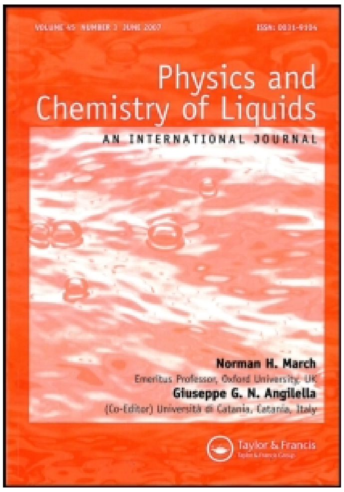

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Dimers and Tetramers in High Temperature Sodium Vapour

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Sodium vapour is modelled as a mixture of monomers, dimers and tetramers and the populations decided by energy minimisation. The analysis shows that the equation of state is consistent with the known binding energy and bond length of Na_2, but the supplementation of dimers by tetramers alone (at least with the geometry at present favoured by theory) is deficient as a fine-tuning mechanism.

Experiments[1] suggest that an alkali metal vapour at high temperature and high pressure contains a substantial fraction of dimers and tetramers. We have undertaken a theoretical study of the case of Na vapour. The system is taken as a mixture of isolated atoms (Na), dimers (Na_2) and tetramers (Na_4), and the compositions are determined by minimisation of the free energy of the system in accordance with the Gibbs-Bogoliubov principle.

Consider a volume Ω of Na vapour at temperature T, containing a total number N of Na atoms. Let n_1N, n_2N and n_4N be the number of free atoms, dimers and tetramers respectively. The total number of "particles" in the system is nN, with $n = n_1 + n_2 + n_4$, and the volume per "particle" is

$$\bar{\Omega} = \frac{\Omega}{nN}.$$

For convenience, we also define the number fractions

$$x_i = \frac{n_i}{n}, i = 1, 2, 4.$$

The Helmoltz free energy per atom then has the form

$$F = n\{\tfrac{3}{2}k_B T - T(S_{\text{gas}} + S_c + S_\eta + S_\sigma)\} + n_2(-E_2) + n_4(-E_4)$$
$$- n_2 k_B T \ln\left(\frac{T}{2\theta_{\text{rot}}}\right) - n_4 k_B T \ln\left\{\frac{\sqrt{\pi}}{\lambda}\left(\frac{T}{\tilde{\theta}_{\text{rot}}}\right)^{3/2}\right\} \qquad (1)$$

Here S_{gas} is the ideal gas entropy term given by

$$\frac{S_{\text{gas}}}{k_B} = \frac{5}{2} + \ln\left[\bar{\Omega}\left(\frac{m_1^{x_1} m_2^{x_2} m_4^{x_4} k_B T}{2\pi\hbar^2}\right)^{3/2}\right]$$

where m_1, m_2 $(=2m_1)$ and m_4 $(=4m_1)$ are the masses of Na, Na_2 and Na_4 respectively. S_c is the entropy of mixing term defined by

$$\frac{S_c}{k_B} = -(x_1 \ln x_1 + x_2 \ln x_2 + x_4 \ln x_4)$$

S_η and S_σ are the total packing and size mismatch entropy contributions; these depend on the hard sphere "diameters" σ_1, σ_2, and σ_4 of Na, Na_2 and Na_4 and detailed expressions are given by Hoshino and Young.[2] The central part of (1) gives the free energy change due to the formation of molecules, where E_2 and E_4 are the binding energies of Na_2 and Na_4 respectively. The final terms of (1) give the free energy of rotation. θ_{rot} and $\tilde{\theta}_{\text{rot}}$ are the characteristic temperatures for rotation of the dimers and the tetramers respectively, and λ is the usual symmetry factor for a polyatomic molecule.

As it stands, the free energy F in (1) contains five variational parameters: n_2, n_4, σ_1, σ_2 and σ_4. (Note that $n_1 + 2n_2 + 4n_4 = 1$). Preliminary calculations have shown that F is quite insensitive to the values of the hard sphere diameters σ_i. Subsequently, we have neglected the terms S_η and S_σ and performed the minimisation of F with respect to n_2 and n_4.

We discuss next the input data for the calculation. First, the binding energy $E_2 = 0.0943$ a.u. and $\theta_{\text{rot}} = 0.22$ K for the dimer Na_2 were obtained from experimental data by Roach and Baybutt.[3] Experimental data for Na_4 are not available, and we have used results of a theoretical calculation[4] giving $E_4 = 0.0690$ a.u., $\tilde{\theta}_{\text{rot}} = 0.080$ K, and $\lambda = 4$ for the lowest energy configuration of a rhombus.

In principle, we can determine the specific volume at a given temperature T and pressure P, by minimisation of the free energy with respect to volume:

$$p = -\left(\frac{\partial F}{\partial \Omega}\right)_T \qquad (2)$$

In this work, we have simply taken the specific volume from experimental data[5] as input and used Eq. (2) to determine the pressure.

TABLE I

Dimer and tetramer populations (unadjusted theoretical input).

T(K)	1491	1547	1602	1658
$2n_2$	0.18 (0.267)	0.15 (0.230)	0.12 (0.203)	0.10 (0.178)
$4n_4$	0 (0.0428)	0 (0.0281)	0 (0.020)	0 (0.0143)
P(atm)	10.9 (10)	—	—	10.6 (10)

Calculations use $E_2 = 0.0268$ a.u., $E_4 = 0.0943$ a.u., $\theta_{\text{rot}} = 0.22$ K, $\tilde{\theta}_{\text{rot}} = 0.080$ K and $\lambda = 4$. Experimental data[5] are in parentheses.

The results of our calculation are shown in Table I, experimental data[5] being in parentheses. Comparison shows that our model can account for the formation of dimers, but not the tetramers.

The values of n_2 and n_4 are quite sensitive to the input binding energies E_2 and E_4. We have adjusted E_2 and E_4 to fit the experiment data at 1491 K, giving $E_2 = 0.030$ a.u. and $E_4 = 0.148$ a.u. Using these adjusted values, the results of Table II are obtained.

TABLE II

Dimer and tetramer populations (adjusted theoretical input).

T(K)	1491	1547	1602	1658
$2n_2$	0.26 (0.267)	0.23 (0.230)	0.19 (0.203)	0.16 (0.178)
$4n_4$	0.042 (0.0428)	0.014 (0.0281)	0.0047 (0.020)	0.0016 (0.0143)

Calculations use adjusted binding energies $E_2 = 0.030$ a.u. and $E_4 = 0.148$ a.u., the other parameters staying the same. Experimental data[5] again in parentheses.

In this case, the weight fraction ($2n_2$) of dimers is well reproduced, but the weight fraction ($4n_4$) of the tetramers decreases much faster with temperature as compared with experiment.

We appear, therefore, to have a satisfactory description of the grosser aspects of the equation of state through the mechanism of dimerisation and the known properties (binding energy and bond length) of Na_2. At a finer level, however, supplementation by tetramers only (at least with the geometry at present favoured by theory) is inadequate.

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