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Thermodynamic Properties of High-Temperature Jupiter-Atmosphere Components

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A study on the thermodynamic properties of Jupiter-atmosphere chemical species important for the high-speed aerodynamics analysis of entry problems is reported. The included species are H_2, H_2^+, H_3^+, H^+, H^-, He, He^+, He^{++}, e^-. Complete tables of thermodynamic properties of these species in the temperature range 50–50000 K have been obtained by using accurate sets of energy levels for both atomic and molecular species. The calculation method is described and relevant results are shown and discussed by comparison with previous data from other sources.

Nomenclature

a_{ij} = stoichiometric coefficient for the formation reaction of the ith species
B_v, D_v, H_v, L_v = rotational spectroscopic constants
C_p = total specific heat
$C_{p,\mathrm{int}}$ = internal specific heat
c = speed of light
E_i = ionization energy
E_{int} = internal energy
E_n = energy of the nth quantum level
D_e = dissociation energy
F = Helmholtz free energy
F_v = rotational energy (polyatomic molecules)
G = Gibbs free energy
$G_0(v_1, \ldots)$ = vibrational energy of the state $(v_1, v_2, \ldots, v_m)$
g_n = statistical weight of the nth quantum level
H_i = molar enthalpy of the ith species
h = Planck constant
J = rotational quantum number
k_B = Boltzmann constant
m_i = mass of the ith species
n = principal quantum number
p_i = statistical weight of the ith electronic states (polyatomic molecules)
p_v = statistical weight of the state $(v_1, v_2, \ldots, v_m)$
Q_i = total partition function of the ith species
$Q_{\mathrm{int},i}$ = internal partition function of the ith species
$Q_{\mathrm{tr},i}$ = translational partition function of the ith species
R = universal gas constant
r_e = equilibrium distance
S = entropy
T = temperature
$T_0^{(i)}$ = excitation energy of the ith electronic states (polyatomic molecules)
V = volume
v = vibrational quantum number
ΔE_i = lowering of the ionization potential
$\Delta H_{f,i}$ = variation of the enthalpy for the formation of the ith species
μ = reduced mass
σ = symmetry factor
ω_n = frequency of the nth vibrational mode (polyatomic molecules)

I. Introduction

THE outburst toward new frontiers of space exploration requires the study of many problems concerning hypersonic aerodynamics to obtain the best spacecraft configuration for reentry. To this end, it is necessary to provide the most accurate thermodynamic data for the chemical constituents of a certain atmosphere. As in the case of Mars-atmosphere components [1–3], here we will deal with chemical species constituting Jupiter-atmosphere. The problem is faster to solve in respect to the previous one, at least for what concerns the number of species (H_2, H_2^+, H_3^+, H^+, H^-, He, He^+, He^{++}, e^-). Also, in this case, the literature [4–7] offers few sources and, when data are present, they are given in a temperature range not adequate to face up to specific requirements. The purpose of this work is then to set up a reference for this kind of necessity.

II. Method of Calculation

A. Partition Functions

The theoretical basis of present calculations is described in [1–3]. Thus, here we will focus our attention just on some particular aspects about the calculation of the internal partition functions of the hydrogen and helium species. The thermodynamic properties of high-temperature gas mixtures can be obtained if the partition functions of single components are known. In general, the partition

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function can be factorized as the product of the translational $Q_{\mathrm{tr},i}$ and the internal $Q_{\mathrm{int},i}$ contributions. Whereas the translational contribution can be easily determined for atoms, biatomic and polyatomic molecules, the internal one strongly depends on the considered species.

For an isolated atom, the internal partition function is the sum over the electronic levels up to the ionization limit

$$Q_{\mathrm{int},i} = \sum_n g_n \exp\left(-\frac{E_n}{k_B T}\right) \tag{1}$$

where g_n and E_n represent the statistical weight and the energy of the nth internal quantum level of the component under consideration. In practice, Eq. (1) assumes different explicit forms for atoms and for molecules. For atomic species, the sum in Eq. (1) diverges because the statistical weight is not bound when the principal quantum number increases indefinitely, thus it must be adequately truncated. There is no universal cutoff criterion. Reviews of various cutoff methods can be found in the literature [7,8]. The existing cutoff criteria yield partition functions and their derivatives that depend on either the electron density or the gas pressure. In our calculations, we choose a class of criteria based on the fact that the ionization energy of an atom in the presence of other components is lowered by a factor which, in general, depends on the number densities of the charged particles, including the electrons [9]. This lowering ΔE_i is set as a parameter. We note that, for those species that do not have electrons (H^+, He^{++}), internal thermodynamic properties do not depend on the cutoff because no electronic levels are present. This is not true when we consider the formation enthalpy and the formation constant; indeed, these quantities depend indirectly on the cutoff because they are connected with the corresponding properties of neutral atoms, i.e., the formation enthalpy and the formation constants for H^+ and He^{++} are calculated taking as a reference H and He whose thermodynamic properties depend on the cutoff. For molecules [10–12], the energy of a particular state is given by three contributions:

$$E_{nJv} = E_{\mathrm{el}}(n) + E_{\mathrm{vib}}(n, v) + E_{\mathrm{rot}}(n, v, J) \tag{2}$$

the electronic excitation energy $E_{\mathrm{el}}(n)$, the vibrational energy $E_{\mathrm{vib}}(n, v)$, and the rotational energy $E_{\mathrm{rot}}(n, v, J)$. The general expression for the vibrational energy can be written as

$$\begin{aligned} \frac{E_{\mathrm{vib}}(n, v)}{hc} &= \omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2 + \omega_e y_e\left(v+\frac{1}{2}\right)^3 \\ &\quad + \omega_e z_e\left(v+\frac{1}{2}\right)^4 + \omega_e k_e\left(v+\frac{1}{2}\right)^5 + \omega_e j_e\left(v+\frac{1}{2}\right)^6 \end{aligned} \tag{3}$$

where ω_e, $\omega_e x_e$, $\omega_e y_e$, $\omega_e z_e$, $\omega_e k_e$, $\omega_e j_e$ are spectroscopic constants for each electronic state, and c is the speed of light. The rotational energy for a nonrigid rotator associated with the v vibrational level of the n electronic state reads

$$\begin{aligned} \frac{E_{\mathrm{rot}}(n, v, J)}{hc} &= B_v J(J+1) - D_v J^2(J+1)^2 \\ &\quad + H_v J^3(J+1)^3 - L_v J^4(J+1)^4 \end{aligned} \tag{4}$$

where

$$\begin{aligned} B_v &= B_e - \alpha_e\left(v+\frac{1}{2}\right) + \gamma_e\left(v+\frac{1}{2}\right)^2 + \delta_e\left(v+\frac{1}{2}\right)^3 \\ &\quad + \sigma_e\left(v+\frac{1}{2}\right)^4 + \zeta_e\left(v+\frac{1}{2}\right)^5 + \theta_e\left(v+\frac{1}{2}\right)^6 + \tau_e\left(v+\frac{1}{2}\right)^7 \end{aligned} \tag{5}$$

$$\begin{aligned} D_v &= D_e - \beta_e\left(v+\frac{1}{2}\right) + \phi_e\left(v+\frac{1}{2}\right)^2 + \varepsilon_e\left(v+\frac{1}{2}\right)^3 \\ &\quad + \eta_e\left(v+\frac{1}{2}\right)^4 + \iota_e\left(v+\frac{1}{2}\right)^5 \end{aligned} \tag{6}$$

$$H_v = H_{v0} + H_{v1}\left(v+\frac{1}{2}\right) + H_{v2}\left(v+\frac{1}{2}\right)^2 + H_{v3}\left(v+\frac{1}{2}\right)^3 \tag{7}$$

$$L_v = L_{v0} + L_{v1}\left(v+\frac{1}{2}\right) + L_{v2}\left(v+\frac{1}{2}\right)^2 \tag{8}$$

The maximum permissible value $J_{\max}$ of the rotational quantum number for each vibrational quantum number is determined by comparing the vibrational-rotational energy with the dissociation energy relative to the electronic level we are considering. This represents a simplification in which the molecule is considered as a nonrotating system, indeed, the rotation of the molecule determines a distortion of the potential energy curve [11], allowing the existence of quasi-bound states above the dissociation limit of the molecule.

Moreover, the description of the thermodynamic properties of homonuclear diatomic gases involves the consideration of the overall symmetry requirements in the combined nuclear and rotational eigenfunctions. If a homonuclear diatomic molecule is composed of fermions, the overall wave function is required to be antisymmetric. Two different summations must be written for the rotational partition functions corresponding to J_{odd} (*ortho*hydrogen) and J_{even} (*para*hydrogen).

$$Q_{\mathrm{rot}}^{\mathrm{ortho}} = \sum_{J_{\mathrm{odd}}} (2J+1)\exp\left[-\frac{E_{\mathrm{rot}}(n, v, J)}{k_B T}\right] \tag{9}$$

$$Q_{\mathrm{rot}}^{\mathrm{para}} = \sum_{J_{\mathrm{even}}} (2J+1)\exp\left[-\frac{E_{\mathrm{rot}}(n, v, J)}{k_B T}\right] \tag{10}$$

At high temperatures, these expressions approach the same limit, which is one-half the value of the rotational partition function for a heteronuclear diatomic molecule, but, at low temperatures, they are quite different. Then, one might expect that the total rotational partition function for homonuclear gases should be a weighted sum according to the abundance of the symmetrical and antisymmetrical nuclear species. Thus, once the maximum number of vibrational levels for each electronic state and the maximum number of rotational states for each vibrational state have been determined, the internal partition function can be calculated by the following expression:

$$\begin{aligned} Q_{\mathrm{int}} &= \frac{1}{\sigma}\sum_n^{n_{\max}} g_n \exp\left[-\frac{E_{\mathrm{el}}(n)}{k_B T}\right] \sum_v^{v_{\max}(n)} \exp\left[-\frac{E_{\mathrm{vib}}(n, v)}{k_B T}\right] \\ &\quad \times \left\{3\sum_{J_{\mathrm{odd}}}(2J+1)\exp\left[-\frac{E_{\mathrm{rot}}(n, v, J)}{k_B T}\right] \right. \\ &\quad \left. + \sum_{J_{\mathrm{even}}}(2J+1)\exp\left[-\frac{E_{\mathrm{rot}}(n, v, J)}{k_B T}\right]\right\} \end{aligned} \tag{11}$$

This expression for the internal partition function implies that all the spin isomers are in equilibrium with each other, meaning that the single term with $J = 0$ will eventually dominate the partition function at low temperature. This term will be unity, while all the other J values, which have higher energies, will give rise to terms that approach zero. This means that all the hydrogen molecules would be able to reach the lowest rotational state, and that all then have become antisymmetric in the spin function. But, if an external agent does not act, the spin isomers continue to exist at low temperature. Therefore, hydrogen gas behaves as a mixture of three-quarters orthohydrogen and one-quarter parahydrogen. The internal partition function of polyatomic molecules by analogy with diatomic molecules can be written in the general case in the following way [7,13]:

$$
\begin{aligned}
Q_{\mathrm{int}} = {} & \frac{1}{\sigma}\sum_i p_i \exp\left(-\frac{hc}{k_B T}T_0^{(i)}\right) \\
& \times \sum_{v_1}\sum_{v_2}\sum_{v_m} p_v \exp\left(-\frac{hc}{k_B T}G_0^{(i)}(v_1, v_2, \ldots, v_m)\right) \\
& \times \sum_J \sum_{k=-J}^{k=J}(2J+1)\exp[-F_v^{(i)}(J,k)] \qquad (12)
\end{aligned}
$$

In this expression, the first sum is taken over the electronic states (in general, the valence ones) of the molecule, characterized by the energy of excitation $T_0^{(i)}$ and the statistical weight p_i; $G_0^{(i)}(v_1, v_2, \ldots, v_m)$ represents the energy of the vibrational states, and $F_v^{(i)}(J, k)$ is the energy of the rotational levels and is expressed differently according to the symmetry of the molecule. It is important to note that different electronic excited states of the same polyatomic molecule can have different geometries, thus affecting the symmetry number and also determining a different rotational behavior. The calculation of the internal partition function of H_3^+ can be tackled as a particular case of this general treatment. The total energy of each rovibrational state can be written as [14]:

$$
\begin{aligned}
\frac{E}{hc} = {} & \frac{E_0}{hc} + \omega_1\left(v_1 + \frac{1}{2}\right) + \omega_2(v_2+1) + (x_{12} + x_{21}) \\
& \times \left(v_1 + \frac{1}{2}\right)(v_2+1) + x_{22}(v_2+1)^2 + x_{l_2 l_2} l_2^2 + J(J+1)B_v \\
& - \kappa^2(B_v - C_v) - J^2(J+1)^2 D_J - J(J+1)\kappa^2 D_{J\kappa} - \kappa^4 D_\kappa \qquad (13)
\end{aligned}
$$

where the quantum numbers v_1, v_2, l_2, κ, and J take on the values

$$
\begin{aligned}
& v_1 = 0, 1, 2, 3, \ldots \qquad v_2 = 0, 1, 2, 3, \ldots \\
& l_2 = v_2, v_2 - 2, v_2 - 4, \ldots, 1 \quad \text{or} \quad 0 \qquad \kappa = 0, 1, 2, 3, \ldots \\
& J = \kappa, \kappa + 1, \kappa + 2, \ldots
\end{aligned}
$$

$$
B_v = B_e - \alpha_0 - \left(v_1 + \frac{1}{2}\right)\alpha_1 - (v_2 + 1)\alpha_2 \qquad (14)
$$

$$
C_v = C_e - \gamma_0 - \left(v_1 + \frac{1}{2}\right)\gamma_1 - (v_2 + 1)\gamma_2 \qquad (15)
$$

$$
D_J = B_e^3\left(\frac{2}{\omega_1^2} + \frac{2}{\omega_2^2}\right) \qquad (16)
$$

$$
D_{J\kappa} = -B - e^3\left(\frac{2}{\omega_1^2} + \frac{4}{\omega_2^2}\right) \qquad (17)
$$

$$
D_\kappa = B_e^3\left(\frac{1}{2\omega_1^2} + \frac{2}{\omega_2^2}\right) \qquad (18)
$$

B. Thermodynamic Properties

From the partition functions and their first and second derivatives, we can calculate all the thermodynamic properties of the components according to the formulas of statistical thermodynamics [15]. The Helmholtz potential, the internal contribution E_{int} to the thermodynamic energy, the entropy, and the internal constant-pressure specific heat $C_{p,\mathrm{int}}$ are obtained, respectively, from

$$
F - H(0) = -RT \ln Q \qquad (19)
$$

$$
E_{\mathrm{int}} = RT^2\left(\frac{\partial \ln Q_{\mathrm{int}}}{\partial T}\right)_V \qquad (20)
$$

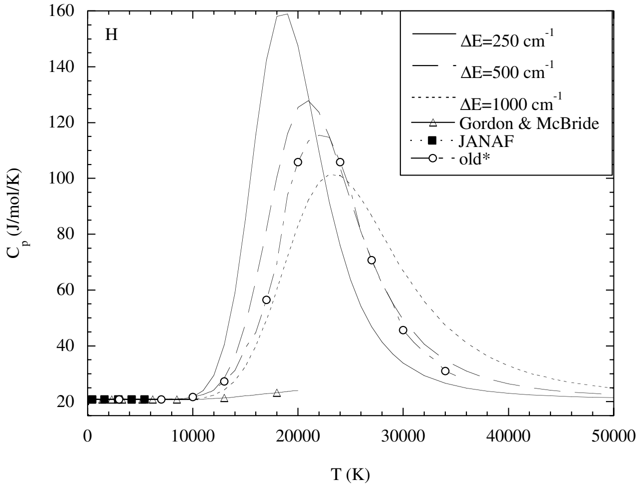
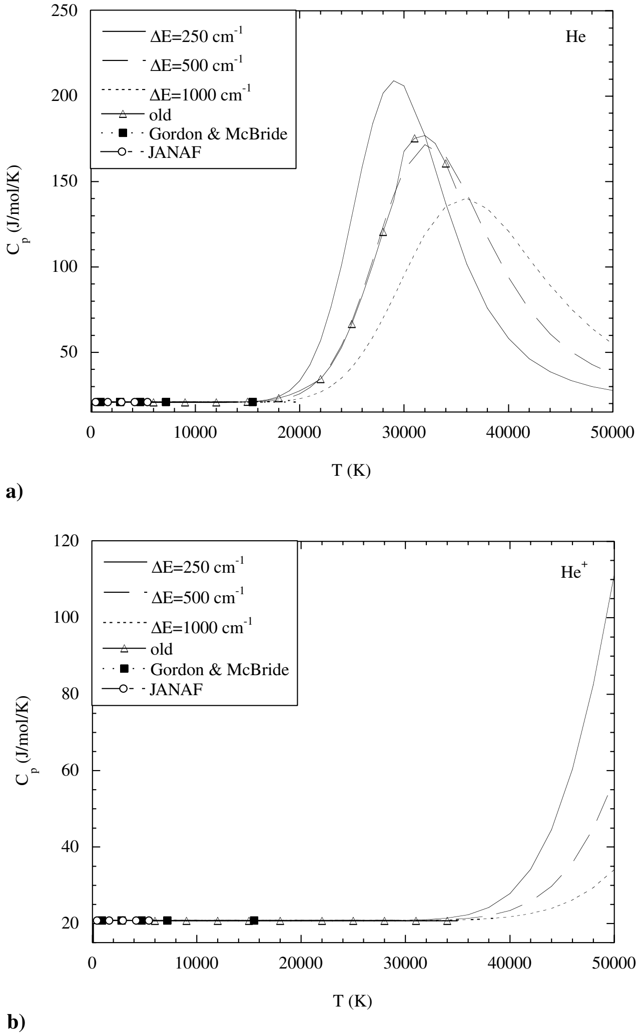


Fig. 1 Comparison of specific heat as a function of temperature for $\Delta E = 250\ \mathrm{cm}^{-1}$, $\Delta E = 500\ \mathrm{cm}^{-1}$, and $\Delta E = 1000\ \mathrm{cm}^{-1}$ for atomic hydrogen.



a)

b)

Fig. 2 Comparison of specific heat as a function of temperature for He and He$^+$ for $\Delta E = 250\ \mathrm{cm}^{-1}$, $\Delta E = 500\ \mathrm{cm}^{-1}$, and $\Delta E = 1000\ \mathrm{cm}^{-1}$.

Table 1 Spectroscopic data for H_2

T_e	g_i	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_e	γ_e	δ_e	D_e	β_e	H_{v0}	r_e
0.0[a]	1	4403.57	123.86	0.8129[b]	60.890	3.170	0.15593	$-4.601e-2$[c]	$4.657e-2$	$-1.5085e-3$[d]	$5.224e-5$[ef]	0.7414
0.0	1	4401.21	121.34	0.8129	60.853	3.062	0.057	−0.0051	0.0471	−0.00274	$4.9e-5$[g]	0.7414
91,700	1	1358.09	20.888	0.7196[h]	20.015	1.185	0.1214	−0.0117[i]	0.0163	$-2.165e-3$[j]	0.0	1.293
100,089.8	2	2443.77	69.524	0.7312[k]	31.363	1.665	0.0296	−0.00296	0.0223	−0.00074	0.0	1.033
100,082.3	1	2588.9	130.5	0.0	32.68	1.818	0.0	0.0	0.0228	0.0	0.0	1.012
100,911	1	1199	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
111,642.8	1	2039.52	83.406	3.533[l]	26.705	2.781	0.540	−0.0917	0.012	0.0	0.0	1.119
113,163	2	742	0.0	0.0	16.3	0.0	0.0	0.0	0.0	0.0	0.0	1.43
112,669	1	2232.59	30	0.0	10.8	0.0	0.0	0.0	0.0	0.0	0.0	1.76
112,834	1	2343.9	55.9	0.0	28.4	0.0	0.0	0.0	0.0	0.0	0.0	1.085
113,142	2	2259.15	78.41	0.0	29.259	0.0	0.0	0.0	0.018	0.0	0.0	1.069
113,550	2	2341.15	63.23	0.0	30.081	0.0	0.0	0.0	0.0189	0.0	0.0	1.055
113,888.7	2	2359.91	68.816	1.0274[m]	30.296	1.42	−0.025	0.0	0.0201	0.0	0.0	1.051
113,899	1	2538	124	0.0	29.5	0.0	0.0	0.0	0.0	0.0	0.0	1.065
114,520	1	1835	0.0	0.0	9.7	0.0	0.0	0.0	0.0	0.0	0.0	1.86
114,485	1	2176	0.0	0.0	13	0.0	0.0	0.0	0.0	0.0	0.0	1.60
116,707.7	1	0.0	0.0	0.0	18.8	0.0	0.0	0.0	0.0	0.0	0.0	1.33
116,287	1	1983.3	0.0	0.0	18.4	0.0	0.0	0.0	0.0	0.0	0.0	1.35
117,984.5	1	2197.50	68.136	0.0	26.68	1.19	0.0	0.0	0.034	0.0	0.0	1.120
119,512.6	1	0.0	0.0	0.0	25.4	0.0	0.0	0.0	0.0	0.0	0.0	1.148
119,531	1	0.0	0.0	0.0	30	0.0	0.0	0.0	0.0	0.0	0.0	1.06
118,688	2	2142.	0.0	0.0	30	0.0	0.0	0.0	0.0	0.0	0.0	1.06
119,870	1	0.0	0.0	0.0	32	0.0	0.0	0.0	0.0	0.0	0.0	1.02
119,893	2	0.0	0.0	0.0	28.8	0.0	0.0	0.0	0.0	0.0	0.0	1.078
118,865.3	2	2329.97	63.140	0.0	29.89	1.11	0.0	0.0	0.025	0.0	0.0	1.058
121,211	2	2319.92	63.041	0.0	30.76	1.45	0.0	0.0	0.03	0.0	0.0	1.043
95,838.5	6	2466.89	63.51	0.552	31.07	1.425	0.0	0.0	0.0195	0.0	0.0	1.0376
95,936.1	3	2664.83	71.65	0.92	34.216	1.671	0.0	0.0	0.0216	0.0	0.0	0.9888
107,774.7	3	2196.13	65.80	−0.433	27.30	1.515	0.0	0.0	0.0	0.0	0.0	1.107
112,700.3	6	2371.58	66.27	0.88	30.364	1.545	0.0	0.0	0.0191	0.0	0.0	1.0496
112,854.4	3	2290.86	105.43	2.403	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
112,913	3	2268.73	0.0	0.0	30.62	0.0	0.0	0.0	0.0	0.0	0.0	1.045
113,132	6	2253.55	67.05	−1.272	29.221	1.506	0.0	0.0	0.0176	0.0	0.0	1.07
113,533	6	2345.26	66.56	0.745	30.085	1.692	0.0	0.0	0.0190	0.0	0.0	1.0545
113,825	6	2596.8	106	0.0	36	0.0	0.0	0.0	0.0	0.0	0.0	0.96
114,234	3	2399.1	91	0.0	35	0.0	0.0	0.0	0.0	0.0	0.0	0.98
116,705	3	2143.6	0.0	0.0	27	0.0	0.0	0.0	0.0	0.0	0.0	1.11
118,366.2	6	2344.37	67.29	0.99	30.074	1.462	0.0	0.0	0.0815	0.0	0.0	1.055
118,330	6	2340.	57	0.0	29.1	0.0	0.0	0.0	0.0	0.0	0.0	1.072
118,509.8	3	2303.1	76.90	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
118,613.7	6	2280.3	57.96	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
118,875.2	6	2291.7	62.44	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
119,317	3	2457.1	121.34	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
120,952.9	6	2321.4	62.86	0.0	29.95	1.24	0.0	0.0	0.023	0.0	0.0	1.057
121,295	3	2172.6	121.34	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
121,292	3	2661.4	121.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
123,488	6	0.0	121.34	0.0	29.3	0.0	0.0	0.0	0.023	0.0	0.0	1.069

[a] JANAF.
[b] $\omega_e z_e = -0.173514$, $\omega_e k_e = 9.93128e-3$, $\omega_e j_e = 4.38015e-4$.
[c] $\sigma_e = 8.72205e-3$, $\zeta_e = -9.59207e-4$, $\theta_e = 5.31722e-5$, $\tau_e = -1.21393e-6$.
[d] $\phi_e = -2.7385e-4$, $\varepsilon_e = 1.0242e-4$, $\eta_e = -1.172e-5$, $\iota_e = 4.684e-7$.
[e] $H_{v1} = -7.24e-6$, $H_{v2} = 9.619e-7$, $H_{v3} = -4.838e-8$.
[f] $L_{v0} = 6.70e-8$, $L_{v1} = -1.426e-8$, $L_{v2} = 1.388e-9$.
[g] $H_{v1} = -0.5e-5$.
[h] $\omega_e z_e = -0.0598$, $\omega_e k_e = 0.00216$.
[i] $\sigma_e = 0.00046$.
[j] $\phi_e = 2.289e-4$, $\varepsilon_e = -1.185e-5$.
[k] $\omega_e z_e = -0.0415$.
[l] $\omega_e z_e = -0.9375$.
[m] $\omega_e z_e = -0.04202$.

Table 2 Spectroscopic data for H_2^+

T_e	gi	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_e	γ_e	δ_e	D_e	β_e	H_{v0}	r_e
0.0[a]	2	2323.23	67.39	0.93[b]	29.946	1.594	0.032	−0.013	0.01991	−0.00087[c]	$1.75e-5$[d]	1.052
0.0	2	2321.7	66.2	0.6	30.21	1.685	0.0412	0.0	0.0	0.0	0.0	1.052
93,804.5	2	437.15	5.247	0.0	1.530	0.0312	0.0	0.0	0.000075	0.0	0.0	4.677
102,696.7	4	266.01	6.454	0.0	1.899	0.0758	0.0	0.0	0.00039	0.0	0.0	4.198

[a] JANAF.
[b] $\omega_e z_e = -0.029$.
[c] $\phi_e = 0.00003$.
[d] $H_{v1} = -6.e-7$, $L_{v0} = 1.6e-8$.

$$U - H(0) = E_{\mathrm{int}} + \frac{3}{2}RT \tag{21}$$

$$S = \frac{F - E}{T} \tag{22}$$

$$C_{p,\mathrm{int}} = R\left[2T\left(\frac{\partial \ln Q_{\mathrm{int}}}{\partial T}\right)_V + T^2\left(\frac{\partial^2 \ln Q_{\mathrm{int}}}{\partial T^2}\right)_V\right] \tag{23}$$

The total specific heat is obtained by adding the translational contribution

$$C_p = C_{p,\mathrm{int}} + \frac{5}{2}R \tag{24}$$

The enthalpy is given by

$$H - H(0) = E_{\mathrm{int}} + \frac{5}{2}RT \tag{25}$$

The Gibbs free energy is calculated from the entropy and the enthalpy as

$$G - H(0) = -RT \ln Q + RT \tag{26}$$

The Helmholtz potential, the internal contribution to the thermodynamic energy, and the internal constant-pressure specific heat strongly depend on the assumed sets of energy levels and adopted cutoff criterion.

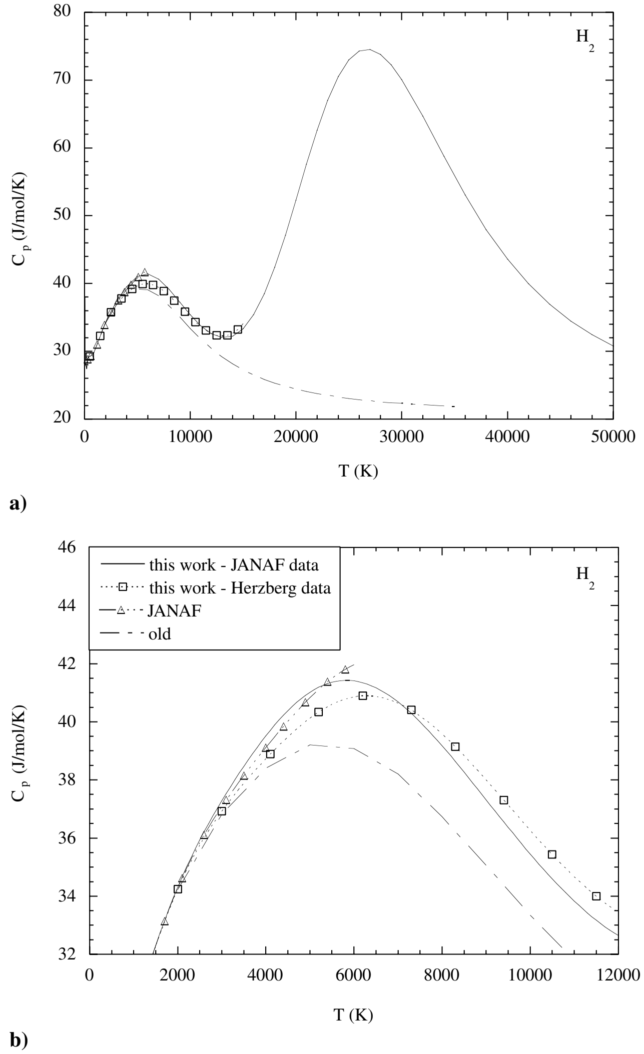


Fig. 3 Comparison of specific heat as a function of temperature for H_2.

Finally, we calculate the formation enthalpy of the component under consideration from

$$\Delta H_{f,j} = H_i - \sum_j \sigma_{ij} H_j \tag{27}$$

where H_i, H_j are the molar enthalpies given in Eq. (25), σ_{ij} are the stoichiometric coefficients of the formation reaction, and the sum runs on all the forming reactants. For example, for H formation

$$\frac{1}{2}H_2 \to H \tag{28}$$

the formation enthalpy is given by

$$\Delta H_{f,H}(T) = \frac{D}{2} + [H(T) - H(0)]_H - \frac{1}{2}[H(T) - H(0)]_{H_2} \tag{29}$$

III. Results and Discussion

A. Monatomic Species

In this section, we compare the present results with similar ones from literature. Figures 1 and 2 show comparisons of present results obtained for H, He, and He^+ with the results obtained by our group some years ago [16,17] (called old) and other calculations performed by Stull and Prophet [4] and by Gordon and McBride [5]. The main differences between the calculations are in the set of levels inserted in the partition function and its derivatives.

The present calculations complete the observed levels reported in the tables by Moore [18] and the National Institute of Standards and Technology (NIST)¶ with Rydberg and Ritz extrapolation laws for principal quantum number less than 20, using the hydrogenlike formulation for $n > 20$. The calculations are then presented with the lowering of the ionization potential as a parameter to control the cutoff. The same procedure was used in our previous calculations [16,17], even though, in this case, we considered a self-consistent approach for calculating ΔE.

In general, we should expect a good agreement about the thermodynamic properties of atomic (neutral and ionized) components for temperatures below 10,000 K. The trend of excited energy levels for H, He, and He^+ species is such that only at high-temperature ($T > 10,000$ K) excited states start contributing on partition function and on related quantities. This point can be understood by looking at Figs. 1 and 2, where the specific heats for these species have been reported as a function of temperature. Calculated values strongly depend on the used ΔE. In the same figure, we have also reported NASA results, as well as our old calculations.

The specific heat presents a flat behavior (i.e., only the translational contribution $C_p = 2.5 \cdot R$) below 10,000 K and a dramatic increase when high-lying excited states are populated. The Gordon and McBride specific heats closely follow our results below 10000 K but are largely underestimated above 10000 K because of the insufficient number of levels considered by these authors (Fig. 1). The insufficient number of levels considered by Gordon and McBride is determined by the cut-off criterion adopted in their calculations [5]. This cutoff criterion is temperature-dependent, the partition function includes only those levels below the ionization potential lowered by kT, then, as temperature increases, fewer energy levels are used, resulting in an underestimation of thermodynamic properties at high temperature. It should also be noted that the present results are close to the old results obtained by our group some years ago [16,17], but it must be noted that those results were self-consistent because they were calculated including the lowering of the ionization potential provided by the Debye-Huckel theory in the equilibrium code. Then, in principle, those results cannot be directly

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¶http://physics.nist.gov/PhysRefData/ASD1/ (reference date Aug. 1997; last update April 2005).

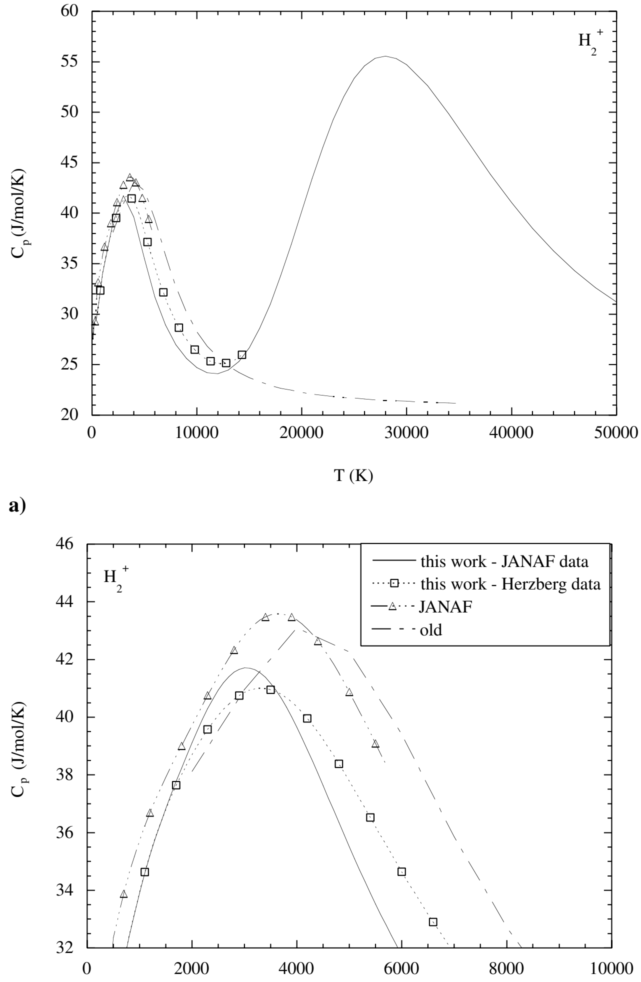
compared with ours. However, the lowering of the ionization potential for atmospheric hydrogen plasmas in the temperature range of 15,000–35,000 K is in an interval of 750–420 cm^{-1} for atomic hydrogen [19]. Keeping in mind these considerations, we can appreciate that the self-consistent results lie between the curves calculated in the present work corresponding to $\Delta E = 500\ \mathrm{cm}^{-1}$ and $\Delta E = 1000\ \mathrm{cm}^{-1}$. Similar considerations apply to the specific heat for He and He^+ (Fig. 2). In this case, the self-consistent lowering of the ionization potential for He is on the order of 500 cm^{-1}. Comparison of the present results calculated with $\Delta E = 500\ \mathrm{cm}^{-1}$ present an excellent agreement with our previous [16,17] self-consistent results in the whole temperature range.

B. Diatomic Species

In this section, we will compare the present results with those given in the JANAF (Joint Army, Navy, Air Force) tables [4] and in old calculations performed by our group some years ago [16,17]. The present results are calculated using two sets of spectroscopic data: the first one is that from Huber and Herzberg [20] for all the excited electronic levels of diatomic species; the second source is the JANAF tables [4] just for the spectroscopic constants of the ground electronic level of H_2 and H_2^+ (see Tables 1 and 2).

The various calculations differ because of the number of electronically excited states included in the partition function and, in some cases, because of the way to account for the rotational and vibrational levels. Results for H_2 and H_2^+ are shown in Figs. 3 and 4. To understand the present comparison, we must note that 1) our "old" results for H_2 and H_2^+ were determined by considering only the electronic ground state, moreover, the simplest method was used to calculate $v_{\max}$ and $J_{\max}$; 2) the reported values of JANAF tables consider a very low-temperature range so that only the ground electronic state is important. This means that both the old results and the JANAF results should present a trend of specific heat with a maximum typical of a finite number of levels in the partition function. Keeping in mind these considerations, we can appreciate a satisfactory agreement of the present calculations with the corresponding ones of [4,16,17] for $T < 12,000$ K. On the other hand, the present calculations show a second maximum in both H_2 and H_2^+ due to the insertion of high-lying electronic levels in the partition function.

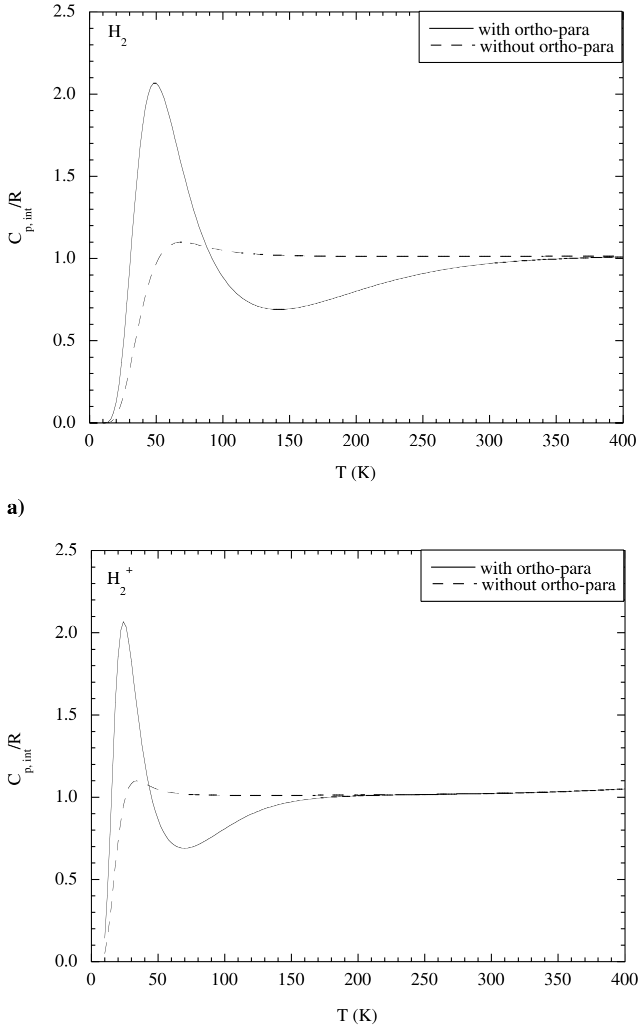
A particular behavior appears at low temperature, below 400 K, connected with the overall symmetry requirements of combined nuclear and rotational eigenfunctions of homonuclear diatomic molecules. The symmetry requirements of homonuclear diatomic molecules give place to two kinds of hydrogen molecules characterized by different J values (odd for orthohydrogen and even for parahydrogen) with a certain relative abundance. To take into account the relative abundance of the symmetrical and antisymmetrical nuclear species, one might consider a weighted sum for the rotational partition function. Fig. 5 reports comparisons between results calculated considering a different weight for even and odd rotational states of H_2 and H_2^+ (called "with ortho-para") and those obtained using the same weight (called "without ortho-para"). Strong differences appear in both cases at low temperature, where the most important contribution to the total energy is given by the rotational one. However, also including the effect of differently weighted J



a)

b)

Fig. 4 Comparison of specific heat as a function of temperature for H_2^+.



a)

b)

Fig. 5 Effect of ortho-para rotational states on specific heat for H_2 and H_2^+.

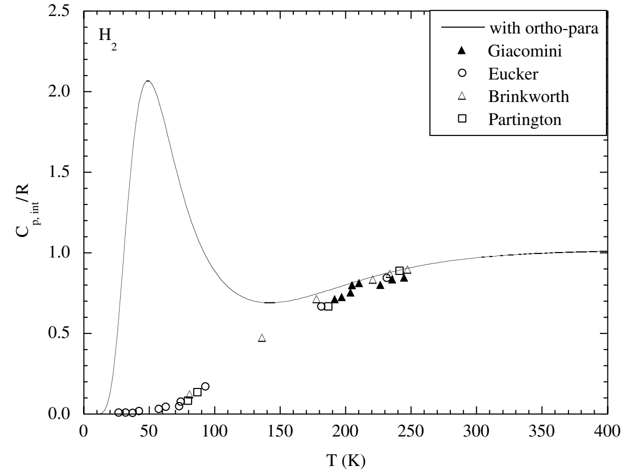


Fig. 6 Comparison between experimental data (see [21]) for the specific heat of H_2 and calculation performed considering a different weight for odd and even rotational states.

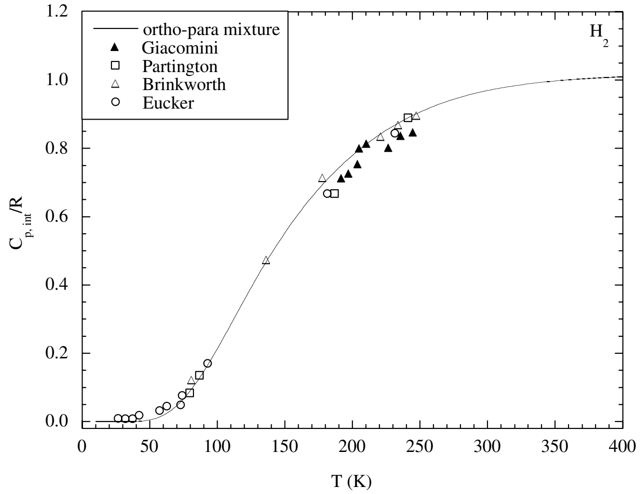


Fig. 7 Comparison between experimental data (see [21]) for the specific heat of H_2 and calculation performed considering the gas as a mixture of ortho- and parahydrogen.

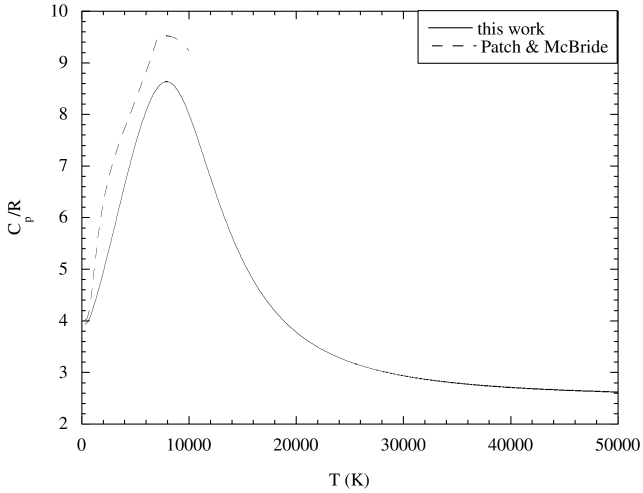


Fig. 8 Comparison of nondimensional specific heat as a function of temperature for H_3^+.

states, results are not in agreement with experimental data (Fig. 6). This means that calculating the rotational partition function by using a different weight for odd and even states is not enough to justify the behavior of the specific heat. Strong differences are evident comparing this calculation with experimental data by various authors (see [21]). This is because this approach implies that all of the spin isomers are in equilibrium with each other causing, at low enough temperature, all the hydrogen molecules to be able to reach the lowest rotational state. But this is not experimentally verified, with both the spin isomers being present at low temperature. Instead, theoretical calculations fit experimental data when hydrogen is considered as a mixture of two independent species ("ortho-para mixture" in Fig. 7): the species with symmetrical spin wave function are called *ortho*; those with antisymmetric spin wave function are called *para*. Thus, ordinary hydrogen gas behaves as a mixture of three-quarters orthohydrogen with a specific heat calculated from $Q_{\rm rot}^{\rm ortho}$ and one-quarter parahydrogen with a specific heat calculated from $Q_{\rm rot}^{\rm para}$.

C. Triatomic Species

Figure 8 reports a comparison of specific heat for the H_3^+ species. Results have been calculated considering only the ground electronic state and compared with those given by Patch and McBride [14]. A satisfactory agreement is observed. The Patch and McBride results, even limited to 10,000 K, present a well-defined maximum in the same position.

IV. Conclusions

In this paper, we have presented recent calculations of thermodynamic properties of high-temperature Jupiter components. In particular, we have presented the partition function and the specific heat of the relevant species, comparing them with existing results. In general, at low temperature, a good agreement is observed, whereas very large deviations occur at high temperatures when electronic excited states start contributing. A more expanded presentation of data and relative method of calculation will appear in a forthcoming ESA technical report, which will include tables of thermodynamic properties according to standard formats and interpolating polynomials. Work is in progress to produce a consistent set of transport properties for the same species.

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