CHAPTER II
LITERATURE REVIEW

2.1 Membrane Separation Processes

2.1.1 Definition of Membrane

A membrane system is defined as two essentially uniform and homogeneous three-dimension fluid phases between which matter and energy may be exchanged at rates governed by the properties of a third phase, or group of phases, which separates them. This third phase is membrane (Meares, 1976).

The versatility of polymers as a source of thin and strong films, which can have a wide range of chemical and physical properties, has made polymer film the natural choice in the search for membranes with selective permeability.

Frequently the submicroscopic arrangement of the polymer molecules may also be characterized fairly precisely by spectroscopic and thermal analysis, by electron and x-ray diffraction, and in other ways.

2.1.2 Types of Membranes

Membranes can be broadly classified into 2 types.

a) Homogeneous Membrane

This type of membrane consists of a single substance or stable mixture of substances not separated by internal interfaces and constrained within the membrane boundaries. This membrane is uniform in any lateral direction but may be non-uniform in the flux direction provided the gradients of composition between its faces are everywhere continuous.

b) Heterogeneous Membrane

This type of membrane consists of a random or ordered array of discrete volume elements with different chemical or physical properties.

2.1.3 The Basic Membrane Process For Gas Separation

The pressure difference across the membrane provides the driving force for the diffusion of gas across the membrane. Components that diffuse more rapidly become enriched in the low pressure *permeate* stream, while the slower components are concentrated in the *retentate* stream. For the gas separation with membranes, the feed and product streams are all gases without the phase change. A membrane will separate gases only if some components pass through the membrane more rapidly than others do. This requirement place constrains on the structure of the membrane's separating layer.

There are 4 types of the constrains on the structure of the membrane's separating layer.

a) Convective Flow

No separation occurs in this type of flow since the membrane contains pores that are large enough to let all gases diffuse through.

b) Knudsen Diffusion Flow

When the size of the pores is smaller than the mean free path of the gas molecules, the convective flow is replaced by Knudsen diffusion flow. In this case the gas molecules interact with the pore walls more frequently than with one another. Low molecular weight gases are able to diffuse more rapidly than the heavier one. In the limit of zero permeate pressure, the difference in transport rates of two components is inversely

proportional to the square root of the ratio of their molecular weights. Normally, the pore size is between 1-5 nm.

    c) Molecular Sieving Flow

        If the pores are small enough, about 5-500 nm, large molecules are unable to pass through them and are excluded by the membrane. This molecular sieving is useful in separating molecules of different sizes.

    d) Solution-diffusion Flow

        The transport in this type of membrane occurs when gas molecules dissolve into the membrane and then diffuse across it. Most of the commercial solution-diffusion membranes are made of polymers.
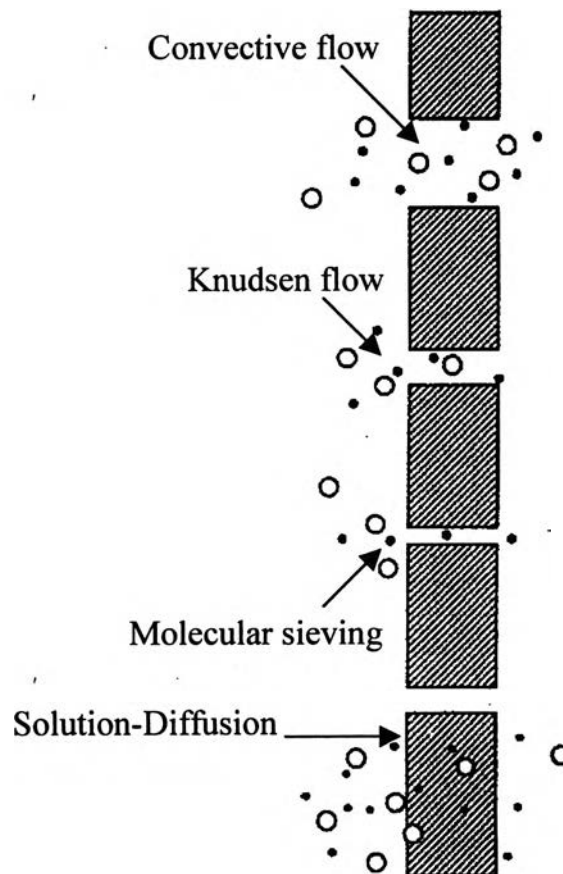

Figure 2.1 Structures of separating layer of membrane (Zolandz, and Fleming, 1992, ch.2).

2.2 Gas Diffusion in Solids

2.2.1 Determination of Diffusivity and Permeability Coefficients

If the material is initially free of the gas then there will be a transient period while the gas concentration reaches its steady state distribution in the material. After this period the gas concentration will be constant at C_1 and C_2 respectively in the material at the two surfaces (See Figure 2.2). The flow rate through an area A of material is given by

$$Q = DA\left(\frac{C_1 - C_2}{L}\right) \quad\quad (2.1)$$

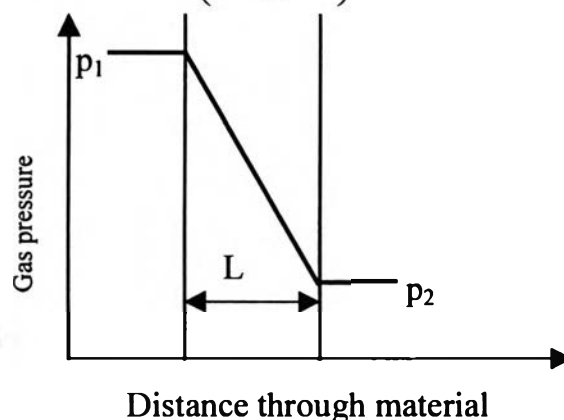

Distance through material

Figure 2.2 Variation of gas pressure through a material.

Gas permeation through a material was quantified in terms of the permeability coefficient, ϕ, defined by the steady-state equation:

$$Q = \phi A\left(\frac{p_1 - p_2}{L}\right) \quad\quad (2.2)$$

where:

Q	= molar flow rate of permeant, mol s^{-1}
A	= cross sectional area to flow, m^2
D	= diffusion coefficient, m^2 s^{-1}
ϕ	= permeability coefficient, mol m^{-1} Pa^{-1} s^{-1}
C_1, C_2	= gas concentrations on either side of interfaces, mol m^{-3}
p_1, p_2	= gas partial pressures on either side of interfaces, Pa

L   = thickness of material, m.

There are many different units for these constants, because the apparatus used to determine them may measure gas volumes or mass changes. In addition, the pressure units and time units can vary. Permeability coefficients are frequently given in units of cm^3 (STP) cm/cm^2 min atm. The conversion factor is,

$$1 \text{ mol m}^{-1} \text{ Pa}^{-1} \text{ s}^{-1} = 1.36 \times 10^9 \text{ cm}^3 \text{ (STP) cm/cm}^2 \text{ min atm.}$$

For multilayer materials made by co-extrusion or coating techniques, the total permeability coefficient, ϕ_T is related to the total thickness L_T by

$$\frac{\phi_T}{L_T} = \frac{\phi_1}{L_1} + \frac{\phi_2}{L_2} + \frac{\phi_3}{L_3} + \dots \qquad (2.3)$$

The resistance to the gas transfer for each layer can be added directly as

$$R_i = \frac{L_i}{\phi_i} \qquad (2.4)$$

2.2.2 The Relation between Diffusion and Permeability Coefficients

a) For Simple Gases

The diffusion coefficient is related to the permeability coefficient, ϕ by

$$\phi = DS \qquad (2.5)$$

where S is the solubility constant for the gas which is affected by the strength of the intermolecular forces between a pair of gas molecules.

b) In Hydrogen/Palladium System

Fick's law governs the diffusion of a gas in a solid material,

$$N = DA \frac{dC}{dx} \qquad (2.6)$$

Equation (2.6) applies for the diffusion of atomic hydrogen within palladium, and molecular hydrogen within the coating.

The solution to this equation for unsteady state diffusion of a gas in a solid of various geometry has been solved by Carslaw and Jaeger (1959, ch.3). The rate of diffusion of hydrogen through the palladium membrane can be measured by the diffusion coefficient, D.

The formulation of diffusion equations based on Fick's 1st law is

$$P = D\left(\frac{C_1 - C_2}{L}\right) \qquad (2.7)$$

where:

P = rate of hydrogen permeation

D = diffusion coefficient, cm^2/s

L = thickness of the material, cm

C_1, C_2 = concentrations of hydrogen dissolved in the membrane at each side of the interfaces.

The diffusion coefficient, D, is dependent on the chemical composition, the concentration gradient across the membrane and on the thickness.

2.2.3 Factors Affecting Diffusion of Gases in Polymers

a) Temperature and Pressure

Mostly, the diffusion coefficient is independent of the concentration due to the very low concentrations encountered at normal pressure. This effect also reflects the comparative lack of interaction between simple gases and polymers.

The temperature effect can be discussed in terms of the nature of gases and the nature of polymers. From the relationship, found by Barrer (1968, ch.2).

$$D = D_0 \exp\left(\frac{-Q}{RT}\right) \qquad (2.8)$$

where:

D   = diffusion coefficient

D_0 = pre-exponential factor

E_A = activation energy.

Therefore, the diffusion coefficient always increases with increasing temperature. Moreover, the size of the diffusing gas also affects the diffusion coefficient and it is found diffusion coefficient to decrease with the increasing in diameter.

b) Nature of Gases

It is clear that the larger holes need to be formed in the polymer for the diffusion of the larger molecules. The larger holes will require a higher amount of energy for their formation. The diffusion of the bigger molecules will have higher activation energy and hence the diffusion coefficient will be smaller.

Table 2.1 Molecular weight and kinetic diameter of interesting feed gases.

Gas	Molecular weight(g/mol)	Kinetic diameter (nm)
H_2	2.0	0.297
N_2	32.0	0.354
O_2	28.0	0.375
Cl_2	35.5	0.412

c) Nature of Polymers

From many studies of the diffusivity, the diffusivity rate will depend on

i) The Number and Size Distribution of Pre-existing Holes   s

This effect depends on the ease and degree of packing of the chains and is related to the free volume and to the density.

ii) The Ease of Hole Formation

The segmental chain mobility has an impact on the ease of the hole formation, for example, the chain stiffness, and on the cohesive energy of the polymer. Silicone rubbers, which have exceptionally high internal chain mobility, have exceptionally high diffusivity with low activation energy.

d) Effect of Glass Transition

The effects of the glass transition have been interpreted in terms of the change in the coefficient of expansion at the glass temperature, T_g. Since this would lead to changes in the rate of increase of the free volume with temperature and then leads to a change in the activation energy. At above T_g, the segmental mobility is greatly increasing and the activation energy increases as a consequence.

e) The Effect of Crosslinking

It is found that as the degree of crosslinking increases, the diffusion coefficients decrease. This effect is caused by the reduction in the mobility of the polymer chains. The magnitude of the change in the diffusion coefficients is greater for the larger penertrant molecule.

f) Effects of Plasticizers and Relative Humidity

The addition of a plasticizer to a polymer decreases the cohesive forces between the chains resulting in an increase in segmental mobility. It is to be understood that this should result in an increased rate of diffusion, caused by the lower activation energy.

The effect of relative humidity on gas diffusion in polymers varies widely. Polymers, which swell greatly in water, always have increasing diffusivity with increasing humidity. It is apparent that when water is highly sorbed into the polymer, the film is plasticized by the water leading to greatly increased permeability, as same as the diffusivity.

2.3 Hydrogen Permeation in Solids

The hydrogen monitoring acts as an important role in the chlor-alkali plant because of the increasing in hydrogen concentration could indicate the lower efficient operational electrolytic cell and cause an explosion when hydrogen exceeds 6% which is the explosive limit of hydrogen in chlorine gas. The understanding for the permeation of hydrogen in the materials is needed.

2.3.1 Diffusivity and Permeability of Hydrogen through Palladium

When palladium is used as a membrane, it is possible to combine the catalytic ability of palladium with the selective permeation of hydrogen through the membrane.

a) Interaction of Hydrogen Molecule with Palladium

The interaction of a hydrogen molecule with palladium is considered as a model of chemisorption and catalytic action of a metal surface. The basic assumption is the local nature of the interaction between hydrogen and palladium. The hydrogen molecule is adsorbed and dissociated very smoothly on the palladium surface with almost no barrier and shows an equilibrium with the two atomic hydrogen radicals. The Pd-Pd bond is not weakened in this process, which is related to the stability of the catalytic surface. The existence of a smooth equilibrium between molecular hydrogen and two atomic hydrogen radicals on the metal surface is,

$$H_2 \leftrightarrow H\bullet + H\bullet \tag{2.9}$$

On the surface $1.5 A^\circ$ apart from the metal, the dissociative form is more stable than the molecular form by 2.2 kcal/mole and the barrier height is 5.6 kcal/mole. From Nakatsuji and Hada study (1985), the attractive interaction of the hydrogen molecule with the palladium is found. And the palladium system is the smallest possible system that shows the

catalytic activity for the dissociative adsorption of the hydrogen molecule. Hydrogen molecule with a binding energy about 104 kcal/mole is dissociated, with almost no barrier, into two atomic hydrogenous on the palladium surface. It is the same as on the extended surface. From the potential energy study, it can determine the excited states of the palladium-hydrogen system are well separated from the ground state and there is almost no chance for the excited states to participate in the dissociative process.

The present result has shown that even palladium molecule has catalytic activity for the hydrogen cleavage shall suggest a design of the palladium catalyst not as a solid but in a more molecular form.

b) Permeation of Hydrogen through Palladium

The high amount of hydrogen is allowed to put on the palladium over a very wide range of temperatures and pressures of hydrogen gas. Figure 2.3 shows the solubility of hydrogen in palladium.
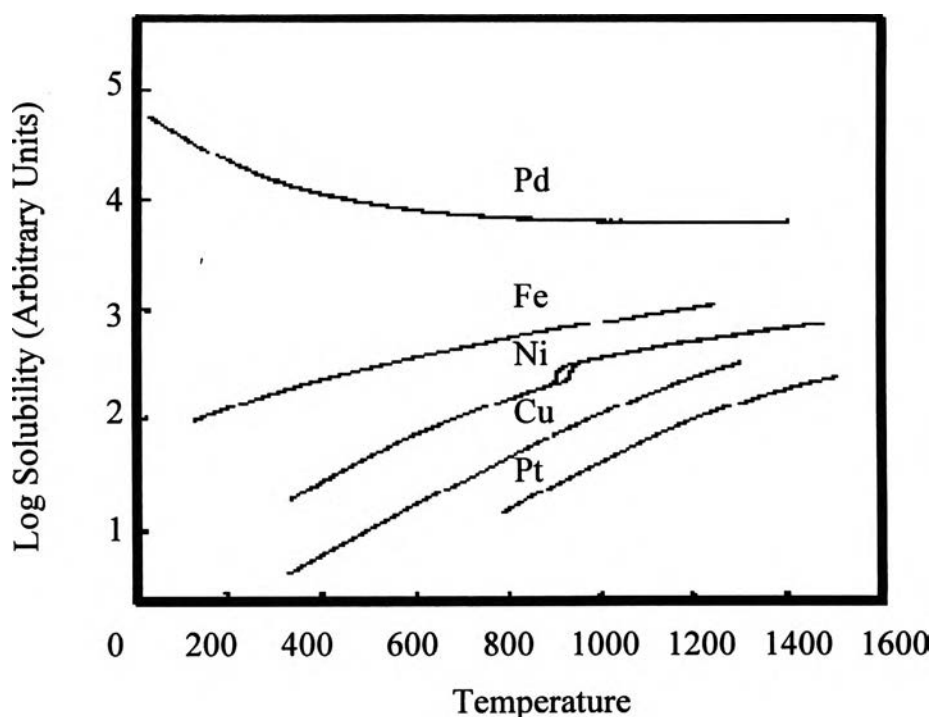

Figure 2.3 Schematic comparison of solubility of hydrogen in metals at a pressure of 1 atm as a function of temperature (Rakotoarevelo, 1995).

c) The Measurement of the Permeation Rates

Using Fick's first law to determine the diffusion coefficient, as the complete equilibrium between solid and gas is reached, diffusion through the solid is the slow and rate-limiting step. Therefore, the concentrations of hydrogen at the surfaces may be derived from the gas pressure through P-C-T relationships as shown in Figure 2.5.

i) Hydrogen Permeation Rate Measurement at Room Temperature

The surfaces of palladium membrane do not readily equilibrate with the hydrogen molecule. Some activation procedures have been succeed recently. For examples, by plating on a layer of Pd black, bombardment by argon ions formed in low-pressure gaseous discharges, contacting the surfaces with materials such as copper or hydrides of uranium and tantalum. Both uranium and tantalum were believed to be more efficient than palladium for dissociating molecular hydrogen and from which the dissociated atoms migrate to the palladium surface.

ii) Hydrogen Permeation Rate Measurement at Temperature Exceeding 250°C

The specimens may need to be heated in oxygen for a period before reproducibly high rates of permeation are recorded. Low solubility of hydrogen can be explained by inhibition of the dissociation of hydrogen molecules to chemisorbed atoms or by the poisoning element which formed a layer of high melting compounds.

To prevent the decrease of permeation rates to negligible low values, Lewis (1967) suggested the necessity for maintaining movement and circulation of the gas at the input or upstream side of the membrane.
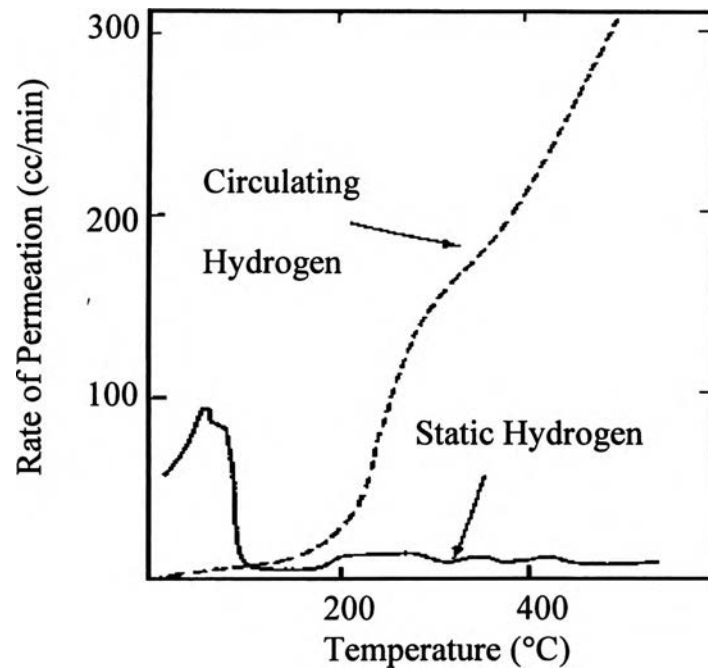
Figure 2.4 Examples of permeability of a palladium tube when hydrogen at the high pressure (upstream) side is kept either static or in circulation by bleeding away some of the gas (Rakotoarevelo, 1995).

d) Isothermal Pressure-Composition Relation in

Hydrogen/Palladium System

Figure 2.5 shows the Phase diagram of the palladium-hydrogen system. At low hydrogen contents, the equilibrium pressure shows a continuous increase. In this region, the solid can be regarded as a solid solution of hydrogen in the original palladium lattice and has become the α-phase of the palladium-hydrogen system.
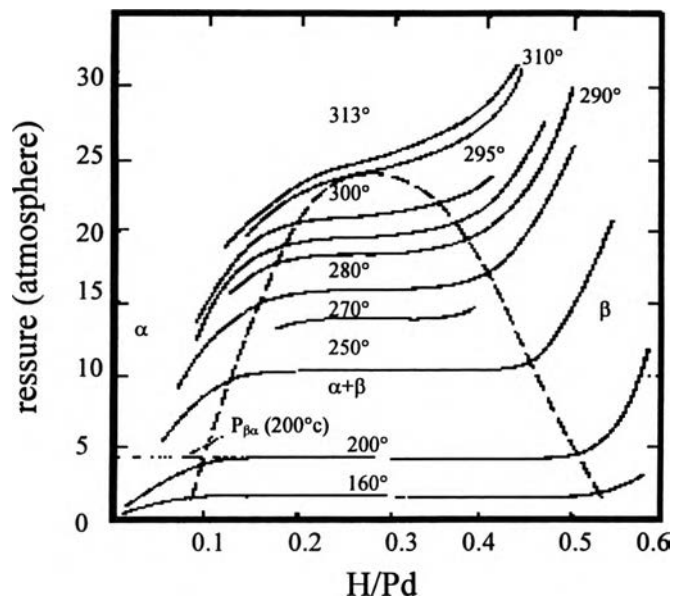
Figure 2.5 Phase diagram for the Pd/H system: isothermal pressure-composition (Rakotoarevelo, 1995).

With the change in temperature, there was an accompanying change in the range of the composition over which the pressure remained constant. There is a continuous transformation of hydrogen from α- to β-phase in this region as the hydrogen content increases.

When the phase transformation has been completed, the hydrogen vapor pressure once again begins to go up with further increases in hydrogen content.

2.3.2 Diffusivity or Permeability of Hydrogen through Alloys of Palladium

There are many kinds of alloy of palladium with metals, such as silver, platinum, nickel, rhodium, copper and gold. The compositions of Pd/Ag alloys have been widely used instead of pure palladium as a material for the membrane construction.

a) Absorption of Hydrogen

Hydrogen has been introduced into Pd alloys by electrolysis in most studies. The hydrogen solubility was evaluated and compared under a pressure of 1atm in series of palladium alloys. Figure 2.6 showed a continuous decline at all temperatures in the case of Pd/Pt series. On the other hand, the curves were exhibited pronounced maximum value that became lower with the increasing temperature in Pd/Au and Pd/Ag series. The peak seemed to be shifting slightly towards a lower percentage content of the alloying metal with an increasing temperature.

b) Existence of critical and supercritical isotherms

There is no longer pressure constant region at a particular composition and the p-C relationships have the appearance of a critical isotherm. The isotherms for alloys with high contents of alloying metals should then be in a supercritical form and the critical temperature decreases with increasing content of alloying metal.
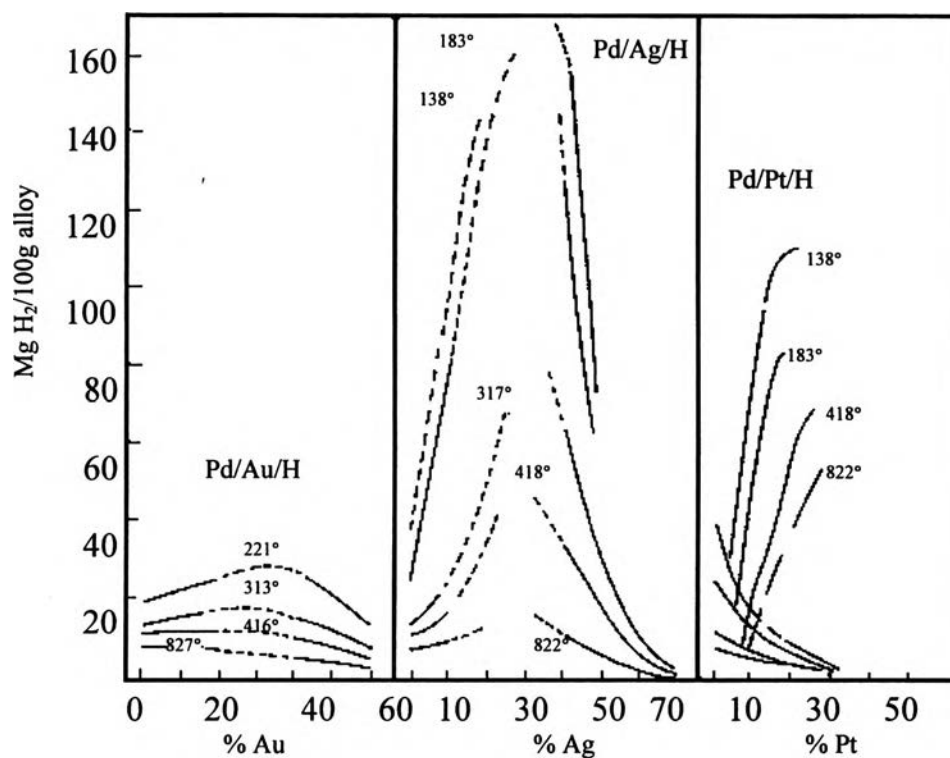
Figure 2.6 Comparison of solubilities of hydrogen under a pressure of 1 atm in series of palladium alloys-from measurements of Sieverts (Rakotoarevelo, 1995).

c) Pd/Ag Study

The maximum solubility was found to be closer to 20%Ag at 155 and 260°C. Lewis (1967) showed that when solubilities were compared to a pressure of 5 atm, there was an apparent maximum about 5%Ag at 155°C. While there was apparently a continuous solubility decline with an increasing silver content at 200°C.

Figure 2.7 shows an invariant pressure regions. There is a complementary decrease of the hydrogen pressure over these plateau regions as the silver contents increase. Similar forms of isotherm were exhibited with 10 to 20%Ag to those of the Pd/H system. There is relatively slow diffusion of hydrogen in alloys with higher silver contents.
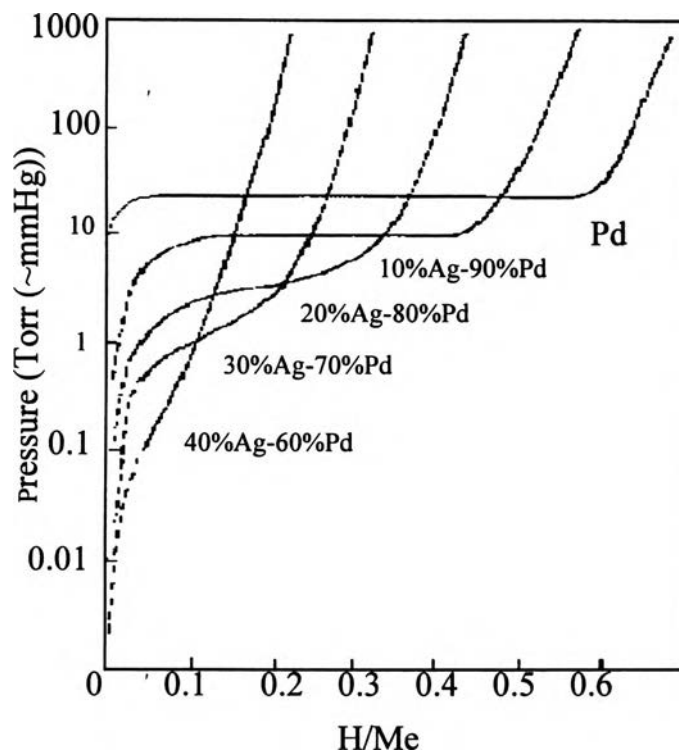
Figure 2.7 Comparison of P-C (absorption) relations for palladium silver alloys at 50°C (Rakotoarevelo, 1995).

i) Critical Isotherm, Tc

It is found that the critical temperature, Tc decreases with increasing contents of the alloying metal.

ii) Diffusion and Permeability Values

Several scientists have studied the data from the studies of hydrogen diffusion coefficient.

Holleck and Wicke (1968) obtained a value of the diffusion of hydrogen in palladium at low hydrogen concentrations. In the metal, D_0 is $17\pm 5.95\times10^3$ cm²/sec and the value of Q equals to 7.1±0.018 cal/g-atm for alloys containing 25%Ag in the temperature range between 0-80°C and at hydrogen concentration of 0.612 in the metal. Diffusion at a fast rate requires the values of diffusion coefficient, D to be high. However, in practice, the value of D over a range of alloy compositions may decrease

sufficiently as to give rise to seriously enhanced experimental limitations under a particular set of conditions.

Some values of D were obtained for a 25% Ag alloy at 25 °C, such as,

Wicke and Holleck: $\sim 7.5 \times 10^{-7}$ cm^2/sec.

Wicke and Bohmholdt: $\sim 6.1 \times 10^{-7}$ cm^2/sec.

2.3.3 Diffusivity or Permeability of Hydrogen through Teflon

a) Nature of Teflon

Teflon PTFE (Polytetrafluoroethylene) resins have a continuous working temperature of 260°C. Great higher temperatures can be satisfactory sustained for shorter exposures (See physical properties of Teflon in Appendix A).

As a fluoropolymer, it has exceptional resistance to chemical attack and high thermal stability. It also retains the main properties over a wide temperature range. Teflon may be used up to about 300°C for long periods without loss of strength. The thin sections of Teflon remain flexible at the temperature lower than 100°C. There is some weight loss when it is heated above 200°C but the weight loss becomes very small up to 350°C. It enters a gel state at 327°C. The processing technique may be varied in order to obtain various physical properties. While some properties relatively do not depend on the fabrication conditions.

b) Diffusion and Permeability Values of Hydrogen in Teflon

The studies of the hydrogen diffusion coefficient for Teflon at 25°C are given as 14.7± 1.54×10^{-8} cm^2/sec at room temperature (Matsuyama *et al.*, 1982).

c) Factors Affecting the Diffusivity

These effects can be discussed in terms of the nature of gases and the nature of polymers. From the relationship of D and T as shown in equation (2.8). It is clear that D always increases with increasing temperature.

2.4 Sensors for Monitoring the Hydrogen Concentration

Three types of sensors have been considered.

2.4.1 The Pd/H Electrical Resistance Sensor

This type of sensor utilizes the dependency of the electrical resistance of palladium, upon the concentration of absorbed hydrogen in the metal, the fabrication of Pd/H electrical resistance sensor used in the present work is shown in Figure 2.8.
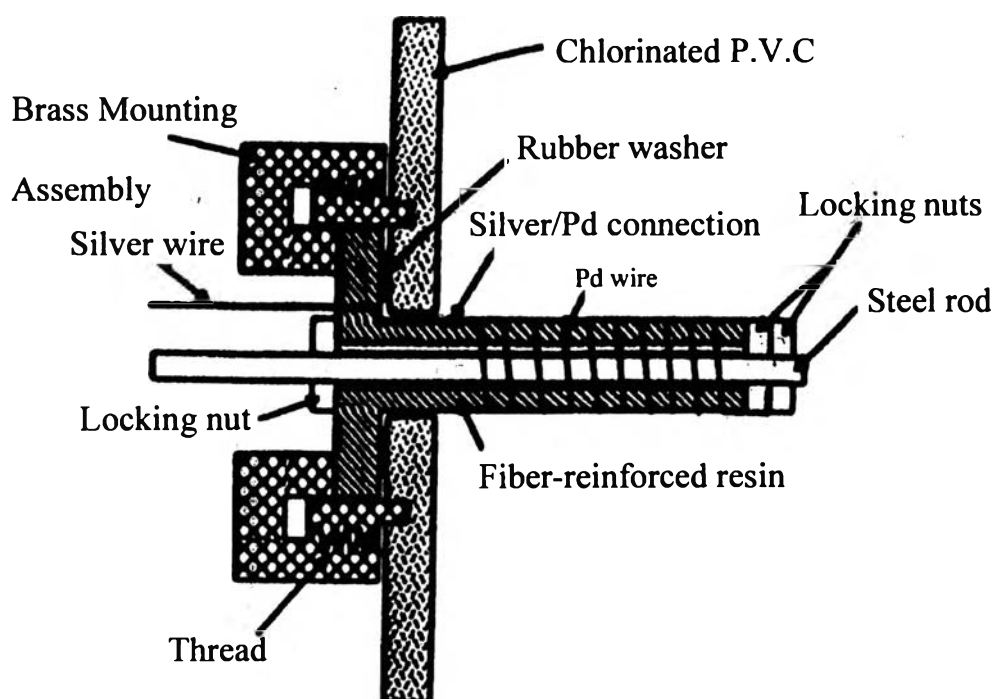

Figure 2.8 Cross section of the Pd/H electrical resistance sensor.

According to Mathiessen's rule (Barrett *et al.*, 1973) states that the presence of solute atoms in a metal cause an increasing in the electrical resistance relative to the pure metal. The electrical resistivity, ρ, of the single phase Pd/H solid solution is given by,

$$\rho = \rho_l + \rho_H$$

(2.10)

Where ρ_l is resistivity due to lattice vibration and ρ_H is resistivity due to the hyrogen atoms. Furthermore, $\rho_l \propto T$ and $\rho_H \propto x_H$ (Nordheim's rule) where x_H is the atom ratio of hydrogen in the palladium. Hence the resistance ratio of a palladium wire, $\overline{R}$ (T, x_H) at temperature T, atom x_H is,

$$\overline{R} \equiv \frac{R(T, x_H)}{R(T, x_H = 0)} = 1.0 + k(T)x_H \qquad (2.11)$$

Where k is linear function of reciprocal absolute temperature.

The results of experiment have been summarized by Morris *et al.* (1995) in the temperature range between 60° to 330°C as:

$$\overline{R}\ (T,\ x_H) = 1.0 + (929.8T^{-1} + 1.1237)\ x_H \qquad (2.12)$$

At T = 80°C, (353K),

$$\overline{R} = 1.0 + 3.758\ x_H \qquad (2.13)$$

The chemical reaction involving hydrogen gas and palladium metal is written as:

$$H_{2(g)} \longleftrightarrow 2H_{(Pd)} \qquad (2.14)$$

The equilibrium constant K_g (T) for reaction (2.14) may be written as:

$$K_g(T) = \frac{a_H^2}{p_{H_2}} = \left(\frac{x_H^2}{p_{H_2}}\right)_{p_{H_2} \to 0} \qquad (2.15)$$

Lasser and Powell (1986) described the relationship between the hydrogen pressure P_{H2} (atm) and the atom ratio x_H accounting for the non-ideality of the metal solution as:

$$\ln\frac{p_{H_2}}{x_H^2} = -\ln K_g(T) - 2\alpha_H(T)x_H \qquad (2.16)$$

With,

$$\left[\frac{\ln K_g(T)}{atm^{-1}}\right] = 2\ln\left[\frac{1 + 1.981\,\exp(-768.0/T)}{[1 - \exp(-800/T)]^3}\right] - \ln\left[4.293 \times 10^{-4} T^{3.5}\right] + \frac{1895.1}{T} \tag{2.17}$$

And

$$\alpha_H = \frac{2265}{T}\left(1 + \frac{445}{T}\right) - 1 \tag{2.18}$$

Equation (2.18) is held over the temperature range 0° to 2000°C.

In the equation (2.15), a_H is activity at the atom ratio x_H in the single phase Pd/H solid solution and p_{H2} is pressure of hydrogen in the equilibrating gas (atm). α_H is empirically determined deviation from ideality; as $x_H \to 0$, $a_H \to x_H$ (Sievert's Law).

It is to be noted that the equilibrium between H_2 and hydrogen atom is established with the pressure of hydrogen in the bulk gas phase only if the gas phase does not contain a component, which is reactive to hydrogen. It is well known that palladium acts as a catalyst to promote chemical reactions involving hydrogen. The present investigation involves mixtures of hydrogen with chlorine and oxygen, which are both chemically reactive toward hydrogen. Hence a usable sensor will require the presence of a coating, which is permeable to hydrogen and impermeable to chlorine and oxygen in order that it shall respond in a reproducible manner to changes of hydrogen concentration in the bulk gas.

The permeation of hydrogen into metals from a gas phase is a complex process involving three steps (Barrer, 1951):

1. Reversible dissociative chemisorption of hydrogen atom on the palladium surface.

2. Reversible dissolution of hydrogen atom on surface in the bulk layers of the palladium.

3. Diffusion of hydrogen atom in the palladium.

The rate-limiting step for the Pd/H system is often the bulk diffusion step 3. However, it is well known that under certain circumstances, step 1 can be rate limiting. In particular Kay *et al.* (1986) found that the rate of absorption of hydrogen by cleaned palladium surface was about 100 times that of an uncleaned surface. The cleaning procedure removed oxygen, sulfur and carbon surface adsorbed atoms.

2.4.2 The Electrochemical Potentiometric Sensor

The electrochemical potentiometric sensor first examined had a conventional concentration cell structure as shown in equation (2.19).

(reference electrode) air, noble metal | proton conductor | noble metal, sample gas (sensing electrode)   (2.19)
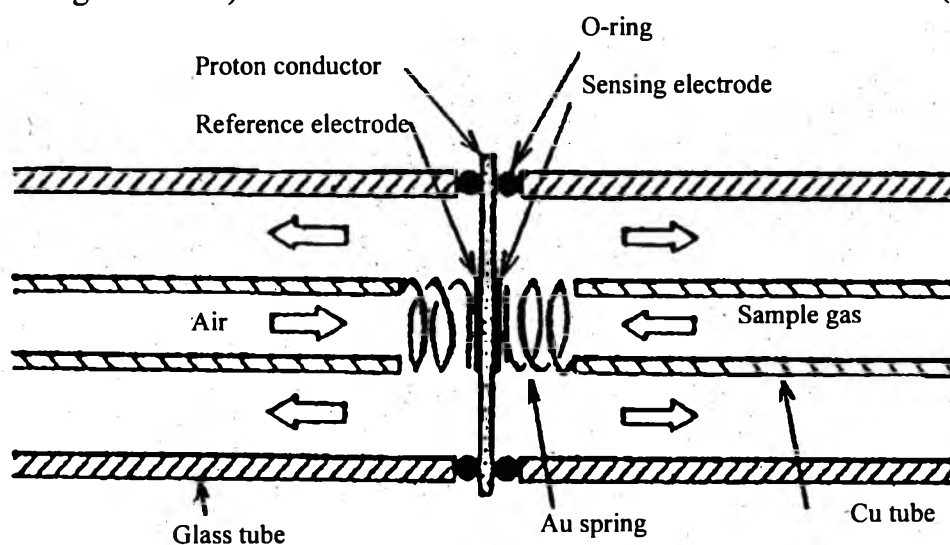

Figure 2.9 The structure of the original potentiometric sensor using proton conductor (Miura *et al.*, 1988).

This type of sensor utilizes the dependency of the electrical potential of platinum on the hydrogen concentration in the equilibrating gas. A cross-section diagram of the potentiometric sensor is shown in Figure 2.10.
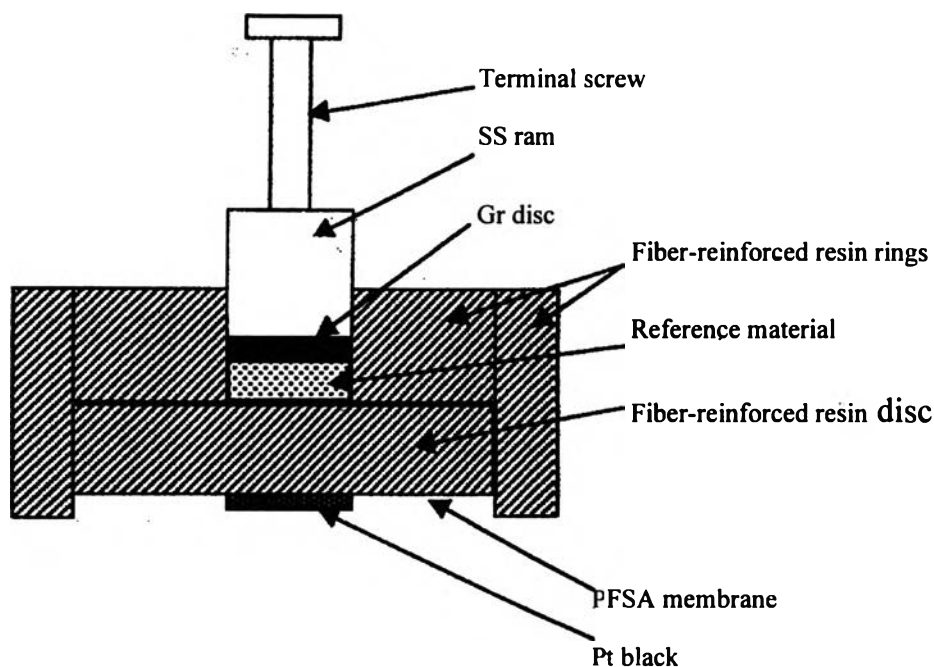
**Figure 2.10** Cross section of the potentiometric sensor.

The polymer electrolyte is a perfluorosulfonic acid (PFSA) membrane conductive to hydrogen ions (Morris, and Sun, 1993). In the phase sequence, Pt represents platinum black applied as slurry to the PFSA membrane surface. The reference mixture is composed of Fe (II) and Fe (III) sulfate hydrates. Gr represents the graphite disc between the stainless steel (SS) ram and the reference mixture. The vertical dashed line represents Fiber-resinforced resin film to prevent access of chlorine and oxygen to the platinum of the sensing electrode. The potentiometric hydrogen sensor may be represented schematically as the sequence of phases.

$$Cl_2, H_2, air, H_2O_{(g)} \quad Pt \mid PFSA \mid reference\ mixture, Gr, stainless\ steel \quad (2.20)$$

$$\text{I} \qquad \text{II}$$

where g indicates gas phase.

The equilibria at the interfaces I and II of the sensor are postulated to be:

I: Hydrogen gas (H₂),

$$H_3O^+ \text{ (PFSA)} + e^-_{(Pt)} \leftrightarrow \frac{1}{2} H_2 \text{ (g)} + H_2O \text{ (PFSA)} \qquad (2.21)$$
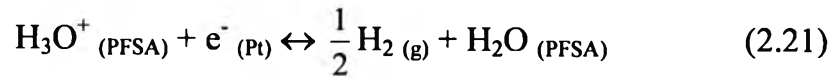
II: Reference mixture,

$$Fe^{3+}_{(s)} + e^-_{(c)} \leftrightarrow Fe^{2+}_{(s)} \qquad (2.22)$$

Where s indicates solid phase and c indicates carbon. The half-cell potentials are given by Nernst equations:

$$E_1 = E_1^0 - \frac{RT}{F} \ln \frac{p_{H_2}^{1/2} a_{H_2O}}{a_{H_3O^+}} \qquad (2.23)$$

$$E_{II} = E_{II}^0 - \frac{RT}{F} \ln \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \qquad (2.24)$$

Where E_I^0 and E_{II}^0 are constants, p_{H2} is the ratio of the H_2 pressure to the standard atmosphere, a is activity of the indicated species, R is gas constant, T is absolute temperature and F is Faraday's constant. The reference mixture comprises the pure hydrated sulfates. Hence, the ionic activities are constant and since the hydrogen ion concentration in the polymer electrolyte is fixed, $a_{H_3O^+}$ is constant. The activity of water in the polymer electrolyte is fixed by the saturation of the Hydrogen mixture in the water.

The voltage developed by the sensor (E) is,

$$E = E_{II} - E_1 = E^0 + \frac{RT}{2F} \ln p_{H_2} \qquad (2.25)$$

Where E^0 is constant ~ 0.65 V.

2.4.3 The Electrochemical Amperometric Sensor

a) Basic Principle of Electrochemical Amperometric Sensor in Present Work

The information from an amperometric sensor is obtained from the current-concentration relationship. The chemical transformation which takes place at the electrodes during the passage of current is governed by Faraday's law.

$$\text{mole} = Q/nF \qquad\qquad (2.26)$$

where:

M = net chemical changes

Q_C = total charge passed through the electrode during the experiment

z = number of moles of electrons involved in electrochemical reaction

F = Faraday's constant.

Such changes can have a cumulative effect on the measurement, particularly when the products of the electrochemical reaction are not removed sufficiently rapidly from the interface. A schematic diagram of an electrochemical amperometric sensor for monitoring hydrogen concentration used in the present work is shown in Figure 2.11.
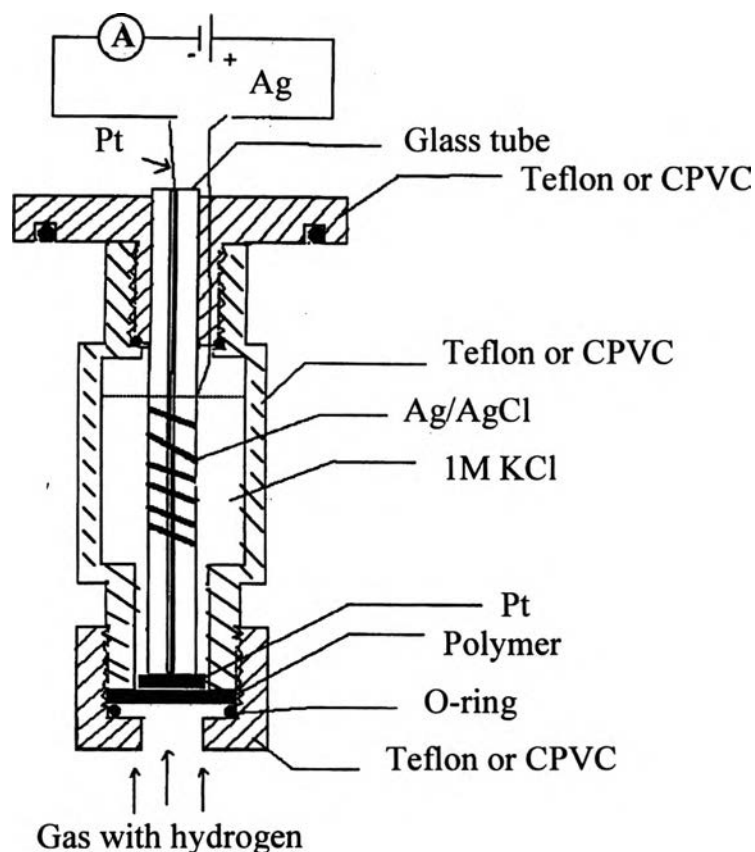

Figure 2.11 Schematic diagram of an amperometric sensor for monitoring hydrogen concentration.

An amperometric sensor is basically identical to the Clark sensor developed for the determination of oxygen in blood (Clark, 1956). The instrument has been developed by Orbisphere for monitoring hydrogen or oxygen in non-reactive mixtures. The principal of operation described by Kalvoda (1987) is well known. The diffusion-limited current I measured in the external circuit is,

$$I = \frac{zFAP_{H_2}}{l} p_{H_2} \qquad (2.27)$$

where:

z = number of moles of electrons involved in electrochemical reaction

F = Faraday's constant
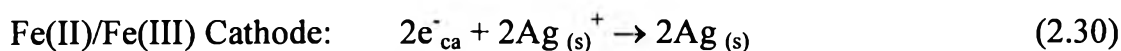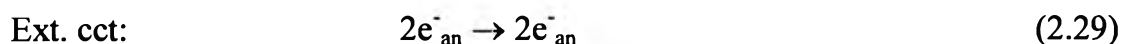
A = cross sectional area to flow

ϕ_{H2} = permeability of hydrogen in membrane material

L = thickness of material

p_{H2} = pressure of hydrogen in gas.

A cross sectional diagram of the sensor is shown in Figure 2.11.

The reactions occur in the sensor are,

Pt Anode:	$H_{2\,(aq)} \rightarrow 2H^+ + 2e^-_{an}$	(2.28)
Ext. cct:	$2e^-_{an} \rightarrow 2e^-_{an}$	(2.29)
Fe(II)/Fe(III) Cathode:	$2e^-_{ca} + 2Ag_{(s)}{}^+ \rightarrow 2Ag_{(s)}$	(2.30)
Total Reaction:	$H_{2\,(aq)} + 2Ag_{(s)}{}^+ \rightarrow 2H^+ + 2Ag_{(s)}$	(2.31)

An example of the response signal from the amperometric sensor in hydrogen, dry chlorine and dry argon mixtures at ambient temperature are presented in Figure 2.12.
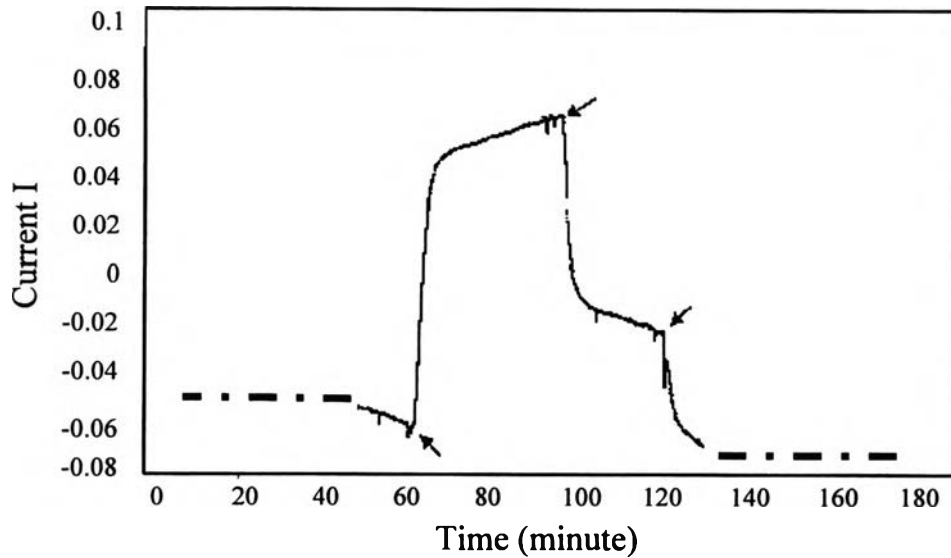
Figure 2.12 An example of the response signal for electrochemical amperometric sensor for H_2 in dry gas mixtures with dry chlorine.

Arrows in Figure 2.12 indicate the point in time at which the gas atmosphere was changed to another value. Clearly the sensor is responding to the change of hydrogen concentration.

The advantage of this sensor relative to the Pd/H electrical resistance is the relative rapidity of response to a change of hydrogen pressure. It follows from the fact that the detection principle is not dependent upon the absorption of hydrogen. However it is believed that the amperometric sensor may require periodic recalibration or regeneration of the platinum anode due to the progressive loss of the electrochemical reactivity.