Nonequilibrium Ionization in Wet Alkali Metal Vapors

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A theoretical model for the transport of electrons in a wet vapor has been formulated. The medium is considered to consist of electrons, neutral gas atoms, positively charged atomic ions, and charged vapor droplets. The degree of ionization of the gas atoms is assumed to be given by Saha's Law evaluated at the electron temperature, whereas the degree of charging of the vapor droplets is obtained by equating the random electron current in the gas to the thermionic emission current of the vapor droplet at its internal temperature. The electron temperature is determined by equating the Joule heating rate of the electrons to their rate of energy loss due to elastic electron-atom, electron-ion, and electron-droplet collisions and inelastic electron-droplet collisions. The droplet internal temperature is determined by equating the rate of droplet heating due to electron bombardment to the rate of cooling due to atom and ion bombardment. The preceding theory is applied to MHD generator considerations for which the predominate effect of the droplets is found to be the absorption of free electrons from the system. The depression of electron density is found to be most severe at high-percent moisture and for small droplets.

NONEQUILIBRIUM ionization, as it shall be referred to in this paper, is the production of a highly-ionized gas at low gas temperatures as a result of applied and/or induced electric fields in the gas, which serve to heat the electrons. These energetic electrons subsequently ionize the gas to a degree commensurable with their energy rather than that of the cooler gas. This phenomenon has been a long-observed fact in gaseous discharges[1, 2] and has recently been considered as a means of producing high electrical conductivities in an MHD generator at gas temperatures compatible with present materials technology.[3, 4]

In Ref. 4, nonequilibrium ionization, as it applies to MHD generators utilizing noble gases seeded with low concentrations of alkali metal vapors as working fluids, was extensively analyzed. An equation for the electron temperature relative to that of the other species in the gas was obtained by equating the rate at which energy is gained by the electrons in an electromagnetic field, $\mathbf{j}\cdot(\mathbf{E} + \mathbf{u} \times \mathbf{B})$ (where $\mathbf{j}$ is the electron current, $\mathbf{E}$ is the electric field, $\mathbf{u}$ is the gas-flow velocity, and $\mathbf{B}$ is the magnetic field), to the rate at which energy is given up by the electrons to other species in the gas due to collisions. This energy balance results in the equation

$$\mathbf{j}\cdot\mathbf{E}^* = \sum_i n_e \nu_{ei}\left(2\delta_i \frac{m}{M_i}\right)\frac{3}{2}K(T_e - T_i) \tag{1}$$

where $\mathbf{E}^* = \mathbf{E} + \mathbf{u} \times \mathbf{B}$, n_e is the electron density, ν_{ei} is the electron collision frequency with the ith species, δ_i is a correction factor that accounts for the possibility of inelastic collisions, m/M_i is the electron to ith species mass ratio, K is the Boltzmann constant, T_e is the electron temperature, and T_i is the temperature of the ith species, generally taken to be identical and equal to the gas temperature T_g. It is then postulated that, as a direct consequence of the fact that ionization is primarily produced by electron-atom impact, the resulting steady-state degree of ionization will be a function of electron energy rather than gas energy. The degree of ionization, assuming only the alkali metal seed ionizes, is then given by Saha's law evaluated at the electron temperature:

$$\frac{n_e n_i}{n_A} = \left(\frac{2\pi m K T_e}{h^2}\right)^{3/2} \exp\left(-\frac{e\varphi_i}{KT_e}\right) \tag{2}$$

where n_i is the ion density, n_A is the density of atoms of ionizing material, h is Planck's constant, e is the unit electric charge, and φ_i is the ionization potential. The increased ionization then results in a subsequent increase in the scalar electrical conductivity:

$$\sigma = n_e e^2 \Big/ m \sum_i \nu_{ei} \tag{3}$$

Verification of the preceding postulates has been obtained in diode experiment,[2] and qualitative agreement has been found in MHD devices[5–10] using mixtures of alkali metal vapors and noble gases. These postulates, therefore, form the basis for the analysis to follow.

In this paper, nonequilibrium ionization is investigated in wet alkali metal vapors in which the condensate is considered to be in the form of homogeneously dispersed droplets of uniform but arbitrary size. The medium is therefore considered to consist of neutral atoms, positively charged atomic ions, electrons, and liquid droplets that, in the regime of interest here, are negatively charged. The percent moisture is an arbitrary input parameter so that electron conduction can be evaluated in the presence of supersaturated or superheated vapor conditions. Also, the droplet size is left arbitrary, which allows the investigation of conduction at the onset of condensation when the droplets are small or at later phases when the droplets have grown to large sizes. The ultimate result is the evaluation of the local scalar conductivity and, with application to the MHD generator, the magnetic field required to produce the considered electron temperature.

Collision Frequencies

In the development of the theory of electron conduction in wet vapors, the electron-neutral atom, electron-ion, electron-droplet, and atom-droplet collision frequencies for momentum transfer are found to be of importance. The electron-neutral atom and electron-ion collision frequencies are evaluated by standard techniques[11] and terms of the order of the ratio of light to heavy-particle mass and of relative flow to mean thermal energy are neglected. The electron-neutral atom interaction is assumed to be hard sphere, whereas the electron-ion interaction is taken to be Coulombic. These frequencies are, respectively,

$$\nu_{eA} = n_A Q_{eA}(8KT_e/\pi m)^{1/2} \equiv n_A Q_{eA}\langle v\rangle_e \tag{4}$$

$$\nu_{ei} = n_i \frac{8(\pi)^{1/2}}{3}\left(\frac{e^2}{m}\right)^2\left(\frac{2KT_e}{m}\right)^{-3/2} \ln\left[\frac{9K^2T_e^2}{e^4/\lambda_D^2} + 1\right] \tag{5}$$

Presented as Preprint 64-381 at the 1st AIAA Annual Meeting, Washington, D. C., June 29–July 2, 1964; revision received December 17, 1964.

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where Q_{eA} is the electron-neutral atom cross section and λ_D is the Debye shielding distance which, by a generalization of the techniques of Ref. 12, is given by

$$\frac{1}{\lambda_D^2} = \frac{2\pi e^2}{KT_g}\left[n_e\left(1 + \frac{T_g}{T_e}\right) + ZN_d(1 + Z)\right] \quad (6)$$

where Z is the charge on the droplet, N_d is the density of droplets Z times charged; and it has been assumed, as it shall be throughout the following work, that the *kinetic* temperatures of all of the heavy particles are equal and equal to the gas temperature. However, the droplet *internal* temperature T_d may differ from either the electron or gas kinetic temperature.

The electron-droplet collision frequency is considered to consist of two parts. All electrons that strike the surface of the droplet are assumed to interact inelastically; the basic process being Coulombic interaction, absorption, and random re-emission. Under these circumstances the inelastic electron-droplet collision frequency has been previously derived[13] and, for the negatively charged droplets to be considered here, is given by

$$\nu_{ed}^{\mathrm{inel}} = N_d\langle v\rangle_e\pi r_d^2 \exp\left(-\frac{|Z|e^2/r_d}{KT_e}\right) \quad (7)$$

Those electrons that do not strike the surface are assumed to interact elastically and Coulombically with the droplet. The collision frequency is then obtained in the same manner as the electron-ion frequency except that a lower limit on the integration over impact parameters is introduced. This limit is the impact parameter for which an electron just touches the surface. Using the results of Ref. 14, this impact parameter is

$$b^2 = r_d^2[1 - (|Z|e^2r_d)/\tfrac{1}{2}mv^2] \quad (8)$$

The electron-droplet elastic collision frequency is found to be

$$\nu_{ea}^{\mathrm{el}} = n_a\frac{8(\pi)^{1/2}}{3}\left(\frac{Ze^2}{m}\right)^2\left(\frac{2KT_e}{m}\right)^{-3/2} \times \ln\left\{\frac{[9K^2T_e^2/(e^4/\lambda_d^2)]+1}{\gamma^2+1}\right\} \quad (9)$$

where

$$\gamma^2 \simeq \frac{2}{(\pi)^{1/2}}\left(\frac{KT_e}{|Z|e^2/r_d}\right)^{1/2}\left[1 + \frac{3}{2}\frac{KT_e}{|Z|e^2/r_d}\right]\exp\left(-\frac{|Z|e^2/r_d}{KT_e}\right) \quad (10)$$

The atom-droplet collision frequency is considered to be entirely inelastic and of the hard-sphere type. The collision frequency is then,

$$\nu_{Ad} = N_d\pi r_d^2(8KT_g/\pi m_A)^{1/2} \equiv N_dQ_{Ad}\langle v\rangle_A \quad (11)$$

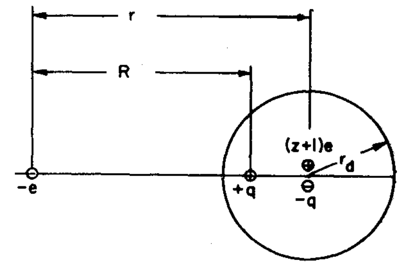
Electron Density

The electron density in the medium is a result of the combined effect of the ionization of gas atoms and the emission absorption of electrons by the droplets. The ionization of the gas is considered to be specifiable by Saha's equation evaluated at the electron temperature. Thus, for the alkali metal vapors

$$\frac{n_en_i}{n_A} = \left(\frac{2\pi mKT_e}{h^2}\right)^{3/2}\exp\left(-\frac{e\varphi_i}{KT_e}\right) \quad (12)$$

Before considering the equation governing the charging of the droplets, a potential model for the removal of an electron from a droplet will be derived. This is accomplished by considering the droplet to be a perfectly conducting sphere. Then, by image theory,[15] the force on the electron due to a droplet Z-times charged prior to the removal of the electron is given by the charge configuration shown in Fig. 1, where

Fig. 1 Image change distribution on a perfectly conducting sphere in presence of a charge $(-e)$.



$$q = (r_d/r)e \quad (13)$$

$$R = r - r_d^2/r \quad (14)$$

The potential is then,

$$\varphi(r) = e\left[\frac{r_d}{2}\frac{1}{(r^2 - r_d^2)} + \frac{Z+1}{r} - \frac{1}{2}\frac{r_d}{r^2}\right] \quad (15)$$

and the work required to remove the electron from an infinitesimal distance δ from the droplet surface to infinity is in the limit as $\delta \to 0$,

$$W \equiv \lim_{\delta\to 0} e\varphi(r_d + \delta) = e^2\left[\frac{1}{4\delta} + \frac{3}{8}\frac{1}{r_d} + \frac{Z}{r_d}\right] \quad (16)$$

In the limit as $r_d \to \infty$, i.e., the sphere approaches a flat surface, $W = e^2/4\delta$, which is therefore associated with the flat surface work function $e\varphi_w$ so that the work to remove an electron from a droplet Z-times charged is

$$W = e\varphi_w + \tfrac{3}{8}(e^2/r_d) + Ze^2/r_d \quad (17)$$

It should be mentioned that, for droplets consisting of a small number of atoms, φ_w will also become a function of r_d since at some point the energy to remove an electron must make a transition toward the ionization energy of a single atom.

In order to simplify the calculation of the elastic and inelastic collision frequencies and the thermionic emission barrier, the actual potential of the droplet is replaced by a pseudo potential consisting of a long range potential $(Z + 1)e/r$, and an abrupt surface potential. For this potential model, the energy to bring the electron to the surface is $-(Z + 1)e^2/r_d$ so that, from Eq. (17), the depth of the surface potential to the Fermi level in the "metal" is

$$\varphi_s = \varphi_w - \tfrac{5}{8}e/r_d \quad (18)$$

The potential barrier of the negatively charged droplets being considered here is depicted in Fig. 2.

The equation for the droplet charging is obtained by considering all droplets to possess the same average charge Z and then equating the random electron current to the droplet to the thermionic emission current from the droplet. Then

$$n_eN_dQ_{ed}^{\mathrm{inel}}\langle v\rangle_e = (J_dA_d/e)N_d \quad (19)$$

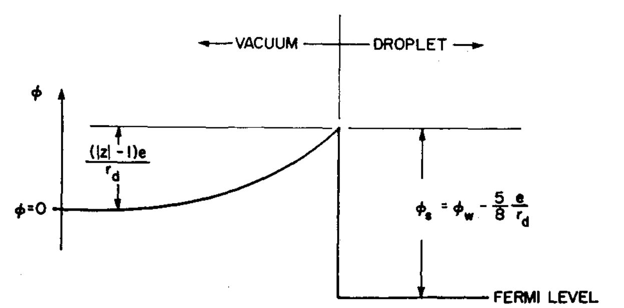


Fig. 2 Pseudopotential well for droplet, Z-times charged.

where J_d is the thermionic emission current and A_d is the surface area of the droplet. This approximation has been previously used[16, 17] and the validity of it demonstrated[18–20] in the limit of large Z.

The thermionic emission current is given in its usual form as follows (see Fig. 2):

$$J_d = (4\pi emK^2T^2/h^3)\exp(-e\varphi_s/KT) \tag{20}$$

A generalization of previous results is now obtained by evaluating the left-hand side of Eq. (20) at the electron temperature and the right-hand side at the droplet internal temperature to obtain

$$n_e = 2\left(\frac{2\pi mKT_d}{h^2}\right)^{3/2}\left(\frac{T_d}{T_e}\right)^{1/2}\exp\left[-\frac{e\varphi_s}{KT_d} + \frac{|Z|e^2/r_d}{KT_e}\right] \tag{21}$$

The charging of the droplets is now completely specified in terms of the neutral atom density, the droplet density, the electron temperature, and the droplet internal temperature by Eqs. (12), (21), and the equation for local charge neutrality

$$n_e = n_i - |Z|N_d \tag{22}$$

Droplet Internal Temperature

The equation for the droplet internal temperature is obtained by equating the rate with which the droplet is heated due to electron bombardment to the rate with which the droplet is cooled due to neutral atom bombardment (cooling due to ion bombardment is neglected with respect to that of the neutral atoms). Assuming a unit accommodation coefficient for both electrons and atoms,

$$n_e\nu_{ed}^{\text{inel}}(T_e - T_d) = n_A\nu_{Ad}(T_d - T_g) \tag{23}$$

Substituting Eqs. (7) and (11) into the preceding expression yields

$$T_d = (\alpha T_e + T_g)/(1 + \alpha) \tag{24}$$

where

$$\alpha = \frac{n_e}{n_A}\left(\frac{m_AT_e}{mT_g}\right)^{1/2}\exp\left(-\frac{|Z|e^2/r_d}{KT_e}\right) \tag{25}$$

Electron Temperature

An expression for the electron temperature as a function of the electromagnetic field in the gas is obtained by modifying Eq. (1) to include the effect of the energy loss resulting from electron-droplet inelastic collisions. Assuming again a unit accommodation coefficient for the process, the inelastic energy-loss term is given by

$$n_e\nu_{ed}^{\text{inel}}2K(T_e - T_d) \tag{26}$$

and Eq. (1) is modified to the form

$$\mathbf{j}\cdot\mathbf{E}^* = \sum_i n_e\nu_{ei}2\frac{m}{M_i}\frac{3}{2}K(T_e - T_g) + n_e\nu_{ed}^{\text{inel}}2K(T_e - T_d) \tag{27}$$

where we have neglected all other inelastic energy losses.

For the numerical considerations to follow, we shall restrict ourselves to the special case of a segmented electrode MHD generator (see Ref. 4) for which Eq. (39) simplifies to

$$\left(e^2\Big/m\sum_j \nu_{ej}\right)u^2B^2 = \sum_i 2\nu_{ei}\frac{m}{M_i}\frac{3}{2}K(T_e - T_g) + n_e\nu_{ed}^{\text{inel}}2K(T_e - T_d) \tag{28}$$

Results and Discussion

As an example of the effect of droplets upon the conduction of electrons we considered a potassium-vapor system at 800°K, 0.1 atm (slightly supersaturated), and 75% moisture, for which

$$n_A \simeq P_g/KT_g$$

$$N_d \simeq n_A\ (\%\ \text{moisture})\ 1/n_d$$

where n_d is the number of atoms per droplet and, for "close packing," is given by

$$n_d = (r_d/r_A)^3$$

where $r_A = 2.38 \times 10^{-8}$ cm (Ref. 21) is the radius of an atom. The work function of the droplet was assumed equal to that of solid potassium, $e\varphi_w = 2.15$ ev (Ref. 21); the ionization potential of the potassium atom was taken to be $e\varphi_i = 4.34$ ev (Ref. 21); and the electron-neutral atom cross section is $Q_{eA} = 3 \times 10^{-14}$ cm² (Ref. 22). The system is then considered as a function of electron temperature in the range of 1500°–3500°K for $r_d = 10^{-6}$ cm ($n_d = 7.5 \times 10^4$) and $r_d = 2.16 \times 10^{-7}$ cm ($n_d = 7.5 \times 10^2$). For the preceding conditions the droplet temperature was found to be equal to the gas temperature.

In Fig. 3 the ratio of the electron density in the system to that with no droplets present is shown. An almost two order-of-magnitude decrease in the electron density is noted at the lower limit of electron temperatures considered. The electron

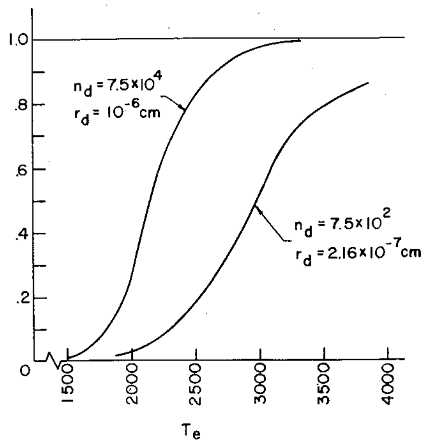


Fig. 4 Ratio of electrical conductivity with droplets to electrical conductivity without droplets vs electron temperature.

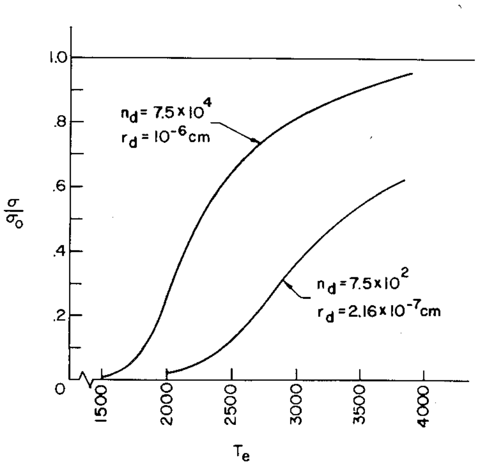


Fig. 3 Ratio of electron density with droplets to electron density without droplets vs electron temperature.

density ratio then rises rapidly to reach approximately unity at the upper range of electron temperature, the depression of electron density being due to electron absorption by the droplets.

The ratio of the electrical conductivity in the system to the electrical conductivity with no droplets is shown in Fig. 4. The variation of the conductivity with electron temperature is primarily due to the electron density variation, in as much as the collision frequence is, within the range considered here, dominated by electron-neutral atom collisions. It is noted that, when the condensate is dispersed in small droplets, the conductivity is more severely depressed.

The effect upon the required magnetic-field strength due to the presence of the droplets is slight and nearly independent of electron temperature. The inelastic energy loss is insignificant except at the lowest temperature where its contribution is approximately 10% as compared to the elastic energy losses. The ratio of magnetic field required to produce a given electron temperature with droplets to that without droplets was found to be approximately 1.08 for $r_d = 10^{-6}$ cm and 1.2 for $r_d = 2.16 \times 10^{-7}$ cm.

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