

Review

Review of absorption and adsorption in the hydrogen–palladium system

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Received 3 January 2006; received in revised form 25 April 2006; accepted 5 May 2006

Available online 5 July 2006

Abstract

The hydrogen–palladium system has been the subject of much study, both experimentally and computationally. In this review article the authors have set out to draw a comparison between the experimentally determined thermodynamic data for this system and the calculated energies, in order to attempt to bridge the gap between computational chemistry and experimental work and so gain insight into the absorption and adsorption of hydrogen on palladium.

Rigorous thermodynamic analysis of the data for the absorption of hydrogen into palladium metal shows that although constant volume measurements have been made, the analysis that has been applied in the literature in several instances is valid only for a constant pressure system. Re-analysis of the data has lead to a heat of formation for β -palladium hydride which is not a function of composition and a weak function of temperature. Values for the internal energy of absorption of -36.7 , -35.2 and -34.4 kJ/mol of H_2 were obtained at $0^\circ C$ and in the temperature ranges from 200 to $313^\circ C$ and from 366 to $477^\circ C$, respectively. There is a good agreement between these values and the calculated values.

The implicit assumptions that underpin the integrated form of the Clausius–Clapeyron equation are that an isobaric system is being analyzed, and that the enthalpy is not a function of composition or temperature. Since heat of adsorption is known to be a function of surface coverage and is generally measured in a constant volume system, the application of the integrated Clausius–Clapeyron equation to determine the enthalpy of adsorption as a function of surface coverage has been questioned and an alternative thermodynamic analysis has been proposed that enables one to calculate the differential change in internal energy of adsorption with surface coverage. It has been found that the internal energy of adsorption varies with increasing surface coverage in a similar manner to the way in which internal energy varies as two atoms approach each other. It is noted that the variation in internal energy with surface coverage ($0.1 < \theta < 0.94$) calculated in this work is of the order of 100 J/mol, while the heat of adsorption in the literature is of the order of $-87,000$ J/mol. Thus, except at very high coverages, the change in internal energy or enthalpy of adsorption with changes in surface coverage is very small compared to the overall heat of adsorption.

The computationally determined energies of adsorption do not reflect this trend and appear to under estimate the electrostatic repulsion (or over estimate the attraction) between gas phase molecules and atoms that are already adsorbed on the surface for this system.

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Keywords: Surface coverage; Experimental and computational determination of heat of adsorption; Heat of absorption; Palladium hydride; Hydrogen adsorbed on palladium

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Nomenclature

A	moment of inertia of a hydrogen atom
E_{ads}	heat of adsorption
f_{H_2}	fugacity of hydrogen
h	interlayer spacing
ΔH	change in enthalpy
ΔH_{abs}	heat of absorption or heat of formation of palladium hydride
ΔH_{ads}	heat of adsorption for M_s atoms of hydrogen
k	Boltzmann constant
l	lattice parameter, length of the unit cell so that $l = \sqrt{3}h$
m	mass of a hydrogen atom
M_s	number of hydrogen atoms adsorbed on the surface, or absorbed into the bulk
M_2	number of hydrogen molecules in the gas phase
n_{H_2}	number of moles of absorbed hydrogen molecules (may be adsorbed as atomic species)
N_A	Avogadro's number
N_s	the number of holes in the palladium lattice available to receive hydrogen atoms, or the number of surface sites available for adsorption
p	pressure of hydrogen in the gas phase
R	ideal gas constant
T	system temperature
ΔU	change in internal energy
ΔU_{abs}	cumulative internal energy of absorption for M_s atoms of hydrogen (to obtain the heat of absorption per molecule of hydrogen, the value obtained would need to be multiplied by 2 and divided by the number of atoms adsorbed)
$\Delta \hat{U}_{\text{ads}}$	the internal energy of adsorption per mole of hydrogen molecules adsorbed
V	volume of M_2 hydrogen molecules in the gas phase at p , T so that M_2/V is the inverse of the specific volume of the gas

Greek symbols

α, α'	constant (of integration)
θ	surface coverage
θ_{ave}	surface coverage that is the average value between θ_1 and θ_2
θ_{min}	surface coverage that corresponds to the minimum in $\theta_{\text{ave}}\chi$
θ_1, θ_2	surface coverage corresponding to a particular point
$\nu(T)$	partition function of a hydrogen atom
$\Delta\phi$	change in work function
$\Delta\phi_{\text{max}}$	maximum change in work function, i.e. at the highest surface coverage observed

χ_0	lowest quantum state of an atom absorbed in the palladium lattice
χ_d	dissociation energy of hydrogen from its lowest quantum state
χ	energy of absorption associated with one hydrogen atom
χ_1, χ_2	energy of absorption associated with one hydrogen atom at θ_1 and θ_2 , respectively

1. Introduction

Palladium is well-known for its selectivity and activity in hydrogenation reactions. The aim of this review is to gain an understanding of the adsorption of hydrogen on palladium, in order to gain insight into catalytic hydrogenation. A major trend in the catalysis literature in the last 15 years is the increase in the number of papers on computational chemistry. In these papers the interactions of molecules with catalytic surfaces are considered, as well as the interaction of adsorbed molecules with one another. Although the authors of computational chemistry papers tend to refer to experimental studies to verify their work, fewer experimentalists appear to be following the computational chemistry literature. In order to unlock the power of computational chemistry the fields need to become more integrated. This review has been written not from the point of view of evaluating different computational methods, but from the viewpoint of evaluating the reliability of the results generated computationally so as to determine where these results can be safely applied. Therefore it focuses on trying to resolve the discrepancies in heats of adsorption and absorption published both in experimental and computational studies for the hydrogen–palladium system.

As mentioned by Watson et al. [1], catalyzed chemical reactions are complex and involve the interaction of the species present with the catalyst surface, so that the isolation of one factor is of limited value. However, since molecular modelling involves building up a system from isolated components, these studies have tended to focus on one or another component. Moreover it is worth examining the components of the system to ensure that when the models are used in the complex systems they at least represent the behavior of the components accurately.

Hydrogen readily dissociates on palladium surfaces. In addition hydrogen atoms diffuse into the subsurface layers of the metal to form palladium hydride. Thus the gas phase hydrogen molecules and the adsorbed surface atoms are in equilibrium and, further, the hydrogen atoms adsorbed on the surface are in equilibrium with the absorbed subsurface hydrogen atoms that form palladium hydride within the metal

lattice [2]. It has been found that hydrogen carries a negative charge in palladium hydride [3] and similarly for hydrogen adsorbed on palladium surfaces [2].

Although it was the intention of the authors of this review to focus on work published in the last fifteen years, it seemed

important to consider earlier work as well, particularly with respect to palladium hydride.

The structure of this review is as follows: the results of various computational studies will be presented, followed by a discussion of the absorption of hydrogen into palladium. The

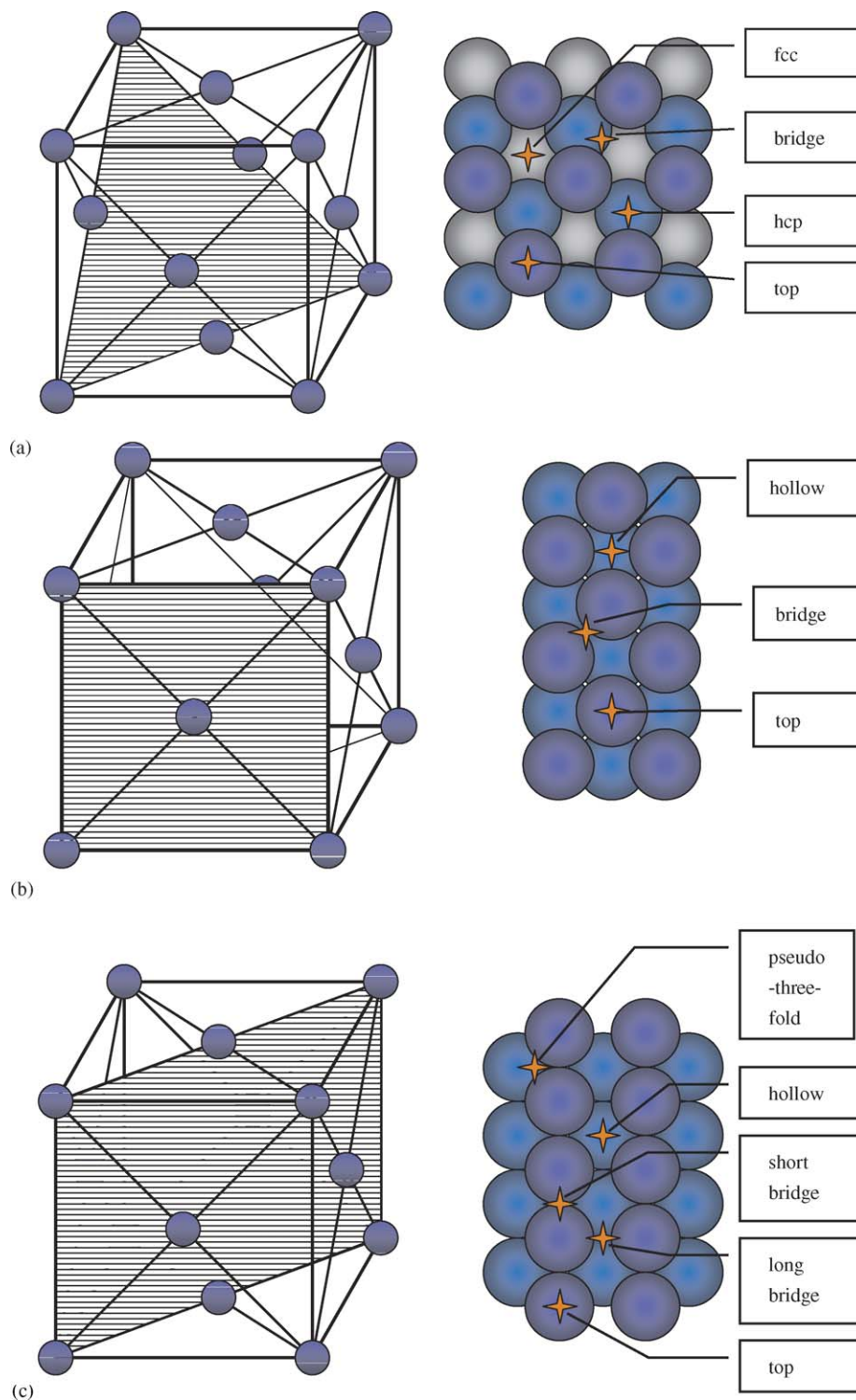


Fig. 1. (a) Palladium unit cell showing (1 1 1) plane; schematic representation of fcc, bridge, hcp and top adsorption sites for palladium (1 1 1) plane. (b) Palladium unit cell showing (1 0 0) plane; schematic representation of hollow, bridge and top adsorption sites for palladium (1 0 0) plane. (c) Palladium unit cell showing (1 1 0) plane; schematic representation of pseudo-three-fold, hollow, short bridge, long bridge and top adsorption sites for palladium (1 1 0) plane.

conventional way of analyzing data to determine the heat of adsorption of hydrogen on palladium will be discussed and an alternative will be proposed. Lastly, surface diffusion will be considered and conclusions will be drawn.

2. Computational chemistry studies of the hydrogen–palladium system

Palladium metal has a face centered cubic (fcc) structure. Several different faces for palladium metal crystals have been considered in computational studies: (1 1 0) and (1 0 0) [4,5] although most studies [1,5–11] focus on the (1 1 1) plane, which is the most densely packed (Fig. 1).

There are four different possible adsorption sites for hydrogen atoms on a palladium (1 1 1) surface: a bridge site between two palladium atoms, on top of a palladium atom, in a hollow between three palladium atoms, termed an hexagonal close packed (hcp) site when there is a palladium atom in the layer directly beneath the surface layer, or fcc when there is a hole in the layer directly beneath the surface layer [9]. The fcc site is consistently found by calculation to be the most stable of these sites, followed by the hcp and bridge sites (see Table 1). Experimental studies concur that hydrogen atoms adsorb on the fcc sites of palladium, see for example Mitsui et al. [12].

For the (1 0 0) palladium surface, there are three possible adsorption sites: a hollow between four palladium atoms, a bridge between two surface atoms or on top of a palladium atom. Computationally the hollow site has been shown to give the most favorable adsorption [4,5], see Table 2.

For palladium (1 1 0), the least densely packed of the surfaces considered, the situation is more complex. The site on which hydrogen adsorbs preferentially, as determined experimentally, is a pseudo-three-fold site [13]. This site is asymmetrical and so the computational requirements are very

high [4]. As a result, calculations have not been done for the pseudo-three-fold site in every instance, although it is thought that the pseudo-three-fold site will be similar to the more symmetric bridge and hollow sites [4], see Table 2.

Authors of computational chemistry papers [1,4,5,7–11] refer consistently to the results of their calculations as heats of adsorption or energies of adsorption, using the symbol E_{ads} or ΔE_{ads} , carefully avoiding terms from classical thermodynamics such as enthalpy or internal energy. Statistical thermodynamics would lead naturally to the calculation of an internal energy [14], usually given the symbol of E in statistical thermodynamics and U in classical thermodynamics. To convert an internal energy to an enthalpy, pressure and volume would need to be specified. However the values reported are not associated with any particular pressure or volume so that one must conclude that the calculated values presented in computational results are in fact internal energies rather than enthalpies. The energies of adsorption are usually reported in units of electron volts per hydrogen atom adsorbed. The data in Tables 1 and 2 (and throughout this paper) have been converted to units of kJ/mol of hydrogen molecules adsorbed, in line with the way in which experimental heat of adsorption data are usually presented. The sign convention used is that an exothermic change is given a negative sign, indicating that the resulting state has a lower energy than the initial state, and vice versa for positive values that represent endothermic changes (note that this sign convention has not been uniformly used in the literature, see for example Ref. [5]).

The surface coverage is taken as 1 when all the fcc sites are occupied and 1/3 when one out of three fcc sites are occupied [9]. In other words on a (1 1 1) surface the bridge, top and hcp sites would be neglected in calculating surface coverage. When all fcc sites are occupied there is one hydrogen atom adsorbed for every surface palladium atom.

Table 1
Heats of adsorption and diffusion calculated for various different surface coverages from Refs. [1,5,7,8,9] for palladium (1 1 1)^a

Source	ΔE_{ads} (kJ/mol)							E_{a} diffusion (kJ/mol)				
	[7] ($\theta = 1$)	[5] ($\theta = 1$)	[9] ($\theta = 1$)	[10] ^b ($\theta = 1$)	[8] ($\theta = 2/3$)	[9] ($\theta = 1/3$)	[1] ($\theta = 1/4$)	[7] ($\theta = 1/4$)	[5] ($\theta = 1$)	[9] ($\theta = 1/3$)	[1] ($\theta = 1/4$)	[7] ($\theta = 1/4$)
$H_{2,g} = 2H_{\text{ads}}$												
fcc–fcc	–82	–98	–68	–52	–111	–102	–100.2	–133	18	14	13	
hcp–hcp	–70	–87		–35	–100		–91	–126				
top–top	32	8		75	1		1.2	–3				
bridge–bridge	–44	–62		–35	–51		–71.2	–78				
fcc–hcp					–81							27
fcc–top											50.7	72
Octahedral subsurface– octahedral subsurface		–37	–46			–81						
Lattice parameter used as basis for calculations, l (Å)	3.876	3.96	4.76 ^c		3.95		3.950					
Bulk interlayer spacing, h	2.24 ^c	2.29 ^c	2.75				2.281					
No. of layers	5	5 or 9	3		5	2	5			2		

^a The convention used in this paper is that energies are reported as negative when they are exothermic; that is, not stable relative to the gas phase.

^b Binding energies have been converted to heats of adsorption by subtracting dissociation energy for H_2 .

^c Calculated from data given in this reference using $l = \sqrt{3}h$ for a uniform lattice.

Table 2

Heats of adsorption and absorption calculated for Pd (1 0 0) and Pd (1 1 0)

Source	E_{ads} (1 0 0) (kJ/mol)			E_{ads} (1 1 0) (kJ/mol)	
	[5] ($\theta = 1$)	[4] ^a ($\theta = 1$)	[4] ^a ($\theta = 2$)	[5] ($\theta = 1$)	[4] ^a ($\theta = 1$)
$H_{2,g} = 2H_{\text{ads}}$					
Pseudo-three-fold				−97	
Hollow	−100	−118		−83	−147
Long-bridge				−75	−212
Short-bridge				−35	−143
Bridge	−77		−37		
On-top	15	87		14	2
Subsurface	−35			−39	
$E_{\text{formation}} (P \text{ dH})$					
Lattice parameter used as a basis for calculations (Å)	3.96	3.90			

^a Bond energies have been converted to heat of adsorption by subtracting dissociation energy for H_2 .

2.1. Heats of adsorption

There is no clear trend from one author to the next for the heats of adsorption, E_{ads} , with change in surface coverage, θ , although drawing a comparison between results from a particular paper shows a clear trend of increasing heat of adsorption (i.e. becoming less negative) with increasing surface coverage. See for example the data of Refs. [7] and [9] in Table 1.

Except for one instance at $\theta = 1/4$ [7], adsorption onto the top site is always endothermic and the top site is consistently the least favorable site [1].

The energies of adsorption calculated by Dong et al. [5] for adsorption to the most favorable site for each surface at $\theta = 1$, are given as −98, −100 and −97 kJ/mol for the (1 1 1), (1 0 0) and (1 1 0) surfaces, respectively. This indicates that the measured heat of adsorption should not be strongly affected by the particular face of the surface.

2.2. Absorption or subsurface adsorption

Three Refs. [4,5,9] consider the subsurface adsorption of hydrogen into the octahedral site. The subsurface sites are less stable than the most stable surface adsorption sites; Dong et al. [5] calculated slightly different subsurface adsorption energies for the different faces, namely (1 1 1) −37 kJ/mol, (1 0 0) −35 kJ/mol and (1 1 0) −39 kJ/mol. Tománek et al. [4] calculated the heat of formation of palladium hydride to be −51 kJ/mol while Paul and Sautet [9] calculated values of −46 kJ/mol at $\theta = 1$ and −81 kJ/mol at $\theta = 1/3$.

Dong et al. [5] calculated a bigger difference between the fcc and subsurface sites for palladium (1 1 1) (−37 kJ/mol for the subsurface site and −98 kJ/mol for the fcc sites, $\theta = 1$) than Paul and Sautet [9] (−46 kJ/mol for the subsurface site and −68 kJ/mol for the fcc sites, $\theta = 1$). The difference in the former case is 61 kJ/mol, while in the latter it is only 22 kJ/mol.

A possible reason for the smaller difference in the values calculated by Paul and Sautet [9], is the large lattice parameter that they used, namely 4.76 Å compared to 3.96 Å used by Dong et al. [5]. (Note that the value used by Dong et al. [5] is much closer to the experimentally measured value of 3.8825 Å

[15] than the value used by Paul and Sautet [9].) The error in the lattice parameter used by Paul and Sautet [9] is 23% compared to 2% error in the value used by Dong et al. [5]. The value used for the lattice parameter has a significant effect on the energies that are calculated [6].

Dong et al. [5] have reported that the percentage lattice relaxation that occurs on adsorption of hydrogen on the various sites is as follows: fcc 1.9%, hcp 3.3%, bridge 2.3%, top 2.7% and subsurface as 7.0%. This would make the lattice parameter for palladium hydride, i.e. hydrogen adsorbed into the subsurface site of palladium, 4.24 Å. This value is higher than the experimentally measured values for the lattice parameter of β -palladium hydride which were reported to be 4.12 Å [4] and 4.043 Å (at 206 °C and 22.3 atm in a hydrogen atmosphere) and are a function of composition [6]. Tománek et al. [4] calculated the lattice parameter for palladium to be 3.90 Å and found a lattice constant of 4.1 Å for palladium hydride. This represents a relaxation of 5.1%. Interestingly, the lattice relaxation calculated by comparing the above experimentally measured values is 6.1%.

Thus the calculated values for lattice expansion on the formation of palladium hydride [4,5] are in good agreement with the experimentally measured data. Further Tománek et al. [4] have found (from calculations) that as hydrogen adsorbs onto the palladium (1 1 0) and (0 0 1) surfaces, the surface layer of palladium atoms relaxes outwards. This expansion is 6% for monolayer coverage, and is similar in magnitude to the lattice expansion that occurs on formation of β -palladium hydride. Note that Tománek et al. [4] assumed that the surface layer of palladium atoms is contracted due to unsaturated surface bonds; however, Felter et al. [16] have shown that the surface layer of clean palladium is in fact expanded by 1.1%.

At first glance it seems counter intuitive that subsurface adsorption should be less exothermic than surface adsorption, since the energy attributed to surface atoms is generally higher than that of subsurface atoms. However, the less exothermic subsurface adsorption can be explained by considering the expansion of the lattice during hydrogen absorption which would require work to be done on the lattice [17]. This also explains the greater difference between surface and subsurface adsorption calculated by Dong et al. [5] who have allowed for

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

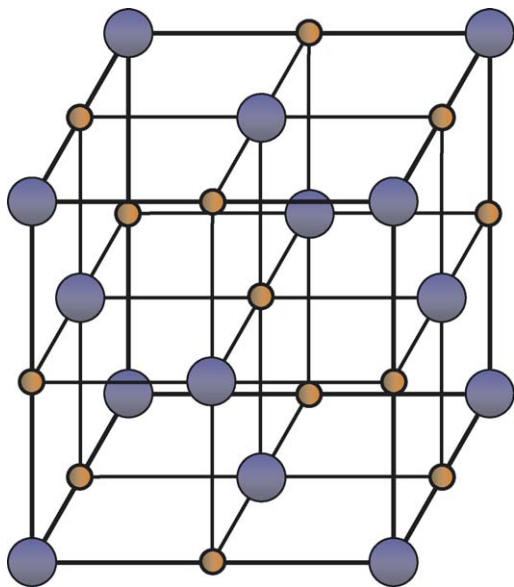


Fig. 2. Unit cell of palladium metal showing octahedral sites that would be occupied by hydrogen in β -palladium hydride, for the limiting H:Pd ratio of 1. Note that the same sites are occupied by hydrogen in α -palladium hydride, at a considerably lower H:Pd ratio.

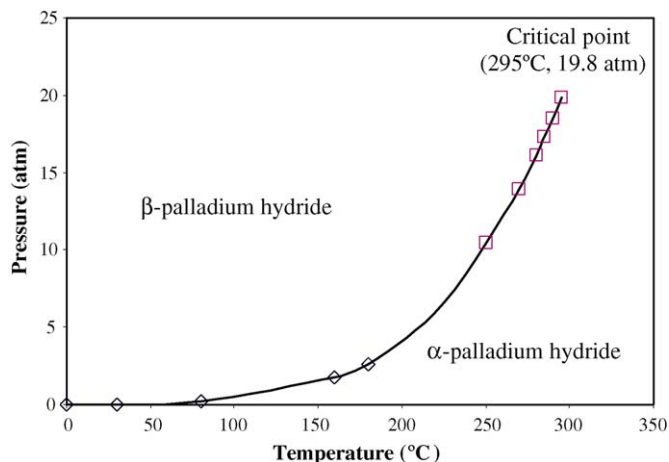


Fig. 3. Pressure–temperature phase diagram for the H:Pd system: \diamond , data of Gillespie and Hall [26] and \square , data of Gillespie and Galstaun [22].

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.

Table 3

Experimental integral enthalpy of absorption for the hydrogen-palladium system: data from Gillespie and Hall [26]

Temperature (°C)	$\Delta\hat{H}$ (kJ/mol)
0	−36.7
30	−36.4
80	−35.4

The values reported for particular temperatures range from −36.7 to −35.4 kJ/mol as shown in Table 3.

Levine and Weale [17] found that the heat of absorption increases (becomes less exothermic) with increasing hydrogen to palladium ratio at higher pressures and at temperatures above the critical point (Table 4). According to Levine and Weale [17] the relationship between enthalpy of absorption and composition is linear, with a change in gradient at approximately 0.5, they attribute this behavior to lattice expansion. The isosteric heats of sorption range from −46.1 to −11.7 kJ/mol.

Gillespie and Ambrose [18] have measured internal energy of absorption over a range of compositions at 0 °C. At first glance these data points also appear to vary linearly with composition. However, Gillespie and Ambrose [18] have presented their data (and the data of Mond et al. [27]) as ΔU in cal/g of palladium. If the basis for this data is taken per mol of hydrogen molecules instead of per gram of palladium, the value of the internal energy of absorption is approximately constant with composition for the 0 °C isotherm ranging from 36.25 to 36.95 kJ/mol, excluding one value that is very low, see Table 5.

Thus some researchers [17] have found that the heat of absorption varies with composition but the data of other authors [18,26] suggest that this is not true. Let us examine the data of Levine and Weale [17] in more detail.

The values for ΔH_{abs} given by Levine and Weale [17] were obtained from the gradient of a straight line fit to a graph of the natural logarithm of f_{H_2} against $1/T$ for a particular composition. The equation on which this is based is:

$$\ln f_{\text{H}_2} = \alpha - \frac{\Delta H}{RT} \quad (1)$$

Gillespie and Galstaun [22] also suggest that $\ln p$ versus $1/T$ for the palladium hydrogen system can be approximated by a straight line.

Table 4

Isosteric heat of sorption data from Levine and Weale [17]^a

mol H ₂ /g Pd	$\Delta\hat{H}$ (kJ/mol H ₂)	H/Pd
0.00106	−46.1	0.225
0.00141	−42.7	0.3
0.00164	−39.4	0.35
0.00188	−34.3	0.4
0.00211	−30.1	0.45
0.00235	−28.5	0.5
0.00258	−22.6	0.55
0.00282	−13.4	0.6
0.00305	−11.7	0.65

^a Data measured above the critical temperature.

Table 5

Internal energy of absorption data from Gillespie and Ambrose [18] for the 0 °C isotherm

mol H ₂ /g Pd	ΔU (kJ/g Pd)	$\Delta\hat{U}_{\text{abs}}$ (kJ/mol H ₂)	H/Pd
0.000699	−0.02565	−36.70	0.1487
0.000863	−0.03179	−36.84	0.1836
0.001893	−0.06891	−36.41	0.4028
0.000089	−0.00239	−26.86 ^a	0.0189
0.000368	−0.01334	−36.25	0.0783
0.000998 ^b	−0.03676	−36.83	0.2124
0.00194 ^b	−0.07138	−36.80	0.4128
0.002809 ^b	−0.10362	−36.89 ^c	0.5978
0.002991 ^b	−0.11053	−36.95 ^c	0.6365
Average (excluding) ^a		−36.71	

^a Gillespie and Ambrose [18] remark that this measurement is low citing experimental error, due to the small amount of energy being measured.

^b Data from Mond et al. [27] at 23 °C recalculated to 0 °C by Gillespie and Ambrose [18].

^c According to Gillespie and Ambrose [18] the data points of Mond et al. [27] at H/Pd of 0.5978 and 0.6363 correspond to the second rising portion of the isotherm, that is they refer to the saturation of the β -phase. Although these values are slightly higher, the difference is within experimental error.

Since the enthalpy of absorption is thought to be a function of composition, equilibrium values of pressure and temperature at constant composition are used to calculate the heat of absorption. The authors of this work remark that this graph is “very roughly a straight line” [17]. See Fig. 4 for a graph based on the data of Levine and Weale [17].

Levine and Weale [17] do not derive this equation or explain its origin. It appears to be an integrated form of the Clausius–Clapeyron equation which is:

$$\frac{d \ln p}{dT} = \frac{\Delta H}{RT^2} \quad (2)$$

where α is the constant of integration and the heat of absorption is assumed not to be a function of temperature. The Clausius–Clapeyron equation is used to calculate the enthalpy of phase change by considering equilibrium points.

There are two reasons for questioning the application of this equation to this system to calculate the heat of absorption.

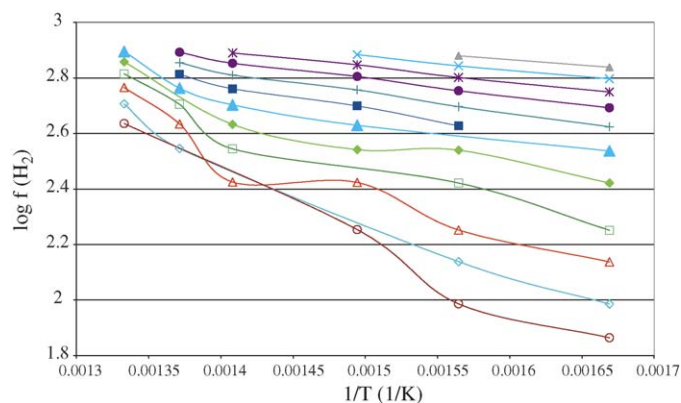


Fig. 4. Isosteric data of Levine and Weale [17] used to determine the heat of absorption. The data is for the following H/Pd ratios: \blacktriangle , 0.68; \times , 0.66; $*$, 0.65; \bullet , 0.54; $+$, 0.45; \blacksquare , 0.63; \blacktriangle , 0.61; \blacklozenge , 0.60; \square , 0.58; \triangle , 0.55; \diamond , 0.53; \circ , 0.50.

Firstly this equation is derived for an isothermal, isobaric closed system [28] and secondly one of the assumptions underlying this equation is that the heat of adsorption is not a function of composition which is in contradiction to what Levine and Weale [17] have found. These points will be discussed in more detail below.

Firstly, the system used by Levine and Weale [17] for their measurements is not a constant pressure system, but rather is a constant volume system, with the pressure free to adjust itself as the equilibrium is attained.

In an analogous way to the derivation of the Clausius–Clapeyron equation, the following equation can be derived for an isothermal closed system with fixed boundaries. (See Appendix A for a discussion of the statistical thermodynamic derivation of this equation that is given by Lacher [21].):

$$\int_0^{M_s} k \left(\frac{\partial \ln(M_2/V)^{1/2}}{\partial(1/T)} \right)_{M_s} dM_s = \Delta U_{\text{abs}} \quad (3)$$

The statistical thermodynamic derivation emphasizes that the energy of absorption is a function of composition, while the equation used by Levine and Weale [17] assumes that the heat of absorption is not a function of composition. If the heat of absorption is in fact not a function of composition or temperature, a graph of the natural logarithm of (M_2/V) against $1/T$ will be a straight line. (See Appendix B for an explanation of how to get from Eqs. (3) and (4).):

$$\ln \hat{V} = \alpha' - \frac{\Delta \hat{U}_{\text{abs}}}{RT} \quad (4)$$

When the data of Gillespie and Galstaun [22] and Levine and Weale [17] are re-analyzed to calculate the internal energy of absorption instead of the enthalpy of absorption, by plotting the natural logarithm of \hat{V} versus $1/T$, straight lines are obtained with correlation coefficients of 0.9995 and 0.9830, respectively, see Fig. 5. The points used in this graph correspond to the horizontal sections of the pressure versus composition isotherms over a range of compositions since this is the region in which the hydride is formed; this is also the region that corresponds to the expansion of the lattice to the lattice

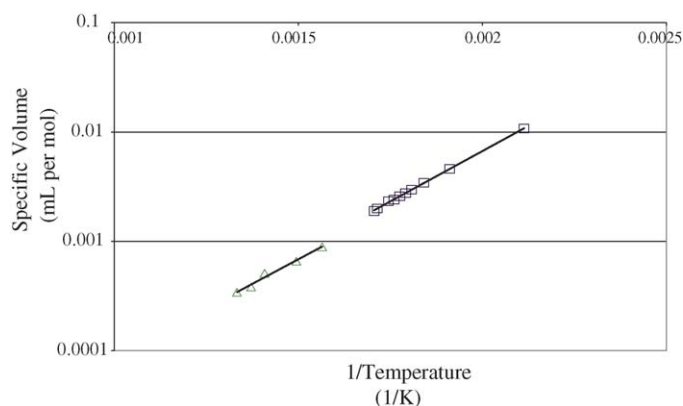


Fig. 5. Re-analyzed data of Gillespie and Galstaun [22]: \square , $\hat{V} = 10^{-6} \text{ ml/mol e}^{(4231.6K/T)}$ ($R^2 = 0.9995$) and Levine and Weale [17]: \triangle , $\hat{V} = 10^{-6} \text{ ml/mol e}^{(4140.2K/T)}$ ($R^2 = 0.9983$).

Table 6

Internal energies of absorption calculated by analyzing the data of Gillespie and Galstaun [22] and Levine and Weale [17] as constant volume systems

Source data	Temperature range ($^{\circ}\text{C}$)	$\Delta \hat{U}_{\text{abs}}$ (kJ/mol H_2)
[22]	200–13	–35.2
[17]	366–77	–34.4

The points used in this analysis represent a range of compositions.

parameters characteristic of palladium hydride [23]. For isotherms measured above the critical point [17] the point of inflection in the isotherm was taken. Since the data points are quite far apart it is in some cases difficult to determine the point of inflection so that it is expected that the values calculated from the data of Levine and Weale [17] are less accurate than those obtained from the data of Gillespie and Galstaun [22].

The broad range of hydrogen:palladium ratios (0.1–0.45) for which data have been included and the good fit of the straight lines indicate that the internal energy of absorption is in fact not a function of composition, in agreement with the data of Gillespie and Ambrose [18]. The values for the heat of adsorption obtained have been summarized in Table 6.

The difference between these two values is within experimental error. Moreover they are quite similar to the values obtained by recalculating the data of Gillespie and Ambrose [18]. The small differences in the internal energies of absorption can probably be explained by the different ranges of temperature over which the data were measured, with a slight decrease with increasing temperature.

Thus, the experimental ΔU_{abs} values are found to be -36.7 kJ/mol [18], -35.2 kJ/mol [22] and -34.4 kJ/mol [17], by recalculating the data in the original references as explained above. These values are independent of composition and are very close to the values (-35 to -39 kJ/mol) calculated by Dong et al. [5] for subsurface adsorption on the different faces of palladium. The absolute values calculated by other authors are larger, namely -51 kJ/mol [4], and -46 kJ/mol [9], but of the same order of magnitude. The value calculated at $\theta = 1/3$ is considerably larger at -81 kJ/mol [9]. This is probably because the hydrogen atoms in palladium hydride at a hydrogen:palladium ratio of $1/3$, are in reality not uniformly distributed throughout the solid (as would be implicit in the calculations), but rather that the solid of this composition consists of (outer) regions of palladium hydride that surround a region of palladium metal. This kind of behavior has been experimentally observed [29].

In conclusion of this section, the internal energy of absorption appears to be a (weak) function of temperature, but not composition. Reported variations in heat of absorption with changing composition appear to be an artifact of the way in which the data have been analyzed. With care, computational chemistry is able to predict the heat of absorption or formation of palladium hydride fairly accurately, suggesting that it could be used to gain insight into the palladium hydride system.

3.2. Adsorption

The source of the experimentally measured value for E_{ads} that is widely used as a comparison for theoretically calculated values

of the heat of adsorption of hydrogen on palladium is the value calculated by Conrad et al. [2], based on measurements of change in work function. The precise relationship between change in work function ($\Delta\phi$) and surface coverage is not known, although it is a measure surface coverage [2]. Therefore, although one cannot say precisely which value of surface coverage corresponds to a particular value of change in work function, a particular change in work function corresponds to a particular surface coverage, irrespective of the temperature or pressure.

Conrad et al. [2] used pressure and temperature measurements to calculate E_{ads} for a particular surface coverage by means of the Clausius–Clapeyron equation, in a similar way to that in which Levine and Weale [17] did for the heat of formation of palladium hydride. The Clausius–Clapeyron equation, in a slightly different form from what is given in Eq. (2), is given by Conrad et al. [2] as follows:

$$\left[\frac{d \ln p}{d(1/T)} \right]_{\theta=\text{const}} = - \frac{E_{\text{ads}}}{R} \quad (5)$$

Firstly it should be noted that although the symbol E_{ads} is used in this Ref. [2], the heat of adsorption that is calculated using this equation is the change of enthalpy on adsorption, namely ΔH_{ads} .

Thus the authors of computational chemistry papers compare their calculated internal energies of adsorption to an enthalpy of adsorption. There is not likely to be a large difference between these quantities, but the discrepancy needs to be noted nonetheless.

Moreover Conrad et al. [2] found that ΔH_{ads} is constant for low surface coverages, but after some point (about 50% of the maximum change in work function observed) the heat of adsorption begins to increase with increased surface coverage; i.e., its numerical value becomes less negative. Conrad et al. [2] stress that the values of ΔH_{ads} that they calculated are only valid at low surface coverages. Yet in a couple of cases [5,7] these ΔH_{ads} data are compared to calculated values for high surface coverage and it is claimed that there is fairly good agreement between the calculated and measured values. However there is less agreement than is claimed because the low surface coverage experimental data are similar to the high surface coverage calculated data. The calculated heats of adsorption for the (1 1 1) and (1 1 0) surfaces have been plotted in Fig. 6a and b, together with the data of Conrad et al. [2], to emphasize the fact that the experimental data are valid only at low surface coverages.

It is known from experiment that subsurface sites become occupied during the adsorption of hydrogen on palladium at higher surface coverages [2,29]. Indeed, Christmann et al. [29] attribute their observations to the formation of palladium hydride in the outer layers of the metal and state that the hydrogen absorption isotherms for the surface region deviate considerably from the data for the bulk. That is, under the conditions of the studies of Conrad et al. [2] and Christmann et al. [29], bulk experimental measurements predict a very small hydrogen: palladium ratio. But their observation for the layer directly beneath the surface indicates surface expansion corresponding to a much larger ratio.

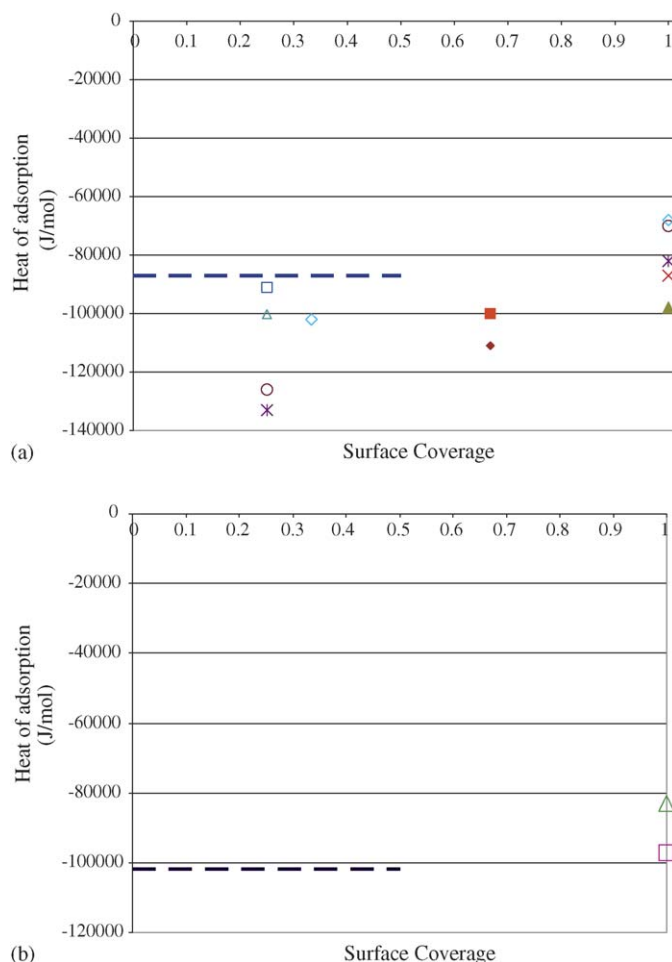


Fig. 6. (a) Heat of adsorption versus surface coverage on the palladium (1 1 1) surface: a comparison of the calculated and experimentally measured values: \triangle , fcc site [1]; \square , hcp site [1]; \blacktriangle , fcc site [5]; \times , hcp site [5]; $*$, fcc site [7]; \circ , hcp site [7]; \blacklozenge , fcc site [8]; \blacksquare , hcp site [8]; \diamond , fcc site [9]; ---, experimental data [2]. (b) Heat of adsorption versus surface coverage on the palladium (1 1 0) surface: a comparison of the calculated and experimentally measured values: \square , pseudo-threefold site [5]; \triangle , hollow site [5] and ---, experimental data [2].

Maeland and Gibb [23] probably observed symptoms of the same phenomenon when they measured the lattice parameters of palladium hydride via X-ray diffraction by both increasing and decreasing the hydrogen pressure. They observed faint diffraction lines for α -palladium hydride during the transition between the two phases (in either direction), but always observed the lines corresponding to β -palladium hydride clearly. This corresponds to the formation of β -palladium hydride first in the outer layers and to β -palladium hydride remaining present last in these layers as the phase equilibrium shifts back to the α -phase (see Fig. 2 for the structures of α - and β -palladium hydride).

Similarly, after forming the β -phase, and then removing the hydrogen from the sample, Owen and Williams [24] (see also Owen and Jones [31]) observed distortion of the palladium lattice. In other words, although the hydrogen had apparently been removed, not all of the atoms had returned to their original positions. It was found that the samples needed to be annealed

at 450 °C before the atoms returned to the original positions [24].

On the basis of the above observations [2,23,24,31] it seems likely that the adsorption isotherms of Conrad et al. [2] were measured not on Pd metal, but rather on Pd metal covered by an outer layer of β -palladium hydride.

Conrad et al. [2] have taken great care to demonstrate that $\Delta\phi$ is not affected by the presence of subsurface hydrogen. They formed palladium hydride, evacuated the chamber of hydrogen and found that the work function returned to the original value that was observed before the initial introduction of hydrogen to the clean palladium surface. Then with time hydrogen diffused out of the subsurface layers and formed an adsorbed layer on the surface, resulting in a change in the work function [2].

This experiment proves that, although palladium hydride formed in the subsurface layers of the palladium metal during the measurements of the adsorption isotherms, $\Delta\phi$, the parameter that has been used as a measure of surface coverage, is unaffected [2]. This means that a particular value of $\Delta\phi$ will correspond to a unique surface coverage.

For Pd (1 1 0) Conrad et al. [2] found that the ΔH_{ads} begins increasing at about 50% of $\Delta\phi_{\text{max}}$. In general, the increase in enthalpy of adsorption is explained by interaction of adsorbed surface species at high surface coverage. These forces are considered to be repulsive or attractive depending on the particular adsorbate and adsorbent and the surface coverage. In this case the forces are interpreted to be repulsive because the heat of adsorption becomes less exothermic as the surface coverage increases.

However, both adsorption and absorption phase equilibria shift as temperature and pressure are changed. Therefore although work function [2], and by implication surface coverage, is not affected by the formation of palladium hydride, the gradient

$$\frac{d \ln p}{d(1/T)} \quad (6)$$

would respond to shifts in both equilibria. This means that the enthalpy of adsorption calculated via the integrated form of the Clausius–Clapeyron equation would reflect not only the marginal or incremental adsorption of hydrogen on the surface of the palladium, but also the formation of palladium hydride in the subsurface layers.

Thus, rather than interaction between adsorbed species, what Conrad et al. [2] may have observed is adsorption onto other sites for which the enthalpy of adsorption is less exothermic [30]. In other words, what they may have observed as a less negative enthalpy of adsorption at 50% surface coverage may in fact be the transition between filling up fcc sites and other less thermodynamically favorable sites such as the subsurface sites, as is known to occur at higher pressures, where the formation of the palladium hydride is favorable.

In addition, the system used by Conrad et al. [2] is a constant volume rather than a constant pressure system, so that the applicability of the Clausius–Clapeyron equation is in question for the sake of correctness. Nonetheless, because of the small

changes in pressure measured on adsorption (compared to absorption) this would probably have an extremely small effect on the results. Moreover, analysis of the results in an analogous fashion to that described above for palladium hydride, yielded curves which could in no way suggest that the internal energy of adsorption is not a function of surface coverage.

3.3. An alternative method for determining the effect of surface coverage on the heat of adsorption

In the light of the above observations it seemed desirable to find an alternative way of analyzing the data of Conrad et al. [2]. Noting that the equations derived by Lacher [21] for the absorption of hydrogen in palladium can be derived in an analogous fashion for adsorption [32,33], the following equation for the internal energy of adsorption when M_s atoms are adsorbed on the surface is considered:

$$\Delta U_{\text{ads}} = -\frac{(1/2)M_s^2\chi}{N_s} - M_s\left(\chi_0 - \frac{1}{2}\chi_d\right) - M_s k T^2 \frac{\partial}{\partial T} \ln \frac{(F'_2)^{1/2}}{v(T)} \quad (7)$$

where

$$F'_2 = \frac{[2\pi(2m)kT]^{3/2}}{h^3} \frac{8\pi^2 A k T}{h^2} \quad (8)$$

By convention, internal energy of adsorption is given per mole of gas phase molecules adsorbed, i.e. $(1/2)M_s$. Dividing the above equation throughout by $(1/2)M_s$, and remembering that $\theta = M_s/N_s$, one obtains:

$$\Delta \hat{U}_{\text{ads}} = -\theta\chi - (2\chi_0 - \chi_d) - 2kT^2 \frac{\partial}{\partial T} \ln \frac{(F'_2)^{1/2}}{v(T)} \quad (9)$$

In the above equation, only θ and χ are functions of surface coverage, all of the other terms would be constant for a particular temperature [21,32]. In other words, the product $\theta\chi$ gives an indication of the variation of $\Delta \hat{U}_{\text{ads}}$ with surface coverage. This is in contrast to the Clausius–Clapeyron equation where the enthalpy of adsorption is (implicitly) assumed not to be a function of surface coverage.

Refer to Appendix C for an explanation of how $\theta\chi$ can be approximated from experimental data if it is assumed that $\chi \approx$ constant for small changes of θ . A graph of differential change in internal energy of adsorption with surface coverage (i.e. $\theta_{\text{ave}}\chi$ versus θ_{ave}) for the Pd (1 1 1) data of Conrad et al. [2] is given in Fig. 7. (It has been assumed that $\theta = \Delta\phi/\Delta\phi_{\text{max}}$ where $\Delta\phi_{\text{max}} = 180$ mV for the Pd (1 1 1) measurements of Conrad et al. [2].) The difference between the values of surface coverage used to calculate a particular value of $\theta\chi$ is: $\theta_2 - \theta_1 = 0.06$.

Figs. 8 and 9 (data from Refs. [2,34], respectively) show the variation of the differential change in internal energy of adsorption with surface coverage (i.e. $\theta_{\text{ave}}\chi$ versus θ_{ave}) for data on the Pd (1 1 0) surface. In the former case the difference between the values of surface coverage used to calculate a

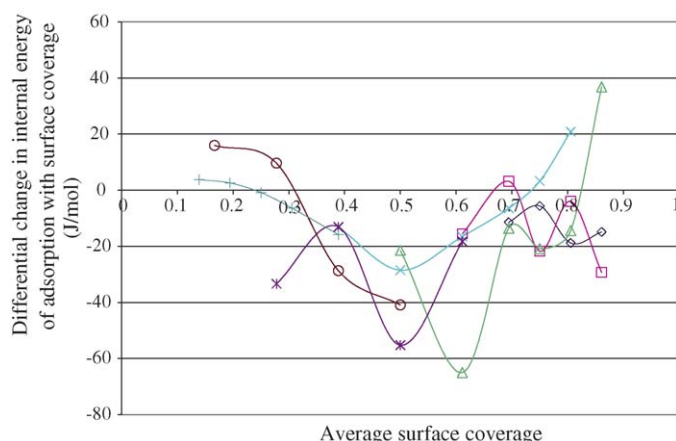


Fig. 7. Relationship between change in internal energy and average surface coverage, data from Conrad et al. [2] for Pd (1 1 1) for different temperatures: \diamond , 35 °C; \square , 50 °C; \triangle , 65 °C; \times , 80 °C; $*$, 95 °C; \circ , 110 °C; $+$, 125 °C. Points calculated for $\varphi_{\max} = 180$ mV.

particular value of $\theta\chi$ is: $\theta_2 - \theta_1 = 0.07$ and in the latter case it ranges from 0.02 to 0.24, with an average of 0.13. Cobden et al. [34] have measured surface coverage over a much wider range of temperature (25–227 °C) than Conrad et al. [2] (35–125 °C). A constant surface coverage interval could be used for the data of Conrad et al. [2] because these authors have plotted $\Delta\varphi$ against pressure for particular temperatures; but Cobden et al. [34] have plotted surface coverage against temperature for particular pressures, so that in order to obtain values at a particular temperature the surface coverage had to be taken as a dependent variable and its value could not be predetermined.

A comparison of Fig. 9 with Figs. 7 and 8 shows that the spread of the values of $\theta_{\text{ave}}\chi$ are far greater for Cobden et al. [34] than for Conrad et al. [2]. This is likely due to the larger and variable intervals of surface coverage used to calculate $\theta_{\text{ave}}\chi$ for this data.

The data show a fairly high degree of variability. Errors in the data may be due to variance in experimental measurements

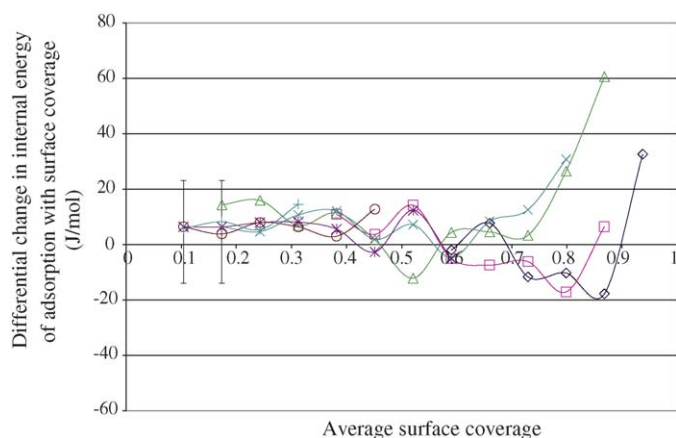


Fig. 8. Relationship between change in internal energy and surface coverage, data from Conrad et al. [2] for Pd (1 1 0) for different temperatures: \diamond , 35 °C; \square , 50 °C; \triangle , 65 °C; \times , 80 °C; $*$, 95 °C; \circ , 110 °C; $+$, 125 °C. The error bars are based on a standard deviation of 5.96 J/mol which was estimated by allowing for variance in the pressure and φ measurements of Conrad et al. [2]. Points calculated for $\varphi_{\max} = 360$ mV.

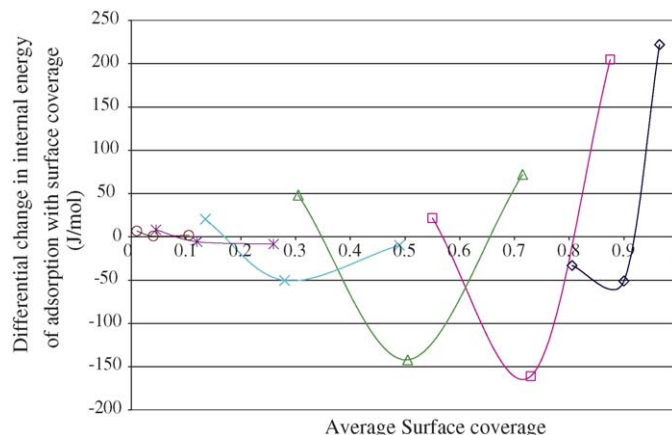


Fig. 9. Relationship between change in internal energy and surface coverage, data from Cobden et al. [34] for Pd (1 1 0) for different temperatures: \diamond , 52 °C; \square , 77 °C; \triangle , 102 °C; \times , 127 °C; $*$, 152 °C; \circ , 177 °C.

of pressure, temperature and work function. Allowance has been made for variance in pressure and $\Delta\varphi$ measurements and the standard deviation has been estimated to be 5.96 J/mol for the data of Conrad et al. [2] on the Pd (1 1 0) surface.

Of particular importance is the value of $\Delta\varphi_{\max}$, since surface coverage is calculated relative to this value. Errors in $\Delta\varphi_{\max}$ have a greater effect on the points at high surface coverage than at low surface coverage. To show the maximum effect that errors in $\Delta\varphi_{\max}$ could have, values for θ_{ave} and $\theta_{\text{ave}}\chi$ have been calculated for several different values of $\Delta\varphi_{\max}$ for the point with the highest surface coverage at 65 °C on the Pd (1 1 1) surface, see Table 7. Note that Conrad et al. [2] have indicated that their data may not be valid at high surface coverage for the Pd (1 1 1) surface, although they do not give an indication of the magnitude of the error in these data, other than to say that all $\Delta\varphi$ values are measured to within 3 mV.

Further errors may have arisen because the values of surface coverage and pressure or temperature have been read off graphs (with logarithmic scales in some cases) in the respective sources [2,34] in order to re-analyze the data. Lastly it should be remembered that the analysis relies on an approximation as described in Appendix C.

From Fig. 8, for which more data points for each temperature are available it can be seen that for a particular value of surface coverage, $\theta_{\text{ave}}\chi$ shows no clear trend with temperature, suggesting that $\theta_{\text{ave}}\chi$ is not a function of temperature, but only of surface coverage.

The general trends of Figs. 7–9 are very similar: a gradual decrease in $\theta_{\text{ave}}\chi$ with increasing surface coverage until a

Table 7
Effect of $\Delta\varphi_{\max}$ on calculated values of θ_{ave} and $\theta_{\text{ave}}\chi$ at 65 °C on the Pd (1 1 1) surface at high surface coverage

$\Delta\varphi_{\max}$	θ_{ave} (mV)	$\theta_{\text{ave}}\chi$ (J/mol)
180	0.861	37.9
175	0.886	69.0
170	0.912	128

minimum is attained at a coverage of ca. 0.6–0.9 (referred to as θ_{\min}) followed by a sharp increase in $\theta_{\text{ave}}\chi$. Remembering that $\theta_{\text{ave}}\chi$ is a measure of the change in $\Delta\hat{U}_{\text{ads}}$ with θ , this suggests that initially the incremental addition of adsorbed molecules is favorable as the internal energy of adsorption of each additional hydrogen molecule is more exothermic. At a particular point, θ_{\min} , this changes and the incremental internal energy rapidly increases and becomes endothermic. This suggests that at low surface coverages (i.e. $\theta < \theta_{\min}$) the species being adsorbed experience attractive forces as they approach the surface. At high surface coverage (i.e. $\theta > \theta_{\min}$) net repulsion is experienced by molecules approaching the surface.

The general trend of $\theta_{\text{ave}}\chi$ (i.e. $\Delta\hat{U}_{\text{ads}}$) with θ_{ave} is reminiscent of the effect of forces of electrostatic repulsion and attraction on internal energy as a function of distance between atoms [35]. This kind of behavior is suggested by Langmuir [36] and discussed by Skottke et al. [13].

Due to the strong repulsion at high coverages, it is probably not possible to achieve a surface coverage of 1. It should be noted that Conrad et al. [2] experienced difficulty in determining $\Delta\varphi_{\text{max}}$ for Pd (1 1 1). It is possible that evidence for the suggested behavior at high surface coverage is also given in the work of Mitsui et al. [12], who observed that adjacent vacant sites are not filled by the dissociation of gas phase hydrogen at high coverages. Rather the vacancies are filled by the diffusion of adsorbed surface atoms, that is the vacancy moves to another location on the surface, and the surface coverage does not increase beyond a particular point at high coverages.

Rather than ascertaining the actual value of the heat of adsorption, the question that is answered by Figs. 7–9 is how the heat of adsorption varies with surface coverage. In the most extreme cases it appears to vary by no more than ± 0.25 kJ/mol. This is a very small amount compared to the variation of heat of adsorption as a function of surface coverage predicted by computational chemistry.

Due to the small value of $\theta_{\text{ave}}\chi$ and the gradual change in this value particularly at low coverages, the effect of $\theta_{\text{ave}}\chi$ on $\Delta\hat{U}_{\text{ads}}$ is small. This means that net values for the heat of adsorption reported by Conrad et al. [2] are likely to be fairly accurate, but only at very low coverages. Moreover, due to the small magnitude of the values of $\theta_{\text{ave}}\chi$ relative to the heat of adsorption, the sign of the overall heat of adsorption would not be affected by the sign of the $\theta_{\text{ave}}\chi$ values.

3.4. Diffusion

In the following section barriers to diffusion will be briefly discussed, both from one surface site to another and into the surface.

Watson et al. [1] suggest that the activation energy for diffusion of 13 kJ/mol from one fcc site to another on palladium (1 1 1) is high relative to that for platinum which is 2–3 kJ/mol. Paul and Sautet [9] found the lowest barrier to diffusion to occur between two fcc sites via a bridge and an hcp site and calculated it to be 14.5 kJ/mol. They suggest that this value is low and therefore means very fast surface diffusion. Mitsui et al. [12] determined the barrier experimentally using

scanning tunneling microscopy (STM) and assuming a pre-exponential factor of 10^{13} /s to be 0.9 kJ/mol. This measured value is considerably lower than the calculated values by a factor of between 14 and 16.

Interestingly Dong et al. [7] found by considering diffusion from an fcc or hcp site to a top site, that the top site represents a local energy minimum, while Watson et al. [1] found only a maximum relative to the hcp and fcc sites.

Calculation of barriers to diffusion into subsurface sites has been done in two different ways: relative to the gas phase, or relative to adsorbed surface atoms. Paul and Sautet [9] give the activation energy for diffusion from an fcc site to an octahedral subsurface site as 32 kJ/mol. Olsen et al. [37] allowed for motion of the surface palladium atoms and calculated the energy barrier for direct absorption of hydrogen atoms into subsurface sites to be 43.4 kJ/mol. This activation energy is considerably lower than that calculated for most hydrogenation reactions, see for example Ref. [38]. Thus, the barrier for diffusion into the surface is in general found to be lower than that for hydrogenation reactions.

Olsen et al. [37] find, by varying the temperature in their calculations (0, 300 and 700 K) that heating the surface would not affect the onset of direct subsurface absorption, that is the barrier for direct subsurface absorption is not a function of temperature. This contradicts the experimental results which suggest that diffusion into subsurface sites is very slow at temperatures below ca. 210–250 K [12,39].

Thus the calculated barriers to surface diffusion appear to be much larger than the experimentally measured value and the behavior predicted by calculation for how the barrier to diffusion into the surface changes with temperature does not agree with experimental observations.

4. Conclusions

Except for a few instances, there appear to be fairly large discrepancies between experimentally measured values of the lattice parameters and the values used as inputs to the models, or values calculated by the models. The ability of a model to predict the strength of bonds between atoms, i.e. heat of adsorption, must be questioned if the model cannot accurately predict the distance between the atoms, or if it relies on data that differ substantially from experimental values as an input. The range of lattice parameters used also makes comparison difficult. Indeed it would be helpful if all authors adopted the approach of Olsen et al. [6], namely to use experimentally determined lattice parameters in order to facilitate comparison.

Analysis of the experimental data for the formation of palladium hydride as a constant volume system, leads to the conclusion that the internal energy of formation is not a function of composition, although it is a slight function of temperature. Computational chemistry is able to predict the internal energy of formation of palladium hydride fairly accurately.

Since the heat of adsorption is a function of surface coverage, the application of the Clausius–Clapeyron equation to isotherm data in order to calculate the ΔH_{ads} is not valid.

Analysis of data in the literature suggests that the internal energy of adsorption as a function of surface coverage follows the behavior of the internal energy of atoms as they come into close proximity, with forces of both attraction and repulsion coming into play.

At low coverages, hydrogen adsorption stabilizes the palladium surface by lowering the surface energy [4]. As surface coverage increases initially, the heat of adsorption becomes more negative (exothermic). At high coverages ($\theta > \text{ca. } 0.7$), repulsion between adjacent adsorbed atoms results in an increase in the surface energy on the addition of each extra hydrogen atom. At this point the heat of adsorption begins to become more positive (endothermic).

The magnitude of the changes in the internal energy of adsorption with surface coverage predicted by the analysis presented in this paper is small compared to the changes predicted by computation. The current work has not examined the effect of competitive adsorption on the variation of heat of adsorption with surface coverage [39,40], although it would certainly be interesting to investigate this in the light of the alternative analysis presented in this review.

The calculated barriers to diffusion and experimentally measured values differ substantially. In addition, it is predicted that absorption into subsurface sites will be unaffected by temperature. This is not what has been observed experimentally.

Finally, it is not surprising that calculations of the heat of absorption of hydrogen into palladium to form palladium hydride are very close to experimentally measured values, considering that computational chemistry has its origins in solid state systems. Indeed computational chemistry may be able to shed light on the elusive H:Pd ratio. However the ability of computational chemistry to predict surface phenomena accurately is in doubt, since surface phenomena seem to be more dependent on electrostatic interactions between the gas phase and the solid surface than the models allow. In computational chemistry, a hypothetical surface is set up with a particular surface coverage and the average energies of the atoms are calculated. The calculations yield the answer for the average, but do not answer the question about the energy that is released on the adsorption of one additional atom. On the basis of the alternative analysis presented in this review, computational chemistry appears to underestimate the electrostatic repulsion (or over estimate the attractive forces) between gas phase molecules and atoms that are already adsorbed on the surface at both low and high surface coverages, so that the calculated heats of adsorption are more exothermic than those calculated from experimental data.

Acknowledgements

L.L. Jewell would like to thank the University of the Witwatersrand for sabbatical leave that made this work possible. The authors would like to thank the library staff both at CAER and at the University of the Witwatersrand for their unstinting willingness to help.

Appendix A

The purpose of this appendix is to discuss the derivation given by Lacher [21]; the derivation will not be given in full. Lacher [21] has derived an equation that has a similar form (once it is integrated) to the equation given by Levine and Weale [17] and in slightly different form by Gillespie and Hall [26]. Lacher's [21] work considers absorption, however the analogous equations can be derived for adsorption [32,33]. Provided that ΔH is not a function of temperature:

$$\int_0^{M_s} k \left(\frac{\partial \ln p^{1/2}}{\partial (1/T)} \right)_{M_s} dM_s = \Delta H \quad (10)$$

Lacher [21] derives this equation using statistical mechanics, by comparing an expression for ΔU with an expression for the left hand side of Eq. (10). The equations are as follows:

$$\begin{aligned} \Delta U = & -\frac{(1/2)M_s^2\chi}{N_s} - M_s \left(\chi_0 - \frac{1}{2}\chi_d \right) \\ & - M_s k T^2 \frac{\partial}{\partial T} \ln \frac{(F'_2)^{1/2}}{v(T)} \end{aligned} \quad (11)$$

and,

$$\begin{aligned} \ln p^{1/2} = & \ln \frac{\theta}{1-\theta} - \frac{(\chi_0 - (1/2)\chi_d + \theta\chi)}{kT} \\ & + \ln \frac{(kTF'_2)^{1/2}}{v(T)} \end{aligned} \quad (12)$$

where $\theta = M_s/N_s$.

Differentiating Eq. (12) with respect to $1/kT$ and integrating with respect to M_s :

$$\begin{aligned} & \int_0^{M_s} k \left(\frac{\partial \ln p^{1/2}}{\partial (1/T)} \right)_{M_s} dM_s \\ = & -\frac{(1/2)M_s^2\chi}{N_s} - M_s \left(\chi_0 - \frac{1}{2}\chi_d \right) - M_s k T^2 \frac{\partial}{\partial T} \ln \frac{(F'_2)^{1/2}}{v(T)} \\ & - \frac{1}{2} M_s k T \end{aligned} \quad (13)$$

A comparison between Eqs. (11) and (13) shows that they differ by $-(1/2)M_s k T$. Thus:

$$\int_0^{M_s} k \left(\frac{\partial \ln p^{1/2}}{\partial (1/T)} \right)_{M_s} dM_s = \Delta U - \frac{1}{2} M_s k T \quad (14)$$

Lacher [21] replaces $-(1/2)M_s k T$ with $p\Delta V$ using the ideal gas law expressed in terms of the number of molecules rather than the number of moles of molecules and bearing in mind that $(1/2)M_s$ atoms is stoichiometrically equivalent to M_2 molecules, i.e.:

$$pV = nRT = M_2 k T \quad (15)$$

Since $H = U + pV$ by definition, Lacher [21] concludes that:

$$\int_0^{M_s} k \left(\frac{\partial \ln p^{1/2}}{\partial (1/T)} \right)_{M_s} dM_s = \Delta H \quad (16)$$

However, the substitution of pV for $(1/2)M_s kT$ is erroneous because M_s is the number of hydrogen atoms absorbed in the palladium lattice, in other words these are not gas phase species. This means that whenever the natural logarithm of p is plotted against $1/T$ in order to obtain ΔH from the gradient, what is found is not ΔH , but rather a rough approximation for $\Delta U - (1/2)M_s kT$. It can never be more than a rough approximation because it ignores the fact that both ΔU and $(1/2)M_s kT$ are functions of temperature. This explains why a straight line is not obtained when the natural logarithm of p is plotted against $1/T$.

An investigation of the derivation of Eq. (12) showed that Lacher [21] substitutes p for V/M_2 using the ideal gas law (V is the volume of M_2 hydrogen molecules in the gas phase at p, T). If this substitution is not made and Eq. (13) is written in terms of V/M_2 , the following equation results:

$$\ln\left(\frac{M_2 kT}{V}\right)^{1/2} = \ln \frac{\theta}{1-\theta} - \frac{(\chi_0 - (1/2)\chi_d + \theta\chi)}{kT} + \ln \frac{(kTF'_2)^{1/2}}{v(T)} \quad (17)$$

Differentiating with respect to $1/kT$ and integrating with respect to M_s :

$$\begin{aligned} \int_0^{M_s} k \left(\frac{\partial \ln(M_2/V)^{1/2}}{\partial(1/T)} \right)_{M_s} dM_s - \frac{1}{2} M_s kT \\ = - \frac{(1/2)M_s^2 \chi}{N_s} - M_s \left(\chi_0 - \frac{1}{2} \chi_d \right) - M_s kT^2 \frac{\partial}{\partial T} \ln \frac{(F'_2)^{1/2}}{v(T)} \\ - \frac{1}{2} M_s kT \end{aligned} \quad (18)$$

Comparing Eqs. (11) and (17):

$$\int_0^{M_s} k \left(\frac{\partial \ln(M_2/V)^{1/2}}{\partial(1/T)} \right)_{M_s} dM_s = \Delta U \quad (19)$$

Thus interestingly, unlike for Eq. (2), there is no extra term on the right hand side of the equation.

Moreover, since measurements of the equilibrium between hydrogen gas, palladium metal and palladium hydride have in all cases [17,18,22,26] been made in constant volume systems, rather than constant pressure systems, and knowing that a constant volume energy balance for a batch system yields an expression in terms of internal energy rather than enthalpy, the data obtained from such systems would be useful for calculating internal energy rather than enthalpy.

Appendix B

Consider Eq. (18):

$$\int_0^{M_s} k \left(\frac{\partial \ln(M_2/V)^{1/2}}{\partial(1/T)} \right)_{M_s} dM_s = \Delta U_{\text{abs}} \quad (20)$$

If ΔU_{abs} was not a function of composition, the heat of absorption would be the same for each new hydrogen atom

that adsorbed into a subsurface site. The change in internal energy per absorbed hydrogen atom would be given by:

$$\frac{\Delta U_{\text{abs}}}{\Delta M_s} = k \left(\frac{\partial \ln(M_2/V)^{1/2}}{\partial(1/T)} \right)_{M_s} \quad (21)$$

Now, $k\Delta M_s = kN_A 2n_{H_2} = R2n_{H_2}$ since by mass balance, two absorbed atoms must have originated as a gas phase molecule. Substituting into the above equation and recalling the conventional definition of $\Delta \hat{U}_{\text{abs}}$ namely, the internal energy of absorption per mole of hydrogen molecules absorbed:

$$\frac{\Delta \hat{U}_{\text{abs}}}{2R} = \left(\frac{\partial \ln(M_2/V)^{1/2}}{\partial(1/T)} \right)_{M_s} \quad (22)$$

Provided that $\Delta \hat{U}_{\text{abs}}$ is not a function of temperature, this equation can be integrated to give:

$$\ln \hat{V} = \alpha' - \frac{\Delta \hat{U}_{\text{abs}}}{RT} \quad (23)$$

Appendix C

In order to calculate $\theta\chi$ from the experimental data, let us consider Eq. (16), remembering that $\hat{V} = V/M_2$:

$$\begin{aligned} \ln \left(\frac{kT}{\hat{V}} \right)^{1/2} = \ln \frac{\theta}{1-\theta} - \frac{(\chi_0 - (1/2)\chi_d + \theta\chi)}{kT} \\ + \ln \frac{(kTF'_2)^{1/2}}{v(T)} \end{aligned} \quad (24)$$

For two different surface coverages, θ_1 and θ_2 at a particular temperature, T :

$$\begin{aligned} \ln \left(\frac{kT}{\hat{V}_1} \right)^{1/2} = \ln \frac{\theta_1}{1-\theta_1} - \frac{(\chi_0 - (1/2)\chi_d + \theta_1\chi_1)}{kT} \\ + \ln \frac{(kTF'_2)^{1/2}}{v(T)} \end{aligned} \quad (25)$$

$$\begin{aligned} \ln \left(\frac{kT}{\hat{V}_2} \right)^{1/2} = \ln \frac{\theta_2}{1-\theta_2} - \frac{(\chi_0 - (1/2)\chi_d + \theta_2\chi_2)}{kT} \\ + \ln \frac{(kTF'_2)^{1/2}}{v(T)} \end{aligned} \quad (26)$$

Subtracting Eq. (23) from Eq. (22):

$$\ln \left(\frac{\hat{V}_2}{\hat{V}_1} \right)^{1/2} = \ln \left(\frac{\theta_1}{1-\theta_1} \right) \left(\frac{1-\theta_2}{\theta_2} \right) - \frac{(\theta_1\chi_1 - \theta_2\chi_2)}{kT} \quad (27)$$

χ_1 and χ_2 are the energies of adsorption associated with an atom of hydrogen at surface coverages of θ_1 and θ_2 , respectively, and at a temperature, T .

Assuming that $\chi \approx$ constant for small changes of θ ; i.e., that χ changes gradually with surface coverage, Eq. (24) can be re-

arranged as follows:

$$\chi_{12} = \left[\ln \left(\frac{\hat{V}_2}{\hat{V}_1} \right)^{1/2} - \ln \left(\frac{\theta_1}{1 - \theta_1} \right) \left(\frac{1 - \theta_2}{\theta_2} \right) \right] \left[\frac{kT}{\theta_1 - \theta_2} \right] \quad (28)$$

Note that for an ideal gas, Eq. (25) is equivalent to:

$$\chi_{12} = \left[\ln \left(\frac{p_1}{p_2} \right)^{1/2} - \ln \left(\frac{\theta_1}{1 - \theta_1} \right) \left(\frac{1 - \theta_2}{\theta_2} \right) \right] \left[\frac{kT}{\theta_1 - \theta_2} \right] \quad (29)$$

since

$$p = \frac{kT}{\hat{V}} \quad (30)$$

\hat{V}_1 and \hat{V}_2 are at the same temperature.

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