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Research Article

Equation of State and Fugacity Models for H_2 and for D_2

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Abstract

When Pd is in equilibrium with H_2 or D_2 in gas, the chemical potentials are equal, and this allows a determination of the chemical potential and other thermodynamic properties of palladium hydride and palladium deuteride. At high loading near room temperature, the gas pressure must be very high, and an ideal gas law no longer applies. In this case a knowledge of the fugacity is required to interpret and understand the results. We examine empirical models for the equation of state and fugacity of H_2 which are relevant to the high pressure regime of interest, including an old model of Holley et al (1958), and the more modern models of Spycher and Reed (1988), Tkacz and Litwiniuk (2002), and Joubert (2010). At high pressure the more recent models are best, but the model of Tkacz and Litwiniuk diverges from the ideal gas equation of state at low pressure, which leads to an offset in the fugacity. We examine the difference between the equation of states for H_2 and D_2 in recent models, and find that the small difference at high pressure in the models of Tkacz and Litwiniuk agree best with experiment, while the larger difference in the models of Joubert (2010) and Joubert and Thiebaut (2011) is probably not reliable. We examine the possibility of developing a difference correction for the fugacity theoretically. It may be possible to account accurately for the zero-point contribution; however, accounting for the difference in inter-molecular potentials due to the different degrees of rotational excitation requires the development of new potential models.

Keywords: Equation of state, Fugacity, Gaseous H_2 and D_2, Nonideal gas, Quantum cell model

1. Introduction

In experiments where thermodynamic equilibrium is established between hydrogen in the gas phase and the metal hydride phase, by definition the hydrogen chemical potential is matched. Early in the last century the entropy of the ideal gas was established theoretically [1,2]; this provides a basis for the computation of the chemical potential, and allows for the determination of the chemical potential of hydrogen in Pd and other metals from pressure-composition-temperature experiments. The subsequent development of theoretical models for the chemical potential of hydrogen in metal hydrides followed [3].

For excess heat to be produced in the Fleischmann-Pons experiment [4,5] a very high deuterium loading in the Pd cathode is required [6]. We have been interested for some time in the development of models relevant to excess heat

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production, and from our perspective it would be of interest to model the deuterium loading in a manner consistent with the occupation of vacancies and other defects. Near room temperature the deuterium pressure that corresponds to the high D/Pd loading required is very high (near 1 GPa), sufficiently high that an ideal gas law model would not give very good results. In this regime in order to develop a relevant model for the chemical potential of deuterium in Pd in this regime, a knowledge of the equation of state of D_2 is necessary. From the equation of state the fugacity of D_2 can be determined [7], and with such a model it is possible to develop a model for the chemical potential of deuterium in Pd from experiments in which the loading is measured at high pressure.

Conceptually this seems straightforward. Ultimately a knowledge of the equation of state derives from experiment, so this motivates an interest in what experimental data is available. As might be expected, the equation of state of hydrogen and deuterium as a dense gas or liquid has been much studied over the years, and there are many data sets in relevant pressure and temperature regimes [8–16]. Considerable effort has also been put into the modeling of the equation of state as well, and one can find empirical models which are in good agreement with experiment [17–34]; some of the more recent of these focus on the temperature and pressure regime that we are interested in.

One might think that this should be the end of the story, but as could be expected there are a number of issues which have remain, and which have drawn our attention. For example, there is a recent empirical model by Tkacz and Litwiniuk [27] which has been widely used. If one compares predictions from this model to an older model favored by Bockris et al. [7], one finds significant differences at high pressure. Since the older model is based on the Beattie–Bridgeman empirical equation of state [35] (which dates from the 1920s), and fitted before 1960 by Holley et al. [19], when pressure–volume–temperature data was available for a much smaller range of pressures than in more modern times, one would expect that the more recent model should be preferred. Probably it would come as a surprise that near room temperature the older model is better, since there is a problem with the form of the fit employed by Tkacz and Litwiniuk [27]. Unfortunately the Tkacz and Litwiniuk model does not go to the ideal gas limit at low pressure.

Our attention is then drawn to the more recent empirical model by Joubert [31] for hydrogen, which looks to be the best available at this time for the parameter regime of interest. A very similar empirical model was put forth by Joubert and Thiebaut [32] for deuterium, which also looks to be very good. Of course, with such good models for hydrogen and for deuterium, the question naturally arises as to whether one might be able to address the relatively small and subtle differences between the fugacity of hydrogen and deuterium with these models reliably. Upon comparing the difference between the two models near room temperature at high pressure, our conclusion is that there is more difference than in experiment. Probably one cannot use these models then to study the relatively small difference between H_2 and D_2 and expect reliable results.

In what follows, we focus first on the equation of state of hydrogen, and then consider the associated fugacity. Subsequently we look at the difference between hydrogen and deuterium equation of state, and then consider the possibility of developing an estimate for the difference based on theory.

2. Equation of State Models for H_2

As discussed in Section 1, our understanding of the chemical potential of hydrogen in palladium hydride at high loading requires an understanding of the equation of state of gaseous and liquid hydrogen at high pressure. In connection with the discussion below, we recall the ideal gas law written as

$$PV = RT, \tag{1}$$

where P is the pressure, V the volume per mole, T the temperature and R is the gas constant. At high pressure where the equation of state is not ideal, we will be working with empirical gas laws which will specify a functional relation between the pressure, volume and temperature. As mentioned above there are many equation of state models in the

Table 1. Fitting parameters for the equation of state of H_2 based on the Beattie–Bridgeman equation from Ref. [19]; the pressure is in atmospheres, and the volume is in l/mol.

Parameter	Value
A_0	0.1975
a	-0.00506
B_0	0.02096
b	-0.04359
c	5.04×10^{-6}
R	0.08206

literature for hydrogen and deuterium which are potentially of interest in our discussion [17–34]; however, only a few of these seem relevant over a range extending up to a few GPa near room temperature, which is the regime of interest to us in connection with the Fleischmann–Pons experiment. We will focus below on the four that seem most interesting.

2.1. Model of Holley et al. [19]

One of these is the Beattie–Bridgeman equation [35] of state, which we can write as

$$PV^2 \;=\; RT\left(1-\frac{c}{VT^3}\right)\left(V+B_0-\frac{bB_0}{V}\right)-A_0\left(1-\frac{a}{V}\right). \tag{2}$$

The five parameters of the model (listed in Table 1) were fit to PVT data for H_2 as reported by Holley et al. [19]. We were initially drawn to this model since it was referenced by Bockris et al. [7] in connection with the Fleischmann–Pons experiment.

2.2. Model of Spycher and Reed [23]

A more modern model in the form

$$\frac{PV}{RT} \;=\; 1+\left(\frac{a}{T^2}+\frac{b}{T}+c\right)P+\left(\frac{d}{T^2}+\frac{e}{T}+g\right)P^2 \tag{3}$$

was published by Spycher and Reed [23]. The version of the model for hydrogen was fit to data up to 3000 bar, over a temperature range from 25 to 600°C. The parameters of the model are given in Table 2.

Table 2. Fitting parameters for the equation of state of H_2 based on the Spycher–Reed model [23]; the pressure is in bar.

Parameter	Value
a	-12.5908
b	0.259789
c	-7.24730×10^{-5}
d	4.71947×10^{-3}
e	-2.69962×10^{-5}
g	2.15622×10^{-8}

Table 3. Fitting parameters for the equation of state of H_2 based on the Tkacz and Litwiniuk model [27]; the pressure is in MPa, and the volume is in cm^3/mol.

Parameter	Value
A	176.330
B	-633.675
C	-304.574
D	731.393
E	8.59805

2.3. Model of Tkacz and Litwiniuk [27]

The equation of state due to Tkacz and Litwiniuk [27] can be written as

$$V \; = \; \frac{A}{P^{1/3}} + \frac{B}{P^{2/3}} + \frac{C}{P^{4/3}} + \frac{D+ET}{P}, \tag{4}$$

where the fitting parameters were optimized taking into account recent high pressure measurements with diamond anvil cells. Model parameters appear in Table 3.

2.4. Model of Joubert [31]

Our last equation of state is given by Joubert [31], and this one is given as

$$V \; = \; \frac{RT}{P} + a_1 \mathrm{e}^{-P/b_1} + a_2 \mathrm{e}^{-P/b_2} + a_3 \mathrm{e}^{-P/b_3} + a_4 \mathrm{e}^{-P/b_4} + a_5 \mathrm{e}^{-P/b_5} + c. \tag{5}$$

This model was developed for use with the CALPHAD thermal physics software packages [36–38], and takes advantage of experimental PVT measurements up to high pressure. Fitting parameters are given in Table 4.

Table 4. Fitting parameters for the equation of state of H_2 based on the model of Joubert [31]; the pressure is in Pa, and the volume is in m^3/mol.

Parameter	Value
a_1	4.29×10^{-6}
a_2	6.35×10^{-6}
a_3	4.25×10^{-6}
a_4	-1.50×10^{-6}
a_5	-1.63×10^{-6}
b_1	5.35×10^{8}
b_2	4.21×10^{9}
b_3	3.99×10^{10}
b_4	2.90×10^{7}
b_5	8.02×10^{7}
c	2.479×10^{-6}
R	8.31451

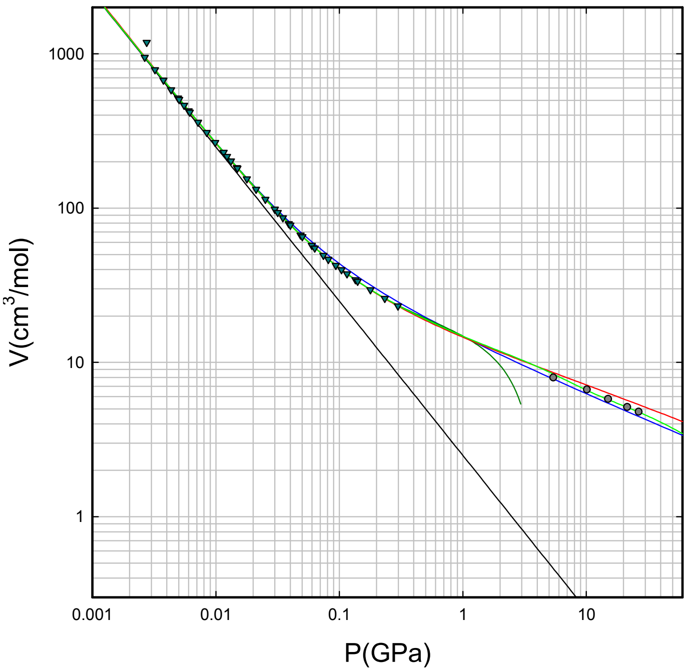

Figure 1. Results for V as a function of P; ideal gas (black line); Beattie–Bridgeman model fitted by Holley et al. (blue line); Spycher and Reed model (dark green line); Tkacz and Litwiniuk model (red line); Joubert model (light green line); data of Hemley et al. [15] (gray circles); data of Michels et al. [8] (dark cyan triangles)

2.5. Volume as a function of pressure

We compare these models with experiment at room temperature in Fig. 1, where we plot the volume V as a function of pressure P. We show data points from the measurements of Michels et al. [8] as quoted in [27], and from the measurements of Hemley et al. [15]. We note that all of the models considered are in good agreement with the measurements of Mills et al. [9] between 0.2 and 2 GPa (not shown).

Perhaps the first thing to note is a substantial increase of the volume relative to the ideal gas law (the low black line), which is why we need an equation of state model to begin with. Next we note that the model of Spycher and Reed (1988) deviates from the other models above 1 GPa, which is due to our extending the model well out of range of the upper limit of pressures use for the fit (0.3 GPa). The other models are reasonably close to the experimental data, even at high pressure which might have been out of range for the Beattie-Bridgeman model.

We note that molecular hydrogen undergoes a phase change between the liquid phase and solid phase near 5.7 GPa at room temperature [11,39,40]. There is a volume change associated with this phase change [13], which is about 0.3 cm^3/mol at a volume of about 8 cm^3/mol. This volume change needs to be taken into account for high precision thermodynamics modeling. However, at this point we have no relevant data for PdH or PdD at such a high pressure, and the effect is small on the scale of our present considerations. We will ignore it in this work.

2.6. Discussion

We see a clear deviation of the equation of state above about 25 MPa from the ideal gas law in Fig. 1, which provides motivation for our interest in the fugacity.

Based on the discussion so far, we conclude that three of the equation of state models appear to give results in good agreement with experiment over the full range from atmospheric pressures up to the the highest data point shown at 26.5 GPa. The Beattie–Bridgeman fit is a bit high in the vicinity of 100 MPa, and the Tkacz-Litwiniuk model seems a bit high around 20 GPa. Nevertheless we are generally pleased, and we would expect that these models might reasonably be used for thermodynamic modeling near room temperature, specifically for the fugacity which we consider next.

3. Models for the Fugacity of H_2

From the equation of state models considered in the previous section, it is possible to construct models for the fugacity by integrating. It will be useful here to review briefly what fugacity is in the context of extending the ideal gas chemical potential.

3.1. Ideal gas chemical potential and fugacity for a nonideal gas

It is possible to derive the entropy of an ideal gas from first principles, which leads to the Sackur–Tetrode entropy, which in a physics notation can be written as

$$S(N,E,v) \;=\; Nk_{\mathrm{B}}\left\{\frac{3}{2}\ln\left(\frac{E}{N}\right)-\ln\left(\frac{N}{v}\right)+\frac{3}{2}\ln\left(\frac{M}{3\pi\hbar^2}\right)+\frac{5}{2}\right\}. \tag{6}$$

Here N is the number of atoms or molecules, k_{B} Boltzmann's constant, E the energy, v the volume, and M is the mass. From this entropy model we can derive the chemical potential according to

$$-\frac{\mu}{T} \;=\; \left(\frac{\partial S}{\partial N}\right)_{E,v}. \tag{7}$$

The chemical potential in this model satisfies

$$-\frac{\mu}{k_{\mathrm{B}}T} \;=\; \frac{3}{2}\ln\left(\frac{E}{N}\right)-\ln\left(\frac{N}{v}\right)+\frac{3}{2}\ln\left(\frac{M}{3\pi\hbar^2}\right). \tag{8}$$

The other partial derivatives of the Sackur–Tetrode relation lead to

$$\frac{E}{N} \;=\; \frac{3}{2}k_{\mathrm{B}}T \tag{9}$$

and

$$Pv = Nk_{\mathrm{B}}T. \tag{10}$$

We can make use of these relations at constant temperature to write the chemical potential in the form

$$\mu \;=\; \mu_0 + kT\ln\frac{P}{P_0}. \tag{11}$$

We see that the chemical potential at constant temperature is logarithmic in the pressure. It was noticed that a very similar formula could be used for the chemical potential at constant temperature in the case of a nonideal gas if one worked with the fugacity f

$$\mu \;=\; \mu_0 + kT\ln\frac{f}{f_0}, \tag{12}$$

where the fugacity satisfies

$$\ln\frac{f}{P} \;=\; \int_0^P \left(\frac{P'v}{Nk_\mathrm{B}T} - 1\right)_T \frac{\mathrm{d}P'}{P'}. \tag{13}$$

It will be convenient to switch back to a chemistry notation to write this as

$$\ln\frac{f}{P} \;=\; \int_0^P \left(\frac{P'V}{RT} - 1\right)_T \frac{\mathrm{d}P'}{P'}. \tag{14}$$

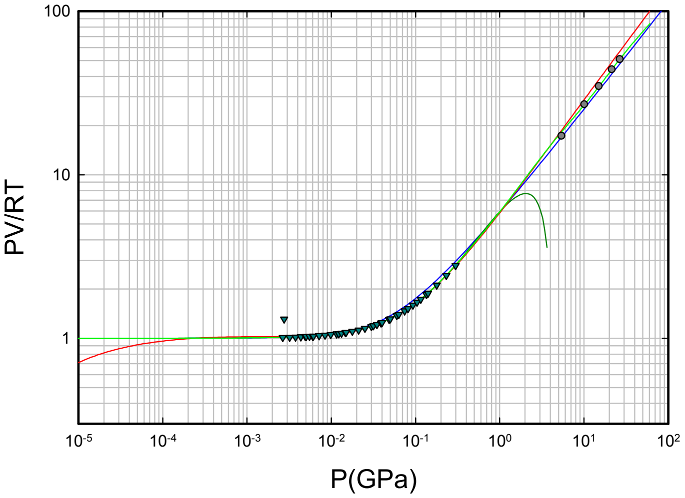

Figure 2. Results for PV/RT as a function of P; Beattie–Bridgeman model fitted by Holley et al. (blue line); Spycher and Reed model (dark green line); Tkacz and Litwiniuk model (red line); Joubert model (light green line); data of Hemley et al. [15] (gray circles); data of Michels et al. [8] (dark cyan triangles)

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3.2. The compressibility factor

We see that the integral appearing in the computation of the fugacity involves the compressibility factor

$$z = \frac{PV}{RT}.$$

This motivates us to examine the compressibility for the different equation of state models considered in the previous section. Results are illustrated in Fig. 2 for the different models compared with experimental data. We notice that the compressibility factor increases at high pressure, which is where we would have expected deviations from the ideal gas law. As was the case previously we see that the model of Spycher and Reed [23] begins to deviate from the other models above 1 GPa.

3.3. Divergence of PV/RT in the model of Tkacz and Litwiniuk

However, this time we notice that the model of Tkacz and Litwiniuk [27] starts dropping below unity at low pressure. We did not see it previously as our earlier plot did not extend down to sufficiently low pressure. The problem in this case is that the form used for the fit does not go to the ideal gas law as $P \to 0$. To illustrate this, we may write

$$\begin{aligned} \frac{PV}{RT} &= 1 + \frac{P}{RT}\left(\frac{A}{P^{1/3}} + \frac{B}{P^{2/3}} + \frac{C}{P^{4/3}} + \frac{D}{P}\right) \\ &= 1 + \frac{1}{RT}\left(AP^{2/3} + BP^{1/3} + \frac{C}{P^{1/3}} + D\right) \rightarrow \frac{1}{RT}\frac{C}{P^{1/3}}. \end{aligned} \tag{15}$$

The compressibility diverges at low pressure in this model. Unfortunately, this will lead to headaches later on.

3.4. Fugacity from the different models

A nice feature of the algebraic form for the different equation of state models we are interested in is that it is possible to carry out the integration required to compute the fugacity analytically. In the case of the Beattie–Bridgeman model, Holley et al. [19] give

$$\ln f = \ln\frac{RT}{V} + \frac{2}{V}\left(B_0 - \frac{c}{T^3} - \frac{A_0}{RT}\right) - \frac{3}{2V^2}\left(bB_0 + \frac{cB_0}{T^3} - \frac{aA_0}{RT}\right) + \frac{4}{3V^3}\frac{cbB_0}{T^3}. \tag{16}$$

For the model of Spycher and Reed [23] we can write

$$\ln\frac{f}{P} = P\left(\frac{a}{T^2} + \frac{b}{T} + c\right) + \frac{P^2}{2}\left(\frac{d}{T^2} + \frac{e}{T} + g\right) \tag{17}$$

Tkacz and Litwiniuk [27] give

$$\ln f = \frac{1.5AP^{2/3} + 3BP^{1/3} + (D + ET)\ln P - 3CP^{-1/3}}{RT}. \tag{18}$$

Finally, we can carry out the integration for the model of Joubert [31] to obtain

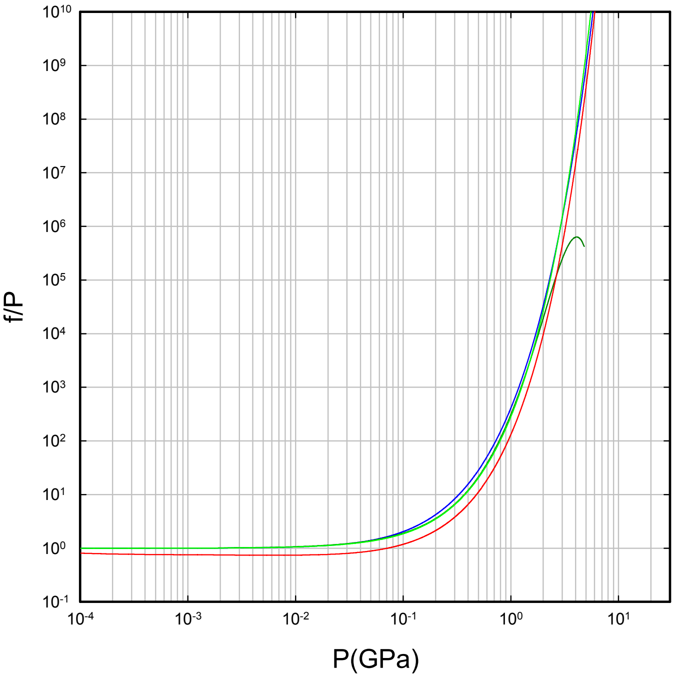

Figure 3. Results for the ratio f/P as a function of P at $T = 300$ K; Beattie–Bridgeman model fitted by Holley et al. (blue line); Spycher and Reed model (dark green line); Tkacz and Litwiniuk model (red line); Joubert model (light green line)

$$\ln\frac{f}{P} = \frac{1}{RT}\Big[a_1b_1(1-\mathrm{e}^{-P/b_1}) + a_2b_2(1-\mathrm{e}^{-P/b_2}) + a_3b_3(1-\mathrm{e}^{-P/b_3}) + a_4b_4(1-\mathrm{e}^{-P/b_4}) + a_5b_5(1-\mathrm{e}^{-P/b_5}) + cP\Big] \qquad (19)$$

Results for the ratio of fugacity to pressure at room temperature (300 K) are shown in Fig. 3. Broadly we see that the ratio increases strongly at high pressure, indicating that the deviations from the ideal gas law are significant above 100 MPa. The ratio based on the model of Spycher and Reed [23] begins to deviate from the results of the other models above a few GPa (which is out of range for the model). We notice that the ratio from the Tkacz and Litwiniuk model is low by a roughly constant offset at low pressure, which is a consequence of model deviating from the ideal gas law below 1 GPa.

3.5. Modification of the Tkacz and Litwiniuk model

We might develop a modification of the model of Tkacz and Litwiniuk in order to remove the low pressure problem. Perhaps the simplest modification is to set the compressibility ratio to unity whenever it goes below; for example we may write

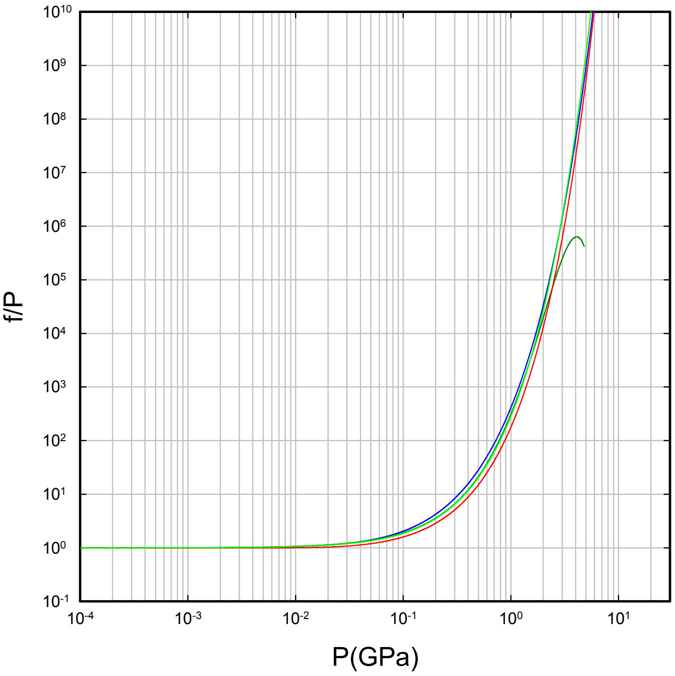

Figure 4. Results for the ration f/P as a function of P at $T = 300$ K; Beattie–Bridgeman model fitted by Holley et al. (blue line); Spycher and Reed model (dark green line); modified Tkacz and Litwiniuk model (red line); Joubert model (light green line)

$$z' = \begin{cases} 1 & \text{for } z < 1, \\ z & \text{for } z > 1. \end{cases} \tag{20}$$

Results are shown in Fig. 4. We see that this modification generally reduces differences with the other models. Nevertheless, the modified version of the model remains noticeably low between 0.1 GPa and a few GPa.

3.6. Fugacity models at different temperatures

The Spycher and Reed model was fit using data between 25 and 600°C, while the Joubert model is based on data at both lower and higher temperature. The data sets available to Holley and coworkers was more limited, so we should expect poorer performance at other temperatures.

A comparison of the different models at 200 and at 500 K is shown in Fig. 5. Above about 0.5 GPa the Spycher and Reed model wanders away from the others; once again we note that this model is fit to data up to 0.3 GPa, and above 25°C, so much of the comparison here exercises the model outside of its range. The older Beattie–Bridgeman model fitted by Holley et al. is clearly the outlier away from room temperature of the remaining three. In general the modified Tkacz and Litwiniuk model tracks the Joubert model reasonably well at both temperatures. We see that the modified Tkacz and Litwiniuk model is a bit lower, similar to the case at 300 K.

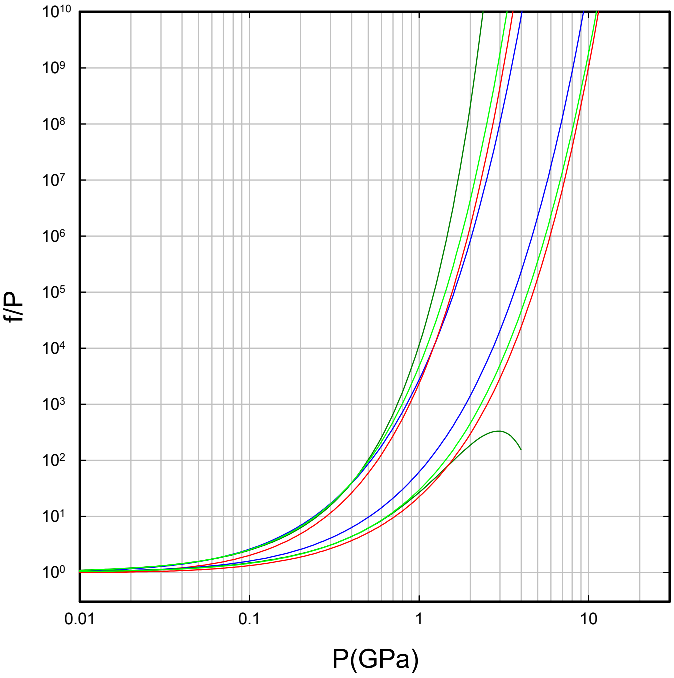

Figure 5. Results for f/P as a function of P at $T = 200$ K (upper curves) and at $T = 500$ K (lower curves); Beattie–Bridgeman model fitted by Holley et al. (blue line); Spycher and Reed model (dark green line); modified Tkacz and Litwiniuk model (red line); Joubert model (light green line)

3.7. Discussion

There are a number of observations the might be made based on this comparison. We were impressed by the older equation of state and fugacity of Holley et al. near room temperature, which does pretty well at pressures much higher than was available when it was constructed; however, we see that the resulting fugacity is not so good away from room temperature. The Spycher and Reed model looks good in the vicinity of the data used for its construction, but the fugacity is not so good when the equation of state is used out of range. The equation of state for the Tkacz and Litwiniuk model looks good except at low pressure where it deviates from the ideal gas law, and the corresponding fugacity is off at low pressure, and also low at higher pressures. The "new" equation of state and fugacity of Joubert is fitted over a wide range of temperatures and pressures, and doesn't suffer from headaches at low pressure. It looks to be superior to all of the others considered in this work.

4. Difference between D_2 and H_2

We are interested in this section in the equation of state for D_2 at high pressure, and in the difference between the equation of state and fugacity between D_2 and H_2. Before focusing in detail, we note that we might expect the two equations of state to be very similar. So one the issue before us is whether we might get good results using an H_2 model

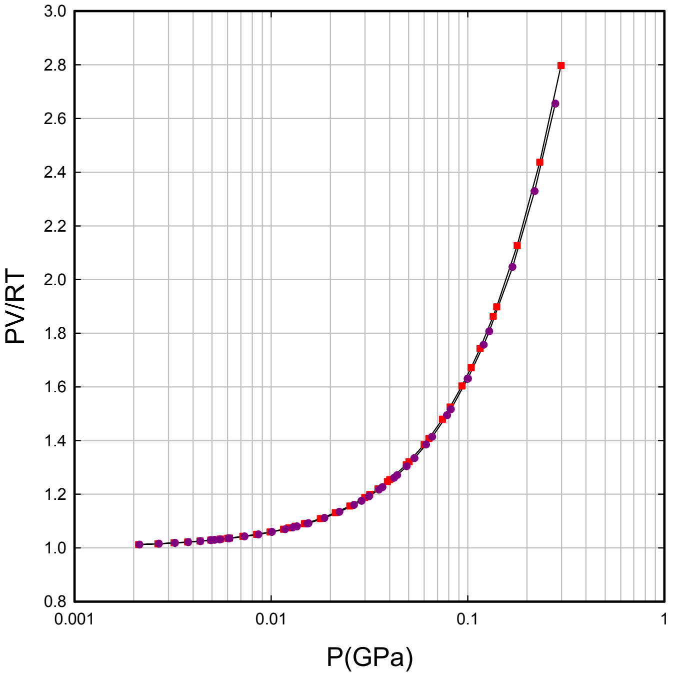

Figure 6. Compression ratio PV/RT for H_2 (light red squares) and for D_2 (dark pink circles) at 25°C as a function of pressure.

for the fugacity of D_2. Another issue is whether we should make use of equation of state models and corresponding fugacity models that have been developed specifically for D_2. And if we do make use of a model that is specific to D_2, would we expect the difference between a D_2 model and an H_2 model to be reliable in capturing the difference between the two gasses?

4.1. Data of Michels et al. [8]

One place to begin the discussion is with the measurements at "low" pressure reported by Michels et al. [8] which are shown in terms of the compression ratio in Fig. 6. At low pressure there does not appear to be a discernible difference in the compression ratio, as would probably be expected since the deviation from the ideal gas compressibility is small, and the difference between deuterium and hydrogen volumes are minimal. At higher pressure, in the vicinity of 0.3 GPa one could argue for a per cent level difference, favoring a larger volume for H_2 as expected due to zero-point nuclear motion contributions.

4.2. Fits of Mills et al. [9,10]

Next we consider the fit for H_2 given in Mills et al. [9], and an equivalent on for D_2 given in Mills et al. [10]. The two fits are

$$
\begin{aligned}
V[\mathrm{H}_2] &= \left(36.716 + 0.0033003T - \frac{22.479}{\sqrt{T}}\right)P^{-1/3} + \left(-17.174 - 0.021393T\right)P^{-2/3} \\
&\quad + \left(-8.9886 + 0.11001T + \frac{69.233}{\sqrt{T}} - \frac{31.395}{T}\right)P^{-1}, \qquad (21)
\end{aligned}
$$

$$
\begin{aligned}
V[\mathrm{D}_2] &= \left(35.283 + 0.00094704T + \frac{3.2843}{\sqrt{T}}\right)P^{-1/3} + \left(-25.090 + 0.0063917T\right)P^{-2/3} \\
&\quad + \left(13.650 + 0.069563T - \frac{158.29}{\sqrt{T}} + \frac{720.00}{T}\right)P^{-1} \qquad (22)
\end{aligned}
$$

with P in kbar and V in cm^3/mol. The ratio $V[\mathrm{H}_2]/V[\mathrm{D}_2]$ is shown as a function of pressure at 300 K between 2 and 20 kbar in Fig. 7. One observes that there is a volume increase for H_2 over D_2 on the order of 1.5%.

4.3. Data of Hemley et al. [15]

Also relevant to the discussion appears to be the PVT measurements of Hemley et al. [15] done for H_2 and for D_2, taken above the liquid/solid phase boundary. One can see from the data points plotted in Fig. 8 that the H_2 volume is larger than the D_2 volume, by a bit more than 1% near 10 GPa. This seems to be generally consistent with the ratio obtained from Mills [9,10].

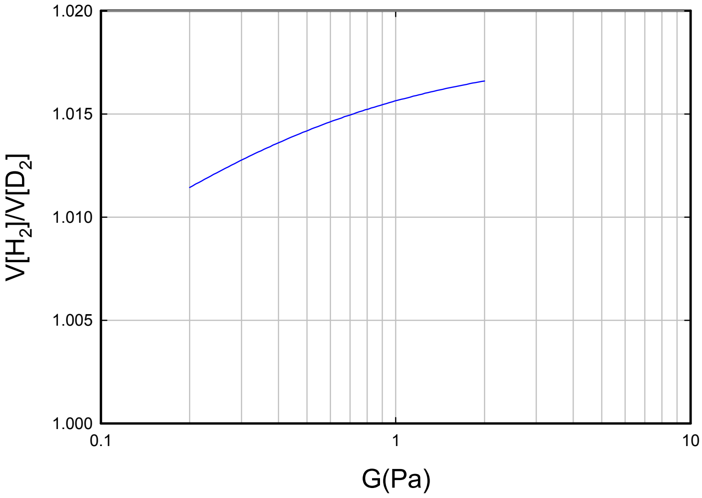

Figure 7. Plot of the ratio $V[\mathrm{H}_2]/V[\mathrm{D}_2]$ as a function of pressure at 300 K based on the fits of Mills [9,10].

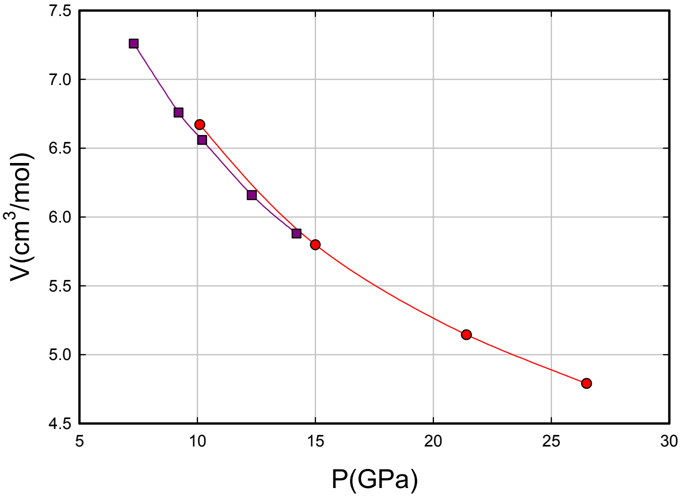

Figure 8. Data points for V as a function of P at 300 K of Hemley et al. [15]. The upper curve with right circles is for H_2, and the lower curve with dark pink squares is for D_2.

4.4. Model of Tkacz and Litwiniuk [27]

Tkacz and Litwiniuk fitted data separately for both H_2 and for D_2. The equation of state model is based on Eq. (4), with the fitting parameters of Table 5. We note the issue that the form of the fit used does not go to the ideal gas law for $P \rightarrow 0$, and that this introduces issues in both the equation of state and the fugacity. Results for the ratio of the volumes as a function of pressure are shown in Fig. 9. One observes that the ratio is generally consistent with experiment at high pressure, but is unreliable at low pressure.

4.5. Model of Joubert and Thiebaut [32]

In the discussion above we found that the empirical model of Joubert [31] seemed to be the best of the lot. A similar equation of state model for D_2 was developed subsequently [32]. This equation of state model is given by Eq. (5) with fitting parameters given in Table 6.

Table 5. Fitting parameters for the equation of state of D_2 based on the Tkacz and Litwiniuk model [27]; the pressure is in MPa, and the volume is in cm^3/mol.

Parameter	Value
A	174.725
B	-643.463
C	-334.258
D	763.862
E	8.63927

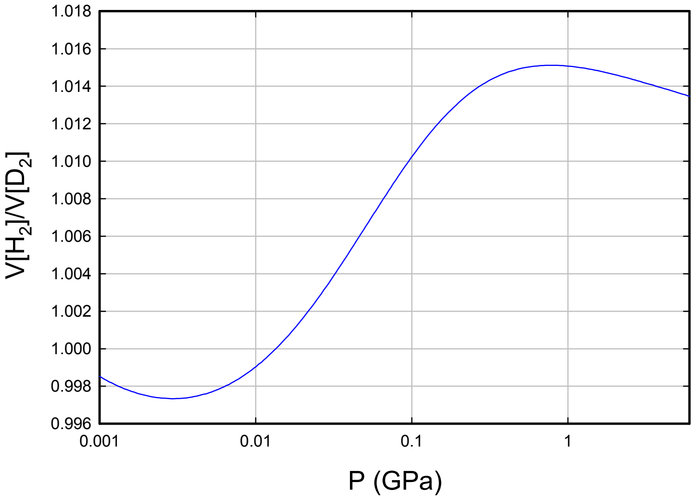

Figure 9. Plot of the ratio $V[\mathrm{H}_2]/V[\mathrm{D}_2]$ as a function of pressure at 300 K based on the fits of the fits of Tkacz and Litwiniuk [27].

Results are shown in Fig. 10. The ratio in this case looks good at low pressure, and increases in a plausible way at somewhat higher pressures. However, the peak ratio goes up over 1.04, which seems too high relative to the experimental data discussed above. Our conclusion in this case is that these most recent models probably overestimate the difference between H_2 and D_2 at room temperature.

Table 6. Fitting parameters for the equation of state of D_2 based on the model of Joubert and Thiebaut [32]; the pressure is in Pa, and the volume is in m^3/mol.

Parameter	Value
a_1	4.86×10^{-6}
a_2	5.46×10^{-6}
a_3	4.342×10^{-6}
a_4	-0.94×10^{-6}
a_5	-1.79×10^{-6}
b_1	5.35×10^{8}
b_2	4.21×10^{9}
b_3	3.99×10^{10}
b_4	2.90×10^{7}
b_5	8.02×10^{7}
c	2.434×10^{-6}
R	8.31451

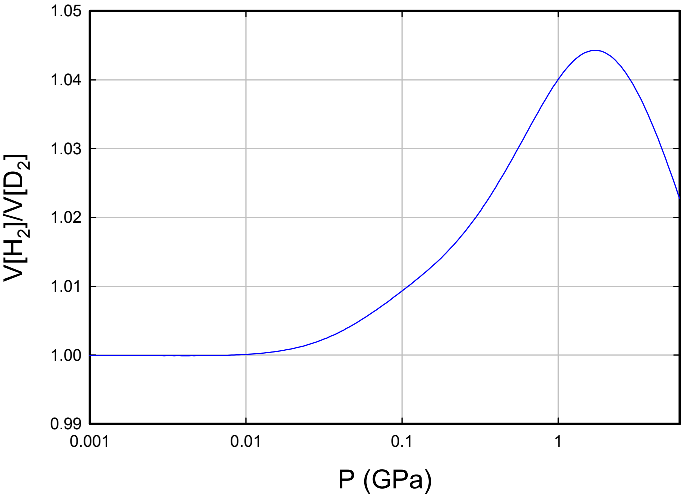

Figure 10. Plot of the ratio $V[\mathrm{H}_2]/V[\mathrm{D}_2]$ as a function of pressure at 300 K based on the fits of the fits of Joubert [31] and Joubert and Thiebaut [32].

4.6. Discussion

From the experimental data sets discussed above we would expect the H_2 volume to be larger than the D_2 volume by up to about 1.5% near 1 GPa. The empirical models of Tkacs and Litwiniuk [27] are consistent with this around 1 GPa, but have issues at lower pressure. The recent models of Joubert [31] and Joubert and Thiebaut [32] are good at low pressure, but overestimate the difference at higher pressure.

Suppose we wished to study the difference between H_2 and D_2 in connection with PdH and PdD near room temperature, and we wanted to understand what difference came about due to differences in the fugacity, then how might we proceed? Based on the discussion above, one way might be to make use the difference in volume at high pressure based on the Tkacs and Litwiniuk [27] equation of state models (use a cut-off factor to suppress the errant low-pressure anomaly), and then use this to modify the Joubert [31] H_2 equation of state to D_2.

5. Theoretical Issues

One could imagine starting with the equation of state model for H_2 of Joubert [31], and then estimating the difference between H_2 and D_2 based on a theoretical model. For example, if one believed that the nuclear zero-point contribution to the equation of state was dominant, it would be possible to develop and estimate of the difference, and then use this estimate to correct the H_2 equation of state to make it applicable for D_2.

Unfortunately, the situation is more complicated than this, as we will see in this section. Moreover, this problem in general has been of interest to researchers in the literature, and it seems worthwhile to think some about the issues involved.

5.1. Absence of a mass difference in a simple classical model

It is possible to make some progress by considering first a classical version of the model in which the interaction potential between two H_2 molecules is the same as the interaction potential between two D_2 molecules. In this case we can compute the pressure from the classical partition function according to

$$P = k_\mathrm{B}T \left[\frac{\partial}{\partial v} \ln Z_\mathrm{C} \right]_T . \tag{23}$$

The classical partition function in this case is given by

$$Z_\mathrm{C} = \frac{1}{(\prod_k N_k!)} \frac{1}{h^{3n}} \int \cdots \int \mathrm{e}^{-H(\mathbf{r}_1 \cdots \mathbf{r}_n, \mathbf{p}_1 \cdots \mathbf{p}_n)/k_\mathrm{B}T} \mathrm{d}^3\mathbf{r}_1 \cdots \mathrm{d}^3\mathbf{r}_n \mathrm{d}^3\mathbf{p}_1 \cdots \mathrm{d}^3\mathbf{p}_n, \tag{24}$$

which is a generalization of the identical molecule formula in Mayer [41]. The momentum integrations can be done analytically for the nonrelativistic version of the problem

$$\int \cdots \int \mathrm{e}^{-\sum_j |\mathbf{p}_j|^2/2m_j k_\mathrm{B}T} \mathrm{d}^3\mathbf{p}_1 \cdots \mathrm{d}^3\mathbf{p}_n = \prod_j \left(2\pi m_j k_\mathrm{B} T \right)^{3/2} . \tag{25}$$

The resulting contribution is independent of the volume V, and so does not contribute to the pressure. In this case, the classical pressure in a simple binary interaction model is given by

$$P = k_\mathrm{B}T \left[\frac{\partial}{\partial V} \ln \int \cdots \int \mathrm{e}^{-\sum_{j<k} U(\mathbf{r}_j - \mathbf{r}_k)/k_\mathrm{B}T} \mathrm{d}^3\mathbf{r}_1 \cdots \mathrm{d}^3\mathbf{r}_n \right]_T . \tag{26}$$

The pressure then is this kind of simple classical model is independent of the mass. This is the reason that we see such similar equation of state curves in the previous section.

5.2. Pressure in a quantum mechanical model

In a quantum mechanical version of the problem the partition function can be defined according to

$$Z_\mathrm{Q} = \sum_j g_j \mathrm{e}^{-E_j/k_\mathrm{B}T}, \tag{27}$$

where the summation is over the states of the (many-particle) quantum system. From this quantum mechanical partition function, we can determine the pressure as before

$$P = k_\mathrm{B}T \left[\frac{\partial}{\partial v} \ln Z_\mathrm{Q} \right]_T . \tag{28}$$

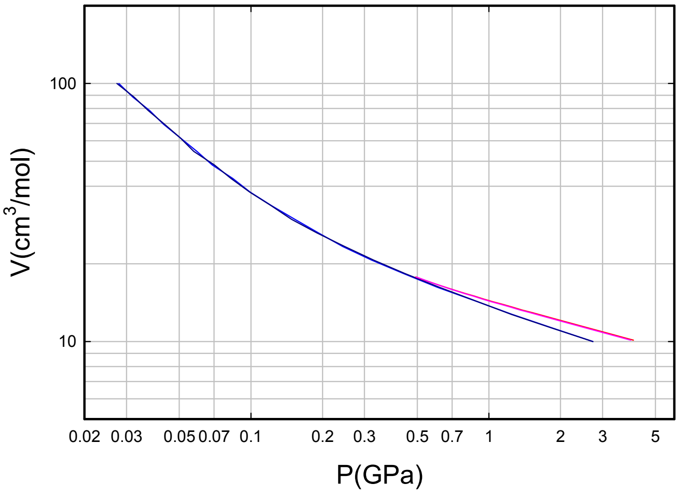

Figure 11. Volume as a function of pressure for the Slater–Kirkwood exp-6 potential model of Ross al. [43]; molecular dynamics for H (blue) and D (dark blue); quantum FCC cell model for H (red) and D (pink).

5.3. Computational results

We examined a specific model for the equation of state based on some classical and quantum mechanical models, in order to try to understand the theoretical problem better. For these calculations we used the Slater–Kirkwood [42] exp-6 model of Ross et al. [43]. For the classical equation of state we computed the pressure at a fixed volume for 200 molecules at room temperature based on a molecular dynamics calculation. As expected we obtained the same pressure for H_2 and D_2 to within the precision of the calculation (see Fig. 11). We worked with a number of different molecular potential models, and found that the Slater–Kirkwood exp-6 model of Ross et al. [43] gave the best agreement with the experimental equation of state at room temperature.

For the quantum mechanical equation of state, we modeled a single molecule as a quantum particle in a fixed FCC lattice with the same exp-6 potential model. The quantum calculation might be considered to be a numerical 3D quantum cell calculation with a realistic potential, as a generalization of the simpler quantum cell calculation used in years past from the literature [44–50]. For these calculations we solve the (discretized) Schrödinger equation directly for up to about 30,000 states, we construct the quantum mechanical partition function, and repeat for different volumes to allow a pressure calculation. The results are shown in Fig. 11.

For the quantum mechanical calculation, we found good agreement with the classical calculation at low pressure, and a systematic deviation from the classical model at higher pressures. This can be attributed to the use of a quantum cell model, in which the collisions between the test molecule and neighboring molecules at fixed locations are harder on average than had we allowed all of the molecules to move. We also found a higher pressure for H_2 than D_2 as a result of the difference in the nuclear zero-point motion at all but the largest volume used (where the computation is most demanding due to many excited state contributions which become difficult to compute accurately in a single calculation as we carried out).

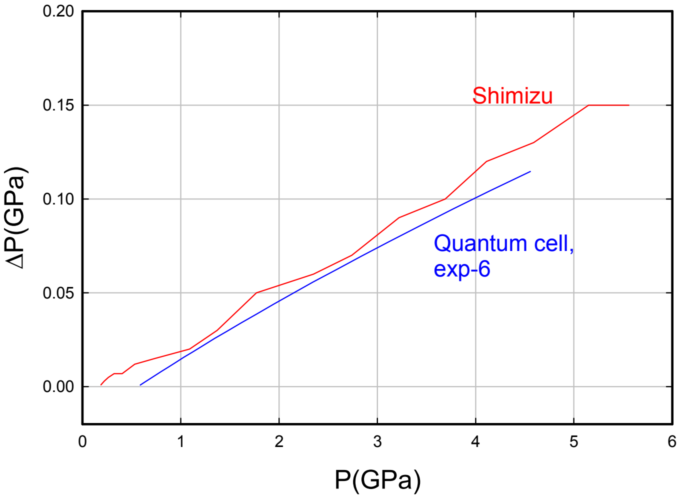

Figure 12. Differential pressure for H_2 and D_2 as a function of H_2 pressure for the quantum cell calculation with the Slater–Kirkwood exp-6 potential model (blue); and from the calculations of Shimizu and Kumazawa [51].

The difference in pressure between H_2 and D_2 was determined at different volumes from the quantum cell model (Fig. 12), with the results in reasonable agreement with the perturbation theory calculation of Shimizu and Kumazawa [51]. The ratio of the volumes from the cell model calculation is shown in Fig. 13. We see that the contribution of the zero-point nuclear motion yields a volume ratio that is less than what is observed in experiment.

5.4. Difference in the binary potentials

We have argued that the zero-point contribution cannot account for the difference between the H_2 and D_2 equation of state, we must turn to other explanations. In this case there is another source of difference between the two problems which is perhaps more subtle, but which should be expected. At room temperature we would expect some degree of excitation of the rotational states. For example, keeping in mind that some of the rotational states are excluded because the overall wavefunction must be anti-symmetric, we can compute the average rotational excitation to be

$$\langle l \rangle = 1.213 \quad \mathrm{H}_2, \qquad \langle l \rangle = 1.856 \quad \mathrm{D}_2. \tag{29}$$

In the case of the molecular hydrogen at near 0 K, the equation of state is different for *ortho*-H_2 and *para*-H_2 [52–54]. Since the masses are the same in this case, the differences can only be attributed to the differences in the inter-molecular potential which is known to differ for the different rotational states. Models for the inter-molecular potential have been developed for some of the low-lying rotational states [55–58]. However, what would be helpful would be an inter-molecular potential model averaged appropriately over the degree of rotational excitation. Such a model would be very useful for the computation of differences between H_2 and D_2.

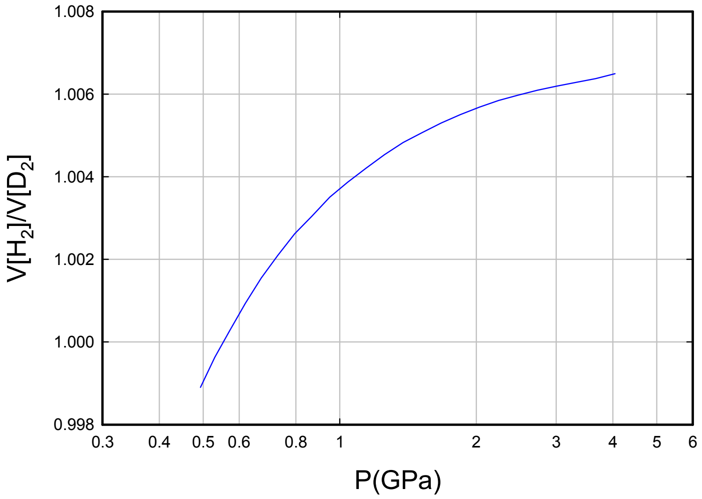

Figure 13. Ratio of V[H_2]/V[D_2] as a function of H_2 pressure from the quantum cell model.

6. Discussion and Conclusions

To interpret experimental results for the loading as a function of pressure, and to understand the chemical potential of hydrogen or deuterium in metals, reliable models for the fugacity are needed. This problem has been of interest now for almost 80 years, so much work has been focused on the problem generally. In the earliest modeling efforts, it was sufficient to make use of an ideal gas model for hydrogen gas and deuterium gas. However, to model the Fleischmann–Pons experiment we are interested in understanding the chemical potential at a loading near unity, which means that we need to understand the equation of state and the fugacity at pressures up to and beyond 1 GPa.

Fortunately, there are available many experimental studies of the H_2 equation of state in the regime of interest, and fewer studies of the D_2 equation of state. The model of Tkacz and Litwiniuk [27] has been important in recent years; however, it is not widely appreciated that the fit employed leads to a divergence from ideal gas relations at low pressure. We noticed differences in the fugacity larger than expected a few years ago [59] when we compared it with results published by Bockris et al. [7] based on the model of Holley et al. [19]. The more recent model of Joubert [31] represents a significant improvement.

In times past people would use the H_2 fugacity freely for D_2, since one would expect the differences to be small. However, in recent years there have become available equation of state and fugacity models that are specific to D_2, which is of great interest for precision thermodynamic modeling. We were interested in whether the differences in the H_2 and D_2 models is reliable, in the sense of being reflected in the equation of state data. In the models of Tkacz and Litwiniuk [27], the difference at room temperature near 1 GPa seems close to the difference seen in experiment. However, the same does not seem to be true for the more recent models of Joubert [31] and Joubert and Thiebaut [32].

Since the differences are small, we thought that it might be possible to arrange for an estimate of the difference based on theory. For example, one can contemplate developing a reliable estimate for the zero-point contribution to the equation of state. As we have seen, this contribution is only part of the difference. The remainder is due to differences in the inter-molecular potential. In principle this could be calculated, if a suitable rotationally averaged inter-molecular potential were available. At present such a model does exist. In the future we would expect such models to be of interest, and once available one might return to the problem of developing a theoretical estimate for the difference in equation of state models.

Given the present situation, probably the most reliable approach to fugacity models that can address differences between the H_2 and D_2 fugacity would be to work with the difference between the two equation of state models of Tkacz and Litwiniuk [27], use a cut-off at low pressure, and then use this difference with the model of Joubert [31] to obtain equation of state and fugacity values for D_2.

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