Effect of Halogens on the Ionization of Alkali Metals in the Hydrogen Flame Ionization Detector for Ultra-Micro Analysis of Alkali and Alkaline Earth Metals

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Quantitative treatment of alkali metals in a small hydrogen flame in the presence or absence of halogens was studied. The proportionality of the ion current to the concentration of alkali metals was found to depend on the applied potential of the electrodes. On adding halogens, the concentration of free neutral alkali atoms decreased. Addition of bromine and iodine increased the ionization of alkali metals, while fluorine decreased it slightly. Addition of chlorine increased or decreased the ionization. The thermionic detection mechanism of halogen-containing compounds in TID of gas chromatograph was discussed.

Ultra-micro analysis of alkali and alkaline earth metals by the hydrogen flame ionization method was developed by the authors.[1–3] The method, in which an electric current caused by ionization of these metals in the hydrogen flame is measured by applying an electric field, has a high sensitivity. It was observed that the ionization of alkali metals was enhanced or suppressed by the addition of hydrogen chloride gas to the flame. Behavior of alkali metals in the small diffusion hydrogen flame without an electric field, distribution of free neutral atoms and charged particles and the mobility of charged particles were also studied.[4] In investigations carried out on the ionization of alkali metals in the presence of halogens,[5–7] large, flat and pre-mixed flames were used, no electric field being applied.

On the other hand, a high sensitive and selective gas chromatographic detector has been used[8,9] for halogen- and phosphorus-containing compounds, known as a thermionic or alkali flame detector. It is a modification of the flame ionization detector making use of different ionization processes in the flame in the presence of an alkali metal. The mechanism of response was discussed from the point of view that halogens and phosphorus increase the ionization or volatilization of alkali metals.

This paper deals with the quantitative treatment of the ionization of alkali metals when halogens are added or not added to a small diffusion flame to which electric field is applied. The study is also related with the thermionic detection mechanism.

Experimental

A double jet type hydrogen flame ionization detector was used, the flow rates of hydrogen and oxygen and also the instrument being the same as those used previously.[4] The electric field is applied to the ionizing flame by two parallel plane electrodes, 5.5×3.5 cm nickel plates plated with silver and gold. The applied potential and distance between the electrodes are variable. The flame photometric method was applied for studying the effect of halogens on the concentration of free neutral atoms.

Alkali metals were intermittently supplied to the ionizing flame (the upper flame) by inserting the tip of a platinum wire coated with 10^{-9}—10^{-11} mol alkali chloride into the evaporating flame (the lower flame). Halogens were continuously added to the ionizing flame by introducing them into the hydrogen gas stream for the ionizing flame. Chlorine was added as hydrogen chloride from a cylinder. Iodine, bromine, and fluorine were added as methyl iodide, diethyl bromide, and fluorobenzene, respectively, from a heated reservoir.

Results and Discussion

In the Absence of Halogens. Alkali chlorides MCl react with hydrogen atoms in the flame as follows:

$$\mathrm{MCl} + \mathrm{H} \rightleftarrows \mathrm{M} + \mathrm{HCl};\ \text{eq. const. } K_1.$$

This gives alkali atoms M which can be readily ionized. Alkali atoms are ionized by collisional process with B, major constituent of the gas products (water molecule in this case):

$$\mathrm{M} + \mathrm{B} \xrightarrow{k_1} \mathrm{M}^+ + \mathrm{e}^- + \mathrm{B}. \qquad \text{(I)}$$

The activation energy of reaction (I) is equal to the ionization potential.[10] Since the concentration of water molecule is constant in a given flame, the reaction is considered to be of first order, depending only on the alkali atom concentration. This indicates that the ionization occurs *via* a thermal rather than a chemical path. If the process completely follows this reaction, then we have

$$\frac{\mathrm{d}[\mathrm{M}^+]}{\mathrm{d}t} = k_1[\mathrm{M}][\mathrm{B}],$$

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where k_1 is the rate constant of reaction (I), [M] and [B] are concentrations of alkali atom and water molecule, respectively. If the recombination in the electric field is neglected, the ion current i which flows into the outer circuit will be proportional to $d[M^+]/dt$:

$$i \propto \frac{d[M^+]}{dt} = k_1[M][B]. \tag{1}$$

If $[M]_0$ and $[Cl]_0$ are total concentrations of metal and chlorine atom, whether combined or free, then

$$[M]_0 = [M] + [MCl] + [MOH], \tag{2}$$

$$[Cl]_0 = [M]_0 = [MCl] + [HCl] + [Cl], \tag{3}$$

where [MCl] is the concentration of undissociated alkali chloride, [MOH], [HCl], and [Cl] are concentrations of alkali hydroxide, hydrogen chloride and chlorine atom, respectively, formed in the flame. Formation of MOH and HCl is governed by the reversible reactions:

$$M + H_2O \rightleftarrows MOH + H,$$

$$Cl + H_2 \rightleftarrows HCl + H.$$

Putting $[MOH]/[M] = \phi$, Eq. (2) becomes

$$[M]_0 = [M]\left(1+\frac{[MCl]}{[M]}+\phi\right)$$

$$= [M]\left(1+\frac{[HCl]}{K_1[H]}+\phi\right). \tag{4}$$

From the previous results, the value of ϕ was 0.1—0.3 for lithium and $\phi \ll 1$ for the other alkali mtals.[4] Equations (2) and (3) give

$$[M](1+\phi) = [HCl]\left(1+\frac{[Cl]}{[HCl]}\right).$$

Since $[Cl]/[HCl] \ll 1$, this becomes

$$[M](1+\phi) = [HCl]. \tag{5}$$

From Eqs. (4) and (5), we obtain

$$[M] = \frac{2[M]_0}{(1+\phi)\{\sqrt{1+4[M]_0/K_1[H](1+\phi)}+1\}}. \tag{6}$$

In our experiment, the amounts of alkali metals added were 10^{-11}—10^{-9} mol. Thus we get for $[M]_0$ 10^{-8}—10^{-6} atm (partial pressure), for $K_1[H](1+\phi)$ about 10^{-2} atm for lithium and 10^{-3} atm for cesium. Equation (6) can therefore be simplified as

$$[M] = \frac{[M]_0}{1+\phi}. \tag{7}$$

This holds also for the other halides of alkali metals. Thus, we have from Eqs. (1) and (7)

$$i \propto \frac{[M]_0}{1+\phi}.$$

This indicates that the ion current is proportional to the total concentration of alkali metals. The experimental results are shown in Fig. 1.

The plot of lithium alone shows a straight line. A deviation from the straight line would be due to the space charge effect caused by insufficient applied potential. The relationship between the saturated ion current i_s and the minimum applied potential V_s at which i_s is obtained is shown in Fig. 2. The slope of straight lines is found to be 2 and i_s-V_s relation is represented by the equation. Since the coefficient a is correlated

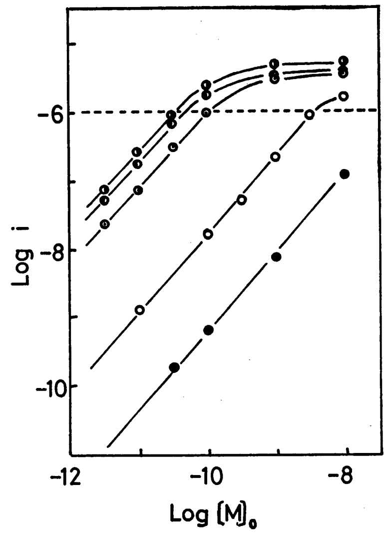

Fig. 1. Relationship between i and $[M]_0$.
i and $[M]_0$ are represented by ampere and mole, respectively. Applied potential: 1000 V; Distance between the electrodes d(cm): 1.8; Sample: ● LiCl, ○ NaCl, ⊙ KCl, ◐ RbCl, ◑ CsCl.

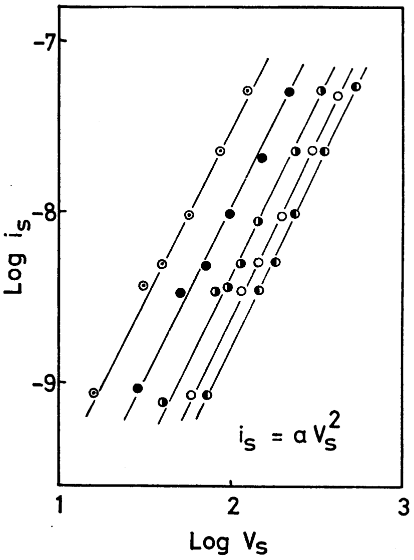

Fig. 2. Relationship between i_s and V_s.
i_s and V_s are represented by ampere and volt, respectively. Distance between the electrodes d(cm): ⊙ 1.4, ● 1.8, ◑ 2.2, ○ 2.6, ◐ 3.0; Sample (mol): NaCl 1×10^{-10}.

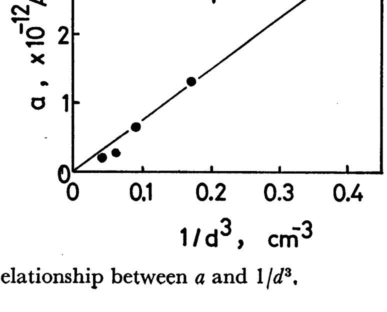

Fig. 3. Relationship between a and $1/d^3$.

with the distance between the electrodes d as shown in Fig. 3, we obtain

$$i_s = 6 \times 10^{-12}\frac{V_s^2}{d^3}(\mathrm{A}). \tag{8}$$

This shows that the saturated ion current depends on the applied potential, if d is kept constant. Under the conditions shown in Fig. 1, where V_s is 1000 V and d 1.8 cm, i_s is calculated to be 1.0×10^{-6} A. This value is represented by a horizontal dotted line. Above this line, linear relation can not be obtained because the applied potential is not sufficient. When the applied potential is larger, the plots should be linear if the secondary ionization do not occur. The working curves became non-linear in the range of large amounts of halide (for example, 10^{-10} mol in sodium chloride).[3] The applied potential was about 300 V, and the linear dynamic ranges of the working curves were not more than 100. These results show that the applied potential was apparently low.

In the Presence of Halogens. On adding halogens, the ionization can be considered to be the following reactions in the electric field:

$$\mathrm{M} + \mathrm{B} \xrightarrow{k_1} \mathrm{M}^+ + \mathrm{e}^- + \mathrm{B}, \tag{I}$$

$$\mathrm{M} + \mathrm{X} \xrightarrow{k_2} \mathrm{M}^+ + \mathrm{X}^-, \tag{II}$$

and halogens take part in two reversible bimolecular reactions,

$$\mathrm{MX} + \mathrm{H} \rightleftarrows \mathrm{M} + \mathrm{HX};\ \text{eq. const. } K_2, \tag{III}$$

$$\mathrm{H}_2 + \mathrm{X} \rightleftarrows \mathrm{H} + \mathrm{HX};\ \text{eq. const. } K_3, \tag{IV}$$

where X is a halogen atom. In reaction (II), it is expected to increase the ion current, and in reaction (III), to decrease the ion current, since ionizable alkali atoms are removed as gaseous alkali halides.

If reaction (II) is of second order, the ion current i' is given by

$$i' \propto \frac{\mathrm{d}[\mathrm{M}^+]'}{\mathrm{d}t} = k_1[\mathrm{M}]'[\mathrm{B}] + k_2[\mathrm{M}]'[\mathrm{X}]', \tag{9}$$

where $[\mathrm{M}^+]'$ and $[\mathrm{M}]'$ are concentrations of the metal ion and the free atom, respectively, in the presence of added halogen, and $[\mathrm{X}]'$ that of atomic halogen. [B] remains constant because of the buffer effect of the flame gases. From Eqs. (1) and (9), the ion current ratio i'/i is obtained:

$$\frac{i'}{i} = \frac{[\mathrm{M}]'}{[\mathrm{M}]}\left(1 + \frac{k_2[\mathrm{X}]'}{k_1[\mathrm{B}]}\right). \tag{10}$$

If $[\mathrm{M}]_0$ and $[\mathrm{X}]'_0$ are the concentrations of total alkali metals and halogens, respectively, the material balance is given by

$$[\mathrm{M}]_0 = [\mathrm{M}]' + [\mathrm{MOH}]' + [\mathrm{MX}]', \tag{11}$$

$$[\mathrm{X}]_0' = [\mathrm{X}]' + [\mathrm{HX}]'. \tag{12}$$

Ions are ignored in the metal balance since the degree of ionization is small. $[\mathrm{MX}]'$ is neglected in the halogen balance since $[\mathrm{X}]_0' \gg [\mathrm{M}]_0$. Equation (12) is rewritten as

$$[\mathrm{X}]_0' = [\mathrm{X}]'\left(1 + \frac{[\mathrm{HX}]'}{[\mathrm{X}]'}\right)$$

$$= [\mathrm{X}]'\left(1 + \frac{K_3[\mathrm{H}_2]}{[\mathrm{H}]}\right). \tag{13}$$

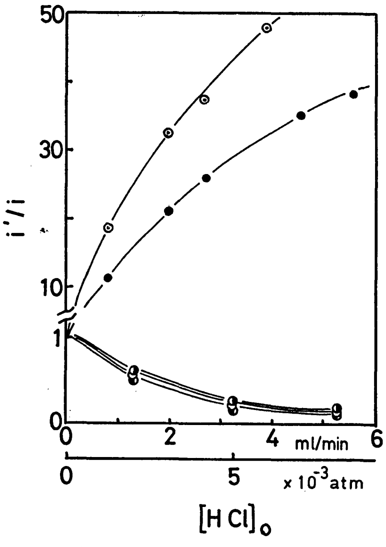

Fig. 4. Plots of i'/i against $[\mathrm{HCl}]_0$.
Applied potential: 1000 V; Distance between the electrodes d(cm): 1.8; Sample (mol): ⊙ LiCl 1×10^{-10}, ● NaCl 1×10^{-11}, ◑ KCl 1×10^{-11}, ○ RbCl 1×10^{-11}, ◐ CsCl 1×10^{-11}

Equation (10) then becomes

$$\frac{i'}{i} = \frac{[\mathrm{M}]'}{[\mathrm{M}]}\left\{1 + \frac{k_2[\mathrm{X}]_0'}{k_1(1 + K_3[\mathrm{H}_2]/[\mathrm{H}])[\mathrm{B}]}\right\}. \tag{14}$$

Change of i'/i, on addition of a few milliliters per minute of hydrogen chloride (an order of 10^{-3} atm in partial pressure), is shown in Fig. 4. We see that the ion currents for lithium and sodium increase, while those for the other alkali metals decrease. This is because $[\mathrm{M}]'/[\mathrm{M}]$ in Eq. (14) decreases the ion current, while the second term in the brace increases it. That is to say, in the case of lithium and sodium, the second term in the brace is much larger than 1, while in the case of other alkali metals, it is much smaller than 1.

Equation (11) is rewritten as

$$[\mathrm{M}]_0 = [\mathrm{M}]'\left(1 + \frac{[\mathrm{MOH}]'}{[\mathrm{M}]'} + \frac{[\mathrm{MX}]'}{[\mathrm{M}]'}\right)$$

$$= [\mathrm{M}]'\left(1 + \phi + \frac{[\mathrm{HX}]'}{K_2[\mathrm{H}]}\right).$$

We have from Eqs. (12) and (13)

$$[\mathrm{M}]_0 = [\mathrm{M}]'\left\{1 + \phi + \frac{[\mathrm{X}]_0'}{K_2[\mathrm{H}](1 + [\mathrm{H}]/K_3[\mathrm{H}_2])}\right\}. \tag{15}$$

ϕ, [H], and $[\mathrm{H}_2]$ remain constant because of the buffer effect of the flame gases. Since $[\mathrm{Cl}]'/[\mathrm{HCl}]' \ll 1$, Eq. (15) for chlorine becomes

$$[\mathrm{M}]_0 = [\mathrm{M}]'\left(1 + \phi + \frac{[\mathrm{Cl}]_0'}{K_2[\mathrm{H}]}\right). \tag{16}$$

From Eqs. (6) and (16), the concentration ratio of free alkali atoms in the presence or absence of added hydrogen chloride is given by

$$\frac{[\mathrm{M}]}{[\mathrm{M}]'} = \frac{2\{1 + [\mathrm{Cl}]_0'/(1+\phi)K_2[\mathrm{H}]\}}{1 + \sqrt{1 + 4[\mathrm{M}]_0/(1+\phi)K_2[\mathrm{H}]}}. \tag{17}$$

$[\mathrm{M}]/[\mathrm{M}]'$ is equal to I/I', where I and I' are emission intensities of alkali atoms in the absence and presence of added hydrogen chloride. Plots of I/I' against $[\mathrm{Cl}]'$ and of $(I-I')$ against I give straight lines as shown in

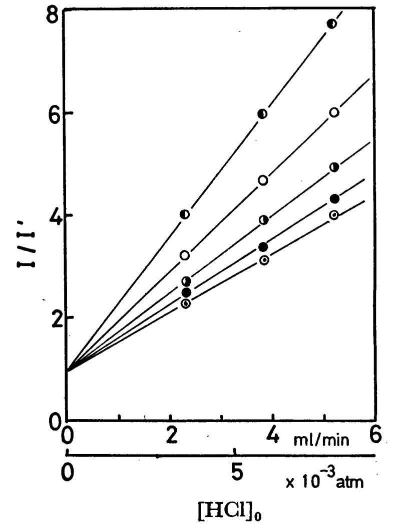

Fig. 5. Plots of I/I' against $[HCl]_0$.
Sample (mol): ⊙ LiCl 1×10^{-9}, ● NaCl 1×10^{-10}, ◑ KCl 1×10^{-8}, ○ RbCl 1×10^{-8}, ◐ CsCl 1×10^{-8}

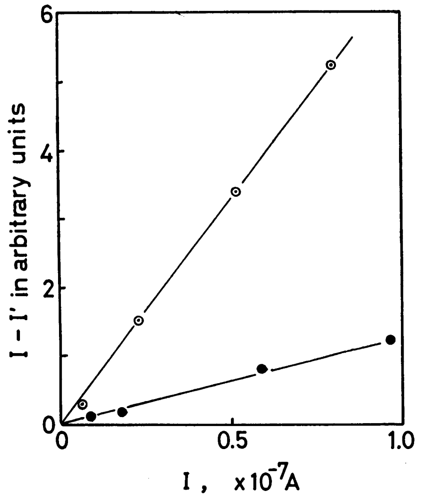

Fig. 6. Plots of $(I-I')$ against I.
Alkali metals were continuously supplied to the flame, while one milliliter of hydrogen chloride was intermittently injected to the hydrogen gas stream. Sample: ⊙ LiCl, ● NaCl

Figs. 5 and 6, respectively. Thus, $4[M]_0/(1+\phi)K_2[H]$ is considered to be negligible compared with 1. Thus Eq. (17) is simplified to

$$\frac{[M]}{[M]'} = 1 + \frac{[Cl]_0'}{(1+\phi)K_2[H]}.$$

Therefore, $(1+\phi)K_2[H]$ can be determined from the slope of straight lines in Fig. 5. They were 10^{-2} atm for lithium and 10^{-3} atm for cesium. The concentration of free alkali atoms was reduced because of the formation of MCl, and $[M]'/[M]$ was in the order of magnitude of 10^{-1}.

The second term in the brace in Eq. (14) should next be considered. The expression for the rate constant k_1 of reaction (I) is

$$k_1 = \pi r^2_{M-B}\sqrt{\frac{8kT(m_M+m_B)}{m_M m_B}}\exp\left(-\frac{E_M}{RT}\right), \quad (18)$$

where r_{M-B} is the collision diameter, m_M and m_B are respectively the atomic and molecular weight of the metal and water and E_M is the ionization potential of the metal. The collision cross-sections πr^2_{M-B} are greater than the normal gas kinetic values by several orders of magnitude and were deduced experimentally.[10] The results indicate that, although reaction (I) seems to be of first order with respect to the metal, it can not be a simple single-step process as given by reaction (I). Nevertheless, Eq. (18) with the appropriate values of the collision cross-sections can still be used to estimate the rate at which alkali metals are ionized.

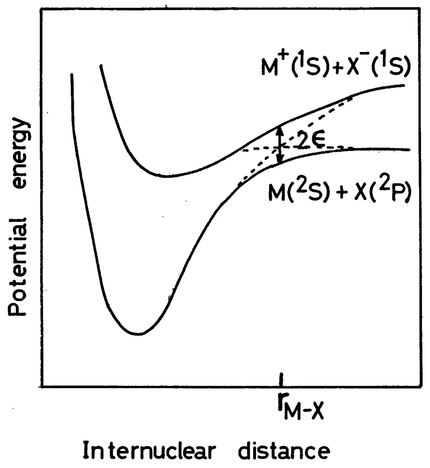

Fig. 7. Potential energy curves for electron transfer reaction.

Electron transfer reaction (II) may be considered with referring to the simple diagram of Fig. 7, which represents the potential curves for the two lowest states of the MX molecule. The rate constant k_2 of reaction (II), with a transition complex in the region of r_{M-X}, is reduced to

$$k_2 = \kappa\pi r^2_{M-X}\sqrt{\frac{8kT(m_M+m_X)}{m_M m_X}}\exp\left(-\frac{E_M-E_X}{RT}\right), \quad (19)$$

Where κ is a transmission coefficient, r_{M-X} the distance between the nuclei of alkali metal and halogen at the crossing point and E_X the electron affinity of halogen atom. The potential energy relative to the separated ions is approximately the same as at infinity, *i.e.*, E_M-E_X. Hence we have at the crossing point

$$r_{M-X} = \frac{e^2}{E_M-E_X}, \quad (20)$$

where e is the electronic charge. The values of r_{M-X} calculated from Eq. (20) give the effective collision diameters for the reaction between the various alkali metals and halogen atoms.

If χ is the probability of crossing from the lower to the upper potential energy surface, then

$$\kappa = 2\chi(1-\chi).$$

The following Landau-Zener formula gives χ in terms of 2ε:

$$\chi = \exp\left(-\frac{4\pi^2\varepsilon^2}{hv\,|s_i-s_f|}\right),$$

where 2ε is the energy equivalent to the closest distance between the upper and lower curves. Thus ε is the resonance energy in the activated state, v the velocity

TABLE 1. CALCULATED VALUES OF k_2/k_1

	F			Cl		
	1400 K	1600 K	1800 K	1400 K	1600 K	1800 K
Li	1.5×10^{10}	3.9×10^{8}	1.6×10^{7}	5.3×10^{10}	1.0×10^{9}	5.4×10^{7}
Na	3.6×10^{9}	1.0×10^{8}	4.7×10^{6}	2.8×10^{10}	6.0×10^{8}	3.2×10^{7}
K	$< 10^4$	$< 10^2$	< 10	10^2	1	10^{-1}
Rb	$< 10^4$	$< 10^2$	< 10	$< 10^2$.	< 1	$< 10^{-1}$
Cs	$< 10^4$	$< 10^2$	< 10	$< 10^2$	< 1	$< 10^{-1}$

	Br			I		
	1400 K	1600 K	1800 K	1400 K	1600 K	1800 K
Li	10^{9}[a)]	10^{7}[a)]	10^{6}[a)]	10^{4}[b)]	10^{3}[b)]	10^{2}[b)]
Na	10^{9}[a)]	10^{7}[a)]	10^{6}[a)]	10^{4}[b)]	10^{3}[b)]	10^{2}[b)]
K	1.5×10^{9}	2.8×10^{7}	2.1×10^{6}	3.1×10^{6}	2.2×10^{5}	1.6×10^{4}
Rb	4.3×10^{7}	8.1×10^{5}	5.9×10^{4}	4.3×10^{7}	2.4×10^{6}	2.0×10^{5}
Cs	$\ll 10^7$	$\ll 10^5$	$\ll 10^4$	5.3×10^{8}	2.4×10^{7}	1.1×10^{6}

a) $\epsilon \approx 100$ cal/mol., b) $\epsilon \approx 1000$ cal/mol.

with which the system passes through this configuration, and $|s_i - s_f|$ is the absolute magnitude of the difference between the slopes of the two common tangents to the curves. There will be little error in taking v as the classical mean velocity, $\sqrt{kT(m_M+m_X)/2\pi m_M m_X}$, s_i as e^2/r^2_{M-X}, and s_f as zero. Magee[11] calculated ε using the Slater one-electron wave functions. Equations (18) and (19) give the rate constant ratio of reactions (I) and (II) as

$$\frac{k_2}{k_1} = \frac{\kappa r^2_{M-X}}{r^2_{M-B}}\sqrt{\frac{(m_M+m_X)m_B}{(m_M+m_B)m_X}}\exp\frac{E_X}{RT}.$$

The calculated values of k_2/k_1 are given in Table 1.

The equilibrium constant of reaction (IV), K_3, was obtained by statistical calculations (Table 2):

TABLE 2. EQUILIBRIUM CONSTANT K_3

	1400 K	1600 K	1800 K
HF	6.9×10^{4}	1.8×10^{4}	6.7×10^{3}
HCl	1.5	1.6	1.7
HBr	5.4×10^{-3}	1.4×10^{-2}	2.6×10^{-2}
HI	3.6×10^{-5}	1.8×10^{-4}	3.8×10^{-4}

$$K_3 = \frac{f_{HX}f_H}{f_{H_2}f_X}\exp\left\{\frac{D(HX)-D(H_2)}{RT}\right\},$$

where the fs are partition functions; D_{HX} and D_{H_2} are the heats of dissociation (positive) of HX and H_2, respectively, at 0 K. $[H_2]/[H]$ was obtained by calculating[12] the composition of the flame gases at a given temperature, assuming a stoichiometric H_2–O_2 flame. It was in the order of magnitude of 10^3 at 1400—1800 K. The concentration of water molecule, [B], was about 0.6 atm, considering the water vapor

TABLE 4. EXPERIMENTAL VALUES OF i'/i ON ADDING HALOGENS[a)]

Amounts of added metal (mol)		F	Cl	Br	I
Li	1×10^{-9}	1.0	22	31	7.1
Na	1×10^{-10}	1.0	11	84	16
K	1×10^{-11}	0.9	0.7	4.5	6.5
Rb	1×10^{-11}	0.9	0.6	3.5	4.4
Cs	1×10^{-11}	0.9	0.6	1.5	1.3

a) Added halogens: C_6H_5F 2.1×10^{-3} atm; HCl 2.0×10^{-3} atm; CH_2BrCH_2Br 4.0×10^{-3} atm; CH_3I 1.6×10^{-3} atm

TABLE 5. PREDICTIONS OF THE EFFECTS OF HALOGEN ADDITION ON ION CURRENT

	F	Cl	Br	I
Li	±	+	+	+
Na	±	+	+	+
K	±	−	+	+
Rb	±	−	+	+
Cs	±	−	+	+

+: Increase, −: Decrease, ±: A little, decrease, or no change

TABLE 3. ORDERS OF MAGNITUDE OF $k_2[X]'_0/k_1\ (1+k_3[H_2]/[H])\ [B]$

	F			Cl			Br			I		
	1400 K	1600 K	1800 K	1400 K	1600 K	1800 K	1400 K	1600 K	1800 K	1400 K	1600 K	1800 K
Li	10^{-1}	10^{-1}	10^{-2}	10^{5}	10^{4}	10^{2}	10^{6}	10^{3}	10^{2}	10^{3}	1	10^{-1}
Na	10^{-1}	10^{-2}	10^{-3}	10^{4}	10^{3}	10	10^{6}	10^{3}	10^{2}	10^{3}	1	10^{-1}
K	$<10^{-1}$	$<10^{-2}$	$<10^{-3}$	$\ll 1$	$\ll 1$	$\ll 1$	10^{6}	10^{3}	10^{2}	10^{5}	10^{5}	10^{2}
Rb	$<10^{-1}$	$<10^{-2}$	$<10^{-3}$	$\ll 1$	$\ll 1$	$\ll 1$	10^{4}	10^{2}	10	10^{6}	10^{6}	10^{3}
Cs	$<10^{-1}$	$<10^{-2}$	$<10^{-3}$	$\ll 1$	$\ll 1$	$\ll 1$	$\ll 10^{4}$	$\ll 10^{2}$	$\ll 1$	10^{7}	10^{7}	10

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11) J. L. Magee, *J. Chem. Phys.*, **8**, 687 (1940).

12) A.G. Gaydon and H.G. Wolfhard, "Flames: Their Structure, Radiation, and Temperature," Chapman and Hall, London (1953), p. 264.

Table 6. Calculated values of i'/i for TID

	F		Cl		Br		I	
	1000 K	1200 K	1000 K	1200 K	1000 K	1200 K	1000 K	1200 K
Li	1	1	10^4—10^7	10—10^4	10^5—10^8	10^2—10^5	1—10^3	1
Na	1	1	10^4—10^7	10—10^4	10^5—10^8	10^2—10^5	1—10^3	1
K	1	1	1	1	10^6—10^9	10^2—10^5	10^3—10^6	1—10^3
Rb	1	1	1	1	10^4—10^7	10—10^4	10^4—10^7	10^2—10^5
Cs	1	1	1	1	$<10^4$—10^7	<10—10^4	10^6—10^9	10^3—10^6

produced in the evaporating (lower) flame. The total concentration of added halogens, $[X]_0'$, was in the order of 10^{-3} atm. Thus the second term in the brace in Eq. (14) was calculated as given in Table 3.

The results shown in Fig. 4 can be easily understood from Table 3 and the values of $[M]'/[M]$ in Fig. 5. The results from the presence of 10^{-3} atm of halogens are given in Table 4. $[M]'/[M]$ was in the order of 10^{-1} for bromine, and was nearly equal to 1 for fluorine and iodine. It can be predicted from the data of Table 3 whether the addition of halogens increases or decreases ion current. The predicted results are compatible with the experimental results as shown in Table 5. The experimental values of i'/i fairly differ from those predicted from the data in Table 3. Exact prediction is difficult in this experiment in which the diffusion flame is used. It is necessary to consider ionization not only from the ground states but also from electronically excited levels.

On TID Response. It has been found that the thermionic detector (TID) has a high sensitivity to halogen-containing compounds in gas chromatography. Karmen[13—15] proposed a TID with two burners placed one above the other and separated by a platinum screen treated with an alkali metal salt. This detector essentially consists of a combination of two self-contained detectors: a flame ionization (lower) detector and a thermionic (upper) detector. It is believed that the TID response depneds on the increase in ionization or volatilization of alkali metals. Karmen explained the sensitivity of the TID to halogen-containing compounds by the increase in volatilization. However, we see from Table 3 that the effect of halogens on ionization can not be neglected. The TID response will be discussed by means of Eq. (14).

Working conditions of the gas chromatographic detector required for the calculations were assumed as follows: the flow rates of hydrogen, air, and carrier gas (nitrogen) are 30, 400, and 40 ml/min, respectively; the flame is a stoichiometric one; mono-halogenated benzenes as halogen-containing compounds are supplied in the rate of 10^{-10}—10^{-7} g/sec (10^{-8}—10^{-5} atm in partial pressure) to the TID. Temperature of the flame used for the TID may be lower than that used for this experiment. It may be about 1000—1200 K.[16] Since $[X]_0'$ is very small, $[M]'/[M]$ is assumed to be nearly equal to 1. Calculated values of i'/i are given in Table 6.

We see that chlorine, bromine, and iodine appear to increase the ionization of all or some alkali metals, while fluorine appears to be ineffective. Karmen showed that the relative sensitivity to butyl bromide, chloride and iodide varied somewhat when screens treated with different alkali metals were used, and that the sensitivity to butyl bromide was greater than that to butyl chloride or butyl iodide for each of the screens. The sensitivity to fluorine-containing compounds was much less, but a definite response was obtained, particularly when a screen treated with a cesium salt was used. These results are consistent with the data in Table 6. However, Karmen also found that when a potassium-treated screen was used, the relative sensitivity to butyl chloride was higher than those treated with any of the other alkalis. This indicates that the increase in the volatilization of alkali metals plays an important role in the increase in sensitivity. It is almost certain that the sensitivity to fluorine-containing compounds and to chlorine-containing compounds when potassium-, rubidium-, and cesium-screens are used is due to the increase in the volatilization of alkali metals. In the case of other combinations of halogen-containing compounds and alkali metals, the response is considered to arise from the increase not only in the volatility, but also in the ionization. The increment of evaporation and ionization should be known in order to study the detection mechanism of TID in detail.

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