Engineering Notes

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An Optimization of the Formation of Negative Ions

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Nomenclature

A = electron affinity of the gas
A_0, B_0 = thermodynamic constants of the surface
k = Boltzmann constant
$K_p(T)$ = gas equilibrium constant
M = atomic or molecular weight of the gas
p = pressure
R = gas constant
s = sticking probability of an incoming atom
T = temperature
α = fraction of dissociated molecules
β_- = ionization efficiency
θ = fractional coverage of ionizer surface
η_i = negative ion evaporation rate
ϕ = surface work function of the ionizer
$\Delta\phi$ = change in work function due to surface coverage

Introduction

A HIGH-INTENSITY negative ion source is desirable for applications in ion propulsion and other areas of space technology. To date, relatively few studies of negative ion sources have been conducted compared to the vast amount of work, both theoretical and experimental, done on positive ion sources. One reason is that negative ion production by conventional methods is usually inefficient and of very low intensity. Recent experimental work done on high-intensity halogen negative ion sources has suggested a theoretical study of the process of formation of negative ions by surface ionization, the most effective method of negative ion creation.[1] A result of the study indicates that gas temperature and pressure can be optimized to achieve higher production of negative ion flux.

Theory of Negative Ion Formation

The theoretical development is analogous to the treatment of positive ion sources by surface ionization.[2] In the case of negative ion formation, the gas should have electron affinity greater than the surface work function of the ionizer to maximize the ionization efficiency as given by

$$\beta_- = \frac{1}{1+4\exp[(\phi-A)/kT]} \tag{1}$$

The general model presented below takes into account the temperature, the pressure of the gas that interacts with the ionizer, and the effect of the monolayer coverage by the adsorbed atoms or molecules on the ionizer surface. The gas is assumed to be in thermal equilibrium with the ionizer surface so that the vapor pressures, condensation rates, evaporation rates, etc., are all functions of the ionizer temperature and the gas pressure.

The fractional surface coverage of adsorbed atoms or molecules as a function of pressure, temperature, gas species, etc., is derived below, following Langmuir.[3] The rate of arrival of an atom species of mass m at a surface is given by

$$\mu = p/\sqrt{2\pi mkT} \tag{2}$$

The evaporation rate ν_l, in terms of thermodynamic constants A_0 and B_0 of the surface, is given as

$$\nu_l = A_0 e^{-B_0/T} \tag{3}$$

For a surface with fractional coverage given by θ the evaporation rate from the whole surface is $\nu = \theta\nu_l$ which, under the equilibrium condition, must be balanced by the atom arrival rate given by Eq. (2). The fractional coverage is thus obtained as

$$\theta = s\mu/A_0 e^{B_0/T} \tag{4}$$

Where Eq. (4) is combined with Eq. (2) and expressed in convenient units,

$$\theta = \frac{s3.5\times 10^{22} p e^{B_0/T}}{A_0\sqrt{MT}} \tag{5}$$

where p is in mm Hg, T in degrees K, and M is nondimensional. The thermodynamic constants A_0 and B_0 are determined from the evaporation data of the surface.

Once the fractional coverage is known, the increase or decrease in surface work function can be found. An ionizer surface can be modeled as having an exposed active area for ionization (determined by θ). For the case in which only the uncovered active areas can undergo ionization, the effective surface area is only $(1-\theta)$ of the total available surface area. For the case of coverage elevating the surface work function by a small increment (which is detrimental to negative ion creation if allowed to build up), an average surface work function elevation per unit ionizer surface area can be derived.

From Page and Goode[4] the work function of a partially covered surface is

$$\phi = \sum_{i=0,1} \chi_i\phi_i + RT^2 \sum_{i=0,1} \chi_i \frac{\mathrm{d}}{\mathrm{d}T} \ell n\theta_i - T \sum_{i=0,1} \chi_i \frac{\mathrm{d}\phi_i}{\mathrm{d}T} \tag{6}$$

where ϕ_i are the work functions and χ_i the fractions of the total electric currents emanating from unit area, associated with the uncovered ($i=0$) and the covered ($i=1$) areas of the ionizer surface. For the case in which the fractional coverage θ is so large that the work function is high enough for the emission current from the covered portion of the surface to be

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neglected, $\chi_l \ll \chi_0$ and Eq. (6) becomes

$$\phi=\phi_0+RT^2\frac{\mathrm{d}}{\mathrm{d}T}\ln(1-\theta) \tag{7}$$

The change in surface work function due to coverage is then

$$\Delta\phi=RT^2\frac{\mathrm{d}}{\mathrm{d}T}\ln(1-\theta) \tag{8}$$

Substitution of Eq. (5) into Eq. (8) yields

$$\Delta\phi=RT\left(\frac{1}{2}+\frac{B_0}{T}\right)\left(\frac{\theta}{1-\theta}\right) \tag{9}$$

Another important factor affecting the ion evaporation rate arises from the fact that gas particles in the atomic state have a higher electron affinity than when they are in the molecular state. As a result, the rate of negative ion production at the surface is essentially determined by the arrival rate of the atomic species produced by the dissociation of the gas molecules.

At thermal equilibrium, the fraction of dissociated molecules of a diatomic gas as a function of gas temperature (in K), pressure (in mm Hg), and $K_p(T)$ (in atm)[5] is given by

$$\alpha=1/\sqrt{1+(4p/750K_p)} \tag{10}$$

Using this formula, the partial pressure of the atomic species resulting from dissociation can be computed

$$p_a=\alpha p \tag{11}$$

Substituting Eq. (11) into Eq. (2) and expressing the result in convenient units, the arrival rate of the neutral atom is then

$$\mu_a=3.5\times10^{22}\alpha p/\sqrt{MT}\quad 1/\mathrm{cm}^2\cdot\mathrm{s} \tag{12}$$

The product of the arrival rate of the neutral atoms and the ionization efficiency will give the negative ion evaporation rate. Thus,

$$\eta_i=\frac{\mu_a}{1+4\exp[(\phi-A)/kT]} \tag{13}$$

where

$$\phi(T)=\phi_0+\Delta\phi$$

and ϕ_0 is the surface work function of an uncovered surface.

Analysis and Optimization

As temperature is increased for a fixed pressure, the arrival rate of dissociated atoms increases and the coverage per unit surface area decreases; however, the ionization efficiency decreases with increasing temperature. Therefore, the ion current will become saturated as the temperature continues to increase at that pressure. Similarly, as the pressure is increased for a fixed temperature, the arrival rate of dissociated atoms increases, the coverage per unit surface area increases, and the incremental change in surface work function increases. The ionization efficiency approaches a constant value. Therefore, there is an actual decrease of ion current emitted as pressure increases for a given temperature until $\theta=1$. Hence, for a given ion current emission, there is an optimum combination of temperature and pressure.

As an example, lanthanum hexaboride is chosen as the ionizer material. In the literature, LaB_6 has been shown to be an excellent electron emitter because of its low surface work function of about 2.7 eV.[6,7] LaB_6 is chemically inert to most toxic gases and has a high melting point.[6] Because of their strong electron affinity, halogens are the most suitable choice for the gas, although they are toxic and must be handled via closed systems. In the past, negative ion current emission has been measured by using iodine on LaB_6.[1]

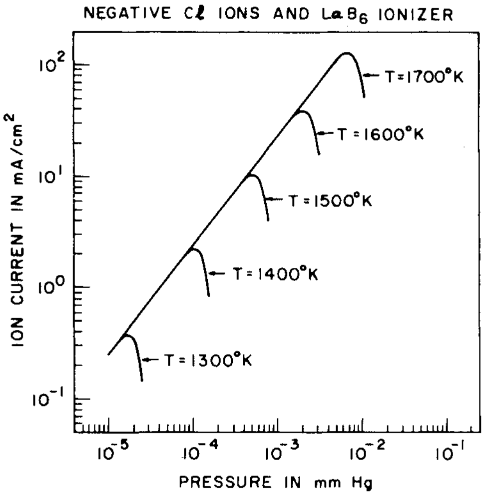

Fig. 1 Negative chlorine ion current from a LaB_6 ionizer.

Because of available thermal data, chlorine is chosen as the gas in this example. One difference between chlorine and iodine atoms is their respective electron affinities (3.6 and 3.0 eV, respectively). Thus, chlorine has the advantage of higher negative ion formation efficiency. In addition, because of its larger mass, chlorine negative ions can produce more thrust from an ion engine. Chlorine exists in molecular gaseous form at room temperature. The electron affinity of chlorine molecules is smaller than the LaB_6 surface work function. Thus adsorbed molecules will not contribute to the ion evaporation rate. Thermal equilibrium data as a function of temperature for chlorine are available to calculate the dissociation fraction.[5]

Because chlorine evaporation data from LaB_6 surface are not available, the thermodynamic constants A_0 and B_0 in Eq. (5) are estimated from the electron emission data of LaB_6.[7] It is assumed that upon being absorbed, a chlorine atom picks up an electron and is then free to be evaporated. The rate of arrival of chlorine atoms is approximately equal to that of the electron emission from the LaB_6 surface and, therefore, the electron emission rate is a good estimate of the evaporation rate of chlorine from LaB_6.

Taking the logarithm of Eq. (3), leads to

$$\log\nu_l=\log A_0-(B_0/T) \tag{14}$$

From the electron emission data, which are on log-log scales, the values of the constants are determined

$$A_0=1.74\times10^{27}\,1/\mathrm{cm}^2\cdot\mathrm{s}$$

$$B_0=3.29\times10^4\ \mathrm{K}$$

Knowing the thermodynamic constants and assuming $s=1$, a plot of chlorine negative ion current as a function of temperature and pressure is shown in Fig. 1. The plots for different temperature curves are stopped when either θ becomes equal to unity or the value of ϕ is equal to A. As Fig. 1 shows, for fixed values of pressure, the ion current saturates as the temperature is increased; for a fixed temperature, the ion current starts to decrease with increasing pressure after reaching a peak. These results show that for a given ion current, there is an optimum combination of temperature and pressure.

The ion currents in Fig. 1 are of the order of magnitude as in the past experimental data conducted with LaB_6 using halogen gas.[1] The parameters in those experiments were not optimized, so lower currents were probably measured (assuming other deionizing effects were negligible). The theory outlined in this paper enables optimization of system parameters for a negative ion source.

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Ideal Ramjet: Optimum M_∞ for Fuel Limit and Material Limit

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THE expression for the specific impulse I_{sp} is given[1] by the expression

$$I_{sp}=\frac{a_\infty M_\infty}{g_c}\left\{\sqrt{1+\frac{\Delta T}{T_{t\infty}}}-1\right\} \tag{1}$$

where a_∞ is the freestream speed of sound, M_∞ is the freestream Mach number, $T_{t\infty}$ is the freestream stagnation temperature, and ΔT is the increase in stagnation temperature due to combustion. The expression, Eq. (1), for I_{sp} is well known. Also for a given ΔT due to combustion, it is also well known that I_{sp} obtains a maximum as a function of M_∞. Also, for the material limited case where a maximum temperature, T_{max}, is specified, it is well known that I_{sp} obtains a maximum as a function of M_∞; here $T_{max}=T_{t\infty}+\Delta T$. The purpose of this Note is to present the derivation of some simple algebraic expressions for the value of M_∞ at which I_{sp} obtains a maximum for both the fuel limited and the material limited cases.

It is believed by the author that these expressions have not been derived previously, but that M_∞ for maximum I_{sp} is normally determined numerically. Thus it would be convenient to have closed form expressions for the value of M_∞ where I_{sp} reaches a maximum.

Material Limited Case

For the material limited ideal ramjet, Eq. (1) becomes

$$I_{sp}=\frac{a_\infty M_\infty}{g_c}\left\{\sqrt{1+\frac{T_{max}-T_{t\infty}}{T_{t\infty}}}-1\right\} \tag{2}$$

or

$$I_{sp}=\frac{a_\infty M_\infty}{g_c}\left\{\sqrt{\frac{T_{max}}{T_{t\infty}}}-1\right\} \tag{3}$$

where

$$T_{t\infty}=T_\infty\left[1+\frac{\gamma-1}{2}M_\infty^2\right] \tag{4}$$

Therefore

$$I_{sp}=\frac{a_\infty M_\infty}{g_c}\left[\left\{\frac{2T_{max}}{T_\infty[2+(\gamma-1)M_\infty^2]}\right\}^{1/2}-1\right] \tag{5}$$

To find the M_∞ value at which I_{sp} is a maximum, set $dI_{sp}/dM_\infty=0$; therefore differentiation yields

$$\frac{[2T_{max}]^{1/2}-[T_\infty\{2+(\gamma-1)M_\infty^2\}]^{1/2}}{[T_\infty\{2+(\gamma-1)M_\infty^2\}]^{1/2}} =\left[\frac{T_\infty\{2+(\gamma-1)M_\infty^2\}}{2T_{max}}\right]^{1/2}\left[\frac{2T_{max}M_\infty^2(\gamma-1)}{T_\infty\{2+(\gamma-1)M_\infty^2\}}\right] \tag{6}$$

Next multiply both sides of Eq. (6) by the denominator on the left-hand side of Eq. (6) and by $[2T_{max}]^{1/2}$. This yields

$$-[2T_{max}T_\infty\{2+(\gamma-1)M_\infty^2\}]^{1/2} =\frac{2T_{max}M_\infty^2(\gamma-1)}{\{2+(\gamma-1)M_\infty^2\}}-2T_{max} \tag{7}$$

Next square both sides of Eq. (7) and collect terms in powers of M_∞. This process yields

$$M_\infty^6[(\gamma-1)^3] +M_\infty^4[6(\gamma-1)^2]+M_\infty[12(\gamma-1)]+8=8T_{max}/T_\infty \tag{8}$$

or

$$[M_\infty^2(\gamma-1)+2]^3=8T_{max}/T_\infty \tag{9}$$

therefore

$$M_\infty=\left[\frac{2}{\gamma-1}\left\{\left(\frac{T_{max}}{T_\infty}\right)^{1/3}-1\right\}\right]^{1/2} \tag{10}$$

For example, consider the case where $\gamma=1.4$, $T_\infty=400°R$ and $T_{max}=5000°R$; thus yields $M_\infty=2.57$ and $I_{sp}=104$ lbf-s/lbm (which agrees well with the values in Ref. 1). Equation (10) shows that to obtain maximum I_{sp} at the highest possible M_∞, T_∞ should be as low as possible for a fixed T_{max}.

Fuel Limited Case

For the fuel limited ideal ramjet, ΔT is fixed and I_{sp} is given by

$$I_{sp}=\frac{a_\infty M_\infty}{g_c}\left\{\left[\frac{T_\infty\{2+(\gamma-1)M_\infty^2\}+2\Delta T}{T_\infty\{2+(\gamma-1)M_\infty^2\}}\right]^{1/2}-1\right\} \tag{11}$$

To find M_∞ at which I_{sp} is a maximum, set $dI_{sp}/dM_\infty=0$,

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