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Temperature Dependence of Thermal Positive Ion Production through Dissociation of Polyatomic Molecules

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The production of a thermal positive ion (M^+) from a polyatomic molecule (MX) incident upon a heated metal surface is investigated theoretically as a function of surface temperature (T). The quantitative expression of the ion emission current (i^+) of M^+ at a constant incident flux (N) of MX is found to change according to the condition whether the work function (ϕ) of the surface is higher or lower than the first ionization energy (I) of M and also to the degree of dissociation (γ) of MX on the surface. Namely,

(1) When $\phi - I > 0$,

$$i^+ \approx \begin{cases} K_1 \text{ for } \gamma \approx 1. \\ K_2\, T^{-1/4} \exp\left[\dfrac{\phi - I - D}{2RT}\right] \text{ for } \gamma \ll 1. \end{cases}$$

(2) When $\phi - I < 0$,

$$i^+ \approx \begin{cases} K_3 \exp\left[\dfrac{\phi - I}{RT}\right] \text{ for } \gamma \approx 1. \\ K_4\, T^{-1/4} \exp\left[\dfrac{\phi - I - D/2}{RT}\right] \text{ for } \gamma \ll 1. \end{cases}$$

Here D is the bond dissociation energy of MX and K's are virtually independent of T. In any other cases i^+ cannot be expressed in such a simple form. The particular temperature regions corresponding to $\gamma \approx 1$ or $\gamma \ll 1$ are evaluated for given sets of N, D, I, and ϕ.

When a beam of an atom (M) with a small value of the first ionization energy (I(M)) is impinged upon a positively biased metal surface at a high temperature, a positive ion (M^+) is emitted after attaining the following equilibrium on the surface.

$$M \rightleftharpoons M^+ + e^-. \tag{1}$$

This phenomenon is usually called thermal positive ion emission or positive surface ionization, and has long been investigated both experimentally and theoretically by great many workers. Nowadays, in consequence, it is generally accepted that the ionization coefficient (α^+(M)) of M is described by Saha-Langmuir's equation.[1,2]

$$\alpha^+(M) \equiv \frac{n(M^+)}{n(M)} = \frac{w^+}{w^0} \exp\left[\frac{\phi - I(M)}{RT}\right]. \tag{2}$$

Here $n(M^+)$ and n(M) are the numbers of M^+ and M emitted per unit time from unit surface area, respectively, w^+/w^0 the statistical weight ratio of M^+ to M, ϕ the work function of the surface, R the gas constant, and T the absolute temperature of the surface. The enthalpy change (ΔH_1) due to the surface reaction ($M \rightarrow M^+ + e^-$) is equal to $-(\phi - I(M))$, which is naturally included in Eq. 2. The ionization efficiency is usually given by

$$\beta^+(M) \equiv \frac{n(M^+)}{N(M)} = \sigma(M) \frac{n(M^+)}{n(M) + n(M^+)}$$

$$= \sigma(M) \frac{\alpha^+(M)}{1 + \alpha^+(M)}, \tag{3}$$

where N(M) and σ(M) are the incident flux per unit time per unit surface area and the accommodation coefficient of M, respectively.

The ion current collected with a Faraday cage is generally expressed by

$$i^+(M) = e S \eta(M^+) N(M) \beta^+(M). \tag{4}$$

Here e, S, and $\eta(M^+)$ are the elementary electric charge, the area of the ionizing surface, and the collection efficiency of M^+, respectively. Substitution of Eqs. 3 and 2 in Eq. 4 yields

$$i^+(M) \approx \begin{cases} C_1 \text{ for } \alpha^+(M) \gg 1. & (5) \\ C_1 \left[1 + \dfrac{w^0}{w^+} \exp\left[\dfrac{\Delta H_1}{RT}\right]\right]^{-1} \text{ for neither} & \\ \quad \alpha^+(M) \gg 1 \text{ nor } \alpha^+(M) \ll 1. & (6) \\ C_1 \dfrac{w^+}{w^0} \exp\left[\dfrac{-\Delta H_1}{RT}\right] \text{ for } \alpha^+(M) \ll 1. & (7) \end{cases}$$

Here C_1 is given by

$$C_1 \equiv e S \eta(M^+) \sigma(M) N(M). \tag{8}$$

Clearly the quantitative expression of i^+(M) changes according to the value of α^+(M), and it is ΔH_1, of course, that is included in the Boltzmann factor governing the thermal positive ion production from the incident atom M. When $\alpha^+(M) \gg 1$, however, i^+(M) is virtually independent of both ΔH_1 and T, as shown by Eq. 5. When α^+(M) is neither much larger nor much smaller than unity, Eq. 6 indicates that the slope of an emission plot ($\log i^+(M)$ *vs.* $1/T$) is not constant. On the other hand, such a plot as is based on Eq. 7 yields a straight line, the gradient (G) of which is equal to $-(0.434/R)\,\Delta H_1$. Only when $\alpha^+(M) \ll 1$, therefore, it is possible to determine I(M)[3-5] or ϕ[6-9] from G.

Such emission of the positive ion M^+ is observed also when a beam of a molecule (MX) including the same element M impinges upon the surface. In the case of this molecular beam incidence, however, M^+ is emitted after attaining Equilibria (9) and (1) on the ionizing surface, and the ion production processes are more complicated than those in the case of the atomic beam incidence described above.

$$MX \rightleftharpoons M + X. \tag{9}$$

The enthalpy change (ΔH_2) due to the surface reaction

($MX \rightarrow M^+ + X + e^-$) is equal to $-(\phi - I(M) - D(MX))$, where $D(MX)$ is the bond dissociation energy of MX. The temperature dependence of the collected ion current ($i^+(MX)$) of M^+ thus produced from MX has long been investigated experimentally by many workers.[1,2] The theoretical investigation of the dependence, however, has not yet fully been made, and a quantitative expression of $i^+(MX)$ as a function of T seems not to be derived theoretically or empirically by any workers. Consequently, the quantitative relation between $i^+(MX)$ and ΔH_2 also seems to be left unknown, in contrast to the case of the atomic beam incidence described above. From analogy with Eqs. 6 and 7, it may possibly be inferred that none other than ΔH_2 can be included in the Boltzmann factor governing the production of M^+ from MX. The validity of this inference, however, should be checked rigorously on the basis of thermochemistry. Previously one of the present authors made a theoretical study of thermal negative ion production from incident molecules.[10,11] A theoretical model developed in the previous work may probably be useful for solving the above problems, too.

From the viewpoints described above, the present authors have applied the theoretical model to the thermal positive ion production from polyatomic molecules. In consequence, they have found that $i^+(MX)$ is expressed as a function of T by seven different equations according to the ionization coefficient and to the degree of dissociation of MX, and also that the Boltzmann factors in some of the equations include ΔH_1, $\Delta H_2/2$, or $(\Delta H_1 + \Delta H_2)/2$, as opposed to the above inference that ΔH_2 alone is included.

This paper describes the theoretical investigation leading to the above findings and also illustrates an application of the present theory to several sample–surface systems.

Theoretical

Expression of the Ionization Coefficient. In a similar way as in the previous work,[10,11] let us consider an isothermal airtight metal vessel, inside of which Equilibria (9) and (1) exist. If the density of the charged particles is so small that the space-charge effect may be neglected, then Eqs. 10—12 are derived from thermochemical considerations.

$$\frac{P(M)\,P(X)}{P(MX)} = \frac{f(M)\,f(X)}{f(MX)} \exp\left[\frac{-D(MX)}{R\,T}\right]. \tag{10}$$

$$\frac{P(M^+)\,P(e^-)}{P(M)} = \frac{f(M^+)\,f(e^-)}{f(M)} \exp\left[\frac{-I(M)}{R\,T}\right]. \tag{11}$$

$$P(e^-) = f(e^-) \exp\left[\frac{-\phi}{R\,T}\right]. \tag{12}$$

Here $P(Y)$ and $f(Y)$ are the equilibrium vapor pressure and the partition function, respectively, of the particle Y, and ϕ is the work function of the surface of the vessel.

The flux of Y evaporating per unit time from a unit area of the surface is given by

$$J(Y) = \frac{N_A\,P(Y)}{\{2\,\pi\,M(Y)\,R\,T\}^{1/2}}, \tag{13}$$

where N_A and $M(Y)$ are Avogadro's number and the molecular (or atomic) weight of Y, respectively. In surface ionization, however, free evaporation occurs in a vacuum. Strictly speaking, therefore, $P(Y)$ should be corrected with a factor of the evaporation coefficient $(\varepsilon(Y))$.[12] Consequently, the flux of Y emitted from an ionizing surface is

$$n(Y) = \varepsilon(Y)\,J(Y). \tag{14}$$

From Eqs. 10—14 we obtain Eqs. 15—17.

$$\frac{n(M)\,n(X)}{n(MX)} = \frac{N_A\,\rho(MX)}{\{2\,\pi\,\mu\,R\,T\}^{1/2}} \exp\left[\frac{\Delta S^\circ(MX)}{R}\right] \times \exp\left[\frac{-D(MX)}{R\,T}\right]. \tag{15}$$

$$\alpha^+(MX) \equiv \frac{n(M^+)}{n(M)} = C_2 \exp\left[\frac{\phi - I(M)}{R\,T}\right]. \tag{16}$$

$$C_2 \equiv \rho(M) \exp\left[\frac{\Delta S^\circ(M)}{R}\right]. \tag{17}$$

Here $\Delta S^\circ(MX)$ and $\Delta S^\circ(M)$ are the standard entropy changes due to the dissociation and the positive ion production, respectively; and $\rho(MX)$, $\rho(M)$, and μ are given by $\varepsilon(M)\,\varepsilon(X)/\varepsilon(MX)$, $\varepsilon(M^+)/\varepsilon(M)$, and $M(M) \times M(X)/M(MX)$, respectively. Essentially C_2 is equal to w^+/w^0 because Eq. 2 is derived on the implicit assumption $\rho(M) = 1$. If the flux of MX or M impinging separately upon the same ionizing surface is so small that ϕ may be regarded essentially constant without being affected by adsorption of MX or M, then the ionization coefficient $\alpha^+(MX)$ given by Eq. 16 is equal to $\alpha^+(M)$ by Eq. 2.

Under such a steady-state condition that all of the particles evaporate from the ionizing surface immediately after attaining Equilibria (9) and (1) on the surface, the following relations hold.

$$n(M) + n(M^+) = n(X) = \sigma(MX)\,\gamma(MX)\,N(MX). \tag{18}$$

$$n(MX) = \{1 - \gamma(MX)\}\,\sigma(MX)\,N(MX). \tag{19}$$

Here $\sigma(MX)$ is the accommodation coefficient of MX incident upon the ionizing surface, and represents the fraction of the MX molecules attaining Equilibria (9) and (1) on the surface. Namely,

$$\sigma(MX) \equiv \frac{n(MX) + n(M) + n(M^+)}{N(MX)}. \tag{20}$$

The ionization efficiency is given by

$$\beta^+(MX) \equiv \frac{n(M^+)}{N(MX)} = \sigma(MX)\,\gamma(MX)\,\frac{\alpha^+(MX)}{1 + \alpha^+(MX)}. \tag{21}$$

Eqs. 16 and 18 yield

$$n(M) = \frac{\sigma(MX)\,\gamma(MX)\,N(MX)}{1 + \alpha^+(MX)}. \tag{22}$$

By substituting Eqs. 18, 19, and 22 in Eq. 15, we obtain

$$\frac{\gamma(MX)^2}{1 - \gamma(MX)} = \{1 + \alpha^+(MX)\}\,B, \tag{23}$$

or

$$\gamma(MX) = \frac{\{1 + \alpha^+(MX)\}B}{2} \times \left[\left\{1 + \frac{4}{\{1 + \alpha^+(MX)\}B}\right\}^{1/2} - 1\right]. \tag{24}$$

Here

$$\begin{cases} B \equiv b\, T^{-1/2} \exp\left[\dfrac{-D(\mathrm{MX})}{R\,T}\right]. & (25) \\ b \equiv \dfrac{N_{\mathrm{A}}\, \rho(\mathrm{MX})}{\sigma(\mathrm{MX})\, N(\mathrm{MX}) \{2\,\pi\,\mu\,R\}^{1/2}} \exp\left[\dfrac{\Delta S^{\circ}(\mathrm{MX})}{R}\right]. & (26) \end{cases}$$

Again, it should be noted that Eq. 2 is based upon simplifying assumptions such as $\rho(\mathrm{M})=1$ and $\sigma(\mathrm{M})=1$ but is nevertheless approved widely as a quantitative expression of $\alpha^{+}(\mathrm{M})$ in usual surface ionization, where the electric field drawing out M^{+} from the surface is so weak that Schottky effect may be neglected. When potassium halide molecules impinge upon a rhenium surface, for example, $\beta^{+}(\mathrm{KX})$ is virtually unity in the range 1200—1900 K.[13] This result may give evidence that both $\sigma(\mathrm{KX})$ and $\rho(\mathrm{KX})$ are essentially unity in the above cases. In addition, cesium chloride molecules are completely accommodated on both iridium and carburized iridium surfaces.[14]

Judging from the experimental results described just above, it may be reasonable at least with alkali halide molecules to regard that both $\sigma(\mathrm{MX})$ and $\rho(\mathrm{MX})$ are virtually unity in usual surface ionization. In a narrow temperature range usually covered in positive surface ionization, therefore, b given by Eq. 26 may be regarded essentially constant for a constant value of $N(\mathrm{MX})$.

Expression of the Ion Emission Current. The ion current collected with a Faraday cage is expressed by Eq. 27, which is derived from Eq. 21.

$$\begin{aligned} i^{+}(\mathrm{MX}) &= e\,S\,\eta(\mathrm{M}^{+})\, N(\mathrm{MX})\, \beta^{+}(\mathrm{MX}) \\ &= C_3\, \gamma(\mathrm{MX}) \frac{\alpha^{+}(\mathrm{MX})}{1+\alpha^{+}(\mathrm{MX})}, \end{aligned} \tag{27}$$

where C_3 is

$$C_3 \equiv e\,S\,\eta(\mathrm{M}^{+})\, \sigma(\mathrm{MX})\, N(\mathrm{MX}). \tag{28}$$

Since C_3 may be regarded constant for a fixed value of $N(\mathrm{MX})$, it is essentially upon $\gamma(\mathrm{MX})$ and $\alpha^{+}(\mathrm{MX})$ that $i^{+}(\mathrm{MX})$ depends. First, therefore, Eq. 27 will be treated as a function of $\gamma(\mathrm{MX})$.

(A) Equation 24 indicates that $\gamma(\mathrm{MX})\approx 1$ when $\{1+\alpha^{+}(\mathrm{MX})\}B \gg 4$. In this case Eq. 27 becomes

$$i^{+}(\mathrm{MX}) \approx C_3 \frac{\alpha^{+}(\mathrm{MX})}{1+\alpha^{+}(\mathrm{MX})}. \tag{29}$$

In usual surface ionization the measurement of $i^{+}(\mathrm{MX})$ is accompanied with an error of about ±5%, and hence a prerequisite for Eq. 29 may be written down

$$\gamma(\mathrm{MX}) \gtrsim 0.95 \text{ or } \{1+\alpha^{+}(\mathrm{MX})\}\, B \gtrsim 18. \tag{30}$$

(B) When $\gamma(\mathrm{MX}) \ll 1$, Eq. 23 reduces to

$$\gamma(\mathrm{MX}) \approx [\{1+\alpha^{+}(\mathrm{MX})\}B]^{1/2}. \tag{31}$$

Substitution of Eq. 31 in Eq. 27 yields

$$i^{+}(\mathrm{MX}) \approx C_3\, B^{1/2} \frac{\alpha^{+}(\mathrm{MX})}{\{1+\alpha^{+}(\mathrm{MX})\}^{1/2}}. \tag{32}$$

Consideration of the experimental error mentioned above leads to the conclusion that a prerequisite for Eq. 32 may be set up

$$\gamma(\mathrm{MX}) \approx [\{1+\alpha^{+}(\mathrm{MX})\}B]^{1/2} \lesssim 0.098. \tag{33}$$

(C) When $\gamma(\mathrm{MX})$ is intermediate, namely,

$$\begin{aligned} &0.95 > \gamma(\mathrm{MX}) > 0.098 \text{ or} \\ &18 > \{1+\alpha^{+}(\mathrm{MX})\}B > 0.0095, \end{aligned} \tag{34}$$

$i^{+}(\mathrm{MX})$ cannot be approximated adequately in such a simple form as in Eq. 29 or 32. In this case, $i^{+}(\mathrm{MX})$ is expressed in a complex form by Eq. 35, which is obtained by substituting Eqs. 16 and 24 in Eq. 27.

$$i^{+}(\mathrm{MX}) = C_4 T^{-1/2}\, \mathrm{F}(T) \exp\left[\frac{\phi - I(\mathrm{M}) - D(\mathrm{MX})}{R\,T}\right]. \tag{35}$$

Here

$$\begin{cases} C_4 \equiv \dfrac{e\,S\,\eta(\mathrm{M}^{+})\, N_{\mathrm{A}}\, \rho(\mathrm{M})\, \rho(\mathrm{MX})}{2\{2\pi\,\mu\,R\}^{1/2}} \\ \qquad \times \exp\left[\dfrac{\Delta S^{\circ}(\mathrm{M}) + \Delta S^{\circ}(\mathrm{MX})}{R}\right], & (36) \\ \mathrm{F}(T) \equiv \left[1 + \dfrac{4}{\{1+\alpha^{+}(\mathrm{MX})\}B}\right]^{1/2} - 1. & (37) \end{cases}$$

It should be noted that Eq. 35 holds not approximately but exactly for any values of $\gamma(\mathrm{MX})$ and $\alpha^{+}(\mathrm{MX})$.

Consideration of the Ionization Coefficient. Secondly, let us treat $i^{+}(\mathrm{MX})$ as a function of $\alpha^{+}(\mathrm{MX})$.

(A) Equation 16 indicates that $\alpha^{+}(\mathrm{MX})$ is much larger than unity when $\phi - I(\mathrm{M}) \gtrsim 10$ kcal mol^{-1}. Because $R\,T$ is less than about 3 kcal mol^{-1} in a temperature range (1100—1800 K) usually covered in positive surface ionization, and also because C_2 is about 1/2 for alkali metal or its salt, which is the most typical sample material in positive surface ionization. Under the above condition we obtain Eqs. 38 and 39 from Eqs. 29 and 32, respectively, while no simple equation other than Eq. 35 holds for the intermediate values of $\gamma(\mathrm{MX})$.

$$i^{+}(\mathrm{MX}) \approx \begin{cases} C_3 \text{ for } \gamma(\mathrm{MX}) \gtrsim 0.95. & (38) \\ C_4\, T^{-1/2}\, \mathrm{F}(T) \exp\left[\dfrac{\phi - I(\mathrm{M}) - D(\mathrm{MX})}{R\,T}\right] \\ \quad \text{for } 0.95 > \gamma(\mathrm{MX}) > 0.098. & (35) \\ C_5\, T^{-1/4} \exp\left[\dfrac{\phi - I(\mathrm{M}) - D(\mathrm{MX})}{2\,R\,T}\right] \\ \quad \text{for } \gamma(\mathrm{MX}) \lesssim 0.098. & (39) \end{cases}$$

Here C_5 is

$$C_5 \equiv \frac{e\,S\,\eta(\mathrm{M}^{+}) \{N_{\mathrm{A}}\, \sigma(\mathrm{MX})\, N(\mathrm{MX})\, \rho(\mathrm{M})\, \rho(\mathrm{MX})\}^{1/2}}{\{2\,\pi\,\mu\,R\}^{1/4}} \times \exp\left[\frac{\Delta S^{\circ}(\mathrm{M}) + \Delta S^{\circ}(\mathrm{MX})}{2\,R}\right]. \tag{40}$$

(B) Under the condition that $\phi - I(\mathrm{M}) \lesssim -10$ kcal mol^{-1}, $\alpha^{+}(\mathrm{MX})$ in the usual temperature range is negligibly small compared with unity, and hence Eqs. 41 and 42 are obtained from Eqs. 29 and 32, respectively. Similarly as in the case (A) described just above, it is only Eq. 35 that holds for the intermediate values of $\gamma(\mathrm{MX})$.

$$i^{+}(\mathrm{MX}) \approx \begin{cases} C_6 \exp\left[\dfrac{\phi - I(\mathrm{M})}{R\,T}\right] \text{ for } \gamma(\mathrm{MX}) \gtrsim 0.95. & (41) \\ C_4\, T^{-1/2}\, \mathrm{F}(T) \exp\left[\dfrac{\phi - I(\mathrm{M}) - D(\mathrm{MX})}{R\,T}\right] \\ \quad \text{for } 0.95 > \gamma(\mathrm{MX}) > 0.098. & (35) \\ C_7\, T^{-1/4} \exp\left[\dfrac{\phi - I(\mathrm{M}) - D(\mathrm{MX})/2}{R\,T}\right] \\ \quad \text{for } \gamma(\mathrm{MX}) \lesssim 0.098. & (42) \end{cases}$$

Here C_6 and C_7 are given by Eqs. 43 and 44, respectively.

$$C_6 \equiv e\,S\,\eta(\mathrm{M}^{+})\, \sigma(\mathrm{MX})\, N(\mathrm{MX})\, \rho(\mathrm{M}) \exp\left[\frac{\Delta S^{\circ}(\mathrm{M})}{R}\right]. \tag{43}$$

$$C_7 \equiv \frac{e\,S\,\eta(\mathrm{M}^+)\,\rho(\mathrm{M})\,\{N_\mathrm{A}\,\rho(\mathrm{MX})\,\sigma(\mathrm{MX})\,N(\mathrm{MX})\}^{1/2}}{\{2\,\pi\,\mu\,R\}^{1/4}} \times \exp\left[\frac{\Delta S^\circ(\mathrm{M}) + \Delta S^\circ(\mathrm{MX})/2}{R}\right]. \qquad (44)$$

(C) When $|\phi - I(\mathrm{M})| < 10\ \mathrm{kcal\ mol^{-1}}$, the condition that neither $\alpha^+(\mathrm{MX}) \gg 1$ nor $\alpha^+(\mathrm{MX}) \ll 1$ holds in the usual temperature range so long as the allowable error due to approximation is restricted to less than about ±5%. In this case, $i^+(\mathrm{MX})$ is expressed as follows:

$$i^+(\mathrm{MX}) \approx \begin{cases} C_6\,\mathrm{G}(T)\exp\left[\dfrac{\phi - I(\mathrm{M})}{R\,T}\right] & \text{for } \gamma(\mathrm{MX}) \gtrsim 0.95. \qquad (45)\\ C_4\,T^{-1/2}\,\mathrm{F}(T)\exp\left[\dfrac{\phi - I(\mathrm{M}) - D(\mathrm{MX})}{R\,T}\right] & \text{for } 0.95 > \gamma(\mathrm{MX}) > 0.098. \qquad (35)\\ C_7\,T^{-1/4}\,\mathrm{G}(T)^{1/2}\exp\left[\dfrac{\phi - I(\mathrm{M}) - D(\mathrm{MX})/2}{R\,T}\right] & \text{for } \gamma(\mathrm{MX}) \lesssim 0.098. \qquad (46)\end{cases}$$

Here $\mathrm{G}(T)$ is given by

$$\mathrm{G}(T) \equiv \left[1 + C_2\exp\left[\frac{\phi - I(\mathrm{M})}{R\,T}\right]\right]^{-1}. \qquad (47)$$

Equations 45 and 46 are derived from Eqs. 29 and 32, respectively. So long as $|\phi - I(\mathrm{M})| < 10\ \mathrm{kcal\ mol^{-1}}$, therefore, $i^+(\mathrm{MX})$ cannot be expressed in such a simple form as in Eq. 38, 39, 41, or 42.

Evaluation of the Degree of Dissociation. For the reasons described just below Eq. 26, the factors $\sigma(\mathrm{MX})$, $\rho(\mathrm{M})$, and $\rho(\mathrm{MX})$ may be assumed to be unity, and hence Eqs. 48—50 may be obtained from Eqs. 23—26.

$$\frac{\gamma(\mathrm{MX})^2}{1 - \gamma(\mathrm{MX})} \approx \frac{2.67 \times 10^{25}}{N(\mathrm{MX})\,\{\mu\,T\}^{1/2}} \times \exp\left[\frac{\Delta S^\circ(\mathrm{MX})}{R}\right]\exp\left[\frac{-D(\mathrm{MX})}{R\,T}\right]$$

$$\times \begin{cases} 1 & \text{for } \alpha^+(\mathrm{MX}) \ll 1. \qquad (48)\\ \left\{1 + \exp\left[\dfrac{\Delta S^\circ(\mathrm{M})}{R}\right]\exp\left[\dfrac{\phi - I(\mathrm{M})}{R\,T}\right]\right\} & \text{for neither } \alpha^+(\mathrm{MX}) \ll 1 \text{ nor } \alpha^+(\mathrm{MX}) \gg 1. \qquad (49)\\ \exp\left[\dfrac{\Delta S^\circ(\mathrm{M})}{R}\right]\exp\left[\dfrac{\phi - I(\mathrm{M})}{R\,T}\right] & \text{for } \alpha^+(\mathrm{MX}) \gg 1. \qquad (50)\end{cases}$$

Here the first figure on the right hand side includes the factor 1.013×10^6, which is necessary because the entropy changes refer to a standard gaseous state for $P(\mathrm{Y}) = 1$ atm. At $\alpha^+(\mathrm{MX}) \gg 1$, $\gamma(\mathrm{MX})$ depends strongly upon ϕ in contrast to the other cases, as may be easily understood from Eqs. 48—50. Obviously Eq. 50 is $\exp[\{\phi - I(\mathrm{M}) + \Delta S^\circ(\mathrm{M})\,T\}/R\,T]$ times as large as Eq. 48, thereby indicating that the dissociation of MX is promoted at $\alpha^+(\mathrm{MX}) \gg 1$. In a high temperature range where $\gamma(\mathrm{MX})$ is close to unity, of course, $\gamma(\mathrm{MX})$ is virtually independent of the factors such as $N(\mathrm{MX})$, $D(\mathrm{MX})$, $I(\mathrm{M})$, and ϕ included in Eqs. 48—50, as will be illustrated below (see Fig. 1).

To take concrete examples, let us consider that a beam of NaF strikes single crystal surfaces of Mo(100), W(100), W(110), and Ir(111), the work functions of which are

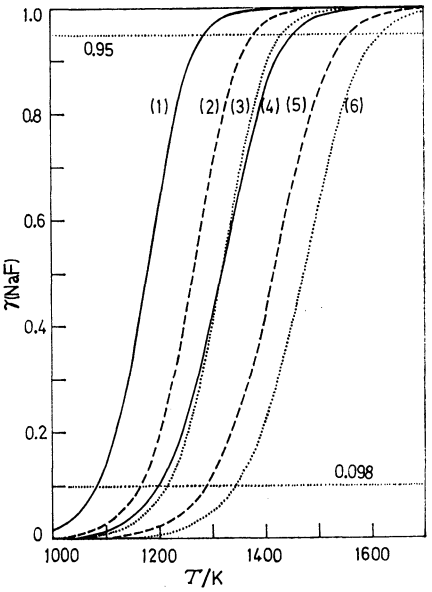

Fig. 1. Temperature dependence of the degree of dissociation of NaF on several surfaces.
Curves (1), (2), and (3); $N(\mathrm{NaF}) = 10^{10}$ molecules $\mathrm{cm^{-2}\,s^{-1}}$ on the surfaces of Ir(111), W(110), and W(100) or Mo(100), respectively. Curves (4), (5), and (6); $N(\mathrm{NaF}) = 10^{12}$ molecules $\mathrm{cm^{-2}\,s^{-1}}$ on the surfaces of Ir(111), W(110), and W(100) or Mo(100), respectively.

TABLE 1. THE BOUNDARY TEMPERATURES ($T_{0.098}$ AND $T_{0.95}$) CORRESPONDING TO γ(NaF) =0.098 AND 0.95, RESPECTIVELY, UNDER VARIOUS EXPERIMENTAL CONDITIONS.

Surface	ϕ / kcal mol^{-1}	α^+(NaF)[a]	Eq.[b]	N(NaF) / molecules cm^{-2} s^{-1}	Curve in Fig. 1	$T_{0.098}$ / K	$T_{0.95}$ / K
Mo(100)	100	1×10^{-4}—3×10^{-3}	48	10^{10}	(3)	1220	1430
				10^{12}	(6)	1340	1620
W(100)	105	1×10^{-3}—1×10^{-2}	48	10^{10}	(3)	1220	1430
				10^{12}	(6)	1340	1620
W(110)	124	7.8—2.7	49	10^{10}	(2)	1170	1380
				10^{12}	(5)	1290	1560
Ir(111)	132	300—25	50	10^{10}	(1)	1080	1280
				10^{12}	(4)	1200	1450

a) The values of α^+(NaF) calculated for 1100—1800 K by using Eq. 16. b) The equation employed to evaluate the boundary temperatures.

100,[15] 105,[15] 124,[16] and 132[17] kcal mol^{-1}, respectively. Since I(Na) is 118 kcal mol^{-1}, it is concluded from Eq. 16 in the usual temperature range (1100—1800 K) that α^+(NaF)$\ll$1 for both Mo(100) and W(100), that α^+(NaF)$\gg$1 for Ir(111), and that α^+(NaF) is intermediate for W(110). The values of γ(NaF) at various temperatures are calculated with the above surfaces by using Eqs. 48—50. The thermochemical data for $\Delta S°$(Na), $\Delta S°$(NaF), and D(NaF) are cited from Refs. 18 and 19. The results thus obtained for γ(NaF) are shown in Fig. 1. The boundary temperatures ($T_{0.098}$ and $T_{0.95}$) corresponding to γ(NaF)=0.098 and 0.95, respectively, at N(NaF)=10^{10} or 10^{12} molecules cm^{-2} s^{-1} may be read off in Fig. 1. The temperatures thus evaluated are summarized in Table 1, which shows that both $T_{0.098}$ and $T_{0.95}$ depend upon N(NaF) and also upon α^+(NaF) unless α^+(NaF) is much smaller than unity. The three temperature regions ($T\lesssim T_{0.098}$, $T_{0.098}<T<T_{0.95}$, and $T\gtrsim T_{0.95}$) are hereafter referred to as T_L, T_M, and T_H, respectively. As may be seen in Fig. 1, γ(NaF) at $T\gtrsim$1700 K is essentially constant at about unity without depending upon both N(NaF) and the nature (ϕ) of the ionizing surface employed. In the temperature range below about 1600 K, however, γ(NaF) at N(NaF)=constant depends upon ϕ unless α^+(NaF)$\ll$1, as already stated above.

Therefore, the following results (A)—(C) are obtained when the present theory as to molecular beam surface ionization is applied to the above sample–surface systems at N(NaF)=10^{12} molecules cm^{-2} s^{-1}.

(A) For the NaF-Ir(111) system where α^+(NaF)$\gg$1,

$$i^+(\mathrm{NaF}) \approx \begin{cases} C_3 \text{ at } T_\mathrm{H} \gtrsim 1450\ \mathrm{K}. & (38) \\ C_4\, T^{-1/2}\, \mathrm{F}(T) \exp\left[\dfrac{-\Delta H_2}{R\,T}\right] & \\ \quad \text{at } 1450 > T_\mathrm{M} > 1200\ \mathrm{K}. & (35) \\ C_5\, T^{-1/4} \exp\left[\dfrac{-\Delta H_2}{2\,R\,T}\right] \text{ at } T_\mathrm{L} \lesssim 1200\ \mathrm{K}. & (39) \end{cases}$$

(B) For the NaF-Mo(100) or NaF-W(100) system where α^+(NaF)$\ll$1,

$$i^+(\mathrm{NaF}) \approx \begin{cases} C_6 \exp\left[\dfrac{-\Delta H_1}{R\,T}\right] \text{ at } T_\mathrm{H} \gtrsim 1620\ \mathrm{K}. & (41) \\ C_4\, T^{-1/2}\, \mathrm{F}(T) \exp\left[\dfrac{-\Delta H_2}{R\,T}\right] & \\ \quad \text{at } 1620 > T_\mathrm{M} > 1340\ \mathrm{K}. & (35) \\ C_7\, T^{-1/4} \exp\left[\dfrac{-\Delta H_1-\Delta H_2}{2\,R\,T}\right] & \\ \quad \text{at } T_\mathrm{L} \lesssim 1340\ \mathrm{K}. & (42) \end{cases}$$

(C) For the NaF-W(110) system where neither α^+(NaF)$\gg$1 nor α^+(NaF)$\ll$1,

$$i^+(\mathrm{NaF}) \approx \begin{cases} C_6\, \mathrm{G}(T) \exp\left[\dfrac{-\Delta H_1}{R\,T}\right] \text{ at } T_\mathrm{H} \gtrsim 1560\ \mathrm{K}. & (45) \\ C_4\, T^{-1/2}\, \mathrm{F}(T) \exp\left[\dfrac{-\Delta H_2}{R\,T}\right] & \\ \quad \text{at } 1560 > T_\mathrm{M} > 1290\ \mathrm{K}. & (35) \\ C_7\, T^{-1/4}\, \mathrm{G}(T)^{1/2} \exp\left[\dfrac{-\Delta H_1-\Delta H_2}{2\,R\,T}\right] & \\ \quad \text{at } T_\mathrm{L} \lesssim 1290\ \mathrm{K}. & (46) \end{cases}$$

Characteristics of the Emission Plots. All of the factors C_1—C_7 in the above equations are virtually independent of T because, σ, ρ, and $\Delta S°$ may be regarded constant in a narrow temperature range usually covered in positive surface ionization and also because N is usually kept constant throughout the course of a run. On the other hand, both F(T) and G(T) depend upon T. The characteristics of an emission plot (log i^+(M) *vs.* 1/T) for atomic beam surface ionization is already outlined below Eq. 8. Similarly those for molecular beam surface ionization will be summarized in this section.

Equation 35 indicates that an emission plot of log[i^+(MX) $T^{1/2}$] *vs.* 1/T does not yield a straight line in the region T_M, irrespectively of the value of α^+(MX). Also when α^+(MX) is neither much smaller nor much larger than unity, no straight line is obtained in any temperature range if log i^+(MX) or log[i^+(MX) $T^{1/4}$] is plotted against 1/T, as may readily be understood from Eq. 45 or 46. In the case of α^+(MX)$\ll$1, on the other hand, the emission plots (log i^+(MX) *vs.* 1/T and log[i^+(MX) $T^{1/4}$] *vs.* 1/T) owing to Eqs. 41 and 42, respectively, yield straight lines except in T_M so long as ϕ is constant in the temperature range covered in a run. The gradients of the plots are equal to $-(0.434/R)\times\Delta H_1$ and $-(0.434/R)(\Delta H_1+\Delta H_2)/2$ in the ranges T_H and T_L, respectively. Similarly the gradients in the case α^+(MX)$\gg$1 are constant for a constant value of ϕ and are equal to null and $-(0.434/R)\,\Delta H_2/2$ in T_H and T_L, as may be proved from Eqs. 38 and 39, respectively. In any case, therefore, the gradient of an emission plot (log[i^+(MX) T^n] *vs.* 1/T where n=0, 1/4, or 1/2) is never equal to $-(0.434/R)\,\Delta H_2$ in any temperature range. If log[i^+(MX) $T^{1/2}$/F(T)] instead of log[i^+(MX) $\times\,T^{1/2}$] is plotted against 1/T, on the other hand, a straight line is obtained even in T_M when ϕ is constant, and its gradient is equal to $-(0.434/R)\,\Delta H_2$, as may readily be concluded from Eq. 35. In a similar way, straight lines with a different slope are obtained in T_H and T_L if log[i^+(MX)/G(T)] and log[i^+(MX) $T^{1/4}$/G(T)$^{1/2}$] are plotted against 1/T according to Eqs. 45 and 46, respectively. For making the plots, however, the accurate values of N(MX), ΔH_2, $\Delta S°$(MX), and $\Delta S°$(M) and of ΔH_1 and $\Delta S°$(M) are required to evaluate F(T) and G(T), respectively.

These characteristics of the above various emission plots should be taken into consideration when an experiment of molecular beam surface ionization is made to confirm the present theory or to determine ϕ, I(M), or D(MX).

Experimental Confirmation of the Present Theory. In this section the conclusions derived theoretically in this work will be compared with experimental results obtained by other workers in order to verify the present theory.

When α^+(MX) is much larger than unity and also γ(MX) is essentially unity, β^+(MX) defined by Eq. 21 is virtually unity and hence i^+(MX) is independent of T, just as concluded by Eq. 38. This conclusion may be supported strongly by the experimental result that i^+(MX) is essentially constant in a high temperature region when a molecular beam of alkali halide (KCl, KBr, KI, or CsCl) impinges upon a surface of Re[13] or Pt.[20]

In the cases other than both $\alpha^+(\mathrm{MX})\gg1$ and $\gamma(\mathrm{MX})\approx1$, the characteristics of the plots described in the preceding section may afford a quite simple method to experimentally confirm the present theory. Namely, the gradient determined experimentally under a certain condition (*e.g.*, $\alpha^+(\mathrm{MX})\gg1$ and $\gamma(\mathrm{MX})\ll1$) may be expected virtually equal to the value (*e.g.*, $-(0.434/R)\,\Delta H_2/2$) predicted by the corresponding theoretical conclusion (*e.g.*, Eq. 39).

When atomic and molecular beams including a common alkali element (Li, Na, or K) impinges separately upon the same polycrystalline surface (Re, Ir, or Pt), the temperature dependence of $i^+(\mathrm{MX})$ shows a strong resemblance to that of $i^+(\mathrm{M})$ in a region above a certain temperature (T_C).[20—22] A similar result is obtained with potassium halide–tungsten systems.[23] These results may suggest with the region that (a) $\gamma(\mathrm{MX})$ is approximately unity, (b) the temperature dependence of both $i^+(\mathrm{MX})$ and $i^+(\mathrm{M})$ is governed by the common Boltzmann factor including ΔH_1, and hence (c) $i^+(\mathrm{MX})$ is expressed by Eq. 41 or 45 at $T\gtrsim T_\mathrm{C}$. Below T_C, on the other hand, a large difference in temperature dependence appears between $i^+(\mathrm{MX})$ and $i^+(\mathrm{M})$, and this difference is concluded to arise from incomplete dissociation of MX.[21,22] Unfortunately the experimental data reported in Refs. 20—23 are not available enough to obtain a definite answer to the question whether the gradient of the emission plot such as $\log[i^+(\mathrm{MX})\ T^{1/2}/\mathrm{F}(T)]$ *vs.* $1/T$ or $\log[i^+(\mathrm{MX})\ T^{1/4}]$ *vs.* $1/T$ is equal to that predicted by the present theory. Firstly because the accurate value of ϕ below T_C is unknown, and secondly because the quantitative relation between $i^+(\mathrm{MX})$ and T in each run is not described in detail but is shown roughly in a figure where a relative value of $i^+(\mathrm{MX})$ is plotted against T. In addition, the comparison of T_C with $T_{0.95}$ is not useful for confirming experimentally the present theory because there is no evidence that the value of ϕ in the ranges both above and below T_C is constant and also identical between the atomic and molecular beam surface ionizations. The workers[20—23] have neither employed single crystal surfaces nor tried to plot $\log[i^+(\mathrm{MX})\ T^n]$ against $1/T$ for each of the sample–surface systems under study. Accordingly, they seem to have eliminated the possibility of finding the following consequences (a)—(c); when ϕ remains unchanged in the whole temperature range investigated in a run, (a) the plot shows a line having constant, inconstant, and constant gradients in the high, middle, and low temperature regions (T_H, T_M, and T_L), respectively, and hence (b) the quantitative expression of $i^+(\mathrm{MX})$ changes according to the condition $\gamma(\mathrm{MX})\gtrsim0.95$, $0.95>\gamma(\mathrm{MX})>0.098$, or $\gamma(\mathrm{MX})\lesssim0.098$, and also (c) the boundary temperatures ($T_{0.95}$ and $T_{0.098}$) depend largely upon $D(\mathrm{MX})$ and $N(\mathrm{MX})$ in the case $\alpha^+(\mathrm{MX})\ll1$ but strongly upon ΔH_2 and $N(\mathrm{MX})$ in the case $\alpha^+(\mathrm{MX})\gg1$.

It should be emphasized that a clean surface of single crystal is homogeneous with respect to ϕ and that the value of ϕ effective for thermal positive ion emission is equal to that for thermal electron emission, in contrast to a polycrystalline surface.[8,12,17,24] Therefore, the possible dependence of ϕ upon T during sample beam incidence upon the single crystal surface under study may be checked definitely by monitoring electron emission current soon after and/or before running positive surface ionization. In other words, the value of ϕ or its change may be determined from a Richardson plot without depending upon any datum obtainable from a Saha-Langmuir plot. This merit of single crystal over polycrystal may be quite helpful for confirming experimentally the theoretical predictions made in this work.

In conclusion, none of the published experimental data that are known to the present authors is available for confirming sufficiently the present theory as to the temperature dependence of $i^+(\mathrm{MX})$ especially in the region $T<T_{0.95}$.

Conclusions

The theoretical investigation described above may be summarized as follows:

(1) In usual positive surface ionization where $N(\mathrm{MX})$ is kept constant during the study of temperature dependence, the quantitative expression of $i^+(\mathrm{MX})$ varies according to the values of both $\gamma(\mathrm{MX})$ and $\alpha^+(\mathrm{MX})$, and hence to the temperature region T_L, T_M, or T_H.

(2) When $\alpha^+(\mathrm{MX})\gg1$ and also $\gamma(\mathrm{MX})\ll1$, $i^+(\mathrm{MX})$ is a function of both $T^{-1/4}$ and the Boltzmann factor, the numerator of which is not $-\Delta H_2$ but $-\Delta H_2/2$. Consequently, the gradient of an emission plot ($\log[i^+(\mathrm{MX})\ T^{1/4}]$ *vs.* $1/T$) in the region T_L is equal to $(0.434/R)\{\phi-I(\mathrm{M})-D(\mathrm{MX})\}/2$.

(3) In such a high temperature region that $\gamma(\mathrm{MX})$ may be estimated to be essentially unity, it is not ΔH_2 but ΔH_1 that is included in the Boltzmann factor governing the production of M^+ from MX, and hence temperature dependence of $i^+(\mathrm{MX})$ is essentially the same to that of $i^+(\mathrm{M})$ when ϕ is virtually identical between the atomic and molecular beam surface ionizations under study.

(4) When both $\alpha^+(\mathrm{MX})\ll1$ and $\gamma(\mathrm{MX})\ll1$, $i^+(\mathrm{MX})$ is proportional to both $T^{-1/4}$ and the Boltzmann factor, the numerator of which is neither $-\Delta H_1$ nor $-\Delta H_2$ but is $-(\Delta H_1+\Delta H_2)/2$. In consequence, the gradient of a plot ($\log[i^+(\mathrm{MX})\ T^{1/4}]$ *vs.* $1/T$) is equal to $(0.434/R)\times\{\phi-I(\mathrm{M})-D(\mathrm{MX})/2\}$.

(5) When neither $\gamma(\mathrm{MX})\approx1$ nor $\gamma(\mathrm{MX})\ll1$, $i^+(\mathrm{MX})$ cannot be expressed by a simple equation, and a plot ($\log[i^+(\mathrm{MX})\ T^{1/2}]$ *vs.* $1/T$) does not show a straight line in the region T_M even if $\alpha^+(\mathrm{MX})\gg1$ or $\alpha^+(\mathrm{MX})\ll1$.

(6) When neither $\alpha^+(\mathrm{MX})\gg1$ nor $\alpha^+(\mathrm{MX})\ll1$, $i^+(\mathrm{MX})$ is not expressed in a simple form, and hence the gradient of a plot ($\log[i^+(\mathrm{MX})\ T^n]$ *vs.* $1/T$ where $n=0$, $1/2$, or $1/4$) is not constant in any temperature region (T_H, T_M, or T_L).

(7) Under any condition the gradient of a plot ($\log[i^+(\mathrm{MX})\ T^n]$ *vs.* $1/T$) is never equal to $-(0.434/R)\times\Delta H_2$.

(8) Under the condition that (a) $\alpha^+(\mathrm{MX})\gg1$ and

$\gamma(MX) \ll 1$, (b) $\alpha^+(MX) \ll 1$ and $\gamma(MX) \approx 1$, or (c) $\alpha^+(MX) \ll 1$ and $\gamma(MX) \ll 1$, either ϕ or $I(M)$ can be determined from the gradient (G) of a plot ($\log[i^+(MX) \times T^n]$ *vs.* $1/T$) while such a determination in atomic beam surface ionization is available only at $\alpha^+(M) \ll 1$. Determination of $D(MX)$ from G, however, can be made under the condition (a) or (c) alone.

(9) For $\alpha^+(MX) \ll 1$, $\gamma(MX)$ is essentially independent of the value of $\alpha^+(MX)$. In any other cases, however, $\gamma(MX)$ increases with increase in $\alpha^+(MX)$.

To the best of the present authors' knowledge, neither theoretical nor experimental investigation arriving at the above conclusions (1)—(9) except (3) has yet been carried out.

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