relaxation as opposed to Paul and Sautet [9] who have considered a frozen palladium lattice, albeit with a very large lattice parameter. The value calculated by Tománek et al. [4] (−51 kJ/mol) is somewhat more negative than the values calculated by Dong et al. [5] (−35 to −39 kJ/mol); however, all of the energies given in Ref. [4] are more exothermic than the values reported in other references.

No experimentally measured heats of formation have been quoted in the above mentioned papers [4,5,9] as a basis for comparison. In the next section, the experimentally measured heats of formation for palladium hydride are examined.

3. Experimental heats of absorption and adsorption

3.1. Heat of formation of palladium hydride

The hydrogen–palladium system has been extensively studied over the last century and a half. (See for example Gillespie and Ambrose [18] and references therein.) As hydrogen dissolves in palladium metal the hydrogen atoms occupy the octahedral interstitial sites of the fcc metal sublattice, see Fig. 2. In these octahedral sites the hydrogen atom occupies a very similar position to the position occupied by hydrogen adsorbed in the fcc sites on a palladium (1 1 1) surface. If all of the octahedral sites were occupied the limiting composition would be PdH with the NaCl structure [19]. However the stoichiometric composition has never been attained [20]. Experimental error, such as the difficulty of attaining equilibrium and sample impurities, is blamed for conflicting data obtained for H:Pd ratios [21,22].

There are two phases in the palladium–hydrogen system. The α-phase is a solution phase and has lattice constants close to palladium metal. At room temperature the hydrogen:palladium ratio for this phase is 0.03. As more hydrogen dissolves in the
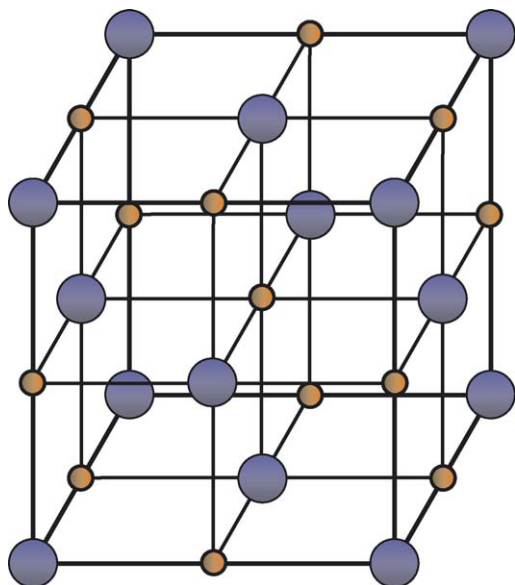
Fig. 2. Unit cell of palladium metal showing octahedral sites that would be occupied by hydrogen in β-palladium hydride, for the limiting H:Pd ratio of 1. Note that the same sites are occupied by hydrogen in α-palladium hydride, at a considerably lower H:Pd ratio.
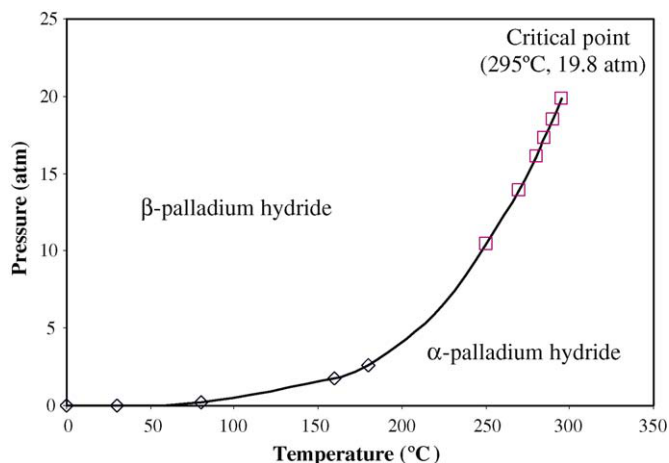
Fig. 3. Pressure–temperature phase diagram for the H:Pd system: ◇, data of Gillespie and Hall [26] and □, data of Gillespie and Galstaun [22].

metal, the lattice constants increase linearly with pressure, until the β-phase appears [23,24]. The composition of the β-phase is approximately 0.6 at room temperature. When the system switches from one phase to the other depends on the pressure and temperature at which the isotherm is being measured.

Unlike all other hydrides (except chromium hydride), both the α- and the β-phase have the same metal lattice structure and consist of octahedrally coordinated hydrogen atoms [20]. For all other metal hydrides the tetrahedral sites (which are equivalent to hcp sites on the surface) fill up first and then the octahedral sites begin to fill [20]. It is thought that there is a critical point at 295 °C and 19.8 atm above which only one phase exists [22]; Maeland and Gibb [23] found the critical temperature to be 308 °C. See Fig. 3 for a pressure–temperature phase diagram drawn using data from Gillespie and Hall [26] and Gillespie and Galstaun [22].

The reason for the atomic ratio for β-palladium hydride being so elusive is probably that as the vacancies in the palladium lattice fill up, the lattice expands, creating more vacancies [21]. In other words, the number of available sorption sites increases continuously as the lattice expands [17]. As a result of this continuous expansion of the palladium hydride lattice as the hydrogen content increases, the heat of absorption (or formation of palladium hydride) is thought to be a function of composition [25].

The heat of absorption is measured [18,22,26] by adding a known volume of hydrogen to an evacuated chamber that contains a sample of palladium metal (free of impurities) of known mass. The pressure and temperature are recorded once the system has equilibrated. Since the volume of the chamber is known, the amount of hydrogen absorbed by the palladium metal can be calculated. By increasing (or decreasing) the pressure, isotherms can be measured and the ratio of hydrogen to palladium atoms can be calculated.

Gillespie and Hall [26] found that the heat of absorption for the α-phase increases with increasing hydrogen content, and obtained the heat of formation of β-palladium hydride by integrating along the isotherms and using the Clausius–Clapeyron equation. The limits of integration are not given.