91. *The Concentration of Artificially Produced Radio-elements by Means of an Electric Field.*

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ALL methods of producing artificial radio-elements have the disadvantage that only a very small fraction of the atoms exposed to the bombarding particles becomes activated. The radio-elements, therefore, are invariably diluted by an overwhelming mass of inactive material, and for their theoretical study as well as their practical use as indicators it is frequently necessary to extract and concentrate them. Methods for doing this with invisible quantities of active materials have been developed in the study of the natural radio-elements. One of the most efficient is the application of an electric field to either the gaseous or the liquid phase; well-known examples, in the former case, are the collection of the " active deposits " produced by the three emanations; in the latter case, the electrolytic deposition of these and other isotopes of lead, bismuth, and polonium.

It seemed worth while to investigate whether an electric field might also be of help in concentrating artificial radio-elements. We have applied this method in both the gaseous and the liquid phase. As the only available neutron source was small, experiments had to be confined to the study of artificial radio-elements produced by slow neutrons, since only this type of activation can be increased by the " hydrogen effect "; whence it follows, further, that in our experiments the artificial radio-elements were necessarily isotopes of the bombarded ones. It should be pointed out, however, that the application of an electric field to the concentration of artificial radio-elements is a general method and can certainly be used with advantage, and frequently even in a still more efficient way, in the case of non-isotopic radio-elements produced by neutron bombardment, and of radio-elements generated by the impact of α-particles or protons.

EXPERIMENTAL.

The source of neutrons for producing the artificial radio-elements consisted of 25 mc. of radio-thorium, mixed with 5 g. of finely powdered beryllium and sealed in a glass tube. The neutrons were " slowed down " by performing the experiments in a large tank of water, 40 cm. in diameter and 30 cm. high.

The activity was measured in the usual way, by counting the β-rays by means of a Geiger–Müller counter, the impulses being amplified by a single-stage amplifier and then fed into the grid circuit of a Thyratron valve, which worked a telephone meter, so that each electron entering the counter was automatically recorded.

(a) *Experiments in the Gaseous Phase.**—The gas employed for these experiments was arsine, because arsenic, as Amaldi, d'Agostino, Fermi, Pontecorvo, Rasetti, and Segrè (*Proc. Roy. Soc.*, 1935, **149**, 522) have shown, when irradiated with neutrons, gives an isotope according to the equation $^{75}_{33}\text{As} + ^{1}_{0}n \longrightarrow ^{76}_{33}\text{As}$, and consequently the activation is increased by surrounding it with water; moreover, the half-life period is of convenient length (26 hours), and the activity is strong. Arsine is one of the few gaseous compounds which satisfy these conditions.

The arsine, prepared by reducing an acid solution of arsenious oxide by means of zinc, was purified by passage over soda-lime and calcium chloride and then frozen out in a liquid-air trap. It was stored in an 8-litre bulb, shielded from light. The spontaneous decomposition, on the

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* A summary of this part of the paper appeared in *Nature*, 1935, **135**, 820.

walls of the vessel, of gas so purified was almost completely suppressed during storage, and in the actual experiments further precautions (see below) were taken.

The experiments were carried out in a silver flask, of 800-c.c. capacity, fitted with a ground-glass stopper having a side-tube and tap; into the top of the stopper a piece of glass tubing was sealed, reaching nearly to the centre of the flask, and containing a copper lead dipping into mercury and so making contact with the inner electrode, which normally consisted of 10 cm. of platinum wire bent into the shape of a flat, compact zig-zag of length about 1·5 cm. and sealed into the central tube. A minimum of grease was used for the ground-glass joint, since grease catalyses the spontaneous decomposition of arsine. The outer electrode was the flask itself.

Arsine was introduced to the required pressure into the evacuated flask *via* the side tube as follows. The gas was condensed out of the storage bulb in a liquid-air trap and, after any hydrogen resulting from its decomposition had been pumped off, it was passed through a cotton-wool plug into the flask, by removing the liquid air and allowing the trap gradually to warm sufficiently for the gas to distil off. The tap on the side tube was then closed. The cotton-wool filter retained any solid arsenic particles, which catalyse decomposition. Rubber connexions were also eliminated for the same reason.

The flask was then placed in the water-bath, with the source, contained in a boiling-tube, clamped beside it. The flask and the source were so arranged as to be as near as possible to the centre of the bath. All experiments were performed with the same relative distribution.

The field was 1300 volts (about 250 volts/cm.), applied from dry batteries, with a water resistance in each lead as a safety precaution. (Experiments were performed without these resistances in the leads and, as expected, they caused no modification in the results.) The glass stopper was shielded from light during the experiments.

Irradiation was first carried out with the electrodes joined together, and no activity whatever was found on the platinum wire. The field was then applied during irradiation, each experiment being performed with the inner electrode charged negatively and positively alternately. An activity could be collected on the electrode, independently of the sign of the charge. As a check in the first few experiments, the decay curve of the activity was taken, and found to have a half-value period of about 1 day, as was to be expected for the arsenic isotope ${}^{76}_{33}\text{As}$. Very occasionally an experiment with the positive charge on the inner electrode during irradiation gave no activity on the electrode; this happened so rarely, however, that we could not study the reason for this failure. The exception did not occur when the inner electrode was negative.

Experimental conditions were varied in different ways; the pressure of the gas and the metal of the electrode were altered; hydrogen and water vapour were added; and the ionisation inside the flask was increased by means of the extra γ-radiation from a 30-mc. radio-thorium source, unmixed with beryllium, placed inside the flask. In some cases these variations caused a deposit of arsenic on the wire about 10^{-4} cm. thick without, in general, increasing the yield of active isotope to any great extent. Hydrogen alone made the collection of the activity completely reliable on either electrode, a fact which may be due to the production of a well-defined platinum–hydrogen surface. In this connexion the effect of cooling the platinum wire in a stream of hydrogen after ignition in a Bunsen flame was tested, but no difference was observed. A few experiments were done with the platinum electrode coated with arsenic, but the yield was appreciably lowered. For all other experiments the platinum wire was carefully ignited.

In order to determine the yield, it is necessary to know the total activity induced in the arsine; for this purpose a small quantity (0·2 g.) of arsenious oxide was irradiated inside the flask under conditions similar to those obtaining during the irradiation of the arsine, and the activity measured directly. As a check, a similar quantity was irradiated inside the flask in solution and precipitated as magnesium ammonium arsenate, after oxidation with nitric acid. The two values agreed within 5%. It was found, as expected, that the yield was proportional to the pressure of arsine in the flask, and for comparison, all results were corrected for 100% activation (*i.e.*, irradiation at a pressure of 76 cm. for 10 days).

In no case was more than 30% of the active isotope collected on the inner electrode, and these higher yields were always accompanied by the deposition of a weighable quantity of inactive arsenic. On the other hand, by very careful purification, up to 15% of the active isotope could be collected on a straight platinum wire of length 3 cm., charged positively or negatively, without the deposition of a visible layer of arsenic. In these experiments, the concentration factor [*i.e.*, the change in the ratio $({}^{76}\text{As}, \%)/({}^{75}\text{As}, \%)$ on the electrode] was certainly greater than 20,000.

A few experiments were performed with a smaller voltage between the electrodes, with the object of finding whether a larger flask could be employed with the available H.T. supply.

A potential of only 250 volts, or 50 volts/cm., was found to be only slightly less effective than the 1300 volts normally employed. Consequently, a copper flask, similar to but larger than the silver flask, was used for a further series of experiments, but the yield did not increase in proportion to the volume.

The results are summarised in Table I.

TABLE I.

Silver flask ; diam. 5 *cm., vol.* 800 *c.c.*

Electrode.	Field.	Kicks/ min.	% Activity deposited.	Wt. of As deposited, g.	Concn. factor.
Before shielding gas from light, etc.; gas at about 70 cm.					
Cu plate	−	15	24	—	—
Cu spiral	−	17	26	0·0015	500
,,	+	22	34	0·0036	300
Conditions modified as described on p. 385; gas at about 70 cm.					
Pt spiral	−	16	25	0·0004	2,000
,,	+	12	19	0·0002	2,900
Effect of addition of water (a few drops in bottom of flask); gas at 70 cm.					
Pt spiral	−	6	9	0·0004	600
,,	+	15	24	0·0003	2,400
Effect of reducing pressure: gas at 35 cm.					
Pt spiral	−	14	22	0·000035 *	19,000
,,	+	12	19	0·000035	16,000
Effect of additional radiation: 30-mc. radio-thorium in flask.					
Pt spiral	−	10	16	0·0001	5,000
,,	+	11	17	0·0001	5,000
Effect of addition of hydrogen : 35 cm. AsH_3 + 35 cm. H_2.					
Pt spiral	−	10	16	0·0001	5,000
,,	+	11	17	0·0002	2,500
Effect of using Pt spiral coated with As; gas at 70 cm.					
Pt spiral with some As already on spiral	−	4	8	0·0001 (extra)	
,, ,, ,, ,, ,,	+	2½	4	No weighable extra quantity deposited	

* Thanks are due to Miss P. M. Sanderson for weighing these very small deposits on the microbalance.

Variation of field : 35 *cm.* AsH_3 + 35 *cm.* H_2. Pt *spiral electrode.*

Field	−1300	+1300	−500	+500	−250	+250
Kicks/min.	10	11	8	9	7	6
% Activity	16	17	12	14	11	10

Copper flask ; diam. 9 *cm., vol.* 3200 *c.c.* Pt *spiral electrode.*

Field	−1300	+1300	−1300 (with H_2)	+1300 (with H_2)
Kicks/min.	13	7	11	18
% Activity	5	3	4	7

It appears from the results that the active arsenic isotope does not retain any characteristic charge which may possibly be imparted to it at the moment of its formation. It seems probable that clusters are formed, which acquire a charge by catching the ions present in the gas. These ions apparently may be produced by the neutrons as well as the γ-rays (Hopwood and Philipps, *Nature*, **1935**, **136**, 1026); as insufficient is known about the relative intensities of both ionisations, our failure to detect any influence by a rather weak γ-ray source is not surprising.

In convenience and general reliability, the results obtained in the gaseous phase are not to be compared with those obtained with liquids.

(b) *Experiments in the Liquid Phase.*—In these experiments the general arrangements of source, sample, and bath as described above were employed. 10 C.c. of the liquid were irradiated in a boiling-tube fitted with electrodes 1 cm. square; the field (360 volts) was obtained from dry batteries, and except where otherwise stated, it was applied during the whole of the irradiation and removed one minute after the source had been taken away.

It was decided to use organic liquids containing bromine and iodine, inasmuch as these elements are both strongly activated in water with an induced activity of half-life 18 and 25 minutes, respectively (Fermi *et al.*, *loc. cit.*), a very convenient period since 30 minutes' irradiation gives over 50% of the maximum activity, and in all experiments this was the period of exposure. In this time no appreciable activation of the bromine isotope of 4-hours' period occurs.

To find the order of the activity to be expected, similar samples were irradiated under the same conditions but without electrodes, and the active isotope was precipitated by the method of Szilard and Chalmers (*Nature*, 1934, **134**, 462). This gave an activity (corrected for incomplete activation and decay) of the order of 100 kicks/minute, and in making comparisons these values are arbitrarily called 100% for each respective sample. Experiments were made on the activity of irradiated ethyl iodide (liquid) before and after precipitation, and only about 60% of the total activity was precipitated by this method.

Experiments with ethyl iodide, using platinum electrodes, gave no activity on either anode or cathode. Silver electrodes, however, resulted in the collection of the activity exclusively on the anode, the yield being slightly higher than that obtained by the precipitation method (*i.e.*, > 100%). Copper electrodes cleaned with emery gave on each electrode a visible deposit of cuprous iodide with some activity, but the condition of the surface of the electrodes had a great influence, and, by carefully polishing each electrode with fine abrasive powder, it was found that the activity was here also confined to the anode, the yield being somewhat under 100%. If the experiment was performed in exactly the same way, except that no field was put on the electrodes, a low yield of active isotope was collected on the rough copper electrodes, showing that there is a definite affinity of the iodine for the copper, irrespective of the electric field, which can, however, be overcome by application of the field and use of smooth electrodes. It would appear that the chemical affinity is necessary to retain the halogen when it reaches the electrode, and this probably explains the absence of activity on the platinum electrodes.

In order to ascertain whether the negative charge, which the ions must have in order to be collected exclusively on the anode, is a lasting property or merely momentary, the experiment was repeated with no applied field during actual irradiation, the field being applied for 30 minutes after irradiation had been stopped. The yield, after allowance for decay, was practically the same as that previously obtained, being, if anything, a little higher, showing that the charge is retained.

These results, summarised in Table II (i), were obtained by using a fresh sample of ethyl iodide for each experiment, but when the same sample was used more than once, after a few hours had been allowed for the old activity to decay, the collected activity was still confined to the anode but the yield decreased continuously until finally practically no activity was collected; this suggests that an exchange of electric charges between the radio-active iodine and a small quantity of iodine ions present in the liquid takes place. This point was investigated subsequently (see p. 388).

A similar series of experiments was carried out, with bromoform instead of ethyl iodide. The results are in Table II (ii).

TABLE II.

			(i) *Ethyl iodide.*				(ii) *Bromoform.*			
			Anode.		Cathode.		Anode.		Cathode.	
Electrodes.	Treatment.	Field.	Kicks/ min.	%.†	Kicks/ min.	%.†	Kicks/ min.	%.†	Kicks/ min.	%.†
Pt	Ignited	360	0	0	0	0	0	0	0	0
Ag	Abrasive powder	360	145	120	0	0	10	6	10	6
Cu	Emery	—	13	11	13	11	21	13	22	13
,,	,,	360	90	75	20	17	17	11	17	11
,,	Abrasive powder	360	100	84	0	0	23	15	23	15
,,	,, ,,	360 *	130	108	0	0	26	16	23	15

* No field during irradiation; field applied for 30 minutes after irradiation was stopped.

† % = % Activity.

It is noteworthy that with bromoform the activity is collected indiscriminately on both electrodes, showing that the active bromine in bromoform, unlike the iodine in ethyl iodide, has no characteristic charge, and that its collection on the electrodes is purely a chemical effect. In view of this striking difference in behaviour between bromoform and ethyl iodide, various liquids were tried. Smooth copper electrodes were used, the field being applied during and for 1 minute after irradiation. Newly purchased materials were employed, the colour being removed, where possible, by standing in contact with copper wire. In some experiments an effort was made to produce ions, in order to facilitate the collection of the active isotope, by passing sulphur dioxide through the liquid. The results are given in Table III and the accompanying notes.

TABLE III.

Smooth copper electrodes ; 360-volt field.

Substance.	Kicks/min. Anode.	Kicks/min. Cathode.	Substance.	Kicks/min. Anode.	Kicks/min. Cathode.
Methyl iodide	38	0	Butyl iodide	118	0
Ethyl iodide	100	0	Butyl bromide	70	0
Ethyl bromide	125	0	Ethylene dibromide	88	0

Bromoform : Field has no apparent effect (see above).

Iodobenzene : Always coloured. No activity can be collected even after 30 minutes' passage of sulphur dioxide. The liquid cannot be decolorised by standing over copper wire.

Bromobenzene : The colourless liquid, after standing with copper wire, gave an activity of 35 kicks/min. on the anode and 15 kicks/min. on the cathode. A similar sample, after addition of a trace of bromine and 5 minutes' passage of sulphur dioxide, gave an activity of 28 kicks/min. on each electrode; after addition of sufficient bromine to impart a dark brown colour to the liquid, followed by 30 minutes' passage of sulphur dioxide (conditions analogous to the iodobenzene experiment), no activity was collected on either electrode.

Methylene iodide : Liquid dark brown, and no activity collected even after 30 minutes' passage of sulphur dioxide.

Methylene bromide : Colourless liquid gave all activity on the anode (113 kicks/min.) ; addition of bromine until liquid was dark brown, and then passage of sulphur dioxide, gave no activity on either electrode.

An interesting feature of the table is that the active bromine in ethyl and butyl bromide and ethylene dibromide, unlike that in bromoform, is collected exclusively on the anode. Methyl bromide, ethylene di-iodide, and iodoform could not be investigated in this way, as the first is a gas and the others are solids.

It seems that no activity is collected on the electrodes in any case where a considerable amount of free halogen is present, and that this absence of activity is due to exchange processes between the active isotope and the excessive quantity of dissolved halogen; *e.g.*, in bromoform, the samples used always had a brown tint which could not be removed by standing with a copper coil. (There would have been no point in trying to remove the colour by distillation, as the experiments with ethyl iodide show that the presence of ions in solution is essential for the collection of the activity on the electrode.) The same explanation is also borne out by the experiments with bromo- and iodo-benzene, and by the fact that in the second experiment described under methylene bromide, a current of the order of 1 m.a. passed through the liquid, showing the presence of ions, and an appreciable deposit of cuprous bromide was left on both electrodes although no activity was collected. In the case of iodobenzene, on the other hand, it is probable that there are no charged particles present, even after passage of sulphur dioxide, as there was an almost complete absence of a deposit on the electrodes and no measurable current passed through the liquid; the non-collection of activity in this case is therefore due to the absence of the minimum amount of ions from which the active isotope, by exchange, could acquire its charge.

From the literature it appears that little is known about the accidental presence of iodine and bromine ions in liquid organic compounds of these halogens. A further investigation was not made of this point, which, however, may be of interest in the study of the mechanism of their reactions.

Investigation of the Behaviour of Ethyl Iodide.—The effect of electrolysing the liquid to zero conductivity had been found to be complete removal of colour, and prevention of the collection of any activity on either electrode (see p. 387). Shaking with phosphoric oxide had no effect upon the colour but removed the conductivity. According to Bodenstein and Jost (*J. Amer. Chem. Soc.*, **1927**, **49**, 1416), phosphoric oxide reacts with hydrogen iodide, and it was thought probable that the presence of the latter would prove to be the explanation. Accordingly, experiments were performed upon electrolysed ethyl iodide, colourless and of zero conductivity, the effect being tested of different substances and treatments which might be expected to produce ions in solution. The arrangements were as before, with smooth copper electrodes, and a 360-volt field. The results are summarised in Table IV.

TABLE IV.

Electrolysed ethyl iodide. Smooth copper electrodes; 360-volt field.

Treatment of sample.	Anode. Kicks/ min.	Anode. % Activity.	Cathode. Kicks/ min.	Cathode. % Activity.	Deposit.
Untreated	0	0	0	0	
10 Days' standing in sunlight	65	54	0	0	
10 Days' standing in dark with Cu wire	85	71	0	0	
Dry HI bubbled through liquid	12	10	0	0	
Crystal of NMe_4I added	25	21	0	0	
Crystal of I_2 added	80	75	10	8	
SO_2 passed	25	21	0	0	Not visible.
Crystal of I_2 added, SO_2 passed	70	58	70	58	
Trace of I_2 added, SO_2 passed	120	100	0	0	Scarcely visible.
Minute trace of I_2 added (not enough to impart a colour to the liquid), and few bubbles of SO_2 passed	65	54	0	0	Not visible.

It will be seen from the table that, in order to obtain a very high concentration factor, with the deposition of a very pure layer of active isotope uncontaminated with inactive material, the best method is to pass a little sulphur dioxide into the electrolysed solution, either with or without the addition of a minute trace of iodine. The presence of too much iodine dilutes the active deposit. Similar efforts to increase the yield of active bromine from bromoform were unsuccessful.

In an endeavour to increase the concentration factor still further, the plate electrodes were replaced by a single-wire anode and a cylindrical copper cathode. The activity on the wire only was measured, but the efficiency of this arrangement was only about one-sixth of that with the plate electrodes (see following table).

Variation in electrodes.

Sample.	Plate anode. Kicks/min.	Plate anode. % Activity.	Wire anode. Kicks/min.	Wire anode. % Activity.
Electrolysed liquid + SO_2	25	21	4	3
Manufacturer's sample, stood with copper wire	85	71	15	12
Electrolysed liquid + trace of I_2 + SO_2	120	100	20	17

Effect of Stirring.—In order to ascertain (*a*) how quickly the active isotope may be collected and (*b*) how long an interval may elapse between interruption of irradiation and collection of the activity, a series of experiments was performed, in which the electrodes were the usual smooth copper plates and the field 360 volts, but the liquid was stirred when required by a mechanical glass stirrer immersed therein. Electrolysed ethyl iodide was used, to which a trace of iodine had been added and through which sulphur dioxide had been passed for 5 minutes. The arrangement of the bath was slightly altered, resulting in diminished activation, but as only comparisons were required, the activity deposited was compared as kicks/minute (allowance being made for incomplete activation and decay) and not as percentages of the total activity obtained by precipitation. The anode activities are given in Table V.

TABLE V.

Effect of stirring electrolysed ethyl iodide + I_2 + SO_2.

Conditions.	Kicks/min.
Field on during irradiation	33
Field on during irradiation + stirring	28
Irradiate without field, remove source, and stir for 2 mins. with field on	24
Irradiate without field, remove source, and have field on for 2 mins. without stirring	15
Irradiate without field, remove source, and stir for ½ min. with field on	15
Irradiate without field, remove source, and have field on for ½ min. without stirring	13
Irradiate without electrodes, then place electrodes in position, and stir with field on for 2 mins. Remove electrodes, and measure activity after 1 hour	14
Irradiate without electrodes, stand for 1 hour, then place electrodes in position, and stir with field on for 2 mins. Measure activity at once	14

It will be seen that stirring during irradiation, with the field on, does not increase the yield. When the field is applied for a short time after irradiation, however, stirring seems to be advantageous.

The experiments involving time intervals necessitated the use of a stronger source, and a 150-mc. radon–beryllium source was employed. The figures are corrected for this and for the decay of the radon source, so comparisons are absolute. It is obvious that the active iodine does not have its charge altered in any way by standing, since the activity on the anode is the same whether the active isotope is collected at once or is allowed to stand and then collected. It was found that the experiments involving stirring always gave a slight activity (about 6 kicks/minute, corrected) on the cathode, even when the field was applied throughout the experiment, but this is not difficult to understand when one recalls that there was evidence in the first few experiments of a definite chemical affinity of the active iodine for the copper electrodes, which must be encouraged by stirring.

Finally, an investigation was made to determine whether the active isotope obtained by the application of an electric field was identical with that obtained by precipitation. It was found that precipitation of all free iodine as silver iodide before irradiation did not affect the collection of the activity on the anode. If, however, the sample was irradiated, sulphur dioxide passed, and the free iodine extracted, no active deposit was collected on the electrodes, even if a trace of iodine and a little sulphur dioxide were added to the liquid after precipitation and before application of the field. This suggests that the active iodine obtained on the electrode is identical with that obtained by precipitation by the method of Szilard and Chalmers (*loc. cit.*), the remaining 40% presumably either never leaving the ethyl iodide molecule or else re-entering it (see following paper).

SUMMARY.

The concentration of artificially produced radio-elements can in many cases be effected by the application of an electric field, for we have found that the active particles are often charged. The radioactive atoms in our experiments were produced by slow neutrons, and the charge acquired by them has nothing to do with the mechanism of the capture of the neutrons, but is due to secondary processes. We have studied in some detail the effects of neutron bombardment on arsine (gaseous phase) and ethyl iodide (liquid phase). The active arsenic isotope ${}^{76}_{33}\mathrm{As}$ does not retain any characteristic charge which may be imparted to it at the moment of its formation, but attaches itself to the positive and negative ions present in the gas and can be deposited on electrodes of either sign. In the case of ethyl iodide, the iodine atoms which are activated and, at the same time, detached from the ethyl groups, acquire by exchange processes the negative charge of iodine ions which are usually present in the liquid or, if not, can be easily imparted to it. By electrolysis, therefore, the active isotope ${}^{128}_{53}\mathrm{I}$ can be concentrated on a copper or silver anode. By the same method it is possible to collect the active iodine from methyl and butyl iodides and the active bromine from ethyl, butyl, methylene, and ethylene bromides.

From these and other experiments described, it appears that the nature of the secondary processes which lead to the acquisition of electric charges varies, but that frequently the application of an electric field is a good method of obtaining the radioactive isotopes in a practically pure state. The concentration factor in some of our experiments exceeded 20,000.

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