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STUDIES ON THE PHYSICOCHEMICAL PROPERTIES OF ASTATINE AND RADON BY RADIOGASCHROMATOGRAPHY

by

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(Thesis)

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To know is nothing at all;
To imagine is everything.

- Anatole France -

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ABSTRACT

The physicochemical properties of astatine and radon, i.e., the chemical form of elementary astatine and the boiling points of astatine and radon, have been studied by means of a newly designed radiogaschromatography.

Astatine used was synthesized by ^{209}Bi(^{3}He, 3n)^{209}At reaction. Astatine zero was extracted into carbon tetrachloride from 1 N HNO_3 solution, and then it was mixed with the $^{131}I_2$ solution which contained a small amount of I_2 carrier. This sample was analyzed by the radiogaschromatography, and then the boiling points of the peaks observed was estimated by the use of a semi-empirical formula relating the retention volume with the boiling point of an object. Further, the chemical form was determined on the basis of the rule found for the boiling points of diatomic interhalogen compounds. The boiling point of radon was estimated too, after the semi-empirical formula was confirmed by using xenon to hold on rare gases.

The boiling points obtained were 503 ± 3 and 198 ± 2 K for astatine and radon, respectively. These values were

much lower than the extrapolated values from the lighter elements in the same groups, and the boiling point of radon was lower than that obtained by Gray and Ramsay.

The deviation was concluded to be well explained by the Pauling's screening constant on both astatine and radon.

I. INTRODUCTION

A. ESTIMATION OF PHYSICOCHEMICAL PROPERTIES OF ASTATINE AND RADON

As well known astatine and radon are the heaviest elements in halogens and rare gases, respectively, the existence of which has been confirmed until now. It is very difficult to study their physicochemical properties by usual method, because they are short-lived radioisotopes and so only the trace amounts can be dealt with. When gross amounts are treated, various effects due to radioactive disintegration must be considered. Hence, the properties of them have been estimated by many ways. The most popular method is to extrapolate the properties of the elements which belong to the same group as the object. The boiling points[I-1], some critical properties (critical temperature, pressure and volume)[I-2, 3], and ionization potentials [I-4], for example, were estimated by this method. As these values are not confirmed experimentally, there are no guarantees that the extrapolation is possible beyond the experimental values. Thus it would be far difficult to estimate the properties of eka-astatine and eka-radon, which are very interesting from the standpoint of nuclear chemistry.

B. CHEMICAL PROPERTIES OF ASTATINE AND RADON

The chemical behavior of astatine has been investigated by many workers[I-5 to I-7]. The chemical behavior of this element is similar to iodine in general, but it is partly different. It is very important when the element is separated from the target and is purified. When it is artificially synthesized, the element is separated with the consideration of the followig behaviors[I-8 to I-11]: (1) Since astatine has a tendency to be adsorbed on surfaces of glass as many other trace species, precautions must be taken to avoid this cause of error. (2) From solutions, in which astatine is only partially reduced by sulfur dioxide, it is partially carried by thallium iodide, but completely carried by silver iodide. (3) In the presence of iodine, astatine is best isolated by the precipitation of an iodide from a reducing solution, but sometimes silver nitrate does not precipitate astatine from a slightly nitric acid solution using potassium iodide as a carrier. This is probably due to losses of astatine from the AgI lattice as pointed out[I-12]. Precipitation with PdI from the solution containing sulfite and an excess of nitric acid is more reliable, because palladium iodide recrystallize more slowly than silver iodide[I-13]. (4) Astatine zero is extracted readily from nitric acid solutions into organic solvents such as benzene and carbon tetrachloride. The partition coefficients are rather variable and depends on mainly on the type of impurities present. Most of astatine is extracted into organic solvents can be back-extracted into aquaous phase containing NaOH, because of hydrorysis.

Although radon has been thought to be chemically inactive, there are some evidences that it forms the compounds with halogens like xenon[I-14,15].

C. RADIOGASCHROMATOGRAPHY

Methods of radiogaschromatography is extraordinarily sensitive. They provide qualitative and quantitative data and require only very small amounts of samples. The technique of radiogaschromatography differs from current gas chromatography only in the detector which records the radioactivity of gaseous mixture and vapours in their exit from the column. The general requirments are the posibility of measuring radioactivity over a wide range and with suficient accuracy. These measurements can be carried out discontinuously or continuously in the flow.

The discontinuous (batch) method is very simple procedure and consists in measuring radioactivity of various fractions of the separated substance at the exit of a column. It is used in the case of low specific activities. The eluate is adsoved on some suitable material. The column should be adjusted to permit the connection of absoption vessels, which are either replaced at regular intervals or after each fraction. Although this method is very sensitive, each radioactive fraction should be collected quantitatively. There are several ways for the collection of sample. Separated fractions are trapped into condensor vessel colled with a dry-ice or liquid-nitrogen[I-16,17] and are adsorbed on active charcoal, millipore filters and adsorption cotton[I-18].

In the continuous analysis the detectors of radiation are placed in series with the column. An advantage of this method is that the samples are always monitored with fairly high sensitivity. The type of radioactivity detector used is determined by the type of radiation to be detected and the working conditions of analysis (e.g., carrier gas, chemical composition of sample etc.), particularly in the case of flow proportional counter or ionization chamber, where the eluted gases form directly the functional component of detector.

Radiation detectors used are changed accorging to the type and energy of the radiation emitted by the detected radionuclides. Though the most suitable detector in the continuous measurement of gamma rays of effluents is a scintillation counter, a proportional counter is suitable to detect beta and alpha rays. In the present study the proportional counter was used.

II. ESTIMATION OF THE CHEMICAL FORM AND THE BOILING POINT OF ELEMENTARY ASTATINE

A. INTRODUCTION

Astatine, the heaviest element in the halogens was artifficially synthesized for the first time by Corson et al.[II-1]. It was produced in the ^{209}Bi(He, 2n)^{211}At reaction using 32 MeV alpha particles at the Crocker Radiation Laboratory cyclotron. A very large number of astatine isotopes, which have various half-lives ranging from 0.1 μsec to 8.3 h, have been discovered until now as shown in Table II-1. The isotopes of importance in the chemical studies of astatine are ^{211}At, ^{210}At and ^{209}At, because their half-lives are the most suitable for the treatment of astatine, and other isotopes are of very short life.

Although the chemical properties of the element (e.g., oxidation state, extractability, reactability etc.)[II-2 to II-5] have been studied since the discovery of the

Table II-1. Isotopes of astatine

Mass	Half life	Decay	Production mode	Reference
196	0.3 sec		$^{185}\mathrm{Re}(^{20}\mathrm{Ne}, 9n)$	II-6
177	0.3 sec		$^{185}\mathrm{Re}(^{20}\mathrm{Ne}, 8n)$	II-6
198	4.9 sec		$^{185}\mathrm{Re}(^{20}\mathrm{Ne}, 7n)$	II-6
199	7.2 sec		$^{185}\mathrm{Re}(^{20}\mathrm{Ne}, 6n)$	II-6
200	42 sec	α, EC+β^{+}	$^{197}\mathrm{Au}(^{12}\mathrm{C}, 9n)$	II-7
201	1.5 m	α, EC+β^{+}	$^{197}\mathrm{Au}(^{12}\mathrm{C}, 8n)$	II-7
202	3.0 m	α, EC+β^{+}	$^{197}\mathrm{Au}(^{12}\mathrm{C}, 7n)$	II-8
203	7.3 m	α, EC+β^{+}	$^{197}\mathrm{Au}(^{12}\mathrm{C}, 6n)$	II-8
204	9.3 m	α, EC+β^{+}	$^{209}\mathrm{Bi}(\alpha, 9n)$	II-9
205	26.2 m	α, EC+β^{+}	$^{209}\mathrm{Bi}(\alpha, 8n)$	II-10
206	31.4 m	α, EC+β^{+}	$^{209}\mathrm{Bi}(\alpha, 7n)$	II-11
207	1.8 h	α, EC+β^{+}	$^{209}\mathrm{Bi}(\alpha, 6n)$	II-9
208	1.6 h	α, EC+β^{+}	$^{209}\mathrm{Bi}(\alpha, 5n)$	II-10
209	5.4 h	α, EC+β^{+}	$^{209}\mathrm{Bi}(\alpha, 4n)$	II-11
210	8.3 h	α, EC+β^{+}	$^{209}\mathrm{Bi}(\alpha, 3n)$	II-12
211	7.2 h	α, EC+β^{+}	$^{209}\mathrm{Bi}(\alpha, 2n)$	II-13
212	0.31 sec	α	$^{209}\mathrm{Bi}(\alpha, n)$	II-14
213	0.11 sec	α	$^{209}\mathrm{Bi}(^{22}\mathrm{Ne}, 2n)$	II-15
214	2 μsec	α	descendant $^{226}\mathrm{Pa}$	II-16
215	0.1 msec	α	descendant $^{227}\mathrm{Pa}$	II-16

Table II-1 (continued)

Mass	Half life	Decay	Production mode	Reference
216	0.3 msec	α	descendant ^{228}Pa	II-16
217	32.3 msec	α, β^-	descendant ^{225}Ac	II-17
218	1.5 sec	α, β^-	daughter ^{226}Ac	II-17
219	0.9 msec	α, β^-	daughter ^{227}Ac	II-18

element, the chemical form of elementary astatine has not been determined untill now. Astatine is usually present in a volatile state, which has been assumed generally to be At_2, when left to its own devices in acidic solution. This state has been reffered to "At(0)"[II-19]. Astatine in this state, either as vapor or in dilute nitric acid, has a tendency to be adsorbed by various metalic surface and glass. This form of astatine can be extracted from dilute nitric acid solutions by ethers, carbon tetrachloride or carbon disulfide. It has usually been assumed that the astatine species present in "At(0)" solutions is At_2, but Aten, Jr. mentioned that pure astatine didn't seem to be At_2 in aquaous solutions in view of the very low concentration of the element[II-20].

The determination of the chemical form of elementary astatine has been attempted by Appleman et al.[II-21]. and Golovkov et al.[II-22] through the use of a mass spectrometer to measure the mass directly. In spite of their efforts the existence of At_2 couldn't be confirmed. One reason of their failure is that the dissociation of At_2 might be occured in the plasuma ion source. Furthermore, even if At_2^+ is observed it may be due to the reaction of $At + At^+ \longrightarrow At_2^+$ in the ion source as pointed out by Golovkov et al.[II-22].

There has been no experimental value on the boiling point of elementary astatine because of the reasons mentioned below:

(1) The direct measurement of the boiling point is very difficult because astatine has no long-lived isotope and a massive preparation of the sample is difficult.

(2) Besides, heat is produced by the radioactive disintegration.

(3) The care for boiling point elevation can not be avoided because astatine produces a considerable amount of polonium by EC-decay.

On the other hand, the boiling points of astatine compounds were estimated indirectly by Samson et al.[II-23] and Meyer et al. [II-24] using a radiogaschromatography (RGC). When the retention volumes of astatine compounds were measured at a constant column temperature, the boiling point was estimated by the extrapolation of the strait line relating the boiling point with the retention volume obtained on the group of nalogous compouds (e.g., CH F, CH_3Cl, CH_3Br ,CH_3I and CH_3At). This rule holds at a constant column temperature only, so that this method cannot be applied to groups which have large variation of the retention volume at a given temperature. This method cannot be applied to elementary halogens.

Though the radiogaschromatographic method is indirect it is very suitable for the estimation of the boiling point of trace radioisotopes. There are no problems on the heat produced by the decay and the boiling point elevation. Further, massive preparation of the sample isn't needed. Also trace samples can be detected with high sensitivity using a radioactive detector. Many studies on the analysis of various radioisotopes have been done by the RGC [II-25, 26].

In the present work $^{131}I_2$ containing carrier I_2 (about ten times the amount of $^{131}I_2$) was mixed into "At(0)" solution, and then the sample was analyzed by means of a newly designed RGC. It has been well known that AtI was formed when I_2 was mixed into "At(0)" solution, so three peaks might be observed in the radiochromatogram, viz., I_2, AtI and "At(0)". These peaks were assigned by a sophisticated procedure, and hence the chemical form of elementary astatine was determined. Further, the boiling point of the element was estimated with the semi-empirical theory[II-27] relating the boiling point to the absolute retention volume of an object on gas chromatography.

Since the absolute retention volume is expressed as the function of moles and solubility parameter of the solvent in a column, the boiling point of an object, mean boiling point of sample's family and the column temperature, the boiling point of an object can be estimated from the measured retention volume at a given column temperature. In this point this method is quite different with Samson's. This method has been widely applied to molecular samples, especially halogens[II-29].

B. EXPERIMENTAL PROCEDURES

B-1. Preparation of Astatine

Astatine-209 was produced by the bombardment of 22 μm thick bismuth, which was deposited onto a 15 μm thick aluminum foil by evapolation in vacuo, with 26 MeV ^{3}He of the OULNS* cyclotron. In Fig. II-1 the seting of the target at bombardment is sketched. The target, which was wrapped up in aluminum foil, was cooled by circulating water. This target assembly was held with a special holder at the irradiation port of the cyclotron. The total beam on the target was measured in terms of the integrator. The irradiation time was 3 to 4 hours, which was an appropriate time for the production of ^{209}At, and the average current was about 2 μA. The yields of astatine isotopes produced were 80 μCi for ^{209}At and 7 μCi for ^{210}At, which were

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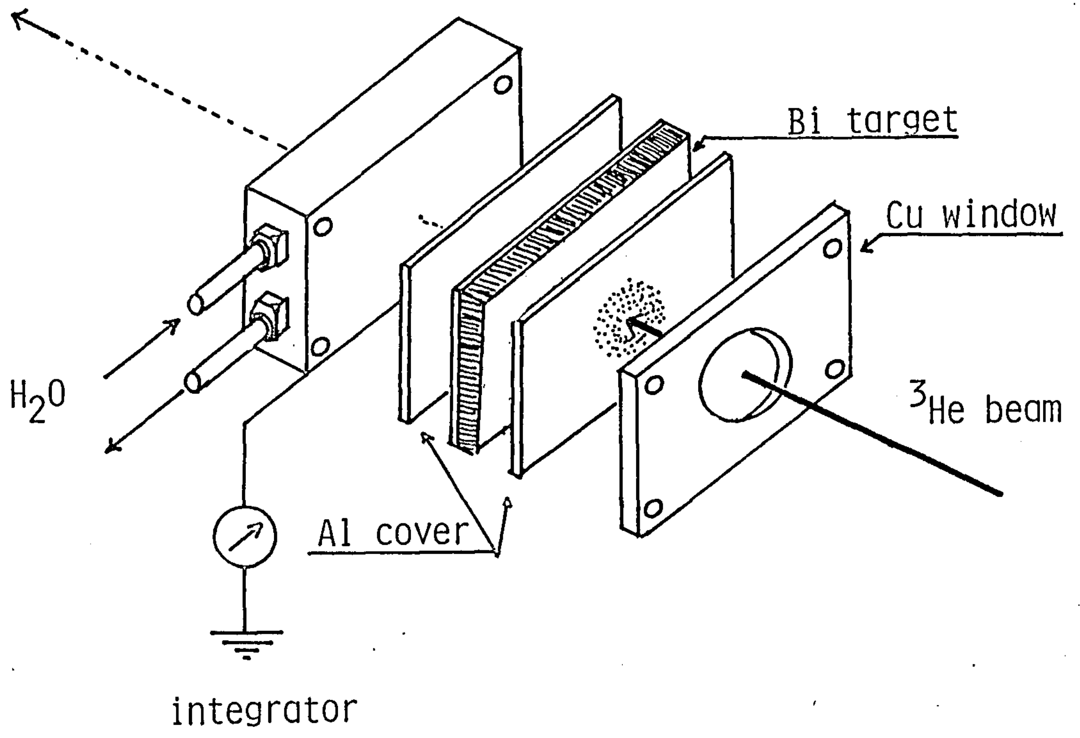


Fig. II-1. Arrangement of the target

calculated on the basis of the excitation function[II-30] shown in Fig. II-2.

After the irradiation the bismuth target was cooled for half an hour, and then it was removed from the target holder. The activities produced in the target was measured by means of a 60 cc Ge(Li) detector. The gamma spectrum which was observed on the target an hour after the end of the bombardment is shown in Fig. II-3. The peaks shown in the gamma spectrum are mostly atributable to ^{209}At and ^{210}At. The target was dissolved into 1 N HNO_3 and then "At(0)" was extracted with carbon disulfide according to the process shown in Fig. II-4. Final activity of ^{209}At was 50 Ci and the volume of the solution was 100 μl. This solution contained a few μCis of ^{210}At.

B-2. Radiogaschromatographyic Apparatus

In Fig. II-5 the block diagram of the RGC that is newly designed for the purpose of this study is shown. This system is constructed from the Bendix Series 2200 Laboratory Gas Chromatograph, a gas-flow type proportional counter and several electric instruments for the measurement of radioactivity. A four meteter stainless steel column with 3 mm inside diameter was packed with 10 %w/w Silicon DC 550

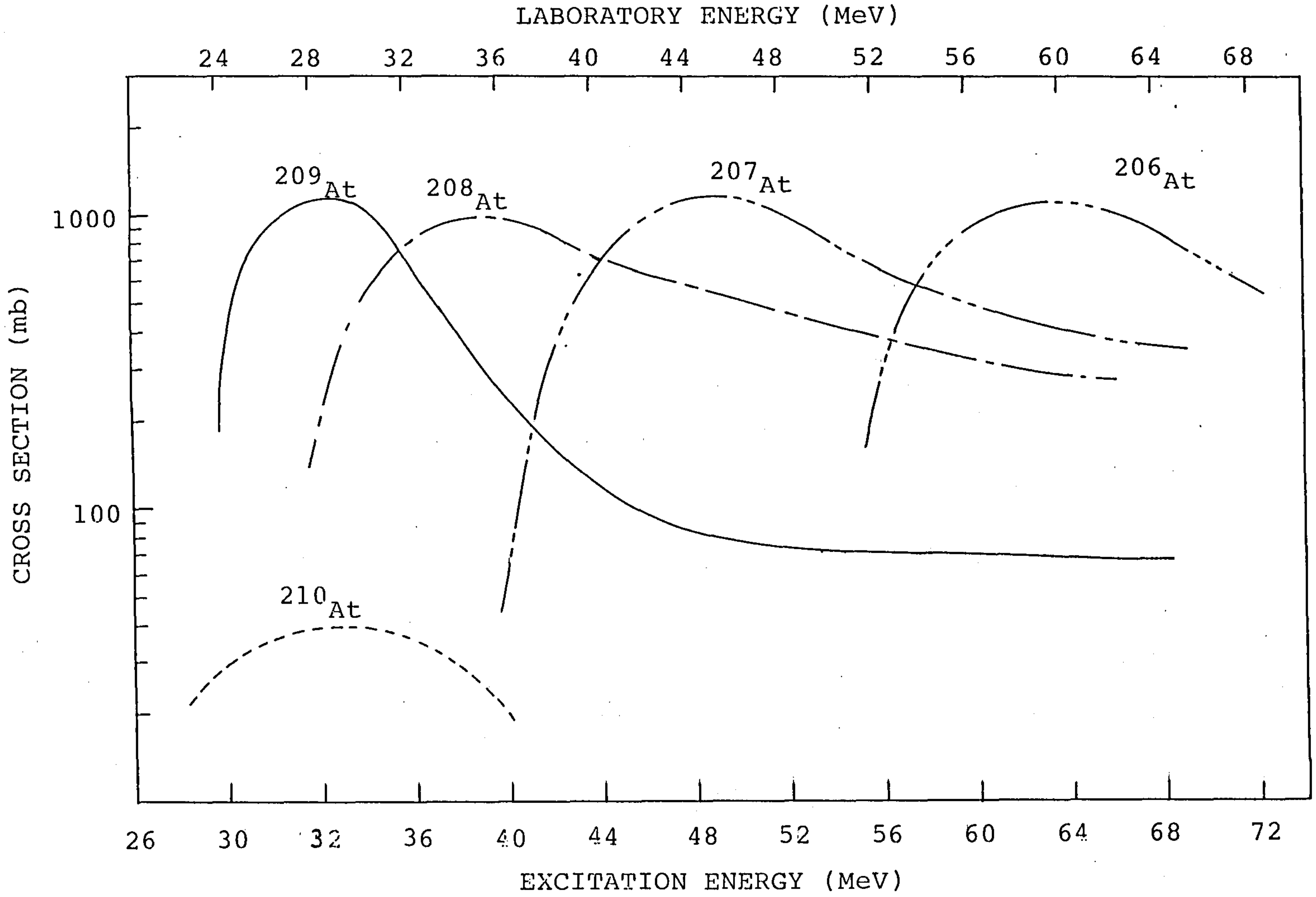


Fig. II-2. Excitation functions for the ^{209}Bi(^{3}He, xn)$^{212-x}$At reactions

----- ^{209}Bi(^{3}He, 2n)^{210}At; ——— ^{209}Bi(^{3}He, 3n)^{209}At.

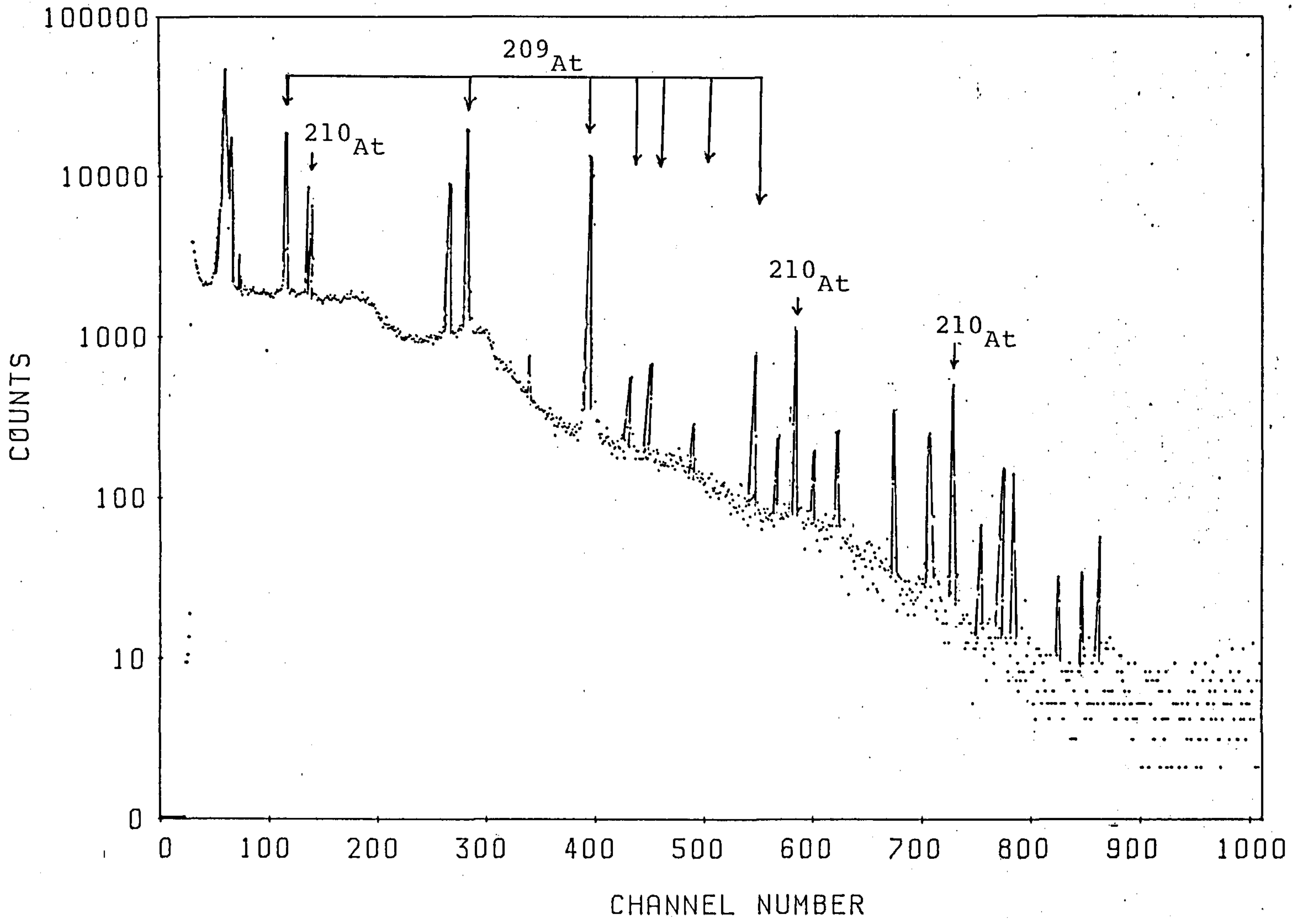


Fig. II-3. Gamma spectrum of bismuth target
1 ch = 2 keV.

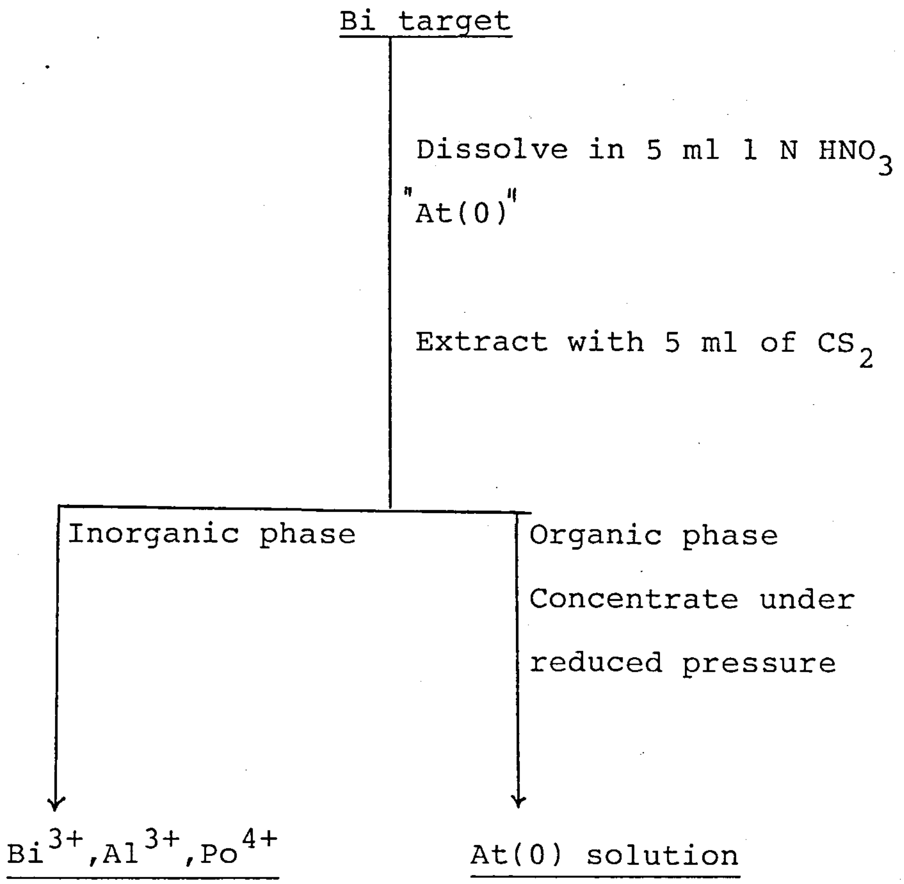


Fig. II-4. Separation of astatine from the bismuth target

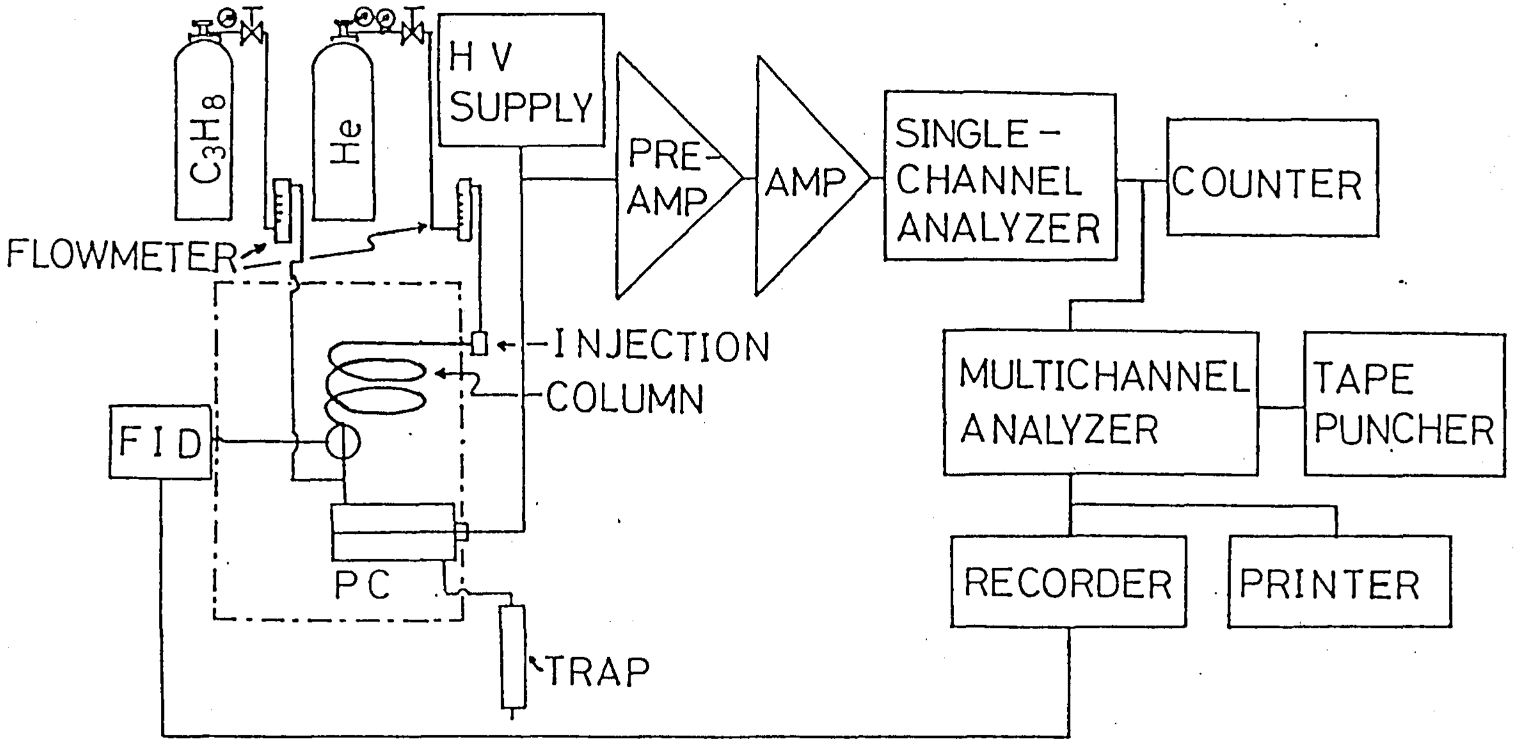


Fig. II-5. BLOCK DIAGRAM OF GAS RADIOCHROMATOGRAPHY on Chromosorb. The column was installed in the thermostat of the RGC.

Although various detecting systems have been applied to RGC, we used a proportional flow counter from next reasons: It has high counting efficiency because of internal counting system with 4 π geometry, and it is bassically of simple design so that it is readily coupled with a flowing gas system. Further, it can be readily cleaned up if it is contaminated. A rough sketch of the counter is shown in Fig. II-6. The counter is constructed out of a cylindrical stainless wall and a tungsten center wire. The size is 30 mm in inside diameter and 95 mm in length, and the effective volume is about 20 cm^3. For decontamination the counter can be easily disassembled by withdrawing the center wire assembly.

Helium was used as the carrier gas and helium-propane mixture was used as the counting gas. Propane was mixed immediately before the counter. The flow rate of the gas was adjusted using a soap film burette at the start, and then observed continuously by a flow meter. Based on the gas flow counter a system can be disassembled for quantitative RGC. Then the quantitative analysis depends on the stability of the counter. The change of plateau was measured using ^{131}I source by varying the propane to helium ratio. The propane to helium ratio was adjusted to 0.07

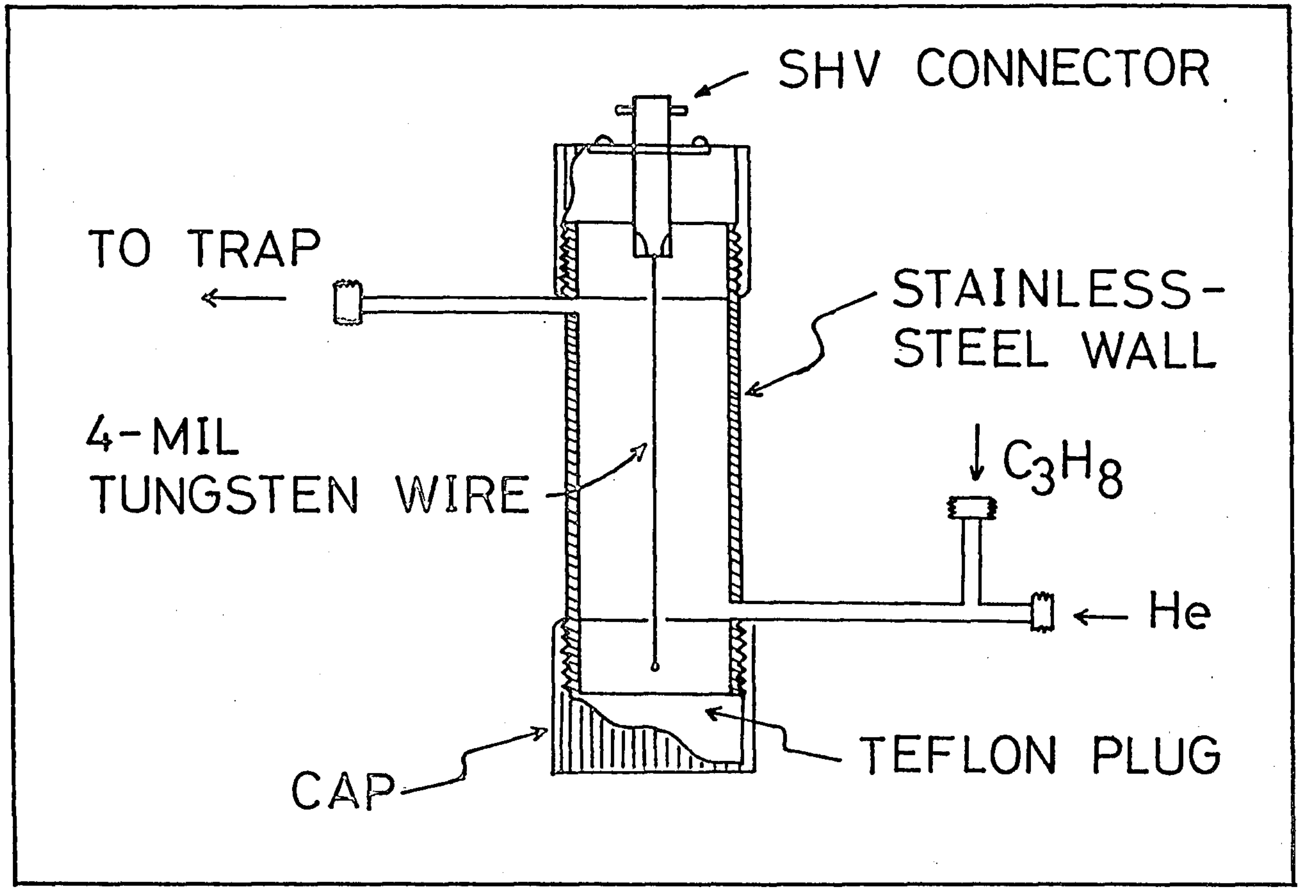


Fig. II-6. Sketch of proportional counter during the later experiments.

B-3. Preparation of Samples for Analysis

Three samples were prepared for the measurement as follows:

(1) After the irradiation the bismuth target was dissolved into 5 ml of 1N HNO_3, and "At(0)" was extracted with 5 ml of carbon disulfide which had previously been washed with a few mls of 1 N HNO_3. The solution was concentrated up to 0.5 μCi/μl under reduced pressure. This procedure is shown in Fig. II-4.

(2) Carrier-free $^{131}I^-$, which was bought from Amersham International Ltd., was oxidized by the H_2O_2-H_2SO system, and then $^{131}I_2$ was extracted with about 5 ml of carbon disulfide which had been washed with acid. The solution was concentrated to 0.3 μCi/μl under reduced pressure by the same manner as in the case of astatine.

(3) Carrier-I_2 (about ten times the amount of $^{131}I_2$) was added to 50 μl of the sample (2), and then 50 μl of the sample (1) was mixed with it.

B-4. Analysis of the Samples

Three samples were analyzed by the RGC. If the β ray from ^{131}I and the α ray from ^{209}At can be measured separately, the assignment of the peak in the chromatogram should be very easy. The signals due to α rays can be selected by discriminating lower pulses since the pulse hight is far higher than that of β rays when these radiations are detected by a proportional counter. The signals due to β rays cannot be measured independently since the signals due to electrons scattered by α rays and EC-Auger electrons mixed. The discriminating revel was determined by the use of ^{210}Po, emitting almost same energy of α rays as those from ^{209}At, and ^{131}I sources.

For determination of the chemical form of elementary astatine about 2 μl aliquots of each sample were analyzed by the RGC. Both α and β rays were detected with samples (1) and (2), whereas the measurement of α rays only was carried out with the sample (3) as well as that of α rays plus β rays. Further, the sample (1) was analyzed by the RGC at several column temperatures for the estimation of the precise boiling point of astatine.

The waste samples were finally trapped on to charcoal. The radioactivity built up in the counter was decontaminated at every ten runs.

C. RESULTS

C-1. Plateus of the Counter

In Fig. II-7 are shown the typical proportional counting plateaus obtained with various propane to helium ratios using an internal ^{131}I source. All plateaus are virtually flat, and higher propane to helium ratios raise both the threshold and the plateau toward higher voltages.

C-2. Gas Radiochromatograms

For the determination of the chemical form of elementary astatine three samples were analyzed by means of the RGC at 393 K. The gas radiochromatograms obtained are shown in Fig. II-8. In the figure the abscissa is absolute retention volume which is corrected for free space and pressure gradient, and the ordinate is counts of activity. Chromatograms I and IV are obtained by detecting both α and β rays on samples (2) and (1), respectively. Chromatograms II and III are obtained by detecting α rays plus β rays and

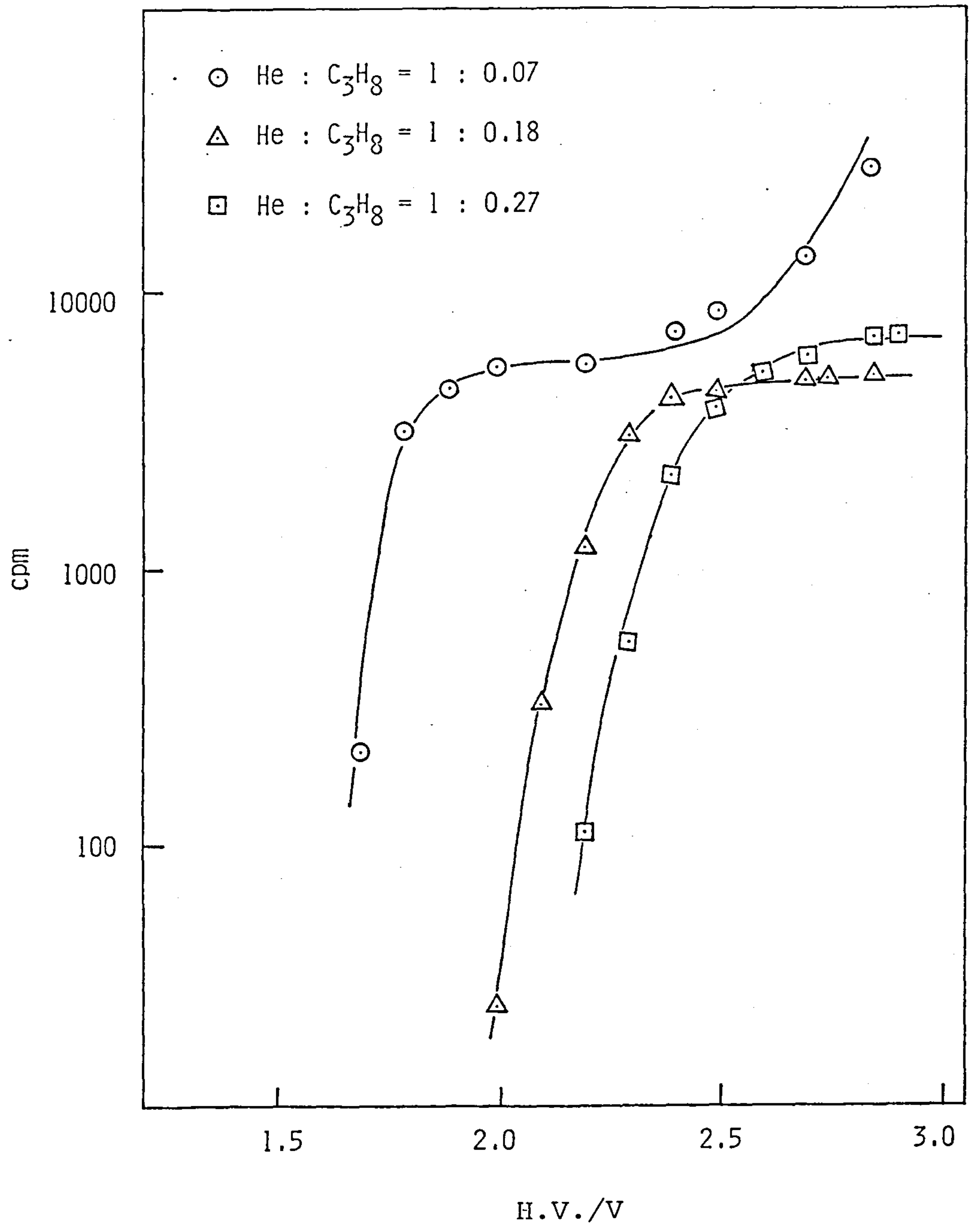
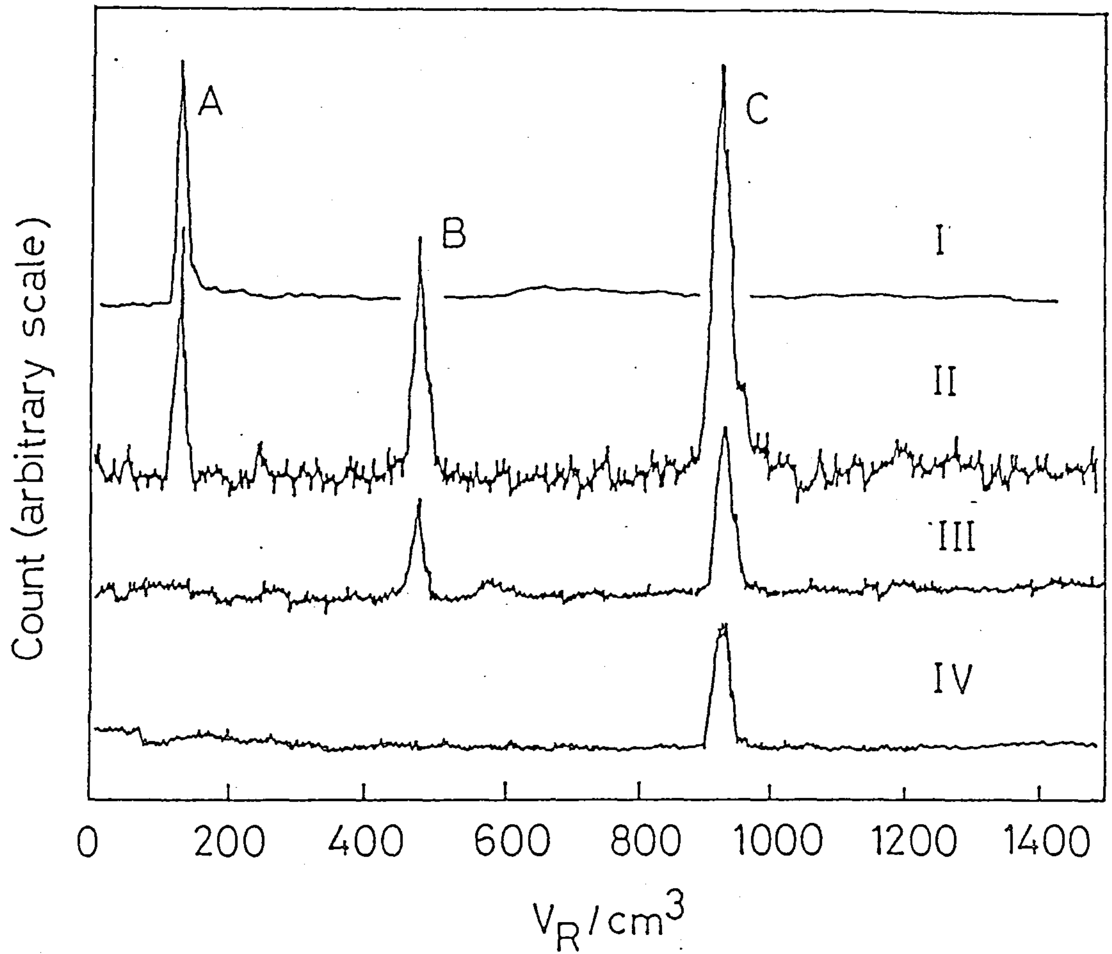


Fig. II-7. Typical proportional counting plateaus obtained with various propane to helium ratios



I: $^{131}I_2$(carrier-free), α ray + β ray

II: $^{131}I_2$(carrier I_2) + At(0), α ray + β ray

III: $^{131}I_2$(carrier I_2) + At(0), α ray

IV: At(0)(carrier-free), α ray + β ray

Fig. II-8. Radiochromatograms of samples (1), (2) and (3) rays only, respectively, on sample (3).

In chromatograms I and IV only a peak is observed, and in chromatograms II and III a few peaks are observed. These peaks shall be assigned later.

Further, the sample (1) was analyzed at several column temperatures by detecting α rays plus β rays. These chromatograms are shown in Fig. II-9.

Peak positions were graphically obtained and were computed by the smoothing and differenciation of the data.

C-3. Estimation of the Boiling Point by Semi-Empirical Theory

For molecular solutes the retention volume, V_R, on gas chromatography is simply expressed as

$$V_R = f(N, \delta_s, T_b, \overline{T}_b, T). \tag{II-1}$$

Here, V_R(cm^3) is the absolute retention volume corrected for free space and pressure gradient, N (mole) the moles of the solvent in a column, δ_s (cal$^{1/2}$cm$^{-3/2}$) the solubility parameter of the solvent, T_b (K) the boiling point of the solute, $\overline{T}_b$ (K) the mean boiling point of the family and T (K) the column temperature. Details will be mentioned in

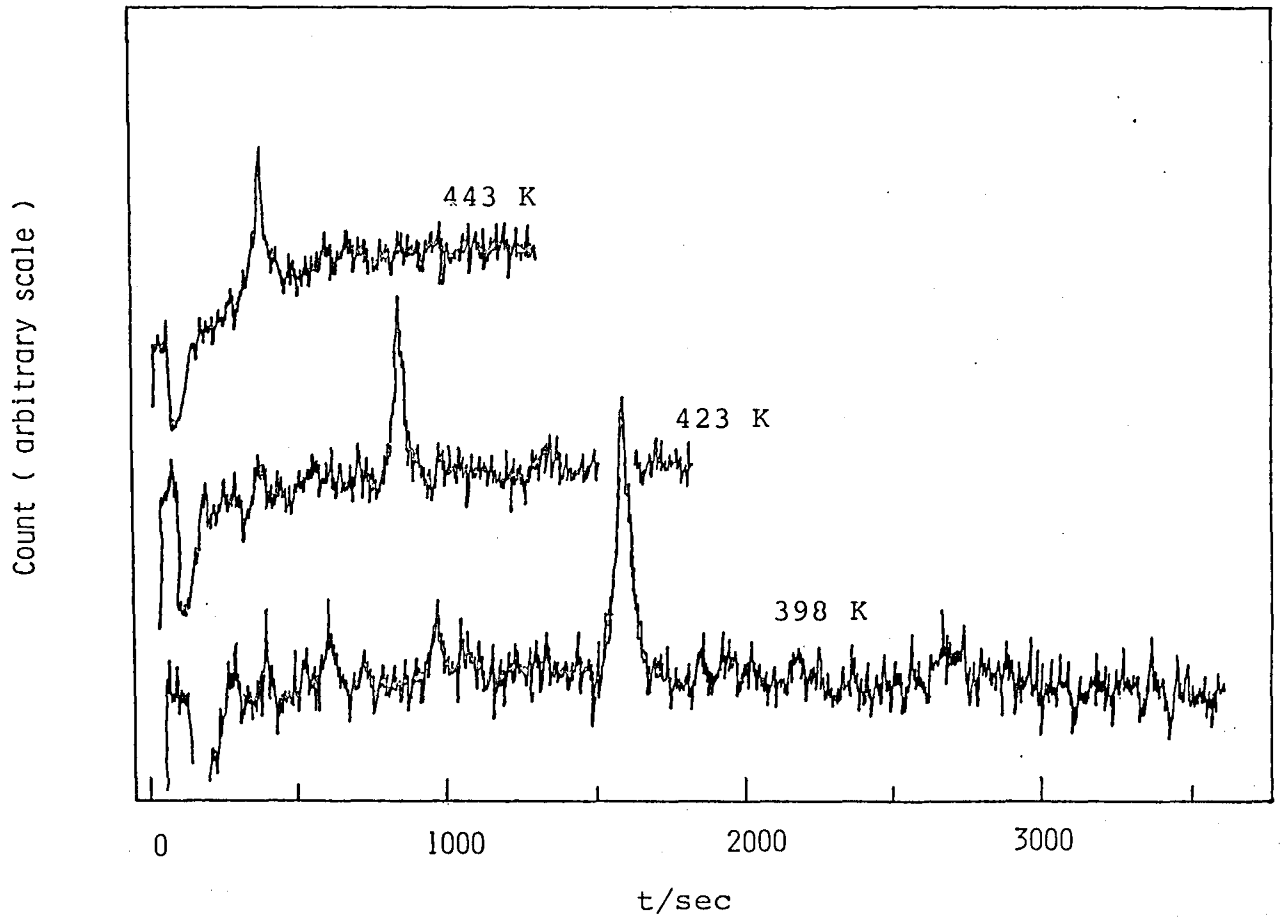


Fig. II-9. Radiochromatograms of At_2 at several column temperatures

Appendix (i).

Now, if N and δ_s which are characteristic of the solvent are known, V_R is expressed as the function of T_b only for a given T. Therefore, T_b can be estimated by measuring V_R at a given column temperature. This method has been well tested on halogens[II-30].

The molecular weight, W_w , and δ_s of the solvent used in this experiment were determined previously and N is calculated from the molecular weight. The quantities of M_w and δ_s are tabulated in Table II-2.

The estimated boiling points for the peaks in Figs. II-8 and II-9 are listed in Table II-3 and II-4, respectively.

The error of the boiling point estimated is mainly derived from the deviation of the retention volume measured by the RGC.

D. DISCUSSION

D-1. Assignments of peaks (Determination of the Chemical Form of Elementary Astatine)

The peaks of A, B and C in Fig. II-8 are assigned to

Table II-2. Molecular weight M_w and solubility parameter δ_s, of the solvents used

Solvent		M_W	δ_S
SIlicon DC	550	50000	8.1
	702	62300	8.0
	710	89200	7.9
PEG	1500	1500	11.7
	4000	3100	11.6
	6000	6750	11.6

Table II-3. Boiling points of peaks A, B and C

Peak	Retention volume (cm^3)	Boiling point (K)
A	120 ± 2	457 ± 2
B	485 ± 2	486 ± 2
C	929 ± 2	504 ± 3

Table II-4. Boiling points of At_2 at several temperatures

Column	Retention	Boiling point (K)	
temp. (K)	volume (cm^3)	calc.	extrap.
393	929 ± 2	504 ± 2	
398	850 ± 2	503 ± 3	
423	339 ± 2	502 ± 3	
443	182 ± 2	502 ± 3	
mean		503 ± 3	585[a]

a; given in Ref. II-29.

I_2, AtI and At_2, respectively, from the following reasons:

(1) Peak A is attributable to I_2 since only this peak is observed in the chromatogram I and there at least exist $^{131}I_2$ molecules. This is consistent with the fact that the boiling point of this peak agrees well with that of I_2, 457.5 K, as shown in Table II-3.

(2) Peak C may be attributable to "At(0)" since only this peak is observed in the chromatogram IV and there at least exist At(0) molecules. If it is due to a compound of astatine with organic impurities, one or more additional peaks should be observed in the chromatogram. The peak C was as well observed when other solvents (e.g., benzene and carbon tetrachloride) were used as with CS_2. Therefre, the possibility of the formation of astatine organic compounds is ruled out though "At(0)" is known to react with organic substances.

(3) Peak B must be attributed to the compound of astatine with iodine since it can be first observed when "At(0)" is mixed with I_2 and α rays are detected at the peak as shown in the chromatogram III. Furthermore, it is well known that AtI is produced by the reaction of "At(0)" with I_2, so the peak may be AtI.

(4) We have found a remarkable relationship holding among halogen molecules and diatomic interhalogen compounds. Namely, the boiling point of a diatomic interhalogen

compound is nearly equal to the mean boiling point of constituent elements as shown in Table II-5. The chemical forms of peaks B and C are AtI and At_2, respectively, as for the other halogens; this rule holds on the boiling point of peaks A, B and C. If the peak C is due to a compound of astatine with impurities, this rule may hardly hold.

D-2. Formation of AtI and the Anomalous Boiling point of At_2

Now, AtI would be produced by the hot atom reaction as

$$^{209}At_2 + I_2 \longrightarrow {}^{209}AtI + XI, \qquad (II-2)$$

in which X is the daughter of astatine in solution, or by the ordinary chemical reaction in the vaporization cell where temperature is higher than the room temperature. The study on the hot atom reaction of At_2 will be discussed in Appendix (ii).

Estimation of the boiling points of At_2 at several column temperatures are mutually compatible, but the value is much lower (by 82 K) than that extrapolated from the other halogens. Although the anomaly of the boiling point will be discussed later together with that of radon, it can

Table II-5. Boiling points of interhalogen compounds

	F_2	ClF	Cl_2	BrCl	Br_2	IBr	I_2	AtI	At_2
observed (K)	85	173	236	278	332	389	457	486	503
mean (K)		160		284		395		480	

mentioned here that the anomalous boiling point of At_2 should not be due to the anomalous behavior of carrier-free species, since no anomaly could not be observed on carrier-free $^{131}I_2$.

III. ESTIMATION OF THE BOILING POINT BY RADIOGASCHROMATOGRAPHY

A. INTRODUCTORY CONSIDERATIONS

Radon has been well known as the decay product of ^{226}Ra (i.e., emanation). This element has no stable isotopes like astatine. We know about thirty isotopes for the element now as shown in Table III-1. In these isotopes ^{222}Rn has the longest half life which is 3.8 day. Radon has been widely used as the so-called emanation method[III-12] which yields information about the characters of solid materials. As well known this element belongs to the group VIII in the periodic table, and it has been seemed to be chemically inactive similarly to the other rare gases. The studies on radon compounds have been done since Batlett et al. synthesized xenon complexes at 1962[III-13].

Although there are a few studies on the chemical properties of radon, the boiling point of the element being the most fundamental property was measured only by

Table III-1. Isotopes of radon

Mass	Half life	Decay	Production mode	Reference
200	1.0 sec	α	Th(p, spall)	III-1
201	3.8 sec	α	^{197}Au(^{14}N, 10n)	III-2
202	< 1 sec	α	^{197}Au(^{14}N, 9n)	III-2
203	45 sec	α, EC+β^+	^{197}Au(^{14}N, 8n)	III-2
204	75 sec	α, EC+β^+	^{197}Au(^{14}N, 7n)	III-2
205	170 sec	α, EC+β^+	^{197}Au(^{14}N, 6n)	III-2
206	5.6 m	α, EC+β^+	^{197}Au(^{14}N, 5n)	III-2
207	9.2 m	α, EC+β^+	^{197}Au(^{14}N, 4n)	III-3
208	24.3 m	α, EC+β^+	^{197}Au(^{14}N, 3n)	III-3
209	28.5 m	α, EC+β^+	daughter ^{213}Ra	III-4
210	2.4 h	α, EC+β^+	^{232}Th(p, spall)	III-4
211	14.6 h	α, EC+β^+	^{232}Th(p, spall)	III-5
212	23 m	α	daughter ^{212}Fr	III-6
213	25 m	α	daughter ^{217}Ra	III-6
214	0.27 μsec	α	descendant ^{222}Th	III-7
215	2.3 μsec	α	^{232}Th(α, 9n)	III-8
216	45 μsec	α	descendant ^{228}U	III-9
217	0.5 msec	α	descendant ^{229}U	III-9
218	35 msec	α	descendant ^{230}U	III-9
219	3.9 sec	α	descendant ^{227}Th	III-9
220	55 sec	α	descendant ^{228}Th	III-9
221	24 m	α +β^-	Th(p, spall)	III-4

Table III-1 (continued)

Mass	Half life	decay	Production mode	Reference
222	3.8 d	α	natural source	III-9
223	43 m	β^-	^{232}Th(p, spall)	III-10
224	1.78 h	β^-	^{232}Th(p, spall)	III-10
225	4.5 m	β^-	^{232}Th(p, spall)	III-11
226	6 m	β^-	^{232}Th(p. spall)	III-11

Rutherford[III-14] and Gray and Ramsay[III-15] at 1909, and there has been few experiments on the boiling point thereafter it except for the measurement by Wertenstein[III-16]. The boiling point was estimated by the measurement of the variation of the vapor pressure with changing temperature on ^{222}Rn. But the decay schem of ^{222}Rn was uncertain at that time, and so the contribution of helium to the vapor pressure of Rn was unable to be estimated. The exact measurement of the pressure of He might not be done because of the trace amount of He. Therefore, these values may include fairly large errors. In an analogous experiment Wertenstein obtained a value higher by 15 K than that measured by Gray and Rasay. As mentioned in the study of astatine, the estimation of the boiling point with the RGC method is superior to the measurement of the vapor pressure, but the shortage of the RGC is that it is indirect. In this method the impurities (decay products) in the sample are separated in a column and so their effects are removed in principle. Further, the sample used is of a trace amount so that the heat involved in the decay needs not to be considered. Since this method is indirect, the applicability must be confirmed for a similar substance, the boiling point of which is known.

Generally the column is set at a lower temperature than the boiling point of the sample when the retention volume is measured by means of a gas chromatography. Since the boiling point of elementary astatine was fairly high, the retention volumes were measured at the range of 390 K to 440 K. No particular attentions for the solvent in the columns had to be paid. On the contrary, if the retention volume of radon is to be measured by the RGC, it should be measured at a lower temperature than 200 K. In this case the temperature is very low, so that the solvent used in the column may solidify. If the solvent solidifies, the semi-empirical relation between the retention volume and the boiling point doesn't hold. Therefore, the solvent which doesn't solidify at such low temperature must be used in the experiment. As there are no solvents, which don't solidify at such temperatures, the retention volume must be measured at a higher column temperature than the boiling point of the object. On the other hand, a large retention volume is desirable for precise estimation of the boiling point. Now we must seek a solvent which realize the operation of the RGC at a temperature as low as possible, so close to the boiling point of Rn that a large retention volume is obtained.

In the present work the boiling point of Rn was estimated with this method and xenon was used as a checking substance.

B. EXPERIMENTAL

B-1. Preparation of Radon and Xenon Samples

The samples of ^{222}Rn, which was the decay product from ^{226}Ra, and ^{133}Xe, which was bought from Amersham International, Ltd., were prepared in a vacuum line shown in Fig. III-1. For the preparation of the Rn sample about 2 μCi of ^{226}Ra was placed in a sample vessel and then the vessel was evacuated. This sample was allowed to stand for three weeks, and the growth of ^{222}Rn was waited. The vessels, which contained Rn and Xe, were attached to the vacuum line as shown in Fig. III-1.

Prior to the introduction of the gases the line was evacuated and dried. Next, the sample vessels were opened, and once the gases were stored in cold trap which was cooled with liquid nitrogen. A finite aliquot of the gas sample was led to the RGC through a stainless steel pipe which was connected to the right side of the glass line.

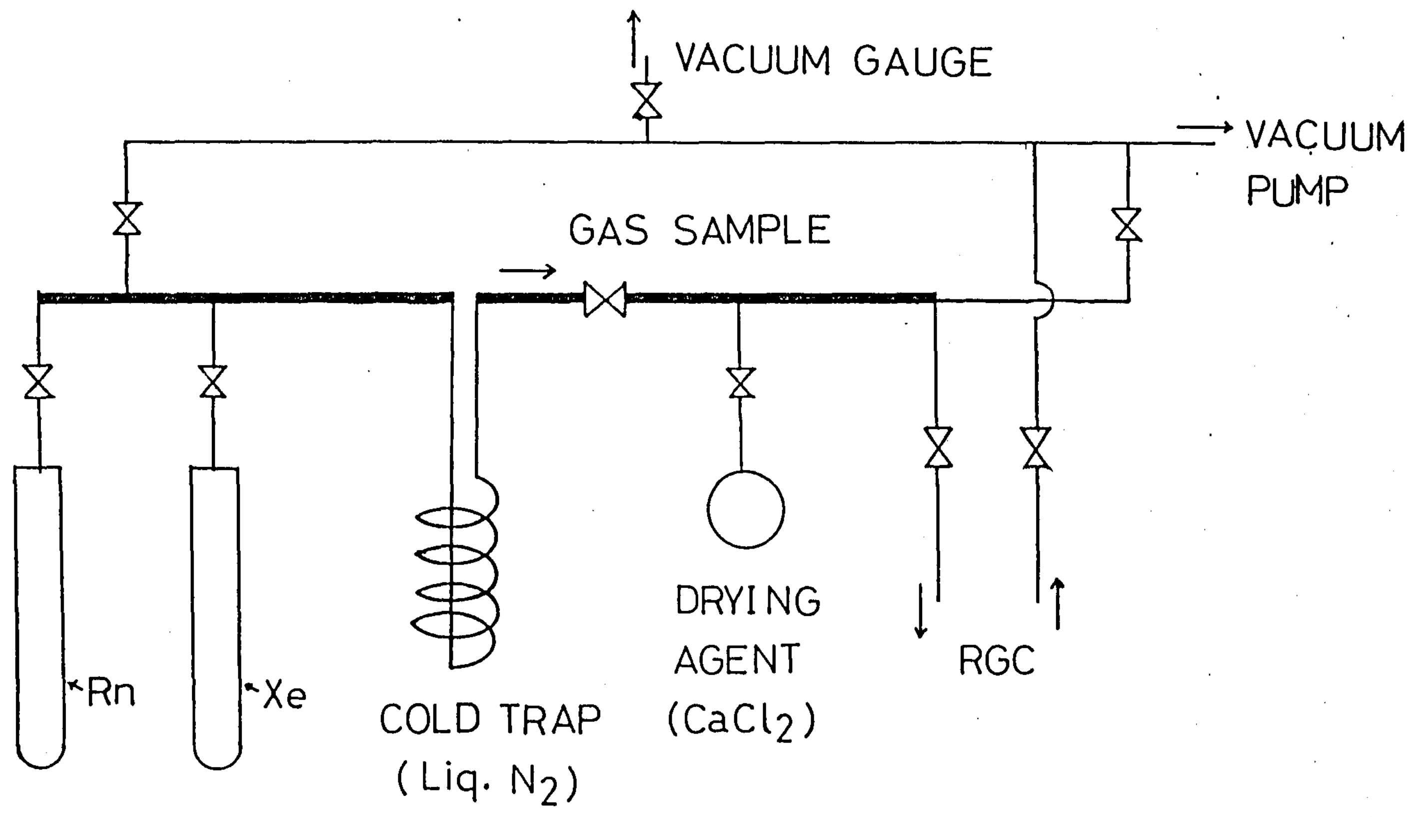


Fig. III-1. Vacuum line for the preparation of gas sample

B-2. Modified RGC System

For the estimation of the boiling point of radon we had to measure the retention volume at the temperature as near to the boiling point of Rn as possible and to use the solvent, which didn't solidify at such low temperature. We reached squalene as a possible candidate of the solvent among several materials surveyed and proved its usefulness. As the RGC used for the experiments on astatine couldn't be operated under the room temperature (about 300 K), the equipment was modified. The block diagram of this system is shown in Fig. III-2. The thermostat in the RGC was cooled by blowing liquid nitrogen via a solenoid valve and was kept at a designed temperature. The solenoid valve and the heater were controlled by the temperature controller. It was possible to operate at a very low temperature (it was possible to operate at 77 K in principle).

In the present work a 8 port rotary valve, which enabled to introduce gas samples on-line, was equipped in the RGC. The schematic diagram of the valve is shown in Fig. III-3. Gas samples are led to "SAMPLE IN" and emerged from "SAMPLE OUT" through "LOOP A". Then, desired aliquots of the sample can be trapped at "LOOP A" by cooling it with liquid nitrogen, while helium as carrier-gas is now led to

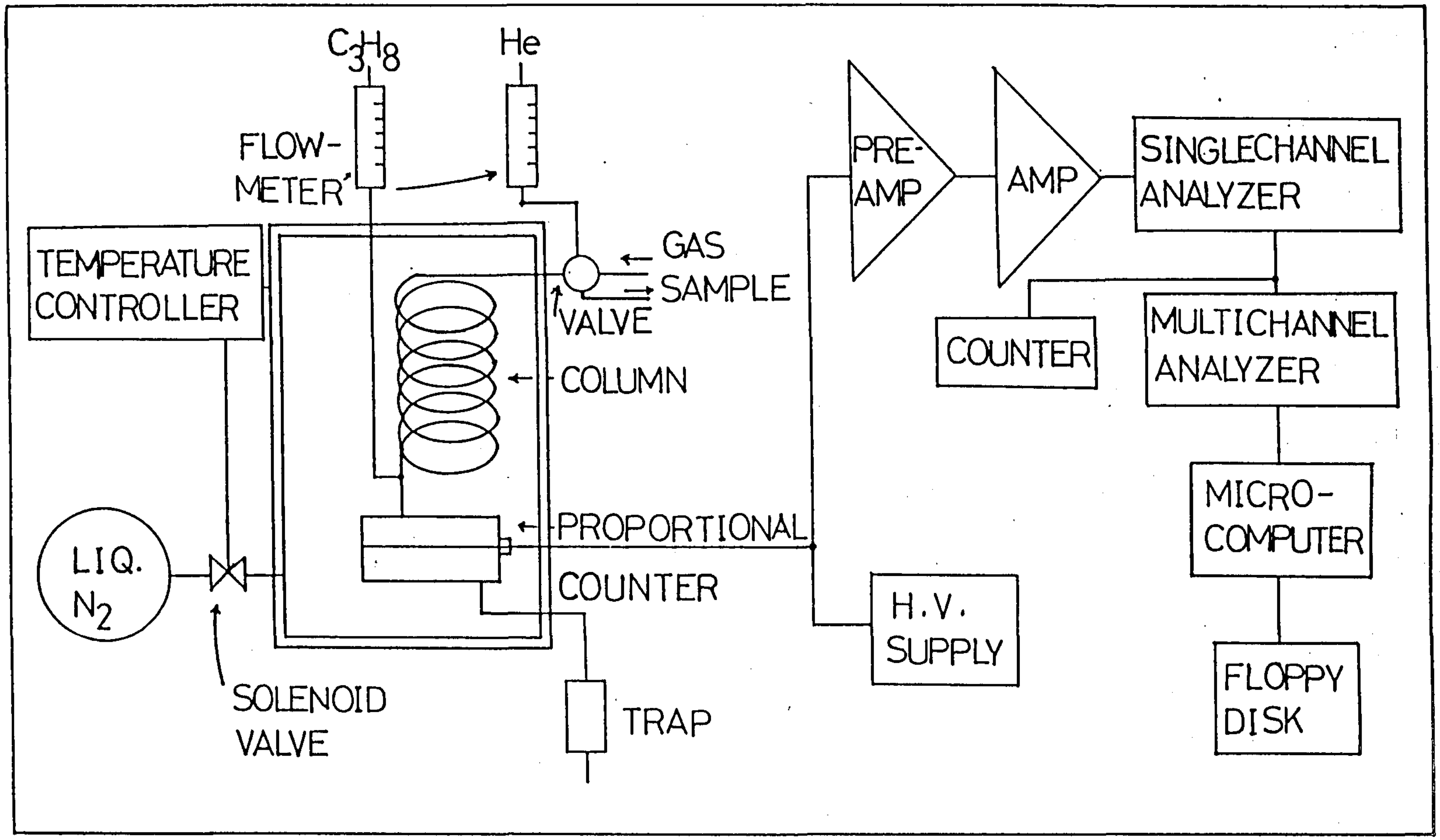


Fig. III-2. Block diagram of modified RGC

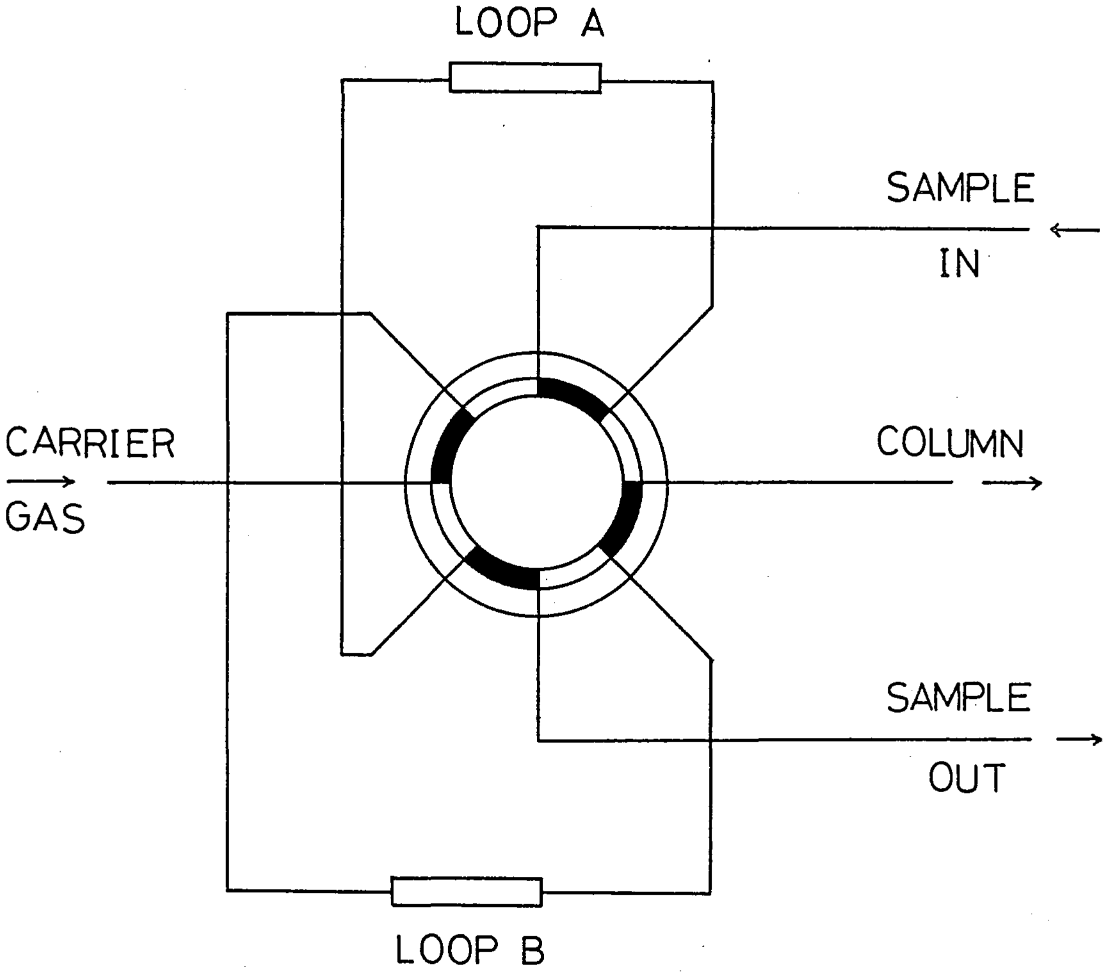


Fig. III-3. Rotary valve for the injection of gas sample the column through "LOOP B". When the valve is turned by 45°, the gas sample stored "LOOP A" is expelled by the carrier-gas and is injected into the column.

A proportional counter was used as a detector. This counter had been used previously on the experiment of astatine. Alpha and beta rays were detected together for ^{222}Rn and ^{133}Xe, respectively, and these signals were stored in a multichannel analyzer in the multiscaling mode. The aquired data were recorded on floppy disks through a microcomputer, and were analyzed by the computer.

B-3. Analysis of Rn and Xe by RGC

Radon and xenon samples prepared in the vacuum line shown in Fig. III-1 were analyzed on-line by the RGC. The retention volumes of radon were measured at several column temperatures using squalene, and further at 323 K using PEG 1500. For xenon the retention volumes were measured at several column temperatures using squalene. The radioactivities of ^{222}Rn and ^{133}Xe were about 0.2 μCi and 0.3 μCi, respectively.

C. RESULTS

C-1. Estimated Boiling Points of Rn and Xe

The typical radiogaschromatograms of Rn and Xe are shown in Figs. III-4 and III-5, respectivery. The radiogaschromatogram shown in Fig. III-4 was obtained on ^{222}Rn using squalene at 273 K, and Fig. III-5 was obtained on ^{133}Xe using squalene at 229 K. In the figures the ordinate is counts of radioactivities and the abscissa is the retention time. In Figs. III-4 and III-5 only one peak is observed, and so these peaks can be attributed to Rn and Xe, respectivery. These peaks shift to a smaller retention time with increasing column temperature.

Then, we calculated the boiling points of Rn and Xe from the absolute retention volumes measured by the semi-empirical formula (II-1). We recall that the formula is expressed as follows:

$$V_R = f(N,\ \delta_s,\ T_b,\ \overline{T}_b,\ T).$$

The molecular weight (M_w) and the solubility parameter (δ_s) were already determined for PEG 1500, and the moles could be

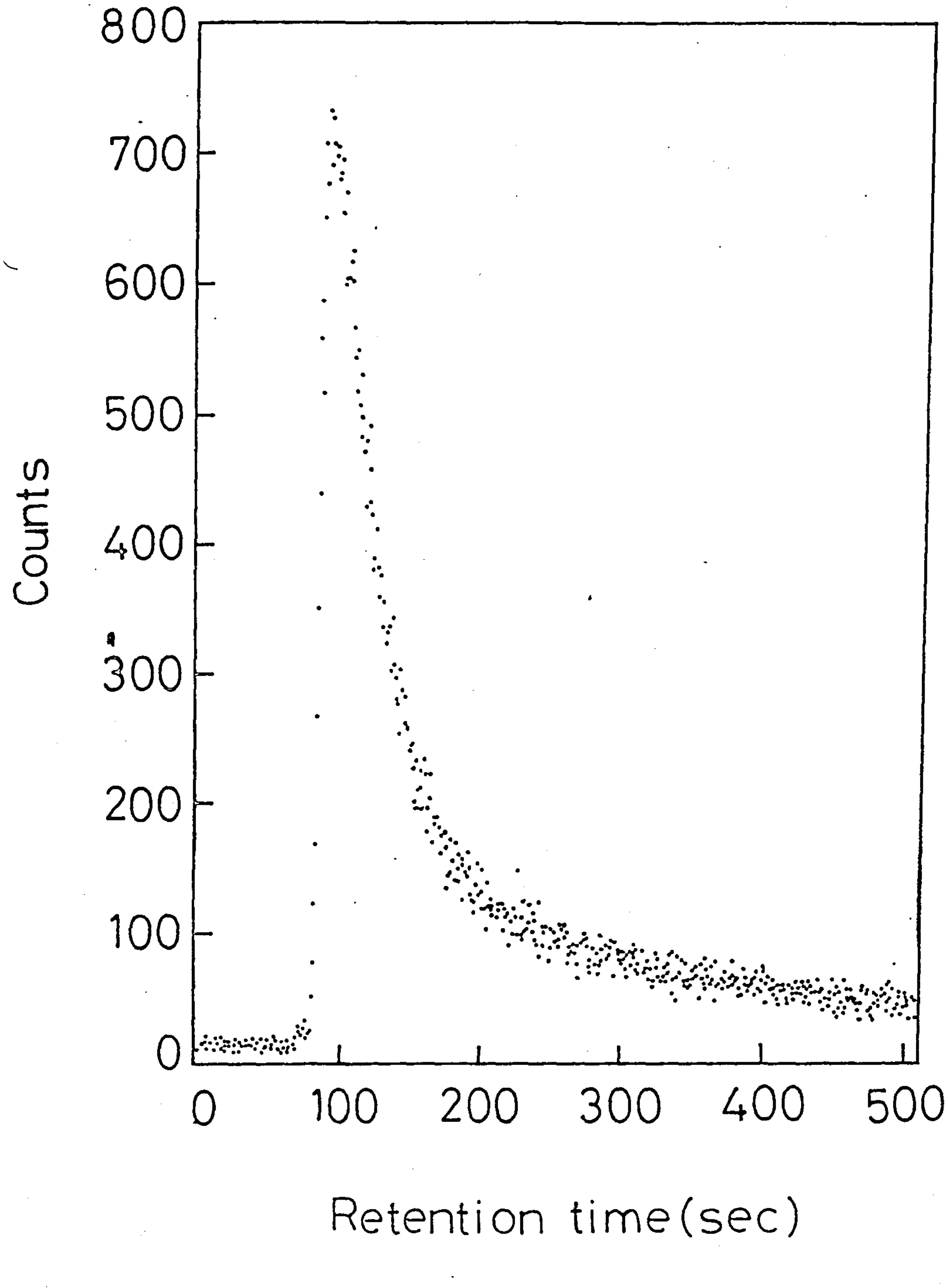


Fig. III-4. Radiochromatogram of Rn at 273 K

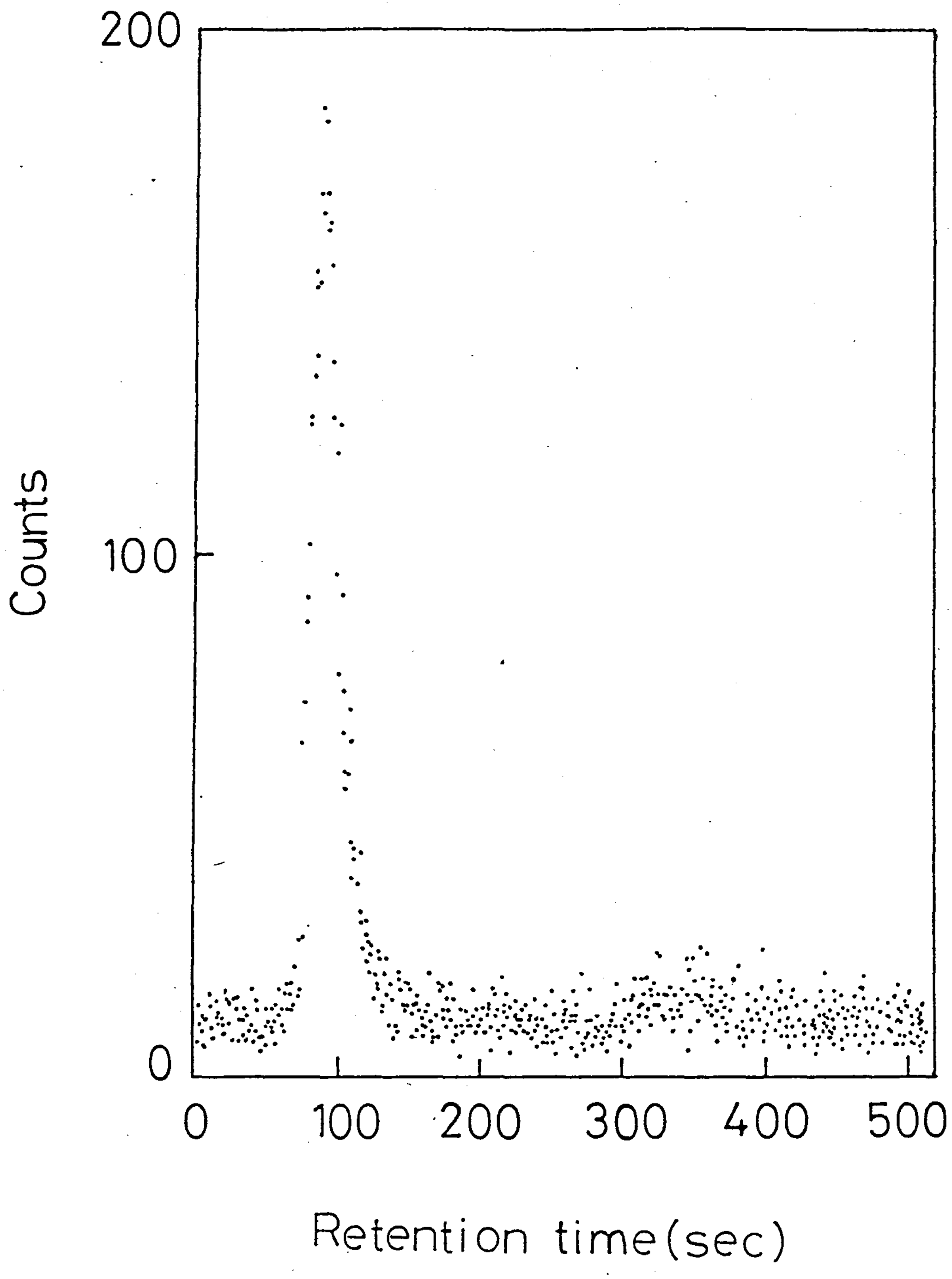


Fig. III-5. Radiochromatogram of Xe at 229 K calculated from M_w. Although M_w of squalene was known, was not determined. The solubility parameter of squalene δ_s was measured using I_2 by a conventional method, which is described closely in Appendix (iii).

The properties of these solvents are tabulated in Table III-2. The resulting boiling points of Rn and Xe are listed in Tables III-3 and III-4, respectively, with the literature values.

D. DISCUSSION

D-1. Appricability of the Semi-Empirical Theory on Rare Gases

Although the semi-empirical theory has been well tested on halogens, it was not tested on rare gases. So there is no guarantee for that the theory holds on rare gas at low temperature. We must confirm that the theory holds on rare gas too. Thus the theory was tested on Xe. The boiling point of Xe was estimated from the retention volume measured by the formula (II-1) and was compared with literature value. The results are given in Table III-3. As shown in the table estimated boiling points at several column temperatures

Table III-2. Properties of the solvents used

Solvent	M_w	δ_s
Squalene	410	9.7
PEG 1500	1500	11.7

Table III-3. Boiling point of Rn measured at various column temperatures

Column temp. (K)	Retention volume (cm^3)	Boiling point (K) obs.	Boiling point (K) liter.
296[a)]	6.9 ± 0.2	198 ± 1	211[c)], 208[d)]
273[a)]	12.2 ± 0.1	201 ± 1	
251[a)]	17.8 ± 0.1	198 ± 1	
229[a)]	27.5 ± 0.5	195 ± 1	
323[b)]	9.2 ± 0.4	197 ± 3	
mean		198 ± 2	

a) Squalene ($N = 1.380\times10^{-4}$ mol, $\delta_s = 9.7\ cal^{1/2}cm^{-3/2}$) was used as solvent in the column.

b) PEG 1500 ($N = 1.513\times10^{-3}$ mol, $\delta_s = 11.7\ cal^{1/2}cm^{-3/2}$) was used as solvent in the column.

c) Obtained by Rutherford.

d) Obtained by Gray and Ramsay.

Table III-4. Boiling point of Xe

Column temp. (K)	Retention volume (cm^3)	Boiling point (K) obs.	liter.
273[a)]	3.3 ± 0.2	164 ± 2	166.0[b)]
254[a)]	5.4 ± 0.2	170 ± 1	
229[a)]	9.3 ± 0.2	170 ± 1	
mean		168 ± 3	

a) Squalene ($N = 1.380\times10^{-4}$ mol, $\delta_s = 8.7$ $cal^{1/2}cm^{-3/2}$) was used as solvent in the column.

agreed well one another, and with the literature value too. This implies that the semi-empirical theory excellently holds on rare gases at a low temperature.

D-2. Choice of the Solvent in RGC and Error of the Boiling Point Estimated

In the present work the retention volumes of rare gases had to be measured at higher temperatures than the boiling points of the samples, since there were no solvents, which din't solidify below such temperatures. Generally the retention volume observed is very small at such a temperature. On the semi-empirical theory the retention volume is expressed as the function of N, δ_s, T_b, $\overline{T}_b$ and T as mentioned previously. The boiling point is given when the object is given, and the range of T is also limited by the solvent used. So the retention volume actually depends on δ_s. We must successfully choose the solvent in order to obtain a large retention volume. Squalene is the best solvent for rare gases from the stadpoint of solidification and the retention volume. The measurement of the retention volume of Rn is, however, possible by using PEG 1500 too.

The relatins between V_R, T_b and T are shown in Figs. III-6 and III-7. Fig. III-6 shows the variation of

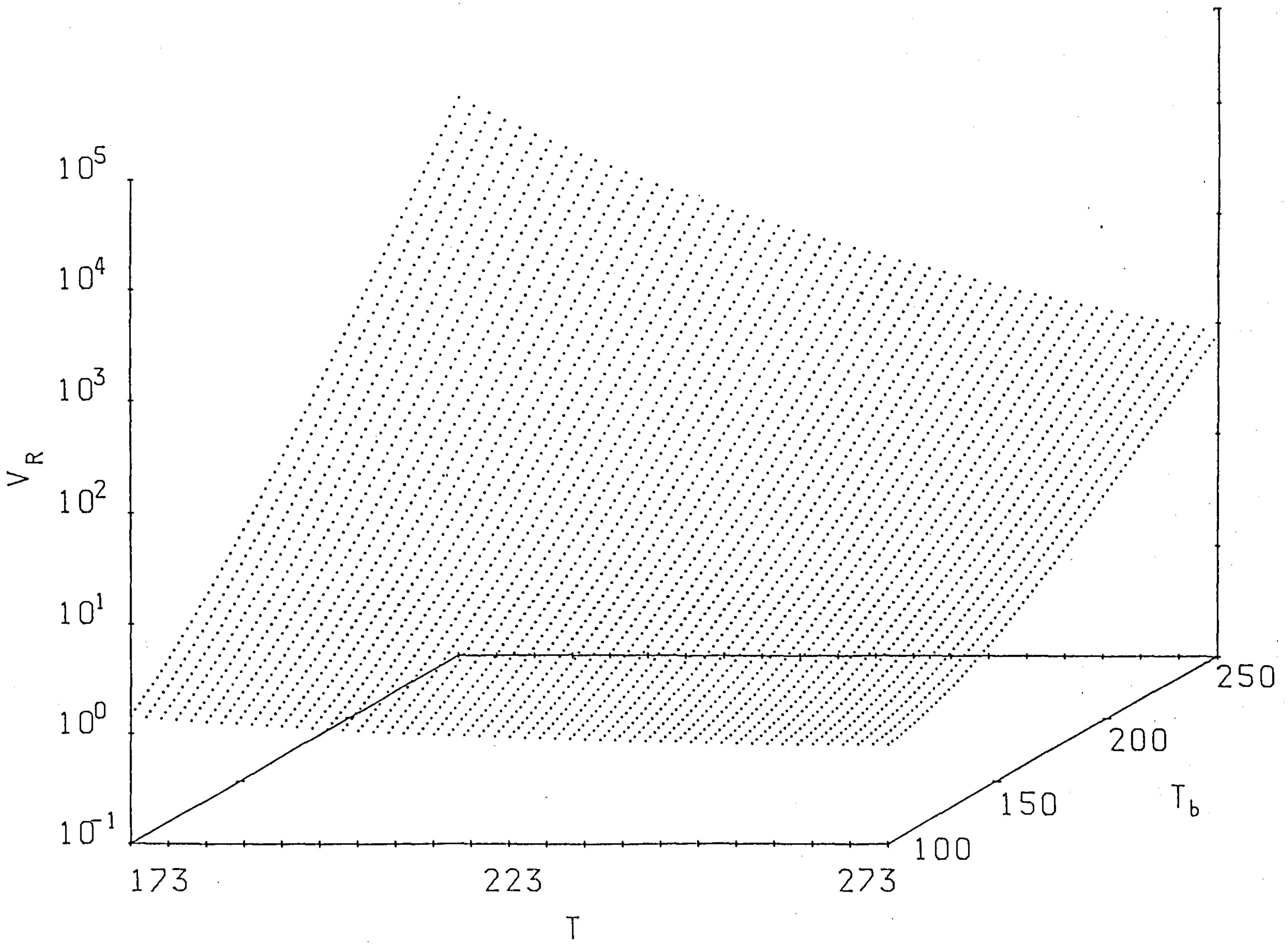


Fig. III-6. Relation between V_R, T_b and T on squalene

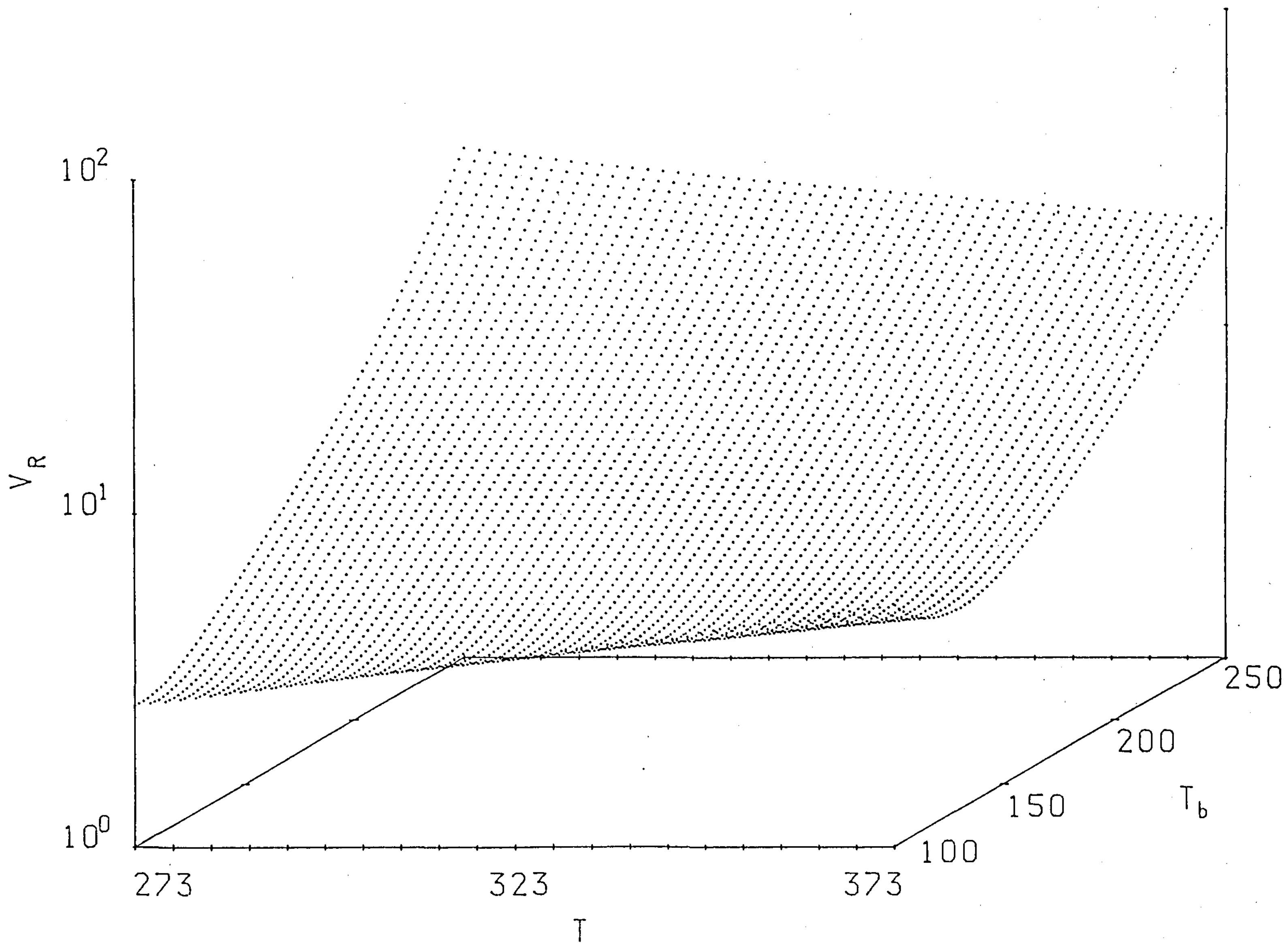


Fig. III-7. Relation between V_R, T_b and T on PEG 1500

V_R, which is calculated from the semi-empirical theory when squalene is chosen. Fig. III-7 shows the variation of V_R when PEG 1500 is chosen. From these figures it is obvious that the retention volumes are very small at lower column temperatures than the boiling points of the objects. The freezing point of PEG 1500 is around 317 K, and it is seen from Fig. III-7 that the retention volume of Rn is about 10 cm^3 near the temperature. Thus, the boiling point of Rn can be estimated even at fairly high temperature.

Further, it is understandable from these figures that the estimated boiling point has a small error even when the error of the retention volume is fairly large. This is due to the steep slope of V_R vs. T_b line at given T. The error of T_b listed in Tables III-2 and III-3 is due to the error of retention volume only.

D-3. Disagreement between the Boiling Point of Rn Obtained and That Given in Literatures

The boiling point of Rn obtained in the present work is 198 ± 2 K and is lower by 13 K than those extrapolated from the lighter rare gases and measured by Gray and Ramsay. This shows the same tendency that was observed on At_2. This may imply that the intermolecular forces of typical elements in the 6th period has a somewhat different tendency from those of the lighter elements in the same group. This will be discussed closely later.

IV. DISCUSSION ON THE BOILING POINTS OF ASTATINE AND RADON

A. EXTRAPOLATION FROM OTHER ELEMENTS IN THE SAME GROUP

A-1. Calculation by Otozai's Empirical Formula

The boiling points of astatine and radon, which were obtained in the present study, were far lower than those extrapolated from other elements, and further for Rn it was lower than the values obtained on the basis of vapor pressure. Thus in this section the boiling points, which are estimated from other elements in the same group, are discussed.

Probably it is the most popular method to find the relation between boiling points and period numbers (m) in the periodic table. In Fig. IV-1 the relations of T_b vs. m are shown on both halogens and rare gases. It is seen from the figure that the boiling point zigzag increases with increase of m. The degree of zigzag is more remarkable in

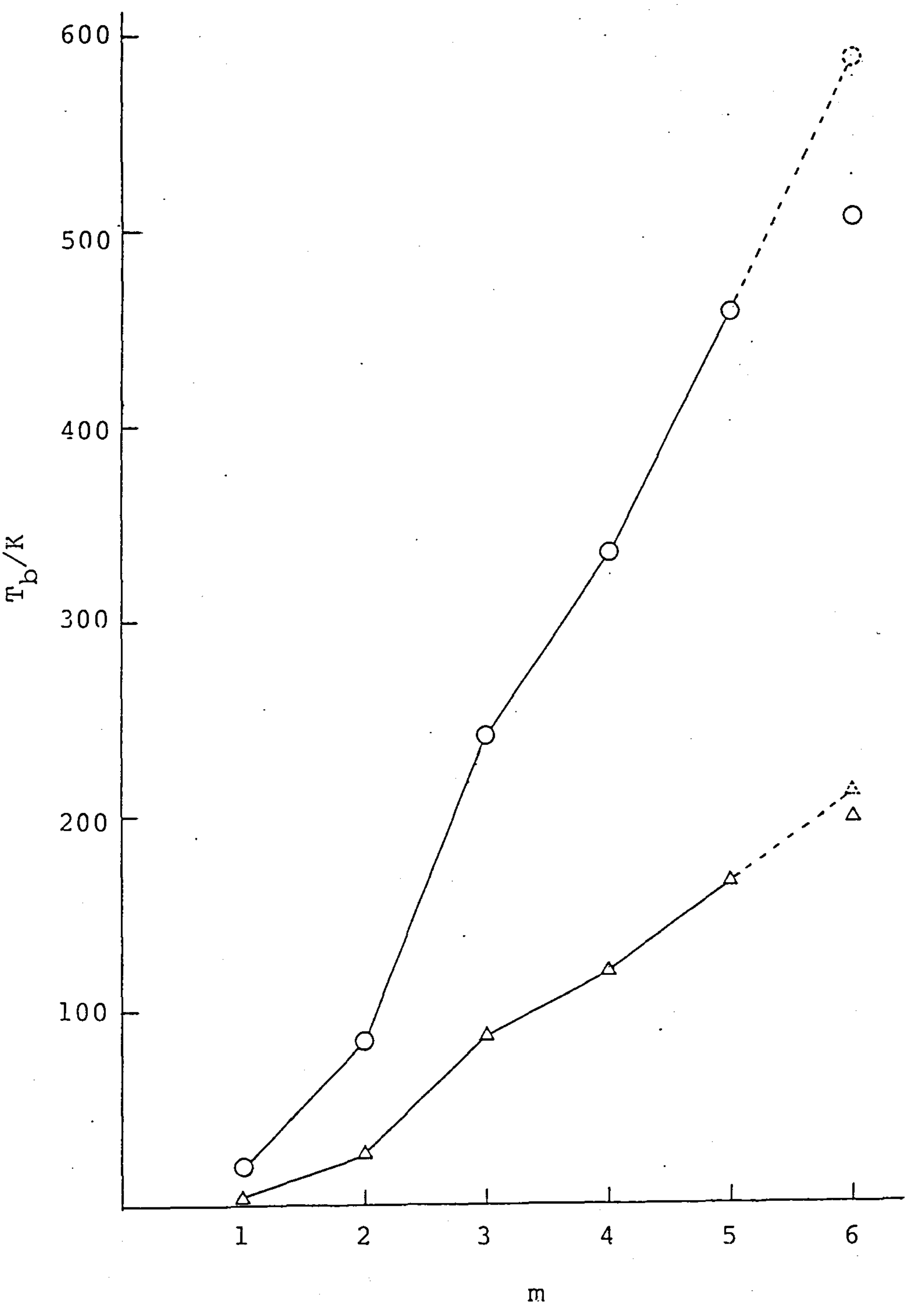


Fig. IV-1. Boiling points of halogens and rare gases (linear scale).

○ : halogen, △ : rare gas.

Dashed lines indicate the extrapolation.

halogens than rare gases. It is difficult to estimate simply an unknown boiling point due the effect. One may find the regularity of the zigzag with m, (the degree decreases with the increase of m).

Now, the next empirical formulae on T_b were led by Otozai[IV-1]. Rare gas sample was the most suitable for leading the empirical relation of T_b with atomic number (Z), because it condenses only by the van der Waals force due to the absence of ionic, permanent dipole and metallic interactions. For the rare gas group the empirical formula

$$T_b = 26.5\ R - 33$$

was obtained with

$$R = (Z + f)^{1/2},$$

where f is defined as

$$f = [30.8\cos m\pi/m\pi][1.15\sin^2(m/2)\pi\{\exp(0.548(1 - m)) - 1\} - \cos^2(m/2)\pi].$$

In these equations the zigzag effect is corrected by a parameter f. For halogens the T_b was represented as

$$T_b = 53m^{0.317}(Z + f)^{1/2} - 33.$$

In Table IV-1 the values, which are obtained with the equations are listed for halogens and rare gases. Further, the experimental values in the present study and the others [IV-2] are listed too. Although the calculated values agree well with experimental values up to the fifth period in both halogens and rare gases, discrepances were found between the calculated and experimental values at the sixth period. So this method may not be applied above the sixth period on both halogens and rare gases.

A-2. Relation between the Boiling Point and the Period Number

In the above calculation the zigzag pattern was well corrected by using a parameter f and the relation between the boiling points and the atomic numbers was found except for the samples in the sixth period. On the other hand, the linear relation between $\ln T_b$ and m is hold in the region of large period numbers as shown in Fig. IV-2. In this figure good linearity of $\ln T_b$ vs. m is found among the 3d, 4th and 5th period groups (the linearity is not found among the 1st, 2nd and 3d period groups).

Table IV-1. Boiling points of halogen and rare gas

m	f	halogen			rare gas		
		Z	T_b (K)		Z	T_b (K)	
			calc.	expt.		calc.	expt.
1	0	1	20	20.28[a)]	2	4	4.22[a)]
2	-4.90	9	85	85.01[a)]	10	27	27.10[a)]
3	+2.50	17	239	238.55[a)]	18	87	87.45[a)]
4	-2.45	35	333	331.93[a)]	36	120	120.85[a)]
5	+2.00	53	457	457.5[a)]	54	165	166.05[a)]
6	-1.63	85	586	503[b)]	86	210	198[b)]
7	+1.55	117	720	-	118	257	-

a) Given in Ref. [IV-2].

b) Obtained in the present study.

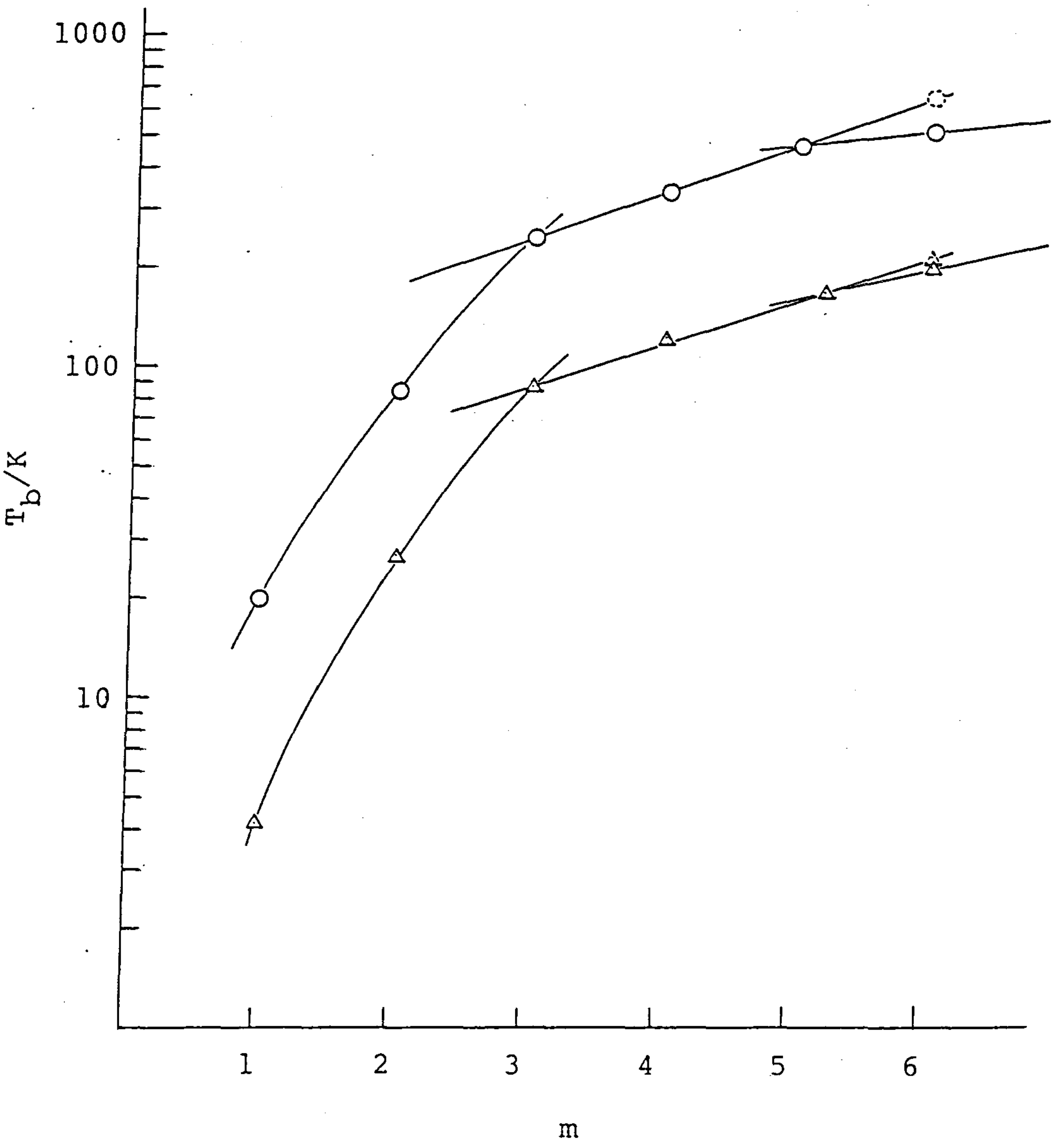


Fig. IV-2. Boiling points of halogens and rare gases (log scale).

○: halogen, △: rare gas.

Thus we tried to fit these values with a linear equation by the least squares method, and the following equations were obtained from the data of the 3d, 4th and 5th periods. For halogens T_b is expressed as

$$\ln T_b = 0.325m + 4.502. \qquad \text{(IV-1)}$$

For rare gases

$$\ln T_b = 0.321m + 3.507 \qquad \text{(IV-2)}$$

is obtained. For the 3d, 4th qnd 5th periods the values estimated by these equations and experimental values are tabulated in Table IV-2 for halogens and rare gases. This method gives boiling point much higher than the present experimental values for the elements of the 6th period.

B. ON THE SEMI-EMPIRICAL FORMULA BETWEEN BOILING POINTS AND RETENTION VOLUMES IN GAS CHROMATOGRAPHY

The boiling points of astatine and radon were obtained by using the semi-empirical theory on the retention volume. The formula has been tested on halogens[IV-1] and was

Table IV-2. Estimated boiling points by least squares method

m	halogen			rare gas		
	element	T_b (K)		element	T_b (K)	
		calc.	expt.		calc.	expt.
3	Cl_2	239	238.55	Ar	87	87.45
4	Br_2	331	331.93	Kr	121	120.85
5	I_2	459	457.5	Xe	166	166.05
6	At_2	635	503	Rn	229	198
7	Eka-At_2	880	-	Eka-Rn	316	-

checked using xenon in the present study. Thus it must be applicable to At_2 and Rn. But the boiling points of At and Rn obtained couldn't be explained by the extrapolation of the other elements in the same groups. Thus we come to a conclusion that the boiling point of the 6th period may be much lower than that extrapolated.

There is another possibility, however; that is, it may be considered that the semi-empirical formula does not hold on At_2 and Rn. The succesive discussion is done from the point of view. The solubility parameter of solute (δ) was expressed as $\delta = (eT^{1/4} - f) + (i/T_b^4 - j)$, which was shown in Appendix (i). Although the values of δ are well known on popular samples in genaral, they are not given exactly as a function of temperature. So the was represented as a function of T_b semi-empirically. Since on both halogens and rare gases the boiling points estimated by the semi-empirical formula well agree with those of other experiments except for At_2 and Rn, it is concluded that the formula of δ holds well in these elements. One may reckon that above formula doesn't hold for At_2 and Rn. But it is quite unlikely that the regularity of the solubility doesn't hold only in the cases of At_2 and Rn.

C. CONSIDERATION ON THE BOILING POINT WITH RELATION TO THE EFFECTIVE NUCLEAR CHARGE

An linear relationship exists between $\ln T_b$ and m as shown in Fig. IV-2, and large changes are found in the slopes of the lines before and after m = 3 both in halogens and rare gases. Furthermore these changes are also found at m = 5 if the presently obtained values are take into consideration. If the values obtained in this study are correct, this behavior of the boiling points may be correlated qualitatively to the configuration of electrons on the elements, because at m = 4 and m = 6 the d-orbital and f-orbital are first fulfilled, respectively.

The wave function, which discribes a many-electron system, can be approximately constructed of a hydrogen-like wave function, which has an effective nuclear charge. The difference between the real and the effective nuclear charge is called as a screening constant (S). The radial part of the wave function of one electron has been simply expressed by Slater[IV-3] as

$$r^{n^*-1} e^{-((Z - S)/n^* r)} .$$

It is an asymptotic form at large distances for a hydrogen-like wave function of quantum number n^* in the field of a nuclear charge $(Z - S)$.

The values of n^* and $(Z - S)$ are given by following rules in literature[IV-3]:

(1) n^* is assigned by the following table, interms of the real principal quantum number n:

for n = 1, 2, 3, 4, 5, 6
n^* = 1, 2, 3, 3.7, 4.0, 4.2

(2) For determining $(Z - S)$, electrons are divided into the following groups, each having different shielding constant: 1s; 2s, p; 3s, p; 3d; 4s, p; 4d; 4f; 5s, p; 5d; etc.

(3) The shielding constant S is formed, for any group of electrons, from the following contributions:

(a) Nothing from any shell outside the one considered.

(b) An amount 0.35 from each other electron in the group considered (except in the 1s group, where 0.30 is used instead).

(c) If the shell considered is an s, p shell, an amount 0.85 from each electron with the total quantum number less by one, and an amount 1.00 from each electron still further in; but if the shell is d or f, an amount 1.00 from every electron inside it.

In Table IV-3 Slater's $(Z - S)$ and S are listed for

Table IV-3. Slater's effective nuclear charges and screening constants for p-orbital electrons

m	orbital	halogen		rare gas	
		Z - S	S	Z - S	S
1	1s	1	0	1.70	0.30
2	2p	5.2	3.8	5.85	4.15
3	3p	6.1	10.9	6.75	11.25
4	4p	7.6	27.4	8.25	27.75
5	5p	7.6	45.4	8.25	47.75
6	6p	7.6	77.4	8.25	77.75

p-orbital electrons of halogens and rare gases.

Separately from Slater, Pauling has been obtained a series of screening constants[IV-4], which were estimated from x-ray terms and mole refraction by semi-empirical considerations. According to Pauling the many physical properties of elements are expressed as a function of (Z - S). The property, which for a hydrogen-like atom is found to vary with $n^r Z^{-t}$, has been considered by Pauling[IV-5].

The screening constant for this property would be such that

$$\mathrm{const.}\,n^r Z^{-t} = \mathrm{const.}\,n^r (Z - S)^{-t}.$$

Here, S is expressed as

$$S = \sum_i Z_i - \frac{r}{\gamma_i}\sum_i Z_i D_i,$$

in which D_i, called the unit screening defect for an electron in the i th shell, is given by the equation

$$D_i = \frac{1}{\pi}\{\beta_i u_i + (1 + \beta_i)\varepsilon \sin u_i\} - \beta_i$$

with

$$1 + \varepsilon \cos u_i = \frac{\gamma_i n_i^2}{n^2}$$

and

$$\beta_i = \frac{n^2}{\gamma_i n_i} - 1.$$

The path of an electron in the *i* th region is a segment of Kepler ellipse defined by the segmentary radial and the azimuthal quantum number n' and k, so that it can be described as follows:

$$r = \frac{a_0 k^2}{Z_i} \cdot \frac{1}{(1 - \varepsilon_i \cos \varphi)} = \frac{a_0 n_i^2}{Z_i} (1 + \varepsilon_i \cos u).$$

$$t = \frac{n_i^2}{4\pi R Z^2} (u + \varepsilon_i \sin u).$$

In these equations φ and u are the segmentary true anomaly and excentric anomaly, respectively, measured from aphelion, while n_i and ε_i are the segmentary principal quantum number and the excentricity given by the equations

$$n = n' + k, \qquad \varepsilon = \sqrt{1 - \frac{k^2}{n_i^2}} \; .$$

Pauling's (Z - S) and S are listed in Table IV-4 for p-orbital electrons of halogens and rare gases. He explained well the physical properties of elements (e.g., sizes of atoms and ions, mole refraction, diamagnetic susceptibility etc.) by using the values.

Since the values of (Z -S), which is given by Slater's rule, satulate and equal to 7.6 and 8.25 on halogens and rare gases, respectively, this cannot explain the present discrepancy of the boiling points at the 6th period. On the other hand, Pauling's values obviously begin to change at m = 5 in both halogenes and rare gases as shown in Figs. IV-3 and IV-4 (it is not clear at the 3d period). This phenomenon is identical with the variation of the boiling points of halogen and rare gas groups.

Thus, we attempted to represent the boiling points as a function of (Z - S). On the boiling points of the elements in 5th, 6th and 7th periods the following equations are obtained with considering the effective nuclear charge:
For halogens

$$T_b = 32.1(Z - S) + 45.9, \qquad \text{(IV-3)}$$

and for rare gases

$$T_b = 16.7(Z - S) + 36.7 \qquad \text{(IV-4)}$$

are obtained. The values estimated from these equations are listed in Table IV-5. Estimated values agreed well with

Table IV-4. Pauling's effective nuclear charges and screening constants for p-orbital electrons

m	orbital	halogen		rare gas	
		Z - S	S	Z - S	S
1	1s	1	0	1.81	0
2	2p	4.85	4.15	5.43	4.57
3	3p	6.6	10.4	7.1	10.9
4	4p	8.9	26.1	9.4	26.2
5	5p	11.9	41.1	12.2	41.8
6	6p	13.2	71.8	14	72
7	7p	16	101	17	101

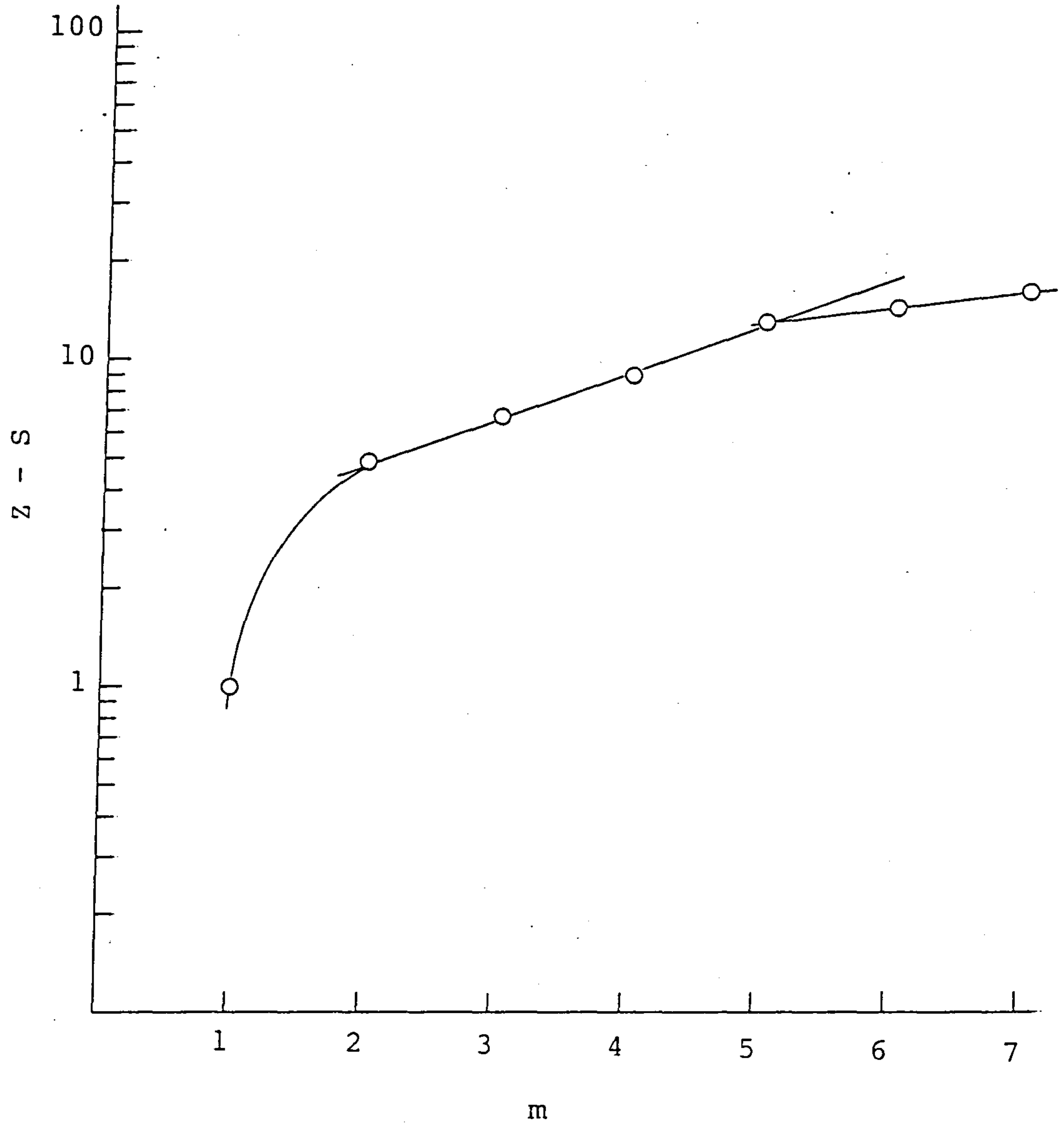


Fig. IV-3. Effective nuclear charges for p-orbital electrons of halogens.

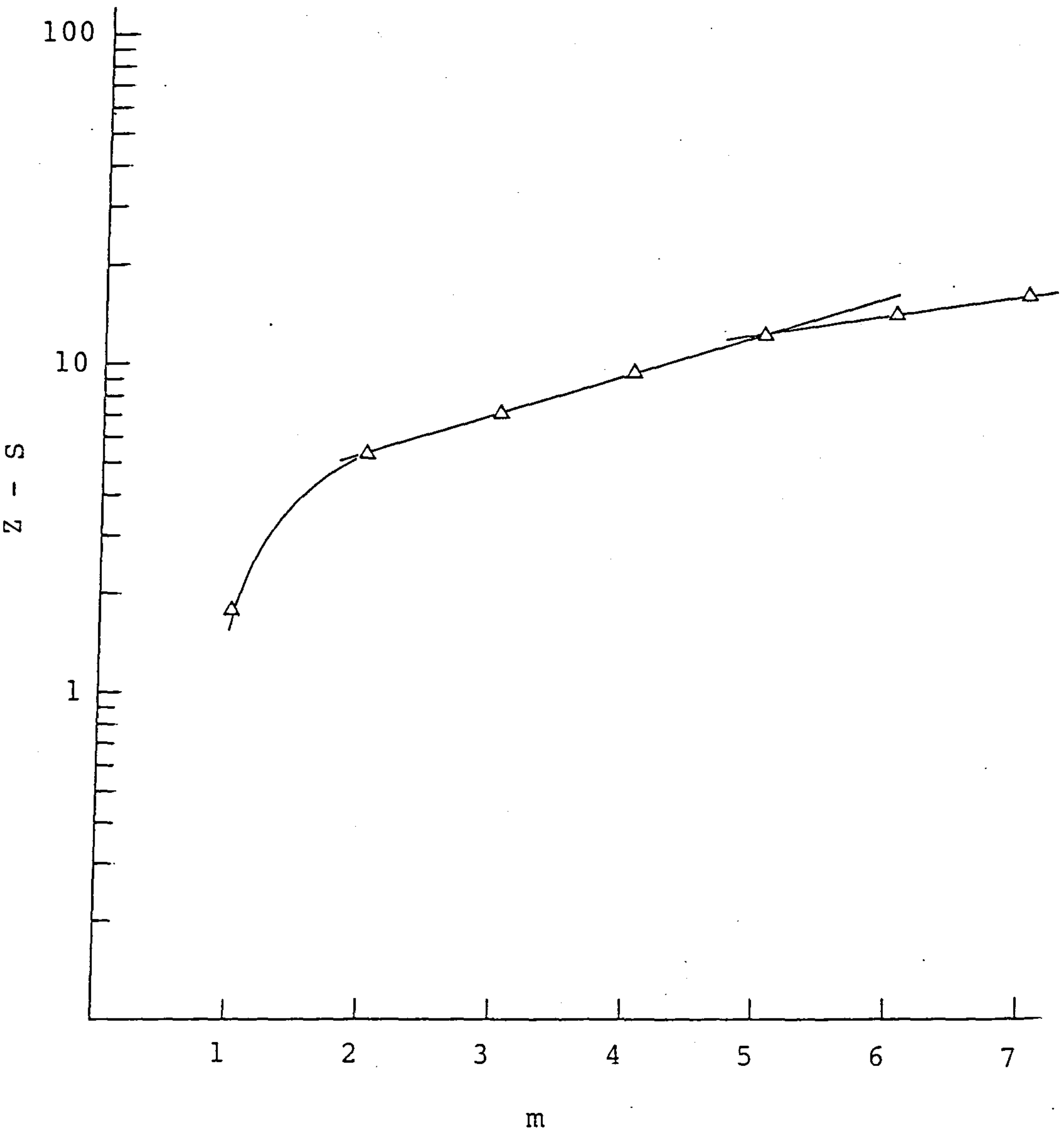


Fig. IV-4. Effective nuclear charges for p-orbital elctrons of rare gases.

Table IV-5. Boiling points of halogens and rare gases

m	halogen			rare gas		
	element	T_b (K)		element	T_b (K)	
		calc.	expt.		calc.	expt.
4	Br_2	331	331.93	Kr	120	120.85
5	I_2	459	457.5	Xe	167	166.05
6	At_2	501	503	Rn	197	198
7	Eka-At_2	559	-	Eka-Rn	247	-

experimental values in both halogens and rare gases at the 5th and 6th periods. Moreover the values agreed well even at the 4th period. For reference, the predicted values for the 7th period are fairly lower than those expected by other extrapolation methods.

In conclusion, we have found a close relationship between the observed boiling point and the screening constant which is based on some physical or physicochemical concepts. Now that it is quite conceivable that the evaporation phenomenon is strongly influenced by the electronic configuration of the molecule, we have a good reason to believe that the present work gave correct boiling points both halogen and rare gas groups. This proves in turn that Otozai's empirical formula is reliable even for the 6th period and very likely for higher periods.

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APPENDIX

APPENDIX (i)

SEMI-EMPIRICAL THEORY ON THE RETENTION VOLUME IN GAS CHROMATOGRAPHY

APPENDIX (ii)

REACTION MECHANISMS OF ELEMENTARY ASTATINE WITH SOME ORGANIC SOLVENTS

APPENDIX (iii)

DETERMINATION OF THE MOLECULAR WEIGHT AND SOLUBILITY PARAMETERS OF HIGH-POLYMERS BY GAS CHROMATOGRAPHY

APPENDIX (i)

SEMI-EMPIRICAL THEORY ON THE RETENTION VOLUME IN GAS CHROMATOGRAPHY[i-1]

It has been found that the retention volume in the gas-liquid partition elution gas chromatography has a close correlation with the boiling point of the sample[i-2 to i-6]. It was attempted to obtain a quantitative expression for the relation by a semi-empirical method (e.g., by the plate theory on retention volume, the regular solution theory and some empirical rules to supply the theories). The practical form of the theory is as follows:

$$\ln V_R = \ln ZRTN\vartheta + Z(1 + hr)\varepsilon - r + \{1 - Z(1 + h)\varepsilon\}rT_b/T, \qquad \text{(i-1)}$$

$$Z = 1 + h\{d - c(T_b/T)^2\}(T_b/TR)\exp\{r(1 - T_b/T\}, \qquad \text{(i-2)}$$

$$\vartheta = 100,\ h = 1/\{1 + (1/aT_b^4 - 1)T/T_b\} + 1/\ln T_bT, \qquad \text{(i-3)}$$

$$r = \mu(aT_b^4 + b)\{1 + aT_b^4(T_b/T - 1)\}T^{1/8} \ln T_b/\ln T_bT, \qquad \text{(i-4)}$$

$$\varepsilon = (\beta\delta_s/\delta - 1)^2,\ \delta = (eT_b^{1/4} - f) + (i/T_b - j), \qquad (i\text{-}5)$$

$$\beta = \{1 + 1.3(\delta - 5.9)/\delta_s\}/\{1 + 0.05(\overline{\delta} - 5.9)\}. \qquad (i\text{-}6)$$

For non-associated sample solutes, for example, $a = 4\times10^{-12}$, $b = 10.35$, $c = 3.45$, $d = 0.15$, $e = 1.87$, $f = 0.75$, $i = 0$, $j = 0$ and $\mu = 1$. The derivation of the theory will be mentioned below in detail.

The usual idealization for low vapor pressure, which leads to the ideal gas behavior and disregard of the molar volume of liquid compared with that of gas, is tried to be amended as far as possible. However, the assumption of dilute solution is left as it is, because of the difficulty for correction.

The formula for retention volume by the plate theory[i-7] is corrected for the deviation from the ideal gas behavior as

$$V_R = ZRTN/\gamma P, \qquad (i\text{-}7)$$

where V_R (cm^3) is the absolute retention volume, Z is the compressibility factor ($Pv_g = ZRT$ for gas low), P (atm) is the vapor pressure of pure liquid solute, v_g (cm^3/mol) is the molar volume in gas state, R is the gas constant, T(K) is the column temperature, N (mol) is moles of solvent in the column and γ is the activity coefficient of solute in the solution at infinite dilution based on Raoult's law.

Under the assumption of low vapor pressure, Hildebrand rule, $\Delta S^V = R(1 + C\ln v_g)$, is derived. Putting this formula into the Clapeyron-Clausius equation, $dP/dt = \Delta S^V/\Delta v$, a solution $\ln P = q\{1 - (T_b/T)\}$ is obtained with a good approximation in the Taylor expansion. Here, ΔS^V (cal/deg. mol) is the entropy of vaporization, C is a constant, $\Delta v = v_g - v_\ell$, T_b (K) is boiling point and $q = 1 + C\ln RT$. In order to correct for the assumption of low vapor pressure, an expression:

$$\ln P = r(1 - T_b/T) \tag{i-8}$$

is assumed, leading the theoretical factor $1 - T_b/T$ as it is, and searching the contents of rT_b/T empirically as mentioned below.

According to the regular solution theory[i-8, 9] the solubility parameter δ (cal$^{1/2}$cm$^{-3/2}$) is defined as $\delta = (-E_\ell/v_\ell)^{1/2}$, where E (cal/mol) is the cohesive energy. If van der Waals equation, $-E = a/v$, is assumed $\Delta E^V = (-E_\ell) - (-E_g) = a(1/v_\ell) - (1/v_g)$, and hence $-E_\ell = a/v_\ell = \Delta E^V/Y$, where, a (cal.cm^{3}mol^{-2}) is van der Waals constant and $Y = (v_g - v_\ell)/v_g$ is the molar volume correction factor. As $\Delta E^V = \Delta H^V - P\Delta v = \Delta H^V - YZRT$, and $\Delta H^V = YZ\Delta H^V_{app}$ from the Claperon-Clausius equation, $d\ln p/dT = \Delta H^V/PT\Delta v = \Delta H^V_{app}/RT$, δ is expressed as

$$\delta = \{(Z/v_\ell)(\Delta H^V_{app} - RT)\}^{1/2}, \qquad \text{(i-9)}$$

where ΔH^V_{app} (cal/mol) is the apparent heat of vaporization. It is seen that the correction factor Y disappears in this expression.

Again the regular solution theory gives $\ln(p/P) = \ln x + (1/RT)v_\ell\varphi_s^2(\delta_s - \delta)^2$ under the assumption of low vapor pressure, where p (atm) is the vapor pressure of the solute, x is the mol fraction of solute, φ_s is the volume fraction of the solvent and δ_s is the solubility parameter of the solvent. Comparing this formula with $p = \gamma xP$, γ is expressed as

$$\ln\gamma = v_\ell\varphi_s^2(\delta_s - \delta)^2/RT. \qquad \text{(i-10)}$$

As $\varphi_s = 1$ in a dilute solution, and by introducing v_ℓ in Eq. (i-3) into Eq. (i-4),

$$\ln\gamma = Z(\Delta H^V_{app}/RT - 1)(\delta_s/\delta - 1)^2 \qquad \text{(i-11)}$$

is obtained.

In order to cover even non-regular solutions, a parameter β (called non-regularity, $\beta \geqq 1$) is introduced, and $\beta\delta_s$ (called an apparent solubility parameter of solvent) is used instead of δ_s. Using the formulae $\Delta H^V_{app} = RT^2(d\ln P/dT)$ and $d\ln P/dT = (dr/dT)(1 - T_b/T) + rT_b/T^2$ derived from Eq. (i-2), γ is represented as

$$\ln\gamma = Z\{(dr/dT)(T - T_b) + rT_b/T - 1\}\varepsilon, \qquad \text{(i-12)}$$

where $\varepsilon = (\beta\delta_s/\delta - 1)^2$. Although δ decrease as temperature increase, the ratio δ_s/δ does not vary so much with temperature. Hence, the temperature dependence of ε is not severe.

Based on experimental vapor pressure data of organic[i-10] and inorganic[i-11] compounds, the parameter r is expressed empirically as follows:

$$r = \rho T_b^{1/8}\ln T_b/\ln T_b T, \qquad \text{(i-13)}$$

$$\rho = \rho_b\{1 + aT_b^4(T_b/T - 1)\}, \qquad \text{(i-14)}$$

and

$$\rho_b = \mu(aT_b^4 + b), \tag{i-15}$$

where subscript b is the symbol for the boiling point.

The values of parameters μ, a and b are listed in Table i-1. The parameter μ may have a physical meaning of effective association. For example, water associated by hydrogen-bond has 1.20 times larger values of ρ_{298} and ΔH_{298}^V than non-associated n-heptane, which has almost the same boilibg point as water shown in Table i-2. Here, subscript 298 is the symbol for 298 K.

From Eqs. (i-7) and (i-8)

$$dr/dT = - hr/T, \tag{i-16}$$

where

$$h = 1/\{1 + (1/aT_b^4 - 1)T/T_b\} + 1/\ln T_bT, \tag{i-17}$$

is derived. Putting Eq. (i-10) into Eq. (i-6), γ is finally expressed as

$$\ln\gamma = Z\{(1 + h)rT_b/T - (1 + hr)\}\varepsilon. \tag{i-18}$$

Putting Eqs. (i-2) and (i-12) into Eq. (i-1), the retention volume is expressed as

$$\ln V_R = \ln ZRTN + \{Z(1 + hr)\varepsilon - r\} + \{1 - Z(1 + h)\varepsilon\}rT_b/T. \qquad \text{(i-19)}$$

Thus, V_R is semi-empirically expressed with variable N, δ, T_b, T and $\beta\delta_s$. As mentioned above, the condition of dilute solution was assumed, the non-regularity was introduced, and the assumption of low vapor pressure was largely corrected.

In the case, when solutes and solvents are chemically similar, ε becomes zero, and so V_R is expressed as $\ln V_R = \ln ZRTN - r + rT_b/T$. As T and N are constant under the same column condition, it becomes $\ln V_R = \text{const} + \text{const}.T_b$ under the assumption that $Z = 1$ and $r = \text{const}$. In such a case $\ln V_R$ vs. T_b plots give a straight line.

In order to apply the theory practically, Z must be calculated. From the formulae $Pv_g = ZRT$ and $Pv_g = RT + BP$, we obtain $Z = 1 + BP/RT$, where second virial coefficient B (cm^2/mol) is empirically expressed from the experimental data[i-12] as

$$-B/T_b = c(T_b/T)^2 - d. \qquad \text{(i-20)}$$

The values of parameters c and d are listed in Table i-3.

Thus, a formula

$$Z = 1 + \{d - c(T_b/T)^2\}(T_b/T)(1/R) \exp\{r(1 - T_b/T)\} \tag{i-21}$$

is obtained.

The values of δ are usually given with two significant figures. To check the theory, however, three significant figures is desirable. The δ values which are not available for any temperature[i-13], can be smoothed by an empirical formula:

$$\delta = (eT_b^{1/4} - f) + (iT_b^4 - j). \tag{i-22}$$

The values of parameters e, f, i and j are listed in Table i-4.

The parameter $\beta\delta_s$ has a proper value for respective combination of the solvent and the chemical group of samples independent of the column temperature. The $\beta\delta_s$ value is approximately constant for each solvent, but shows some systematic increase with increase of $\bar{\delta}$, which is the average value of δ's of the sample in the chemical group. Since is naturally proper to the solvent, systematic increase is due to β. It was found that $\beta\delta_s$ corrected by $-\bar{\delta} + 0.05(\beta\delta_s - 5.9)(\delta - 5.9)$ becomes a constant value characteristic of the solvent and independent of $\overline{\delta}$, the nature of the chemical group. Here, the value (5.9) is the smallest value of the ever found experimentally within many substances.

Thus the formula:

$$\beta\delta_s \text{ (corrected)} = \beta\delta_s - \overline{\delta} + 0.05(\beta\delta_s - 5.9)(\overline{\delta} - 5.9) \qquad \text{(i-23)}$$

is obtained. β deduced from Eq. (i-15) is expressed as

$$\beta = 1 + 1.3(\overline{\delta} - 5.9)/\delta_s/ \{1 + 0.05(\overline{\delta} - 5.9)\}. \qquad \text{(i-24)}$$

Table i-1. Values of parameters μ, a and b

Substance	μ	a	b
n-Alkane and other non-associated	1.00	4×10^{-12}	10.35
Water	1.20	4×10^{-12}	10.35
n-Alkyl alcohol	1.20-1.30	4×10^{-12}	10.35

Table i-2. Meaning of parameter μ

Substances	T_b(K)	ρ_{298}	ΔH^{V}_{298}(cal/mol)
n-C_7H_{16}	371	10.71	8.75
H_2O	373	12.87	10.51
Ratio		1.20	1.20

Table i-3. Values of parameters c and d

Substance	c	d
n-Alkane and sat. Hydrocarbons	3.45	0.15
SO_2, CO_2	2.05	0.15
H_2O	1.15	0.15

Table i-4. Values of parameters e, f, i and j

Substance	e	f	i	j
n-Alkane	1.87	0.75	0	0
Methyl n-alkyl	1.87	0.75	0	0
ketone	1.87	0.75	3.63×10^{10}	0.50
n-Alkyl alcohol	1.87	0.75	6.60×10^{10}	-0.98

APPENDIX (ii)

REACTION MECHANISMS OF ELEMENTARY ASTATINE WITH SOME ORGANIC SOLVENTS[ii-1]

It has been pointed out that elementary asttaine is liable to react with other halogens and organic substances[ii-2]. For example, it was shown by Neumann et al.[ii-3] that astatobenzene was produced when elementary astatine was extracted with benzene. Since elementary astatine tends to react with organic impurities and to be adsorbed on the glassware,the extractability into solvent is not always constant. Appleman et al.[ii-4] have observed some astatine compounds (e.g., HAt, CH_3At, AtCl, AtBr and AtI) in a plasma ion source. These compounds were identified by means of a time-of-flight mass spectrometer. However, it was difficult to discuss the reaction mechanisms because of the uncertain chemical form of elementary astatine. Since astatine is a short-lived radioisotope, the experiment must be done only at very low concentrations and so the assignment and the determination of the species produced are very difficult in ordinary methods.

Many studies on the reaction of halogens following to the decay (i.e. known as a hot atom reaction) have been done [ii-5 to ii-10]. Replacement reactions of astatine in benzene and halobenzene following to the EC-decay of radon was studied by Vasaros et al.[ii-11]. Energetic astatine produced by the EC-decay participates in this reaction.

We found that several astatine compounds were always produced when elementary astatine was extracted into benzene[ii-12]. The amounts of the compounds tended to increase up to saturated amounts with increasing the time after extraction, and the rate was closely related to the half life of astatine used[ii-13]. Since the chemical form of elementary astatine had be confirmed[ii-14], the reaction mechanism of elementary astatine with benzene, toluene and monochlorobenzene could be discussed. The compounds were analyzed by means of the RGC, which enabled the assignment and the determination of compounds produced.

Astatine was produced by the $^{209}Bi(^{3}He, 3n)^{209}At$ reaction as described before. After the irradiation the bismuth target was dissolved in 5 ml of 1 N HNO_3, and then At was extracted with 5 ml of benzene, toluene and monochlorobenzene which were previously washed with acid. The astatine samples were contaminated with about 6 percents of ^{210}At. The solutions which contained At_2 were concentrated up to 100 μl under reduced pressure at room temperature. The specific activity were about 0.5 μCi/μl.

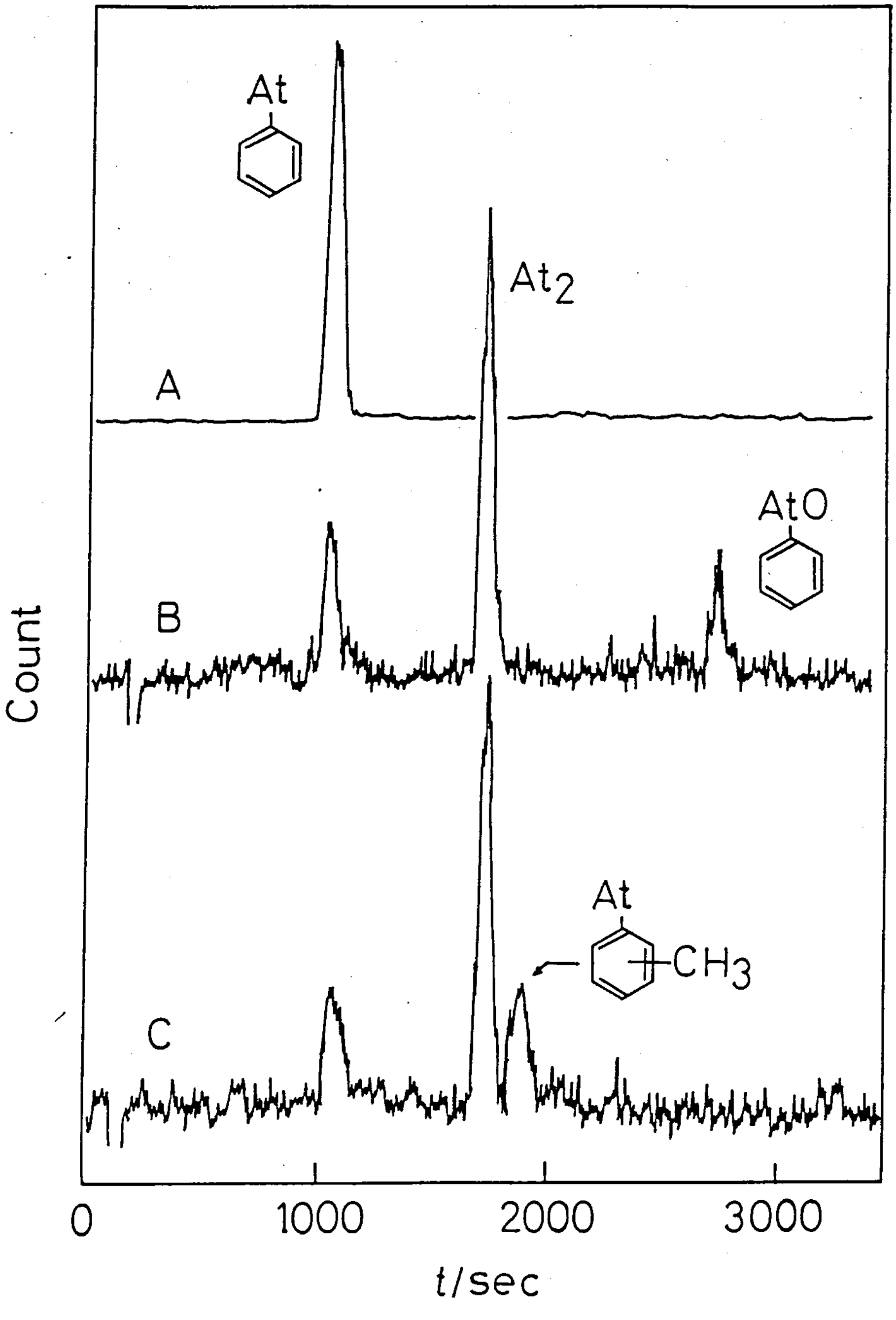


Fig. ii-1. Radiogaschromatograms of astatine compounds at 406 K

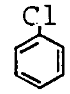
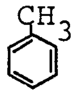
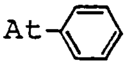
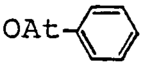
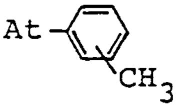
A: At_2 + , B: At_2 +  , C: At_2 + .

Table ii-1. Boiling points of astatine and astatine compounds

Compound	Boiling point (K)	
	obsd.	lit.
At_2	503 ± 3	586[a)]
	484 ± 3	485 ± 2[b)]
	517 ± 3	-
	505 ± 4	512 ± 4[c)]

a) given in Ref. ii-16.

b) given in Ref. ii-17.

c) given in Ref. ii-18.

basis of the reasons that iodosobenzene analogous to astatosobenzene was observed in the reaction of carrier-free iodine-131 with benzene and no simple astatine compound having such a boiling point could be considered. For reference the radiogaschromatogram obtained for the sample of $^{131}I_2$ plus benzene are shown in Fig. ii-2 and the boiling point of the peaks are listed in Table ii-2.

Now, it is reasonable to think that the reaction of carrier-free astatine with organic solvents is caused by the At-At bond cleavage by the decay of astatine from the following reasons:

(1) Though other inactive elementary halogens generally don't react with benzene and toluene at ordinary temperature, only carrier-free species react with them when they are mixed.

(2) Though in the thermal reaction the amounts of products depend on the temperature, in this case the amounts of them don't vary so much when the temperature is changed.

(3) When carrier I_2 was added in the At_2 solution, the compouds of astatine with solvents were not produced in the present work. This may show that At-radicals produced in the solution are caught by I_2 as radical collector.

(4) The rate constants for the reactions, this is most important, are proportional to the half life of astatine used as described below.

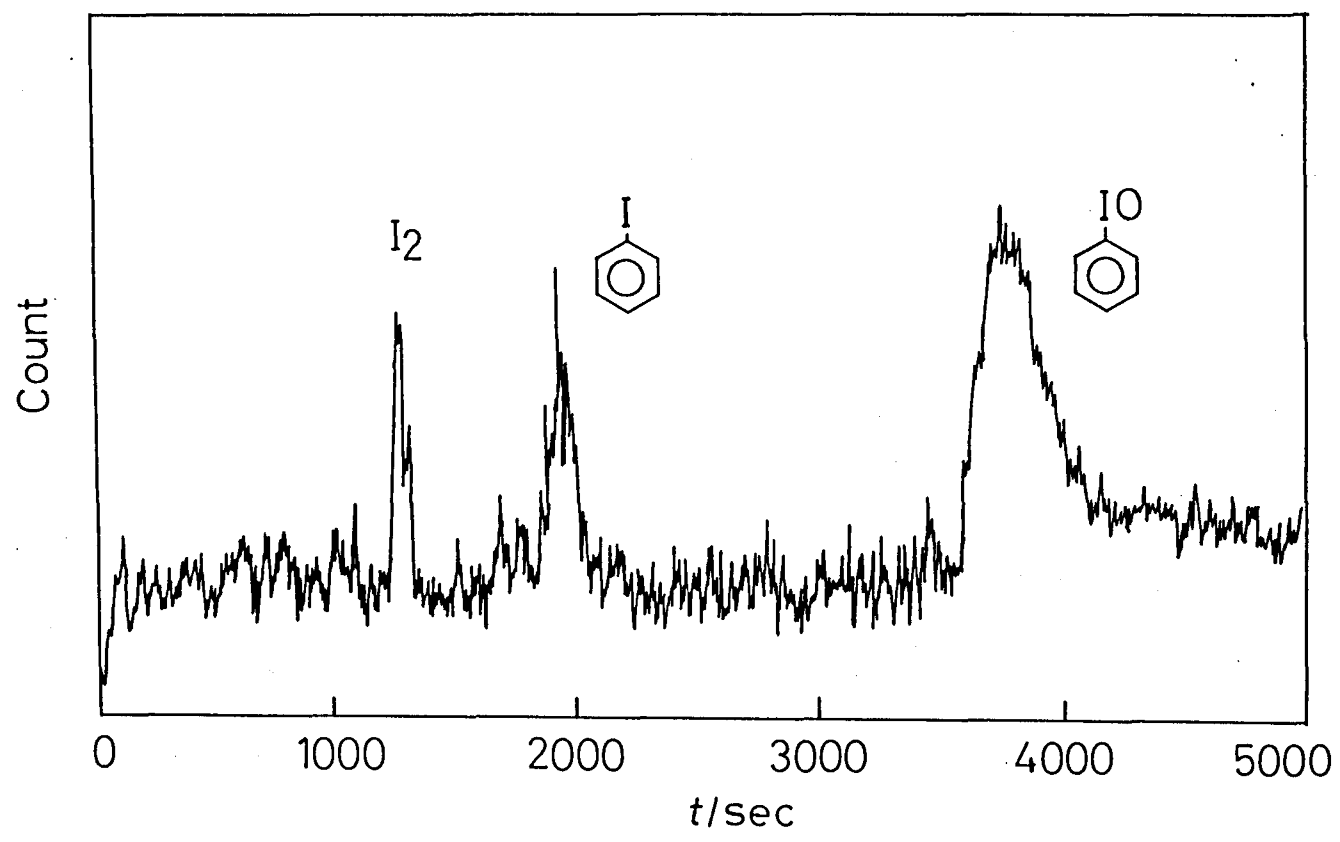
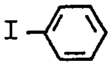
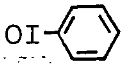


Fig. ii-2. Radiogaschromatogram of iodine compound at 377 K

Table ii-2. Boiling points of iodine and iodine compounds

Compound	Boiling point (K)		
	obsd.		lit.
I_2	453	1	457.5[a)]
	462	2	463.6[a)]
	483	3	483[a)]

a) given in Ref. ii-16.

This reaction may be divided into 2 steps as follows:

Step 1; the bond of At-At is cleaved by the disintegration of either astatine in At_2, and the remained reacts with solvents.

Step 2; the compounds produced at step 1 is started to decompose by the decay of astatine.

As the number of molecule of the solvent is in large excess of At_2 at step 1, the reaction depends only on the number of At_2 molecules and is first-order for At_2. As the reaction is of a decomposition type in step 2, it depends only the number of At-compound and is first-order for At-compound. We assume here that these reactions proceed faster than thermal reactions. If the rate constants of steps 1 and 2 are k_{i1} and k_{i2}, respectively, the reaction is represented as

$$At_2 + \text{organic solvent} \xrightarrow[\text{step 1}]{k_{i1}} \text{At-compound} \xrightarrow[\text{step 2}]{k_{i2}}. \qquad (ii-1)$$

Here, subscript i indicates the kind of the compound produced in the same system, hence i takes 1 and 2 in the present work since two kinds of compounds are observed in both benzene and toluene systems. When the number of At_2 molecule and At-compound in formula (ii-1) are N_{01} and N_{i2}, respectively, then

$$\frac{dN_{01}}{dt} = -2\sum_i k_{i1} N_{01} \qquad \text{(ii-2)}$$

and

$$\frac{dN_{i2}}{dt} = 2k_{i1} N_{01} - k_{i2} N_{i2} \qquad \text{(ii-3)}$$

hold. If the activity of At_2 and the compound are A_{01} and A_{i2}, respectively, the following equations are obtained:

$$A_{01} = 2\lambda N_{01}^0 = 2\lambda N_{01}^0 \exp(-2\sum_i k_{i1} t), \qquad \text{(ii-4)}$$

$$A_{i2} = \lambda N_{i2} = \frac{2k_{i1}}{k_{i2} - k_{i2}} \lambda N_{01}^0 \{\exp(-2\sum_i k_{i1} t) - \exp(k_{i2} t)\}. \qquad \text{(ii-5)}$$

Here, N_{01}^0 is the number of At_2 molecule at $t = 0$ and λ is the decay constant of astatine used. The activity ratio is represented as

$$\frac{A_{i2}}{A_{01}} = \frac{k_{i1}}{k_{i2} - 2\sum_i k_{i1}}\{1 - \exp(-k_{i2}t + 2\sum_i k_{i1}t)\}. \qquad \text{(ii-6)}$$

The curve of A_{i2}/A_{01} vs. time was analyzed by the analogous method to the analysis of decay curve, and k_{i1} and k_{i2} were calculated. The time-courses of A_{i2}/A_{01} for At_2 plus benzene and toluene are shown in Figs. ii-3 and ii-4, respectively. The analysis for At_2 plus monochlorobenzene was not carried out, because At_2 couldn't be observed in the present work as shown in Fig. ii-1 and subsequently the activity ratio couldn't be obtained. In Table ii-3 k_{i1} and k_{i2} (divided by λ for convenience of discussion) obtained by the analysis for benzene and toluene systems are listed. All values of k_{11}/λ and k_{21}/λ are nearly constant and k_{11}/λ plus k_{21}/λ equals to unit for both benzene and toluene systems. This shows that the reaction can occur only when the bond of At-At is cleaved by the disintegration of either astatine in At_2 as assumed above and the remained astatine reacts immediately with surrounding solvents. Further, the reaction at step 2 may be caused by the disintegration of astatine too because k_{i2}/λ is almost constant.

In the reaction of At_2 plus monochlorobenzene system At_2 may react too rapidly to be observed. If this mechanism is accepted, k_{i1}/λ and k_{i2}/λ should have very large values.

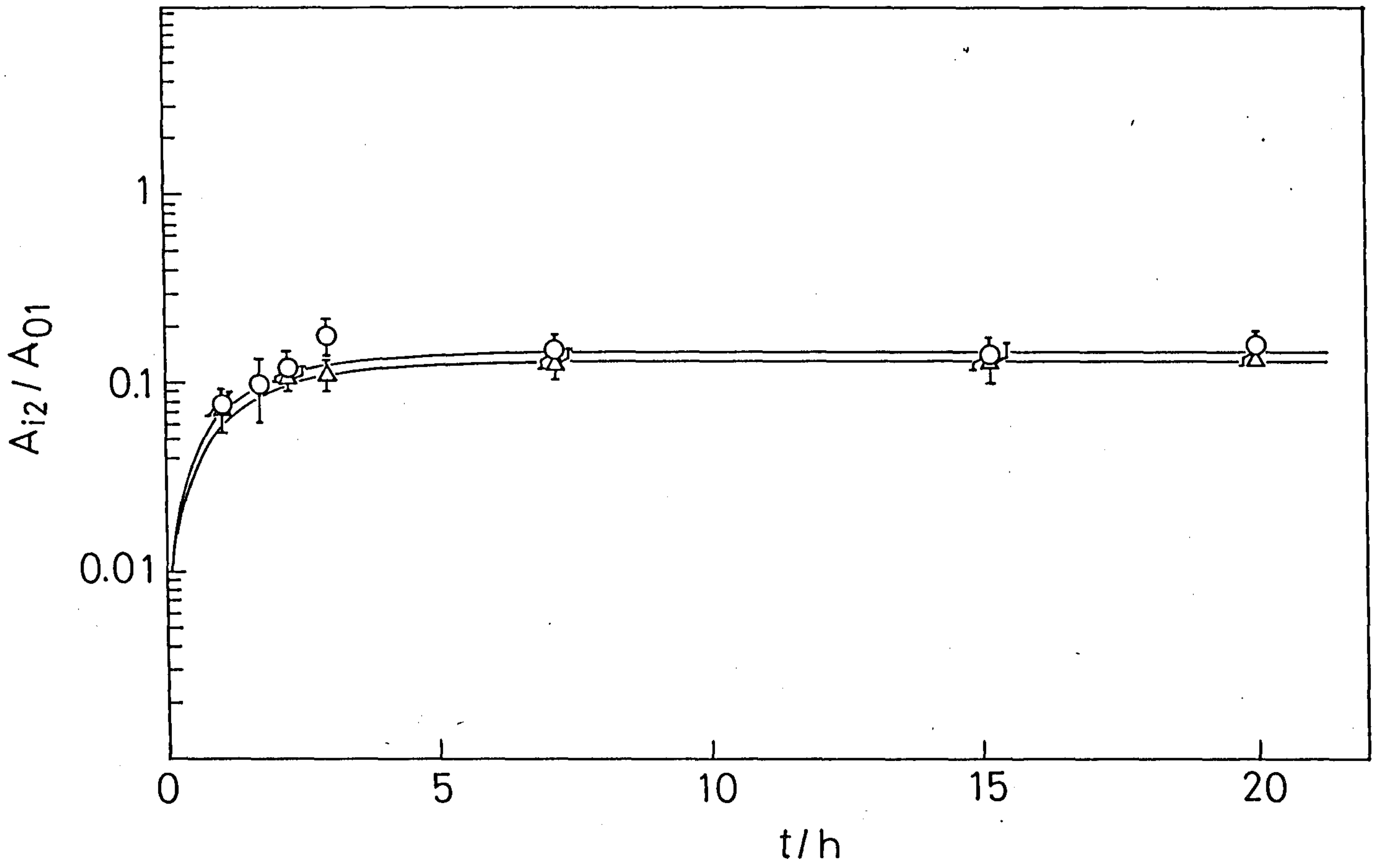
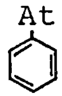
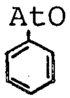


Fig. ii-3. Time-courses of activity ratio in benzene system

○:  , Δ:  .

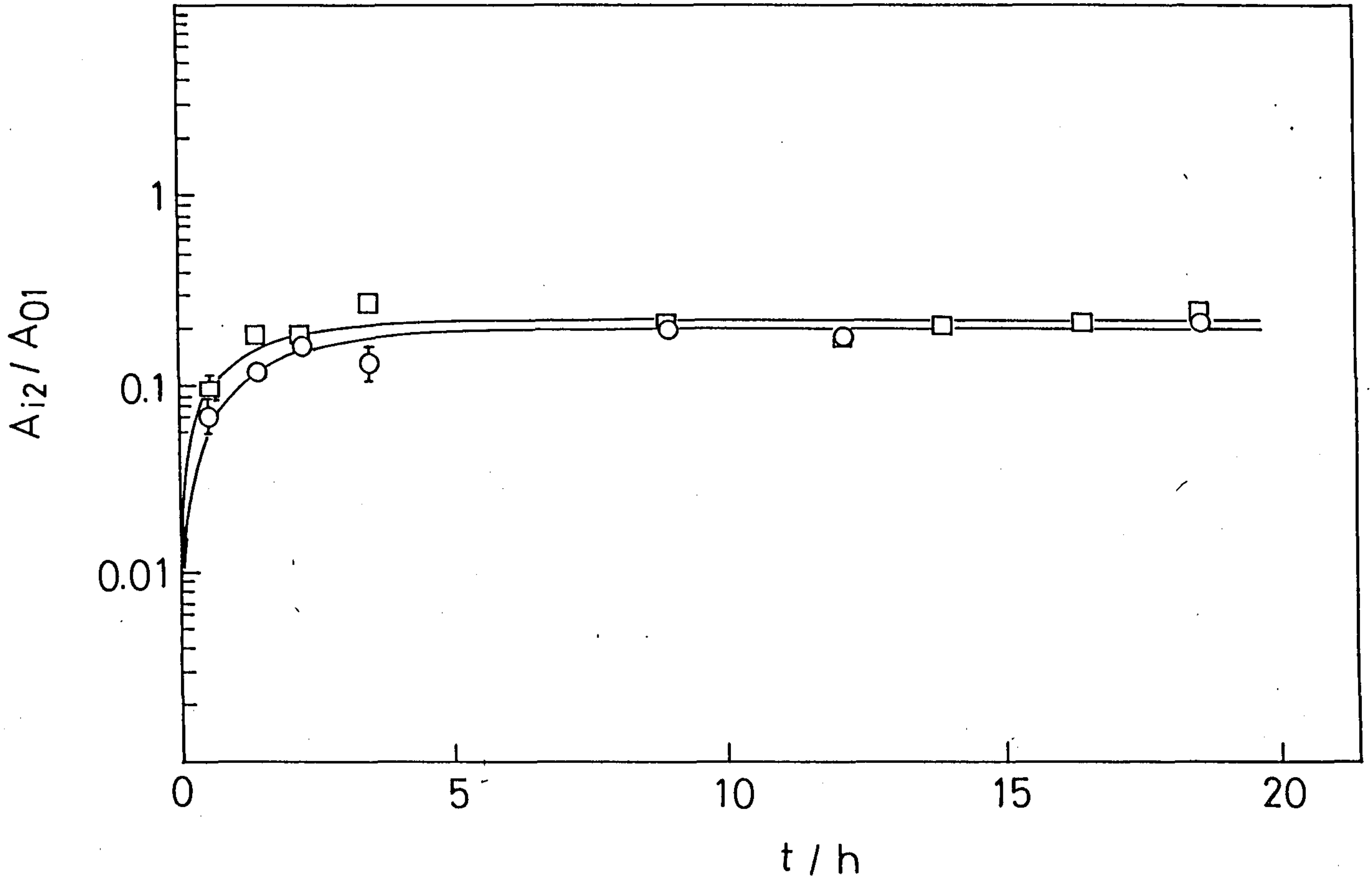


Fig. ii-4. Time-courses of activity ratio in toluene system

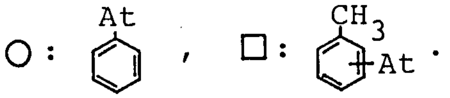
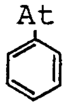
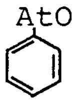
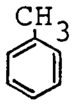
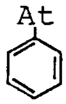
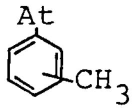


Table ii-3. Rate constants for the reaction of astatine with benzene and toluene

Reaction	i	compd.	k_{i1}/λ	k_{i2}/λ
At_2 + 	1		0.5 ± 0.2	5.2 ± 1.8
	2		0.4 ± 0.2	5.2 ± 1.8
At_2 + 	1		0.6 ± 0.2	6.0 ± 2.0
	2		0.7 ± 0.3	6.2 ± 2.1

In $^{131}I_2$ plus benzene system the sum of k_{i1}/λ and k_{i2}/λ are larger than unit. This implies that in these reactions the ordinary chemical reaction may occur with high speed too.

APPENDIX (iii)

DETERMINATION OF THE MOLECULAR WEIGHT AND SOLUBILITY PARAMETERS OF HIGH-POLYMERS BY GAS CHROMATOGRAPHY[iii-1]

Since the formulae in the reference [iii-2] are cited so frequently, they are expressed in abbreviated forms as below.

$$\ln V_R = \ln N - \mu\varepsilon + \nu + c \qquad \text{(iii-1)}$$

with

$$\mu(T_b, T) = Z\{(1 + h)rT_b/T - (1 + hr)\}, \qquad \text{(iii-2)}$$

$$\nu(T_b, T) = r(T_b/T - 1), \qquad \text{(iii-3)}$$

and

$$c(T_b, T) = \ln ZRT\vartheta. \qquad \text{(iii-4)}$$

If the retention volume of a halogen for the solvent of the sample polymer is measured at two column temperatures of T_1 and T_2, the formulae

$$\ln V_{R1} = \ln N - \mu_1 \varepsilon + \nu_1 + c_1 \qquad \text{(iii-5)}$$

and

$$\ln V_{R2} = \ln N - \mu_2 \varepsilon + \nu_2 + c_2 \qquad \text{(iii-6)}$$

are obtained. Here, the subscripts 1 and 2 correspond to T_1 and T_2, respectively. In formulae (iii-5) and (iii-6) V_R can be experimentally obtained, and μ, ν and c are easily calculated with formulae (iii-2), (iii-3) and (iii-4) for given values of T_b and T. Thus, unknown N and ε can be calculated from the two simultaneous equations.

From N the average molecular weight M_w of the solvent is calculated by $M_w = W/N$, where W is the weight of sample used. From ε the solubility parameter δ_s of the solvent is calculated.

For iodine solute (T_b = 457 K) at two column temperatures T_1 = 353 K and T_2 = 403 K, for example, simulteneous equations (iii-5) and (iii-6) become

$$\ln V_{R1} = \ln N - 15.67\varepsilon + 18.64 \qquad \text{(iii-7)}$$

and

$$\ln V_{R2} = \ln N - 12.54\varepsilon + 16.57. \tag{iii-8}$$

The quantity M_w is determined easily by $M_w = W/N$ as mentioned above, and δ_s is obtained by

$$\delta_s = 8.462\varepsilon^{1/2} + 6.599, \tag{iii-9}$$

which is derived from Eqs. (i-6) and (i-7) using $T_b = 457$ K, $\overline{\delta} = 7.333$, which is derived from Eq. (i-6) with $\overline{T}_b = 349$ K given in reference [iii-3].

For three kinds of Slicon Oil DC and PEG, which are the most popular solvents for gas chromatography, the values of M_w and δ_s are listed in Tables (iii-1)and (iii-2), respectively.

Table iii-1. Molecular weights of silicon oil and PEG

Sample	M_w			
	This method		Usual method	lit.$^{a)}$
	I_2	Br_2		
Silicon DC 550	50000	50000	50000$^{b)}$	
702	62300	62500	62500$^{b)}$	
710	89200	89300	89300$^{b)}$	
PEG 1500	1500	1500	1500$^{c)}$	1500
4000	3100	3050	3100$^{c)}$	3000-3700
6000	6750	6760	6750$^{c)}$	6000-7500

a) Stecker[iii-3].

b) Osmotic method.

c) Vapour pressure method.

Table iii-2. Solubility parameters of silicon oil and PEG

Sample		δ_s		
		This method		lit.$^{a)}$
		I_2	Br_2	
Silicon DC	550	8.1	8.1	
	702	8.0	8.0	
	710	7.9	7.9	
PEG 1500		11.7	11.7	
4000		11.6	11.6	8.9-12.7$^{b)}$ 8.5-14.7$^{c)}$ 9.5-14.5$^{d)}$
6000		11.6	11.6	

a) Brandrap and Immergut[iii-1].

b), c) and d) For poorly, moderately and strongly hydrogen bonded solvents, respectively.

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Nuclear Physics A352, 461 (1981)

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ESTIMATION OF BOILING POINT OF RADON BY RADIOGASCHROMATOGRAPHY
submitted to Nature

Naruto Takahashi and Kiyoteru Otozai
REACTION MECHANISMS OF ELEMENTARY ASTATINE WITH SOME ORGANIC SOLVENTS
to be published