"Frozen" Properties and Cut-off Criteria of High Temperature Gases

M. CAPITELLI and E. FICOCELLI V.

Centro di studio per la Chimica dei plasmi del C. N. R.
Istituto di Chimica Generale ed Inorganica dell'Università
Bari (Italy)

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The importance of the contribution coming from electronic excitation for the evaluation of the "frozen" properties of a plasma and the strong dependence of the electronic contribution on the adopted cut-off criterion are shown.

In the evaluation of electronic partition functions Q_{ej} of a species j

$$Q_{ej} = \sum_{n}^{n\max} g_{nj} \exp\{-E_{nj/kT}\}$$

or (1)

$$Q_{ej} = \sum_{0}^{E_{nj\max}} g_{nj} \exp\{-E_{nj/kT}\}$$

one has to resort to some cut-off criterion [1] of the Q_{ej} in order to avoid the divergence of the summation. The following criteria have most extensively been used in recent times:

The Criterion of MARGENAU *and* LEWIS [2, 3]

The partition function is cut at a value of the quantum number n given by

$$n_{\max} = 36.11 \cdot 10^3 \cdot \left(\frac{Z_j{}^2{}_{\text{eff.}}\, T}{\sum n_j z_j{}^2}\right)^{1/4} \tag{2}$$

where $Z_{j\,\text{eff.}}$ is the effective charge of the j-th species and n_j is the number density (cm^{-3}) of the species with charge z_j.

The criterion of GRIEM [4, 5]

The partition function is cut at a maximum value of E_n given by

$$E_{nj\,\max} = E_{0j} - \Delta E_{0j}$$

with (3)

$$\Delta E_0 = 2\,(z_j + 1)\; e^3 (\pi/k\,T)^{1/2}\; (\sum n_j\, z_j{}^2)^{1/2}$$

where E_{0j} and ΔE_{0j} are the ionization potential and lowering of ionization potential respectively.

The ground state criterion

$$Q_{ej} = g_{0j}\,.$$

Once the cut-off criterion has been selected the procedure for the calculation of equilibrium compositions and thermodynamic properties is straightforward as already discussed in previous works [5, 6]. The purpose of the present work is to emphasize the importance of the contribution coming from electronic excitation in evaluating the "frozen" properties of a plasma and the strong dependence of the electronic contribution on the cut-off criterion adopted.

Frozen properties are important quantities indeed for the analysis of heat transfer in plasmas where their values are needed for the evaluation of the adimensional PRANDTL and LEWIS numbers.

The observation [5, 7–9] that thermodynamic properties and total specific heats of high temperature gases are practically insensitive to the cut-off criteria adopted has often led to the neglection [10, 11] of the contribution coming from electronic excitation in the evaluation of the equilibrium properties of plasmas.

The results obtained according to this procedure are however accurate only as far as total thermodynamic quantities are concerned (i. e. properties which include ionization effects). The contribution of electronic excitation to these quantities is indeed small when compared with the contribution coming from ionization.

However, when "frozen" properties are calculated, which do not include the contribution from ionization, the neglect of the electronic contribution can lead to very inaccurate results, as will be shown below. This point has been overlooked in recent calculations [11].

Helium plasma (He, He^+, e) in the temperature range $10{,}000 - 35{,}000$ °K and in the pressure interval $0.1 - 10$ atmospheres will be taken as an example.

Results obtained for N_2 plasma (N_2, $N_2{}^+$, N, N^+, N^{++}, N^{+++}, e) will also be presented. The conclusions reached from analysis of these systems should be considered of general validity for high temperature gases.

Frozen properties and cut-off criteria

The frozen enthalpy (H_f) of a mixture of monatomic gases composed of atoms, ions and electrons, is made up of a translational contribution (H_{tr}) and a term coming from electronic excitation (H_{int}). In the par-

Reprints request to Dr. M. CAPITELLI, Istituto di Chimica Generale ed Inorganica dell'Università di Bari, Via Amendola 173, *I-70 125 Bari* (Italy).

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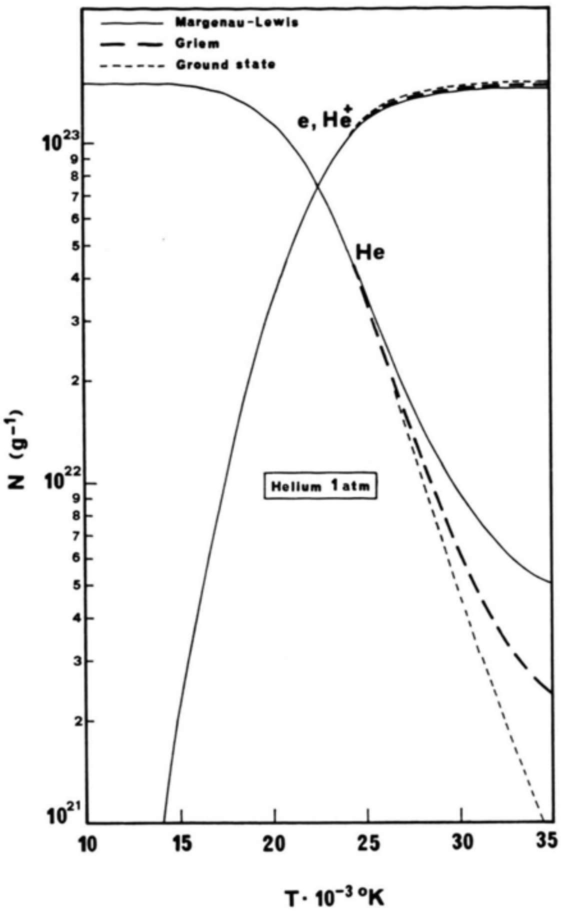

Fig. 1. Equilibrium composition of Helium plasma ($p=1$ atm) as a function of temperature.

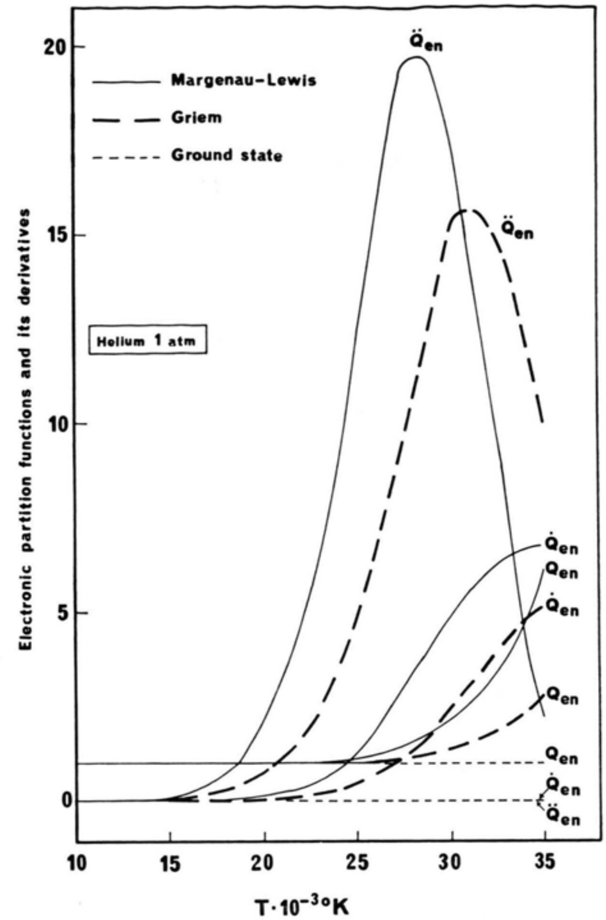

Fig. 2. Electronic partition function and its derivatives as a function of temperature for the He species ($p=1$ atm) (for the He^+ species: $Q_{ei}=2$; $\dot{Q}_{ei}=\ddot{Q}_{ei}=0$).

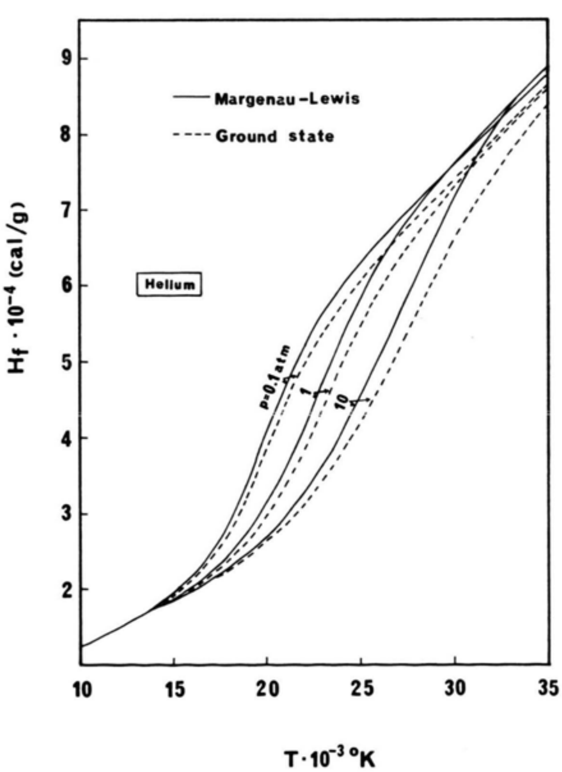

Fig. 3. "Frozen" enthalpy as a function of temperature for a Helium plasma.

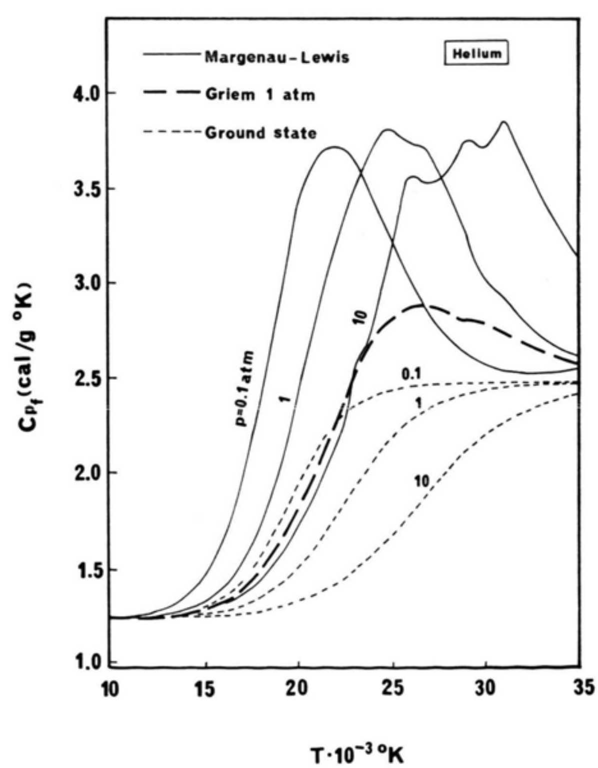

Fig. 4. "Frozen" specific heats as a function of temperature for a Helium plasma.

ticular case of the Helium plasma ($\underset{n}{He}\ \underset{i}{He^+}\ \underset{e}{e}$), for the temperature and pressure ranges considered in the present work, the contribution coming from electronic excitation is simply due to the neutral species, because excitation energies of the He^+ are too high.

One can write for this case:

$$H_f = H_{tr} + H_{int} \tag{4}$$
$$= (5/2)\ k\,T\,(N_n + N_i + N_e) + k\,T \left(\frac{d \ln Q_{en}}{d \ln T}\right) N_n .$$

Deriving Eq. (4) with respect to temperature, at constant composition, one obtains the frozen specific heat:

$$C_{pf} = \left(\frac{\partial H_f}{\partial T}\right)_{pN_j} = C_{p\,tr} + C_{p\,int} \tag{5}$$
$$= (5/2)\ k\,(N_n + N_i + N_e) + k\left[\frac{d \ln Q_{en}}{d \ln T} + \frac{d^2 \ln Q_{en}}{d^2 \ln T}\right] N_n$$

where N_j is the number of particles of j-th species per gram of plasma. From Eqs. (4) and (5) we can see that the quantities H_f und C_{pf} can be influenced by the different cut-off criteria either through H_{tr} and $C_{p\,tr}$ or through H_{int} and $C_{p\,int}$.

Differences in H_{tr} and $C_{p\,tr}$ can arise from variations in the N_j's. The equilibrium composition is in fact determined by the Saha equation [12]

$$\frac{n_i\, n_e}{n_n} = \frac{2\,(2\,\pi\, m_e\, k\, T)^{3/2}}{h^2} \frac{Q_{ei}}{Q_{en}} \exp - \{E_{0n} - \Delta E_{0n}/k\,T\} . \tag{6}$$

Fig. 1 shows that the criterion adopted is felt by the minority species only. The meaning of these results is that the partition function of He becomes appreciably different from its ground state value, g_{0He}, only when the concentration of this species is markedly diminishing and its contribution becomes therefore small.

Differences in H_{tr} and $C_{p\,tr}$ calculated according the Margenau-Lewis criterion and the ground state method do not differ by more than 3%. The quantities H_{int} and $C_{p\,int}$ depend upon

$$\dot{Q}_{en} \equiv d \ln Q_{en}/d \ln T \quad \text{and} \quad \ddot{Q}_{en} \equiv d^2 \ln Q_{en}/d^2 \ln T .$$

Values of $\dot{Q}_{en}$ and $\ddot{Q}_{en}$ calculated at atmospheric pressure according to the three cut-off criteria have been plotted in Fig. 2 as a function of temperature, along with Q_{en}. One sees that $\dot{Q}_{en}$ increases in a temperature range where the He species is sharply decreasing. The contribution of the terms $k\,T\,N_n\,\dot{Q}_{en}$ in Eq. (4) is therefore rather small and values of H_f do not differ by more than 10% (Fig. 3). The plots of $\ddot{Q}_{en}$ do on the contrary show the presence of a maximum in a temperature region where He is not a minority species. A marked contribution to $C_{p\,int}$ is therefore to be expected (Fig. 4). When use is made of the Griem's method the maxima of the quantities $\dot{Q}_{en}$ and $\ddot{Q}_{en}$ are shifted toward higher temperatures (Fig. 2). This is immediately reflected by the frozen quantities, as can be seen from Fig. 4.

Results for the N_2 plasma given in Fig. 5 are in general agreement with those obtained for the Helium plasma.

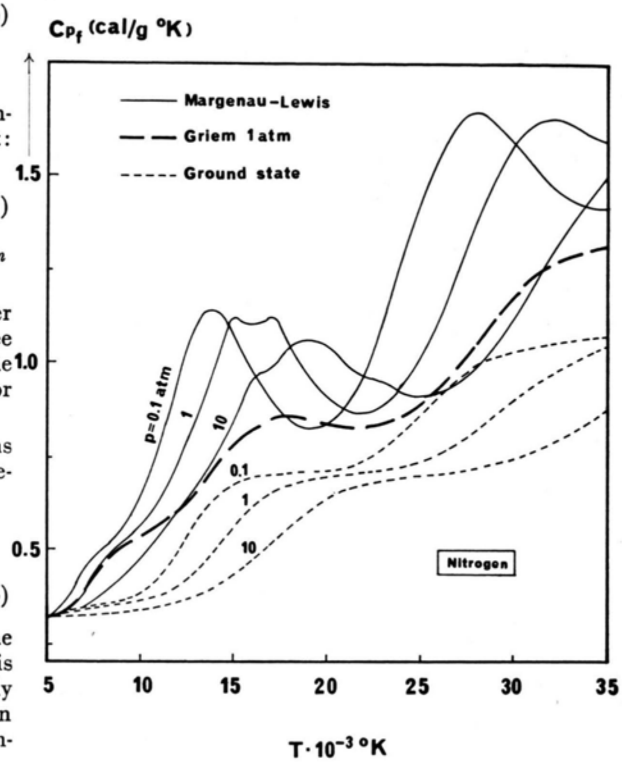

Fig. 5. "Frozen" specific heats as a function of temperature for a Nitrogen Plasma.

The behaviour of the frozen quantities as illustrated by the results for the He and the N_2 plasmas should be of a rather general validity. It is in fact a rather general situation with equilibria of the type

$$A^Z \rightleftarrows A^{Z+1} + e$$

that the z-charged species is excited and ionized in a temperature range where the energy levels of the $(z+1)$ ion are too high to be considerably populated.

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[12] The following expressions have been used for the calculations of the ΔE_{0j}'s:
a) MARGENAU-LEWIS: $\Delta E_{0j} = E_{0j}/n^2_{max}$;
b) Griem: Eq. (3); c) Ground state: $\Delta E_{0j} = 0$.