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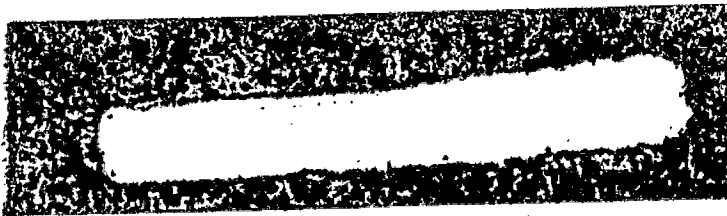
CHEMICAL PROPERTIES OF ASTATINE

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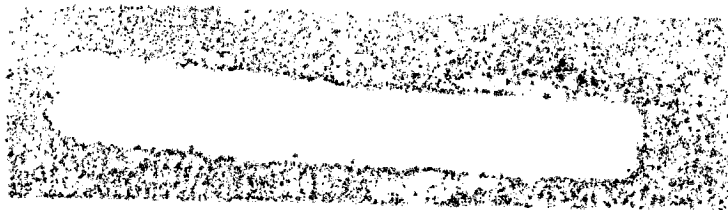
CHEMICAL PROPERTIES OF ASTATINE

Evan H. Appelman

(Thesis)

January 1960

Printed for the U. S. Atomic Energy Commission



Printed in USA. Price \$2.50. Available from the
Office of Technical Services
U. S. Department of Commerce
Washington 25, D.C.

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

-- Anatole France

CHEMICAL PROPERTIES OF ASTATINE

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January 1960

ABSTRACT

The aqueous solution chemistry of astatine has been investigated by extraction of the astatine into benzene and carbon tetrachloride and by its coprecipitation with insoluble iodides, iodates, and periodates. Some of the experiments of previous workers have been repeated and amplified.

A systematic study of the behavior of astatine as a function of the emf of an acid aqueous solution has been carried out. This study has confirmed the existence of the (-1), (0), and (+5) oxidation states, and of at least one intermediate positive state. A rough potential diagram for acidic astatine solutions has been proposed. No evidence for a (+7) state has been found. Iodine has been used as a nonisotopic carrier to fix the identity of the (0) state as AtI. In the course of this study photochemical reactions involving astatine have been observed for the first time.

The distribution of astatine between aqueous solutions and carbon tetrachloride in the presence of other halogens and halide ions has been investigated quantitatively, and evidence has been adduced for the species AtI, AtI_2^- , AtIBr^- , AtICl^- , AtBr, AtBr_2^- , and AtCl_2^- . The equilibrium constants relating these species have been determined. In connection with these studies the distribution of IBr between CCl_4 and aqueous bromide solutions has been accurately determined.

A report is given of an unsuccessful attempt to obtain quantitative information regarding the At (-1) -- At (0) couple from the reactions of astatine with the As (III) -- As (V) couple.

Incidental data is presented on the half-lives of At^{211} and Bi^{207} .

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I. INTRODUCTION

Astatine, the heaviest member of the halogen family, has no isotope of half life longer than 8.3 hr and exists in nature only in minute quantities resulting from the decay of long-lived natural radioactivities.¹ The element was first identified in 1940 after synthesis by alpha particle bombardment of bismuth.² Since then the chemistry of astatine has been the subject of a rather limited number of original papers³ and a virtually unlimited number of reviews.⁴

The dearth of original work on astatine chemistry probably results from the difficulties involved in studying a short-lived material which is available only in quantities comparable with the least of the impurities present in one's experimental system, and for which there exists no entirely satisfactory nonisotopic carrier. Grim testimony to the magnitude of these difficulties comes from the recent studies of iodine chemistry at very low concentrations.⁵ The investigators of tracer iodine have been singularly unsuccessful in attempts to explain their results in terms of the known macrochemistry of iodine. And the quantities of iodine involved in these experiments are still several orders of magnitude greater than the readily available quantities of astatine!

The investigations of astatine chemistry which have been conducted to date have established the following: When left to its own devices astatine usually is present in a relatively volatile state which has been generally assumed to be elemental At or At₂. This state will be referred to henceforth as "At(0)." Astatine in this state, either as vapor or in dilute nitric acid, has a tendency to be adsorbed by

various metallic surfaces and, less strongly, by glass. This form of astatine can be extracted from dilute nitric acid solutions by ethers, carbon tetrachloride, or hydrocarbons, although the distribution of the astatine in such extractions is variable.

From these nitric acid solutions the astatine does not coprecipitate with AgI or TlI, but partially coprecipitates with (or is adsorbed by) insoluble sulfides and hydroxides, and with metallic silver or tellurium precipitated in situ. In acid solution At (0) may be reduced by SO_2 or metallic zinc to an unextractable state which coprecipitates more or less completely with AgI and TlI and is taken to be At^- . Strong oxidants such as HOCl or persulfate oxidize astatine to an unextractable state which coprecipitates completely with AgIO_3 and which is assumed to be AtO_3^- . Less powerful oxidants such as bromine convert the astatine to a state which, although unextractable, does not coprecipitate with AgIO_3 . This is considered to be an intermediate positive oxidation state.

From several molar HCl solutions, oxidized astatine is extractable into ethers but not into hydrocarbons or CCl_4 , suggesting the formation of species such as HAtCl_2 or HAtCl_4 . Addition of hydrohalic acids to At (0) solutions renders the astatine unextractable into CCl_4 or hydrocarbons, but does not significantly alter its extractability into ethers, giving further evidence for polyhalide complexes.

An At (0) solution becomes unextractable when made alkaline, and the extractability is usually partially or completely restored when the solution is reacidified. The astatine in these alkaline solutions coprecipitates completely with AgI. This behavior is taken to indicate disproportionation of the At (0), although the complete coprecipitation with AgI is not expected.

In all solutions investigated, astatine was found to migrate in an electric field as a negative ion. It could be electrodeposited at either the anode or the cathode.

II. EXPERIMENTAL METHODS

A. Preparation and Purification of Astatine⁶

Astatine was produced by bombardment of bismuth with alpha particles in the University of California's 60-in. cyclotron. The reaction $\text{Bi}^{209}(\alpha, 2n)\text{At}^{211}$ has a threshold of 19 Mev.⁷ Above 29 Mev the $(\alpha, 3n)$ reaction sets in to give At^{210} . In order to avoid this, the alpha beam was degraded to 29 Mev or less with aluminum absorbers.

The target was reagent-grade bismuth fused or vaporized onto a 10- to 30-mil aluminum backing. The thickness of the bismuth layer was at least 100 mg/cm^2 to make full use of the beam. The back of the target was water-cooled. Heat was conducted from its face either by a flow of helium at one atmosphere or by a static half-atmosphere of helium. In some cases the target was covered with an 0.5- to 1-mil copper or 1-mil stainless steel foil. Targets were bombarded from 1 to 4 hr with a beam current of 12 to 30 μamps . Yields measured by dissolution of targets in nitric acid and direct assay agreed with the reported yield of 1.3×10^9 disintegrations/min/ $\mu\text{amp-hr}$.^{3a} This figure was therefore then taken to be 100% in estimating the yields of various purification procedures.

The investigators of the nuclear properties of astatine,⁸ as well as those who have studied its effects on biological systems,⁹ have contributed greatly to the development of methods of separating and purifying the element. These may be divided into wet methods and dry methods. The most successful wet method involves dissolving the bismuth in nitric acid, making the solution 6 to 12 M in HCl, extracting the astatine into diisopropyl ether, and back-extracting into basic solution.

The dry methods take advantage of the volatility of At (0) to remove it directly from the target. Since these methods seemed to offer less threat of introducing unknown chemical impurities than did the wet methods, they were utilized almost exclusively in this study.

Johnson et al., using bismuth targets less than 40 mg/cm^2 thick on 1-mil aluminum were able to remove the astatine quantitatively

by heating to the melting point of bismuth (271°C) in high vacuum.^{3a} The astatine could be collected on glass at liquid-nitrogen temperatures and, if desired, could be redistilled from the glass at room temperature.

In our experiments, working with much thicker bismuth layers, we found that the astatine did not leave the target in high vacuum at temperatures below 600°C . Above this temperature the bismuth itself distilled, carrying the astatine with it. A stream of nitrogen at a few millimeters pressure permitted the removal of 5 to 15% of the astatine from the target.

The redistillation from glass was not as straightforward as Johnson et al. found it. It was usually necessary to heat the glass to well above room temperature before the bulk of the astatine distilled. The astatine was very probably being adsorbed by impurities which condensed along with it. A discoloration of the glass was frequently observed at the point where the astatine was deposited.

We did, however, find it possible to distill the astatine from the target in air, as was done by Barton et al.⁸ The astatine began to come off at the melting point of the bismuth, but was most nearly completely removed at 700 to 800°C . From 40 to 80% of the astatine could be removed from the target in this way.

The discrepancy between this behavior and that reported by Johnson et al. is marked and hard to explain. Bismuth is a rather poor thermal conductor. Possibly the interior of a thick target is heated by the alpha beam to a temperature at which the bismuth reacts with the astatine, forming a relatively nonvolatile astatide which is decomposed upon heating in air to bismuth oxide and free astatine. We have found that hot bismuth reacts rapidly and completely with iodine vapor in a vacuum system.

If distilled in air, the astatine may be collected on a cooled platinum or silver foil suspended above the heated target. The condensed astatine is held on these foils with surprising tenacity. Very little of the astatine is normally removable when the foil is washed with hot water, methanol, or benzene. When the foil is heated in vacuum the

astatine does not distill below about $130^{\circ}\text{C}.$, and complete removal from the plate often requires temperatures as high as $500^{\circ}\text{C}.$

On the basis of these observations the following purification method for astatine was devised and utilized throughout most of this study: The target was placed in a stainless steel vessel open to air and the vessel was heated to $270^{\circ}\text{C}.$ in an electric furnace to remove volatile impurities. A water-cooled 1-mil platinum plate was suspended over the target, the temperature of which was then raised to $800^{\circ}\text{C}.$ over about 30 min. The apparatus was agitated occasionally to break up any oxide film which might trap the astatine within the bismuth.

The platinum plate, containing the astatine and a small quantity of bismuth and bismuth oxide, was transferred to a quartz tube which was attached to the end of a vacuum line incorporating a detachable u-tube. The line was evacuated to a pressure less than 10^{-4} mm of Hg, and the platinum was heated to $130^{\circ}\text{C}.$ with a small electrical furnace to further remove volatile impurities. A slush bath of dry ice in a 1:1 CCl_4 - CHCl_3 mixture was placed around the u-tube, to which the astatine was transferred by heating the platinum foil to $500^{\circ}\text{C}.$ in about 10 min. The dry-ice bath was used in preference to liquid nitrogen to minimize condensation of impurities.

After the transfer of astatine was complete, the cooling bath was removed, the vacuum broken, and the u-tube taken off the line and washed with 0.5 to 1 ml of an aqueous solution appropriate to the experiments to be carried out with the astatine. The yield of astatine for the entire process was 20 to 30%, and the resulting stock solution contained about 10^{10} disintegrations/min of At^{211} and was about 10^{-8} M in astatine. (In typical experiments the At concentration would be 10^{-13} to 10^{-15} M.)

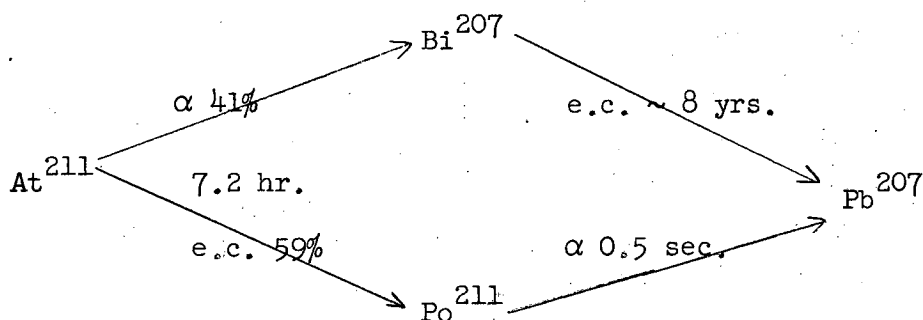
Nitric acid stock solutions (0.01 to 1 M) were used for most of the experiments in Section III, but perchloric acid stocks were used in all later experiments.

Astatine is rather strongly absorbed by ordinary hydrocarbon vacuum greases, but not by Dow Corning silicone vacuum grease. The latter was used in early vacuum work, but was later abandoned because

of its tendency to spread over the glassware in its vicinity. Instead a heavy fluorocarbon fraction -- Hooker Chemical Corporation's Fluorolube HG 1200 -- was used. Although the physical properties of this material make it a rather poor grease, it should have complete chemical inertness, and it was, in fact, found to have only a slight tendency to absorb astatine.

B. Assay Methods

At²¹¹ has the following decay scheme:¹⁰



Thus the astatine may be assayed either by counting the alpha particles or by counting the x-rays accompanying its electron capture.

Alpha counting was carried out in either an argon-flow ionization chamber or in a methane-flow alpha proportional counter, both with closely the same geometry of approximately 51%. The alpha-assay techniques relied on the fact that under certain conditions metallic foils tend to retain the astatine present in solutions evaporated to dryness on them, even though the astatine is present in the solution in what would normally be considered a volatile form. The effect of varying conditions has been investigated, and the results are shown in Table I.

The relative retention of astatine from benzene and CCl₄ solutions was obtained by comparison of the alpha-counting results with the results of direct x-ray counts of aliquots of the solutions, with the efficiency of the latter assumed to be the same for organic and aqueous solutions (see discussion of scintillation counting to follow). The ratio of x-ray

Table I

Retention of astatine from solutions evaporated on various metals ^a		
Composition of solution	Metal	Relative retention
12 M HCl	Pt	1.0
3 M HCl	Pt or Ag	1.0 ± .01 ^{b,c}
1 M HCl	Pt	1.0
0.2 M HCl	Pt	0.9
16 M HNO ₃	Pt	~0.5 ^{b,d}
3 M HNO ₃	Pt	0.7 ± .1 ^b
1.5 M HCl + 1.5 M HNO ₃	Pt	1.0
15 M NH ₄ OH	Pt	0.9
0.1 M NaOH	Pt	0.9
0.01 M NaOH	Pt	0.9
Water	Pt	0.8 ± .1
Benzene or CCl ₄	Pt or Ag	0.64 ± .07 ^e
CCl ₄	Pt	0.14, 1.0 ^e
3 M HCl or 3 M HNO ₃	Ta	0.5 ^{d,f}
3 M HNO ₃	Al	0.4 ^{d,f}
3 M HNO ₃	Stainless steel	0.1 ^{d,f}

^aIn the case of aqueous solutions 5 to 50 microliters (μl) of an At(0) stock were added to ~100 μl of the indicated solution on the metal plate. The mixture was then evaporated to dryness under an infrared heat lamp. Aliquots of organic astatine solutions were placed in depressions stamped into the metal plates and were allowed to dry at room temperature.

^bThe activity was not changed by prolonged heating of the dried plate under an infrared lamp.

^cSaturation of the 3 M HCl stock solution with SO₂ did not alter the retention.

^dResults varied by as much as a factor of 2.

Notes to Table I (concluded)

^e"Normal" values around 0.64 were obtained from CCl_4 and benzene solutions of astatine which were made by extracting aqueous At(0) stocks containing no reagents other than dilute HNO_3 or HClO_4 . The low value was obtained from a CCl_4 solution which had been washed repeatedly with portions of an aqueous solution 0.1 M in HClO_4 , 0.1 M in $\text{Fe(ClO}_4)_3$, and 0.001 M in $\text{Fe(ClO}_4)_2$. The high value was obtained from a CCl_4 solution which had been washed repeatedly with a solution 0.1 M in HClO_4 , 0.01 M in $\text{Fe(ClO}_4)_3$, and 0.1 M in $\text{Fe(ClO}_4)_2$. Solutions of astatine in CCl_4 prepared by extracting the astatine from either of these ferrous-ferric solutions with fresh CCl_4 gave "normal" retention values.

^fMuch activity was lost from the dried plate upon prolonged heating under the infrared lamp.

activity to alpha activity was always constant to within a few percent in the case of aqueous solutions if the alpha assays were made by evaporation of 3 M HCl solutions on platinum or silver. However, when this ratio was measured for different benzene or CCl_4 solutions, the considerable variations shown in the table were found, even though duplicate alpha counts of the same benzene or CCl_4 solution agreed to within a few percent. These variations were confirmed by the material balance in solvent-extraction experiments.

It is not unlikely that the retention of astatine when organic solutions are evaporated on metallic foils is strongly dependent on impurities in the solutions. The observed effect of reagents such as ferric and ferrous ions may be on these impurities rather than directly on the astatine.

Even from aqueous solutions the causes of the retention remain unknown. The highest and most reproducible retention was obtained when astatine solutions were evaporated on silver or platinum foils from 3 M HCl, although it has not been established that the retention is complete even in this case. However this method of evaporation was routinely used for alpha assay of aqueous astatine solutions.

All in all, analysis of solutions by alpha counting left much to be desired. Even aside from the irreproducibility sometimes encountered, self-absorption by solid residues on the plates often made the results quite uncertain. Therefore methods were developed for counting the x-ray activity of the unevaporated solutions with a sodium iodide scintillation counter.

Aliquots of the solutions were added to a quantity of solvent sufficient to yield a constant final volume (either 0.5 or 1.0 ml) in a small glass vial. Either 2 M HClO_4 or 2 M H_2SO_4 was used as the solvent for assay of aqueous astatine solutions, and technical-grade butyl carbitol (Griffin Chemical Co.) for organic assays. In the earlier part of this study, vials 1/2 in. in diam. and 1/2 in. high were counted beneath a standard cylindrical thallium-activated sodium iodide crystal 1 in. thick and 1-1/2 in. in diam. with a 0.032-in.-thick aluminum cap.

Later a special crystal 1 in. thick and 1-3/4 in. in diam. with a 0.01-in.-thick aluminum cap and containing a well of 5/8 in. diam. and 1/2 in. depth was used, and the vials were placed in the well. For some experiments a second crystal 1/2 in. thick and 1-3/4 in. in diameter with a cap 0.01 in. thick was mounted above the well so that after the vial had been put in place the two crystals could be brought together face-to-face. The photomultipliers attached to the two crystals were connected to the same counting unit, giving a 4π counting geometry. However, the high geometry was found not to be worth the added background from the second crystal, and it was later eliminated, reducing the geometry to about 70%. Samples were thereafter placed in standard 1-dram vials (Kimble Glass Co.). All sodium iodide crystals used were made by the Harshaw Chemical Co.

In order to reduce the high background ordinarily encountered with sodium iodide scintillators, the counter was operated as a single-channel analyser with a large window "sitting on" the ~ 90 kev K-x-ray peak of the Po^{211} . In this way, backgrounds as low as 7 counts/min could be obtained, while still counting 40% of the x-rays to which the crystals responded.

Since butyl carbitol is miscible with water as well as with benzene and CCl_4 , its absorption of the x-rays could be compared directly with that of water. The difference was found to be negligible, as was the difference in absorption between aqueous solutions of various compositions. However, in cases in which appreciable amounts of CCl_4 were added to the carbitol with the astatine, a correction of a few percent was necessary to account for the greater absorption of x-rays by the CCl_4 .

Precipitates were slurried into the vials with n-propanol for counting. Since the precipitate settled to the bottom of the vial, it counted with a higher efficiency than did solutions, and a suitable correction had to be made. This amounted to 4% relative to solutions assayed at a volume of 0.5 ml, and 10% relative to those assayed at a volume of 1 ml. This correction was not applied for samples counted with the 4π -geometry setup. A small correction was also necessary for

x-ray absorption by the precipitates themselves. For the precipitates used in this study, this correction amounted to about 4% per 10 mg of precipitate.

Unless otherwise specified, alpha counting was used for all assays in Section III except the assay of precipitates. X-ray counting was used exclusively for the assays of Sections IV and V.

Decay corrections were, of course, always necessary in this work. Since there was some disagreement in the literature¹⁰ over the half life of At^{211} , a reasonably accurate determination of its value seemed worthwhile. Samples were prepared for alpha counting by evaporation onto platinum from 3 M HCl and were counted long enough to obtain 10,000 counts, except in some cases when the activity had decayed to such a level that this was impractical. Coincidence correction was made at a rate of 1% per 100,000 counts/min.

Larger aliquots of the same stock solutions were plated to determine the residual alpha activity after the decay of the astatine. This residue was identified by pulse-height analysis as Po^{210} and corresponded to an initial $\text{At}^{211}/\text{At}^{210}$ ratio of ~ 2500 .

Half-life values were determined by a visually fitted best straight line on a semi-logarithmic plot to give the results shown in Table II.

In accordance with these results, a half life of 7.22 hr was used in correcting for decay. In general, related samples were counted at nearly the same time to minimize this correction. When it was necessary to compare samples counted at considerably different times, a decay curve was usually obtained for a standard made from the same stock solution as the samples.

Samples of precipitates and aqueous solutions which were x-ray counted 3 days or more after the end of a bombardment were allowed to decay for several more days and were then recounted for residual Bi^{207} activity, which had to be subtracted from the original count. The amount of radiobismuth found varied erratically, much of it tending to deposit on the walls of reaction vessels, from which it could be dislodged by

Table II

Half-life of At ²¹¹		
Initial activity (counts/min)	Days followed	Half life (hr)
18,000	2.3	7.28
8700	2.1	7.04*
18,000	2.1	7.24
8300	2.0	7.18
75,000	2.7	7.19
73,000	3.1	7.23
Mean (excluding *)		7.22 ± .03
Literature Values: ¹⁰		7.20
		7.5

concentrated HCl. The results seemed to indicate that in solutions of low acidity the bismuth was not in solution but was present as a "radiocolloid," probably deposited on dust particles in the solution.

The ratio of At^{211} activity at the end of the bombardment to residual Bi^{207} activity appeared to be within a factor of two of 1×10^5 . If the half life of Bi^{207} is really 8 yr, this ratio should be only 7×10^3 . The most plausible explanation of the enormously greater observed ratio is that the true half life of Bi^{207} is of the order of 100 yr. Values as high as 50 yr have been reported.¹⁰

All assays in the rest of this study were counted to a total of at least 400 counts, except for a few assays of extremely low-activity solutions and precipitates, which were counted to a total of at least 100 counts. Assays in Section V were counted to at least 1600 counts.

C. Reagents

All reagents were commercial products of reagent grade unless otherwise specified. Mallinckrodt low-sulfur CCl_4 and water redistilled from an alkaline permanganate solution were used for the experiments of Sections IV and V, and for those of Section III in which their use is specifically indicated. Otherwise, singly distilled water and Baker and Adamson reagent grade CCl_4 were used.

Sodium and barium perchlorate solutions were prepared by dissolving the respective hydroxides in a stoichiometric quantity of perchloric acid. A lead perchlorate solution was prepared from lead carbonate and an excess of perchloric acid, resulting in a 1 M $(\text{Pb}(\text{ClO}_4)_2)$ solution 0.1 M in HClO_4 . When a smaller excess of acid was desired, it was necessary to filter the solution to free it from basic lead salts. In this way a 1 M $\text{Pb}(\text{ClO}_4)_2$ solution 0.01 M in HClO_4 was obtained.

Thallous perchlorate was prepared in two ways. Chemically pure grade (cp) thallous chloride (Fisher Scientific Co.) was fumed with HClO_4 to remove chloride. The solution was diluted and boiled to reduce any thallic ion which might have been formed. The resulting 0.25 M TlClO_4 -- 0.5 M HClO_4 solution was tested for thallic ion by precipitation of TlI . If thallic ion was present, TlI_3 would be precipitated,¹¹

and I_2 could be removed from the precipitate by washing with acetone, giving the wash a yellow color. A positive test was obtained in the freshly prepared solution, but after the solution had stood for a few weeks a negative test resulted. At this later time also, the electromotive force (emf) of a platinum electrode immersed in the solution was within 10 millivolts of its value in a $TlNO_3$ solution prepared by dissolving the cp salt (Fisher). Nor was the emf altered after the solution had been boiled with metallic thallium.

Later a quantity of cp $Tl_2(CO_3)$ (Fisher) was obtained, from which a $TlClO_4$ solution was prepared by addition of a stoichiometric quantity of $HClO_4$. It was necessary to filter the solution to free it from an insoluble residue. Thallium perchlorate solutions prepared in these two ways gave indistinguishable results in astatine experiments, nor were different results obtained with $TlNO_3$ solutions.

Ferrous perchlorate solutions were prepared by dissolving iron wire in excess hot 0.5 M $HClO_4$. The solution was cooled and filtered before the iron was quite completely dissolved. An 0.2 M $Fe(ClO_4)_2$ -- 0.2 M $HClO_4$ solution made in this way could be kept several months without more than a few percent of the ferrous ion being oxidized. Ferric perchlorate solutions were made by fuming ferrous perchlorate solutions with perchloric acid and diluting; they were found by potentiometric titration to contain less than 0.05% of the iron as Fe^{++} .

Solutions of VO_2ClO_4 were prepared by dissolving cp NH_4VO_3 (City Chemical Corporation of New York) in dilute NaOH and rapidly adding an excess of perchloric acid. City Chemical Corporation's cp vanadyl sulfate was used as a source of vanadium (IV).

Because certain experiments in Section V involved high Cl^-/I^- or Br^-/I^- ratios (see Tables XXV and XXVII), NaCl and NaBr stock solutions were tested for iodide by oxidation to iodate, followed, after boiling to remove excess oxidant, by reduction with iodide to I_3^- and detection with starch.¹² Bromine was the oxidant used for analysis of the chloride solutions, while the bromide solutions were oxidized with excess chlorine in 0.2 M acid. Lower limits of 2×10^6 and 1×10^6 were found respectively for Cl^-/I^- in the NaCl solutions and Br^-/I^- in the NaBr solutions.

In general the concentrations of solutions were determined simply on the basis of the weight of air-dried reagent, or the volume of concentrated acid used, leaving the concentration known to $\pm 10\%$ in the worst cases. Exceptions are the sodium perchlorate, sodium halide, and halogen solutions used in Section V. The NaClO_4 solutions were analysed gravimetrically by conversion to Na_2SO_4 .¹³ The halide solutions were analysed either gravimetrically or volumetrically by the Fajans method.¹⁴ Determination of the concentrations of the halogen solutions will be discussed in the following paragraphs.

Saturated iodine solutions were prepared in low-sulfur CCl_4 and in 0.001 M HClO_4 , and were stored in teflon-stoppered bottles (q.v.) at $21 \pm 0.5^\circ\text{C}$. A small volume of 0.001 M HClO_4 was kept in equilibrium with the CCl_4 solution to wash out any iodide that might form, although the saturated aqueous iodine solution did not develop a detectable halide concentration over several months. From solubility data the I_2 concentrations of the saturated aqueous and CCl_4 solutions should be respectively 0.00117 and 0.099 M .¹⁵ The concentration of the CCl_4 solution was measured by titration with thiosulfate¹² and was found to be 0.100 . This value was used in calculations, along with the literature value for the concentration of the aqueous iodine solution.

Bromine solutions in low-sulfur CCl_4 were generally made up directly from a measured volume of liquid bromine equilibrated with and stored under 0.01 M HClO_4 at 21 to 23°C . The molarity of the bromine was taken to be 19.5 .¹⁶ For some experiments a freshly prepared saturated solution of bromine in 0.01 M HClO_4 at $21.5 \pm 0.5^\circ\text{C}$ was used, its concentration being taken as 0.215 M .¹⁵

Fisher Scientific Co. "Purified" IBr was dissolved in low-sulfur CCl_4 to make a 0.5 M solution, which was tested for an excess of either parent halogen by extracting away the IBr with several portions of 1 M NaBr and examining the residual CCl_4 . In this way the solution was found to be about 0.02 M in excess bromine. It was then titrated with a saturated iodine solution in CCl_4 to give a final solution with a $1 \times 10^{-4} \text{ M}$ excess of iodine. The solution was analysed iodometrically,¹² and it was stored in a Teflon-stoppered bottle in equilibrium with a small volume of 2 M HClO_4 .

Solutions of these halogens, particularly bromine solutions and aqueous iodine solutions, were generally made up from these stocks within a few days of their use. All halogens were kept in black-taped, Teflon-stoppered vessels.

A 0.0015 M I_2 solution in CCl_4 was found to be completely stable over two weeks. However the concentrations of unsaturated aqueous iodine solutions often decreased visibly within a few days. Solutions of Br_2 in CCl_4 decreased slowly in concentration, the decrease amounting to 0.5 to 1% per day. A 0.001 M IBr solution in CCl_4 , stored under a small quantity of 1 M $HClO_4$, did not show a detectable concentration change in a week.

Chlorine stock solutions were prepared by saturating water or dilute perchloric acid with Matheson chlorine passed in through Teflon and glass tubing. The solutions were prepared within a few days of their use and were stored in the dark at 1 to 2°C in Teflon-lined screw-capped bottles. Some of the solutions were analysed by adding an aliquot to excess iodide and determining the resulting triiodide spectrophotometrically. When initially prepared, the solutions were approximately 0.07 M in stoichiometric chlorine (if no acid was present) but lost chlorine at the rate of 30 to 40% per day. Chlorine solutions used in individual experiments were not usually analysed, the loss of chlorine being only roughly estimated. Therefore the chlorine concentrations quoted for various experiments are probably accurate to no better than $\pm 50\%$.

D. Apparatus

Solutions used in this work were allowed to contact only glass and Teflon. Teflon stoppers machined to fit standard taper sockets were found very convenient, particularly in solvent-extraction experiments, since liquid did not leak around them.

Volumetric ware, consisting of 1- μ l to 1-ml micropipets, 1-ml and larger conventional volumetric flasks and pipets, and, in less critical work, 5-ml and larger graduated cylinders, was generally used without further calibration. Micropipets of 100 μ l and smaller capacity were used "to contain," and were rinsed. Larger micropipets were used either "to

contain" or "to deliver," the difference amounting to no more than 0.5%. In quantitative studies, micropipets smaller than 5 μ l were rarely used.

Glassware was routinely cleaned with 5% aqueous HF and/or hot fuming nitric acid. Teflonware was cleaned by treatment successively with boiling aqua regia, methanol, boiling benzene, and CCl_4 . It was then baked overnight at 230°C.

E. Solvent-Extraction Procedures

Solvent extractions were carried out in glass- or Teflon-stoppered 1 to 2 ml volumetric flasks, or, occasionally, in small graduates. The former were centrifuged to separate the phases; the latter were allowed to settle until no droplets of either phase were visible in the other. Unless otherwise specified, extraction mixtures were agitated 1 to 2 min in the experiments of Sections III and IV, and 2 to 6 min in the experiments of Section V.

The cross-contamination problem was most severe when it was necessary to assay a carbon tetrachloride phase through an aqueous phase of much greater activity. Even in this case, with suitable care it was possible to keep cross contamination below 0.02%. When the CCl_4 contained less than 0.1% of the activity, it was separated and recentrifuged before an aliquot was taken for assay.

F. Coprecipitation Procedures

Coprecipitations were carried out by mixing the carrier, (iodide, iodate, or periodate) with the astatine solution in a centrifuge cone, and then adding an excess of the precipitating ion. In the case of all precipitates except $\text{Ba}(\text{IO}_3)_2$ and possibly KIO_4 , precipitation was complete within a few minutes. The precipitate was centrifuged, the supernate was withdrawn and assayed, and the precipitate was washed one or more times with a suitable aqueous wash solution. When the precipitate carried only a very small portion of the activity, at least two washes were always used. In certain cases the precipitate was also washed with acetone.

The aqueous washes were either assayed independently or were combined with the supernates. Acetone washes were always assayed independently.

The precipitates were slurried into counting vials with n-propanol (Eastman Kodak Co., White Label), which was effective in dislodging them from the walls of the cones. In a few of the experiments in Section III, the precipitates were filtered rather than centrifuged and were mounted on flat aluminum cards for counting under the conventional type of sodium iodide crystal.

Table III gives the procedures generally used for specific precipitations. Exceptions will be noted as they arise.

G. Temperature Control

Experiments were carried out at room temperature, usually 21 to 23°C, unless otherwise specified. The controlled-temperature experiments in Section V were carried out in a room thermostated at $21 \pm 0.5^\circ\text{C}$.

Table III

Precipitate	Carrier conc. (M)	pH before precipitation	Precipitation procedures		Wash solution
			Excess conc. of precipitant (M)	Precipitant solution used	
AgI	0.02	1 to 3	0.04	0.5 M AgNO ₃	0.01 M AgNO ₃ -- 0.01 M HClO ₄
PbI ₂	0.04	1 to 3	0.1	1 M Pb(ClO ₄) ₂ , pH 1 ^a	0.05 M Pb(ClO ₄) ₂ , pH 2.3, followed by acetone ^b
TlI	0.02	1 to 7	0.04	0.25 M TlNO ₃ or TlClO ₄ ^c	0.05 M TlNO ₃ -- 1% HOAc ¹⁷ followed by acetone
Ba(IO ₃) ₂	0.05	2	0.1	0.6 M Ba(ClO ₄) ₂ , pH 2 ^{a,d}	0.1 M Ba(ClO ₄) ₂ , pH 2
AgIO ₃	0.05	0.3	0.1	0.5 M AgNO ₃	0.1 M AgNO ₃ -- 0.4 M HClO ₄
Pb(IO ₃) ₂	0.02	1 to 3	0.05	1 M Pb(ClO ₄) ₂ , pH 1	0.05 M Pb(ClO ₄) ₂ , pH 2.3
KIO ₄	0.2 M H ₂ IO ₆ -- 0.04 M NaIO ₃	2	0.9	2 M KNO ₃ -- ^{a,e} 0.1 M NaOH	no wash

^a Precipitation was carried out at 0°C.

^b Only a single aqueous wash was used.

^c The neutral 0.25 M TlNO₃ or a 0.25 M TlClO₄ solution at pH 3 was used as the source of precipitant for experiments in Section III. A solution 0.25 M in TlClO₄ and 0.5 M in HClO₄ was used in Section IV unless otherwise specified.

^d After the precipitant had been added, the mixture was allowed to stand for 1 to 2 hr in an ice bath before being centrifuged.

^e The mixture was allowed to stand for 30 to 60 min in an ice bath before being centrifuged. Note that addition of the precipitant doubles the volume of the solution. After the precipitation, the supernate is ~0.05 M in HNO₃.

III. PRELIMINARY EXPERIMENTS

In view of the irreproducible behavior generally attributed to astatine, it seemed worthwhile to initiate this study with efforts to duplicate some of the earlier work. In general these efforts resulted in confirmation of the earlier results. In this section I shall report the few discrepancies which were observed, as well as such of my results which augment the previous studies.

A. Adsorption of Astatine on Glass

The tendency of astatine to be adsorbed onto the walls of vessels has always interfered greatly with attempts to study its chemistry. This tendency seems to be primarily a property of At (0) in aqueous solutions. Organic solutions and solutions of oxidized or reduced astatine are reported to be much more stable to loss of activity to the walls. On the other hand, it has appeared that this property of astatine might provide a method for separating it from other elements.

Two types of experiment were conducted. In the first type about 0.3 g. portions of washed Pyrex wool were added to 1 ml volumes of various solutions containing At (0). The solutions were allowed to stand undisturbed except for periodic withdrawal of aliquots for assay. A comparison experiment, covering a more limited range of solution compositions, was conducted with carrier-free solutions of RaDEF (Pb^{210} , Bi^{210} , and Po^{210}).

In the experiment of the second type, 0.1 g. of glass wool was added to 1 ml of a 0.05 M HNO_3 solution containing At (0) and RaDEF. Four ml of a 0.1 M NH_4NO_3 -- 0.2 M NH_3 solution were added. The mixture was agitated briefly and then allowed to stand for 30 min, after which it was filtered with suction through a sintered-glass frit. The glass wool was leached first with water, then with concentrated HCl.

In all of the experiments, the astatine and polonium were determined by alpha counting dried aliquots at once and again after the astatine had decayed away. The bismuth was determined by immediate beta counting

through 12 mg/cm² of aluminum with an end-window methane-flow proportional counter, and the lead was determined by repeating the beta count several years later, after secular equilibrium had been reestablished. The results of these experiments appear in Tables IV and V.

It appears that undisturbed alkaline At (0) solutions, or those in strong HCl are stable to loss of activity to glass, while others show a partial loss which varies erratically in magnitude. The losses are greatly enhanced by agitation, but in no case is the removal of astatine from solution complete. This is in marked contrast to the behavior of bismuth and polonium, which under at least some conditions can be almost quantitatively removed from solution. It appears that the deposited activity can be largely, but not completely, brought back into solution by leaching the glass with HCl.

Efforts have been made to explain the adsorption of tracer metal ions on glass in terms of replacement of the hydrogen in Si--O--H groups.¹⁸ This explanation does not appear too likely in the case of astatine, which does not seem to form positive ions in solution. It is more probable that the astatine is adsorbed as a neutral molecule. It may also be that the adsorption behavior is influenced as much by the impurities in the solution as by its macro components.

B. Solvent Extraction Behavior of At (0)

In the early solvent-extraction experiments, astatine has shown a characteristic behavior pattern. If an aqueous At (0) solution is extracted with benzene or CCl₄, the distribution coefficient,

$$D = (\text{total At in organic phase})/(\text{total At in aqueous phase}),$$
is found to have a variable value between one and ten. If the organic phase is washed with successive portions of fresh aqueous solution, the amount of At back-extracted decreases gradually from wash to wash until the activity left in the organic phase is almost completely unextractable into water. Likewise, if the initial aqueous phase is washed with successive portions of the organic solvent, one is ultimately left with an aqueous solution from which very little activity can be extracted.

Table IV

Adsorption of At(0) onto glass from undisturbed aqueous solutions ^a		
Solution	Time (hr)	Fraction of At left in solution
0.5 M HNO ₃	24	0.7
0.5 M HNO ₃ ^b	44	0.25
0.15 M HNO ₃	6	0.93
	20	0.69
	48	0.52
0.01 M HNO ₃	12	0.62
	39	0.44
0.001 M HNO ₃	5	0.88
	20	0.84
	40	0.80
3 M HCl	22	1.0
	49	0.91
0.5 M HCl	46	0.59
0.1 M HCl	24	0.62
0.1 M NH ₄ NO ₃	27	0.89
0.1 M NH ₄ NO ₃ ^b	19	0.79 ^c
0.1 M NH ₄ NO ₃ ^b	46	0.69
Water in equilibrium with air	5	0.70
	49	0.70
0.1 M NH ₄ NO ₃ -- 0.2 M NH ₃	27	1.0
	49	0.95 ^d
0.1 M NaOH (carbonate-free)	49	1.0
0.1 M NaOH (carbonate-free) ^b	46	0.95

^aInitial At concentrations were $\sim 5 \times 10^{-13}$ M. Comparison experiments were run with RaDEF in 0.12, 1.2, and 12 M HCl and in 0.2, 1.5, and 15 M HNO₃. All of these solutions were stable over one day to loss of bismuth or lead. All but the 0.2 M HNO₃ solution were stable over 12 days to loss of polonium. The 0.2 M HNO₃ solution retained 79% of its polonium over one day and 73%

Notes to Table IV (concluded)

over 12 days. Initial concentrations were: $\text{Pb}^{210} \sim 4 \times 10^{-10}$, $\text{Bi}^{210} \sim 3 \times 10^{-13}$, and $\text{Po}^{210} \sim 10^{-11}$ M. The total Pb and Bi concentrations may have been much greater, however, due to contamination with impurity lead and bismuth.

^b Duplicate experiments.

^c This solution was now agitated and filtered. The filtrate contained only 33% of the initial astatine.

^d See Table V for the behavior of an agitated solution of this composition.

Table V

Adsorption onto glass of At(0), and of tracer lead, bismuth, and polonium from an agitated and filtered solution of pH 9.7 ^a				
Solution	Fraction of initial activity			
	Pb	Bi	Po	At
Filtrate	0.54	0.06	0.06	0.34
H ₂ O leach	0.07	0.01	0.01	0.02
First conc. HCl leach	0.16	0.63	0.66	0.20
Second conc. HCl leach	<u>0.01</u>	<u>0.02</u>	<u>0.01</u>	<u>0.01</u>
Total recovered	0.78	0.72	0.74	0.57

^aInitial At concentration $\sim 2 \times 10^{-12}$ M. Concentrations of RaDEF were were approximately half those in the experiments of Table IV (note a).

This behavior would seem to indicate the presence of at least three astatine species of varying degrees of extractability. Eiland observed similar behavior with iodine at low concentrations, and was able to isolate, but not identify, the species involved.^{5d}

A series of experiments was carried out to determine to what extent this behavior was affected by variations in the nature and purity of the phases, by control of the oxidation potential of the aqueous phase, or by the exclusion of air and light. The results of these experiments are shown in Table VI. It appears that the general trend of the behavior is but little dependent on these factors. However it is of interest that my D values tend to be consistently lower than those of Johnson *et al.*^{3a} The time dependences noted are probably due to impurity reactions. Similarly, the apparent effect of dilution (note d) is more likely due to impurities introduced with the diluting solvent than to any true concentration dependence of the extraction.

Table VII shows the results of some experiments on the effects of halide ions on the extractability. The extractability is depressed at halide concentrations considerably below the $>1M$ concentration range investigated by earlier workers, bromide ion having a greater effect than chloride. However, the rather marked and erratic time dependences displayed in some of these experiments suggest that something other than a simple complexing reaction is involved. The effect of iodide on the extraction of astatine is investigated at length in Section V.

C. Coprecipitation Behavior of Astatine

In Table VIII certain of my coprecipitation results are compared with the results of similar experiments reported by Johnson *et al.* It is seen that in some cases At (0) is partially coprecipitated with AgI and TlI, while in other cases it does not appreciably coprecipitate with either. In the former cases redistilled water was used, and the astatine was stocked in perchloric acid solutions. In the latter cases, only single-distilled water was used, and the astatine was stocked in nitric acid. The fact that addition of nitric acid to systems of the first type

Table VI

Solvent extraction of At(O) ^a						
Experiment						
	I	II	III ^b	IV	V	VI ^c VII ^c
Nature of stock ^d	0.02 M HNO ₃	0.01 M HClO ₄	0.001 M HClO ₄ , redistilled H ₂ O	0.01 M HClO ₄	0.001 M HClO ₄	Conc. HNO ₃ diluted to 0.5 M before stock was used.
Aqueous medium	0.01 M HNO ₃	0.01 M HClO ₄	0.001 M HClO ₄ redistilled H ₂ O	0.1 M HClO ₄ 0.1 M Fe(ClO ₄) ₃ 0.01 M Fe(ClO ₄) ₃	0.1 M HClO ₄ 0.001 M Fe(ClO ₄) ₃ 0.1 M Fe(ClO ₄) ₃	0.0001 M HNO ₃
Organic phase	Benzene	CCl ₄	Low sulfur CCl ₄	CCl ₄	CCl ₄	Benzene CCl ₄
Assay method	α	α	X-ray	X-ray	X-ray	? ?
D value	5.7	5.9	2.2	2	3	46 10
Initial aqueous phase + Fresh organic phase 1.0(1.6) ^f		0.39	0.88	0.64	0.64	
2nd fresh organic	0.39	0.39	0.41	0.15	0.54	
3rd fresh organic	0.26	Not assayed		0.15(0.33) ^g	0.32(1.0) ^g	
4th fresh organic	0.16	0.41 ^g				
5th fresh organic	0.12					
6th fresh organic	0.11					
7th fresh organic	0.10 ^g					

Table VI (cont'd)

Initial organic phase ^a	Experiment					
	I	II	III ^b	IV	V	VII ^c
Fresh aqueous phase	22	12	9.5	18	6	53
2nd fresh aqueous	35	21	13	35	13	64
3rd fresh aqueous	21(?)	Not assayed		51(17) ^g	22(11) ^g	90
4th fresh aqueous	37	31 ^g				242
5th fresh aqueous	53					227
6th fresh aqueous	60					
7th fresh aqueous	64					
8th fresh aqueous	69					
9th fresh aqueous	70 ^g					

^aThe volumes of the two phases were approximately equal. Agitation times were 1 min, except in Expt. III, in which they were 5 min.

^bThis experiment was carried out at $21 \pm 0.5^\circ\text{C}$ in black-taped tubes with solutions saturated with pure nitrogen. All operations were performed under the illumination of a Wratten series-1 Safelite, using a 40-watt bulb.

^cThese experiments were reported by Johnson, Leininger, and Segre. ^{3a}

^dAll At was separated by double distillation.

^eInitial D values, while varying from system to system, showed little or no change when the two-phase system was allowed to stand for as long as 24 hr with intermittent agitation.

Notes to Table VI

f The value in parentheses was obtained after the system had stood overnight and was reagitated for 1 min.
g If a repeatedly washed aqueous phase was allowed to stand overnight in contact with a fresh organic phase and then was reagitated, a several-fold increase in D was generally noted. If, on the other hand, a repeatedly washed organic phase was allowed to stand overnight in contact with a fresh aqueous phase and was then reagitated, a several-fold reduction in D was usually found. The altered values are indicated in parentheses for several of the experiments.

When a portion of a repeatedly washed benzene solution showing a D of 73 was diluted 80-fold and washed with 0.01 M HNO_3 , a D value of 43 was obtained.

Table VII

Effect of halide ions on the extractability of At(0) into CCl_4 ^a		
Halide	Time	D
Series I ^b		
0.1 M NaCl	1 hr	0.95
0.1 M NaCl	3.5 hr	0.055 ^d
0.01 M NaCl	1 hr	12
0.001 M NaCl	1 hr	12
Series II ^c		
0.09 M NaCl	5 min	0.45
	30 min	1.2
0.011 M NaBr	5 min	0.54
	30 min	2.6

^aEqual volumes of the two phases were used.

^bThe astatine was introduced as a portion of an organic phase which gave a D of 30 when extracted with 0.01 M HClO_4 . Mixtures were agitated approximately 1 min out of every fifteen for the total time indicated. The aqueous phase was 0.01 M in HClO_4 plus the indicated concentration of NaCl. The astatine stock had been 0.01 M in HClO_4 .

^cThe astatine was introduced as a portion of an aqueous phase, 0.001 M in HClO_4 , another portion of which had given a D of 2.2 when extracted with low-sulfur CCl_4 . Mixtures were agitated continuously for the time indicated in black-taped tubes. The aqueous phases were 0.001 M in HClO_4 plus the halide concentration indicated. Redistilled water and low-sulfur CCl_4 were used in this series, and assays were made by x-ray counting of solutions. The original astatine stock was 0.001 M in HClO_4 and was made with redistilled water.

^dThis was a duplicate of the first experiment, using another preparation of astatine. When the aqueous phase was re-extracted for 1 min with fresh CCl_4 , a D of 0.1 was obtained.

Table VIII

Coprecipitation of At(O) and SO ₂ -reduced At with AgI, TlI, and Pb(IO ₃) ₂					
History	Solution from which precipitated	Precipitant	% on precip. after all washes	% in acetone wash	
Distilled At(O) stock ^a in conc. HNO ₃ , diluted to 0.5 M before stock was used.	0.01 M HNO ₃ + KI	Ag ⁺	< 2	Not used	
	0.01 M HNO ₃ + KIO ₃	Ag ⁺	40 to 80	Not used	
	SO ₂ + KI	Ag ⁺	100	Not used	
	SO ₂ + KI	Tl ⁺	Partial	Not used	
Distilled At(O) stock in 0.02 M HNO ₃	0.01 M HNO ₃ + 0.02 M NaI	AgNO ₃	0.1	< 0.1 ^e	
	Same as above	TlNO ₃	4	5 ^e	
	Same as above	AgNO ₃	1	Not used	
	Same as above	TlNO ₃	10	Not used	
	0.01 M HNO ₃ + 0.02 M NaIO ₃	Pb(NO ₃) ₂	0.3	0.5 ^e	
	Same as above	Pb(NO ₃) ₂	3	Not used	
Distilled At(O) stock in ^c 0.001 M HClO ₄	0.001 M HClO ₄ ^d	AgNO ₃	90 to 100	Not used	
	0.001 M HClO ₄	AgNO ₃	39	Not used	
	0.001 M HClO ₄ + 1 M NaClO ₄ ^d	AgNO ₃	37	Not used	
	0.01 M HClO ₄ + 1 M NaClO ₄ ^d	AgNO ₃	16	Not used	
	0.1 M HClO ₄ + 1 M NaClO ₄ ^d	AgNO ₃	10	Not used	
	0.01 M HNO ₃	AgNO ₃	11	Not used	
	0.01 M HNO ₃ + 1 M NaClO ₄ ^d	AgNO ₃	10	Not used	
	0.001 M HClO ₄ ^d	TlClO ₄	55	23 ^e	
	0.001 M HClO ₄	TlClO ₄	53	38 ^f	
	0.01 M HClO ₄ ^d	TlClO ₄	51	41 ^f	

Table VIII (cont'd.)

History	Solution from which precipitated	Precipitant	% on precip. after all washes	% in acetone wash
Distilled At(O) stock in ^c 0.001 M HClO ₄	0.01 M HNO ₃ ^d	TiClO ₄	39	54 ^f
	0.003 M SO ₂ + 0.00015 M H ₂ SO ₄ ^g	TiClO ₄	91	1 ^e
	0.003 M SO ₂ + 0.00015 M H ₂ SO ₄ + 0.1 M HClO ₄ ^g	TiNO ₃	89	0.6 ^e
Distilled At(O) stock in 0.01-0.02 M HNO ₃	0.01 M SO ₂ ^h + 0.02 M NaI	TiNO ₃	30	j
	0.005 M SO ₂ ⁱ¹ + 0.02 M NaI	TiNO ₃	<10	j

^aThese are results reported by Johnson et al.^{3a}

^bThese precipitations were made from portions of a 0.01 M HNO₃ solution from which 98% of the astatine had been removed by extraction ten times with its own volume of benzene. The last of these extractions gave a D of 0.17.

^cThis stock was made up in redistilled water, and redistilled water was used in all experiments carried out on it. All assays of these experiments were made by x-ray counting of solutions.

All solutions were made 0.02 M in NaI for precipitations.

^dThe astatine solutions for these precipitations were obtained by backextraction of At(O) solutions in low-sulfur CCl₄ with 0.001 M HClO₄, or with 0.001 M HClO₄ + NaI. When the At(O) solutions were backextracted with the iodide-free acid, D's between 5 and 10 were obtained.

^eOnly one acetone wash was used.

^fTwo successive acetone washes were used. They were combined in the same vial for assaying.

Notes to Table VIII (cont'd.)

^gMade by dilution of a 0.1-M SO_2 -- 0.005 M H_2SO_4 solution in which At(O) had stood for 4 hr, at which time it gave a D of 0.039 when diluted threefold and extracted for 5 min under a series-1 safelite with low-sulfur CCl_4 .

^hThe astatine was introduced into this solution prior to the addition of the iodide by backextraction of an extensively washed benzene solution of At(O) ($D > 300$) with intermittent agitation over 6 hr.

A final D of 0.42 was obtained.

ⁱThe astatine was backextracted into a 0.01 M SO_2 solution from a benzene solution of $D = 43$ by intermittent agitation over 10 hr after which it had a D of 1.9. This aqueous solution was diluted with an equal volume of water, and iodide was added to give the indicated composition.

^jThe single acetone wash was not assayed.

does not entirely eliminate coprecipitation is not a conclusive argument against the nitric acid being the significant factor, since a stock stored in nitric acid might slowly develop astatine species different from those present in the perchloric acid solutions. Furthermore, different nitric acid solutions may contain various amounts of lower nitrogen oxides.

The partial coprecipitation could conceivably result from extensive hydrolysis of the astatine due to the removal of astatide by coprecipitation. Such hydrolysis should be inhibited by acid, but there is no reason why the coprecipitation with AgI should be strongly diminished when the acidity is increased, while that with TlI is hardly affected. Nor is the partial removal of the activity from the TlI by acetone easily explained in terms of a hydrolytic process. I have found that a single acetone wash removes nearly completely moderate amounts of iodine that have been taken up by a TlI precipitate.

It seems more likely that the coprecipitation of At (0) with TlI and AgI is actually a process of adsorption, rather than of true isomorphous replacement of similar ions in the crystal lattice.¹⁹ We shall see in Section IV that drastically different behavior is encountered if the solution contains an appreciable I_2 concentration.

It would appear that reduction of At (0) to At^- by SO_2 is slow and incomplete when the SO_2 concentration is 0.01 M but is completed fairly rapidly in 0.1 M SO_2 . However, it is also possible that astatine species formed in nitric acid solutions are less readily reduced than those formed in perchloric acid solutions. The decrease in D when an SO_2 solution is used to backextract an organic astatine solution apparently need not be indicative of reduction to At^- , since such a decrease may occur even when the astatine does not coprecipitate with TlI. It is possible that the SO_2 forms a nonextractable complex with the astatine before reducing it.

The incomplete precipitation with TlI reported by Johnson et al. may then be due to incomplete reduction, while the complete precipitation they observed with AgI may, as they suggest, result from deposition of At (0) on metallic silver formed by the reduction of Ag^+ by SO_2 .

On the other hand, Johnson et al. observed a great deal more coprecipitation of At (0) with insoluble iodates than I do.^{3a} They suggested that the iodate itself was oxidizing the astatine to astatate. However, my results indicate that no appreciable oxidation of astatine to astatate takes place within a few minutes in 0.02 to 0.04 M iodate solutions at pH 1 to 3 (see Table VIII and the iodate coprecipitation data in Section IV). In Section IV we will also note that even a periodate-iodate mixture only slowly oxidizes At (0) to AtO_3^- . Thus the cause of the extensive coprecipitation of At (0) with AgIO_3 found by Johnson et al. remains a mystery.

D. Discussion

Irreproducibility has keynoted all the early work on astatine. Results have been strongly dependent on seemingly minor variations in experimental conditions and in the history of the astatine used. One tends to conclude that the unknown impurities in the systems are at least as influential as the known components. This unpleasant state of affairs can be attributed to two causes. Firstly, the oxidation potentials of solutions used have not been adequately controlled. In most of the studies characterizing At (0), no redox control at all was employed, while even in the oxidation and reduction studies the potential was often poorly defined, due both to failure to fix the concentrations of both members of a redox couple, and to the use of more or less irreversible couples.

Strict redox control of a system requires a couple which reacts much faster with astatine than do impurities in the system. Such couples are not always easy to come by, nor is there any way to be sure that a couple fulfills this condition other than to try it and obtain reproducible and intelligible results. Still, even the use of a redox couple that only does the job poorly is better than having no redox control at all.

The second difficulty, which is not unrelated to the first, is the failure to define the state of the so-called "At (0)". Without knowing the nature of this state -- or states -- the explanations advanced

for much of the observed behavior of astatine must be classed as the sheerest speculation.

It is usually tacitly assumed that At (0) is either At_2 or, because of the very low concentration, $\text{At}\cdot$. While $\text{At}\cdot$ might be formed in nonpolar solvents, in aqueous solution disproportionation, e.g. to At^- and HOAt , seems much more likely.

However, there is precious little reason to believe that At (0) consists merely of astatine-hydrogen-oxygen compounds. As the halogens get heavier, they become increasingly labile in almost all of their reactions. Thus astatine should be the most labile member of the group. Further, at the extremely low concentrations at which the astatine is present, any reaction which acts to split the At_2 molecule tends to become thermodynamically favored. In the light of these considerations it does not seem improbable that "At (0)" solutions contain a veritable zoo of compounds of astatine with sundry organic impurities in the reaction media. The exact composition of this tracer-scale witch's brew probably varies from one solution to another, and the compounds may be destroyed by powerful reducing or oxidizing agents, yielding such less-controversial species as At^- and AtO_3^- .

It is unlikely that different workers would have the good fortune to deal with the same impurity complement, and widely discrepant results are to be expected. Thus the fact that Johnson et al. found "At (0)" to be much more extractable than I did merely indicates that we were probably working with entirely different impurity compounds of astatine.

The only hope of remedying this unhappy situation would seem to lie in converting the astatine into a known compound before getting started, and the most likely candidate is an interhalogen. All of the interhalogens are stable with respect to their elements, and the reactions forming them are very rapid. Further, a halogen present in macro quantities in a system might be expected to react first with most of the impurities that could otherwise react with the astatine. However, although the possible advantages of iodine as a nonisotopic carrier for astatine were pointed out by Aten et al.,²⁰ no one has heretofore acted on his suggestions.

In the work reported in the following sections, I have attempted to design most of the experiments in such a way that the oxidation potentials of the solutions are more or less adequately controlled, and so that, whenever possible, the At (0) is encouraged to form such respectable interhalogen compounds as AtI and AtBr.

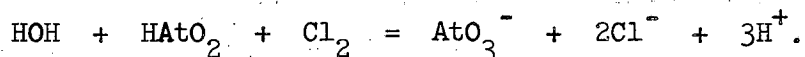
IV. A SYSTEMATIC SURVEY OF THE REDOX BEHAVIOR OF ASTATINE

A. Introductory Considerations

If the oxidation potential of an astatine solution can be controlled through the use of redox couples with which the astatine reacts more rapidly than it reacts with impurities in the system, it is possible to bracket the oxidation potential between astatine states A and B, by determining the potential at which A is converted to B, and the least different potential at which B is converted to A.

In principle it is possible to find a couple which has a potential very close to the potential of the astatine couple and then, if equilibrium can be obtained, to determine the dependence of the reaction on various constituents of the reaction mixture. In this way, if one of the two astatine states involved is known, the other may be identified.

For example, if AtO_3^- were reduced to an intermediate state by the $\text{Cl}^- \text{ -- } \text{Cl}_2$ couple in such a way that the ratio $(\text{AtO}_3^-)/(\text{At intermediate})$ was proportional to the quotient $(\text{Cl}_2)/(\text{Cl}^-)^2(\text{H}^+)^3$, we could be pretty certain that the intermediate state was HAtO_2 and the reaction was



The qualitative method of bracketing potentials has become a standard technique of tracer chemistry.¹⁹ However, only in a few cases has it been possible to obtain even limited quantitative information about a redox reaction involving species present at tracer concentrations.²¹

Application of these methods requires some means of distinguishing among the astatine states. In this work such distinctions have been made in accordance with the following assumptions:

(a) Only elemental halogens, interhalogens, and organohalogen compounds containing astatine extract appreciably into CCl_4 .

(b) Only At^- , AtO_3^- , and AtO_4^- will coprecipitate extensively with insoluble iodides, iodates, and metaperiodates, respectively, and not be removed from the precipitates by washing.

The second assumption is far less secure than the first. Isomorphous replacement of similar ions is ~~about~~ one of several mechanisms by which a tracer can be incorporated into a nonisotopic carrier precipitate. Surface adsorption, inclusion of mother liquid within the crystals, "internal adsorption" at active lattice sites, and "anomalous mixed-crystal formation" by dissimilar ions are all processes which must not be ignored.¹⁹

The only way to be certain that isomorphous replacement is taking place is to determine that the equilibrium distribution of tracer between the aqueous and crystal phases is indeed a constant. Such studies of equilibrium distribution involving precipitates have not been conducted in the work reported in this section. Therefore we must utilize assumption (b) with considerable reservation, particularly in those cases in which the coprecipitation is incomplete.

B. Experimental Method

The following general procedure was used in these experiments: Portions of solutions of astatine in a previously identified state were treated with various redox couples, and the behavior of the astatine was noted. Intermediate astatine states were approached from both sides, assuring that the absence of reaction in a particular case was not due merely to the slowness of the reaction. All reactions were tested for photosensitivity by repeating the experiments either in black-taped, opaque-stoppered tubes, or under a Wratten series-1 safelite with a 40-watt bulb, which will henceforth be identified simply as the "series-1 safelite."

C. Results

The results are shown in Tables IX to XIX.

Explanation of Tables

The ~~natures~~ of the stock solutions from which astatine was taken to react with each couple are indicated in the tables by capital letters,

plus the principal astatine species believed to be in the stock. The letters refer to the following solutions: (Stocks A to C were used only for the experiments of Table IX.)

Solution A. Hydrolysed At (0) stock -- no iodine. A target was dissolved in nitric acid and fumed down with HClO_4 . The astatine was extracted into CCl_4 from 2 M hydroxylamine sulfate, and was backextracted into 0.05 M NaOH to give this stock.

Solution B. Chlorine-oxidized At (0) stock -- no iodine. The astatine was separated by the wet method of Neumann.^{3b} In order to make the stock solution the astatine was backextracted from the isopropyl ether with aqueous NaOH. The aqueous solution was then acidified, saturated with Cl_2 , and heated to oxidize impurities that might have been introduced during the separation.

Solution C. Hydrolysed At (0) stock -- no iodine. The astatine was separated by double-distillation and was removed from the u-tube with 0.01 M NaOH to give this stock solution.

Solution D. At^- stock. Double-distilled astatine was removed from the u-tube with 0.01 M HIO_4 . Thirty hours later the solution was made 0.1 M in SO_2 (0.06 M excess after reaction with the periodate) to give this stock, which was allowed to stand for 3 hr before use. From a portion of the stock diluted 1000-fold with 0.01 M HClO_4 , 90% of the At was co-precipitated with PbI_2 . Another portion, diluted 1000-fold with 0.1 M HClO_4 and extracted for a minute with an equal volume of CCl_4 gave a D of 0.026.

Solution E. AtI stocks. These stocks were made by removing double-distilled astatine from the u-tube with solutions 0.001 to 0.01 M in HClO_4 , 10^{-4} to 5×10^{-3} M in stoichiometric I_2 , and 10^{-4} to 10^{-2} M in NaI.

Solution E'. AtI stock. The double-distilled astatine was washed from the u-tube with 0.001 M HClO_4 , and within 10 min the solution was made

5×10^{-4} M in I_2 and in NaI. It was allowed to stand one hour before use.

Solution E". AtI stock. The double-distilled astatine was removed from the u-tube with 0.01 M HIO_4 . Nine hours later an aliquot of this solution was diluted 33-fold with a solution 0.1 M in $HClO_4$, 0.009 M in NaI, and 0.001 M in NaI_3 to make this stock, which was allowed to stand 13 hr before use. (Final concentrations were NaI = 0.005 M and NaI_3 = 0.002 M.)

Solution E''' . AtI stock. The organic phase from an extraction of an E-type stock with CCl_4 .

[When aliquots of E, E', and E" stocks were extracted with CCl_4 they yielded D values in agreement with Eq. (V-1) (q.v.).]

Solution F. AtO_3^- stock -- no iodine. The double-distilled astatine was washed from the u-tube with 0.01 M NaOH. It was oxidized at $100^\circ C$ with 0.01 M Ce^{+4} in concentrated $HClO_4$ to provide this stock solution. From an aliquot of the solution diluted 1000-fold the astatine was 83% precipitated with $Pb(IO_3)_2$.

Solution F'. AtO_3^- stock -- only trace iodine. This solution is similar to F, except that I_2 , NaBr, and Br_2 were added during the oxidation process. They were subsequently removed largely, but by no means completely, by fuming with $HClO_4$. The final stock solution was 1 M in $HClO_4$ and 0.01 M in $(NH_4)_2Ce(NO_3)_6$ with traces of bromine and iodine species. From an aliquot of this solution diluted 300-fold with 0.01 M $HClO_4$, 77% of the astatine coprecipitated with $Pb(IO_3)_2$. An aliquot diluted 150-fold with 1 M $HClO_4$ gave a D of 0.003 when extracted for 1 min with an equal volume of CCl_4 .

Solution F". AtO_3^- stock. A portion of the E' stock was made 0.02 M in $(NH_4)_2Ce(NO_3)_6$ and 1.2 M in $HClO_4$ and was heated at $100^\circ C$ for an hour. From an aliquot diluted 1000-fold in 0.01 M $HClO_4$, the astatine was 99% coprecipitated with $Pb(IO_3)_2$. An aliquot diluted 10-fold with 1 M $HClO_4$

gave a D of 0.025 when extracted for one minute with an equal volume of CCl_4 .

Solution G. AtO_3^- stocks. Portions of E-type stocks were oxidized at 100°C with 0.1 to 0.4 M HIO_4 to give solutions from which 98 to 100% of the astatine could be coprecipitated with $\text{Pb}(\text{IO}_3)_2$ (see Expt. 9-5). The astatine was essentially unextractable into CCl_4 ($D < 0.005$).

Solution H. Bromine-oxidized AtI stock. An E'' stock 0.005 M in I_2 was backextracted with an equal volume of a solution 0.1 M in HClO_4 , 2 M in NaClO_4 , 0.01 M in Br_2 , and 0.01 M in NaBr . The value of D was 0.005. The aqueous phase comprised stock H.

Solution H'. Bromine-oxidized AtI stock. A portion of a type-E stock was made 0.01 M in Br_2 , 0.01 M in NaBr , and 0.1 M in HClO_4 , with a final stoichiometric IBr concentration of 2×10^{-4} M to make stock H'. When an aliquot of this solution was diluted 200-fold with 0.1 M HClO_4 and extracted for 1 min with an equal volume of CCl_4 it gave a D of 0.05.

Solution I. At (0) stock -- no iodine. The double-distilled astatine was removed from the u-tube with 0.001 M HClO_4 . The solution gave a D of 4.8 when extracted for 1 min with an equal volume of CCl_4 .

Solution I'. At (0) stock -- no iodine. This solution is the organic phase from the extraction of stock I.

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The compositions of the reaction mixtures include species introduced with the stock. Concentrations are generally stoichiometric, and do not indicate the actual species present. However, the pH is indicated in parentheses for buffered systems, and the free Cl^- , Br^- , and H^+ concentrations are indicated in parentheses in those of the Cl^- -- Cl_2 , and Br^- -- Br_2 experiments in which they receive an appreciable contribution from hydrolysis of the halogen.

Equilibrium has been assumed to have established itself between all oxidizing and reducing agents present in macro concentrations in the solution, with the following two exceptions: On the basis of experimental observations the reduction of iodate by VO^{++} and the oxidation of iodine by $\text{Cr}_2\text{O}_7^{=}$ are assumed not to proceed appreciably in the course of the experiments.

Electromotive forces of the solutions have been calculated from the data of Latimer.²² Rough activity corrections have been applied on the basis of his table of activity coefficients and the additional data of Harned and Owen.²³ The emf's of the ferro-ferricyanide experiments are based on the data of Kolthoff and Tomsicek.²⁴ The emf's may easily be in error by ± 0.01 volt. In Tables XI and XIII the emf's calculated from the I_2 -- IO_3^- couple are given in parentheses beneath those calculated from the Cr (III) - (VI) or VO^{++} -- VO_2^+ couples. All emfs are given with respect to the standard hydrogen electrode.

"Time" generally refers to the interval between the time of preparation of the mixture and the time at which aliquots were withdrawn for precipitation or extraction.

Unless otherwise specified, solvent extractions were carried out with equal volumes of aqueous solution and low-sulfur CCl_4 agitated for about 1 min. Volume ratios appreciably different from unity are indicated as R = organic volume/aqueous volume. Again D is total organic At/total aqueous At.

Unless otherwise noted, precipitations were carried out in accordance with the procedures described in Table III. The percentage of the initial activity remaining in the precipitate after all washes is given as "% Precip." If an acetone wash was used, the percentage of the activity found in it is also given. When more than a few percent of the activity washed off in the acetone, at least two consecutive acetone washes were used, and the activity indicated to be in the acetone is their sum. The activity of an aqueous wash is not usually indicated unless it amounted to more than 5% of the total activity.

"Dilution" entries should be interpreted in accordance with the following example: " $\frac{1}{2}$ (0.2 M HClO_4)" means that one volume of the reaction

mixture was diluted with an equal volume of 0.2 M HClO_4 . No entry in the "dilution" column means either that no dilution was employed or that the diluent was a solution of the same composition as the reaction mixture exclusive of new species introduced into the latter with the stock.

The results of duplicate precipitations or extractions are indicated in parentheses below the original values. If a "% Percip." or D value is given as an upper limit, it means that the activity of the precipitate or organic phase, respectively, was below the limit of detection in the particular experiment. Similarly, a lower limit is given for "% Percip." if the activity of the supernate was below the limit of detection.

Unless otherwise specified, all reactions and operations were carried out at room temperature in glass vessels exposed to more or less daylight and fluorescent illumination. No effect of variation in astatine concentration per se was ever noticed, indicating that radiation-induced reactions did not play a significant role.

Small Roman letters (a) refer to footnotes following the individual tables. Greek letters (α) refer to the following footnotes which pertain generally to Tables IX to XIX:

(α) The tubes containing the reaction mixtures and solvent extraction mixtures for these experiments were covered with black tape to protect them from light. However, transfer of aliquots, coprecipitations, and assays of solvent-extraction mixtures were performed under ordinary fluorescent light.

(β) These experiments differed from those described in note (α) only in that all operations which required removal of solutions from the black-taped tubes were carried out in the light of a series-1 safelite.

(γ) In these experiments the reaction mixtures themselves were 2-phase solvent-extraction mixtures, and the "time" refers to the duration of continuous agitation of the mixtures before aliquots were withdrawn.

(8) In these precipitations the low-acid TlClO_4 and $\text{Pb}(\text{ClO}_4)_2$ solutions described in Section II-C were used instead of the high-acid solutions used in the other experiments.

D. Discussion

1. The Highest Attainable Oxidation State of Astatine (Table IX)

The experiments of Table IX were designed to identify the highest oxidation state of astatine. Barium iodate precipitated from a mixture of a large amount of iodate with a moderate amount of periodate has been found to carry very little of the periodate. Similarly, KIO_4 precipitated from a solution containing a large quantity of periodate in the presence of a somewhat smaller quantity of iodate contains very little of the iodate.²⁵

If we assume that AtO_3^- and AtO_4^- behave like their iodine counterparts, we then have a method for distinguishing the two astatine states. But how good is this assumption? The principal species in a perchloric acid solution are H^+ and ClO_4^- , while a periodic acid solution contains primarily H_5IO_6 . This tendency toward expanded coordination should be even more pronounced with the larger astatine atom, and an octahedral H_5AtO_6 would have little tendency to coprecipitate with KIO_4 . But neither would such an ion be likely to coprecipitate with $\text{Ba}(\text{IO}_3)_2$. The nearly quantitative coprecipitation of the astatine with $\text{Ba}(\text{IO}_3)_2$ would therefore suggest that the principal astatine species present is AtO_3^- rather than a perastatate.

Throughout the remainder of this thesis, then, we shall assume that the astatine species which coprecipitates with insoluble iodates is AtO_3^- . As a matter of experimental convenience, Pb^{++} will be most often used for such precipitations, since $\text{Pb}(\text{IO}_3)_2$ is precipitated rapidly and very nearly completely, even from 0.1 M acid.

Although the most powerful oxidant used has an oxidation potential of less than -2 v, it is possible for perastatate formed at such a potential to be reduced by the iodate present during the subsequent precipitations. Therefore we cannot set the limit for the astatate-

Table IX

The highest attainable oxidation state of astatine						
Expt. Stock	Reaction mixture	Emf (volts)	Time	Dilution	Coprecipitation behavior	
					Special conditions	Precipitate % precip.
9-1 A Hydrolysed At(O)	0.1 M HIO_4 + 0.01 M NaIO_3	~ -1.6	40 min ^a	1/10		$\text{Ba}(\text{IO}_3)_2$ 86 (92) KIO_4 8(5)(3)
9-2 B Oxidized At states	Supernatant from 1st KIO_4 precipitation 0.1 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ + 1 M HClO_4 low sulfate ^b	< -2	5 min ^a	1/25	0.02 M HIO_4	AgIO_3 82 $\text{Ba}(\text{IO}_3)_2$ >99 KIO_4 4
9-3 B	Same as 9-2 but + 3×10^{-4} M AgNO_3	< -2	5 min ^a	1/25	0.02 M HIO_4	$\text{Ba}(\text{IO}_3)_2$ 97 KIO_4 6
9-4 C Hydrolysed At(O)	0.02 M $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ 12 M HClO_4 low Ce^{+++}	< -1.7	15 min ^a	1/200 ^c 1/200 ^c	0.02 M HIO_4	$\text{Ba}(\text{IO}_3)_2$ 97 KIO_4 11
9-5 E AtI	0.1 M HIO_4 + 0.05 M NaIO_3	~ -1.6	10 min ^a + 3 hr room temp.	1/200	0.02 M HIO_4	$\text{Pb}(\text{IO}_3)_2$ 99
9-6 D At ⁻	0.1 M HIO_4 + 0.05 M NaIO_3 + 0.6 M HClO_4 + 0.003 M H_2SO_4	~ -1.6	25 hr ^d	1/10		$\text{Pb}(\text{IO}_3)_2$ >99

^aAt 100°C.^bAn appreciable sulfate concentration was built up from decomposition of the persulfate during the heating.^cThe cerium was first precipitated by the addition of excess NaOH, after which the supernatant was reacidified for the iodate and periodate precipitations. If the ceric ion was not removed, most of the astatine accompanied the ceric iodate which precipitated when iodate was added.^dAn aliquot diluted 5-fold with 0.5 M HClO_4 gave a D of 9×10^{-4} when extracted for 1 min with 1.2 times its volume of CCl_4 .

perastatate couple more negative than about -1.6 v in the 0.01 M HClO_4 solutions from which the barium iodate was precipitated. We have still neglected the possibility of a shift in the astatate-perastatate equilibrium during the precipitation itself.

The ease with which lower states of astatine could be oxidized to astatate was not always predictable. Experiment 9-6 appears exceptional, since heating was usually necessary to obtain a material completely coprecipitable with lead iodate. One E-type stock could not be oxidized completely by even the most vigorous periodate oxidation and required the use of Ce (IV). The reason for these differences is not known, but they may be due to interference from reducing impurities.

2. The Cl^- -- Cl_2 Couple

The Table X experiments seem to indicate that at low chloride concentrations this couple partially oxidizes astatine to AtO_3^- , while at high chloride concentrations the astatate is reduced. In all cases the astatine is essentially unextractable into CCl_4 , even when diluted to chloride concentrations so low as to make polyhalide-ion formation highly improbable. Apparently, then, the reduced astatine species is not At (0) but some intermediate positive oxidation state.

In those cases in which appreciable coprecipitation with lead iodate takes place, the precipitation appears to be independent of the total salt content and acidity of the solution from which it is carried out (Expts. 10-7 and 10-8). From Expt. 10-9 we see that the coprecipitation is also independent of the excess of Pb^{++} used and of the iodate concentration up to 0.02 M IO_3^- . Further increase in the iodate concentration, however, causes a larger fraction of the astatine to coprecipitate. Both barium and lead iodate precipitations show this effect.

The experiments of Table Xa show that at 0.005 M IO_3^- a second lead iodate precipitation gleans relatively little astatine, but when the iodate concentration is between 0.01 and 0.02 M, the astatine can be almost completely removed from the solution by several successive precipitations. This unexpected behavior at high iodate concentration may be due to adsorption of astatine when a large quantity of precipitate is formed.

Table X

Reaction of astatine with the $\text{Cl}^- - \text{Cl}_2$ couple									
Expt.	Stock	Reaction mixture	Emf (volts)	Time (hr)	Extraction		Cocprecipitation		Iodate precipitate % precip.
					Dilution	D	Dilution	Special conditions	
10-1 ^B	G AtO ₃	0.05 M Cl ₂ , 0.1 M HClO ₄ , 0.002 M NaIO ₃ (Cl ⁻ = 0.015; H ⁺ = 0.11)	-1.46	25					Lead 68
10-2 ^B	G AtO ₃	0.04 M Cl ₂ , 0.2 M NaCl, 0.1 M HClO ₄ , 0.002 M NaIO ₃	-1.40	25					Lead 0.5
10-3	F' AtO ₃	0.01 M Cl ₂ , 0.1 M NaCl, 0.5 M HClO ₄ , 0.001 M Ce(NO ₃) ₃ , 0.002 M NH ₄ NO ₃	-1.40	11	1/100 (0.5 M HClO ₄)	0.02	1/10 (0.05 M HClO ₄)		Lead 0.5
10-4	G AtO ₃	0.03 M Cl ₂ , 0.5 M NaCl, 0.4 M HClO ₄ , 2 x 10 ⁻⁴ M NaIO ₃	-1.38	24			1/5		Lead 1
10-5	F AtO ₃	0.003 M Cl ₂ , 8 M HCl 0.004 M Ce(ClO ₄) ₃	-1.24	1.5	1/1000	0.03	1/200		Lead 0.6
10-6	E AtI	0.06 M Cl ₂ , 0.4 M HClO ₄ , 2 x 10 ⁻⁵ M NaIO ₃ (Cl ⁻ = 0.013)	-1.48	24			1/5		Lead 36
10-7 ^B	E AtI	0.06 M Cl ₂ , 0.1 M HClO ₄ , 6 x 10 ⁻⁵ M NaIO ₃ (Cl ⁻ = 0.019; H ⁺ = 0.12)	-1.47	14	1/10 (0.1 M HClO ₄)	5x10 ⁻⁴		0.2 M NaClO ₄	Lead 6 ^a Lead 6
10-8 ^a	E' AtI	0.03 M Cl ₂ , 0.08 M HClO ₄ , 3 x 10 ⁻⁴ M NaIO ₃ (Cl ⁻ = 0.012; H ⁺ = 0.09)	-1.46	55			1/20 (0.1 M HClO ₄) 1/20		Lead 70 (10% in wash)
									Lead 74 (2% in wash)
									Lead 12 (4% in wash)
									Lead 45 (23% in aqueous wash, 7% in acetone wash)
				66			1/20 (0.1 M HClO ₄)		
				78		<0.002			
10-9	E AtI	0.05 M Cl ₂ , 2x10 ⁻⁴ M NaIO ₃ (H ⁺ = Cl ⁻ = HCl = 0.024)	-1.45	14				0.02 M NaIO ₃ 0.01 M excess Pb ⁺⁺	Lead 17(25) ^b
								0.02 M NaIO ₃ 0.04 M excess Pb ⁺⁺	Lead 18
								0.04 M NaIO ₃ 0.03 M excess Pb ⁺⁺	Lead 60 (20% in wash)
				38				0.02 M NaIO ₃ 0.01 M excess Pb ⁺⁺	Lead 19
								0.002 M NaIO ₃ 0.02 M excess Pb ⁺⁺	Lead 15
								0.005 M NaIO ₃ 0.02 M excess Pb ⁺⁺	Lead 17 ^b
								0.02 M NaIO ₃	Barium 17
								0.04 M NaIO ₃	Barium 31
10-10 ^B	E AtI	0.05 M Cl ₂ , 0.2 M NaCl, 0.1 M HClO ₄ , 6 x 10 ⁻⁵ M NaIO ₃	-1.41	14	1/10 (0.1 M HClO ₄)	6x10 ⁻⁴			Lead 0.4
10-11	D At ⁻	0.02 M Cl ₂ , 0.5 M NaCl, 0.6 M HClO ₄ , 0.005 M H ₂ SO ₄ , 5 x 10 ⁻⁴ M NaIO ₃	-1.38	20	1/50 (0.5 M HClO ₄)	<0.002	1/10		Lead 3

^aThe same result was obtained when the precipitation was repeated under fluorescent light.

^bReprecipitations were carried out from the supernates obtained from these initial precipitations. The results appear in Table XA.

Table XA

Successive precipitations of lead iodate from aliquots of the Expt. 10-9 reaction mixture ^a						
Expt.	Precipitate No.	Iodate added		Pb ⁺⁺ added		Original activity on precipitate(%)
		Mmoles	Excess(M)	Mmoles	Excess(M)	
10-9a	1	0.02	0.02	0.02	0.01	25
	2	0.04	0.016	0.02	0.008	57
	3	0.04	0.014	0.02	0.007	13
	4	0.04	0.012	0.03	0.012	4
10-9b	1	0.02	0.02	0.02	0.01	17
	2	0.03	0.008	0.02	0.008	28
10-9c	1	0.005	0.005	0.005	0.0025	17
	2	0.01	0.005	0.005	0.0025	6

^aThe aliquot was diluted with an iodate-containing solution of the same acidity and chlorine content, and an excess of Pb⁺⁺ was added to give precipitate No. 1. To the separated supernate was added an excess of iodate. The solution was well mixed and an excess of Pb⁺⁺ was added. The total precipitate thus formed was precipitate No. 2. The process was repeated to give further precipitations as indicated.

Experiment 10-8 indicates that the coprecipitation of the astatine is markedly inhibited by the presence of chlorine and its hydrolysis products in the precipitation mixture. This observation is difficult to explain, and again suggests that the astatine is being held by some mechanism other than isomorphous replacement of ions in the crystal lattice.

Considerably lower D's are obtained in Expts. 10-7, -8, and -10 than in Expts. 10-3 and 10-5. The extraction mixtures of only the former were protected from light, and the higher D's of the unprotected mixtures may result from a photochemical reduction of astatine to At (0). Other photochemical reactions of this nature will be mentioned later in connection with the bromine systems.

The irregularities we have just discussed cast considerable doubt on the interpretation of the coprecipitation of astatine in this system as due to a simple redox reaction. However, if we assume that at least part of the coprecipitation results from the formation of AtO_3^- , and if we represent the intermediate state as At (X), we may set the At (X) -- AtO_3^- potential between -1.46 and -1.5 v in 0.1 M HClO_4 .

There are numerous possibilities for At (X). The most likely candidates would seem to be HOAt , HAtO_2 , and interhalogens such as AtCl , and AtCl_3 , although we would expect the latter two to be hydrolysed in at least some of the experiments. Nor can we really rule out organoastatine compounds like ROAt .

3. The Cr(III) -- Cr(VI) Couple (Table XI)

This is a notoriously sluggish couple and can scarcely be considered to control the emf of a solution. Nonetheless, its reaction with astatine is of interest. Once more we seem to have a case of partial oxidation of the astatine to astatate and partial reduction of AtO_3^- to lower states. Since under at least some conditions the astatine is largely unextractable into CCl_4 , an intermediate positive state is again indicated. However, the extractability of the astatine shows a marked but erratic dependence on dilution which is quite puzzling.

Experiments 11-6, -8, and -14 show the coprecipitation with lead iodate to be independent of the concentration of chromium species in the

Table XI

Reaction of sstatine with the Cr (III) -- Cr (VI) couple									
Expt.	Stock	Reaction mixture	Emf (volts)	Time (hr)	Extraction		Precipitation		
					Dilution	D	Dilution	Special conditions	Precipitate ^a % precip.
11-1	G AtO ₃	0.1 M Cr(NO ₃) ₃ 0.05 M Na ₂ Cr ₂ O ₇ 0.3 M HClO ₄ 3x10 ⁻⁴ M NaIO ₃	-1.26	15			1/16 (0.006 M HClO ₄)	Pb(IO ₃) ₂	45
11-2 ^B	G AtO ₃	0.008 M Cr(NO ₃) ₃ 0.04 M H ₂ Cr ₂ O ₇ 0.09 M HClO ₄ 0.002 M NaIO ₃ 8x10 ⁻⁵ M I ₂	-1.22 (-1.09)	25			1/20 (0.1 M HClO ₄)	Pb(IO ₃) ₂	85
11-3 ^B	G AtO ₃	0.08 M Cr(NO ₃) ₃ 0.04 M Na ₂ Cr ₂ O ₇ 0.1 M HClO ₄ 0.002 M NaIO ₃ 8x10 ⁻⁵ M I ₂	-1.20 (-1.09)	25			1/20 (0.1 M HClO ₄)	Pb(IO ₃) ₂	52(56)
11-4	F AtO ₃	1 M Cr(NO ₃) ₃ 0.01 M NaHCrO ₄ 0.04 M HClO ₄ 4x10 ⁻⁴ M Ce(ClO ₄) ₃	~ -1.1	1.5			1/10	Pb(IO ₃) ₂	26
				4	1/10 (0.005 M HClO ₄)	0.024	1/10	Pb(IO ₃) ₂	20
11-5	E AtI	0.1 M Cr(NO ₃) ₃ 0.05 M Na ₂ Cr ₂ O ₇ 0.3 M HClO ₄ 10 ⁻⁵ M I ₂	-1.26	17			1/16 (0.006 M HClO ₄)	Pb(IO ₃) ₂	57
							1/16 (0.006 M HClO ₄)	No Pb ⁺⁺	Basic chromic iodate 30
							1/16 (0.006 M HClO ₄)	No iodate	PbCrO ₄ 5
11-6 ^B	E AtI	8x10 ⁻⁴ M Cr(NO ₃) ₃ 0.04 M H ₂ Cr ₂ O ₇ 0.09 M HClO ₄ 9x10 ⁻⁵ M I ₂	-1.24	20			1/100 (0.1 M HClO ₄)	Pb(IO ₃) ₂	40
				44			1/20 (0.1 M HClO ₄)	Pb(IO ₃) ₂	(7% in wash)
									(8% in wash)
11-7 ^C	E AtI	0.08 M Cr(NO ₃) ₃ 0.04 M Na ₂ Cr ₂ O ₇ 0.2 M HClO ₄ 10 ⁻⁴ M I ₂	-1.24	72			1/100 (0.1 M HClO ₄)	0.05 M NaIO ₃ Pb(IO ₃) ₂	49
							1/100 (0.1 M HClO ₄)	0.01 M NaIO ₃ Pb(IO ₃) ₂	47 ^b (60)
11-8 ^B	E AtI	0.08 M Cr(NO ₃) ₃ 0.04 M Na ₂ Cr ₂ O ₇ 0.1 M HClO ₄ 9x10 ⁻⁵ M I ₂	-1.20	20			0.0016 1/100 (0.1 M HClO ₄)	Pb(IO ₃) ₂	70
				44			1/20 (0.1 M HClO ₄)	Pb(IO ₃) ₂	(5% in wash)
									67
									(12% in wash)
11-9 ^C	E' AtI	0.1 M Cr(NO ₃) ₃ 0.05 M Na ₂ Cr ₂ O ₇ 0.1 M HClO ₄ 2x10 ⁻⁴ M I ₂	-1.20	4			1/40 (0.1 M HClO ₄)	Pb(IO ₃) ₂	43
				20	1/25 (0.1 M HClO ₄)	2.0			
					1/13 (0.1 M HClO ₄)	0.5(0.17) ^c			
11-10 ^C	E' AtI	0.08 M Cr(NO ₃) ₃ 0.04 M Na ₂ Cr ₂ O ₇ 0.08 M HClO ₄ 1.3x10 ⁻⁴ M I ₂	-1.19	55			1/10 (0.1 M HClO ₄)	Pb(IO ₃) ₂ ^B	4(5)
							1/20 (0.1 M HClO ₄)	Pb(IO ₃) ₂ ^B	30
							1/20 (0.005 M HClO ₄)	Ba(IO ₃) ₂	4
				78	1/10 (0.1 M HClO ₄)	2.1			
					no dilution	0.004			
11-11	E' AtI	0.001 M Cr(NO ₃) ₃ 10 ⁻³ M NaHCrO ₄ 0.01 M NaIO ₃ 0.1 M HClO ₄ , 10 ⁻⁵ M I ₂	-1.19 (-1.10)	0.1			No dilution or further addition of carrier	Pb(IO ₃) ₂	5
11-12	E AtI	Same as 11-11 but no dichromate	(-1.10)	0.1			No dilution or further addition of carrier	Pb(IO ₃) ₂	0.5
11-13 ^C	E' AtI	0.1 M Cr(NO ₃) ₃ 0.1 M HClO ₄ 2x10 ⁻⁴ M I ₂		7	1/25 (0.1 M HClO ₄)	5	1/50 (0.1 M HClO ₄)	Pb(IO ₃) ₂	0.5
				20	1/8 (0.1 M HClO ₄)	4.1			
					above mixture made 0.007 M in H ₂ Cr ₂ O ₇	1.8	(1 min agitation)		
						2.0	(30 min standing plus 1 min agitation)		
11-14	D At ⁻	0.1 M Cr(NO ₃) ₃ 0.05 M Na ₂ Cr ₂ O ₇ 0.5 M HClO ₄ , 10 ⁻⁴ M I ₂ 0.003 M H ₂ SO ₄	-1.29	24			1/5 (0.5 M HClO ₄) (R=1.2)	Pb(IO ₃) ₂	48
							1/50 (0.1 M HClO ₄)	Pb(IO ₃) ₂	53
							1/10 (0.05 M HClO ₄)	Pb(IO ₃) ₂	55

^aPb, CrO₄, BaCrO₄, and basic chromic iodate also precipitate under appropriate conditions.

^bThe supernate from this precipitation was made 0.03 M excess in NaIO₃; then, after mixing, it was made 0.04 M excess in Pb⁺⁺. The resulting second precipitate contained 4% of the initial activity. A third precipitate obtained in the same manner contained only 2% of the initial activity.

^cThe lower D value rose to 0.53 after 20 min of agitation under fluorescent light.

solution from which the precipitation is made. Experiment 11-7 shows it to be independent of the iodate concentration, and also shows that relatively little astatine is brought down by successive lead iodate precipitations from the same solution (note b).

From Expt. 11-5 we see that not much astatine coprecipitates with lead chromate in the absence of iodate carrier, but a considerable amount comes down with the basic chromic iodate precipitated by the addition of iodate to the diluted reaction mixture.

Experiment 11-10 shows the coprecipitation to be greatly diminished when H^+ is reduced to 0.004 M and also shows that very little astatine coprecipitates with barium iodate at pH 2. On the other hand, 20 to 26% of the astatine precipitates with lead iodate from 0.004 M acid in Expt. 11-4 and 57% coprecipitates from 0.02 M acid in Expt. 11-5. This behavior is quite disconcerting, and is hardly what one would expect for a case of straightforward isomorphous replacement.

Experiments 11-11, -12, and -13 serve as "blanks." They indicate that chromic ion alone neither reduces the extractability of At (0) nor renders it coprecipitable with lead iodate. Further, when the astatine has been exposed to low concentrations of dichromate for only a few minutes, its extractability is only slightly reduced and only a few percent of it coprecipitates with lead iodate. This indicates that some slow process involving the dichromate is involved, and oxidation of the astatine is the most obvious interpretation.

All in all, the situation regarding the behavior of the astatine in the presence of this couple is far from clear. The irregularities we have noted, as well as the lack of any clear-cut emf dependence of the fraction of the astatine coprecipitated, indicate that we are probably dealing with something more complicated than a redox equilibrium. This might have been anticipated in view of the irreversibility of the chromium couple, which makes it a rather poor choice for this type of study.

4. The Br^- -- Br_2 Couple. (Table XII)

This couple reduces astatate and oxidizes extractable astatine to a state which is neither extractable nor coprecipitable with lead iodate,

Table XII

Reaction of astatine with the Br ⁻ -- Br ₂ couple								
Expt.	Stock	Reaction mixture	Emf (volts)	Time (hr)	Coprociipitation with Pb(IO ₃) ₂			
					Extraction		Dilution	
					Dilution	D		% precip.
12-1 ^α	F ^{II}	0.2 M Br ₂ , 10 ⁻⁴ M NaBr, 0.1 M HClO ₄	-1.28	12			1/2	45(47)
	AtO ₃ ⁻	7x10 ⁻⁵ M NaIO ₃ , 8x10 ⁻⁵ M Ce(NO ₃) ₃ 2x10 ⁻⁴ M NH ₄ NO ₃ (Br ⁻ = 3.4x10 ⁻⁴)		40	<0.02		(0.05 M HClO ₄) 1/2 (0.05 M HClO ₄)	37% (38%) in 4 aqueous washes, 1% in acetone wash 17 (55% in 3 aqueous washes)
12-2 ^α	F ^{II}	0.2 M Br ₂ , 10 ⁻³ M NaBr, 0.1 M HClO ₄	-1.24	27	<0.006		1/2 (0.05 M HClO ₄)	12 (17% in 3 washes)
12-3	F	0.02 M Br ₂ , 0.6 M NaBr, 3 M HClO ₄	-1.04	12	1/100	0.05	1/70	5
	AtO ₃ ⁻	0.005 M Ce(ClO ₄) ₃						
12-4 ^α	E ^I	0.2 M Br ₂ , 5x10 ⁻⁴ M NaBr, 0.1 M HClO ₄	-1.26	48		0.003	1/2 (0.05 M HClO ₄) 1/10 (0.1 M HClO ₄)	11 (40% in 2 washes) (nothing in third) 22 (49% in 3 aqueous washes) (nothing in acetone wash)
	AtI	3x10 ⁻⁴ M IO ₃ ^{-a} (Br ⁻ = 6x10 ⁻⁴)						
12-5 ^α	E	0.05 M Br ₂ , 0.005 M NaBr, 0.05 M HClO ₄	-1.19	0.25		0.005		
	AtI	7x10 ⁻⁴ M IBr ^b , 1 M NaClO ₄		0.7		0.005		
12-6 ^r	E	Aqueous phase:	-1.11	0.1 ^c		0.002		
	AtI	0.009 M NaBr, 0.06 M HClO ₄ , 0.36 M NaClO ₄						
		Organic phase: 0.01 M Br ₂ , 0.03 M IBr ^b		0.1 ^d		0.002		
				0.1 ^e		0.003		
12-7	D	0.2 M Br ₂ , 0.1 M NaBr, 0.6 M HClO ₄	-1.13	22	1/50	0.005	1/10	0.6
	At ⁻	3x10 ⁻⁴ M IBr, 0.003 M H ₂ SO ₄				(0.5 M HClO ₄)		

^a 2x10⁻⁴ M NaIO₃ was added to the reaction mixture; the rest of the iodate came from oxidation of I₂.

^b A considerable fraction of the IBr enters the aqueous phase, both as (IBr)_{aq} and as IBr₂⁻ (see Section V-C). Thus the free Br⁻ concentration is around 0.003 M in Expt. 12-6. The oxidation of iodine to iodate in Expts. 12-5 has not been considered, due to the brevity of the experiment.

^c Mixtures agitated and assays taken in the dark.

^d Mixtures agitated and assays taken under series-1 safelite with 40-watt bulb.

^e Mixtures agitated and assays taken under series-00 safelite with 100-watt bulb.

^f Mixtures agitated and assays taken under fluorescent light.

although the data do suggest that under the most oxidizing conditions the couple may oxidize a small fraction of the astatine to astatate. Presumably we are again dealing with an intermediate oxidation state.

In the most oxidizing systems, a large fraction of the astatine coprecipitates initially with lead iodate but is washed off in the first one or two aqueous washes of the precipitate. Little more is removed by exhaustive washing, either with aqueous wash solution or with acetone. The effect does not appear to be greatly altered by the extent to which the reaction mixture is diluted prior to the precipitation. The explanation of this phenomenon is by no means apparent.

If AtO_3^- is indeed formed under the most oxidizing conditions, the intermediate state must be different from that formed in the chloride-chlorine system, since the latter is only oxidized to astatate at a much more negative potential. However, the unexplained irregularities in the coprecipitation behavior of both systems make such conclusions rather shaky, to say the least.

The photochemical effects apparent in Expt. 12-6 are fairly typical. However, the limited results do not warrant much speculation regarding the nature of the photochemical reaction. The Wratten series-1 filter is a red filter cutting off between 6100 and 6200 Å.²⁶ The series-00 is a yellow filter with a short-wavelength cutoff between 5200 and 5300 Å. However, the effects observed with filtered light may be partly due to the reduction in over-all light intensity accompanying the use of the filters. Since the extractions in Expts. 12-3 and 12-7 were performed under fluorescent light, it is likely that the observed D's are higher than they would have been in the dark.

The bromine system will be discussed further in Section V.

5. The Vanadium Couple. (Table XIII)

It appears that in the dark this couple reduces both AtO_3^- and the product of bromine oxidation at least partially to extractable $\text{At}(0)$ and does not greatly affect $\text{At}(0)$ itself.

Under the action of light, however, the astatine is slowly rendered unextractable, and the extractability is restored when the mixture is again

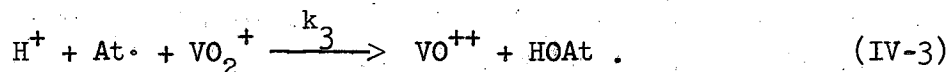
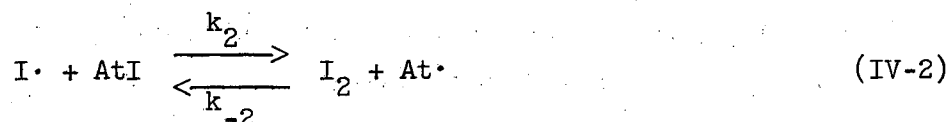
Table XIII

Reaction of astatine with the VO^{++} -- VO_2^+ couple									
Expt.	Stock	Reaction mixture	Emf (volts)	Time(hr) and lighting	Extraction Dilution	D	Coprecipitation with $\text{Pb}(\text{IO}_3)_2$ Dilution	% precip.	
13-1 ^B	G AtO ₃ ⁻	0.007 M VOSO_4 , 0.09 M VO_2ClO_4 , 0.3 M HClO_4 , 8×10^{-4} M NaIO_3 , 8×10^{-5} M I_2	-1.00 (-1.11)	21 dark	2/5 (0.1 M HClO_4)	0.27	1/20 (0.1 M HClO_4)	4	
13-2 ^B	G AtO ₃ ⁻	0.08 M VOSO_4 , 0.01 M VO_2ClO_4 , 0.3 M HClO_4 , 8×10^{-4} M NaIO_3 , 8×10^{-5} M I_2	-0.89 (-1.11)	21 dark	2/5 (0.1 M HClO_4)	3.4			
13-3 ^{A, Y}	H	Aqueous phase: 0.09 M VOSO_4 , 0.045 M VO_2ClO_4 , 0.4 M HClO_4 , 0.2 M NaClO_4 , 6×10^{-4} M NaBr	-0.95	0.5 dark		0.23			
13-4 ^B	E AtI	Organic phase: 0.01 M I_2 0.009 M VOSO_4 , 0.09 M VO_2ClO_4 0.3 M HClO_4 , 9×10^{-5} M I_2	-1.00	37 dark	2/5 (0.1 M HClO_4)	-5.8 ^a (4.3)			
13-5 ^Y	E' (AtI)	Aqueous phase: 0.1 M VOSO_4 , VO_2ClO_4 , 0.3 M HClO_4 Organic phase: 0.001 M I_2 Same as 13-5	-0.95	19 dark 19 dark + 7 fluorescent	2/5 (0.1 M HClO_4)	0.05	1/5 ^b (0.05 M HClO_4)	2.5	
13-6 ^Y	E' (AtI)	Same as 13-5	-0.95	19 fluorescent 19 fluorescent + 7 dark		0.003	1/10 ^b (0.1 M HClO_4)	1.5	
13-7 ^Y	I At(O)	Same as 13-5 but no I_2 present	-0.95	19 dark		1.9 9.4			
13-8 ^Y	I At(O)	Same as 13-7	-0.95	19 fluorescent 19 fluorescent + fluorescent ^c		4.9 ≤ 0.007			

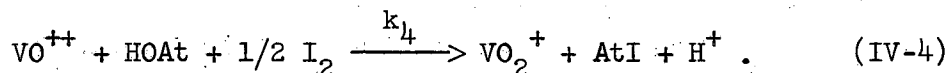
^aDuplicate extraction agitated 2 min under fluorescent light.^bAliquot taken from aqueous phase of reaction mixture.^cAfter organic phase was made 0.001 M in I_2 .

protected from the light. The unextractable species does not coprecipitate with lead iodate, and presumably represents an intermediate positive oxidation state. The photochemical effect appears largely dependent on the presence of iodine in the system.

In this case, then, the photochemical reaction does not merely produce a small shift in an equilibrium, but actually converts the bulk of the astatine to a thermodynamically unstable state. While such an effect would be remarkable on a macro scale, it is perfectly reasonable with tracer amounts of astatine. Consider the possible photochemical reaction sequence:



This competes with the thermal reaction, which we need not consider mechanistically:



The steady-state concentration of iodine atoms may be quite small compared with the total iodine concentration and still be much greater than the AtI concentration. In that case, reaction (IV-2) will not appreciably alter the (I·) concentration. A steady state with respect to astatine species will be reached at which the HOAt will be formed by reactions (IV-2) and (IV-3) just as fast as it is consumed by the thermal back-reaction (IV-4). There is no reason why this steady state cannot have most of the astatine in the form of HOAt.

In general, a gross shift of an equilibrium is a reasonable possibility in a tracer system if the primary photochemical process does not involve the tracer species. It therefore becomes apparent that gross

qualitative as well as quantitative misinterpretations can result from failure to consider photochemical effects when working with species at tracer levels.

6. The Fe(II) -- Fe(III) Couple. (Table XIV)

This couple and the vanadium couple appear to affect astatine rather similarly. However, in the iron system the photochemical reaction comes into play only when the Fe(III)/Fe(II) ratio is quite high. It seems to be more rapid than the vanadium photochemical reaction, although the latter renders the astatine less extractable.

The absence of iodine seems to slow down the photochemical reaction without greatly altering the final state that is reached. Since a primary process involving astatine could not easily convert the bulk of the astatine to an unstable state, Fe^{+++} seems like the most probable participant in the primary photochemical step in the iodine-free systems. However, it is not unlikely that the addition of iodine alters the entire mechanism of the reaction.

It is of interest to note that the equilibrium in the reaction $\text{Fe}^{++} + 1/2 \text{I}_2 = \text{Fe}^{+++} + \text{I}^-$ is shifted to the right by light, the light-absorbing species being either I_2 or I_3^- .²⁷

Johnson *et al.* reported that while ferrous ion reduced higher oxidation states of astatine to At (0), nearly pure ferric ion seemed to oxidize At (0).^{3a} Since they made no effort to exclude light, it seems almost certain that the oxidation they observed was a photochemical reaction.

It is worth noting that Expts. 14-2 and 14-6, in which no macro amounts of iodine species are present, do not in the dark give grossly different results from the other experiments. This indicates that the At (0) species formed in the absence of iodine is not significantly less stable than AtI, although it may be more so. This, in turn, tends to exclude At \cdot and At $_2$, both of which would be much less stable than AtI under these conditions.

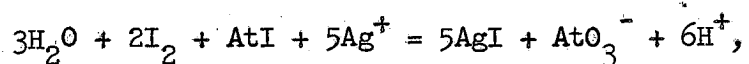
Table XIV

Reaction of astatine with the Fe (II) -- Fe (III) couple						
Expt. Stock	Reaction mixture	Emf (volts)	Time (hr) and lighting	Extraction Dilution D	Coprecipitation with $Pb(IO_3)_2$	
14-1 ^a F ⁺	0.04 M $Fe(ClO_4)_2$, 0.03 M $Fe(ClO_4)_3$	-0.74	34	3.8	1/2	0.5
AtO ₃ ⁻	0.13 M $HClO_4$, 6×10^{-4} M I_2					(0.1 M $HClO_4$)
14-2 F	4×10^{-4} M $Ce(NO_3)_3$, 8×10^{-4} M NH_4NO_3	-0.75	2	(R = 1.4)	0.19	
AtO ₃ ⁻	0.1 M $Fe(ClO_4)_2$ = $Fe(ClO_4)_3$, 0.3 M $HClO_4$		7	(R = 1.4)	0.88	
14-3 ^b H ⁺	Aqueous phase: 0.001 M $Fe(ClO_4)_2$	-0.87	0.5 standing		1.9	
Br ₂ -oxidized At	0.1 M $Fe(ClO_4)_3$, 0.3 M $HClO_4$		+0.1 agitating			
	Organic phase: 0.01 M I_2		2.5 standing			
			+0.1 agitating		3.6	
14-4 ^c E	Aqueous phase: 5×10^{-4} M $Fe(ClO_4)_2$, 0.1 M $Fe(ClO_4)_3$, 0.03 M $HClO_4$	-0.89	1 dark		5.2	
AtI	Organic phase: 0.005 M I_2		1 dark +0.3 fluorescent		0.26	
			Same as above +0.3 dark		4.9	
14-5 ^d E	Aqueous phase: 4×10^{-4} M $Fe(ClO_4)_2$	-0.89	0.3 fluorescent		0.09	(0.01 M $NaIO_3$) 0.1
AtI	0.1 M $Fe(ClO_4)_3$, 0.1 M $HClO_4$					
	Organic phase: 10^{-4} M I_2					
14-6 ^e I ⁺	Same as 14-5 but no I_2	-0.89	0.5 dark		2.6	
At(O)			0.5 dark +0.5 fluorescent		0.64	
			Same as above +0.7 dark		1.7	
			Same as above +3.7 light		0.13	1/3 (0.1 M $HClO_4$)
			Same as above +1 dark	(R = 2)	0.4	
14-7 D	0.1 M $Fe(ClO_4)_2$ = $Fe(ClO_4)_3$	-0.75	16	1/9	6.2	
At ⁻	0.2 M $HClO_4$			(0.2 M $HClO_4$)		
	2×10^{-5} M I_2 , 5×10^{-4} M H_2SO_4			(R = 1.2)		

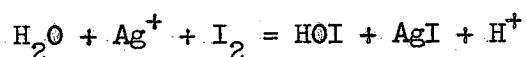
7. The Iodide-Iodine Couple (Tables XV and XVI)

This couple is seen to be capable of reducing higher astatine states and oxidizing lower ones to extractable At (0). The extraction behavior will be examined in detail in Section V, where evidence will be presented that the At (0) species are AtI, with a distribution constant of 5.5, and unextractable AtI_2^- .

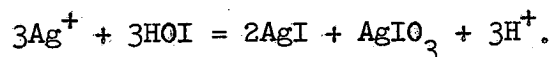
In the presence of this couple the astatine does not usually coprecipitate with AgI, even on repeat precipitations. The astatine in the supernate is unextractable, and precipitates nearly completely with lead iodate. The following reaction seems plausible:



since under these conditions the I_2 -AgI couple has a potential of about -1.4 v. The iodine in the solution is of course consumed by the reactions:



and



However, the precipitation of the silver iodate may be slow and incomplete under the experimental conditions employed, explaining the failure of the AtO_3^- to be carried. On the other hand, the cause of the extensive coprecipitation of the astatine in Expt. 16-6 is not known.

To understand the coprecipitation results with TlI and PbI_2 we must note that both of these precipitates take up iodine from solution -- the latter to a small extent from solutions containing a great deal of I_3^- , the former much more extensively.¹¹ The iodine may be removed nearly completely from either precipitate by one or two washes with acetone.

It appears that the astatine shows behavior similar to that of the iodine, carrying essentially completely on the TlI, even at quite low iodine concentrations; carrying partially on the PbI_2 , particularly at high iodine concentrations; and being nearly completely washed off either by acetone. This is the behavior one might expect for AtI, and we may

Table XV

Reaction of astatine with the I_2 -- I^- couple
(Emf -0.60 to -0.61)

Expt. Stock	Reaction mixture	Time (hr)	Extraction		Coprecipitation	
			Dilution	D	Dilution	Precipitate % precip.
15-1 F AtO_3^-	0.1 M NaI = NaI ₃ , 1 M HClO ₄ , 0.002 M Ce(ClO ₄) ₃	3 10	1/30	0.5	1/10 1/10	AgI 4 TlI·xI ₂ ^a 99 (no acetone wash)
15-2 F' AtO_3^-	0.05 M NaI, 0.025 M NaI ₃ , 0.16 M HClO ₄ 0.002 M Ce(NO ₃) ₃ , 0.003 M NH ₄ NO ₃	12	1/100 (0.2 M HClO ₄)	3.7	1/10	TlI ^a 4 (96% in 2 acetone washes)
15-3 D At^-	0.02 M NaI, 7x10 ⁻⁴ M NaI ₃ , 0.1 M HClO ₄ 5x10 ⁻⁴ M H ₂ SO ₄	2 27	1/5 (0.1 M HClO ₄) (R = 1.2)	0.77	4/5	PbI ₂ 1 (2% in acetone wash)

^a Precipitated with a neutral 0.25 M TlNO₃ solution.

Table XVI

Coprecipitation of astatine from solutions containing I_2 and I^- (astatine taken from E-type stocks)						
Expt.	(M)			Precipitate	% in precipitate after all washes	% in acetone wash(TlI and PbI_2 only)
	I_3^-	I^-	$HClO_4$			
16-1	--	0.02	0.001	AgI	40(90)	
16-2	--	0.02	0.01	AgI	16	
16-3	--	0.02	0.1	AgI	10	
16-4 ^B	2×10^{-4}	0.01	0.001	AgI	1.6 ^b	
16-5 ^B	10^{-3}	0.01	0.01	AgI	3 ^c	
16-6 ^B	0.0035	0.01	0.01	AgI	48 ^{c,d}	
16-7	--	0.02	0.001	TlI ^δ	55(53)	23(38)
16-8	--	0.02	0.01	TlI ^δ	51	41
16-9	6×10^{-7}	0.02	0.001	TlI ^δ	42	52
16-10	2×10^{-5}	0.02	0.001	TlI	16	81
16-11 ^B	3×10^{-5}	0.02	0.01	TlI	9	73
16-12	10^{-4}	0.02	0.001	TlI ^δ	8	90
16-13 ^B	0.007	0.02	0.016	TlI	13	82
16-14	2×10^{-5}	0.04	0.001	PbI_2	0.2	0.3
16-15 ^B	0.001	0.04	0.01	PbI_2	3	5
16-16 ^B	0.007	0.04	0.016	PbI_2	6	75
16-17	6×10^{-7}	5×10^{-7}	0.001	$Pb(IO_3)_2^{a,δ}$	0.5	

^aSolution made 0.02 M in $NaIO_3$ immediately prior to precipitation.

^bAn excess of NaI, followed after stirring by an excess of $AgNO_3$, was added to the supernate. Two percent of the activity was found in the resulting precipitate.

^cWhen an excess of $NaIO_3$, followed after stirring by an excess of Pb^{++} , was added to the supernate under the series-1 safelite, 91% of the activity of the supernate came down with the mixed $AgIO_3$ -- $Pb(IO_3)_2$ precipitate.

^dAn aliquot of the supernate was extracted with CCl_4 under the safelite. The D value was < 0.01.

relate it to the observation that astatine is gradually incorporated into solid iodine in equilibrium with an aqueous solution.²⁰

The coprecipitation of astatine from these mixtures with all three iodides appears independent of acidity between pH 1 and pH 3.

In Table XVI some of the results in iodine-free solutions which were discussed in Section III are compared with the results in the presence of macro quantities of I_2 . When no iodine is present, both AgI and TlI precipitate appreciable quantities of astatine, and only a portion of the astatine can be removed from the TlI by acetone washes. In these cases the coprecipitation with AgI is greatly reduced when the acidity is increased. The "macro iodine behavior" sets in when the I_3^- concentration exceeds about 10^{-5} M.

All of this suggests that at vanishingly small iodine concentrations the astatine is strongly adsorbed at active sites on or in the crystal lattices. These sites might then be preferentially occupied by iodine molecules when these are present at a sufficiently high concentration. Increasing the acidity may result in formation of appreciable I_2 by air oxidation of iodide -- perhaps enough to reduce the coprecipitation with AgI, while not enough to affect the coprecipitation with the more strongly adsorbing TlI.

8. The I^- -- I_2 -- Br^- -- IBr -- Br_2 System.

This system bridges the emf gap between the iodide-iodine and the bromide-bromine couples and is investigated in Section V. In this system the astatine displays varying degrees of extractability, and the species $AtBr$, $AtBr_2^-$, and $AtIBr^-$ are postulated in addition to AtI and AtI_2^- .

9. The As(III) -- As(V) Couple (Table XVII)

This couple is known to react quite rapidly and reversibly with the iodine-iodide couple,²⁸ and therefore it should be extremely suitable for use with astatine. The experiments indicate extractable $At(0)$ to be the equilibrium species for $pH < 3$, but at higher pH the extractability falls off. Experiment 17-3 shows that the extractability is restored quickly

Table XVII

Reaction of astatine with the As (III) -- As (V) couple									
Expt.	Stock	Reaction Mixture	Emf (volts)	Time (hr)	Extraction		Cocrecipitation		% precip.
					Dilution	D	Dilution	Precipitate	
17-1	F ⁻	0.02 M As(III) = As(V), 0.2 M HClO ₄	-0.51	4		4.2			
	AtO ₃ ⁻	4x10 ⁻⁴ M Ce(NO ₃) ₃ , 10 ⁻³ M NH ₄ NO ₃ trace I ⁻							
17-2	E	0.01 M As(III) = As(V), 6x10 ⁻⁴ M NaI	-0.06	0.2		0.67			
	AtI	0.1 M NaH ₂ PO ₄ = Na ₂ HPO ₄ (pH 6.8)		6		0.55			
				12			TlI	(3% in acetone wash)	94
17-3	E	0.01 M As(III) = As(V), 0.1 M HOAc =	-0.25	0.2		0.16			
	AtI	NaOAc, 6x10 ⁻⁴ M NaI (pH 4.6)		12		0.14		TlI	86
		An aliquot of this mixture made 0.5 M in HClO ₄ and agitated 3 min with an equal volume of CCl ₄ :	-0.53			3.2		(3% in acetone wash)	
17-4	E	0.01 M As(III) = As(V),	-0.38	0.2		3.5			
	AtI	6x10 ⁻⁴ M NaI (pH 3) ^a		6		1.5			
				12			PbI ₂	(3% in acetone wash)	91
17-5	E	0.01 M As(III) = As(V),	-0.49	0.2		6			
	AtI	6x10 ⁻⁴ M NaI, 0.1 M HClO ₄		6		3.4			
				12			PbI ₂	(3% in acetone wash)	57
							TlI	(3% in acetone wash)	96
17-6 ^B	E	0.01 M As(III) = As(V),	-0.48	48		1/20	PbI ₂	(no acetone wash)	28
	AtI	0.06 M HClO ₄ , 0.024 M NaI				(0.1 M HClO ₄) (0.02 M NaI)			
						1/20	PbI ₂	(no acetone wash)	36
						(0.1 M HClO ₄) (0.05 M NaI)			
17-7	D	0.1 M As(III) = As(V), pH 3 ^a	-0.38	2	1/5	2.2			
	At ⁻	5x10 ⁻⁵ M NaI, 5x10 ⁻⁴ M H ₂ SO ₄			(0.001 M HClO ₄) (R = 1.2)				
				17	1/5	2.4	1/10	PbI ₂	95
					(0.001 M HClO ₄)	(0.001 M HClO ₄)	(2% in acetone wash)		
					(R = 1.2)				
					1/20	2.0	1/5	TlI	93
					(0.001 M HClO ₄)	(0.001 M HClO ₄)	(4% in acetone wash)		
17-8	D	0.08 M As(III), 0.04 M As(V),	-0.52	7					
	At ⁻	0.5 M HClO ₄ , 0.003 M NaI				1/40	PbI ₂	(6% in acetone wash)	16
		5x10 ⁻⁴ M H ₂ SO ₄				1/10	TlI	(2.5% in acetone wash)	97
				17	1/9	4.3	1/20	AgI	94
					(0.6 M HClO ₄) (R = 1.3)	(0.3 M HClO ₄)			
						1/3	TlI	(2% in acetone wash)	95
						(0.3 M HClO ₄)			

^aBuffered by the H₃AsO₄ -- H₂AsO₄⁻ system

after acid is added to a system at a high pH. This may be interpreted as reversible reduction of the astatine to At^- by the arsenic couple as the latter's potential becomes less negative. In Section V further data on the extraction behavior of astatine in this system will be given and an attempt at a quantitative interpretation will be made.

Although the astatine is extractable at $\text{pH} < 3$, it coprecipitates nearly completely with TlI and AgI at all acidities. With PbI_2 it precipitates completely at $\text{pH} 3$, but only incompletely from 0.1 M acid. These results suggest that the precipitation is somehow shifting the equilibrium to favor reduction of the astatine.

Considering the effect of the precipitation on the arsenic species, we find that none of the precipitating cations precipitate As(III) under the conditions employed. The Tl^+ ion does not precipitate As(V) either; Ag^+ precipitates it incompletely at $\text{pH} 3$ and not at all when the pH is much lower; and Pb^{++} precipitates As(V) even at the highest acidities used. Thus it does not seem that changes in the concentrations of the arsenic species can explain the experimental results.

The results do make a little sense if we postulate that the equilibrium shift results from the reduction of the At^- concentration by its inclusion in the insoluble iodide precipitate. Exactly the same shift should result from the removal of I^- from the solution during the precipitation, in accordance with the reaction:



where M^+ is a precipitating cation. The relatively soluble PbI_2 would then cause the least shift and thus might only partially coprecipitate the astatine at the highest acidities when the normal equilibrium most strongly favors $\text{At} (0)$. Of course the Pb^{++} is also rendering the solution more reducing by precipitating the As (V) .

We must observe that the free-iodine concentrations in these solutions are extremely low. Thus Expts. 17-2, -3, -4, and -5 have respective I_2 concentrations of the order of 10^{-25} M , 10^{-19} M , 10^{-15} M , and 10^{-11} M . In the former two cases, the iodine concentrations are actually considerably lower than the astatine concentrations (10^{-13} to 10^{-15} M), and under

such conditions AtI is probably completely dissociated. Even though the iodine is in excess of the astatine at the highest acidities, it is still probably lower than typical impurity levels, and while the iodine itself will be maintained in concentration by the relatively large iodide reservoir, we cannot feel particularly confident of the ability of such a low iodine concentration to protect the astatine from reaction with impurities.

Thus we again find ourselves in a situation in which we are uncertain of the nature of the At (0) species. It is now an unavoidable situation, however, which arises from the fact that iodine is more readily reduced to the (-1) state than is astatine. Despite these ambiguities, we will use these results to estimate the $\text{At}^- \text{ -- At (0)}$ potential to be about -0.3 volt.

10. The Ferro-Ferricyanide Couple (Table XVIII)

This couple also reacts fairly rapidly with iodine and iodide, but much mystery still surrounds the reaction.²⁹ The equilibrium is photosensitive in much the same way as the $\text{I}^- \text{ -- I}_2 \text{ -- Fe}^{++} \text{ -- Fe}^{+++}$ equilibrium.³⁰ The situation is complicated by the fact that the ion HFe(CN)_6^{-3} is a weak acid, and its salts are also somewhat weak.²⁴ Therefore the reducing power of the couple decreases both with increasing acidity and with increasing salt concentration.

These factors are evident in the solvent-extraction behavior of astatine in the experiments of Table XVIII. Even the photochemical effect is seen in Expt. 18-4 (note g). We shall interpret the decrease in extractability as indication of reduction to At^- . It appears that equilibrium is attained fairly rapidly, making it necessary to consider equilibrium shifts accompanying dilution of the reaction mixture for extraction or coprecipitation. Therefore the emf's of the extraction and coprecipitation mixtures are indicated in the table.

Once more we are confronted with a difficulty in identifying the At (0) species. In the most reducing of the solvent-extraction mixtures (Expt. 18-3), the aqueous I_2 concentration is of the order of 10^{-17} M. If the At (0) species is still AtI, the reaction is

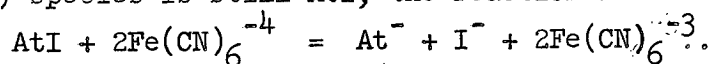


Table XVIII

Reaction of AtI (Stock E) with the ferrocyanide-ferricyanide couple ^a									
Expt.	Reaction mixture	Emf (volts)	Time (hr)	Extraction		Cocipitation		Precipitate % precip.	
				Dilution	Emf	Dilution	Emf		
18-1 ^a	0.01 M $K_4Fe(CN)_6$, 4×10^{-4} M $K_3Fe(CN)_6$, 0.025 M NaI, 0.002 M $HClO_4$ (pH 4.8) ^b	-0.33	4			1/3	-0.31	40	AgI
						1/3	-0.31	99	TlI_2 ^c (1% in acetone wash)
						1/3	-0.31	4	PbI_2 ^d (2% in acetone)
18-2 ^b	0.09 M $K_4Fe(CN)_6$, 5×10^{-4} M $K_3Fe(CN)_6$, 6×10^{-4} M KI, 0.007 M H_2SO_4 (pH 4.95) ^b	-0.32	11	1/10 (0.01 M $HClO_4$)	-0.36	1/20	-0.26	> 99	TlI_2 ^c (1% in acetone)
			23			1/100 ^e (0.012 M H_2SO_4)	-0.41	> 99	TlI_2 ^c (< 3% in acetone)
						1/10 (0.006 M H_2SO_4)	-0.42	7	PbI_2 ^d (4% in acetone)
18-3 ^{a, r}	0.01 M $K_4Fe(CN)_6$, 2.6×10^{-4} M $K_3Fe(CN)_6$ = KI, 5×10^{-4} M H_2SO_4 + CCl_4 Same as 18-3, but: KI = $K_3Fe(CN)_6$ = 0.0014 M	-0.32	0.1		-0.32	1/20 (0.012 M H_2SO_4)	-0.42	21(18) ^e	AgI
18-4 ^{a, r}		-0.36	0.1		-0.36				

^aThe ferricyanide was formed in situ by the oxidation of ferrocyanide with iodine, a reaction which appeared to be quite rapid under these conditions.

^bThese solutions are buffered by the $HFe(CN)_6^{3-} \rightleftharpoons Fe(CN)_6^{4-}$ system, which has an acid dissociation constant 6×10^{-5} .²⁴

^cAfter the thallium was added, the first of these solutions became 0.2 M and the second 0.1 M in $HClO_4$ because of the acidity of the stock $TlClO_4$ solution used (see Sections II-C and II-F).

^dAn 0.1 M excess of Pb^{++} was added, making the final solution 0.01 M in $HClO_4$ (see Sections II-C and II-F).

^eThese precipitations were carried out under fluorescent light.

^fThere was no change in D after another 20 min agitation. The organic phase was removed and the aqueous phase was agitated for 5 min with fresh CCl_4 , again giving D = 0.056.

^gNo change in D after another 20 min agitation. However, a further 25 min agitation under fluorescent light caused D to rise to 0.45.

The variation in D between Expt. 18-3 and Expt. 18-4 is compatible with this interpretation, but comparison of Expt. 18-2 with Expt. 18-4 does not reflect the expected I^- dependence. However, the conditions of Expt. 18-2 are considerably different from those of Expts. 18-3 and 18-4, and the emf computed for Expt. 18-2 may be in error.

No extensive quantitative study of this equilibrium has been made, although such a study may well prove rewarding. A prior clarification of the iodine-ferrocyanide system might be in order, however. The limited results presented here would indicate an $At^- \rightleftharpoons At(0)$ potential of about -0.4 v, which is 0.1 v more negative than the potential obtained from the study of the arsenic system. The discrepancy may be due to an inaccurate estimate of the ferro-ferricyanide potential. The difference is of considerable importance, since if the reduction occurs at -0.3 v, it is virtually certain that the $At(0)$ species is not AtI , while at -0.4 v there remains some ambiguity.

It is a little surprising that the astatine in these solutions can be completely coprecipitated with TlI , but only partially with AgI and hardly at all with PbI_2 . This may relate to the extent to which the various precipitants disturb the ferro- and ferricyanide ions in the solution. The Tl^+ ion does not precipitate ferricyanide under any of the conditions used. It does not precipitate ferrocyanide if the pH is 2 or less, and only incompletely precipitates it at lower acidity. The Pb^{++} ion does not precipitate ferricyanide, but precipitates ferrocyanide under all conditions employed. The Ag^+ ion precipitates both ferro- and ferricyanide under all conditions.

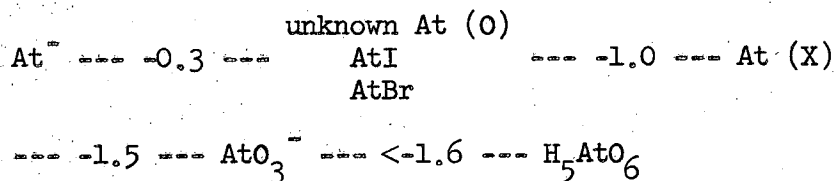
Thus Tl^+ causes the least disturbance of the emf of the solution. The fact that AgI coprecipitates considerably more astatine than PbI_2 may be due to the fact that Ag^+ precipitates ferricyanide while Pb^{++} does not, or it may be the consequence of a shift in the astatine equilibrium resulting from removal of At^- and I^- by the highly insoluble AgI . Or it may simply result from part of the astatine being gobbled up by the rapidly precipitated AgI before it can be affected by the equilibrium shifts.

11. The Reaction of Astatine with SO_2 (Table XIX)

While nobody in his right mind would consider the sulfite-sulfate couple to be reversible, SO_2 does rapidly reduce iodine species, and it was one of the first reducing agents used in astatine studies. The results obtained by Johnson et al. have already been discussed in Section III. My results show that regardless of whether or not the reaction mixture contains macro amounts of iodine, the astatine is converted by SO_2 to a nonextractable state which coprecipitates nearly completely with AgI , PbI_2 , and TlI (though only the last was precipitated from iodine-free systems). It seems reasonable to identify this state as At^- .

12. Conclusions

The results of the work reported in this section are summarized in Table XX. The identity, and even the multiplicity of the intermediate positive oxidation states of astatine remain indeterminate, as do the precise potentials relating such states at AtO_3^- and $\text{At} (0)$. However, it is clear that at least one intermediate positive state does exist, and we shall continue to designate it as $\text{At} (X)$. We have also seen that the nature of the $\text{At} (0)$ species present in reducing solutions is highly ambiguous. Subject to these uncertainties, we may construct the following rough potential diagram for astatine at $\text{pH} \sim 1$ (assuming no pH dependence for the $\text{At} (0) \rightleftharpoons \text{At}^-$ couples):



This potential scheme probably represents a modest improvement over that estimated by Latimer on the basis of the work of Johnson et al.²²

It appears, then, that astatine differs markedly from the other halogens, since none of them have positive valence states between 0 and +5 that are stable to disproportionation. Such a stabilization of lower positive states in astatine might be expected from analogy with the nitrogen-group elements.

Table XIX

Reaction of astatine with the SO_2 -- $\text{SO}_4^{=}$ couple (emf = 0 to + 0.1)

Expt.	Stock	Reaction mixture	Time (hr)	Extraction		Coprecipitation	
				Dilution	D	Dilution	Precipitate % precip.
19-1	F'	0.1 M SO_2 , 0.01 M H_2SO_4 , 0.2 M HClO_4	4	(R = 2)	0.002	1/4	TlI^a 87
	AtO_3^-	0.002 M $\text{Ce}(\text{NO}_3)_3$, 0.004 M NH_4NO_3 trace I $^-$				(0.1 M HClO_4)	(0.3% in acetone)
19-2 $^\alpha$	F''	0.1 M SO_2 , 0.05 M H_2SO_4 , 0.001 M NaI	48		0.05	1/3	TlI^δ 94
	AtO_3^-	4×10^{-4} M $\text{Ce}(\text{NO}_3)_3$, 8×10^{-4} M NH_4NO_3				(0.07 M HClO_4)	(0.6% in acetone)
19-3 $^\beta$	E	0.1 M SO_2 , 0.1 M H_2SO_4 , 0.02 M NaI	48			1/20	TlI^b > 99.5
	AtI					(0.1 M HClO_4)	
						1/20	PbI_2^b 91
19-4	E	0.06 M SO_2 , 0.04 M H_2SO_4 , 0.001 M NaI	4	1/1000	0.026	1/1000	PbI_2^b 90
	AtI			(0.1 M HClO_4) (R = 1.5)		(0.01 M HClO_4)	
19-5	E''	0.1 M SO_2 , 2×10^{-4} M H_2SO_4	4			1/17	PbI_2^b 97
	AtI	0.001 M NaI				(0.01 M HClO_4)	
19-6 $^\beta$	I	0.1 M SO_2 , 0.005 M H_2SO_4	4	1/3	0.04	1/17	AgI > 99.5
	At(O)					1/30	TlI 91
						(0.001 M HClO_4)	(1% in acetone)

^a Precipitated with a neutral 0.25 M TlNO_3 solution.^b No acetone wash was used.

Table XX

Redox behavior of astatine		
Emf (volts)	Couple used	Behavior of astatine
-1.6	$\text{IO}_3^- \text{ -- HIO}_4$	Unextractable; coprecipitates completely with insoluble iodates, not at all with KIO_4
-1.4 to -1.5	$\text{Cl}^- \text{ -- Cl}_2$	Unextractable; coprecipitates partially with insoluble iodates from the more oxidizing solutions
-1.1 to -1.3	Cr(III) -- Cr(VI)	Variable extractability; partial coprecipitation with lead iodate ?
-1.0 ^a to -1.3	$\text{Br}^- \text{ -- Br}_2$	Unextractable; not coprecipitated with insoluble iodates except to a small extent from the most oxidizing solutions
-0.9 to -1.0	Fe(II) -- Fe(III) $\text{VO}^{++} \text{ -- VO}_2^+$	Extractable in dark. Unextractable in light; not coprecipitated with lead iodate
-0.4 to -1.0	$\text{I}^- \text{ -- I}_2$ -- IBr -- Br As(III) -- As(V) Fe(II) -- Fe(III)	Varying degrees of extractability; not coprecipitated with AtI , AtBr , AtI_2 , insoluble iodides or iodates (except in arsenic system, in which coprecipitation with iodides occurs); absorbed by TLI along with the I_2 from an I^- -- I_2 mixture
-0.3 to -0.4	Ferro-ferril-cyanide As(III) -- As(V)	Varying degrees of extractability, decreasing as conditions become more reducing; more or less completely coprecipitated with insoluble iodides
0 to -0.3	As(III) -- As(V)	Reduced extractability; completely coprecipitated with insoluble iodides
+0.1 to 0	$\text{SO}_2 \text{ -- SO}_4^{--}$	Unextractable; completely coprecipitated with insoluble iodides

^aBased on the results of Section V.^bOnly if the system contains macro concentrations of iodine. Otherwise unknown At(O) species will be present.

V. QUANTITATIVE STUDIES OF THE SOLVENT

EXTRACTION OF ASTATINE INTO CCl_4

A. Introduction

In the course of the work described in the previous section, a number of solvent-extraction systems involving astatine seemed to warrant detailed study in order to obtain more positive identification of the species involved. Certain of these are examined in this section.

The studies of the previous section indicated that in the presence of iodine and iodide, astatine was more or less extractable into CCl_4 , and that it was not coprecipitated with insoluble iodides, but did carry with I_2 absorbed by a TlI precipitate. This was the behavior expected from an interhalogen such as AtI . If the species is AtI , it should in general show properties similar to those of the homologous IBr . This conclusion is tested in the first three parts of this section, which deal with the reactions of $\text{At}(\text{O})$ with other halogens and interhalogens. The last part of the section concerns an unsuccessful attempt to study quantitatively a redox reaction of $\text{At}(\text{O})$ not involving another halogen.

B. The I^- -- I_2 System

1. Experimental

Astatine was added to the two-phase systems as an aliquot of either an iodine solution in CCl_4 or an aqueous iodine-iodide solution. The "early" group of experiments was performed at room temperature (21 to 23°C) in daylight or fluorescent light. The "later" experiments were carried out at $21 \pm 0.5^\circ\text{C}$ in black-taped, opaque-stoppered tubes.

2. Results and Discussion

The principal results appear in Tables XXI and XXIA. The systems appeared to reach equilibrium after 1 minute of agitation, although some mixtures occasionally showed slow drifts in D over several hours, both when the mixtures were agitated continuously and when they were allowed

Table XXI

Carbon tetrachloride extraction of astatine from iodide-iodine systems ^a							
Expt.	(I ⁻) (M)	(I ₂) CCl ₄	D _{initial}	D _{final}	Time (hr)	Notes and special conditions	D _{calc}
Early experiments (21 to 23°C)							
1	10 ⁻⁵	0.0010	6.3	6.3	0.5	c	5.4
2	1.0x10 ⁻⁴	0.0010	9.4	6	0.1		4.6
3	1.0x10 ⁻⁴	0.0010	6.5				4.6
4	9x10 ⁻⁵ (1.0x10 ⁻⁴)	0.010	5.7				4.7
5	9x10 ⁻⁵ (1.0x10 ⁻⁴)	0.010	8.7 ^b			c	4.7
6	0.00107	1.0x10 ⁻⁴	3.1	2.5	24 ^d		1.8
7	0.00115	1.0x10 ⁻⁴	2.6 ^b			c	1.7
8	0.00103	1.0x10 ⁻⁴	3.8	3.5	0.3	1.1 M NaClO ₄	1.8
9	0.00120	6x10 ⁻⁴	3.3			0.1 M HClO ₄	1.6
10	0.00120	6x10 ⁻⁴	3.3	3.3	30 ^d	0.001 M HClO ₄	1.6
11	0.00120	6x10 ⁻⁴	3.1	2.5	6 ^d	0.03 M HOAc = NaOAc pH 4.6	1.6
12	0.00120	6x10 ⁻⁴	2.2	1.7	30 ^d	0.035 M NaH ₂ PO ₄ , 0.015 M NaH ₂ PO ₄ pH 7.2	1.6
13	0.00114	0.0010	2.8 ^b	2.2	4 standing + 0.5 agitating		1.7
14	0.00103 (0.00107)	0.004	2.6	2.6	1 ^d	0.00075 M HClO ₄	1.8
15	0.00104 (0.00107)	0.004	3.3	3.2	1 ^d	1 M NaClO ₄ , 0.00075 M HClO ₄	1.8
16	0.00105 (0.00115)	0.010	2.8	e			1.8
17	0.00105 (0.00115)	0.010	3.1 ^b			c	1.8
18	0.00112 (0.00213)	0.097	2.0			Aqueous phase: 1 count/min/μl	1.7
19	0.00117 (0.00223)	0.098	2.1			Aqueous phase: 300 counts/min/μl	1.65
20	0.00120 (0.0023)	0.098	3.1	2.2	4 standing + 0.5 agitating		1.6
21	0.00111 (0.00214)	0.10	1.9			R = 4	1.7
22	0.00108 (0.00182)	0.097	3.0 ^b	2.6	1	1.1 M NaClO ₄	1.74
23	0.0104	0.0009	0.33	0.30	1		0.25
24	0.0103 (0.0107)	0.0036 (0.0040)	0.39	0.34	1	0.00075 M HClO ₄	0.25
25	0.0104 (0.0107)	0.0036 (0.0040)	0.44	0.43	1	1.0 M NaClO ₄ , 0.00075 M HClO ₄	0.25
26	0.101	1.1x10 ⁻⁴ (2.2x10 ⁻⁴)	0.034				0.027
27	0.74	7x10 ⁻⁶ (5x10 ⁻⁵)	0.0046			R = 1.1	0.0037
28	0.75	1.6x10 ⁻⁵ (1.2x10 ⁻⁴)	0.0041				0.0037

Table XXI (cont'd.)

Expt.	(M)		D _{initial}	D _{final}	Time (hr)	Notes and special conditions	D _{calc}
	(I ⁻)	(I ₂) CCl ₄					
Later experiments (21 ± .5°C) ^f							
29 ^f	5.9x10 ⁻⁶ (1.08x10 ⁻⁵)	0.088		12.1	0.5		5.4
29a ^f	5.3x10 ⁻⁶ (8.8x10 ⁻⁶)	0.088		9.0	0.5	0.9 M NaClO ₄ , 0.0008 M HClO ₄	5.4
29b ^f	5.0x10 ⁻⁶ (8.4x10 ⁻⁶)	0.088		8.6	0.5	0.9 M NaClO ₄ , 1.0 M HClO ₄	5.4
30 ^f	6.6x10 ⁻⁶ (1.08x10 ⁻⁵)	0.087		5.7	0.5	0.9 M NaClO ₄ , 0.010 M NaH ₂ PO ₄ = Na ₂ HPO ₄ = pH 6.3	5.4
31	8.1x10 ⁻⁵		3.8			c	4.7
32	8.1x10 ⁻⁵	0.0010	4.4				4.7
33	8.1x10 ⁻⁵	0.0010	6.0			1.0 M NaClO ₄	4.7
34	9.6x10 ⁻⁵	0.0010	4.4				4.6
35	1.26x10 ⁻⁴	0.0010	4.5 ^b	4.3	5		4.4
36	1.23x10 ⁻⁴	0.0010	5.0 ^b			0.9 M NaClO ₄	4.4
37	1.26x10 ⁻⁴	0.0010	4.8 ^b			0.10 M HClO ₄	4.4
38	1.24x10 ⁻⁴	0.0010	4.7 ^b			0.009 M NaOAc 0.010 M HOAc, pH 4.6	4.4
39	1.24x10 ⁻⁴	0.0010	3.5 ^b			0.010 M NaH ₂ PO ₄ = Na ₂ HPO ₄ , pH 6.9	4.4
40	3.05x10 ⁻⁴	0.0010	3.3				3.4
41	9.7x10 ⁻⁴	0.0010	1.87 ^b				1.87
42	0.00105 (0.0010)	0.0009 (0.0010)	1.79 ^b	1.51 1.55	5 5+0.5	under fluorescent light	1.77
43	0.0046		0.66	0.59	0.1 ^g		0.54
44	0.0089	3x10 ⁻⁵	0.30 ^b				0.29
45	0.0107	0.0009 (0.0010)	0.255				0.245
46	0.0088	0.0009 (0.0010)	0.28 ^b				0.30
47	0.0088	0.0009 (0.0010)	0.28 ^b			Ordinary Baker and Adamson reagent CCl ₄ used.	0.30
48	0.0086	0.0009 (0.0010)	0.35 ^b			0.8 M NaClO ₄	0.30
49	0.0096 (0.017)	0.084 (0.093)	0.30 ^b				0.27
50	0.0195	0.0008 (0.0010)	0.138				0.138
51	0.097	0.0005 (0.0010)	0.031			R = 0.9 ^h	0.028
52	0.093	0.0006 (0.0011)	0.033 ^b			R = 0.88 ^{c,i}	0.029
53	0.98	1.8x10 ⁻⁵ (8x10 ⁻⁵)	0.0034	0.0032	0.1 in R = 2.6 ^{c,i} fluorescent light		0.0028
54	0.97	8x10 ⁻⁵ (0.0010)	0.0046			h	0.0028
55	0.68 (0.98)	0.036 (0.096)	0.0033			R = 5.0 ⁱ	0.0040

Notes to Tables XXI and XXIA

^aUnless R = organic volume/aqueous volume is specified, the two phases were approximately equal in volume, and the aqueous solutions were 0.0009 to 0.0010 M in HClO_4 with no inert salt. Acid, buffer, and inert salt concentrations are given to $\pm 5\%$. Iodide was added as NaI , and the iodide concentrations are indicated to $\pm 5\%$ for the "early" experiments, and to $\pm 1\%$ for the "later" ones. Iodine concentrations around 0.1 M are given to the same accuracy as the iodide, while iodine concentrations of 0.01 M and less are given to $\pm 10\%$. The corrections for the distribution of the iodine and for the formation of I_3^- and (in Expt. 55) of I_6^- were made using the data of Table XXII. These data are strictly applicable only at 21°C , and the corrected concentrations may be in error by a few percent in the room-temperature experiments. When the I_3^- correction resulted in appreciable changes, the uncorrected $\Sigma \text{I}^- = \text{I}^- + \text{I}_3^- + 2\text{I}_6^-$ and $\Sigma \text{I}_2(\text{CCl}_4) = \text{I}_2(\text{CCl}_4) + [\text{I}_2(\text{aq}) + \text{I}_3^- + 2\text{I}_6^-]/R$ are indicated in parentheses beneath the corrected (I^-) and (I_2) CCl_4 values. Values of D_{initial} were obtained after 1 to 5 min of agitation unless otherwise specified. Values of D_{final} were observed after the system had been agitated for the time indicated in the "time" column, except when it is specified that for some or all of the "time" the mixture had been allowed to stand.

^bValue of D_{initial} obtained after 10 to 15 min of agitation.

^cThe phases of these experiments were separated. To the aqueous phase was added a fresh iodine solution in CCl_4 of the same concentration as the original; to the organic phase was added a fresh iodide-triiodide solution of the same composition as the original aqueous phase. The results of these secondary extractions appear in Table XXIA. When entries in Table XXIA are marked with (a), as in Expt. 1, another similar extraction was carried out, the results being entered as Expt. 1'. Thus the original aqueous phase of Expt. 1 was contacted with a second fresh organic phase to give a D of 1.6, while its original organic phase was extracted with a second fresh aqueous solution to give a D of 8.3.

^dThe mixtures stood undisturbed for the indicated time, after which they were agitated for 1 to 5 min.

^eThe value of D oscillated with time between 2.6 and 3.2.

^fExpts. 29 and 30 were carried out at room temperature. Experiments 29a and 29b resulted from modification of the solutions of Exp. 29.

^gAfter organic phase had been made 0.0010 M in I_2 .

^hThe astatine was added in the aqueous phase (indicated only for selected experiments).

ⁱThe astatine was added in the organic phase (indicated only for selected experiments).

Table XXIA

Re-extraction of separated phases from experiments of Table XXI ^a									
		Original organic phase + + fresh organic phases				Original aqueous phase + + fresh aqueous phase			
Expt.	Original D	D _{calc}	D _{initial}	D _{final}	Time (hr)	D _{initial}	D _{final}	Time (hr)	
1	6.3 ^b	5.4	4.5 ^a			7.0 ^a			
1'			1.6			8.3			
5	8.7	4.7	6.5	8.2	1 standing + 0.5 agitating	6.1	6.7 ^a	2 standing + 0.5 agitating	
							11.3	Same as above + 4 agitating	
5'						6.3	6.3	4	
7	2.6	1.7	2.3 ^b			2.5 ^b	2.2	2 standing ^d + 0.5 agitating	
17	3.1	1.8	2.9 ^b			3.2 ^b	2.3	2 standing + 0.5 agitating	
31	3.8	4.7	2.0 ^c			5.5 ^a			
31'						6.0			
52	0.033	0.029	0.028 ^a						
52'			0.028						
53	0.0034	0.0028	0.0027 ^a						
53'			0.0027 ^a						

Notes to Table XXIA

^aThe phases of these experiments were separated. To the aqueous phase was added a fresh iodine solution in CCl_4 of the same concentration as the original to the organic phase was added a fresh iodide-triiodide solution of the same composition as the original aqueous phase. The results of these secondary extractions appear in Table XXIA. When entries in Table XXIA are marked with (a), as in Expt. 1, another similar extraction was carried out, the results being entered as Expt. 1'. Thus the original aqueous phase of Exp. 1 was contacted with a second fresh organic phase to give a D of 1.6, while its original organic phase was extracted with a second fresh aqueous solution to give a D of 8.3.

^bValue of D_{initial} obtained after 10 to 15 min of agitation.

^cWhen the organic phase was made 9×10^{-5} M in I_2 and the system was agitated for 5 min, D did not change. When the organic phase was made 0.010 M in I_2 and the system was again agitated for 5 min, D rose to 2.3.

^dAfter organic phase had been made 0.0010 M in I_2 .

to stand undisturbed. The distribution ratio appears independent of the relative volumes of the two phases (Expts. 21, 53, and 55) and usually remains nearly unchanged when the phases are separated and either is contacted with a fresh portion of the other. The distribution shows no systematic dependence on I_2 concentration or on H^+ concentration between pH 1 and 5 (Expts. 9 to 12 and 37 to 39). There does seem to be a slight but real dropoff of D at pH 7. The presence of 1 M $NaClO_4$ increases D some 20 to 30%. Comparison of Expts. 18 and 19 indicates the distribution to be independent of total astatine concentration, ruling out the possibility of radiation-induced reactions. The same D may be obtained regardless of whether the astatine is added in the aqueous or the organic phase (Expts. 51 to 55). Experiments 35, 42, and 53 indicate the absence of photochemical effects. The substitution of ordinary reagent-grade CCl_4 for our low-sulfur reagent does not alter the distribution (Expt. 47).

If the astatine species present were AtI distributed between the two phases and AtI_2^- in the aqueous phase, then we have

$$D = \frac{\text{total organic astatine}}{\text{total aqueous astatine}} = \frac{K_D^{AtI}}{1 + K_{AtI_2^-}(I^-)} \quad , \quad (V-1)$$

$$\text{where } K_D^{AtI} = \frac{(AtI)_{CCl_4}}{(AtI)_{aq}} \quad \text{and} \quad K_{AtI_2^-} = \frac{(AtI_2^-)}{(AtI)_{aq}(I^-)} \quad .$$

In Table XXI values of D_{calc} have been computed for $K_D^{AtI} = 5.5$ and $K_{AtI_2^-} = 2000$. The fit appears reasonably good between 10^{-4} and 1 M I^- , particularly for the "later" experiments. The "early" experiments give D's which are almost uniformly some 50% higher than the calculated values and those of the "later" experiments. It is hard to explain such a large difference. The "early" experiments also show more internal scatter and appear more prone to erratic time dependence than the "later" experiments.

The "early" experiments were carried out over a three-month period, using various batches of astatine. The "later" experiments

were conducted a year later, again over a three-month period. During the interval between the two sets of experiments, various reagent solutions were replaced and new stocks of double-distilled water were made up. It is possible that a systematic impurity accounts for the discrepancy.

Because of their greater internal consistency, and the greater care with which they were conducted, I have fitted D_{calc} to the "later" experiments.

Systems with low D sometimes show a decrease in D the first time the aqueous phase is extracted with fresh CCl_4 . Another extraction with fresh CCl_4 does not alter D , and the final value agrees well with D_{calc} (Expts. 52 to 53). It may be that the initial D is raised by the presence of small quantities of extractable astatine species other than AtI . Accordingly, we would expect that systems of low D which are not reextracted might give D 's higher than the calculated values (see Expt. 54).

For the $\text{IBr} \rightleftharpoons \text{IBr}_2^-$ system at 21°C , the corresponding constants are $K_D^{\text{IBr}} = 4.31$ and $K_{\text{IBr}_2^-} = 444$ (see part C of this section). The similarity of the K_D 's supports our identification of the astatine species as AtI . The difference between $K_{\text{IBr}_2^-}$ and $K_{\text{AtI}_2^-}$ is not surprising if we consider that the polyhalide ions tend to become increasingly stable as the central halogen becomes heavier. Thus the formation constant of I_3^- is 800, while that of Br_3^- is only 17.^{31,32}

If we consider the effect of inert salt to be due primarily to the salting of AtI out of the aqueous phase, we obtain a salting coefficient of approximately 0.1, i.e.:

$$\log_{10} D = \log_{10} D_0 + 0.1 (\text{NaClO}_4).$$

The analogous coefficient for IBr is 0.12 (Table XXII). The experiments at high I^- are also subject to a salt effect. However, data on other systems suggest that NaI has a considerably smaller salting coefficient than has NaClO_4 -- probably less than 0.05.²³ No salt correction has been included in the D_{calc} values.

Table XXII

Summary of interhalogen equilibrium constants used in astatine computations (21°C unless otherwise specified)			
Quotient	K	Salt effect ^a	References
$(I_2)_{CCl_4}/(I_2)_{aq}$	86 ^b	$\log K = \log K_o + 0.13 (NaClO_4) + 0.13(NaCl)^c + 0.1(NaBr)^c + 0.05(NaI)^c + 0.03(HClO_4)$	15,23,32
$(Br_2)_{CCl_4}/(Br_2)_{aq}$	27.1	Assumed the same as for I_2	15
$(IBr)_{CCl_4}/(IBr)_{aq}$	4.31	$\log K = \log K_o + 0.12(NaClO_4) + 0.096(NaBr) + 0.03 (HClO_4)$	Section V-C
$(I_3^-)/(I^-)(I_2)_{aq}$	800	$\log K = \log K_o + 0.02(NaX)^d + 0.05 (HClO_4)$	32
$(I_2Br^-)/(I_2)_{aq}(Br^-)$	14.3	Assumed the same as for I_3^-	33
$(IBr_2^-)/(IBr)_{aq}(Br^-)$	444	$\log K = \log K_o + 0.02(NaX)^d + 0.053(HClO_4)$	Section V-C
$(I_2Cl^-)/(I_2)_{aq}(Cl^-)$	~3	Assumed the same as for I_3^-	33
$(Br_3^-)/(Br_2)_{aq}(Br^-)$	17	Assumed the same as for I_3^-	31
$(I_6^-)/(I_3^-)^2$	~1	Neglected	34
$\left[\frac{(IBr)}{(I_2)^{1/2}(Br_2)^{1/2}} \right]_{CCl_4}$	19.6 ^e	Assumed independent of salt	22,35
$\frac{(I^-)(IBr)_{CCl_4}}{(Br^-)(I_2)_{CCl_4}}$	1.10×10^{-7}	Assumed independent of salt	15,22,35

^aAll logarithms are to the base 10. Stoichiometric salt concentrations are used. Thus IBr_2^- is assumed to have the same effect as Br^- .

^bTaken as the ratio of the solubilities (see Section II-C).

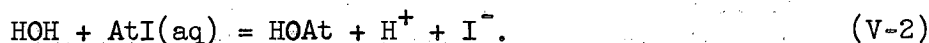
^cEstimated from the general salting behavior of these ions.²³

^dHere NaX is any sodium halide or sodium perchlorate.

^eCalculated from the value at 25°C³⁵ with the heat of dissociation of IBr in CCl_4 assumed equal to the vapor phase value of 1.36 kcal.²²

The lack of iodine dependence means that no redox reaction is coming into play, even at the most reducing potential of -0.42 v in Expt. 27. It also indicates that the reaction $\text{AtI}_2^- + \text{I}_2 = \text{AtI}_4^-$ is not important.

From the lack of pH dependence, we may set an upper limit of 10^{-11} to the constant for the reaction:



The corresponding constant for IBr is 1.5×10^{-7} .³⁶ We might expect the heavier interhalogen to be more stable to hydrolysis.

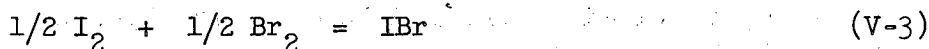
It is not clear to what reaction we should actually attribute the slight decrease in D around pH 7. Its independence of (I^-) (compare Expts. 9 to 12 with Expts. 37 to 39) precludes its representing the onset of reaction (V-2).

The experiments carried out at very low iodide concentrations (Expts. 1, 29, and 30), and in the absence of iodine (Expts. 31 and 43) are of interest, since they tend to bridge the gap between the experiments of this section and those detailed in Table VI. In both cases the experiments begin to show the presence of species both more and less extractable than AtI, similar to the three or more species needed to explain the solvent-extraction behavior of solutions free of both iodine and iodide.

C. The IBr -- IBr_2^- System

Introduction

The reaction



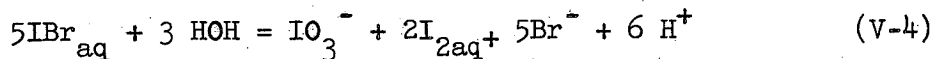
in CCl_4 has an equilibrium constant of 19.1 at 25°C .³⁵ Faull determined rough values of 3.9 and 380 for K_D^{IBr} and $K_{\text{IBr}_2^-}$, respectively, at this temperature.³⁶ (The more recent paper by Pungor et al. claiming that IBr_4^- is the principal complex ion suffers from fundamental thermodynamic

errors in interpretation.³⁷ When these are corrected, approximate agreement with Faull's work is obtained.) For the calculations needed to interpret the results of experiments with astatine in this system, it was desirable to know these two constants to well within $\pm 10\%$ at 21°C . The following experiments were designed to obtain this information.

Experimental

The two-phase reaction mixtures were prepared in Teflon-stoppered glass vessels which were agitated in the dark for 30 min at 21 to 21.5°C . Aliquots of each phase were added to solutions containing excess iodide, and the liberated I_3^- was titrated with standardized 0.01 M sodium thiosulfate, using starch indicator.¹² All volumetric ware used was calibrated.

Excess I_2 was added to systems in which Br^- was 0.01 M or less, and they were made 1 M in HClO_4 to suppress the reaction



for which $K_{250} \sim 10^{-20}$.²²

Results and Calculations

The results are shown in Table XXIII. The constants of Table XXII were used to calculate the quantities of iodine and bromine in the two phases.

From the data of Table XXIII it is possible to calculate directly $K_{\text{D}}^{\text{IBr}}$ and K_{IBr_2} for a 1 M HClO_4 medium. However to obtain values for the other media we must evaluate six correction parameters -- the effect of each of the reagents HClO_4 , NaClO_4 , and NaBr on K_{D} and on K_{IBr_2} . Since the limited data do not allow the determination of all of these, certain assumptions must be made. I have assumed that the effect of HClO_4 on K_{D} is equal to its salting out effect on iodine (salting coefficient = 0.03),³² and I have further assumed that NaClO_4 and NaBr affect K_{IBr_2} to the same extent that NaClO_4 affects the formation constant of I_3^- (see Table XXII).

Table XXIII

Distribution of IBr between CCl ₄ and aqueous bromide solutions ^a									
(21-21.5°C)									
A. Experimental Results									
Expt.	HClO ₄	NaClO ₄	R ^b	Stoichiometric amount added (M)			Titer (as IBr) (M)		
				NaBr	(IBr) CCl ₄	(I ₂) CCl ₄	CCl ₄	Aqueous	
1	1.0	--	1.136	0.001438	0.00694	0.01058	0.01591	0.001822	
2	0.99	--	2.028	0.01218	0.00240	0.001953	0.00335	0.001930	
3	0.06	--	4.48	0.1094	0.00488	1x10 ⁻⁶	0.001622	0.01449	
4	0.06	0.28	4.52	0.1103	0.00488	1x10 ⁻⁶	0.001694	0.01439	
5	0.06	0.78	4.48	0.1094	0.00488	1x10 ⁻⁶	0.001829	0.01374	
6	0.89	--	4.50	0.1100	0.00488	1x10 ⁻⁶	0.001579	0.01484	
7	0.065	--	47.3	0.960	0.00488	1x10 ⁻⁶	0.002051	0.1344	
B. Calculated Values									
Expt.	CCl ₄ (M)			Aqueous (M)				D _{exptl}	D _{calc}
	I ₂	Br ₂	IBr	"I ₂ "	"Br ₂ "	"IBr"	Br ⁻		
1	0.01049	7x10 ⁻⁶	0.00543	1.15x10 ⁻⁴	2x10 ⁻⁷	0.001707	9.05x10 ⁻⁴	3.18	3.18
2	0.001944	3x10 ⁻⁶	0.001404	2.5x10 ⁻⁵	1x10 ⁻⁷	0.001905	0.01058	0.737	0.734
3	7.6x10 ⁻⁵	7.5x10 ⁻⁵	0.001471	2x10 ⁻⁶	7x10 ⁻⁶	0.01448	0.0952	0.1016	0.1014
4	7.9x10 ⁻⁵	7.8x10 ⁻⁵	0.001538	2x10 ⁻⁶	7x10 ⁻⁶	0.01438	0.0962	0.1070	0.1071
5	8.6x10 ⁻⁵	8.5x10 ⁻⁵	0.001658	2x10 ⁻⁶	7x10 ⁻⁶	0.01373	0.0960	0.1208	0.1205
6	7.4x10 ⁻⁵	7.3x10 ⁻⁵	0.001432	2x10 ⁻⁶	7x10 ⁻⁶	0.01483	0.0955	0.0966	0.0968
7	9.6x10 ⁻⁵	9.5x10 ⁻⁵	0.001860	1x10 ⁻⁵	5x10 ⁻⁵	0.1343	0.826	0.01385	0.01384

^aThe quantities "I₂", "Br₂", and "IBr" include the concentrations of I₂Br⁻, Br₃⁻, and IBr₂⁻, respectively, and D = (IBr)_{CCl₄}/"IBr"_{aq}. Concentrations of HClO₄ and NaClO₄ are only accurate to ± 1%. The other "raw data" concentrations in part A of the table are accurate to ± 0.5%.

^bR = organic volume/aqueous volume.

With these assumptions we can evaluate the other parameters and conclude (see note (a) to Table XXII):

$$\log K_D^{\text{IBr}} = \log (4.31) + 0.12 (\text{NaClO}_4) + 0.03 (\text{HClO}_4) + 0.096 (\text{NaBr})$$

$$\log K_{\text{IBr}_2} = \log (444) + 0.02 (\text{NaClO}_4) + 0.02 (\text{NaBr}) + 0.053 (\text{HClO}_4).$$

The NaClO_4 correction to K_D and the HClO_4 correction to K_{IBr_2} turn out to be nearly the same as the analogous values in the I_2 -- I_3^- system.

The distribution ratios calculated from these expressions are tabulated as D_{calc} in Table XXIII, and can be seen to yield an adequate fit to the data. Since the data have obviously been overinterpreted, this serves only as a check of internal consistency. However, the results should easily provide the accuracy needed for interpretation of the astatine experiments.

D. Astatine in the I^- -- I_2 -- Br^- -- IBr -- Br_2 System

Since IBr is an oxidant intermediate between I_2 and Br_2 , it represents a possible means of investigating the region of transition from AtI to the unknown, unextractable, intermediate positive astatine state or states. This possibility has been pursued in the following experiments.

Experimental

The IBr was usually introduced into these systems as an aliquot of either an IBr solution or a Br_2 solution in CCl_4 . In a few experiments an aqueous bromine solution was used. Astatine was added from either an aqueous I_2 -- I^- solution or from a CCl_4 solution containing I_2 . The mixtures were generally agitated for 5 min.

At first reactions were carried out in black-taped tubes under ordinary room lighting. However, it was found that in systems with D less than about 0.05, the distribution could be altered by the exposure of the system to light while aliquots were being withdrawn for assay.

Thereafter, experiments were carried out in a darkroom illuminated by a Wratten series-1 red safelite using a 40-watt bulb. Certain of the mixtures were found to be sensitive even to this illumination, and ultimately it was necessary to work in black-taped tubes under the safelite, taking assays with minimal exposure of the systems to the light and with the least possible mixing of the phases. In this way it was possible to obtain results that did not differ from the results of awkward parallel experiments executed in total darkness.

When it was desired to re-extract an aqueous phase with a fresh organic phase of the same composition as the first, the latter was usually obtained from a suitably agitated duplicate experimental system to which no astatine had been added.

Results

The results are compiled in Tables XXIV through XXVI.

Calculations

The data of Table XXII were used in the calculations. Reaction (V-3) had to be considered for systems which did not contain a considerable excess of I_2 over IBr . The reaction



had to be invoked for systems containing a fairly high bromide concentration but little or no IBr (see Table XXII).³⁸

Discussion

The experiments of Tables XXIV and XXV appear to reach equilibrium within 5 min. The astatine distribution appears to be largely independent of the concentration of the astatine, the phase into which it is introduced, the type of CCl_4 used (Expt. 5, note b), and of the acidity between pH 0 and 3. The salt effect appears generally to be no greater than than found in the $I_2 \rightleftharpoons I^-$ system.

The lack of acidity dependence is particularly significant in the case of Expts. 6 -7 and 15-16, since it indicates that although

Table XXIV

Carbon tetrachloride extraction of astatine in Br ⁻ -- I ₂ -- IBr system ^a									
(21 ± .5°C)									
Expt.	R ^a	ΣBr ⁻	Br ⁻	I ₂	IBr	CCl ₄ IBr	IBr/I ₂	D _{exptl}	D _{calc}
Br ⁻ ~ .0009 M									
1	1.89	0.00094	0.00093	0.095	0.0000374	0.000032	0.00034	2.36	2.2
2	1.89	0.00094	0.00091	0.095	0.0000374	0.00032	0.0034	0.33	0.37
3	2.07	0.00094	0.00092	0.0087	0.000171	0.000150	0.0173	0.097	0.101
4	1.96	0.00108	0.00093	0.092	0.00182	0.00158	0.0171	0.110	0.101
5	1.89	0.00094	0.00093	0.00094	0.0000374	0.000032	0.034	0.052 (0.060) ^b	0.066
6	1.86	0.00164	0.00091	0.098	0.0096	0.0083	0.085	0.049	0.045
7 ^c	1.86	0.00164	0.00086	0.098	0.0096	0.0082	0.084	0.049	0.045
8 ^{d,f}	0.92	0.00116	0.00113	0.00079	0.000382	0.00028	0.36	0.0215	0.033
9 ^{d,f}	0.91	0.00094	0.00091	0.00080	0.000390	0.00030	0.37	0.040	0.034
10 ^{e,g}	1.89	0.00094	0.00091	0.00078	0.000374	0.00032	0.41	0.034	0.034
11 ^{h,d}	0.94	0.00094	0.00093	0.000072	0.000150	0.000113	1.6	0.036	0.032
12 ^e	1.93	0.00108	0.00093	0.00094	0.00185	0.00160	1.7	0.035	0.032
13 ^d	0.92	0.00094	0.00092	0.0000254 (0.0000243)	0.000154	0.000114	4.5	0.029	0.031
14 ^e	1.88	0.00163	0.00093	0.00111 (0.00097)	0.0094	0.0079	7.1	0.030	0.031
15 ^d	2.02	0.00163	0.00097	0.00042 (0.000109)	0.0088	0.0071	17	0.0265	0.031
16 ^{c,d}	2.02	0.00163	0.00092	0.00042 (0.000109)	0.0088	0.0071	17	0.025	0.031

17	0.91	0.0091	0.00232	0.076	0.0462	0.031	0.41	0.022	0.025
18	0.98	0.0116	0.0060	0.00117 (0.00096)	0.0185	0.0101	8.6	0.0104	0.0138
19 ⁱ	0.98	0.0116	0.0060	0.00055 (0.000102)	0.0185	0.0098	18	0.0076	0.0137
Br ⁻ ~ 0.009 M									
20 ^j	0.91	0.0091	0.0090	0.099	0.0000364	0.000021	0.00021	1.09	1.16
21 ^j	0.90	0.0090	0.0088	0.099	0.000138	0.000064	0.00065	0.60	0.53
22	0.91	0.0091	0.0091	0.0099	0.0000426	0.000020	0.0020	0.184	0.20
23 ^j	0.87	0.0087	0.0084	0.099	0.000452	0.00021	0.0021	0.172	0.20
24 ^g	0.91	0.0091	0.0088	0.099	0.000430	0.00020	0.0020	0.167	0.20
25 ^{f,k,l}	0.93	0.0093	0.0090	0.097	0.000372	0.000165	0.00171	0.163	0.21
26 ^c	0.94	0.0091	0.0087	0.095	0.000468	0.00021	0.0022	0.147	0.173
27 ^m	0.97	0.0092	0.0089	0.092	0.000456	0.00022	0.0024	0.162	0.174
28	0.91	0.0092	0.0089	0.0294	0.000452	0.00021	0.0071	0.080	0.067
29 ^h	0.88	0.0089	0.0083	0.098	0.00127	0.00060	0.0061	0.073	0.080
30 ^j	0.86	0.0086	0.0079	0.098	0.00147	0.00069	0.0071	0.085	0.074
31	0.93	0.0092	0.0091	0.00096	0.0000460	0.000021	0.022	0.029	0.028
32 ^j	0.91	0.0092	0.0089	0.0097	0.000452	0.00021	0.022	0.029	0.029
33	0.91	0.0092	0.0090	0.0097	0.000488	0.00023	0.023	0.025	0.028
34 ^{d,f}	0.93	0.0108	0.0091	0.095	0.00380	0.00177	0.0186	0.028	0.032
35 ^{e,n}	0.93	0.0108	0.0091	0.085	0.00382	0.00178	0.021	0.031	0.030
36 ^{e,r}	0.93	0.0092	0.0077	0.095	0.00386	0.00192	0.020	0.033	0.034
37 ^{d,j,n}	0.90	0.0090	0.0073	0.097	0.00461	0.0023	0.024	0.032	0.032
38	0.90	0.0097	0.0092	0.0092	0.00136	0.00062	0.068	0.0165	0.0161
39	0.90	0.0097	0.0092	0.0092	0.00136	0.00062	0.068	0.0188	0.0161
40	0.90	0.0167	0.0090	0.0695	0.0195	0.0090	0.13	0.0165	0.0135
41	0.91	0.0108	0.0092	0.0080	0.00388	0.00178	0.22	0.0133	0.0120
42	0.93	0.0092	0.0091	0.000080	0.0000460	0.0000214	0.27	0.0095	0.0117
43	0.93	0.0092	0.0090	0.000755	0.000474	0.00022	0.29	0.0116	0.0117
44	0.93	0.0094	0.0093	0.000088	0.000167	0.000077	0.87	0.0104	0.0105
45 ^{k,l}	0.91	0.0094	0.0093	0.000053	0.000126	0.000054	1.0	0.0106	0.0104
46	0.92	0.0094	0.0094	0.0000300	0.000146	0.000066	2.2	0.0079	0.0102
47	0.99	0.0100	0.0095	0.000305	0.00127	0.00060	2.0	0.0095	0.0101
48	0.91	0.0147	0.0093	0.00320	0.0136	0.0062	1.9	0.0115	0.0103

Table XXIV (cont'd.)

Expt.	R ^a	ΣBr ⁻	Br ⁻	CCl ₄				D _{exptl}	D _{calc}
				I ₂	ΣIBr	IBr	IBr/I ₂		
49	0.91	0.0234	0.0086	0.0105	0.0390	0.0183	1.75	0.0118	0.0109
50	0.91	0.0093	0.0092	0.0000245	0.000154	0.000070	2.9	0.0098	0.0103
51 ^o	1.36	0.0185	0.0092	0.00213 (0.00201)	0.0195	0.0107	5.0	0.0114	0.0102
52	0.93	0.0101	0.0093	0.000067 (0.0000402)	0.00190	0.00085	13	0.0097	0.0101
53	0.91	0.0234	0.0087	0.00114 (0.000429)	0.0393	0.0178	16	0.0039	0.0106

54	0.91	0.0276	0.0275	0.000088	0.000167	0.000041	0.47	0.0045	0.0044
55	0.92	0.0281	0.0280	0.0000240	0.000154	0.000038	1.6	0.0043	0.0041
Br ⁻ ~ 0.09 M									
56	1.86	0.094	0.093	0.097	0.0000356	0.0000163	0.000168	0.157	0.189
57	1.86	0.094	0.092	0.097	0.000372	0.000066	0.00069	0.055	0.066
58	1.86	0.094	0.094	0.00095	0.0000356	0.0000062	0.0065	0.0074	0.0090
59	1.84	0.101	0.094	0.098	0.00485	0.00082	0.0084	0.0063	0.0073
60	1.86	0.094	0.093	0.00080	0.000372	0.000063	0.079	0.0024	0.00195
61 ^p	2.00	0.160	0.089	0.090	0.0446	0.0084	0.094	0.0031	0.00193
62 ^p	0.96	0.119	0.118	0.000308 (0.000316)	0.00127	0.000101	0.33	0.00129	0.00116
63 ^p	0.92	0.121	0.121	0.0000236 (0.0000243)	0.000154	0.0000115	0.49	0.00113	0.00109
64 ^{1,p}	0.89	0.101	0.101	0.0000693 (0.0000713)	0.000479	0.000041	0.59	0.00177	0.00128
65 ^p	0.90	0.102	0.102	0.000057 (0.0000585)	0.000486	0.000042	0.73	0.0022	0.00126
66	1.84	0.103	0.096	0.00099	0.00485	0.00080	0.81	0.0022	0.00132
67 ^p	0.93	0.103	0.095	0.000255	0.0096	0.00090	3.5	0.0020	0.00129
68 ^{p,q}	0.91	0.101	0.093	0.000134 (0.000121)	0.0096	0.00089	6.7	0.00195	0.00131
69 ^p	2.00	0.184	0.110	0.00104 (0.00093)	0.0446	0.0071	6.8	0.00143	0.00111

70 ^a	0.91	0.283	0.283	0.000055 (0.0000585)	0.000486	0.0000161	0.29	0.00141	0.00050
Br ⁻ ~ 0.9 M (no NaClO ₄)									
71	1.86	0.94	0.93	0.091 (0.098)	0.0000368	0.0000142	0.000157	0.021	0.023
72	1.86	0.94	0.93	0.091 (0.098)	0.000380	0.0000186	0.000206	0.0176	0.020
73	1.86	0.94	0.92	0.089 (0.096)	0.00382	0.000088	0.00099	0.0057	0.0057
74	1.87	0.94	0.94	0.00087 (0.00097)	0.0000356	0.00000150	0.00173	0.00335	0.0034
75	1.87	0.94	0.94	0.00073 (0.00079)	0.000380	0.0000085	0.0117	0.00161	0.00064
76	1.90	1.02	0.94	0.072 (0.077)	0.0374	0.00085	0.0119	0.00158	0.00064
77	1.95	1.00	0.90	0.085 (0.091)	0.0446	0.00109	0.0128	0.00107	0.00063
78	1.82	0.93	0.92	0.00093 (0.00100)	0.00485	0.000107	0.115	0.00131	0.000188
79 ¹	1.94	0.90	0.87	0.000123 (0.000127)	0.0172	0.00042	3.4	0.00026	0.000146
80	2.04	0.96	0.92	0.000093 (0.000099)	0.0172	0.00043	4.6	0.00115	0.000137
81 ^r	2.04	0.96	0.92	0.000093 (0.000099)	0.0172	0.00043	4.6	0.00105	0.000137

Notes to Table XXIV

- ^aAll concentrations are moles/liter (M). Bromide ion was added as NaBr. Unless otherwise specified, $(\text{HClO}_4) = 0.063 \pm .003 \text{ M}$, and $(\text{NaClO}_4) = 0.40 - (\Sigma \text{Br}^-) \pm .02 \text{ M}$. Again, $R = \text{organic volume/aqueous volume}$. The quantities ΣBr^- , $\Sigma \text{IBr}(\text{CCl}_4)$, and $\Sigma \text{I}_2(\text{CCl}_4)$ are the concentrations that would be present if reaction (V-3) went to completion, if no I_2Br^- or IBr_2^- were formed, if reaction (V-5) did not take place, and if all the I_2 and IBr remained in the organic phase. In most cases $\Sigma \text{I}_2 \sim 1.01 (\text{I}_2)_{\text{CCl}_4}$ and the former has not been tabulated. In cases in which the organic iodine concentration has been increased by the dissociation of IBr or decreased by reaction (V-5) or by the formation of I_2Br^- to such an extent that ΣI_2 and $(\text{I}_2)_{\text{CCl}_4}$ differ by more than 2%, ΣI_2 is indicated in parentheses beneath the tabulated (I_2) value. The tabulated volume ratios and "raw data" concentrations are accurate to $\pm 1\%$. The derived concentration, e.g. $(\text{IBr})_{\text{CCl}_4}$, may be in error by $\pm 2\%$. Small apparent discrepancies in calculated quantities result from rounding off after computation.
- ^bThe value in parentheses was obtained from a duplicate experiment using ordinary Baker and Adamson reagent-grade CCl_4 instead of our low-sulfur reagent.
- ^c $\text{HClO}_4 = 1.02 \pm 0.05 \text{ M}$. No NaClO_4 was added.
- ^dAstatine was added in the aqueous phase (indicated only for selected experiments.)
- ^eAstatine was added in the organic phase (indicated only for selected experiments.)
- ^fAqueous phase activity: 100 to 200 counts/min/ μl .
- ^gAqueous phase activity: 10 to 20 counts/min/ μl .
- ^hNo change when agitated under fluorescent light.
- ⁱWhen black-taped tube was uncovered and agitated for 5 min under Series 1 safelite, D rose to 0.012. After 5 min agitation under fluorescent light D rose to 0.037.
- ^jUnchanged after another 30 minutes agitation.
- ^kNo NaClO_4 added.
- ^lThe aqueous phases of these systems were re-extracted with fresh CCl_4 of the same composition as the original organic phases. The results appear in Table XXVA.
- ^m0.03 M HClO_4 , 0.03 M HOAc , 0.43 M NaClO_4 .
- ⁿAqueous phase activity: ~ 50 counts/min/ μl .
- ^oNo change when black-taped tube was uncovered and agitated under Series 1 safelite.
- ^p $\text{NaClO}_4 = 0.485 - (\Sigma \text{Br}^-) \pm .035 \text{ M}$.
- ^qWhen black-taped tube was uncovered and agitated for 5 minutes under Series 1 safelite, D rose to 0.0023.
- ^r0.0063 M HClO_4 .

Table XXV

Carbon tetrachloride extraction of astatine in I^- -- Br^- -- I_2 systems ^a ($21 \pm .5^\circ C$)								
Expt.	R	$I^- \times 10^4$	Br^-	CCl_4			D_{exptl}	C_{calc}
				I_2	$IBr \times 10^7$	$IBr/I_2 \times 10^5$		
82 ^b	0.91	1.90	0.00089	0.00194	0.0100	0.051	4.1	4.1
			$Br^- \sim 0.01 M$					
83	0.99	42.0	0.0101	0.00095 (0.00100)	0.0025	0.026	0.48	0.52
84	0.99	10.5	0.0101	0.00098	0.0104	0.106	1.31	1.27
85	0.95	3.64	0.0097	0.00099	0.029	0.29	2.01	1.88
86 ^b	0.92	1.92	0.0089	0.00194	0.099	0.51	2.5	2.4
87	0.99	1.26	0.0101	0.00099	0.087	0.88	2.16	2.1
88	1.00	0.387	0.0102	0.00099	0.29	2.9	2.0	2.0
89 ^b	0.90	0.114 (0.0470)	0.0088	0.099	84	8.5	1.81	1.83
90	1.01	0.130	0.0103	0.00099	0.86	8.7	1.13	1.50

91	0.95	3.01	0.0188	0.00096	0.066	0.69	1.63	1.37
			$Br^- \sim 0.1 M$					
92	0.98	102	0.098	0.00089 (0.00100)	0.0094	0.106	0.192	0.169
93 ^{b,c}	0.92	19.4	0.102	0.00094 (0.00098)	0.054	0.58	0.46	0.35
94 ^c	0.94	9.5	0.090	0.00092	0.095	1.04	0.45	0.38
95	1.01	10.5	0.101	0.00097	0.102	1.05	0.37	0.34
96	0.85	5.4	0.086	0.00095	0.168	1.76	0.44	0.39
97 ^b	0.89	2.80	0.099	0.00095	0.37	3.9	0.32	0.34
98 ^d	0.92	2.32	0.093	0.00095	0.42	4.4	0.27	0.32
99 ^{c,e}	0.89	2.23	0.090	0.00095	0.42	4.4	0.32	0.36
100 ^b	0.93	1.95	0.091	0.00191	0.98	5.1	0.255	0.34
101	1.01	1.27	0.101	0.00097	0.85	8.7	0.164	0.23
102	1.03	0.194 (0.130)	0.103	0.00097	5.7	58	0.041	0.064
103 ^g	0.98	0.138 (0.130)	0.103	0.000079	0.65	82	0.028	0.048

Table XXV (cont'd.)

Expt.	R	$I^- \times 10^4$	Br^-	CCl_4			D_{exptl}	C_{calc}
				I_2	$IBr \times 10^7$	$IBr/I_2 \times 10^5$		
104 ^f	1.80	0.116 (0.0243)	0.093	0.00098	8.6	88	0.031	0.054
105 ^f	1.80	0.116 (0.0243)	0.093	0.00098	8.6	88	0.031	0.054
$Br^- \sim 1 \text{ M}$								
106 ^c	0.98	109	0.87	0.00074 (0.00091)	0.065	0.88	0.075	0.049
107 ^c	0.98	9.6	0.90	0.00081 (0.00094)	0.83	10.3	0.043 (0.044) ^g	0.030
108 ^d	1.82	6.7 (.0245)	0.92	0.092 (0.100)	140	15.2	0.022	0.024
109 ^d	0.93	2.80 (2.36)	0.91	0.00166 (0.00196)	5.9	36	0.0133	0.0128
110 ^{c,d}	1.80	0.91	0.93	0.00089 (0.00101)	9.9	111	0.0042	0.0051
111 ^{c,h}	1.80	0.91	0.93	0.00089 (0.00101)	9.9	111	0.0041	0.0051

^aAll concentrations are moles/liter (M). Unless otherwise specified, solutions are 0.0009 to 0.001 M in $HClO_4$ with no added $NaClO_4$. I^- and Br^- were added as the sodium salts. Usually (I^-) is just the concentration resulting from the added iodide, less 1 to 2% which goes to form I_3^- when $(I_2)_{CCl_4} \sim 0.001$ to 0.002 M. Sometimes, however, (I^-) is appreciably greater because of reaction (V-5). In such cases the concentration that would have resulted solely from the added NaI appears in parentheses beneath the corrected value. The $(I_2)_{CCl_4}$ values have been corrected for formation of $(I_2)_{aq}$, I_3^- , and I_2Br^- , and for reaction (V-5). When this correction exceeds 4%, ΣI_2 is indicated in parentheses in the $(I_2)_{CCl_4}$ column. The greatest deviations of Br^- from ΣBr^- are of the order of 1 to 2%, because of I_2Br^- formation in systems nearly saturated with iodine, and ΣBr^- is not indicated. Accuracies are comparable to those of Table XXIV.

^b0.040 M $NaClO_4$, 0.063 M $HClO_4$.

^cSee note 1 to Table XXIV.

^d0.063 M $HClO_4$.

Notes to Table XXV (concluded)

^e 0.40 M NaClO₄, 0.0009 to 0.001 M HClO₄.

^f 0.29 M NaClO₄. In Expt. 104: 0.063 M HClO₄, In Expt. 105: 0.009 M HClO₄.

^g The values in parentheses are the results of a duplicate experiment carried out immediately after the first.

^h 0.0063 M HClO₄.

Table XXVA

Re-extraction of aqueous phases of experiments from Tables XXIV and XXV

Expt.	D			Calculated
	Original	First re-extraction	Second re-extraction	
25	0.163	0.180		0.21
45	0.0106	0.0102		0.0104
64	0.00177	0.00142	0.00173	0.00128
79 ^a	0.00026	0.00018	0.000135	0.000146
93	0.46	0.45		0.35
94	0.45	0.43		0.38
99	0.32	0.30		0.36
103	0.028	0.025		0.048
106	0.075	0.069	0.067	0.049
107	0.043 (0.044) ^b	0.022 (0.022) ^b	0.022 (0.024) ^b	0.030
110	0.0042	0.0033	0.0033	0.0051
111	0.0041	0.0039		0.0051

^aIn this case the aqueous phase was re-extracted with pure CCl_4 to which no halogen had been added. Thus in the two re-extractions the ratio $(\text{IBr}/\text{I}_2)_{\text{CCl}_4}$ approached the limiting value of 19.6 resulting from the dissociation of IBr.

^bThe values in parentheses are the results of a duplicate experiment carried out immediately after the first.

reaction (V-4) is thermodynamically possible in the 0.06 M HClO_4 experiment of each pair, it does not proceed to an appreciable extent during the experiment. This agrees with the reported sluggishness of the reaction under most conditions.³⁶

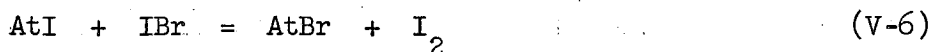
With the exception of Expts. 79 and 107, re-extraction of an aqueous phase with a fresh organic phase does not greatly alter D.

The systems with moderately great I_2 and IBr concentrations show a sensitivity to fluorescent light, while some of those with quite high IBr and relatively low I_2 concentrations appear sensitive even to illumination with a series-1 safelite.

Looking first at Table XXIV, we see that for the most part the distribution of the astatine is dependent only on Br^- and on the ratio IBr/I_2 . At roughly constant Br^- , D decreases as the ratio of IBr to I_2 increases, finally leveling off when the ratio exceeds about 0.2. Increasing Br^- decreases D regardless of the value of IBr/I_2 .

Such behavior indicates the formation of a second species from a first by introduction of IBr and elimination of I_2 , the second species having a K_D which is considerably smaller than that of the first but is still not negligible. Further, both species must react with Br^- to form new species of low extractability.

If we consider the first species to be the AtI we have already proposed, we may further postulate the following equilibria:



and the corresponding equilibrium quotients:

$$\frac{(\text{AtBr})_{\text{aq}}(\text{I}_2)_{\text{CCl}_4}}{(\text{AtI})_{\text{aq}}(\text{IBr})_{\text{CCl}_4}} = Q_{\text{Br}} \quad (\text{V-6}')$$

$$\frac{(\text{AtIBr}^-)}{(\text{AtI})_{\text{aq}}(\text{Br}^-)} = K_{\text{AtIBr}^-} \quad (\text{V-7}')$$

$$(\text{AtBr}_2^-)/(\text{AtBr})_{\text{aq}}(\text{Br}^-) = K_{\text{AtBr}_2^-}, \quad (\text{V-8'})$$

where the phases of the neutral interhalogens have been chosen for computational convenience. We also have the new distribution constant $K_D^{\text{AtBr}} = (\text{AtBr})_{\text{CCl}_4}/(\text{AtBr})_{\text{aq}}$, as well as the constants K_D^{AtI} and $K_{\text{AtI}_2^-}$ determined in Part B of this section. Then the distribution coefficient is given by:

$$D = \frac{(\Sigma \text{At})_{\text{CCl}_4}}{(\Sigma \text{At})_{\text{aq}}} \quad (\text{V-9})$$

$$= \frac{K_D^{\text{AtI}} + K_D^{\text{AtBr}} Q_{\text{Br}} (\text{IBr}/\text{I}_2)_{\text{CCl}_4}}{1 + K_{\text{AtI}_2^-}(\text{I}^-) + K_{\text{AtIBr}^-}(\text{Br}^-) + Q_{\text{Br}} (\text{IBr}/\text{I}_2)_{\text{CCl}_4} [1 + K_{\text{AtBr}_2^-}(\text{Br}^-)]}$$

Using the values of 5.5 and 2200 obtained in Part B, I have fitted the present data to Eq. (V-9) with $K_D^{\text{AtBr}} = 0.04$, $Q_{\text{Br}} = 3800$, $K_{\text{AtIBr}^-} = 120$, and $K_{\text{AtBr}_2^-} = 320$ to obtain the "D_{calc}" values in Tables XXIV and XXV. Because most of the experiments were carried out with rather high salt concentrations, K_D^{AtI} was corrected by the relation

$$\log K_D^{\text{AtI}} = \log (5.5) + 0.1 (\text{Na}^+). \quad (\text{V-10})$$

This salting coefficient was estimated from the results of Part B. The effect of inert salt on the other astatine equilibria should be considerably smaller, and no other corrections were applied.

Most of the results of Table XXIV show satisfactory agreement with the calculated D values. The principal discrepancies appear in systems of high Br^- and IBr/I_2 for which D's of 0.001 or less are predicted. In these systems the experimental D's are usually considerably too high. The magnitude of the discrepancy seems to vary erratically, as does the behavior upon repeated extraction of the aqueous phase with fresh organic phases (see Expts. 60 to 70 and 75 to 81). Re-extraction of the aqueous phase of Expt. 79 brings D to the calculated value, but in no other experiment was a D of less than 0.001 obtained. It is not

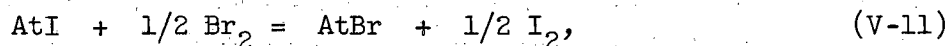
at all unlikely that small amounts of more-or-less extractable impurity compounds of astatine are responsible for these deviations.

On the other hand, certain experiments of high IBr/I_2 and high total (IBr) show D's considerably below the limiting value for their bromide concentrations (see Expts. 18, 19, and 53). This may represent the onset of a further oxidation of the astatine under these relatively highly oxidizing conditions, e.g. to AtBr_3 or to HAtO_2 . This idea will be considered again when we discuss systems containing an excess of Br_2 .

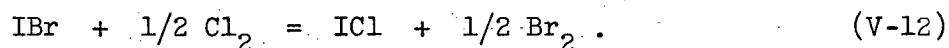
The experiments detailed in Table XXV, which contain I_2 , I^- , and Br^- but no added IBr, give rather remarkable results. At constant Br^- , D goes through a maximum as I^- is increased. It is difficult to envisage any explanation for this phenomenon other than the series of reactions we have just been considering. The initial addition of iodide suppresses the formation of IBr by reaction (V-5), increasing D.³⁸ After the IBr concentration has been rendered negligible, further addition of iodide forms AtI_2^- , causing D to decrease again. The calculated and experimental D's for the most part show satisfactory agreement, but the observed drop-off at low iodide is appreciably greater than that calculated.

It is of interest to compare the parameters of the astatine extraction with the constants for the homologous iodine system. The distribution constant of ICl is 0.34, compared with 0.04 for AtBr .³⁶ The difference is greater than one might expect. The formation constant of IBrCl^- is 43, and that of ICl_2^- is 170, analogous to 120 and 320 for AtIBr^- and AtBr_2^- , respectively.³⁶ As we observed when comparing AtI_2^- with IBr_2^- , this is the trend we would expect as the central atom of the complex gets larger.

Since BrCl has not been well characterized, we must recast Eq. (V-6) into the form



which may be compared with



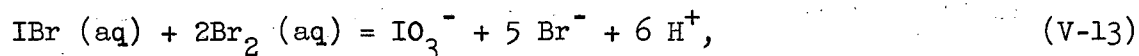
Considering all concentrations in terms of 1 M aqueous solutions, we find the equilibrium constant of Eq. (V-11) to be 4.2×10^4 at 21° . The corresponding constant for Eq. (V-12) is 270 at 25° .³⁶ Although we might have anticipated that the astatine constant would be the greater, the 150-fold difference seems surprisingly large.

From the lack of hydrogen-ion dependence (see, for example, Expt. 27) we may set an upper limit of $\sim 10^{-4}$ for hydrolysis reaction $\text{HOH} + \text{AtBr}_{\text{aq}} = \text{HOAt} + \text{Br}^- + \text{H}^+$. The analogous constant for ICl is about 10^{-4} .³⁶

As in previous cases, the data are too scanty, and the possibilities are too numerous to permit worthwhile speculation regarding the nature of the photochemical reactions that have been observed.

Table XXVI summarizes the results of experiments in which bromine was present in excess over the stoichiometric iodine. These experiments are characterized by relatively low D's which show quite severe scatter. Within the limits of this scatter can be detected no clearcut dependence on concentrations of Br_2 , IBr , H^+ , Br^- or astatine. It does not matter into which phase the astatine is introduced. The reactions do not show appreciable time dependence over half an hour. The value of D is increased by exposure to fluorescent light, but it is not appreciably affected by the series-1 safelite. Re-extraction of an aqueous phase with fresh organic phases causes D to drop sharply.

We should bear in mind that some of these systems are unstable to the reaction



for which K_{250} is about 7×10^{-11} .²² However it is unlikely that the reaction proceeds to any great extent during the experiments.

About the only conclusion we can draw from these experiments is that some further reaction is taking place -- possibly an oxidation to AtBr_3 or HAtO_2 . The oxidation product may be virtually unextractable, with the observed D's being entirely due to accidental impurities. We should note that these are essentially the conditions of the bromine experiments in Section IV, and save for the presence of IBr , they are

Table XXVI

Carbon tetrachloride extraction of astatine in Br^- -- IBr -- Br_2 systems^a
($29 \pm .5^\circ\text{C}$)

CCl_4 (M)		D	Notes
$\Sigma\text{IBr} \times 10^3$	$\text{Br}_2 \times 10^3$		
0.02	0.02	0.007-0.011	
0.02	0.2	0.004-0.006	
0.2	0.2	0.0016-0.006	Independent of astatine concentration, and of phase in which astatine is added.
0.2	0.2	0.0008-0.006	0.9 M HClO_4 , no NaClO_4
1	0.3	0.004-0.006	The lowest value was obtained after 20 min. agitation
1	0.3	0.006	0.9 M HClO_4 , no NaClO_4
0.02	2	0.001-0.003	A duplicate experiment in total darkness also gave a D of 0.001
0.2	2	0.0005-0.002	
2	2	0.0006-0.002	
30	10	0.002	$\Sigma\text{Br}^- = 0.009$ M. D did not change in total darkness but increased to 0.01 under fluorescent light (see Expt. 12-6, Table XII).
0.02	20	0.0006-0.0015	
0.2	20	0.0005-0.0013	
2	20	0.001-0.0013	Independent of phase in which astatine is added; D increased to 0.004 under fluorescent light. ^b
2	20	0.0008	$\Sigma\text{Br}^- = 0.126$
20	20	0.0013	$\Sigma\text{Br}^- = 0.017$

^a Except when otherwise indicated, mixtures were agitated for 5 min in uncovered tubes under a series 1 safelite. ΣBr^- and ΣIBr mean the same as in Tables XXIV and XXV. Unless otherwise specified, ΣBr^- (added as NaBr) was such that the free Br^- was between 0.008 and 0.009 M, NaClO_4 was 0.40 M and HClO_4 was 0.063 M. R = organic volume/aqueous volume ~ 0.9 . Most of the entries represent several experiments, and experimental spread is indicated by a range of D values (e.g. 0.001 to 0.003).

^b One of these experiments was re-extracted with three successive portions of CCl_4 of the same halogen content as the original organic phase and gave successive D's of 0.00031, 0.00021, and 0.00022.

the conditions under which Johnson et al. reported astatine to form an unextractable species that did not coprecipitate with insoluble iodates.

We can recognize indirectly an effect of iodine on these systems. Thus, for example, Expts. 49, 51, and 53 of Table XXIV all have free bromine concentrations of 10^{-4} M or greater in the CCl_4 phase because of dissociation of IBr . Yet only Expt. 53 deviates from Eq. (V-9), although systems in Table XXVI which have similar Br_2 and Br^- concentrations have considerably lower D's. Since the emf of the solution is determined by the bromine and bromide concentrations, we have systems of the same emf which behave differently. The only apparent difference is that the free iodine concentration is very much lower in the Table XXVI experiments than in those of Table XXIV.

However, if our interpretation of the earlier data has been correct, the principal astatine species in the Table XXIV experiments in question are AtBr and AtBr_2^- . Since these contain no iodine, there is no way in which iodine can inhibit the equilibrium of any further reaction with bromine. It is possible that iodine could inhibit such a reaction kinetically. But it is also possible that our interpretations have been in error. The data could be equally well satisfied if our original species were AtI_3 , rather than AtI . Then the first reaction with bromine would give AtI_2Br , leaving us still two iodine atoms to play with. However, we would not expect AtI_3 to have a distribution constant so similar to that of IBr as we have observed.

Further elucidation of the situation will require better information on just what is happening when bromine is in excess. The use of polar solvents to extract such species as HAtBr_4 may provide a suitable tool.

E. The I_2 -- I^- -- Cl^- System

The experiments carried out in this system are shown in Table XXVII. Equilibrium appears to have been reached within 2 min. The mixtures seem insensitive to light, and D was not changed by re-extraction of an aqueous phase with fresh CCl_4 of the same iodine

Table XXVII

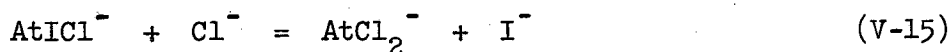
Carbon tetrachloride extraction of astatine in I^- -- I_2 -- Cl^- systems ^a ($21 \pm 0.5^\circ C$)					
$(I_2)_{CCl_4}$	$(I^-) \times 10^4$	(Cl^-)	D_{exptl}	D_{calc}	Notes
0.0019	1.90	0.0095	3.9	4.1	0.40 M $NaClO_4$
0.00022	0.084	0.106	1.52	1.61	0.97 M $NaClO_4$
0.0019	1.92	0.096	2.4	2.6	0.40 M $NaClO_4$
0.00021	2.24	0.106	2.6	2.8	0.97 M $NaClO_4$
0.00022	0.54	1.02	0.162	0.154	1.5 counts/min/ μl
0.00095	0.58	0.95	0.180	0.182	0.001 M $HClO_4$ ^b 9 counts/min/ μl
0.0019	2.30	0.96	0.37	0.40	
0.00095	9.5	0.94	0.53	0.52	0.001 M $HClO_4$ ^b
0.00021	53	1.00	0.35	0.33	

^aIodide and chloride were added as the sodium salts. Unless otherwise specified, the organic volume/the aqueous volume is about unity, the $HClO_4$ concentration is $0.063 \pm .003$ M, and mixtures were agitated 5 to 10 min in black-taped tubes. The $(I_2)_{CCl_4}$ has been corrected by 1 to 2% for distribution and for the formation of I_2Cl^- . A slight correction for I_3^- (2% or less) has been applied to (I^-) . The iodide formed by the reaction $I_2(aq) + 2 Cl^- = ICl_2^- + I^-$ ($K_{250} = 1.1 \times 10^{-6}$)²² is negligible. Concentrations of $NaClO_4$, Cl^- , and I^- are accurate to $\pm 1\%$, while I_2 concentrations are accurate to $\pm 2\%$.

^bThese experiments were agitated only 2 min. Their D's were unchanged when the tubes were uncovered and agitated another three min under fluorescent light. When each of the aqueous phases was agitated for 2 min with fresh CCl_4 0.001 M in I_2 , respective D values of 0.171 and 0.57 were obtained.

content as the original organic phase. In addition, D is independent of acidity, I_2 concentration, and total astatine concentration.

At constant Cl^- , increasing I^- causes D to pass through a maximum, reminiscent of the situation in the $I_2 \rightleftharpoons I^- \rightleftharpoons Br^-$ system. Accordingly, I have postulated the new species $AtICl^-$ and $AtCl_2^-$, and the equilibria:



with the corresponding equilibrium constants:

$$(AtICl^-)/(AtI)_{aq}(Cl^-) = K_{AtICl^-} \quad (V-14')$$

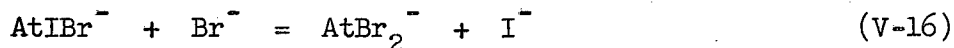
$$(AtCl_2^-)(I^-)/(AtICl^-)(Cl^-) = P. \quad (V-15')$$

Then we can write

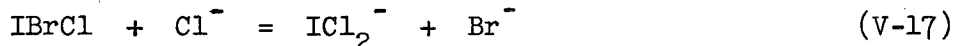
$$D = \frac{K_D^{AtI}}{1 + K_{AtI_2}^-(I^-) + K_{AtICl^-}^-(Cl^-) [1 + P(Cl^-)/(I^-)]}$$

In Table XXVII, D_{calc} has been obtained by setting $K_{AtICl^-} = 9$ and $P = 2 \times 10^{-4}$. The values of $K_{AtI_2}^-$ and K_D^{AtI} , and the salt correction to the latter, are the same as were used in Part D.

The resulting agreement is embarrassingly good. Further analysis of this system will require direct introduction of ICl into the solution, so that ICl and Cl^- concentrations can be varied independently, as was done in the IBr experiments. For purposes of comparison we may write the $AtBr$ and IBr analogs to (V-15):



and



which have equilibrium constants of 0.0011 and 0.005, respectively, the latter at 25°C.^{22,36}

The various interhalogen equilibria involving astatine are tabulated in Table XXVIII.

F. The Arsenic (III) -- Arsenic (V) System

Introduction

As we observed in Section IV, the arsenic system should be a good one in which to investigate the At (0) -- At (-1) couple. The pH dependence of the arsenic couple allows its emf to be varied over a very wide range, making it especially useful for such a study.

Experimental

Reaction mixtures were agitated in black-taped tubes at room temperature (21 to 23°C). Iodine was usually added to the two-phase systems from either aqueous or CCl₄ solutions of I₂, and the mixtures were agitated for a few minutes before the astatine was introduced. Reduction of the iodine appeared to be complete within a minute. However no differences were observed in the astatine distribution if the iodine was added directly as NaI or if the systems were not agitated prior to the addition of the astatine. The astatine itself was introduced either from an aqueous I₂ -- I⁻ solution or from an I₂ solution in CCl₄. Occasionally the manner in which the astatine was added did alter the results; the effect, however, was erratic and unpredictable. Solutions were buffered with acetate or phosphate mixtures, or, when possible, with the arsenate system itself. The pH values were measured with a Beckman model-G pH meter.

Results and Discussion

In solutions more acid than pH 3, the distribution of the astatine seems largely independent of acidity and concentrations of arsenic (III) and (V), and the D's are usually within a factor of two

Table XXVIII

Interhalogen equilibria involving astatine	
Reaction	$K_{eq} (21^\circ\text{C}) \pm 10\%$
$\text{AtI (aq)} = \text{AtI (CCl}_4\text{)}$	5.5^a
$\text{AtI (aq)} + \text{I}^- = \text{AtI}_2^-$	2000
$\text{AtI (aq)} + \text{Br}^- = \text{AtIBr}^-$	120
$\text{AtI (aq)} + \text{Cl}^- = \text{AtICl}^-$	9
$\text{AtBr (aq)} = \text{AtBr (CCl}_4\text{)}$	0.04
$\text{AtBr (aq)} + \text{Br}^- = \text{AtBr}_2^-$	320
$\text{AtI (aq)} + \text{IBr (CCl}_4\text{)} = \text{AtBr (aq)} + \text{I}_2 \text{ (CCl}_4\text{)}$	3800
$\text{AtI (aq)} + 1/2 \text{ Br}_2 \text{ (aq)} = \text{AtBr (aq)} + 1/2 \text{ I}_2 \text{ (aq)}$	4.2×10^4
$\text{AtIBr}^- + \text{Br}^- = \text{AtBr}_2^- + \text{I}^-$	0.0011
$\text{AtICl}^- + \text{Cl}^- = \text{AtCl}_2^- + \text{I}^-$	2×10^{-4}

^aThe observed salt effect is given by: $\log K_D = \log (5.5) + 0.1 (\text{NaClO}_4)$.

The same salting coefficient has been assumed to apply to NaCl and NaBr.

of the values calculated from Eq. (V-1). However the results tend to be somewhat erratic, and irregular time variations were sometimes noted (See Table XVII). The results at higher pH are summarized in Tables XXIX to XXXI.

Additional experiments have shown that the astatine distribution is not discernibly affected by exposure of the mixtures to light, saturation of the solutions with nitrogen, introduction or elimination of either phosphate or acetate, or variation of the astatine concentration.

The data in general show disheartening scatter and perplexing time dependences. Re-extraction of a phase gives a D which may differ from the original value by as much as a factor of two. There is good evidence that the distribution is extremely sensitive to impurities. Thus experiments using one particular astatine stock solution gave initial D's very much higher than those obtained previously. The deviation depended on what volume of the stock solution was used and nearly disappeared after many hours of agitation.

The data obviously do not warrant quantitative interpretation. However certain qualitative observations can be made. Thus D decreases with both decreasing acidity and decreasing $\text{As(V)}/\text{As(III)}$, as would be expected for the reduction of extractable At^{O} to unextractable At^{I} . The magnitude of the observed dependence, however, is smaller than that needed for any reasonable reaction.

The lack of a clear-cut iodide dependence indicates that the extractable species cannot be AtI . This should not surprise us, since we have concluded in Section IV that at pH values greater than 3, the astatine in these systems is present in considerable excess over the I_2 . Thus the astatine is susceptible to reaction with any impurity that happens to be around to grab it, and we are probably studying the reduction to At^{I} of astatine-impurity compounds whose exact nature varies from one solution to the next.

Table XXIX

Carbon tetrachloride extraction of astatine from As(III) -- As(V) solutions^a
Dependence on pH: $(I^-) = 0.001\text{ M}$

As(III)	As(V)	pH	D	Notes
0.09	5×10^{-4}	4.8	2	
		5.1	0.6	
		5.6	0.2	
		6.3	0.03-0.15	
	0.009	4.8	0.7-1.6	Highly variable
		4.9	0.8	After 30 min ^b
		5.2	1.7	Constant after 20 min
		5.4	0.4	
		5.7	0.3	
		6.1	0.1	
		6.3	0.05-0.1 ^c	After 1 to 2 hr ^{b,d}
		6.4	0.025-0.1	After 1 to 2 hr ^{b,d}
		6.8	0.04	
		7.25	0.024	
		7.6	0.023	
	0.09	4.8	2 ^e	e
		5.6	0.5	f
		5.7	0.5	
		6.2	0.3 to 0.4	
0.02	0.02	4.5	0.3 → 1	(5 min → 1 hr)
		5.3	1.4	
		5.9	2	g
		6.7	1.4	g

^aThe two phases were of approximately equal volume. The aqueous phases contained sufficient NaClO_4 to make the ionic strength approximately unity. Iodide was introduced either as I_2 or as NaI . Arsenic (III) and arsenic (V) were introduced either as the free acids or as their sodium salts. All concentrations are moles/liter and are accurate to $\pm 10\%$.

Notes to Table XXIX concluded

Most of the entries represent several experiments, and the experimental spread is indicated by a range of D's, e.g. "0.05-0.1." A D entry such as "0.3. → 1 (5 min → 60 min)" means that a D of 0.3 was observed after 5 min of agitation, while after 60 min of agitation a D of unity was measured. If no further remark is made, D did not change thereafter. If no time dependence at all is indicated, a constant value of D was reached within 60 min.

^b When the last measurement was made D was still rising.

^{c,e,f} The aqueous phase of each of these experiments was re-extracted with fresh CCl_4 , and the organic phase was re-extracted with a fresh aqueous phase of the same composition as the original. The results follow:

Note	D		
	Original	Aqueous phase + fresh CCl_4	Organic phase + fresh aqueous phase
c	0.1	0.13 → 0.06 (1 min → 60 min)	Not carried out
e	2	1.1	1.8
f	0.5	0.7	0.7

^d Among duplicate experiments were some in which D decreased with time and others in which it increased with time.

^g Within 5 min D reached a steady value.

Table XXX

Carbon tetrachloride extraction of astatine from As(III) -- As(V) solutions. ^a Dependence on As(III)/As(V). (I^-) = 0.001 M.					
pH	As(III)	As(V)	$\frac{As(III)}{As(V)}$	D	Notes
4.8	0.02	0.2	0.1	1.5	b
	0.09	0.09	1	2	c
	0.08	0.008	10	0.7 - 1.6	highly variable
	0.08	5×10^{-4}	160	2	
5.2	0.002	0.02	0.1	1 → 1.8	(1 hr → 5 hr) ^d
	0.02	0.02	1	1.4	
	0.09	0.009	10	1.7	
	0.09	5×10^{-4}	180	0.6	
5.7	0.09	0.09	1	0.5	
	0.1	0.009	11	0.3	
	0.09	5×10^{-4}	180	0.22	
6.4	0.09	0.025	3.6	0.07 - 0.13	
	0.09	0.009	10	0.03 - 0.1	e
	0.09	0.003	30	0.05	
	0.08	0.002	40	0.03	
	0.08	9×10^{-4}	90	0.05 - 0.11	
	0.08	5×10^{-4}	160	0.15	

^aSee note a, Table XXIX.

^{b,c}The aqueous phase of each experiment was re-extracted with fresh CCl_4 , and the organic phase was re-extracted with a fresh aqueous phase of the same composition as the original. The results follow:

Note	D		
	Original	Aqueous phase + fresh CCl_4	Organic phase + fresh aqueous phase
b	1.5	0.7	1.6
c	2	1.1	1.8

^dSee note b, Table XXIX.

^eSee note d, Table XXIX.

Table XXXI

Carbon tetrachloride extraction of astatine from As(III) -- As(V) solutions ^a Iodide dependence.					
pH	As(III)	As(V)	(I ⁻)	D	Notes
4.5	0.02	0.02	1 - 3 x 10 ⁻⁴	0.3 → 3	(5 min → 7 hr) ^b
			0.001	0.3 → 1	(5 min → 1 hr)
5.2	0.09	0.009	5 x 10 ⁻⁵	0.09 → 0.34	(20 min → 3 hr) ^b
			0.001	1.7	
5.6	0.09	0.0005	0.001	0.2	
			0.18	0.4	
		0.09	0.0001	1 - 2	c
			0.001	0.5	d
5.7	0.1	0.008	0.00012	0.09 → 0.2	(15 min → 80 min) ^b
			0.001	0.3	
6.2	0.1	0.08	0.00022	0.4	
			0.001	0.4	
6.3	0.09	0.008	5 x 10 ⁻⁵	0.06 → 0.14	(30 min → 3 hr) ^b
			0.001	0.05 - 0.1 ^e	After 1-2 hr ^{f, b}
			0.0044	0.09 → 0.06	(20 min → 100 min)
			0.008	0.06	
			0.02	0.06 → 0.09	(20 min → 150 min) ^b
			0.085	0.07 → 0.13	(20 min → 4 hrs) ^b
			0.85	0.06 → 0.09	(20 min → 150 min)

^aSee note a, Table XXIX.

^bSee note b, Table XXIX.

^cOver several hours of agitation D alternately rose and fell.

^{d, e}The aqueous phase of each of these experiments was re-extracted with fresh CCl₄, and the organic phase was re-extracted with a fresh aqueous phase of the same composition as the original. The results follow:

D			
Note	Original	Aqueous phase + fresh CCl ₄	Organic phase + fresh aqueous phase
d	0.5	0.7	0.7
e	0.1	0.13 → 0.06 (1 min → 60 min)	not carried out

^fSee note d, Table XXIX.

ACKNOWLEDGMENTS

I wish to thank Professor Isadore Perlman and Dr. Earl K. Hyde for their untiring support and encouragement throughout the trials and tribulations of this work. I also want to thank Professor Burris B. Cunningham, Dr. Allan Stoner, and Messrs. Marshall Parrott and Ralph McLaughlin for many helpful discussions and not inconsiderable practical assistance.

Thanks are due to the Lawrence Radiation Laboratory analytical chemistry group under Dr. Eugene H. Huffman for performing some of the analyses incidental to this work, and to Mr. George V. Shalimoff for certain spectrographic analyses.

To the crew of the University of California's 60-in. cyclotron under Messrs. William B. Jones and the late Bernard G. Rossi, and to the Radiation Laboratory Health Chemistry group under Mr. Nels Garden go my thanks for their invaluable assistance in the preparation and safe handling of the astatine.

I am greatly indebted to the Radiation Laboratory electronics groups and especially to Messrs. Alfred Wydler and Almon Larsh for designing and maintaining the counting equipment required for this work.

I wish to acknowledge a special debt to Professor Robert E. Connick, who has devoted innumerable hours of his time to battling around the problems of astatine chemistry. From his stubborn insistence that traces of one halogen could best be studied in the presence of macro amounts of another arose most of the positive results of this thesis.

During the first two years of this work I was the recipient of a National Science Foundation Fellowship, for which I want to express my appreciation. I am also grateful to the United States Atomic Energy Commission for its support of the investigation.

REFERENCES

1. The work on the natural occurrence of astatine is reviewed by E. K. Hyde, J. Phys. Chem. 58, 21 (1954).
2. D. Corson, K. MacKenzie, and E. Segrè, Phys. Rev. 8, 672 (1940).
3. (a) G. Johnson, R. Leininger, and E. Segrè, J. Chem. Phys. 17, 1 (1949).
(b) H. M. Neumann, J. Inorg. Nuclear Chem. 4, 349 (1947).
(c) H. M. Neumann, unpublished paper presented at the American Chemical Society meeting, San Francisco, April 1958.
4. The latest and probably the most comprehensive review of astatine chemistry is that by E. Anders, Ann. Rev. Nuclear Sci. 9, 203 (1959).
5. (a) M. Kahn and A. C. Wahl, J. Chem. Phys. 21, 1185 (1953).
(b) M. L. Good and R. R. Edwards, J. Inorg. and Nuclear Chem. 2, 196 (1956).
(c) R. G. Wille and M. L. Good, J. Am. Chem. Soc. 79, 1040 (1957).
(d) H. M. Eiland, "The Chemical Behavior of Iodine at Tracer Concentrations." Doctoral Thesis, University of New Mexico, 1957.
6. A portion of the work reported in Section II-A was carried out in cooperation with Dr. Allan Stoner, and another portion was carried out in cooperation with Mr. Ralph D. McLaughlin.
7. E. Kelly and E. Segrè, Phys. Rev. 75, 999 (1949).
8. Typical is the paper of G. Barton, Jr., A. Ghiorso, and I. Perlman, Phys. Rev. 82, 13 (1951).
9. Typical is the paper of W. Garrison, J. Gile, R. Maxwell, and J. Hamilton, Anal. Chem. 23, 204 (1951).

10. D. Strominger, J. Hollander, and G. T. Seaborg, Revs. Modern. Phys. 30, Part 2 (1958).
11. Gmelins Handbuch der Anorganischen Chemie (Verlag Chemie, Berlin, 1936) System No. 38, p. 330.
12. I. Kolthoff and R. Belcher, Volumetric Analysis (Interscience, New York, 1957), Vol. III, Chap. VI-VII.
13. W. Hillebrand, G. Lundell, H. Bright, and J. Hoffman, Applied Inorganic Analyses (Wiley, New York, 1953), p. 651.
14. I. Kolthoff and V. Stenger, Volumetric Analysis (Interscience, New York, 1947), Vol. II, Chap. 8.
15. A. Seidell, Solubilities of Inorganic and Metal Organic Compounds (Van Nostrand, New York, 1940), Vol. 1.
16. International Critical Tables (McGraw-Hill, New York, 1926), Vol. I, p. 102.
17. W. Hillebrand, G. Lundell, H. Bright, and J. Hoffman, Applied Inorganic Analyses (Wiley, New York, 1953), p. 479.
18. I. E. Starik, Zhur. Neorg. Khim. III, 6 (1958).
19. A. Wahl and N. Bonner, Radioactivity Applied to Chemistry (Wiley, New York, 1951), Chap. 6.
20. A. Aten, T. Doorgeest, U. Hollstein, and H. Moeken, Analyst 77, 774 (1952).
21. For example: N. Matsuura and M. Haissinsky, J. Chim. Phys. 55, 475 (1958) - (polonium chemistry).
22. Wendell M. Latimer, The Oxidation States of the Elements (Prentice-Hall, New York, 1952).

23. H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolytic Solutions (Reinhold, New York, 1943).
24. I. M. Kolthoff and W. J. Tomsicek, J. Phys. Chem. 39, 945, 955 (1935).
25. H. H. Willard and J. J. Thompson, J. Am. Chem. Soc. 56, 1827 (1934).
26. Eastman Kodak Company, Rochester, New York, private communication, 1959.
27. G. B. Kistiakowsky, Photochemical Processes, (Chemical Catalogue Co., New York, 1928), p. 62.
28. H. A. Liebhafsky, J. Phys. Chem. 35, 1648 (1931).
29. W. L. Reynolds, J. Am. Chem. Soc. 80, 1830 (1958).
30. R. G. Dickinson and S. F. Ravitz, J. Am. Chem. Soc. 52, 4771 (1930).
31. Gmelins Handbuch der Anorganischen Chemie (Verlag Chemie, Berlin, 1931), System No. 7, p. 283.
32. L. I. Katzin and E. Gebert, J. Am. Chem. Soc. 77, 5814 (1955).
33. Gmelins Handbuch der Anorganischen Chemie (Verlag Chemie, Berlin, 1933), System No. 8, p. 427.
34. M. Davies and E. Gwynne, J. Am. Chem. Soc. 74, 2748 (1952).
35. D. Yost, T. Anderson, and F. Skoog, J. Am. Chem. Soc. 55, 552 (1933).
36. J. H. Faull, Jr., J. Am. Chem. Soc. 56, 522 (1934).
37. E. Pungor, K. Berger, and E. Schulek, J. Inorg. and Nuclear Chem. 11, 56 (1959).
38. The possible importance of this equilibrium was called to my attention by Professor William Jolly of the University of California Chemistry Department.

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