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TRANSLATIONAL HEAT CAPACITY IN SMALL CUBIC BOXES: A POSSIBLE CONTRIBUTION TO TEMPERATURE HEAT CAPACITY MAXIMUM IN Pd–HYDROGEN SYSTEMS *

ZDENĚK SLANINA **
Max-Planck-Institut für Chemie (Otto-Hahn-Institut), Mainz (F.R.G.)

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ABSTRACT

The behaviour of the partition function of translation of an ideal gas particle in a cubic box of gradually decreasing dimensions has been studied. For the thermodynamic term of molar translational heat capacity at constant volume this process leads to distinct deviations from the conventional term of $\frac{3}{2}R$ when considering very small dimensions of the cube. The dependence on the cube-edge magnitude exhibits a maximum which exceeds $\frac{3}{2}R$ by about 1.56 J K^{-1} mol^{-1}. These results have been applied to hydrogen isotopes occluded in elementary cubic cells of Pd. It has been shown that the effects of translation in small volumes can contribute to the observed temperature heat capacity maximum of the Pd–hydrogen system.

INTRODUCTION

The first available information [3–13] concerning the presumed low-temperature nuclear fusion in Pd fed with deuterium has naturally revived interest in the various physicochemical characteristics of this system. The former quantum chemical studies of energetics [14–20] can now be meaningfully extended to the thermodynamic aspects of the behaviour of this system. These also include the heat capacity of hydrogen in Pd which shows a remarkable temperature anomaly [21–24]. The heat capacity at constant pressure exhibits a local maximum at a temperature of about 55 K (the position of this maximum is similar for isotopes H and D). This peak can be interpreted using arguments similar to those employed to explain the Schottky anomaly in a system with two energy levels. In the case given, two phases

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[*] Dedicated to the memory of the late Academician A.D. Sakharov (1921–1989) who as early as 1948 had indicated [1,2] the possibility of muon-catalysed fusion.

[**] Author to whom correspondence should be addressed at The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Dolejškova 3, CS-182 23 Prague 8, Czechoslovakia.

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coexist, namely an α phase with low hydrogen content and an expanded, hydrogen-rich β phase [25]. The presence of these two phases can be treated [26–29] within a quasi-chemical model [30,31].

Recently, attention has been paid to limiting the behaviour of the partition functions of motions whose quantum models show a quadratic dependence of the energy spectrum on the quantum number(s) [32–42]; this is true of the partition functions of free internal rotation or translation in a rectangular prism. These studies have shown the need for transition from the conventional one-term partition functions [43] to multiterm expressions [32,37,44,45]. From our viewpoint, the possible dependence of translational partition function on vessel shape is of interest [38–42]. Such a dependence could be important when studying the motions in systems represented by a large number of relatively isolated spaces of very small dimensions, e.g. cavities of various types [46,47]. Hydrogen isotopes occluded in Pd have recently been approximated in this way, and it has been shown that the molar internal energy of translation can increase above any limit when decreasing the dimensions of the elementary cells to the zero limit [42]. This paper is a continuation of this work and develops the model, focusing on the aspects related to the heat capacity term.

RESULTS AND DISCUSSION

General formulation

The energy of an ideal gas particle of mass m in a cubic box of edge a is given by the well-known relation [43]

$$E_{n_1 n_2 n_3} = \frac{h^2}{8ma^2}\left(n_1^{\,2} + n_2^{\,2} + n_3^{\,2}\right) \tag{1}$$

where n_1, n_2 and n_3 are the quantum numbers ($n_i = 1, 2, \ldots$) and h denotes the Planck constant. The translational partition function for this cube is given by the summation

$$q = \left[\sum_{i=1}^{\infty} \exp\left(-\frac{h^2 i^2}{8mkTa^2}\right)\right]^3 = \left[\sum_{i=1}^{\infty} \exp\left(-\sigma_i^{\,2}\right)\right]^3 \tag{2}$$

where k is the Boltzmann constant and T is the absolute temperature.

The partition function of 1 mol of this ideal gas (corrected boltzons) is

$$Q = q^N/N!, \tag{3}$$

where N is the Avogadro number. In these terms the contribution of translation to heat capacity at constant volume is [43]

$$\delta C_v = (\partial E/\partial T)_v \tag{4}$$

where the molar translational energy E is given by the relation

$$E = kT^2(\partial \ln Q/\partial T)_{v,N} \tag{5}$$

After carrying out the respective operations we obtain

$$\frac{\delta C_v}{R} = 3\sigma^2\left\{\frac{\sum_{i=1}^{\infty} i^4 \exp(-\sigma i^2)}{\sum_{i=1}^{\infty} \exp(-\sigma i^2)} - \left[\frac{\sum_{i=1}^{\infty} i^2 \exp(-\sigma i^2)}{\sum_{i=1}^{\infty} \exp(-\sigma i^2)}\right]^2\right\} \tag{6}$$

Clearly, in the conventional limiting case $\sigma \rightarrow 0$ (e.g. $a \rightarrow \infty$)

$$\lim_{\sigma \rightarrow 0} \delta C_v = \tfrac{3}{2}R \tag{7}$$

Also it is obvious that although eqn. (6) allows for a dependence on edge length a (cf. eqn. (2)), the conventional relation (7) does not involve such a residual dependence.

Application to the Pd–hydrogen isotope system

In order to simulate Pd elementary cells, let us adopt the same approach as used in ref. 42. Hence we consider (i) a cell derived directly from the face-centred cubic (f.c.c.) lattice of the metal with a lattice constant [48] of $a = 3.884 \times 10^{-10}$ m and (ii) a lattice constant $a = 4.020 \times 10^{-10}$ m corresponding [48] to a sufficient occlusion of hydrogen. (For our purposes it is not important that the lattice constants for the coexisting α and β phases differ: 3.894×10^{-10} m and 4.025×10^{-10} m respectively [25].) Finally, a third value of the edge length a is also considered as recommended in ref. 42, i.e. a value derived from the term of 4.020×10^{-10} m by subtracting the reported [49] twofold metallic radius of Pd ($a = 1.280 \times 10^{-10}$ m). The hydrogen isotopes ^{1}H, ^{2}D and ^{3}T (as well as the most stable helium isotope ^{4}He) are considered to be present in the elementary cell as free atoms (although their real form is still rather an open question [50]).

The derivation given above presumes the occlusion of 1 mol of ideal gas particles in a common cube. However, in the real situation for the Pd–hydrogen system, the bulk of Pd metal is represented by a large number of (mutually interacting) elementary cubic cells, which dramatically reduces the number of particles in one cube. If we assume that the motion of any occluded particle represents translation in a single small cube, the one-particle partition function will continue to represent the starting point. Although the combinatorial reasoning will be different, the resulting formula (6) can also be considered to be significant for the particular situation treated.

Figure 1 presents the dependence of the $\delta C_v/R$ term on the dimensionless parameter σ. It can be seen that with increasing value of the σ parameter the

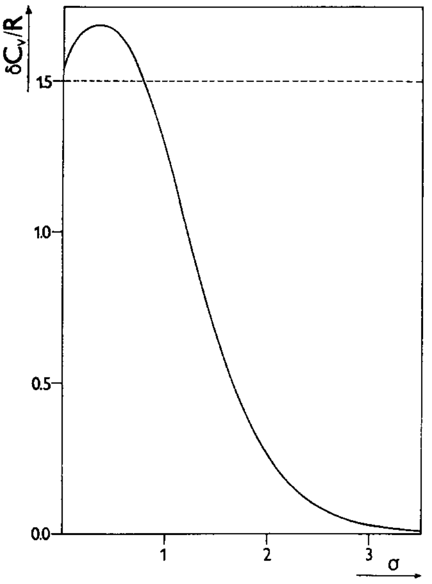

Fig. 1. Dependence of the reduced molar heat capacity at constant volume for translation in a cubic box ($\delta C_v/R$) on the reduced dimensionless quantity σ in the region of moderate values (the broken line indicates the result for the limit $\sigma \to 0$, i.e. from the conventional translational partition function approach).

$\delta C_v/R$ term increases above the conventional limiting value of $\frac{3}{2}$. The maximum is attained at about $\sigma = 0.349$, the height of this maximum being equal to about 1.687. A rapid decrease to zero is then observed.

Table 1 shows the temperatures at which the maximum of Fig. 1 is reached for individual choices of the parameters a and m. It can be seen that, with regard to the observed maximum in the heat capacity at constant pressure in the Pd–hydrogen system at about 55 K [21–25], the phenomenon of translation in a small volume cannot be used as an exclusive (alternative [25]) explanation of the origin of this maximum. Nevertheless, this phenome-

TABLE 1

Temperature position T_0 of the maximum[a] of the translational heat capacity at constant volume δC_v for species accommodated in Pd cells

a (10^{-10} m)	T_0 (K)			
	^{1}H	^{2}D	^{3}T	^{4}He
4.020	42.1	21.1	14.1	10.6
3.884	45.1	22.6	15.1	11.4
1.280	415.3	207.8	138.8	104.6

[a] The maximum height is 14.030 J K^{-1} mol^{-1}, i.e. by 1.559 J K^{-1} mol^{-1} larger than the conventional term $\frac{3}{2}R$.

non can be taken as a mechanism contributing to this maximum. For a final evaluation of the importance of the contribution of this mechanism, it will be necessary to elaborate further (cf. refs. 42,51) the model used in this work.

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