A useful test of temperature dependency of cluster populations under saturation conditions: the Ar_2 case [1]

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Abstract

The argon vapour in equilibrium with the condensed Ar phase is treated as mixture of the monomer and dimer. The gas-phase composition is evaluated using the calculated dimerization equilibrium constant and the observed saturated pressure (in the temperature region 80–150 K). Regardless of the approximation used for the equilibrium constant evaluation, the dimer mole fraction x_2 in its equilibrium mixture with monomer at saturated pressure exhibits a clear temperature increase in the temperature interval. This conclusion is consistent with recent findings of such a temperature increase with other saturated cluster-containing vapours.

INTRODUCTION

Recently, the saturated vapours of three considerably different species, water [1], carbon [2], and magnesium [3] have been investigated from a common point of view. The vapours were understood as an equilibrium mixture of related clusters (primarily monomers and dimers). The stabilities of the clusters were deduced from calculated equilibrium constants of dimerization, etc. The saturated vapour was described by the observed (or estimated) saturated pressure. It was found that the equilibrium mole fraction x_2 of the dimer (for two-membered mixtures) or the sum of mole fractions of dimers and higher clusters increases with temperature in the temperature interval studied. The interesting observation was interpreted as a result of competition and compensation between temperature and pressure.

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The composition of saturated vapours is of interest to several branches of current research. For example, composition of saturated carbon vapour at high temperatures can be useful in optimizing the conditions for synthesis of C_{60} and other fullerenes [4–8]. Similarly, atmospheric chemists [9–14] are also interested in such information because, for example, atmospheric humidity can in some situations be close to saturation. Very recently, the composition of the atmosphere of Venus has been investigated in terms relative to the carbon dioxide dimer [15], and even the atmosphere of Comet Halley with regard to the water dimer [16].

The cluster equilibrium constants are to be, typically, calculated in the approximation of the rigid rotor and harmonic oscillator (RRHO). The choice is dictated by computational demands which are quite enormous for quantum-chemical generation of the molecular parameters needed for the partition-function construction even in the RRHO approximation. There is one exception: two-atomic clusters [17]. For the special species the dimerization constant can be calculated in approximations beyond the RRHO approach. This report focuses on the dimer Ar_2 and studies its equilibrium mole fraction in saturated argon vapour with regard to the temperature dependency.

CALCULATIONS

We shall deal with an equilibrium mixture of a species and of its dimer, i.e. all higher aggregates are neglected. The population of the monomer and dimer will be described by their mole fractions x_1 and x_2, respectively. The mole fractions are, inter alia, given as ratios of the respective partial pressures (p_1 or p_2) and the total pressure ($P = p_1 + p_2$). The key term in the evaluations is the dimerization equilibrium constant K_p given by

$$K_p = \frac{p_2}{p_1^2} \tag{1}$$

Then, the dimer mole fraction x_2 is given by [18–20]

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

In fact, we still have not used the saturation condition. The total pressure P could have any value between zero and the related saturated pressure (and even beyond if supersaturated conditions are considered). However, hereafter the P term will exclusively denote the saturated pressure.

The equilibrium constants K_p for the dimerization

$$2Ar(g) = Ar_2(g) \tag{3}$$

was recently calculated [21] in a number of approximations, employing several analytical potentials. In addition to the sophisticated KMA

TABLE 1

Mole fraction x_2 of $Ar_2(g)$ in its equilibrium mixture with $Ar(g)$ calculated under saturation conditions for various evaluations [21] of the dimerization equilibrium constant K_p for temperature $T = 100$ K

Approach [a]	K_p (atm^{-1})	x_2 (%)
KMA/Q	0.0159	4.60
KMA/QRR	0.0334	8.82
LJ1	0.0333	8.80
Morse	0.0248	6.85
Harmonic	0.0222	6.21

[a] See text and ref. 21 for explanation of the labels.

potential [22] also two Lennard–Jones (LJ1 and LJ2), Morse, and harmonic interaction potentials were selected. Moreover, various approximations of partition functions were studied, especially the numerically exact (Q) and the quantum rigid rotor (QRR). In this study, five types of equilibrium constants (1) are considered: KMA/Q, KMA/QRR, LJ1, Morse, and harmonic (the last three potentials in conjunction with the QRR approximation). Table 1 lists the K_p values [21] in the approximations at temperature $T = 100$ K.

The temperature region, for which the saturated pressure P of argon is available, is rather narrow [23, 24]. In practice it is limited by the argon triple point (83.8 K) and its critical temperature (150.7 K). From the K_p values calculated [21] for five selected temperatures, an analytical fit in the six-term form

$$\log_{10} K_p = A + \frac{B}{T^2} + \frac{C}{T} + D \log_{10} T + ET + FT^2 \qquad (4)$$

was developed (a limiting condition of vanishing K_p term in the high temperature limit was incorporated). The same analytical fit is also used for evaluation of the observed temperature dependence of the saturated pressure P of argon vapour [23] (57 observed points). Both functions have been applied in the temperature interval 80–150 K.

RESULTS AND DISCUSSION

The values of the dimerization equilibrium constant K_p differ considerably at some temperatures for some approximations (there is even a modest temperature increase present with the harmonic K_p values at high temperatures). Thus, the dimeric mole fraction x_2 under the saturation conditions can vary substantially in some cases (as also indicated by the values of Table 1). In any case, they reach quite high values. This is a consequence of relatively high values of the saturated pressures (for
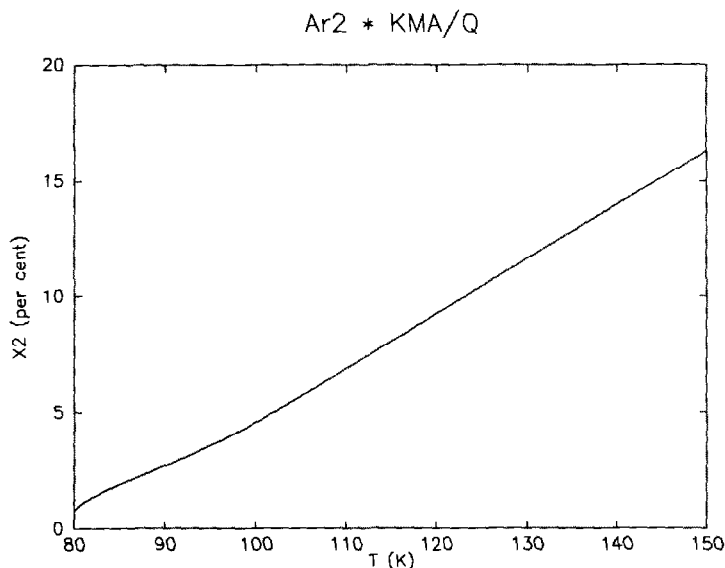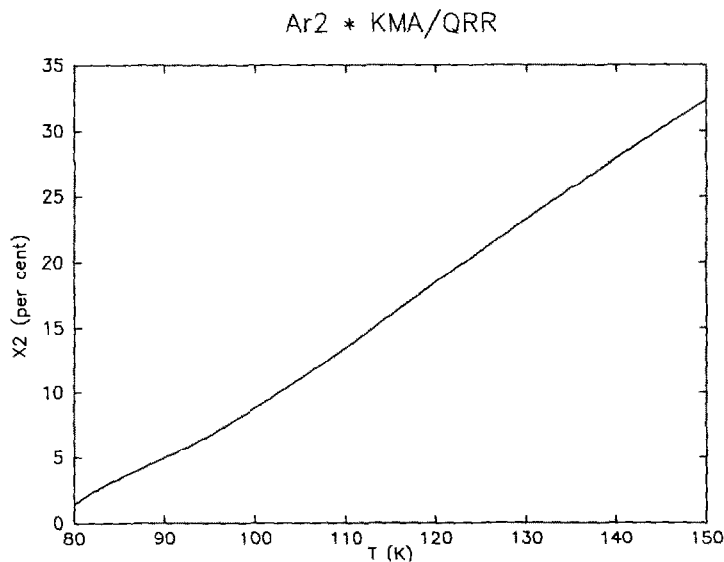
Ar2 * KMA/Q

Fig. 1. Temperature evolution of the $Ar_2(g)$ mole fraction x_2 in its equilibrium mixture with Ar(g) at the saturated pressure P derived for the KMA/Q approximation (see Table 1).

Ar2 * KMA/QRR

Fig. 2. Temperature evolution of the $Ar_2(g)$ mole fraction x_2 in its equilibrium mixture with Ar(g) at the saturated pressure P derived for the KMA/QRR approximation (see Table 1).

example, the critical pressure of argon [23] reaches 48 atm) though potential depth is essentially small (the LJ1 term for Ar_2 equals [21] to 1 kJ mol^{-1}).

Figures 1–3 present calculated temperature dependence of the dimeric mole fraction x_2 in the saturated argon vapour in the interval 80–150 K for three selected representative approximations (KMA/Q, KMA/QRR, and harmonic). The selected temperature interval is in fact somewhat wider (in the low temperature region) than that in which the K_p values were calculated [21]. In spite of the considerably different approximations used for the K_p evaluations, the qualitative behaviour does not differ in the three cases. The dimeric mole fraction x_2 systematically increases with temperature (in spite of the temperature decrease of the K_p terms (if we ignore the harmonic high-temperature irregularity)). The clear x_2 temperature increase is just another illustration of the over-compensation of the K_p temperature decrease by the saturated pressure P increase with temperature. The competition between these two trends creates the final x_2 temperature behaviour.

This study offers a useful test of the effects of the corrections with respect to the standard RRHO functions. It shows that the x_2 temperature increase is certainly not an artefact of the latter partition functions. The fact that higher clusters were ignored is not critical. However, one should still investigate what kind of changes a replacement of the partial pressures by activities in eqn. (1) could bring (actually, at least in principle, computations could produce pressure dependent K_p values).
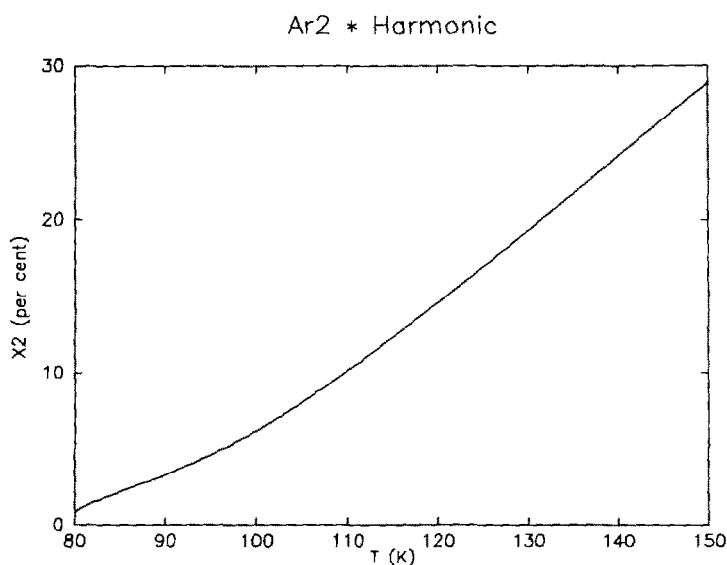

Fig. 3. Temperature evolution of the $Ar_2(g)$ mole fraction x_2 in its equilibrium mixture with Ar(g) at the saturated pressure P derived for the harmonic approximation (see Table 1).

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