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Non-uniformity in Surface Properties of a Thick Potassium Fluoride Layer-Platinum Substrate System and Influence of the Non-uniformity upon Thermal Positive and Negative Ion Emission*

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The emission of thermal positive ion (K^+), negative ion (F^-) and of neutral molecules (mainly KF) from a KF -Pt system is investigated as a function of both surface temperature (T) and mean sample layer thickness ($\bar{\theta}$). Thermochemical analysis of the results obtained indicates that K^+ , F^- and KF are emitted from respectively different surface sites ($Q(K^+)$, $Q(F^-)$ and $Q(KF)$) of the system. The actual surface areas ($S(K^+)$, $S(F^-)$ and $S(KF)$) for the emission of K^+ , F^- and KF from the respective sites are found to be quite different from the apparent surface area. $S(KF)$ is strongly dependent upon $\bar{\theta}$ in contrast to $S(K^+)$. Both $S(K^+)$ and $S(F^-)$ are estimated to be smaller by a factor of at least 10^2 than $S(KF)$. The difference in average effective work function between the active sites $Q(K^+)$ and $Q(F^-)$ is evaluated to be about 3 eV at $\bar{\theta} \simeq 10^2$ molecular layers at $T \simeq 700-750^\circ K$.

1. Introduction

Thermal positive ion emission from systems of thick polycrystalline layers of potassium fluoride coated on a metal surface has been investigated as a function of surface temperature, sample layer thickness, residual gas pressure, and the species of substrate metal.¹⁾⁻³⁾ The results thus obtained indicate that some of the positive

ion emission patterns observed with the above *coated* systems are quite different from those with a usual *incident* system where sample molecules are impinged upon a glowing metal surface, and also suggest that Saha-Langmuir's equation is not applicable to the thick layer systems. In order to elucidate the mechanism of thermal positive or negative ion emission from such a thick layer system, it seems necessary to

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estimate the degrees of both non-uniformity in physico-chemical surface properties of the system and influence of the non-uniformity upon thermal ion emission from the system. As some of the measures of this non-uniformity, the following three factors are adopted in this work; (1) the actual surface area for neutral or ionic emission, (2) evaporation coefficient for a neutral molecule or an ion, and (3) average work function effective for positive or negative ionic emission. These factors have been studied with a KF-Pt system as a function of both surface temperature and number density of the sample molecules present on the substrate metal surface. The results thus obtained suggest that the emitting surface is composed of patchy faces of different work functions and that positive-ionic, negative-ionic and neutral emission occurs on respectively different faces of the thick layer system.

This paper describes the above results and a patchy face model, on the basis of which a mechanism of the ion emission is briefly discussed.

2. Experimental Method

In this work was used a specially designed dual ion source,²⁾ which has a platinum ribbon (F-1) and a platinum wire (F-2) functioning as substrate metal and a neutral vapor detector, respectively, and also has a grid (G) between F-1 and F-2 in order to retard the ions emitted from F-1 or F-2. Both of the walls surrounding F-1 and F-2 were cooled to about 274 °K by circulating ice water lest the sample molecules gradually accumulating on the walls should evaporate again. The poten-

tials (V_1 , V_2 and V_G) applied to F-1, F-2 and G were 4.0 (or -4.0 for negative ion emission), 4.0 and 10.0 volts, respectively, with regard to the surrounding walls, all of which were connected to the earth through a microammeter. With a hypodermic microsyringe, 1.00 μ l of an aqueous solution of KF (0.0746 mole/l) was transferred only to F-1 (1.0 mm in width and 2.0 mm in length) in order to limit the coating area (S_c) exactly to 0.020 cm², and it was dried in an air bath at about 350 °K. Therefore, the initial number (N_0) of the sample molecules coated on F-1 in each run is 4.49×10^{16} . The temperature of F-2 is 1258 °K, at which F-2 was found to have no effect upon ionic and neutral emission from F-1.²⁾ In order to keep F-2 from changing in neutral vapor detection efficiency, the residual gas pressure (P_r) around the ion source region was maintained at about 2×10^{-7} Torr throughout the course of measurements in each run. Temperature (T) of F-1 was measured by using a calibrated chromel-alumel thermocouple.

In this way, primary (positive or negative) and secondary (positive) ion currents ($i_1^\pm$ and i_2^+) emitted from F-1 and F-2, respectively, were separated at high efficiency without employing any additional separator, and simultaneously measured at a given temperature of F-1 by using two vibrating reed electrometers. At such a low temperature as below 800 °K, thermal electron current was too weak to be detected with one of the electrometers having a maximum sensitivity of 1×10^{-16} A per scale division.

Ionic and neutral emission rates ($n^\pm$ and n^0) were evaluated from Eqs. (1) and

(2), respectively.

$$n^{\pm} = \frac{i_1^{\pm}}{e\gamma_1^{\pm}}. \quad (1)$$

$$n^0 = \frac{i_2^+}{e\gamma_2^+}. \quad (2)$$

Here, e is the elementary electric charge, and $\gamma_1^{\pm}$ and γ_2^+ are the collection efficiency (about 0.41) of the primary positive (or negative) ions and the detection efficiency (about 4×10^{-5} , fluctuant up to about $\pm 50\%$ from run to run) of the neutral molecules, respectively, evaporating from F-1. Both of the efficiencies were directly determined by the methods described in Ref. 2.

The number (N_r) of the sample molecules remaining on F-1 at the time (t) that had elapsed after F-1 was heated at various temperatures is given by

$$N_r = N_0 - \sum_t n^{\pm} \cdot t - \sum_t n^0 \cdot t \simeq N_0 - \sum_t n^0 \cdot t. \quad (3)$$

At $T < 770^\circ\text{K}$, N_r was found to be kept virtually constant for longer than an hour, and hence it was intermittently decreased by heating F-1 at $T \gtrsim 810^\circ\text{K}$ for several minutes or more. The average layer thickness ($\bar{\theta}$) of potassium fluoride on F-1 is estimated from Eq. (4)²⁾

$$\bar{\theta} \simeq 3.56 \times 10^{-14} N_r \text{ molecular layers}. \quad (4)$$

In this way, both n^+ (or n^-) and n^0 were simultaneously measured as a function of T and N_r (or $\bar{\theta}$).

3. Results and Discussion

3.1. Neutral Emission

An example of the dependence of both n^0 and n^+ upon N_r at several temperatures is shown in Fig. 1, the data of which were

obtained in the same run by alternating the following procedures (a) and (b).

(a) In a usual range between about 650 and 750 °K, T was gradually increased or decreased at about 5 °K intervals, and both i_1^+ and i_2^+ were simultaneously measured. Both of the currents were nearly constant in time while T was kept constant.

(b) In order to decrease N_r intermittently, T was held at about 820 °K for several minutes or more.

Fig. 1. Dependence of the positive-ionic and neutral emission rates (n^+ and n^0) and of the neutral evaporation parameter ($W(\text{KF})$) upon the sample density (N_r) on the substrate metal surface, where n^+ , n^0 , N_r , and $W(\text{KF})$ are evaluated from Eqs. (1), (2), (3), and (8), respectively. The curves A, B, and C correspond to n^0 , n^+ , and $W(\text{KF})$, respectively, and the subscripts 1, 2, and 3 refer to 650, 700, and 750 °K, respectively.

With decreasing N_r at a given value of T , n^0 decreases sharply, in contrast to n^+ , as shown in Fig. 1. This result indicates that a condition of the surface from which the neutral molecules evaporate changes remarkably according to change in N_r . The evaporation parameter (W) which is the product of the evaporation coefficient (ε) and the actual surface area (S) is adopted as one of the measures defining the surface condition. The results obtained for N_r -dependence of the parameter will be described together with a brief discussion in this section.

When molecules (X) evaporate from crystals directly into vacuum, the evaporation rate is given by

$$J(X) = W(X) \cdot P(X) \cdot N [2\pi \cdot M(X) \cdot R \cdot T]^{-1/2}. \quad (5)$$

Here, N is Avogadro's number; R the gas constant; $M(X)$ the molecular weight of X ; and $P(X)$ the equilibrium vapor pressure to be observed when an equilibrium concerning X holds between gaseous and condensed phases inside of an isothermal enclosure such as a Knudsen cell system. When the vapor under study consists of a mixture of monomeric and polymeric molecules, $M(X)$ is replaced with the properly averaged molecular weight ($\overline{M(X)}$). In this work the actual surface area is given by

$$S(X) = f(X) \cdot r \cdot S_0 = 2.0 \times 10^{-2} r \cdot f(X) \text{ cm}^2, \quad (6)$$

where r and $f(X)$ are the roughness factor for the sample layer surface area and the fractional surface area for the emission of X , respectively.

The evaporation coefficient which is

sometimes called condensation coefficient is given by

$$\varepsilon(X) = \frac{p(X)}{P(X)}. \quad (7)$$

Here, $p(X)$ is the crystal vapor pressure to be observed when free evaporation occurs in such an open system as the potassium fluoride layers on a platinum surface in this work. In other words, ε is the ratio of the total flux of molecules per unit area of a crystal surface to that of saturated vapor effusing from an orifice of unit area in an isothermal enclosure at the same temperature as the crystal. With various metals and compounds the values of ε have been measured by many workers and found to widely range from 1 to 10^{-7} depending upon their physico-chemical properties.^{1), 2)}

Since $J(KF)$ can readily be determined as n^0 in this work and also since $P(KF)$ is known to us as shown in Table 1, we can evaluate the evaporation parameter by using Eq. (8), which is derived from Eq. (5).

$$\begin{aligned} W(KF) &\equiv \varepsilon(KF) \cdot S(KF) \\ &= 2.19 \times 10^{-22} \frac{n^0 \cdot T^{1/2}}{P(KF)} \text{ cm}^2. \end{aligned} \quad (8)$$

Here, $P(KF)$ is expressed in Torr unit, and $\overline{M(KF)}$ is estimated to be 59.4 on the basis of published data,³⁾ which indicate that the relative abundance of the dimer K_2F_2 in the potassium fluoride vapor at 650–750 °K ranges from about 1.7 to 3.0 %. As shown in Table 1, the heat of sublimation (ΔH) determined from the slope of a plot ($\ln n^0 \cdot T^{1/2}$ vs. $1/T$) in this work is in good agreement with that obtained with the monomer by other workers, there

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Table 1. Equilibrium vapor pressure (P) and heat of sublimation (ΔH) determined with potassium fluoride by several groups of workers. The figures with * and ** are the values separately determined with monomeric and dimeric molecules, respectively. The other data for ΔH and P were obtained with a mixture of monomer and dimer.

P (μ Torr)		ΔH (eV)		Ref.
650°K	700°K	750°K	298°K	
0.0228	0.471	6.51	2.50 $\pm$ 0.03	14)
0.0019	0.041	0.61	2.49 $\pm$ 0.02*	6)
.....			2.77 $\pm$ 0.03**	6)
0.0041	0.092	1.36	2.557 $\pm$ 0.005	15)
0.0179	0.277	3.02	2.48*	16)
.....			2.79**	16)
.....			2.50 $\pm$ 0.17	This work
0.0117	0.220	2.88		Average
$\pm$ 0.0103	$\pm$ 0.196	$\pm$ 2.62		Deviation

by suggesting that the monomer is the main composition of the neutral molecules emitted from the KF-Pt system. In this paper the average values at the bottom of Table 1 are tentatively adopted as $P(\text{KF})$ in order to evaluate from Eq. (8) the values of $W(\text{KF})$ at the three specified temperatures. The result thus evaluated with nine runs does not clearly indicate that $W(\text{KF})$ at a given value of N_r depends upon T , and suggests that $W(\text{KF})$ should be considered to be rather independent of T within the experimental errors in this work. In the temperature range mentioned above, however, $W(\text{KF})$ strongly depends upon N_r , as shown as the dotted line (C_{1-3}) in Fig. 1, where $W(\text{KF})$ decreases from about 4×10^{-2} to 5×10^{-8} according as N_r decreases from about 4×10^{18} to 7×10^{13} molecules/0.020 cm². This result suggests that the sample layer thickness is non-uniform all over the surface and that $S(\text{KF})$ and possibly also $\varepsilon(\text{KF})$ change largely during the course of measurements

in a given run.

Usually ε depends upon various factors such as crystallographic orientation of an evaporating sample surface, density of crystal dislocation, and purity of sample crystal.¹⁰ The values of ε determined with seven alkali halides by several groups of workers are summarized together with experimental conditions in Table 2. With respect to other alkali halides including KF, ε does not seem to have been measured by any workers. Judging from the data in Table 2, however, it seems unlikely that ε of some alkali halide crystal under a usual condition is smaller than 0.01. Even if $\varepsilon(\text{KF})$ is roughly estimated to fluctuate in a wide range between 1 and 0.01 while $W(\text{KF})$ varies by a factor of 10^6 in the run illustrated in Fig. 1, $S(\text{KF})$ is concluded to change by a factor of at least 10^4 in the above range of N_r . Provided that $\varepsilon(\text{KF})$ is constant at 0.5 throughout the course of the above measurement, then Eqs. (6) and (8) give us the result that

Table 2. Published data for the evaporation coefficient (ε) determined with some alkali halides. The figures with * and ** are the values separately determined with monomeric and polymeric molecules, respectively. The others were obtained with a mixture of monomer and polymers.

Sample	ε	Crystallographic orientation	T (°K)	Ref.
LiF	0.5*	(100)	980 - 1070	17)
	0.6 - 1.0**	(100)	980 - 1070	17)
	0.17	(100)	960 - 1090	9)
	0.75	(?)	950 - 1110	18)
NaCl	0.14 - 0.28*	(100)	874 - 935	17)
	0.10 - 0.22**	(100)	874 - 935	17)
	0.073 - 0.390	(100)	770 - 870	19)
	0.5 - 1.0	(100)	750 - 920	20)
	0.7	(100), (110) or (111)	800 - 940	21)
	0.15	(100), (110) or (111)	1074	21)
	0.74	(?)	830 - 910	18)
	0.78 ± 0.07	(100)	763	13)
	0.72 ± 0.05	(100)	868	13)
KCl	0.72 ± 0.015	(100)	681 - 742	22)
	0.63	(110) and (100)	681 - 742	22)
	0.56	(110)	681 - 742	22)
	0.11 - 0.70	(?)	750 - 870	23)
KBr	0.79	(?)	710 - 790	18)
KI	0.07 - 0.43	(?)	700 - 800	23)
	0.086 - 0.46	(100)	710 - 770	19)
CsBr	0.22 - 0.38	(?)	785 - 830	17)
CsI	0.31 - 0.42	(?)	757 - 772	17)
	0.88	(100), (110) or (111)	660 - 760	18)

$r \cdot f(\text{KF})$ is about 4 and 5×10^{-6} at $N_r \simeq 4 \times 10^{16}$ and 7×10^{13} molecules/ 0.020 cm^2 , respectively, in the range $650 - 750 \text{ }^\circ\text{K}$. Namely, $S(\text{KF})$ remarkably decreases from about 4×10^2 to $5 \times 10^{-4} \%$ of S_e according

to decrease in N_r from about 90 to 0.15% of N_0 . This estimation suggests that r is larger than unity at an early stage ($N_r \gtrsim 70 \%$ of N_0) in the above run.

3.2. Ionic Emission

As shown in Fig. 1, N_r -dependence of n^+ is entirely different from that of n^0 . This result suggests that ionic emission also should be investigated from the viewpoint of ϵ and S , and hence that K^+ and KF are emitted from respectively different sites on the surface. The results achieved in the previous work³⁾ show that KF -Pt and KF -W systems are essentially the same with each other in regard to both positive ionization coefficient (n^+/n^0) and thermochemical properties (work function, for example) of the emitting surface, and hence suggest that K^+ is not emitted from a bare surface of the substrate metal (Pt or W) but emitted from a surface of polycrystalline potassium fluoride or from a face of a part of the dissociation products of potassium fluoride.

The above results and considerations may lead to the conclusion that a patchy face model should be taken into account in order to gain an important clue to a mechanism of ion emission from the non-uniform surface. The characteristics of the model adopted in this work may be summarized as follows:

(1) The sample layer surface under study is composed of a large number (n) of those patchy faces (Q_n) which are mutually different in fractional surface area (f_n) and also in physico-chemical properties such as evaporation coefficient and particularly work function.

(2) Almost all of the positive ions are emitted from those active faces ($Q_i(K^+)$) which have high work functions (ϕ_i). The total area ($r \cdot S_c \cdot \sum_i f_i(K^+) \equiv r \cdot S_c \cdot f(K^+)$)

of the faces and the average work function effective for this emission are hereafter referred to as $S(K^+)$ and $\bar{\phi}^*$, respectively.

(3) On the other hand, it is mainly from the faces ($Q_j(F^-)$) of low values (ϕ_j) that F^- is emitted. Similarly, $S(F^-)$ and $\bar{\phi}^{**}$ are adopted to represent the two important features of these active faces.

(4) The majority of neutral molecules is emitted from inactive faces ($Q_k(KF)$), the average work function ($\bar{\phi}^0$) of which is probably intermediate between $\bar{\phi}^*$ and $\bar{\phi}^{**}$.

(5) Both $\bar{\phi}^*$ and $\bar{\phi}^{**}$ in addition to $W(K^+)$ and $W(F^-)$ depend upon N_r (or $\bar{\theta}$) in a given run because both $Q(K^+)$ and $Q(F^-)$ vary in surface density according to progress in evaporation. All of these factors at a given value of N_r (or $\bar{\theta}$) change greatly in value from run to run because it is extremely difficult or rather virtually impossible to control them. This is the main reason why n^+ and n^- at given values of both N_r (or $\bar{\theta}$) and T are notably poor in reproducibility among different runs.

In order to examine the model mentioned above from the viewpoint of thermochemistry, let us consider Equilibria (9)–(12) existing inside of an isothermal metal enclosure, where the presence of K_2F_2 is neglected because the abundance ratio of K_2F_2 to KF is estimated to be very small, as already mentioned in the previous section.

If the density of the charged particles is so small that space-charge effect may be neglected, then Eqs. (13)–(16) hold with respect to Equilibria (9)–(12), respectively.

$$\frac{P(K^+) \cdot P(F_2)^{1/2} \cdot P(e^-)}{P(KF)} = \frac{Z(K^+) \cdot Z(F_2)^{1/2} \cdot Z(e^-)}{Z(KF)} \times \exp \left[\frac{-2D(KF) - 2I(K) + D(F_2)}{2kT} \right]. \quad (13)$$

$$\frac{P(K) \cdot P(F^-)}{P(KF) \cdot P(e^-)} = \frac{Z(K) \cdot Z(F^-)}{Z(KF) \cdot Z(e^-)} \times \exp \left[\frac{-D(KF) + A(F)}{kT} \right]. \quad (14)$$

$$\frac{P(F)}{P(F_2)^{1/2}} = \frac{Z(F)}{Z(F_2)^{1/2}} \exp \left[\frac{-D(F_2)}{2kT} \right]. \quad (15)$$

$$\frac{P(KF)}{P(K) \cdot P(F)} = \frac{Z(KF)}{Z(K) \cdot Z(F)} \exp \left[\frac{D(KF)}{kT} \right]. \quad (16)$$

Here $P(X)$, $Z(X)$, $D(X)$, $I(X)$, and $A(X)$ are the partial pressure, partition function, dissociation energy, first ionization energy, and electron affinity, respectively, of the particle (X).

Richardson-Dushman's theory on thermal electron emission gives

$$P(e^-) = Z(e^-) \exp \left[\frac{-\phi}{kT} \right], \quad (17)$$

where ϕ is the work function of the wall of the enclosure. Combinations of Eqs. (13), (15) and (17), and of Eqs. (14) and (17) give the following relations.

$$\frac{P(K^+) \cdot P(F)}{P(KF)} = \frac{Z(K^+) \cdot Z(F)}{Z(KF)} \times \exp \left[\frac{-D(KF) - I(K) + \phi}{kT} \right]. \quad (18)$$

$$\frac{P(K) \cdot P(F^-)}{P(KF)} = \frac{Z(K) \cdot Z(F^-)}{Z(KF)} \times \exp \left[\frac{-D(KF) + A(F) - \phi}{kT} \right]. \quad (19)$$

Under the above discussion, the wall of the enclosure is regarded to be uniform

with respect to work function. According to the present model, on the other hand, the emitting surface is composed of many patchy faces of different work functions, as already stated. Therefore, the three of ϕ in Eqs. (17)–(19) are replaced with $\bar{\phi}^e$, $\bar{\phi}^*$, and $\bar{\phi}^{**}$, respectively, where $\bar{\phi}^e$ is the average work function effective for thermal electron emission from various faces ($Q_h(e^-)$). It should be noted that $\bar{\phi}^e$, $\bar{\phi}^*$, and $\bar{\phi}^{**}$ are the same with each other only when all of the faces including $Q_h(e^-)$, $Q_i(K^+)$, and $Q_j(F^-)$ on the emitter are uniform in work function. Such a condition, however, is not satisfied in general with any surface other than a clean surface of a single crystal made up by simple substance. This consideration and also combination of Eqs. (16), (18) and (19) lead up to

$$\frac{P(K^+) \cdot P(F^-)}{P(KF)} = \frac{Z(K^+)}{Z(K)} \cdot \frac{Z(F^-)}{Z(F)} \cdot \frac{Z(K) \cdot Z(F)}{Z(KF)} \times \exp \left[\frac{-D(KF) - I(K) + A(F) + \bar{\phi}^* - \bar{\phi}^{**}}{kT} \right]. \quad (20)$$

The three pre-exponential terms in Eq. (20) can readily be evaluated from published data for $\Delta S^\circ(K)$, $\Delta S^\circ(F)$ and $\Delta S^\circ(KF)$, which are the changes in standard entropy for these processes $K \rightarrow K^+$, $F \rightarrow F^-$ and $KF \rightarrow K + F$, respectively. Since the relation between $P(X)$ and $J(X)$ is represented by Eq. (5), Eq. (21) is derived from Eq. (20).

$$\begin{aligned} \frac{J(K^+) \cdot J(F^-) \cdot T^{1/2}}{J(KF)} &= 1.013 \times 10^6 N \\ &\times \frac{W(K^+) \cdot W(F^-)}{W(KF)} \left[\frac{M(KF)}{2\pi \cdot M(K) \cdot M(F) \cdot R} \right]^{1/2} \\ &\times \exp \left[\frac{\Delta S^\circ(K) + \Delta S^\circ(F) + \Delta S^\circ(KF)}{R} \right] \\ &\times \exp \left[\frac{-D(KF) - I(K) + A(F) + \bar{\phi}^* - \bar{\phi}^{**}}{kT} \right], \quad (21) \end{aligned}$$

where the first term on the right hand side is necessary because all of the entropy changes refer to a standard gaseous state for which $P(X)$ is 1 atm. In the temperature range (about 650 – 750 °K) investigated in this work, the thermochemical values in Eq. (21) are evaluated from published data.^{7),8)} Namely, $\Delta S^\circ(K) = -1.39$ eu, $\Delta S^\circ(F) = -3.44$ eu, $\Delta S^\circ(KF) = 23.41$ eu, $D(KF) = 5.16$ eV, $I(K) = 4.46$ eV, and $A(F) = 3.67$ eV. Since $J(K^+)$, $J(F^-)$ and $J(KF)$ are experimentally determined as n^+ , n^- and n^0 , respectively, in this work, Eq. (21) becomes:

$$\frac{n^+ \cdot n^- \cdot T^{1/2}}{n^0} = 8.66 \times 10^{28} \frac{W(K^+) \cdot W(F^-)}{W(KF)} \times \exp \left[\frac{-5.95 + \bar{\phi}^* - \bar{\phi}^{**}}{kT} \right]. \quad (22)$$

Fig. 2 shows an example of temperature dependence of the emission rates observed at $N_r = 4.0 \times 10^{15}$ molecules/0.020 cm² and hence at $\bar{\theta} = 1.4 \times 10^2$ molecular layers. After simultaneous measurement of n^0 and n^+ , the data of which are expressed with open circles around the lines (1) and (2), respectively, the polarity of V_1 was changed to minus without any change in V_2 and V_6 . Then the data for n^0 and n^- were simultaneously obtained, as shown with solid circles along the lines (1) and (3), respectively. It should be noted that there exists no systematic difference between the two series of the open and solid circles around the line (1), thereby indicating that the measurement of n^0 was not affected by the change in polarity of V_1 and also that N_r remained virtually constant during the above measurements. These plots in Fig. 2 afford the line (4), which is well

Fig. 2. Temperature dependence of the positive-ionic, negative-ionic and neutral emission rates (n^+ , n^- , and n^0) and of the neutral evaporation parameter ($W(KF)$) observed at $N_r = 4.0 \times 10^{15}$ molecules/0.020 cm² or $\bar{\theta} = 1.4 \times 10^2$ molecular layers. The lines (1) - (5) correspond to n^0 , n^+ , n^- , $n^+ \cdot n^- \cdot T^{1/2}/n^0$, and $W(KF)$, respectively.

represented by

$$\frac{n^+ \cdot n^- \cdot T^{1/2}}{n^0} = 2.69 \times 10^{19} \exp \left[\frac{-2.78}{kT} \right]. \quad (23)$$

Therefore, Eqs.(22) and (23) bring out

$$\frac{W(K^+) \cdot W(F^-)}{W(KF)} = 3.11 \times 10^{-10} \text{ cm}^2, \quad (24)$$

and

$$\bar{\phi}^* - \bar{\phi}^{**} = 3.17 \text{ eV}. \quad (25)$$

As shown as the line (5) in Fig. 2, $W(KF)$ evaluated from Eq. (8) changes in the

range $1.4 \times 10^{-4} - 1.8 \times 10^{-4} \text{ cm}^2$ at $T \simeq 700 - 750^\circ\text{K}$, but it may be regarded to be constant at about $1.6 \times 10^{-4} \text{ cm}^2$ by considering the facts that the average values of $P(\text{KF})$ in Table 1 have such a large standard deviation as about $\pm 90\%$ and that n^0 measured at given values of both T and N_r changes from run to run by about $\pm 30\%$ at $\bar{\theta} = 5 \times 10^2$ molecular layers³⁾ or by much larger percentage at a smaller value of $\bar{\theta}$. Substitution of the above mean value into Eq. (24) yields $W(\text{K}^+) \cdot W(\text{F}^-) = 5.0 \times 10^{-14} \text{ cm}^4$, which suggests that both $W(\text{K}^+)$ and $W(\text{F}^-)$ are much smaller than $W(\text{KF})$. Theoretical consideration shows that respective values of $W(\text{K}^+)$ and $W(\text{F}^-)$ cannot be evaluated even if $J(\text{K}^+) / J(\text{K})$ or $J(\text{F}^-) / J(\text{F}_2)$ instead of $J(\text{K}^+) / J(\text{KF})$ or $J(\text{F}^-) / J(\text{KF})$ is successfully measured as a function of T . Assuming that $\varepsilon(\text{K}^+)$, $\varepsilon(\text{F}^-)$ and $\varepsilon(\text{KF})$ at $N_r \simeq 10^{15}$ molecules/ 0.020 cm^2 lie within the interval from 0.1 to 1.0, then both $S(\text{K}^+)$ and $S(\text{F}^-)$ at $\bar{\theta} \simeq 10^3$ molecular layers may be estimated to be smaller by a factor of at least 10^2 than $S(\text{KF})$, and hence both $f(\text{K}^+)$ and $f(\text{F}^-)$ under the above condition may be evaluated to be less than 1% of $f(\text{KF})$.

Several investigations indicate that non-stoichiometry exists at the surface of alkali halides,⁹⁾ and it seems quite likely that a part of the emitting surface under study is composed of the dissociation products (potassium and fluorine of ionic or neutral state) of potassium fluoride, as already mentioned above. If all of the coefficients of $\varepsilon(\text{K}^+)$, $\varepsilon(\text{F}^-)$, $\varepsilon(\text{K})$, $\varepsilon(\text{F})$, $\varepsilon(\text{F}_2)$ and $\varepsilon(\text{KF})$ are not the same with each other, then surface composition of the sample

layers may possibly result in a greater deviation from stoichiometry during the course of evaporation, and hence such active sites as $Q(\text{K}^+)$ and $Q(\text{F}^-)$ probably increase in surface density. This conjecture may be supported by the example shown in Fig. 2, where measurement of n^- at such a low temperature as about 710°K was successfully performed after F-1 coated with KF was heated at 810°K for 65 minutes at $V_1 = +4.0$ volts, and the ratio n^-/n^+ is about 5×10^{-3} at 710°K . As already stated in the previous papers,^{1),2)} usually i_1^- can hardly be detected below about 770°K . Therefore, the above pre-heating, during which N_r decreased from 100 to about 9% of N_0 , seems to result in increasing $S(\text{F}^-)$ and/or decreasing $\bar{\phi}^{**}$, thereby promoting negative ion emission. Much more work, however, must be done in order to gain definite information on the correlation between the active sites and non-stoichiometry of the sample layer surface.

Eq. (25) indicates that there exists a large difference between the two average effective work functions. This difference is much larger than the experimental error (about $\pm 1 \text{ eV}$) observed from run to run in this work. It is well known that work function of a clean metallic emitter depends upon crystallographic orientation of the emitting surface. Tungsten, for example, is reported to range in ϕ from about 4.3 to 5.8 eV, and a well aged polycrystalline tungsten surface is about 4.5 eV in $\bar{\phi}^0$.¹⁰⁾ Judging from data obtained with *incident* systems,¹¹⁾ the average work function ($\bar{\phi}^-$) effective for negative ion emission seems to be virtually equal to $\bar{\phi}^0$. Another example observed with *incident* systems shows that

the average work function ($\bar{\phi}^+$) effective for positive ion emission from a polycrystalline surface of Mo, Ta, W or Re is higher by about 0.5 – 0.7 eV than $\bar{\phi}^0$,¹²⁾ and hence suggests that $\bar{\phi}^+ - \bar{\phi}^- \simeq 0.6$ eV in the above cases. This difference is much smaller than that between $\bar{\phi}^*$ and $\bar{\phi}^{**}$ observed in this work. On the other hand, $\bar{\phi}^+$ and $\bar{\phi}^-$ of the surface of a thick potassium fluoride layer-substrate metal system or of potassium fluoride crystals, upon which sample molecules or atoms are impinged, do not seem to have been determined by any workers. At present, therefore, we have no reference datum to be compared with the result given by Eq. (25), and also no clue to the question whether $\bar{\phi}^*$ and $\bar{\phi}^{**}$ are the same in value with $\bar{\phi}^+$ and $\bar{\phi}^-$, respectively.

The previous work shows that both n^+ and n^0 are essentially independent of the nature of substrate metal at $\bar{\theta} \simeq 5 \times 10^2$ molecular layers and that n^+ and n^0 vary by about ± 70 and ± 30 %, respectively, from run to run.³⁾ Application of the patchy face model to this result offers us helpful suggestions as follows.

- (1) The density of the active faces $Q(K^+)$ is independent of the nature of substrate metal at $\bar{\theta} \gg 1$ molecular layer.
- (2) At a given value of $\bar{\theta}$, both $Q(K^+)$ and $Q(KF)$ markedly change in surface density from run to run. This is probably inherent in coating the aqueous sample solution in each run.
- (3) Both $S(K^+)$ and $\bar{\phi}^*$ are apt to vary more greatly from run to run than both $S(KF)$ and $\bar{\phi}^0$.

In the preliminary experiment²⁾ i_1^+ was found to remarkably increase according as the residual gas pressure (P_r) increased

from about 1×10^{-5} Torr, below which i_1^+ was essentially independent of P_r . This result suggests that $W(K^+)$ and/or $\bar{\phi}^*$ can be greatly changed by adsorption of foreign gas molecules. Therefore, measurement of i_1^+ , i_1^- and i_2^+ as a function of the pressure of introduced foreign gas such as oxygen may give us useful information as to the natures of respective emission sites on the sample layer system. From this point of view, an experimental study is now in progress.

4. Conclusions

The essence of the results obtained in this work may be summarized by the following statements.

- (1) The emitting surface of the thick potassium fluoride layer-platinum substrate system is quite far from uniformity in physico-chemical properties. It is composed of many patchy faces, which are mutually different in work function and probably also in evaporation coefficient.
- (2) Positive and negative ions and neutral molecules are emitted from respectively different faces, both the actual areas and the average effective work functions of which remarkably change from run to run and also vary during the course of emission in a given run.
- (3) The total area of those active faces from which positive or negative ions are emitted is much smaller than that of the inactive faces from which virtually neutral molecules alone evaporate.
- (4) At $\bar{\theta} \simeq 10^2$ molecular layers the average work function effective for positive ion emission is larger by about 3 eV than that for negative ion emission.

References and Notes

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Keywords

Thermal ion emission
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