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β-DECAY OF RADIOACTIVE LEAD TETRAMETHYL

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Abstract—A study of the decay of gaseous $^{210}Pb(CH_3)_4$ under conditions where the product is not under the influence of neighbouring molecules has shown that 100 per cent of the daughter ^{210}Bi is deposited on the walls of the containing vessel. This may be interpreted in accordance with the predictions that the daughter species $Bi(CH_3)_4^+$ disproportionates to give a charged bismuth-containing fragment, rather than $Bi(CH_3)_3$.

THIS work is concerned with a system in which the chemical effects of the nuclear event can be distinguished so that the subsequent chemical reactions of the species formed by decay can be studied. In order to minimize reaction between the daughter species and its environment, it is necessary to work in the gas phase. A readily volatile parent molecule, with the possibility of daughter reaction products which are also volatile, is therefore desirable. The system

$$^{210}Pb(CH_3)_4 \rightarrow \beta + {}^{210}Bi(CH_3)_4^+$$

was chosen as being one of the few which were suitable. Only three other isotopes, viz. ^{144}Ce, ^{228}Ra and ^{234}Th, have decay energies which are sufficiently low to exclude the possibility of bond rupture by recoil, and all of these are unsuitable for various reasons. The ^{210}Pb β-decay is accompanied by γ-ray emission and internal conversion, which could be troublesome, but previous workers(1,2) investigating the decay of ^{210}Pb as gaseous lead tetramethyl at pressures from 4 to 40 mm Hg and in the presence of inert gases up to 700 mm Hg pressure(3) have shown that such effects are small. In addition the system chosen has the following favourable features: lead tetramethyl (a) is easily prepared in a high state of purity; (b) has a convenient vapour pressure (25 mm at 21°C(4)) for handling in a vacuum line; (c) is unreactive with water, oxygen or carbon dioxide at room temperature; (d) is the volatile compound of lead with the simplest stereochemistry; (e) has two suitable isotopes (^{210}Pb and ^{212}Pb) which decay with different β-energies, so that the contributory effects of nuclear recoil, electronic excitation, and thermodynamic instability may be checked.

EXPERIMENTAL

Materials. Lead tetramethyl was prepared by the method of GILMAN and JONES(5) by adding a solution of methyl magnesium iodide (prepared from 7·3 g of magnesium and 18·7 ml (43 g) of methyl iodide) in 125 ml of ether to a slurry of lead chloride (26·9 g) in methyl iodide (6·2 ml) and ether

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(1) R. A. MORTENSEN and P. A. LEIGHTON, *J. Am. chem. Soc.* **56,** 2397 (1934).

(2) R. R. EDWARDS and C. D. CORYELL, U.S. Atomic Energy Commission unclassified document No. 50 (1948).

(3) R. R. EDWARDS, J. M. DAY and R. F. OVERMAN, *J. chem. Phys.* **21,** 1555 (1953).

(4) D. R. STULL, *Ind. Engng. Chem. analyt. Edn.* **39,** 517 (1947).

(5) H. GILMAN and R. G. JONES, *J. Am. chem. Soc.* **72,** 1760 (1950).

(50 ml) with stirring. All operations were carried out under an inert (nitrogen) atmosphere. The mixture was refluxed for 2 hr, cooled and slowly added to 70 g of crushed ice. The ethereal phase was separated and dried over calcium chloride; the ether was distilled off and the lead tetramethyl was distilled. The fraction boiling at 108–110°C was collected. Yield 13·4 g (52%). *Anal.* Theor. Pb, 77·6%; C, 17·9%; H, 4·5%. Found: Pb, 77·0%; C, 18·3% and H, 4·8%.

Bismuth trimethyl was prepared by the method of LONG and SACHMAN,⁽⁶⁾ by slowly adding a solution of methyl magnesium iodide (from 3·1 g of magnesium and 8·1 ml of methyl iodide) in ether (50 ml) to a stirred slurry of anhydrous bismuth trichloride (13 g) in ether (25 ml). The mixture was refluxed for 2 hr and then poured into cold ammonium chloride solution (50 ml of 10% solution, initially at −3°C). The ethereal phase was separated and dried over anhydrous sodium sulphate; ether was distilled off and the bismuth trimethyl was distilled. The fraction boiling at 110°C was collected. All steps of the preparation were carried out under nitrogen and the product was stored under nitrogen. Yield 3·04 g (30%). *Anal.* Bi theoretical 82·2%. Found: 80·8%.

^{210}Pb-*labelled lead tetramethyl.* Lead chloride having a specific activity of 1·5 μc of ^{210}Pb per mg of $PbCl_2$ was prepared by dissolving the Ra D–E–F mixture from a spent radon seed in concentrated nitric acid containing 100 mg lead nitrate as carrier and precipitating the lead with hydrochloric acid. Lead tetramethyl was prepared as above using $\frac{1}{8}$th the above quantities of materials. The lead chloride used was a mixture of 2·97 g of inactive material and 0·03 g of the ^{210}Pb-labelled material. Micro-size apparatus was used and the yield was 2·4 g (83% theor.), b.p. 109–110°C. This material was stored in a glass-stoppered tube for 30 days before it was used, when it was diluted with inactive lead tetramethyl carrier to give a suitable activity for bond rupture studies.

^{212}Pb-*labelled lead tetramethyl.* The short half-life (10·64 hr) of ^{212}Pb made it necessary to work as quickly as possible with this isotope after separating it from the thorium decay chain. Lead iodide, labelled with ^{212}Pb, was prepared by dissolving aged thorium carbonate (200 g) in conc. nitric acid (160 ml), diluting to 400 ml with water, adding lead nitrate carrier (2·5 g) and precipitating lead iodide with a slight excess of potassium iodide. The precipitated lead iodide was filtered, dried at 140° for 1 hr and used immediately to prepare ^{212}Pb-labelled lead tetramethyl by the method described above, substituting lead iodide (3·03 g) for lead chloride and using equivalent quantities of materials. In a typical preparation the b.p. of the product was 108–110°C, yield 1·0 g (57% theor.). This was used immediately for bond rupture studies.

Nitrogen. "Oxygen-Free Dry Nitrogen", supplied by Commonwealth Industrial Gases Ltd. was used after passing through concentrated sulphuric acid and then over solid potassium hydroxide in a drying tube.

All other reagents used were of AR grade purity.

Apparatus. The all-Pyrex apparatus used in this work is shown in Fig. 1. The apparatus was connected to the pumping system at U and to a sensitive McLeod gauge (10^{-1}–10^{-6} mm Hg pressure range) at V. Air or nitrogen could be admitted by alternately opening the stopcocks A and B. Radioactive lead tetramethyl was stored in K, which was connected to the line by a B7 standard joint (waxed with Apiezon "W") and the stopcock C. Bismuth trimethyl was stored in L, and a small tube M, connected to the line, was used for sampling lead tetramethyl by distillation from K. Reaction vessels W were connected to the system by a B14 joint N. Liquid air traps T were used to prevent lead tetramethyl from contaminating the pressure guage and the pumping system. Material collecting in these traps (mainly lead tetramethyl) was periodically condensed with liquid air into a tube attached at N, diluted with carbon tetrachloride and converted to lead bromide with liquid bromine. This material was never returned to the system, because of possible contamination and depletion of the volatile bismuth content of the lead tetramethyl by reaction with air from the pressure gauge S.

Pressure measurement. A mechanical spoon gauge P was used to measure the pressures of lead tetramethyl and bismuth trimethyl; it was connected to the system through the stopcock G and surrounded by the envelope O. The deflection of the 25-cm glass pointer Q (with a fine tungsten wire fused to the end) was read through the flat window R with a calibrated microscope. The tip of Q was immersed in Apiezon oil "B" to dampen spurious vibrations. The gauge was used as a null instrument; the pressure in the envelope was pre-set by admitting air at J and the pressure of lead tetramethyl in the system was made equal to the pressure in O by controlled evaporation from the storage tube, K. The McLeod gauge S (pressure range 0·02–15 mm Hg) was used to measure the

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⁽⁶⁾ I. H. LONG and J. F. SACKMAN, *Trans. Faraday Soc.* **50**, 1177 (1954).

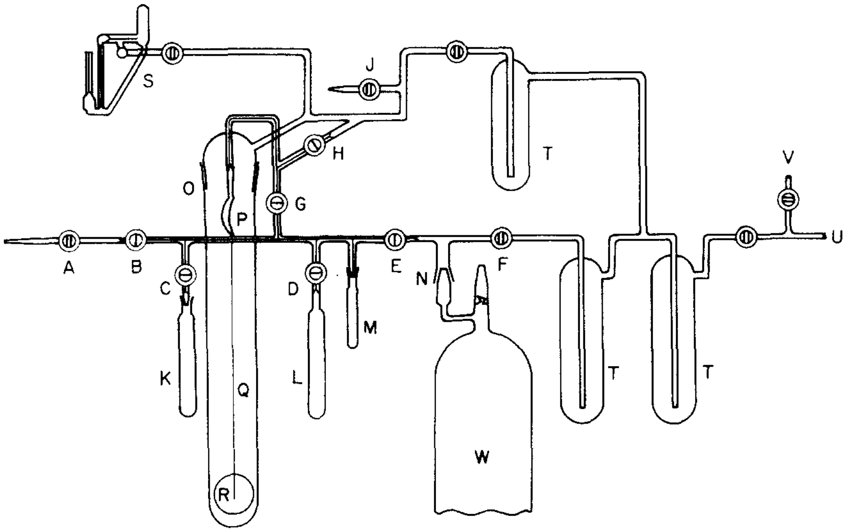

FIG. 1.—The apparatus.

pressure in O. Pressures could be measured to ±0·03 mm Hg by averaging three readings of the gauge.

Pressures below 0·7 mm Hg were calculated, assuming ideal gas laws, from the determined pressure of a sample of lead tetramethyl, in the capillary section of the apparatus, which was then expanded into the reaction vessels of known volumes. The volumes of the portions of the line enclosed by stopcocks A and B (v_1) and by B, C, D, E and G (v_2) were measured prior to the final assembly of the line by weighing mercury. The volume enclosed by the stopcocks G and H and the spoon gauge (v_3) was determined by expanding a known pressure (3–10 mm Hg) of air from v_3 into v_2, measuring the final pressure and calculating v_3 from the ideal gas laws. These volumes were $v_1 = 0{\cdot}824 \pm 0{\cdot}006$ cm^3, $v_2 = 2{\cdot}80 \pm 0{\cdot}01$ cm^3 and $v_3 = 2{\cdot}42 \pm 0{\cdot}03$ cm^3 (v_2 was measured with M not included; the volume with M in place was 5·09 ± 0·02 cm^3).

Reaction vessels. Six reaction vessels W were constructed from 7·6-cm dia. glass tubing, fitted with break-off seals and filling arms as shown, and filled with glass tubing (9-mm dia.) so that the ratio of molecular collisions with the vessel walls to the intramolecular collisions in the gas phase would be increased. Break-off seals were used so that lead tetramethyl in the reaction vessel did not come in contact with grease during the reaction period. Trial runs in which greased stopcocks were used to seal the reaction vessel showed that 15–20% of the lead tetramethyl (at 50 mm Hg pressure) was absorbed by the tap grease after standing for 3 days. The six vessels had free volumes of 1000–1100 ml and geometric surface areas of 5100–5800 cm^2.

Analytical procedures. All activity measurements were made under identical conditions and corrected for counter fluctuations using a standard ^{36}Cl source.

^{210}Bi *content of lead tetramethyl.* A weighed sample of liquid lead tetramethyl (20–50 mg) was dissolved in carbon tetrachloride (15 ml) and treated with a slight excess of bromine in the presence of 1 M nitric acid (20 ml) containing 1 ml of a standard bismuth nitrate solution (8·65 mg of bismuth per ml) to act as carrier. The carbon tetrachloride and excess bromide were boiled off, and excess neutral sodium phosphate solution added to precipitate bismuth phosphate. The precipitate was centrifuged, washed three times with hot water, slurried in acetone, transferred to a weighed aluminium planchette, dried under an i.r. lamp and re-weighed. Corrections for chemical losses were made by comparing the sample weight with the weight of bismuth phosphate expected. The activity of all samples was measured with an end-window Geiger counter at 4 or 5-day intervals for 30 days in order to determine the radiochemical purity of the bismuth phosphate. In all cases long-lived activity (due to ^{210}Pb contamination) was less than 2% of the total activity (i.e. absent within experimental limits) and the measured half-life of the ^{210}Bi was 5·0 ± 0·1 days (quoted value for ^{210}Bi 5·00 days(7)).

(7) D. STROMINGER, J. M. HOLLANDER and G. T. SEABORG, *Rev. Mod. Phys.* **30**, 585 (1958).

^{210}Pb *and* ^{210}Bi *contents of stock lead tetramethyl.* A portion of the stock material was distilled from K into M, the latter being cooled in liquid air. M was filled with nitrogen, removed from the line, warmed to room temperature, and a weighed sample of lead tetramethyl was treated as above to separate ^{210}Bi as bismuth phosphate. This was assayed for radioactivity over a period of 50 days at 4–5-day intervals. The solution remaining after precipitation of bismuth phosphate was treated with excess sodium sulphate to precipitate lead sulphate, which was centrifuged, washed with water, transferred to a weighed aluminium planchette with acetone, dried and weighed. The ^{210}Pb content was obtained by measuring the growth of ^{210}Bi daughter activity in the lead sulphate over a period of 50 days under the end-window Geiger counter. (This was not sensitive to the weak β-particles emitted by ^{210}Pb.) The chemical yield of lead sulphate was determined from the weight of lead tetramethyl sample taken for analysis.

Involatile ^{210}Bi *deposited on the vessel walls.* Concentrated nitric acid (9 ml) and standard bismuth nitrate solution (1 ml) were placed in the reaction vessel and refluxed through the vessel for 1½–2 hr. Preliminary tests showed that refluxing for ½–¾ hr removed all ^{210}Bi from the vessel walls. After cooling, the solution was removed and the vessel rinsed twice with 35 ml water. To the combined nitric acid solution and washings, excess sodium phosphate was added followed by solid sodium hydroxide pellets until precipitation was complete (care being taken that the solution remained acidic). The bismuth phosphate was centrifuged, washed, mounted, weighed and assayed for radioactivity as above. All activity measurements in this work were, so far as possible, made under identical conditions. The usual corrections for absorption, counter fluctuations, and, where appropriate, decay, were made throughout. Tests for involatile ^{210}Pb deposited on the walls were made by adding lead nitrate carrier (50 mg) to the concentrated nitric acid–bismuth nitrate solution in the reaction vessel, treating as above, separating bismuth phosphate and then precipitating lead sulphate. The lead sulphate was prepared for radio-assaying as above, allowed to stand 30 days and assayed for radioactivity. In all cases the activity of the lead sulphate was not detectably different from the natural background activity.

Preliminary investigations with ^{210}Pb(CH$_3$)$_4$. The stock of lead tetramethyl, consisting of 0·4 ml of the labelled ^{210}Pb(CH$_3$)$_4$ prepared as above, diluted with inactive material, was placed in the tube K; after waxing in position below C, this was frozen with liquid air, evacuated and degassed by normal procedures. C was closed, and the contents of K allowed to stand at room temperature for 30 days for radiochemical equilibrium between ^{210}Pb and ^{210}Bi to be attained. The specific activity of this sample of lead tetramethyl under our standard conditions of assay was 226 ± 2·5 counts/min per mg.

Several samples of lead tetramethyl were distilled under vacuum from K to M (cooled in liquid air). These were weighed and treated as above to determine the ^{210}Pb and ^{210}Bi contents, the former being determined by following the growth of ^{210}Bi daughter over a period of 50 days. Since the sum of the measured activities of both samples was constant over the whole counting period, the gas distilling from the liquid lead tetramethyl also contained ^{210}Pb and ^{210}Bi in radiochemical equilibrium. These isotopes were also in radiochemical equilibrium in the liquid phase, indicating that all the ^{210}Bi is present as volatile ^{210}Bi(CH$_3$)$_3$ in the liquid phase, in agreement with Mortensen and Leighton.(1) To ensure that the stock lead tetramethyl in K always contained the ^{210}Pb–^{210}Bi pair in radiochemical equilibrium in a volatile form, air was rigorously excluded from K throughout the investigation, since bismuth trimethyl reacts with oxygen to give involatile Bi$_2$O$_3$.(8)

To determine the material and activity recovery after a decay experiment a reaction vessel was connected to the vacuum line at N by means of the filling arm and evacuated to 10^{-5} mm Hg. The storage vessel K, which had previously been cooled in liquid air, was allowed to warm to room temperature with stopcocks C, G and E open and B, D, F and H closed. Lead tetramethyl was admitted to the reaction vessel until the pressure reached 10 mm Hg. Stopcock E was closed, and the reaction vessel was cooled in liquid air and sealed at the constriction in the filling arm. Meanwhile, the vapour in the line and gauge was condensed back into K with liquid air and C was closed. The reaction vessel was removed from the liquid air and allowed to stand for 30 days at room temperature. The reaction vessel was then connected to the line at N by the B14 cone above the break-off seal; the line was evacuated, the seal broken by a magnetically operated, glass-encased, steel plunger and the lead tetramethyl condensed into M using liquid air. The ^{210}Bi activity in the condensate (which was weighed) and on the vessel walls was determined as above. This was repeated at various pressures and reaction periods ranging from 35 min to 24 days. The results of these runs (Table 1) show that,

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(8) G. E. Coates, *Organo-metallic Compounds*, p. 158. Methuen, London (1956).

within experimental error, the recovery of materials and activity was quantitative. The half-life of the involatile activity was not significantly different from that of ^{210}Bi. EDWARDS and CORYELL(2) were unable to obtain a quantitative recovery of ^{210}Bi after a run, probably because some of the lead tetramethyl vapour dissolved in the grease lubricating the ground glass joints of their reaction vessels. Since quantitative activity recovery is possible using grease-free reaction vessels, it is only necessary to measure the yields of involatile bismuth deposited on the vessel walls in order to determine the fraction of decays which produce free, involatile bismuth as a result of bond rupture of the daughter molecule.

The results in Table 1 for the 35-min and 16-hr runs at 10·2 mm and 7·0 mm respectively show that the amount of involatile ^{210}Bi on the walls of the reaction vessels is very much greater than would be expected from the decay process alone, even if every decay resulted in the complete fragmentation of the daughter molecule. Thus, volatile ^{210}Bi in the gases admitted to the reaction vessels is absorbed on the vessel walls and/or is reacting with traces of oxygen in the vessels. Several runs were performed as above at 7 and 10 mm for periods from 30 min to 30 days. In all cases where the reaction vessels were not specially treated to remove oxygen, the involatile ^{210}Bi activity increased very rapidly at first, then decreased, reaching a steady value after about 14 days (See Fig. 2, Curve A).

TABLE 1.—RECOVERY OF ^{210}Bi

				^{210}Bi Activity†			
					Recovered		
Time	Pressure of $Pb(CH_3)_4$ (mm Hg)	Added* weight of $Pb(CH_3)_4$ (mg)	Recovered weight of $Pb(CH_3)_4$ (mg)	Total‡ added (cpm)	Involatile (cpm)	Volatile (cpm)	Total (%)
30 days	10·5	174·7	173·0	39600	1274	37800	98·7 ± 5·0
24 days	9·9	166·6	165·1	37700	2050	34900	98·0 ± 4·8
20 days	10·0	168·0	169·1	38000	1067	38100	103·1 ± 5·0
13 days	10·0	168·3	160·5	38100	940	35200	94·9 ± 5·1
5 days	10·0	146·3	142·7	33100	12400	19900	97·6 ± 4·5
35 min	10·2	169·0	170·3	38200	6724	31400	99·6 ± 4·8
16 hr	7·0	116·4	115·0	26350	16700	9367	98·9 ± 4·0
12 days	6·9	101·5	99·8	23000	1675	20700	97·3 ± 5·0
12 days	4·3	72·9	71·9	16500	2049	14200	98·5 ± 5·4
11 days	2·3	34·0	33·6	7690	3547	4005	98·2 ± 5·7
10 days	1·0	16·7	17·0	3778	1778	2021	100·6 ± 6·0
						Mean recovery	98·7 ± 1·5

* Determined from the pressure of $Pb(CH_3)_4$ and the volume of the vessel.

† Corrected for decay during the sample preparation and expressed in counts/min (cpm).

‡ Estimated from the weight and specific activity of $Pb(CH_3)_4$.

All errors quoted on activity measurements are standard deviations (68·5% confidence limits).

The fact that this plot goes through a maximum indicates that some secondary reaction is occurring between ^{210}Bi deposited on the glass walls and gaseous lead tetramethyl. Flaming the vessels improved matters but did not entirely eliminate these unwanted side effects (Fig. 2, Curve B). Flushing the hot vessel (at 140°C) with "oxygen-free" dry nitrogen (which reduced the residual oxygen pressure in the vessels by at least a factor of $\sim 10^{-5}$, i.e. to $< 10^{-11}$ mm at 140°C) lead to curve C of Fig. 2. After this pretreatment, reproducible yields of involatile ^{210}Bi independent of (a) the surface area of the vessel and (b) the amount of inactive bismuth trimethyl added to the system, were obtained in subsequent experiments. Thus, after this treatment $^{210}Bi(CH_3)_3$ is not irreversibly absorbed on the vessel walls and the amount of oxygen remaining on the vessel walls or in the residual gases in the vessel is so small that no significant reaction occurs between oxygen and $^{210}Bi(CH_3)_3$. Checks on the material on the walls for ^{210}Pb activity at the end of a run were always negative, indicating that $^{210}Pb(CH_3)_4$ is not irreversibly absorbed on the vessel walls.

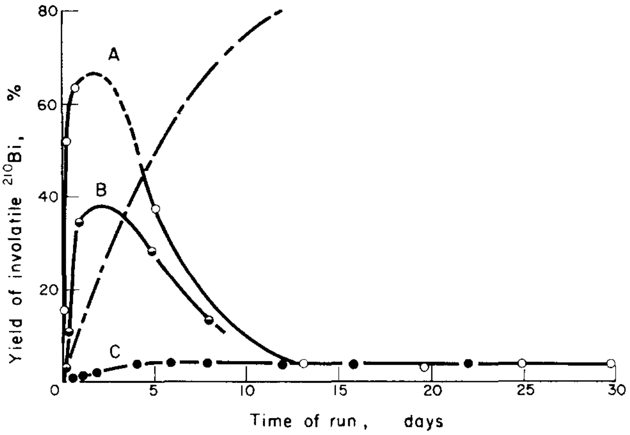

FIG. 2.—The effect of reaction vessel pretreatment on the yield of involatile ^{210}Bi as a function of the time of reaction at 10 mm Hg; ○ no pretreatment; ◒ flamed; ● heated, flushed with nitrogen; dotted curve—calculated for 100% rupture.

Method of investigation of main problem

Determination of ^{210}Bi *deposited on the vessel walls by nuclear decay processes.* The reaction vessel W was thoroughly washed and rinsed with distilled water and a fresh break-off seal, filling arm and B14 cones sealed in position (Fig. 1) The vessel was flushed with nitrogen and heated to 140°C in an oven while nitrogen was passing through it to remove water vapour and air. The filling arm was connected to the vacuum line at N and the vessel evacuated to 10^{-5} mm Hg, refilled with nitrogen (admitted to the line at A) evacuated again and kept at 10^{-5} mm Hg for 2 hr while the vessel cooled to room temperature (which was noted). Lead tetramethyl or a mixture of lead tetramethyl and bismuth trimethyl was admitted to the desired pressure, the reaction vessel was cooled in liquid air and the filling arm was sealed. The vessel was placed in a darkened cupboard at room temperature for the duration of the run. At the completion of the run the vessel was connected to the vacuum line at N, the break-off seal shattered, and the vapours condensed into M, the last traces being removed by successively evacuating to 10^{-5} mm with the pumps, and flushing the vessel with nitrogen to atmospheric pressure. The vessel was refilled with nitrogen, removed from the line and the involatile ^{210}Bi determined as above. The condensate in M was then volatilized and condensed in the stock lead tetramethyl in K. No further vessels were filled from K until radiochemical equilibrium had been re-established to within 1% in the stock sample; usually 7–14 days was required for this, depending on the amount of condensate in M and the degree of depletion of ^{210}Bi during the experiment.

The effect of inactive bismuth trimethyl on the yield of involatile ^{210}Bi was determined by a similar procedure to that given above. Bismuth trimethyl stored in L (Fig. 1) was admitted to the reaction vessel to the desired pressure by a similar procedure to that used for admitting lead tetramethyl. Stopcock E was closed and the bismuth trimethyl remaining in the gauge and line was condensed in L with liquid air. Stopcock D was closed and C opened, and lead tetramethyl allowed to evaporate until the pressure in the line was about 10 mm Hg. E was next opened and lead tetramethyl was admitted to the reaction vessel to the desired pressure. This procedure prevented contamination of the lead tetramethyl in K with bismuth trimethyl. After sealing the reaction vessel it was stood for the desired time at room temperature and the yield of involatile ^{210}Bi measured as above. Details of the runs are given in Table 2.

Bond rupture experiments with ^{212}Pb(CH$_3$)$_4$. The apparatus was used as in Fig. 1 with the following modifications. The stock of ^{210}Pb-labelled lead tetramethyl in K was replaced by a stock of ^{212}Pb-labelled material. This was frozen in liquid air, evacuated, and left for 12 hr at room temperature before use to ensure that radiochemical equilibrium between ^{212}Pb and ^{212}Bi was attained. The reaction vessels (free volume 460–500 cm^3, surface area 2300–3000 cm^2) were made from 6·0-cm dia. tubing filled with pieces of 8·0-mm dia. tubing and fitted with 18/9 B.S. ball joints. Four standard 18/9 B.S. sockets were connected by 2-mm bore stopcocks to a standard B14 cone attached to the

TABLE 2.—DETAILS OF CONDITIONS FOR STUDYING THE EFFECT OF BISMUTH TRIMETHYL ON THE YIELD OF INVOLATILE ^{210}Bi

Pressure (mm Hg)		Time of experiment (days)
$Bi(CH_3)_3$	$Pb(CH_3)_4$	
1·0	9·0	0·22$_2$, 0·75, 2·81, 5·76, 9·70, 13·81, 18·69, 21·93.
0·5$_4$	4·8$_6$	13·90
0·5$_0$	4·5$_0$	6·21
0·4$_6$	4·0$_4$	11·03

vacuum line at N. This arrangement enabled the four vessels to be operated separately or simultaneously. Since the experiments with ^{212}Pb were of short duration, no break-off seals were necessary, as the uptake of lead tetramethyl by tap grease was relatively slow. The desired pressure of lead tetramethyl was admitted to the gauge and the line enclosed by stopcocks B, C, D, E and H. This was expanded into the four reaction vessels and the pressure in the vessels calculated from the measured pressure and the appropriate volumes. At the end of an experiment lead, tetramethyl was pumped from a particular vessel and the pressure maintained at 10^{-5} mm Hg for 10 min; the vessel was then flushed with nitrogen, evacuated, refilled with nitrogen, removed from the line and the ^{212}Bi deposited on the walls determined as for ^{210}Bi. This system was studied at pressures of $3·5 \times 10^{-3}$–5×10^{-2} mm for times of 35–180 min.

Reaction between involatile bismuth and gaseous lead tetramethyl. In order to investigate this reaction which preliminary experiments indicated might be significant, radioactive bismuth was volatilized on to the walls of a reaction vessel and allowed to exchange with inactive lead tetramethyl. A glass vessel of 114 cm^3 capacity was fitted with a standard B14 cone on a side arm and a standard B24 cone. Two tungsten electrodes were sealed through a standard B24 stopper. The vessel was washed, dried at 140°C, filled with nitrogen and connected to the vacuum line (Fig. 1) at N. Meanwhile, a platinum spiral was suspended in the gases emanating from thorium hydroxide, with a potential of -200 V on it with respect to the metal container of the thorium hydroxide.(9) After 4 days, 0·5–1·0 μc of an equilibrium mixture of ^{212}Pb/^{212}Bi collected on the spiral. After removal, the spiral was connected across the ends of the tungsten electrode assembly and placed in the reaction vessel (via the B24 socket). The vessel was evacuated and the ^{212}Pb/^{212}Bi mixture distilled on to the vessel walls by heating the spiral electrically to bright yellow heat (1200–1500°C). Nitrogen was admitted to the vessel, the electrodes and platinum coil removed, a B24 stopper placed in the socket and the system re-evacuated. Inactive lead tetramethyl, which had been stored in M, was vapourized into the vessel to a pressure of 10 mm Hg. This was left for 5 hr at room temperature (21°C). The lead tetramethyl was then condensed back into a clean, empty sample tube attached at M, dissolved in carbon tetrachloride and treated with bromine in the presence of 9 ml of 1 M nitric acid and 1 ml of the standard bismuth solution (see above). The carbon tetrachloride and bromine were boiled off and the aqueous phase concentrated to 5 ml. The activity of this solution was measured with a Geiger Muller counter, type DM6, over a period of 10 hr. The walls of the reaction vessel were rinsed with 5 ml nitric acid (1 M) containing 1 ml of standard bismuth solution and 10 mg lead nitrate. The activity of this solution was measured with the same counter over a period of 30 hr. The above procedure was repeated for runs of 8-hr and 16-hr duration. The results of these experiments are listed in Table 3.

RESULTS AND DISCUSSION

Before any meaningful interpretation of the results can be given, the extent of chemisorption of lead tetramethyl and bismuth trimethyl on the walls of the vessel and the extent of any possible side reactions must be known. Chemisorption errors are shown to be negligible by the preliminary experiments reported above. However,

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(9) D. L. BAULCH and J. F. DUNCAN, *Austr. J. Chem.* **10**, 112 (1957).

TABLE 3.—EXCHANGE OF ^{212}Pb AND ^{212}Bi ON THE VESSEL WALLS WITH GASEOUS LEAD TETRAMETHYL*

Duration of exchange	Time after completion of exchange (min)	Gas phase activity (cpm)	Time after completion of exchange (hr)	Activity remaining on walls (cpm)
5 hr	65	298·2 ± 11·6	1·33	3736 ± 39
	130	170·9 ± 7·5	6·00	2773 ± 29
	190	106·3 ± 5·5	17·33	1302 ± 14·4
	250	74·0 ± 4·5	25·75	756·6 ± 15·8
	355	47·6 ± 4·7	30·17	549·0 ± 12·1
	950	21·0 ± 2·9		
7 hr 55 min	61	604·7 ± 21·6	3·50	5638 ± 58
	107	361·6 ± 8·9	5·33	5230 ± 54
	155	241·1 ± 10·3	15·92	2651 ± 28
	215	144·8 ± 7·3	21·58	1747 ± 19
	235	128·6 ± 6·7	28·17	1163 ± 13
	303	84·1 ± 5·4		
	785	33·0 ± 3·2		
15 hr 55 min	72	181·4 ± 8·3	1·83	1139 ± 13
	126	158·0 ± 7·6	3·83	1032 ± 21
	185	139·2 ± 7·2	4·78	1006 ± 20
	235	128·0 ± 6·7	5·05	938 ± 19
	278	119·9 ± 6·4	7·33	831·5 ± 17
	360	107·1 ± 5·9	22·27	301·0 ± 7·6
	435	96·1 ± 5·5	29·08	195·2 ± 8·7

* All activities corrected for counter fluctuations and natural background.

the amount of ^{210}Bi deposited on the walls of the vessel is affected by an exchange reaction with the gaseous lead tetramethyl (see Fig. 2).

Exchange reactions of lead tetramethyl

Since only about one molecule in 10^{11} in the gas phase contains ^{210}Bi (estimated from the specific activity) a reaction such as the following seems to be occurring,

$$^{210}Bi_{(walls)} + Pb(CH_3)_4 \rightarrow {}^{210}Bi(CH_3)_3 + Pb + \cdot CH_3 \qquad (1)$$

LEIGH-SMITH and RICHARDSON(10) report a similar interchange between deposits of both lead and bismuth on metal surfaces with their respective methyl compounds in ethereal solutions. When a mixture of ^{212}Pb, ^{212}Bi, ^{212}Po and ^{208}Tl, deposited on gold foil, was immersed in an ethereal solution of bismuth trimethyl for 2 hr a volatile compound of ^{212}Bi (presumably bismuth trimethyl) was formed. Similar results were observed when ^{210}Bi deposited on nickel was used. When the gold foil containing ^{212}Pb, ^{212}Bi, ^{212}Po and ^{208}Tl was immersed in an ethereal lead tetramethyl solution volatile compounds of both ^{212}Bi and ^{212}Pb were formed. Insufficient detail is given to decide whether the volatile bismuth arises from one or both of the following processes,

$$^{212}Pb_{(gold)} + Pb(CH_3)_{4(ether)} \longrightarrow {}^{212}Pb(CH_3)_{4(ether)} \xrightarrow{\beta} {}^{212}Bi(CH_3)_3 \qquad (2)$$

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(10) A. LEIGH-SMITH and H. O. W. RICHARDSON, *Nature, Lond.* **135**, 828 (1935).

and/or

$$^{212}\mathrm{Bi}_{(\mathrm{gold})} + \mathrm{Pb(CH_3)_{4(ether)}} \rightarrow {}^{212}\mathrm{Bi(CH_3)_3} + \text{other products} \tag{3}$$

LEIGH-SMITH and RICHARDSON favour reaction (2) on the assumption that $^{212}\mathrm{Pb(CH_3)_4}$ is completely converted to $^{212}\mathrm{Bi(CH_3)_3}$ on β-decay.

Further evidence of the labile nature of the heavy metal alkyls is given by MAHER and EVANS(11) who showed that mixtures of $\mathrm{Tl(CH_3)_3}$ and $\mathrm{Tl(C_2H_5)_3}$ undergo rapid exchange in dichloromethane and toluene solutions to give the mixed trialkyls $\mathrm{Tl(CH_3)(C_2H_5)_2}$ and $\mathrm{Tl(CH_3)_2(C_2H_5)}$. The activation energy of this exchange reaction in dichloromethane was estimated to be 6 kcal/mole.

Exchange between involatile $^{212}\mathrm{Pb}/^{212}\mathrm{Bi}$ *on the vessel walls and gaseous lead tetramethyl.* In order to interpret the results of the experiments (Table 3) we must know the relative contributions that the isotopes present in the rather complex decay system make to the measured activities. The decay scheme under study is as follows,(7)

$$\begin{tikzcd}
\begin{array}{c} {}^{212}\mathrm{Pb} \\ 10{\cdot}64\ \mathrm{hr} \end{array} \arrow[r, "\beta"] & \begin{array}{c} {}^{212}\mathrm{Bi} \\ 60{\cdot}5\ \mathrm{min} \end{array} \arrow[r, "\beta", "64\%"'] \arrow[d, "\alpha"', "36\%"] & \begin{array}{c} {}^{212}\mathrm{Po} \\ 0{\cdot}3\ \mu\mathrm{sec} \end{array} \arrow[d, "\alpha"] \\
 & \begin{array}{c} {}^{208}\mathrm{Tl} \\ 3{\cdot}08\ \mathrm{min} \end{array} \arrow[r, "\beta"] & {}^{208}\mathrm{Pb(stable)}
\end{tikzcd} \tag{4}$$

The total disintegration rate of a mixture of these isotopes at time t, A_T^t, is given by

$$\begin{aligned} A_T^t = {} & E_\mathrm{A}\lambda_\mathrm{A}N_\mathrm{A}^0 \exp(-\lambda_\mathrm{A}t) + 0{\cdot}64E_\mathrm{B}\{\lambda_\mathrm{B}\lambda_\mathrm{A}N_\mathrm{A}^0/(\lambda_\mathrm{B} - \lambda_\mathrm{A})\}\{\exp(-\lambda_\mathrm{A}t) - \exp(-\lambda_\mathrm{B}t)\} \\ & + 0{\cdot}64E_\mathrm{B}\lambda_\mathrm{B}N_\mathrm{B}^0 \exp(-\lambda_\mathrm{B}t) + \frac{0{\cdot}36E_\mathrm{C}}{(\lambda_\mathrm{C} - \lambda_\mathrm{A})}\{\lambda_\mathrm{B}\lambda_\mathrm{C}\lambda_\mathrm{A}N_\mathrm{A}^0/(\lambda_\mathrm{B} - \lambda_\mathrm{A})\} \\ & \times\{\exp(-\lambda_\mathrm{A}t) - \exp(-\lambda_\mathrm{C}t)\} + \frac{0{\cdot}36\,E_\mathrm{C}}{(\lambda_\mathrm{C} - \lambda_\mathrm{B})}\{\lambda_\mathrm{C}\lambda_\mathrm{B}N_\mathrm{B}^0 - [\lambda_\mathrm{B}\lambda_\mathrm{C}\lambda_\mathrm{A}N_\mathrm{A}^0/(\lambda_\mathrm{B} - \lambda_\mathrm{A})]\} \\ & \times\{\exp(-\lambda_\mathrm{B}t) - \exp(-\lambda_\mathrm{C}t)\} + E_\mathrm{C}\lambda_\mathrm{C}N_\mathrm{C}^0 \exp(-\lambda_\mathrm{C}t) \end{aligned} \tag{5}$$

where E_A, E_B, E_C are the relative counting efficiencies, λ_A, λ_B, λ_C are the disintegration constants, and N_A^0, N_B^0 and N_C^0 are the numbers of atoms present at $t = 0$, of $^{212}\mathrm{Pb}$, $^{212}\mathrm{Bi}$ and $^{208}\mathrm{Tl}$ respectively.(12) Insertion into (5) of the values for E_A $(0{\cdot}031 \pm 0{\cdot}008)$, E_B $(0{\cdot}97 \pm 0{\cdot}08)$, E_C $(1{\cdot}00)$, λ_A $(1{\cdot}08_6 \times 10^{-3}\,\mathrm{min}^{-1})$, λ_B $(1{\cdot}14_6 \times 10^{-2}\,\mathrm{min}^{-1})$ and λ_C $(0{\cdot}0223_6\,\mathrm{min}^{-1})$ gives

$$\begin{aligned} A_T^t = {} & \lambda_\mathrm{A}N_\mathrm{A}^0\{1{\cdot}12\exp(-\lambda_\mathrm{A}t) - 1{\cdot}10\exp(-\lambda_\mathrm{B}t) + 0{\cdot}019\exp(-\lambda_\mathrm{C}t)\} \\ & + \lambda_\mathrm{B}N_\mathrm{B}^0\{1{\cdot}00\exp(-\lambda_\mathrm{B}t) - 0{\cdot}379\exp(-\lambda_\mathrm{C}t)\} + 1{\cdot}00\lambda_\mathrm{C}N_\mathrm{C}^0\exp(-\lambda_\mathrm{C}t) \end{aligned} \tag{6}$$

The relative detection efficiencies were calculated from the absorption curves for the various β-particles emitted. The degree of absorption of each β-particle in the counter walls (35 mg cm^{-2} thickness) and the self-absorption losses in the liquid sample (mean thickness 170 mg cm^{-2}) were first determined. Using the known decay schemes(7) the relative detection efficiencies of the β-particle alone were found to be $E_\mathrm{A}^\beta : E_\mathrm{B}^\beta : E_\mathrm{C}^\beta = 0{\cdot}028 \pm 0{\cdot}007 : 1{\cdot}08 \pm 0{\cdot}05 : 1{\cdot}00$. Internal conversion electrons occur in about 38 % of the $^{212}\mathrm{Pb}$ decays, 24 % of the $^{212}\mathrm{Bi}$ decays and 5 % of the $^{208}\mathrm{Tl}$ decays. These contributions to the activities of each isotope were corrected for self and external

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(11) J. P. MAHER and D. F. EVANS, *Proc. Chem. Soc.* 208 (1961).

(12) D. L. BAULCH and J. F. DUNCAN, *Proc. R. Soc.* **A265**, 181 (1962).

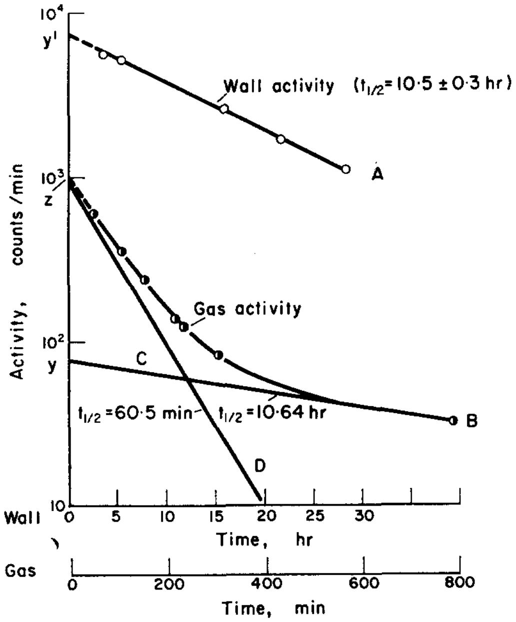

FIG. 3.—Decay curves for ^{212}Pb/^{212}Bi mixtures. A. Wall activity; B. Gas activity; C. 10·64-hr component of B; D. 60·5-min component of B.

(counter wall) absorption and, together with the contribution of the γ-rays to the measured activities, were added to activities due to the β-particles alone. The α-particles emitted are completely absorbed in the counter walls and hence can be ignored. The relative efficiencies of detecting the three isotopes under study in the counter used, when all radiations detected by the GM counter are considered, are respectively 0·031 ± 0·008:0·97 ± 0·08:1·00. The decay curves in Fig. 3 for the gas phase and residual wall activities after the ^{212}Pb–^{212}Bi was allowed to exchange with inactive lead tetramethyl for 7 hr 55 min are typical of those obtained for each run. Zero time for these plots was taken as the time when lead tetramethyl was condensed from the reaction vessel. The values of the various disintegration rates computed by standard methods from Fig. 3 are shown in Table 4.

The ratios of ^{212}Pb in the gas phase to that in the walls at the end of the exchange reactions in three cases were $\lambda_A(N_A^0)_G/\lambda_A(N_A^0)_W = 0{\cdot}014$, 0·010 and 0·121 respectively. The corresponding ratios for ^{212}Bi are more difficult to estimate, since ^{212}Bi

TABLE 4.—EXCHANGE OF ^{212}Pb AND ^{212}Bi WITH GASEOUS LEAD TETRAMETHYL

Duration of exchange	Wall activity y' (cpm)	Component gas activities y (cpm)	z (cpm)	$\lambda_A(N_A^0)_W$ (cpm)	$\lambda_A(N_A^0)_G$ (cpm)	$\lambda_B(N_B^0)_G$ (cpm)
5 hr	4090 ± 50	59·3 ± 8·6	548 ± 25	3680 ± 350	53·1 ± 21·4	606 ± 50
7 hr 55 min	7400 ± 80	76·4 ± 7·4	932 ± 35	6620 ± 680	68·3 ± 16·7	1007 ± 95
15 hr 55 min	1290 ± 20	156·0 ± 8·9	83 ± 6	1154 ± 140	139·7 ± 22·2	237 ± 30

From Equation (6) $y = 1{\cdot}12\lambda_A(N_A^0)_G$
$z = 1{\cdot}00\lambda_B(N_B^0)_G - 1{\cdot}10\lambda_A(N_A^0)_G$
$y' = 1{\cdot}12\lambda_A(N_A^0)_W$.

may enter the gas phase by three processes: (a) direct exchange with lead tetramethyl, (b) exchange of ^{212}Pb with lead tetramethyl, which then decays to give ^{212}Bi which remains in the gas phase, and (c) recoil from the surface of ^{212}Bi, which reacts with lead tetramethyl in the gas phase. The last process can be ignored, since BAULCH and DUNCAN(12) have shown that ^{212}Bi recoil from glass surfaces is negligible at temperatures below 80°C. The importance of process (b) is unknown. However, if it is assumed that ^{212}Bi formed in the gas phase in this manner is completely retained in a volatile form and is in transient equilibrium with the ^{212}Pb in the gas phase, then the measured ratio of $(^{212}\text{Bi})_{\text{gas}}/(^{212}\text{Bi})_{\text{wall}}$ will be a lower limit. Conversely, an upper limit for this ratio is obtained if it is assumed that none of the ^{212}Bi in the gas phase arises from process (b), i.e. that ^{212}Bi appears in the gas phase only by process (a).

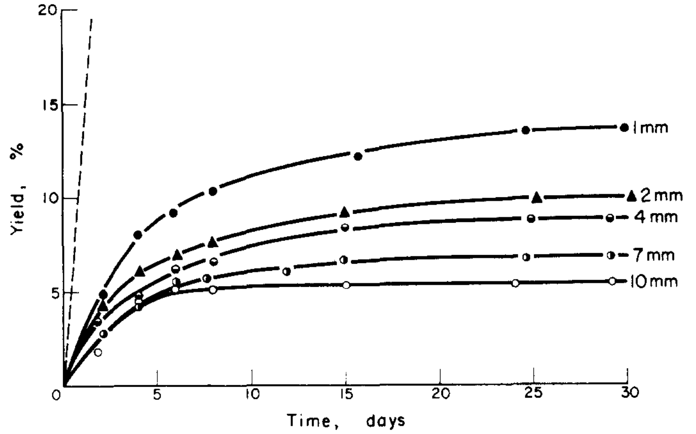

FIG. 4.—Yield of involatile ^{210}Bi deposited on vessel walls as a function of the time of the experiment at various pressures of lead tetramethyl; ● pressures were 1 mm; ▲ 2 mm; ⊖ 4 mm; ◑ 7 mm; ○ 10 mm. The dotted line indicates 100% deposited.

Since the ^{212}Pb/^{212}Bi mixture volatilized from the platinum spiral at 1200°C on to the glass walls is in transient equilibrium, the activity of the ^{212}Bi which enters the gas phase directly from the walls by exchange is: (a) $\lambda_B(N_B^0)_G - \dfrac{\lambda_B}{\lambda_B - \lambda_A} \cdot \lambda_A(N_A^0)_G$ when all the ^{212}Pb decaying in the gas phase gives a volatile ^{212}Bi species, and (b) $\lambda_B(N_B^0)_G$ when none of the ^{212}Pb decaying in the gas phase gives rise to volatile ^{212}Bi species. Hence, from these relationships and the data of Table 4, the lower limits for the ratio $(^{212}\text{Bi})_{\text{gas}}/(^{212}\text{Bi})_{\text{walls}}$ due to exchange alone were calculated to be 0·135, 0·127 and 0·065 respectively for the three experiments. The corresponding upper limits for this ratio are 0·149, 0·138 and 0·186.

Thus both ^{212}Pb and ^{212}Bi, when deposited on glass by a distillation technique, react with gaseous lead tetramethyl (at 10 mm, Hg pressure) and bismuth enters the gas phase at a much faster rate than does lead. Hence, before any correlation can be made between the yield of involatile ^{210}Bi and the pressure and decay process of ^{210}Pb(CH$_3$)$_4$, the observed yields must first be corrected for the effects of the heterogeneous exchange reaction.

Exchange of ^{210}Bi *with lead tetramethyl.* Figure 4 gives the yields of involatile ^{210}Bi deposited on the walls in the experiments in the pressure range 1–10 mm Hg as a function of the time the lead tetramethyl was in the reaction vessel. The yield Y of involatile ^{210}Bi deposited on the vessel walls, expressed as a percentage of the total ^{210}Bi activity, is given by

$$Y = a_e/a_T \times 100 \tag{7}$$

where a_e is the activity on the walls at the end of the experiment (t_e days duration), determined from the measured activity of the $BiPO_4$ sample containing the involatile ^{210}Bi deposited on the vessel walls, corrected for decay during sample preparation and for the chemical yield of $BiPO_4$; a_T is the total ^{210}Bi activity present (equal to the disintegration rate of lead tetramethyl in radiochemical equilibrium). The value of a_T was calculated from the pressure and temperature of the gas, the volume of the reaction vessel, and the specific activity of the admitted material.

In this work all activities are measured in terms of ^{210}Bi activity, since the low energy radiation from ^{210}Pb is not detected. Hence the activities are directly comparable after correcting for chemical losses and decay during source preparation.

If the yields of involatile ^{210}Bi deposited on the vessel walls were determined by decay-induced rupture alone, then this yield would be governed by the growth law

$$Y_R = F_R[1 - \exp(-\lambda_E t_e)] \tag{8}$$

where Y_R is the yield due to decay-induced rupture alone; F_R is the fraction of decays in which the initially-formed daughter species is ruptured giving free ^{210}Bi, all of which deposits on the walls, and $\lambda_E = 0{\cdot}1386$ day^{-1} is the decay constant of ^{210}Bi (*RaE*). Thus Y_R is not expected to reach a steady state until t_e is greater than 30 days. However, Fig. 4 shows that a steady value of Y_R is reached after approx. 7 days, 15 days, 20 days, 26 days and 30 days at 10, 7, 4, 2 and 1 mm Hg pressure respectively. This is believed to be due to reaction between the gaseous lead tetramethyl and the deposit of involatile ^{210}Bi, which results in the ^{210}Bi deposit being removed from the wall, thus competing with the decay-induced deposition process.

To determine the rate at which bismuth is deposited on the vessel walls the subsequent reactions of the initially-formed daughter species $^{210}Bi(CH_3)_4{}^{n+}$ must be considered. Since the molecules originally present contain only methyl groups, the probability of forming stable volatile bismuth species other than $Bi(CH_3)_3$ is unlikely. There are two general ways in which radio-bismuth may deposit on the walls. Ignoring the charge distribution for simplicity, their essential features are described by the following sequences of reactions:

(i) $$Bi(CH_3)_4(g) \rightarrow Bi(g) + 4CH_3(g) \tag{9a}$$

which might occur spontaneously, or after collision with other molecules. This reaction might be followed by either

$$Bi(g) + Pb(CH_3)_4 \rightarrow \cdot BiCH_3 + \cdot Pb(CH_3)_3 \xrightarrow[\text{steps}]{\text{several}} Bi(CH_3)_3 \tag{9b}$$

or $$Bi(g) \rightarrow Bi\ (walls) \tag{9c}$$

(ii) $$Bi(CH_3)_4(g) + Pb(CH_3)_4 \rightarrow Bi(CH_3)_3 + Pb(CH_3)_4 + \cdot CH_3 \tag{10a}$$

and $$Bi(CH_3)_4(g) \rightarrow Bi(CH_3)_4\ (walls) \rightarrow Bi\ (walls) + 4CH_3 \tag{10b}$$

When n is greater than or equal to 2, reaction (9a) is the most likely primary step.

The free bismuth thus produced in the gas phase could react with lead tetramethyl or deposit directly on the walls, so that two simultaneous reactions occur. The rate of deposition of bismuth via reaction (9c) will be first order with respect to the amount of bismuth in the gas phase. Reaction (9b) on the other hand will depend on the pressures of both lead tetramethyl and bismuth in the gas phase. However, since the bismuth pressure in the system is 10^{-11}–10^{-12} of that of the lead tetramethyl, reaction (9b) will be pseudo-unimolecular. Hence at constant pressure, the ratio of the rate constants of these two simultaneously-occurring reactions (9b and 9c) will be constant with time.

The rate of production of free bismuth from $^{210}Pb(CH_3)_4$ via $^{210}Bi(CH_3)_4$ [reaction (9a)] is given by the radioactive growth law

$$d[\mathrm{Bi}]_g/\mathrm{d}t = f[1 - \exp(-\lambda_E t_e)] \,.\, a_T \tag{11}$$

where f is the fraction of decays in which complete rupture of the daughter molecule-ion occurs to give free ^{210}Bi, and the amount of ^{210}Bi is expressed in counts/min. Since a constant fraction of the free bismuth activity will be deposited on the walls at constant pressure, then

$$(d[\mathrm{Bi}]_d/\mathrm{d}t)_P = f_d[1 - \exp(-\lambda_E t_e)] \,.\, a_T \tag{12a}$$

where $[\mathrm{Bi}]_d$ is the amount of bismuth deposited and $f_d(=f.f')$ is the fraction of decays which lead to bismuth being deposited on the vessel walls (f' is the fraction of free bismuth produced by reaction (9a) which deposits on the walls).

In the second sequence of reactions the bismuth tetramethyl ion reacts with lead tetramethyl {acting as a "second body" to remove excitation energy [reaction (10a)], or deposits directly on the walls [reaction (10b)]}. The former reaction is first order with respect to the bismuth tetramethyl ion and is also a pseudo-unimolecular reaction. The rate of deposition of bismuth on the walls via reaction (10b) is first order with respect to $[Bi(CH_3)_4{}^{n+}]$. This reaction will be insignificant at high pressures because the charged ion is unlikely to survive many collisions with lead tetramethyl molecules without charge transfer and disruption occurring. Using similar reasoning as for (12a), the rate of deposition of involatile ^{210}Bi on the walls is given by

$$(d[\mathrm{Bi}]_i/\mathrm{d}t)_P = f_i[1 - \exp(-\lambda_E t_e)] \,.\, a_T \tag{12b}$$

where $[\mathrm{Bi}]_i$ is the amount of bismuth deposited on the walls via Equation (10b) and f_i is the fraction of decays which result in bismuth being deposited by this method. The total rate of deposition of involatile ^{210}Bi on the vessel walls at constant pressure is thus

$$(d[\mathrm{Bi}]_w/\mathrm{d}t)_P = F[1 - \exp(-\lambda_E t_e)] \,.\, a_T \tag{13}$$

where $[\mathrm{Bi}]_w$ is the total amount of involatile ^{210}Bi deposited on the walls by both processes, and $F = f_d + f_i$.

There are two other processes which would prevent free bismuth produced by reaction (9a) from reaching the vessel walls. Firstly, bismuth atoms (or ions) formed by the break-up of the primary $\{Bi(CH_3)_4\}^{n+}$ ion may recombine with the methyl radicals produced before they have time to disperse. This "cage effect" type of reaction has been allowed for in the definition of f in Equation 11. Secondly, reaction may occur between free bismuth atoms and free methyl radicals in the system. However, both these species are in such low concentrations that this reaction would be insignificant. In any case the reaction would be first order with respect to bismuth and therefore contribute a constant (but insignificant) fraction of the overall reaction rate.

In order to determine F, the fraction of $^{210}Pb(CH_3)_4$ decays which result in ^{210}Bi being deposited on the walls, the effect of the subsequent surface reaction (Equation 1) must be eliminated. While this cannot be done experimentally, values of F may be obtained from the plots of Fig. 4 by the following method. Considering each pressure in turn, values of the yield Y of involatile ^{210}Bi were interpolated from the curves of Fig. 4 for various values of t_e. From the decay laws Y_T, the total yield of ^{210}Bi in all forms produced by the decay of $^{210}Pb(CH_3)_4$, was calculated for these values of t_e and from this the ratio R of involatile ^{210}Bi to volatile ^{210}Bi (produced by the decay) was calculated from

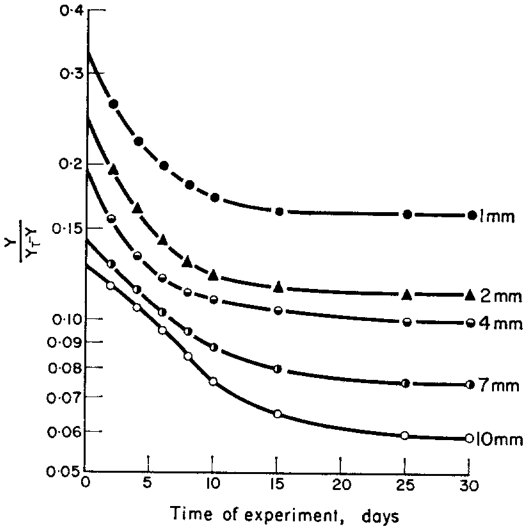

FIG. 5.—Plot of the ratio of ^{210}Bi deposited on the walls to that remaining in the gas phase, from the decay of $^{210}Pb(CH_3)_4$ as a function of the time of the experiment. Pressures were ● 1 mm; ▲ 2 mm; ⊖ 4 mm; ◑ 7 mm; ○ 10 mm.

$$R = Y/(Y_T - Y) \tag{14}$$

and plotted against t_e (Fig. 5). On extrapolating R to zero time the ratio R_0 so obtained can be used to calculate limiting values of F at the various pressures from the relation

$$F = R_0/(1 + R_0) \tag{15}$$

As $t_e \rightarrow 0$ the amount of ^{210}Bi on the walls $\rightarrow 0$; hence the surface exchange reaction is stopped by lack of one of the exchanging species (^{210}Bi) and $Y/Y_T \rightarrow F$. The extrapolated values of R_0 and corresponding values of F in the pressure range 1–10 mm Hg are given in Table 5. F is, in fact, the yield of involatile ^{210}Bi reaching the vessel walls, corrected for the subsequent surface exchange reaction. The results of experiments at lead tetramethyl pressures of 0·0168 and 0·124 mm Hg (Table 6) were analysed in a like manner, but for clarity these results are not plotted in Figs. 4 and 5. However, inspection of the values of $Y/(Y_T - Y)$ (Table 6) at these pressures shows that at the

TABLE 5.—FRACTION OF INVOLATILE ^{210}Bi DEPOSITED ON THE VESSEL WALLS AT VARIOUS PRESSURES

$Pb(CH_3)_4$ pressure (mm Hg)	10	7	4	2	1
R_0	0·127	0·145	0·197	0·248	0·331
F	0·113	0·127	0·165	0·199	0·249
σ_F	0·002	0·002	0·003	0·004	0·006

Errors in F, σ_F, were estimated graphically from the spread in the values of R_0, the errors in the plotted values of R being determined from the errors in the interpolated values of Y (after considering the errors in the experimentally determined values of Y).

lower pressure the ratio is constant, indicating that the surface exchange reaction between involatile ^{210}Bi on the vessel walls and gaseous lead tetramethyl is negligible under these conditons. At low pressures ($<5 \times 10^{-2}$ mm) the ratio of the measured value of Y to Y_T is identical with $F (= Y/Y_T)$ within experimental error. The values of F at 0·124 mm and $0{\cdot}016_8$ mm were 0·450 ± 0·011 and 0·790 ± 0·016 respectively.

TABLE 6.—RATIO R OF INVOLATILE ^{210}Bi TO VOLATILE ^{210}Bi

t_e (days)	Y	Y_T	$Y/(Y_T - Y)$
$Pb(CH_3)_4$ pressure $= 0{\cdot}12_4$ mm Hg			
4	0·176	0·426	0·705
6	0·226	0·565	0·667
8	0·260	0·670	0·634
10	0·284	0·750	0·610
15	0·324	0·875	0·588
$Pb(CH_3)_4$ pressure $= 0{\cdot}016_8$ mm Hg			
2	0·190	0·242	3·65
4	0·335	0·426	3·69
6	0·444	0·565	3·68
8	0·528	0·670	3·72
10	0·589	0·750	3·65
15	0·685	0·875	3·61

Nature of the exchange reaction. The exchange reaction between lead tetramethyl and involatile ^{210}Bi on the walls can be written

$$r\mathrm{Pb(CH_3)_4} + s\,{}^{210}\mathrm{Bi} \rightarrow \text{products} \tag{16}$$

where r and s are the numbers of lead tetramethyl molecules and involatile ^{210}Bi atoms respectively involved in the exchange and the products include ^{210}Bi in a volatile form. Since the surface concentration of ^{210}Bi on the walls is very small (only one atom per 3×10^{11} Å^2 of wall area, even in the case of the highest wall activity) it is unlikely that two ^{210}Bi atoms are sufficiently close to each other to react simultaneously with the same $Pb(CH_3)_4$ molecule, and hence it is reasonable to assume that $s = 1$ in Equation (16). The rate of reaction (16) (with $s = 1$) is given by

$$\text{Rate} = k[^{210}\mathrm{Bi}]_w\{p_{\mathrm{Pb(CH_3)_4}}\}^r \tag{17}$$

and can be measured by the rate of disappearance of ^{210}Bi from the walls. This becomes

$$\text{Rate of removal} = k'(a_T Y)\{p_{\text{Pb(CH}_3)_4}\}^r \tag{17a}$$

when $[^{210}\text{Bi}]_w$ is expressed in terms of the measured activity. On the other hand, the rate of deposition of ^{210}Bi on the walls is given by Equation 13, and at equilibrium these two rates must be equal, i.e.

$$F[1 - \exp(-\lambda_E t_e)]a_T = k' a_T Y_{\text{eq}}\{p_{\text{Pb(CH}_3)_4}\}^r \tag{18}$$

where Y_{eq} is the equilibrium value of the yield. Using $t_e = 30$ days, after which time $Y = Y_{30}$ and equilibrium is attained at the five pressures plotted in Fig. 4, we have

$$F = k' Y_{30}\{p_{\text{Pb(CH}_3)_4}\}^r \tag{18a}$$

Insertion of values of F, Y_{30}, and P into Equation (18a), and using all possible pairs of simultaneous equations, gives mean values of $r = 0{\cdot}111 \pm 0{\cdot}016$ and $k' = 1{\cdot}64 \pm 0{\cdot}12$. The low fractional power dependence of the rate on the lead tetramethyl pressure suggests that the surface exchange reaction takes place in the lead tetramethyl adsorbed on the vessel walls, since this is given by the Freundlich equation

$$[\text{Pb(CH}_3)_4]_w = A(p_{\text{Pb(CH}_3)_4})^{1/m} \tag{19}$$

where $[\text{Pb(CH}_3)_4]_w$ is the surface concentration of adsorbed lead tetramethyl, and A and m are constants ($m > 1$).

Hence if the exchange reaction is assumed to be

$$^{210}\text{Bi}_w + (\text{Pb(CH}_3)_4)_w \xrightarrow{k''} (^{210}\text{Bi(CH}_3)_3)_w + \text{Pb}_w + (\text{CH}_3)_w \tag{20a}$$

$$(^{210}\text{Bi(CH}_3)_3)_w \xrightarrow{\text{fast}} (^{210}\text{Bi(CH}_3)_3)_g \tag{20b}$$

the rate of Equation (20a) is given by

$$\text{Rate} = k''[^{210}\text{Bi}]_w[\text{Pb(CH}_3)_4]_w = k''A[^{210}\text{Bi}]_w(p_{\text{Pb(CH}_3)_4})^{1/m}$$

which agrees with the experimental results, with $m \simeq 9$ and $k''A = k'$.

While the experimental results do not enable anything more detailed to be said about the mechanism of this exchange reaction, they do give sufficient information to enable the observed yields of involatile ^{210}Bi on the vessel walls to be corrected for this exchange. We can now interpret the yields of involatile ^{210}Bi in terms of the initial nuclear event and the properties of the initial daughter species.

Nuclear decay of radio-lead tetramethyl

Dependence of the yield of involatile ^{210}Bi on the vessel walls on pressure. The number of collisions that the initial products of the decay undergo with lead tetramethyl before they reach the vessel walls varies with the lead tetramethyl pressure. Since these collisions cause deactivation of the decay products, a certain amount of reaction may result (as in Equations 9 and 10). Thus the retention of ^{210}Bi in the gas phase is expected to be greatest at the higher pressure. EDWARDS and CORYELL(2) report no significant variation in the yield of involatile ^{210}Bi with the pressure of lead tetramethyl in the range 4–40 mm Hg. However, (i) they made no allowance for the effects of the heterogeneous exchange reaction, (ii) they ignored the possibility of reaction between $^{210}\text{Bi(CH}_3)_3$ and oxygen absorbed on the vessel walls, despite the fact that their mean yield when lead tetramethyl containing both $^{210}Pb(CH_3)_4$ and $^{210}Bi(CH_3)_3$ was used was 11% (compared to a mean yield of 7·2% when freshly-prepared $^{210}Pb(CH_3)_4$ containing negligible $^{210}Bi(CH_3)_3$ was used), and (iii) they failed to achieve a quantitative recovery of their gaseous reaction products. Thus the conclusions of these workers cannot be accepted.

In the current work, F, the fraction of involatile ^{210}Bi deposited on the walls as obtained above is the yield corrected for the effects of the exchange reaction occurring on the vessel walls. These values of F are plotted in Fig. 6 as the points "corrected for exchange". At lower pressures the ratios of the observed yields to the theoretical total yields, Y_T, are plotted in Fig. 6 as "single determinations". This ratio is identical with F within experimental error (see above). Figure 6 shows that the amount of involatile ^{210}Bi reaching the vessel walls depends markedly on the pressure of lead tetramethyl and increases, as expected, with decreasing pressure, i.e. decreasing number of collisions in the gas phase between the ^{210}Bi species and lead tetramethyl. At lower pressures the collision of the ^{210}Bi species with the walls becomes more important than their collision with lead tetramethyl in the gas phase, since for the reaction vessels used the ratio Total wall collisions/Total gas collisions for each ^{210}Bi species $\sim 10^{-1}/P$. Thus below 10^{-2} mm collision of ^{210}Bi species with the walls predominate, and below 10^{-3} mm the measured yields of involatile ^{210}Bi would be essentially free of the effects of concurrent gas phase reactions. Unfortunately the specific activity of $^{210}Pb(CH_3)_4$ used prevented any meaningful results being obtained at pressures below 3×10^{-3} mm Hg. Nevertheless, the results indicate that, within experimental error ($\sim$7%), the yield of involatile ^{210}Bi at very low pressures is 100%.

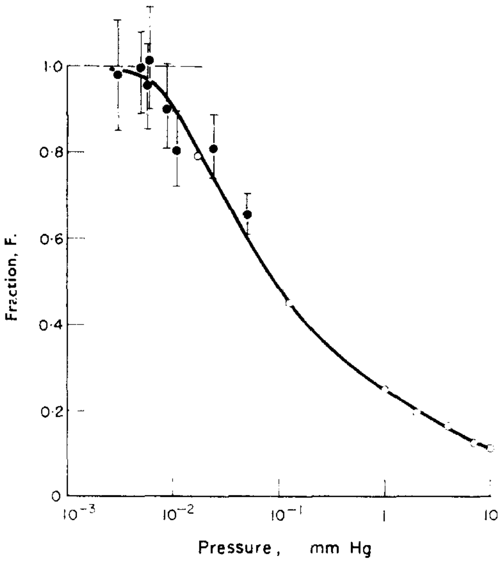

FIG. 6.—Fraction of ^{210}Bi deposited on the vessel walls as a function of the $Pb(CH_3)_4$ pressure; ○ corrected for exchange; ● single determination with maximum experimental error indicated by bar.

Correlation of results with the nuclear decay energetics. The nuclear decay scheme of ^{210}Pb is shown in Fig. 7.(7) The frequencies of the 0·017 MeV and 0·064 MeV

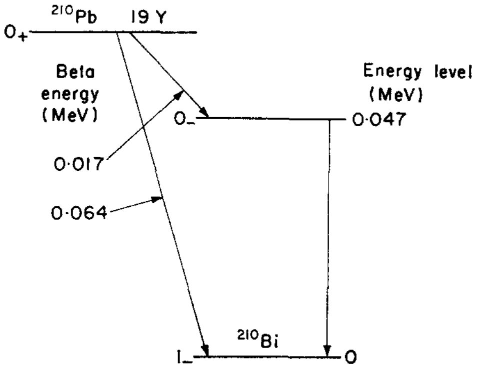

FIG. 7.—Nuclear decay scheme of ^{210}Pb.

transitions are quoted as 85 ± 3% and 15 ± 3%, respectively.(7,13) The 0·047 MeV γ-ray associated with the 0·017 MeV β-particle is internally converted, mainly in the L shell and to a lesser extent in the M shell, in all but 3–4%(13,14) of the transitions giving rise to this γ-ray, i.e. in ~82% of the decays extranuclear electrons are ejected by internal conversion processes giving multi-charged ions. In addition to internal conversion, appreciable electronic excitation and ionization due to the sudden change in the nuclear charge is expected. Unfortunately, both theoretical and experimental studies of the ionization probability of orbital electrons in the decay of heavy isotopes has been confined to the K, L and M shells, and no information about the probabilities of ionization of the outer shells is available. The probability of ionization of an orbital electron, P_{ion}, for the atomic case is $P_{\text{ion}} = k/(Z_{\text{eff}})^2$. An estimate of the total ionization probability for all the orbital electrons of the daughter bismuth atoms can be made, using (a) the values of k given by SCHWARTZ(15) or GREEN(16) for the inner electrons, (b) SLATER's relationships(17) for Z_{eff}, and (c) the known trends in k for the inner electrons, to estimate k for the outer electrons. This leads to a total ionization probability of 0·4 ± 0·2 for the atomic case, which can only be regarded as approximate for the molecular case (probably an upper limit). Nevertheless, we may conclude from this estimation that of the 18% of decays of ^{210}Pb which lead to $(^{210}\text{Bi})^+$ a fraction of the order of 0·4 will be further ionized by excitation processes. Hence only ~11% of the decays will lead to singly-charged ions.

Extrapolating to the molecular case we expect about 10% of the decays to lead to $\{^{210}\text{Bi(CH}_3)_4\}^{n+}$ with $n = 1$. In all other cases, internal conversion, excitation ionization and Auger processes will produce multi-charged ions which will be completely disrupted because of the shortage of electrons in the bonding orbitals.

While the experimental results indicate that at low pressures complete (100%) conversion of the decay products to involatile ^{210}Bi occurs, they do not show whether the $\{^{210}\text{Bi(CH}_3)_4\}^+$ ion produced initially in 10% of the decays ruptures immediately

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(13) W. STANNERS and M. A. S. ROSS, *Proc. Phys. Soc.* **69A**, 836 (1956); C. S. WU, F. BOEHM and E. NAGEL, *Phys. Rev.* **91**, 319 (1953).

(14) R. W. FINK, *Phys. Rev.* **106**, 266 (1957).

(15) H. M. SCHWARTZ, *J. chem. Phys.* **21**, 45 (1953).

(16) A. E. S. GREEN, *Phys. Rev.* **107**, 1646 (1957).

(17) J. C. SLATER, *Phys. Rev.* **36**, 57 (1930).

to produce ^{210}Bi (atoms or ions), or is stable while isolated and only undergoes fragmentation on collision with other molecules or with the vessel walls. Possible paths by which an *isolated* $^{210}Bi(CH_3)_4^+$ ion can lead to involatile ^{210}Bi on the vessel walls are

$$Bi(CH_3)_4^+ \rightarrow Bi(CH_3)_3^+ + \cdot CH_3; \tag{21a}$$

followed by

$$Bi(CH_3)_3^+ \rightarrow Bi + 2CH_3 + CH_3^+; \quad Bi \rightarrow Bi_w \tag{21b}$$

or

$$Bi(CH_3)_3^+ \rightarrow Bi^+ + 3 \cdot CH_3; \quad Bi^+ \rightarrow Bi_w \tag{21c}$$

and

$$Bi(CH_3)_4^+ \rightarrow CH_3^+ + Bi(CH_3)_3 \rightarrow \{Bi(CH_3)_3\}_w \rightarrow Bi_w \tag{21d}$$

$$Bi(CH_3)_4^+ \rightarrow \{Bi(CH_3)_4^+)_w \rightarrow Bi_w \tag{21e}$$

All species are in the gas phase and isolated unless indicated as being on the vessel walls by the subscript *w*. Equations (21b), (c) and (d) are equivalent except for charge distribution.

By comparison, the rupture of $\{Pb(CH_3)_4\}^+$ ⁽¹⁸⁾ gives principally $\{Pb(CH_3)_3\}^+$ (31 %), $PbCH_3^+$ (28 %), Pb^+ (22 %), $\{Pb(CH_3)_2\}^+$ (8 %) and CH_3^+ (4 %), so that one might expect that the fragmentation of $\{Bi(CH_3)_4\}^+$ to give $Bi(CH_3)_3 + CH_3^+$ would be insignificant. Experimental evidence that ^{210}Bi is not deposited as a result of bismuth trimethyl reacting with the walls is confirmed by studies at high pressures. Preliminary experiments (see experimental section) showed that careful preparation of the reaction vessels eliminated the initial rapid build-up of ^{210}Bi on the walls attributed to reaction of $^{210}Bi(CH_3)_3$ with traces of oxygen, and also the addition of inactive bismuth trimethyl to the system at higher pressures did not significantly affect the yield of involatile ^{210}Bi (see Table 7). Since the dilution of the decay-produced $^{210}Bi(CH_3)_3$ by the inactive carrier would be $\sim 10^{10}$, no involatile ^{210}Bi would be detected on the vessel walls if Equation (21d) were significant. Hence mechanism (21d) is unimportant in the production of involatile bismuth from the singly-charged $Bi(CH_3)_4^+$ ion at the gas pressures studied (4–10 mm). At low pressures, where we are dealing with an isolated $Bi(CH_3)_4^+$ ion, these results indicate that fragmentation of this ion via mechanism (21d) to produce bismuth trimethyl in its ground state is also unimportant, since the yield of involatile ^{210}Bi is 100 %.

It is now important to determine whether or not the yield of involatile bismuth at low pressures does in fact approach 100 % and not some other figure, say 95 %, the difference being masked by experimental error. If the thermodynamic properties of the daughter ion produced by the decay are the dominant features of this system, then the same result (i.e. 100 % yield at low pressure) should be obtained using a lead isotope decaying in a different way.

The β-decay of $^{212}Pb(CH_3)_4$. The decay scheme of ^{212}Pb is given in Fig. 8.⁽⁷⁾ The 0·350 MeV and 0·579 MeV β-particles have emission frequencies of $\sim$84 % and $\sim$12 % respectively. Lower energy transitions make up the remainder (4 %). The three principal γ-rays, 0·300 MeV (5 %), 0·239 MeV (84 %) and 0·115 MeV (3 %), have internal conversion coefficients of 0·22, 0·5 and 9·9 respectively.⁽¹⁹⁾ Thus 44 %

⁽¹⁸⁾ V. H. Dibeler, *J. Research N.B.S.* **49**, 235 (1952).

⁽¹⁹⁾ D. G. E. Martin and H. O. W. Richardson, *Proc. Phys. Soc.* **63A**, 223 (1950).

TABLE 7.—YIELD OF INVOLATILE ^{210}Bi IN THE PRESENCE OF INACTIVE Bi(CH$_3$)$_3$

Pb(CH$_3$)$_4$ pressure (mm Hg)	Bi(CH$_3$)$_3$ pressure (mm Hg)	Time of experiment (days)	Yield of ^{210}Bi (%)*	Yield of ^{210}Bi (%)† No carrier present
9·0	1·0	0·22$_2$	0·48 ± 0·04	0·35 ± 0·05‡
9·0	1·2	0·74$_7$	1·65 ± 0·06	1·05 ± 0·05‡
8·9	1·0	2·81	3·11 ± 0·11	3·3 ± 0·1‡
9·0	1·0	5·76	5·06 ± 0·12	5·0 ± 0·1‡
9·0	1·0	9·70	5·22 ± 0·14	5·3 ± 0·1‡
8·9	1·0	13·81	5·68 ± 0·15	5·35 ± 0·18‡
9·0	1·0	18·69	5·54 ± 0·15	5·4 ± 0·1‡
9·0	1·0	21·93	5·13 ± 0·14	5·45 ± 0·1‡
4·8$_6$	0·5$_4$	13·90	7·56 ± 0·38	8·1 ± 0·2§
4·5$_0$	0·5$_0$	6·21	5·57 ± 0·20	6·1 ± 0·1§
4·1$_4$	0·4$_6$	11·03	6·53 ± 0·22	7·7 ± 0·2§

* Errors calculated from standard deviations of counting rates.
† Errors estimated from errors in results used to plot Fig. 4.
‡ Interpolated from Fig. 4, 10 mm Hg curve.
§ Interpolated from Fig. 4, 4 mm Hg curve.

of the transitions lead to multi-charged ions as a result of internal conversion processes. Of the remaining 56% of decays, a fraction, 0·4 ± 0·2, will form multi-charged ions due to excitation effects, and hence the singly-charged ion is expected to be formed in ~34% of decays. In addition to the effect of the multiple charge, some bond rupture may be caused by recoil effects. (The maximum recoil energy of ^{212}Bi due to the decay is 2·38 eV, or 55 kcal/mole.) Using the recoil spectra calculated for this decay by BAULCH and DUNCAN,(12) and assuming that all the recoil energy is available for the rupture of one bond, only $(15/(212 + 15) \times 55) = 3{\cdot}6$ kcal/mole (see Refs. (12) and (20)) is available for bond rupture. Since the Bi—CH$_3$ bond energy is 31 kcal/mole,(21) bond rupture from this cause can be ignored.

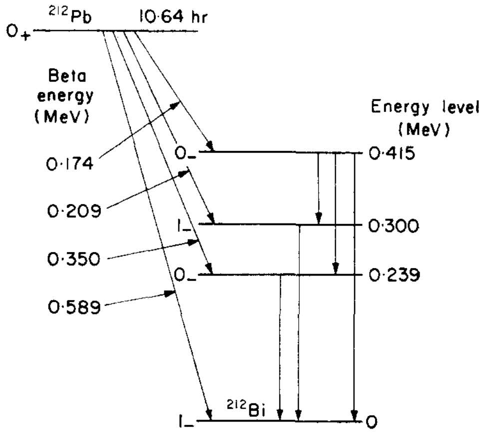

FIG. 8.—Nuclear decay scheme of ^{212}Pb.

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(20) D. L. BAULCH and J. F. DUNCAN, *Q. Rev. chem. Soc.* **12,** 133 (1958).

(21) T. L. COTTRELL, *The Strengths of Chemical Bonds* (2nd Edn.). Butterworths, London (1958).

If some of the $Bi(CH_3)_4^+$ ions lead to volatile bismuth trimethyl [Equation 21(d)] and do not give involatile bismuth in all cases, then the yield of involatile bismuth at low pressures should be appreciably less in the case of the $^{212}Pb(CH_3)_4$ decay than for the $^{210}Pb(CH_3)_4$ decay. The results of the study of the decay of $^{212}Pb(CH_3)_4$ are given in Table 8. Despite the large experimental error, these results show that the yield of involatile bismuth deposited on the walls is independent of the nature of the decay and approaches 100% at low pressures. Hence we conclude that at low pressures, where an isolated $Bi(CH_3)_4^+$ ion is involved, the simple ejection of a methyl ion [Equation 21(d)] from the primary ion to give $Bi(CH_3)_3$ in its ground state does not occur to any measurable extent. However, at higher pressures, where the initial ion undergoes many collisions with the surrounding molecules before reaching the vessel walls, the production of bismuth trimethyl in the gas phase becomes the dominant process, since the yields of involatile bismuth are low (Fig. 6), even after correction for the surface exchange reaction. The collision of $Bi(CH_3)_4^+$ with lead tetramethyl must therefore lead to charge exchange reactions, methyl ions or radicals being produced from the initial ion together with bismuth trimethyl. The formation of involatile bismuth probably results from rupture of the multi-charged ions, the bismuth atoms being too energetic to react with the lead tetramethyl to produce $Bi(CH_3)_3$. Thus at high pressures reactions such as (9a), (9b), (9c) and (10a) must be invoked to describe the dominant reactions occurring, since it is highly unlikely that $Bi(CH_3)_4^+$ would survive sufficient collisions in the gas phase to cause deposition of involatile bismuth on the walls.

TABLE 8.—β-DECAY OF $^{212}Pb(CH_3)_4$

$Pb(CH_3)_4$ pressure (mm Hg)	t_e (min)	Y_{obs} (%)	Y_0 (%)	$F = \frac{Y_{obs}}{Y_0}$	Mean F for each pressure	F for $^{210}Pb(CH_3)_4$*
0·0035	35	35·1 ± 17·9	33·0	1·06 ± 0·54	0·99 ± 0·18	0·99
0·0035	64	49·8 ± 18·8	52·0	0·96 ± 0·36		
0·0035	120	63·4 ± 20·9	74·7	0·85 ± 0·28		
0·0035	180	97·4 ± 28·4	87·3	1·11 ± 0·32		
0·0130	30	23·7 ± 20·1	29·1	0·82 ± 0·69	0·89 ± 0·22	0·84
0·0130	61	52·8 ± 22·7	50·3	1·05 ± 0·45		
0·0130	120	53·4 ± 24·1	74·7	0·71 ± 0·32		
0·0130	180	84·9 ± 27·7	87·3	0·97 ± 0·32		
0·0224	210	59·7 ± 23·5	91·0	0·66 ± 0·26	0·70 ± 0·18	0·75
0·0224	247	69·8 ± 23·5	94·1	0·74 ± 0·25		
0·0501	79	46·3 ± 12·6	59·6	0·78 ± 0·21	0·67 ± 0·14	0·60
0·0501	107	39·2 ± 12·5	70·7	0·56 ± 0·18		

* Interpolated from Fig. 5.

CONCLUSION

From this experimental study we conclude that an isolated $Bi(CH_3)_4^+$ ion formed by decay from $Pb(CH_3)_4$ immediately disproportionates to give $Bi(CH_3)_3^+$. Since radioactive decay is normally complete in 10^{-12} sec, the period of a typical molecular vibration, the product $Bi(CH_3)_4^+$ is expected to be formed with the same stereochemical arrangement as its parent, i.e. with the methyl radicals tetrahedrally arranged about the metal atom, and with the metal–carbon distances the same as in the lead tetramethyl. Indeed, the one feature which seems to be indisputable in this method of making the reactive species is its initial stereochemical arrangement. There are, of course, a variety of ways in which the $Bi(CH_3)_4^+$ might subsequently be found, which would very likely cause reaction to occur in different ways. But since the Pb–C distance in the parent is not likely to be very different from the Bi–C distance in a $Bi(CH_3)_4^+$ ion in the lowest energy state in which a tetrahedral structure is maintained, it is a reasonable inference that the observed properties of the synthesized species will be similar to those of $Bi(CH_3)_4^+$ of similar structure formed in other different ways. This work can therefore be used to predict chemical reactions of a different type, depending on the view taken of the structure of $Bi(CH_3)_4^+$. There are two possible ways in which these results might be interpreted.

(a) If $Bi(CH_3)_4^+$ were regarded as a synthesized derivative of pentavalent bismuth, then a tetrahedral symmetry would be most stable. One might then conclude that Bi^V in this form is unstable and is spontaneously reduced to Bi^{IV},

$$Bi^V(CH_3)_4^+ \rightarrow Bi^{IV}(CH_3)_3^+ + \cdot CH_3$$

(b) Perhaps a more satisfactory way of regarding the species $Bi(CH_3)_4^+$ is as a transition state in a chemical reaction. Such a species has the stereochemistry and charge expected for isotopic exchange reactions of the following types, where the asterisk refers to the isotopic species:

$$Bi(CH_3)_3 + {}^*CH_3^+ \rightleftharpoons [Bi(CH_3)_3({}^*CH_3)]^+ \rightleftharpoons Bi(CH_3)_2({}^*CH_3) + CH_3^+ \qquad (22a)$$

$$Bi(CH_3)_3^+ + {}^*CH_3 \rightleftharpoons [Bi(CH_3)_3({}^*CH_3)]^+ \rightleftharpoons [Bi(CH_3)_2({}^*CH_3)]^+ + CH_3 \qquad (22b)$$

This work shows that reaction (22a) is impossible since $Bi(CH_3)_4^+$ cannot be a transition state for this reaction. It could, however, be one for reaction (22b).

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