Improving the JANAF Thermodynamic Data for Ammonia and Phosphine at High Temperatures

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Ammonia and phosphine are of great interest for a variety of terrestrial and extra-terrestrial studies and have already been found in many astrophysical objects and interstellar media. Access to accurate thermodynamic data on these molecules is therefore of great importance. In particular, the partition function is necessary to establish the correct temperature dependence of spectral lines and their intensity. At elevated temperatures evaluating this function is often not straightforward.

The primary source of thermodynamic species data is the JANAF tables [1]. The JANAF data on ammonia and phosphine cover temperatures up to 6000 K and are based on the use of simplified semi-empirical models. One of the largest sources of error is that these models do not take into account the effect of the dissociation of a molecule, which has previously been shown to be important [2].

In the work presented here, the thermodynamic properties of ammonia and phosphine are calculated by the explicit summation of many millions of rotation-vibrational energy levels calculated using both accurate theoretical models and potential energy surfaces. Additionally, high accuracy estimates are obtained for the specific heat capacity, the Gibbs enthalpy function, the Helmholtz function and the entropy of gas phase as a function of temperature.

We show that the JANAF data significantly overestimates the partition functions for these molecules at high temperature, which has a detrimental effect on other thermodynamic properties for temperatures above 1500 K. We demonstrate that the JANAF data are mainly affected by an incorrect or absence of consideration for the dissociation energy.

[1] JANAF Thermochemical Tables, 3rd edition, M.W. Chase Jr., C.A. Davies, J.R. Davies, Jr., D.J. Fulrip, R.A. McDonald, and A.N. Syverud, *Journal of Physical and Chemical Reference Data*, **14**, Supplement 1, 1985.

[2] M. Vidler, J. Tennyson, J. Chem. Phys. 113, **2000**, 9766.