



Ionization and Dissociation of Molecules and Atoms by Electron Impact I. Relative Abundance, Relative Efficiency of Ionization, and Natural Isotope Abundance.

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# Ionization and Dissociation of Molecules and Atoms by Electron Impact

## I. Relative Abundance, Relative Efficiency of Ionization, and Natural Isotope Abundance.

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Mass spectra of eleven polyatomic molecules and two inert gas atoms have been measured with a 90° type single focussing mass spectrometer.

The present results on the relative abundance and the relative efficiency of ionization of these molecules and atoms are considerably in good agreement with that of our previous experiments and other investigators'. The dependence of the ionization upon ionizing voltage has been measured in details. The natural abundance of some stable isotopes (<sup>36</sup>A, <sup>15</sup>N, and <sup>13</sup>C) has also been measured and compared with the results obtained by A. O. Nier.

### 1. Introduction

The recent advances in mass spectrometric techniques have revealed many distinguished results on kinetic and analytical investigations.

In the course of these mass spectrometric investigations, it is necessary to measure the relative abundance of ions and the efficiency of ionization of pure materials. This is, of course, very labouring work, but one cannot unfortunately use the results obtained by other investigators since each instrument has usually shown the different characteristics.

Moreover, very little has been published concerning the dependence of the ionization upon ionizing voltage (mean kinetic energy of impacting electrons). The present results on these characteristics mentioned above are a part of a general study of the ionization and the dissociations by electron impact.

Data are also given on the natural isotope abundance of argon, nitrogen, carbon monoxide, carbon dioxide, ethylene, and propylene for the purpose of comparison with the results obtained by our previous investigations and other investigators'.

### 2. Experimental

**Materials.** Argon and helium of extra pure grade were obtained from Teikoku Sanso K. K.

Nitrogen was prepared from the thermal decomposition of sodium azide, and purified by passage over anhydrous phosphoric acid and passing through cold traps cooled by liquid nitrogen.

Oxygen was prepared from the thermal decomposition of silver oxide, purified by passage over solid potassium hydroxide and anhydrous phosphoric acid, and then by several fractionations.

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Hydrogen was prepared from the electrolysis of 30% solution of potassium hydroxide, purified by passing through heated palladium asbestos and cold traps cooled by liquid nitrogen, and drying on anhydrous phosphoric acid.

Hydrogen enriched in deuterium was prepared from the decomposition of heavy water (D content, 41%) on heated metallic zinc, and purified by passing through cold traps cooled by liquid nitrogen.

Carbon monoxide was prepared from the decomposition of formic acid dropped in heated phosphoric acid, purified by passage over solid potassium hydroxide and anhydrous phosphoric acid, and through cold traps cooled by liquid nitrogen.

Carbon dioxide was prepared from the thermal decomposition of magnesium carbonate, purified by passage over anhydrous phosphoric acid and then by several fractionations.

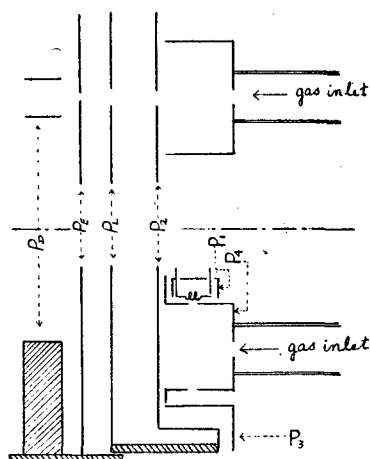
Ammonia was taken from cylinders, purified by passing through recently ignited lime and by several fractionations.

Methane was prepared from the reduction of methyl iodide by zinc-copper couple, purified by passing through fuming sulphuric acid and heated palladium asbestos, and then by fractionation using liquid nitrogen under the reduced pressures.

Ethylene and propylene were prepared from the decomposition of ethyl alcohol and propyl alcohol respectively, purified by passage over anhydrous phosphoric acid and then by several fractionations.

The purity of each material was determined by using a mass spectrometer, and no impurity could be detected within the experimental error.

**Instrument.** The present results were obtained by using a 90° single focussing Hitachi RMC mass spectrometer. The radius of curvature of the ion path and the maxi-



- P<sub>1</sub> ... Electron withdrawal plate,
- P<sub>2</sub> ... Ion accelerator "
- P<sub>3</sub> ... Electron trapper "
- P<sub>4</sub> ... Ion withdrawal "
- P<sub>D</sub> ... Differential charger "
- P<sub>E</sub> ... Earth plate,
- P<sub>L</sub> ... Lensed "

Fig. 1. Schematic diagram of the ionization chamber.

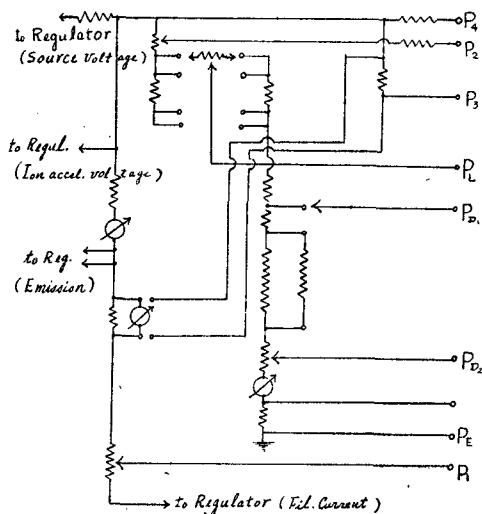


Fig. 2. Circuit diagram of the ionization chamber.

imum resolution in mass units of this instrument are 13.0 cm and 250 respectively.

The schematic and the circuit diagram of the ionization chamber are shown in Fig. 1 and Fig. 2. The schematic diagram of the gas-handling system is also shown in Fig. 3.

**Procedure.** Mass spectra have been measured at any definite ionizing voltage in the range of 20 to 150 volts. Spectra were obtained with constant ion accelerating voltage (1400 volts) and constant electron emission current. A lower magnetic field was applied for the mass range 1 to 4.

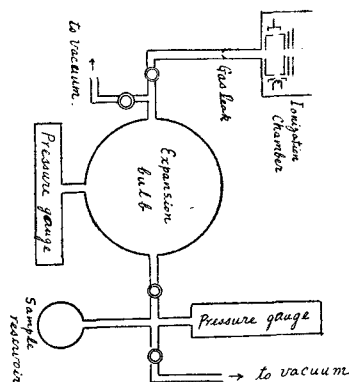


Fig. 3. Gas-handling system.

### 3. Results

Some examples of mass spectra are shown in Plate 1 to Plate 4. In these plates, ordinates indicate the peak intensity of each ion beam (arbitrary units), and abscissae indicate the numerical value of  $M/e$  ( $M$ , mass of each ion reduced to hydrogen atom mass units;  $e$ , number of the positive charge). Lower two figures in these plates were recorded by employing the different kinds of galvanometers (sensitivity ratio is about 10), and upper two belong to the blank experiment.

Table 1 and Table 2 list the abundance ratio of ions relative to each parent ion, and the last two columns give the results obtained by one of us, and other investigators.

The dependence of the ion currents upon impacting electron energy is plotted in Fig. 4 to Fig. 10.

To avoid confusion, only a few principal ion is plotted in Fig. 5 to Fig. 9.

In these figures (Fig. 4 to Fig. 10), the ion current is indicated by the value reduced to the standard conditions, then the total ion current in Fig. 10 coincides with the "relative efficiency" of ionization\*. The relation between the total ion current and the pressure in the expansion bulb (see Fig. 3) are plotted in Fig. 11 and Fig. 12. Such relation, i. e., the total ion current of each sample gas is simply proportional to its pressure in the expansion bulb, was obtained for any definite ionizing voltage within the experimental error.

Table 3 gives the relative efficiency of ionization obtained from the results shown in Fig. 10, Fig. 11, and Fig. 12. The relative efficiency of deuterium ( $HD$  and  $D_2$ ) in this

\* Other investigators occasionally use the term "the probability of ionization". "The probability of ionization" is defined as the number of ionizing collisions made per cm of path through a gas at 1 mmHg. and  $0^\circ\text{C}$ . But this quantity is not observed in the usual mass spectrometric investigations except the case of Tate and Smith<sup>5</sup>, and it varies with the design of a gas flow system (especially with the geometry of a gas leak) of each instrument. The present results were represented by the total ion current (proportional to the number of ionizing collisions) relative to that of argon and reduced to the pressure of 0.1 mmHg. (pressure in the expansion bulb) and the temperature of the ionization chamber. Since the term "relative efficiency" is used,

Table 1. Relative abundance of inorganic substances.

(Ionizing voltage, 100 V. Total emission current, 200  $\mu$ A)

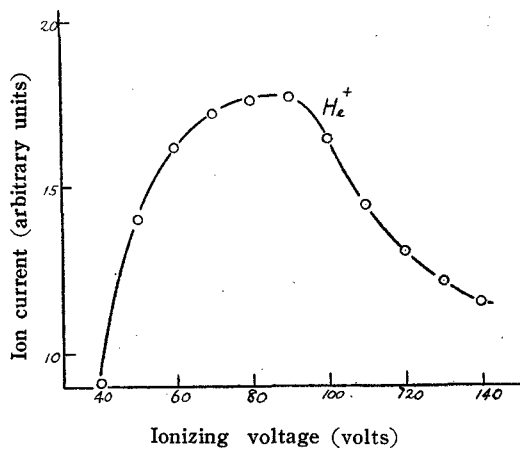
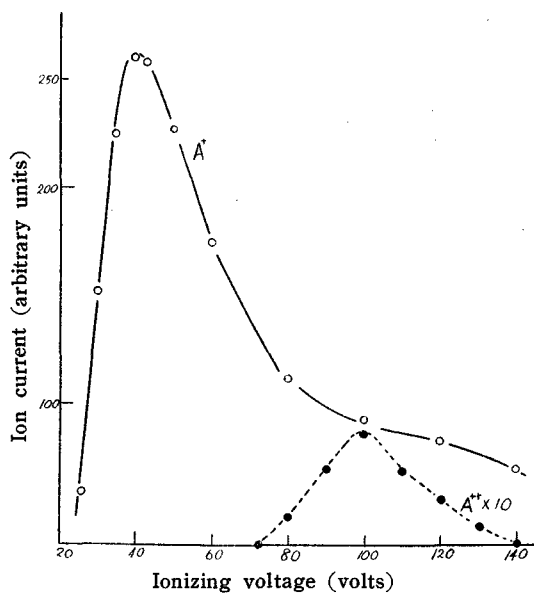
(Ion accelerating voltage, 1400 V.)

Substance	M/e	Ion	Present authors	T. Hayakawa <sup>1)</sup>	Other investigators <sup>2)</sup>
Argon	13.3	A <sup>+++</sup>	0.041		
	20	A <sup>++</sup>	8.53		
	36	<sup>36</sup> A <sup>+</sup> .....isotope	0.308		
	38	<sup>38</sup> A <sup>+</sup> .....isotope	0.061		
	40	A <sup>+</sup>	100		
Nitrogen	14	N <sup>+</sup>	17.3	3.50	
	28	N <sub>2</sub> <sup>+</sup>	100	100	
	29	<sup>15</sup> NN <sup>+</sup> .....isotope	0.75	0.49	
Oxygen	16	O <sup>+</sup>	28.2	4.55	
	32	O <sub>2</sub> <sup>+</sup>	100	100	
	34	<sup>18</sup> OO <sup>+</sup> .....isotope	0.41	—	
Hydrogen	1	H <sup>+</sup>	2.82	1.94	
	2	H <sub>2</sub> <sup>+</sup>	100	100	
Ammonia	14	N <sup>+</sup>	2.23	—	
	15	NH <sup>+</sup>	58.1	—	
	16	NH <sub>2</sub> <sup>+</sup>	78.0	—	
	17	NH <sub>3</sub> <sup>+</sup>	100	—	
Carbon monoxide	12	C <sup>+</sup>	5.49	1.83	
	14	CO <sup>++</sup>	0.19	0.47	
	16	O <sup>+</sup>	3.04	1.02	
	28	CO <sup>+</sup>	100	100	
	29	<sup>13</sup> CO <sup>+</sup> , C <sup>17</sup> O <sup>+</sup> ..... .....isotope	1.13	1.16	
Carbon dioxide	12	C <sup>+</sup>	11.2	2.67	6.67
	16	O <sup>+</sup>	13.9	5.00	9.40
	22	CO <sub>2</sub> <sup>++</sup>	1.14	1.11	—
	28	CO <sup>+</sup>	16.25	47.08	8.17
	29	<sup>13</sup> CO <sup>+</sup> , C <sup>17</sup> O <sup>+</sup> ..... .....isotope	0.22	1.01	0.10
	32	O <sub>2</sub> <sup>+</sup>	1.84	0.88	—
	44	CO <sub>2</sub> <sup>+</sup>	100	100	100
	45	<sup>13</sup> CO <sub>2</sub> <sup>+</sup> , C <sup>17</sup> OO <sup>+</sup> ... .....isotope	1.20	1.19	—

Table 2. Relative abundance of hydrocarbons.

 (Ionizing voltage, 100 V.  
 Total emission current, 200  $\mu$ A.  
 Ion accelerating voltage, 1400 V.)

Sub-stance	M/e	Principal ion	Present authors	Other investi-gators <sup>2),3)</sup>	Sub-stance	M/e	Principal ion	Present authors	Other investi-gators <sup>2),3)</sup>
Methane	1	H <sup>+</sup>	9.40	5.93	Propylene	1	H <sup>+</sup>	5.37	
	2	H <sub>2</sub> <sup>+</sup>	0.80	0.59		2	H <sub>2</sub> <sup>+</sup>	1.21	
	12	C <sup>+</sup>	2.01	1.18		12	C <sup>+</sup>	1.09	1.26
	13	CH <sup>+</sup>	5.03	3.35		13	CH <sup>+</sup>	1.61	1.80
	14	CH <sub>2</sub> <sup>+</sup>	14.6	8.28		14	CH <sub>2</sub> <sup>+</sup>	3.27	3.61
	15	CH <sub>3</sub> <sup>+</sup>	80.8	77.9		15	CH <sub>3</sub> <sup>+</sup>	4.83	5.40
	16	CH <sub>4</sub> <sup>+</sup>	100	100		16	<sup>13</sup> CH <sub>3</sub> <sup>+</sup> ...isotope	0.15	0.16
Ethylene	1	H <sup>+</sup>	12.5			19	C <sub>3</sub> H <sub>2</sub> <sup>++</sup>	3.47	3.23
	2	H <sub>2</sub> <sup>+</sup>	1.10			19.5	C <sub>3</sub> H <sub>3</sub> <sup>++</sup>	2.16	1.96
	12	C <sup>+</sup>	1.89	2.14		20	C <sub>3</sub> H <sub>4</sub> <sup>++</sup>	1.82	2.35
	13	CH <sup>+</sup>	3.26	3.52		20.5	C <sub>3</sub> H <sub>5</sub> <sup>++</sup>	0.41	0.67
	13.5	C <sub>2</sub> H <sub>3</sub> <sup>++</sup>	0.37	0.42		24	C <sub>2</sub> <sup>+</sup>	0.58	0.52
	14	CH <sub>2</sub> <sup>+</sup>	6.20	6.31		25	C <sub>2</sub> H <sup>+</sup>	2.27	2.16
	15	CH <sub>3</sub> <sup>+</sup>	0.27	0.56		26	C <sub>2</sub> H <sub>2</sub> <sup>+</sup>	10.0	10.5
	24	C <sub>2</sub> <sup>+</sup>	3.24	3.71		27	C <sub>2</sub> H <sub>3</sub> <sup>+</sup>	36.1	38.3
	25	C <sub>2</sub> H <sup>+</sup>	8.59	11.7		28	C <sub>2</sub> H <sub>4</sub> <sup>+</sup>	2.34	1.34
	26	C <sub>2</sub> H <sub>2</sub> <sup>+</sup>	55.8	62.3		36	C <sub>3</sub> <sup>+</sup>	2.14	2.42
	27	C <sub>2</sub> H <sub>3</sub> <sup>+</sup>	58.8	64.8		37	C <sub>3</sub> H <sup>+</sup>	12.3	13.6
	28	C <sub>2</sub> H <sub>4</sub> <sup>+</sup>	100	100		38	C <sub>3</sub> H <sub>2</sub> <sup>+</sup>	16.8	19.3
	29	C <sup>13</sup> CH <sub>4</sub> <sup>+</sup>	2.46	2.24		39	C <sub>3</sub> H <sub>3</sub> <sup>+</sup>	68.3	71.1
						40	C <sub>3</sub> H <sub>4</sub> <sup>+</sup>	26.2	28.9
				41	C <sub>3</sub> H <sub>5</sub> <sup>+</sup>	100	100		
				42	C <sub>3</sub> H <sub>6</sub> <sup>+</sup>	68.9	67.7		


 Fig. 4. Helium (Total emission current, 200  $\mu$ A.  
 Ion accelerating voltage, 1400V.)

 Fig. 5 Argon (Total emission current, 200  $\mu$ A.  
 Ion accelerating voltage, 1400V.)

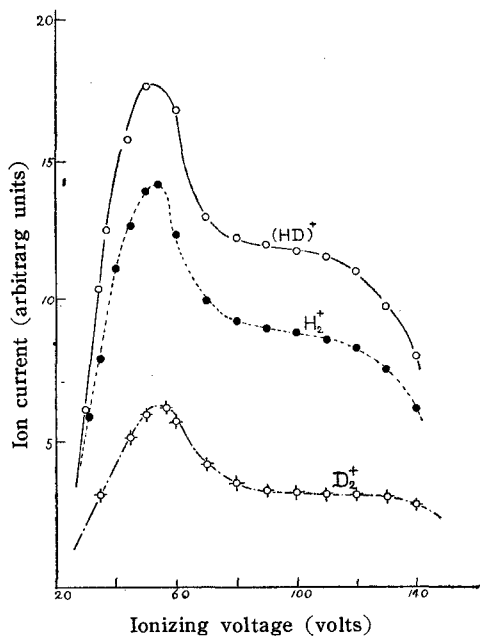


Fig. 6.  $H_2$ -HD- $D_2$  mixture ( $H_2$ , 35 mol.%)  
 (HD, 48 "  
 ( $D_2$ , 17 "  
 (Total emission current,  $200\mu A$ .)  
 (Ion accelerating voltage, 1400V.)

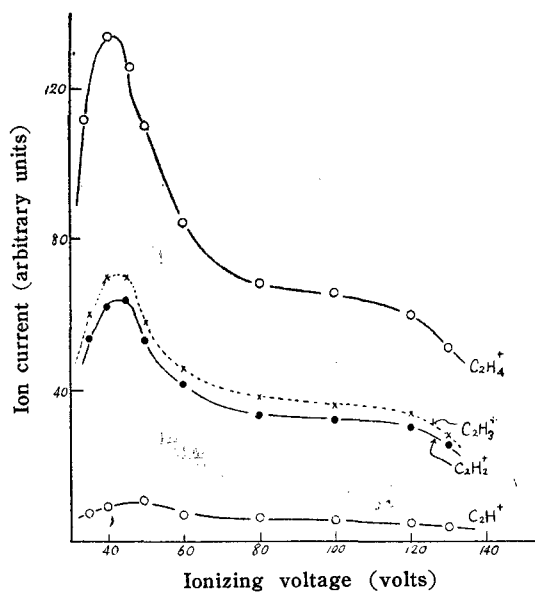


Fig. 8. Ethylene (Total emission current,  $200\mu A$ )  
 (Ion accelerating voltage, 1400V)

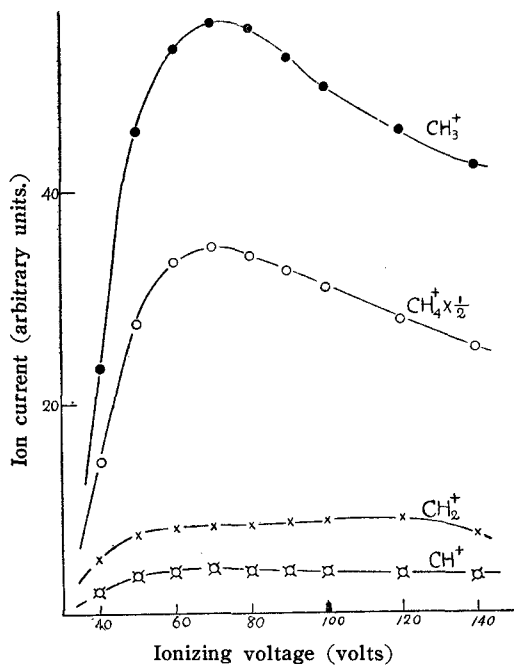


Fig. 7. Methane (Total emission current,  $200\mu A$ )  
 (Ion accelerating voltage, 1400V)

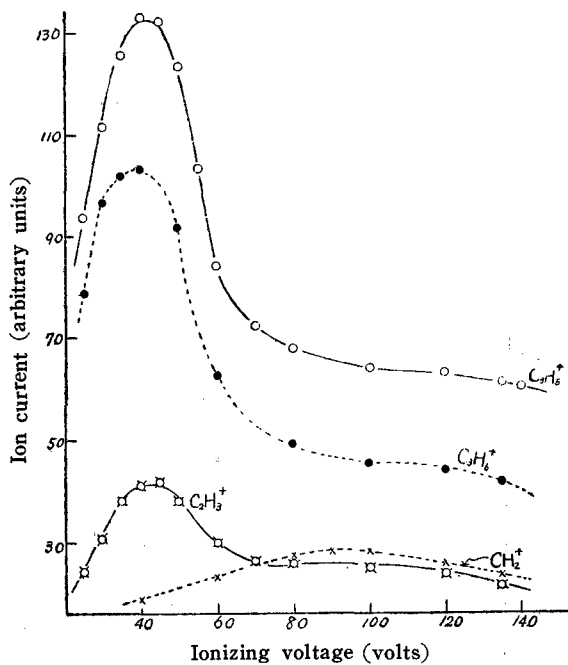


Fig. 9. Propylene (Total emission current,  $200\mu A$ )  
 (Ion accelerating voltage, 1400V)

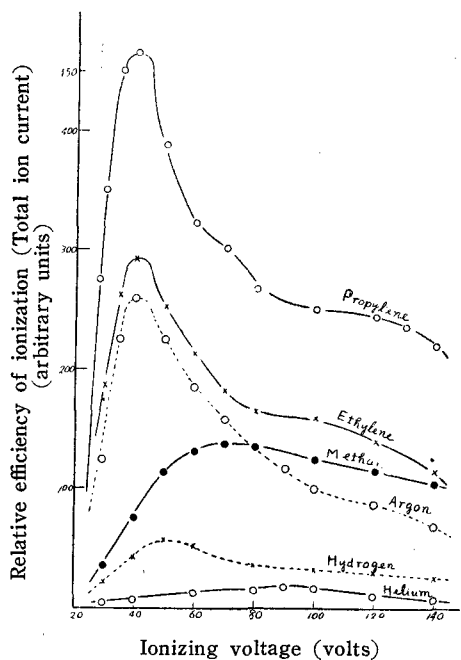


Fig. 10. Relative efficiency of ionization.

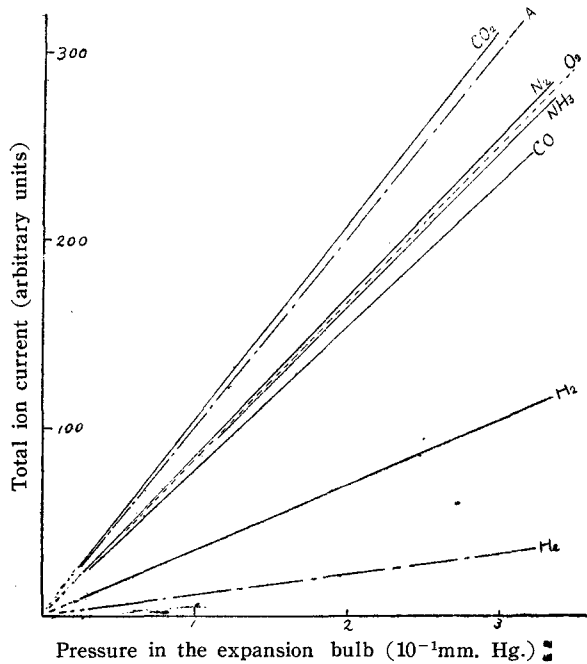


Fig. 11. Dependence of the total ion current upon the pressure.

(Ionizing voltage, 100V.  
Total emission current,  $200\mu A$ .  
Ion accelerating voltage, 1400V.)

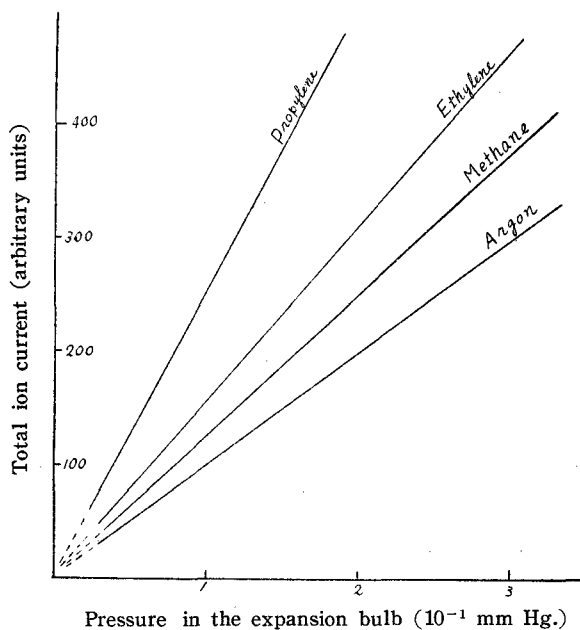


Fig. 12. Dependence of the total ion current upon the pressure.

(Ionizing voltage, 100V.  
(Total emission current,  $200\mu A$ .  
Ion accelerating voltage, 1400V.)



table was calculated from the present results (Fig. 6, Fig. 10, and Fig. 11) and other analytical results on the composition of heavy water ( $H_2$ , 35; HD, 48;  $D_2$ , 17 in mole %), on the assumption that heavy water was completely decomposed over zinc surfaces.

The natural isotope abundance of  $^{36}A$ ,  $^{15}N$ , and  $^{13}C$  measured in the present experiments is listed in Table 4.

Table 3. Relative efficiency of ionization.

(Ionizing voltage, 100 V.  
Total emission current, 20  $0\mu A$ .  
Ion accelerating voltage, 1400 V.)

Substance	Present authors	T. Hayakawa <sup>1)</sup>	T. Kambara <sup>4)</sup>	Tate and Smith <sup>5)</sup> (Probability of ionization)
A	100.0	100.0	100.0	100.0
He	10.6	—	—	—
N <sub>2</sub>	83.4	82.7	81.4	83.4
O <sub>2</sub>	83.0	37.4	85.0	83.6
H <sub>2</sub>	34.8	31.6	29.7	29.3
HD	34.3	—	—	—
(D <sub>2</sub> )	(30.4)	—	—	—
CO	80.6	101.3	—	92.1
CO <sub>2</sub>	102.0	90.9	—	—
NH <sub>3</sub>	82.4	—	—	—
CH <sub>4</sub>	126.2	—	—	—
C <sub>2</sub> H <sub>4</sub>	161.2	—	—	—
C <sub>3</sub> H <sub>6</sub>	251.1	—	—	—

Table 4. Natural abundance ratio of  $^{15}N$ ,  $^{13}C$ ,  $^{36}A$  and  $^{38}A$ .

Material	Source	Natural abundance ratio	Investigators
Nitrogen	Sodium azide	$^{15}N/^{14}N$ , $0.38 \times 10^{-2}$	Present authors
"	Atmospheric	" , 0.37 "	Tate et. al. <sup>6)</sup>
Argon	Atmospheric	$^{36}A/^{40}A$ , $0.308 \times 10^{-2}$	Present authors
"	"	$^{38}A/^{40}A$ , 0.061 "	"
"	"	$^{36}A/^{40}A$ , 0.307 "	A. O. Nier <sup>7)</sup>
"	"	$^{38}A/^{40}A$ , 0.058 "	"
Carbon dioxide	Magnesium carbonate	$^{13}C/^{12}C$ , 0.0112	Present authors
Carbon monoxide	Formic acid	" , 0.0109	"
(Ethylene)	(Ethyl alcohol)	( " , 0.0128 ?)	"
(Propylene)	(Propyl alcohol)	( " , 0.0120 ?)	"
Carbon dioxide	Calcium carbonate	" , 0.0113	Nier et. al. <sup>8),9)</sup>
"	(Natural distribution)	( " , 0.0106~0.0114)	"
"	Sodium bicarbonate	" , 0.0108	T. Kambara <sup>10)</sup>
"	Magnesium carbonate	" , 0.0111	T. Hayakawa <sup>11)</sup>
Carbon monoxide	Formic acid	" , 0.0110	"

#### 4. Discussion

Table 1 and Table 2 indicate that the present results on the relative abundance are, despite of the fact that the different types of mass spectrometers were employed, rather in good agreement with the results obtained by other investigators. Though the present results for nitrogen, oxygen, carbon monoxide, and carbon dioxide are somewhat different from our previous results, probably this may be attributed to the difference in the types of the ionization chambers.

Comparing our results with that of Tate and Smith<sup>5)</sup>, the maximum of the total ionization (Fig. 10) for argon, hydrogen, and helium respectively seems to appear at the lower ionization voltage. This is not so surprising, since the geometry of the ionization chambers (especially in the electron path) was considerably different.

As seen in Table 3, the present results on the relative efficiency of ionization are generally in good agreement with the results previously reported by one of us and by other investigators.

Table 4 indicates that the present measurements on the natural abundance ratio of some stable isotopes, <sup>36</sup>A, <sup>38</sup>A, <sup>15</sup>N, and <sup>13</sup>C, well coincide with the results obtained by Nier, and Tate.

The variations of the natural abundance ratio <sup>13</sup>C/<sup>12</sup>C according to source were extensively investigated by Nier. Though our results (both for the present and the previous investigations<sup>11)</sup>) remain in the distribution range obtained by Nier, further researches must be made for discussing the dependence of the natural abundance ratio on each source.

In order to estimate the natural isotope abundance of <sup>13</sup>C in hydrocarbon molecules, Washburn<sup>12)</sup> has given an equation by means of which a monoisotopic peak may be calculated from measured polyisotopic peaks.

$$M_r = P_r - P_{r-1}\{cn + h(r-1)\} + P_{r-2}[\{cn + h(r-2)\}\{cn + h(r-1)\} - \{n(n-1)c^2/2 + nch(r-2) + (r-2)(r-3)h^2/2\}],$$

where  $n$  = number of carbon atoms in the ion,  
 $r$  = number of hydrogen atoms in the ion,  
 $h$  = ratio D/H,  
 $c$  = ratio <sup>13</sup>C/<sup>12</sup>C,  
 $M_r$  = monoisotopic peak of formula  $C_nH_r$ ,  
 $P_r$  = polyisotopic peak of principal formula  $C_nH_r$ .

The present results obtained from applying this equation for ethylene and propylene, are also listed in table 4. Unfortunately, since this method is not so adequate, the no reliable results obtained from these calculations.

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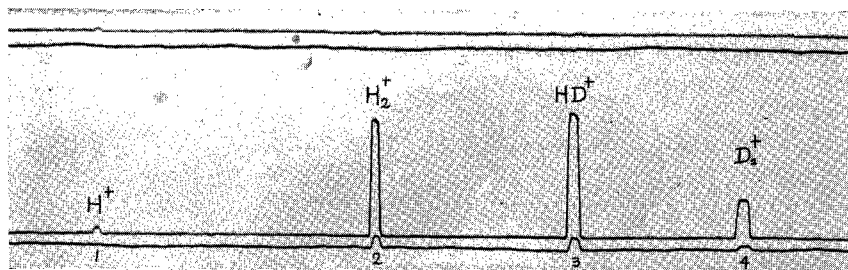


Plate 1. Hydrogen-deuterium mixture. ( $H_2$ , 35; HD, 48;  $D_2$ , 17 in mole %)

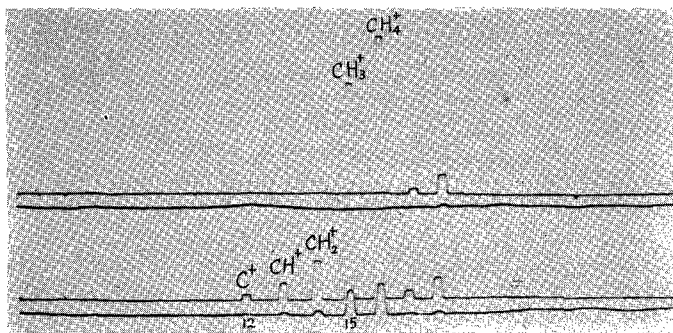


Plate 2. Methane.

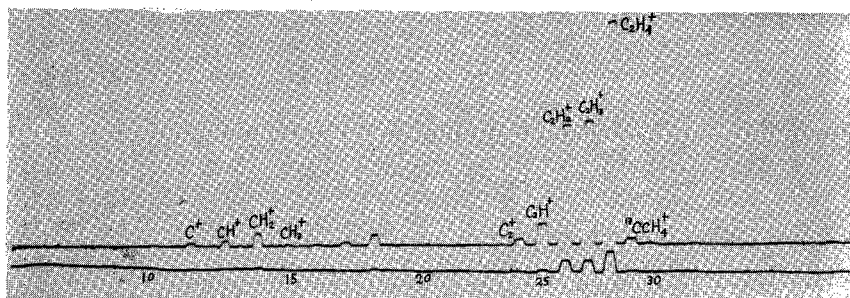


Plate 3.  
Ethylene.

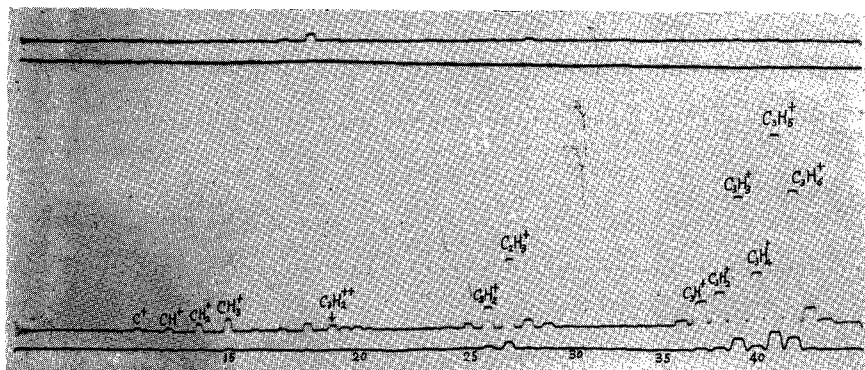


Plate 4.  
Propylene.