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Thermodynamics of Ar–N_2 complexes and their abundance in Titan's atmosphere [1]

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Abstract

The equilibrium constants of formation of the gas phase species Ar–N_2 (T-shape and linear isomer, their equilibrium mixture) are evaluated from recently computed quantum-chemical data. It is shown that the isomeric relative stabilities can be interchanged so that the isomers can exhibit comparable concentrations in some temperature regions. The computed overall equilibrium constant is combined with the observed temperature and pressure profiles in Titan's atmosphere and the altitude profile of the heterodimer mole fraction in equilibrium with N_2 and Ar is estimated. The mole fraction decreases with altitude and close to Titan's surface is found to be 8×10^{-2}%.

INTRODUCTION

Distributions of various molecular complexes in atmospheres of cosmic bodies have been the subject of increasing interest [1–9]. Under equilibrium conditions the distributions represent a particular thermodynamic problem. The Ar–N_2 heterodimer serves as a pertinent example of such a complex. The species can be particularly relevant to Titan's atmosphere with respect to its contents [10–13] of N_2 and Ar. The complex of Ar with N_2 has been studied by various experimental and computational techniques [14–25]. Recent quantum-chemical treatment [26] supplied a consistent

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data set which serves in the present study for an evaluation of Ar–N_2 thermodynamics and the complex altitude profile in Titan's atmosphere.

COMPUTATIONS

Ab inito computations in the 6-31G* basis set with the second order perturbation treatment of electron correlation [26] found two different minimum energy structures, T-shape (C_{2v} symmetry) and $C_{\infty v}$ linear isomers. Although the linear species is lower in potential energy, the T-shape structure is in fact the ground state structure (i.e. the latter species is lower after addition of the zero-point vibrational energy). Basis set superposition error (BSSE) [27, 28] was estimated [26]; however, it produced positive dimerization energy changes so it is not considered here.

We shall deal with three dimerization processes

$$\mathrm{Ar(g)} + \mathrm{N_2(g)} = \mathrm{Ar \cdot N_2}(C_{2v}, \mathrm{g}) \tag{1}$$

$$\mathrm{Ar(g)} + \mathrm{N_2(g)} = \mathrm{Ar \cdot N_2}(C_{\infty v}, \mathrm{g}) \tag{2}$$

$$\mathrm{Ar(g)} + \mathrm{N_2(g)} = \mathrm{Ar{-}N_2(g)} \tag{3}$$

The third process is the total equilibrium considering the equilibrium mixture of both isomers. Hence, we deal we three equilibrium constants; for example the total equilibrium constant is

$$K_p = \frac{p_{\mathrm{Ar-N_2}}}{p_{\mathrm{Ar}} p_{\mathrm{N_2}}} \tag{4}$$

The equilibrium constants can be expressed in the partial pressures p_i or in the equilibrium mole fractions of the components x_i and the total pressure of the mixture P.

According to Samuelson et al. [11] Titan's atmosphere has two major components, N_2 and Ar with mole fractions of 82.2 and 11.6%, respectively. For our purposes we shall neglect all other components, so that we shall deal with a three component model: N_2, Ar, Ar–N_2. The total observed pressure P will therefore be scaled by a reduction factor of 0.938. It holds for the mole fractions in the simplified model

$$x_{\mathrm{N_2}} + x_{\mathrm{Ar}} + x_{\mathrm{Ar-N_2}} = 1 \tag{5}$$

while the nitrogen/argon ratio still has to obey the observed term 82.2/11.6.

The equilibrium constants were evaluated by means of partition functions supplied with parameters from our ab initio computations [26]. With respect to the amount of the computed information available, the partition functions were of the usual rigid-rotor and harmonic-oscillator (RRHO) quality [29]. As mentioned above, the dimerization energetics could not be corrected for the BSSE error. Hence, the interaction energies are probably somewhat overestimated. We followed two approaches to the equilibrium constant evaluation: **A** and **B**. In the **A** case, the ground-state energy changes and the full RRHO partition functions were employed. In the **B** case, the vibrational partition functions are neglected and also the zero-point vibrational contributions (i.e. the treatment deals with the potential energy changes). It can be expected that the **B** case will produce smaller values of the equilibrium constants and hence, it could compensate the interaction energy overestimation.

Finally, the observed profiles [12] of temperature and pressure in the region of the altitude $z = 0–204$ km are used (the profiles were adopted from Voyager results). The nitrogen/argon ratio [11] was supposed to be constant over the region.

RESULTS AND DISCUSSION

Table 1 reports the computed partial and overall dimerization constants

TABLE 1

Temperature dependence of the calculated partial and total dimerization equilibrium constants[a] $K_p = p_{ArN_2}/p_{Ar}p_{N_2}$

T/K	Term	K_p/atm^{-1}	
		A	**B**
50.0	C_{2v}	2.6×10^{-1}	3.0×10^{-2}
	$C_{\infty v}$	1.5×10^{-1}	1.1×10^{-2}
	Total	4.1×10^{-1}	4.1×10^{-2}
100.0	C_{2v}	1.3×10^{-1}	3.5×10^{-3}
	$C_{\infty v}$	9.8×10^{-2}	9.0×10^{-4}
	Total	2.3×10^{-1}	4.4×10^{-3}
150.0	C_{2v}	1.0×10^{-1}	1.2×10^{-3}
	$C_{\infty v}$	9.3×10^{-2}	2.5×10^{-4}
	Total	1.9×10^{-1}	1.5×10^{-3}
200.0	C_{2v}	8.8×10^{-2}	6.1×10^{-4}
	$C_{\infty v}$	9.4×10^{-2}	1.1×10^{-4}
	Total	1.8×10^{-1}	7.1×10^{-4}
250.0	C_{2v}	8.2×10^{-2}	3.6×10^{-4}
	$C_{\infty v}$	9.7×10^{-2}	5.7×10^{-5}
	Total	1.8×10^{-1}	4.2×10^{-4}
298.15	C_{2v}	7.8×10^{-2}	2.4×10^{-4}
	$C_{\infty v}$	1.0×10^{-1}	3.5×10^{-5}
	Total	1.8×10^{-1}	2.8×10^{-4}
300.0	C_{2v}	7.8×10^{-2}	2.4×10^{-4}
	$C_{\infty v}$	1.0×10^{-1}	3.4×10^{-5}
	Total	1.8×10^{-1}	2.7×10^{-4}

[a] The standard state is an ideal gas at 1 atm = 101 325 Pa pressure.

for reactions (1)–(3) evaluated in the **A** and **B** approaches. As expected, the **A** values are higher. Moreover, they exhibit a rather slow temperature decrease; the K_p values are of the same order of magnitude throughout the whole temperature interval considered. This does agree with regularities known for molecular complexes [29]. Hence, for the altitude profile evaluation we shall use the results from the **B** treatment.

Data in Table 1 also allow for a consideration of the inter-isomeric proportions. However Table 2 addresses the question in a more specific manner; it presents the composition of the two-component isomeric mixture. At the lowest temperatures the species lower in energy must be dominant. With respect to our approach it is the T-shape and linear isomer in the **A** and **B** case, respectively. However, in both treatments we can notice a relative stability interchange. It takes place at about 176 and 12 K in the **A** and **B** treatments. Hence, in fact we deal with a coexistence of the two structures. The mixture is, at temperatures relevant to Titan's atmosphere, closer to equimolarity in the **A** approach. Such isomeric

TABLE 2

Temperature dependence of the equilibrium mole fractions w_i of the $Ar \cdot N_2$ isomers [a]

T/K	w_i/%		$\delta C_{p,1}$ [b]/J K^{-1} mol^{-1}
	C_{2v}	$C_{\infty v}$	
Approach **A**			
1.6 [c]	95.6	4.4	3.1
50.0	63.9	36.1	
100.0	56.6	43.4	
150.0	51.9	48.1	
176.0 [d]	50.0	50.0	
200.0	48.5	51.5	
250.0	45.8	54.2	
298.15	43.7	56.3	
300.0	43.6	56.4	
Approach **B**			
3.4 [c]	17.4	82.6	4.5
12.2 [d]	50.0	50.0	
50.0	72.6	27.4	
100.0	79.7	20.3	
150.0	83.0	17.0	
200.0	85.0	15.0	
250.0	86.4	13.6	
298.15	87.4	12.6	
300.0	87.5	12.5	

[a] See Table 1. [b] Isomerism contribution to heat capacity related to the structure more stable in low temperaure region (**A**, C_{2v}; **B**, $C_{\infty v}$). [c] Maximum in the $\delta C_{p,1}$ term. [d] Point of two-structure equimolarity.

TABLE 3

Altitude z profiles of the temperature T, total pressure P, and dimeric mole fraction [a] $x_{\mathrm{Ar-N_2}}$ in the atmosphere of Titan

z/km	T/K	P^{b}/atm	$x_{\mathrm{Ar-N_2}}$/%
0	93	1.5	8.7×10^{-2}
3	86	1.1	8.2×10^{-2}
6.5	80	0.74	6.8×10^{-2}
9.3	76	0.56	6.0×10^{-2}
17	72.1	0.30	3.8×10^{-2}
25.6	70	0.17	2.3×10^{-2}
41	70.3	0.074	1.0×10^{-2}
60.4	80	0.030	2.7×10^{-3}
106	140.7	0.0074	1.4×10^{-4}
153	165	0.0022	2.8×10^{-5}
204	172	0.00056	6.2×10^{-6}

[a] $x_{\mathrm{N_2}} + x_{\mathrm{Ar}} + x_{\mathrm{Ar-N_2}} = 1$. [b] The total pressure scaled by a factor of 0.938.

coexistence has effects for overall thermodynamic terms [29], in particular for the heat capacity term. The enhancement can be measured [29] by means of the isomerism contribution $\delta C_{p,1}$ term which frequently exhibits a sharp temperature maximum. In the Ar–N_2 case the maxima are located at extremely low temperatures.

Table 3 presents the primary results of this study; the computed dimeric mole fraction of Ar–N_2 in the simplified (three component) Titan's atmosphere at selected altitudes z. It turns out that the dimeric mole fraction decreases with increasing altitude. This may be surprising as the temperature decreases in lower parts of the atmosphere which should stabilize the dimers. However, the pressure also decreases, which supports dissociation. The competition between temperature and pressure effects creates the final altitude decrease. Hence, the highest population of the heterodimer should be close to Titan's surface. The estimated value of 8×10^{-2}% is certainly of spectroscopic significance.

One can imagine still a more general treatment within our simplified Titan's atmosphere; inclusion of two other dimers, Ar_2 and $(N_2)_2$. Then, we would deal we three competing dimerization equilibria. Such a treatment would also be interesting from the point of view of thermodynamic methodology. Among other improvements of the computational treatment one has to think of the BSSE correction and hence an application of still larger basis sets. Moreover, anharmonicity of the intersystem vibrations are to be respected in some way in the partition functions. As the system is composed of three particles only a whole analytical potential hypersurface could be considered for its description at a latter stage of research.

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REFERENCES

1 J.M. Calo and J.H. Brown, J. Chem. Phys., 61 (1974) 3931.
2 J.M. Calo and R.S. Narcisi, Geophys. Res. Lett., 7 (1980) 289.
3 K. Fox and S.J. Kim, J. Quant. Spectrosc. Radiat. Transfer, 40 (1988) 177.
4 A.R.W. McKellar, Astrophys. J., 326 (1988) L75.
5 Z. Slanina, J. Atmos. Chem., 6 (1988) 185.
6 J.F. Crifo, Icarus, 84 (1990) 414.
7 A.J. Colussi, S.P. Sander and R.R. Friedl, Chem. Phys. Lett., 178 (1991) 497.
8 Z. Slanina and J.F. Crifo, Thermochim. Acta, 181 (1991) 109.
9 Z. Slanina, K. Fox and S.J. Kim, J. Quant. Spectrosc. Radiat. Transfer, 47 (1992) 91.
10 V.G. Kunde, A.C. Aikin, R.A. Hanel, D.E. Jennings, W.C. Maguire and R.E. Samuelson, Nature, 292 (1981) 686.
11 R.E. Samuelson, R.A. Hanel, V.G. Kunde and W.C. Maguire, Nature, 292 (1981) 688.
12 S.J. Kim, unpublished results, 1982.
13 J.W. Chamberlain and D.M. Hunten, Theory of Planetary Atmospheres, Academic Press, New York, 1987.
14 M.D. Pattengill, R.A. La Budde, R.B. Bernstein and C.F. Curtiss, J. Chem. Phys., 55 (1971) 5517.
15 C.A. Long, G. Henderson and G.E. Ewing, Chem. Phys., 2 (1973) 485.
16 G. Henderson and G.E. Ewing, Mol. Phys., 27 (1974) 903.
17 P.G. Kistenmaker and A.E. de Vries, Chem. Phys., 7 (1975) 371.
18 G. Rotzoll, Chem. Phys. Lett., 88 (1982) 179.
19 R. Candori, F. Pirani and F. Vecchiocattivi, Chem. Phys. Lett. 102 (1983) 412.
20 M.S. Bowers, K.T. Tang and J.P. Toennies, J. Chem. Phys., 88 (1988) 5465.
21 F.R.W. McCourt, F.B. van Duijneveldt, T. van Dam and R.R. Fuchs, Mol. Phys., 61 (1987) 109.
22 A.R.W. McKellar, J. Chem. Phys., 88 (1988) 4190.
23 W. Rijks, M. Gerritsen and P.E.S. Wormer, Mol. Phys., 66 (1989) 929.
24 A.G. Ayllón, J. Santamaria, S. Miller and J. Tennyson, Mol. Phys., 71 (1990) 1043.
25 W. Jäger and M.C.L. Gerry, Chem. Phys. Lett., 196 (1992) 274.
26 Z. Slanina, S.J. Kim and K. Fox, J. Mol. Struct. (Theochem), 288 (1993) 67.
27 S.F. Boys and F. Bernardi, Mol. Phys., 19 (1970) 553.
28 D.W. Schwenke and D.G. Truhlar, J. Chem. Phys., 82 (1985) 2418.
29 Z. Slanina, Contemporary Theory of Chemical Isomerism, Reidel, Dordrecht, 1986.
30 Z. Slanina, S.J. Kim and K. Fox, J. Geophys. Res., in press.