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By J. B. Stuart 8-20-79

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Chemistry-Transuranic Elements

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Special Review of Declassified Reports
Authorized by USDOE JK Bratton
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CHEMISTRY DIVISION

QUARTERLY REPORT

March, April and May, 1949

Berkeley, California

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I QUARTERLY PROGRESS REPORT. PROJECT 48

A. Chemistry of the Rare Earths and Actinide Elements

I. Perlman, B. B. Cunningham and Co-workers

The Heat of Solution of AmO_2 and the Estimation of the Formal Potential for the Am^{+3}-Am^{+4} + e^- Couple

LeRoy Eyring and B. B. Cunningham

Progress reports on the general problem of estimating the aqueous oxidation potentials of the Am^{+3}-Am^{+4}, and Pr^{+3}-Pr^{+4} couples have appeared in UCRL-327 and UCRL-311.

Measurements have since been made of the heats of solution of AmO_2 and PrO_2 in 6.0 M HNO_3 - 0.1 M HBF_4 at 25° C. The measurements were made in the same calorimeter as described previously. The technique employed differed slightly in that the glass sample bulb was replaced by one made of polymono-chloro-trifluoro ethylene (fluorethene) which was resistant to the acid solution containing fluoride ion.

The type of bulb employed is shown in diagrammatic form in Figure 1.

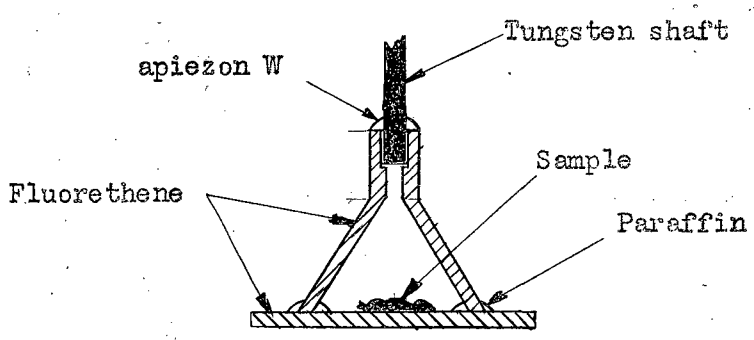

Figure 1. Plastic Calorimeter Bulb

The results obtained on AmO_2 are listed in Table I.

Table I

Heat of Solution of AmO_2 in 6.0 M HNO_3, 0.1 M HBF_4

Run No.	Wt. of Sample (mg)	Calories	Heat of Solution per mole (kcals)
1	0.834	0.09062	-29.7
2	0.672	0.07466	-30.3
3	1.177	0.1326	-30.8
4	1.449	0.1636	-30.8
			-30.4 ± 0.4

From the results of these experiments plus thermodynamic data available for the other actinide oxides, it is possible to estimate the free energy change and hence the oxidation potential for the reaction

$$Am^{+3} + H^{+} \longrightarrow Am^{+4} + 1/2\ H_2.$$

The estimation yields -2.6 ± 0.2 v for the potential. It is to be noted that the reaction written assumes that there is no appreciable hydrolysis of the ions in the acid concentration used in the calorimetric runs. The assumption appears to be reasonable in view of the known hydrolytic behavior of Pu^{+4}.

The stability constant of the fluoride complex of Am^{+3} is not known, but it is believed that at the very low fluoride ion concentration existing in the acid fluoborate solution only a negligible fraction of the Am^{+3} would exist as a fluoride complex ion. This assumption may not be valid, however. The heat of mixing of Am^{+3} in 6.0 M HNO_3 - 0.1 M HBF_4 will be measured, to check this possible correction to the data obtained.

Composition and Thermal Decomposition of "Americium Dioxide"

L. B. Asprey and B. B. Cunningham

The composition of "americium dioxide" at a known temperature and pressure of oxygen was determined by adding a known amount of O_2 to a sample of Am_2O_3 and measuring the oxygen uptake. Americium sesquioxide was prepared by hydrogen reduction of the higher oxide at 700° C. The quantity of oxygen absorbed by the sesquioxide at 300° C and 50 mm O_2 pressure corresponded to a final composition of $AmO_{1.98 \pm 0.02}$.

This work is reported fully in UCRL-329.

The thermal decomposition of AmO_2 was investigated by the same type of apparatus as that used for Pr_6O_{11} (see UCRL-264).

Because of the greater stability of AmO_2 the decomposition could be carried out only to $AmO_{1.85}$.

An average ΔH value for the decomposition

$$13.3\ AmO_2 \longrightarrow 13.3\ AmO_{1.85} + O_2$$

was computed from the log p vs $\frac{1}{T}$ curves obtained. The value obtained was 21 ± 3 kcals. This is substantially different from the average ΔH value of 49 kcals estimated from Eyring's heat of solution data for the reaction

$$4\ AmO_2 \longrightarrow 2\ Am_2O_3 + O_2$$

The results suggest that as in the case of the decomposition

$$Pr_6O_{11} \longrightarrow 3\ Pr_2O_3 + O_2$$

the principal contribution to the heat for the overall reaction occurs after the decomposition has proceeded to a considerable extent. (see UCRL - 329).

Lanthanum Trichloride - Lanthanum Oxychloride Equilibrium

A. Broido and B. B. Cunningham

The equilibrium constant for the reaction

$$LaCl_3 + H_2O \longrightarrow LaOCl + 2\ HCl$$

has been redetermined, using the apparatus and techniques described previously. (Quarterly report UCRL-311). The remeasured value of K_{500^oC} is 0.95 - 1.3. This is in good agreement with the value 1.0 ± 0.2 reported previously.

Heat of Solution of PrO_2 and Estimation of the Formal Potential for the $Pr^{+3}=Pr^{+4} + e^-$ Couple

LeRoy Eyring and B. B. Cunningham

Heats of solution of samples of PrO_2 (prepared by heating Pr_6O_{11} in 100 atms. of O_2 to 500°C) were measured, using apparatus and techniques similar to that described for AmO_2 (see section on americium, this report). The solvent used was 6.0 M HNO_3 - 0.1 M $NaBF_4$.

The results of the measurements are tabulated in Table I.

Table I

Heat of Solution of PrO_2 in 6.0 M HNO_3, 0.1 M $NaBF_4$ at 25° C

Run No.	Weight (mg)	Heat evolved calories	$-\Delta H$ kcal/mol
1	0.827	0.2002	41.9
2	1.430	0.3471	42.0
3	1.229	0.3031	42.7
4	1.177	0.2818	41.4
			42.0 ± 0.4

From these results and other thermodynamic data estimates of the free energies of formation of Pr^{+4} and Pr^{+3} have been made.

The free energy of the reaction

$$Pr^{+3} + H^+ \longrightarrow Pr^{+4} + 1/2\ H_2$$

has been estimated to correspond to an aqueous oxidation potential of -3.1 ± 0.2 v.

The Thermal Decomposition of Pr_6O_{11}

L. B. Asprey and B. B. Cunningham

Curves representing the log p versus $\frac{1}{T}$ relationship for the thermal decomposition of Pr_6O_{11} to Pr_2O_3 have been obtained as described previously (UCRL-311).

A ΔH value was computed for the overall reaction on the assumption that the pressures measured represented equilibrium values. A value of 47 ± 5 kcals was obtained (Decomposition temperature range 400° - 1200° C). The ΔH value is to be compared with that of 48 kcals obtained by calculation from the heats of solution of Pr_6O_{11} and Pr_2O_3 listed in Bichowski and Rossini . It would appear that over much of the decomposition range equilibrium pressures were actually measured.

Preparation of Pure Praseodymium Metal

Winifred Heppler, LeRoy Eyring and B. B. Cunningham

As mentioned in UCRL-311 attempts to prepare pure Pr metal on the milligram scale were only moderately successful, in that small amounts of the reductant and crucible material were found to be present in the metal. Crucibles moulded from 200 mesh BeO were used for these earlier runs, and barium metal was used as reductant.

Subsequent experiments using fused BeO, MgO crystals, powdered and moulded ThO, and TaC as refractory materials have been made. Lithium was used as reductant in most cases.

Results are summarized in Table I. The spectrographic analysis by John G. Conway are reported in μg of impurity per 50 μg of Pr metal.

Table I

Analysis of samples of Pr metal prepared in various ways.

Run	Reductant	Crucible Material	Impurities Present					
			Ba	Be	Li	Mg	Ta	Th
1	Li	fused BeO		.01	0.1			
6	Ba	" "	1.0	0.8				
10	Li	MgO		.01	Nd < .5	1.0		1.0
12	Li	MgO		.06	Nd < .5	6.0		
11	Li	ThO		.03	Nd < .5	<.01		
14	Li	ThO		.04	Nd < .5	0.2		2.0
15		fused BeO		.04		0.2		.1
16		" "		.8		.04		
17		" "		.8		.04		
18		TaC		.05			Nd < .5	
19		TaC		.06			Nd < .5	

Nd = not detected

The presence of Be, Mg and Th in some samples prepared in the apparent absence of these elements is difficult to explain. Analysis of the crucible material, reductant and rare earth fluoride failed to reveal their presence in any of the starting materials.

Lithium impurities in the early runs were eliminated by prolonged heating to insure their complete volatilization.

Magnetic Susceptibility of Apparent Reduction Products of NdF_3, SmF_3 and EuF_3

James C. Wallman and B. B. Cunningham

Magnetic susceptibility measurements on the products resulting from treatment of various rare earth trifluorides with Na vapor at 1125° C have been continued. (see UCRL-311).

Some results are summarized in Table I.

Table I

Magnetic susceptibilities of rare earth trifluorides and reduction products.

Material	χ (observed (1)
NdF_3 (taken as standard)	26
NdF_3 redn. product	18
SmF_3	3
SmF_3 redn. product	14
EuF_3	19
EuF_3 redn. product	141
GdF_3	126

(1) in units of 10^{-6} ergs.

Except for SmF_3 (which has a very low susceptibility) the observed susceptibility of the trifluorides are in fair agreement with results reported previously in the literature.

Measurements on the reduction products are consistent with partial or complete reduction to a lower oxidation state.

Experiments are now in progress to obtain accurate chemical analyses of the reduction products.

Anion Exchange Separation of Zirconium and Hafnium

E. H. Huffman and R. C. Lilly

A separation of zirconium and hafnium by the anion exchange resin Amberlite IR-400 has been demonstrated. A quantity of 2.5 mg. each of zirconium and hafnium containing the tracers Zr^{95} and Hf^{191} were converted to fluo-ions by the addition of somewhat over six times the molar quantity of hydrofluoric acid. The adsorption of these negative ions on a little over twenty times as much resin, by weight, as of combined zirconium and hafnium was 98 percent. This portion of resin was then slurried onto the top of a column of 60-80 mesh resin contained in a tygon tube with lucite fittings. The bed of resin was 18.5 cm. long and 1.0 cm. in diameter.

Elution of the zirconium and hafnium was carried out with a solution of 0.2 M hydrochloric acid and 0.01 M hydrofluoric acid. Earlier work had already shown the possibility of colloid formation and sticking to the resin if fluoride was not present when dilute acid solutions alone were used. The flow rate was about 4.5 ml. per hour.

The results shown in the curve, Figure 1, are based on the tracer count of the eluate, with supplementary spectrographic and gravimetric data.

Spectrographic analysis showed no detectable hafnium up to point A and no detectable zirconium beyond point B and also corroborated the form of the rest of the curve. About 80 percent of the zirconium is contained in the eluate to point A and a similar proportion of hafnium beyond point B.

It is interesting to note that the order of elution of the elements is the reverse of that reported by a cation-exchange separation.(1)

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(1) Street, K., Jr., and Seaborg, G. T., J. Am. Chem. Soc. 70, 4286 (1948).

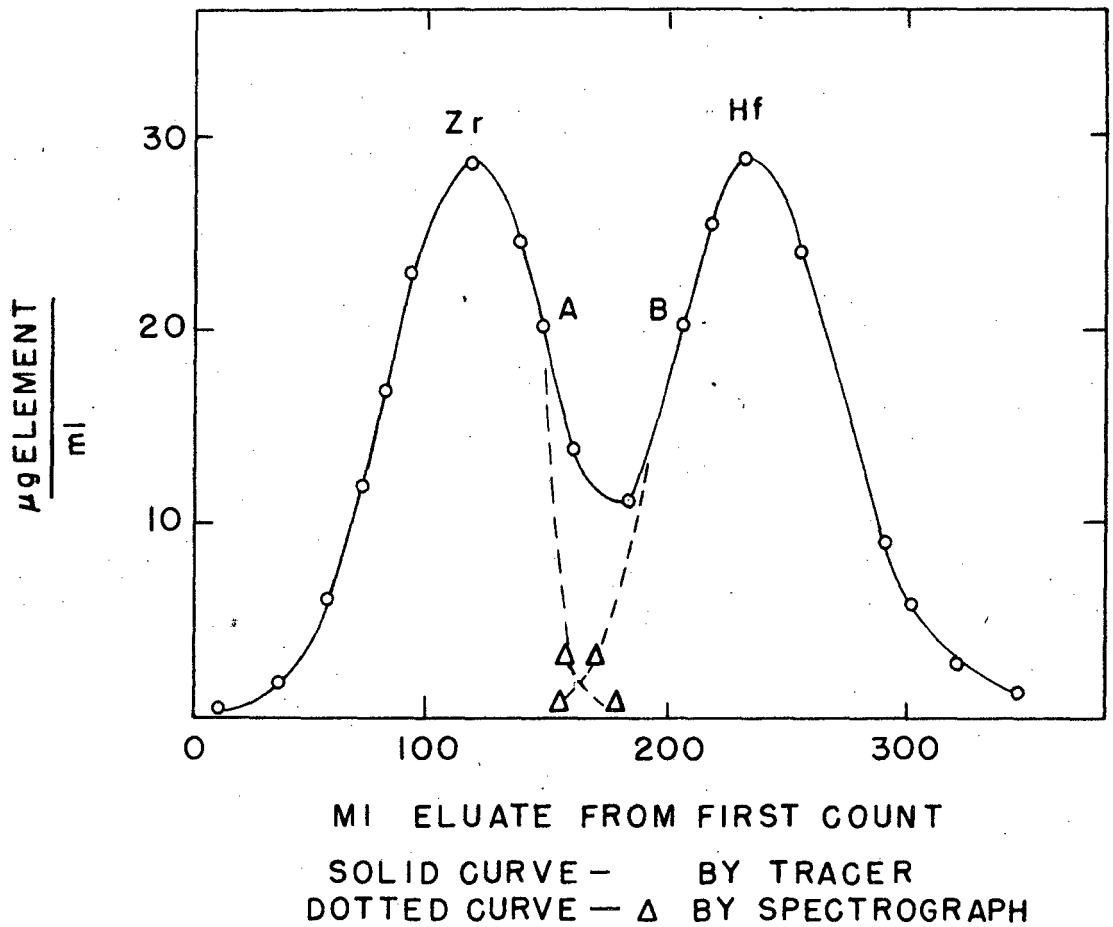

Zr
Hf
A
B
30
20
10
0
100
200
300
μg ELEMENT / ml
MI ELUATE FROM FIRST COUNT
SOLID CURVE — BY TRACER
DOTTED CURVE — Δ BY SPECTROGRAPH

FIG. 1

Solubility and Extraction of Zirconium Thenoyltrifluoroacetonate

E. H. Huffman and G. M. Iddings

This work has been done in accordance with a decision made at the Oak Ridge conference in Dec., 1948, on the separation of zirconium and hafnium by chelation-extraction. The solubilities have been determined for ZrT_4 in benzene at three different temperatures and in benzene solutions of TTA at 20° C, both anhydrous and saturated with water.

Solubility of ZrT_4 in Anhydrous Benzene

Temp.	mg ZrO_2 per 5 ml
20° C	10.7 ± 0.2
30°	15.8 ± 0.4
40°	23.5 ± 0.2

Solubility of ZrT_4 in Anhydrous Benzene-TTA at 20° C.

TTA Conc.	mg ZrO_2 per 5 ml
0.0	10.7 ± 0.2
0.01 M	10.7 ± 0.3
0.02	10.7 ± 0.3
0.04	10.6 ± 0.3
0.08	10.9 ± 0.1

Solubility of ZrT_4 in Water-saturated Benzene and Benzene-TTA at 20° C.

TTA Conc.	mg ZrO_2 per 5 ml
0.0	11.2 ± 0.1
0.06 M	10.9 ± 0.3

The solubility of the chelate is seen to increase about 50 percent for each 10° C. rise in temperature. The amount of zirconium dissolved as ZrT_4 is independent of the concentration of the TTA in benzene. This is in contrast to the distribution ratio dependence on the TTA concentration when zirconium is extracted from 2 M perchloric acid.(1) Some preliminary extractions from a 0.086 M zirconium solution in 5 M perchloric acid show distribution ratios as high as 161. This means that the zirconium concentration in the benzene phase is essentially 0.086 M at this ratio, a value approximately five times as high as those shown above, where it is about 0.018 M. The zirconium species in the benzene is evidently not the simple ZrT_4 when it is extracted from perchloric acid.

The hydrate of TTA itself is soluble in benzene and is not readily formed again after it has been dehydrated.(2) If a hydrated species accounts for the greater solubility of ZrT_4 on extraction than on dissolving the anhydrous chelate it also must not be readily formed from the simple ZrT_4. This is shown above by the fact that the same solubility is obtained when water is present as when anhydrous benzene is used.

(1) Huffman, E.H., and Beaufait, L.J., AECD-2387 (UCRL-194) Oct. 7, 1948.
(2) Calvin, M., Private communication.

Crystal Structure of Mo_3Si

D. H. Templeton and C. H. Dauben

Mixtures of various ratios of molybdenum and silicon have been heated by A. Searcy and L. Brewer to prepare binary compounds of these two elements. The new compound Mo_3Si has been identified from its x-ray diffraction pattern and its crystal structure has been determined.

The lattice is cubic, with $a_o = 4.888 \pm 0.002$ and 4.901 ± 0.002 for two different samples. In both cases other phases were present, and it is not known what dimension corresponds to the ideal composition. The structure is like that of β-tungsten, with two silicon atoms and six molybdenum atoms to each unit cell, arranged as follows:

Space group O_h^3 - Pm3n

2 Si in (a) : 000; 1/2 1/2 1/2.

6 Mo in (c) : ± 0 1/2 1/4; 1/2 1/4 0; 1/4 0 1/2.

The isomorphous compounds Cr_3Si and V_3Si are already known.

B. Nuclear Properties and Transformations

Further Work on Pa^{235} and Some Excitation Functions

W. W. Meinke and G. T. Seaborg

Deuteron bombardment of uranium foil in the Berkeley 60-inch cyclotron with 18 Mev deuterons gave a 23.7 ± 0.5 minute and a 27 day Geiger activity in a highly purified Pa fraction.[1] A small amount of two intermediate periods were present but these most probably can be attributed to a small amount of Zr and Cb fission products coming through the chemistry.

The chemistry involved four manganese dioxide cycles, two solvent extractions with di-isopropyl-ketone and two extractions with TTA in benzene. The manganese dioxide cycles consisted of precipitating the MnO_2 from the solution of uranium in nitric acid, centrifuging, dissolving in hydroxylamine, diluting and reprecipitating. The dissolved precipitate from the last cycle was acidified and the protactinium extracted with di-isopropyl ketone, several washings with salted solutions being made to insure good separation from fission products. The protactinium, washed back into a pH 1 solution from the organic solvent, was acidified, extracted into TTA, and washed once with acid. The TTA was then evaporated on a platinum plate and flamed, leaving a weightless deposit of protactinium.

The cross section for formation of the 23.7 minute period is about 2×10^{-3} barns, a reasonable value for the (d,α) or (d,αn) reactions on U^{238} giving Pa^{236} or Pa^{235}. The 27 day period is formed with a cross section of about 4×10^{-3} barns (corrected for abundance), reasonable for a (d,α) reaction on the U^{235} present naturally in the uranium foil, giving Pa^{233}.

The 23.7 minute activity was checked in a 9 Mev proton bombardment of U^{238} (Q metal) foil and found to be present in a yield corresponding to a cross section of about 3×10^{-5} barns. This cross section has already been corrected for yield due to deuteron contamination (about 1 percent) in the proton beam. This small but definite yield with protons appears to rule out the possibility of the isotope being Pa^{236} and is consistent with the yield one would expect for a (p,α) reaction at such low proton energies.

An aluminum absorption curve of this 23.7 minute period shows a β-particle whose Feather range is about 610 mg/cm^2, corresponding to an energy of about 1.4 Mev.

It is interesting to note that by closing energy cycles in the heavy region one can calculate a decay energy of 1.24 Mev for Pa^{235}, while an energy of 2.09 is calculated for Pa^{236}.

Hence it would seem that the most likely assignment for this new protactinium isotope of 23.7 minute half-life is to Pa^{235}.

Excitation functions have been obtained for various reactions using the particles available at the 184-inch cyclotron. One reason for this interest is of course the practical one of knowing the optimum energy for obtaining a certain reaction although there is also the added aspect of determining by what mechanism a certain reaction is produced.

Preliminary experiments have been made bombarding stacked 1 inch squares of thorium and copper (the latter to cut down the beam energy) with particles in the electrostatically deflected alpha and deuteron beam of the 184-inch cyclotron. The results were not very satisfactory since a background as high as 1/10 maximum activity was found in the foils of "zero calculated energy" due to full energy particles hitting the side of the stack of foils.

Consequently a new apparatus has been designed in which the energy is degraded by 2 1/2 in. x 3 in. copper sheets of various thicknesses with sides milled parallel to within 0.2 mil and the mg/cm^2 determined by weighing. The target material (5 mil thorium foil in this case) is in the form of 3/4 in. discs and is held in a mask of 5 mil copper, about 3/4 in. from the beam side edge and midway between top and bottom of the copper absorbers. This 3/4 in. of copper on the beam side of the target material lowers the background due to particles coming in from the side to about 100th maximum.

Even though the electrostatically deflected beam is used in these experiments a considerable amount of activity is obtained in a bombardment of these 5 mil, 3/4 in. discs of thorium. For a proton bombardment to produce an isotope of 38 minute half-life we obtained the order of 1.5×10^6 alpha disintegrations/minute for a cross section of about 10^{-3} barns.

Protactinium is an excellent product to study in this excitation function work since the 38 minute Pa^{227} is the main alpha activity in evidence in the Pa fraction for a matter of 4-5 hours after shutdown and since an extraction with a solution of TTA in benzene removes the majority of Pa from the solution of target material. Of course when Pa is allowed to stand for any length of time it tends to go into the colloidal state. However, it was hoped that if the foils were worked up simultaneously with identical amounts of reagents, stirring time, etc. that the chemical yields could be assumed to be equivalent, at least to within 5 or 10 percent. This assumption appears to be fairly accurate since in the thorium bombardments to date smooth curves have been obtained with check points differing only a small amount from the mean.

In the chemical procedure the thorium discs are dissolved in 10 cc. of concentrated nitric acid and one drop of 0.2 M ammonium fluosilicate (heating gently on a hot plate until the reaction starts). Ten cubic centimeters of water is then added and the solution poured into separatory funnels (40 ml centrifuge cones with stopcocks sealed onto the bottom.) Ten cubic centimeters of 0.4 M TTA in benzene solution is then added and the mixture stirred for 5 minutes. The aqueous and organic layers are collected in separate tubes and about half of the organic layer (containing the Pa) is plated onto platinum plates, flamed, and counted for gross alpha counts. Two counts are made of the plates within an interval of about 40 to 80 minutes to see that the alpha counts do go down with the 38 minute half-life of Pa^{227}. Pulse analyses are made if needed to check any further question about impurity. Further pulse analyses about two weeks after shutdown give an idea of the amount of Pa^{230} (growing U^{230} and daughters) present in the samples.

So far it has been possible to work up 16 of these thorium foils simultaneously doing Pa chemistry and to start counting the plates about 1 1/2 hours after shutdown.

The only results reportable at this time are those for the $Th^{232}(p,6n)Pa^{227}$ reaction. Observed yield values are plotted in the figures, no attempt being made to correct for the energy distribution in the proton beam. The energy values for the points were determined from theoretical range-energy values for copper and lead calculated by the Theoretical Physics Group at Berkeley[2]. Since the range of the full energy proton

beam of the 184-inch cyclotron is about 4.5 inches of copper it can be seen that these energy values are quite uncertain at low energies. However these curves do give a good idea of the general shape of the excitation functions and if one assumes a calculated threshold for a certain reaction and normalizes the curve to that value one can obtain a fairly true picture of yield peaks, etc. The relative yield scale of each graph is independent of the others and no attempt has been made to normalize them to one scale or set of conditions.

Figure 1 represents our first experiments with our new apparatus, giving no apparent peak in the curve for the few foils worked up. Figure 2 represents a second experiment in which we worked up 12 foils and here found some evidence for a peak in the (p,6n) reaction yields.

To insure against this peak being caused by erratic chemical yields we performed a third experiment in which 16 foils were used, most of them being placed around the "peak" position of Figure 2. The results are shown in Figure 3. Figure 4 is a magnification of the peak in Fig. 3.

It can be seen that the (p,6n) reaction does definitely peak, its maximum activity being about 10 times higher than the activity at full beam energy. Thus since most targets are effectively "thin targets" to the high energy proton beam, it is very important in doing bombardments for (p,xn) reactions to bombard at or near this yield peak.

The (p,6n) excitation function seems to indicate that the reaction does go primarily through the formation of a compound nucleus, although there is an effect due to nuclear transparency[3] that gives a small but definite yield of the reaction at full proton energy.

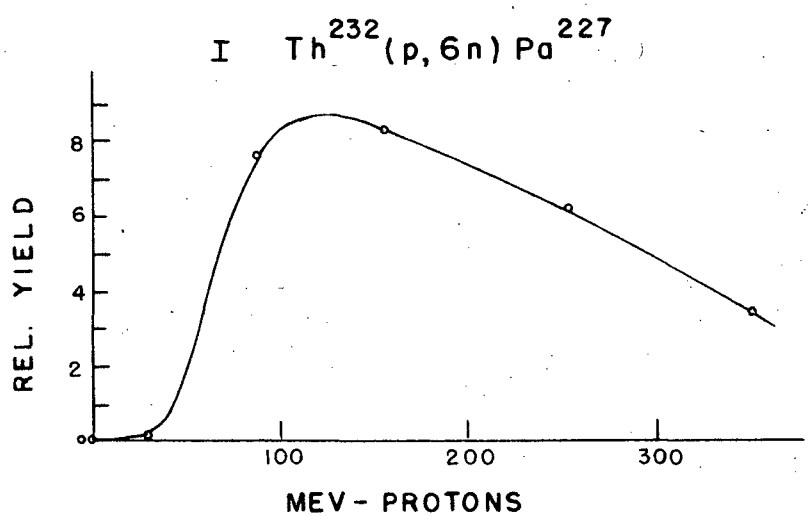
References

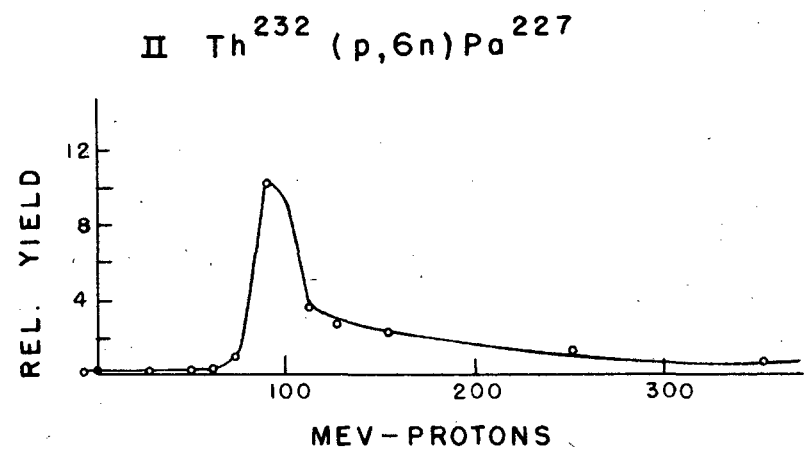
1. W. W. Meinke, A. Ghiorso and G. T. Seaborg, UCRL-311.

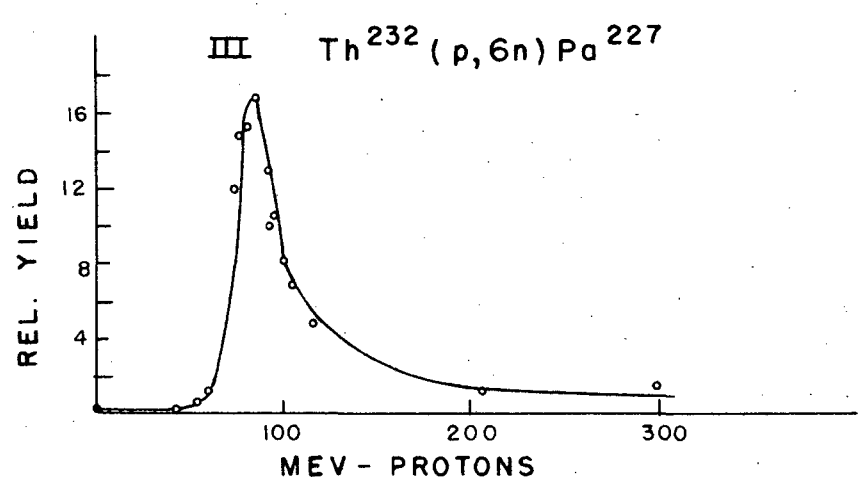
2. W. A. Aron, B. G. Hoffman and F. C. Williams, UCRL-121 (revised), and personal communication.

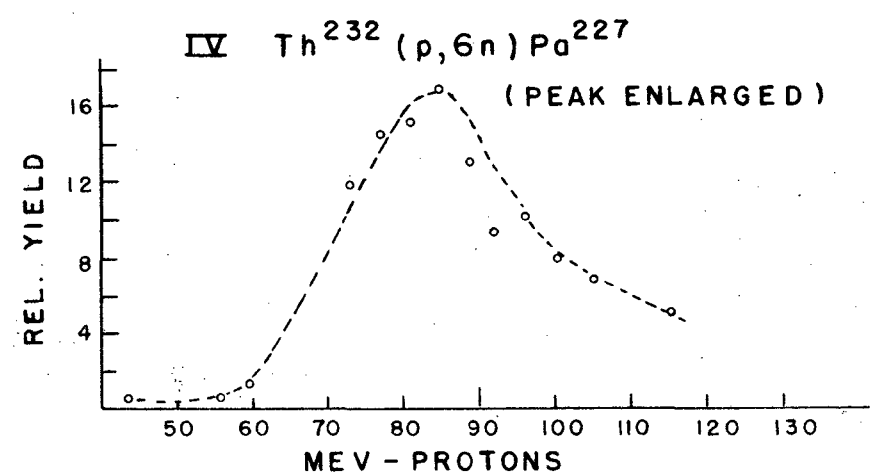
3. R. Serber, Phys. Rev. 72, 1114 (1947).

EXCITATION FUNCTIONS









13868-1

Isotopes of Americium

K. Street and G. T. Seaborg

The milking of neptunium from the americium fraction of a sample of Am^{241} irradiated with thermal neutrons for 15 months was repeated. The results obtained were the same as in the previous milking. The aluminum absorption of the neptunium fraction again shows the presence of Np^{239} as well as Np^{238} and thus the presence of a long-lived Am^{243} decaying at least partially by alpha-emission. An americium fraction containing 4.8×10^8 disintegrations per minute of Am^{241} yields at equilibrium 7.7×10^4 dis./min. of Np^{238} and 9.0×10^4 dis./min. of Np^{239}. Using the value 29 β^- dis./min. of Am^{242} per 10^3 alpha dis./min. of Am^{241} obtained from the growth of Cm^{242} in the same americium fraction one gets alpha-branching of Am^{242} to the extent of about 0.5 percent.

Assuming 400 barns for the slow neutron capture cross sections of Am^{241} and Am^{242} gives a half-life for beta disintegration of Am^{242} of 1400 years and an alpha half-life of 2.6×10^5 years. The same assumption gives 10^4 years for the alpha half-life of Am^{243}. Actually these neutron capture cross sections are not known.

Half-life and Alpha Energy of Pu^{234}

D. A. Orth and G. T. Seaborg

In an attempt to determine the radiation characteristics of Pu^{234}, U^{235} was bombarded with 100 Mev He^{++} ions on the 184-inch cyclotron and a plutonium fraction isolated.

The half-life and energy were accurately determined by pulse analysis as 9 hrs. and 6.15 Mev, respectively. The K/α branching ratio is being determined by following the L x-rays by pulse analysis on a proportional counter.

Spallation Products of Copper with 350 Mev Protons

R. E. Batzel and G. T. Seaborg

The yields of some of the isotopes formed in the spallation of copper with 350 Mev protons have been obtained. These yields are calculated relative to the number of atoms of $_{29}Cu^{61}$ formed during bombardment. The results are as follows:

Isotope	Yield	Isotope	Yield
$_{30}Zn^{63}$	0.15	$_{25}Mn^{56}$	0.12
$_{30}Zn^{62}$	0.11	$_{25}Mn^{52}$	0.30
$_{29}Cu^{64}$	1.36	$_{25}Mn^{51}$	0.04
$_{29}Cu^{61}$	1.00	$_{24}Cr^{51}$	0.08
$_{28}Ni^{57}$	0.05	$_{24}Cr^{49}$	0.07
$_{27}Co^{61}$	0.36	$_{20}Ca^{45}$	0.004
$_{27}Co^{55}$	0.15	$_{20}Ca^{47}$	0.0006
$_{26}Fe^{53}$	0.12	$_{20}Ca^{49}$	0.00008
$_{26}Fe^{52}$	0.02	$_{17}Cl^{38}$	0.004

The cross section for the formation of $_{29}Cu^{64}$ from the bombardment of elemental copper with 350 Mev protons has been determined and found to be 0.02 barns. The value is probably correct to within ± 20 percent.

Yield Distribution in the Fission of Uranium with 350 Mev Protons

R. L. Folger, H. G. Hicks and G. T. Seaborg

Some 5 mil strips of uranium foil have been bombarded with 350 Mev protons in the 184-inch cyclotron, and chemical separation of the fission products made. Preliminary yield data (Table I) seem to indicate a possible shift of the peak in the yield vs. mass curve to a mass less than 110. (The peak in the yield - mass curve from 350 Mev helium ion bombardment of uranium is in the neighborhood of mass 115.) Experiments are underway to better define the curve in the region A = 100 to A = 200. It is also proposed to measure independent yields along several of the fission chains in order to determine the primary fission products.

Table I

Yields Relative to Ba^{140} = 1.00

Fe^{59}	0.00043	Rb^{86}	7.4	Cd^{115}	5.4
Ni^{66}	0.028	Sr^{89}	3.5	Ba^{140}	assumed 1.0
Cu^{67}	0.095	Sr^{91}	7.5	$Au^{198,9}$	0.0005
Zn^{72}	0.054	Zn^{97}	12.	Ra^{224}	spallation 0.24

Properties of U^{231}

W. W. T. Crane and I. Perlman

U^{231} was prepared by bombarding Th^{232} with 150 Mev alphas. The 4.2 day U^{231} was chemically purified by ether extractions and scavenging the solution with $ZrO(IO_3)_2$. The radiation properties of U^{231} were investigated. A 9.5 Kev gamma-ray was found in addition to L and K x-rays. No gamma-radiation harder than the K x-rays was found. In terms of counts the 9.5 Kev gamma was 20 percent of the L x-rays. The ratio of K x-ray counts to L x-ray counts was 0.076

Based on the assumptions that the counting yield of the L x-rays (in Xenon counter) is 0.005 on Step 2 of the counter and that one L x-ray should appear per disintegration, a value for the conversion of L x-rays was determined. The number of orbital electron capture disintegrations was obtained by milking Pa^{231} from U^{231}. The yield of Pa^{231} indicated that 50 percent of the L x-rays undergo Auger conversion. A source of possible error in this measurement is the uncertainty of equilibrium between the tracer (Pa^{233}) and Pa^{231}.

From milkings of Th^{227} an alpha half-life of 200 years for U^{231} was obtained.

Work is being continued on this isotope in an attempt to measure the number of conversion electrons from K as well as L x-rays.

Low Mass Isotopes of Astatine

George W. Barton, Jr. and I. Perlman

Attempts are being made to identify the lower mass isotopes of astatine. Several experiments were performed in which an attempt was made to milk the polonium daughters of the known astatine activities. In one of these, Bi^{209}+ 100 Mev alpha-particles, the decay products were measured in the pulse analyzer after the astatine activity had died in astatine fractions purified at various times. The Po^{208} alpha peak showed that the At^{208} decayed with a 6.6 hour half-life. No alpha has been observed which corresponds with this. Resolution of the Po^{209} peak was much more difficult. Two points indicated something of the order of 3 1/2 hours. A bombardment at 55 Mev produced a heretofore unseen alpha peak at 5.73 Mev, which decayed with a 5.2 hour half-life. This isotope is presumed to correspond to At^{209}. Experiments are being continued to identify these activities by milking of daughter activities, by direct observations of the radiations and by measurements of yield as a function of energy.

The x-ray spectrometer as originally assembled has been found to require 5×10^6 counts per minute of x-ray activity on the standard argon counters, corrected to 100 percent geometry. This was determined from measurements of Cd^{107} (6.7 hr K-capture). An attempt is being made to increase this sensitivity by the use of high pressure proportional counters. Preliminary experiments with a discriminator circuit wheel which reduces the background, while at the same time increasing the sensitivity were extremely encouraging. Work is going forward on the rebuilding of the electronic circuits of the spectrometer and results are expected in a few weeks.

Bismuth Isotopes of Masses 198-203

H. M. Neumann and I. Perlman

Further milking experiments have been performed in an attempt to prove the mass assignment of various light Bi isotopes. The procedure used was generally the following. Bi was separated as BiOCl from the lead target. Pb was milked from the Bi parent by adding Pb carrier, separating Bi as BiOCl, and precipitating the lead as $PbCrO_4$. The resulting Pb fraction was repurified by adding inactive Bi and repeating the precipitation of BiOCl and $PbCrO_4$. This Pb fraction was allowed to stand for a specified length of time and Tl then milked from it by extraction of $TlCl_3$ into ether from 6 N HCl. Decay of the Tl fractions was followed, and initial activities of various Tl isotopes plotted to determine lives of the Bi grandparents.

In a bombardment of Pb with 60 Mev protons for 1 hour, the Bi was purified 2 hrs. after bombardment, Pb milked from Bi at 1 hr. intervals, and each Pb fraction allowed to stand for 24 hrs. before removal of Tl. Results showed an 87 ± 13 min. Bi grandparent of 72 hr. Tl^{201} (improved value for half-life, previously reported as 75 hr.) and a 40 ± 17 min. Bi grandparent of 27 hr. Tl^{200}. The deviations listed are considered to be maximum error possible in this particular experiment.

In a bombardment of Pb with 180 Mev deuterons for 15 min. the Bi was purified 2 hrs. after bombardment, Pb milked from Bi at 20 min. intervals, and each Pb fraction allowed to stand for 4 hrs. before removal of Tl. Results showed a 25 ± 4 min. Bi grandparent of 7 hr. Tl^{199}. The twenty-seven and the 72 hr. thalliums were present in lower yield, and gave half-lives of ~40 min. and ~80 min. for their respective grandparents.

In a bombardment of Pb with 150 Mev protons for 10 min. the Bi was purified 30 min. after bombardment, Pb milked from Bi at 10 min. intervals, and each Pb fraction allowed to stand for 110 min. before removal of Tl. The great bulk of Tl activity decayed with a 7 hr. half-life and only the first two milkings yielding 1.8 hr. Tl^{198}. These two points gave a 10 min. life for the Bi grandparent.

These results confirm the assignment of the 25 min. Bi α-emitter to mass number 199, and the 9 min. α-emitter to Bi^{198}. The α-emitter previously reported as 62 min. would from these results seem to be a mixture of 40 min. Bi^{200} and 87 min. Bi^{201}. The resolution of this α-activity from mixtures with 9 and 25 min. activities produced with 180 Mev deuterons has yielded values from 55 to 80 min. The 62 min. value was obtained from bombardment with 60 Mev deuterons where the 9 and 25 min. activities are not produced. If the 62 min. activity is actually a mixture, the α energies must be nearly the same since the two activities are not resolved by the alpha pulse analyzer.

Measurement of K/α branching ratio for the 9 min. and 25 min. activities, based on the yield of Tl grandaughters and observed Bi α-decay, gives values of 7×10^3 and 6×10^4 respectively. Since these values depend on the counting efficiencies of the Tl isotopes and the lives of the intermediate Pb isotopes, the branching ratios may be in considerable error.

The absorption characteristics of the 7 hr. and 27 hr. Tl activities obtained by these milking experiments have been checked with the activities produced by alpha-

particle bombardment of gold, and found to agree with them. Characteristics previously unreported:

7 hr. Tl:	160 Kev e^- (bender)
27 hr. Tl:	340 Kev e^- (bender)
	1.3 Mev γ (Pb absorption)
	$\sim$0.3 Mev γ (Pb absorption)
72 hr. Tl:	$\sim$0.3 Mev e^- (Al absorption)
	K,L x-rays (Al absorption)
	No γ of $>$1 Mev

In a bombardment with 60 Mev protons for 30 min. the Bi was purified 4 hrs. after bombardment and Pb milked from the Bi at 25 hr. intervals. Results showed a 13 $\pm$ 2 hr. Bi parent of 52 hr. Pb^{203}.

These results are summarized in isotope chart form:

	198	199	200	201	202	203
Bi	9 min. α,K	25 min. α,K	40 min. α(?), K	87 min. α(?), K	2 hr.	13 hr. K
Pb	? min. K	$\sim$80 min. K	18 hr. K	8 hr. K	long	52 hr. K
Tl	1.8 hr. K	7 hr. K	27 hr. K	72 hr. K	12 day K	////////

The chains at mass 199, 200, 201, and 203 have been proven. Further work is necessary to prove the chain at mass 198, and to determine the half life of Pb^{198}. No evidence of Bi^{202} has been obtained in these experiments. See Karraker and Templeton in the following section of this report.

Bi Activities from Neutron Irradiated Bi

Approximately 3 1/2 grams of Bi that had been irradiated for 131 days (June 26, 1946 - November 4, 1946) in the Hanford pile is being examined for the Bi activities produced. The five day Bi^{210} has already decayed out and the sample has been thoroughly purified from Po and probably from other contaminants. A small fraction of the resulting Bi was electroplated on Pt, and pulse analyzed. An α-emitter of 5.02 Mev was observed, confirming the results obtained previously by Howland in a similar experiment. The total α-activity amounted to about 2500 disintegrations/minute. Tl was milked from the Bi by precipitation of Tl_2PtCl_6 from a 2 N HCl solution. The daughter Tl decayed with a 4.2 minute half-life (Tl^{206}), indicating the α-emitter to be an excited state of Bi^{210}. The yield of Tl daughter corresponded to 2,550 alpha disintegrations/minute in total Bi solution. The Geiger activity of the Bi fraction was $\sim$8,000 c/m.

Half of the Bi solution has been set aside to allow Po to grow in, and at a later date Po will be removed to determine presence or absence of Po^{208} and Po^{210}. The other half of the solution is undergoing intensive purification, after which the sample will be examined for evidence of Bi^{208} and for other modes of decay of Bi^{210m}.

Light Isotopes of Polonium

D. G. Karraker and D. H. Templeton

Po^{205}

A new polonium activity, assigned to mass 205, has been produced by 40 Mev alpha bombardment of enriched (about 27 percent) lead 204. The branching ratio, as estimated from L x-rays observed in a rough aluminum absorption, and a 10 percent decay in the alpha counts in the sample, is $K/\alpha \sim 10^4$. The presence of an equal amount of Po^{207} in these samples prevents any better estimate at this time. The energy of the alpha-particle was determined from the decay of a series of pulse analyses as 5.2 ± 0.1 Mev.

Po^{202}, Bi^{202}

It has been previously reported(1) that a 2 hr. Bi activity has been milked from a 40 minute Po activity produced by bombardment of Bi. A better value of the half-life of Po^{202} has been obtained by periodic milkings of the Bi daughter. The yield of 2 hr. Bi^{202} decreases with a 40 ± 5 minute half-life, over 5 half-lives. The mass assignment is not absolute but is supported by the discovery of Po^{203}.

Po^{203}

The discovery by H. Neumann and I. Perlman(2) of a 13 hr. Bi at mass 203 complicates the work on Po^{203}, so two methods were used. In the first a mixture of Po activities was prepared by proton bombardment of Bi, and the Po milked at regular intervals for Bi. A plot of the yield vs. time for the 12 hr. Bi activity obtained this way gave a two-component decay curve, with an initial parent activity of about 45 minutes tailing into the previously reported 4 hr. Po^{204}.

In the second, instead of counting the Bi, the Bi^{203} was allowed to decay into the 52 hr. Pb^{203}, which was separated at appropriate times and its yield compared with the time of milking. A half-life of ~30 minutes was obtained by this method, but neither value is very accurate.

Several attempts were made in an effort to milk the Tl end products of the alpha-decay for both Po^{202} and Po^{203}. None have been fruitful, as the two Tl activities produced, 2 hr. Tl^{198} and 7 hr. Tl^{199} are mutually irresolvable in their decay curve. Different experiments will be necessary to characterize these activities.

The 68 minute Pb^{204} was shown to grow from the 12 hr. Bi activity having a 4 hr. Po parent, by milking 12 hr. Bi from the Po fractions which had been purified after 12 hours, and then milking the 68 min. Pb^{204} from the 12 hr. Bi obtained.

Bi^{205}

A plot of the yield of 6.4 day Bi^{206}, milked from a sample of Po, shows a two component decay curve. Instead of the 9 day curve predicted, the curve shows also a 1.5 hr. decay. This corresponds to the half-life for Po^{205}, so it is suspected the Bi^{205} is also of the order of 6 days in half-life. Further experiments are in progress.

(1) See UCRL-311
(2) See UCRL-382

Work on Neutron Deficient Rare Earth Isotopes

Betsy Jones, LeRoy Eyring and B. B. Cunningham

Two bombardments of Pr_2O_3 with 40 Mev protons have been made on the 184-inch cyclotron. A new 5.2 hr. activity was found, and tentatively assigned to Nd^{139}. Known isotopes of this region are shown below.

	138	139	140	141
Nd			3.3 d. K	2.5 hr.
Pr			~3.5 min. β^+	Stable (100%)
Ce	Stable	140 d. K	Stable	28 d.

The 5.2 hr. activity and the 3.3 d. Nd^{140} were seen, but the 2.5 hr. Nd^{141} was not, as is to be expected from the energy of the bombarding particles.

Some radiation characteristics of the 5.2 hr. activity are as follows: 2.1 Mev positrons by aluminum absorption, 1.2 Mev gammas by lead absorption, K and L x-rays, and conversion electrons of about 0.3 Mev.

A cation exchange resin column run to determine chemical identity of the 5.2 hr. activity has been carried out. Separation of cerium from the bombarded material at 5.2 hr. intervals was done to establish the genetic relationship to Ce^{139}. Because of the long half-life of Ce^{139} positive identification of this isotope in the milkings has not yet been made.

Mass Spectrograph

F. L. Reynolds, R. W. Fink, R. A. Naumann and D. H. Templeton

Mass identification of one radioactive isotope of lanthanum (19.5 hr. La^{135}) has been completed. This isotope was made by bombarding a cesium salt with alpha particles. Transfer plates were made from the original mass spectrograph plate to ascertain the mass position of the radioactivity relative to stable La^{139}, and the half-life was determined directly by counter-slit technique from the activity on the original plate. No evidence was found for La^{136} in these experiments.

Spectra of plutonium, americium, neptunium, and uranium on Ilford plates have been obtained using a thermal source as an ionization means. Of the four, plutonium is the most efficient emitter. Both metal and metal oxide ions appear, the ratio metal to metal oxide increases at more elevated filament temperatures.

A systematic study on new Eastman emulsions sensitive to 8000 volt positive ions has been made. Two emulsions known as J2327 and J2609 required less than 1×10^6 positive ions to produce a visible line 0.2 mm.x 10.0 mm.

Loss factors on cesium and neodymium proved to be interesting. Three different salts of cesium gave values : $CsNO_3$, 1.4×10^6; CsCl, 8.3×10^4; and Cs_2SO_4, 180 as loss factors. Thus, with Cs_2SO_4, the Cs is almost 100 percent converted to positive ions on the thermal source, the other salts are low in efficiency because of greater volatility in vacuum. The loss factor on neodymium is 5.3×10^3. This checks quite well with the University of Chicago workers who found it to be 5×10^3 on their instrument.

A previous report[1] of work on two new neutron-deficient isotopes of cesium outlined experiments giving substantial evidence for the existence of Cs^{127}, (β^+, 5.5 hours), and Cs^{129} (K-capture, 32 hours), and the genetic relationship $Cs^{127} \xrightarrow{\beta^+} Xe^{127}$, where Xe^{127} has a 34-day half-life.

These mass assignments have recently been confirmed by means of the mass spectrograph transfer-plate technique, in which lines of radioactivity at mass numbers 127 and 129 were obtained which transferred from the original plate to another. A second transfer plate exposed after the 5.5 hour Cs^{127} had decayed, showed only one longer-lived activity at mass 129.

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1. UCRL-311 (Quarterly for December, 1948-February, 1949.)

A Fast Quenching Circuit

H. H. Hopkins, Jr.

An attempt was made to make a fast quenching circuit using a multivibrator to reverse the potential on the central wire after each pulse. Square pulses of 10 μ sec. width were obtained. Further work is necessary to reduce the dead time sufficiently below that of the conventional circuit to be useful.

A windowless proportional counter for betas is being worked on. The counting gas, a mixture of methane and argon, will flow through the counting tube at atmospheric pressure. Proportional pulses are fed into a high gain amplifier.

Ionization Chamber for Spontaneous Fission Energy Measurements

R. L. Shuey

An experiment has been started to study the energy distribution of spontaneous fission fragments. Initial experiments have indicated that with an ionization chamber rise times of at least 0.3 μs are obtainable. It is intended to use a double ionization chamber, extend the pulse length to 5 seconds and plot the pulse height with a graphic plotter. At the same time provision is being made to photograph the initial pulse shape.

At present the initial versions of the ionization chamber, pulse extender and some of the associated equipment have been completed.

A Scintillation Counter for Spontaneous Fissions

W. C. Orr

A scintillation counter has been constructed for the purpose of observing spontaneous fissions. The sample is mounted on a very thin film placed between two phosphor screens so that coincident flashes are produced which may be detected by two separate photomultiplier tubes. Only coincident pulses are counted. A high background of alpha radiation can be tolerated because spurious counts arise only when a number of alpha-particles appear in coincidence and give pile-ups on both sides of the thin sample.

Beta-Ray Spectrometer

F. L. Reynolds

Sample testing on the recently constructed double focusing beta-ray spectrometer is to begin in the next few days. Delay in operation has been due to power supply stability troubles which have taken considerable time to correct. Plans are to first check beam characteristics using conversion lines from ThB and recording the spectra photographically. Initial field measurements have been made and a straight line function of gap field strength against current has been established up to a particle energy maximum equal to 3 Mev.

C. Chemistry of Astatine and the Preparation of Certain Compounds

R. F. Leininger and E. Segrè

Astatine

Work on chemistry of astatine was stopped temporarily due to alterations and repairs on the 60-inch cyclotron.

Half-life of Be^7

The experiment to determine the effect of atomic electrons on the half-life of Be^7 has been concluded with the following result.

$$\lambda_{BeO} - \lambda_{BeF_2} = (+1.375 \pm 0.0053) \times 10^{-3}$$

This work has been reported in detail in UCRL-370.

D. Bio-Organic Chemistry Group

B. M. Tolbert

Synthetic and Experimental Chemistry

M. Calvin, B. Tolbert, P. Adams, R. T. Arnold, R. Bartsch, A. Fry, H. Hauptmann, D. Hughes, E. Jorgensen, J. Krone, B. Neivelt, R. Ostwald, R. Selff, Y. Stone and W. Tarpey

Lactic Acid-C^{14}

An important intermediate in both plant and animal metabolism. As the procedure for the bromination of propionic acid had been worked out in connection with the preparation of labeled alanine and the synthesis of the three labeled propionic acids had already been completed, the preparation of all three of the labeled lactic acids was undertaken by the hydrolysis of the bromo acids in zinc oxide slurry as follows:

$$CH_3CH_2CO_2Na + HCl\ (anhyd.) \longrightarrow CH_3CH_2CO_2H + NaCl$$

$$CH_3CH_2CO_2H + Br_2 \xrightarrow[100^\circ,\ 2\text{-}1/2\ hours]{0.04\ g.\ P_4,\ 0.02\ g.\ I_2;\ 0.2\ cc.\ propionylchloride} DL\ CH_3CHBrC(=O)\text{-}OH$$

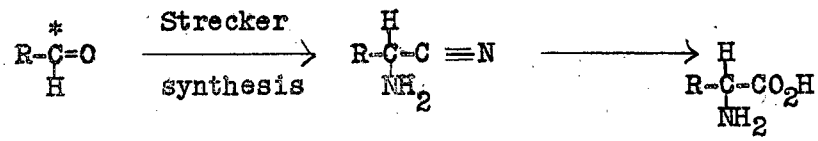
$$H_3CCHBrCO_2H + H_2O \xrightarrow[100^\circ,\ 24\ hours]{ZnO} DL\ (H_3CCHOHCO_2)_2Zn.3\ H_2O$$

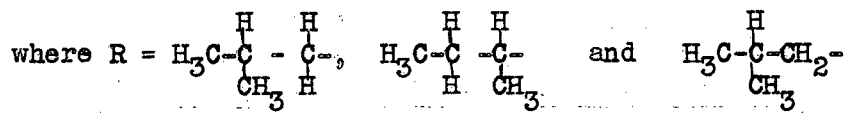
In this manner lactic acid-1-C^{14} has been prepared using 0.601 g. of sodium propionate-1-C^{14} and 0.2 ml. propionyl chloride. A first crop yield of 55 percent based on propionate was obtained and an additional 20 percent can probably be obtained in a second crop. The identity of the compound was determined by carbon and hydrogen analyses, and a paper chromatographic analysis of the product indicated the material to be free of tracer impurities. The preparation of the two- and three-labeled compounds is in progress.

C^{14} alpha-labeled Leucine, Isoleucine and Valine.

The preparation of these three amino acids labeled in the alpha-position with C^{14} has been undertaken for use in biological studies. Calculations of the overall yields from CO_2 based on the yields indicated in the literature showed that probably the best method for making those acids should be through the Strecker synthesis as follows:

$$\overset{*}{C}O_2 \xrightarrow{RMgBr} R\text{-}\overset{*}{C}O_2H \longrightarrow R\text{-}\overset{*}{C}OCl \xrightarrow[H_2]{Pt}$$



where R = 

The first step, reaction of $\overset{*}{C}O_2$ with the Grignard compound, was done with isobutylmagnesium bromide and the yield of sodium isovalerate was 94.2 percent. The second step, transformation of the sodium isovalerate into isovaleryl chloride, presented some difficulty since the separation of this reagent and reaction products was difficult when thionyl chloride was used. With this reagent it was impossible to avoid fractional distillation of the isovaleryl chloride which could not be done on the small scale desired for this preparation. The preparation of the acid chloride could not be executed as had previously been worked out for benzoic acid. Even with fractionation of the reaction product a not quite pure acid chloride was obtained as is shown in the case of n-butyryl chloride. After fractionating and refractionating, the boiling range of the product was 79-93° and this in 39 percent yield.

It seems now that this difficulty can be overcome by carrying out the preparation of the aliphatic acid chloride using a higher boiling aromatic acid chloride. Benzoyl chloride and phthalyl chloride have been tried. The former gave the better results but no definitive conclusions can be drawn at this moment. Three experiments are listed to illustrate the advantage of the method:

a. Sodium n-butyrate was heated with benzoyl chloride in a hydrogen chloride stream. After fractionation 46.5 percent of n-butyryl chloride was obtained, b.p. 100-105° (b.p. indicated, 101-102°).

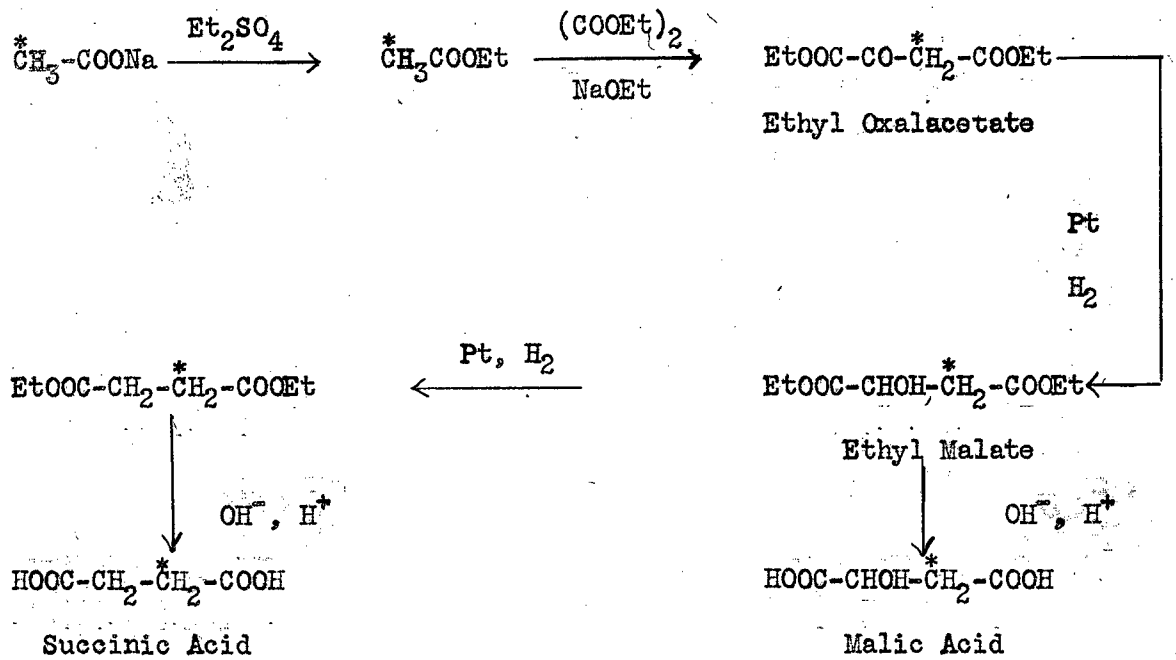
b. Sodium n-valerate heated in the same manner. 50.9 percent of n-valeryl chloride was obtained, b.p. 126-129° (b.p. indicated, 127-128°).

c. n-Valeric acid and benzoyl chloride heated and fractionated. After fractionation 65.2 percent n-valeryl chloride, b.p. 126-129°.

Malic, Succinic, Fumaric and Tartaric Acids-C^{14}

Because of their importance in plant and animal metabolism the earlier work on the synthesis of these compounds has been expanded, and high specific activity preparations of these materials will be undertaken as soon as good synthetic procedures can be worked out.

As a key intermediate, the primary objective was the preparation of malic acid from sodium acetate according to the following scheme:



The conversion of sodium acetate to ethyl acetate was achieved in 97 percent yield on the basis of radioactive residues left on distillation from the reaction mixture, but the condensation between ethyl acetate and ethyl oxalate in ether using sodium methoxide as a catalyst went only in yields of about 60 percent on the basis of subsequent hydrogen pickup. More recent work with absolute ethanol and sodium ethoxide gave a yield of 68 percent, also on the basis of hydrogenation data. After neutralization of the condensation mixture, the hydrogenation is carried out at pressures slightly above atmospheric in the presence of platinum and a trace of ferrous salt to inhibit the hydrogenation of the malic acid. The mixed esters are saponified by shaking at room temperature with a slight excess of dilute base. After acidification, the excess oxalic acid is removed as its calcium salt and the mixed acids ether extracted from the reaction mixture. The separation of the components of the crude residue, left on removal of the ether, is being studied and it is hoped that by partition between ether and water and recrystallization of the enriched fractions from ethyl acetate-hexane solutions fairly pure malic acid can be obtained in good yield.

Demerol-I-Methyl-C^{14}

Attempts to prepare labeled Demerol (1-methyl-4-phenyl-4-carbethoxypiperidine) by the action of C^{14}-labeled methyl iodide on 4-phenyl-4-carbethoxypiperidine resulted in low yields (7-12 percent). A low activity preparation showed that the desired tertiary amine reacts rapidly with methyl iodide to give the quaternary salt.

In an attempt to find a better way to carry out this reaction, the reductive methylation of 4-phenyl-4-carbethoxypiperidine with formaldehyde and formic acid was tried and found to give a 70 percent yield of Demerol on a 2mmole scale.

Four hundred and sixty-six milligrams (2 mmoles) of 4-phenyl-4-carbethoxypiperdine was heated under reflux with 258 mg. (5.0 mmoles) of 90 percent formaldehyde and 175 mg. (2.3 mmoles) of 40 percent formic acid solution for five hours. The resulting pale yellow solution was acidified with 1 ml. of 2 N hydrochloric acid and heated on a steam bath to remove excess formaldehyde and formic acid. The reaction mixture was

evaporated to dryness in vacuo at room temperature, mixed with 1 ml. water and again evaporated to dryness. The dry residue was then heated under reflux for twenty-two hours, with 3 ml. of 11 percent alcoholic hydrochloric acid. The solvent was removed from the product (HCl salt of 1-methyl-4-phenyl-4-carbethoxypiperidine) which was crystallized from dry acetone to give 20 percent yield white salt, m.p. 189-190°. An additional 50 percent of product, m.p. 186-188°, was recovered from the filtrate by crystallization with ethanol-ether.

Synthesis of I^{131}-labeled Monoiodotyrosine, Diiodotyrosine and Thyroxine on a Microgram Scale.

The technique of paper chromatography has been used in the isolation and identification of I^{131}-labeled monoiodo-L-tyrosine, diiodo-L-tyrosine and L-thyroxine which have been synthesized on a microgram scale. In this manner it has been possible to obtain very high specific activity products for animal work.

The hypoiodite method described previously for the preparation of diiodotyrosine on a hundred microgram scale gave three radioactive spots on the paper chromatogram which had been developed in both directions with butanol-acetic acid-water solvent. A large part of the activity was in the form of inorganic iodide near the origin of the paper. About 15 percent of the starting activity was found in two well-defined spots in the far corner of the chromatogram. The upper spot was identified as diiodotyrosine by rechromatographing the eluted product with a known sample of diiodotyrosine which had been synthesized on a 100 mg. scale. The lower spot was identified as monoiodotyrosine by rechromatographing with a known sample obtained from Prof. C. R. Harington.

The specific activities of the products were 520 and 1040 μc/μmole. A semi-quantitative estimation of the yield of diiodotyrosine was made by spectrophotometry.

I^{131}-labeled thyroxine was prepared by means of the exchange reactions with inorganic iodide described by Frieden, Lipsett and Winzler, Science, 107 353 (1948). In a typical experiment, 140 ± 5 μg. of recrystallized thyroxine and 1.7 mc. of I^{131} as sodium iodide were dissolved in 2 ml. of 9:1 butanol-water mixture and the solution adjusted to pH of 5-6 with hydrochloric acid. The solution was heated under reflux for twelve hours, evaporated to about ~0.5 ml. and transferred to the corner of the chromatographic paper. The paper was developed in one direction with butanol-water solution. The radioautograph of the chromatogram showed three spots: inorganic iodide near the origin, a rather diffuse spot of thyroxine and a spot of free iodine along the solvent front.

The thyroxine spot was eluted with approximately 3 ml. of 50 percent alcohol. Spectrophotometry of the eluate showed 120 μg. (83-89 percent) of the thyroxine was recovered. This contained 11 percent of the I^{131} used and had a specific activity of 9.75 μc/μg. The product was identified by rechromatographing with a known sample of thyroxine.

Codeine-3-Methoxy-C^{14}

In connection with the Pharmacology and Chemistry Departments of the University of California we have prepared labeled codeine from morphine by methylation with labeled methyl iodide. The methylation of morphine with this material in the presence of alkali was studied in the late nineteenth century, but all workers reported an extremely small yield of codeine base which was due to the fact that in the morphine molecule there are three reactive groups capable of undergoing methylation, namely the phenolic group,

the tertiary amino group and the allylic alcohol group. An active methylation agent such as methyl iodide when allowed to react with morphine in the presence of alkali will methylate all three groups in such a manner that the final product consists of a mixture of codeine, thebaine and the methiodides of these alkaloids.

Since the reactive group in the morphine molecule that interferes most with this reaction is the tertiary amino group rather than the allylic secondary alcohol group, it was hoped that by protecting this group with oxygen, that is, by using morphine N-oxide for the methylation, the entering group could go under proper control as to time, temperature and reagent proportions almost exclusively to the phenolic group. The methylation of morphine N-oxide with dimethyl sulfate had been previously studied and patented, but the use of methyl iodide in this reaction does not seem to have been investigated.

The direct oxidation of morphine with hydrogen peroxide to the N-oxide did not give a product of sufficient purity for use in the preparation of codeine, so a protective oxidation method was used to obtain high purity morphine N-oxide. Morphine was first converted to the morphine-Na derivative and then allowed to react with chloromethyl ether. The methoxy-methyl ether of morphine thus obtained was oxidized with 30 percent hydrogen peroxide and the product, methoxy-methyl ether of morphine N-oxide, was isolated in the form of a crystalline acetone derivative from which the morphine N-oxide was obtained after hydrolysis with dilute sulfuric acid and subsequent alkalination with ammonia.

Six grams (20 mmoles) of the pure morphine N-oxide was dissolved in a chilled solution of 20 mmoles of sodium methoxide in 20 ml. methanol. The flask was then connected to the vacuum manifold and 2.3 g. (16.2 mmoles) of methyl iodide-C^{14} distilled in. The flask containing the frozen mixture of sodium morphine N-oxide and methyl iodide was removed to the hood and the mixture re-fluxed on the steam bath for four hours. After cooling, 5 ml. of water was added and sulfur dioxide passed through the solution for one hour to reduce the codeine N-oxide. Thirty milliliters of water was added to the flask and the methanol was vacuum distilled off. Then 10 ml. of 6 N sodium hydroxide was added to dissolve excess morphine and the codeine extracted repeatedly with chloroform, which chloroform portions after washing with water and drying, were evaporated to dryness. The codeine was recrystallized from a mixture of benzene and petroleum ether, after which the free base was dissolved in a minimum amount of absolute ethanol and dry hydrogen chloride gas was passed into the solution to form the salt. After evaporation of this solution to dryness the codeine hydrochloride was recrystallized from 95 percent ethanol.

The yield of codeine was 3.3 g. or 55.4 percent based on methyl iodide. The carbon, hydrogen and methoxy analyses checked accurately for codeine, and a paper chromatographic analysis of the material indicated only one radioactive spot, thus confirming the radioactive purity of the material.

Glucose-1-C^{14} and Mannose-1-C^{14}

The synthesis of these compounds by the condensation of labeled nitromethane with D-arabinose has been described in a previous progress report. In the early work the two compounds formed were separated by fractional crystallization, but due to difficulty in obtaining a pure compound on the small scale desired this method has been abandoned.

However, it has been found that as much as 30-40 mg. of mixed mannose and

glucose may be separated by partition chromatography on filter paper sheets using butanol-propionic acid-water solution as a solvent although the arabinose and mannose are not separable under these conditions. The radioactive sugars may be located by radioautographic technique and then eluted from the paper with water, concentrated and crystallized.

Partition chromatography of the sugars on a packed filter paper pulp column was tried with butanol-water as an eluting agent. A partial separation of the sugars was obtained, but it was found impossible to pack the column with the paper pulp available so that the density of the column bed was constant and comparable with that of the paper sheets. Since the density of the paper effects the amount of material which may be separated by chromatography and because the column work did not give a very satisfactory separation, further work with this method has been temporarily abandoned and the straight filter paper sheets are being used instead.

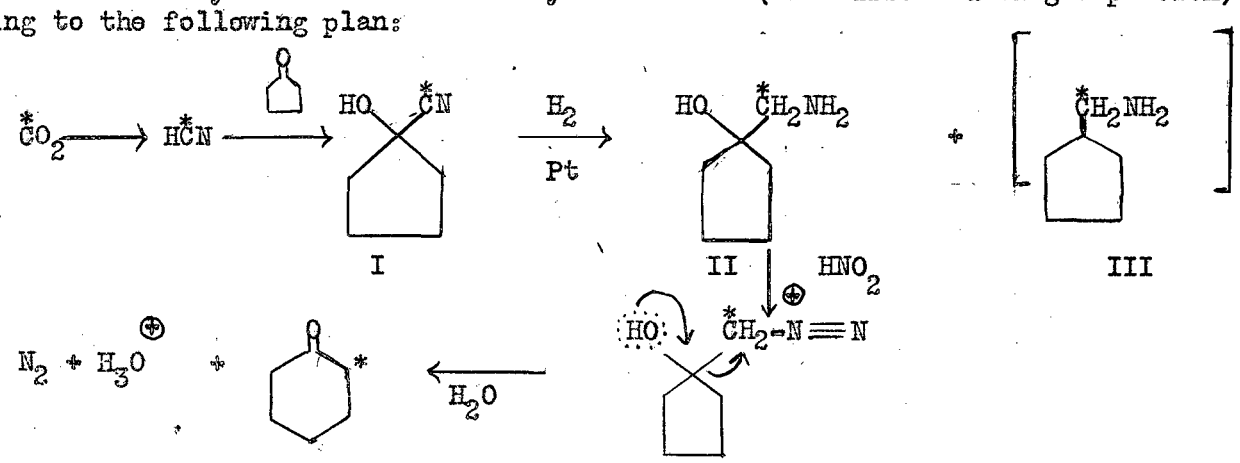
An important advantage of the paper chromatographic method of purification is that the preparation scheme may be simplified. Thus, the crude nitro-sugar mixture may be hydrolyzed directly with either hydrochloric or sulfuric acid, deionized on resin exchange columns, concentrated at room temperature and chromatographed. Using some material from a previous run, pure glucose with a specific activity of 1.8×10^6 dis./min./mg. and mannose with approximately the same specific activity but contaminated with unlabeled arabinose may be obtained.

At present, a low specific activity (28 μc/16 mmoles) preparation is in progress. The efficiency of the two acids in the hydrolysis of the nitrosugars is being checked and it is hoped that high specific activity preparations will be made in the near future.

Because the scale of operation can be reduced below that previously used, labeled sugars with a specific activity of several microcuries per milligram may be prepared by this method. It is also possible that at least a partial separation of the sugars may be effected by distribution between two immiscible solvents using a modified Craig extraction apparatus.

Cyclohexanone-2-C^{14}.

An attempt is being made to use the action of nitrous acid on 1-aminomethylcyclopentanol in a synthesis of labeled cyclohexanone (the Tiffeneau ring expansion) according to the following plan:



A careful examination of various experimental conditions for obtaining maximum yields of I and II is now underway. Compound I has been synthesized (a) by bringing

together liquid HCN and cyclopentanone in the presence of a catalytic trace of KCN; (b) by treating the $NaHSO_3$ addition compound of cyclopentanone with KCN solution; and (c) by generating HCN from aqueous KCN and HCl (at -5°) and allowing the HCN formed to equilibrate with cyclopentanone in ether.

Catalytic reduction of compound I in acetic acid gives considerable hydrogenolysis to yield III. This is perhaps due in part to intermediate formation of the acetate ester of I. Consequently, ethanol is now being examined as a useful solvent. It has now been established that compound II is a powerful catalyst poison (due to strong adsorption of the amino group). As a result it is necessary to have one full equivalent of H^+ present during the reduction.

That the course of the reaction actually goes as postulated will be determined, and, in addition, if yields are satisfactory it is planned to use the products as possible intermediates in the synthesis of ring-labeled aromatic compounds.

Decomposition of Acetyl Peroxide in Acetic Acid.

In the study of the presumed free radical decomposition of acetyl peroxide in methyl-labeled acetic acid it has been shown that of the four identifiable products formed (carbon dioxide, methane, succinic acid and methyl acetate) the succinic acid has about the same specific activity as the acetic acid, the carbon dioxide contains no activity and the methane has a small fraction of the specific activity of the acetic acid.

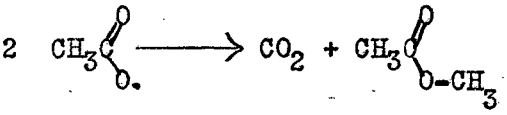
In the last Quarterly Progress Report it was stated that the methyl acetate obtained from the decomposition of acetyl peroxide in C^{14} methyl-labeled acetic acid contained some of the activity. It was also shown that methyl acetate and acetic acid did not undergo an exchange reaction in twelve hours at room temperature. In order to be sure that the source of activity in the methyl acetate from the decomposition of acetyl peroxide was not an exchange reaction under the conditions of the decomposition, i.e., $\sim 100^{\circ}$ for five hours, these conditions were simulated with a synthetic mixture of unlabeled methyl acetate and labeled acetic acid. The acetic acid and methyl acetate were then separated as previously described, and the methyl acetate was found to contain as an upper limit 0.8 percent of the activity calculated for the complete exchange. The probable value is somewhat less than this.

The distribution of activity between the acetic acid and the methyl alcohol obtained from the decomposition of acetyl peroxide was then studied by hydrolyzing the methyl acetate in sodium hydroxide solution and separately burning the sodium acetate and methyl alcohol so obtained. The CH_3 group of the sodium acetate was found to have a specific activity of 3.24×10^3 dis./min./mg.C while that of the methyl alcohol was 318 dis./min./mg.C. The specific activity of the CH_4 obtained from this run was found to be 249 dis./min./mg.C while that of the original acetic acid used was 9.96×10^3 dis./min./mg.C.

In another experiment, the ratio of acetyl peroxide to acetic acid was increased in order to obtain a greater yield of methyl acetate. The methyl acetate so obtained was washed with sodium bicarbonate solution to remove acetic acid and hydrolyzed and burned as before. The specific activities of the CH_3 groups in the various positions were as follows: Original acetic acid, 9.96×10^3 dis./min./mg.C; acetic acid from methyl acetate, 668 dis./min./mg.C; methyl alcohol, 270 dis./min./mg.C; methane, 36 dis./min./mg.C.

From these results it is immediately obvious that the source of the methyl

acetate cannot be the reaction



as has been proposed by Kharasch and Gladstone. If this were the exclusive route of formation of methyl acetate the specific activities of the two methyl groups would necessarily be the same. Likewise, it is obvious that the original acetic acid is not the exclusive source of the acetate in the methyl acetate, since if this were the case the activity of the methyl group would necessarily be 9.96×10^3 dis./min./mg.C as in the original acid.

Many attempts have been made to formulate a mechanism for this reaction, but up to the present time it has been impossible to propose a single path source for the methyl acetate which is consistent with the above facts. Further work is underway in an attempt to clarify the points of inconsistency.

Preparation of Aliphatic Halides Labeled with C^{14}.

Work on high yield preparation methods that will give pure propyl bromide-1-C^{14} or propyl bromide-2-C^{14} is continuing as part of a study of general methods of preparation of the aliphatic halides labeled with C^{14}. We have temporarily discontinued the use of lithium aluminum hydride as a reductant in the case of simple aliphatic compounds due to trace contaminants encountered by the splitting of ethers with this reagent.

Among the other compounds whose preparation is being studied are: isobutyl bromide-1-C^{14}, 2-bromopropane-1-C^{14}, potassium cyanide-C^{14}, alanine-3-C^{14}, leucine-β-C^{14}, valine-methyl-C^{14} and cycloheptanone-2-C^{14}.

Activity Determinations:

Geiger-Müeller Counters. Experiments using a commercial flow-gas counter ("Q" gas counter, Nuclear Instrument and Chemical Corp.) and a counting gas mixture composed of helium (commercial grade) saturated with ethanol at 0° C and dried with Drierite have been performed. The results thus far look very satisfactory. The coincidence correction is normal, about one percent per thousand counts, and the counting rate is quite reproducible. The efficiency of the counter is approximately 2.5 dis./count for C^{14}. The results are better using this gas than the argon-butane mixture supplied with this commercial counter.

Ionization Chambers. The development of ionization chambers for use as a routine instrument in the measurement of very low activity C^{14} samples from biological experiments has progressed to where a fairly standard set up has been developed and calibrated. The unit consists of an ionization chamber of our own design and manufacture, a vibrating reed electrometer made by the Applied Physics Corporation and a Brown "Electronik" potentiometer recorder for continuous recording of the output voltage of the electrometer.

A considerable amount of difficulty was first experienced in the use of ionization chambers due to the piezo electric effect in the insulators associated with the induced strains of evacuation and filling the chambers. After trying a number of different materials including kovar, polystyrene and teflon, it was finally found that teflon gave very satisfactory results with practically no hysteresis effect.

With the present units which hold the carbon dioxide generated from one gram of barium carbonate it is possible to detect radioactivity in the sample to the extent of about 0.07 dis./min./mg. of barium carbonate which is only about three times the natural concentration of C^{14} in living organic materials due to the cosmic bombardment of nitrogen in the atmosphere by neutrons. Activities of about 0.2 dis./min./mg. up can be measured with satisfactory precision for biological work.

Biological Chemistry

M. Calvin, L. Daus, J. Govaerts, M. Kirk, J. Krone, B. Krueckel, M. Meinke and Y. Stone

The Fate of Radiocarbon taken into the Lungs or Blood Stream as $BaC^{14}O_3$

Very little information can be found in the literature on the danger encountered by those who work with $BaC^{14}O_3$. Since this compound is one of the most suitable chemical forms in which radiocarbon is measured and handled, the dangers possibly encountered in its use due to inhalation of barium carbonate were investigated.

It was decided to study this problem by two methods. If barium carbonate injected in the blood stream of a mouse would exchange carbon with that of the carbon dioxide in the blood stream and would be exhaled as carbon dioxide, then barium carbonate inhaled into the lungs would also exchange since the pH of the lungs and the blood stream is the same. Secondly, an actual attempt at insulfation of barium carbonate into the lungs would be tried, but the results would be more uncertain in the latter case as the amount of carbon taken in and the amount eaten would not be known for sure.

The $BaC^{14}O_3$ was administered either as a dust into the nose or as a very fine suspension in isotonic glucose solution. During experiments the mice were maintained continuously in a metabolic cage and the expired carbon dioxide was collected and analyzed. The animals were sacrificed one to two days after the injection, and the radioactivity of the lungs, spleen, liver, kidneys and excreta determined together with the amount of activity in the carbon dioxide expired.

Our experiments show that the C^{14} appears very rapidly in the expired carbon dioxide and that the cumulative excretion of C^{14} by the mouse is approximately the same either if it is introduced in the nose in the form of $BaC^{14}O_3$ or when injected in the blood stream in a suspension. About 45 percent of the injected dose is expired during the first hour after administration. Later on the excretion is slowed down progressively, and after twelve hours 85 percent of the dose has been expired as $C^{14}O_2$. No significant activity is found in the spleen, liver, kidneys or lungs one to two days after injection. The same applies for the excreta collected during the same period of time. In one series of experiments the lungs were tested three to sixty minutes after injection and it was found that $BaC^{14}O_3$ is rapidly filtered out by the lungs and that no significant activity is to be found in the soft tissues.

When the percentages of the injected carbon fixed by the mouse are plotted on semi-logarithmic graph paper it is found that the excretion shows an exponential law. This curve may be broken down into two straight line segments corresponding to biological half-lives of one and nine hours, respectively. From the data we can conclude that most of the C^{14} absorbed by animals as $BaC^{14}O_3$ is expired by the lungs as $C^{14}O_2$.

Metabolism of Propionic Acid-C^{14}

A series of Warburg manometric experiments designed to study the metabolism of normal and neoplastic tissues with C^{14}-labeled compounds has been undertaken. As a preliminary step in this work the metabolic rate of carbon dioxide evolution from tissue slices and homogenates from carboxyl-labeled sodium propionate has been determined.

In this experiment livers from year-old strain "A" male mice were sliced by the Warburg technique and suspended in Ringer phosphate solution at pH 7 in a two-armed Warburg flask. The flasks were equilibrated at 37° C, and a water solution containing the labeled propionate tipped in and shaking continued for the desired incubation time. The acid was then added from the second side-arm to terminate the reaction and the evolved carbon dioxide was absorbed in a sodium hydroxide center well so that the activity could later be determined as $BaC^{14}O_3$. The incubation periods lasted two, three, four, five and six hours, and, in general, the percent of activity in the carbon dioxide increased with time, but variations in the shape of the curve from experiment to experiment were encountered. Attempts are being made to minimize these differences. In general, however, 10 percent of the added activity was present in the carbon dioxide after two hours and about 30 percent after five hours.

As a continuation of this work the chemical forms in which the propionic acid activity was found after the metabolic period were investigated. In this process the flask contents were homogenized and the unmetabolized sodium propionate together with added inactive sodium propionate removed by steam distillation or by vacuum distillation. The p--bromphenyl ester was precipitated from this distillate and recrystallized to constant specific activity. The possibility of co-precipitation of small amounts of other acids such as acetic acid was shown to be considerable in a separate experiment in which the ratio of acetate to propionate decreased only from 1:10 to 1:100 after three recrystallizations. The presence of other fatty acids would, therefore, pass unnoticed in this ester process.

The dry residue from the distillation was separated into fractions by water solubility, ether solubility and absorption on ion exchange resins. The distribution of activity after five-hour incubation was as follows: 32 percent in carbon dioxide, 48 percent as unmetabolized sodium propionate, 1 percent as a water-insoluble residue and 12 percent as water-soluble residues. Ether extraction and ion exchange column work showed that approximately 50 percent of the activity of the water-soluble residue was acidic in nature. It is hoped that a paper chromatographic analysis may be made to identify its components.

At present, however, most of the energy of this work is being directed toward the development of sufficiently refined techniques that reproducible results can be obtained as needed.

Work on the metabolism of C^{14}-labeled stilbamindine in mice is continuing and will be reported in more detail in another section of the Radiation Laboratory Quarterly Progress Reports as will also the reports on the rate studies of the conversion of metabolic intermediates and amino acids to $C^{14}O_2$ in mice.

Photosynthetic Chemistry

M. Calvin, A. Benson, V. Haas, J. Bassham, T. Goodale,
A. Hall, W. Routson and J. Weigl

Investigations of the path of carbon in photosynthesis from carbon dioxide to new cell material has been continued along the lines reported in previous Quarterly Progress Reports. Enough basic information and techniques have been accumulated to allow considerable branching out into separate lines of endeavor. Such projects now include kinetics of photosynthesis and respiration in plants, as determined simultaneously in $C^{14}O_2$, isotope effects involved in such reactions, analytical techniques in separation and identification of photosynthetic intermediates, organic and biosynthesis of these intermediates (labeled and unlabeled) for comparison with the unknown substance, chemical degradation of photosynthetic intermediates necessary for determination of the path of carbon, examination of the high molecular insoluble products of short photosynthesis which include fats, proteins and carbohydrates and studies on plants photosynthesizing under abnormal conditions. These abnormal conditions included such projects as studying the effects of malonate and fluoride inhibition. The different intermediates formed under these conditions yield clues to the mechanism of carbon reduction in the normal cell. Since the process of respiration is closely associated with photosynthesis, it is necessary to investigate both simultaneously. Fixation of carbon dioxide by reversal of respiration and fermentation decarboxylation reactions in the dark has been investigated and corroborates the results obtained when plants are allowed to form normal photosynthetic products for a short time in the light and then are allowed to respire these products in the dark under various conditions. The compounds most readily respired and their path of respiration can be readily ascertained.

Method for Investigation of Radioactive Intermediates.

Paper chromatography has been found almost universally applicable for separating the early intermediates in synthesis of cell material. The value of this tool has increased with our ability to identify more compounds, which appear as black spots in characteristic areas on radioautographs of the chromatogram. At present, four classes of compounds are being separated and identified chromatographically. These are sugars, amino acids, carboxylic acids and phosphate esters. Enough compounds have been studied to enable us to formulate several general principles. The most important of these is the calculation of R_F values (chromatographic coordinates) from solvent distribution coefficients which may be readily measured on known samples. Identity of the calculated coordinates with the position of an unknown spot on a chromatogram (or radiogram) suggest identity of the known and authentic specimen. Further chemical and physical comparisons are necessary for unequivocal identification.

Carboxylic Acids

According to Consden, Gordon and Martin the R_F of a solute is given by

$$R_F = \frac{A_L}{A_L + \alpha A_S}$$

where A_L is the fraction of cross-sectional area occupied by the mobile phase, A_S is

the fraction of cross-sectional area occupied by the stationary phase, and α, the distribution coefficient of the solute, is the concentration of solute in the stationary phase divided by the concentration of solute in the mobile phase. This expression can be written as

$$R_F = \frac{1}{1 + \alpha A_S/A_L}$$

The term A_S/A_L is a constant for a given paper and set of solvents while α is a characteristic of the solute and determines its position on the paper.

The gross distribution of a carboxylic acid between the stationary aqueous phase and the mobile organic phase depends on the distribution coefficient of the undissociated acid and on the degree of dissociation of the acid. The degree of dissociation depends on the pH of the aqueous phase and on the dissociation constant of the acid. Consequently, the gross distribution of a given acid, and hence its R_F value, is in general a function of two physical properties of the acid, its distribution coefficient and its dissociation constant(s) and one experimental condition, the pH of the aqueous phase of the chromatogram.

If neutral, non-buffered solvents are employed the pH of the aqueous phase at a given point depends only on the concentration of carboxylic acid at that point, and as the mobile phase carries the acid past this point there is a decreasing concentration and increasing degree of ionization of the acid with a resultant changing distribution of the acid between phases. The rate of movement of the acid, therefore, decreases when its concentration decreases and streaking is produced.

This effect can be avoided by maintaining the pH of the aqueous phase at a constant value. This is accomplished either by employing an acidic solvent or a buffered solvent. Lugg and Overell have used an acidic solvent to effect the separation of carboxylic acids. By using formic acid as a "swamping" acid, they suppressed the ionization of the test acids so that the R_F values depend principally on the distribution coefficients of the free acids.

It is possible to adjust the pH of the aqueous phase by employing buffers. This can be accomplished either by applying the buffer to the origin or by dissolving the buffer in the solvent beforehand. The R_F value then depends on both the distribution coefficient and the dissociation constant of the carboxylic acid.

It is desirable in two-dimensional paper chromatography to employ a low pH solvent in one direction and a higher pH solvent in the other direction so that a different order and degree of separation is obtained in the two directions. While it is possible to obtain good separations of a number of carboxylic acids with two-dimensional chromatograms which employ acidic solvents in both directions, the resultant positions of the acids tend to overlap those of amino acids, sugars and other plant constituents. The use of solvents of differing pH moves the acids to a region of the paper apart from the rest of the plant constitutents. Such "area" separation is desirable in analysis of plant extracts in that it circumvents preliminary fractionations.

The usual method of buffering in the phenol direction has been to apply the buffer to the origin along with the mixture of acids or cell extract. Since the buffer capacity thus obtained is limited, it is necessary to use very small amounts of acids. From one to five micrograms of acid gives satisfactory results. The colorimetric methods described by Lugg and Overell give best results for twenty micrograms or more so the tracer method of detection is preferable for this purpose.

Several carboxylic acids labeled with C^{14} have been synthesized and chromatographed to determine their positions with the solvents employed. In addition to malic, succinic, fumaric and tartaric acids, which were studied by Lugg and Overell, isocitric, glycolic and glyceric acids have been separated.

The relation of R_F values in an acidic solvent to the distribution coefficients is shown in Table 1. The R_F values and the distribution coefficients of the acids, of alanine and glucose were measured. Using the constants of alanine as a standard, the term $A_S \neq A_L$ was calculated and found to be 0.55. The R_F values of other solutes can then be calculated according to the expression

$$R_F = \frac{1}{1 + 0.55\ \alpha}$$

Comparison of the calculated R_F values with measured R_F values shows fairly good agreement and affords additional evidence that paper chromatograms of this type are partition chromatograms.

Table 1

Comparison of Measured and Calculated R_F Values in Butanol-Propionic Acid-Water Solvent

Solute	α	R_F (calculated)	R_F (measured)
Alanine	3.65	----	0.333
Fumaric	0.50	0.78	.72
Succinic	1.02	.64	.65
Glycolic	2.06	.47	.51
Malic	2.40	.43	.45
Isocitric	2.75	.40	.41
Glyceric	2.95	.38	.38
Tartaric	3.20	.36	.32
Glucose	5.75	.24	.20

Isolation and Identification of the "First" Product of Photosynthesis.

The radiogram of the products of 5 seconds of photosynthesis showed one major compound had been synthesized. It was assumed that this compound was directly in the path of carbon from carbon dioxide to hexose since its amount increased to a maximum with longer photosynthesis, and in experiments where the supply of labeled carbon dioxide was removed from the plants this compound was the first to disappear. It had been known from our earlier work that phosphoglyceric acid appeared in this area in the radiograms. Other laboratories working in this field had not been able to identify phosphoglyceric acid as an intermediate in photosynthesis. It was considered appropriate to isolate and identify this compound by the classical methods.

Six grams of Scenedesmus D-3 cells, which had been allowed to photosynthesize for 5 seconds in $C^{14}O_2$ before rapid killing in acetic acid-hydrochloric acid, was diluted with 18 g. of normal cells. The aqueous cell extract was concentrated and subjected to the usual isolation procedure for phosphoglyceric acid with several modifications. When the acid solution was neutralized to pH 7, the activity came down with a precipitate.

This phenomenon of adsorption is particularly pronounced with phosphoglyceric acid. When the solution was adjusted to pH 9, the activity was apprently displaced and readily washed off the solid. Addition of barium to the re-acidified solution gave a precipitate which was active, not at all characteristic of pure phosphoglyceric acid. The activity could be removed from this precipitate by repeated washing with 0.05 N hydrochloric acid but when this solution was neutralized no insoluble barium phosphoglycerate separated. This was due to the moderate solubility of the salt which was precipitated by addition of a volume of ethanol. Repeated dissolution in 0.05 N hydrochloric acid and precipitation on addition of alcohol gave a crystalline salt which had the properties of barium phosphoglycerate.

The phosphorus analysis and specific rotation, characteristically enhanced by molybdate ion, and solubilities were identical to those of the authentic material. The chromatographic coordinates of the material were those of authentic compound. When absorbed on the strong base anion exchange resin, Dowex A-1, and eluted with dilute sodium chloride, the elution curve of the radioactivity coincided exactly with the elution curve for phosphate analyses. This precluded the mixture of a trace amount of adsorbed high specific activity substance. Further evidence was obtained by hydrolyzing radioactive phosphoglyceric acid and demonstrating that the glyceric acid so obtained was homogeneous (by paper chromatography)and possessed correct distribution coefficient between water and ether.

This aggregate of evidence for the identity of the first stable product of carbon dioxide uptake by green plants during photosynthesis constitutes unequivocal proof of its identity as phosphoglyceric acid and has been accepted by the laboratories working in this field.

Malonate Inhibition Experiments

A study of the effect of inhibitors on the path of carbon dioxide reduction during photosynthesis has been started. Malonic acid has been employed and found to block the conversion of oxaloacetate to malate.

A twenty-four hour growth of Scenedesmus from a continuous culture was centrifuged and the resulting 1.3 cc. of wet, packed cells divided into two equal portions. One portion was suspended in sodium malonate buffer, pH 4.3, containing 5 mg. malonic acid per ml., the other portion was suspended in 50 ml. water. Both suspensions were kept in the dark for three and one-half hours after which they were again centrifuged and then resuspended in 100 ml. water with a small amount of fumarate buffer (pH 5). The suspensions were placed in thin water-jacketed vessels illuminated from both sides. After a forty-five minute period with unlabeled carbon dioxide and air, radioactive bicarbonate was added and the cells permitted to photosynthesize 90 seconds. The cells were killed, concentrated and analyzed by paper chromatography according to procedures previously described. The treatment for the inhibited and the non-inhibited cells was essentially the same.

The most pronounced effect of the inhibition was the disappearance of over 90 percent of the radioactive malic acid. It would appear that if malic acid were an intermediate in the regenerative reductive cycle, the operation of this cycle would be greatly reduced by malonate inhibition. To test this possibility the alanine from both cell extracts was degraded. It was found that the activity in the alpha- and beta-carbon atoms of the alanine was about the same in both cases, namely 35-40 percent. Consequently, it is believed that the cycle operation is not diminished by malonate inhibition and that malic acid is not, therefore, an intermediate in photosynthesis. It is further

indicated that malonate blocks the conversion of oxaloacetate to malate which may indicate a similarity to the enzyme system in animal tissues studied by Das (Biochem. J., 31, 1124 (1937)) where malonate was found to inhibit malic dehydrogenase. The amounts of succinic and fumaric acids were too small in both cases to permit any measurement of malonate inhibition of the formation of these acids.

High Molecular Weight Early Products (insoluble in 80 percent alcohol or water) of Photosynthesis.

Preliminary experiments have been done to determine the rate of incorporation of newly formed amino acids into proteins during photosynthesis. In day-old Scenedesmus, which are actively dividing and producing proteins, several radioactive amino acids are found in the protein hydrolysate after 5 minutes of photosynthesis. Serine and alanine are in largest amounts with lesser amounts of aspartic acid, glycine, tyrosine, phenylalanine and leucine. Others are believed to be methionine or valine and threonine. In barley seedlings, which are producing a cellulose structure, only serine and alanine are radioactive after 5 minutes of photosynthesis.

Hydrolysis of the insoluble radioactive products formed by barley in 5 minutes photosynthesis gave one major spot on the radiogram. This has been tentatively identified as levulinic acid derived from dehydration and decomposition of polyhexose structures.

Separation of Phosphate Esters by Ion Exchange Resins.

The sodium chloride elution curves of "Bios" brand phosphorylated compounds, glucose-1-phosphate, phosphoglyconic acid, glucose-6-phosphate, fructose-1, 6-diphosphate acid, 3-phosphoglyceric acid, from Dowex A-1 resin in the chloride form are being determined. It is intended that these elution curves can be used as a means of identification of the phosphorylated intermediates of photosynthesis.

The electrophoretic behavior of a mixture of radioactive inorganic phosphate and radioactive hexose monophosphates was investigated. A technique described by Garrison, Haymond and Maxwell of Crocker Laboratory of the University of California was used. The liquid sample was placed on a small filter paper and dried. This paper was then put in the center of a stack of filter paper (chromatopile) wetted with an electrolyte. The stack of papers was then placed between platinum electrodes and a ten volt potential placed across the stack of papers. After air drying, the radioactivity of each paper was determined. With sodium acetate as the electrolyte all of the radioactivity was found on the papers adjacent to the anode. No movement in the electrical field was observed when ferrous sulfate or ferric sulfate was used as the electrolyte. Nickelous acetate, cupric acetate and cobaltous acetate gave two regions of activity, one at the origin and the other at half the distance to the anode. Slight movement to the cathode resulted with use of aluminum chloride. These results indicate that complex formation of the phosphate ion occurs with some metallic ions, and the degree of complexing varies with the type of phosphate compound and electrolyte under investigation.

Kinetics of CO_2 Absorption in Plants.

The CO_2-analyzer which is used in this laboratory utilizes infra-red absorption by CO_2 gas. The isotope effect in photosynthesis was first observed with this instrument and it suggested possible differences in infra-red spectra of $C^{14}O_2$ and $C^{12}O_2$.

The infra-red spectrum of $C^{14}O_2$ has been measured and compared to that of $C^{12}O_2$.

The observed isotope shifts of the infra-red-active fundamentals are in accord with those calculated by means of the Teller-Redlich product rule:

$C^{12}O_2$	(obs.)	667.3	2349.3
$C^{14}O_2$	(obs.)	632 ± 2	2220 ± 5
	(calc.)	631.6	2223.7

This work was carried out in collaboration with R. K. Sheline of the Chemistry Department.

Photosynthesis in Higher Plants.

It was thought that there was a possibility photosynthesis in higher plants would differ considerably from that in the green algae. It had been shown in our earlier work that Chlorella and Scenedesmus utilized the same set of intermediates in photosynthesis except for minor variations in the sizes of the reservoirs of certain intermediates. We find that size of reservoirs of many intermediates such as glycine, glycolic acid and malic acid change considerably with the treatment given the plants. It was shown that phosphoglyceric acid was the first radioactive compound to be formed in appreciable amount and the maximum time for it to account for over 60 percent of the activity fixed was about 5 seconds of normal steady-state photosynthesis. Two higher plants, geranium, a dicotyledon, and barley, a monocotyledon, have been studied and shown to produce almost the same intermediates as found in the algae. The first products, the phosphoglyceric acids, are the same in all four plants. Radiograms of 2-5 seconds photosyntheses with these plants show only one major spot on the radiogram, phosphoglyceric acid. The most apparent difference between the higher plants and the algae is the participation of glycolic acid and glycine in photosynthesis by barley and geranium. If the plants are rapidly killed without any dark period after photosynthesis, glycolic acid and glycine appear in the radiograms. With a dark period subsequent to the photosynthesis no glycolic acid and glycine appear. This phenomenon is true to a very limited extent in Scenedesmus and to a marked extent in malonate-inhibited Scenedesmus. The role of glycolic acid in the cycle for regeneration of the two-carbon carbon dioxide accepting molecule is being investigated.

Relationships between Respiration and Photosynthesis.

A series of experiments have been peformed with barley seedlings and the algae Chlorella and Scenedesmus in which photosynthesis intermediates have been respired in the dark or light immediately following their synthesis. The analysis of the radiograms so obtained is not yet complete but the following general phenomena have been observed.

The intermediates from carbon dioxide to sucrose apparent after 30 seconds of photosynthesis have been identified as the phosphate compounds involved in the breakdown of hexoses in animal tissue by respiration. A fraction of this intermediate, drained off at the three-carbon stage, adds another active carbon dioxide to form four-carbon compounds which are split to regenerate new two-carbon carbon dioxide acceptors. During photosynthesis we have found that the Krebs cycle for oxidation of two-carbon compound fractions proceeds only very slowly. In the dark, the Krebs cycle begins to operate immediately and the characteristic respiration intermediates, succinic, fumaric, isocitric and glutamic acids, appear. These appear at the expense of the phosphate esters involved in sucrose synthesis. It now appears that the barley leaves are not capable of oxidizing sucrose whereas they rapidly respire the phosphate esters intermediate in its synthesis. Apparently, the free sucrose prepared in the leaf is protected from oxidation and reserved for use as an energy source in the growing, non-photosynthesizing parts of the plants

such as new leaves and roots.

If carbon dioxide is withheld from the plants in the light after short photosynthesis in $C^{14}O_2$, respiration of active intermediates occurs at a rate considerably less than that in the dark. It is felt that light inhibits plant respiration. This is borne out by independent measurements of respiration rates during photosynthesis previously reported from this laboratory.

The effect of preillumination of barley leaves in the absence of carbon dioxide followed by dark fixation of $C^{14}O_2$ demonstrated that higher plants as well as algae can synthesize sucrose and fats in the dark provided the energy is supplied by preillumination.

II QUARTERLY PROGRESS REPORT PROJECT 48B

W. H. Latimer, Director

A. Metals and High Temperature Thermodynamics

L. Brewer, L. A. Bromley, A. Searcy, L. Templeton, R. Edwards, R. McKisson, G. Elliott, Leonard Phillips and Donald Mastick

Thermal Conductivity of Gases

Construction of the apparatus for the determination of thermal conductivities of gases at high temperature has been completed and experiments are in progress.

Thermodynamics of CN gas

The values obtained for the heats of formation of Cn and C_2 are being checked to determine their accuracy.

Vapor Pressures of Metals

Work is progressing on the determination of the vapor pressure of aluminum. BeO is a satisfactory container at 1400 - 1500° C. TaC is satisfactory even at 2000°C. The vapor pressure of Fe is being checked using BeO and TaC containers.

Preliminary work on the determination of the vapor pressures of very refractory metals such as Re, Os, etc. by spectroscopic methods has been carried out.

Liquid Metal Systems

The construction of a new high temperature calorimeter for determination of heats of formation of metal alloys at high temperature is under way. The study of the U-Bi-Na system is continuing. A new technique of using a high temperature x-ray camera to speed up study of ternary phase diagrams is being tried. A new high temperature x-ray camera has been obtained.

Thermodynamics of Gaseous Oxides and Hydroxides

The study of the vapor pressure of Al_2O_3 by the effusion method is continuing. Mo has been found to be a satisfactory container up to 2200°C. TaC is oxidized by Al_2O_3 unless Al metal is present. AlO does not appear to be important, but it has not yet been established whether Al_2O_3 vaporizes undecomposed. The stability of FeO gas is being studied as a prelude to a search for FeOH. Work is starting on the study of the gaseous Mo oxides and hydroxides.

B. Basic Chemistry, including Metal Chelates

Z. Z. Hugus and K. L. Mattern

Lanthanum Chemistry

Repeated attempts to specify hydrogen ion concentrations have been met with a greater degree of irreproducibility than can be accounted for. The glass electrode has proven unsatisfactory for use in the presence of appreciable concentrations of tripositive ions and in the ionic strengths being used. With more reproducible buffering (measured values) the complexing constant for the(LaK^{++}) formation can be assigned and used in the study of complexing by other ions.

The Exchange of I^{131} Between Iodine and Iodate Ion

Runs in 1.0 M $HClO_4$ and in 0.2 M $HClO_4$, 0.8 M $LiClO_4$ show that the exchange rate varies as the 0.8 power of the iodate ion concentration.

It has been possible to assign a tentative value for the dimerization constant of iodic acid on the basis of measurements of the equilibrium, $6IO_3^- + 6H^+ + 5AgIO_3(s) + 3I_2 + 3H_2O$. The value is such that dimerization is very slight in any of the runs on the exchange reaction.

Measurements of the ultra-violet absorption spectra of KIO_3 and $NaIO_3$ solutions have been discontinued temporarily.

C. Ore Reduction

E. F. Orlemann, M. Lusby, Lewis Myers and Sterling Sorenson

Investigation of macro scale potentiometric determinations of U^{VI} by direct titration with chromous ion (Cr^{++}) has been dropped because of difficulty in establishing the same indicating electrode potentials during any single run. No progress was noted by further investigation into this problem.

A Model 512 Photovolt photometer used in conjunction with a Model R fluorimeter is being employed in the study of chelate formation between UO_2^{++} and TTA. The results of this study will be used in investigations of uranyl and uranous phosphate complexes which have just gotten under way. The precision fluorimeter mentioned elsewhere in this section will be employed in this investigation.

Amperometric microtitration of U^{VI} with Chromous Ion.

The difficulty with microtitration of U^{VI} using polarographic methods is probably inefficient stirring. Apparatus involving a Pt electrode functioning as a stirrer rotating at constant speed is under construction. The problem has been temporarily postponed.

U^{IV} - U^{VI} Studies with the Dropping Mercury Electrode

Diffusion currents of UO_2^{++} have been investigated in HCl, H_2SO_4 and H_3PO_4. Reproducible values are obtained in the first two media, and an examination of possible interferring ions is planned.

Results are erratic in H_3PO_4 over a range of hydrogen ion and phosphate ion concentrations. An attempt has been made to complex $PO_4^{\equiv}$ by adding $AlCl_3$, but this was ineffective. Fe^{+++} was found present in the reagent grade H_3PO_4 and $AlCl_3$ used. The study of the UO_2^{++} diffusion current in H_3PO_4 is postponed until more is known from solubility studies of uranyl phosphates. Reagents of higher purity will then be used.

The half wave potential of U^{IV} in 1.0 M and 0.1 M H_3PO_4 has been roughly located.

To measure the ratio of U^{IV} and U^{VI} concentrations, a pilot system that will come to equilibrium with a U^{VI} - U^{IV} mixture is being looked into. The potential of such a mixture will be a measure of the ratio of concentrations of reduced and oxidized forms. It is planned to use the dropping mercury electrode as the investigating tool. Possible systems are: $Fe(CN)_6^{\equiv}$ - $Fe(CN)_6^{\equiv\equiv}$, V^{+++} - VO^{++}, and I_2 - I^-. Considerable difficulty is being experienced in storing U^{VI} solutions.

A precision fluorimeter, designed to measure U^{VI} in quantities down to 1 x 10^{-9} grams has been designed and is under construction. Principle involves simultaneous measurement of fluorescence from a standard and an unknown solid solution of U^{VI} in NaF - KN_2CO_3 flux, comparison being made through a bridge circuit. Low order of fluorescence is picked up by the use of photomultiplier units.

D. Engineering Development of Plutonium Separation

T. Vermeulen, T. Hicks, Barney Rubin and Milton Davis

Pilot Scale Synthesis of TTA

TTA is now available in semi-commercial quantities from the Dow Chemical Company and accordingly, large batch preparations in this laboratory have been discontinued.

Kinetic investigation of the synthesis reactions has led to results that are usable for reactor design and a report on this subject is in preparation. The rate has been shown to be first-order in respect to addition compound (which is in equilibrium with methoxide and trifluoro ester), first-order in acetothienone and inverse first-order with respect to total alcohol concentration.

Solvent Extraction Utilizing the Chelate Process

A calculation method has been developed utilizing batch rate data to predict recoveries and purifications of the various elements. This method has been verified experimentally using tracer concentrations. Calculations indicate that two seven-stage mixer-settler units can recover 99.95 percent of the plutonium produced at Hanford with a decontamination factor of 10^{-6}.

Plans are in progress for the building of shielded equipment in order to study the recovery and decontamination of plutonium and uranium at high level activity so that above calculations may be checked experimentally.

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