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Astatine

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Astatine is the rarest element on our planet. The Earth's crust contains ~70 mg, among the short-lived members of the natural radioactive families[1]. Astatine became available to investigators only after it had been obtained as a result of nuclear synthesis, therefore it is justifiable to classify it among the synthetic elements.

Despite the fact that the chemical properties of astatine began to be studied a quarter of a century ago, much concerning the behaviour of this element is uncertain and at present we know relatively little about it. This is due primarily to the absence of stable and long-lived isotopes of astatine, which makes it inevitable that all investigations be made at the ultramicro-level with all the associated difficulties. Moreover, it must be borne in mind that astatine is capable of forming a large number of valence states, some of which exhibit high reactivity.

By exhibiting non-metallic properties in some instances and metallic in others, astatine is one of the most interesting elements of the Periodic System.

I. HISTORY OF DISCOVERY

Mendeleev first predicted the existence of the 85th element of the Periodic System. At the start of the nineteen-twenties Wagner[2], starting from the physical basis of the Periodic Law, again predicted the existence of a fifth member of the halogen subgroup. At this time intensive searches for it in natural materials began. Reports of the discovery of element 85 appeared one after another[3-7]. Definite chemical properties were ascribed to the newly discovered element and it was given sonorous names: alabamine[6], helvetium[7], anglo-helvetium[8], leptine[9], daccine[10]. A more thorough verification of the separation and methods of identification of element 85, which were used in studies noted earlier, led to the conclusion that its existence was not proved[11-14]. The mass-energy dependence for heavy nuclei[15] shows that in element 85 the proton : neutron ratio is such that considerable stability cannot be expected for the nucleus of the element, and consequently of its isotopes of long half-life also. In natural materials element 85 is encountered solely in trace amounts as a short-lived daughter product in the natural radioactive series. The search for this element in natural materials by use of chemical methods of separation developed for its nearest analogue, iodine, was unsuccessful. Above all this was due to the time consumption of the methods for separation from the natural materials and the absence of sufficiently long-lived isotopes of element 85. Karlik[16] and Hulubie[17] reviewed critically the unsuccessful searches for the missing halogen and the erroneous reports of its discovery.

The first reliable report of the discovery and identification of element 85 appeared in 1940 in a paper by Corson and coworkers[18], who obtained it in the bombardment of a bismuth target by helium ions in the 60-in cyclotron of California University, by the reaction:

$$^{209}\text{Bi}\,(\alpha,\,2n)\,^{211}\text{At}.$$

Subsequently, the discoveries of this element gave it the name astatin[19] from the Greek αστατοσ (unstable): this name well describes its nature. Until 1960 the name астатин [astatin] was widely used in the Russian chemical literature but the name of this element has now been shortened to астат [astat].

2. ISOTOPES OF ASTATINE

Twenty isotopes of astatine are now known. Their main radioactive characteristics and the nuclear reactions by which they were obtained and identified are shown in Table 1.

It must be noted here that almost all the known isotopes of astatine are also formed by reactions of deep fission of thorium and uranium by high-energy protons[21-23].

Fig. 1 shows a plot of the relation between the α-particle energies and the mass numbers (and number of neutrons) of the isotopes of astatine[24]. As Table 1 and Fig. 1 show, the most long-lived isotopes of astatine have a number of neutrons close to 126, which corresponds to the formation of a completed nuclear shell[25,26]. The form of the curve in Fig. 1 shows that the light isotopes should have very short half-lives and disintegrate with the expulsion of high-energy α-particles. Moreover, in possessing a considerable neutron deficiency they will certainly be unstable to the capture of an orbital electron. On passing to the neutron-surplus region ($A - Z = 126$) the curve has a break, which shows a sharp decrease in the strength of the bonding of the nucleons in the nucleus—all the isotopes of astatine with $A > 211$ have very short half-lives. The heaviest isotopes of astatine ($A \geqslant 219$) show some stability towards α-decay. However, in this range transitions by β-decay are also possible[27,28]. Several authors have suggested that astatine, like elements 43 and 61, cannot have β-stable nuclei at all[29].

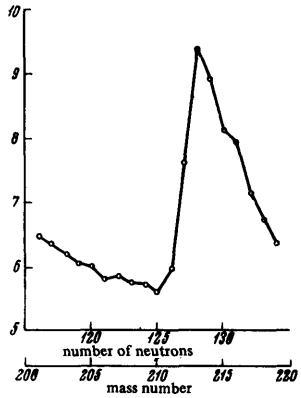


Figure 1. Energy of the α-particles of the isotopes of astatine plotted against mass number (and number of neutrons).

Table 1. Isotopes of astatine[20].

Isotope	Half-life	Type of decay	Energy of α-particles, MeV	Method of production
^{200}At	0.8 min	α	6.42 (~60%) 6.47 (~40%)	Au + ^{12}C
^{201}At	1.5 min	α	6.348	Au + ^{12}C, ^{14}N, ^{16}O
^{202}At	3 min	α (12%) e.c. (88%)	6.133 (64%) 6.231 (36%)	Au + ^{12}C, ^{14}N, ^{16}O
^{203}At	7.1–7.4 min	α (14%) e.c. (86%)	6.09	Bi (α, 10n) Pt + ^{14}N Au + ^{12}C, ^{14}N, ^{16}O
^{204}At	9–9.3 min	α (4.5%) e.c. (95.5%)	5.95	Bi(α, 9n) Au + ^{12}C, ^{14}N, ^{16}O
^{205}At	22.7–26.2 min	α (18%) e.c. (82%)	5.90	Bi (α, 8n) Au + ^{12}C, ^{14}N, ^{16}O Pt + ^{14}N
^{206}At	22–29.5 min	α (0.9%) e.c. (>99%)	5.7–5.9	Bi (α, 7n) Au + ^{12}C, ^{14}N, ^{16}O
^{207}At	1.8–2 h	α (~10%) e.c. (~90%)	5.75	Bi (α, 6n) Au + ^{14}N daughter ^{207}Rn
^{208}At	1.7 h	α (0.5%) e.c. (99.5%)	5.65	Bi (α, 5n) daughter ^{212}Fr
^{209}At	5.5 h	α (~5%) e.c. (~95%)	5.642	Bi (α, 4n) daughter ^{209}Rn
^{210}At	8.3 h	α (0.17) e.c. (>99%)	5.519 (32%) 5.437 (31%) 5.355 (37%)	Bi (α, 3n) daughter ^{210}Rn
^{211}At	7.2–7.5 h	α (40.9%) e.c. (59.1%)	5.862	Bi (α, 2n) daughter ^{211}Rn
^{212}At	0.22–0.305 s.	α	7.60 (20%) 7.66 (80%)	Bi (α, n)
^{212m}At	0.120 s.	α	7.82 (80%) 7.88 (20%)	Bi (α, n)
^{213}At	≪1 s.	α	9.2	decay product of ^{225}Pa
^{214}At	2×10^{-6} s.	α	8.78	daughter of ^{218}Fr in ^{226}Pa series
^{215}At	short	α	8.04	natural daughter of AcA
^{215}At	10^{-4} s.	α	8.00	daughter of ^{219}Fr in ^{227}Pa series
^{216}At	3×10^{-4} s.	α	7.79	daughter of ^{220}Fr in ^{228}Pa series
^{217}At	0.018 s.	α	7.05	daughter of ^{221}Fr in ^{233}U series
^{218}At	1.5–2.0 s.	α	6.6976 (94%) 6.653 (6%)	natural daughter of RaA
^{219}At	0.9 min	α (97%) β (3%)	6.27	natural daughter of AcK

The regularities mentioned show that the longest-lived isotope of astatine is ^{210}At, with a half-life of 8.3 h. ^{209}At and ^{211}At have comparable half-lives (5.5 h and 7.3 h respectively).

In some papers devoted to the study of astatine isotopes it was noted that ^{208}At has an isomer with a half-life of 6.3 h.[30] The isomers ^{204m}At (25 min) and ^{206m}At (2.9 h) have also been observed[30]. A more thorough check of the half-lives of ^{208}At, ^{206}At, and ^{204}At from the periodically separated daughter polonium did not show the presence of the long-lived isomers noted above[31]. Probably the information on the existence of the isomers is due to methodological errors.

The chemical properties of astatine are most conveniently studied on its relatively long-lived isotopes with mass numbers 209, 210, and 211. These isotopes are usually obtained by irradiating bismuth with α-particles.

The excitation function of ^{209}Bi(α, 2n)^{211}At has been studied in sufficient detail[32,33]. Its threshold is 21 MeV, and the yield of ^{211}At reaches a maximum at an α-particle energy of 26 MeV. It is important to note that for the production of pure ^{211}At free from other isotopes as impurities the energy of the helium ions should not exceed 29 MeV—the threshold of the (α, 3n) reaction. These conditions must be observed when the activity of the astatine is measured by recording α-particles, since ^{210}At decays

by 99% into the 138-day ^{210}Po, which also emits α-particles. True, the decay of ^{211}At by 59.1% is effected by capture of an orbital electron with the formation of ^{211}Po but the latter has the half-life of only 0.52 s, and almost any act of decay of ^{211}At leads to the loss of an α-particle. The α-particle spectrum of ^{211}At has a very characteristic appearance: a line at 5.862 MeV for the α-particles of ^{211}At itself and a line at 7.43 MeV for the α-particles of ^{211}Po. A guarantee of the purity of a specimen of ^{211}At is the ratio of the intensities of the 5.862 and 7.430 energies, which should be 40/60.

The isotope ^{210}At was first obtained[32] by the reaction ^{209}Bi(α, $3n$)^{210}At. As already noted above, the threshold of this reaction is 29 MeV and the maximum yield occurs at 40 MeV. The isotope ^{210}At disintegrates by only 0.17% with expulsion of α-particles with energies of 5.519 (32%), 5.437 (33%), and 5.355 (37%) MeV. The decay proceeds mainly through the capture of an orbital electron and the scheme of the conversions is rather complex[34].

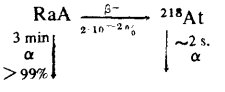
The reaction ^{209}Bi(α, $4n$)^{209}At is most often used for the production of large quantities of the isotope ^{209}At. True, specimens obtained by this method are necessarily contaminated by other isotopes of astatine. A small quantity of completely pure ^{209}At can be isolated as a daughter product from ^{213}Ra, obtained in the irradiation of thorium with protons of energy 350 MeV [21,30].

The isotope ^{209}At decays by capture of an orbital electron and expulsion of α-particles with energy 5.642 ± 0.005 MeV. The α-decay branch totals 5%.[30] Gamma radiation of ^{209}At, which is accompanied by electron capture, consists of four lines.

The principal nuclear properties and the schemes for the γ-transitions for some isotopes of astatine have been reviewed in detail[20].

3. ASTATINE IN NATURE

Starting from the processes of radioactive decay in the uranium series, Hahn[35] predicted the possibility of the formation of isotopes of astatine in the β-decay of polonium[35]. Karlik and Bernert[36], and then Walen[37], observed, in studying the radioactivity of the daughter products of radon, that an insignificant part of RaA (^{218}Po) disintegrates by the scheme:



The presence in a freshly formed specimen of RaA, in addition to α-particles with energy of 5.99 MeV due to the decay of this isotope of polonium, of α-particles with energy 6.63 MeV, served as proof of the formation of ^{218}At in the β-decay of RaA.

The discovery of β-branching in the decay of RaA served as an impetus for studying the polonium fractions of other natural radioactive series with the aim of discovering new natural isotopes of astatine. Karlik and Bernert[38] reported the β-decay of AcA (^{215}Po). They found that AcA undergoes 5×10^{-4}% β-decay, to form ^{215}At, which decays with a period of 10^{-4} s, expelling α-particles with energy 8.4 MeV. Avignon[39] made a more careful investigation and defined the energy of the ^{215}At α-particles (8.00 MeV) and the β^-/α ratio (0.9×10^{-7}) more accurately. This isotope was also observed[40] as the product of the successive α-disintegrations of ^{227}Pa.

On the basis of the regularities in the α- and β-decays in the natural radioactive series it was suggested that as a result of rare instances of α-decay ^{227}Ac forms a little chain parallel to the main series[9]. Hyde and Giorso[41] isolated from the ^{227}Ac source 20 mC francium, in which, ^{219}At was then identified by chemical means. It was shown that ^{219}At has a half-life of 0.9 min, and disintegrates 97% with the expulsion of α-particles with energy 6.27 MeV and 3% undergoes β-decay. This work[41] is the only instance of the chemical identification of an isotope of astatine from a natural source. It has been reliably established that in natural radioactive sources only three short-lived isotopes of astatine, ^{215}At, ^{218}At, and ^{219}At can be detected; these are members of radioactive families. This explains why interest in the search for and investigation of natural astatine has decreased somewhat recently.

4. METHODS OF OBTAINING AND ISOLATING ASTATINE

In the production of astatine in cyclotrons by the (α, xn) reaction a layer of bismuth (50–100 mg cm^{-2}) is applied to an aluminium substrate either as the molten metal or by sputtering. When bismuth oxide is to be irradiated a copper support is employed in the openings of which the Bi_2O_3 is pressed. To avoid loss of astatine at the time of irradiation due to sublimation the back of the support is cooled with water†.

The astatine which is formed as a result of the irradiation of bismuth by α-particles is the main product of the reaction ($\sigma \simeq 10^{-24}$ cm^2) and the contribution of the radioactive isotopes of the other elements is insignificant ($\sigma \simeq 10^{-26}$ cm^2).[42,43] To separate the astatine formed from the main mass of metallic bismuth and from polonium use is frequently made of the high volatility of astatine. The distillation is done in a current of nitrogen (at a few mmHg) or in a vacuum with the target heated to 300–600°C. The astatine vapour is condensed on the surface of a glass trap cooled with liquid air or dry ice. Radiochemically pure astatine is obtained by redistillation[18,44]. The yield of ^{210}At is 5–15%. This is due to the incomplete separation of astatine from bismuth in the gas phase at 600°C. At a higher temperature bismuth starts to distil.

It has been suggested[30] that the retention of astatine in the bismuth target is due to the formation of involatile compounds of it with bismuth inside the target irradiated with α-particles. This is confirmed by the fact that distillation at 700–800°C in air leads to the removal of up to 80% of the astatine from the bismuth target[30]. Evidently on heating in air the compound of bismuth with astatine decomposes with the formation of bismuth oxide and free astatine. From these results Appelman[45] developed the following scheme for the separation of astatine from the bismuth target.

The irradiated bismuth target is put in a stainless steel beaker and heated to 270°C to remove volatile impurities. The subsequent distillation of the astatine is carried out at 800°C. The distillate is collected on a water-cooled platinum plate suspended above the molten target. For the final purification of the astatine the platinum is put in a quartz tube and the impurities are removed at 130°C and a pressure of 10^{-4} mmHg, after which the astatine is redistilled at 500°C. The pure astatine is condensed in a

† When the astatine is produced by deep fission or irradiation of thorium by high-energy protons, such precautions are not needed since usually the intensity of the beam of protons is not so great as to cause strong overheating of the target. [It appears that the terms "deep fission" and "division" used in this review refer to *fission* and *spallation* respectively of Western literature (see especially Ref.50) (Ed. of Translation)].

U-tube cooled with dry ice. The astatine is washed from the walls of the tube with 0.5 ml dilute nitric acid. In this instance the yield reaches 30% and the concentration of astatine in the solution is $\sim 10^{-8}$ M.

The distillation method is also used for the separation of astatine from other targets, for example, gold[46]. Here the irradiated target is dissolved in molten lead or bismuth, after which the astatine is distilled off.

In addition to distillation, astatine is also separated from the target by the so-called "wet method". In this the irradiated bismuth or bismuth oxide can be dissolved in perchloric acid containing a little iodine as a carrier for the astatine, and the bulk of the target is thrown out of solution by precipitating bismuth phosphate. The astatine passes into the filtrate at AtI[47]. However, the preparation contains some polonium.

Neuman[48] made use of its extractibility by isopropyl ether for the separation of astatine from bismuth. The bismuth target is dissolved in nitric acid, the solution evaporated, but not to dryness, since a little nitric acid does not interfere with subsequent operations, and concentrated hydrochloric acid is added to bring the solution of 8 M in HCl. Then the solution is cooled and the astatine extracted with isopropyl ether, saturated with 8 M HCl. The organic phase is washed with 8 M HCl and then the astatine is back-extracted by NaOH solution containing a little iron(III). Iron hydroxide retains the remaining impurities completely and the loss of astatine here does not exceed 5%. The yield is $\sim$ 90%.

An interesting method of extraction separation of astatine from polonium and bismuth has been described[30]. The extractant used to separate astatine from concentrated hydrochloric acid solutions is di-isopropyl ether containing a little of a 20% solution of tributyl phosphate in isobutyl ether, and the extraction was effected in the presence of iron(II) as a reductant. Traces of polonium, bismuth, and lead are washed out of the organic phase by a mixture of 2 M nitric and 4 M hydrochloric acid. The back-extraction is carried out with alkali.

In the production of astatine by the deep fission of thorium the formation cross-section of the isotopes of astatine is two or three orders of magnitude less than the total formation cross section of the products of division and deep fission[49,50]. In the present instance to obtain radiochemically pure astatine effective purification from most of the elements of the Periodic System is necessary.

A method for separating astatine from lead, bismuth, and thorium irradiated with high-energy protons has been described[23]. According to this method, 1 g metallic thorium irradiated with protons of 660 MeV energy, is dissolved in 5 ml concentrated nitric acid by heating in a flask with a reflux condenser. 40 ml 8 M hydrochloric acid saturated with chlorine are added to the nitric acid solution. The extraction is performed with 60 ml di-isopropyl ether in an extractor with a mechanical stirrer. The organic layer is washed twice with 15 ml 8 M hydrochloric acid. The astatine is back-extracted from the ether with 40 ml 0.1 M solution of sodium stannite in 2 M NaOH. 10–15 mg sodium tellurite, 4–5 mg lanthanum chloride, and 1–2 mg sodium chloroaurate were added to the alkaline solution. The solution is separated from the residue by filtration through a glass filter. The precipitation of tellurium with sodium stannite is repeated twice. In this way polonium, gold, mercury, and several other metals which are co-precipitated with metallic tellurium from the alkaline solution in the presence of a reductant or of difficultly soluble hydroxides which are formed are separated from the solution. The alkaline filtrate is acidified with 20 ml concentrated hydrochloric acid containing $\sim$ 4 mg tellurium. The precipitation of tellurium, and astatine with it, from acid solution is carried out with vigorous mixing. After coagulation of the precipitate 5 mg tellurium are twice added to complete the precipitation of the astatine. The precipitate of tellurium containing the astatine is separated from the solution by centrifuging, washed with 6 M hydrochloric acid, and dissolved in a few drops of concentrated nitric acid. 20 ml 6 M hydrochloric acid is added to the solution obtained and the tellurium precipitated with tin(II) chloride. After coagulation of the precipitate the precipitation of tellurium (5 mg) is repeated once more. The precipitate is centrifuged off, washed with concentrated acid and dissolved in 5 ml 8 M HCl whilst passing gaseous chlorine. The astatine is separated from the tellurium by extraction into di-isopropyl ether. The ethereal layer (6 ml) is washed twice with 1.5–2 ml 8 M hydrochloric acid and the astatine is re-extracted with water (twice with 5 ml). After extraction a solution of radiochemically pure astatine is obtained $\sim$ 0.01 M in HCl and containing traces of solvent is obtained.

To separate astatine from tellurium and to obtain a concentrated preparation the chromatographic method can be used[51]. A solution of 8 M HCl saturated with chlorine which contains tellurium and astatine is passed through a layer of Dowex 50 × 8 cation-exchange resin. The tellurium is not retained on the resin; the astatine is adsorbed and is subsequently eluted with chlorine water. The yield of astatine in this method is 60 ± 10%, the degree of purity $\sim 10^{7}$.

Lefort and coworkers[22,52] give the following scheme for the separation of astatine which is formed as a result of the fission of ^{232}Th under the action of protons with energy 160 MeV. The thorium target is dissolved in concentrated hydrochloric acid with the addition of small amounts of hydrofluoric acid. The solution is diluted to 3 M HCl and the astatine coprecipitated by tin(II) chloride with elemental tellurium. To remove the polonium coprecipitated during this the tellurium is dissolved by heating in the minimal quantity of concentrated nitric acid and again precipitated with a milder reductant—sulphur dioxide from dilute hydrochloric acid solution. The precipitate, which contains the astatine, is dissolved in a little concentrated nitric acid, made alkaline until 2 M in NaOH; the astatine is separated from the tellurium and traces of polonium and other radioactive contaminants during their coprecipitation with elemental tellurium after addition of sodium stannite. The filtrate is acidified with nitric acid to 0.3–0.5 M. To prevent the capture of astatine by colloidal tin at the moment of change of the acidity of the medium, small portions of hydrofluoric acid are added. Astatine is isolated from the acid solution by spontaneous deposition on silver foil. This gives an α-radioactively pure preparation of astatine. To bring the astatine into solution, the silver foil is dissolved in concentrated nitric acid and the silver precipitated as chloride. To avoid retention of astatine by the silver chloride precipitate, the latter operation is done in a darkened place.

5. PHYSICAL PROPERTIES OF ASTATINE

Owing to its short half-life, astatine cannot be obtained in ponderable amounts; because of this the physical properties of this element and of its compounds have been incompletely studied. The information was mainly obtained by interpolation and extrapolation of data for its nearest analogues or on the basis of theoretical calculations.

The predicted melting and boiling points are 411° and 299°C respectively [53] [sic (Ed. of Translation)]. The radius of the At^{7+} ion calculated on the basis of theoretical data is 0.62 Å. [54] The crystalline ionic radius of At^- evaluated by several investigators [55-57], is close to 2.3 Å. The radius of At^- in gaseous molecules is calculated to be [57] 1.97 Å. Calculations of the ionisation potentials give the following values: first 9.6, [58-60], second 18.2, [58-59], third 30, fourth 41, fifth 51, sixth 78, and seventh 91 eV. [59]

The relative electronegativity of the astatine atom is estimated [61] to be 2,2 and the atomic refraction, calculated on the basis of this quantity, is 19.3 cm^3. [62]

Starting from the well-known data on the vibration frequencies of the diatomic molecules F_2, Cl_2, Br_2, and I_2, this quantity was also found by extrapolation for At_2 ($\omega_e \simeq 160$ cm^{-1}). [60] The graphical dependence of ω_e plotted on the coordinates $\lg \omega_e$ against $\lg n^2 I$ (where n is the principal quantum number, and I the ionisation potential of a molecule of type XX) gives for At_2 a value $I(At_2) = 8.3$ eV. The dissociation energy of an astatine molecule $D(At_2)$, found by a similar method, is 1.2 eV. In the same study [60] the dissociation energy of an ionised astatine molecule $D(At_2^+)$ was found to be 2.4 eV by use of a thermodynamic cycle. By calculations, some thermodynamic characteristics were obtained for atomic astatine [57,63], for At_2 molecules [64], and for several compounds of astatine with alkali and alkaline earth elements [57-63].

It should be noted that although many chemical and thermodynamic parameters have been calculated for a diatomic astatine molecule, the At_2 molecule was not detected in extremely thorough experiments made by a mass spectrometric method [65].

The most modern equipment now allows several physical constants of astatine to be determined experimentally using indicator amounts of the element. For example, the absorption spectrum of astatine was investigated with the aid of a highly sensitive spectrograph with a capillary absorption cell and use of gaseous specimens of astatine weighing 0.2 mg. [66]

Two lines were observed with wavelengths 2244.01 and 2162.25 Å, and were assigned respectively to the transitions

$$6p^5\ ^2P^0_{3/2} - 6p^4\ 7s^4\ P_{5/2} \text{ and } 6p^5\ ^2P^0_{3/2} - 6p^4\ 7s^4 P_{3/2}. \qquad (E)$$

6. CHEMICAL PROPERTIES OF ASTATINE

As noted above, astatine does not have long-lived isotopes, in consequence of which only ultra-small amounts of the element are available for studying its properties. The investigation was mainly carried out with concentrations of 10^{-11}–10^{-15} M. The most concentrated solution of astatine (10^{-8} M) was obtained by Appelman [45]. It is known that 650 atoms of astatine lead to one α-decay per minute. For this reason a 1 M solution would exhibit an activity of 1.54×10^{16} α-particles min^{-1} cm^{-3}. At such a high specific activity an effervescence of the solutions being tested would be unavoidable and there would be intensive radiolysis of the water with the formation of considerable quantities of hydrogen peroxide. Under these conditions it would be impossible to stabilise the astatine in a desired oxidation state. Astatine, like any other element, present in ultra-small concentrations, must react with traces of impurities in the solutions, be sorbed on dust particles to form radio-colloids, etc.

Usually in studying the behaviour of an element present in indicator amounts the carrier method is used. But astatine does not have either stable isotopic carriers or a sufficiently satisfactory non-isotopic carrier. Being the heaviest element of the halogen subgroup it should exhibit the properties of the latter. However, astatine shows electronegative properties more rarely than iodine, and in some instances it is reminiscent of a metal. The position is greatly complicated by the fact that the chemistry of trace amounts of iodine differs greatly from the chemistry of its macro-quantities [67-69]. At low concentrations iodine not only forms new species (for example, in the oxidation of iodide by Cr^{VI} or Ce^{IV} at iodide concentrations of $\sim 10^{-7}$ M in 1 M sulphuric acid three unidentified iodine species unknown in the macrochemistry of iodine were found), but its interaction with traces of dust and micro-impurities was noted [70].

Four states of oxidation of astatine are now known: At^- the astatide ion, At^0 the zero state, At^X some unidentified valence state, and At^{5+} in the form AtO_3^-. Appelman [71] gives the following scheme for the redox potentials of astatine at pH = 1:

$$At^- \xrightarrow{-0.3\,V} At^0 \xrightarrow{-1.0\,V} At^X \xrightarrow{-1.5\,V} AtO_3^- \xrightarrow{-1.6\,V} H_5AtO_6\ (?)$$

1. Astatine in the Zerovalent State, At^0

Like elemental iodine, astatine in the zerovalent state of oxidation exhibits very high volatility. On this property, in particular, is based the method of isolating astatine from a fused bismuth target.

In the gaseous state astatine is readily sorbed by surfaces of various materials. Table 2 shows data on the simultaneous adsorption of astatine on the surfaces of various metals in a high vacuum [44]. In each instance the surface of the metals was previously purified by heating at ~ 400°C in an atmosphere of hydrogen.

Table 2.

Metal	Quantity of adsorbed astatine, relative %		
	20°	325°	
		expt. 1	expt. 2
Aluminium	0.3	0.2	0.3
Nickel	0.2	0.6	0.7
Copper	0.5	0.6	4.3
Platinum	36.3	33.5	6.5
Gold	38.4	0.1	0.7
Silver	24.3	65.0	87.5
	100.0%	100.0%	100.0%

The vaporisation and adsorption of astatine depends on the nature of the substrate. The low volatility from the surface of gold and platinum is evidently explained by the formation of a new valence form of astatine or its reaction with the material of the substrate [44].

Astatine in the zerovalent state in solutions cannot be identified with any definite chemical species. This can be the products of the reaction of astatine with traces of organic impurities, interhalogen compounds of astatine, and elemental astatine [45]. The latter is undoubtedly present in dilute nitric acid solutions. This happens although

a considerable amount of astatine is lost during the evaporation of the solution. In the drying of a nitric acid solution on platinum substrates ~26% of the astatine volatilises[44]. However, the loss of astatine due to its volatility is not so great as the loss of iodine during the evaporation of the solutions which contain micro-amounts of elemental iodine. The retention of astatine on various surfaces during the evaporation of aqueous solutions varies with the nature of the surface, the composition of the solution, and the conditions of evaporation[15].

Sorption on glass from dilute nitric acid solutions is inherent to astatine in the zerovalent state[45]. An increase in the nitric acid concentration leads to a decrease in sorption, probably as a result of a change in the valence state of the astatine[45].

At^0, like elemental iodine, is extracted very well from nitric acid solutions by almost all organic solvents. This property of astatine is widely used in studying its chemistry. Observation of the change in extraction coefficients of astatine from HNO_3 solutions with change in the concentration of the latter on adding other acids, complex-formers, or various oxidants and reductants makes it possible to find the form of the compound extracted, the degree of complex formation, and the oxidation potential.

At^0 is completely extracted from the organic phase on shaking with 0.1 M NaOH. Probably in this instance the At^0 disproportionates to astatide and a higher oxidation state[44]. Acidification of the solution converts astatine into its initial state and it is again extracted by organic solvents with the initial partition coefficient.

At^0 is partly coprecipitated from aqueous solutions with some hydroxides and also with AgI and TlI, probably as a result of its sorption by the developed surface of these precipitates. Increasing the acidity of the solution completely suppresses the adsorption. Washing the AgI and TlI precipitates with acetone completely removes the astatine from their surface.

Astatine(0) can be isolated from solution by precipitation with elemental tellurium, metallic silver, and on various heavy metal sulphides[18,72]. It is also coprecipitated with PdI_2.[47]

Study of the electrochemical behaviour of astatine showed that the critical potential for the deposition of At^0 from nitric acid solutions on a cathode is −1.22 V and at the anode −1.45 V[44] [Both potentials referred to a normal hydrogen electrode (Ed. of Translation)]. Thin gold foils were used as electrodes in these experiments.

The nature of the astatine compounds liberated in electrolysis is unknown.

The extraction of astatine by polar solvents from solutions of mineral acids in the presence of oxidants or reductants is widely employed in studying the chemistry of astatine[44,45,48,73] but the distribution coefficients for At^0 between aqueous and organic phases depend quite strongly on the purity of the reagents used. Impurities, even those found in micro-concentrations, can bring a considerable part of the astatine into a form with another distribution coefficient. Thus, the repeated extraction of astatine from the same solution with an organic solvent leads to a fall in the partition coefficient with each extraction and finally the astatine stops being extracted. Similarly for repeated re-extraction from an organic phase by an aqueous solution the amount of astatine re-extracted falls[44,45]. Consequently in using extraction as a method of studying the chemistry of astatine, conclusions can be drawn about the change in the state of the latter only when there are very large differences in the partition coefficients of the astatine forms being studied[15].

An important contribution to the study of the chemistry of astatine by the extraction method was made by Johnson and coworkers[44], Neumann[48], and Appelman[45,73]. During the action of reductants of the type of SO_2, H_3AsO_3, or metallic zinc on acid solutions which contain At^0 a sharp decrease in the partition coefficients was observed, evidently the astatine(0) is reduced to At^-, which is confirmed by its coprecipitation with silver or thallium iodides. With Br_2 astatine is oxidised to an unidentified valence state[45].

The addition of strong oxidants of the $S_2O_8^{2-}$ type converts astatine into AtO_3^-, which is coprecipitated with $AgIO_3$.[44]

2. Astatide Ion

The astatide ion is the most studied state of astatine because this form is the most similar in properties to the iodide ion. At^- is formed in solutions which contain astatine(0) in the presence of strong reductants such as SO_2, H_3AsO_3, hydrogen at the moment of liberation in acid solution, or Na_2SO_3 in alkali. This is shown by the results of experiments on electromigration and on coprecipitation with iodides at any acidities and in the presence of various anions[18,44]. At^- is not removed from precipitates of insoluble iodides on washing them with acetone (as happened in the coprecipitation of At^0). These results show that At^- is isomorphously coprecipitated with iodides.

The ratio of the diffusion coefficients of I^- and At^- in 1% NaCl solution which contains 1.2×10^{-3} M KI and 4×10^{-3} M Na_2SO_3 is $D_{I^-}/D_{At^-} = 1.41 \pm 0.02$.[74]

It is thought that the astatide ion absorbs ultraviolet radiation of wavelength ~3000 Å.[75]

The work with At^- in acid solution must be carried out with great precaution since there are indications of the formation of volatile astatides[18,44].

3. The Unidentified Valence State At^X

Oxidants such as the vanadate ion, bromine, chlorine, dichromate, concentrated nitric acid, and Fe^{3+} ions oxidise At^0 to some valence form the state of oxidation of which lies between At^0 and AtO_3^-.[15,44,45] This form is not extracted by carbon tetrachloride and is not coprecipitated with iodides.

Some investigators ascribe to this state of astatine the charge 3+,[76] others the form AtO^- [77,78] (by analogy with iodine) or AtO_2^-.[78] Although the existence of the latter for iodine is also not established, this form could be more stable for astatine[76].

The main regularities in the change in the properties of the elements in the Periodic System show that astatine ought to be more "metallic" than the other halogens. This signifies, in particular that astatine should acquire a positive charge more readily than iodine. In several studies it was found that in its properties astatine shows more resemblances to polonium and bismuth—its nearest neighbours in the Table—than to iodine[18,79].

Experimental results have been obtained[44] which show the reversibility of the electrochemical deposition of astatine on a gold cathode from sulphate solutions oxidised with dichromate, which can be held as proof of the existence of astatine in the form of a cation.

The investigation of the behaviour of astatine oxidised by dichromate in solutions of nitric acid showed that it is present as a singly-charged cation[80]. This was shown by experiments on migration, from the results of which it is clear that the astatine ion in this medium moves predominantly towards the cathode[80]. It appeared that astatine in

this form is sorbed on monofunctional sulphonic-cation-exchange resins. This allowed the charge on the ion of astatine oxidised by dichromate in nitric acid solutions to be determined, and it was found to be unity[80].

In a series of chemical properties the astatine cation is similar to the heavy singly-charged cations, for example, thallium and caesium, and is absorbed well by precipitates of caesium tungstophosphate, thallium dichromate, and silver iodate (Table 3)[81,82].

The astatine cation is spontaneously deposited on metallic platinum coated with an oxide film (Fig. 2).[83] The rate of deposition (at a time of deposition $\tau \leqslant 40$ min) is satisfactorily described by the equation for a first-order reaction:

$$\frac{dx}{d\tau} = K(a-x)\frac{S}{V}$$

where a is the initial amount of the element in the solution, S the surface of the platinum, V the volume of solution, and K a constant.

Table 3. Retention of the singly charged astatine cation by various precipitates from nitric acid solutions containing the dichromate ion. (0.005 M $H_2Cr_2O_7$) (solution volume 5 ml).

Precipitate and its weight	Process of retention of astatine	Composition of solution over precipitate (other than dichromate ion)	Astatine in ppt., %
$Tl_2Cr_2O_7$ 20 mg	retention at moment of formation of ppt	2 M HNO_3	94 ± 5
ditto	ditto	2 M HNO_3 + 10 mg/ml La^{3+}	94
»	sorption on existing ppt	2 M HNO_3	84 ± 1
»	ditto	2 M HNO_3 + 10 mg/ml La^{3+}	80 ± 5
$Ag_2Cr_2O_7$ 40 mg	retention at moment of formation of ppt	2 M HNO_3	74 ± 6
ditto	sorption on existing ppt	ditto	4.5 ± 1.5
$AgIO_3$ 15 mg	retention at moment of sorption formation of ppt	0.5 M HNO_3 + 0.01 M KIO_3	96 ± 1
ditto	ditto	0.5 M HNO_3 + 0.01 M $AgNO_3$	91 ± 2
$Ba(IO_3)_2$ 40 mg	»	0.5 M HNO_3 + 0.02 M KIO_3	95
ditto	»	0.5 M HNO_3 + 0.02 M $Ba(NO_3)_2$	59 ± 4
$Th(IO_3)_4$ 40 mg	»	0.5 M HNO_3 + 0.01 M KIO_3	47 ± 5
ditto	»	0.5 M HNO_3 + 0.01 M $Th(NO_3)_4$	9.5 ± 1.5
Cs_2HPW^* 100 mg	sorption on existing ppt	3 M HNO_3	6 ± 0.5
Cs_3PW^* 100 mg	ditto	3 M HNO_3	78 ± 4
ditto	»	3 M HNO_3 + 0.3 M $CsNO_3$	87 ± 0.2
Rb_3PW^* 100 mg	»	3 M HNO_3 + 0.3 M $RbNO_3$	74 ± 1
$(NH_4)_3PW^*$ 100 mg	»	3 M HNO_3 + 0.3 M NH_4NO_3	24 ± 4

* $(PW)^{3-} = [P(W_{12}O_{40})]^{3-}$.

The adsorption is affected positively by raising the temperature and negatively by increasing the acidity. The astatine deposited on the platinum is held strongly on the metal surface. However, it can be easily desorbed by anodic polarisation of the platinum.

The spontaneous liberation of astatine at platinum covered with an oxide film with subsequent anodic dissolution allows solutions of astatine to be obtained in almost all strong acids, and, moreover, opens the possibility of using this phenomenon in the production of radiochemically pure astatine[83].

4. States 5+ and 7+

The existence of an astatate ion (AtO_3^-) was inferred on the basis of the results of experiments on the coprecipitation of astatine with silver, lead, and barium iodates from nitric and hydrochloric acid solutions containing strong oxidants: $S_2O_8^{2-}$, Ce^{IV}, IO_4^-, $NaBiO_3$.[44,73] The astatate ion is not extracted by carbon tetrachloride or benzene. The negative charge of this form of astatine produced in oxidation by $Na_2S_2O_8$ in nitric acid was shown by electromigration experiments[44]. It was found[44] that astatine oxidised by a hot $Na_2S_2O_8$ solution is coprecipitated very well with

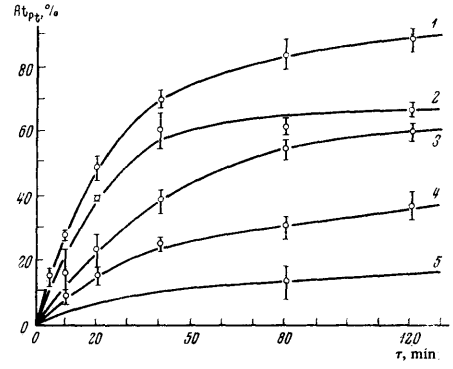


Figure 2. Liberation of astatine at platinum from nitric acid solutions as a function of time. Temperature 23°C; $[H_2Cr_2O_7] = 5 \times 10^{-3}$ M; $S_{Pt} = 4$ cm^2; $V_{soln} = 10$ ml; HNO_3 concentration, M: *1*) 1; *2*) 3; *3*) 5; *4*) 7; *5*) 10.

lanthanum hydroxide. It is assumed that in this instance a compound of the type $La(AtO_3)_3$ insoluble in alkaline medium, is formed.

However, Appelman[72] did not observe the coprecipitation of astatine oxidised by Ce^{IV} in 6 M $HClO_4$ with cerium(IV) hydroxide. It is reported[84] that astatine oxidised by Ce^{IV} is readily extracted by di-isopropyl ether from 4–5 M solutions of nitric, sulphuric, and perchloric acids. Under these conditions micro-amounts of iodine are not extracted. It is known that Ce^{IV} in solutions of strong mineral acids oxidises iodine in indicator amounts to IO_3^-.[67]

Experimental results proving the existence of At^{7+} as perastatate do not exist at present.

Thus Appelman[71], using vigorous oxidants such as H_5IO_6 or Ce^{IV} in 6 M $HClO_4$ did not obtain astatine in a form coprecipitable with potassium periodate. And under these conditions astatine is retained solely by iodates. However, bearing in mind the various forms of periodates[85], a definite conclusion about the absence of a 7+ state cannot be drawn without further studies.

All the above valence states of astatine are formed, as already noted above, at such low concentrations that to stabilise these forms it is necessary to hold the oxidation potential of the solution within strictly defined limits. Therefore to study the chemical properties of any state of astatine the solution must contain an oxidant (a reductant, for the astatide ion), not only for converting the astatine into the required form but also for protecting this form at the time of the experiment from micro-impurities which are unavoidably present in the reagents used.

5. Interhalogen Compounds of Astatine

In studying the chemistry of astatine in solutions which do not contain stabilising agents irreproducible results are

usually obtained. When the stabilising buffer is the halogen pair I^-/I_2, the predominant state will be interhalogen compounds of the types AtI and AtI_2^-. In the presence of elemental iodine the zero valency of the element is represented exclusively by AtI molecules. For the last instance Appelman[73] determined with great accuracy the value of the partition coefficient between carbon tetrachloride and water, 5.5 (Table 5).

Detailed studies have been made[23,48] of the extraction of astatine by di-isopropyl ether from chlorine-treated hydrochloric acid solutions of various concentrations (Fig. 3). On the basis of the results of extraction experiments Neumann[48] drew conclusions about the existence of chloroastatates of composition $AtCl_2^-$ or $AtCl_4^-$. In his review[77], Bagnall states that the composition of the complex probably corresponds to the formula $AtCl_2^-$, that is, the astatine is in oxidation state +1.

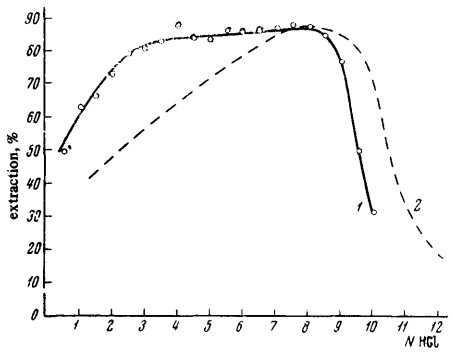


Figure 3. Extraction of astatine from hydrochloric acid solutions by di-isopropyl ether:
1) after the results of Belyaev and coworkers[23]; *2*) after the results of Vinogradov and coworkers[48].

This assumption found confirmation in a study of the adsorption of the astatine cation on platinum covered with an oxide film[83] from nitric acid solutions as a function of the chloride ion concentration. It was found that chloride ion has a negative effect on the adsorption of astatine on platinum (Table 4).

The distribution of astatine between the solution and the platinum depends on the chloride ion concentration:

$$(K_d D - 1) = \frac{1}{K_n}[Cl^-]^n$$

where $K_d = At_{Pt}/At_{soln}$ is the ratio of the amount of astatine on platinum (At_{Pt}) to the amount of (At_{soln}) in solutions which do not contain chloride ion, $D = At_{soln}/At_{Pt}$ the ratio of the amount of astatine in the solution to the amount of it on the platinum in the presence of chloride ion, and K_n the instability constant of the most stable chloro-complex of astatine with n ligands.

In the graph of $\lg(K_d D - 1)$ against $\lg[Cl^-]$ the points calculated from the results in Table 4 lie along a straight line with a slope of 2. Paper electromigration shows that under these conditions astatine is present in an anionic form[81,83]. These results suggest the singly-charged astatine cation adds two Cl^- ions to form an anionic complex of type $[(AtX)Cl_2]^-$. The stability constant of this complex is $(7.4 \pm 0.8) \times 10^5$ M^{-2}‡.

The anionic chloro-complex exhibits one property which is very interesting from the preparative point of view: it is adsorbed on sulphonic cation-exchange resins of the type of KU-2§ and Dowex 50 from solutions of hydrochloric acid and alkali metal chlorides first saturated with chlorine (Fig. 4).[51]

The interhalogen compounds of astatine in various systems in the presence of iodine with the use of liquid extraction by carbon tetrachloride was studied in detail by Appelman[45,73]. Table 5 gives the partition coefficients of the halogens and interhalogen compounds between carbon tetrachloride and the aqueous phase.

On the basis of the distribution results Appelman[45] calculated the formation constants of various astatine complexes (Table 6).

Table 4. Deposition of astatine on platinum in the presence of hydrochloric acid from 1 M HNO_3–5 x 10^{-3} M H_2CrO_4. $S_{Pt} = 4$ cm^2; $V = 10$ ml; $\tau = 40$ min.

[HCl], M	%At on Pt	[HCl], M	%At on Pt
0	53.7±31	$8 \cdot 10^{-3}$	2.1±0.12
$2 \cdot 10^{-3}$	23.5±2.8	$1.3 \cdot 10^{-2}$	0.91±0.13
$3 \cdot 10^{-3}$	12.5±2	$2 \cdot 10^{-2}$	0.52±0.2
$5 \cdot 10^{-3}$	4.9±0.3		

It is interesting to note that astatine always forms a more stable complex than iodine under analogous conditions. The formation constants of identical interhalogen complexes of astatine and iodine differ by a factor of 5–8.[45]

It is well known that molecules which consist of two identical halogen atoms are extracted by carbon tetrachloride considerably better ($D_{I_2} = 86$) than molecules which contain two different atoms ($D_{AtI} = 5.5$, $D_{IBr} = 4.3$, $D_{ICl} = 0.34$). This is because the molecules of the first type are completely non-polar, whereas the interhalogen compounds are dipoles.

The coprecipitation of AtI with elemental iodine in chloroform solutions has been studied[86]. It was shown that the introduction of AtI into iodine crystals obeys Dorner and Hoskins' logarithmic law of distribution. The partition coefficient is

$$\lambda = \frac{\lg(AtI_{soln})/(AtI_{soln} + AtI_{solid})}{\lg(I_{2soln})/(I_{2soln} + I_{2solid})} = 4.$$

Interhalogen compounds are formed in the solid state[87]. Thus CsI_3 which contains $CsAtI_2$ is easily obtained on adding an excess of solid iodine to an aqueous solution of CsI(At). When the system is heated and then cooled, CsI_3 containing astatine is obtained.

‡ When this article was being prepared for press the stability constants of this complex were checked and defined more accurately by the cation-exchange method and β_2 was found to be 2.5×10^5 M^{-2}; moreover, the same method was used to determine the stability constant of a chloro-complex with one ligand, $\beta_1 = 7 \times 10^2$ M^{-1}.[33a]

§ KU-2 is a monofunctional, strongly acid cation-exchange resin with $-SO_3H$ active groups, prepared by treating a swollen styrene–divinylbenzene copolymer with chlorosulphonic acid, then saponifying the sulphonyl chloride (Ed. of Translation).

The thermal decomposition of $CsAtI_2$ obeys the general rule for the decomposition of polyhalogen compounds (in such instances an involatile monohalide is formed—the lighter halogen with the metal), that is, involatile CsI is formed and the astatine is volatilised in the form AtI.[88]

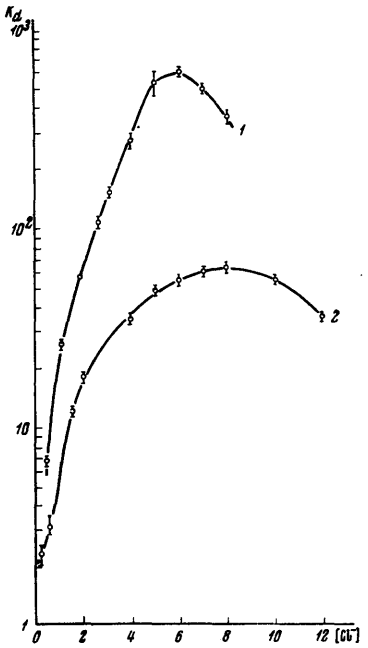


Figure 4. Distribution of astatine, oxidised by chlorine, between the sulphonic cation-exchange resin Dowex 50 x 8 and a solution, as a function of the concentration: *1*) LiCl; *2*) HCl.

Table 5.[73] Partition coefficients of the halogens and interhalogen compounds (21°C), $D = (XY)_{CCl_4}/(XY)_{aq}$.

XY	D	XY	D
AtBr	0.040	AtI	5.5
ICl	0.34 (25°)	Br_2	27
IBr	4.3	I_2	86

Table 6.[45] Formation constants of the various interhalogen complexes of astatine.

Reaction	$K_{form} \pm 10\%$ (21°)
$AtI_{aq} + I^- = AtI_2^-$	2000
$AtI_{aq} + Br^- = AtIBr^-$	120
$AtI_{aq} + Cl^- = AtICl^-$	9
$AtBr_{aq} + Br^- = AtBr_2^-$	320
$AtI_{aq} + IBr_{CCl_4} = AtBr_{aq} + I_{2CCl_4}$	3800
$AtI_{aq} + \frac{1}{2}Br_{aq} = AtBr_{aq} + \frac{1}{2}I_{2aq}$	4.2×10^4
$AtICl^- + Cl^- = AtCl_2^- + I^-$	2×10^{-4}

7. ASTATINE IN ORGANIC COMPOUNDS

A rather large number of organoelemental compounds of iodine have now been obtained and their properties studied in more or less detail. This cannot be said about astatine although the existence of stable alkyl and aryl derivatives of this element follows from its position in the Periodic System (the stability of organic derivatives in Periodic Group VII corresponding to valencies of +3 and over increases from chlorine to iodine).

The difficulty encountered in working with the inorganic forms of astatine is greatly increased in studying the organic derivatives of this element.

One of the features of the preparation of organoelemental compounds of radioactive elements is that they can be produced only with vanishingly small amounts of materials. This is due on the one hand to the impossibility of obtaining ponderable amounts of individual radioactive elements (francium, astatine, radon) even with the aid of modern equipment, and of the necessity of using special, quite complicated techniques of investigation. On the other hand, and this is most important, the undertaking of investigations with considerable amounts of certain radioactive substances is accompanied by such radio-chemical changes (both in the substances studied and in the surrounding medium), which rules out the possibility of obtaining correct information about the properties and state of the substances being studied.

One of the important consequences of the fact that in the preparation of organoelemental compounds of the radioactive elements one is dealing with submicro-amounts of substance is the impossibility of finding the qualitative and quantitative composition of the compounds being studied by direct methods of analysis. For this reason indirect methods based on a comparison of the behaviour of the substance being studied with that of known compounds of analogous elements play the determining role in such investigations. Here the most convenient method is observation of the chromatographic behaviour of the elements and their compounds.

Since astatine does not have long-lived isotopes, almost the only method of making its organic derivatives is preparation with a non-isotopic carrier—iodine.

Until recently only a few papers[48,78,89-91] had been published on the preparation of organoastatine compounds.

From data on the extraction of astatine in an intermediate state of oxidation from 0.5 M sulphuric acid with benzene and a 10^{-3} M solution of phenol in carbon tetrachloride and the back-extraction of astatine from these solvents with 0.5 M NaOH, Neumann draws conclusions about the existence of astatobenzene and astatophenol[48]. However, these compounds were not isolated and identified.

Contradictory results were obtained in an attempt to make iodo(astato)form and *p*-iodo(astato)aniline[78].

Aten's statement (based on the known chemical properties of astatine) that astatine is probably most readily introduced into an organic molecule when it is found in a positively charged state in some intermediate product obtained at the time of reaction merits attention[78].

A large number of organic compounds of astatine also of interest for biological investigations has been obtained[89-91]. Astatobenzene, astatinated serin albumen, and *p*-astatobenzoic acid were obtained through diazo-compounds. *p*-Astatobenzoic acid offers the possibility of introducing astatine into various proteins. Direct astatination in the presence of KI_3 gave astatinated egg albumin and γ-globulin and the reaction of astatine with *N*-iodosuccinimide gave astatinated tyrosine.

Methods of making astatinated compounds of the types RAt, $RAtCl_2$, R_2AtCl, and $RAtO_2$ (where R is phenyl or *p*-tolyl radical) have been described[92,93].

Both phenyl and *p*-tolyl derivatives of astatine were obtained by the same scheme:

$$R_2ICl + KI(At) \rightarrow R_2I \cdot I(At) \xrightarrow{170-180^\circ} RI(At) \xrightarrow{Cl_2} RI(At)Cl_2 \begin{cases} \xrightarrow{R_2Hg} R_2I(At)Cl \\ \xrightarrow[NaOCl]{} RI(At)O_2 \end{cases}$$

To prepare $RAtCl_2$, KI(At) solution was added to aqueous R_2ICl solution, to give a crystalline precipitate which was subjected to thermal decomposition at 170–190°C:

$$R_2I.I(At) \rightarrow 2RI(At).$$

A little chloroform was added to the reaction product and after cooling to 0°C the RI(At) was chlorinated until a yellow crystalline precipitate of $RI(At)Cl_2$ no longer separated.

$RI(At)Cl_2$ was used to make R_2AtCl. The crystals were dissolved in chloroform, the solution was heated to boiling and a hot chloroform solution of R_2Hg was slowly added to it. The mixture was heated for several minutes on the water-bath and then cooled. The precipitate was centrifuged off and R_2AtCl was extracted with water from the mixture of products remaining in the solution.

Table 7. Value of R_f for the tolyl derivatives of astatine and iodine in the chromatographic of various solvents on mixtures of silica gel KSM No.5 and gypsum. Fixed layer.

Substance	R_f				
	methanol	water-25% methanol	water-25% ethanol	butanol	acetone
p-$CH_3C_6H_4ICl_2$	0.33±0.02	0.1±0.01	0.68±0.02	0.6±0.02	0
p-$CH_3C_6H_4AtCl_2$	0.32±0.03	0.11±0.02	0.68±0.04	0.61±0.03	0
$(p$-$CH_3C_6H_4)_2ICl$	0.1±0.02	0.23±0.02	0.1±0.03	0.67±0.02	0.55±0.02
$(p$-$CH_3C_6H_4)_2AtCl$	0.1±0.05	0.25±0.03	0.1±0.04	0.68±0.03	0.54±0.03
p-$CH_3C_6H_4IO_2$	0.65±0.05	0	0.75±0.04	0	0
p-$CH_3C_6H_4AtO_2$	0.65±0.05	0	0.72±0.05	0	0

To prepare $RAtO_2$, crystals of $RI(At)Cl_2$ were put in a centrifuge tube, to which were added 2 ml 50% NaOH solution and 0.5 ml acetic acid. The mixture was heated to 70°C and chlorinated to complete conversion of the yellow crystalline precipitate of $RI(At)Cl_2$ into a white amorphous precipitate of $RI(At)O_2$. Then the temperature was raised to 100°C, the precipitate rapidly centrifuged off, and on cooling the solution to 0°C $RI(At)O_2$ crystallised out.

The compounds obtained were identified by thin layer and paper chromatography.

The results of the analysis of the organoastatine compounds agree well, within the limits of error of the experiment, with the results obtained in the analysis of analogous iodine compounds (Table 7).

In a study of the properties of astatinated derivatives a large part has undoubtedly been played by their preparation using a method based on the change of chemical state of the atoms during nuclear transformations. In this instance it is possible to obtain organic compounds of astatine without a carrier. This method, which has played a large part in studying the chemistry of organopolonium compounds[94,95], has not yet been extensively employed for astatine. Apparently this is connected with the difficulty of obtaining a corresponding organic medium containing radon—the initial substance from which "hot" atoms of astatine are formed as the result of *K*-electron capture.

8. BIOLOGICAL BEHAVIOUR OF ASTATINE

It has been found that astatine, like iodine, is selectively concentrated in the thyroid gland[96]. In this connection the study of the biological properties of astatine started immediately after its discovery[96]. For this purpose At^{211} is usually employed, for which, as noted above, any act of disintegration leads to the expulsion of an α-particle, and the daughter ^{207}Bi exhibits so great a half-life that it does not affect the results of the investigation. Preparations of astatine for biological purposes are obtained by a standard method: distillation in a vacuum from a bismuth target and condensation in a trap on a thin ice surface. After melting the ice, an aqueous solution of astatine in minimal volume is obtained. The physiological solution used in injections is prepared by the addition of the appropriate amount of sodium chloride to the aqueous solution of astatine.

In studying the biological properties of astatine very small quantities of it are usually employed ($< 10\ \mu C$). To obtain sufficiently precise information about the distribution of astatine in organisms a very precise analytical method of separating it from biological specimens is needed. This requirement is satisfied by the method of radiochemical determination in biological materials developed by Hamilton and coworkers[72]: the organic substance is destroyed by wet combustion with a mixture of perchloric and nitric acids (9 M $HClO_4$ containing 30 vol.% 16 M HNO_3). Subsequently the solution is evaporated until perchloric acid fumes appear (during which the nitric acid distils off completely), diluted with distilled water to 3 M in perchloric acid, and the astatine separated from this solution for recording by coprecipitation with metallic thallium or by sorption on a silver disk. The separation on silver requires less time (73.5% is sorbed in the first 10 min and 100% after the next 20 min) and this method is more suitable for the serial analysis of biological materials.

Investigation of the radiobiological properties of ^{211}At showed that the α-particles emitted in the disintegration of this isotope produce some decay in the tissues of the thyroid and, unlike iodine, do not harm the neighbouring parathyroid gland[97]. This shows that astatine is perhaps the only means of therapeutic treatment for enlarged thyroid gland.

The radiobiological action of α-particles of astatine on the thyroid gland is 2.8 times greater[98] than deeply penetrating β-particles of ^{131}I.

It has been found that propylthiouracil suppresses the concentration of iodine in the thyroid gland but with astatine the effect is the reverse—its concentration is observed when this preparation is introduced into rats[99].

It is interesting to note that when astatine is introduced in the form of a radiocolloid it is deposited mainly in the

liver[100]. This reflects the general tendency for most elements which are capable of forming colloidal solutions.

In comparing the metabolism of astatine and radioiodine it was found that their excretion by the stomach and kidney is almost the same. In other instances with the exception of the thyroid the metabolism of astatine is completely different from that of iodine. Even on the introduction of a lethal dose of astatine in the form of true solutions into rats and apes, morphological changes in organs and tissues other than the thyroid were not noted[101]. The observation of the accumulation of ^{211}At in the human thyroid in the breakdown of some of the functions of this organ also showed the absence of concentration of astatine in other organs[102].

On the repeated introduction of large doses of astatine into rats and apes their growth is stopped, probably as a result of a change in the functions of the thyroid secretions due to deficiencies of the thyroid hormones[103]. This could also explain the complete destruction of tumours of the mammary gland in rats on the repeated introduction of small doses of astatine[103]. In some studies it is stated that astatine is partly concentrated in the mammary gland[104].

When very large doses of astatine were introduced into rats over 26 months almost complete destruction of the thyroid gland and highly developed tumours of the mucous and mammary glands were observed[105].

The accumulation of astatine by the thyroid gland is under the control of the pituitary body, and leads to the suppression of the concentration of astatine in the thyroid[106]. It was also shown that the thiocyanate ion blocks the accumulation of astatine in the thyroid, probably by forming a sufficiently stable complex. Consequently the thiocyanate ion can be used to remove astatine from this organ[106].

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In conclusion it must be noted that the experimental difficulties associated with the study of the chemistry of astatine were evidently due to factors that are now understood: it does not have long-lived isotopes and consequently is found in amounts commensurate with accidental contamination. Reviews on the chemistry of astatine[15,76-79,107-113] appear more frequently than original studies. A recently published paper[114] gives information about the [half-life] periods and α-particle energies of the lightest isotopes of astatine.

REFERENCES

1. K.W.Bagnall, "Chemistry of the Rare Radioactive Elements. Polonium-Actinium" (Translated into Russian), Inostr. Lit., Moscow, 1960, p.158.
2. E.Wagner, Z.Electrochem., **26**, 260 (1920).
3. F.Loring and J.Druce, Chem.News, **131**, 305 (1925).
4. G.Toshniwal, Bull.Acad.Sci.U.P.Agra, **2**, 107 (1933).
5. E.Anderson and K.Dansk, Vidends.Selsk, **16**, 1 (1938).
6. F.Allison, E.Bishop, and A.Sommer, J.Amer.Chem.Soc., **54**, 616 (1932).
7. W.Minder, Helv.Phys.Acta, **13**, 144 (1940).
8. A.Leigh-Smith, and W.Minder, Nature, **150**, 767 (1942).
9. C.Martin, Nature, **151**, 309 (1943).
10. R.De Separate, Bani Press, Dacca, 18 (1937).
11. F.Loring, Chem.News, **132**, 407 (1926).
12. H.Herzfinkiel, Compt.rend., **184**, 968 (1927).
13. B.Karlik and T.Bernert, Naturwiss., **30**, 685 (1942).
14. B.Karlik and T.Bernert, Sitzungsber.Akad.Wiss.Wien, IIa 151, 255 (1942).
15. E.K.Kyde, J.Chem.Educ., **36**, 15 (1959).
16. B.Karlik, Monatsh., **77**, 348 (1947).
17. H.Hulubie J.Chem.Phys., **44**, 225 (1947).
18. D.R.Corson, K.R.MacKenzie, and E.Segrè, Phys.Rev., **57**, 458, 672, 1087 (1940).
19. D.R.Corson, K.R.MacKenzie, and E.Segrè, Nature, **159**, 24 (1947).
20. E.K.Hyde, I.Perlman, and G.T.Seaborg, "The Nuclear Properties of the Heavy Elements", Englewood Cliffs, N.Y., 1964, Vol.II, p.1081.
21. F.F.Momyer, Jnr. and E.K.Hyde, J.Inorg.Nuclear Chem., **1**, 274 (1955).
22. M.Lefort, G.Simonoff, and X.Torrago, Bull.Soc.chim. France, 1726 (1960).
23. B.N.Belyaev, Wang Yung-yü, E.N.Sinotova, L.Nemet, and V.A.Khalkin, Radiokhimiya, **2**, 603 (1960).
24. E.K.Hyde, J.Perlman, and G.T.Seaborg, Ref.20, p.1080.
25. A.Berthelot, Compt.rend., **227**, 829 (1948).
26. B.Karlik, Acta Phys.Austria, **2** 182 (1948).
27. L.Perlman, A.Ghiorso, and G.T.Seaborg, Phys.Rev., **74**, 1730 (1948).
28. I.Perlman A.Ghiorso, and G.T.Seaborg Phys.Rev., **75**, 1096 (1949).
29. B.M.Foreman, Jnr. and G.T.Seaborg, J.Inorg.Nuclear Chem., **7**, 305 (1958).
30. G.Barton, Jnr., A.Ghiorso, and I.Perlman, Phys.Rev., **82**, 13 (1951).
31. P.E.Thoseren, F.Asaro, and I.Perlman, J.Inorg.Nuclear Chem., **26**, 1341 (1964).
32. E.L.Kelly and E.Segrè, Phys.Rev., **75**, 999 (1949).
33. W.J.Ramler, J.Wing, B.J.Henderson, and J.K.Huitzenga, Phys.Rev., **114**, 154 (1959).
34. R.W.Hoff and J.M.Hollander, Phys.Rev., **109**, 447 (1958).
35. O.Hahn, Naturwiss., **14**, 758 (1926).
36. B.Karlik and T.Bernert, Naturwiss., **32**, 44 (1943).
37. R.J.Walen, J.Phys.Radium, **10**, 95 (1949).
38. B.Karlik and T.Bernert, Z.Physik, **123**, 51 (1944).
39. P.Avignon, J.Phys.Radium, **11**, 521 (1950).
40. W.Meinke, A.Ghiorso, and G.T.Seabrog, Phys.Rev., **75**, 314 (1949).
41. E.K.Hyde and A.Giorso, Phys.Rev., **90**, 267 (1953).
42. B.V.Kurchatov, V.N.Mekhedov, L.B.Chistyakova, M.Ya.Kuznetsova, N.I.Borisova, and V.G.Solov'ev, Zhur. Eksper.Teor.Fiz.,
43. M.Linder and R.N.Osborne, Phys.Rev., **103**, 378 (1956).
44. G.L.Johnson, R.F.Leininger, and E.Segrè, J.Chem.Phys., **17**, 1 (1949).
45. E.H.Appelman, U.S.Atomic Energy Commission Report No.UCRL-9025, January 1960.
46. W.E.Burcham, Proc.Phys.Soc., **67A**, 555 (1954).
47. A.H.W.Aten, T.Doorgust, V.Hollstein, and H.P.Moeken, Analyst, **77**, 777 (1952).
48. H.M.Neumann, J.Inorg.Nuclear Chem., **4**, 349 (1957).
49. A.P.Vinogradov, I.P.Alimarin, V.I.Baranov, A.K.Lavrukhina, T.V.Baranova, A.A.Bragina, and Yu.V.Yakovlev, in

"Sessiya AN SSSR, po Mirnomu Ispol'zovaniyu Atomnoi Energii 1–5 Iyulya 1955 g. Zasedaniya Otdelenii Khimicheskikh Nauk" (Sessions of the Academy of Sciences of the USSR on the Peaceful Uses of Atomic Energy 1–5 July 1955. Meeting of the Section of Chemical Sciences), Izd. Akad. Nauk SSSR, Moscow–Leningrad, 1955, p. 97.
50. R. Wolfgang, E. W. Baker, A. A. Caretto, T. B. Cumming, G. Friedlander, and T. Hudis, Phys. Rev., **103** 394 (1956).
51. Wang Fu-chiung, Kang Mêng-hua, and V. A. Khalkio, Radiokhimiya, **4**, 94 (1962).
52. M. Lefort, G. Simonoff, and X. Torrago, Compt. rend., **248**, 216 (1959).
53. J. F. Durand, Bull. Soc. chim. France, **3**, 1382 (1936).
54. L. H. Ahrens, Geochim. Cosmochim., **2**, 155 (1952).
55. V. Zacharaisen, in "The Actinide Elements" (Edited by G. T. Seaborg and J. J. Katz) (Translated into Russian), Inostr. Lit., Moscow, 1955, p. 627.
56. L. Genov, Zhur. Obshch. Khim., **29**, 689 (1959).
57. G. A. Kristov, Radiokhimiya, **4**, 690 (1962).
58. W. Finkelnberg and F. Stern, Phys. Rev., **77**, 303 (1950).
59. R. Parsons, "Handbook of Electrochemical Constants", Butterworth, London, 1959.
60. R. W. Kiser, J. Chem. Phys., **33**, 1265 (1960).
61. W. Gordy and W. Thomas, J. Chem. Phys., **24**, 439 (1956).
62. I. L. Agafonov, Zhur. Neorg. Khim., **4**, 1270 (1959) [Russ. J. Inorg. Chem., 573 (1959)].
63. M. F. C. Ladd and W. H. Lee, J. Inorg. Nuclear Chem., **20**, 163 (1961).
64. D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements", Advances in Chemistry, Ser. No. 18, Washington, American Chemical Society, 1956.
65. E. H. Appelman, E. N. Sloth, and M. H. Studier, Inorg. Chem., **5**, 766 (1966).
66. R. McLaughlin, J. Opt. Soc. Amer., **54**, 965 (1964).
67. M. Kahn and A. C. Wahl, J. Chem. Phys., **21**, 1185 (1953).
68. M. L. Good and R. R. Edwards, J. Inorg. Nuclear Chem., **2**, 196 (1956).
69. H. M. Eiland and M. Kahn, J. Phys. Chem., **65**, 1317 (1961).
70. J. H. Wolfenden, Analyt. Chem., **29**, 1098 (1957).
71. E. H. Appelman, J. Amer. Chem. Soc., **83**, 805 (1961).
72. W. M. Garrison, J. D. Gile, R. D. Maxwell, and J. G. Hamilton, Analyt. Chem., **23**, 204 (1951).
73. E. H. Appelman, J. Phys. Chem., **65**, 325 (1961).
74. M. Johnston, C. W. Asling, P. W. Durbon, and G. G. Hamilton. Report No. UCRL-3013 (1955), pp. 35, 36.
75. R. L. Platzman and J. Franck, Res. Council Israel, Spec. Publn., No. 1, 21 (1952).
76. E. Anders, Ann. Rev. Nuclear Sci., **9**, 203 (1959).
77. K. W. Bagnall, see Ref. 1, p. 164.
78. A. H. W. Aten, Adv. Inorg. Chem. Radiochem., **6**, 207 (1964).
79. J. Klivenyi and B. Lakotos, Magyar Kém. Folyóirat, **60**, 136 (1954).
80. Wang Fu-chiung, Yu. V. Norseev, V. A. Khalkin, and Ch'ao T'ao-nam, Radiokhimiya, **5**, 351 (1963).
81. Wang Fu-chiung, N. G. Krylov, Yu. V. Norseev, Ch'ao T'ao-nan, and V. A. Khalkin, in Collected Papers. "Soosazhdenie i Adsorbtsiya Radioaktivnykh Elementov" (Coprecipitation and Adsorption of Radioactive Elements), Izd. Nauka, Moscow, 1965, p. 80.
82. Yu. V. Norseev, V. A. Khalkin, and Ch'ao T'ao-nan, Izv. Sibir. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, No. 11, 3, 21 (1965).
83. Yu. V. Norseev, Ch'ao T'ao-nan, and V. A. Khalkin, Preprint OIYaI R-2159, Dubna, 1965.
83a. Yu. V. Norseev and V. A. Khalkin, Preprint OIYaIR i2-3529, Dubna, 1967.
84. Wang Yung-yü and V. A. Khalkin, Radiokhimiya, **3**, 662 (1961).
85. N. V. Sidgwick, "The Chemical Elements and Their Compounds", Oxford University Press, 1950, Vol. II, p. 1237.
86. A. H. W. Aten, Jnr., J. G. van Raaphorst, G. Nooterboom, and G. Blasse, J. Inorg. Nuclear Chem., **15**, 198 (1960).
87. G. A. Brinkman, J. T. Vunboer, and A. H. W. Aten, Jnr., Radiochim. Acta, **2**, 48 (1963).
88. N. V. Sidgwick. ref. 85, Vol. II p. 1195.
89. W. L. Hughes and D. Gitlin, U. S. Atomic Energy Commission Document BNL 314 (1954).
90. W. L. Hughes and J. Klinenberg, U. S. Atomic Energy Commission Document BNL 367 (1955).
91. W. L. Hughes, E. Smith, and J. Klinenberg, U. S. Atomic energy Commission Document BNL 406 (1956).
92. V. D. Nefedov, Yu. V. Norseev, Kh. Savlevich, E. N. Sinotova, M. A. Toropova, and V. A. Khalkin, Dokl. Akad. Nauk SSSR, **144**, 806 (1962).
93. Yu. V. Norseev, Candidate's Thesis, United Institute of Nuclear Research – Leningrad State University, 1965.
94. A. N. Murin, V. D. Nefedov, V. M. Zaitsev, and S. A. Grachev, Dokl. Akad. Nauk SSSR, **133**, 123 (1960).
95. V. D. Nefedov, V. M. Zaitsev, and M A. Toropova. Uspekhi Khim., **32**, 1367 (1963) [Russ. Chem. Rev., 604 (1963)].
96. J. G. Hamilton and M. H. Soley, Proc. Nat. Acad. Sci. USA, **26**, 483 (1940).
97. J. G. Hamilton, C. W. Asling, W. M. Garrison, K. G. Scott, and D. Axelrod-Heller, Proc. Soc. Exp. Biol. Med., **73**, 51 (1950).
98. J. K. Basson and C. J. Shellabarger, Radiation Res., **5**, 502 (1956).
99. P. W. Durbin, J. G. Hamilton, and M. W. Parrot, Proc. Soc. Exp. Biol. Med., **86**, 369 (1954).
100. M. W. Parrot, W. M. Garrison, P. W. Durbin, M. E. Johnston, H. Powell, and J. G. Hamilton, U. S. Atomic Energy Commission Report No. UCRL 3065 (1955).
101. J. G. Hamilton, C. W. Asling, W. M. Garrison, and K. Scott, Pharmacol. Rev., **2**, 283 (1953).
102. J. G. Hamilton, P. W. Durbin, and M. W. Parrot, Proc. Soc. Exp. Biol. Med., **86**, 366 (1954).
103. J. G. Hamilton, P. W. Durbin, M. W. Parrot, and J. Clin, Endrocrin. and Metabolism, **14**, 1161 (1954).
104. C. W. Asling, P. W. Durbin, M. E. Johnston, and M. W. Parrot, Endrocrinology, **64**, 579 (1959).
105. K. Yokaro, A. Kunit, J. Furth, and P. W. Durbin, Cancer. Research, **24**, 683 (1964).
106. C. J. Shellabarger, P. W. Durbin, M. W. Parrot, and J. G. Hamilton, Proc. Soc. Exp. Biol. Med., **87**. 626 (1954).
107. M. Haissinsky, Bull. Soc. chim. France, **16**, 668 (1949).
108. H. J. Emeléus, Sci. Progr., **38**, 609 (1950).
109. Yu. B. Gerlit, F. I. Pavlotskaya, and S. S. Rodin, Khim. Nauka i Prom., **4**, 465 (1959).
110. A. G. Maddock, Uspekhi Khim., **29**. 1388 (1960) [Translated into Russian from "A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. II. Supplement 1. F, Cl, Br, 1, At", Longmans, Green, 1958, Ch. 44].
111. C. Duval, Chim. Anal. (Paris), **45**, 557 (1963).
112. V. D. Nefedov and M. A. Toropova, in "Radiokhimiya i Khimiya Yadernykh Protsessov" (Radiochemistry and Chemistry of Nuclear Processes) (Edited by A. N. Murin, V. D. Nefedov, and V. P. Shvedov), Gos. Nauchn.-Tekhn. Izd. Khim. Literat., Leningrad, 1960, p. 470.
113. J. Sedlet, in "Treatise on Analytical Chemistry" (Edited by I. M. Kolthoff and P. J. Elving), Interscience, New York, 1964, part II, Vol. 6, p. 487.
114. W. Treytl and K. Valli, Nucl. Phys., **A97**, 405 (1967).

United Institute of Nuclear Research, Dubna