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THERMAL IONIZATION OF ROCKET EXHAUST PLASMAS

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ABSTRACT

Thermal or equilibrium processes contribute to the total ionization of the exhaust plasmas attending a missile in flight. Such equilibrium ionization is the principal contributor to the total ionization in some cases of interest. Calculations of the equilibrium values of ionization for various rocket-propellant components are presented in graphical form to make numeric values readily available and to simplify their utilization.

PROBLEM STATUS

This is an interim report on one phase of the problem; work on this problem is continuing.

AUTHORIZATION

NRL Problem R07-07
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THERMAL IONIZATION OF ROCKET EXHAUST PLASMAS

The plasmas attending a missile in flight may stem from a number of sources, such as from shock ionization, chemi-ionization, thermal ionization, photoionization, etc. One of the important ionization mechanisms is the thermal (or equilibrium) process. Any of the ionization sources may control in a particular case, but only the thermal ionization will be presented in this report.

The subject of equilibrium excitation and ionization is considered in treatises on physical chemistry (see item 1 in bibliography, for example). It has been treated in some detail by Saha (2) and, for this reason, is sometimes called Saha ionization. For the simple case of a single ionizing component, the expression for the ionization is written as

$$\log_{10}\left(\frac{x^2}{1-x^2}\,p\right) = -\frac{5041\,I}{T} + \frac{5}{2}\log_{10}(T) - 6.49 + \log_{10}\left(\frac{g_e g_i}{g_a}\right),$$

where

x = fraction of the ionizable component which is ionized

p = partial pressure of the ionizable component (atmospheres)

I = ionization potential of the ionizable component (electron volts)

T = temperature (degrees Kelvin)

g_e = weight factor for the electron (=2)

g_i = weight factor for the ion

g_a = weight factor for the atom

and the weight factor is $2j + 1$, where j is the inner quantum of the ground term for the particular atom or ion.

If there is more than one component that is ionized, either in different excited states of a single type of atom or in different atoms, the relation then becomes

$$\log_{10}\left(\frac{x_k}{1-x_k}\,\frac{f}{1+f}\,p_k\right) = -\frac{5041\,I_k}{T} + \frac{5}{2}\log_{10}(T) - 6.49 + \log_{10}\left(\frac{g_e g_i}{g_a}\right),$$

where

x_k = fraction of the particular ionizable component that is ionized

p_k = partial pressure of the particular component

f = fraction of free electrons to the original number of undecomposed atoms.

Similar equations are required for each excited state of each type of atom or radical contributing to the total ionization. A simultaneous solution of the set of equations is then required for a solution. Further refinements are required for multiple ionization.

A knowledge of the conditions that exist is usually inadequate to permit a high degree of accuracy in the calculation of chemical kinetic processes which lead to the observed ionization. As a consequence, the first of the above equations with the assumption of a single source of electrons is adequate for most computations. Usually the accuracy desired from the calculations is such that further simplications can be made. As a consequence, plotted values of ionization, such as those illustrated in the following figures, are frequently of utility.

The solution of the equilibrium equation gives curves as plotted in Fig. 1,* which illustrates the steep rise in ionization at the lower temperatures. The ionization of the total gas rather than of the ionizable component is usually of more interest. The curves of Fig. 1 appear as shown in Fig. 2 when expressed in terms of the total gas. Use of an inverse temperature scale simplifies the graphical presentation, as shown in Figs. 3, 4, 5, and 6. The weight function $\log_{10}(g_e g_i / g_a)$, which has a value of zero for the alkaline earth metals and for aluminum, i.e., for most of the curves presented in this report, was assumed to be zero for the general curves. Thus, in Figs. 5 and 6 and other similar plots, a nonzero value of this function would cause a relatively small shift of all the curves along the temperature axis. The effect is illustrated in Fig. 7. Similarly, a change in the pressure causes a shift in the T direction as illustrated in Fig. 8.

The curves for the ionization of all gases are very similar when plotted as a function of the ionization potential divided by the temperature (I/T). This is illustrated in Fig. 9 for various single-component gases having widely varying ionization potentials (11.0 to 2.0 ev) and for a total pressure of one atmosphere. Usually, the range of ionization potentials of the elements of interest are much narrower than the total spread illustrated in this figure and fall within the range of the two inner curves, i.e., between cesium (3.893 ev) and aluminum (5.984 ev). Thus, a single intermediate curve would give results accurate to within 30 percent for most cases. (This accuracy is sufficient for most cases of interest.) A set of curves for an average ionization potential is illustrated in Fig. 10. If results at pressures other than one atmosphere are desired, the curve should be shifted horizontally by an amount determinable from Fig. 8.

In many cases of interest, the electron density rather than the fraction of electrons present is of interest. Curves for the electron density at twelve atmospheres, the approximate pressure at the throat of many rocket motors, are shown in Fig. 11 for various ionizable components of interest. The decrease in electron density at high temperatures is a consequence of the reduced gas density with increasing temperature and constant pressure.

The ionization in a gas at one atmosphere pressure containing cesium is shown in Fig. 12. The curves for the various ionizing components may be combined on a single family of curves when the electron density is plotted against the dimensionalized parameter I/T, similar to those used for the fraction ionized. Curves of this general type for two pressures, one and twelve atmospheres, are shown in Fig. 13. A simpler curve with sufficient accuracy for most applications is illustrated in Fig. 14.

Caution must be exercised in applying these curves, particularly because of the large number of cases in which they are inapplicable because equilibrium processes are not controlling. Further discussions of their applicability may be found in papers referenced in the bibliography.

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*All figures are located at the end of this report.

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APPENDIX

CALCULATION OF SINGLE IONIZABLE COMPONENT X

The equilibrium equation for a single ionizable component may be rewritten in the form

$$x = \left[\frac{10^{-(6.49 + 5041\, I/T)}}{p/T^{5/2} + 10^{-(6.49 + 5041\, I/T)}}\right]^{1/2}$$

For $p/T^{5/2} \ll 10^{-6.49 + 5041\, I/T}$, i.e., for either small pressure (p) or large temperature (T), this equation gives $x \to 1$, as shown on the various curves of Figs. 1 to 10.

Similarly, for T small (or I large) so that $10^{-(6.49 + 5041\, I/T)} \ll p/T^{5/2}$ and $5041\, I/T \gg 6.49$,

$$x \to \frac{T^{5/4}}{p^{1/2}}\, 10^{-(5041\, I/T)/2}.$$

Since T varies slowly compared to $10^{-(5041\, I/T)/2}$, $x \approx 10^{-(2520\, I/T)}$, or $\log_{10} x \approx -(2520\, I/T)$. Thus, on the log linear plots used, the ionization varies approximately linearly with I/T throughout much of the region, as shown on the curves using an inverse temperature scale. A single set of curves will suffice for all ionization potentials whenever this approximation applies. Figures 9 and 13 show the range of values encountered for various ionization potentials. Figures 10 and 14 show approximate values suitable for many purposes.

An approximate equation may also be written in the form

$$x \approx \left[\frac{10^{-(6.49 + 5041\, I/T)}}{p/T^{5/2}}\right]^{1/2}$$

whenever $p/T^{5/2} \gg 10^{-(6.49 + 5041\, I/T)}$. Thus,

$$\frac{x p^{1/2}}{T^{5/4}} \approx 10^{-1/2(6.49 + 5041\, I/T)},$$

or

$$\log_{10} x = -1/2 \log_{10} p + 5/4 \log_{10} T - 1/2(6.49 + 5041\, I/T).$$

Thus, a change in pressure p shifts the value of the ionization much in the same manner as a negative change in temperature. Such a shift is illustrated in Fig. 8.

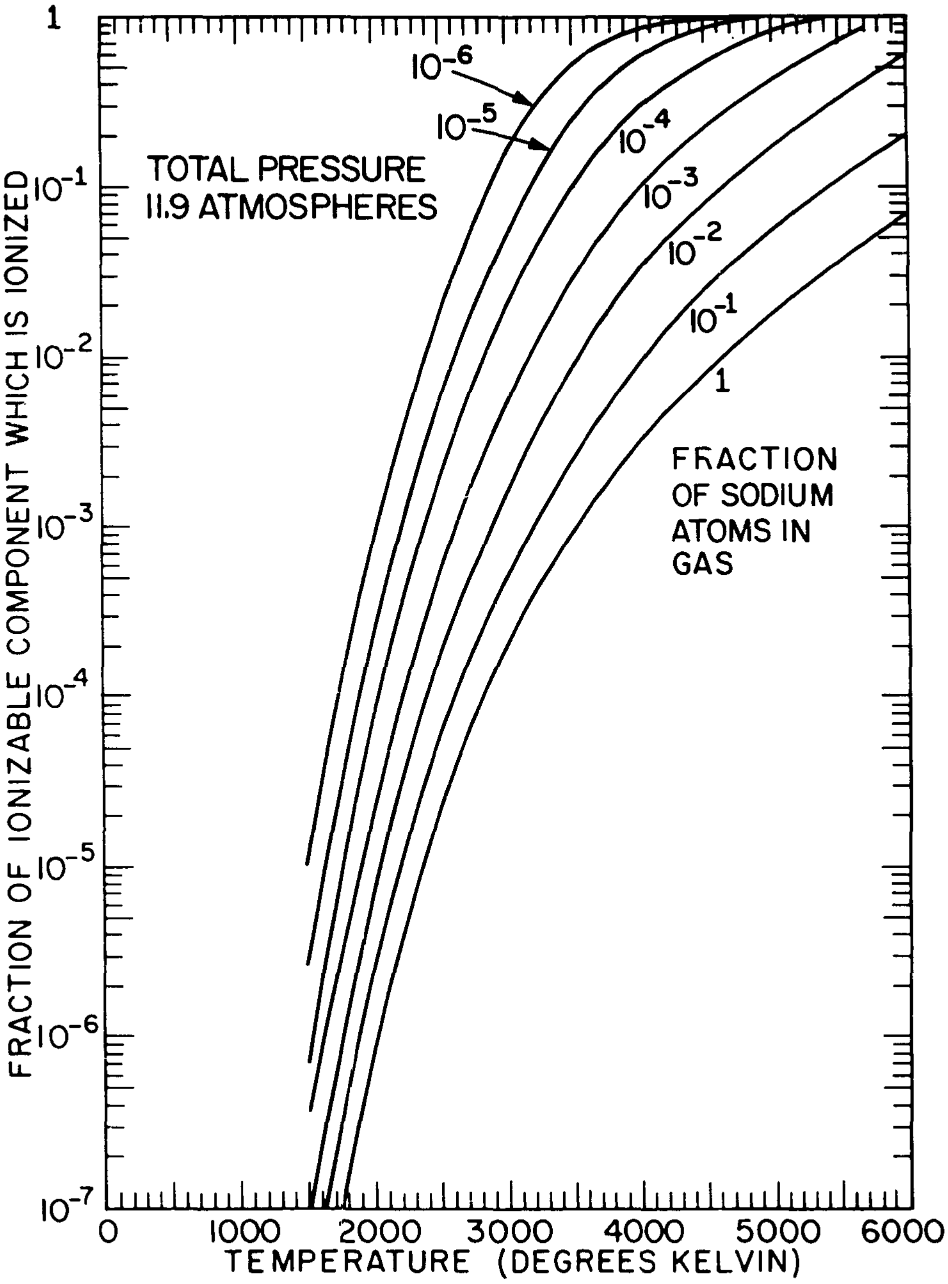

Fig. 1 - Fraction of ionizable component which is ionized varies with partial pressure

The fraction of a low-ionization-potential component which is ionized at a given temperature decreases as the partial pressure of the component increases. The fraction of sodium which is ionized as a function of its partial pressure and the temperature is illustrated in the family of curves shown above. Even though the fraction ionized decreases with increasing pressure, the total electron density increases because of the increasing density of parent atoms.

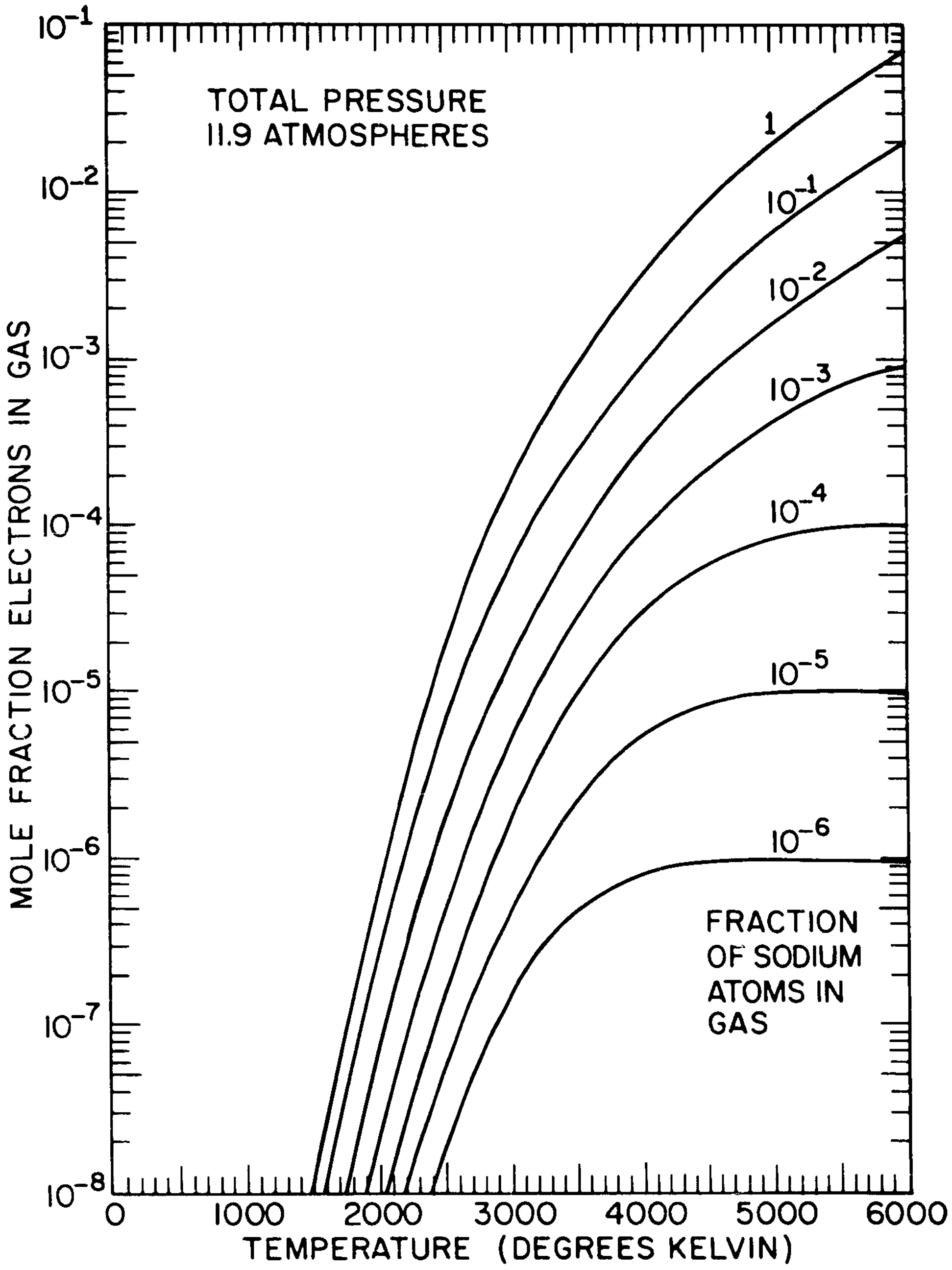

Fig. 2 - Mole fraction of total gas which is ionized increases with partial pressure

The curves of Fig. 1 are replotted with the fraction of total gas which is ionized as the ordinate. Plots such as this with the electron density expressed as a fraction, or sometimes called a mole fraction, are of particular utility when considering frozen expansion of a gas.

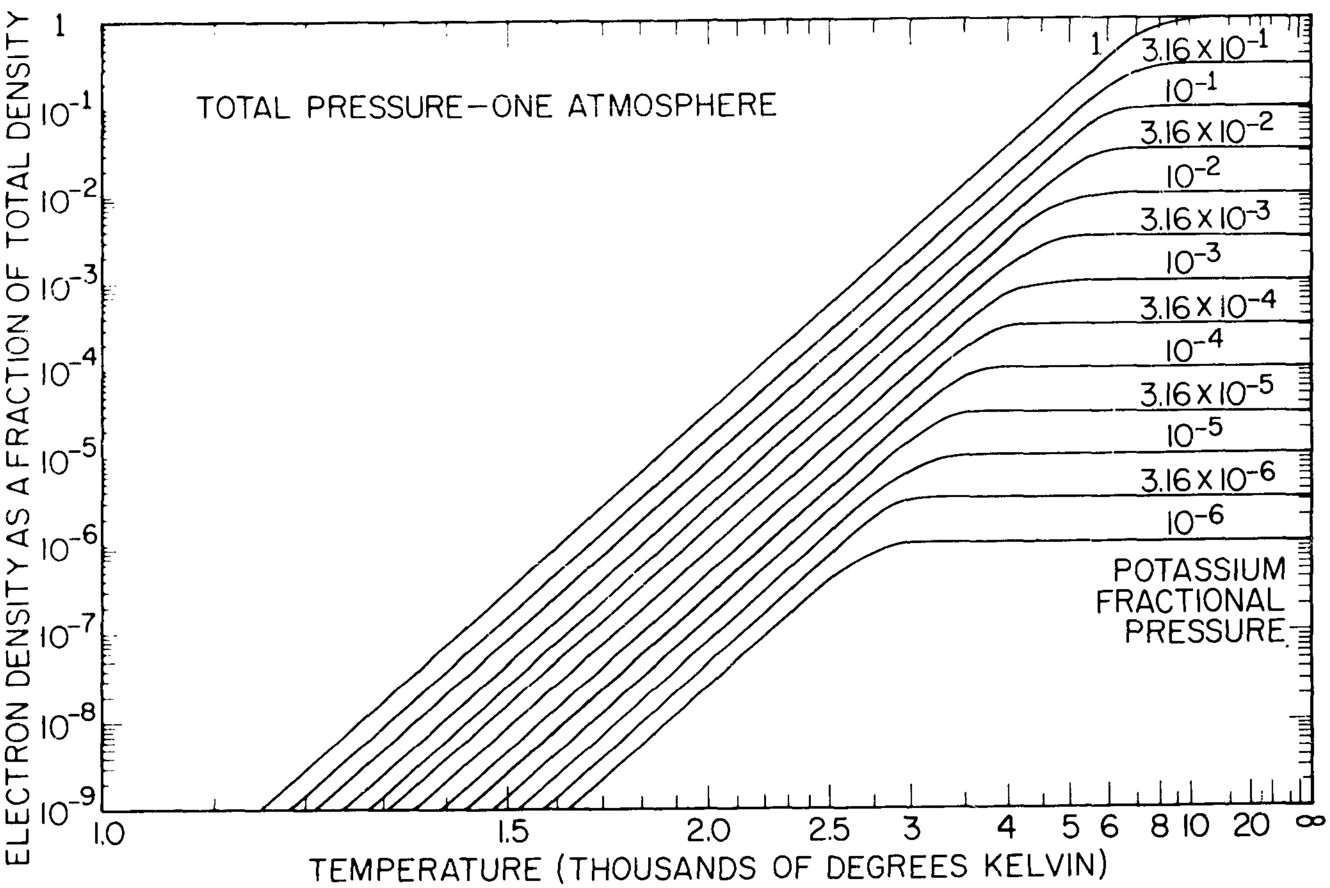

Fig. 3 - Potassium ionization plotted on an inverse temperature scale

The use of an inverse temperature scale reduces the labor in plotting curves and spreads the data, thus making curve reading easier. The abscissa is plotted as an inverse temperature scale, but the temperatures are as indicated to simplify curve reading.

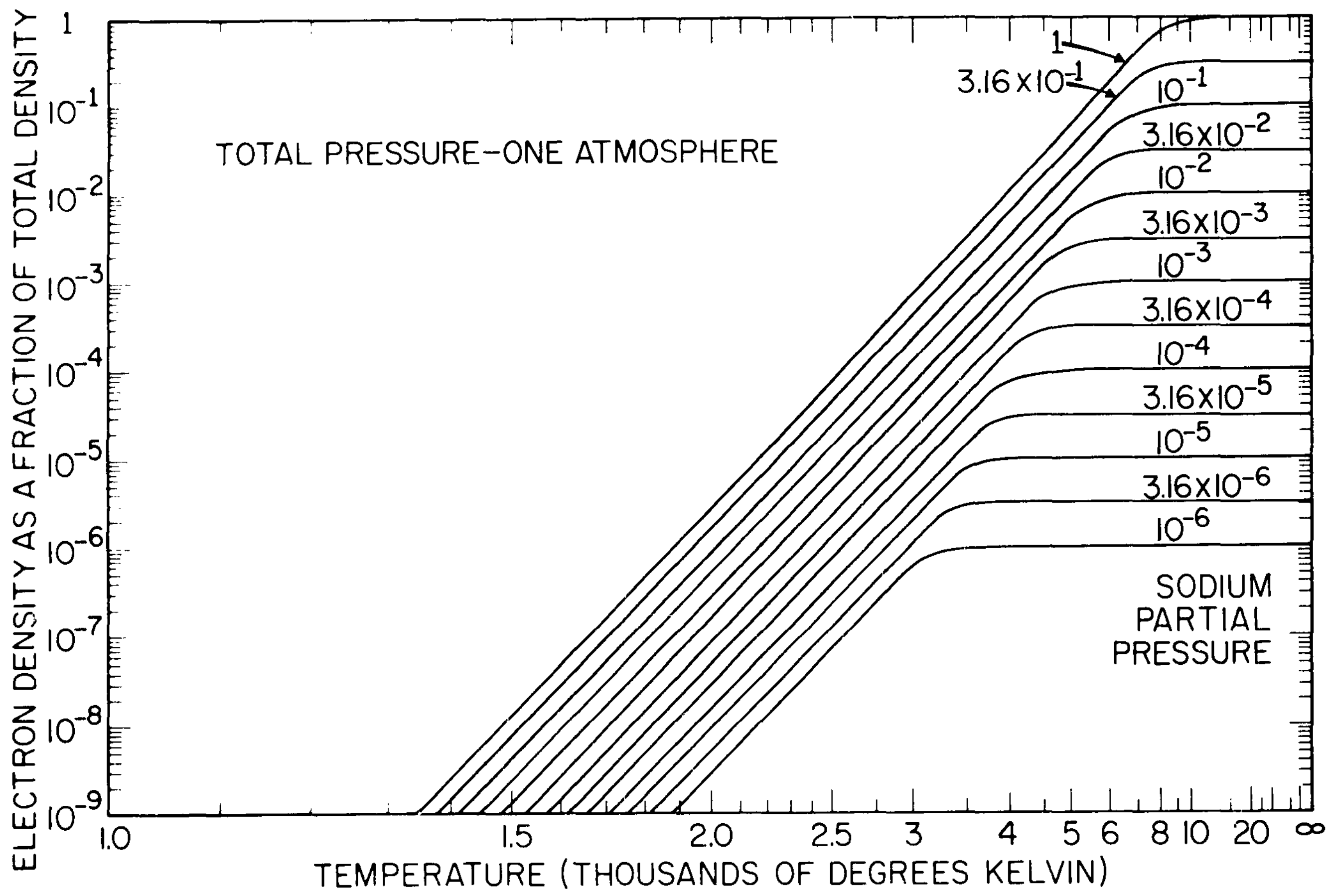

Fig. 4 - Sodium ionization plotted on an inverse temperature scale

Sodium and potassium are two of the principal contributors to thermal ionization. Their low ionization potential plus their widespread use and universal presence make them the prime suspects whenever thermal ionization is encountered.

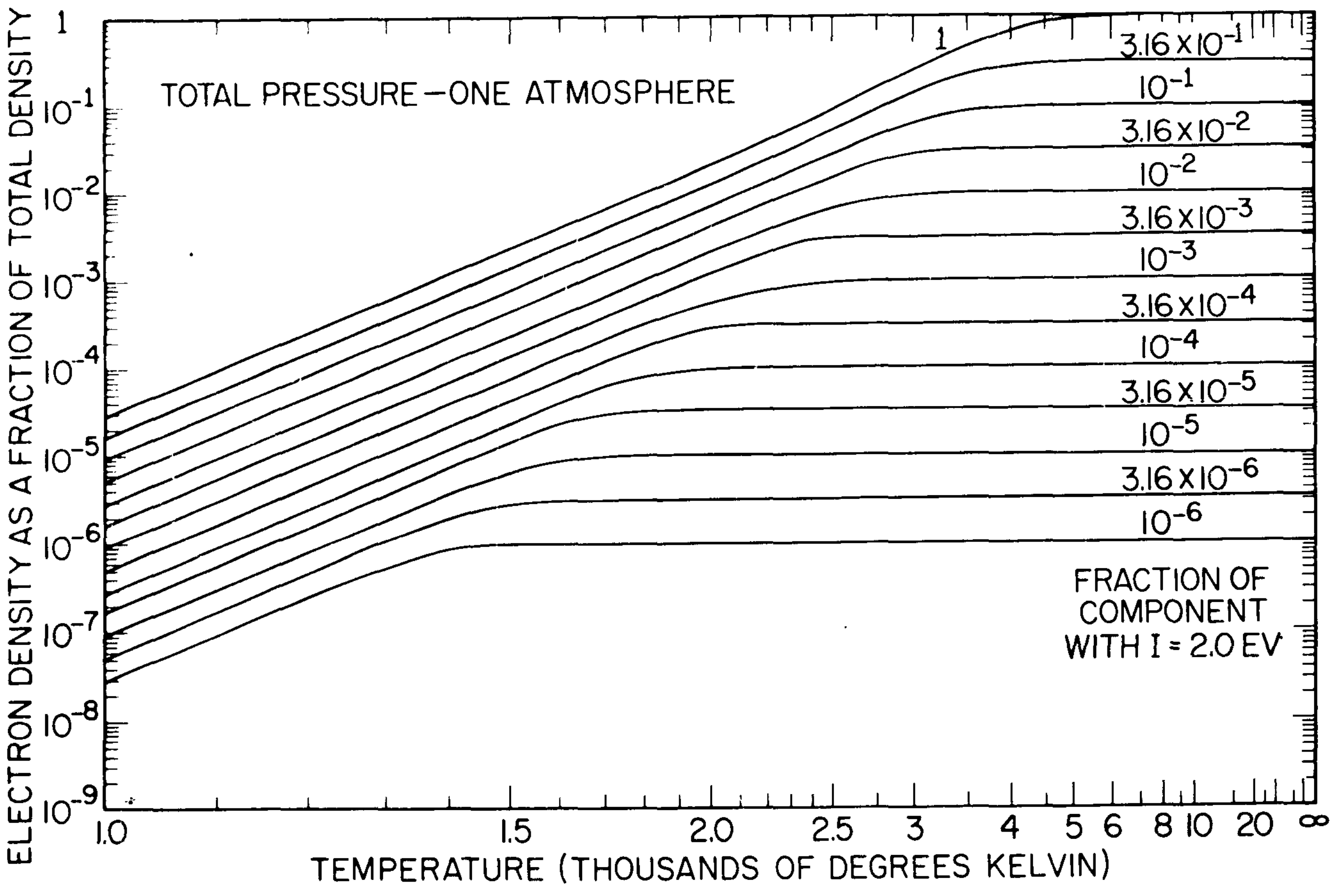

Fig. 5 - Low ionization potentials produce plasmas at low temperatures

No normal element has ionization potentials this low. However, the electron affinity of some atoms and ions produces negative ions by electron capture, such ions having low ionization potentials. They capture electrons at low temperatures and give them up at higher temperatures.

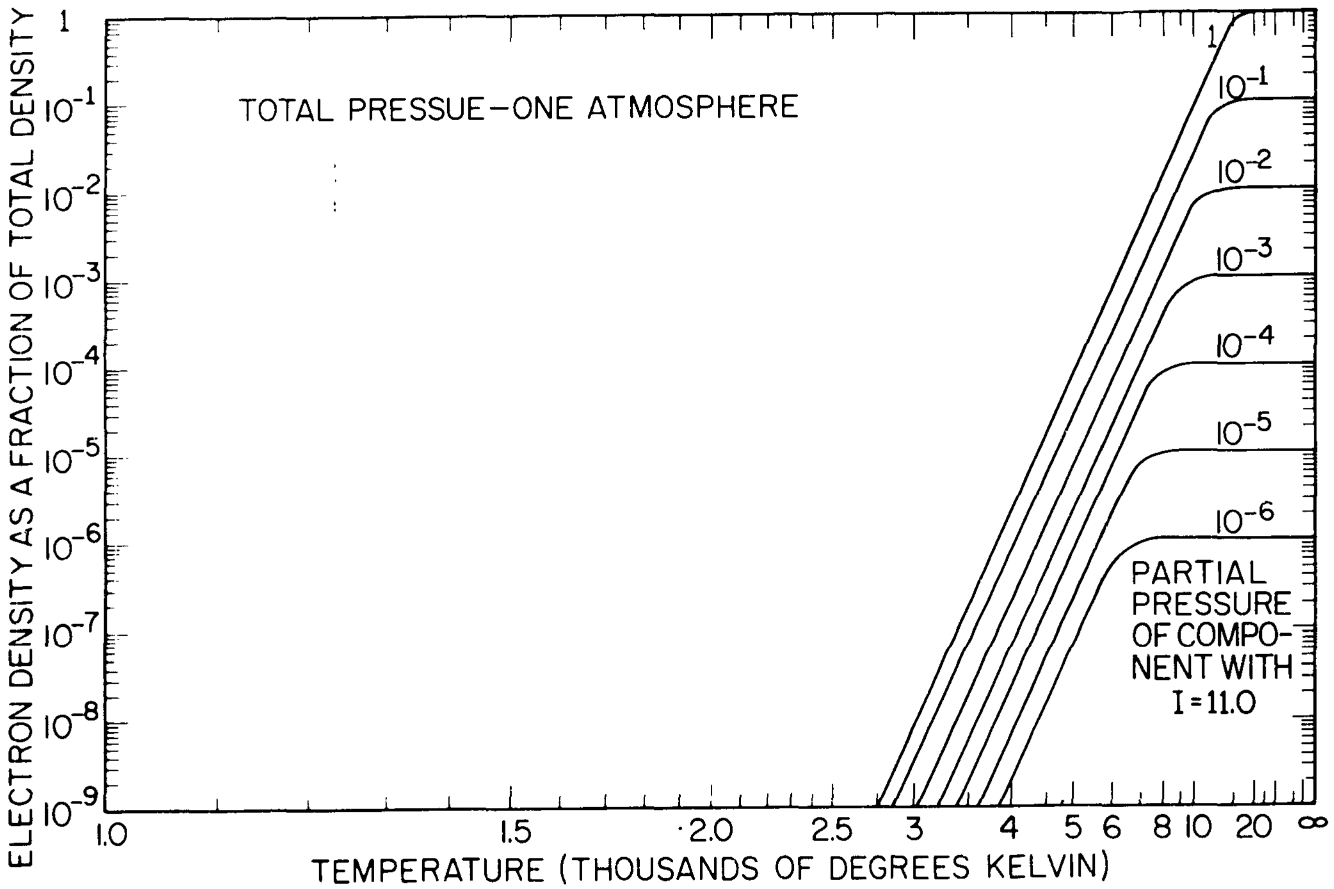

Fig. 6 - High temperatures are required to ionize most atoms

Most atoms and molecules have ionization potentials of 11 volts or more. Temperatures higher than attained in normal combustion processes are required to produce appreciable ionization for such elements or compounds.

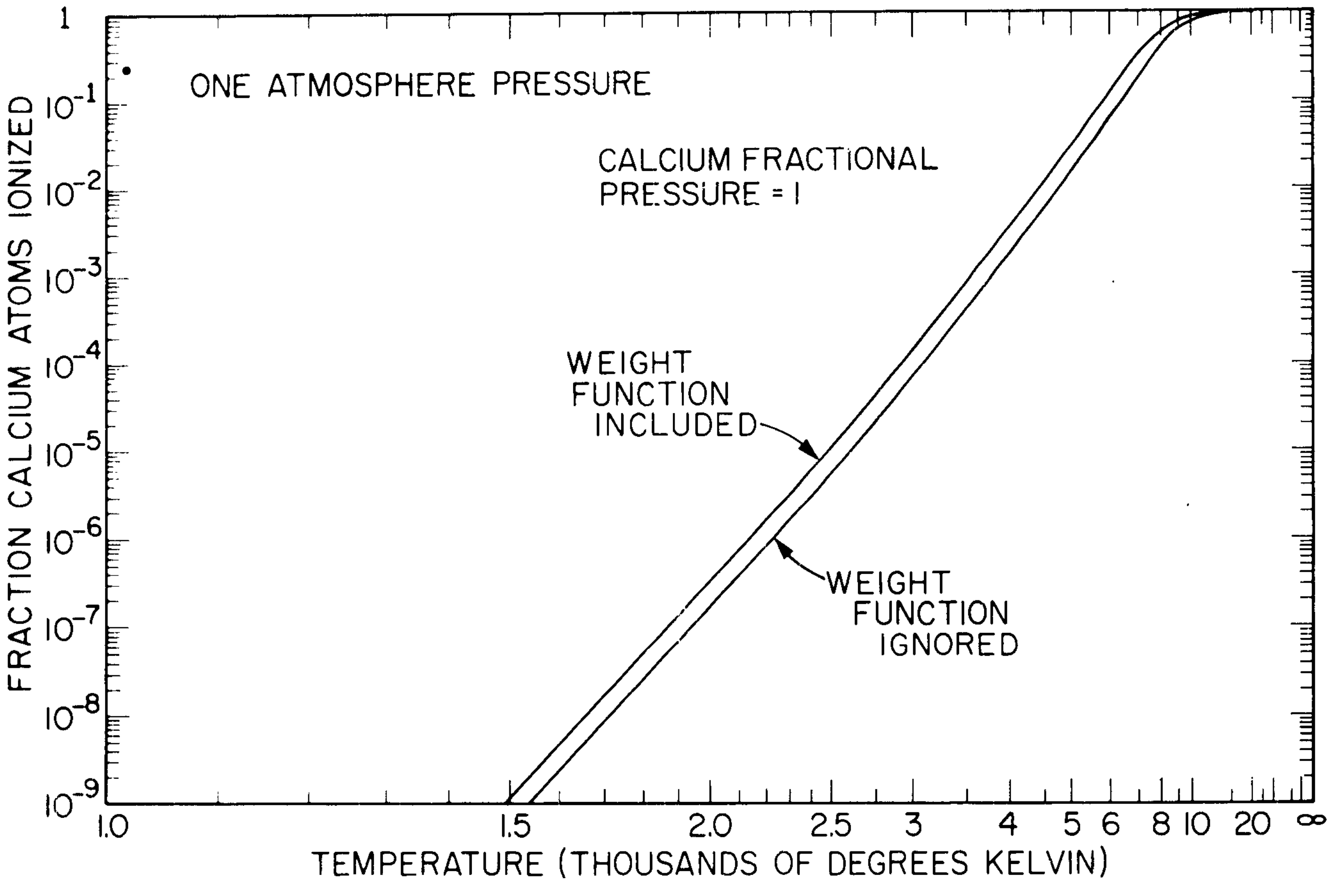

Fig. 7 - The weight function influences calcium ionization calculations

The weight functions $\log_{10}(g_e g_1/g_a)$ must be evaluated if accurate ionization calculations are desired. The ratio $g_e g_1/g_a$ is unity for sodium, potassium, cesium, aluminum, and related elements. The ratio appears as a logarithm and consequently makes no contribution for these elements (i.e., $\log_{10} 1 = 0$). For calcium, however, the ratio is four, giving an increase in the calculated ionization as shown in the figure. Similar corrections will be required for many ionization calculations if high accuracy is required. The 2-to-1 difference for calcium is in many cases negligible, thus permitting use of the dimensionalized curves of Fig. 10.

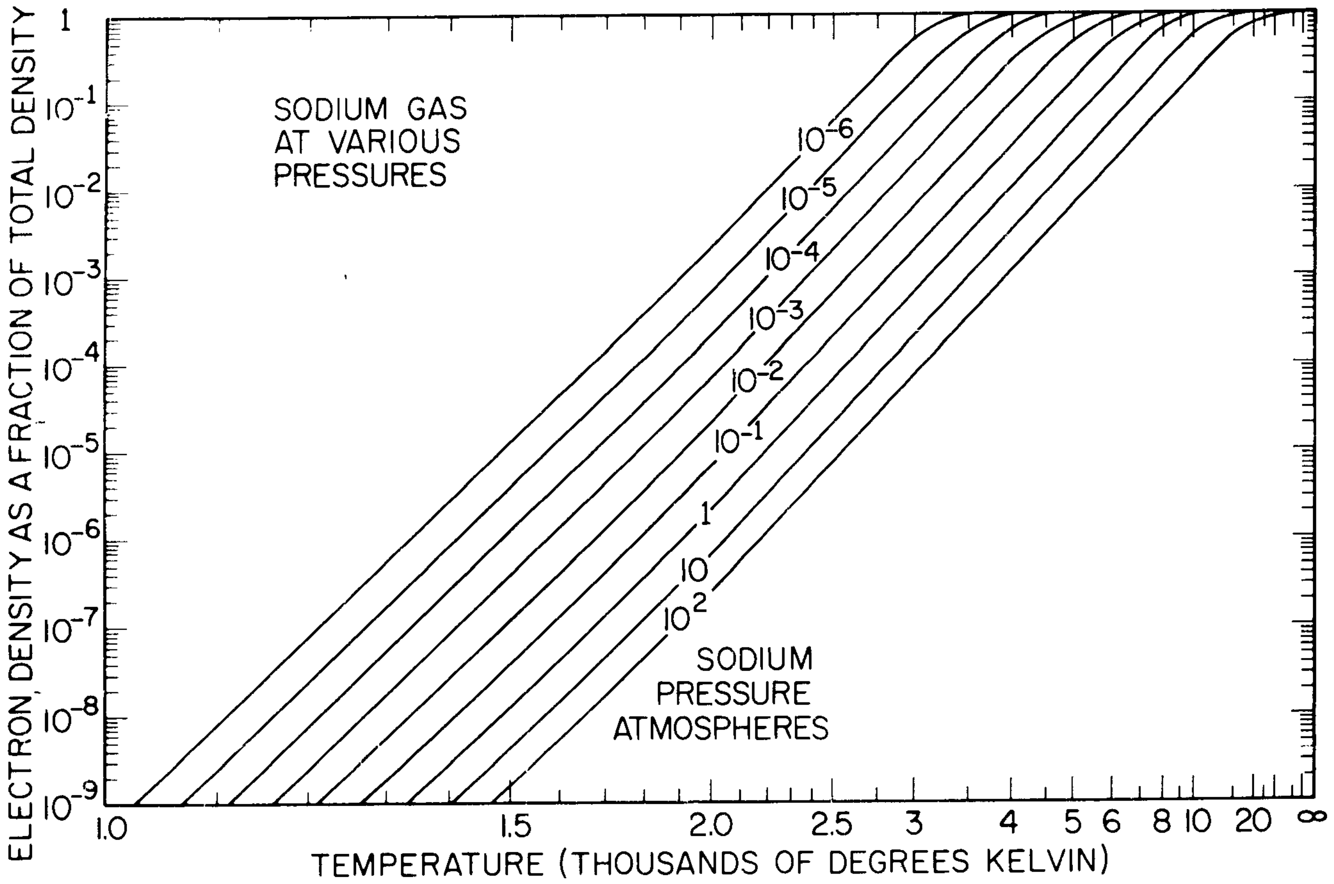

Fig. 8 - Sodium ionization varies with pressure

The ionization of all atoms and molecules varies similarly with pressure, i.e., as the pressure increases at a given temperature, the fraction of ionized atoms decreases.

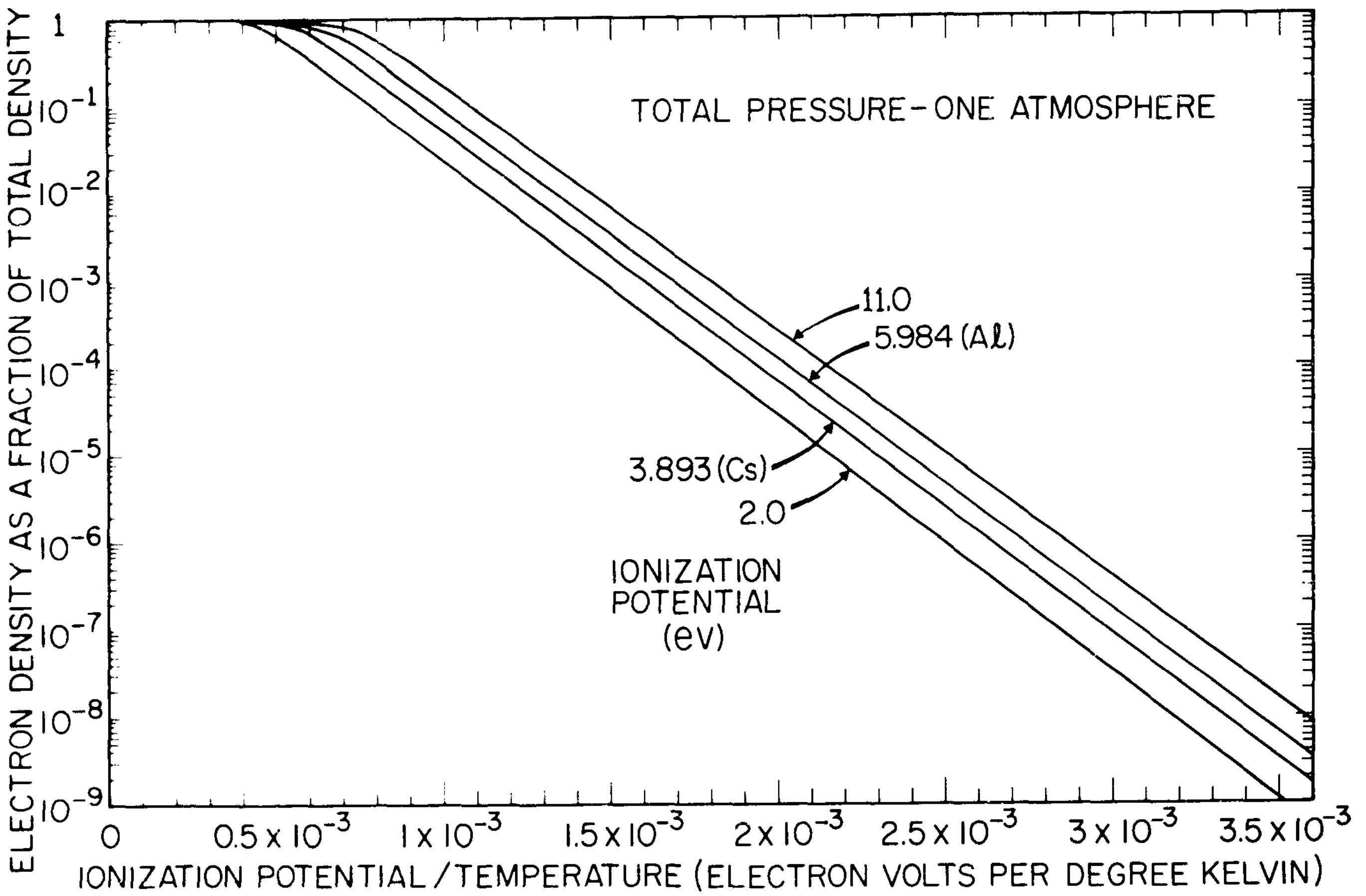

Fig. 9 - A family of curves showing the effect of a wide variety of ionization potentials on the ionization at a total pressure of one atmosphere

The ionization potential of most elements of interest falls between the two inner curves. Thus, a single curve midway between these two provides sufficient accuracy for many calculations. The use of the dimensionalized parameter I/T as illustrated in this plot simplifies graphical presentations.

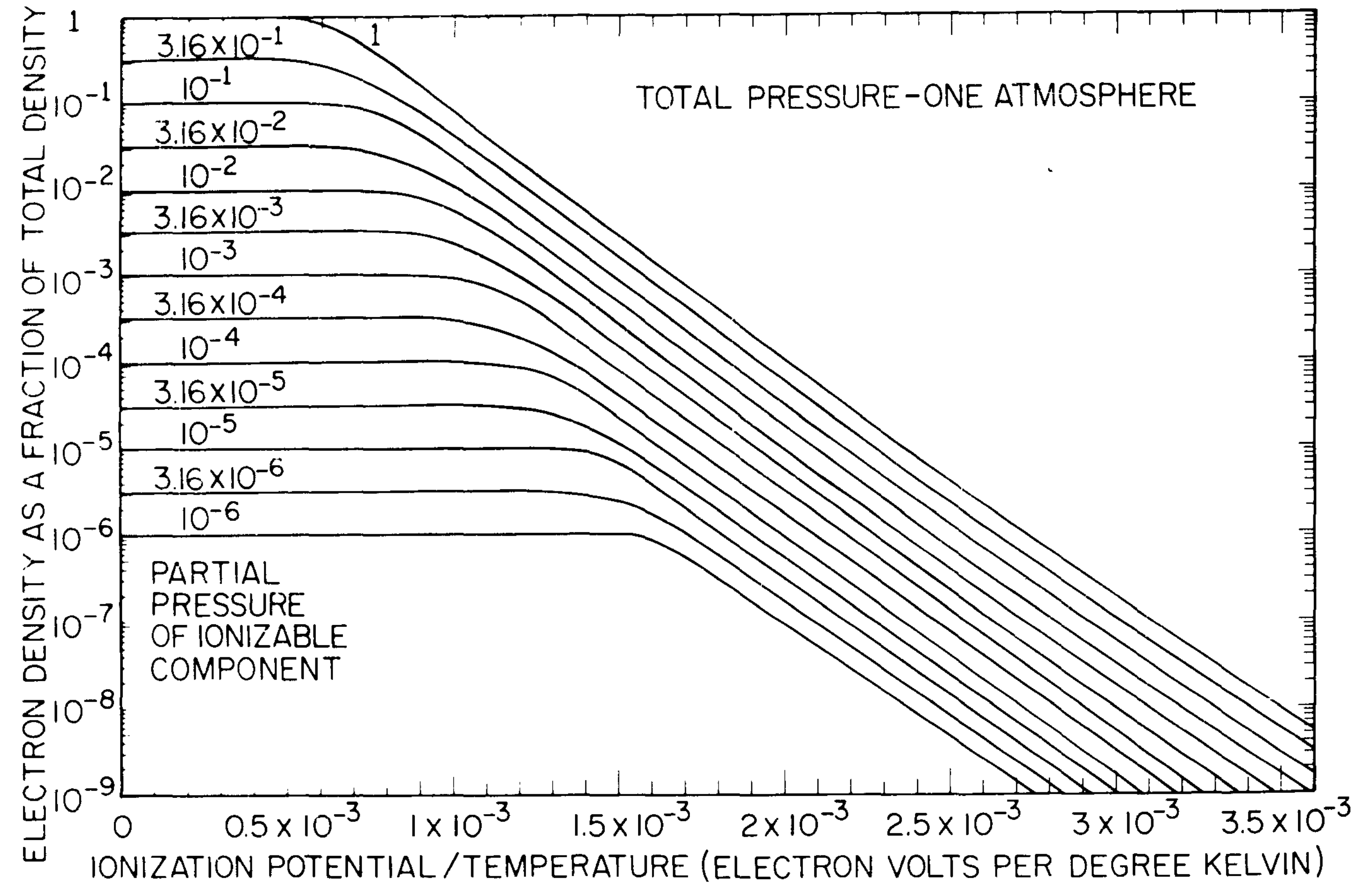

Fig. 10 - A family of partial pressure curves suffices for most calculations

The value of the parameters contributing to thermal ionization are not normally known with sufficient accuracy to permit accurate calculations of the electron density. In such cases, a single family of partial pressure curves plotted against I/T, using a mean of the family shown in Fig. 8, gives results with an accuracy sufficient for most purposes.

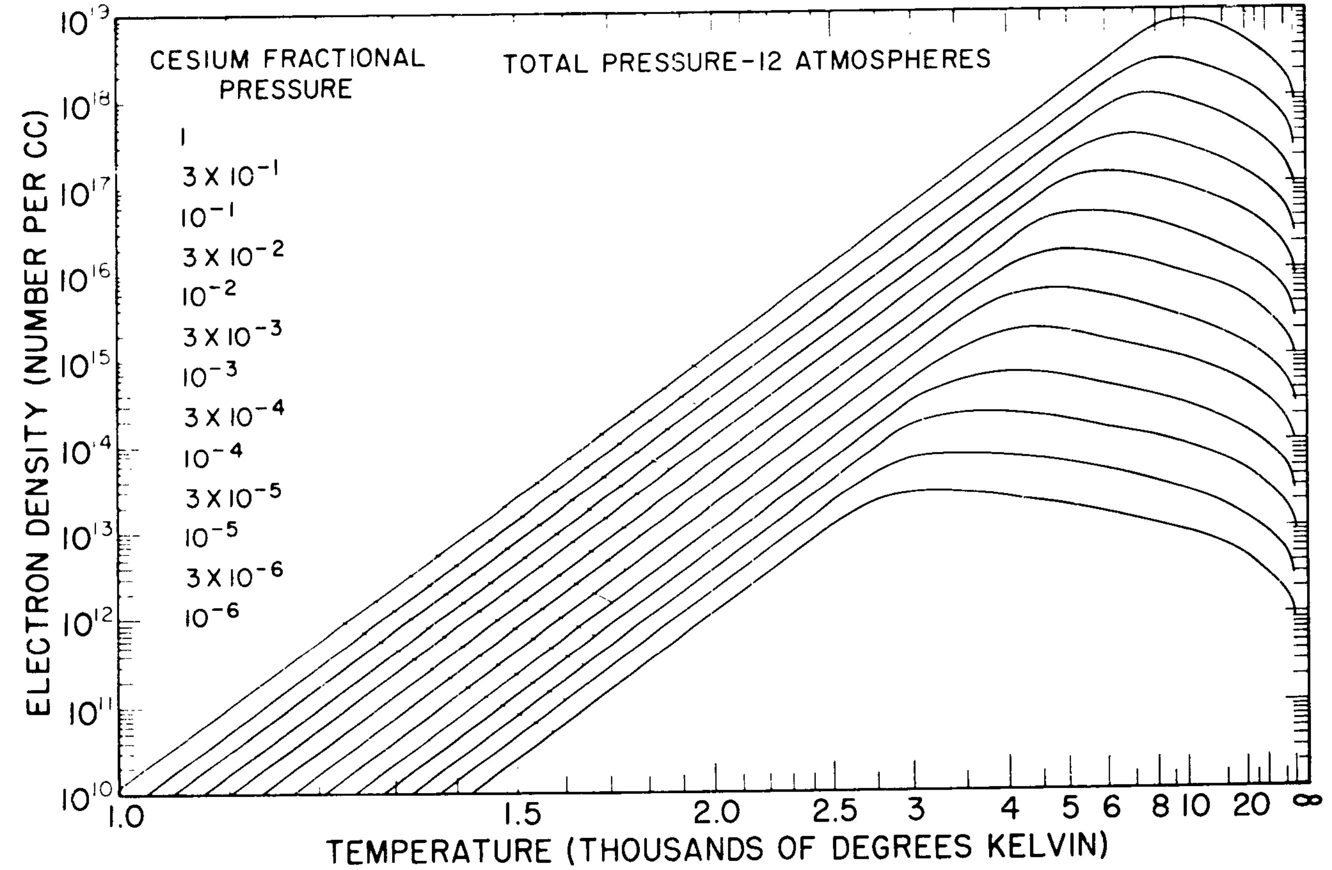

Fig. 11(a) - Electron density for cesium ionization

Previous ionization curves were expressed as a fraction of the total density. The use of the electromagnetic equations requires a number density, as shown in this figure. Twelve atmospheres pressure was selected as an average value for the throat pressure for many rocket motors, and calculations at this pressure are shown for four components. The electron density decreases at the higher temperature because the total density of the gas decreases with increasing temperature when the pressure is held constant. Electron density for (a) cesium, (b) potassium, (c) sodium, and (d) aluminum, all at twelve atmospheres total pressure are shown.

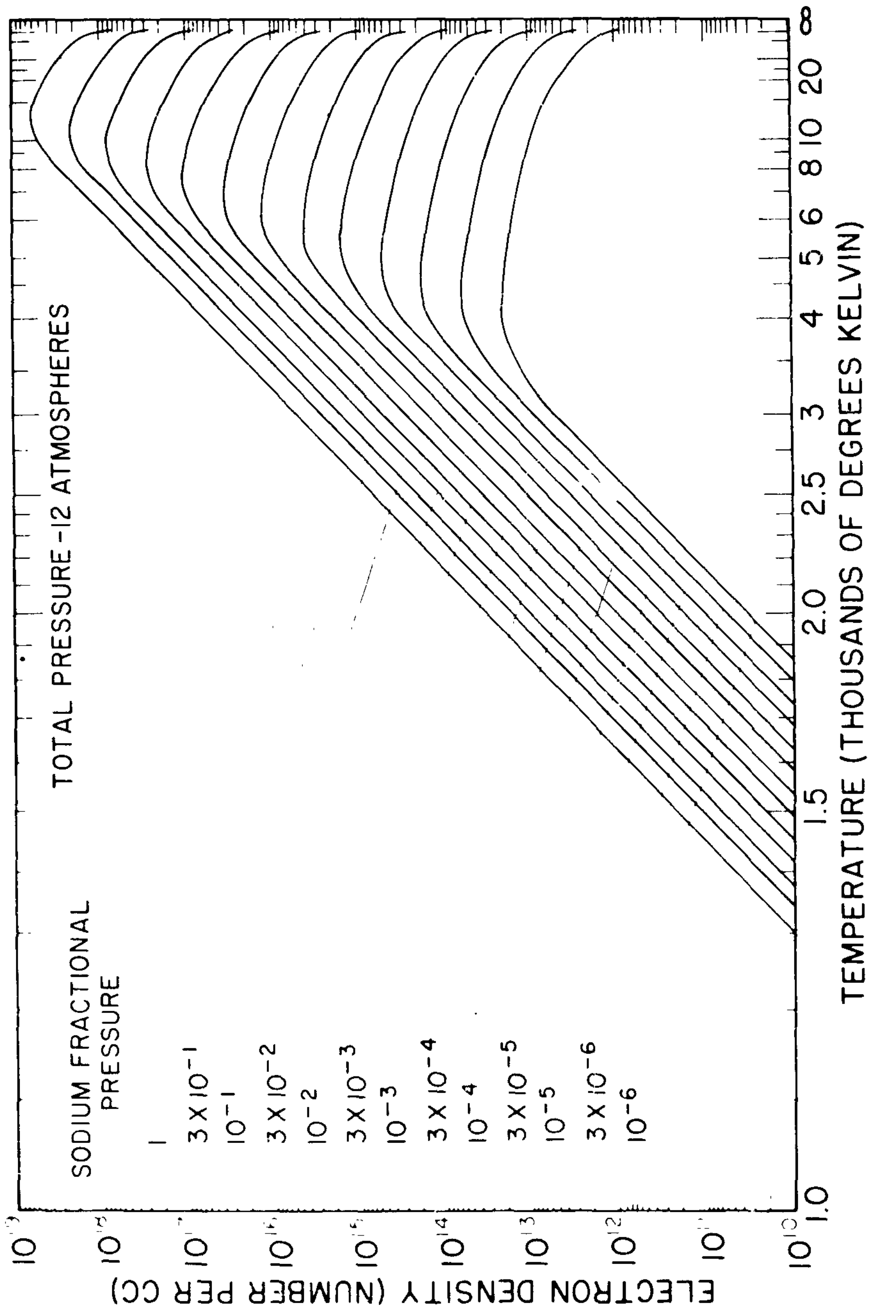

Fig. 11(b) - *Electron density for potassium ionization*

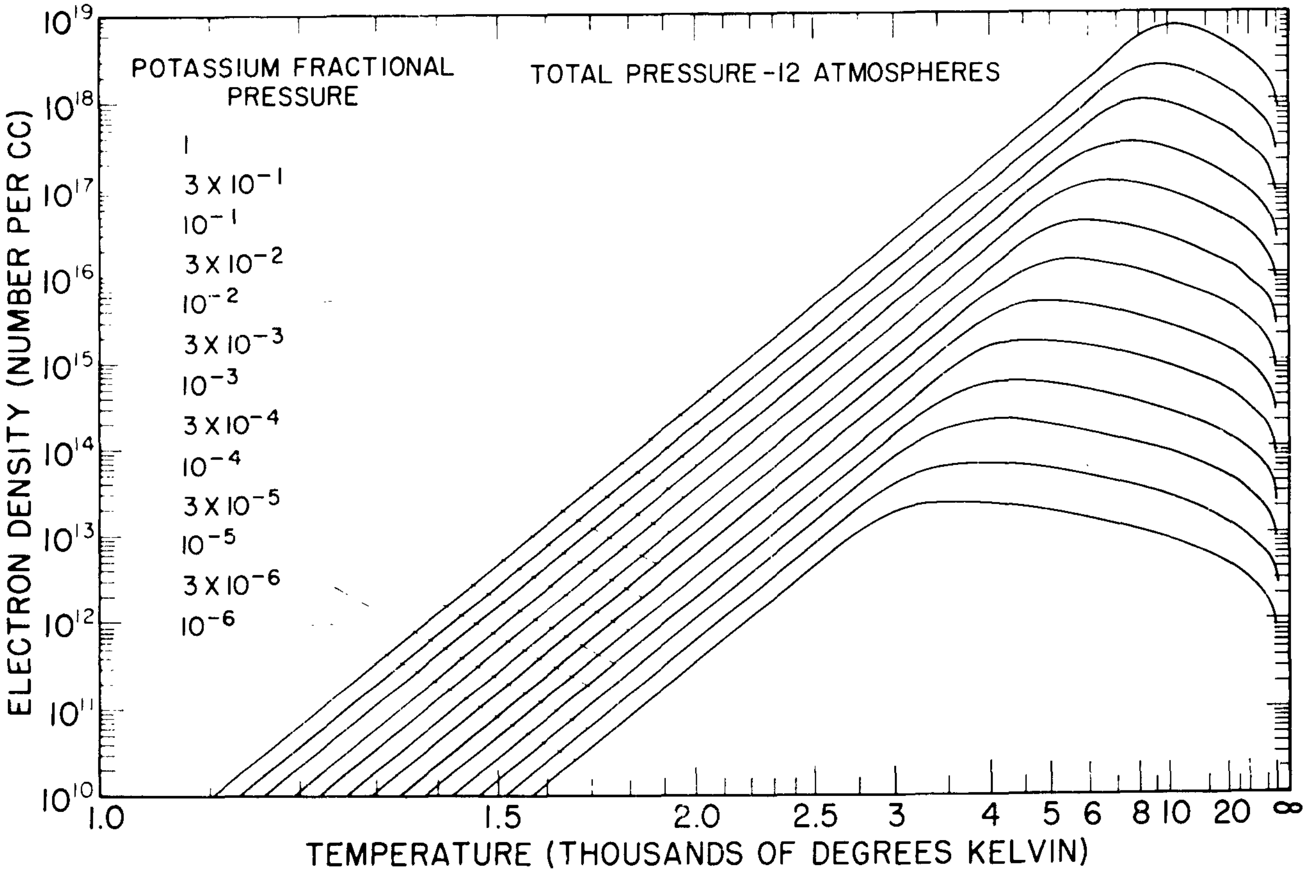

Fig. 11(c) - Electron density for sodium ionization

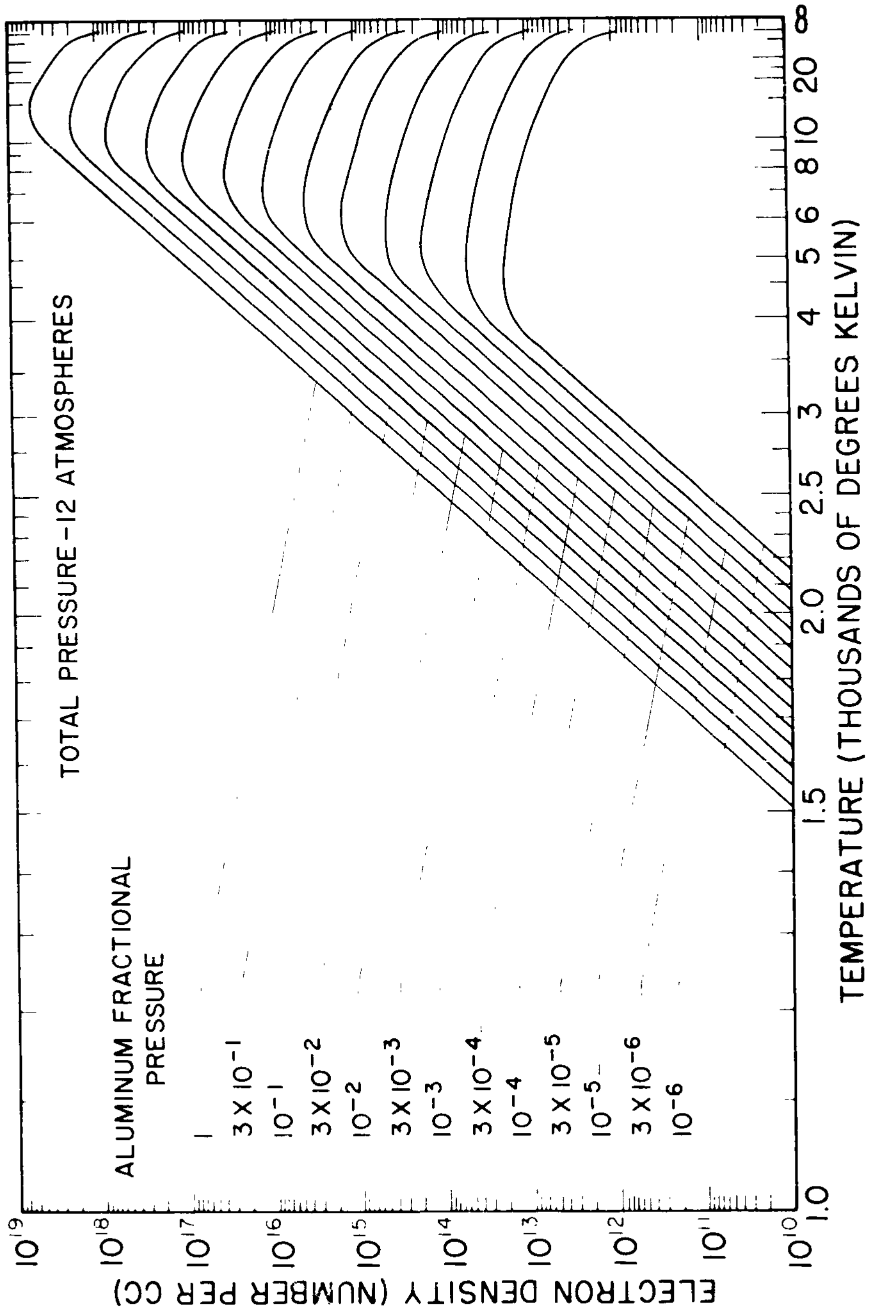

Fig. 11(d) - Electron density for aluminum ionization

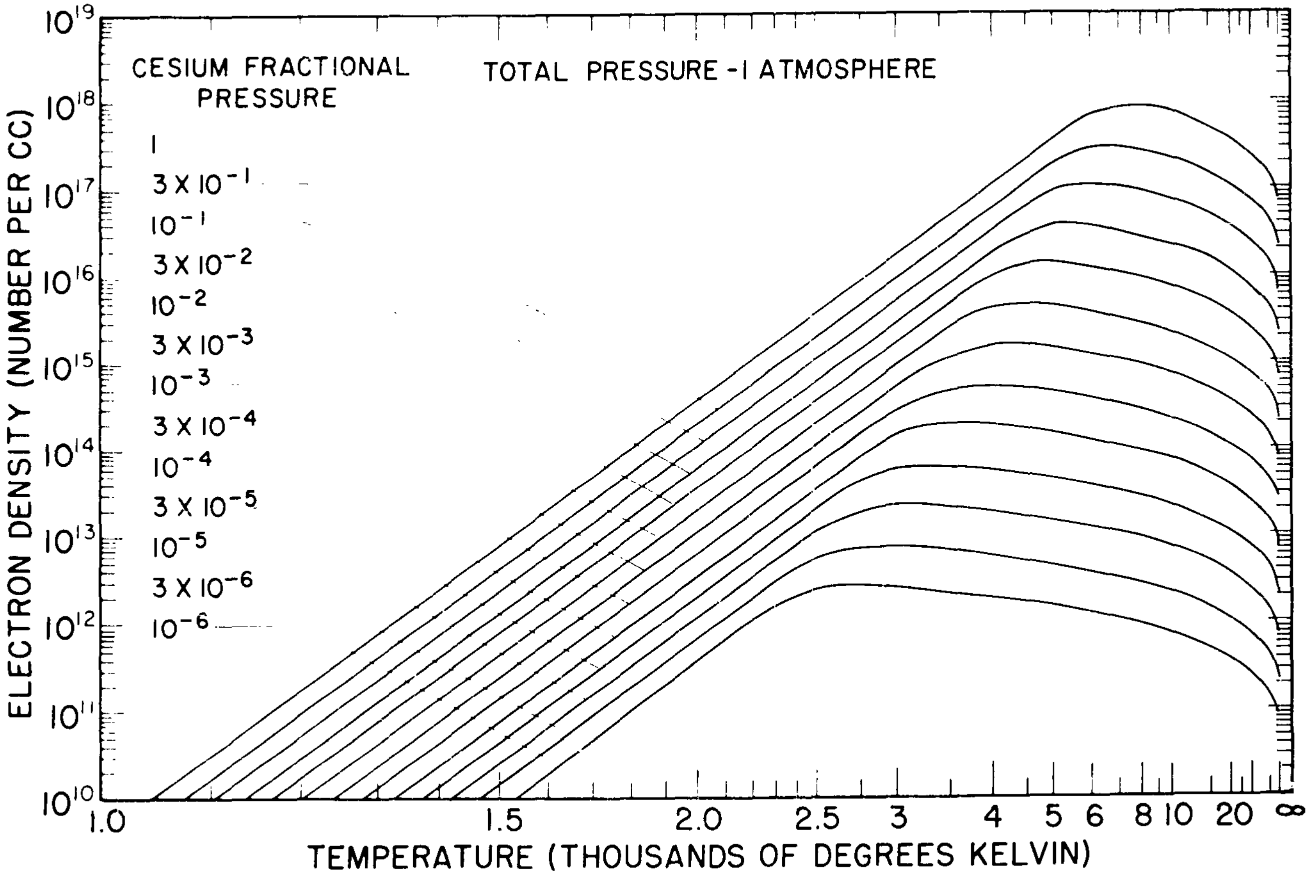

Fig. 12 - Cesium ionization at one atmosphere

Cesium is used to provide dense plasmas because of its low ionization potential. Studies conducted at atmospheric pressure provide knowledge to be used at other pressures.

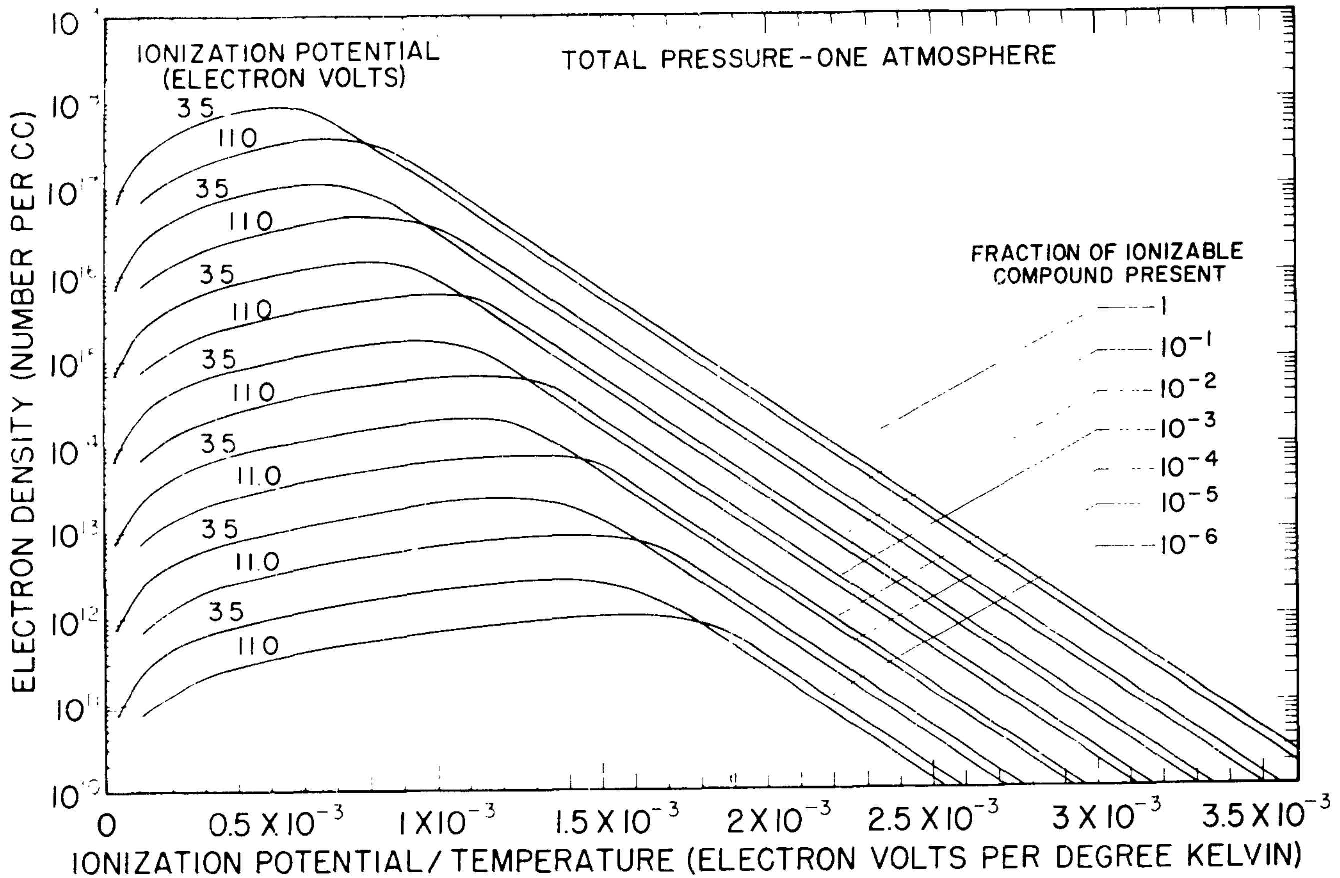

Fig. 13(a) - Plasma strength for various ionization potentials at one atmosphere pressure

Electron density versus the dimensionalized parameter I/T shows relatively little difference in plasma characteristics with varying ionization potentials. The curves shown in (a) are similar to those in Fig. 9, which showed the fraction ionized versus I/T. A comparison of (b) with (a) shows a greater electron density at the higher pressure. This may be contrasted with the variation in the fractional ionization which increases as the total pressure is decreased.

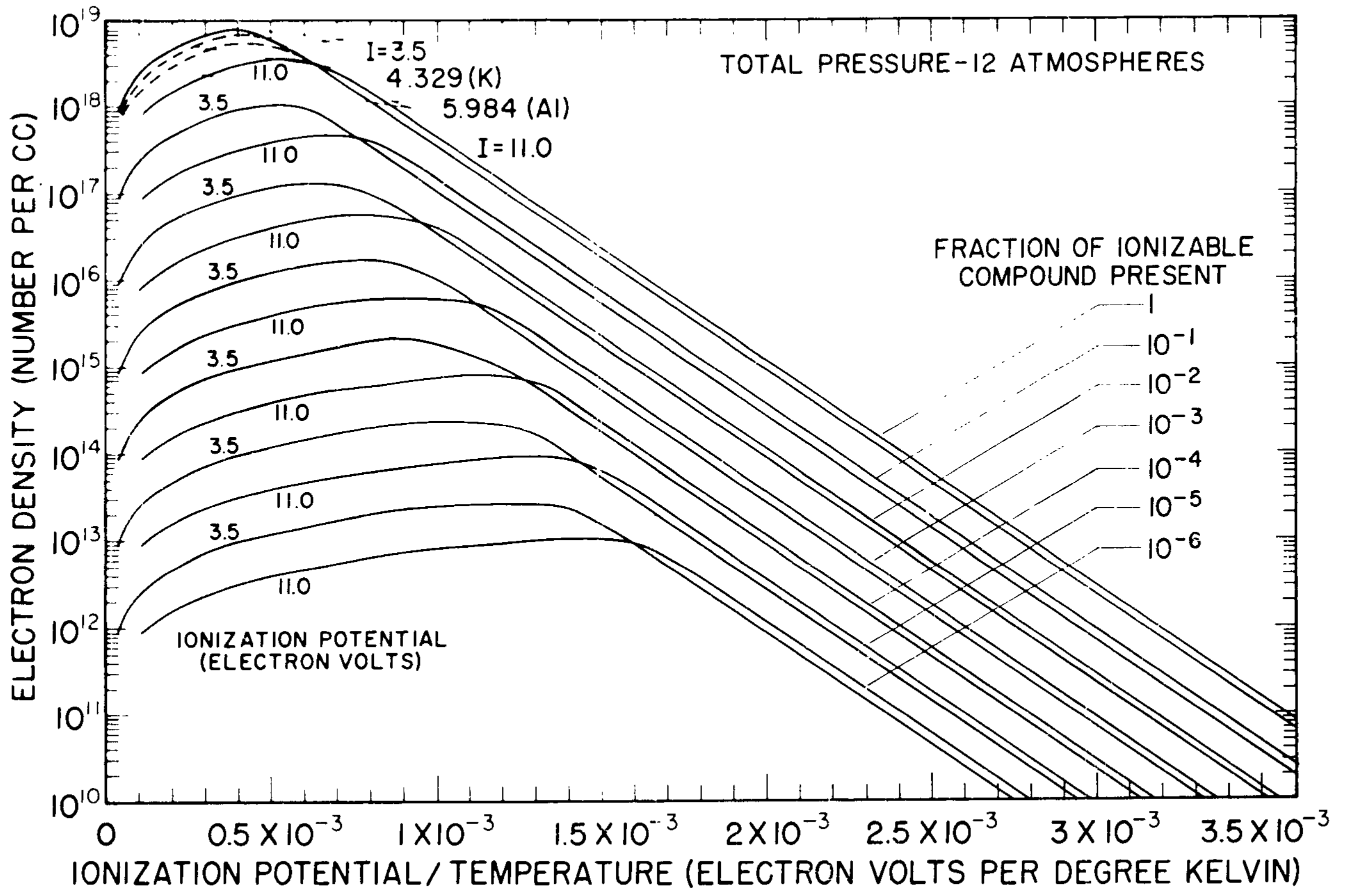

Fig. 13(b) - Plasma strength for various ionization potentials at twelve atmospheres pressure

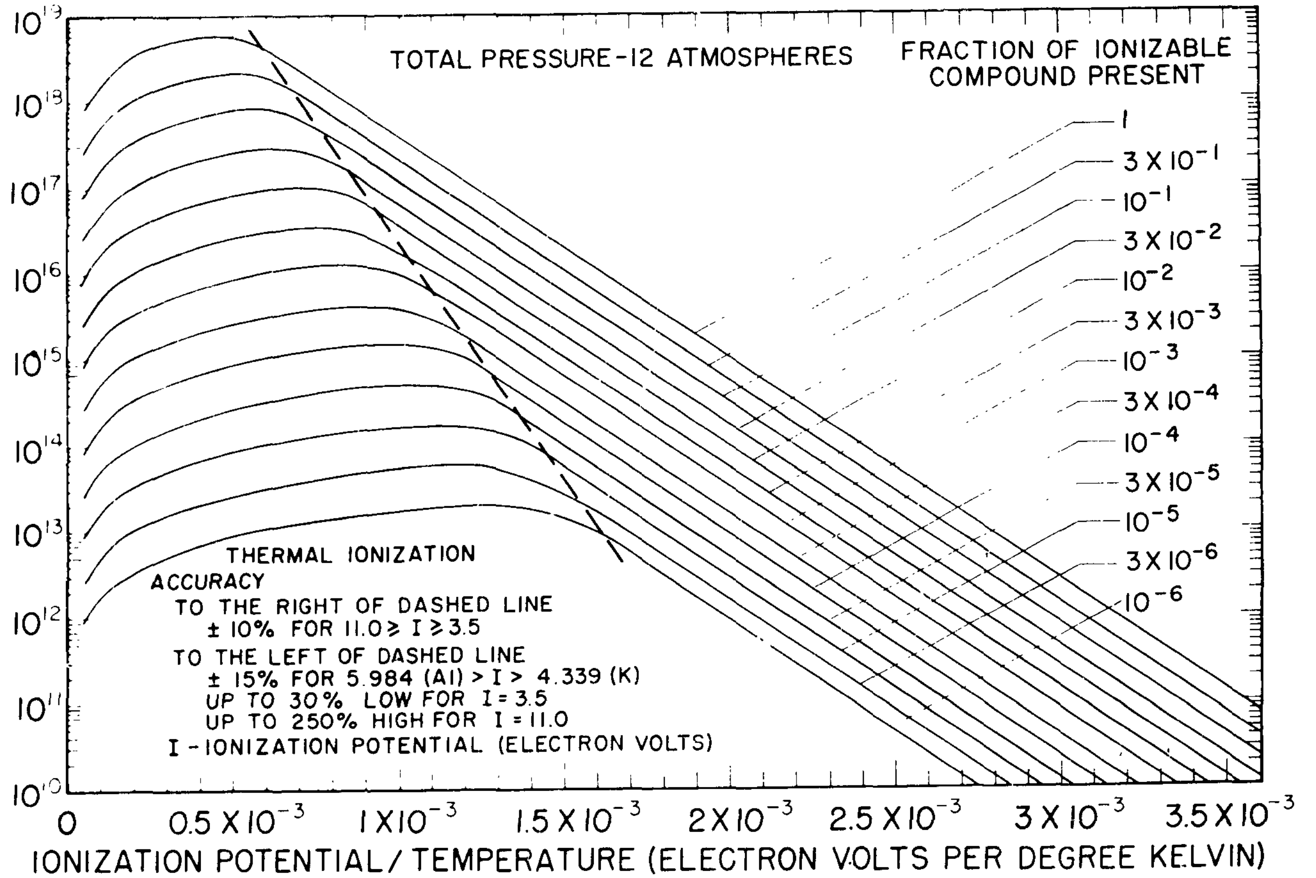

Fig. 14 - A single family of ionization curves for approximate solutions for gases at a pressure of twelve atmospheres

The total electron density may be calculated by this approximation family of curves. The limiting errors brought about by its use are as indicated above. Use for calculation of ionization for elements having a weight function ratio other than unity, as shown in Fig. 7, may add to the error.

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2. Rocket motors - Exhaust gases - Ionization

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