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**Influence of Sample Species upon the Positive Lithium Ion Production
from Lithium Halides Incident on a Glowing Tungsten Surface**

INTRODUCTION

When a sample molecule (MX) including an atom (M) with a relatively low ionization energy (I) is impinged upon a positively-biased glowing metal surface, a positive ion (M^+) is emitted after attaining to thermal equilibria ($MX \rightleftharpoons M + X$ and $M \rightleftharpoons M^+ + e^-$) on the surface. This phenomenon, usually termed positive surface ionization (PSI), has long been treated as a very interesting subject to study physico-chemical processes occurring on solid surfaces and to determine thermochemical properties of impinging molecules and their fragments. In addition, it has been widely utilized as one of the most convenient techniques to generate ion beams, to detect neutral beams, to analyze chemical or nuclear reaction products, to monitor air pollutants, to determine the isotopic ratios of nuclear fuels, and so on [1-3]. The mechanism of PSI, however, has not yet been fully understood. Therefore, further work is necessary to clarify the mechanism in more detail and also to establish the practical method by which the best condition for operating a PSI type ion source may readily be selected.

From the viewpoint mentioned above, we have been studying PSI both experimentally and theoretically. Namely, the emission current (I^+) of thermal positive ion M^+ (Li^+ , Na^+ , K^+ , Cs^+ or Tl^+) produced from either (1) alkali halide molecule MX (LiF , $LiCl$, $LiBr$, LiI , $NaCl$, $NaBr$, NaI , KCl , CsF or $CsCl$) impinging upon a polycrystalline surface of Re [4-22], (2) MX ($NaCl$, $NaBr$, NaI or KCl) or $TlCl$ upon W [20-24], or (3) $NaCl$ upon Ta [20] has been measured as a function of either (1) surface temperature ($T \simeq 900 - 2400$ K) [4-9,11-14,17,20-24], (2) incident sample beam flux ($N \simeq 10^{11} - 10^{14}$ molecules $cm^{-2}s^{-1}$) [15-17], (3) elapsed time ($t \simeq 0 - 10$ min) after flashing the surface at a high temperature with a beam shutter closed [4,6,10,11,13,18,19], or (4) residual gas pressure ($P_r \simeq 10^{-7} - 10^{-5}$ Torr) around the surface [13,14,20,22], in order to find all of the factors governing the ionization efficiency (β^+) of each sample molecule and also to clarify the quanti-

tative relation between β^+ and the factors. Since the sticking probability (σ) [2] of MX to an ionizing surface heated in high vacua is usually regarded as unity [4,13,21], β^+ is given by the product of γ and ε^+ , where γ is the degree of dissociation of MX and ε^+ is that of ionization of M. Temperature dependence of β^+ for NaCl on W at $P_r \simeq 2 \times 10^{-7}$ Torr is exemplified in Fig. 1A. Theoretical analysis of the data therein yields the results on the effective work function (ϕ^+) for PSI, as shown in Fig. 1B and Table 1 [23]. Here, $T_1 - T_3$ are the boundary temperatures around which ϕ^+ and hence β^+ begin to show a considerable or drastic change with an increase or decrease in T . Consideration of our experimental data and analytical results achieved to date leads to the following conclusions.

Table 1. Summary of the data obtained with an NaCl/W system under the residual gas pressure of $\sim 2 \times 10^{-7}$ Torr (see Fig. 1)

Curve	Flux (N ; molecules $\text{cm}^{-2}\text{s}^{-1}$)	Effective work function (ϕ^+ ; eV)							Boundary temperature (K)		
		1000K	1200K	1400K	1600K	1800K	2000K	2200K	T_1	T_2	T_3
(1)	1.60×10^{13}	6.40	6.51	6.16	5.72	5.45	5.22	5.23	1250	1395	~ 1950
(2)	3.10×10^{13}	6.25	6.47	—	5.76	5.48	5.22	5.22	1280	1410	~ 1950
(3)	7.35×10^{13}	6.22	6.44	—	5.75	5.41	5.20	5.22	1325	1415	~ 1950
(4)	2.20×10^{14}	6.13	6.40	—	5.81	5.44	5.23	5.25	1345	1430	~ 1950
Mean (1)-(4)	—	—	—	—	5.76	5.45	5.22	5.23	—	1413	~ 1950
Stand. dev.	—	—	—	—	± 0.03	± 0.03	± 0.01	± 0.01	—	± 13	—

(1) Only in the high temperature range above T_3 , W as well as Re and Ta is kept essentially clean and hence ϕ^+ is almost independent of T . This is the reason why β^+ is little dependent upon T . In this range, β^+ is generally equal to ε^+ since γ is kept ~ 1 . In other words, β^+ is governed mainly by the ionization energy (I) of M without depending upon the dissociation energy (D) of MX under study.

(2) With a decrease in T in the middle temperature range ($T_3 - T_2$), ϕ^+ of W as well as that of Re is monotonically increased by up to ~ 1 eV mainly by adsorption of residual gas molecules (RGM) and hence β^+ is remarkably increased up to ~ 1 without depending upon N . With respect to Ta, on the other hand, the increase in ϕ^+ does not exceed ~ 2 eV and hence β^+ for NaCl, for example, remains below ~ 0.03 . In this temperature range, too, β^+ is determined mainly by ε^+ because γ is still kept nearly unity.

(3) In the threshold temperature range below T_1 , the above increase in ϕ^+ is greatly suppressed by sample adsorption, thereby leading to a reduction in ϕ^+ with a decrease in T . In consequence, β^+ at a given temperature below T_1 becomes smaller with an increase in N and strongly depends upon the species of MX. In most cases, β^+ is determined mainly by γ since ε^+ is usually kept around ~ 1 .

The above conclusions, however, should be checked by a further investigation because γ of MX above T_1 is usually kept ~ 1 and hence because the work function increase found in the middle temperature range ($T_3 - T_2$) may possibly be caused by adsorption of X liberated from MX. In addition, it is very important to confirm

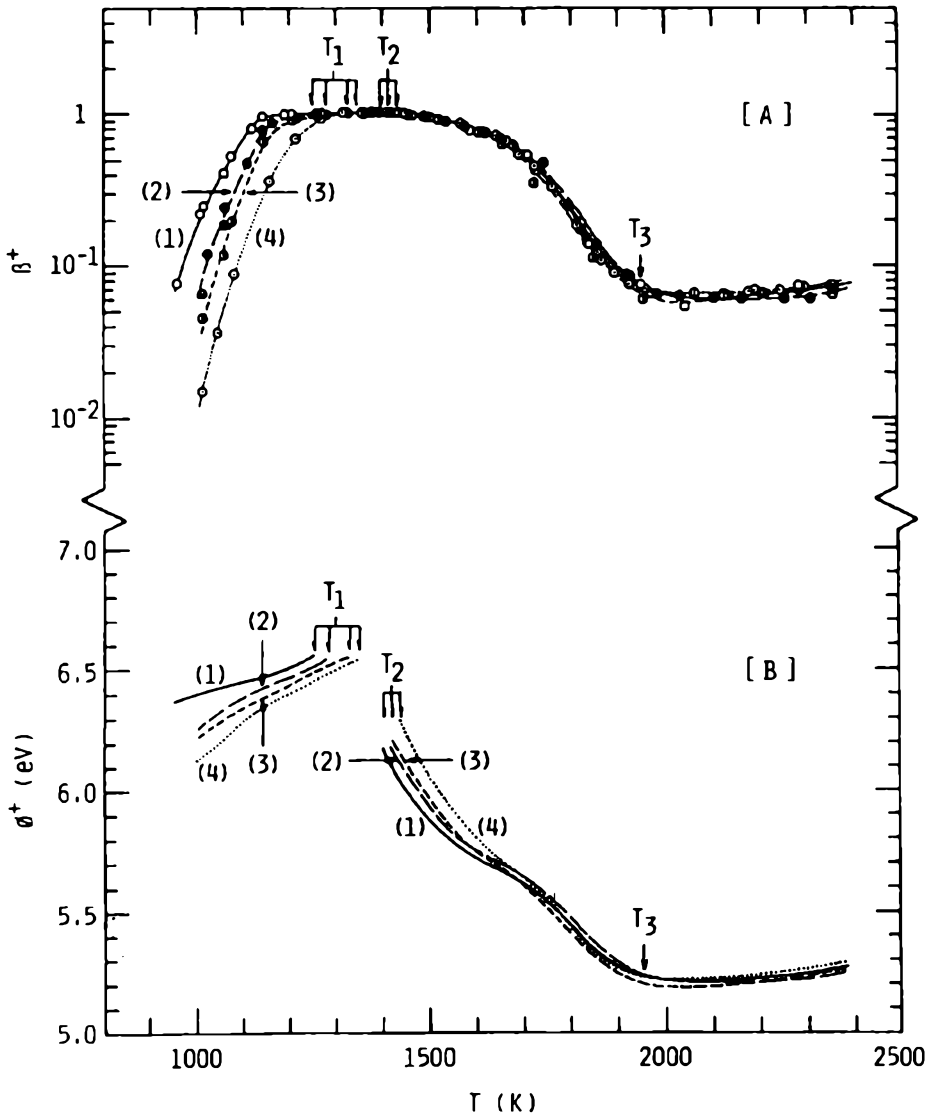


Fig. 1. Surface temperature (T) vs. [A] the ionization efficiency (β^+) of NaCl and [B] the effective work function (ϕ^+) for the ionization on W. Curves (1)-(4) are observed at different fluxes (N). Further information on each curve is given in Table 1

the strong dependence of ϕ^+ upon sample species in the threshold temperature range, which is governed mainly by ϕ^+ , D and I [14]. From these points of view, ϕ^+ of W is investigated by additional experiments using LiCl, LiBr and LiI as sample molecules. This paper summarizes the results thus achieved, showing that the values of ϕ^+ found with the three systems of LiX/W at a given temperature are virtually the same among the three in the range from ~ 2200 to 1700 K but that they have a tendency to deviate with each other by up to $\sim \pm 0.2$ eV as T decreases from ~ 1700 to 1400 K and also that the decrease in ϕ^+ found below ~ 1250 K strongly depends upon both N and the species of LiX. In conclusion, it is below ~ 1700 K alone that β^+ for Li^+ production has a weak or strong dependence upon the species of LiX under study.

EXPERIMENTAL

The experimental apparatus used here was described in detail elsewhere [4,15] and the method was virtually the same as that in the previous work [20–24]. Therefore, only their brief outline will be given here. A beam of LiX effusing from a Knudsen cell (C) kept at a constant temperature (T_c) was directed onto a polycrystalline tungsten filament (F) heated to a high temperature (T) at $P_r \simeq 2 \times 10^{-7}$ Torr. The residual gases mainly consisted of H_2O , CO , CO_2 , O_2 and various hydrocarbons [12]. The total ion current (in A) of Li^+ emitted from F and the saturated vapor pressure (in atm) in C kept at T_c (in K) are given by Eqs. (1) and (2), respectively [4,6].

$$I^+ = eSN\beta^+ = 6.09 \times 10^{-22}N\beta^+ \quad (1)$$

$$P = \frac{\pi L^2 [2\pi M R T_c]^{1/2}}{1.01 \times 10^6 N_A S_C} \cdot \frac{\pi N}{2} = 1.64 [M T_c]^{1/2} \frac{I^+}{\beta^+} \quad (2)$$

Here, e is the elementary electric charge, S is the ionizing surface area (3.80×10^{-3} cm²) of F exposed to the incident beam of LiX, L is the distance (6.5 cm) between C and F, M is the molecular weight of MX, R is the gas constant, N_A is Avogadro's number, and S_C is the effusing slit area (7.83×10^{-3} cm²). The values of T_C and T were determined with calibrated chromel-alumel thermocouples and an optical pyrometer, respectively.

RESULTS AND DISCUSSION

Some examples observed with an LiBr/W system are shown in Fig. 2, where T was successively increased or decreased at ~ 10 min intervals and the lithium ion current (I^+) was reproducible to within the experimental error of about $\pm 5\%$ without any temperature hysteresis. The beam flux (N) of LiBr has a larger value according to an increase in curve number. In each curve, I^+ has such a maximum value (I_m^+) as little depends upon T in an intermediate temperature range ($T_1 - T_2$), indicating that I_m^+ correspondent to $\beta^+ \simeq 1$ and hence $\sigma \simeq 1$ in

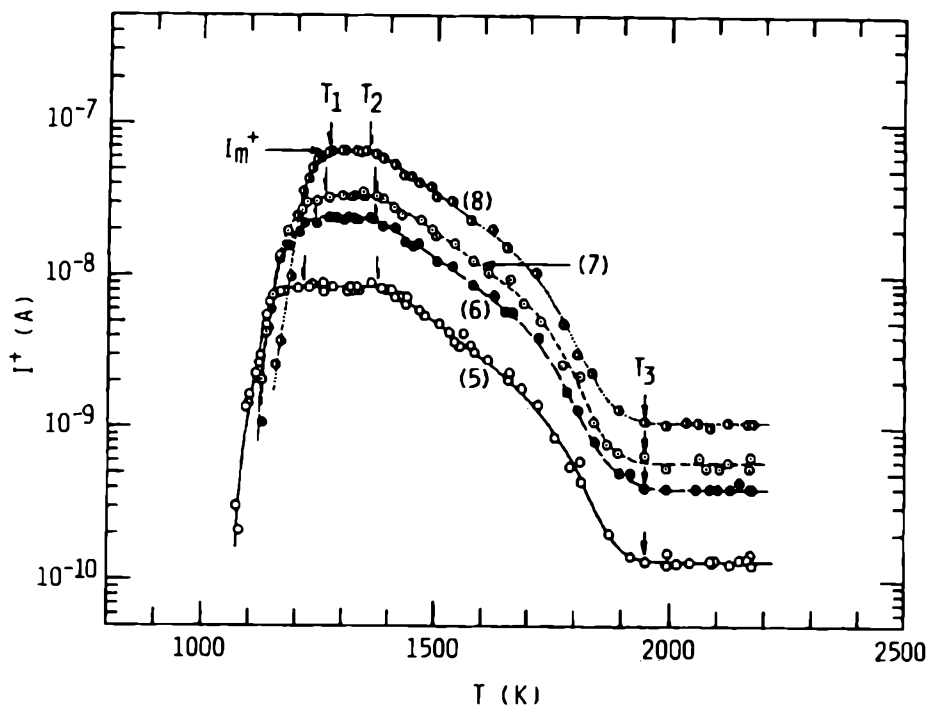


Fig. 2. Temperature dependence for the emission current (I^+) of Li^+ produced from LiBr on W . According to an increase in curve number, the cell temperature (T_C) becomes higher (see Table 2) and hence the incident beam flux (N) increases (see Table 3)

the range. In fact, the values of P evaluated by substitution of our experimental data (T_C , $I^+ = I_m^+$, $\beta^+ \approx 1$) in Eq. (2) are in good agreement with literature values [25–27], as shown in Table 2. This result gives an additional evidence to support our previous conclusion that σ of MX to an ionizing metal surface heated in high vacua is usually estimated to be unity [4,13,21].

The temperature dependence of β^+ for LiBr is shown in Fig. 3A, which is readily obtained from the data in Fig. 2 using the relation of $\beta^+ = I^+ I_m^+$. Fig. 3B shows the temperature dependence of ϕ^+ , which is evaluated from the data in Fig. 3A

Table 2. Vapor pressure (P) determined from the maximum current (I_m^+) of Li^+ produced from LiBr (see Fig. 2) and that determined by different methods by other workers

T_C (K)	This work			Other work			
	Curve	I_m^+ (nA)	P (μ atm)	P (μ atm)			Mean
				Ref. 26	Ref. 26	Ref. 27	
789	(5)	8.46 ± 0.13	3.63 ± 0.05	3.44	3.39	3.44	3.42 ± 0.02
813	(6)	24.4 ± 0.3	10.6 ± 0.1	8.18	8.08	8.18	8.15 ± 0.05
829	(7)	33.6 ± 0.2	14.8 ± 0.1	—	13.3	13.4	13.3 ± 0.1
856	(8)	66.8 ± 0.8	29.9 ± 0.3	—	28.1	28.2	28.1 ± 0.1

using the following equations [4,7], where σ is taken as unity according to the conclusion described above.

$$\beta^+ = \gamma\epsilon^+ = \gamma\alpha^+/(1 + \alpha^+) \quad (3)$$

$$\alpha^+ = \exp[\Delta S^+/R] \exp[(\phi^+ - 1)/kT] \quad (4)$$

$$\frac{\gamma^2}{1 - \gamma} = \frac{1.01 \times 10^6(1 + \alpha^+)}{N[2\pi\mu kT]^{1/2}} \exp\left[\frac{\Delta S}{R}\right] \exp\left[\frac{-D}{kT}\right]. \quad (5)$$

Here, α^+ is the ionization coefficient of Li, ΔS^+ is the entropy change due to ionization of Li, μ is the reduced mass of LiX, and ΔS is the entropy change due to dissociation of LiX. In the range of 1000–2200 K, the values of ΔS^+ , I , ΔS and D for LiBr, for example, are calculated to be $-1.38 - -1.38$ cal mol⁻¹K⁻¹, 5.61–5.87 eV, 23.0–23.9 cal mol⁻¹K⁻¹, 4.44–4.50 eV, respectively, using compiled thermochemical data [26].

In the range of $T_1 - T_2$ corresponding to $\beta^+ \simeq 1$, it is impossible to evaluate ϕ^+ accurately from the data on β^+ using Eqs. (3)–(5) because both γ and ϕ^+ are virtually unity. This is the reason why Fig. 3B has no line in the range. The values of ϕ^+ at selected temperatures are listed together with our experimental conditions in Table 3. Here, T_3 is the boundary temperature above which the surface under study is kept virtually clean, irrespective of the incidence of both sample and residual gas molecules [21–24]. As shown in Fig. 3, both β^+ and ϵ^+ at any temperature below T_1 become smaller with an increase in N . In addition, T_1 itself becomes higher as N increases (see Table 3), thereby suggesting that the steep decrease in ϕ^+ is caused by sample adsorption, quite similarly as in the case of an LiI/Re system [13,18]. Above T_2 , on the other hand, not only β^+ and ϕ^+ but also T_2 and T_3 have little dependence upon N and hence it seems unlikely that the gradual increase in ϕ^+ with a temperature decrease from ~ 1950 to 1400 K is mainly caused by sample adsorption.

Temperature dependence of β^+ and ϕ^+ observed with an LiCl/W system is illustrated in Fig. 4. Here, β^+ is determined by substitution of our experimental data (I^+ and T_C) in the following equations.

$$\beta^+ = 10.7T_C^{1/2}I^+/P \quad (6)$$

$$\log_{10} P = -10230/T_C + 7.03, \quad (7)$$

which are obtained from Eq. (2) and the literature [28], respectively. According to our previous work [16], however, any value of P to be determined from such an empirical formula as Eq. (7) cited from a literature may probably be accompanied with an error of up to $\pm 20\%$. Above T_3 , in fact, the standard deviation of β^+ for LiCl ($\pm 15\%$) is larger than that for LiBr ($\pm 4.2\%$) and for LiI ($\pm 7.2\%$). In addition, the values of β^+ above T_3 do not well agree with each other among the three: 0.014 ± 0.002 for LiCl, 0.017 ± 0.001 for LiBr, 0.021 ± 0.002 for LiI. It should be emphasized that ϕ^+ above T_3 generally corresponds to the essentially clean surface of the filament employed, that γ for any MX in such a high temperature range is

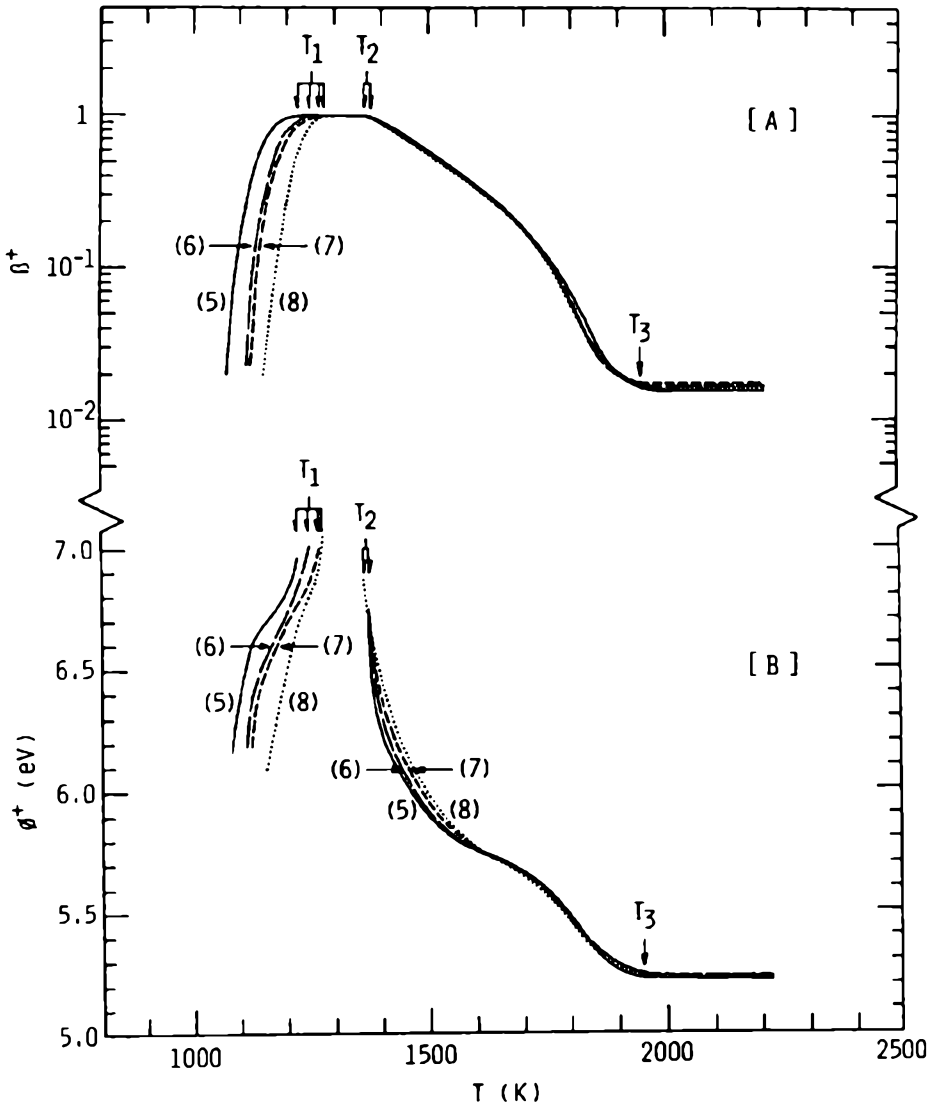


Fig. 3. Surface temperature (T) vs. [A] the ionized efficiency (β^+) of LiBr and [B] the work function (ϕ^+) of W. Curves (5)-(8) correspond to those (5)-(8) in Fig. 2

Table 3. Summary of the experimental and analytical results achieved with LiX/W systems under the residual gas pressure of $\sim 2 \times 10^{-7}$ Torr. Curve numbers are common among Figs. 2-7

Curve	Sample	T_C (K)	Flux (N ; molecules $\text{cm}^{-2}\text{s}^{-1}$)	Effective work function (ϕ^+ or ϕ^c ; eV)						Boundary temperature (K)		
				1200K	1400K	1600K	1800K	2000K	2200K	T_1	T_2	T_3
(5)	LiBr	789	1.39×10^{13}	6.85	6.23	5.75	5.48	5.22	5.22	1220	1375	~ 1950
(6)	LiBr	813	4.01×10^{13}	6.75	6.29	5.76	5.46	5.24	5.24	1244	1370	~ 1950
(7)	LiBr	829	5.52×10^{13}	6.71	6.38	5.76	5.47	5.23	5.23	1266	1370	~ 1950
(8)	LiBr	856	1.10×10^{14}	6.54	6.44	5.76	5.45	5.23	5.23	1274	1360	~ 1950
Mean (5)-(8)	—	—	—	—	6.34	5.76	5.47	5.23	5.23	—	1369	~ 1950
Stand. dev.	—	—	—	—	± 0.08	± 0.00	± 0.01	± 0.01	± 0.01	—	± 5	—
(9)	LiCl	809	1.30×10^{13}	6.70	6.31	5.72	5.37	5.18	5.18	—	—	~ 1950
(10)	LiCl	831	2.76×10^{13}	6.72	6.45	5.80	5.42	5.18	5.18	—	—	~ 1950
(11)	LiCl	854	5.77×10^{13}	6.75	6.60	5.91	5.46	5.20	5.20	—	—	~ 1950
(12)	LiCl	874	1.11×10^{14}	6.79	6.67	6.01	5.51	5.24	5.24	—	—	~ 1950
Mean (9)-(12)	—	—	—	6.74	6.51	5.86	5.44	5.20	5.20	—	—	~ 1950
Stand. dev.	—	—	—	± 0.03	± 0.14	± 0.11	± 0.05	± 0.02	± 0.02	—	—	—
(13)	LiI	697	5.47×10^{12}	—	6.06	5.74	5.43	5.28	5.28	1142	1370	~ 1950
(14)	LiI	716	1.61×10^{13}	5.75	6.02	5.73	5.46	5.27	5.27	1204	1365	~ 1950
(15)	LiI	734	4.34×10^{13}	—	6.15	5.75	5.52	5.25	5.26	1223	1375	~ 1975
Mean (13)-(15)	—	—	—	—	6.08	5.74	5.47	5.27	5.27	—	1370	~ 1958
Stand. dev.	—	—	—	—	± 0.05	± 0.01	± 0.04	± 0.01	± 0.01	—	± 4	± 12
Mean (5)-(15)	—	—	—	—	6.33	5.79	5.46	5.23	5.23	—	1369	1952
Stand. dev.	—	—	—	—	± 0.20	± 0.09	± 0.04	± 0.03	± 0.03	—	± 5	± 7
(16)	—	—	—	—	—	5.06	4.75	4.43	4.42	—	—	~ 2000
(17)	—	—	—	—	—	5.10	4.61	4.50	4.50	—	—	~ 1880
Mean (16)-(17)	—	—	—	—	—	5.08	4.68	4.47	4.46	—	—	1940
Stand. dev.	—	—	—	—	—	± 0.02	± 0.07	± 0.04	± 0.04	—	—	± 60

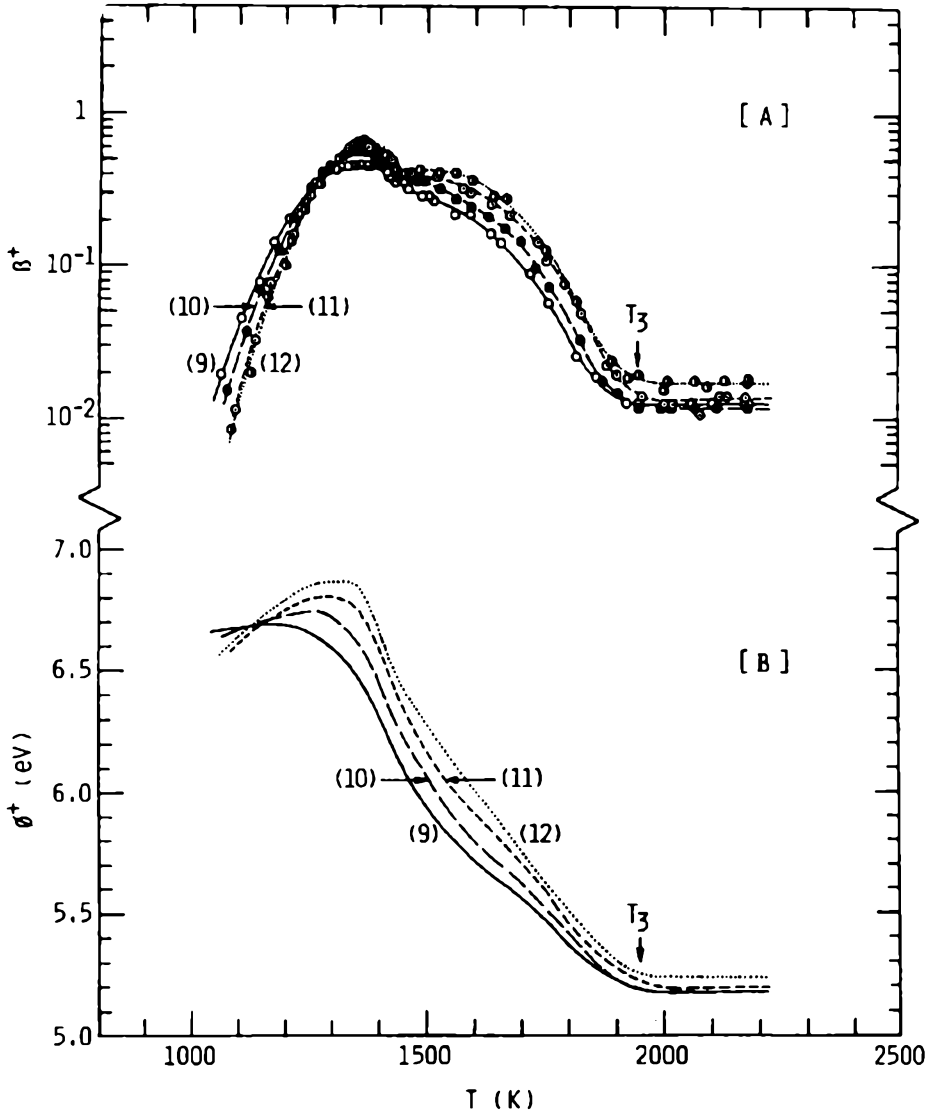


Fig. 4. Temperature dependence of [A] the ionization efficiency (β^+) of LiCl and [B] the work function (ϕ^+) of W. For further information, see Table 3

unity and hence that β^+ in the range is common (0.060 ± 0.002) among NaXs, for example, irrespective of the species of NaX [24]. Comparison between the present and previous results indicates that the data on β^+ and ϕ^+ determined with the LiCl/W system are less accurate than those with the LiBr/W and LiI/W systems. In the system of LiCl, both T_1 and T_2 do not exist because β^+ is always smaller than unity (see Fig. 4). As T decreases from T_3 (~ 1950 K) to ~ 1300 K, ϕ^+ increases from ~ 5.2 up to 6.9 eV and ϕ^+ at any temperature is slightly larger with a larger value of N , thereby suggesting that this increase is partly due to adsorption of Cl liberated from LiCl.

Some of the data on β^+ achieved with an LiI/W system are summarized in Fig. 5A. Above T_2 curves (13)–(15) in Fig. 5B overlap with each other within the experimental error of about ± 0.05 eV, irrespective of a large difference in N among the three (see Table 3). At any temperature below T_1 , on the other hand, ϕ^+ shows quite different values among them, and T_1 itself has a considerable dependence upon N , in contrast to T_2 and T_3 .

Temperature dependence of β^+ determined with nearly the same flux ($N \approx 5 \times 10^{13}$ molecules $\text{cm}^{-2}\text{s}^{-1}$) of LiBr, LiCl and LiI is summarized as curves (7), (11) and (15), respectively, in Fig. 6A, while the data on γ and ε^+ are shown in Figs. 6B and 6C, respectively. Above ~ 1700 K, β^+ for any LiX is determined mainly by ε^+ because γ is kept around unity. In the range of $\sim 1700 - 1400$, γ for LiBr and LiI still remains ~ 1 and hence ε^+ is the predominant factor of β^+ for them. For LiCl, however, β^+ is governed by both γ and ε^+ since γ is much smaller than unity in this range. This is mainly because D of LiCl (~ 5.0 eV) is larger than D of LiBr (~ 4.5 eV) and LiI (~ 3.8 eV). Below ~ 1250 K, β^+ for LiBr and LiCl is governed by γ alone since ε^+ for them is kept unity. On the other hand, β^+ for LiI is governed by both γ and ε^+ and hence shows the sharpest decrease from ~ 1 to less than 0.01 within a very narrow range of ~ 10 K.

Temperature dependence of ϕ^+ observed with the three systems is summarized in Fig. 7. Curves (16) and (17) cited from the previous work [23] show the temperature dependence of the effective work function (ϕ^e) for thermal electron emission from the tungsten surface under study. Below ~ 1500 K, the electron emission current was too weak (much less than ~ 1 pA) to be measured by our present detection system. It should be emphasized that ϕ^e was determined without sample beam incidence and hence that the observed change in ϕ^e is caused not by adsorption of LiX, Li and/or X but by that of RGM.

In the low temperature range below ~ 1250 K, curves (7), (11) and (15) for ϕ^+ in Fig. 7 are quite different in both pattern and position with each other among the three, suggesting that the change in ϕ^+ is caused by sample adsorption and hence that β^+ has a large dependence upon the sample species of LiX (see Fig. 6A). Such a decrease in β^+ with a lowering temperature is caused not by a decrease in σ but mainly by that in γ (see Fig. 6B) owing to a reduction in ϕ^+ (see Fig. 7), just as concluded previously [13,14]. In an early work on MX/Pt systems [29], a sharp decrease in β^+ observed in the threshold temperature range is concluded to be a reduction in γ , but no data are given on γ and ϕ^+ . Above ~ 1700 K, the three curves of ϕ^+ in Fig. 7 nearly overlap with each other within the experimental

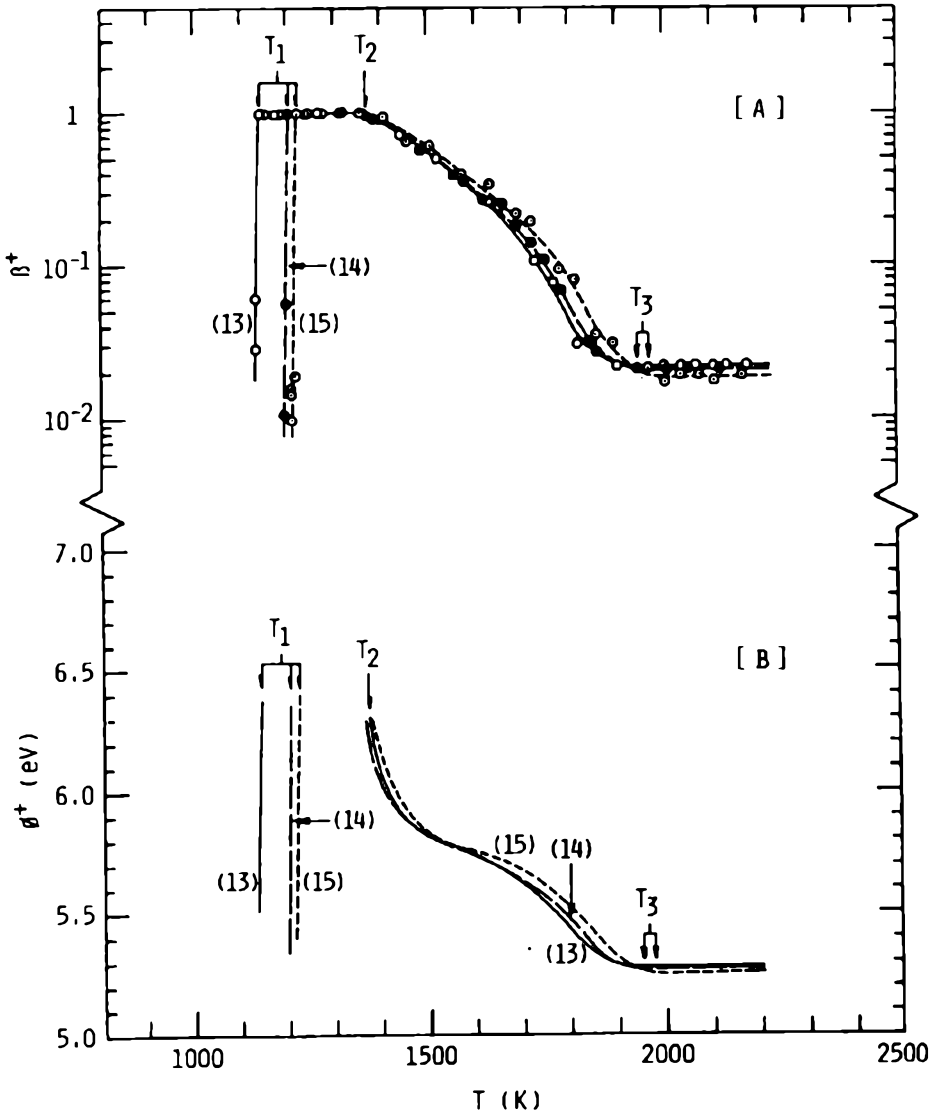


Fig. 5. Data on [A] the ionization efficiency (β^+) and [B] the work function (ϕ^+) determined with an LiI/W system. Further information is given in Table 3

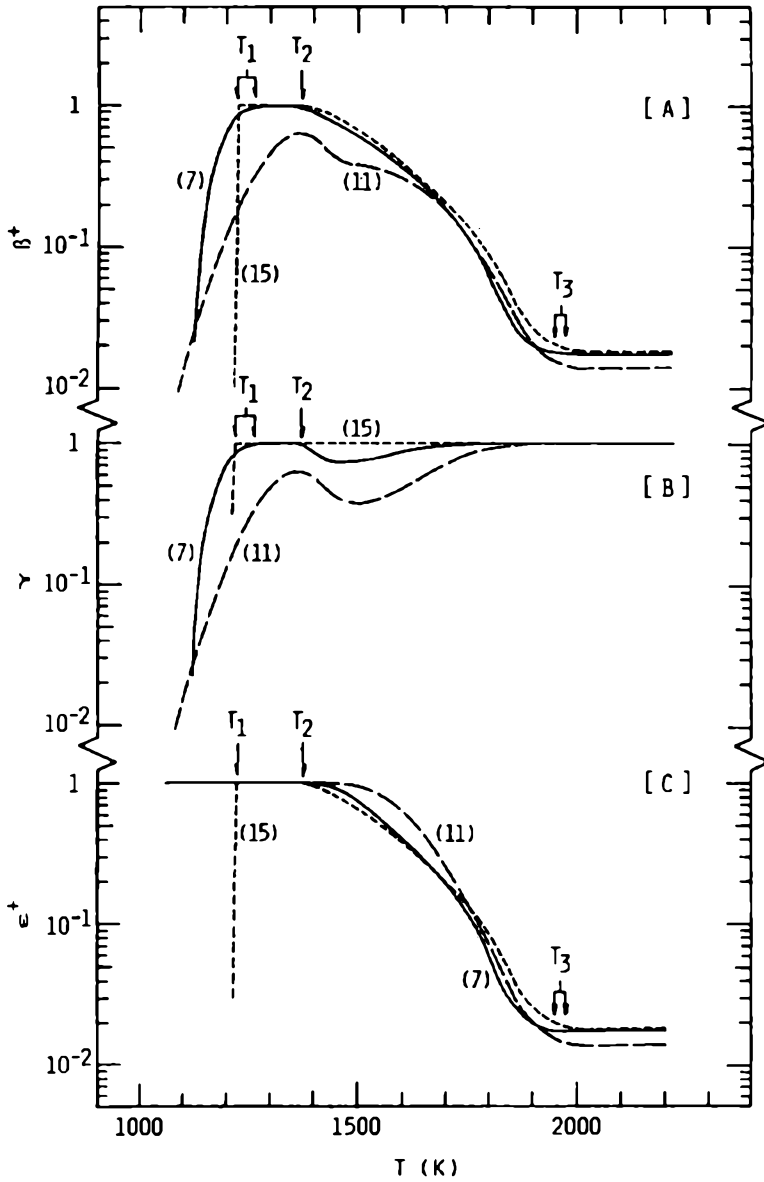


Fig. 6. Comparison of the data on [A] the ionization efficiency (β^+), [B] the degree of dissociation (γ), and [C] that of ionization (ϵ^+) determined with a nearly equal flux of LiX on W. Curves (7), (11) and (15) are observed with LiBr, LiCl and LiI, respectively (see Table 3)

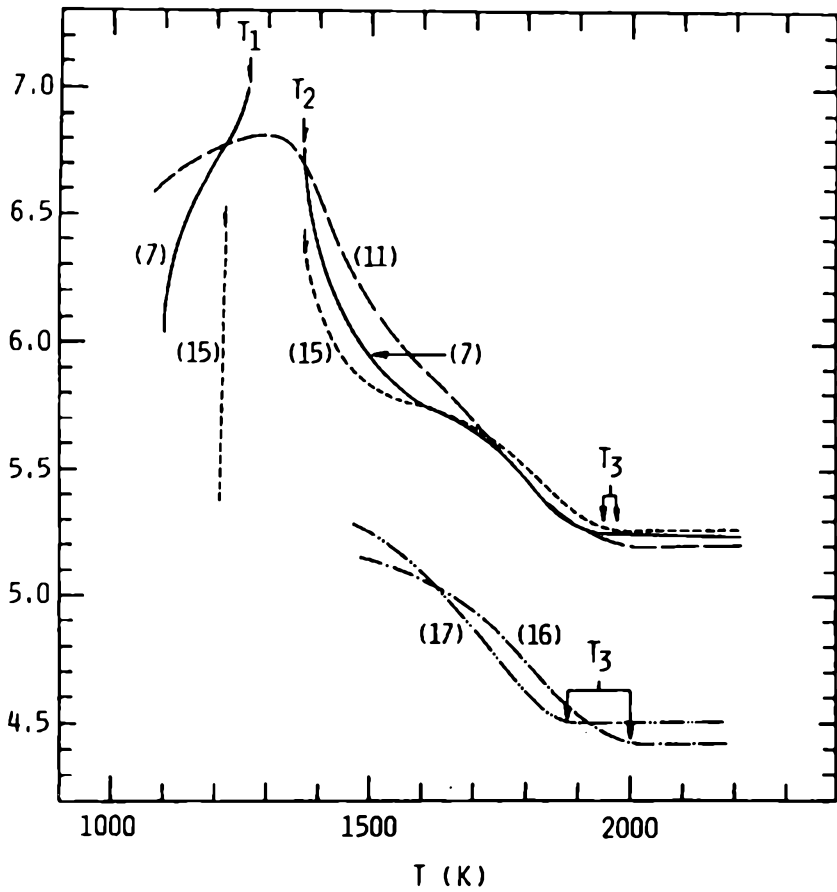


Fig. 7. Temperature dependence of the effective work functions (ϕ^+ and ϕ^-) for positive-ionic and electronic emissions from W. Curves (7), (11) and (15) for ϕ^+ correspond to those (7), (11) and (15) for β^+ in Fig. 6A, respectively. Curves (16) and (17) for ϕ^- are determined without sample beam incidence

error of about ± 0.05 eV and they are virtually the same in pattern with the two curves of ϕ^e . In addition, the thermionic contrast ($\phi^+ - \phi^e$) is essentially constant at ~ 0.8 eV throughout the temperature range. These results give an additional evidence to support our previous conclusion that the increase in ϕ^+ in the range of $T_3 - T_2$ is caused mainly by adsorption of RGM (especially of oxygen) [22]. Below ~ 1700 K, on the other hand, the increase in ϕ^+ due to a temperature decrease has a tendency to become slightly larger according to the reduction in molecular weight of LiX even when N is similar among the three (see Fig. 7). At ~ 1400 K, for example, the mean values of ϕ^+ determined with the four or three different fluxes (see Table 3) are 6.51 ± 0.14 , are 6.34 ± 0.08 and 6.08 ± 0.05 eV for the samples of LiCl, LiBr and LiI, respectively. These results suggest that the work function increase around T_2 is partly due to adsorption of X liberated from LiX. This contribution, however, may be estimated to be less than ~ 0.02 eV, which is much smaller than the work function increase (~ 1 eV) mainly due to residual gas adsorption. It may be noted that the determination of ϕ^+ around T_2 using Eqs. (3)–(5) is subject to a large error of up to $\sim \pm 0.2$ eV either because β^+ for both LiBr and LiI near T_2 tends to have a large experimental error up to $\sim \pm 5\%$ or because the errors inherent in the determination of β^+ for LiCl by using Eqs. (6) and (7) may be at least $\sim \pm 15\%$, as already stated above.

With respect to NaX/W systems, on the other hand, such a halogen effect as suggested above has not been observed in the previous work [24]. Namely, the values of ϕ^+ determined at T_2 (~ 1400 K) using NaCl, NaBr and NaI are 6.06, 6.00 and 5.95 eV, respectively, nearly the same among the three within the limit of ± 0.07 eV. Consideration of the present and previous results suggests that the work function increase due to halogen adsorption on W below ~ 1700 K is much smaller in general than that due to residual gas adsorption so long as $N < 10^{14}$ molecules $\text{cm}^{-2}\text{s}^{-1}$ and $P_r > 10^{-7}$ Torr.

CONCLUSIONS

Consideration of the experimental data and analytical results achieved with the LiX/W systems in this work leads to the conclusions as follows.

(1) The boundary temperature (T_3) above which all of β^+ , ε^+ , γ and ϕ^+ are almost independent of T is common (~ 1950 K) without depending upon both flux (N) and sample species (LiX) under study. In addition, this temperature is virtually the same with that (~ 1940 K) observed with thermal electron emission, thereby indicating that the surface above T_3 is kept essentially clean even when the surface is exposed to a strong sample beam in addition to RGM. In fact, the work function values ($\phi^+ = 5.23 \pm 0.03$ eV, $\phi^e = 4.47 \pm 0.04$ eV) determined above T_3 are in good agreement with literature values ($\phi^+ = 5.1 \pm 5.3$ eV, $\phi^e = 4.4 \pm 4.6$ eV) generally accepted today [2, 30].

(2) According to a temperature decrease from ~ 1940 to 1700 K, all of β^+ , ε^+ and ϕ^+ increase monotonically, while γ still remains around unity. The pattern ϕ^+ is virtually identical with that of ϕ^e and the difference ($\phi^+ - \phi^e$) is constant at

~ 0.08 eV with little dependence upon T , N and the species of LiX. This result indicates that the work function increase found in the range is caused partly by adsorption of sample components (particularly of halogen) but mainly by that of RGM (especially of oxygen).

(3) The values of ϕ^+ observed in the range of $\sim 1700 - 1400$ K, on the other hand, have a slight dependence upon the species of LiX, thereby suggesting that the work function increase found in the range is partly due to adsorption of X liberated from LiX and also that Cl has the largest effect upon the increase among the three halogens investigated. The increase possibly due to halogen adsorption, however, is estimated to be less than ~ 0.02 eV, much smaller than that (~ 1 eV) due to adsorption of RGM.

(4) With a decrease in T from ~ 1250 K, β^+ shows such a steep decrease as depends upon both N and the species of LiX. This is caused not by a decrease in σ but mainly by that in γ , and the latter originates from a reduction in ϕ^+ owing to co-adsorption of LiX and RGM.

Further work, however, is necessary to clarify the mechanism of work function changes due to adsorption of RGM and/or MX. From this point of view, measurements of the amounts of these molecules adsorbed on the ionizing surface are now in progress using a new technique [13] developed in our laboratory and also high-temperature flashing mass spectrometry.

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