Table 1 Air properties at outer edge of boundary layer

No.	h_e	P_e	V	T_e	ρ_e	μ_e	Le	h_D
1	8800	2.0	1800	10,600	3.5×10^{-4}	8.3×10^{-5}	0.85	5000
2	6800	2.0	1800	10,000	4.0	7.8	0.97	3600
3	5100	2.0	1900	9,100	4.7	7.2	1.09	2400
4	8700	4.1	2000	10,700	7.1	8.4	0.87	4200
5	5800	5.8	1500	9,200	13.5	7.2	1.10	2000
6	2800	6.2	1900	6,300	23.6	5.6	1.35	900
7	5100	10.0	1800	9,400	22.9	7.4	1.10	1500

Table 2 Measured and calculated heat fluxes

		Calculated by model		
No.	Measured	1	2	3
1	80	185	183	77
2	73	154	154	70
3	66	123	124	63
4	170	291	288	146
5	153	220	220	141
6	90	131	133	87
7	228	271	274	190

is coated with a material such as SiO, catalytic activity is reduced remarkably. Winkler and Griffin[6] have reported that, in a 9000-Btu/lbm dissociated nitrogen stream, a calorimeter coated with SiO decreased heat transfer by 50% over that of a polished copper cylinder. Mavroyannis and Winkler,[7] at freestream densities comparable to those given here, report that, although copper appeared to be catalytic to the recombination of atomic oxygen and nitrogen, oxide-coated copper was only partially catalytic.

In the present case, heat flux to the copper calorimeter was measured in an arc facility that employed carbon electrodes, some of the carbon subliming and reacting with oxygen of the air to form CO. Since it is known that copper oxide strongly adsorbs a surface layer of CO,[8] it is hypothesized that the calorimeter had an oxide layer on its surface and that either this layer was itself noncatalytic to recombination or the strong adsorption of CO rendered it noncatalytic. Work in this area is continuing in our laboratories.

The possibility that a catalytic surface can be rendered so easily noncatalytic makes it imperative that calorimeter-catalytic activity be determined for each test series. Only in this way can there be assurance that the effective heats of ablation calculated from the measured heat rates are realistic. It is strongly suspected that this possible variation in surface catalytic activity often may be responsible for the wide variations reported in effective heats of ablation.

Conclusions

Heat flux measurements are as important in determining effective heats of ablation as are the ablation rates themselves. The fact that flow appears to remain substantially frozen at relatively high pressures in the present experiments makes it imperative that calorimeter poisoning be held to a minimum and catalytic activity towards atomic recombination be determined if accurate and reproducible effective heats of ablation are to be obtained.

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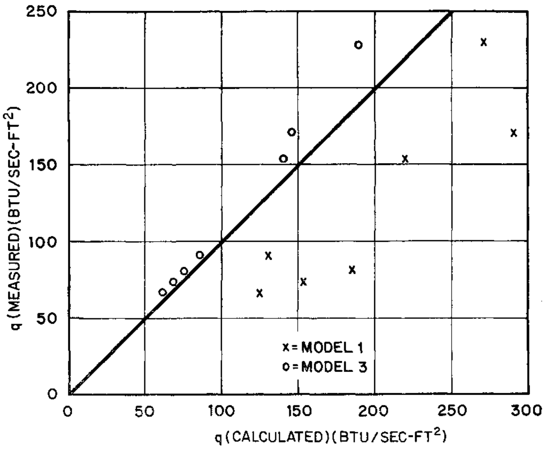

Fig. 1 Comparison of measured and calculated heat rates for two models

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Debye-Huckel Plasma Corrections

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The physical model recently used by McGee and Heller to compute the thermodynamic properties of gaseous plasma is questioned. For the medium-density plasma, the Debye-Huckel theory of point charges is adequate and provides both a cutoff for the electronic partition function and a lowering of the ionization potential. The difficulties of the high-pressure plasma model are mentioned briefly.

IN a recent paper, McGee and Heller[1] have computed the thermodynamic properties of the first three elements treated as plasmas in the pressure and temperature ranges 0.0001 to 100 atm and 2000° to 50,000°K, respectively. The physical model that they chose was as follows:

1) The plasma consisted of atoms, ions and, electrons, all of which obeyed classical (Boltzmann) statistics.

2) Neutral gas thermal imperfections were neglected.

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3) Electrostatic interactions between charged species were allowed for by using the Debye-Huckel theory for point charges.

4) The ionization potentials χ of the atomic and ionic species were lowered by an amount $\Delta\chi$, depending on the sum of the energy level lowering effects due to the plasma microfield (the so-called Unsold term), together with the energy level lowering effects due to the Debye polarization effect, viz.,

$$\Delta\chi = 0.67 \times 10^{-6} N_e^{1/3} + 0.37 \times 10^{-7} (N_e/T)^{1/2} \text{ ev}$$

where N_e is the electron density. This result first was given by Ecker and Weizel.[2]

5) The electronic partition functions of the atomic and ionic species were made nondivergent by using the Inglis-Teller cutoff,[3] which gives for the principal quantum number $n_{\max}$ of the last bound state

$$\log_{10} n_{\max} = 3.11 - 0.133 \Sigma z N_z$$

where z is the charge on an ion, and N_z is its number density.

The purpose of this note is to question the internal consistency of the forementioned physical model. Equilibrium calculations of plasma properties have been made by many workers during the war and in the postwar period. Alpher,[4] in 1957, when commenting on some of these calculations, remarked that "There exists no unique and universally accepted procedure for computing the electronic partition functions." However, since that time, considerable theoretical advances in imperfect gas plasma behavior have been made, and the regions of validity of various physical models of plasma have been established quite convincingly.

It appears that the Debye-Huckel theory of point charges indeed is valid in what may be termed the medium-density, medium-temperature range. For a good discussion of its range of validity, see Duclos and Cambel.[5] In general, Debye theory for point charges likely is valid if the following two criteria are obeyed: 1) the electrostatic interaction energies are small compared with the thermal energies; and 2) the Debye sphere contains a large number of charged particles. A mathematical description of this second criterion cannot be framed accurately, but one plausible statement is that of Fowler and also Berlin and Montroll (see Ref. 5):

$$N_e \leq (1/2\pi)(kT/e^2)^3$$

where N_e is the electron density, T the temperature, e the electrostatic charge on the electron, and k the Boltzmann constant. This has the numerical value

$$N_e \leq 3.4 \times 10^7 T^3$$

This latter inequality holds only for a gas consisting of electrons and singly charged ions. For multiply ionized plasmas, Griem[6] gives it as

$$\frac{(N_e + \Sigma z^2 N_z)^{3/2}}{N_e + \Sigma N_z} \leq \frac{(kT)^{3/2}}{\pi^{1/2} e^3}$$

In view of the second Debye criterion, it is doubtful if the theory is applicable for the total gas pressures of 100 atm and the lower temperatures considered by McGee and Heller. Furthermore, if it is decided that Debye-Huckel theory is valid for a given plasma, then care must be taken in deciding what model to use for the lowering of the ionization potential. It already has been remarked that McGee and Heller used the Ecker-Weizel result. As originally given, this considered the effects of a nearest-neighbor interaction (the Unsold term) superimposed on a "background" Debye polarization, although there is some dispute as to whether the Unsold term and the first term of the Ecker-Weizel analysis are comparable physically. Many authors have used either the Unsold term alone or the Ecker-Weizel two terms to express the lowering of the ionization potential; these two expressions are all but equal, since the Unsold term is the dominant term in the Ecker-Weizel expression. However, the Unsold analysis is applicable only at high electron densities such that $N_e > (kT/e^2)^3$. This inequality is given by Olsen[7] and also by Griem; it will be seen that it is in direct contradiction to the second Debye validity criterion for point charges. The appropriate expression for the lowering of the ionization potential in a Debye-Huckel gas of point charges is the Debye polarization term alone, which involves the Debye radius rather than the (smaller) mean distance between ions such as was used by Unsold. It has been given by Griem in the form

$$\Delta\chi_z = 2(z + 1)e^3(\pi/kT)^{1/2}(N_e + \Sigma z^2 N_z)^{1/2}$$

Griem comments also that the Debye polarization term given by Ecker and Weizel is, in fact, incorrect and arose because of an incorrect use of Debye-Huckel theory.

If the correct Debye polarization term is used, it is found that McGee and Heller have cut off considerably more electronic states than are warranted; this clearly is of importance, since they state that the lowering of the ionization potential by other ions "significantly affects the enthalpy of the plasma." As McGee and Heller do not quote their computed electron densities, their errors cannot be assessed in this note. However, a typical example can be given by considering the atmospheric pressure argon plasma at 16,000°K. For ionization of the neutral atom, the lowering of the ionization potential using Griem's expression is 0.11 ev, whereas use of the Ecker-Weizel expression of McGee and Heller gives a value of 0.45 ev.

Two comments can be made on the foregoing results. First, it hardly can be said that an electrostatic interaction energy of 0.45 ev obeys the first Debye validity criterion just given; secondly, the Griem cutoff excludes 28 levels and one level of the ${}^2P_{3/2}{}^0$ and ${}^2P_{1/2}{}^0$ AI configuration, respectively, whereas the Ecker-Weizel cutoff excludes 87 and 59 levels, respectively. At the higher temperatures (such as considered by McGee and Heller), these incorrectly excluded terms will affect the enthalpy considerably.

The Inglis-Teller relation used by McGee and Heller is that appropriate to energy level broadening and merging by ionic first-order Stark effect, i.e., the electrons are ignored. First-order Stark effect broadens the energy levels but does not displace them, whereas quadratic Stark effect shifts the level centers of gravity. Strictly speaking, the Inglis-Teller result is applicable only for hydrogen or hydrogen-like elements or ions where first-order Stark effect predominates. It therefore should be used with caution for other elements of a nonhydrogenic nature. The question of whether a quantum level of an atom shows a linear or quadratic Stark effect depends on whether that level has a permanent or only an induced net electric moment associated with it. The majority of quantum levels for most atoms do not possess such a permanent electric moment and therefore exhibit a quadratic Stark effect; it would be incorrect to apply the Inglis-Teller relation as originally given for these cases. Linear Stark effect, which is the exception rather than the rule, is obtained only when the running electron moves in a Coulomb field and in a nonpenetrating orbit; hence, linear Stark effect can be obtained for hydrogen and hydrogen-like atoms and ions. It can be argued that a highly excited but bound electron in any element is near-hydrogenic, since it can be regarded as an ion together with an electron moving around it in a very large orbit (see Bethe[8] and more recent discussions by Rouse[9] and by Harris[10]). However, it really is unnecessary to invoke the Inglis-Teller relation, since the Debye-Huckel theory of point charges provides its own electronic partition function cutoff, viz., the partition functions should include all levels whose energies ϵ fulfill the inequality

$$(\epsilon_m)_z \leq \chi_z - \Delta\chi_z$$

where the levels m refer to an element in ionization stage z. Clearly, this cutoff would have added to the consistency of the McGee-Heller calculations if it had been used. It appears therefore that the Debye-Huckel theory of point charges provides a consistent model for medium-density, medium-temperature plasmas. What model therefore is appropriate for denser plasmas, where the Debye validity criteria are invalid and into which regime the McGee and Heller calculations likely encroach? If it is desired to extend the pressure range beyond the range of the Debye criteria, then the theory must be generalized to avoid not only the divergence of the collision integrals at long range (Debye length) but also the divergence at short range. This latter divergence can be removed by assuming that the ions have a finite, nonzero diameter; this point is discussed by Duclos and Cambel. Now it will be recalled that Debye-Huckel theory avoided the statistical aspects of the ionized medium by assuming that the electrostatic potential obeyed the Poisson-Boltzmann equation. When linearized, the resulting equation could be solved exactly and yielded the thermodynamic functions used by McGee and Heller. However, when finite ionic diameters are introduced into the linearized equation, inconsistencies arise which unfortunately do not disappear on removal of the linearization. To avoid these difficulties, Meyer[11] made a fresh statistical approach (cluster theory using ring-integrals), and this theory has been extended by several workers; their results recently have been discussed by Brush, DeWitt, and Trulio.[12] These analyses show that the pressure decrease predicted by Debye-Huckel theory of point charges is overestimated if finite ionic diameters are considered. The problem of pressure ionization becomes relevant here, viz., at a fixed temperature the degree of ionization of a gas decreases with pressure as decreed by the Saha equation but then passes through a minimum and then increases with pressure. Pressure ionization that is attributed to the squeezing of the electronic levels of an atom into the continuum due to increasing atom density in the immediate vicinity has been treated simply by Bethe and more exactly by Timan[13] using the Debye-Huckel theory of point charges. It also has been studied by Brush[14] for the case of finite ionic diameter; he found that the pressure p^*, where the degree of ionization became a minimum, was given by the approximate expression

$$p^* = \left[1 + \frac{4e(\pi p^*)^{1/2}}{\beta kT}\right]\left[\frac{k^4T^4}{4\pi e^6}\right]$$

where β^{-1} is the mean radius of the electronic charge distribution of an ion. The analysis giving this result is suitable for a gas with two stages of ionization but with a preponderance of one stage. If the value of 10^{-8} cm is taken for the mean ionic radius, then at a temperature of 10,000°K, the foregoing formula gives a pressure of 36 atm, whereas if the ionic radius is put equal to zero at the same temperature, then a pressure of 23.6 atm is found, i.e., the introduction of a finite ionic diameter increases the gas pressure above that predicted by the Debye theory of point charges. Bearing this in mind, it would appear that the higher-pressure, lower-temperature results of McGee and Heller for hydrogen and for lithium should be re-examined, since it is likely that their tabulated Debye-Huckel point charge excess functions will be in error. Strictly speaking, although there are well-developed theories for discussing the high-temperature, high-pressure gas, such as those reviewed by Brush et al.,[12] they all suffer from the one defect, viz., the gas imperfections that they predict are sensitive functions of the mean radius of the ion, and this quantity cannot be decided unambiguously at the present time.

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Integrated Laminar Heat Transfer in the Windward Plane of Yawed Blunt Cones

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THE ratio of local to stagnation heat-transfer rates on a blunt body in axisymmetric laminar flow is given by Ref. 1:

$$\frac{q}{q_0} = \frac{\rho_w\mu_w u_e r}{(2\xi)^{1/2}[2\rho_{w0}\mu_{w0}(du_e/ds)_0]^{1/2}} \frac{1 + 0.096(\beta)^{1/2}}{1.068} \left(\frac{H_0 - h_w}{H_0 - h_{w0}}\right) \tag{1}$$

where

$$\beta = 2(d \ln u_e/d \ln\xi) \tag{2}$$

and

$$\xi = \int_0^s \rho_w\mu_w u_e r^2 ds \tag{3}$$

with s being the distance along a streamline at the edge of the boundary layer.

According to Ref. 2, the heating-rate distribution over an axisymmetric body may be expressed by replacing the cylindrical radius r in Eqs. (1) and (3) by a curvilinear variable h_2. In the windward plane h_2 is expressed by the differential equation

$$\frac{1}{h_2}\frac{\partial h_2}{\partial s} = \frac{1}{r}\frac{\partial r}{\partial s} + \frac{1}{u_e}\frac{\partial w}{r\partial \phi} \tag{4}$$

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