

# Hydrogen Solubility in Liquid and Solid Pure Aluminum—Critical Review of Measurement Methodologies and Reported Values

Prince N. Anyalebechi

School of Engineering, Grand Valley State University, Grand Rapids, MI, USA

Email: anyalebp@gvsu.edu

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## Abstract

Reliable information on the solubility of hydrogen in aluminum and its alloys is critical to the effort of the aluminum industry to control and ameliorate the usually deleterious effects of hydrogen on the properties and performance of pure aluminum and aluminum alloy products. Unfortunately, there is a significant disparity between published values of hydrogen solubility in pure aluminum and aluminum alloys. This is because the measurement of the extremely low soluble hydrogen concentration in aluminum and its alloys is experimentally difficult. Also, the reproducibility, accuracy, and reliability of the hydrogen solubility values are very sensitive to the measurement techniques, test conditions, chemical composition, and state of the aluminum sample. Thus, no serious discussion of the reliability of reported values of hydrogen solubility in aluminum and its alloys can be undertaken without a critical assessment of the fundamental principles of the experimental techniques used in the determination of the reported values. In this article, a critical review of the fundamental principles of the experimental techniques used in the measurement of hydrogen solubility in liquid and solid pure aluminum and aluminum alloys is presented. In addition, the reliability and possible accuracy of reported values of hydrogen solubility in solid and liquid pure aluminum are critically assessed. Empirical equations for calculating hydrogen solubility in liquid and solid pure aluminum as a function of temperature and pressure, derived from the most reliable sets of data are recommended. At 101.3 kPa (1 atm.) hydrogen partial pressure, the most reliable values of hydrogen solubility at the melting point (833 K) of pure aluminum are 0.71 cm<sup>3</sup>/100g (*i.e.*,  $6.32 \times 10^{-5}$  wt.% H) and 0.043 cm<sup>3</sup>/100g (*i.e.*,  $3.81 \times 10^{-6}$  wt.% H), in the liquid and solid state, respectively. So, the partition coefficient of hydrogen in pure aluminum is 0.061.

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## Keywords

Hydrogen Solubility, Sieverts' Isotherm, Van't Hoff Isobaric Relationship, Pure Aluminum

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## 1. Introduction

The aluminum industry spends a significant portion of its financial resources (which amounts to millions of dollars a year) and manpower to ensure the exclusion of hydrogen from its products, from the beginning to the end of the production and manufacturing cycles. The deleterious effects of hydrogen on the properties of aluminum and its alloys are very well documented in the technical literature [1] [2] [3] [4] [5]. Some of the defects whose presence is directly attributable to undue concentration of hydrogen in aluminum include gas-induced porosity, blisters, hydrogen embrittlement, stress corrosion cracking, and associated poor tensile strength and fatigue properties [1] [2] [3] [4] [5]. Control and amelioration of these deleterious effects require knowledge of the solubility of hydrogen in the liquid and solid states of aluminum and its alloys. Reliable hydrogen solubility limit data are required for: 1) mathematical modeling of melt treatment (degassing) processes; 2) explaining why lithium-containing aluminum alloys such as 2090, 2091, 2195, etc. are much more difficult to degas than other aluminum alloys but are less prone to porosity formation [6]; 3) modeling and simulation of the formation and evolution of hydrogen-induced gas porosity during solidification of cast, welded, and additive manufactured aluminum alloy products [7] [8] [9] [10] [11]; 4) assessing the propensities of different aluminum alloys to hydrogen-induced defects such as gas porosity [12] [13], blisters [14], bright flakes in forgings, and hydrogen embrittlement; 5) developing and explaining the mechanisms for the formation of hydrogen-induced defects; 6) alleviation of formation and/or exacerbation of hydrogen-induced defects during thermal treatments such as as-cast ingot homogenization, preheat prior to deformation, annealing and age hardening heat treatments [15]; 7) for comparison with prevailing hydrogen contents of aluminum and aluminum alloy products in production, 8) characterization of the nature of hydrogen solutions in aluminum and its alloys, and 9) calibration of instruments used to measure hydrogen concentration in aluminum alloy melts such as Telegas, ALSCAN, Northop, ALSPEK, Hycal, and CHAPEL [16]. In fact, hydrogen solubility limit data are required for the development of the theory of solutions of hydrogen in metallic systems and understanding of the mechanisms for the formation of gas-induced defects. For example, prior to 1947, the greater predisposition of aluminum and its alloys to hydrogen-induced defects than other metals such as Mg, Cu, Zn, Ni, Fe, and their alloys could not be properly explained. This became possible only after Ransley and Neufeld [17] reported reliable data on the hydrogen solubility in both liquid and solid pure aluminum.

However, despite the afore-mentioned practical importance of the knowledge of hydrogen solubility in aluminum and its alloys, reliable data on the solubility of hydrogen in aluminum and aluminum alloys are limited. This is because the solubility of hydrogen in both the liquid and solid aluminum and its alloys are relatively low and are therefore difficult to measure accurately. This is particularly the case with the solubility of hydrogen in the solid state of pure aluminum, where, by the inherent nature of the measurement techniques and the ubiquitous nature of hydrogen, it is difficult to discern between hydrogen from the sample and that from the surrounding equipment and contaminants. Also, the melting temperatures of aluminum and its alloys are relatively high, compounding the difficulty in reliable determination of the solubility of hydrogen in aluminum and its alloys. Consequently, there is a significant disparity in the reported values of hydrogen solubility in liquid and solid aluminum and its alloys. This, unfortunately, has resulted in significant discrepancies in the results of mathematical models and calculations on melt treatment processes and porosity formation in aluminum products.

The reliability of the reported solubility of hydrogen in aluminum and aluminum alloys has been cursorily reviewed in several articles [1] [2] [18]-[29]. The majority of the discussions involved partial collation and a cursory examination of reported values of hydrogen solubility in primarily liquid pure aluminum with little or no critical examination or discussion of the measurement methodologies [1] [2] [18] [19] [20] [21] [25] [27] [28]. None of the reviews has addressed the solubility of hydrogen in solid aluminum and aluminum alloys. Others have involved some limited discussion of some of the techniques used to determine the solubility of hydrogen in liquid pure aluminum and aluminum alloys [21] [22] [23] [24] [27]. The most notable reviews to date are those by this author [22] [23] [24] and Harvey and Chartrand [26]. However, Harvey and Chartrand's [26] review was limited only to reported values of hydrogen solubility in liquid pure aluminum obtained with only the Sieverts' method. Notably, some of the discussions and cursory reviews were by authors who attempted to justify the reliability of the results of their modeling calculations [18] [25] [26]. Some discussions were limited to only the latest published hydrogen solubility values. Unfortunately, the majority of the authors who have attempted to discuss the reliability of reported hydrogen solubility in pure aluminum and its alloys have never experimentally studied or measured hydrogen solubility [18] [19] [20] [21] [25] [27] [28]. It has sometimes led to technically incorrect assertions and erroneous recommendations on what constitutes the correct values of solubility of hydrogen in liquid and solid pure aluminum and aluminum alloys [25] [28]. This is exemplified by Tiryakioğlu [28] who recently claimed to have arrived at the "most reliable values" of hydrogen solubility in liquid pure aluminum by supposedly reanalyzing some of the reported values. As discussed later, this claim is erroneous because it is based on a technically flawed premise that reveals a lack of understanding of how hydrogen solubility values are experimentally determined.

It is noteworthy that none of the previous discussions or aforementioned cursory reviews critically examined the effects of the fundamental principles of measurement techniques, test conditions, sample conditions, and chemical composition on the reliability of hydrogen solubility results. Thus, the primary objective of the first part of this article is to critically examine the principles of the experimental techniques and methodologies used in determining the solubility of hydrogen in liquid and solid aluminum and its alloys. Also, with the exception of this author's previous review [24] more than twenty-three years ago, there is no critical assessment or review of the published values of the hydrogen solubility of hydrogen in solid pure aluminum and its alloys. So, in the second part of this article, the reliability of the reported values of hydrogen solubility in liquid and solid pure aluminum is critically assessed. They are assessed based on five criteria, namely: 1) reliability of experimental technique and methodology; 2) potential sources of error in the experimental conditions, 3) agreement with theoretically predicted and well established empirical relationships, such as the Sieverts' isothermic and Van't Hoff isobaric relationships; 4) self-consistency of results reported by the same investigators; and 5) comparison of results with hydrogen activities in equilibrium with arbitrary hydrogen concentrations. Deference is given to studies conducted over a wider range of temperatures and pressures, and to investigators that reported results of more than one test per experimental condition as opposed to single average values. An unfortunate notable feature of most published experimental studies on the hydrogen solubility of hydrogen in aluminum and its alloys is that the reported values are usually insufficient for statistical analysis. Even worse is the fact that replicate hydrogen solubility values are not reported by the majority of the investigators. This makes it difficult to assess the reproducibility of the reported experimental results. The overarching goals of this study are to: a) provide the technical basis for future evaluation of the reliability of reported values of hydrogen solubility in both liquid and solid states of aluminum and its alloys, b) to identify the most reliable sets of published studies of hydrogen solubility in liquid and solid pure aluminum, and c) develop empirical equations for calculating the most reliable values of solubility of hydrogen in liquid and solid pure aluminum.

## 2. Theoretical Considerations for Hydrogen Solution in Aluminum

The solubility of a gas such as hydrogen, nitrogen, and oxygen in metal, is the quantity of the gas in a state of thermodynamic equilibrium with the metal at a specific temperature and unique partial pressure of the gas. It can also be defined as the equilibrium between a metal and the gas-induced intermediate phase such as an oxide, nitride, or hydride at a specific temperature and a unique partial pressure of the gas. So, hydrogen solubility is the concentration of hydrogen in a liquid, semi-solid, or solid metal that is in equilibrium with hydrogen in the surrounding atmosphere at a given temperature and hydrogen partial pressure.

It is therefore the maximum amount of hydrogen that can dissolve in a given state of metal of a given chemical composition under equilibrium conditions at a specific temperature and hydrogen partial pressure.

On the basis of the effects of temperature on the solubility of hydrogen, metals can be separated into two groups. In the first group, the solubility of hydrogen is very small and increases with an increase in temperature. These metals are referred to as endothermic occluders of hydrogen. The amount of hydrogen absorbed increases with increasing temperature because endothermic absorption occurs with the absorption of heat. Aluminum and its alloys are endothermic occluders of hydrogen [17] [22] [24]. In the second group, the solubility of hydrogen is much greater and at a given pressure, decreases with an increase in temperature. These metals are referred to as exothermic occluders of hydrogen. They usually form hydrides, so the concentration of dissolved hydrogen is limited to that in equilibrium with the hydride at the appropriate temperature and pressure. The solubility of hydrogen in exothermic occluders decreases with increase in temperature because exothermic absorption occurs with the liberation of heat.

Dissolution of atomic hydrogen in liquid and solid aluminum and its alloys follows Sieverts' law. That is, it is atomistic rather than molecular in nature. It involves: 1) dissociation of the diatomic hydrogen gas into the atomic form at the boundary layer; 2) dissolution of the atomic hydrogen in the melt boundary layer; and 3) transport of hydrogen to the bulk of the melt or solid metal by diffusion. This process in liquid and solid pure aluminum is described by the reaction:



The underlined symbol  $\bar{H}$  denotes hydrogen dissolved in liquid or solid pure aluminum. It is assumed that: 1) hydrogen solution in solid pure aluminum is interstitial in nature and that the hydrogen atoms are accommodated as non-interacting atoms all occupying equivalent interstitial sites, and 2) the solution of hydrogen in both liquid and solid aluminum is very dilute so that Henry's law applies. According to Henry's law, at a constant temperature, the activity of the dissolved gas in a very dilute solution is proportional to its concentration,  $[H]$ , *i.e.*:

$$a_H = K_H [H]^2 \quad (2)$$

where  $a_H$  = activity of the dissolved hydrogen in a very dilute solution, and  $K_H$  = equilibrium constant.

If the ideal gas laws are assumed for the hydrogen gas phase and the standard states selected are: 1) the infinitely dilute atomic fraction for the solute, and 2) the pure element at 101,325 Pa, for the gas phase, the equilibrium constant is given by:

$$K_H = \frac{a_H^2}{a_{H_2}} = \frac{N_H^2 \cdot P_{H_2}^o}{P_H} \quad (3)$$

where  $K_H$  = equilibrium constant,  $a_H$  = activity of the dissolved hydrogen in very dilute solution referred to the atomic fraction at infinite dilution as the standard

state,  $a_{H_2}$  = activity of the hydrogen referred to pure hydrogen at standard pressure,  $p_H^o$ , and  $N_H$  = atomic fraction of hydrogen in equilibrium with an arbitrary gas pressure  $p_H$ .

If Equation (3) is rearranged to express the proportionality between the solute concentration and pressure of hydrogen, then

$$\frac{N_H}{N_H^o} = K_H \left( \frac{p_{H_2}}{p_{H_2}^o} \right)^{0.5} \quad (4)$$

where  $N_H^o$  = atomic fraction of solute in equilibrium with the standard pressure,  $p_H^o$ .

Equation (4) is known as Sieverts' law. From the equation

$$K_H = \left( \frac{N_H}{N_H^o} \right)^{0.5} \cdot \left( \frac{p_{H_2}^o}{p_{H_2}} \right) \quad (5)$$

Hence,

$$\ln K_H = 2 \ln \left( \frac{N_H}{N_H^o} \right) + \ln \left( \frac{p_{H_2}^o}{p_{H_2}} \right) \quad (6)$$

Differentiating Equation (6) with respect to temperature at constant pressure gives

$$\frac{\partial}{\partial T} (\ln K_H)_p = 2 \frac{\partial}{\partial T} \ln \left( \frac{N_H}{N_H^o} \right)_p + \frac{\partial}{\partial T} \ln \left( \frac{p_{H_2}^o}{p_{H_2}} \right)_p \quad (7)$$

The relationship between the free energy change,  $\Delta G^o$ , of a reaction and the equilibrium constant is given by the Van't Hoff isotherm:

$$\Delta G^o = -RT \ln K_H \quad (8)$$

Rearranging and differentiating Equation (8) gives

$$\frac{\partial}{\partial T} (\ln K_H)_p = - \frac{\partial}{\partial T} \left( \frac{\Delta G^o}{RT} \right)_p \quad (9)$$

Using the Gibbs-Helmholtz equation,

$$\frac{\partial}{\partial T} \left( \frac{\Delta G^o}{T} \right)_p = - \frac{\Delta H^o}{T^2} \quad (10)$$

an equation may be derived which expresses the variation of the equilibrium constant with temperature at constant pressure,

$$\frac{\partial}{\partial T} (\ln K_H)_p = - \frac{\Delta H^o}{RT^2} \quad (11)$$

Combining Equations (7) and (11) gives

$$\frac{\partial}{\partial T} (\ln K_H)_p = 2 \frac{\partial}{\partial T} \ln \left( \frac{N_H}{N_H^o} \right)_p = - \frac{\Delta H^o}{RT^2} \quad (12)$$

This means that application of Van't Hoff isobar gives the variation of the equilibrium solute concentration as a function of temperature, and it is determined by the sign and magnitude of the standard enthalpy of solution,  $\Delta H^\circ$  for the reaction. For a small or restricted range of temperature, where the change in heat capacity is negligible, it is possible to disregard the temperature dependence of enthalpy of solution so that integration of Equation (12) yields:

$$\ln \frac{N_H}{N_H^\circ} = -\frac{\Delta H^\circ}{2RT} + \text{constant} \quad (13)$$

Combining Equations (6) and (13) yields the relationship between hydrogen solubility, gas pressure, and temperature:

$$\ln \left( \frac{N_H}{N_H^\circ} \right) - 0.5 \ln \left( \frac{P_{H_2}}{P_{H_2}^\circ} \right) = -\frac{\Delta H^\circ}{2RT} + \text{constant} \quad (14)$$

A more fundamental derivation of Equation (14) characterizes the integration constant:

$$\ln \left( \frac{N_H}{N_H^\circ} \right) - 0.5 \ln \left( \frac{P_{H_2}}{P_{H_2}^\circ} \right) = -\frac{\Delta G^\circ}{2RT} = -\frac{\Delta H^\circ}{2RT} + \frac{\Delta S^\circ}{2R} \quad (15)$$

where  $\Delta G^\circ$  = Gibbs free energy change for the solution of one diatomic hydrogen,  $\Delta S^\circ$  = entropy of solution, and  $\Delta H^\circ$  = heat of solution.

It is a long-established practice to express the concentration of dissolved hydrogen in terms of the unit defined as  $\text{cm}^3$  of hydrogen per 100 g of metal measured at 101,325 Pa (1 atm) gas pressure and 273 K. Thus, for concentration measured in this unit it is often convenient to rewrite Equation (15) in this logarithmic form:

$$\log_{10} \left( \frac{S_H}{S_H^\circ} \right) - 0.5 \log_{10} \left( \frac{P_{H_2}}{P_{H_2}^\circ} \right) = -\frac{\Delta H^\circ}{4.606R} \left( \frac{1}{T} \right) + \frac{\Delta S^\circ}{4.606R} \quad (16)$$

where  $S_H$  = the solubility of hydrogen in  $\text{cm}^3/100\text{g}$  of metal,  $S_H^\circ$  = the standard value of hydrogen solubility equal to  $1 \text{ cm}^3$  of diatomic hydrogen per 100 g of metal measured at 273 K and 101,325 Pa gas pressure,  $p_H$  = hydrogen pressure surrounding the metal,  $p_H^\circ$  = the standard value of pressure equal to 101,325 Pa,  $T$  = temperature in K,  $\Delta S^\circ$  = entropy of solution, and  $\Delta H^\circ$  = heat of solution.

It is noteworthy that based on the theoretical assumption implicit in the Sieverts' law, the solubility of hydrogen in a metal is zero at zero hydrogen pressure, thus Equation (16) can be rewritten simply as:

$$\log_{10} S_H, \text{cm}^3/100 \text{ g} = -\frac{\Delta H^\circ}{4.606R} \left( \frac{1}{T} \right) + \frac{\Delta S^\circ}{4.606R} + 0.5 \log_{10} \left( \frac{P_{H_2}}{P_{H_2}^\circ} \right) \quad (17)$$

The values of hydrogen solubility can also be expressed in terms of mass of hydrogen absorbed in a given mass of the metal as wt.% hydrogen measured at 101,325 Pa (one atmosphere) gas pressure and 273 K. So, for hydrogen solubility

measured in this unit Equation (15) can also be written in the form:

$$\log_{10} (\text{wt. \% } \underline{H})_{\text{in Al-H}} = -\frac{\Delta H^{\circ}}{4.606R} \left( \frac{1}{T} \right) + \frac{\Delta S^{\circ}}{4.606R} + 0.5 \log_{10} \left( \frac{P_{H_2}}{P_{H_2}^{\circ}} \right) \quad (18)$$

A general form of Equations (17) and (18) is:

$$\log_{10} S_H = -\frac{A}{T} + B + 0.5 \log_{10} \left( \frac{P_{H_2}}{P_{H_2}^{\circ}} \right) \quad (19)$$

In principle, standard enthalpy and entropy of hydrogen solution in metals can be evaluated from experimental results fitted to either Equation (17) or (18). Although, the values of standard enthalpy of the solution obtained are subject to significant errors from any slight variation or small change in the gradient of the graph of the logarithm of hydrogen solubility against the reciprocal of temperature. If the enthalpy of solution is positive, the hydrogen solubility at constant pressure increases with an increase in temperature, whereas for negative enthalpy of solution, the solubility decreases with an increase in temperature. A positive enthalpy of the solution indicates an endothermic hydrogen solution, whereas a negative enthalpy of the solution is an indication of an exothermic hydrogen solution.

### Units of Measurement of Hydrogen in Aluminum and Its Alloys

The concentration of hydrogen absorbed by metals can be described by a variety of units. In general, the units can be classified into about six main groups, in terms of:

1) Volume of hydrogen (in  $\text{cm}^3$ ,  $\text{m}^3$ , or mL) at 273 K and 101,325 Pa per a given weight (such as g, 100 g, or 1 kg) of metal. This includes the non-S.I., but commonly used units:  $\text{cm}^3/100\text{g of Al}$ ,  $\text{cm}^3/\text{g of Al}$ ,  $\text{mL}/100\text{g of Al}$ , and  $\text{m}^3/\text{kg of Al}$ . This unit of measurement of the hydrogen content in aluminum and its alloys is the most commonly used in the aluminum industry. Its popularity originates from the determination of the hydrogen content in aluminum and its alloys by the measurement of the volume of hydrogen absorbed by or evolved from a given mass of the metal sample in a vacuum system. The actual measurements of absorption (or adsorption) of hydrogen phenomena usually involve observing the pressure changes, on absorption or degassing, in an apparatus of known volume. The observed pressure change is simply converted into the volume of the gas at 273 K and 101,325 Pa using the general gas equation. Like the other volume units, this is a physical picture of the amount of gas absorbed or contained in a given mass of the metal. It is noteworthy that prior to 1982, a temperature of 273.15 K and absolute pressure of 101,325 Pa (1 atm) were defined as the standard temperature and pressure (STP), respectively.

2) Volume of hydrogen (in  $\text{cm}^3$ ,  $\text{m}^3$ , or mL) at 273 K and 101,325 Pa per volume of metal (also in  $\text{cm}^3$ ,  $\text{m}^3$ , or mL); this is sometimes referred to as the "relative volume", the units are:  $\text{cm}^3/\text{cm}^3 \text{ of Al}$ ,  $\text{m}^3/\text{m}^3 \text{ of Al}$ , or  $\text{mL}/\text{mL of Al}$ .

3) Weight of hydrogen (in mg, g, or kg) absorbed in a given weight of metal (such as 1 g,  $10^3$  g, or  $10^6$  g); when expressed as 1 g/ $10^6$ g of Al (or 1 mg/ $10^3$ g of Al), the unit is referred to as “parts per million by weight,” that is, *ppm*. The notation *ppm* has been universally used to represent parts per million by weight for more than seventy years despite the recent suggestion by Werner *et al.* [29] that it is unclear. They have suggested the use of the less well known *wppm* or unknown *ppmw* to represent the unit. When the weight of hydrogen is expressed in terms of percentage by weight of the metal, the unit of concentration is wt.%.

4) Number of atoms of hydrogen per a given number of atoms of metal; this is referred to as atomic fraction. When expressed as 1 atom of hydrogen per  $10^6$  atoms of Al, the unit is referred to as “atomic parts per million,” that is, *appm*. When the number of atoms of hydrogen is expressed in terms of the percentage of atoms of Al, the unit of concentration becomes at.%.

5) Volume of hydrogen (in  $\text{dm}^3$ ,  $\text{cm}^3$ , or  $\text{m}^3$ ) at 273 K and 101.33 kPa absorbed onto a given surface area (in  $\text{cm}^2$ ) of the metal surface. This best describes gas adsorption which is a surface-controlled process rather than a volume process. When expressed as per  $1 \text{ cm}^2$  of Al surface, the unit is  $\text{cm}^3/\text{cm}^2$  of Al surface or  $\text{m}^3/\text{m}^2$  of Al.

6) Number of moles of hydrogen per mole of aluminum; this is referred to as *mole fraction*.

The relationship between the most common unit,  $\text{cm}^3/100\text{g Al}$  and the other units can be derived from first principles; for example:

a)  $1 \text{ cm}^3$  of hydrogen/100g of Al = 0.8922 ppm (*i.e.*, 0.892 g H/ $10^6$ g Al), *i.e.*,

$$\text{ppm} = \left( \frac{1 \text{ cm}^3 \text{ H}_2}{100 \text{ g Al}} \right) \times \left( \frac{1 \text{ mol H}_2}{22400 \text{ cm}^3 \text{ H}_2} \right) \times \left( \frac{2 \text{ g H}_2}{1 \text{ mol H}_2} \right) \times \left( \frac{10^6 \text{ g Al}}{1} \right) \quad (20)$$

b)  $1 \text{ cm}^3$  of hydrogen/100g of Al =  $8.929 \times 10^{-5}$  wt.%, *i.e.*,

$$\text{wt.\%} = \left( \frac{1 \text{ cm}^3 \text{ H}_2}{100 \text{ g Al}} \right) \times \left( \frac{1 \text{ mol H}_2}{22400 \text{ cm}^3 \text{ H}_2} \right) \times \left( \frac{2 \text{ g H}_2}{1 \text{ mol H}_2} \right) \times 100 \quad (21)$$

c)  $1 \text{ cm}^3$  of hydrogen/100g of Al =  $2.409 \times 10^{-11}$  appm, *i.e.*,

$$\text{appm} = \left( \frac{1 \text{ cm}^3 \text{ H}_2}{100 \text{ g Al}} \right) \times \left( \frac{1 \text{ mol H}_2}{22400 \text{ cm}^3 \text{ H}_2} \right) \times \left( \frac{2 \text{ g H}_2}{1 \text{ mol H}_2} \right) \times \left( \frac{26.98 \text{ g Al}}{1 \text{ atom Al}} \right) \times \left( \frac{1}{10^6 \text{ atoms Al}} \right) \quad (22)$$

d)  $1 \text{ cm}^3$  of hydrogen/100g of Al =  $2.409 \times 10^{-3}$  at.%, *i.e.*,

$$\text{at.\%} = \left( \frac{1 \text{ cm}^3 \text{ H}_2}{100 \text{ g Al}} \right) \times \left( \frac{1 \text{ mol H}_2}{22400 \text{ cm}^3 \text{ H}_2} \right) \times \left( \frac{2 \text{ g H}_2}{1 \text{ mol H}_2} \right) \times \left( \frac{26.98 \text{ g Al}}{1 \text{ atom Al}} \right) \times 100 \quad (23)$$

The most commonly used units in describing the concentration of hydrogen in aluminum such as solubility limits and gas contents are  $\text{cm}^3/100\text{g Al}$  (or  $\text{mL}/100\text{g Al}$ ), ppm, wt.%, appm, and at.%. However,  $\text{cm}^3/100\text{g Al}$ , the most popular unit used in the aluminum industry, is not a recognized unit in the SI system. Also, it is not rational to express a quantity of atomic solute in terms of the volume occupied by its gaseous diatomic equivalent, especially when the

temperature and pressure at which the volume of the diatomic gas is to be measured are not explicitly given.

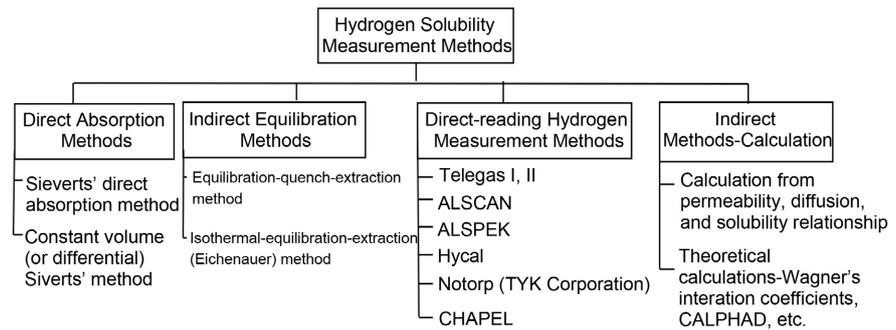
However, since hydrogen is virtually an ideal gas at the temperatures of interest, the unit  $\text{cm}^3/100\text{g of Al}$  can be assimilated into the SI unit system by equating it to unit *molality* for the atomic solute by selecting a standard value of molality,  $m^\circ$ , equal to  $8.93 \times 10^{-4}$  mol/kg [3]. This is the molality of a solution of atomic hydrogen formed when  $1 \text{ cm}^3$  of diatomic hydrogen measured at 273 K and 101.325 kPa (1 atm), dissolves in 100 g of metal.

As a matter of convenience, any of the above units may be used for the comparison of hydrogen absorption data in any one metal such as aluminum (and its alloys) under a variety of conditions (temperature, pressure, etc.). However, solubility limits and the effects of hydrogen on the physical and mechanical properties of metals, depend, to a large extent, on the relative concentration of hydrogen atoms within the metal. Thus, the only means of directly comparing the behavior of hydrogen within two different metals or metal alloys is by the expression of the hydrogen content in terms of the atomic percentage (at.%) of hydrogen in the various metals.

### 3. Hydrogen Solubility Measurement Methods

The disparities in reported hydrogen solubility limits in aluminum and its alloys are largely due to the different methods used by different investigators. For a given method, the reliability and accuracy of reported hydrogen solubility limits depend on several factors. These include: 1) methodology, 2) physical state of the sample (*i.e.*, liquid, semi-solid, or solid), 3) sample size, 4) alloy chemistry, 5) gas purity, 6) precision of the measurement of the amount of hydrogen absorbed, and 7) proper control of the experimental conditions (*i.e.*, sample temperature and gas pressure). It is, therefore imperative that before the use of published sets of values of hydrogen solubility in aluminum and its alloys in important modeling calculations and in critical production decision making, one must critically assess how the values were obtained. As will become apparent later, there are sources of error associated with every method; it is the variable ability to minimize and/or eliminate these errors that leads to the different results by different investigators.

Taxonomy of experimental and non-experimental methods used in the last ninety-nine years to determine the solubility of hydrogen in aluminum and its alloys is shown in **Figure 1**. The classical method for determining the solubility of hydrogen or gasses in metals is to measure the mass or volume of gas absorbed by a known mass of metal equilibrated (*i.e.*, saturated) with the gas phase at prescribed temperatures and pressures. There are four variations of this method, namely, the: 1) Sieverts direct absorption method [17] [30]-[46]; 2) constant volume (or differential) Sieverts' method [47], 3) equilibration-quench-extraction technique [17] [45] [48] [49] [50] [51] [52], and 4) isothermal equilibration-extraction (or Eichenauer's) technique [53] [54] [55] [56] [57].



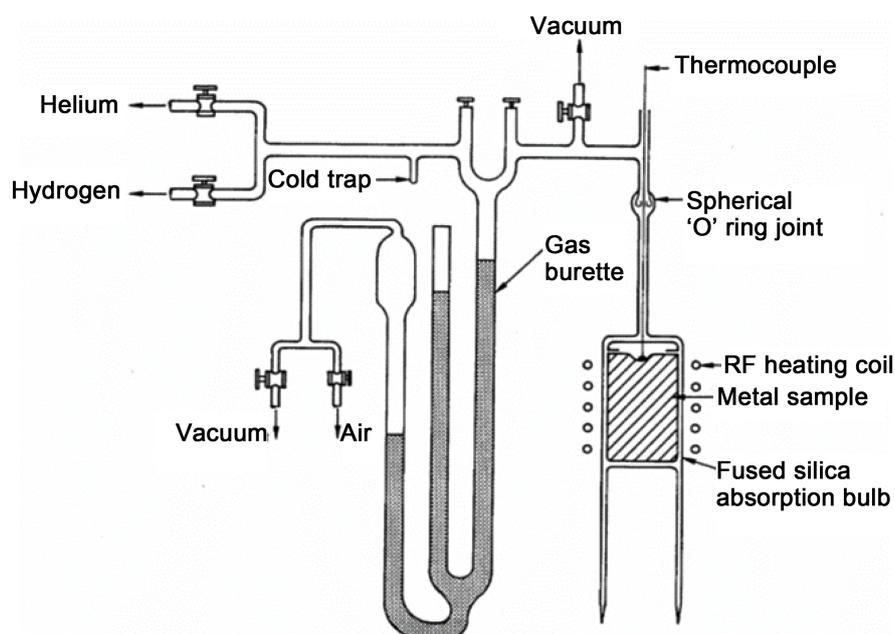
**Figure 1.** Taxonomy of experimental and non-experimental methods used to determine the solubility of hydrogen in aluminum and its alloys.

Another approach that can be used to determine the solubility of hydrogen in aluminum and its alloys involves the measurement of the activity of hydrogen in the gas phase in equilibrium with arbitrary hydrogen contents [58] [59] [60]. This is accomplished in effect when values for hydrogen contents in molten aluminum are determined using any one of the following instruments: 1) Telegas I or II™ instruments [16] [61] [62]; 2) ALSCAN™ instrument [63]; 3) the continuous hydrogen analysis pressure evaluation in liquids (CHAPEL) technique [60] [64] [65]; and 4) the proton-conducting solid electrolyte hydrogen analyzers such as Notorp (TYK Corporation) [66] [67], the hydride ion-conducting solid electrolyte probe [68], and ALSPEK and Hycal™ which are based on an indium-doped calcium zirconate solid electrolyte [69] [70] [71] [72]. Other attempts to determine the solubility of hydrogen in aluminum and its alloys include derivation of solubility from experimentally determined values of the diffusion coefficient and permeability of hydrogen in aluminum and its alloys [73] [74] [75], and by theoretical calculations [18] [25] [26] [76] [77] [78] [79] [80].

As will become apparent in the following sections, the choice of a given experimental method is first determined by whether the desired hydrogen solubility is to be determined in the liquid or solid state of the pure aluminum and aluminum alloys. Also, every method has potential sources of error that must be correctly identified, corrected for, and or alleviated.

### 3.1. Sieverts' Direct Absorption Technique

The Sieverts' direct absorption technique involves direct measurement of the volume of gas absorbed by a known mass of metal contained in a crucible and enclosed in an evacuated absorption bulb or reactor [17] [30]-[46] [81]. In the Sieverts' direct absorption method, the melt is contained in a closed chamber or absorption bulb (Figure 2). The apparent or dead volume of this absorption bulb is usually determined at the desired temperature and pressure, by introducing a known quantity of inert gas that has very closely the same general thermal and physical characteristics as the experimental gas, which in this case is hydrogen. Sometimes referred to as the *hot volume*, the dead volume is the volume of gas at standard temperature (273 K) and pressure (101,325 Pa)



**Figure 2.** The modified Sieverts' apparatus for measuring hydrogen solubility by the direct absorption method (Anyalebechi *et al.* [45] [46] [81]).

necessary to fill the physical space between the sample, absorption bulb, and the connecting glassware at a specific temperature and reaction system pressure. Alternatively, the experimental gas (*i.e.*, hydrogen) is used with an inert specimen having similar physical characteristics as the experimental metal (melt or solid). Subsequently, the experimental metal is equilibrated with the experimental gas by introducing a known quantity of the gas into the calibrated absorption bulb. The desired quantity of gas absorbed is thus derived from the difference between the two relatively large volumes. When the solubility is small as it is in most solid metals and their alloys the Sieverts' direct absorption technique leaves much to be desired. In the Sieverts' method, the following mathematical expressions are used to calculate the maximum amount of hydrogen absorbed by the aluminum melt determined at a constant melt temperature and hydrogen pressure:

$$S_H = \left[ (V_a - V) \times \left( \frac{P_H}{101325 \text{ Pa}} \right) \times \left( \frac{273 \text{ K}}{T} \right) \times \left( \frac{100 \text{ g}}{W} \right) \right]_{p \neq 1, T_m} \quad (24)$$

and

$$\text{wt. \%H} = \left[ (V_a - V) \times \left( \frac{2}{22400 \text{ cm}^3} \right) \times \left( \frac{P_H}{101325 \text{ Pa}} \right) \times \left( \frac{273 \text{ K}}{T} \right) \times \left( \frac{100 \text{ g}}{W} \right) \right]_{p \neq 1, T_m} \quad (25)$$

where  $S_H$  = equilibrium solubility of hydrogen in the aluminum melt at a given melt temperature and hydrogen pressure in  $\text{cm}^3/100\text{g}$ ,  $V_a$  = total volume of hydrogen gas admitted into the absorption bulb throughout the test run to maintain the hydrogen pressure at a constant value in  $\text{cm}^3$  or milliliters at standard temperature and pressure;  $V$  = hot volume of the absorption bulb, in  $\text{cm}^3$  or milliliters at standard temperature and pressure;  $P_H$  = hydrogen pressure in Pa;  $T$  =

melt temperature, in K;  $W$  = mass of the aluminum metal charge in grams, and wt.% H = equilibrium solubility of hydrogen at a given melt temperature and hydrogen pressure, in wt.% H.

Accurate measurements can be made only by reducing the dead space to as small a volume as possible; although, this is not very critical if the solubility is large, such as the hydrogen solubility in Fe-Co alloys at 1865 K and 101.3 kPa which is 23.0 cm<sup>3</sup>/100g [82]. The physical volume of the absorption bulb or reactor is affected by the temperature of the molten metal which alters the temperature distribution in the region of the molten aluminum. Consequently, the hot volume must be determined as a function of molten metal temperature and reaction system pressure. It is also essential that the solution of the gas in the crucible containing the metal, and in the material of which the bulb is constructed should be either negligible or at least known with sufficient accuracy to enable suitable correction to be made.

The principal sources of error in the Sieverts' direct absorption technique are:

1) Errors in the measurement of the hot dead space volume of the absorption bulb due to: a) thermal mismatch with hydrogen, if an insoluble gas of high relative molar mass and different thermal properties is used, such as the use of argon instead of neon or preferably helium [17] [26] [45]; b) permeation of the inert gas through the walls of the absorption bulb if heated externally with an electric resistance furnace instead of a radio frequency (RF) induction heater [17] [45]; c) small variability in sample size and mass, crucible size, chemical composition of the molten metal, and the temperature of the melt could alter the temperature distribution in the region of the molten aluminum and consequently the hot dead space volume and the hydrogen solubility values obtained; and d) the reaction of the experimental gas with any components of the melt which may have distilled onto the cooler parts of the absorption bulb. The latter problem can be an appreciable source of error with alloys containing reactive volatile elements such as Mg, Li, Cr, and Zn. For example, the metallic vapor may react with hydrogen to form hydrides or with nitrogen to form nitrides or the gas may be adsorbed on finely divided deposits. These conditions tend to increase the apparent absorption or hydrogen solubility limit values obtained.

2) Failure to reach equilibrium due to slow permeation of hydrogen through the oxide film if the metal is quiescent, as it is when the sample temperature is maintained by external heating with an electric resistance furnace [17]. The use of radio frequency induction heater with its induced magnetic stirring alleviates this problem.

3) Loss of hydrogen or the inert gas used for calibration of the hot volume by permeation through and solution in the absorption bulb material if it is directly heated [17] [37]. This is circumvented by surrounding the absorption bulb with an outer jacket, which is filled with hydrogen at the same pressure as that in the inner bulb and thus compensates for any outward flow of hydrogen [17]. This does not, however, prevent some solution of hydrogen in the glass from the in-

side. Since the solubility of hydrogen in silica is high ( $0.01 \text{ cm}^3 \text{ (STP)/cm}^3$  of silica) and does not vary greatly with temperature, it can amount to an appreciable fraction of the observed solubility of hydrogen in the aluminum sample and has to be corrected for. This problem may be exacerbated by attack of the surface of the absorption by reactive volatile elements such as Li and Mg. A better solution is the use of radiofrequency heating and experimental conditions that will reduce the temperature of the absorption bulb and the time required for equilibration [45].

4) Insensitivity due to the use of small samples or inadequacies in the design of the gas burette system used to measure the volumes of hydrogen or insoluble gas admitted to the absorption bulb.

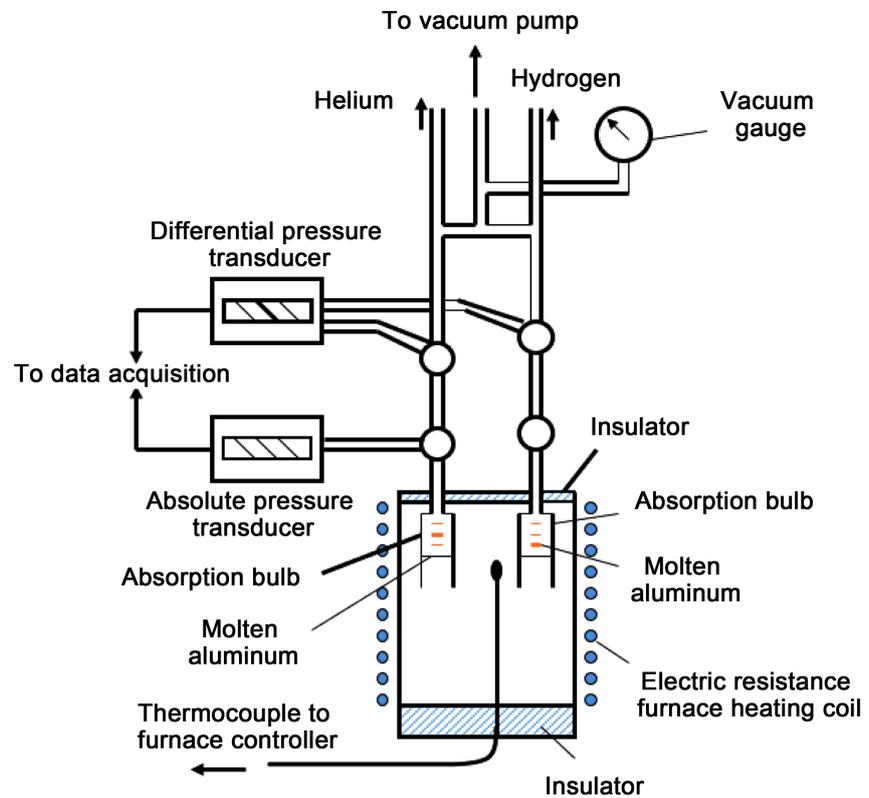
5) Change in the composition of the melt due to evaporation of the volatile components during the measurement. Any deposits formed can also affect the temperature distribution in the absorption bulb. Both effects can be significant if the melt is held under vacuum for an extended period.

6) Oxygen which is not completely removed from the metal can react with hydrogen in the absorption bulb and thus increase the apparent solubility.

### 3.2. The Constant Volume (or Differential Sieverts') Method

The Constant Volume Method of hydrogen solubility measurement is conceptually similar to the Sieverts' direct absorption technique so it is sometimes referred to as the Differential Sieverts' method [47]. Its principal difference from the Sieverts' direct absorption technique is that gas solubilities are measured by measuring pressure changes at constant volume, rather than measuring volume changes at constant gas partial pressure. The pressure difference generated is a measure of the solubility of the gas of interest in the alloy being investigated. The Sieverts' direct absorption method, originally devised by Sieverts [30] is sometimes referred to as the *constant pressure Sieverts' method* because the gas dissolution reaction occurs in an absorption reactor in which the pressure of the gas phase is kept constant. In contrast, with the constant volume Sieverts method, dissolution of the gas in the absorption reactor occurs in a closed system in which the volume remains constant. In the constant volume method, an initial pressure is first established in the absorption reactor and is then allowed to evolve as a function of the progress of the dissolution reaction.

The constant volume method involves the use of two absorption bulbs or reactors and two arms instead of one (Figure 3) as used in the Sieverts' direct absorption method. These absorption bulbs, constructed of quartz, are reportedly of the same volume, and contain identical crucibles of the same volume and metal samples. Both absorption bulbs are placed inside an electric resistance furnace so that their temperatures are identical; one bulb contains an insoluble gas (such as argon or helium) and the other contains the dissolving gas (hydrogen). The pressure difference ( $\Delta P$ ) caused by the absorption of hydrogen in one reactor gives rise to a pressure difference which is measured by a set of co-active



**Figure 3.** Schematic of apparatus for the constant volume (or differential sieverts' method) for the measurement of the solubility of hydrogen in liquid aluminum and its alloys (Verma [47]).

capacitance-type pressure transducers. An absolute pressure transducer is connected to the limb that contains argon and a differential pressure transducer is connected across the limb that contains the insoluble gas (argon or helium) and the other limb which contains hydrogen.

The hydrogen solubility in  $\text{cm}^3$  (STP)/100g of metal is derived from the ideal gas equation:

$$\Delta P = \frac{\Delta n RT}{V} \quad (26)$$

where  $\Delta P$  = the pressure difference due to hydrogen absorption in mmHg,  $V$  = constant volume of the absorption bulb,  $\Delta n$  = number of moles of hydrogen dissolved in the sample,  $T$  = absolute temperature in K, and  $R$  = gas constant =  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$  ( $= 62,400 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ ).

Thus,

$$\Delta n = \frac{\Delta P V}{RT} \quad (27)$$

and

$$S_H = \frac{1.12 \Delta n M_{H_2}}{W} \quad (28)$$

where  $S_H$  = hydrogen solubility in  $\text{cm}^3(\text{STP})/100\text{g}$ ,  $\Delta n$  = number of moles of hydrogen dissolved in the sample,  $M_{H_2}$  = the molecular weight of hydrogen, and  $W$  = the mass of the sample in grams (g).

Unlike in the Sieverts' direct absorption technique where relatively large samples (>100 g) are used to produce gas volume changes that can be precisely measured with a calibrated burette, in the constant volume method, comparatively small samples (5 - 7 grams per bulb) are used. Also, the latter reportedly has a smaller hot "dead space" volume ( $6 \text{ cm}^3$ ) than in the classical Sieverts' apparatus ( $10 - 15 \text{ cm}^3$ ).

The constant volume method is a novel approach; theoretically, it could be used to determine the solid state solubility of hydrogen in aluminum alloys because of the sensitivity of the pressure transducers to low pressures. However, despite the novelty of the constant volume method, there are several sources of error that will make the hydrogen solubility values obtained with it less accurate than the Sieverts' direct absorption method. These errors include:

1) *Slow and direct heating of the quartz absorption bulbs, and Long equilibration time.* The use of an electric resistant furnace for heating or melting samples imposes an extra 1 to 2 hours on the test time while the sample is raised to the desired test temperature. This is compounded by the poor thermal transfer through the intervening vacuum between the external resistance furnace and the samples. Experience shows that a 10 mm diameter  $\times$  50 mm long cylinder weighing about 6 to 8 g (depending on the alloy composition) contained in a quartz tube in a vacuum of  $1.33 \times 10^{-4}$  Pa and heated by an external resistance furnace takes at least 1 hour to reach a temperature of 773 - 873 K [83] [84]. This is because radiation is the dominant heat transfer mechanism and solid aluminum has a low thermal absorptivity. In severe cases, the sample, located in the hottest zone of the furnace does not attain the set furnace temperature.

The slow and prolonged direct heating of the quartz absorption bulb is an undesirable feature of the constant volume method since it is expected to result in the gas diffusion through, and dissolution in, the walls of the quartz absorption bulbs. With this method of heating, the absorption bulb temperature will inevitably be at or above the test temperature. At test temperatures of 973 K and above, a measurable loss of helium and hydrogen by diffusion and dissolution in quartz is expected to occur at such elevated temperatures [85]. However, the diffusivity of hydrogen and helium through the quartz is only expected to give rise to significant experimental errors in hydrogen solubility determinations if the following conditions exist: 1) the temperature of the quartz absorption bulb exceeds 473 - 573 K; and 2) test time, *i.e.*, the time helium or hydrogen is inside the absorption bulb, exceeds 30 - 60 minutes.

Furthermore, attainment of equilibrium between hydrogen and the molten metal in this method seems to take a relatively long time, at least one hour, during which the loss of helium and hydrogen via diffusion through and dissolution in the quartz could be substantial. The long equilibration time is not surprising,

since the oxide film which is inherently present on the surface of the melt tends to impede the rate of diffusion of hydrogen into the melt sample. Ransley and Neufeld [17] have shown that the loss of hydrogen by diffusion through quartz at temperatures of 973 K and above, for 2 to 24 hours yields a significant error in the hydrogen solubility results obtained with a resistance furnace heated absorption bulb.

2) *Chemical composition changes of the alloy due to loss of volatile elements (e.g., Mg, Li, Zn)*: Another potential source of error in the differential Sieverts' method is the loss of volatile elements from the sample. This is expected to be significant in a 1-hour test, especially in a small (<25 g) sample.

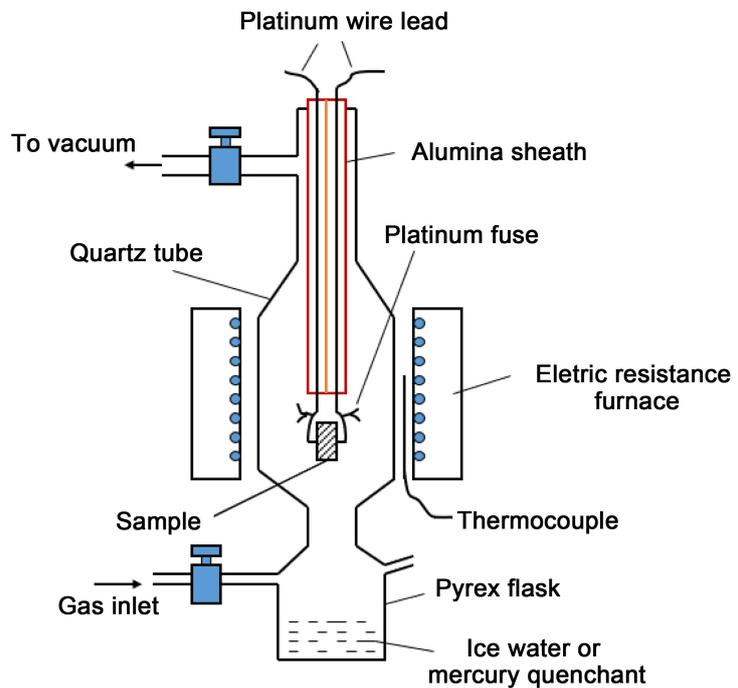
3) *Attack of absorption bulbs by volatile and reactive elements like lithium and magnesium*: Reactive elements such as Li and Mg attack the walls of the quartz tube. This interaction has also been found to be exacerbated by high temperature (>773 K) and long contact times [16] [84]. It results in degradation (and cracking, in the most severe cases) of the quartz bulb; this, in turn, enhances the diffusion and dissolution of both helium and hydrogen gases from and in the quartz material.

4) *Questionable melt temperature*: The location of thermocouples inside the furnace, instead of inside the bulbs could result in melt sample test temperatures being either above or below the desired test temperature. This will result in a significant error since the solubility is a direct function of temperature.

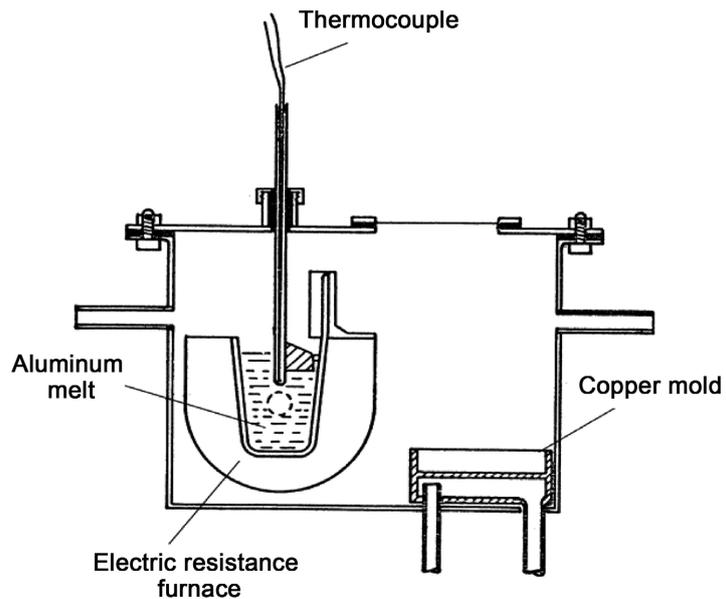
5) *Presumed equal volume of absorption bulbs*: The accuracy and reliability of the constant volume method depend on both accurate pressure measurement and the equality of the volumes of both absorption bulbs. However, it is extremely difficult and impractical to construct two bulbs with exactly the same volume. Proponents of this technique realize that dilemma and as a result, conduct two tests per sample [47]. The first test is conducted with a gas that is insoluble in aluminum and its alloys but is thermally comparable to hydrogens such as helium or neon in both absorption bulbs to determine the dead space volume. A second test is conducted with hydrogen gas in one absorption bulb and argon or helium in the other.

### 3.3. The Equilibration-Quench-Extraction Technique

In the equilibration-quench-extraction technique, the solid or liquid sample is equilibrated with the gas under the prescribed conditions and quenched to retain the absorbed gas which is then extracted for measurement in a separate operation [17] [48] [49] [50] [51] [52]. If the sample is solid, it is quenched with either a strong cold air blast applied to the outside of the vessel containing the sample in the gas atmosphere [17] [45] [51] [56] [75] [86], in a water-cooled jacket [87], or in a cold water or mercury quench tank [55] [88] (Figure 4). If it is a liquid, the melt surface is skimmed during equilibration to keep it free from impeding oxide films. It is quenched by casting into a water-cooled metal chill mold (Figure 5 and Figure 6) while still in the gas atmosphere to provide a solid sample of



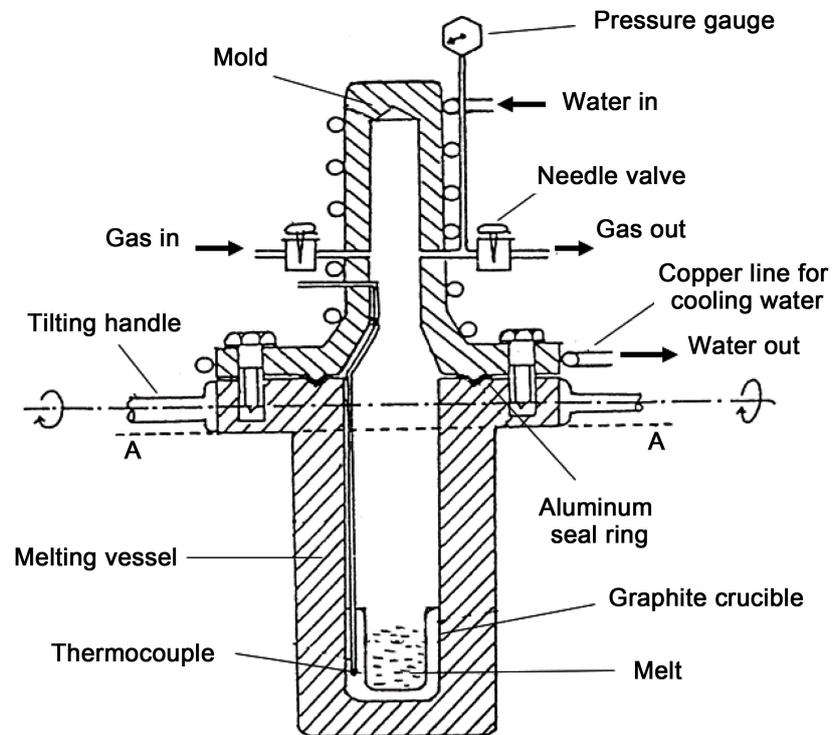
**Figure 4.** Gas equilibrium and quench apparatus for solid state hydrogen Solubility measurement (Jones and Pehkle [88]).



**Figure 5.** Apparatus for saturation of molten aluminum with hydrogen and quenching in a copper mold (Ransley and Talbot [48]).

a form suitable for gas content measurements [48] [49] [51] [52]. In both cases, the samples are exposed to the atmosphere after equilibration and must be given a surface preparation, such as machining, which may be necessary for the subsequent determination of hydrogen content.

Application of the equilibration-quench-extraction technique to hydrogen



**Figure 6.** Apparatus for the determination of the solubility of hydrogen in molten aluminum by the equilibration-quench-extraction technique (Imabayashi *et al.* [52]).

solubility measurements in liquid metals suffers from the limitation that some gas may be gained (as is the case in Cr-Fe alloys [84] or lost, as is the case of hydrogen in Fe-Ni alloys [89], and aluminum and its alloys [48] [52] during solidification and cooling of the quenched molten metal sample. In the case of the solid, however, the equilibration-quench-extraction technique can be used with more confidence since the loss of gas by diffusion can be readily assessed. Also, subsequent measurement of hydrogen retained in the quenched sample involves hydrogen content analysis by hot vacuum sub-fusion extraction technique. As expounded in previous publications [16] [83] [84] [90], this requires great care and is prone to several potential sources of errors.

### 3.4. The Isothermal Equilibration Desorption (or Eichenauer's) Technique

In this method developed by Eichenauer and his co-investigators [53] [54] [55], a sample is allowed to absorb hydrogen from the gas phase and then desorbed isothermally into a low pressure system for measurement. Kocur *et al.* [56] [57] used the same methodology to determine the solubility of hydrogen in liquid aluminum. Unlike the equilibration-quench-extraction technique, in the isothermal equilibration-desorption technique the temperature of the sample is not changed between equilibration or saturation with the gas phase and extraction of the hydrogen for measurement. This is accomplished by terminating the equili-

bration stage by rapidly evacuating the gas from the absorption system and then diverting the gas subsequently evolved from the sample into the low pressure system for measurement.

The primary limitation of this method is the difficulty of distinguishing clearly between the gas evacuated from the vessel and the gas subsequently evolved from the sample. The procedure requires an intermediate operation to evacuate the hydrogen from the absorption system before connecting it to the low pressure collection system. The reliability of the technique depends critically on the correction required for hydrogen desorbed from the sample and consequently lost during the intermediate stage. The technique is inherently more reliable for the determination of hydrogen solubility in solid metals where the desorption of hydrogen is diffusion-controlled and relatively slow, permitting accurate back extrapolation of the hydrogen evolution curve by application of standard diffusion theory to determine the correction for the lost hydrogen. For liquid aluminum, the method is less appropriate because the expected correction is higher and difficult to assess. For example, it is well known that the sudden application of vacuum to liquid aluminum causes hydrogen bubbles to nucleate within the bulk of the liquid metal. In fact, Eichenauer *et al.* [54] admitted that the desorption of hydrogen from liquid aluminum was not controlled by diffusion but by other undefined processes. Corrections for the lost hydrogen were made by applying empirical “velocity constants” of an undisclosed nature and no information was given from which to assess the validity of the procedure.

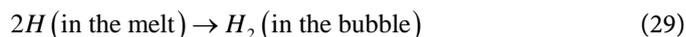
Furthermore, another possible source of error in the application of the isothermal equilibration-extraction technique to the determination of hydrogen solubility in solid aluminum and its alloys is the hydrogen adsorbed onto the surface of the silica quartz (or graphite) absorption system during the equilibration stage of the test. The adsorption is exacerbated by an attack on the surface of the absorption vessel by aluminum and the corresponding increase in the surface area of the absorption bulb. The adsorbed hydrogen tends to subsequently evolve during the evacuation and extraction stages of the test and will contribute to the result. This problem is expected to be worse when the technique is applied to aluminum alloys which contain volatile and more reactive alloy elements such as Mg, Li, and Zn [16] [45] [83] [90]. The results obtained with the isothermal equilibration-quench technique are therefore susceptible to systematic errors.

### 3.5. The Direct Reading Control Hydrogen Measurement Methods

Theoretically, the direct reading control hydrogen measurement methods used to determine the hydrogen content of molten aluminum can also be used to measure the solubility of hydrogen in liquid aluminum and its alloys. The methods include the Telegas I and II™ [16] [58] [59] [61] [62], AISCAN™ [63], CHAPEL method [60] [64] [65], Notorp [66] [67], ALSPEK [69] [70] [71] [72], and Hycal [72] instruments. This is accomplished in effect when the values of the hydrogen content of molten aluminum determined using these instruments

are compared with corresponding values of the hydrogen contents of quenched solid samples of the molten aluminum determined by hot vacuum extraction or LECO hydrogen analyzer on quenched samples [58] [59] [60].

The Telegas I and II™, and AISCAN™ instruments are sometimes referred to as the Close Loop Recirculating method [59] [61]. They are designed to indirectly measure the activity of hydrogen (*i.e.*, hydrogen solution pressure) in the liquid metal, by measuring the induced thermal conductivity of the gas mixture with a katharometer (thermal conductivity cell). Melt hydrogen content is obtained from a calibration chart which relates Telegas and AISCAN™ instrument meter reading, hydrogen solubility as affected by melt temperature, and hydrogen content in cm<sup>3</sup> of hydrogen per 100 g of metal. They operate on the principle of monitoring the hydrogen activity developed in the bubbles of a small quantity of inert gas or nitrogen continuously recirculated through the molten metal in equilibrium with the solute hydrogen in the molten metal in accordance with the equation [61]:



At equilibrium, Sieverts' relationship between the concentration of dissolved hydrogen atoms and the pressure of the molecular hydrogen gas is established as follows:

$$S_H^{eq}(T, P_{H_2}) = K_s(T) \sqrt{P_{H_2}} \quad (30)$$

where  $S_H^{eq}$  = the amount or solubility of hydrogen in the aluminum melt which is a function of melt temperature, hydrogen gas pressure above the melt, and alloy composition,  $K_s$  = the Sieverts' constant which varies with the melt temperature and alloy composition, and  $P_{H_2}$  = equilibrium hydrogen pressure above the melt.

This equation can be rewritten in a slightly different form. If the solubility of hydrogen in the alloy is for example  $S_{Alloy}$  at 101.3 kPa, then a given hydrogen content,  $C_H$ , will give rise to an equilibrium pressure or internal solution pressure of hydrogen  $P_i$  (Pa) such that:

$$\frac{C_H}{S_{alloy}} = \sqrt{\frac{P_i}{101325}} \quad (31)$$

Thus, determination of the hydrogen content,  $C_H$  and the partial pressure of the hydrogen  $P_i$  under known conditions of temperature and pressure and application of Equation (31) yields the required hydrogen solubility. The hydrogen content,  $C_H$  of the molten metal is obtained by determining the hydrogen content of the quenched samples of the molten metal by the hot vacuum sub-fusion extraction technique.

The proton-conducting hydrogen analyzers such as Notorp [66] [67], ALSPEK [69] [70] [71], and Hycal [72] instruments are designed to indirectly measure the activity of hydrogen (*i.e.*, hydrogen solution pressures) in the liquid metal with an electrochemical sensor, by measuring induced electromotive force (emf). For example, the sensor in the ALSPEK instrument and its successor, the

Hycal™ instrument is an indium-doped calcium zirconate (CaZrO<sub>3</sub>-In) solid electrolyte which allows the free movement of hydrogen ions [69] [70] [71] [72]. The sensor is contained or housed in a refractory probe that protects it from molten aluminum and permits gas exchange [71]. The probe consists of refractory graphite or SIALON sheath that is chemically inert to aluminum melt and a porous carbon plug at the bottom end. The hydrogen sensor is located in a gas chamber or cavity inside the probe. The porous plug allows the diffusion of the hydrogen dissolved in the melt into the gas chamber in contact with the solid electrolyte until it attains a state of equilibrium with the hydrogen in the melt. The solid electrolyte is also in contact with a solid state reference (a zirconium and zirconium-hydrogen mixture) with known hydrogen partial pressure [71]. The solid state reference generates a known hydrogen concentration. The part of the solid electrolyte in contact with the gas chamber is referred to as the “measuring electrode” and the part in contact with the solid state reference is the “reference electrode”. Both sides of the solid electrolyte are coated with a porous film of platinum. The electrochemical sensor compares the known hydrogen partial pressure of the reference electrode with that of the unknown hydrogen partial pressure of the measuring electrode. The proton-conducting hydrogen analyzers are essentially hydrogen concentration cells that obey the Nernst law:

$$E = -\frac{RT}{2F} \ln \frac{P_{H_2}^m}{P_{H_2}^{ref}} \quad (32)$$

where  $E$  = electromotive force (emf) in mv,  $P_{H_2}^m$  = hydrogen partial pressure at the measuring electrode which is related to the dissolved hydrogen content in the melt,  $P_{H_2}^{ref}$  = hydrogen partial pressure at the reference electrode,  $T$  = temperature in K,  $R$  = gas constant, and,  $F$  = Faradays constant. The melt hydrogen content is obtained by determining the emf of the hydrogen concentration cell which is a function of the difference between the hydrogen partial pressure in the gas chamber and that at the solid state reference. According to Sieverts' law shown mathematically in Equation (28), the hydrogen concentration in the melt is a function of the square root of hydrogen partial pressure in the surrounding atmosphere, hence:

$$P_{H_2}^m = \left( \frac{S_H}{K_s} \right)^2 \quad (33)$$

where  $S_H$  = the amount or solubility of hydrogen in the aluminum melt which is a function of melt temperature, hydrogen gas pressure above the melt, and alloy composition,  $K_s$  = the Sieverts' coefficient or constant which varies with the melt temperature and alloy composition, and  $P_{H_2}$  = equilibrium hydrogen pressure above the melt. A direct determination of the hydrogen content in the melt is obtained by combining Equations (32) and (33):

$$E = -\frac{RT}{2F} \ln \frac{(S_H)^2}{(K_s)^2 P_{H_2}^{ref}} \quad (34)$$

Thus, Equation (34) establishes the direct correlation between the measured electromotive force or cell potential,  $E$ , with the proton conducting gas analyzer and the unknown hydrogen content of the melt. The melt hydrogen content is obtained from a calibration chart which relates emf, hydrogen solubility as affected by melt temperature, and hydrogen content in  $\text{cm}^3$  of hydrogen per 100 g of metal. Thus, like with the Telegas I and II<sup>™</sup>, and AISCAN<sup>™</sup> instruments, the potential use of the proton-conducting gas hydrogen gas analyzers also requires the determination of the hydrogen content of quenched samples of the pure aluminum or aluminum alloy melt by hot vacuum sub-fusion extraction technique.

The CHAPEL method is a direct-reading method for the continuous measurement of the hydrogen content in molten metals. It involves the continuous measurement of the activity of hydrogen in molten metals by measuring the equilibrium hydrogen pressure with a sensor cell. The sensor cell consists of a porous degassed electrographite disk that is permeable to hydrogen in the melt connected to a vacuum gage via a gas-tight alumina tube [60] [64] [65] [91]. The porous graphite is cylindrical in shape, 12 mm diameter  $\times$  15 mm height, with 16 - 18 vol.% porosity. A modified version of CHAPEL has been used by Szokefalvi-Nagy *et al.* [60] to directly measure the solubility of hydrogen in liquid aluminum.

The principle of this methodology is based on the premise that Sieverts' constant at a given temperature can be determined by adding or removing a given amount of hydrogen to or from a known mass of molten aluminum, even if its hydrogen content is not known at the beginning of the experiment. For example, at a given temperature, an aluminum melt with a given concentration of dissolved hydrogen  $C_1$  will have an initial hydrogen partial pressure of  $P_1$ . A new equilibrium partial pressure  $P_2$  will be established after a brief degassing of the melt. If no hydrogen exchange through the outer surface of the melt takes place, the concentration of dissolved hydrogen in the melt will decrease to  $C_2$ , because the sensor cell has to be filled again with hydrogen from the melt to attain the new equilibrium state. Thus, the change of the hydrogen concentration is given by the following equation [60]:

$$C_1 - C_2 = K_s (\sqrt{P_1} - \sqrt{P_2}) \quad (35)$$

where  $K_s$  = Sieverts' constant at the given melt temperature.

The change of the hydrogen concentration is also given by the following equation based on the knowledge of the experimental conditions and the volume of the sensor cell or probe:

$$C_1 - C_2 = \frac{P_2 V_{cell}}{RT N_{Al}} \quad (36)$$

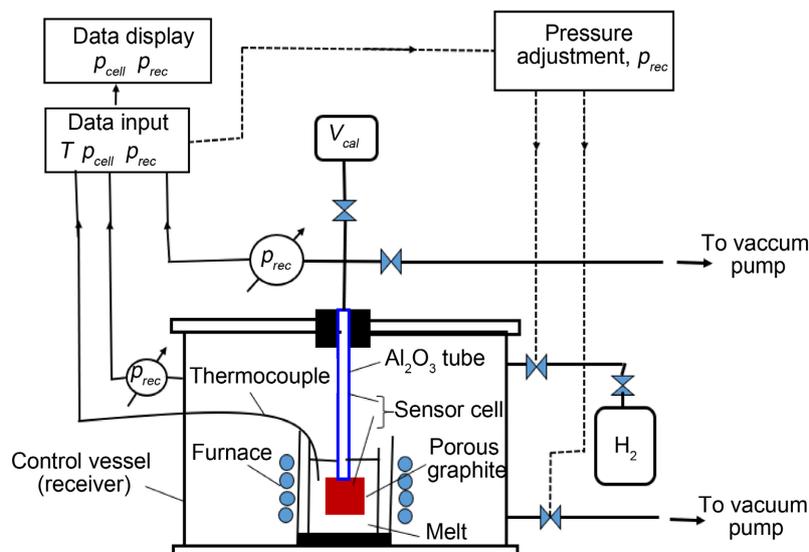
where  $V_{cell}$  = effective volume of the sensor cell,  $T$  = temperature,  $N_{Al}$  = number of moles of the molten metal sample, and  $R$  = gas constant. The Sieverts constant can be obtained by combining the two equations:

$$K_s = \left( \frac{V_{cell}}{RTN_{Al}} \right) \frac{P_2}{(\sqrt{P_1} - \sqrt{P_2})} \quad (37)$$

The first part of the right-hand side of this equation is a constant parameter for a test at a given temperature.

As described by Szokefalvi-Nagy *et al.* [60], the modified version of the CHAPEL method involves the placement of the molten metal sample and the sensor cell in a control vessel (or receiver) where the sensor system is used to continuously adjust the hydrogen pressure to the actual hydrogen activity in the melt. The addition or removal of hydrogen through the sensor cell is used to achieve quantitative changes in the hydrogen content of the test melt. As shown in **Figure 7**, the experimental apparatus consists of the following contained in a control vessel: 1) about 80 - 100 g of molten aluminum contained in an alumina crucible heated by an electric resistance furnace, and 2) the CHAPEL sensor cell that consists of a 12 mm diameter  $\times$  15 mm long cylindrical porous (16 - 18 vol.% porosity) electrographite disk attached to a vacuum-tight alumina tube which connects the sensor cell to a pressure gage. The control vessel serves as a pressure reservoir and is where the hydrogen pressure can be adjusted. Both the control vessel and the sensor can be evacuated and filled with hydrogen gas separately. The pressure in the control vessel can be adjusted to any desired value.

The measurement of hydrogen solubility involves: 1) the measurement of the volume of the sensor cell,  $V_{cell}$  from the change in pressure caused by opening the valve that connects the sensor to the evacuated calibrated volume,  $V_{cal}$ ; 2) measurement of the equilibrium hydrogen pressure in the system ( $p_0$ ); that is the hydrogen pressure in the sensor cell ( $p_{cell}$ ) is equal to that in the control vessel or receiver ( $p_{rec}$ ); 3) rapid evacuation of the sensor cell immersed in the molten



**Figure 7.** A schematic of the modified CHAPEL method for direct determination of the solubility of hydrogen in molten aluminum and its alloys (Szokefalvi-Nagy *et al.* [60]).

metal to remove a given amount of hydrogen from the molten metal resulting in a new equilibrium pressure in the sensor cell; 4) simultaneous to 3), the hydrogen pressure in the controlled vessel is adjusted to the actual activity of dissolved hydrogen in the molten metal, based on the assumption that the relatively high rate of diffusion of hydrogen in molten aluminum will ensure quick uniform hydrogen distribution in the melt, and thus result in a quasi-equilibrium during the measurement.

On the basis of Equations (35), (36) and (37), the change in the concentration of hydrogen in the melt is obtained from the above measurements using the following equation [60]:

$$C_0 - C(t) = K_s \left( \sqrt{p_o} - \sqrt{p_{eq}(t)} \right) = \left( \frac{V_{cell}}{RTN_{Al}} \right) p_{rec}(t) \quad (38)$$

where  $C_0 = C(0)$  = initial concentration of hydrogen dissolved in the melt,  $C(t)$  = hydrogen concentration at time  $t$ ,  $K_s$  = Sieverts' constant at the given melt temperature,  $p_o = p(0)$  = initial equilibrium pressure corresponding to  $C_o$ , and  $p_{eq}(t)$  = actual equilibrium pressure over the melt. The equilibrium pressure,  $p_{eq}(t)$  is calculated from the pressure in the sensor cell as:

$$p_{eq}(t) = \left( \sqrt{p_o} - \frac{p_{cell}(t)V_{cell}}{K_s RTN_{Al}} \right)^2 = p_{rec}(t) \quad (39)$$

This equation defines the pressure adjustment in the control vessel since the hydrogen pressure over the melt has to be kept equal to the actual equilibrium pressure,  $p_{eq}(t)$ . However, the equation contains the unknown Sieverts' constant which is apparently determined by trial and error by adjusting the pressure in the control vessel. This appears to be the greatest drawback of the use of this method to measure the solubility of hydrogen in aluminum alloys.

Some of the drawbacks of the possible application of direct reading control methods for the measurement of the solubility of hydrogen in aluminum and its alloys include: 1) the instruments measure the activity and not the concentration of hydrogen in the melt, 2) loss (or pick-up) of hydrogen during sampling of the melt, 3) non-attainment of equilibrium because of the impedance of hydrogen diffusion into the melt by the oxide film on the melt surface; 4) the fact that the accuracy of the hydrogen solubility measurement results will depend on the accuracy and reproducibility of both the direct hydrogen measuring instruments and the hot vacuum extraction and LECO tests, with reported standard deviations of 0.008 - 0.09 cm<sup>3</sup>/100g [16]. Except for the first, the other possible sources of error are addressed and can be potentially alleviated with the modified CHAPEL instrument, especially the fact that there is no need for the determination of the hydrogen content of the quenched melt samples of the molten metal by hot vacuum extraction.

### 3.6. Other Approaches Used to Determine Hydrogen Solubility

In addition to the use of experimental methods, the solubility of hydrogen in

aluminum and its alloys can also be potentially determined by two other approaches, namely:

1) *Calculation of hydrogen solubility from the relationship between permeability, diffusivity, and solubility*—There is a fundamental relationship between permeability, diffusivity, and solubility. This is because dissolution is one of the several steps involved in the permeation of hydrogen in dense metallic systems. The steps include the: a) adsorption and dissociation of a hydrogen molecule on the aluminum metal surface; b) dissolution of the hydrogen into the aluminum in an atomic; c) diffusion of the atomic hydrogen inside the aluminum; and d) recombination of the hydrogen atoms and desorption and desorption in molecular form from the metal surface. Consequently, the solubility of hydrogen in both liquid and solid aluminum and its alloys can be derived from available hydrogen permeability and diffusivity data [73] [74]. The combination of Sieverts' law and Fick's first law gives permeability, an intrinsic property of a metallic membrane. It is the product of Sieverts' or solubility constant and diffusivity, *i.e.*,

$$Q_p = K_s D \quad (40)$$

where  $Q_p$  = permeability in  $\text{cm}^3$  (STP)/ $\text{s}\cdot\text{cm}\cdot\text{Pa}^{1/2}$ ,  $D$  = diffusivity in  $\text{cm}^2/\text{s}$ , and  $K_s$  = Sieverts' solubility constant in  $\text{cm}^3$  (STP)/ $100\text{g}\cdot\text{Pa}^{1/2}$ . Assuming Sieverts' law holds, according to Equation (28),  $K_s = S_H (P_{H_2})^{-1/2}$ , so Equation (38) becomes:

$$Q_p = K_s D = S_H (P_{H_2})^{-1/2} D \quad (41)$$

Thus,

$$S_H = \frac{Q_p (P_{H_2})^{1/2}}{D} \quad (42)$$

where  $S_H$  = hydrogen solubility in  $\text{cm}^3$ (STP)/ $100\text{g}$ ,  $D$  = diffusivity in  $\text{cm}^2/\text{s}$ ,  $Q_p$  = permeability in  $\text{cm}^3$ (STP)/ $\text{s}\cdot\text{cm}\cdot\text{Pa}^{1/2}$ , and  $P_{H_2}$  = the pressure of the molecular hydrogen.

This method of determining hydrogen solubility is fraught with experimental and procedural difficulties. This is particularly the case in the liquid state where accurate measurement of diffusivity is made difficult by the convective currents in the liquid metal and the inability to suppress or accurately account for the errors associated with them. This problem is compounded in alloys by the vaporization of alloying elements from the melt [92]. Also, in the solid state experimentally determined values of permeability are affected by several factors such as formation, growth and structural and associated allotropic transformation of oxide films on the surface of the aluminum specimens, dynamic grain recrystallization, and phase transformations in the bulk of the melt [93]. All of these factors can either reduce or increase the movement of hydrogen through the specimen and consequently invalidate results obtained from permeability tests. The effects of these factors increase with an increase in temperature.

2) *Theoretical Calculations*—The solubility of hydrogen in metals have been

calculated by various methods ranging from statistical treatment [76] [77] to thermodynamic methods such as the regular solution [25], the Wagner's interaction parameter [22] [24] [80], and the modified quasichemical with the pair approximation [26] models. The thermodynamic methods used by Oiu *et al.* [25] and Harvey and Chartrand [26] are sometimes referred to as the Calculation of Phase Diagrams (CALPHAD) modeling method [94]. This is because they involve the description of Gibbs energies of individual phases in a given system, which are combined to predict the phase diagram for Al-H binary and Al-X-H multicomponent phase diagrams. The theoretical approaches and the reliability of predicted values of hydrogen solubility in pure aluminum and aluminum alloys will be the subject of a separate article.

### 3.7. Selection of Hydrogen Solubility Measurement Methodology

The reproducibility, accuracy, and hence, reliability of the values of hydrogen solubility obtained in a given experimental study profoundly depend on the measurement methodology. Thus, the selection of an appropriate measurement methodology is in turn affected by factors such as: 1) the state of the material, i.e., liquid, semi-solid, or solid, 2) alloy chemical composition, 3) temperature and pressure conditions, and 4) expected nominal volume of hydrogen absorbed by the sample at the given experimental conditions.

In spite of the above described difficulties and potential sources of error, Sieverts' direct absorption method appears to be the most reliable available method for the measurement of the solubility of hydrogen in liquid aluminum and its alloys. It offers better prospects for reliable measurement. In addition, the error due to indeterminate loss of hydrogen during quenching or evacuation, and the difficulty in preventing loss from these effects are avoided. The equilibration-quench-extraction (EQE) technique is another feasible method, but it is useful only when it can be demonstrated by an independent experiment that there is no appreciable loss of hydrogen by diffusion during the quenching operation. Besides, the rate of absorption of hydrogen in the metal cannot be obtained and hence the kinetics of the dissolution reaction cannot be determined. The accuracy of the results obtained with the equilibration-quenching-extraction technique also depends on the reliability of the gas analysis technique subsequently applied to the equilibrated samples. Some of the same concerns about the use of the equilibration-quenching-extraction also apply to the use of the direct reading hydrogen measurement methods such as Telegas I and II™ ALS-CAN™, CHAPEL, Notorp, ALSPEK, and Hycal™ instruments. However, with any method, care must be taken to ensure the attainment of gas-metal equilibrium and the alleviation of identified potential sources of error described in this article.

For the determination of the solubility of hydrogen in solid aluminum and its alloys, the equilibration-quench-extraction technique is the most reliable method. The solubility of hydrogen in solid aluminum and its alloys is much lower than that in the liquid state. Consequently, the expected volume of gas absorbed

and measured in the solid state is so small that it is below the range for which Sieverts' direct absorption method is feasible. The equilibration-quench-extraction technique is also preferred to Eichenauer's isothermal equilibration-extraction technique because it is easier to assess and correct for small errors introduced by hydrogen loss during quenching than for the larger and more uncertain errors due to hydrogen absorption on the apparatus walls and hydrogen loss during intermediate pumping which is inherent in the isothermal equilibration-extraction technique. An additional advantage of the equilibration-quench-extraction technique is that if the extraction of hydrogen from the reheated sample is conducted isothermally and the hydrogen evolution monitored continuously, the information can be used to derive the diffusion coefficients of hydrogen in the aluminum and its alloys [92] [95].

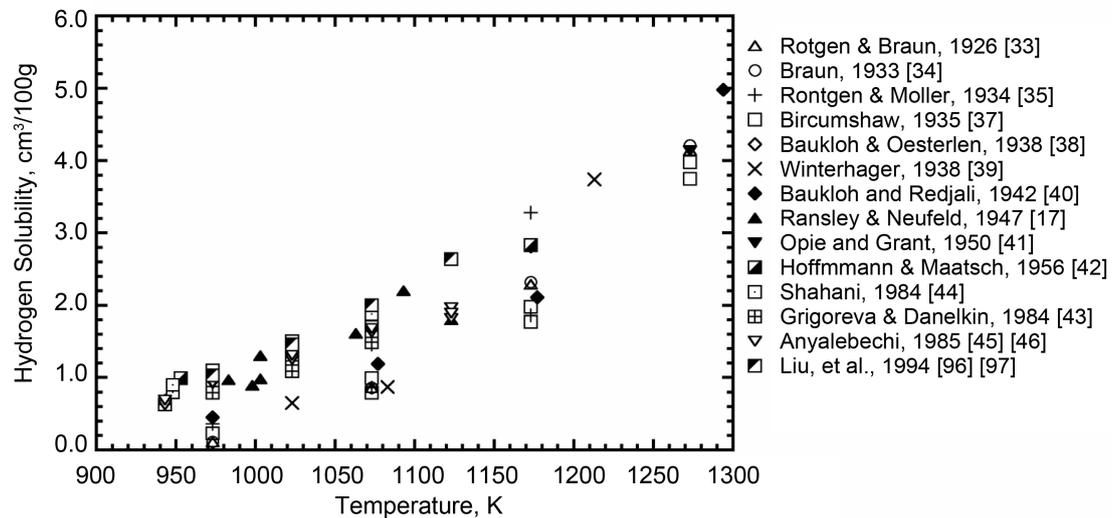
#### 4. Critical Assessment of Reported Hydrogen Solubility Values

In this review, the experimentally determined values for the solubility of hydrogen in liquid and solid pure aluminum are critically assessed against four criteria: 1) *ab initio* or inherent reliability of experimental techniques and methodologies; 2) agreement of reported hydrogen solubility limits with theoretically predicted and well established empirical relationships, such as the Sieverts' isothermic and Van't Hoff isobaric relationships; 3) self-consistency of results reported by investigators; and 4) comparison of results with hydrogen activities in equilibrium with arbitrary hydrogen concentrations. For clarity, the assessment of the published hydrogen solubility values will be classified under two subheadings: *Liquid (or Molten) State and Solid State*. For brevity and completeness, all of the reported hydrogen solubility values are compared graphically and are also given in form of tabulated equations.

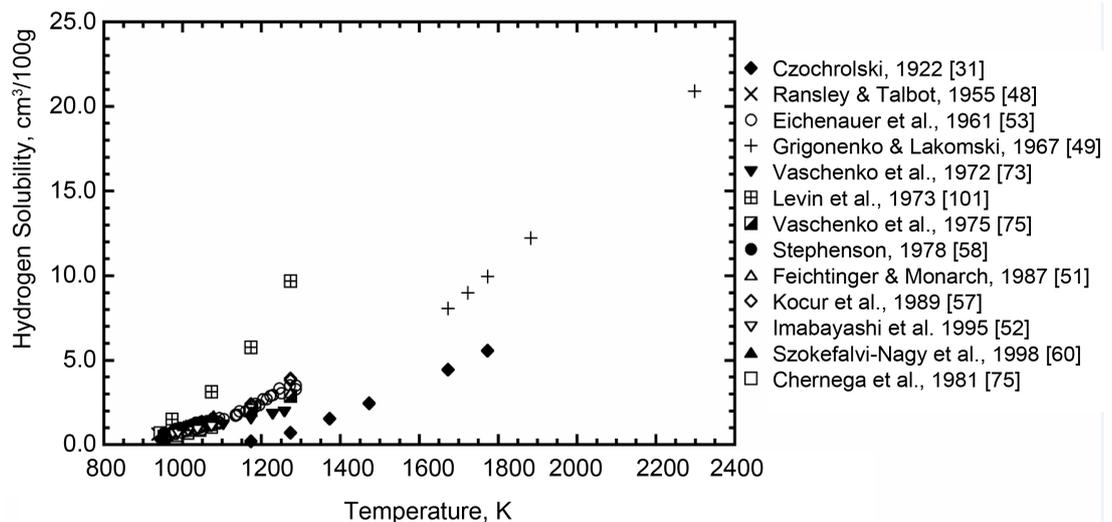
##### 4.1. Liquid (or Molten) Pure Aluminum

The reported values of hydrogen solubility in liquid pure aluminum since 1922 by different investigators and determined with different methods are presented graphically in **Figure 8** and **Figure 9**. For completeness, empirical equations derived from each set of the results are given in **Table 1**. The nominal values of hydrogen solubility at specific temperatures obtained with the different methods are compared in **Table 1**. As apparent in **Figure 8** and **Figure 9**, the twenty-eight sets of reported determinations in the past one hundred years are inconsistent, with significant disparity between different investigators.

For clarity and brevity, the hydrogen solubility values obtained with the Sieverts' method, judged above to be fundamentally the most reliable method for the measurement of hydrogen solubility in liquid metals, will be first critically examined. Then the reliability of the hydrogen solubility values obtained with the other (non-Sieverts') methods will be examined in relation to how they compare with the most reliable results obtained with the Sieverts' method.



**Figure 8.** Comparison of reported hydrogen solubility limits in liquid pure aluminum at 101.3 kPa hydrogen partial pressure determined with the Sieverts' direct absorption method. Iwase's [43] extremely high results are omitted.



**Figure 9.** Reported hydrogen solubility limits in liquid pure aluminum at 101.3 kPa hydrogen partial pressure determined with indirect non-Sieverts' absorption methods by various investigators.

#### 4.1.1. Hydrogen Solubility Results Obtained with the Sieverts' Method

As shown in the preceding sections, Sieverts' direct absorption method is inherently the most reliable method for obtaining accurate gas solubility limits in molten metals. Consequently, in this study, for clarity, results obtained with other methods and techniques are compared against what are deemed to be the most reliable and potentially accurate results obtained with the Sieverts' direct absorption method. Of the twenty-eight reported experimental measurements of hydrogen solubility in liquid pure aluminum in the last ninety-four years, fifteen were determined by the Sieverts' method [17] [32]-[46] [96] [97]. The results of these studies are shown graphically in **Figure 8**. Iwase's [32] results, the earliest reported values of hydrogen solubility in liquid pure aluminum are not included

**Table 1.** Empirical constants for the calculation of hydrogen solubility (in cm<sup>3</sup>/100g) in *liquid* pure aluminum as reported (or derived from reported raw data or graphs) by various investigators.

Investigators	Year	Measurement Method	Temperature range, K	H solubility constants		Reference	Reliable
				A	B		
Czochralski**	1922	Weight	1173-1773	-4733.22	3.510	31	No
Iwase**	1926	Sieverts	973-1198	-4930.86	5.456	32	No
Rontgen and Braun**	1932	Sieverts	973-1273	-6502.28	5.868	33	No
Braun**	1933	Sieverts	973-1273	-6535.91	5.872	34	No
Rontgen and Moller	1934	Sieverts	973-1273	-4008.82	3.687	35	No
Bircumshaw	1935	Sieverts	973-1273	-4877.82	4.439	37	No
Baukloh and Oesterlen***	1938	Sieverts	973-1173	-2567.42	2.635	38	No
Winterhager	1938	Sieverts	1023-1213	-5109.45	4.480	39	No
Baukloh and Redjali**	1942	Sieverts	973-1294	-4005.41	3.772	40	No
Ransley and Neufeld	1948	Sieverts	943-1123	-2638.20	2.672	17	Yes
Opie and Grant	1950	Sieverts	973-1273	-2555.00	2.624	41	Yes
Ransley and Talbot	1955	EQE <sup>#</sup>	937-1073	-2257.40	2.245	48	No
Hofmann and Maatsch	1956	Sieverts	953-1173	-2411.60	2.497	42	Yes
Eichenauer <i>et al.</i>	1961	IED <sup>##</sup>	942-1287	-3178.10	3.046	53	No
Grigonenko & Lakomski	1967	EQE <sup>#</sup>	1673-1883	-2535.50	2.426	49	No
Vaschenko <i>et al.</i>	1972	Permeability <sup>+</sup>	950-1258	-1864.80	1.769	73	No
Levin <i>et al.</i>	1973	EQE	973-1273	-3346.20	3.615	101	No
Vaschenko <i>et al.</i>	1975	Permeability	943-1273	-2260.20	2.236	75	No
Stephenson	1978	Telegas I/EQE	953-1048	-2946.70	2.954	58	Yes
Chernega <i>et al.</i>	1981	Permeability <sup>+</sup>	953-1073	-2888.20	2.708	75	No
Shahani	1984	Sieverts	948-1073	-2680.80	2.771	44	Yes
Grigoreva & Danelkin**	1984	Sieverts	943-1073	-3000.30	2.995	43	No
Anyalebechi & Talbot	1985	Sieverts	943-1123	-2582.90	2.602	45, 46	Yes
Feichtinger & Monarch	1987	EQE <sup>#</sup>	973-1273	-2959.90	2.813	51	No
Kocur <i>et al.</i>	1989	IED <sup>##</sup>	973-1273	-2799.00	2.780	57	Yes
Liu <i>et al.</i>	1994	Sieverts	973-1123	-2964.40	3.062	96, 97	No
Imabayashi <i>et al.</i>	1995	EQE <sup>#</sup>	975-1073	-2357.00	2.222	52	No
Szokefalvi-Nagy <i>et al.</i>	1998	CHAPEL	1003-1078	-2757.90	2.795	60	Yes

<sup>#</sup>For the equation:  $\log_{10} S_H = -\frac{A}{T} + B + 0.5 \log_{10} \left( \frac{P_{H_2}}{P_{H_2}^o} \right)$ ; \*\*Interpolated from graph; <sup>#</sup>EQE—equilibration-quench extraction technique; <sup>##</sup>IED—iso-thermal-equilibration-desorption technique; <sup>+</sup>Calculated from hydrogen permeability and diffusivity data; <sup>++</sup>Telegas instrument and hot vacuum extraction (Ransley) method for determination of hydrogen content. \*\*\*Just three temperature data points.

in the graph because they are unduly high. Although Iwase [32] used the Sieverts' method, his results were unduly high because the conditions of his test resulted in the loss of hydrogen by permeation through the containing vessels of the apparatus, resulting in erroneous hydrogen solubility values. However, the remainder of the hydrogen solubility values obtained with the Sieverts' direct absorption method tend to converge at higher temperatures (1150 - 1325 K) but show considerable divergence at temperatures near the freezing point of pure aluminum. It is also evident in **Figure 9** that there is a significant disparity between the results of some of the earlier studies [32]-[40] with the Sieverts' direct absorption method from 1932 to 1942 and those of later studies from 1947 to 1994 [17] [41]-[46] [96] [97] with the same method. Also, there is significant variability (0.20 - 0.23 cm<sup>3</sup>/100g) within some of the given sets of results at a given temperature. The only set of data from an earlier study that compares reasonably well with the later results is reported by Baukloh and Oesterlen [38] in 1938. This is surprising considering the fact that Baukloh and Oesterlen [38] used argon for determining the dead space of their absorption bulb. However, these results should be ignored for a variety of reasons, namely: 1) they are single test results obtained at just three temperatures, 2) the hydrogen solubility values reported for a wide range of aluminum alloys in the same article have been found to be unreliable [22] [23] [24], and 3) later hydrogen solubility results published by Baukloh and Redjali [40] in 1942 are too low and also unreliable.

The disparity between earlier and most recent results is not surprising considering the significant improvement in measurement technology since those tests were conducted. The lower solubility values reported by earlier investigators and the greater disparity between the reported results of the different investigators at lower temperatures can be ascribed to some of the previously described potential sources of error in the use of Sieverts' direct absorption method. These include failure to reach equilibrium due to the slow permeation of hydrogen through the oxide film of the aluminum melt when the melt is quiescent. This is the case when the molten metal sample temperature is maintained by external heating (with an electrical resistance furnace) as in earlier studies. The second source of error in the earlier studies was the measurement of the hot dead space volume of the absorption bulb through thermal mismatch with hydrogen if an insoluble gas of high relative molar mass, such as argon, is used instead of neon or preferably helium. Also, some of the earlier investigators like Bircumshaw [36] [37] and Iwase [32], used clear silica glass which was directly heated by the electric resistance furnace resulting in the solution and permeation of hydrogen in and through the glass, respectively, leading to erroneous hydrogen solubility values. This problem was circumvented by some of the earlier investigators such as Baukloh and Oesterlen [38], and Ransley and Neufeld [17] by using double-walled quartz absorption vessels. However, later hydrogen solubility limits reported by Grigoreva and Danelkin [43] in 1984 are also too low. This confirms the fact that methodology and experimental conditions are critical to the accuracy and relia-

bility of experimentally determined values of hydrogen solubility even with the Sieverts' direct absorption method. Although they did not give full details of their experiments, it appears that Grigoreva and Danelkin [43] used electric resistant furnace heating. This resulted in long saturation times and the associated loss of hydrogen (and helium used for calibration of volume of absorption vessel) through the walls of the silica absorption bulb or reactor.

It is noteworthy that the last reported experimentally determined values of hydrogen solubility in pure liquid aluminum obtained with the Sieverts' direct absorption method by Liu *et al.* [96] [97] in 1994 are deemed unreliable. This conclusion is contrary to this author's (Anyalebechi [22] [23]) previous inclusion of Liu *et al.*'s [96] and Baukloh and Oesterlen [38] results as part of the reliable sets of data on hydrogen solubility in liquid pure aluminum in an earlier review twenty-six years ago [22] [23]. Liu *et al.*'s results are unreliable for the following reasons:

- 1) The results are inconsistent and generally higher than the previous results that are deemed to be reliable and accurate;
- 2) The values of hydrogen solubility values in Al-Cu alloys reported by the Liu *et al.* [96] have been found to be unreliable [22] [24] because they are 1.5 to 2 times greater than those of previously determined reliable results for the same alloys;
- 3) All of the solubility measurements were strangely made at less than 101.32 kPa (1 atm) hydrogen partial pressure with greater potential for error because of the smaller difference between the hot or dead volume and the actual volume of hydrogen absorbed by the aluminum melt sample;
- 4) The use of argon instead of helium as reference gas in the measurement of the dead or hot volume of the measurement system;
- 5) An absorption bulb (hence measurement system) with large dead volume, 50 cm<sup>3</sup> compared to the much preferred 10 - 15 cm<sup>3</sup>; and
- 6) The use of excessively large samples (300 g compared to 30 - 120 g by other investigators) with its associated overheating of the absorption bulb and attendant diffusion of hydrogen and the calibrating argon or helium gas through the walls of the reactor.

Despite their claims, Liu *et al.*'s results lack self-consistency. In their original study, Liu *et al.* [96] used argon instead of helium as the reference gas to calibrate the dead or hot volume of their absorption bulb. They obtained comparatively higher (10% - 17%) hydrogen solubility values in liquid pure aluminum than the previously reported reliable values, especially at temperatures above 973 K. The difference increased **with an increase in temperature**. In an attempt to explain the disparity between their results and the accepted reported hydrogen solubility limits and their claim that argon should be the preferred reference gas, Liu *et al.* [97] conducted a second but somewhat cursory study using helium as a reference gas. Using helium as reference gas, they re-determined the solubility of hydrogen in liquid pure aluminum at just two temperatures and pressures below

101.32 kPa. They surprisingly obtained much lower (11% - 21% lower) hydrogen solubility values than the previously reported reliable values obtained with the same reference gas and method (**Table 2**). Both sets of the authors' results are clearly inconsistent and unreliable. Despite Liu *et al.*'s [96] [97] claims, helium has long been recognized as the best reference for the measurement of hot volume in the use of the Sieverts' direct absorption method in the measurement of the solubility of hydrogen in metals in general [17] [41] [45] [81] [82] [86]. Helium is the preferred reference gas because its physical and thermal properties are closer than those of argon to the physical and thermal properties of hydrogen (**Table 2**). The thermal conductivity of helium is significantly greater than that of argon but closer to that of hydrogen and is therefore more nearly equivalent to hydrogen in its behavior [98] [99]. Liu *et al.* erroneously attributed their poor hydrogen solubility results to an unlikely and never reported solubility of helium in liquid aluminum. Using argon as a reference gas, they apparently observed measurable solubility of helium in liquid aluminum at two temperatures and at pressures less than 101.3 kPa. Their reported solubility of helium in liquid aluminum is surprising, especially since previous investigators [17] [41] [45] [46] who also used helium for measurement of dead volume with Sieverts' apparatus with even better sensitivity did not observe any discernible helium solubility in aluminum or aluminum alloy melts. This author and my colleagues [45] [46] [81] [100] did not observe any discernible helium solubility in liquid aluminum and Al-Li alloys in a careful investigation over much wider ranges of temperature (943 - 1123 K) and pressure (67 - 113 kPa) than those reported by Liu *et al.* [96] [97]. It is also noteworthy that all of their tests were conducted at hydrogen partial pressures lower than 101.3 kPa. It appears that the apparent "solubility" of helium in molten aluminum observed by Liu *et al.* [96] [97] is not due to the solution of helium in aluminum but due to the diffusion and dissolution of helium in the hot quartz absorption bulb. Large size samples (>200 g) of the aluminum heated by a radiofrequency induction heater tend to raise the temperature of the absorption bulb by radiation more than smaller size samples (100 g). Thus, with

**Table 2.** Comparison of the physical properties of some of potential reference gases [99] [100].

Gas	Atomic wt., g/mol	Atomic radius, nm	Thermal conductivity, mW/m·K		Specific heat, kJ/kg·K	Density, kg/m <sup>3</sup>	Crystal structure
			300 K	600 K			
H	1.008	46	186.6	309.1	14.304	0.089	HCP/cubic
He	4.003	176	155.7	251.6	5.193	0.166	HCP/cubic
Ar	39.95	174	17.7	30.3	0.52	1.66	FCC
Ne	20.18	160	49.4	78.5	1.03	0.839	FCC
Xe	131.29	12.4	5.5	10.3	0.158	5.898	FCC
N <sub>2</sub>	14.01	71	26	41.8	1.040	1.165	Cubic/HCP

300 g sample, it is conceivable that the temperature of Liu *et al.*'s [96] [97] quartz absorption bulb probably exceeded 573 K and resulted in a measurable loss of helium (and probably hydrogen). According to Dushman [85], at 101.3 kPa pressure and 433 K and 703 K, temperatures, 0.1 and 1 cm<sup>3</sup> of helium, respectively, diffuses through 1 cm<sup>2</sup> of 1 mm thick quartz material in 1 hour. In comparison, the same amount of hydrogen diffuses through the same material at 683 and 1108 K, respectively. Also, 0.1 cm<sup>3</sup> of neon diffuses through the same material for the same length of time at 959 K. Ransley and Neufeld [17] have demonstrated that the loss of hydrogen by diffusion through quartz at temperatures of 973 K and above for 2 to 24 hours, yields a significant error in hydrogen solubility results. It is also noteworthy that Liu *et al.*'s Sieverts' apparatus did not have the required sensitivity for the measurement of low gas solubility values such as hydrogen solubility in liquid pure aluminum and their reported apparent helium solubility. This is because the hot (or dead) volume of their Sieverts' apparatus was too large. It was 50 cm<sup>3</sup> compared to the dead volume of 10 - 15 cm<sup>3</sup> reported for other investigators' Sievert apparatus.

Hence, the most reliable and accepted results obtained by the Sieverts' direct absorption method are those reported by Ransley and Neufeld [17], Opie and Grant [41], Hoffman and Maatsch [42], Shahani [44], and Anyalebechi and Talbot [45] [46].

#### 4.1.2. Hydrogen Solubility Results Obtained with Indirect (*i.e.*, Non-Sieverts') Methods

Thirteen of the twenty-eight reported measurements of hydrogen solubility in liquid pure aluminum were obtained with indirect (non-Sieverts') methods. Five of the thirteen measurements were by the equilibration-quench-extraction technique [48] [49] [51] [52] [101], and two by the Eichenauer's isothermal-equilibration-extraction technique [53] [57]. Two sets of results were obtained with the direct reading hydrogen measurement methods by the measurement of known activities of hydrogen in the aluminum melt with the Telegas instrument and the hot vacuum extraction technique [58], and by using a modified CHAPEL [60] instrument. Three other sets of results were calculated from experimentally determined diffusivity and permeability data [73] [74] [75], and the other by saturation of the sample with hydrogen and measurement of the change in weight of the sample purportedly caused by the absorption of hydrogen [31]. The reliability of the reported values of hydrogen in liquid pure aluminum obtained with the indirect methodologies is evaluated by comparing them to the five most reliable hydrogen solubility values obtained with the Sieverts' method. The first reported measured hydrogen solubility values in liquid pure aluminum by Czochralski [31] in 1922 were obtained by measuring the change in the specific weight of aluminum melts saturated with hydrogen at given temperatures. This method is insensitive since the amount of hydrogen absorbed in aluminum is so small that it does not cause any measurable change in the weight of the aluminum melt. This explains why Czochralski's hydrogen

solubility values are the lowest of the values reported (**Figure 9**) and should be disregarded.

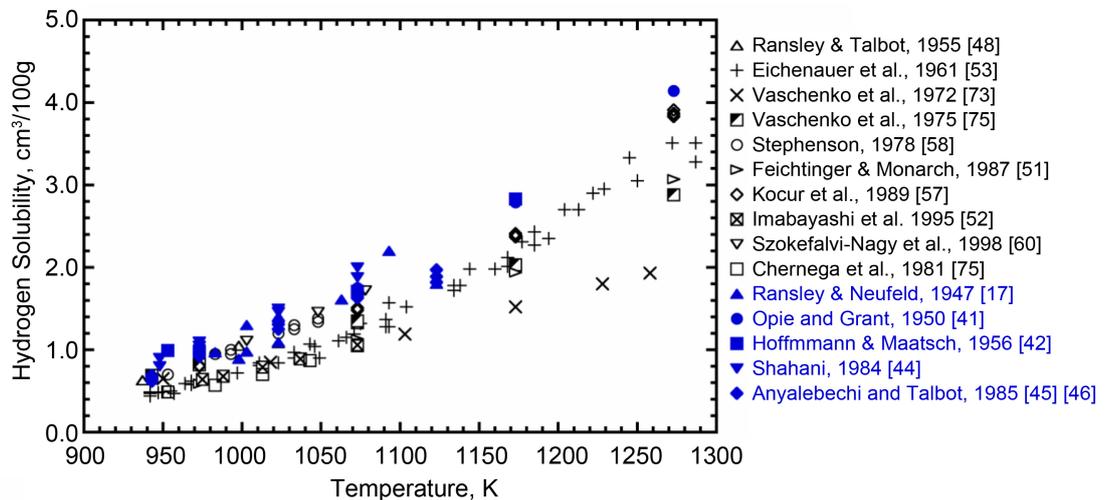
As apparent in **Figure 9**, the hydrogen solubility limits in liquid pure aluminum obtained by Eichenauer *et al.* [53] with the isothermal absorption-desorption technique are significantly lower, especially at the lower temperatures. This is ascribed to the differences in the reliabilities of the two methods rather than to subjective variation between the works of different investigators. As alluded to earlier, the merit of the Sieverts' method is that equilibrium values are measured under equilibrium conditions and it is possible to isolate and evaluate at leisure every potential source of error by suitable supporting and blank determinations. However, the technique used by Eichenauer *et al.* [53] which involves isothermal equilibration of the sample with hydrogen and subsequent desorption of the absorbed hydrogen into a low pressure system requires an intermediate operation. The latter involves the evacuation of the hydrogen from the absorption bulb before connecting it to the collection system. The reliability of the technique therefore depends critically on a correction required for hydrogen desorbed from the melted sample and therefore lost during the intermediate operation. For liquid aluminum, the isothermal-absorption-desorption technique is less appropriate because the expected correction is higher and difficult to assess. For example, it is well known that the sudden application of vacuum to liquid aluminum causes hydrogen to nucleate within the bulk of the liquid metal. In fact, Eichenauer *et al.* [53] admitted that desorption of hydrogen from liquid aluminum was controlled not by diffusion but by other undefined processes. Corrections for the lost hydrogen were made by applying empirical "velocity constants" of an undisclosed nature and no information was given from which to assess the validity of the procedure. The results obtained by Eichenauer *et al.* [53] are therefore inherently subject to systematic error and it is prudent to disregard them. However, the hydrogen solubility values obtained with a modified version of the isothermal absorption-desorption technique by Kocur *et al.* [56] [57] compare fairly well with the accepted results obtained with the Sieverts' direct absorption method. Their study involved isothermal saturation of 18 g sample of molten aluminum with hydrogen followed by immediate isolation of the reaction bulb and more gradual extraction of the absorbed hydrogen into an inert argon gas stream and is subsequently analyzed using a thermal conductivity detector. This approach limited the loss of hydrogen from the melt during the sudden evacuation of the absorption bulb before connecting it to the collection system. The automation of the procedure improved the consistency of their results. Thus, Kocur *et al.*'s [57] results are accepted as being reliable because their self-consistency and reproducibility. Also, their tests were conducted over a wide range of temperature and pressure conditions.

Examination of the results obtained with the equilibration-quench-extraction technique reveals a disparity between the results of five different investigators (**Figure 9**). For example, Levin *et al.*'s [101] results can be disregarded since they

are grossly higher than the reported hydrogen solubility limits by other investigators, including those reported by Ransley and Talbot [48], Feichtinger and Morach [51], Imabayashi *et al.* [52], and Grigonenko and Lakomskii [49], who used a similar method. The reason for the markedly much higher hydrogen solubility values is not clear; it may be because they were calculated from results of tests conducted at very high temperatures, 1770 - 1970 K.

The hydrogen solubility limits reported by Feichtinger and Morach [51] and Imabayashi *et al.* [52] are lower than those reported by Ransley and Talbot [48]. However, solubility limits extrapolated from the results obtained by Grigonenko and Lakomskii [49] at very high temperatures are even lower than those reported by Feichtinger and Morach [51] and Imabayashi *et al.* [52]. The disparity between the reported results obtained with the same equilibration-quench technique is not surprising since the specifics of the tests by the different investigators differed significantly. For example, Grigorenko and Lakomskii [49] conducted their tests at high temperatures (1673 - 2563 K) and they used the high frequency induction heater for melting and maintaining the temperature of the melt. Equilibrium between the melt and hydrogen was reportedly reached in 65 - 90 seconds and the melt was subsequently poured into copper molds. The relatively low values obtained by Grigorenko and Lakomskii [49] may be attributed to the fact that they were extrapolated from solubility values obtained at very high temperatures. At these temperatures, the solubility of hydrogen is expected to be affected by the comparatively high vapor pressure of aluminum. In fact, they found that hydrogen solubility in aluminum increased to a maximum of 20.9 cm<sup>3</sup>/100g at 2,298 K and decreased sharply at higher temperatures approaching the boiling point of pure aluminum. However, they recommended the calculation of hydrogen solubility in liquid aluminum with results obtained at temperatures between 1673 and 1873 K. Other possible sources of error in Grigorenko and Lakomskii's [49] results include loss of hydrogen during pouring of the melt into the copper mold and the short saturation time of 65 - 90 seconds which may have been too short for the attainment of equilibrium between hydrogen and the aluminum melt.

A comparison of the hydrogen solubility values obtained with the equilibration-quench-extraction technique and the reliable values obtained with the Sieverts' direct absorption method confirms the fact that the reported hydrogen solubility limits by Feichtinger and Morach [51] and Imabayashi *et al.* [52] are too low (Figure 10). This may be attributed to the methodologies and experimental conditions used by the different investigators. Feichtinger and Morach [51] used small 9 - 12 g samples heated with an electric resistance furnace. After saturation for 30 minutes, the melt was poured into a copper chill mold through an alumina tube without exposing the melt to the atmosphere. The hydrogen solubility values they reported were relatively low probably because of the short saturation time and the loss of hydrogen from the melt during pouring into and during solidification in the copper chill mold. As shown earlier by Ransley and



**Figure 10.** The hydrogen solubility limits in liquid pure aluminum at 101.3 kPa hydrogen partial pressure obtained with the Non-Sieverts' methods compared to the most reliable hydrogen solubility values obtained with the Sieverts' direct absorption method.

Neufeld [17] and later by Kocur *et al.* [57], the use of electric resistance furnace heating delays the attainment of equilibrium between hydrogen and the aluminum melt, requiring at least 1 hour of equilibration time. Unlike radiofrequency induction heating which induces magnetic-induced stirring, electric resistance heating results in a quiescent melt surface and the presence of a uniform oxide film on the melt surface which impedes the absorption of hydrogen by the melt. Although Kocur *et al.* [56] [57] also used electric resistance furnace heating their reported hydrogen solubility values in the pure aluminum melt are higher than those reported by Feichtinger and Morach [51], Grigonenko and Lakomskii [49]. Kocur *et al.*'s results are much closer to the hydrogen solubility values obtained with the Sieverts' absorption method. This is probably because of their longer saturation times of 60 - 180 minutes. However, despite saturating for longer time (80 - 117 minutes), Imabayashi *et al.*'s [52] results were still low; most likely because of the loss of hydrogen during pouring and solidification of the 40 - 50 g melt. Kocur *et al.*'s [56] [57] results compare much better with those obtained with the Sieverts' direct absorption method than those obtained by Ransley and Talbot [48] who used the same method and saturated for 30 - 60 minutes. Ransley and Talbot's [48] results show fairly good agreement with the reliable hydrogen solubility results obtained with Sieverts' method at lower than 1000 K. At higher temperatures, Ransley and Talbot's [48] results, like the majority of those obtained with the equilibration-quench-extraction technique become progressively lower. Thus, in general, results of hydrogen solubility in liquid pure aluminum obtained with the equilibration-quench-extraction technique are consistently lower than those obtained with the Sieverts' direct absorption method at temperatures above 1073 K because of an increasing loss of hydrogen from the melt during pouring and solidification of the cast samples (Figure 10). Thus, data reported by Ransley and Talbot [48], Grigorenko and Lakomskii [49],

Feichtinger and Morach [51], and Imabayashi *et al.* [52] can be disregarded.

The only set of data of hydrogen solubility in liquid pure aluminum obtained with the Telegas instrument followed by hot vacuum extraction by Stephenson [58] compares fairly well with the hydrogen solubility results accepted to be reliable (Figure 10). Also, the very limited number of values of hydrogen solubility in liquid pure aluminum obtained using a modified CHAPEL method by Szokefgalvi-nagy *et al.* [60] compare fairly well with the hydrogen solubility results accepted to be reliable.

In contrast, the solubility data calculated from experimentally determined hydrogen diffusivity and permeability data in liquid pure aluminum by Chernega *et al.* [75] and Vaschenko *et al.* [73] are markedly lower than the accepted reliable hydrogen solubility limits. They should be disregarded. However, the hydrogen solubility values derived from the diffusivity and permeability results reported by Vaschenko *et al.* [74] in a later study with a modified technique are slightly closer to the other reported results deemed to be reliable (Figure 10). As previously explained, accurate measurement of diffusivity of hydrogen in liquid aluminum is difficult because of the effects of convective currents and the inability to suppress or accurately account for errors associated with it.

#### 4.1.3. The Most Reliable Reported Hydrogen Solubility Limits in Liquid Pure Aluminum

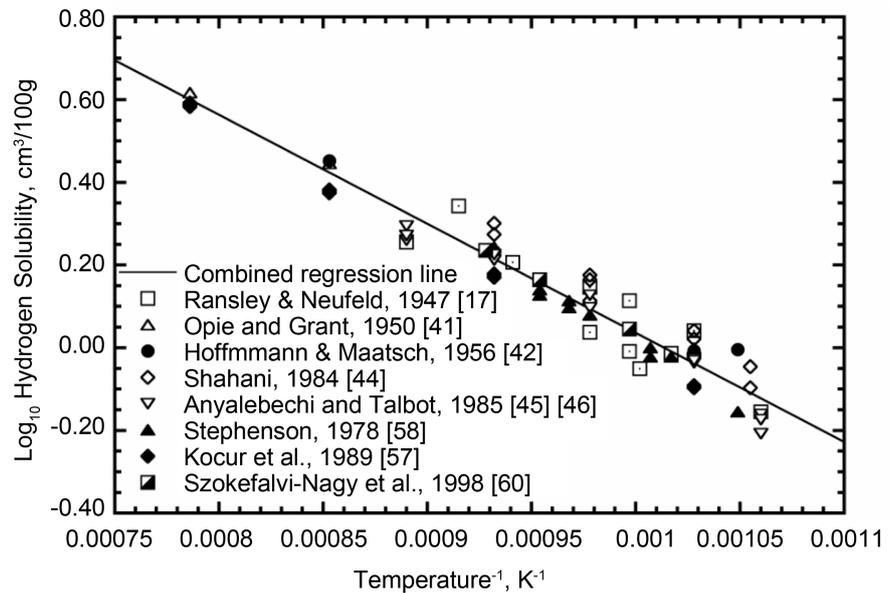
Based on the above critical review, the most reliable available values for the solubility of hydrogen in liquid pure aluminum are those reported by Ransley and Neufeld [17], Opie and Grant [41], Hoffman and Maatsch [42], Shahani [44], Anyalebechi and Talbot [45] [46], Kocur *et al.* [57], Stephenson [58], and Szokefgalvi-nagy *et al.* [60]. Close scrutiny of the fundamental principles of the measurement methodologies and the descriptions of the experimental conditions given by the investigators revealed that the studies were carried out meticulously and with full appreciation of the sources of systematic errors. So, there is no *a priori* reason to prefer any one of the eight sets of results over the others. The most logical approach is to combine the eight sets of experimental results and to recommend values given by linear regression analysis of the common Van't Hoff isobars, using the method of least squares, *i.e.*, assigning the scatter to random errors (Figure 11). This yields the following equation for calculating the solubility at 101.3 kPa (1 atm) hydrogen pressure:

$$\log_{10} S_H, \text{cm}^3/100 \text{ g} = \frac{-2587.50}{T} + 2.623 \quad (R = 0.974) \quad (43)$$

where  $S_H$  = hydrogen solubility in liquid pure aluminum at a given temperature, in  $\text{cm}^3/100\text{g}$ ,  $T$  = temperature in K, and  $R$  is the correlation coefficient.

It can also be given as the following when the hydrogen solubility limit is expressed in wt.%:

$$\log_{10} S_{\text{wt.\%H}} = \frac{-2587.50}{T} - 1.426 \quad (R = 0.974) \quad (44)$$



**Figure 11.** Van't Hoff isobar at 101,325 Pa of the recommended reported hydrogen solubility in liquid pure aluminum and the regression line for the combined results.

where  $S_{wt.\%H}$  = hydrogen solubility in liquid pure aluminum at a given temperature, in wt.%,  $T$  = temperature in K, and  $r$  is the correlation coefficient.

#### 4.1.4. Effect of Hydrogen Partial Pressure on Hydrogen Solubility in Liquid Pure Aluminum

Of the investigators who reported reliable hydrogen solubility values, only Opie and Grant [41], Anyalebechi [45] [46], and Kocur *et al.* [57] examined the effects of pressure. Their results compare very well with each other's at the various temperatures (Figure 12). Regression analyses of the four sets of data at different temperatures yield an equation relating pressure to hydrogen solubility of the form:

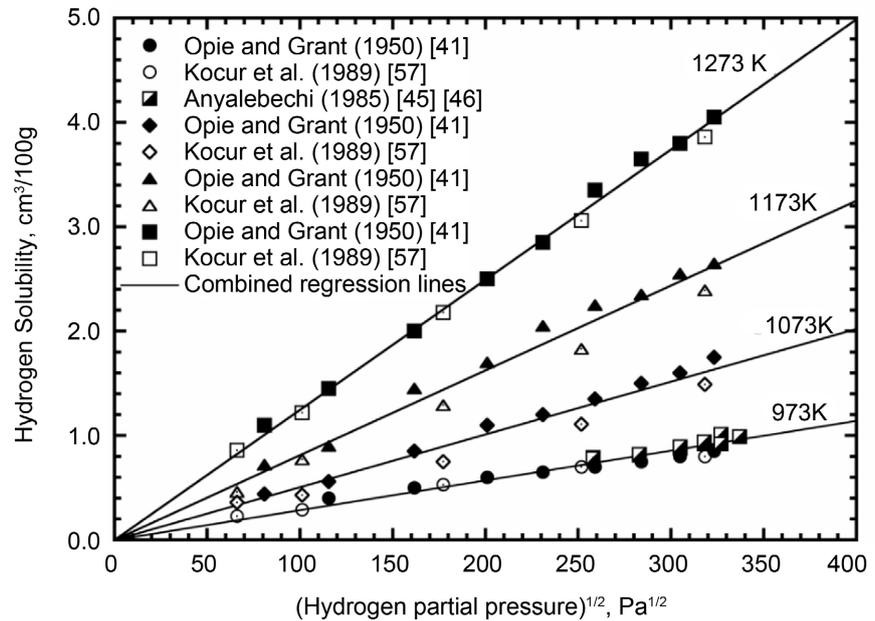
$$S_{wt.\%H} = k_T \sqrt{P_{H_2}} \quad (45)$$

where  $S_{wt.\%H}$  = hydrogen solubility in liquid pure aluminum at a given temperature, in  $\text{cm}^3/100\text{g}$  or wt.%;  $P_{H_2}$  = the hydrogen partial pressure in Pa; and  $k_T$  = a temperature-dependent Sieverts' equilibrium constant in  $\text{cm}^3/100\text{g}/\text{Pa}^{1/2}$  or wt.%H/ $\text{Pa}^{1/2}$ .

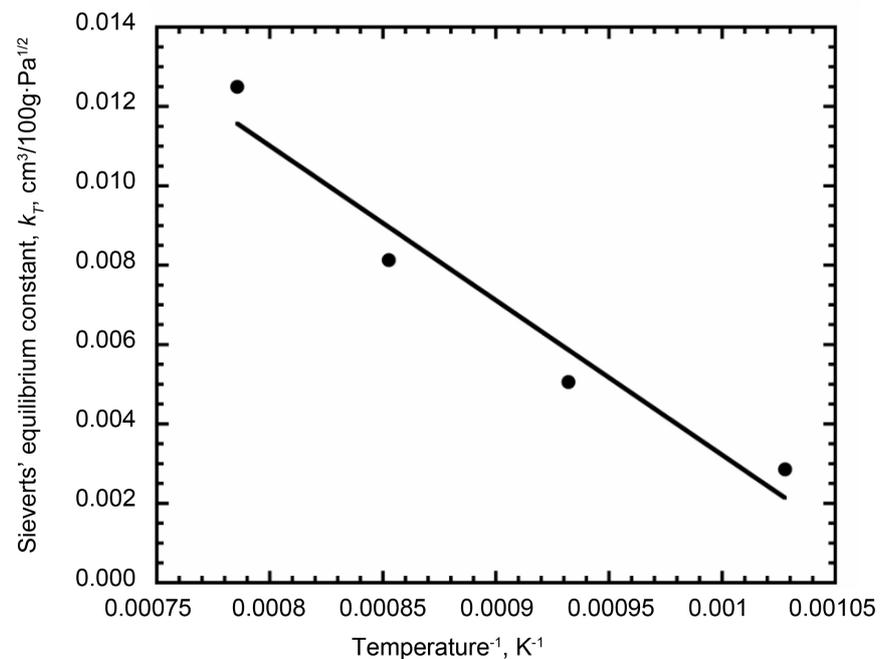
The Sieverts' equilibrium constant as a function of temperature obtained from the combined regression analysis of the reliable hydrogen solubility limits reported by Opie and Grant [41], Anyalebechi [45] [46], and Kocur *et al.* [57] are given in Table 3. As shown in Figure 13,  $k_T$  increases with increase in melt temperature in accordance with the following equation:

$$k_T = \frac{-38.958}{T} + 0.04218 \quad (R = 0.974) \quad (46)$$

where  $k_T$  = a temperature-dependent Sieverts' equilibrium constant in  $\text{cm}^3/100\text{g}\cdot\text{Pa}^{1/2}$ , and  $T$  = temperature in K.



**Figure 12.** Effect of hydrogen partial pressure on the solubility of hydrogen in liquid pure aluminum at different temperatures reported by different investigators.



**Figure 13.** Effect of melt temperature on Sieverts' equilibrium constant for hydrogen solubility in liquid pure aluminum [41] [45] [46] [57].

As Equation (45) shows, hydrogen solution in liquid pure aluminum follows Sieverts' law. That is, the solubility of hydrogen is directly proportional to the square root of the hydrogen pressure. It is noteworthy that, based on the theoretical assumption implicit in the Sieverts' relation, the solubility of hydrogen in metal is zero at zero hydrogen pressure. Thus, introducing pressure as a

**Table 3.** Sieverts' equilibrium constant for the solubility of hydrogen in liquid pure aluminum as a function of temperature.

Temperature, K	Sieverts' equilibrium constant, $k_T$ $\text{cm}^3/100 \text{ g}/\text{Pa}^{1/2}$	Correlation coefficient, $R$	References of combined results
973	$2.855 \times 10^{-3}$	0.985	Anyalebechi [45] [46] Opie and Grant [41] Kocur <i>et al.</i> [57]
1073	$5.059 \times 10^{-3}$	0.987	
1173	$8.128 \times 10^{-3}$	0.989	Opie and Grant [41] Kocur <i>et al.</i> [57]
1273	$12.475 \times 10^{-3}$	0.999	

variable, Equation (44) becomes:

$$\log_{10} S_{\text{wt.\%H}} = -\frac{2587.50}{T} - 1.426 + 0.5 \log_{10} \left( \frac{P_{\text{H}_2}}{P_{\text{H}_2}^o} \right) \quad (47)$$

where  $S_{\text{wt.\%H}}$  = hydrogen solubility in liquid pure aluminum at a given temperature, in wt.%;  $P_{\text{H}_2}$  and  $P_{\text{H}_2}^o$  are, respectively, the hydrogen pressure in Pa, and a standard value of hydrogen pressure equal to 101.3 kPa (*i.e.*, 1 atm).

This equation replaces the previous one recommended by Talbot and Anyalebechi [46] which was based on only the three sets of reported experimental results obtained with the Sieverts' direct absorption method by Ransley and Neufeld [17], Opie and Grant [41], and Anyalebechi and Talbot [45] [46]. It also replaces the equations recommended by this author (Anyalebechi [22] [24]) in an earlier review. Comparison of Equation (45) with the Van't Hoff relationship (*i.e.*, Equation (16)) yields a value for the solution enthalpy and entropy of diatomic hydrogen of 99.1 kJ/mol and 54.61 J/mol·K, respectively.

Equation (45) yields a value for solubility in liquid pure aluminum at the melting point, 933 K, of 0.71  $\text{cm}^3/100\text{g}$  (or  $6.32 \times 10^{-5}$  wt.% H) at 101.3 kPa (*i.e.*, 1 atm) hydrogen partial pressure. This is remarkably consistent with the value of 0.67  $\text{cm}^3/100\text{g}$ , predicted by Anyalebechi and Talbot [33] [56] and by this author (Anyalebechi [22] [24]) in previous reviews twenty six years ago. However, it is clearly different from the recent erroneous claim that the solubility of hydrogen in liquid pure aluminum at 933 K is 0.92  $\text{cm}^3/100\text{g}$  by Tiryakioğlu [28]. The claim is based on a technically wrong interpretation of reported experimentally determined hydrogen solubility limits and a premise that is devoid of any relevant technical reason. It is based on the erroneous assumption that in sixteen data sets, the highest or maximum hydrogen solubility values at different temperatures are supposedly the most reliable hydrogen solubility values. The author [28] claimed, without giving any cogent technical reasons or justification, that the "maximum points" supposedly represent those cases in which the solubility of hydrogen happened to have been reached under experimental conditions. Tiryakioğlu's [28] only reason for this technically flawed recommendation

is that the reported highest hydrogen solubility limit at a given temperature clearly follows a linear trend. This simplistic and incorrect approach revealed the author's [28] lack of fundamental understanding of reported hydrogen solubility values and how they are experimentally determined. Each group of investigators' reported hydrogen solubility values is in fact the maximum concentrations of hydrogen in the metal that are in equilibrium with hydrogen in the surrounding atmosphere at the respective temperatures and partial pressures of hydrogen. It is therefore illogical to capriciously choose the highest or maximum values out of a group of data sets at each temperature and erroneously claim that those are the most reliable values.

## 4.2. Solid Pure Aluminum

Unlike in the liquid state, published values of hydrogen solubility in solid pure aluminum are limited [17] [50] [53] [54] [55] [102]-[115]. As discussed in the preceding section, this is because the solubility of hydrogen in the solid state of pure aluminum is significantly lower than that in the liquid state. In fact, earlier attempts to measure it resulted in the erroneous conclusion that hydrogen was not soluble in solid aluminum [30] [31] [32] [39] [40]. The primary reason for the inability to determine the solubility of hydrogen in solid pure aluminum in the very early experimental attempts was because of the use of the wrong method, namely the Sieverts' method. As previously explained, the Sieverts' method while is good for liquid aluminum is insensitive to the very small hydrogen solubility limits in the solid state of aluminum and its alloys. Determination of the solubility of hydrogen in solid pure aluminum is a much more formidable experimental task than the determination of the hydrogen solubility in the liquid state. This problem is also compounded by the fact that the diffusion of hydrogen into aluminum in the solid state is several orders of magnitude less than that into the liquid [92]. This requires significantly longer saturation times and a small sample size [45] [112]. The latter reduces the measurable amount of hydrogen to even smaller volumes and it becomes much more difficult to determine. All of the above problems associated with the determination of the solubility of hydrogen in solid aluminum are reflected in the comparatively fewer number of determinations and published results (Table 4). Because of the limitations of the measurement of the low hydrogen volume, the solubility of hydrogen in the solid state is measured primarily by two techniques, namely, the equilibration-quench-extraction and the isothermal equilibration-extraction techniques. The latter was developed and exclusively used by Eichenauer and his co-workers [53] [54] [55].

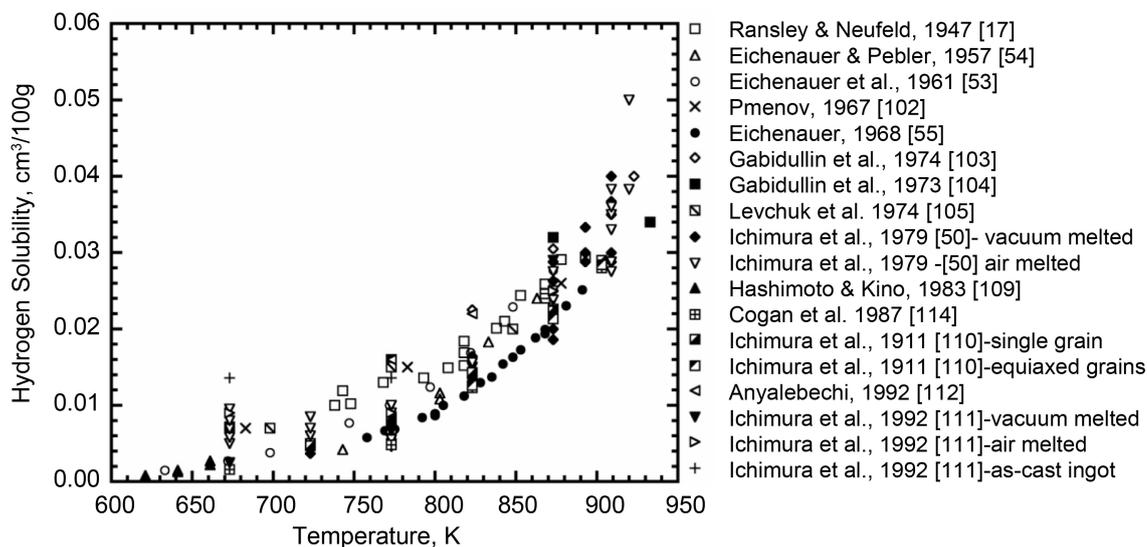
Only nineteen investigators or groups of investigators [17] [50] [53] [54] [55] [102]-[116] have attempted to measure the solubility of hydrogen as a function of temperature in solid pure aluminum. Even fewer investigators have examined the effect of hydrogen pressure in the surrounding atmosphere [17]. Some of the investigators [102] [105] [106] [112] [115] [116] measured the solubility of

**Table 4.** Empirical constants for the calculation of hydrogen solubility (in cm<sup>3</sup>/100g) in *solid* pure aluminum as reported (or derived from reported raw data or graphs) by various investigators.

Investigators	Year	Temperature range, K	Hydrogen solubility constants		H solubility, cm <sup>3</sup> /100g		Sample conditions
			A	B	773 K	823 K	
Ransley and Neufeld	1947	738 - 893	-1942.20	0.628	0.013	0.018	Cold rolled
Eichenauer and Pebler	1957	743 - 863	-4088.60	3.148	0.007	0.015	Cast ingot
Eichenauer <i>et al.</i>	1961	633 - 873	-2942.50	1.815	0.010	0.017	As-cast
Pmenov	1967	683 - 878	-1783.60	0.452	0.014	0.019	?
Eichenauer	1968	758 - 891	-3347.40	2.155	0.007	0.012	Extruded bar
<i>Zhukhovitsky et al.</i>	1972	823	-	-	-	0.062	
<i>Gelman</i>	1972	823	-	-	-	0.026	?
Gabidullin <i>et al.</i>	1974	773 - 923	-1901.00	0.663	0.016	0.023	
Gabidullin <i>et al.</i>	1973	673 - 933	-1695.50	0.394	0.016	0.022	
Levchuk <i>et al.</i>	1974	698 - 848	-1847.70	0.509	0.013	0.018	
<i>Andreev et al.</i>	1976	773, 823	-4300.00	3.325	0.006	0.013	<i>Extruded rod,</i>
Ichimura <i>et al.</i>	1979	723 - 909	-3360.90	2.237	0.008	0.014	Vacuum melted
		673 - 920	-2081.60	0.777	0.012	0.018	Air melted
Ichimura & Imabayashi	1980	673 - 913	-981.40	0.066	0.063	0.075	Air melted
Hashimoto and Kino	1983	621 - 661	-4901.00	4.790	0.028	0.068	
Cogan <i>et al.</i>	1987	673 - 903	-5931.90	4.884	0.002	0.005	
Ichimura <i>et al.</i>	1991	723 - 903	-2945.10	1.735	0.008	0.014	Single grain
		773 - 903	-3400.53	2.235	0.007	0.013	Equiaxed grain
<i>Anyalebechi</i>	1992	773, 823	-1975.70	0.753	0.016	0.022	<i>Extruded rod</i>
			-3063.10	1.908	0.009	0.015	Vacuum melted
Ichimura <i>et al.</i>	1992	673 - 873	-1215.60	-0.305	0.013	0.017	Air melted
			-625.21	-0.971	0.017	0.019	As-cast ingot
		673 - 825	-3233.99	2.368	0.013	0.023	Air melted, 0.05 wt.% Ti
		673 - 826	-3301.00	2.411	0.014	0.025	N <sub>2</sub> melted, 0.05 wt.% Ti
Ichimura and Sasajima	1993	673 - 827	-2707.60	1.629	0.013	0.022	Air melted, 0.10 wt.% Ti
		673 - 828	-2707.60	2.182	0.021	0.037	N <sub>2</sub> melted with 0.10 wt.% Ti

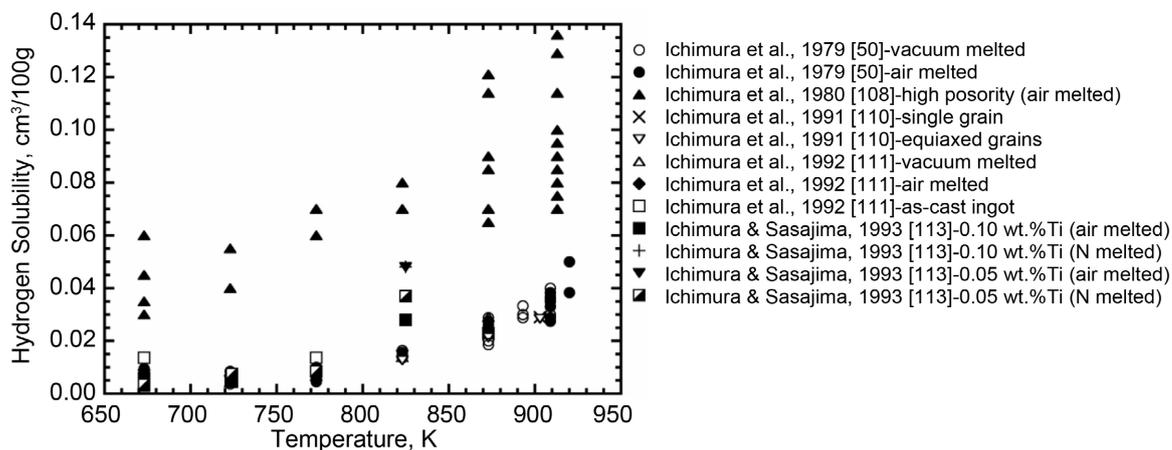
hydrogen at less than four different temperatures as part of programs designed to investigate the effects of alloying elements (or chemical composition) on the solubility of hydrogen in solid aluminum.

As apparent in **Figure 14**, there is a significant disparity between the reported



**Figure 14.** Reported hydrogen solubility in solid pure aluminum as a function of temperature at 101,325 Pa by different investigators.

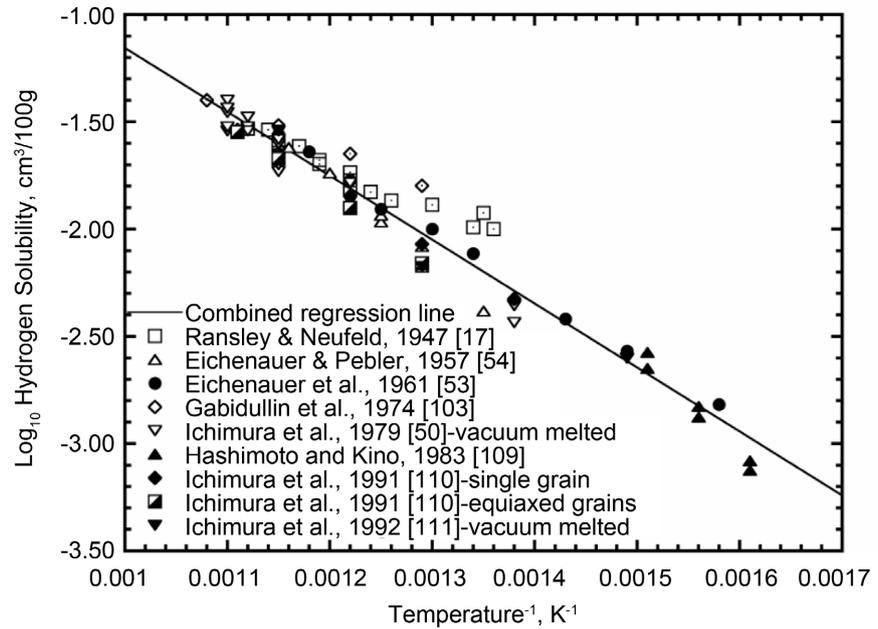
hydrogen solubility limits in solid pure aluminum. The disparity is not only between results reported by different investigators but in results published by the same group of investigators. The reason for the latter is partly due to the different sample conditions, and in some cases, different methodology. For example, the results published by Eichenauer [55] in 1968 is consistently lower than the hydrogen solubility limits reported by other investigators' and his previously reported results [53] [54] (Figure 14) and should be disregarded. Eichenauer [55] did not provide any explanation for the lower solubility values, although he speculated that coarsening of the grains in the sample could have caused it. However, it appears that the discrepancy was due to the different types of samples used in the different investigations. For example, in his first study with Pebler [54], Eichenauer used samples from a continuously cast ingot which were kept at test temperature for two weeks and repeatedly saturated with hydrogen (gassed) and degassed until reproducible hydrogen gas desorption curves could be obtained. In the second study [53], super purity aluminum samples etched in a hydrofluoric-chromic acid mixture were used; whereas in the last study [55] that yielded lower hydrogen solubility results, extruded super purity aluminum samples were used. Another example is the significant disparity between the results published by Ichimura with different co-workers [50] [108] [110] [111] [113] from 1979 to 1993 (Figure 15). This is not necessarily because of an inherent flaw in their technique and methodology, but rather a clear demonstration of the significant effects of sample condition on the solubility of hydrogen in solid pure aluminum. As apparent in Figure 15, the condition of the sample used profoundly affects the hydrogen solubility limits in solid pure aluminum. For example, the pre-existence of porosity and oxide films and inclusion in the sample results in much higher hydrogen solubility limits. This is not surprising since interdendritic and gas pores, oxide films and inclusions in ingots act as sites for additional



**Figure 15.** Effect of porosity on measured hydrogen solubility in solid pure aluminum as a function of temperature at 101,325 Pa hydrogen partial pressure reported by Ichimura and his co-investigators [50] [108] [110] [111] [113].

hydrogen solution and thus increase hydrogen solubility. They are considered to be molecular traps. Because the presence of porosity, oxide films, and inclusions cannot be controlled, they also cause significant scatter and non-reproducibility of the hydrogen solubility limits at any given temperature, especially at higher temperatures. Consequently, Ichimura *et al.*'s values of hydrogen solubility in solid pure aluminum determined with samples that contain both shrinkage and gas porosity should be disregarded. These are results obtained with samples cast in air or nitrogen atmosphere [50] [108] [111] [113].

For statistical reasons, the results of measurements conducted at less than three different temperatures by Andreev *et al.* [107], Anyalebechi [112], Gelman [115], and Zhukhovitsky *et al.* [116], will be excluded from further consideration and the regression analysis. Thus, the results to be evaluated are those determined within an acceptable range of temperature. Of these, results of Gabidullin *et al.* [103] [104] are much higher than the other published values at both the high and low temperature test conditions and should be ignored (Figure 14). Cogan *et al.*'s [114] results should also be ignored because they are consistently low at both low and high temperatures. More importantly, details of Gabidullin *et al.* [103] [104] and Cogan *et al.*'s [114] experimental conditions and methodology are not given in the publications. This makes it difficult to determine whether the disparity between their results and those of other investigators is due to experimental errors or due to flaws in their methodology. Consequently, the most reliable and preferred hydrogen solubility limits for solid pure aluminum are those reported by Ransley and Neufeld [17], Eichenauer and Pebler [54], Eichenauer *et al.* [53], Hashimoto and Kino [109], Levchuk *et al.* [105], and some of Ichimura *et al.*'s results obtained with carefully prepared vacuum melted cast samples [50] [110] [111]. It is noteworthy that the results deemed to be reliable were obtained with both as-cast, cold and hot rolled, single, equiaxed, and columnar grains. A Van't Hoff isobaric plot of the results is presented in Figure 16.



**Figure 16.** Van't Hoff isobar at 101,325 Pa of the recommended reported hydrogen solubility in solid pure aluminum and the regression line for the combined results.

Combined regression analysis of these results yields the following equation for the solubility of hydrogen in the solid state of pure aluminum:

$$\log_{10} S_H, \text{cm}^3/100 \text{ g} = -\frac{2981.6}{T} + 1.827 \quad (R = 0.978) \quad (48)$$

where  $S_H$  = the solubility of hydrogen in  $\text{cm}^3/100\text{g}$ ,  $T$  = temperature in K, and  $r$  is the correlation coefficient.

It can also be given as the following equation when the hydrogen solubility limit is expressed in wt. %:

$$\log_{10} S_{\text{wt.\%}H} = -\frac{2981.9}{T} - 2.222 \quad (R = 0.978) \quad (49)$$

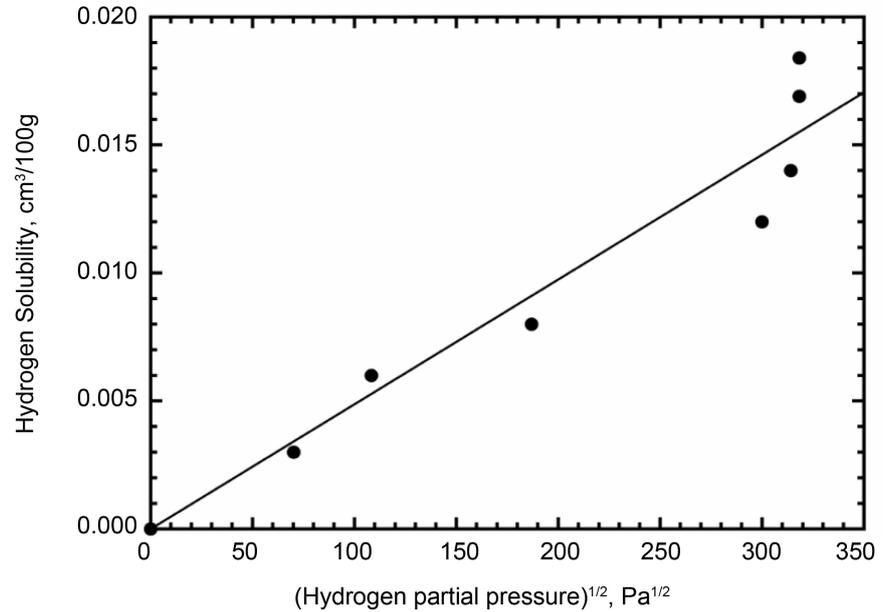
where  $S_{\text{wt.\%}H}$  = hydrogen solubility in solid pure aluminum at a given temperature, in wt. %, and  $T$  = temperature in K.

### Effect of Hydrogen Partial Pressure on Hydrogen Solubility in Solid Pure Aluminum

Of the above investigators, only Ransley and Neufeld [17] measured the solubility in solid pure aluminum as a function of hydrogen partial pressure (Figure 17). They found that at 818 K and within a pressure range of 4.9 - 101.3 kPa, the solubility of hydrogen in solid pure aluminum obeys Sieverts' law, in accordance with the following equation:

$$S_{H,818 \text{ K}}, \text{cm}^3/100 \text{ g} = 4.875 \times 10^{-5} \sqrt{P_{H_2}} \quad (R = 0.966) \quad (50)$$

where  $S_{\text{wt.\%}H,818 \text{ K}}$  = solubility of hydrogen in solid pure aluminum at 818 K, and  $P_{H_2}$  = hydrogen partial pressure of hydrogen in Pa. If the solubility of hydrogen expressed in wt. %, Equation (50) becomes:



**Figure 17.** Effect of hydrogen partial pressure on the solubility of hydrogen in solid pure aluminum at 818 K (Ransley and Neufeld [17]).

$$S_{wt.\%H,818K} = 4.350 \times 10^{-9} \sqrt{P_{H_2}} \quad (R = 0.966) \quad (51)$$

where  $S_{wt.\%H,818K}$  = solubility of hydrogen in solid pure aluminum at 818 K, and  $P_{H_2}$  = hydrogen partial pressure of hydrogen in Pa.

Thus, introducing pressure as a variable, Equation (29) becomes:

$$\log_{10} S_{wt.\%H} = -\frac{2981.9}{T} - 2.222 + 0.5 \log_{10} \left( \frac{P_{H_2}}{P_{H_2}^o} \right) \quad (52)$$

where  $S_{wt.\%H}$  = hydrogen solubility in solid pure aluminum at a given temperature, in wt.%;  $P_{H_2}$  and  $P_{H_2}^o$  are, respectively, the hydrogen pressure in Pa, and a standard value of hydrogen pressure equal to 101.3 kPa (*i.e.*, 1 atm).

Comparison of Equation (48) with the Van't Hoff Equation (16) yields a value for the solution enthalpy of 114.19 kJ/mol and entropy of 85.09 J/mol·K. Equation (52) yields a value for solubility in solid pure aluminum at the melting point, 933 K, of 0.043 cm<sup>3</sup>/100g (*i.e.*,  $3.81 \times 10^{-6}$  wt.% H) at 101.3 kPa hydrogen partial pressure. Consequently, the partition coefficient of hydrogen solution in pure aluminum is 0.0606. The partition coefficient is defined as:

$$k = \frac{S_{H,solid}}{S_{H,liquid}} \quad (53)$$

where  $k$  = partition coefficient, and  $S_{H,solid}$  and  $S_{H,liquid}$  are the solubility of hydrogen in solid and liquid pure aluminum, respectively, at the solidification front (*i.e.*, melting temperature).

## 5. Conclusions

The following have been deduced from a comprehensive and critical examina-

tion of the fundamental principles of the methods used in the measurement of the solubility of hydrogen in liquid and solid aluminum and the reported values in the literature:

1) The reproducibility, accuracy, and hence, reliability of the values of hydrogen solubility obtained in a given experimental study depends on: a) measurement method, b) the state of the material, *i.e.*, liquid, semi-solid, or solid, c) alloy composition, d) temperature and pressure conditions, and e) expected nominal volume of hydrogen absorbed by the sample at the given experimental conditions.

2) The most reliable techniques for the measurement of hydrogen solubility in liquid and solid aluminum and its alloys are the Sieverts' direct absorption method and isothermal equilibration-quench-extraction method, respectively.

3) Equations for calculating the most reliable values of the solubility of hydrogen in liquid and solid pure aluminum as a function of temperature and pressure have been obtained from combined regression analyses of the most reliable sets of published hydrogen solubility values.

4) At 101.3 kPa (*i.e.*, 1 atm) hydrogen partial pressure and the melting point (933 K) of pure aluminum, the solubility of hydrogen is 0.71 cm<sup>3</sup>/100g (or 6.32 × 10<sup>-5</sup> wt.% H) and 0.043 cm<sup>3</sup>/100g (*i.e.*, 3.81 × 10<sup>-6</sup> wt.% H) in the liquid and solid state, respectively. Thus, the partition coefficient of hydrogen in pure aluminum is 0.061.

## Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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