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Chemical Properties of Astatine. I.

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This work is a report on studies of the chemistry of astatine on a tracer scale, using the various methods of tracer chemistry. A general discussion of preparation of materials and analytical methods is included. The properties of astatine and its solutions as they appear in work on a tracer scale are discussed. Migration experiments show that astatine when ionized in aqueous solution is negatively charged. Electro chemical, solvent extraction, and carrying studies are presented.

In general, (a) elemental astatine is extractable by organic solvents; (b) the -1 state may be prepared by powerful reducing agents; and (c) at least two positive oxidation states exist.

I. INTRODUCTION

EARLIER work on the radioactive element 85, astatine, has been reported in 1940.¹ At that time the nature of the various radiations produced by astatine 211 were well worked out, and, in addition, the chemical properties of this new element were briefly sketched. Soon after, all work on the subject was dropped because of the pressure of war activities. This paper is the first report of a more detailed investigation of the chemistry of astatine; we hope to continue this research.

As a first step in extending our knowledge of astatine, we have tried to find some isotope of longer life than At^{211} , with the hope of accumulating visible amounts of the substance. This quest has been unsuccessful, although two new isotopes, astatine 212 and 210, with half-lives of 0.2 second and 8.3 hours, respectively, have been

recognized.² Astatine 212 is an alpha-emitter, and astatine 210 decays by K -capture. Other reported isotopes of astatine^{3,4} have even shorter half-lives, and from this it appears that at the present time all of the chemical research on astatine must be done on a tracer scale. For reasons of convenience we have used almost exclusively astatine 211 of 7.5-hour half-life. 650 atoms of this isotope produce one alpha-particle per minute. The most concentrated solution so far prepared is approximately 10^{-8} molar, and the usual experiments are performed with 10^{-11} to 10^{-15} molar astatine; a molar solution of At^{211} would emit $1.54 \times 10^{16} \alpha \text{ cm}^{-3} \text{ sec}^{-1}$. Since tracer scale experiments are difficult to interpret, wherever there is any doubt we shall include sufficient experimental data to enable

² At^{210} : E. Kelly and E. Segrè, to be published elsewhere; At^{212} : T. Putnam and M. Weissbluth, to be published elsewhere.

³ At^{217} , $T_{1/2}$ 0.02 sec.: Hageman, Katzin, Studier, Ghiorso, and Seaborg, *Phys. Rev.* **72**, 252 (1947); English, Cranshaw, Demers, Harvey, Hincks, Jelley, and May, *ibid.* **72**, 253 (1947).

⁴ At^{215} , At^{216} , At^{218} : B. Karlik and T. Bernert, *Zeits. f. Physik* **123**, 51 (1944).

¹ D. R. Corson, K. R. Mackenzie, and E. Segrè, *Phys. Rev.* **57**, 672 (1940). For the name "astatine," see D. R. Corson, K. R. Mackenzie, E. Segrè, *Nature* (London) **159**, 24 (1947).

the reader to draw his own conclusions. Also, in work at these dilutions the concentration effects on the thermodynamic properties are very large. The correction to macro quantities of astatine will be very large in all cases except when the same numbers of astatine atoms or molecules appear on both sides of the reaction equations. As this is a report of current work, some of our conclusions are rather hypothetical and may be corrected in future articles. The experimental parts of this paper will be described in general sections according to the property of astatine used in the experiment (volatility, solvent extraction, etc.). Since the details of the experiments will not be of interest to all readers, the final section includes a summary of the results with the conclusions which we have drawn from them.

II. PREPARATION OF MATERIALS

Bismuth, when bombarded by alpha-particles in the energy range 21–29 Mev, produces astatine 211 free of other activities. Above 28 Mev astatine 210 is also produced by the reaction ($\alpha, 3n$).⁵ This substance decays by orbital electron capture to polonium 210, the presence of which is very undesirable in all of our experiments.

The bismuth samples that were bombarded were produced by evaporating bismuth from a molybdenum boat in a high vacuum upon aluminum disks of one-mil thickness. Bismuth samples prepared in this way were of uniform thickness and could be made up to 40 milligrams per square centimeter thick. These samples were subsequently clamped in a water-cooled target holder and bombarded by the sixty-inch cyclotron of the Crocker Radiation Laboratory. The beam energy was reduced to less than 28 Mev by aluminum absorbers in front of the target in order to avoid producing polonium 210. In some bombardments an additional bismuth-aluminum foil was exposed to the full energy of the beam to produce polonium 210 for comparison experiments. A detailed study of the bismuth-alpha-excitation function by E. Kelly will be published elsewhere. Here it suffices to say that if we limit the energy to 29 Mev to prevent production of polonium 210, the thick target yield for a short

bombardment is approximately 1.2×10^9 disintegrations per minute per microampere hour.

For most of our experiments we wished to extract the activity from the bombarded target. As the high volatility of astatine from bismuth was known,¹ we used a high vacuum distillation method to concentrate the activity.

The procedure used was to distill the astatine from bismuth at its melting point in an all-glass system, and collect the carrier-free element in a four-millimeter diameter U tube cooled by liquid nitrogen. The U tube while still cold was washed with one drop of concentrated nitric acid, allowed to stand 1 hour, and then washed with distilled water into a stock bottle. By this method three-milliliter solutions were prepared containing 0.5-molar nitric acid and 10^7 disintegrations/sec. of astatine. Such a solution is 2.1×10^{-10} molar with respect to astatine. Yields up to 0.95 were obtained with less than 0.001 of any polonium present in the original target coming over.

Experiments to be described later in the volatility section indicate that astatine evaporated on glass is very poorly held by this surface at room temperature. Based on this information, a double separation of astatine from bismuth and polonium was accomplished. A bismuth plate was bombarded in such a way as to accumulate in it approximately equal numbers of polonium and astatine atoms, after which a first distillation was carried out in the usual way. The tube containing the bismuth was sealed off and the astatine then distilled at room temperature to a second U tube cooled by liquid nitrogen. The yield of this experiment was 0.83 of the astatine present on the original target, with less than 10^{-6} of the polonium coming over.

III. ANALYTICAL METHODS

Astatine 211 can be measured by its alpha or x-ray radiations, and either radiation can be used to follow a chemical process. For most purposes the alpha-particles are counted because of the higher counting efficiency of the equipment used to detect this type of radiation. However, for certain experiments where self-absorption prohibits the use of alpha-counting techniques, x-ray counters were used. At^{210} is even more favorable than At^{211} for thick sample counting because it emits γ -rays in addition to the x-rays. However,

⁵ E. L. Kelly and E. Segrè, *Phys. Rev.* **72**, 746 (1947).

because in our alpha-bombardments At^{210} is always produced together with polonium and with relatively small yield, we did not use it extensively.

For alpha-counting, the samples were mounted on flat platinum disks 2 mils thick and one inch in diameter. A slurry of the precipitate to be studied was pipetted on a freshly flamed platinum disk and allowed to dry. In general, the thickness of the sample was limited to one milligram per square centimeter except in cases where poor spreading of the precipitate made the sample thicker in spots.

Samples for x-ray measurement were placed in three-milliliter centrifuge cones. These samples were counted with a Geiger-Müller counter; the efficiency of the counter was not accurately known, but was kept constant during the various experiments.

Frequently during the course of this investigation weightless samples of astatine and its compounds were deposited on supports of a variety of materials for analytical purposes. It was easily recognized that such samples occasionally lost more activity by evaporation than by decay, and for this reason studies were made on their volatilities under various conditions.

The volatility of astatine from glass is most striking. When elemental astatine was evaporated upon glass the loss of astatine from that surface at room temperature was so rapid that, if the evaporation follows an exponential law, the "half-life for evaporation" is approximately 1 hour. From metallic surfaces the losses were much less; for instance, about sixteen hours were required for half of the astatine to evaporate from a gold or platinum surface. When the astatine was initially dissolved in cold concentrated nitric acid, and the samples dried at 80°C on the surface investigated, the losses were much smaller. From glass the "half-life for evaporation" of the residue was approximately four hours. There was no observable loss from gold and platinum in a period of 24 hours after the samples were evaporated at 80°C on these supports.

These experiments indicated that elemental astatine would not provide samples suitable for counting but that nitric acid solutions of astatine dried on gold or platinum would give satisfactory

samples if we knew the loss undergone in the drying process. Furthermore, since gold consistently showed a higher initial loss than platinum when identical amounts of the same tracer solution were evaporated upon them at 80°C , platinum was used in all cases. The absolute loss of astatine, when a nitric acid solution was dried, was measured by counting the x-rays from a small sample as the solution went to dryness. In three experiments on different solutions, the losses were 26, 26, and 28 percent, respectively. Subsequent experiments with solvent extraction have shown that astatine dissolved in cold concentrated nitric acid is present principally as the zero state.

The losses in the experiment just described are attributed to partial loss of some astatine zero. The principal losses always took place just as the samples were going to dryness.

IV. VOLATILITY EXPERIMENTS

Since our analytical experiments indicated that astatine had variable affinities for various surfaces, an experiment was devised to measure the relative adsorption power of various metals. A 0.3×2.5 -cm strip of each of the metals listed in Table I was suspended in an evacuated Pyrex tube of one-inch diameter. In the first experiments the metals were exposed to astatine vapor for approximately 16 hours at room temperature. In the second experiment the metal foils were heated in an evacuated system to 325°C for one-half hour together with a previously bombarded bismuth foil. The data are given in Table I. Since Al, Ni, and Cu showed low adsorption, in some of the later experiments we omitted them and used duplicate strips of the other metals. The surfaces of the metals in each

TABLE I. Adsorption of astatine on metallic surfaces in high vacuum expressed as percent of the total astatine on the surfaces.

Metal	Room temperature		325°C		
	(1)	(2)	(1)	(2)	(3)
Al	0.3		0.2	0.3	
Ni	0.2		0.6	0.7	
Cu	0.5		0.6	4.3	
Pt	36.3	20	33.5	6.5	16
Au	38.4	65	0.1	0.7	4
Ag	24.3	15	65.0	87.5	80
	100.0%	100%	100.0%	100.0%	100%

TABLE II. Distillation of astatine solutions.

Initial solution	Initial volume 10 ml Percent of At in each successive ml of distillate									Percent left in still	(a)
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)		
16M HNO ₃	0.1	0.1	0.1	0.3	0.1	0.2				86	0.87
5M HNO ₃ +3 mg I ⁻	2.0*									98	—
12M HCl	0	0	0	0.4	0.1	0.8	3.7	9.5		70	0.84
1:1 H ₂ SO ₄	0.6	0	0.2	0.3	0.4	0.2	0.1	0		91	0.92
60% HClO ₄	0	0.1	0	0	0	0.1	0	0.2	0.4	101	1.02
0.5M H ₂ SO ₄ +0.05M Fe ⁺⁺	48	21	5.0	4.0	3.6	2.6	3.0	4.0		7.4	—
CCl ₄	1.1	0.8	0.7	0.6	0.6	0.8	1.0	2.0	7.8	64	0.78
Benzene	3.5	3.5	3.4	3.2	3.5	3.6	4.6	4.8	7.7	62	—

* Amount of astatine in distillate and still pot divided by initial amount of astatine.

* First 10 percent of distillate contained all of the I₂ but only 2 percent of the At.

case were previously cleaned in the apparatus by heating to $\sim 400^\circ\text{C}$ in a hydrogen atmosphere.

The selective nature of the adsorption indicates a special affinity of astatine for some metallic surfaces. Aluminum (certainly oxidized on the surface) and glass showed very poor adsorption; bismuth too is not a good adsorber.

We have also run some experiments on the distillation of various solutions containing astatine. Table II lists the various combinations tested, the yields of astatine in the distillate, and the material balances when obtained. In all experiments the astatine was detected by thick sample counting of the x-rays.

Special attention is called to the differing behavior of astatine and iodine. The dissimilarity of astatine and iodine under these conditions was noted in the paper of 1940.¹ The failure of astatine to distill under conditions in which iodine distills, therefore, was not surprising. This anomaly will be explained further in the section on solvent extraction.

These results indicate that astatine in aqueous

solution may be manipulated without loss in the presence of oxidizing agents. Organic solvent solutions and aqueous solutions containing reducing agents (Fe⁺⁺ or better) must be handled with care.

V. MIGRATION EXPERIMENTS

We performed some experiments to determine the direction of migration of astatine in a solution subject to an electric field. The simple apparatus⁶ used consisted of a U tube, the bottom section of which was made of one-millimeter capillary tubing (see Fig. 1). The capillary tubing, which was about two inches long, could be isolated from the rest of the U tube by one-millimeter bore stopcocks.

Solutions containing astatine were placed in the capillary tube with care so that no bubbles were left. The stopcocks were then closed and the excess material in the side arms of the U tube carefully washed out. A solution of the same composition but without astatine was placed in the U tube arms, two platinum electrodes inserted, and the entire apparatus clamped in a thermostat. The solutions in the side arms were leveled by opening the connecting stopcock, which was above the capillary section of the U tube containing astatine. The leveling stopcock was then closed and the two capillary stopcocks opened. A voltage difference of 100 volts was applied across the cell for approximately one hour, after which the stopcocks were closed and the side arms analyzed for astatine. The normal migration current was less than 10 milliamperes; however, in concentrated acid solutions, currents

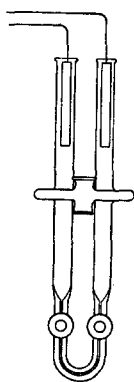


FIG. 1. Migration apparatus.

⁶ See, e.g., M. Haissinsky, *Electrochimie des Substances Radioactives* (Hermann and Company, Paris, 1946), p. 19.

as high as 90 milliamperes occurred. In all solutions tested the astatine migrated as a negative ion. The conditions checked are listed in Table III.

VI. ELECTROCHEMISTRY

The electrochemistry of astatine has been studied using the method of Hevesy and Paneth⁷ with the refinements of Joliot.⁸ The electrolysis was carried out in a glass cell (*a*) made in the form of a tee (see Fig. 2). Gold windows (*b*), eight to ten milligrams per square centimeter in thickness, were fastened over the ends of the tee by a rigid clamping arrangement similar to that used by Joliot. The windows were one centimeter in diameter, and the cell had a volume of ten milliliters. The alpha-particles of astatine were deposited on the gold windows, penetrated the thin gold, and caused ionization in the air beyond. These ions were collected by an electric field and the resultant current measured by an FP-54 electrometer. By this arrangement the ionization of 50 alpha-particles per minute was easily detected.

Joliot used a system of parallel plates perpendicular to the thin gold window to collect the ions formed. We used this arrangement at first, but later abandoned it in favor of another which gave better results. The changes were as follows: A thin aluminum leaf (*c*) was mounted by Aquadag on a brass ring spaced one centimeter from and parallel to the gold windows. A potential difference of 700 volts was maintained on this ring with respect to ground by a battery. Behind the ring and spaced two centimeters from it was a brass disk (*d*) of the same size. The disk was insulated by polystyrene and was connected to the grid of the FP-54 tube. In addition, a movable shutter was arranged over the gold windows to absorb the alpha-particles coming through so that the FP-54 circuit could be adjusted to zero while an electrolytic process was in progress. Since both windows were equipped with electrometers, the activity deposited on either window could be measured at any time.

Considerable difficulty was experienced in

⁷ G. v. Hevesy and F. Paneth, *Wien Ber.* **123**, 1619 (1914), and **122**, 1049 (1913).

⁸ F. Joliot, *J. de Chemie Phys.* **27**, 119 (1930).

TABLE III. Composition of solutions in which astatine migration experiments were run; astatine was initially dissolved in concentrated nitric acid and then treated as described below.

- (1) Made 1M in HNO_3
- (2) Made 0.1M in HNO_3
- (3) pH = 3 in phosphate buffer
- (4) pH = 5 in phosphate buffer
- (5) pH = 7 in phosphate buffer
- (6) pH = 9 in phosphate buffer
- (7) pH = 11 in phosphate buffer
- (8) pH = 13 0.1M NaOH
- (9) Reduced by SO_2 in 0.1M HNO_3
- (10) Reduced by NaSO_3 in 0.1M NaOH
- (11) Oxidized by hot $\text{K}_2\text{S}_2\text{O}_8$ in 0.1M HNO_3
- (12) Oxidized by HClO in 0.1M NaOH
- (13) Oxidized by Br_2 in 0.5M HNO_3

finding thin gold free from pin holes. The gold foils were finally manufactured by evaporating gold from a tungsten boat in a high vacuum upon freshly split mica. When the gold-coated mica was placed in water, the gold films were detached cleanly from the mica by the wetting power of the water.

Initially, the electrolysis was carried on between the two gold windows. The potentials of the gold windows with respect to a saturated calomel reference electrode were measured with a Beckman Laboratory type pH meter. Later, however, the two electrodes were connected together and the electrolysis conducted between the combined electrodes and a working calomel electrode. Figure 2 is a schematic diagram of the apparatus and electrical circuit used.

The results of the cathode electrolytic experiments are shown in Table IV. The critical deposition potentials listed are obtained by extrapolation of deposition rate *vs.* potential curves back to zero rate. An example of typical data and their extrapolation are given in Figs. 3 and 4.

Special experiments performed were as follows:

(a) When the astatine was previously oxidized

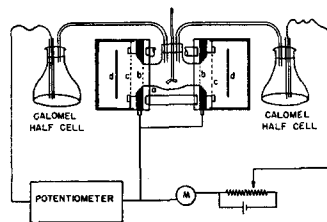


FIG. 2. Schematic diagram of the electrolytic apparatus and the electrical circuit.

TABLE IV. Critical deposition potential of astatine at the cathode from various solutions.

Solution	Concentration of At mole/liter	Critical deposition potential/normal H ₂ electrodes
0.066 <i>M</i> HNO ₃	2.8×10^{-13}	-1.225 ± 0.025 v
1.0 <i>M</i> HNO ₃	5×10^{-14}	-1.24 ± 0.025 v
0.075 <i>M</i> H ₂ SO ₄ 0.1 <i>M</i> Na ₂ Cr ₂ O ₇	6×10^{-13}	-1.20 ± 0.025 v
0.066 <i>M</i> HNO ₃ + 3 mg Au	1×10^{-13}	-1.22 ± 0.025 v
0.066 <i>M</i> HNO ₃ (repeat)	4×10^{-14}	-1.22 ± 0.025 v

by hot (60°C) persulfate for 15 minutes there was no consistent deposition at the cathode. The initial spontaneous deposition was smaller than in any previous experiment. The possible ions present in the oxidized solution will be discussed in the sections on solvent extraction and carrying.

(b) When astatine zero was dissolved in sulfuric acid no deposition took place at the cathode until dichromate ion was added to the cell.

We endeavored to determine the reversibility of the cathodic deposition. In every experiment tried the deposition appeared to be quite reversible. After depositing astatine on the cathode at potentials greater than the critical deposition potential, the material was rapidly removed by lowering the cathode potential below -1.25 v by a few hundredths of a volt. A further decrease of the gold potential to about -1.45 v caused the astatine to deposit on the gold anodically.

A study of this anodic deposit was also attempted (Table V). Since the potentials involved are close to those required to decompose water and dissolve gold, the problems are more difficult than those involved in the cathodic work. The experiments were run in 0.1*M*, or less, nitric acid to avoid excessive electrolytic currents.

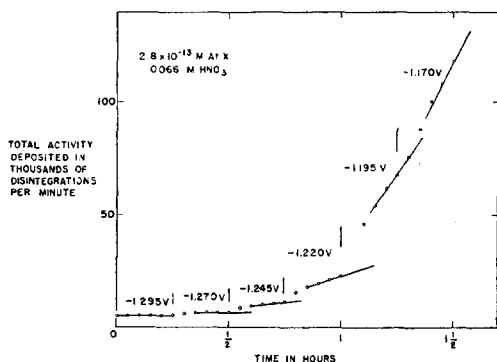


FIG. 3. Typical data showing the total activity deposited on the gold window as a function of the deposition potential and the time.

TABLE V. Critical deposition potential of astatine at the anode from various solutions.

Solution	Concentration of At in mole/liter	Critical deposition potential/normal H ₂ electrode
0.066 <i>M</i> HNO ₃	2.4×10^{-13}	-1.46 ± 0.02 v
0.066 <i>M</i> HNO ₃	5.3×10^{-13}	-1.45 ± 0.02 v
0.1 <i>M</i> HNO ₃ 0.1 <i>M</i> K ₂ S ₂ O ₈	5.4×10^{-13}	-1.445 ± 0.02 v

The anodic deposition was not reversible. Vigorous treatment, such as concentrated nitric acid or strong electrolytic currents with repeated reversals of direction, was necessary to remove the deposited material.

The nature of the astatine compounds deposited in the electrolytic experiments is as yet unknown. A large variety of products are possible at both the anode and the cathode.

VII. SOLVENT EXTRACTION

Solvent extraction studies proved to be our most powerful single tool in the study of astatine chemistry. Since solvent extraction methods work well in very dilute solutions, the method is particularly adaptable to our problems and although no quantitative results were attempted for the time being, solvent extraction methods should prove to be very useful in determining the thermodynamics of astatine even in these extremely dilute solutions. As an example, the reaction



would be unaffected by astatine concentration, whereas



would be greatly affected. Concentration studies of solvent extraction in solutions stabilized with respect to oxidation-reduction are contemplated.

The solvents used were Baker's analyzed carbon tetrachloride and benzene. Initially, it was believed that in the case of carbon tetrachloride astatine might conceivably react with or replace the chlorine of the solvent, affecting the results of the experiments. No such effect was observed in the work, and the behavior of CCl₄ is qualitatively identical with that of benzene.

Solutions were prepared by dissolving astatine in the various solvents, and using them as

stock solutions for the experiments involved. All extraction experiments were run in the range of 3×10^{-11} to 10^{-12} molar astatine. When such a stock solution was repeatedly extracted with $0.01M$ HNO_3 , a series of partition coefficients was obtained which increased to a maximum value. This maximum value is not necessarily the true partition coefficient but approaches it as a limit, the limit being set by the mechanics of the experiment and the presence of traces of oxidizing or reducing agents. All work was done on a one-milliliter scale. Since the extraction experiments involved usually a series of consecutive extractions on a single sample of astatine, the results of the experiments are recorded in tabular form in Table VI with comment at the end.

It is noteworthy that the experiment on tracer I_2 falls far short of the accepted value of 85.

In basic solution the behavior of astatine is very different. The experiments were as follows. A stock solution of astatine in organic solvent was extracted three times by $0.01M$ HNO_3 until a large partition coefficient was obtained. The solvent phase was then extracted with $0.1M$ $NaOH$ and the partition coefficient measured. Finally, the water layer was acidulated and the partition coefficient remeasured. The results are given in Table VII.

The simplest interpretation of this experiment is that in alkaline solution astatine disproportionates to At^- and an oxidized state, and passes from the solvent to the water layer. In this hypothesis a fractional part of the astatine in the water layer should precipitate with AgI as a carrier, and another fraction should not precipitate because it is in a higher oxidation state. However, when we precipitated silver iodide from the $0.1M$ $NaOH$ solution in the presence of

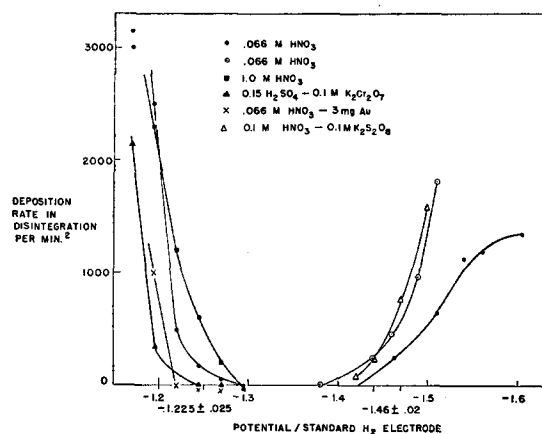


FIG. 4. The rate of electrochemical deposition of astatine on gold at the cathode and the anode from various acid solutions. All points below zero indicate zero rate of deposition.

excess ammonia, the silver iodide carried all the astatine. This objection to the hypothesis of the disproportionation of astatine in alkaline solution does not seem of great importance, however, because we are not certain that the higher oxidation states of astatine would not coprecipitate in alkaline solution with silver iodide. In acid solution they do not coprecipitate with silver iodide.

So far we have discussed simple extractions in acid and basic solutions of astatine. Solvent extraction has been used also to study oxidation and reduction of astatine zero by adding an oxidizing or reducing agent to the water phase and observing the effect on the partition coefficient. In the experiments to be described, astatine dissolved in the organic solvent was repeatedly extracted by $0.01M$ HNO_3 to give the partition coefficient listed in column 3 of Table VIII. The solvent layer was then extracted by the final aqueous phase, listed in column 2, to give a new value of partition coefficient, listed in column 4.

TABLE VI. Partition coefficient of At and tracer I in successive extractions.

Extraction	At $CCl_4-0.01M$ HNO_3		At $C_6H_6-0.01M$ HNO_3		I $CCl_4-0.01M$ HNO_3	
	Exp. 1	Exp. 2	Exp. 1	Exp. 2	Exp. 1	Exp. 2
1	58	9.8	46	40	18	14
2	86	53	86	83	15	17
3	91	64	140	112	21	25
4		90	155	106	31	28
5			242	89		
6			227			

TABLE VII. Comparison of partition coefficients of At in acid and basic solution.

Solvent	CCl_4	C_6H_6
First acid extraction	58	29
Second acid extraction	86	42
Third acid extraction	91	52
Extracted by $0.1M$ $NaOH$	0.85	1.5
Aqueous layer made $0.1M$ in HNO_3 , the layers recombined and reextracted	25.0	21

In addition to the experiments listed above we have also dissolved astatine in 16M HNO₃ from a glass surface by 2-hour treatment with the cold acid. This solution was then diluted to 0.1M HNO₃ and extracted with carbon tetrachloride. A partition coefficient as high as 10 was found, showing that cold concentrated nitric acid oxidizes astatine slowly and incompletely.

VIII. CARRYING EXPERIMENTS

Carrying experiments have been made in an effort to determine the nature of the ions in solution. Experimental results have been found which emphasize the resemblance of astatine to iodine. Reference should also be made to the paper of 1940¹ which described many more of the carrying experiments.

Since astatine has a slight tendency to stick to glass surfaces, as do many other substances on tracer scale, precautions must be taken to avoid this cause of error. In general, confusion

TABLE VIII. Oxidation reduction studies using solvent extraction.

Solvent	Final aqueous layer	Partition coeff. in 0.01M HNO ₃	Partition coeff. with final aq. layer	Comments
(1) C ₆ H ₆	0.25M FeSO ₄ 0.01M HNO ₃	91	89	At ⁰ is neither reduced nor oxidized
(2a) CCl ₄	saturated H ₂ AsO ₃	90	49	after 10 minutes
(2b)	solvent reextracted with same aqueous layer	—	31	after 20 minutes
(3) CCl ₄	1.1M KI in 0.01 HNO ₃	50	0.4	approx. 10 minute extraction. Decrease of coefficient due to formation of inter halogen compounds
(4) C ₆ H ₆	saturated I ₂ 0.01M HNO ₃	200	64	slight effect
(5a) C ₆ H ₆	saturated SO ₂ 0.01M HNO ₃	200	3	reduction of At ⁰ to At ⁻ , AgI precipitated from this solution carries all the activity.
(5b) CCl ₄	same	85	0.8	same
(6) CCl ₄	0.25M Fe(NO ₃) ₃ 0.01M HNO ₃	85	2	partial oxidation of astatine
(7) 0.5M	Hg(NO ₃) ₂ 0.01M HNO ₃	200	0.01	possible complexing by Hg ⁺⁺ causing At ⁰ to disproportionate
(8) CCl ₄	Br ₂ < 0.1M 0.01M HNO ₃	85	0.05	rapid oxidation of astatine by bromine; see carrying experiments.
(9a) C ₆ H ₆	cold 0.01M K ₂ S ₂ O ₈	200	5	slow oxidation of astatine
(9b) C ₆ H ₆	50°C 0.1 K ₂ S ₂ O ₈	200	0.1	rapid oxidation by hot K ₂ S ₂ O ₈
(10) C ₆ H ₆	3M HCl	50	0.66	possible compound formation with Cl ⁻
(11) C ₆ H ₆	0.1M KIO ₃ 0.01M HNO ₃	200	16	slight oxidation by IO ₃ ⁻ in 10 minutes

from this source has been avoided by measuring separately the activities of the supernatant, precipitate, and precipitation vessel. X-ray counting methods have been used extensively for these measurements.

(a) When the stock solutions were centrifuged, erratic losses were observed in different solutions of the same composition. However, no additional loss was produced by repeated centrifuging of an astatine tracer solution which had lost activity to the glass walls in the initial centrifugation. Since fresh centrifuge tubes were used each time, the loss was not dependent on the glass surface but on impurities (i.e., dust, etc.) in the initial solution. In general, centrifugation of the stock solutions improved the consistency of the subsequent experiments. Two-hour centrifugations at 2000 times gravity have produced negligible losses from 10-M HNO₃, 0.5-M HNO₃, and 0.1-M NaOH solutions.

(b) Various hydroxides carry astatine differently. The results are summarized in Table IX.

It is noteworthy that lanthanum hydroxide carries astatine differently, according to the oxidation of the solution. The reason for this behavior may be related to the insolubility of compounds of the type La(AtO₃)₃ in alkaline solution.

(c) Precipitation of mercuric sulfide in HCl solution carries astatine. The percent carried as a function of acidity is given below.

M HCl	0.5	1	5	10
Percent of At carried by HgS	69	81	93	92
Same in repeat exp.	88			96

(d) Astatine when reduced by sulfur dioxide in acid solution, is partially carried by TII. Silver iodide carries At completely, but this effect is due to the formation of metallic silver on which astatine deposits (see under (e) below).

(e) If astatine is reduced by zinc in 1M sulfuric acid, and potassium iodide and silver nitrate are added *after the zinc is completely dissolved*, the astatine is carried completely by silver iodide. The carrying is also complete when TII is used. If, however, we start from AgI containing astatine and reduce it by zinc, all of the astatine is found on the precipitated metallic silver which is formed, whereas all the iodine is in the solution.

(f) When silver iodide or chloride is precipitated from nitric acid solution of astatine, less than 2 percent of the activity is found in the precipitate.

(g) When silver iodate is precipitated from a nitric acid solution of astatine, the carrying depends upon the order of addition of the reagents. When silver is added first, poor carrying (5–20 percent) is observed; when iodate is added first, fair carrying (40–80 percent) occurs. This may be due to the fact that iodate can oxidize astatine, as discussed in the section on solvent extraction.

(h) When silver iodate is precipitated from a bromine oxidized solution, the iodate carries astatine poorly (5–15 percent).

(i) When silver iodate is precipitated from an oxidized solution of astatine (hot $K_2S_2O_8$ or $HClO$), carrying (90–100 percent) is independent of the order of addition of the reagents.

IX. CONCLUSIONS

In a work of this nature, the interpretation of the experimental data is often difficult because of the extreme dilution at which the experiments are run. This circumstance affects the results not only through dilution effects, but also through the presence of impurities in the reagents, which although negligible under ordinary circumstances, may materially influence some reactions. For the time being we have not tried to purify reagents beyond the ordinary quantitative analysis standards. For these reasons, although the facts and the results which have been described seem to us reasonably established, we may later change some of our current interpretations as additional research uncovers further facts in the complicated study of astatine chemistry.

The problem of data interpretation would be greatly simplified if the chemistry of iodine on a tracer scale were known. At the present time little is known of the behavior of iodine at concentrations of the order of 10^{-10} – 10^{-16} molar. Studies on this subject would also be highly desirable from the general point of view of radio-chemistry. However, such a study would be very difficult since any reagent, even of highest quality, would be likely to increase the iodine concentration unwittingly manifold.

TABLE IX. Carrying of astatine by various hydroxides.

Precipitant	Starting material			
	HNO ₃ stock solution NaOH	NH ₄ OH	HNO ₃ stock solution oxidized by hot $K_2S_2O_8$ NaOH	NH ₄ O
Aluminum hydroxide		7–15%		7–15%
Bismuth hydroxide	40–60%		50–60%	
Ferric hydroxide	40–50%	30–40%	97–99%	85–90%
Lanthanum hydroxide	5–8%		97–99%	

Unfortunately, astatine is one of the few elements which can be studied in truly carrier free solutions.

In conclusion, we shall discuss individually the various oxidation species thus far ascertained.

The Zero State

The solvent extraction experiments give ample evidence for the existence of the zero state. Since the extraction coefficients which have been measured for the halogens show a trend increasing from chlorine to iodine, we expected the corresponding coefficients for astatine to exceed numerically those of iodine. The maximum values so far determined are

	I ₂		I ₂ on tracer scale
	At	literature	experiments
Benzene	240	400	—
Carbon tetrachloride	91	85	31

The attempt at solvent extraction of I_2 on a tracer scale, using carrier free iodine from Oak Ridge, yielded the coefficient included in the data.

The zero state is very easy to prepare and is stable in water solution. It is reduced by SO_2 and oxidized by ferric salts. (See solvent extraction.) It is the form obtained when astatine is distilled from bismuth at elevated temperatures, as proved by the fact that initial extraction coefficients as high as 40 have been obtained from such distilled materials.

The zero state is slowly oxidized by cold concentrated nitric acid. Oxidized solutions, however, are readily reduced to the zero state by ferrous compounds. These same ferrous compounds are incapable of reducing the zero state to the -1 state. (There is no effect on the distribution coefficient in CCl_4 with 0.25M $FeSO_4$.)

Astatine zero appears to disproportionate in basic solutions with $pH = 13$.

The -1 State

There is little doubt as to the assignment of the -1 state. As was pointed out, the zero state is not reduced by the -1 by $0.25M$ $FeSO_4$. There is slight evidence for a slow reduction by arsenious acid (see solvent extraction data). However, sulfur dioxide and zinc reduce astatine zero. Silver iodide, precipitated after SO_2 reduction, carries astatine completely in both acid and basic solutions (see (d) under carrying experiments). Zinc reduction in sulfuric acid solution followed by silver or thallous iodide precipitation carries astatine completely. On the other hand, if the reduction is performed in the presence of silver, the astatine is found entirely in the precipitated metallic silver. Experiments described in the section on volatility of astatine showed a strong affinity of At^0 in the gaseous state for silver. This may be due to either compound formation (astatides) or adsorption upon the metallic lattice. The carrying of the astatine by the reduced silver is perhaps to be regarded as a related phenomenon, rather than as an electrochemical deposition. The difficulties described in the earlier paper¹ regarding the method of purification used by Buch-Anderson in his search for element 85 in nature are easily resolved by these results.

The Plus States

Ferric compounds are sufficiently strong oxidizing agents to oxidize the zero state to a plus

state. Br_2 rapidly and completely oxidizes astatine. (See solvent extraction studies.)

Carrying experiments with $AgIO_3$ have shown a difference between the plus states formed by Br_2 oxidation and those formed by $HClO$ oxidation. One-half hour oxidation by cold Br_2 oxidizes the astatine completely (CCl_4 extraction coefficient of 0.1 and less), and the astatine so oxidized carries poorly on $AgIO_3$ (less than 15 percent). However, oxidation by $HClO$ produces an astatine state which carries completely on $AgIO_3$, when the iodate is precipitated under the same condition as just described for the Br_2 experiment.

These experiments make it plausible that there are two positive oxidation states, one of which is formed by Br_2 oxidation, and the other by more powerful oxidation ($HClO$ or $K_2S_2O_8$).

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