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QUARTERLY REPORT

June, July and August 1949

September 27, 1949

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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

Chemistry of Neodymium, Samarium and Gadolinium

James C. Wallman and B. B. Cunningham

Chemistry of Neodymium.

An improved balance for measuring magnetic susceptibilities has been constructed. A permanent magnet is placed in an upright position to give a vertical displacement to the sample; this deflection is measured by a quartz fiber torsion balance of the Kirk-Craig-Gulberg type. The balance has a sensibility of approximately 0.001 micrograms. With the aim of elucidating the composition of the sodium vapor reaction products of rare earth trifluorides, the magnetic susceptibility of several compounds has been determined using this apparatus. Calibration of the balance is based upon observations using Mohr's salt, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, as the standard. The value of the effective moment of Mohr's salt used for calculating the specific susceptibility is 5.25 Bohr magnetons: $X = 29.6 \times 10^{-6}$.

Three preparations of NdF_3 gave specific susceptibilities of 28.94, 30.84 and 29.39 (unit of X is 1×10^{-6} cgs electromagnetic units). Seven sodium reductions of these trifluorides were made of which four resulted in black-coated pellets with pink cores. X-ray analysis indicated the presence of principally NdF_3 with only partial reaction to give the fluorite-patterned product presumed to be NdOF or NdF_2. Magnetic susceptibility measurements indicated no reduction: X values of 29.66, 30.02, 29.23 and 30.25 were obtained. Reduction of NdF_3 to NdF_2 should decrease the susceptibility by about 28 percent. Coprecipitation of CaF_2 and NdF_3 resulted in a product of susceptibility about 1/3 that of NdF_3 and reaction with sodium metal caused the susceptibility to increase, probably due to traces of iron impurity in the sample.

Chemistry of Samarium.

Reduction to SmF_2 is to be expected in the case of SmF_3 and magnetic measurements for two runs indicate reductions of 35 and 60 percent completeness: X of value 6.23 increasing to 12.32 and 19.99. Reaction of coprecipitated $CaF_2 \cdot SmF_3$ with Na resulted in a change of susceptibility indicating 100 percent formation of samarium difluoride.

Chemistry of Gadolinium.

The susceptibility of GdF_3 was measured as 132.6 and 127.0. Treatment of the GdF_3 with Na vapor at 1125°C gave products with susceptibilities of 126.8, 139.8, and 131.5. As in the case of NdF_3, no reaction product gave a susceptibility indicating even partial reduction to the difluoride and no product was obtained with

a pure fluorite x-ray pattern. One reaction did result in formation of GdF_3 with hexagonal lattice symmetry and of UCl_3 structure type, as opposed to the hexagonal LaF_3 type usually formed.

Contrary to results obtained earlier (see UCRL-311 and UCRL-382) the magnetic measurements on the rare earths indicate that the trifluoride-sodium metal reaction product is probably not a difluoride; however, none of the products tested exhibited a pure fluorite structure: an indeterminate amount of trifluoride is always present. Further work to obtain a pure fluorite-patterned product is in progress.

Chemical analysis of the reaction products would also indicate the composition and much effort has been devoted to developing a method of analysing for fluoride content. There are no semimicro gravimetric or volumetric analysis yields results of the accuracy required. A gravimetric analysis for the rare earth ion has been developed and appears to be the most feasible method of chemical analysis.

The Vapor Phase Hydrolysis of Lanthanum Trichloride

A. Broido and B. B. Cunningham

Notably absent from standard compilation of thermochemical data (such as those of Bichowski and Rossini, or those of Brewer, Bromley, Gilles and Lofgren) are data pertaining to the rare earth oxyhalides. Existing methods for the preparation of these compounds are based on purely empirical procedures. The oxyhalides nevertheless constitute an important class of compounds. The ease of formation of the oxychlorides and oxybromides, for example, is a major source of difficulty in the attempted preparation of pure samples of the corresponding trihalides. The presence of oxyhalide impurities not only introduces an element of uncertainty in all observations on the properties of the trihalide sample, but may have a notably deleterious effect on some of the chemical reactions of the trihalide - the reduction to metal by metallic reductants, for example. We have therefore undertaken a systematic investigation of the free energy of the reaction

$$RCl_3 + H_2O = ROCl + 2HCl$$

by measurement of the equilibrium constants at various temperatures. In the equation R symbolizes a rare earth cation.

It is intended that this investigation shall cover not only the available rare earths, but several of the actinide elements as well.

The initial measurements, some of which have been reported before, have been made on lanthanum.

We have now measured the equilibrium constant for the reaction

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

at several temperatures in the range 600-800° K. The constant was determined by a flow method in which samples of La_2O_3, mounted in a 12 mm diameter pyrex tube, were treated with N_2-H_2O-HCl mixtures of various chosen compositions. If the HCl/H_2O ratio exceeded the value of the quilibrium constant, the sample would be converted completely to the trichloride; if not, the oxychloride would result, regardless of which of the lanthanum compounds was present at the start.

The temperature of the sample was maintained at the desired value by means of an electrically heated tube furnace, the temperature being measured by an iron constantan thermocouple placed inside the furnace and in contact with the outside of the reaction tube. Previous measurements had indicated that the temperature inside and outside the tube agreed within 2°C.

The composition of the gas phase entering the tube was fixed at various values by bubbling pure nitrogen gas through aqueous solutions of HCl of carefully established composition and known temperature. The partial pressure of HCl was

occasionally checked by absorption in standard NaOH solution and titration of the excess NaOH with standard HCl.

For the most part, however, the partial pressures of HCl and H_2O used in the calculation of the equilibrium constants were computed from the known temperature and composition of the aqueous HCl solution by reference to the compilation of data by F. C. Zeisberg (International Critical Tables, Vol. III, p. 301)

For the early experiments, performed at 500° C, the identification of the products obtained were carried out by x-ray diffraction methods. The diffraction patterns were obtained and interpreted by members of the x-ray diffraction group working under Dr. D. H. Templeton. No measureable change in the lattice constants of any of the products, and no change in the value of the equilibrium constant with change in composition of the initial solid phase were taken as indications that the range of solid solution formation was negligibly small. The fact that the same value for the constant was obtained at flows of 6 cc/min and of 40 cc/min indicated that no appreciable error in computing partial pressures of the gaseous species inside the furnace was introduced by thermal diffusion effects.

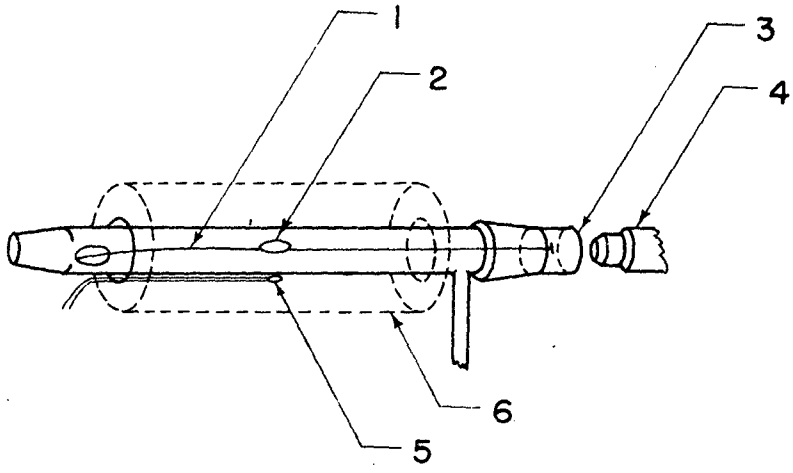
The method of investigating the equilibrium which has now been adopted is based on the fact that a weight change of about 20 percent results when $LaCl_3$ is converted to LaOCl. The sample is now mounted on a cantilever type quartz figer microbalance contained inside the reaction tube (See Fig. 1). The balance and optical system now in use is such that with a sample of ca 4 mg, the weight change during the reaction results in a displacement of the balance pointer of ca 4 mm and the position of the pointer may be measured to ± .02 mm. It was found that once the tube temperature reached a constant value no drift of the balance pointer occurred, and, except for occasional disturbances, vibration of the pointer was not serious.

This method of following the progress of the reaction may be used, not only to determine the equilibrium constant but also to determine the rate of reaction without disturbing the reaction itself. The equilibrium constant may be determined much more rapidly by this method, since it is necessary only to determine the direction of swing of the balance pointer (for a fixed HCl/H_2O ratio), and not to follow the reaction to completion.

As a check, the value for K 500° C ± 10, previously determined as 1.18 by x-ray diffraction methods, was redetermined using the microbalance. The value obtained for $K_{500° C \pm 2}$ was 1.14. The values determined to date are listed in Table I.

Table I

$T_{(°K)}$	K	ΔF
775 ± 2	1.14 ± .07	-0.2_0
739 ± 2	0.47 ± .03	1.1_1
701 ± 2	0.136 ± .012	2.7_8
665 ± 2	.036 ± .003	4.3_9



1. CANTILEVER TYPE QUARTZ FIBER MICROBALANCE

2. PLATINUM PAN CONTAINING SAMPLE

3. OPTICAL WINDOW

4. MICROSCOPE

5. THERMOCOUPLE

6. FURNACE

FIG. 1

Chemistry of Vitamin B_{12}

B. B. Cunningham and James C. Wallman

A sample of vitamin B_{12} for magnetic susceptibility analysis was obtained from Dr. Melvin Calvin. Previous work elsewhere has shown that the material has a molecular weight of about 1490 and contains one cobalt atom per molecule; the oxidation state and nature of the bonding of the cobalt is unknown and the present magnetic measurement was undertaken to provide this information. An organic Cu(II) compound was used as a check on the Mohr's salt standardization of the balance. The measured effective moment for the copper compound was 1.83 Bohr magnetons, in good agreement with many measurements on organic cupric compounds. The vitamin B_{12} had an effective moment of 4.46 Bohr magnetons indicating an ionic cobaltous compound. It is conceivable that cumulative errors in the measurement might permit of an actual value of 5.0 Bohr magnetons -- the lower limit for an ionic cobaltic compound. The presence of impurities in the B_{12} would lead to a misinterpretation of the data and measurements on material from different sources will be made. Restandardization of the balance with standards of more accurately known purity is also necessary.

B. Nuclear Properties and Transformations

Bombardment of Copper with Protons

R. Batzel and G. T. Seaborg

The reaction $_{29}Cu^{63}(p, 13z26a)\ _{17}Cl^{38}$ or $_{29}Cu^{65}(p, 13z28a)_{17}Cl^{38}$ has a calculated threshold of 100 ± 5 Mev if the reaction is considered to proceed $_{29}Cu^{63} + {}_1H^1 \longrightarrow 6\,{}_2He^4 + {}_1H^1 + n + {}_{17}Cl^{38}$. $_{17}Cl^{38}$ has been detected at energies considerably below this threshold. In order to determine an actual threshold for the reaction an excitation curve was run and the value obtained was 65 Mev. The cross section for the reaction at 85 Mev has been calculated to be $\sim 10^{-8}$ barns. Since the reaction cross section is so small, impurities in the copper might explain the yield below the calculated threshold. The copper is specified as 99.999 + percent pure, and the amount of impurities necessary to explain the activity is 10^{-3} percent with a cross section of 10^{-3} barns. To rule out contributions from some of the possible impurities cross sections for the formation of $_{17}Cl^{38}$ from K, Ca, Ti, Cr were determined. To rule out Sc and V impurities low energy bombardments were made and suitable fractions removed. All cross sections were found to be less than 10^{-3} barns and impurities checked found to be less than 10^{-3} percent. The results thus far indicate that the activity cannot be explained by impurities. Work has been started on the determination of the yield of recoils given off in the spallation of copper with 350 Mev protons. Thin copper foils alternated with 1 mil polystyrene sheets are bombarded with the beam intensity cut in half. At full intensity the polystyrene has been found to melt and burn. The recoils from copper are collected on the polystyrene and the yields determined.

Table I gives a list of the yields determined:

Table I

Isotope	Recoils Poly-Fraction	Copperfoil
$_{29}Cu^{61}$	1	1
$_{29}Cu^{64}$	0.70	1.36
$_{28}Ni^{57}$	0.31	0.05
$_{27}Co^{61}$	0.60	0.36
$_{27}Co^{55}$	0.80	0.15
$_{26}Fe^{52}$	0.17	0.02
$_{25}Mn^{56}$	1.14	0.12
$_{25}Mn^{52}$	1.33	0.30

All Yields are Calculated Relative to $_{29}Cu^{61}$.

Alpha Particle Decay in Rare Earth Isotopes

S. G. Thompson, A. Ghiorso, and J. O. Rasmussen

Several periods of alpha radioactivity have been discovered in the heavy rare earth isotopes. The bombardments and the results are summarized in Table I.

The 4 hour and ~ 1 day periods were identified as terbium isotopes by separations using an ion exchange column. The α/electron capture branching ratio of the 4 hour terbium isotope is at least 1 percent. An attempt to determine the mass number of the 4 hour isotope using the mass spectrograph with the transfer plate technique to observe alpha particle tracks was unsuccessful due to high background in the photographic plates. The low energy threshold for its production and the high α/electron capture branching ratio in the 4 hour Tb isotope indicates that alpha particle decay occurs in heavy rare earth isotopes of moderate neutron deficiency in contrast with the high neutron deficiency necessary to produce alpha particle decay in isotopes of gold and mercury. This fact together with the experimental observation above, that alpha particle decay was not observed in elements below europium suggests that the 82 neutron configuration is important just as the 126 neutron configuration is important in producing high alpha particle energies in isotopes above lead.

Table I

Summary of Results of Bombardments

In Production of Light Alpha Emitters

Target	Bombardment (Proton Energy) Mev	Time of Bomb. (Minutes)	Results		
			Alpha Period	Alpha Energy	Element Assignment
Sm_2O_3	200	12	No significant alphas		
Gd_2O_3	200	12	~7 minutes	4.2	
			4 hours	4.0	
Gd_2O_3	50	15	4 hours only (small yield)	4.0	
	75	15	4 hours only (fair yield)		
	100	15	4 hour 7 min. (small yield)		
	150	15	4 hours ~7 min. (both in good yield)		
Dy_2O_3	200	15	Possibly some ~4 minute		
			~7 minute	4.2	
			~20 minute	4.1	
			4 hours	4.0	
Pd metal	200	15	no alpha activity		
Dy_2O_3	200	140	~7 minutes	4.2	
			~20 minutes	4.1	
			possibly ~2 hours	?	
			4 hours	4.0	Terbium (by ion exchange column)
			~1 day	~3.65	Terbium (by ion exchange column)
			~6 weeks	~3.1	
Yb_2O_3	200	15	Many alpha periods similar to above not well resolved yet. 4 hour period observed.		
Pr_2O_3	50	10	No significant alphas.		
Te	200	15	No significant alphas.		
Nd_2O_3	200	15	No significant alphas.		
Sm_2O_3	75	120	No significant alphas.		

Neutron Deficient Rare Earth Isotopes

Betsy Jones and B. B. Cunningham

The characterization of Nd^{139} has been completed. Decay of the hard gamma radiation through ten half-lives gives a half-life value of 5.50 hrs. The Pr daughter is probably of the order of 1 min., and the mass number assignment was made by milking the 140 d. Ce^{139} which grew in with a 5.5 hr. half-life.

Chemical identification was affected by separating Nd and Pr on a 4 cm. ion exchange column. The activity breakthrough preceded the Pr by 5 hrs. and the peak separation was 9 hrs.

The radiation characteristics of Nd^{139} and its Pr^{139} daughter are as follows:

Radiation	3.1 Mev β^+	0.28 Mev e^-	K x-rays	1.1 Mev γ
Relative Abundance	0.06	0.06	1	0.15

Work is in progress on neutron deficient isotopes of Nd, Pr, Ce, and Os.

Bismuth Isotopes, Masses 198-203

H. M. Newmann and I. Perlman

Milking experiments of the type described in our previous report UCRL-382 have been continued in an attempt to prove the mass assignments of various Bi isotopes. A careful study has been made of the Bi parent-Pb daughter separation to determine if the separation were introducing trends that would affect the experimentally observed half-life of the parent. This study has shown that < 2 percent of the Bi parent is lost, and ~ 8 percent of the Pb daughter is retained with the parent per separation. The latter effect would cause one to observe a longer life of parent than actually existed. All previously reported values have been corrected for this effect, and are listed below along with new experimental results.

Bi^{203} (half-life based on yields of 52 hr. Pb): A 13 hr. half-life was previously reported on the basis of milkings performed at 25 hr. intervals. Correction for Pb retention changes this value to 12 hr. Milkings at 12 hr. intervals also give a value of 12 hr.

Bi^{202}, Pb^{202}: failure to observe 12 day Tl^{202} makes it impossible to learn anything about Bi^{202} from these experiments. This is consistent with Pb^{202} being long-lived or stable. In the most favorable experiment performed Tl^{202} should have been observed if Pb^{202} had a half-life less than 950 yr. This calculation is based on assumption that Bi^{202} and Bi^{201} yields are the same at the energy used (120 Mev), that Tl^{202} counts with one-half the efficiency of Tl^{201}, and that the half-life of Bi^{202} is 2 hrs. (See Templeton and Karraker, Quarterly report, UCRL-382.)

Bi^{201} (half-life based on yields of 72 hr. Tl obtained via 8 hr. Pb intermediate): The previously reported value of 87 min. has been shown to be incorrect by subsequent work. By extending the number of milkings over a long time it was shown that two Bi parents must lead to production of 72 hr. Tl. The longer isomer was shown to have a half-life of 110 minutes by milkings at 155 min. intervals following initial purification of Bi 4 hr. after end of bombardment. Both parents were observed in milkings at 50 min. intervals following initial purification of Bi 1 hr. after end of bombardment. Using the 110 min. value as the longer component gave 55 min. for the shorter. Milkings at 30 min. intervals beginning 1 hr. after bombardment also gave 55 min. for the shorter component.

Bi^{200} (half-life based on yields of 27 hr. Tl obtained via 18 hr. Pb intermediate): The previously reported value of 40 ± 17 min. was not expected to be very reliable. Milkings at 50 min. intervals following initial purification of Bi 1 hr. after end of bombardment gave a half-life of 33 min. Milkings at 30 min. intervals beginning 1 hr. after bombardment gave a value of 30 min. Weighted average = 32 min.

Bi^{199} (half-life based on yields of 7 hr. Tl obtained via 80 min. Pb intermediate): Previously reported half-life 25 min. is decreased to 22 min. when corrected for retention of Pb daughter in Bi-Pb separation. No new experimental results.

Bi^{198} (half-life based on yields of 1.8 hr. Tl via 25 min. Pb intermediate): Two attempts to repeat the previously reported results yielded no Tl activity shorter than 7 hr. Tl^{199}.

Assignment of Bi alpha activities: The 62 min. α-emitter would now seem most likely assigned to the shorter isomer of Bi^{201}. The 25 min. α-emitter still seems most likely to be Bi^{199}, although it may be a mixture of Bi^{199} and Bi^{200}. Enough bombardments of varying energy have been run to give the following thresholds for production of these α-emitters by proton bombardment of natural lead.

α activity	threshold
62 min.	<40 Mev
25 min.	50-60 Mev
9 min.	60-80 Mev

Bi^{205}, Po^{203}, Pb^{198}, Rb^{81} and Kr^{81}

D. G. Karraker and D. H. Templeton

Bi^{205}.

The previously reported Bi^{205} has been verified by a repetition of earlier experiments. It was produced by decay of cyclotron-produced Po, and from milking experiments it has been shown to be the daughter of the 1.5 hr. Po^{205}.

Its half-life, obtained by following samples containing about 90 percent Bi^{205}, is 14 days, over 5 half-lives. An aluminum absorption curve shows about 14 percent of the gross activity counted is due to electromagnetic radiation, and about half of the electromagnetic counts are due to a 1.7 Mev gamma ray, as shown by a Pb absorption curve.

Po^{203}

The half-life of Po^{203} has been determined to be 37 ± 7 minutes, over 5 half-lives by milking the 52 hr. Pb^{203} as the end-product of the K-capture decay chain $Po^{203} \xrightarrow{37\ min.} Bi^{203} \xrightarrow{12\ hr.} Pb^{203} \xrightarrow{5\ hr.}$

Pb^{198}

Milkings of the 1.8 hr. Tl^{198} from Pb produced in a cyclotron-bombardment of Tl has shown Pb^{198} to have a half-life of about 25 minutes.

Rb^{81}

An examination of mixed Rb^{81} and Rb^{82} activities on the Beta-ray spectrometer has revealed the K and L conversion lines of a 187 Kev gamma ray. These lines of electron are known from other work to be associated only with Rb^{81}, and furthermore, coincide exactly with the conversion line of a 13 sec. Kr isotope[1].

Although previous attempts had failed to detect the Kr daughter, it was found by flaming a sample of Rb in a crude spectrometer, then watching the growth of the β^--activity. The growth period corresponded to a half-life of 10 ± 8 sec.

Thus, the 13 sec Kr must be at mass 81, and the 5.5 sec Kr is probably mass 79, since these activities were produced with low energy protons on mixed Br^{79} and Br^{81}.

---

[1] Creutz, et. al. Phys. Rev. 58 88 (1940), also Barkas, et.al. P.R. 57 1087 (1940)

Search for Heavy Polonium Isotope

Jack M. Hollander and I. Perlman

The production and identification of heavy isotopes of Po and At is desirable, in order to relate their properties to the systematics of alpha decay. We have been attempting to produce these isotopes by means of spallation reactions induced in thorium and uranium by high energy protons from the 184-inch cyclotron.

The predicted half-lives for these isotopes are as follows:

	α	β (min)
Po^{219}	~1 hr.	1-10 min.
At^{219}	~10 min.	~5 min.
Po^{220}	~1 day	~1 day
At^{220}	1-10 days	~5-15 min.

We first timed the chemical separation of polonium such that isotopes of intermediate half-lives could be seen. A polonium fraction was examined in an alpha energy pulse analyser about one hour after bombardment, but no evidence for the characteristic α-daughters of Po^{219} or Po^{220} was found. The yield of Po^{210} was quite high, but was cut down considerably when bombardments were done at 100 Mev. Since it is desirable to have the Po^{210} heavy Po ratio as small as possible, subsequent bombardments have all been done at 100 Mev. (It is felt that the yield of heavy Po's will be roughly the same at 100 Mev as at higher energies.)

As a result of the foregoing experiments, we felt that the Po^{219} might be too short to observe after an hour's lapse, and that possibly we had not waited long enough to observe the growth of daughters from a long-lived Po^{220}. Thus experiments had to be designed separately for these two isotopes.

A subsequent 15 min. bombardment of uranium with 100 Mev protons, in which a polonium fraction was pulse analysed 25 minutes after bombardment, yielded no detectable Po^{219}. Pulse analysis showed only Po^{210} in the polonium fraction.

This experiment established that either:

(a) the half-life of Po^{219} is shorter than 5 min, or
(b) the yield of Po^{219} in thorium spallation is extremely small compared to that of Po^{210} where this is the case, the cross section for this reaction would have to be only ~0.01 percent that for Po^{210}.

Attempts to produce Po^{220} have been equally as fruitless. A 2-1/2 hour bombardment of thorium yielded only Po^{210}*, but no trace of α-daughters of Po^{220}

* No attempts were made to determine the yields or establish the presence of isotopes of Po lighter than 210.

grew into the sample in almost 24 hours. It is most probable in this case that the absence of Po^{220} is due to a very low yield, for with even quite a long half-life, we would certainly observe some activity due to the α-daughters Em^{220}, Po^{216} and Bi^{212}, if a significant number of Po^{220} atoms were present.

This work is being continued.

Low Mass Isotopes of Astatine

G. W. Barton and I. Perlman

Using the circulating beam of the 184-inch cyclotron, bombardments were made to determine the Bi(α,xn)At excitation function. By means of these bombardments it was hoped to be able to determine the most desirable energies for milking experiment bombardments. As a consequence of these experiments, though, it is possible to give the probable mass assignments to two known alpha groups, as well as half-lives for these isotopes. The pulse analyzer was used to watch the decay of the groups, and to determine the Po's remaining after decay.

Quantitative milking experiments have also been performed in an effort to associate Po daughters with At parents. In particular we have tried to find the 1.7 hr. At^{208} described by Earl K. Hyde in the next section of this report. The latest attempt still awaits pulse analysis, others show only the 7.0 hr. At with no perceptible alpha branching. A quick, easy satisfactory milking chemistry yet remains to be devised and some experiments were performed in hopes of improving it. All reactions so far tried were slow.

In view of the experiments performed the following is suggested.

At^{209}	$T_{1/2}$ = 5.7 hr.	α = 5.65 Mev
At^{208}	7.0 hr.	α not obs., $\sim$100% elec capt.
At^{207}	1.8 hr.	α = 5.76 Mev

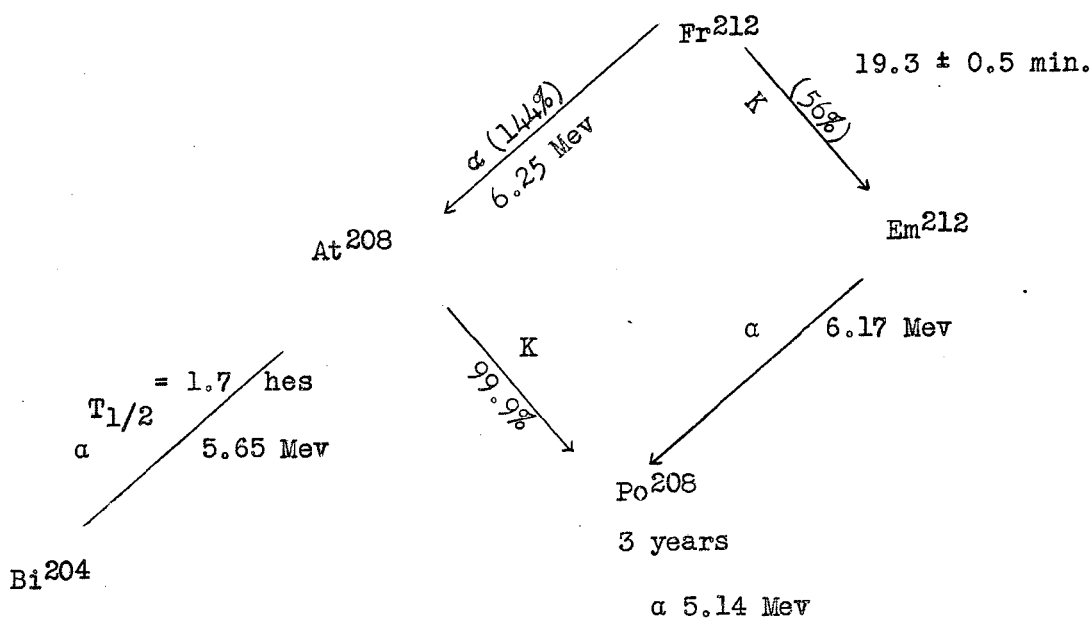
The redesign and rebuilding of the x-ray spectrometer so as to use a proportional counting tube is proceeding.

New Isotopes of Francium

Earl K. Hyde

Recent correlations in alpha decay systematics (Phys. Rev. 74, 1730 (1948)) in the heavy region have indicated that francium (element 87) in analogy to bismuth, polonium and astatine might have isotopes of abnormally high alpha stability in the region of 126 neutrons or less, i.e., $\leqslant Fr^{213}$.

These have been looked for in francium fractions isolated from short bombardments of thorium metal with 350 Mev protons in the 184-inch cyclotron. Fr^{212} has been found, and its decay scheme worked out as diagrammed below.



Some evidence has been found for Fr^{211} decaying by successive orbital electron capture to At^{211} with a half-life of roughly 8 minutes.

In a further search for new isotopes of francium, Fr^{222} has been prepared and identified in a thorium target bombarded with 100 Mev protons. Fr^{222} is a 14 ± 2 minute β^--emitter decaying to the α-chain Ra^{222}, Em^{218}, RaC'. The identification of these daughter activities by pulse analysis constitutes the proof for Fr^{222}.

Excitation Function Work on Thorium

W. W. Meinke and G. T. Seaborg

The proton excitation function work previously reported[1] has been extended to deuteron and alpha particle bombardments of thorium, protactinium being separated and counted each time.

The curve obtained for the (d,7n) reaction is very similar to the one reported for the (p,6n) reaction[1] in that it rises to a peak (with a maximum 8 times the value at full energy) immediately after the threshold.

The (α,p8n) reaction on thorium gives a slowly varying excitation function with a broad maximum at about 150 Mev gradually dropping to 1/3 maximum at 380 Mev.

A curve for the Al^{27} (d,αp) Na^{24} reaction for 194 Mev deuterons has also been determined.

These excitation functions are being rechecked and will be published later in a report.

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[1] W. W. Meinke and G. T. Seaborg, UCRL-382, pp. 15-17, June 30, 1949.

Fission Product Yield Distribution from Bombardment of Natural Uranium with 350 Mev Protons

R. L. Folger, H. G. Hicks, J. M. Miller, G. H. Higgins and G. T. Seaborg

An indication of the β^- Energy of Ni^{66}.

A nickel fraction was separated from other fission product activities and its decay characteristics studied. An aluminum absorption curve was obtained soon after separation, and 2.6 hr. Ni^{65} identified both by its β^- energy and its half-life. The decay curve was followed through several half-lives of the 56 hr. Ni^{66} tail. Determination of the fission yield of Ni^{65} placed it on the curve drawn through Fe^{59}, Co^{61} and Cu^{67}. Assuming that the yield of Ni^{66} should also fall on the curve, the required growth factor $Ni^{66} \longrightarrow Cu^{66}$ (5 min. Cu) becomes 1. This indicates that within the limits of error (5-10 percent), the β^- particles from Ni^{66} were not counted through 5.1 mg/cm^2 absorber (air space and counter window). Therefore, it is suggested that the β^- energy of Ni^{66} is $<$150 Kev.

Independent Yield Determinations.

a) Chain 97 - $Zr^{97} \xrightarrow[\beta^-]{17\ h} Cb^{97} \xrightarrow[\beta^-]{68\ m}$

Independent determinations were made on the fission yields of Zr^{97} and Cb^{97}. All of the Cb^{97} found could be accounted for by growth from Zr^{97}. The independent yield of Cb^{97} is therefore zero within 10 percent error (rel to Zr^{97}).

b) Chain 111 $Pd^{111} \xrightarrow[\beta^-]{26\ m} Ag^{111} \xrightarrow[\beta^-]{7.5\ d}$

The independent yields of these isobars were measured by separating the Ag^{111} daughter immediately after bombardment and (from another aliquot of the same target solution) after all of the Pd^{111} had decayed. From the equations for radioactive decay one can derive an expression for A_2 (the activity of the daughter) of the form

$$A_2 = aR_1 + 6R_2$$

where R_1 and R_2 represent independent rates of formation (proportional to σ) of the parent and daughter respectively. α and b are functions of the parameter = (time after end of bombardment at which Ag separated from Pd). By obtaining the activities at two different times of separation, it is possible to solve for the unknowns R_1 and R_2. The independent yield of Ag^{111} has been determined to be zero within 10 percent error (rel. to Pd^{111}).

c) Experiments are in progress to determine the relative yields of Ba, La, and Ce in chain ^{141}.

Ba Isotopes Obtained in Fission of Uranium with 350 Mev Protons.

The Ba fraction from an 8 hour bombardment of uranium with 350 Mev protons was purified for mass spectrographic analysis by carrying 100 μgm of Ba carrier alternately on $Sr(NO_3)_2$ and $PbCrO_4$. The final $PbCrO_4$ ppt was metathesized with HCl-ether reagent which complexed the Pb and left a precipitate of $BaCl_2$. This precipitate was metathesized to $BaSO_4$ with 1 drop H_2O and 1 drop 0.5 N H_2SO_4. A transfer plate was placed over the mass spectrograph collector plate after the run was completed. After about 3 days the transfer plate was developed, showing lines for Ba^{131}, Ba^{133}, Ba^{135} and developed, showing lines for Ba^{131}, Ba^{133}, Ba^{135} and Ba^{140}. A second transfer, kept in contact with the collector plate for about two weeks, showed lines for Ba^{131} and Ba^{140}. These results may be taken as confirmatory evidence for the mass assignment of the 12.0 d K-capture activity to Ba^{131}. Analysis of the Ba fraction decay curve shows a 30 hr. line in independent abundance 0.59 relative to Ba^{140}. It seems likely that this is largely due to Ba^{135m}. The appearance of light isotopes in the Ba fraction casts doubt upon the validity of Ba^{140} as a true measure of the yield of mass 140. The primary product of mass 140 might be La^{140}, Ce^{140} or even Pr^{140}. Independent measurements along chain 141 should help to answer this question.

Plutonium and Neptunium Isotopes

D. A. Orth and G. T. Seaborg

Attempts have been made to determine the branching ratio of Pu^{234} and Pu^{232} for decay by orbital electron capture and by alpha emission and hence determine the alpha half-life.

Pu^{234}(9 hr. α,k) was made by α's on U^{235}. The alpha decay of the samples was followed on the pulse analyzer and the L x-rays were followed on a proportional tube also connected to the pulse analyser. The L x-rays contained an unusually large component from Pu^{237} (40 d K) so that experiments were repeated on Pu^{234} made from U^{233} in order to eliminate Pu^{237} and to attempt to observe the growth of Np^{237} (4.4 d K) in the x-rays.

From these experiments a value for associated x-rays and α's were obtained, but the interpretation rests on several assumptions. Work by A. Ghiorso indicates that the counting yield for x-rays on the proportional counter is 1 percent, and experimental results are that 1/2 to 1 L x-ray is seen per capture depending on the amount of gamma conversion. Assuming 1/2 L observed per disintegration to get an upper limit, and the 1 percent counting yield, then $K/\alpha \leq 33$ or the $\alpha T_{1/2} \leq 13$ d.

Pu^{232}(37 min. α,K?) was re-examined in an attempt to determine a branching ratio: Samples of Pu^{232} were milked for Np^{232} (14 min K). No L x-ray activity was observed in the milking, however, the Pu^{232} α counting rate was very small ($\sim$ 20 dis/min.) so that the assumed counting yield and limits of detection for x-rays allows a limit of $K/\alpha < 100$.

The absence of x-rays in the milked Np fraction also indicates the absence of any appreciable amount of the unknown Pu^{233} activity, since the daughter, Np^{233} (32 min. K), would have been observed.

Previous attempts to measure the beta energy of Np^{236}(22 hr. β^-) produced by bombarding U^{235} with deuterons failed since there was 5 percent U^{238} contamination in the target, which produced sufficient Np^{238} and Np^{239} to mask the Np^{236} beta completely. The availability of high purity U^{235} for bombardment work allowed absorption curves to be taken on Np^{236}; Be absorptions indicate a beta energy of 0.5 Mev. No gamma rays are observed to be associated with this isotope.

Beta-Spectrometer

F. L. Reynolds and G. D. O'Kelley

A magnetic beta spectrometer of the double focusing type has been under construction for several months, and is now in operation. The double focusing principle was used because of the high transmission which may be obtained with good resolution. There have been adequate treatments of the principle elsewhere, and only a brief description of this instrument will be given here.

The magnet is ring-shaped, of 1010-Hat Rolled steel. Double focusing is achieved by shaping the magnetic field according to the relation $H(r) = Ho \sqrt{ro/r}$.

The necessary preface shape was calculated, and the steel was carefully machined to $\pm$ 0.003 inch. A flip coil and ballistic galvanometer were used to establish the linearity of the field current relation from about 10 gauss at minimum current up to 575 gauss. From the characteristics of the steel used, there is no reason to suspect any deviation from linearity at our present maximum current of 12 amperes (800 gauss). Having proved the linear dependence of field upon current, the latter is used in actual practice as a measurement of the momentum.

The magnet current is supplied by selenium rectifier and regulated electronically to about 0.1 percent.

An electron trajectory with an equilibrium radius, ro = 25 cm., is used. The electron beam is defined by two polystyrene baffles placed 18° and 239° from the source, with a 1/4 inch collimator over the detector (G-M tube). The double focusing principle dictates that for the field shape employed, the detector must be located at a point $\pi\sqrt{2}$ radius, or about 255°, away from the source.

Resolution measurements on the "F" line of ThB, using thin, "point" sources indicate the optimum resolution to be about 1 percent, for a measured geometry of 0.42 percent. This figure for the geometry is probably low, and it is hoped that better measurements will indicate a geometry of 0.5 percent or greater.

Counters have been used with both mica and thin (0.4 mg/cm^2) nylon windows. The counter is placed in the vacuum tank and pumped out with the vacuum tank, and then filled with a mixture of 10 percent alcohol and 90 percent argon to a total pressure of 4.0-4.5 inches of mercury. The pressure in the vacuum tank is about 2×10^{-5} mm of mercury.

Calibration runs have been made using the "F" and "I" lines of ThB, as well as 330 day Cd^{109}, which decays by electron capture to Ag^{109m}, a 45 sec. isomer with an 87 Kev internally converted gamma-ray. Annihilation radiation calibrations have been made, but with rather poor resolution on the photoelectron lines. The 0.4112 Mev gamma ray of Au^{198} will be run in the near future.

Some of the isotopes investigated are 18 hr. Pb^{200}, 52 hr. Pb^{203}, 5 hr. Rb^{81} and several Bismuth isotopes. However, more detailed investigations will be necessary before interpretation of the data becomes possible. A sample of Am^{241} shows electron peaks at 30, 33, and 46 Kev. Again, no interpretation of the data will be attempted at this time.

Current plans include a program of more extensive calibration, especially in the low energy region, and improvement of the counting equipment, including the possible installation of a proportional counter.

Mass Spectrograph

F. L. Reynolds

In addition to the radioactive lanthanum (19.5 hr. La^{135}) reported in the last quarterly report UCRL-382 a shorter life lanthanum (4.5 hr. La^{133}) has been identified on the mass spectrograph. This isotope was made by bombarding a cesium salt with alpha radiation. Transfer plates made from the original mass spectrograph plate showed after 24 hours transfer time both the 19.5 hr. La^{135} and the 4.5 hr. La^{133}. An additional tranfer plate placed on the original for a subsequent 72 hours showed only the longer life isotope La^{135}. Mass assignment was made by the position of these radioactive isotopes relative to stable La^{139} present on the original plate. La^{135} decays by K-capture, while La^{133} is a positron emitter.

After several attempts on trying to get a normal tin spectra from a thermal source for mass spectrograph work a successful tin spectra was obtained from tin oxide on a tungsten filament at temperatures around 2300°C. The "loss factor" is greater than 10^7 and considerable amount of activity will be needed to work this element satisfactory in the mass spectrograph.

Considerable work has been done during this period on the element plutonium. Abundance ratio determinations on neutron irradiated samples from the Hanford pile were obtained. This data is of value for cross section calculations and has helped in checking half-life calculations. In addition to the isotopes already known a new isotope of plutonium was found at mass 242. Attempts have been made to separate enough Pu^{239}, Pu^{240}, Pu^{241} and Pu^{242} isotopes on a platinum foil to be able to transfer the alpha radiation as visible tracks on an Eastman N.T.A. photographic plate. From this experiment an interesting check on the half-life of Pu^{240} was obtained. By counting the number of tracks from Pu^{239} and from Pu^{240} and knowing their abundance ratio, the half-life of Pu^{240} calculated to be about 5.54×10^3 years $\pm$ 2 percent. Insufficient number of tracks at mass 242 indicates that the half-life of Pu^{242} must be long. The chemical work connected with the above determinations was done by Thompson and Street of this laboratory.

An active Ba sample submitted by R. L. Folger showed the presence of four radioactive isotopes at masses 131, 133, 135 and 140 after a 3 day transfer from the original plate. An additional transfer exposed for two weeks to the original plate showed only radioactive masses 131 and 140. This showed that Ba^{131} and Ba^{140} were longer life isotopes than Ba^{133} and Ba^{135}. All of these isotopes have been previously reported, this work may augment the class status of Ba^{131} and Ba^{135}. This experiment will be reported in full by R. L. Folger. The above constitutes the findings as far as the mass spectrograph work is concerned.

Spontaneous Fission

R. L. Shuey

Experiments studying spontaneous fission are being continued. This experiment fits into two classes: spontaneous fission rates and spontaneous fission fragment energy distribution.

Spontaneous fission rates are being studied in the equipment indicated in Figure 1.

So far the equipment has been used to study fission rates of the order of 1 count per minute and the accuracy to date is only 5 percent. The plotting equipment, primarily designed for energy distribution work, has been included just for interest and not as an energy measuring device. All ionization chambers use an argon and CO_2 mixture and operate on a flat portion of the E/p vs velocity curve.

An attempt is being made to install this equipment in a Standard Budd cabinet with line filters and complete r.f. shielding added. If successful, it will provide a convenient laboratory instrument.

The present limitation on the accuracy is the generation of spurious counts originating in the preamplifier. These counts are not an extension of the noise spectrum and it is believed they can be eliminated by preamplifier redesign. The construction of a new ion chamber and preamplifier is almost complete.

The fission fragment energy distribution equipment is essentially that previously shown in the block diagram connected to each side of a double ionization chamber. The source is mounted on a thin foil between the chambers. This equipment has been run on alpha particles and test pulses and as yet is not satisfactory. It is expected that the following steps will be necessary to insure adequate performance.

a. Electrical shielding like the fission rate apparatus.
b. Redesign and modification of ionization chamber to give less energy spread for mono-energetic particles.
c. Redesign of pulse extender for greater accuracy.

These modifications are at present being made.

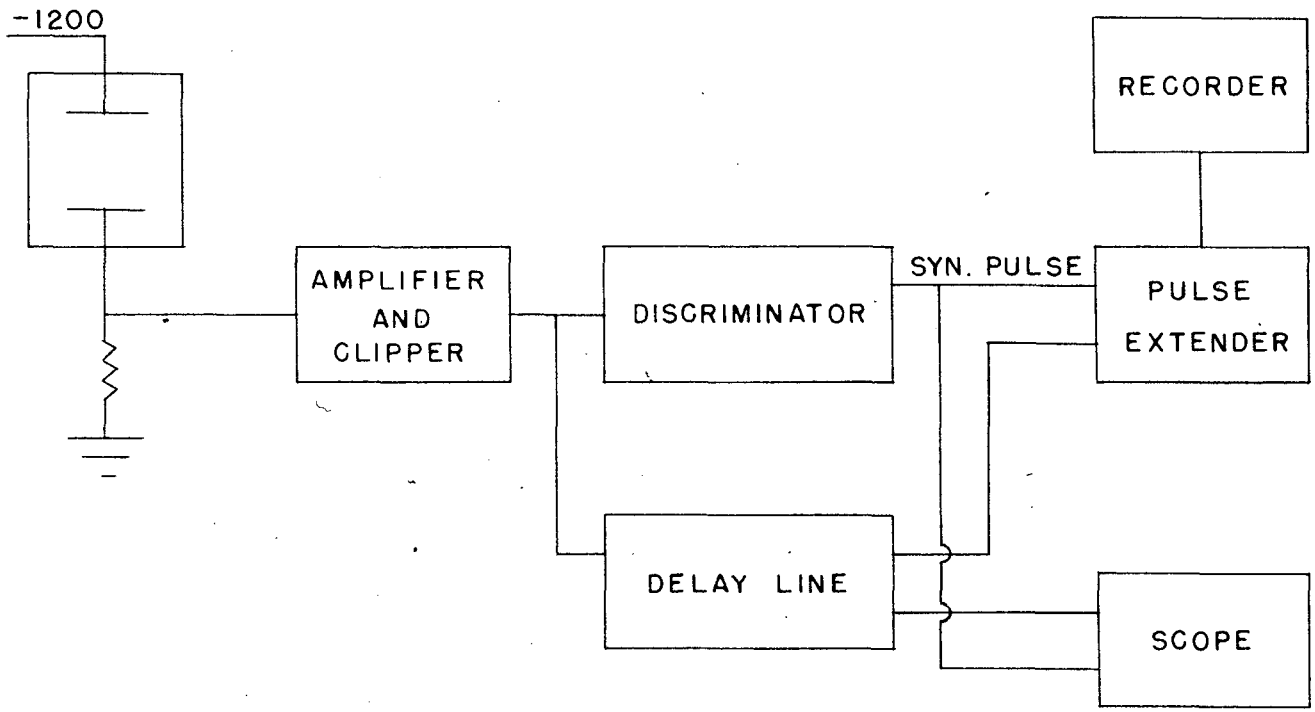

-1200
AMPLIFIER AND CLIPPER
DISCRIMINATOR
SYN. PULSE
RECORDER
PULSE EXTENDER
DELAY LINE
SCOPE

FIG 1

14178-1

C. Chemistry of Astatine and the Preparation of Certain Compounds

R. F. Leininger

The chemistry of this group has been somewhat inactive during the period being reported since the 60-inch cyclotron has been down for repair. All of the materials used in this research are produced in the 60-inch cyclotron.

Special equipment has been prepared, however, for future experiments on astatine.

1. Special glass ware.
2. A still for redistilling all water used.
3. A new form of the electrolysis apparatus described in previous quarterly reports.

The following special samples have also been prepared:

1. Astatine from the 184-inch for Hugh Bradner.
2. Special collimated alpha samples for proportional counter experiments.
3. Alpha standards were prepared from natural Uranium to replace those in use made of enriched materials.

D. Bio-Organic Chemistry Group

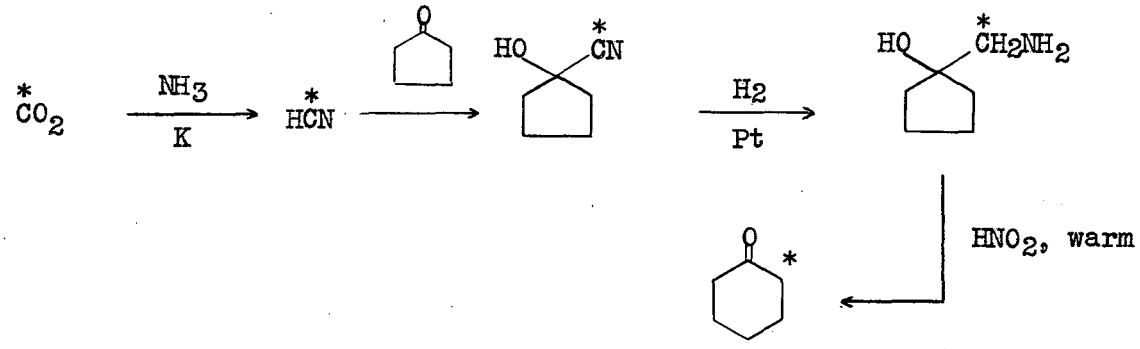
B. M. Tolbert

Synthetic and Experimental Chemistry

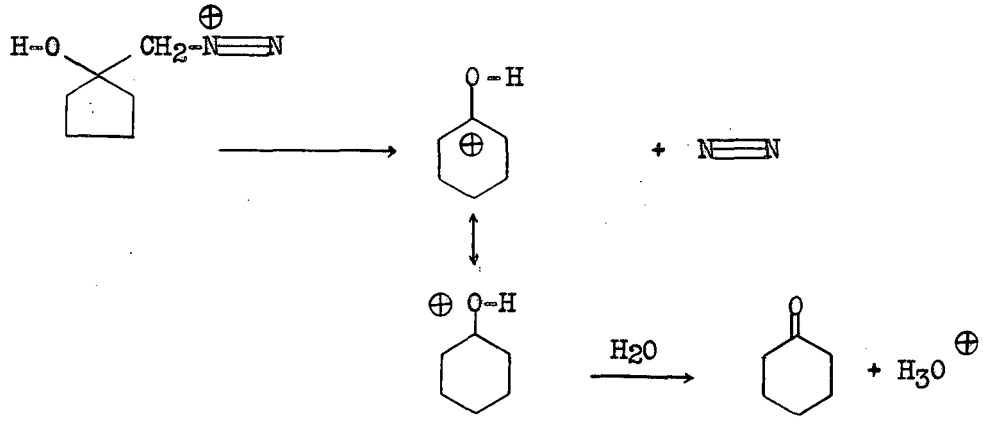
M. Calvin, B. Tolbert, P. Adams, R. T. Arnold, R. Bartsch, A. Fray, H. Hauptmann, D. Hughes, E. Jorgensen, B. Neivelt, R. Ostwald, R. Selff, Y. Stone and W. Tarpey.

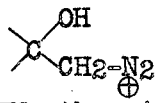
Experimental Chemistry.

Cyclohexanone-2-C^{14} -Conversion of 1,2-Amino Alcohols to Carbonyl Compounds. The study of the Tiffeneau ring expansion has continued and a preliminary phase of the work completed. The reactions involved are:



This rearrangement offers possibilities for the preparation of cyclic ketones containing isotopic carbon. Unfortunately, no detailed directions were published for the conversion via the cyanhydrin of cyclopentapentanone into cyclohexanone. The reaction mechanism probably involves an intermediate diazonium cation which rearranges spontaneously



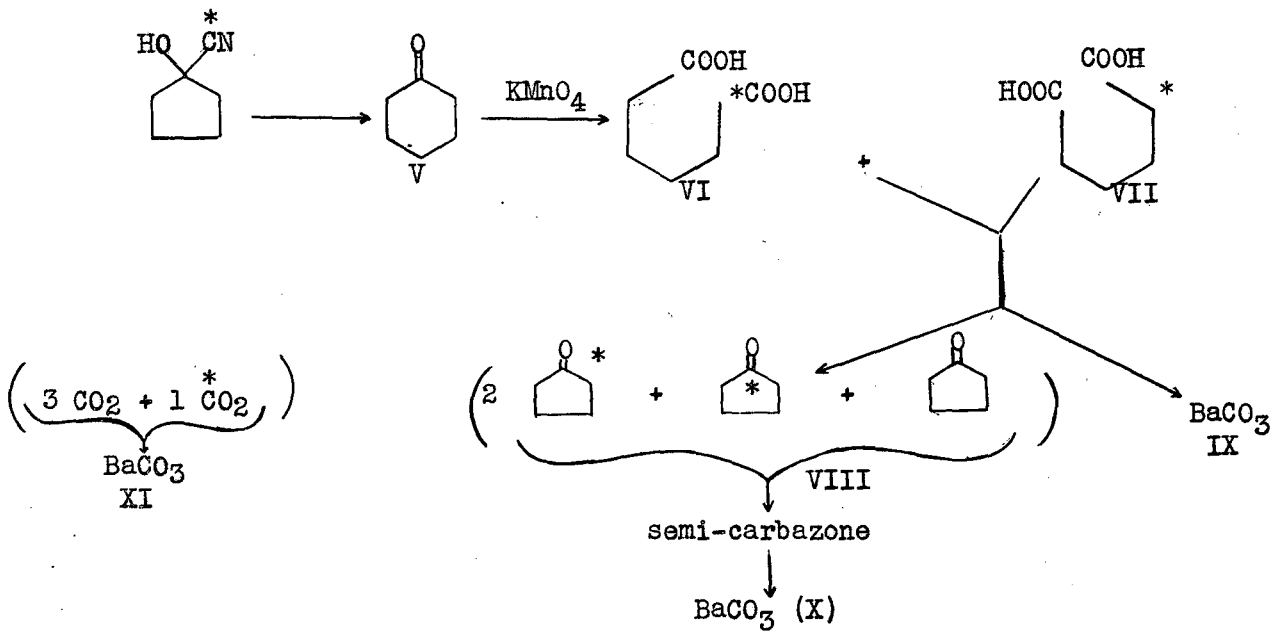
according to an intramolecular S_N^2 reaction in which a methylene group (bonded to the  group) makes a back attack against the methylene group of $-CH_2-\overset{\oplus}{N}\equiv\overset{\oplus}{N}$, the nitrogen molecule being eliminated from the front of the tetrahedron.

Several routes to cyanhydrins are in common use: (a) Direct reaction between cyanide ion and bisulfite addition compounds; (b) Direct addition of anhydrous hydrogen cyanide to carbonyl compounds in the presence of cyanide ion as a catalyst; (c) A modification of method (b) in which the carbonyl compound (dissolved in ether) is supported over a solution of aqueous cyanide and HCN is liberated slowly at low temperature by the dropwise addition of a strong acid. In this work all three procedures were examined, and (c) was finally chosen as being best adapted to the current problem. Cyanhydrin prepared from bisulfite addition compounds contained some poison which interfered with the subsequent reduction. Method (b) gave mechanical difficulties and inconsistent results were obtained.

Hydrogenation of Cyanhydrin. During the catalytic hydrogenation of cyanhydrins in acetic acid solution containing hydrochloric acid, considerable hydrogenolysis of the tertiary hydroxyl group occurs and, in the present case, leads to the formation of cyclohexanol (from + HONO) and this contaminates the final ketone unless a careful fractionation is carried out after the hydrogenation step. It is believed that less reductive cleavage occurs and a more pure cyclohexanone obtained when the cyanhydrins were reduced in ethanol (with either platinum or Raney nickel) containing acetic acid, but no concentrated hydrochloric acid. For unknown reasons cyanhydrin prepared from synthetic cyanide samples gave considerable trouble in the hydrogenation and the high specific activity preparation was a failure on this account.

Location of Labeled Carbon Atom. Using C^{14}-labeled cyanide, the previously proposed scheme should lead to C_2^{14} isotopically homogeneous cyclohexanone (V). In order to establish this fact, (V) was oxidized to the two isotopic adipic acids (VI) and (VII) and these cyclized to the mixture of isotopic cyclopentanones (VIII). The carbon dioxide liberated was collected in alkali and precipitated as barium carbonate (XI) for measurement of activity.

If "X" represents the total activity per mole of adipic acid cyclized, "3X/4" should be present in the cyclopentanones (VIII) and "X/4" in the carbon dioxide liberated (assuming no isotope effect). For measurement the adipic acid (VI + VII) and cyclopentanone semi-carbazone were converted to barium carbonate, giving (IX) and (X).



From the above it can be seen that the activities expressed in terms of dis/min/mg of barium carbonate in (IX), (X) and (XI) should be found in the following ratios:

X/IX = 0.750; XI/IX = 1.50

Two sets of data on differently combusted samples and measured separately are as follows:

IX	982		IX	1026	
	982	aver. = 982 dis/min/mg		1004	
				1005	
				986	aver. = 1005 dis/min/mg
X	754		X	713	
	730	aver. = 742 dis/min/mg		761	
				776	
				769	aver. = 755 dis/min/mg
XI	1487		XI	1491	
	1508			1496	
	1481			1530	aver. = 1506 dis/min/mg
	1457	aver. = 1482 dis/min/mg			

X/IX = 0.756; XI/IX = 1.509 X/IX = 0.751; XI/IX = 1.499

There can be little doubt that all of the C^{14} is in the 2-position in the synthetic cyclohexanone.

Experimental work is now in progress to simplify and improve the procedure.

Isotope Effect in the Decarboxylation of Malonic Acids: - Previous work in this laboratory has indicated that there is an isotope effect in the decarboxylation of malonic acid and bromolalonic acid. In an extension of this work a substituted malonic acid which would decarboxylate at a lower temperature was sought. Blicke and Feldkamp (J. Am. Chem. Soc., 66 1087 (1944)) have reported that methyl-α-naphthyl malonic acid decarboxylates at room temperature, and so the preparation of this compound labeled in the carboxyl group with C^{14} was undertaken.

A review of the literature indicated that one of the best methods in the synthesis of this and similar compounds would be to use α-naphthyl glycolic acid as the first intermediate. The plan was to replace the hydroxy group of this compound with halogen, the halogen with C^{14}-labeled cyanide and to hydrolyze the resulting nitrile in basic medium. Upon making this solution acid it was hoped that the resulting substituted malonic acid would spontaneously decarboxylate.

If desired, the α-naphthyl glycolic acid could be readily oxidized to α-naphthyl glyoxylic acid, which could then be converted to variously substituted α-naphthyl glycolic acids by the addition of the desired Grignard reagent to the keto group.

Of the several methods of preparing α-naphthyl glycolic acid, McKenzie and Dennler (J. Chem. Soc., 1599, (1926)) had indicated that addition of α-naphthyl Grignard reagent to chloral followed by hydrolysis of the resulting trichloro alcohol was the best. Some time was spent attempting to duplicate their results but with little success; only 5-10 percent yield could be obtained where yields of 50 percent were reported. The chief difficulty seemed to be in the hydrolysis step but various modifications of the procedure failed to materially improve yields.

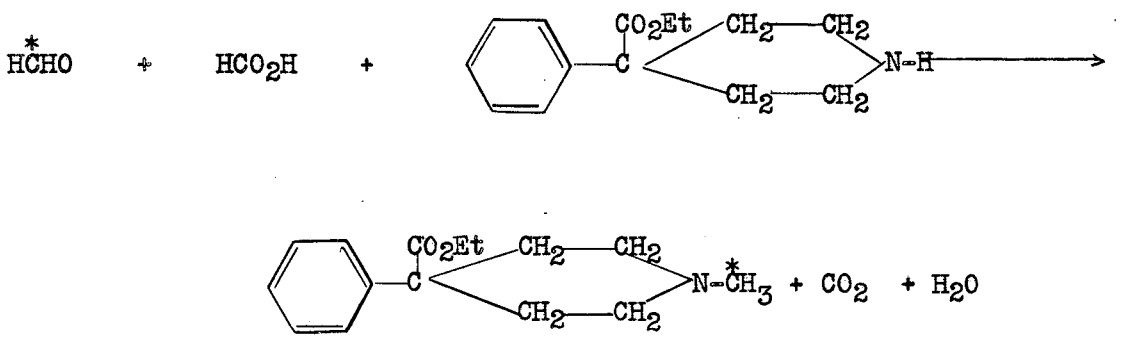
An attempt was next made to prepare α-naphthyl methyl glycolic acid directly by the addition of α-naphthyl Grignard reagent to ethyl pyruvate. The corresponding reaction with isoamyl pyruvate had been studied by Grignard (Compt. rend., 135, 628 (1902)). This reaction gave α-naphthyl methyl glycolic acid in 40 percent yield.

The replacement of the hydroxy group in the α-naphthyl methyl glycolic acid by halogen was first attempted by the method of Fittig and Kast (ann., 206, 28 (1881)) for the corresponding phenyl compound. This consisted of reacting the hydroxy acid with concentrated HBr or HCl at room temperature, but, in this case, no reaction took place under these conditions. Upon heating the concentrated HCl solution to boiling and immediately cooling, impure chloro acid was obtained. With longer heating no chloro acid was obtained but a new acid, M.P. - 161.5-162.5° C, which did not contain halogen was obtained. If the hydroxy acid was heated with concentrated HBr solution to boiling and immediately cooled, this same unknown acid, M.P. - 161.5-162.5°, was obtained.

With $SOCl_2$ or PBr_3 as halogenating agents, equally unsatisfactory results were obtained. It was finally found that on heating the hydroxy acid at 50° C for several hours with concentrated HCl saturated with $ZnCl_2$, fairly pure chloro acid, M.P. 147-8°, was obtained. The preparation of intermediates in the synthesis of α-naphthyl methyl malonic acid is continuing.

Synthetic Chemistry

The Role of Formaldehyde and Formic Acid in the Preparation of Demerol-N-Methyl-C^{14}: - In the last Quarterly Progress Report, UCRL-382, the preparation of labeled Demerol, a sedative and analgesic, was described using formaldehyde-C^{14} and inactive formic acid in a reductive methylation:



The role of the two reagents, formaldehyde and formic acid, in this reaction is still questioned. In a recent study, Staple and Wagner (J. Org. Chem., 14, 559 (1949)) state that in methylations by formaldehyde and formic acid the reduction is affected by both compounds. By the use of C^{14} labeled reactants it seemed possible to clarify this question.

When the alkylation of 4-phenyl-4-carbethoxy piperidine was carried out using 4-phenyl-4-carbethoxy piperidine, formaldehyde-C^{14} and inactive formic acid (Run 1 Table I), only the demerol formed and the recovered formaldehyde were radioactive, while the carbon dioxide given off contained only traces of C^{14}. Within the experimental error, the demerol had the same specific activity as the formaldehyde used.

When the reaction was carried out with C^{14}-labeled formic acid and inactive formaldehyde (Run 2 Table I), neither the resulting demerol nor the unreacted formaldehyde was radioactive. The carbon dioxide produced had the same specific activity as the starting formic acid. The excess formic acid was recovered and found to be radioactive.

The fact that the carbon dioxide evolved was radioactive only when C^{14}-labeled formic acid was used but not when C^{14} labeled formaldehyde was employed indicates that in the case of demerol the reduction is effected by the formic acid. It does not seem likely that there can be exchange between the formaldehyde and the formic acid under the conditions employed.

Table I

Reactants Products, etc.	Run 1 (e) Molar Ratio	Spec. Act. μc/mmole	Run 2 (f) Molar Ratio	Spec. Act. μc/mmole
Reactants				
4-phenyl-4-carbethoxy piperidine	1.0	--	1.0	--
Formaldehyde	1.0	210	1.0	--
Formic Acid	2.6	--	2.1	0.433
Products				
Demerol-C^{14}	0.39 Fr. 1 0.22 Fr. 2 0.17 Fr. 3	215 248 (b) 238	~0.65 (d)	0.003
Carbon Dioxide	1.2 (a)	0.08	1.0	0.418
Recovered Formaldehyde (dimedone derivative)	3 mg.	155 (c)	3.4 mg.	0
Recovered Formic Acid	--	--	1.0	0.312 (c)

(a) The source of the excess carbon dioxide in this reaction is unknown but it may have resulted from the solution of C^*H_2O; (b) the higher specific activity of the less pure product indicates the presence of a radioactive impurity; (c) radioactivity measurements were taken of the crude material; (d) the demerol was not recovered from the filtrates; (e) radioactive formaldehyde and inactive formic acid were used in Run 1; (f) inactive formaldehyde and radioactive formic acid were used in Run 2.

Preparation of Labeled Glucose and Mannose: - A modification of the Victor Meyer reaction as previously used permits the synthesis of small quantities of pure nitromethane of high specific activity in 70 percent yield based on methyl iodide. The nitromethane is suitable for condensation with arabinose in the synthesis of labeled sugars. In this modification methyl iodide is distilled directly onto a 0.9 mole excess of silver nitrite contained in a small side-neck flask attached to a reflux condenser on the vacuum line. The reaction flask is closed off from the line, the reflux condenser filled with

dry ice-isopropyl alcohol mixture at -30° C and the reaction mixture heated slowly to 40° C and kept at this temperature for one hour with a water bath. The reaction mixture is then brought to room temperature, the reflux condenser to -10° C and the side product methyl nitrite, swept into a dry ice cooled spiral trap with a slow stream of dry nitrogen. The nitromethane is then distilled into a suitable receiver on the vacuum line.

Unsuccessful attempts have been made to separate the radioactive sugars by adsorption chromatography on a Fuller's earth type of clay as described by Lew, Wolfrom and Goepp (J. Am. Chem. Soc., 68, 1449 (1946)). The radioactive sugars have been separated in 100 mg. quantities from unreacted arabinose by paper chromatography on a chromatopile consisting of a stack of one thousand 9 cm. Whatman No. 1 filter discs with water-saturated phenol as solvent. The glucose and mannose did not completely separate under the conditions used although some pure glucose could be obtained on each pass with such a procedure.

Dicarboxylic Plant Acids: - Work is contuing on the synthesis of labeled malic and succinic acids. In this preparation methyl-labeled sodium acetate is converted to ethyl acetate (95-98 percent yield) using diethyl sulfate. This is then condensed with diethyl oxalate in the presence of sodium methoxide in ether to yield ethyl oxalacetate which is hydrogenated in 95 percent ethanol with a platinum catalyst to a mixture of diethyl malate and diethyl succinate. Previous attempts to use a ferrous ion catalyst poison to stop reduction at the malate stage has resulted in very inconsistent results in hydrogenation. From 30-75 percent of theoretical reduction to malate was observed in these cases. Without the catalyst poison, two hydrogenations have taken up 65 percent and 66 percent of theoretical amount of hydrogen.

The mixture of esters, malate, succinate and excess oxalate can be separated by saponification and removal of the oxalate as its insoluble calcium salt, then separation of the free malic and succinic acids by a tedious fractional extraction between ether and water, but the yields are low. Work is now proceeding on the direct separation of the three esters on an alumina column. Succinic acid is eluted first in this process while the malic and oxalic acids were found to be held tenaciously on the column; this may be due to saponification of the esters while on the column by traces of sodium carbonate present in the alumina. Therefore, an attempt is being made to remove this carbonate by washing the alumina with 2 N hydrochloric acid, then to neutrality with water and drying to the desired activity. On the basis of hydrogenation data and the amount of pure succinic acid obtained, the condensation between ethyl acetate and diethyl oxalate is a yield step of about 60 percent.

The earlier work on the preparation of β-labeled pyruvic acid by saponification and decarboxylation of ethyl oxalacetate has been repeated. The yield of 8.5 percent from sodium acetate agrees with the previous low yields obtained and so the method does not seem too satisfactory.

Lactic Acid-C^{14}: - The preparation of zinc lactate-1-C^{14} by the bromination and hydrolysis of propionic acid-1-C^{14} has been described. Similar reactions have been carried out with the 2- and 3- labeled propionic acids with overall yields based on the carbon dioxide used to begin the synthesis of 20 percent and 55 percent, respectively. These molecules were built up from carbon dioxide by reduction of the lower acids to alcohols, bromination, conversion to the Grignard and carbonation with inactive carbon dioxide. The actual yield on the bromination and hydrolysis, followed by repeated (three-four) crystallizations usually ran as high as 80 percent. Batches of each of these compounds have been

prepared for distribution by the Isotopes Division at Oak Ridge.

C^{14} -labeled Valine, Leucine and Intermediates: - The study of α-labeled leucine and valine has been continued. The procedure discussed in the last Quarterly Progress Report, UCRL-382, has been studied and the difficulty in the preparation of the acid chlorides overcome. By letting phthalylchloride react with the free carboxylic acids the chlorides were obtained in yields up to 75 percent. However, the reduction of the chlorides to the aldehydes could not be carried out in a satisfactory yield. The Rosenmund reaction neither in different solvents nor in the gas phase yielded more than 30 percent of aldehyde and frequently less. Other methods, too, e.g., the Reissert reaction, were unsatisfactory in their yields. It seems that the considerable volatility of the chlorides and the aldehydes as well as the autoxydation tendency of the latter are mainly responsible for the low yields. Therefore, this method was abandoned.

In search of other possibilities, the preparation of leucine from malonic ester was tried. The nitrosation of isobutylmalonic ester and the reduction of the resulting isonitrosoisocaproic ester was successful and could have been improved by nitrosating the free isobutylmalonic acid and reducing the resulting product. This method now awaits the preparation of methylene-labeled malonic ester. In the meantime, an alternative method has been studied and this promises somewhat better results.

$$\overset{*}{C}O_2 \xrightarrow{RMgX} R\overset{*}{C}O_2Na \xrightarrow{C_{16}H_{33}Br} R\overset{*}{C}O_2C_{16}H_{33}$$

$$\xrightarrow[\text{Cu Chromite}]{H_2} R\overset{*}{C}H_2OH \xrightarrow{PBr_2} R\overset{*}{C}H_2Br \xrightarrow[CO_2]{Mg}$$

$$R\text{-}\overset{*}{C}H_2\text{-}CO_2H \xrightarrow{Br_2} R\text{-}\overset{*}{C}HBr\text{-}CO_2H \xrightarrow{NH_3\ (l.)}$$

$$R\text{-}\overset{*}{C}HNH_2CO_2H$$

R = $(CH_3)_2$-CH- for valine, $(CH_3)_2$-CH-CH_2- for leucine

The method that is being developed for the synthesis of isoamyl-alcohol and isoamyl bromide from sodium isovalerate is a general one and it is hoped that it will make possible the high purity synthesis of many alcohols. The sodium salt is allowed to react with cetyl bromide to form the ester and this ester is subjected to high pressure hydrogenation. Since the cetyl alcohol and cetyl bromide left after the reaction is essentially non-volatile, the alcohol, together with water, etc., may be separated by an <u>in vacuo</u> distillation and the

crude hydrogenation product can be treated with PBr_3 and the resulting bromide washed with water and dried over phosphorus pentoxide. Yields have not yet been determined, but both alcohol and bromide have been characterized by boiling point and index of refraction determinations.

Isoamyl bromide: n_D. Theory n_D^{20} - 1.4412; found n_D^{21} - 1.4410

Boiling point. Theory - 120.6; found - 121.

Isoamyl alcohol: n_D. Theory n_D^{17} - 1.4084; found n_D^{20} - 1.4028.

Boiling point. Theory - 132; found 128-38.

It can also be seen from the above reaction scheme that this method offers a possibility of preparing carboxyl-labeled valine and leucine by bromination and amination of the corresponding carboxyl-labeled acid:

$$\overset{*}{C}O_2 \xrightarrow{R\text{-}CH_2\text{-}MgBr} R\text{-}CH_2\text{-}\overset{*}{C}O_2H \xrightarrow[2.\ NH_3\ (l.)]{1.\ Br_2,\ P_4} R\text{-}CHNH_2\text{-}\overset{*}{C}O_2H$$

R = $(CH_3)_2$-CH- for valine, $(CH_3)_2$-CH-CH_2 for leucine.

Low activity preparations of all three of the carboxyl-labeled acids, isobutyric, isovaleric and isocaproic acids, with yields of 90-95 percent have been made. Low activity preparations of valine -1-C^{14} and leucine-1-C^{14} have given yields of 35-40 percent based on radioactive carbon dioxide. High activity preparations are now in progress.

Biological Chemistry

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M. Kirk, J. Krone, B. Krueckel, M. Meinke and J. Weaver

Purines and Nucleic Acids. I.

Recent work by Kidder, et.al. (Science, 109, 511 (1949)) has indicated that differences exist between normal and cancer cells in the manner in which they metabolize certain purines. Other workers have also reported differences in nucleic acids in normal and tumor-bearing animals. As an aid in the study of these and other problems of purine metabolism, we have undertaken the synthesis of several labeled naturally occurring purines and analogs including adenine, guanine and guanazole (5-amino-7-hydroxy-1 H-v-triazolo-(d)-pyrimidine).

Adenine is being synthesized substantially by the method used by Cavalieri, et. al., (J. Am. Chem.Soc., 71, 533 (1949)) to incorporate C^{14} into carbons 4 and 6. Difficulty was experienced in repeating the preparation of ethyl forminimo ether hydrochloride as described by these authors, but by control of temperature and the amount of hydrogen chloride added, a satisfactory preparation was obtained. Trial preparations of cyanoacetamide from chloroacetic acid via the ethyl ester using inactive cyanide have indicated that it may be prepared in 50-60 percent yield based on cyanide. We have modified the procedure used by Cavalieri. Following conversion of chloroacetic acid to cyanoacetic acid, the product is extracted with ether in a continuous liquid-liquid extractor. The ethyl ester is prepared using absolute ethyl alcohol and sulfuric acid as the catalyst, and subsequently it was converted in cyanoacetamide using aqueous ammonia.

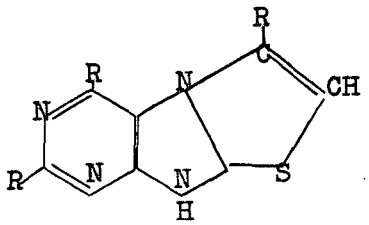
Inactive phenylazomalononitrile has been prepared by the same method as described by Cavalieri, et. al., in 50-60 percent yield from cyanoacetamide. At the present time, factors which influence the yield in the coupling of phenylazomalononitrile and formamidine to prepare 4,6-diamino-5-phenylazoprimidine are being investigated. Methods of reduction of this compound to 4,5,6-triamino-pyrimidine are also being studied.

It is planned to prepare guanine and guanazole with 4-C^{14}. As an intermidiate ethyl cyanoacetate is used. It is condensed with guanidine to form 2,4-diamino-6- hydroxy-pyrimidine and the isomeric cyanoacetyl guanidine. At the present time, factors which influence the yield in this condensation are being investigated.

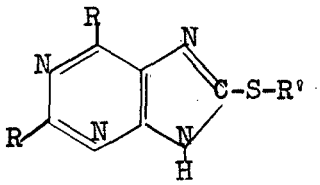
Purines and Nucleic Acids. II.

Treatment of experimental mice with nucleotides results in tissue and blood changes which are very similar to those occurring in tumor growths. (Parsons, J. Path. Bact., 57, 9 (1945) ; Barker, Gulland and Parsons, Nature, 157, 482 1946)). These results indicate that there may be excellent opportunities for the treatment of cancer in the use of synthetic nucleotides which contain purines, closely resembling those involved in enzyme systems but unusable for this purpose, which would be concentrated in the proliferating area.

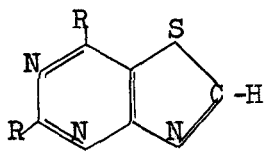
In this connection, the synthesis of the following purine derivatives and isoteres has been proposed:



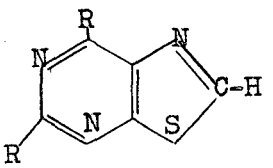
Thiazolidinopurine



8-Mercaptopurine



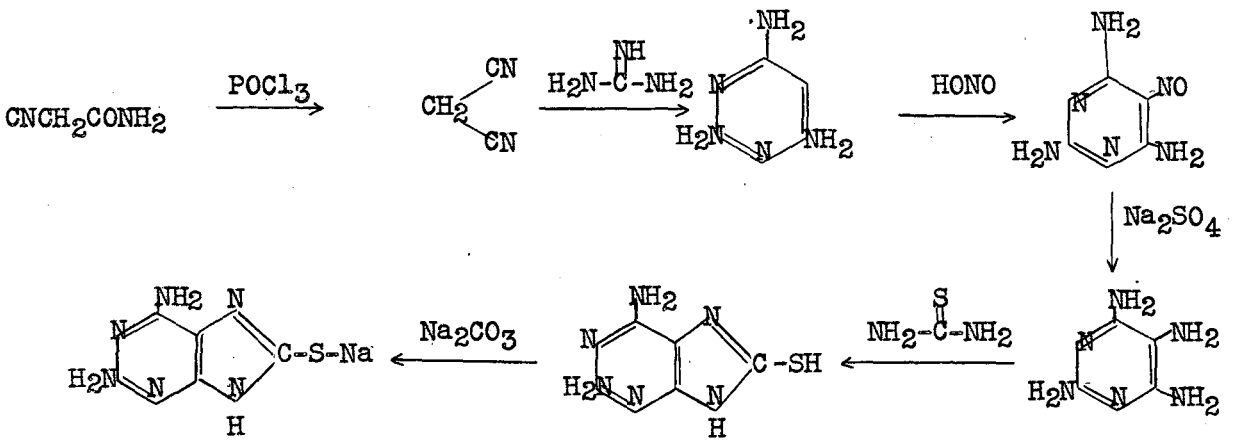
7-Thiaxanthine



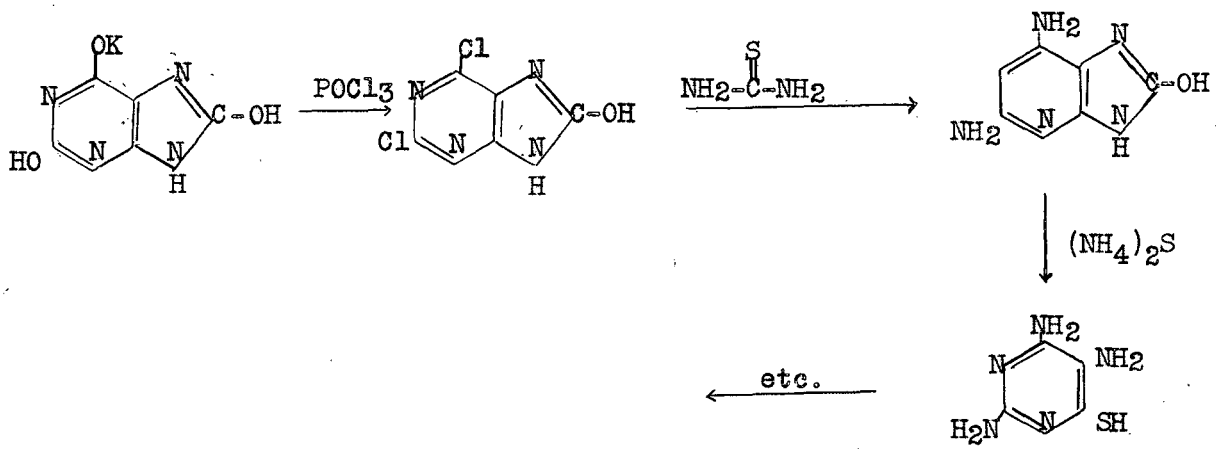
9-Thiaxanthine

R = Alkyl or NH_2 or OH; R' = NH_4^+, or Na^+ or H

To date the following synthetic work has been accomplished:



Toxicity tests are in progress on the last named compound.



This work is still in progress.

Metabolism of Propionic Acid-C^{14}.

Investigation of the metabolites resulting from incubation of mouse liver slices with carboxyl-labeled sodium propionate is being continued by use of paper chromatography. Samples have been prepared as described in the last Quarterly Progress Report, UCRL-382. The undesirability of large quantities of sulfate ion introduced when the metabolism is stopped with sulfuric acid has led to a study, now in progress, of other acids for this purpose.

The water soluble-ether insoluble fractions of each sample, after further fractionation and salt removal by ion exchange resins, are chromatographed. Phenol and butanol-propionic acid are the solvents used for the two-dimensional separation. Radioautographs of these papers show many distinct spots. On of the most intense has been identified as alanine. Of the other prominent spots, one is an amino acid while the others are acidic in nature; efforts toward their identification are continuing.

In hopes of establishing the mechanism by which the alanine was formed, the components of the ether soluble fractions are being studied and attempts will be made to determine the position of the alanine carbon label.

Immunochemistry.

It has been shown that an animal will incorporate administered amino acids into antibodies which it is actively producing. The question of whether or not this is true with passively transferred antibodies is still unsettled. Therefore, the preparation of labeled antibodies to human A and B cells in rabbits was undertaken by feeding glycine-2-C^{14} to sensitized animals. If the tagged antibody can be obtained with fairly high specific activity, it can be used in a possibe antibody transfer and compared with the uptake of C^{14} by actively produced antibody and finite quantitative rate data can be obtained therefrom.

Rabbits which had been given four weekly courses of immunization against

human A cells were given 60 μc of $\overset{*}{C}H_2NH_2COOH$ over a period of three days by means of interperitoneal injection. The titer of two rabbits was 160. The serum of the rabbits had 5000 dis/min/cc. After absorption and discarding the non-specific antibodies and the agglutination of the A-antibodies, the supernate had 1084 dis/min/cc. The A-antibody contained almost the same activity as the background and, therefore, could not be detected with the Nucleometer. A passive transfer of B-antibody to these rabbits at the same time as the administration of the radioactive glycine gave similar results. The isolation of the antibodies was done in two different ways and the results were duplicated.

Previous workers have shown that certain human amniotic fluids can inhibit the in vitro agglutination of Rh+ cells by anti-Rh+ sera. This work has been repeated with not equal success.

An attempt has been made to isolate the Rh antigen from the amniotic fluid of mothers who had given birth to Rh positive babies. The factor is detectable in a 1:1 or 1:2 dilution. We are at present determing this titer per unit weight and attempting to concentrate the antigen.

Metabolism in Mice of C^{14}-Labeled Compounds.

The studies in the rate of elimination of C^{14} fed to mice in the form of simple organic compounds or amino acids has continued. Among others, the following labeled compounds have been investigated: sodium acetate-1-C^{14}, sodium acetate-2-C^{14}, methionine-methyl-C^{14}, sodium butyrate-4-C^{14}, urea-C^{14} and glucose-1-C^{14}. The details of this work will appear elsewhere in the reports from this project.

Photosynthesis Chemistry

M. Calvin, A. A. Benson, G. Dorough, A. G. Hall, V. H. Lynch, J. A. Bassham, T. Goodale, W. Stepka, P. Warrington and J. Weigl

The mechanism and kinetics of photosynthesis by green plants are being investigated in this study. As primary tools, labeled carbon, hydrogen and oxygen have extended research in this field. Thus, by using labeled carbon dioxide it has been possible to study the path of carbon from the atmosphere to the constituents of cellular material; with labeled hydrogen it is hoped to investigate the formation of reducing agents during photoreduction. This report also contains a summary of work done to determine the possibility of a path from water to oxygen gas using Oxygen 18 as a tracer.

Degradation of Intermediates.

In order to determine the path of carbon in photosynthesis the known intermediates and related compounds in sugar synthesis are being degraded and the positions of labeled carbon atoms in each compound determined as a function of time of photosynthesis in $C^{14}O_2$. Previous results from this laboratory showed that C^{14} was first incorporated in the C-1 atom of a three-carbon intermediate and in the 3,4-carbon atoms of the hexose molecules. The results reported in Table I verify and extend the earlier results. Perhaps the most important data are those for glyceric acid. Phosphoglyceric acid has been shown to be the earliest radioactive product of photosynthesis in $C^{14}O_2$ and this is converted to glyceric acid by enzymatic or acid hydrolysis. In the degradation the glyceric acid is first purified by two-dimensional paper chromatography, eluted from the paper and oxidized with periodic acid. Formaldehyde is obtained from the β-carbon atom and is separated and counted as the dimedone derivative. Further oxidation of the glyoxylic acid with excess periodate gives formic acid from the α-carbon and carbon dioxide from the carboxyl carbon. The two are separated and counted as barium carbonate.

Alanine, another important three-carbon intermediate, was degraded by ninhydrin oxidation as reported earlier and sucrose, a sugar, was degraded after conversion to lactic acid by E. coli. Serine was oxidized with periodate by the same method as used for glyceric acid. Since the glyceric acid is most closely related to the direct path of carbon, the C^{14} distribution in glyceric acid is of greatest importance.

From Table I it is seen that barley functions much more rapidly than the algae; C^{14} is incorporated into the α-and β-carbon atoms of glyceric acid from barley much earlier than in that from algae. This rapid turnover in barley may be due to smaller reservoirs of intermediates in the regeneration of C-2 acceptor molecule cycle in barley which would require less time to be saturated with radiocarbon after which the succeeding intermediate becomes increasingly active. Additional experiments, then, will be carried out with algae to further elucidate the path of carbon.

Experiments have been done at lower temperatures and at lower light intensities in order to slow down the process. The major difficulty is the

Table I

	5 sec. PS Scen.	15 sec. PS Barley	60 sec. PS Barley	30 sec. PS Scen.	90 sec. PS Scen.	90 sec. PS Scen. Malonate	PI-30 min.D Chlor.	5 sec. Chlor.	2 sec. Barley
Glyceric Acid									
C_1	95	49	44					95	85
C_2	2.5	25	30					3	
C_3	1-2	26	25					2	15
Alanine									
C_1		61	48		56	47-67	89		
C_2					44	? -33	10		
C_3		30	44				0.5		
Serine									
C_1			28-?						
C_2			15-?						
C_3			11-?						
Glycine									
(g)C_1(C_2)		60							
(g)C_2(C_3)		40							
Sucrose									
(S)$C_{3,4}$(C_1)		52(54)	35-37(42)	87			76		
(S)$C_{2,5}$(C_2)		25	34	7			17		
(S)$C_{1,6}$(C_3)		24	32	6			7		
Malic Acid									
(m)$C_{1,4}$(C_2)				93.5					
(m)$C_{2,3}$(C_3)				6.5					
Aspartic Acid									
(a)$C_{1,4}$(C_2)				96					
(a)$C_{2,3}$(C_3)				4					

increasing formation and effect of respiration intermediates (citric acid, glutamic acid, succinic acid, fumaric acid) upon the path of carbon in photosynthesis. Preliminary results with lower light intensities have shown that the same products are formed except that the relative amounts differ. Phosphoglyceric acid is the major product formed in 30 seconds. Some evidence now exists for the formation of a precursor of phosphoglycerate which may be phosphoenol-pyruvate. Phospho-enol-oxalacetate may also be formed.

Feeding Experiments with Labeled Intermediates.

The fate of several labeled compounds related to the photosynthetic intermediates has been investigated in a preliminary manner. Labeled acetates, formate, alanines and glycine have been fed to the algae Scenedesmus, in both light and dark. The radioactive products formed are separated and identified on two-dimensional paper chromatograms.

The experiment was performed so that substrate could penetrate the cells during 30 minutes in the dark immediately after a period of normal photosynthesis. A sample is taken in the dark, the radioactive constituents of which represent the products of dark metabolism of the substrate. The light is then turned on for 10 minutes and the remainder of the algae are killed and analyzed. During all this time, the system was flushed with 4 percent carbon dioxide in nitrogen to dilute and remove any $C^{14}O_2$ formed. Since the amount of substrate taken (5-8 mg. per gram of packed cells in 70 ml. of water) is large compared to the aliquot part that may be effectively chromatographed on one sheet of paper, it was necessary to remove the cells from the medium. This was done by filtering the algae with Celite on a 9 cm. filter as quickly as possible (3-5 seconds). The cells on the filter were rapidly killed and extracted by boiling ethanol which was diverted into a second receiver.

Glycine-1-C^{14}. The major product formed from feeding glycine as described above was serine which was about one-third as active as the glycine itself. There was also a large number of less active compounds formed among which alanine, hexose phosphates, triose phosphate, and phospho-glyceric, malic, glutamic and aspartic acids were identified. In the dark there was no conversion of glycine to serine.

Glycine-2-C^{14}. The major conversion product here was also serine. In this case, however, the serine contained about two-thirds of the total activity while the glycine contained only one-third. The conversion of glycine to serine can be explained by the known reaction:

$$C^2H_2NH_2\text{-}C^1O_2H \longrightarrow HC^2O_2H + C^1O_2$$

$$HC^2O_2H + C^2H_2NH_2\text{-}C^1O_2H \longrightarrow C^2H_2OH\text{-}C^2HNH_2\text{-}C^1O_2H$$

This would explain the relative activity of serine from the two glycines. The serine would contain twice the relative number of C^{14} atoms if the C^2 were active than if the C^1 were active. By appropriate degradations it will be

possible to verify the possibility of this mechanism for algae. With methylene-labeled glycine the other active compounds were similar to those found with carboxyl-labeled glycine, but the activities were much less. In the dark there was also no conversion of glycine to serine.

Alanine-2-C^{14}. After feeding alanine-2-C^{14} to the algae in the dark there was considerable activity found in the alanine, glutamic acid and proteins and fats. Lesser amounts of activity appeared in hexose monophosphate and aspartic, phosphoglyceric, citric, malic and succinic acids. Triose phosphate, hexose diphosphate and glutamine also contained some activity. In the light the picture was similar except that the early photosynthetic intermediates were missing or very low in activity. The important active compounds found in the light were glutamic, aspartic, citric and malic acids.

The alanine feeding experiment was repeated using carbon dioxide-free air. In this case, both in light and dark, the activity was confined to the proteins and fats.

Acetate-2-C^{14}. In the dark after feeding methyl-labeled acetate activity was found in glutamic, citric, aspartic, malic, succinic, and fumaric acids and glutamine. In the light the same compounds were present in similar amounts but, in addition, the fats were active with half of the total.

Respiration and Photosynthesis.

Work described earlier has been continued in order to determine the relationships between the photosynthetic path of carbon and normal respiration processes. In these experiments labeled intermediates were formed during short photosynthesis periods with $C^{14}O_2$. The light was then stopped and respiration allowed to proceed for a determined time before the plant was rapidly killed. The products formed were determined on the radioautograph of a filter paper chromotogram ("radiogram").

Preliminary results with algae were described in our preceding Quarterly Progress Report, UCRL 382; the experiments have now been extended to include barley seedling leaves. Chromatograms of extracts from sixteen such experiments were counted after determining the exact position of the spot on an x-ray film and the results are listed in Table II. Certain comparisons may be made upon examination of the table. When barley and Chlorella are exposed to $C^{14}O_2$ in the dark the products formed are those related to the tricarboxylic acid cycle. Fixation occurs largely by virtue of reversibility of decarboxylation processes. When, however, the plants are illuminated immediately prior to dark fixation of $C^{14}O_2$, the products are quite different and almost identical with those of normal photosynthesis (30 seconds photosynthesis, Chlorella or barley). We can thus confirm the suggestion, at first made on the basis of kinetic studies, that all of the reactions between carbon dioxide and surcrose are dark reactions.

One effect is immediately apparent. In those cases in which the algae have not been given a dark period either during or after exposure to $C^{14}O_2$ there is little or no labeled glutamic and citric (iso) acid formed (see 30s.PS.C., 30s.PS.-150s.L(He)C. and 5m.PS.C., Table II). If, however, they are given as little as 150 seconds of dark time following 30 seconds photosynthesis in $C^{14}O_2$, relatively large amounts of labeled glutamic and citric (iso) acids appear. See 30s.PS.-150s.D.(He)C., Table II). If the dark period is aerobic the amounts of

Table II

Percentage Distribution of Radioactivity Among Aqueous Alcohol-Soluble Non-lipid Products

	Alanine	Aspartic	Glutamic	Glutamine	Glycine	Serine	Succinic	Fumaric	Glycolic	Isocitric (Citric ?)	Malic	Sucrose	Phosphate Esters
30s.PS.C.[a]	6.1	0.8				1.3			0.5		0.9	0.5	89[l]
2m.D.PI.C.[a]	39	5.5	0.4			7.3	0.4			0.2	2.4	6.7	38
45m.D.C.[a]	11	8.7	23	1.5		4.0	17	7.5		1.9	21	1.2	1.2
30sPS.B.[b]	1.1	0.1			12	4.9			8.3		0.5	15	59[m]
2mD.PI.B.[a]	33	3.4	1.2			2.2					4.9	1.9	53[n]
50mD.B.[a]	2.2	28[z]	17	8.2		4.7				6	31		2.9
30s.PS.-150s.L[c].(He)C	23	17	0.4			3.8					8.4	27	21[p]
30s.PS.-150s.D.(He)C[d]	27	3.6	3.1			4.5		0.9		0.5	3.4	7.2	50[q]
30s.PS.-150s.L.C.[e]	8.0	6.1	0.5		4.1	8.3			6.7	0.6	6.7	31	25[r]
30s.PS.-150s.L.Sc.[f]	1.2	39	1.5		0.9	3.7			3.7	2.2	25	1.9	56[s]
5m.PS.C.[g]	1.9	3.0	0.4			2.0	0.2			0.1	1.9	23	65[t]
30s.PS.-2m.L.B.[h]	2.2	1.4			7.4	6.7			23		2.3	45	11[u]
30s.PS.-2m.D.B.[b]	4.6	0.8			0.7	17			0.2	0.5	0.7	34	42[v]
30s.PS.-40m.D.B.[i]	6.4	1.6	2.3	1.4		7.3				0.8	2.1	62	16[w]
60s.PS.B.[j]	7.7	2.6			3.3	3.7			2.0		3.3	27	50[x]
5m.PS.B.[k]	8.1	0.7	0.8		4.5	4.3			6.4	0.2	2.6	65	6[y]

Percentages were determined by direct counting of areas on the paper chromatogram defined by the radiogram.

S.- seconds, m. - minutes, PS. - photosynthesis with $C^{14}O_2$, C. - Chlorella pyrenoidosa, Sc. - Scenedesmus D-3,. -light, D. - dark, B. - barley seedling leaves, PI. - 5-10 min. preillumination in helium, He. - helium. All treatments subsequent to photosynthesis were done in carbon dioxide-free air unless specified as in He.
a.- in these experiments less than 5% of the total radioactivity fixed was insoluble in alcohol-water; b. - 2.5% insol.; c. - 25% insol.; d. - 6% insol.; e. - 30% insol.; f. - 30% insol.; g. - 45% insol.; h. - 10% insol.; i.- 6% insol.; j. - 3.2% insol.; k. - 4.5% insol.; l. - includes phosphoglyceric acid 24 (PGA), hexose monophosphates 60 (HMP), hexose diphosphates 3.9 (HDP), triose phosphates 0.5 (TrP); m. - includes free glyceric acid 10; n. -includes free glyceric acid 2; p. - includes PGA 1.3, HMP 14, HDP 4, p-pyruvic 1.8; q. - includes PGA 6, HMP 35, HDP 7, p-pyruvic 1.8; r. - includes PGA 3.2, HMP 13, HDP 7; s. - includes PGA 25, HMP 11, HDP 18 p-pyruvic 2.2; t. - includes PGA 26, HMP and HDP 39, p-pyruvic 0.6; u. - includes free glyceric acid 0.7; v. - includes free glyceric acid 15; w. - includes free glyceric acid 9; x. - includes free glyceric acid 6; y. - includes free glyceric acid 0.6; z. - includes asparagine 2.

these compounds which appear are somewhat larger than under anaerobic conditions. It is thus clear that the light not only initiates a series of reactions constituting the photosynthetic reduction of carbon dioxide but also in some way inhibits certain other reactions. Although the nature of the inhibition is as yet unknown, it is clear that light prevents some of the newly formed photosynthetic intermediates from participating in the tricarboxylic acid cycle as represented by glutamic and (iso) citric acids. In the barley leaves the formation of labeled glutamic acid is so slight even after relatively long dark periods that we cannot yet say whether the same phenomenon occurs or not. It is indicated by a comparison of the isocitric contents of 30s.PS.B., 5m.PS.B., 30s.PS.-2m.L.B. and 30s.PS.-2m.D.B. in which the last contains more of this acid than any of the first three. In the barley experiments another effect can be seen, which involves the conditions under which labeled glycine and glycolic acid are found. Glycine and glycolic acid, formed in the light from radiocarbon dioxide, disappear in as little as two minutes in the dark. They appear in detectable amounts in as short a period as 5 seconds of photosynthesis in radiocarbon dioxide and are maintained in the light in the absence of carbon dioxide with the glycolic acid increasing. (See 30s.PS.B., 30s.PS.-2mD.B., 30s.-2m.L.B.). The same effect has been observed with algae. Additional experiments with algae showed that the presence of oxygen during the subsequent illumination enhanced the formation of labeled glycine and glycolic acid. In the case of glycine, for which the total amount present may be estimated from the amount of the ninhydrin color produced on the paper it appears that the short dark periods reduce not only the amount of labeled glycine but the total glycine as well. This would seem to indicate that the size of the reservoirs of free glycine and presumably of glycolic acid vary considerably with illumination and may possibly be related to the photosynthetic path of carbon. Degradation studies now underway should lead to a detailed exposition of the sequence of compounds involved.

The Path of Oxygen in Photosynthesis.

Since the work of S. Ruben et. al. in 1941 no information has been obtained regarding the source of the oxygen evolved during photosynthesis. Calvin and Karrer have independently suggested that the oxygenated carotenoid pigments might be such intermediates. Carotenoids are invariably associated with chlorophyll in green plants. Karrer has isolated a number of epoxide structure among the oxygenated carotenoids which conceivably could be involved in the oxidation of water. A straightforward way of testing such a hypothesis would be to photosynthesize a plant of high carotenoid content with water containing Oxygen 18, isolate and purify the various epoxide and furan carotenoid pigments, and determine whether or not these pigments contain a higher percentage of Oxygen 18 than an identical sample kept in the dark. Such an experiment has been carried out; the details of the experiment will be reported as soon as the mass spectrographic analysis of the sample is available.

Separation of Phosphate Esters by Ion Exchange Resins.

Fructose-1,6-diphosphate, the hexose-6-phosphates and inorganic phosphates have been separated by elution from a Dowex A-1 anion exchange resin column with 0.2 N sodium chloride. The barium salts of fructose-1,6-diphosphate and of the hexose-6-phosphates were obtained in 98-100 percent yield by alcohol precipitation after addition of barium acetate to the sodium chloride effluate. Ion exchange resins may be used for the preparation of fructose-1,6-diphosphate and a mixture of the hexose-monophosphates in pure form and in good yields greater than 98 percent of theoretical. The ion exchange method of separation is superior to the classical method of separation

by repeated fractional precipitations and crystallizations of the barium salts with regard to both purity and yield.

Work is continuing on the separation of fructose-1,6-diphosphate and 3-phosphoglyceric acid by ion exchange methods. A Dowex A-1 resin column in the chloride form and eluting solutions containing both sodium chloride and hydrochloric acid are being used.

Infra-Red Absorption Spectra of Photosynthetic Intermediates.

Work has been started on the systematic identification of photosynthetic intermediates by means of their infra-red absorption. One method that may be used involves thin films on silver chloride plates. Even 150-500 γ of a solid deposit suffice to give good bands; however, before plating, equivalent amounts of inert sodium chloride have to be added to the solution before it is evaporated onto the silver chloride plate. The sodium chloride may bring out the bands in the absorber by causing it to form very fine crystals capable of lengthening the effective light path. Some solid deposit measurements have been carried out on a Perkin-Elmer, Model B spectrophotometer. The spectra of a few samples of organic-insoluble sugar phosphates have also been measured in water solution using a Baird double-beam recording spectrophotometer. No definite results have yet been obtained on this project.

II QUARTERLY PROGRESS REPORT Project 48B

W. H. Latimer, Director

A. Metals and High Temperature Thermodynamics

L. Brewer, L.A. Bromley, A. Searcy, D. Mastick,
Raleigh McKissen, G. Elliott, D. Sawyer, L. Templeton, Alexander Lindsay

Thermodynamics of CN and N_2 Gas.

This work has been brought to a successful conclusion with the determination of the heats of formation of CN, N_2, and NO from the gaseous atoms. A complete report of this work is being written up at present.

Vapor Pressure of Metals.

The vapor pressures of aluminum and iron have been determined. A complete report of the work is being written up.

Gaseous Oxide Species.

It has been established that FeO vaporizes by decomposition to the atoms. The existence of gaseous sub-oxides of aluminum has been demonstrated. Work is starting on the study of NiO and the molybdenum oxides.

Gaseous Hydroxide Species.

It has not been possible to detect gaseous iron or aluminum hydroxides within the experimental conditions available to us. Molybdenum and tungsten apparently do form gaseous hydroxides and further studies are continuing to fix their formulas.

Liquid Metal Systems.

The new high temperature calorimeter has been virtually completed. The high temperature camera is in operation and studies of ternary metal systems has commenced.

Refractory Studies.

The silicides and borides of Ce, Ti, Zr, Cb, Ta, Mo, W, U, and Th have been investigated. The phases of most of the diagrams have been established. The crystal structures of a number of the phases have been determined. A complete report of the silicide work has already been submitted. A complete report of the boride work is being written at present.

Lattice and Gaseous Energy Calculations.

The previous calculations using the Born-Haber cycle and lattice energy calculations has been extended with some success to gaseous molecules. Most of the unipositive and dipositive solid halides and oxides can be treated with reasonable

accuracy. Unipositive gaseous halides and oxides give good results, but solid nitrides and gaseous dipositive oxides do not give good results because of the large contribution of repulsive energy due to the considerable penetration of the ions when their charges are high. The poor state of the theory of repulsive forces does not allow one to calculate them accurately enough to evaluate compounds with large repulsive contributions.

Thermal Conductivity of Gases.

The work is continuing but has been greatly handicapped by the difficulty of determining pressures accurately when gases are subjected to sudden temperature changes.

Heat Transfer in Forced Convection Film Boiling.

An apparatus has been designed and is under construction.

B. Basic Chemistry, including Metal Chelates

Z. Z. Hugus and K. L. Mattern

Lanthanum Chemistry.

Former attempts to fix hydrogen ion concentration were met with failure, due to an unexplained fault in the $LiClO_4$ stock solution, used to maintain ionic strength. Recent experiments, using differently prepared $LiClO_4$ solutions, have given reproducible results and have permitted the calculation of the complexing constant for the formation of (LaK^{++}) in ionic strengths of one, while varying the (H^+) concentration and (ΣLa) concentration over a five fold range. When an attempt was made to account for background absorption in the area of the (LaK^{++}) peak, difficulty was encountered. The molar extinction coefficient for enolate ion and the pK for TTA, as given in BC-63, indicated a discrepancy factor of about two in either the pK or the ϵ enolate. This is probably due to an ionic strength effect on the pK of TTA and experiments are underway to determine this factor more carefully.

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

Several samples of $AgIO_3$ and AgI were submitted to X-ray analysis in order to check variations in the specific rate constant of the Abel reaction.

The Thermodynamics of Rhenium.

The precision calorimeter and associated apparatus used by B. J. Fontana, has been overhauled and several trial runs made in order to determine features of performance and to calibrate the equipment. A satisfactory technique has been perfected and the first measurements will be made shortly.

Several compounds of rhenium have been synthesized. From an impure sample of rhenium metal, pure Re, K_2ReCl_6, $ReO_2 \cdot xH_2O$, and NH_4ReO_4 have been made. Another sample of pure Re has been used in syntheses of ReO_3. However, the method used in this latter preparation, viz. heating (120-150°C) Re in a limited supply of air has not resulted in complete conversion to ReO_3.

It is planned to use the NH_4ReO_4 as a source of ReO_2, by subjecting it to thermal decomposition in vacuo at 500°C.

C. Ore Reduction

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

The phase equilibrium constant for the reaction: UO_2^{++} (aq) + 2 TTA (benzene) = 2 H^+ (aq) + UO_2K_2 (benzene) has been determined at several values of the various concentrations. The method of study involved the fluorimetric determination of the concentration of UO_2^{++} in the aqueous phase and UO_2K_2 in the benzene phase. The fluorimeter used in these experiments was that reported in the last quarterly Report, UCRL-382. Difficulties in experimental procedure have been numerous but have been pretty well overcome. In the above studies ionic strength has been kept constant by working in a 1.5 M ClO_4^- aqueous phase, the only other negative ion present being a small amount of the TTA ion. Studies are now under way in which various amounts of phosphate are present to gain information regarding the complexing of UO_2^{++} by that species.

About 25 ions were investigated to determine their interference or lack of interference in the polarographic analysis of uranyl ion. To use in determining the ratio of U^{IV} to U^{VI} in mixtures of the two, pilot systems having a normal potential near that of the U^{VI}-U^{IV} couple, and establishing immediate equilibrium were investigated. The $Fe(CN)_6^{\equiv}$ - $Fe(CN)_6^{\equiv\equiv}$ couple fails because complexing occurs with uranium. The half-wave potential of I_2 is so close to that of UO_2^{++} as to point to some other analytical tool (possibly spectrophotometer) to follow the attainment of equilibrium with the I_2 - I^- couple. The polarographic double curves obtained from VO^{++} - U^{IV} mixtures have not been interpreted. It is difficult to assign the waves to the proper components of the mixture. Both the VO^{++} - V^{+++} and I_2 - I^- couples bear further investigation.

This line of investigation has been abandoned since overall emphasis in the Raw Materials division has been shifted. More pertinent investigations will be undertaken.

The study of microamperometric titration of uranyl with chromous ion is being resumed. Stirring efficiency is the main difficulty here.

D. Engineering Development of Plutonium Separation

T. Vermeulen, Thomas Hicks, Howard Crandall, Barney Rubin, Hugh Lehman, Alexander Kaminski, Homer Raey, Milton Davis.

Pilot Scale Synthesis of TTA.

Preliminary design of continuous plant for TTA production at rate of two tons a day has been completed. All available information is now in form for publication as a Radiation Laboratory report.

No further work with TTA manufacture is contemplated.

Solvent Extraction Utilizing the Chelate Process.

Work is continuing on the design and construction of shielded equipment for processing 1 percent Hanford level β-γ activity and full Hanford level plutonium activity by the chelate process.

It is planned that mixer-settlers are to be used in the recovery of plutonium where the rate of extraction is relatively slow while pulse columns are to be used in the recovery of uranium where the rate of extraction is rapid. Construction of a 1/2 inch pulse column has been started so that its operation may be observed and analyzed.

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