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TOWARDS MOLECULAR-THERMODYNAMIC ASPECTS OF POSTULATED Pd/D LOW-TEMPERATURE NUCLEAR FUSION: A USEFUL EXAMPLE OF A FAILURE OF THE CONVENTIONAL TRANSLATIONAL PARTITION FUNCTION

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ABSTRACT

The partition function of translation in a cubical box of very small volume has been studied. Decreasing dimensions of the cube have been found to cause gradually larger deviations from the conventionally used partition function. This is manifested in the corresponding values of thermodynamic quantities. Special attention was paid to the molar internal energy of translation, and marked differences from the conventional term of $3RT/2$ were observed for very small dimensions of the cube, this energy term being increased without limitation in the limiting case. These results were applied to the hydrogen isotopes occluded in elementary cubic cells of Pd. The results are interpreted as a possible auxiliary contribution to the overall mechanism of the low-temperature nuclear fusion presumed to take place in a Pd electrode fed with deuterium.

INTRODUCTION

Recently, attention has been paid to the limiting behaviour of the partition functions of motion with quantum models exhibiting a quadratic dependence of the energy spectrum on the quantum number(s). This especially applies to the partition function of free internal rotation in molecules [1–6] as well as to that of translation in a rectangular prism [7–10]. From a practical standpoint, the more interesting results have been those for free internal rotation, especially in the case of small molecular complexes. These species can exhibit relatively very small values of reduced moments of inertia and fairly low temperatures are needed for their observation. Under such conditions, the free internal rotation should make a rather low, but always positive, contribution to the entropy values. However, the conventional one-term partition function [11] can, under these conditions, lead to a contribution which is paradoxically negative and decreases without limitation with decreasing temperature [1,2]. In spite of this, the partition function

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was used in a number of studies without this serious defect being recognized. It is already obvious that this failure of the conventional partition function of free internal rotation is caused by replacement of rigorous summation in its usual derivation by approximative integration. On this basis, several-term formulas have been constructed [1,6,12,13] which apply well, at least within the sections of intervals where the conventional formula fails. Nevertheless, the technique of direct summation with an evaluation of the summation residuum was recommended [4,5] as the single universal means for this purpose.

The situation in the case of the translational partition function has been less interesting up to now, although it was shown that there exists, in principle, some residual dependence of the exact form of this function upon the vessel shape [7–10]. Nevertheless, it was obvious that this dependence would be quite insignificant in usual chemical situations. Potential applications were expected either at low temperatures (with the presumption of a transition to the relevant quantum statistics) or in vessels of very small dimensions, e.g. in the region of inclusion phenomena, in clathrates or zeolites or in cavities serving to simulate the dissolution of gases [14]. The carbon aggregates C_{60} and C_{70} [15] are recent examples of such type of cavities. The first pieces of information [16] about the presumed low-temperature nuclear fusion in the Pd electrodes fed with deuterium provide another impetus to study the thermodynamics of translational motions in small volumes.

RESULTS AND DISCUSSION

General reasoning

The energy spectrum of a particle of ideal gas of mass m in a cubical box of edge a is given by the well-known relation [11]

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

where $n_i = 1, 2, \ldots$ are quantum numbers and h stands for the Planck constant. The translational partition function for this cube is then given by the summation

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

where k is the Boltzmann constant and T is the absolute temperature. For sufficiently small σ values it is possible to replace the summation (2) by the integration from which the conventional formula of the translational partition function is obtained [11]. For 1 mol of ideal gas the partition function of the whole system reads as follows (corrected boltzons)

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

where N is Avogadro's number. In these terms the molar internal energy E generally is [11]

$$E = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N} \tag{4}$$

where V is the volume of the system. In terms of the rigorous summation (2) we obtain eqn. (5) for the molar internal energy of translational motion

$$\frac{E}{RT} = 3\sigma \frac{\sum\limits_{i=1}^{\infty} i^2 \exp(-\sigma i^2)}{\sum\limits_{i=1}^{\infty} \exp(-\sigma i^2)} \tag{5}$$

where R stands for the gas constant. If the transition from the summation to integration is applied to sufficiently small σ, then eqn. (5) is reduced to the usual expression $3RT/2$. For higher values of the reduced quantity σ eqn. (5) can be determined with any chosen precision by the technique of direct summation [5]. The results thus obtained are shown in Fig. 1. The conventional formula for the translational partition function, which provides the uniform term of $3RT/2$, does not allow for any dependence of the molar internal energy upon the mass of particle of the ideal gas or upon the dimensions of the cube. Figure 1, however, demonstrates that in a more rigorous approach such dependences do exist, even though they are not very distinct except at small values of a (and/or of the particle mass and/or of the temperature). In our context, it is significant that if the parameter σ grows without limitations, then the energy eqn. (5) also grows without limitations.

Application to the system Pd–hydrogen isotopes

The first pieces of information [16] about the potential low-temperature nuclear fusion in the Pd electrode fed with deuterium indicate that this problem also has molecular-thermodynamic aspects. These, first of all, include the question of accommodation and behaviour of deuterium in elementary cells of Pd. This metal has an f.c.c. lattice with a lattice constant [17] of 3.884×10^{-10} m. The hydrogen occlusion being sufficient, this lattice is broadened [17] up to a lattice constant value of 4.020×10^{-10} m. It seems appropriate to treat the motions of hydrogen isotopes in the elementary cells of Pd simply as translations in small cubes. There is, of course, a certain difference here. The above discussion dealt with 1 mol of ideal gas compressed in a single cube. Now, the whole bulk of metal Pd is to be

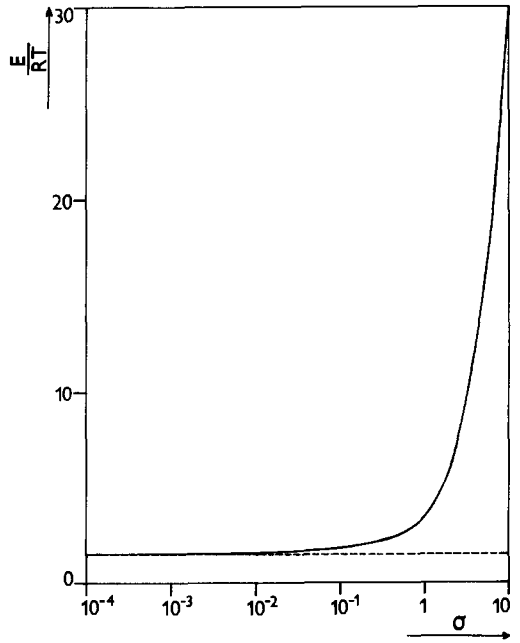

Fig. 1. Dependency of the reduced molar internal energy of translation in a cubical box, E/RT, on the reduced, dimensionless quantity σ (the dashed line indicates the result from the conventional translational partition function approach).

represented by a large number of (mutually interacting) elementary cubic cells, thereby reducing dramatically the number of particles moving in a single cube. Nevertheless, in a state of thermodynamic equilibrium it is possible to consider the motion of each occluded particle as approximately translation in a small cube and, hence, to adopt the energy spectrum (1). Although a different combinatorial reasoning is now valid for the system partition function (3), nevertheless the one-particle partition function q is significant for the temperature differentiation (4). Therefore, in this case we also can evaluate the molar internal energy according to eqn. (5).

The situation in the elementary cell of Pd, of course, corresponds only approximately to the rectangular potential in a cubic box; the real potential will have a more rounded shape. This can be interpreted also as an effective lowering of the edge length a of the model cube. Therefore, three different dimensions of the model cube were considered (Table 1). Besides both the above-mentioned values, a third value of the edge length a was considered which was derived from the value of 4.020×10^{-10} m by subtracting the reported [18] twofold metallic radius of Pd (1.37×10^{-10} m). The results of Table 1 indicate that, even at room temperature, the motion in a small area can lead to a significant increase in the kinetic energy of the occluded species as compared with the conventional description of translational motion.

TABLE 1

Molar internal energy [a] E of species accommodated in Pd cells at room temperature

a (10^{-10} m)	$\frac{E}{RT}$ [b]			
	^{1}H	^{2}D	^{3}T	^{4}He
Any [c]	1.5 [c]	1.5 [c]	1.5 [c]	1.5 [c]
4.020	1.715	1.646	1.617	1.601
3.884	1.723	1.651	1.622	1.604
1.280	2.473	2.078	1.942	1.869

[a] The translational energy contribution is considered only.

[b] Reduced dimensionless representation; R denotes the gas constant and T room temperature ($T = 298.15$ K).

[c] Results from the conventional translational partition function formula.

Further progress in understanding these problems will be possible after a more detailed investigation of the potential profiles in the Pd cells and elucidation of the form of the hydrogen isotopes present (e.g. the form of positively charged clusters [19]). Also, it will be necessary to pay attention to a more complete statistical–mechanical description of the occlusion of hydrogen in Pd inclusive of the transition towards quantum statistics. In conclusion, this work indicates a possible substantial increase in kinetic energy of particles placed in small spaces. This represents a possible auxiliary contribution which also should be considered when constructing [20–22] the overall mechanism of the low-temperature nuclear fusion presumed to occur [16] in the Pd electrode fed with deuterium.

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