NOTES AND CORRESPONDENCE

The Mechanism of Charge Transfer Associated with Evaporation of Ice

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Latham and Stow (1965) described ice evaporation experiments demonstrating that charge is carried away on the particles leaving the specimen if temperature gradients exist in its surface. The results were qualitatively explicable in terms of the temperature-gradient theory, but Latham and Stow concluded that it is impossible to determine whether quantitative consistency with Mason's (1961) equations exists until the charge and temperature distributions within ice specimens subjected to temperature gradients have been established. However, the approximate computation presented here shows that the concept of charging by the removal of individual singly-charged molecules, the process envisaged by Latham and Stow, is totally inconsistent with the charging rate predicted by Mason's equations, even under the clearly incorrect hypothesis that all the charge separated by the temperature gradients resides on the ice surface. The argument is related to the typical observation by Latham and Stow that if the temperature gradient in the surface, dT/dx , was 90°C cm^{-1} , and the rate of disappearance of the surface, dl/dt , was $2 \times 10^{-6} \text{ cm sec}^{-1}$, then the rate of charging of their ice specimen by evaporation was $8.9 \times 10^{-6} \text{ esu cm}^{-2}$. In this experiment the surface was colder than the interior of the ice specimen, which became negatively charged.

Brook (1965) remarked that the work which must be performed by a singly-charged individual molecule in order to escape from an ice surface is significantly greater than that required to remove an electrically neutral molecule because the charged molecule has to overcome attractive image forces. Let this additional increment of energy be Σ . Assuming a cubical ice molecule of side L , the additional work required for a molecule to overcome its electrostatic image charge is given by

$$\Sigma = \int_{x=L}^{x=\infty} \frac{e^2}{x^2} dx = e^2/L, \quad (1)$$

where e is the electronic charge. If we take $L = 5 \times 10^{-8} \text{ cm}$, then $\Sigma = 4.6 \times 10^{-12} \text{ ergs}$.

The ratio of the probability of escape of a charged molecule to that of an uncharged molecule can be expressed approximately by

$$P = e^{-\Sigma/KT}, \quad (2)$$

where K is Boltzmann's constant. If we take a typical temperature of 250°K , then

$$P = e^{-131} = 10^{-57}.$$

The rate of evaporation, dN/dt , of molecules from unit area of the surface of an ice specimen is given by the product of the surface density of molecules, D , and the rate of disappearance of monomolecular surfaces, R . Our approximate treatment gives $D = L^{-2} = 4 \times 10^{14} \text{ cm}^{-2}$ and $R = L^{-1} dl/dt = 40$.

Therefore,

$$\frac{dN}{dt} = 1.6 \times 10^{16} \text{ molecules sec}^{-1} \text{ cm}^{-2}.$$

The maximum surface density of charge, S , predicted by Mason's equations is given by

$$\begin{aligned} S &= 5 \times 10^{-6} \frac{dT}{dx} = 4.5 \times 10^{-3} \text{ esu cm}^{-2} \\ &= 9.4 \times 10^6 \text{ charged molecules cm}^{-2} \end{aligned} \quad (3)$$

and, since $R=40$, the total number of charged molecules available for evaporation from unit area of the ice surface is $3.8 \times 10^8 \text{ sec}^{-1}$. This analysis assumes that all the charge separated by the temperature gradient resides in the monomolecular surface layer and that a charged molecule removed from the ice surface by evaporation is instantaneously replaced by another charged molecule. Both of these assumptions lead to an overestimate of the theoretical charging rate.

The number of charged molecules leaving unit area of the ice specimen per unit time is given by

$$\frac{dn}{dt} = FP \frac{dN}{dt}, \quad (4)$$

where $F=S/D$ is the fraction of surface molecules that are charged. For $F=2.4 \times 10^{-8}$, the theoretical rate of charging by evaporation from unit area of the ice surface is given by

$$\frac{dg}{dt} = e \frac{dn}{dt} = 1.85 \times 10^{-58} \text{ esu cm}^{-2}, \quad (5)$$

which is over fifty orders of magnitude less than the experimentally determined charging rate given earlier. This extremely low value of dg/dt results from the fact that the work required to remove a charged molecule from an otherwise neutral ice surface is much greater than that required to remove an uncharged molecule.

Since the surface carries a charge of the same sign as that of the evaporating charged molecules, and since it is possible that the vacancy left by a charged molecule leaving the ice surface is immediately filled by another charged molecule, repulsive forces exist between the ice surface and the charged molecules leaving it, which will reduce the value of Σ . The following calculation demonstrates that the reduction is negligible.

The repulsive field at the surface of the ice specimen owing to the distribution of positive charge is given by

$$F_R = 4\pi S = 5.6 \times 10^{-2} \text{ esu} = 18 \text{ v cm}^{-1}. \quad (6)$$

This field will diminish rapidly as the distance from the surface increases.

The attractive field at the surface produced by the mirror-image charge is given by

$$F_A = \frac{-e}{L^2} = -1.9 \times 10^5 \text{ esu} = -5.7 \times 10^7 \text{ v cm}^{-1}. \quad (7)$$

This field will also decrease rapidly with distance from the surface but it can easily be shown that over 99 per cent of the work required to completely remove a charged molecule from the ice surface has been performed when it has reached a distance from the surface of 10^{-5} cm where the repulsive field is about 100 times

the attractive field at the surface of the specimen. The surface density of charge has therefore a negligible influence on the removal of a charged molecule from the ice. The probability that the vacancy left by the removal of a charged molecule from the ice surface is instantaneously filled by another charged molecule is simply $F=2.4 \times 10^{-8}$ and is therefore remote. It can easily be shown that even when this does occur the evaporating molecule has already performed the greater part of its work before the other charged molecule can be accommodated into the vacancy. The distribution of charge on the surface of an evaporating ice specimen therefore has an insignificant effect on the ease of removal of a charged molecule.

It must be concluded from this analysis that the charging of an evaporating ice specimen is not a consequence of the removal of *individual* charged molecules. However, the measured electrification is entirely explicable qualitatively in terms of the temperature gradient effect, and would also be in quantitative agreement with the theory if the ratio P were increased to about 5×10^{-5} . An enhancement in the value of P would ensue if the evaporation occurred by means of the removal of clusters of neutral molecules carrying a single charged molecule. A calculation will now be made of the size of a cluster which will reduce the value of Σ so that the ratio $P=5 \times 10^{-5}$.

We assume for simplicity that the cluster leaving the ice surface is comprised of one charged molecule in the center of $(n-1)$ uncharged ones, and that this agglomerate is cubical of side x . We see from Eq. (2) that $P=4.8 \times 10^{-5}$ when $\Sigma=3.5 \times 10^{-13} \text{ ergs}$. The critical value of x which satisfies (1) with $\Sigma=3.5 \times 10^{-13} \text{ ergs}$ is therefore

$$x = 6.6 \times 10^{-7} \text{ cm}.$$

Quantitative consistency between the experimental and theoretical values for the rate of charging of an evaporating ice specimen is therefore achieved if each charged molecule is removed in the center of a cluster of side $6.6 \times 10^{-7} \text{ cm}$, containing $n=(x/L)^3=2.2 \times 10^3$ molecules. The energetic problems involved in the creation and removal of such an agglomerate indicate that this suggestion is unlikely to be correct although some latitude is afforded by the deviations of the theoretical charge separation within the ice specimen from that predicted by Mason (1961). A more detailed treatment of this problem should consider quantitatively the charge and temperature distributions within an ice specimen subjected to temperature gradients and also the possibility, advanced by Schaefer (1965), that submicroscopic foreign particles may be the agents by which charge is removed during the evaporation process; this mechanism is isolated from the energetic difficulties which, as has been shown in this analysis, eliminate the possibility that the charge is removed on individual molecules.

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