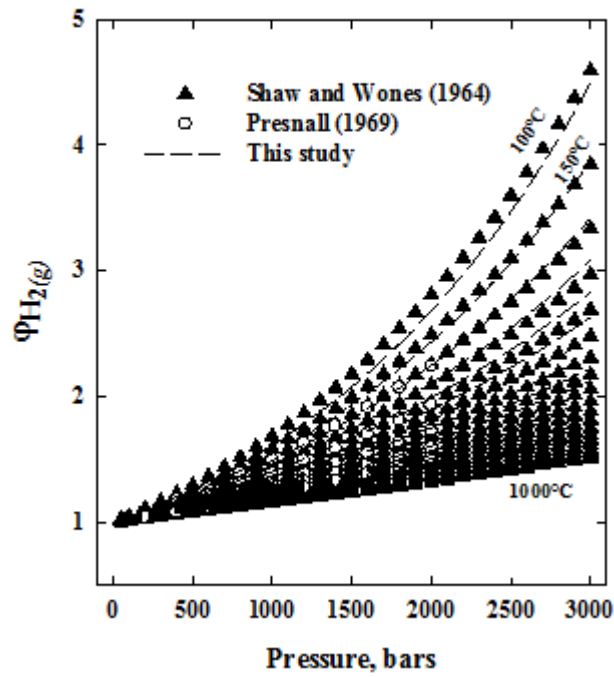


Fig. 12. Fugacity coefficient of  $H_2$  gas function of pressure determined in this study (dashed line) and by Shaw and Wones (1964) and Presnall (1969) (triangle and circle, respectively) for temperatures comprised between  $0^\circ\text{C}$  and  $1000^\circ\text{C}$ .

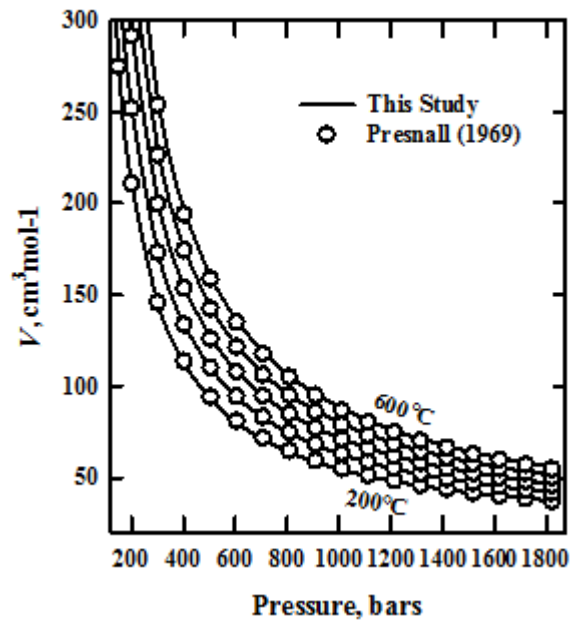


Fig. 13. Pressure-volume-temperature relations for hydrogen gas. The circles represent the experimental values find by Presnall (1969). The curve corresponds to the value calculation with the aid of this study.

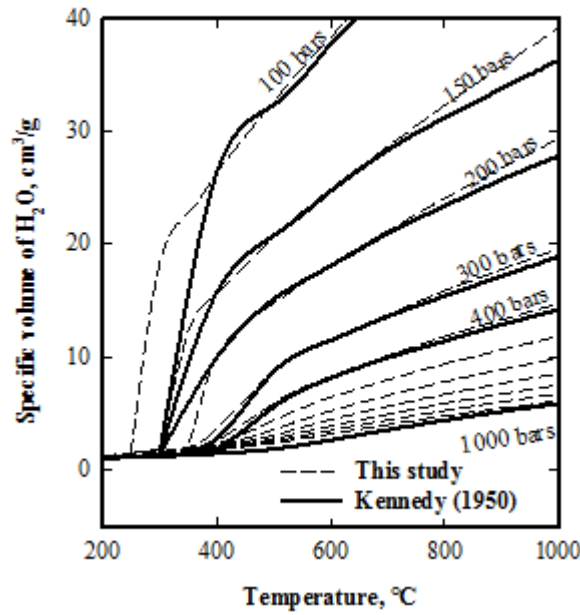


Fig. 14. Specific volume of  $\text{H}_2\text{O}$  reproduced in this study. The dashed lines are the results of this study for  $\text{H}_2\text{O}$ , and the dark lines are the results of the experimental study of Kennedy (1950) for the some pressures. The results correspond to the fluid when  $V^l = M$ ,  $V^{\text{fluid}} = M/x^l$ .

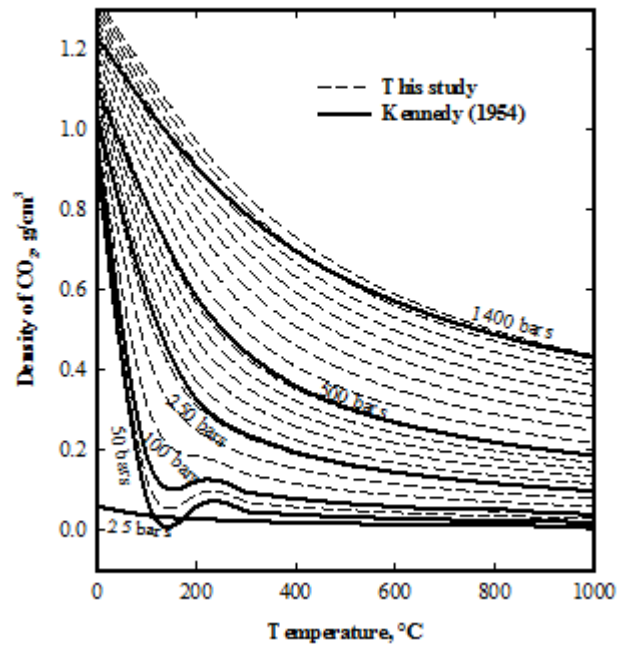


Fig. 15. Density of  $\text{CO}_2$  reproduced in this study. The dashed lines are the results of this study for  $\text{CO}_2$ , and the dark lines are the results of the experimental study of Kennedy (1954) for the some pressures. The results correspond to the fluid when  $V^l = M$ ,  $V^{\text{fluid}} = M/x^l$ .

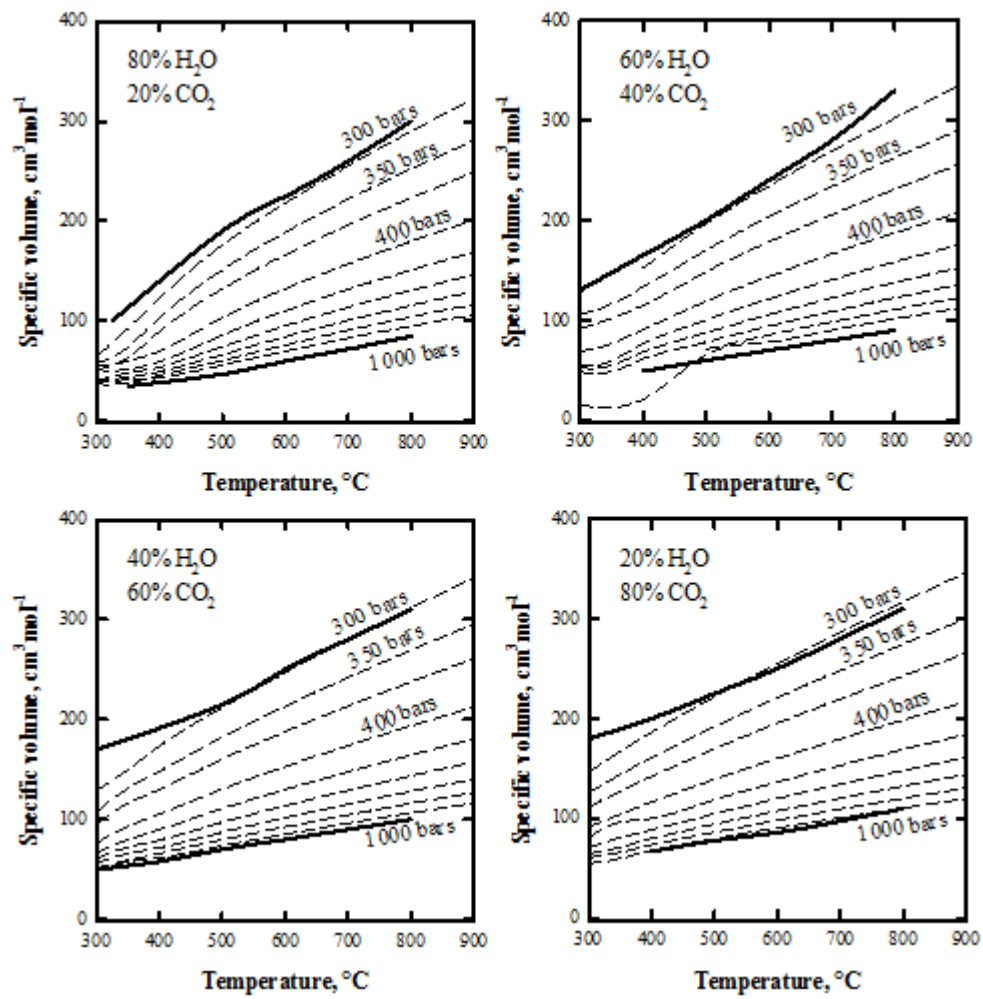


Fig. 16. Specific volume of  $\text{H}_2\text{O}$ - $\text{CO}_2$  system reproduced in this study. The dashed lines are the results of this study, and the dark lines are the results of the experimental study of Plyasunov and Zakirov (1991) for the extreme pressures. Both results are in good agreement.

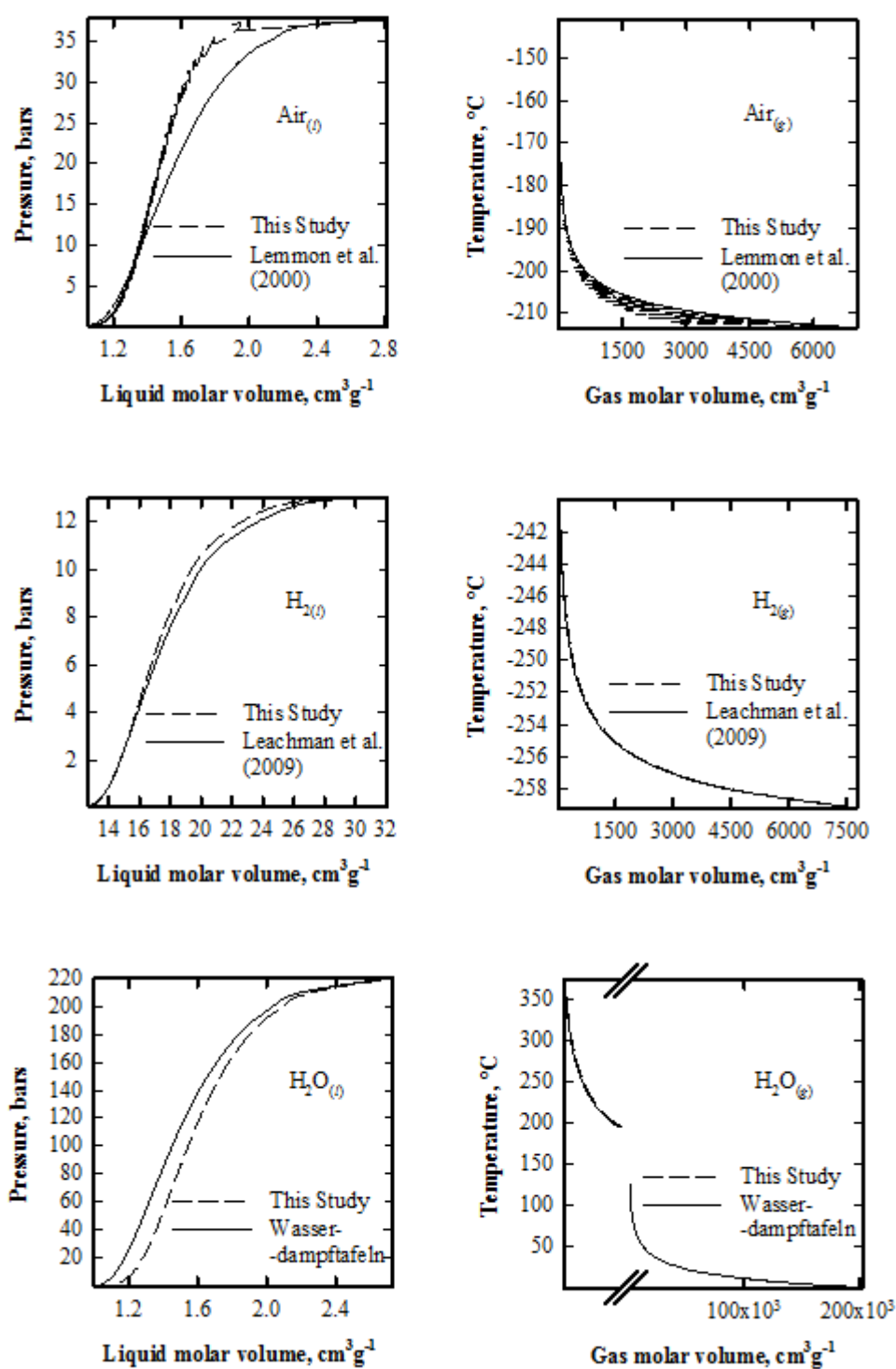


Fig. 17. Critical curves function of pressure-liquid molar volume and temperature-gas molar volume for Air, hydrogen and water. The curves determined by this study (dashed lines) are closed to the curves which the values are listed in the studies of Lemmon et al. (2000), Leachman et al. (2009) and the international steam tables in the Wasserdampftafeln by Grigull (1984) (full lines).



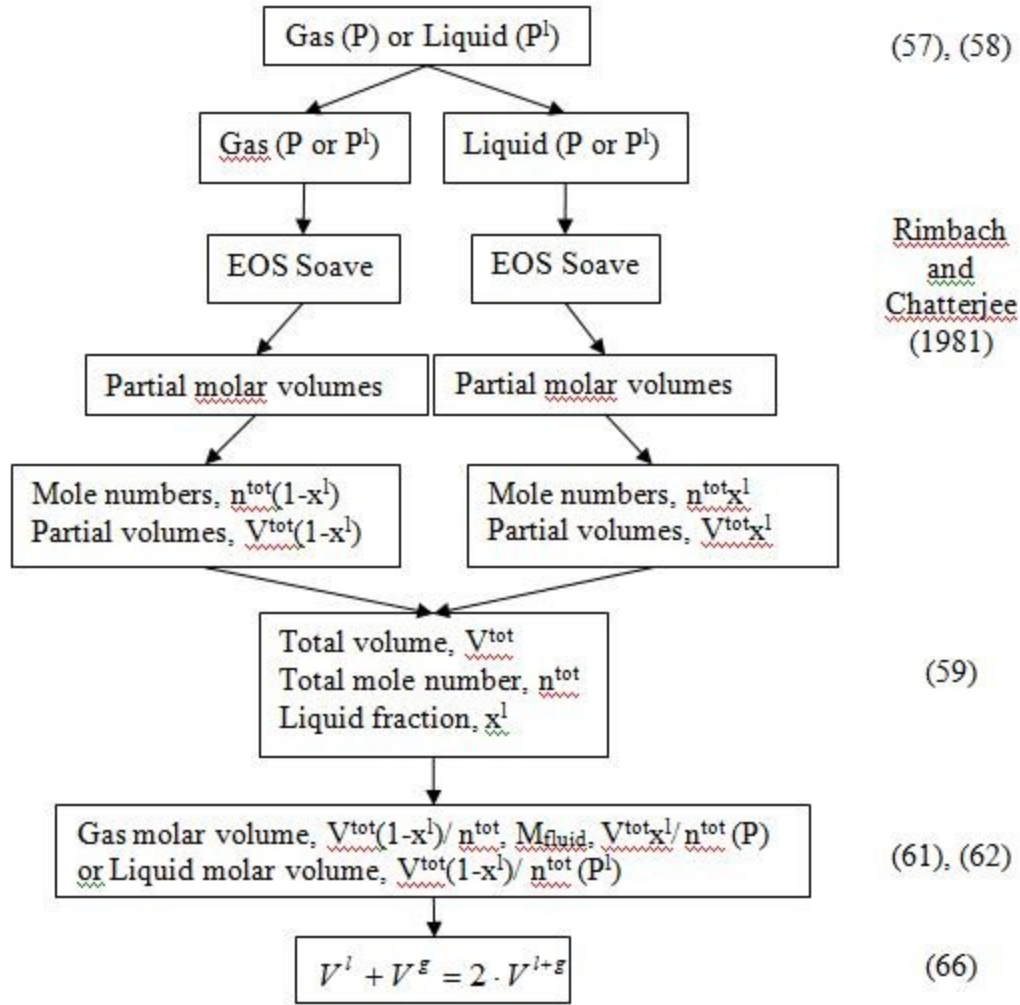


Fig. 20. Some explications and related equations of the calculation represented in a scheme.



## **7. Use and Agreement Contract**

**Owner:** Michael Andre Franiatte.

**Contact:** [michael.franiatte@gmail.com](mailto:michael.franiatte@gmail.com).

**Owning:** All works from scratch of the owner.

**Proof of Owning:** Works published, and writings/speakings all over.

**Requirements of Use:** Pay the owner, quote the owner, agreement of the owner.

**Availability of Works:** Only under the shapes of the owner built, only for personal use.

**Subjects of Claims:** Works published by the owner on Google Play and Google Books.

**Concerning Author Rights:** Equations and codes from scratch of the owner, softwares built from it, all things of people arising from it.

**End User License Agreement:** A commercial license is required to use in personal manner. Do not redistributing in any manner, including by computer media, a file server, an email attachment, etc. Do not embedding in or linking it to another programs, source codes and assistances including internal applications, scripts, batch files, etc. Do not use for any kind of technical support including on customer or retailer computer, hardware or software development, research, discovery, teachery, talk, speech, write, etc. Do not use for win money or for commercialisation of any products arising from my programs, source codes and assistances. Do not use and do not copy the way it run in other programs, source codes and assistances. Do not use without pay me, quote me and my agreement. Do not steal or copy or reproduce or modify or peer or share. Do not use in other manner than personal. It stand for my programs, source codes and assistances or programs, source codes and assistances stealing or copying or reproducing or modifying or peering or sharing my programs, source codes, and assistances. If you aren't agree you shall not use.

**Terms of License and Price:** The present contract acceptance is required to use works of the owner and built from it in all kind of manner. The price for each user shall be defined with the owner by contacting him and this for each subject of works the owner claims. Each user shall contact the owner for asking his agreement. It can be refused by the owner depending who asking and the price defined. People don't respecting the present contract shall not use the works of the owner.