

On temperature increase of the Mg_2 mole fraction in saturated magnesium vapour¹

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Abstract

The composition of saturated magnesium vapour is investigated in terms of the dimerization equilibrium constant and the observed saturated pressure in the temperature region 700–1000 K. The highest reported value of the dimer mole fraction x_2 in its equilibrium mixture with the monomer at the saturated pressure is quite small (0.004%). It is found that (at least in the interval 850–1000 K) the x_2 term increases with temperature. This is in agreement with recent findings of such temperature increase with other associating vapours.

INTRODUCTION

Molecular complexes represent a subject of considerable and wide chemical and physical interest [1,2]. They are essentially present in any gas phase; however their amounts can vary considerably with conditions. Accurate data on their concentrations are usually lacking and computational evaluations can thus be helpful. From a physicochemical point of view conditions in saturated vapours are quite distinct and should therefore be investigated concerning the molecular-complex contents. The situation is of considerable interest to atmospheric chemistry [3–10] because for atmospheric steam, for example, the conditions are close to saturation. In this connection it has been found [11–13] that the water dimer and trimer populations increase with temperature. As the finding is based on harmonic vibrational partition functions there is an important question concerning effects of higher approximations on the partition function. Owing to computational difficulties the question cannot at present be answered for the water dimer. However, it can be investigated for two-atom species

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[14]. Magnesium vapour, i.e. an equilibrium mixture of Mg(g) and Mg₂(g), represents a convenient system [15]. The present report deals with the problem in detail.

COMPUTATIONS

Let us consider an equilibrium monomer–dimer mixture (i.e. we shall neglect any higher aggregates). For the dimer mole fraction x_2 the relationship [11–13]

$$x_2 = \frac{2PK_p + 1 - (4PK_p + 1)^{1/2}}{2PK_p} \quad (1)$$

holds, where P stands for the total pressure of the mixture. For the limiting case $PK_p \ll 1$, eqn. (1) can be reduced to the simple form $x_2 \approx PK_p$. The total pressure can take any value between zero and the related saturated pressure, and in fact even beyond if we allow for super-saturated conditions. However, in this report P will exclusively denote the saturated pressure.

Equilibrium constants K_p of the dimerization



were recently calculated [15] in a number of approximations, in particular for harmonic, Morse, Lennard–Jones (LJ) and Varandas–Dias da Silva (VD) [16] potentials. Moreover, various approximations of partition functions were tested, e.g. the numerically exact (Q) and the quantum rigid rotor (QRR). For our purposes we shall consider five sources of the K_p values (VD/Q, VD/QRR, LJ, Morse, and harmonic, the last three potentials being combined with the QRR approximation). Table 1 presents K_p values [15] in the approximations at 1000 K.

TABLE 1

Mole fraction x_2 of Mg₂(g) in its equilibrium mixture with Mg(g) calculated under saturated pressure for various evaluations [15] of the dimerization equilibrium constant K_p for 1000 K

Approximation ^a	K_p (atm ⁻¹)	x_2 (%)
VD/Q	0.00062	0.00097
VD/QRR	0.00258	0.00404
LJ	0.00198	0.00310
Morse	0.00151	0.00236
Harmonic	0.00177	0.00276

^a See text and ref. 15 for explanation of the abbreviations.

From the K_p values calculated at selected temperatures in the interval 100–1000 K we passed to an analytical fit in the six-term form

$$\lg K_p = A + \frac{B}{T^2} + \frac{C}{T} + D \lg T + ET + FT^2 \quad (3)$$

(We added a limiting condition of vanishing K_p term in the high temperature limit.) The same analytical fit is used in this report for evaluation of the observed temperature dependence of the saturated pressure P of magnesium vapour [17].

RESULTS AND DISCUSSION

The values of the dimerization equilibrium constant K_p can differ considerably in some approximations. Consequently, the dimeric mole fraction x_2 under the saturation conditions varies significantly (Table 1). Even the highest value at $T = 1000$ K (about 0.004%) is however considerably smaller than those reported at lower temperatures for the water dimer [11–13]. This is a consequence of considerably lower saturated pressures (for example, at $T = 1000$ K the saturated pressure is [17] $P = 0.016$ atm) and lower potential depth (the LJ term for Mg_2 equals [15] about 5 kJ mol⁻¹).

Figures 1–3 present calculated temperature dependences of the dimeric mole fraction x_2 in saturated magnesium vapour in the interval 700–1000 K for three selected representative approximations (VD/Q, VD/QRR, and harmonic). The selected temperature interval in fact represents the

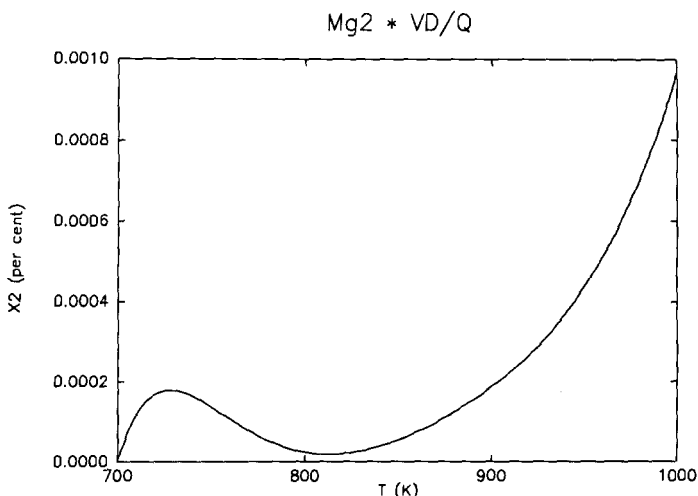


Fig. 1. Temperature dependences of the $Mg_2(g)$ mole fraction x_2 in the equilibrium mixture with $Mg(g)$ at saturated pressure evaluated in the VD/Q approximation (see Table 1).

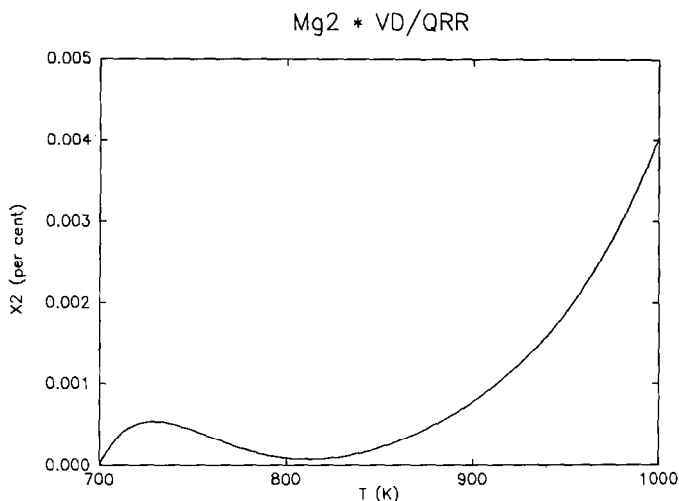


Fig. 2. Temperature dependences of the $\text{Mg}_2(\text{g})$ mole fraction x_2 in the equilibrium mixture with $\text{Mg}(\text{g})$ at saturated pressure evaluated in the VD/QRR approximation (see Table 1).

overlap between the intervals in which the K_p values [15] were calculated and the saturated pressures P are available [17] from observations. In fact, there are only six pressure values available for the gas–liquid equilibrium, which cannot be considered enough for a reliable fitting (3). Moreover, there is a melting point involved in the interval. A higher number of measured P values would certainly increase the quality of the fit.

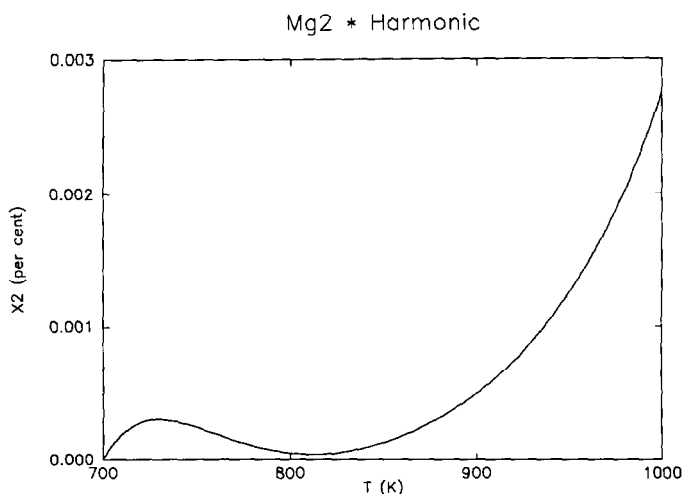


Fig. 3. Temperature dependences of the $\text{Mg}_2(\text{g})$ mole fraction x_2 in the equilibrium mixture with $\text{Mg}(\text{g})$ at saturated pressure evaluated in the harmonic approximation (see Table 1).

In spite of considerably different approximations used for the K_p evaluations, the qualitative behaviour is the same in all the three figures. At higher temperatures, the dimeric mole fraction x_2 considerably increases with temperature (in spite of the temperature decrease of the K_p terms). At lower temperatures there is a temperature decrease; however, our analysis indicates that it should be considered only as an artefact of fitting formula (3) (when supplied with too few values). The clear x_2 temperature increase at higher temperatures can be interpreted as an over-compensation of the K_p decrease by the saturated pressure P increase with temperature. It is the competition between these two trends which creates the final x_2 temperature behaviour.

This report for the first time provides a test of the effects of corrections with respect to the standard harmonic-oscillator and rigid-rotor partition functions. The finding that the dimeric mole fraction x_2 under saturation conditions increases at higher temperatures regardless of the rotational-vibrational motion description is thus important.

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