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OCTOBER, NOVEMBER, AND DECEMBER 1952

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D. W. Osborne, Assistant Division Director

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CHEMISTRY DIVISION, SECTION C-I

QUARTERLY REPORT

OCTOBER, NOVEMBER, AND DECEMBER 1952

NUCLEAR CHEMISTRY AND RADIOCHEMISTRY

Alpha Half-Life of Am²⁴³ - H. Diamond, P. Fields, J. Mech, M. Inghram,¹
and D. Hess¹

Americium rich enough in Am²⁴³ to allow measurement of its alpha half-life has been produced by irradiation of plutonium for two years in the Chalk River pile. The alpha half-life of Am²⁴³ has been previously reported to be roughly 10⁴ years.²

Americium and curium were separated from the irradiated plutonium by elution from a Dowex A-1 anion exchange column with concentrated hydrochloric acid that was 3 per cent in nitric acid. Further purification from fission products was obtained by elution from two successive Dowex-50 cation exchange columns with concentrated hydrochloric acid.³ This was followed by elution from two successive heated cation exchange columns of Dowex-50 with citric acid whose pH had been adjusted to 3.5 with NH₃. The americium and curium were combined.⁴

A portion of the above sample was analyzed with a mass spectrometer. The molal ratio of Am²⁴³ to Am²⁴¹ was found to be 0.3346 ± 0.003 . The possibility of appreciable contamination of the americium peaks by curium was eliminated by the observation that a threefold variation in americium to curium ratios (obtained by varying the electrode temperatures) caused no variation in the 243:241 ratio.

¹Physics Division.

²K. Street, Jr., A. Ghiorso, and G. T. Seaborg, Phys. Rev. 79, 530 (1950).

³R. M. Diamond, K. Street, Jr., and G. T. Seaborg, Phys. Rev. 85, 482 (1950).

⁴The Health Chemistry Group, Radiation Laboratory, University of California, under the direction of N. B. Garden and William G. Ruehle, designed and operated the remote control equipment used for the initial separations.

Lanthanum carrier was added to another portion of the americium curium mixture, and the americium was oxidized with persulfate.⁵ The curium was precipitated on LaF_3 ; the americium was recovered from the solution. Three such oxidation cycles resulted in a 10^4 fold separation of curium from the americium. The americium was electrodeposited⁶ on a tantalum cathode from 0.2 M K_2CO_3 solution and was then alpha pulse analyzed.

The average alpha activity ratio of 5.21 Mev Am^{243} to Am^{241} , from five pulse analyses, was 0.0179 ± 0.0006 . The partial alpha half-life of Am^{243} was calculated from these data and the half-life of Am^{241} (470^{+5}_{-10} years)⁷ to be $8.8 \pm 0.6 \times 10^3$ years. The estimated error reported is based upon the standard deviation in the alpha counting data (3.5 per cent), the mass spectrometer error (1 per cent), the estimated error in the half-life of Am^{241} (2 per cent), and the estimated error due to the uncertain correction for the overlap of Am^{241} alpha in the Am^{243} peak.

Neutron Capture Cross-Section of Actinium²²⁷ - R. K. Sjolom and P. Fields

A measurement of the Ac^{227} (n, γ) cross-section has been made by studying the following reactions:

A sample of Ac^{227} , purified from Th^{227} before bombardment, was irradiated in the Argonne CP-3' pile. From the ratio of Th^{228} to Th^{227} , as measured by pulse analysis, the Ac^{227} neutron capture cross-section was calculated.

300 micrograms of Ac^{227} in 0.1 N HCl were extracted several times with 0.25 M TTA in benzene to remove the Th^{227} daughter. The actinium sample was then irradiated for two weeks in the maximum flux of the central thimble in the Argonne CP-3' pile. A Np^{237} flux monitor was attached to the sample. After bombardment the thorium was again separated from the actinium by the above method, and the ratio of $\text{Th}^{228}:\text{Th}^{227}$ obtained by pulse analysis.

⁵M. W. Asprey, S. E. Stephanou, and R. A. Penneman, J. Am. Chem. Soc. 72, 1425 (1950).

⁶H. Diamond, R. Barnes, and P. Fields, private communication.

⁷B. G. Harvey, Phys. Rev. 85, 482 (1952).

Since the amount of Th^{228} present is small in comparison to the amount of Th^{227} the first pulse analyses are not reliable. Periodic purifications of the thorium fraction from its decay products were made and pulse analyses run as the 18.6 da. Th^{227} decayed. Three samples of Ac^{227} were irradiated, and the results of analyses are shown in Table 1. Further pulse analyses must be made of samples 2 and 3 when the Th^{227} peak has decayed further.

Table 1

DETERMINATION OF THE THERMAL NEUTRON CAPTURE
CROSS-SECTION OF Ac^{227}

Sample	Flux	$\sigma_c(\text{Ac}^{227})$ (barns)
1	3.30×10^{12}	$633 \pm 30^*$
2	3.14×10^{12}	573 ± 75
3	3.72×10^{12}	580 ± 85

*The errors quoted are those arising only from the pulse analyses.

In order to correct for the resonance contributions to the neutron capture in Ac^{227} , a cadmium-shielded sample was also irradiated with the unshielded sample. 1.6 per cent of the Th^{228} activity was due to capture of neutrons whose energy was above the cadmium cutoff (0.3 ev). The cross-section of the Ac^{227} in the unshielded sample was corrected for this fast effect to give the thermal neutron cross-section.

Np^{237} was used as the flux monitor. In order to determine how much of the $\text{Np}^{237} (n, \gamma) \text{Np}^{238}$ activation was due to thermal neutrons, the activation in a cadmium-covered sample was measured. Pulse analysis of the data shows that 4.8 per cent of the activation was due to neutrons above the cadmium cutoff. The monitors have been corrected for this resonance effect.

Studies on Sea Water - D. C. Stewart

The extractants were used as received from the manufacturers in all cases save the dibutyl orthophosphoric acid, which was separated from the monoalkyl acid by the method of Stewart and Crandall.⁹ In all cases, one ml of the indicated organic phase was agitated for two hours or more in a water bath at 25°C with an equal volume of Pacific Ocean coastal sea water (pH = 7.8) to which 7300 counts min⁻¹ ml⁻¹ of U²³³ had been added (equivalent to 2×10^{-6} M UO₂⁺⁺). After equilibration, the tubes were centrifuged and each phase was assayed by alpha counting.

A plating technique was developed which gave count reproducibility to 5 per cent standard deviation on sea water labeled with 1500 counts min⁻¹ ml⁻¹ of U²³³. The distribution ratios shown on the table are not as precise, however, primarily because in most cases the actual level of activity in one or the other phase was only of the order of a few counts per ml or less, and also because material balances indicated that some radioactivity loss due to absorption by the sea water solids always occurred on the aqueous phase counting plates. Distribution ratios above 100, particularly, are order of magnitude indications only.

The alkyl phosphates and phosphites are such effective extractants that it was of interest to test the effect of replacing the phosphorus atom in the center of the surrounding oxygen-alkyl structure with other elements in the same or nearby groups of the periodic table. Accordingly, the following (Eastman) materials were made up in 10 volume per cent concentrations in technical carbon tetrachloride and tested in the same fashion as those shown in Table 2: Dibutyl carbonate, diisobutyl carbonate, n-butyl formate, n-butyl nitrite, and di-n-butyl sulfite. A 0.1 g/ml preparation of n-butyl sulfone was also tested. A 10 volume per cent n-butyl oxalate solution was also prepared to see whether results comparable to those with tributyl citrate could be obtained. A distribution ratio of about 0.03 was obtained with the oxalate, all the others being less than 0.01. Material balances were very poor in the n-butyl sulfone system, and some evidence was obtained that the losses were due to volatilization of the compound formed with the uranium tracer.

⁹D. C. Stewart and H. W. Crandall, J. Am. Chem. Soc. 73, 1377 (1951).

Table 2

SOLVENT EXTRACTION OF LOW LEVELS OF U^{233} FROM SEA WATER

Organic Extractant*	Source of Extractant	K_D $\left(\frac{\text{Organic}}{\text{Aqueous}}\right)$
Tributyl phosphate	Commercial Solvents	<0.01
0.73 M Dibutyl orthophosphoric acid	Eastman	>500
0.14 M Dibutyl orthophosphoric acid	Eastman	>500
0.073 M Dibutyl orthophosphoric acid	Eastman	>500
0.014 M Dibutyl orthophosphoric acid	Eastman	240
0.0073 M Dibutyl orthophosphoric acid	Eastman	45
Monooctyl orthophosphoric acid	Victor Chemical	>300
Dioctyl pyro phosphoric acid	Victor Chemical	>500
Triethyl phosphite	Virginia-Carolina Chemical	0.015
Triisopropyl phosphite	Virginia-Carolina Chemical	0.09
Tributyl phosphite	Virginia-Carolina Chemical	0.12
Trihexyl phosphite	Virginia-Carolina Chemical	~500
Triisooctyl phosphite	Virginia-Carolina Chemical	~200
Tri (2-ethyl hexyl) phosphite	Virginia-Carolina Chemical	~600
Dimethyl phosphite	Virginia-Carolina Chemical	0.002
Diethyl phosphite	Virginia-Carolina Chemical	0.003
Dibutyl phosphite	Virginia-Carolina Chemical	35
Dibutyl phosphite	Victor Chemical	0.5
Dioctyl phosphite	Victor Chemical	50
Di (2-ethyl hexyl) phosphite	Virginia-Carolina Chemical	>500
Dioctyl isooctene phosphonate	Victor Chemical	0.007
Diisooctyl isooctene phosphonate	Victor Chemical	0.014
Tributyl citrate	Commercial Solvents	2.0
Tributyl citrate	Eastman	<0.005
10% hepta-fluorobutyric acid in fluoro-ether 0-75	Minnesota Mining	<0.01
100% technical grade dibutoxy tetraethylene glycol (pentaether)	Carbide and Carbon	0.03

*10 volume per cent in technical carbon tetrachloride, unless otherwise noted.

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Of the substances tested, the preliminary survey indicates that the following might be worth further investigation as extractants for removing low levels of uranium from unacidified sea water: the dialkyl phosphoric acids with alkyl groups higher than butyl, the trialkyl phosphites higher than hexyl, and the dialkyl phosphites above butyl. The tributyl citrate system also promises to be of considerable interest. The Commercial Solvents material was from a bottle which had been in stock for 5-10 years, whereas the Eastman product was newly purchased. The simplest explanation is that the older sample had partially hydrolyzed, and that the dibutyl or monobutyl citrates actually were responsible for the extraction. (A second preparation from the same bottle some two months later gave an even higher distribution ratio.) Differences in the amount of hydrolysis also probably account for the results obtained with the two samples of dibutyl phosphite obtained from different suppliers.

The failure of the two phosphonates to give good extraction is of interest in view of the efficiency of this group of compounds in extracting uranium from acidified systems.¹⁰

Other Nuclear Work - H. Diamond, P. Fields, S. Fried, A. Hirsch, J. Mech, G. Pyle, and M. Studier

A substantial amount of nuclear work done during the past quarter will be reported in a forthcoming Los Alamos report on Operation Ivy.

Heats of Formation of Uranium Hydride, Uranium Deuteride and Uranium Tritide - B. M. Abraham and H. E. Flotow

The calorimetric determination of the heat of reaction of powdered uranium metal with the isotopes of hydrogen has now been completed with the measurement of the heat of formation of UT_3 . The calorimeter used for the measurements was described in a previous report.¹¹

The heats of formation of UH_3 , UD_3 and UT_3 at 30°C are given in Table 4. Included for comparison are the values, extrapolated to 30°C, obtained by Spedding *et al.*¹² and by Flotow and Abraham¹³ from dissociation pressure measurements.

Table 4

HEATS OF FORMATION OF UH_3 , UD_3 , AND UT_3 AT 30°C

Substance	ΔH_f (kcal/mole of hydride)	
	Calorimetric Measurements	Dissoc. Press. Data
UH_3	-30.34	-30.8 ¹²
	-30.35	
	-30.34	-31.8 ¹³
	Mean -30.34 $\pm$ 0.03	
UD_3	-31.00	-30.8 ¹²
	-31.03	
	-31.00	-31.9 ¹³
	Mean -31.01 $\pm$ 0.03	
UT_3	-31.15	-30.1 ¹³
	-31.10	
	-31.12	
	Mean -31.12 $\pm$ 0.05	

¹¹B. M. Abraham and H. E. Flotow, ANL-4942 (1952).

¹²Spedding, *et al.*, Nucleonics 4, 10 (1949).

¹³H. E. Flotow and B. M. Abraham, unpublished results.

A slightly larger error was attached to the UT_3 results because of the much greater drift rate arising from the beta decay energy absorbed in the calorimeter. The calorimetric data show that the heat of formation becomes progressively more negative from UH_3 to UD_3 to UT_3 , a result which is not observed in the dissociation pressure measurements. On the basis of the UH_3 and UD_3 results the heat of formation of UT_3 was calculated to be 0.2 kcal/mole more negative than was actually observed. The calculated value was obtained by making the simple assumption that the zero point energies of the hydride compounds varies as $(\mu_i)^{1/2}$, where μ_i is the reduced mass for U-H, U-D, or U-T. The agreement is considered very satisfactory.

Since the calorimetric values given in Table 4 are reliable to the indicated accuracy, the values calculated from the dissociation pressures must be uncertain to about 1 kcal/mole. Possibly the dissociation pressure measurements are not true equilibrium values but are values that are readily reproducible in a given apparatus. It should also be borne in mind that the heats reported here are for the reaction of powdered uranium with hydrogen and that, as pointed out by Giaque,¹⁴ the value for massive uranium may be quite different.

¹⁴W. F. Giaque, J. Am. Chem. Soc. 71, 3192 (1949).

The Entropy and Low Temperature Heat Capacity of Uranium Tetrafluoride -
H. R. Lohr, D. W. Osborne, and E. F. Westrum, Jr.¹⁵

A comparison¹⁶ of the entropies of uranium tetrafluoride and of thorium tetrafluoride has indicated that the extrapolation by Brickwedde, Hoge, and Scott¹⁷ of the heat capacity of UF_4 below 20°K may be in error. Therefore, the measurements on UF_4 have been extended down to 5°K in the apparatus described previously.¹⁸

The sample of UF_4 , which was from a lot manufactured by Mallinckrodt for metal production, was found by H. R. Hoekstra¹⁹ to contain 0.34 per cent oxygen. This amount of oxygen corresponds to 3.3 per cent UO_2F_2 , but the purity is regarded as adequate for the present purpose.

The results between 5 and 23°K are presented in Table 5 and in Figure 4. It can be seen that the measured values are appreciably higher than the extrapolated values of Brickwedde, Hoge, and Scott. Further, the shape of the curve suggests that there may be an anomalous maximum in the heat capacity below 5°K.

Table 5
MOLAL HEAT CAPACITY OF URANIUM TETRAFLUORIDE

Molecular Weight = 314.07

0°C = 273.16°K

T (°K)	Approx. ΔT (°K)	C _p (cal/deg)
5.19	0.45	0.261
5.85	0.88	0.268
6.84	1.11	0.272
8.14	1.53	0.281
9.71	1.60	0.315
11.25	1.49	0.373
12.78	1.57	0.461
14.32	1.54	0.576
15.82	1.56	0.708
17.45	1.73	0.871
19.35	2.07	1.098
21.38	1.99	1.374
23.33	1.91	1.670

¹⁵Chemistry Department, University of Michigan, Ann Arbor, Michigan.

¹⁶Lohr, Osborne, and Westrum, ANL-4942 (1952), p. 35.

¹⁷Brickwedde, Hoge, and Scott, J. Chem. Phys. 16, 429 (1948).

¹⁸D. W. Osborne and E. F. Westrum, Jr., ANL-4686 (1951), p. 9.

¹⁹H. R. Hoekstra and J. J. Katz, ANL-4942 (1952), p. 14.

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Figure 4

The Heat Capacity of UF_4 from 5 to 23°K

It seems desirable, therefore, to make heat capacity measurements on UF_4 below 5°K . For this purpose it is intended to construct a calorimeter suitable for measurements in the range 1 to 20°K and to prepare a purer sample of UF_4 .

In the course of this work it was found that the heat capacity of UF_4 at 300°K is 1.3 per cent lower than reported by the National Bureau of Standards.¹⁷ In order to compare the calorimetric techniques at this laboratory with those at the National Bureau of Standards, heat capacity determinations were made on an NBS standard sample of benzoic acid. The agreement with the NBS results²⁰ was better than 0.1 per cent between 30 and 305°K , increasing to only 2 per cent at 14°K . This agreement is within the accuracy claimed, and it indicates that the discrepancy in the UF_4 measurements is due to a difference in the samples. The purer sample that is to be made for measurements below 5°K will also be used for measurements from 5 to 300°K .

Reaction of Thorium Nitrate Tetrahydrate with Nitrogen Pentoxide in Anhydrous Nitric Acid - John R. Ferraro and Leonard I. Katzin

In an attempt to prepare anhydrous thorium nitrate, the reaction of thorium nitrate tetrahydrate with nitrogen pentoxide in anhydrous nitric acid was studied. The experimental procedure was as follows: 2 grams of thorium nitrate tetrahydrate were dissolved in 10 ml of anhydrous nitric acid, and nitrogen pentoxide was condensed in the mixture by means of a dry ice-acetone bath. The mixture was allowed to warm up to room temperature, and then the excess anhydrous nitric acid was distilled off under vacuum.

It was found that whenever 2 grams or less of nitrogen pentoxide were condensed in the thorium nitrate tetrahydrate-anhydrous nitric acid mixture, the solid isolated was an NO_2 addition compound. This solid has about 41 per cent ThO_2 with 17 to 20 per cent NO_2 and about 1 per cent water. In one experiment the solid obtained corresponded to the composition 3 moles of NO_2 , 0.2 mole of N_2O_5 , and 0.2 mole of H_2O per mole of $\text{Th}(\text{NO}_3)_4$. The NO_2 addition compound is a creamy white, flaky solid with an NO_2 atmosphere above the solid. When water is added it gives off NO_2 gas.

If the amount of nitrogen pentoxide added was greater than 2 grams, an N_2O_5 addition was obtained. This solid has about 38 per cent ThO_2 , only about 2 to 4 per cent NO_2 , and practically no water. In one experiment the solid obtained corresponded to the composition 1.7 moles of N_2O_5 , 0.4 moles of NO_2 and 0.1 mole of H_2O per mole of $\text{Th}(\text{NO}_3)_4$. The N_2O_5 solid is a white granular material, which gives off fumes of anhydrous nitric acid when water is added, if the NO_2 content of the solid is not greater than 4 per cent.

²⁰Furukawa, McCoskey, and King, J. Research National Bureau of Standards 47, 256 (1951).

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X-ray powder diagrams of the above solids have shown that in both the NO_2 and N_2O_5 addition compounds the patterns are different from the hydrate pattern and different from one another.

Thermal decomposition experiments have shown that the NO_2 addition compound is less stable than the N_2O_5 solid. The NO_2 in the NO_2 addition compound can for the most part be removed in less than an hour at a temperature of $160\text{--}170^\circ\text{C}$ at a pressure of 3 mm. At 10^{-5} mm the NO_2 can be removed in 30 to 40 minutes at temperatures around 130°C . Even these conditions may be too drastic, because in some experiments some decomposition of the nitrate took place.

With the N_2O_5 addition compound, it takes 4 to 5 hours at 170°C and a pressure of 3 mm to remove most of the N_2O_5 . At 10^{-5} mm this can be done in 4 hours at $150\text{--}160^\circ\text{C}$.

The anhydrous solids obtained by the thermal decomposition of the NO_2 and N_2O_5 addition compounds are white and powdery. X-ray powder diagrams showed that the pattern for the anhydrous solid was different from the hydrate pattern, and different from the patterns of the addition compounds. No oxide lines were detected.

These anhydrous solids dissolved rapidly in water to give clear solutions spectrophotometrically identical with solutions of thorium nitrate hydrates. The solids are very soluble in methyl alcohol, slightly soluble in wet ether, and difficultly soluble in anhydrous diethyl ether. The ultraviolet absorption spectra of such a solution in anhydrous diethyl ether was compared with the spectra of ether solutions of the tetrahydrate and pentahydrate. It was observed that the nitrate peak at $275\text{ m}\mu$ is missing in the spectra of the anhydrous solids in anhydrous diethyl ether. Total nitrogen on an anhydrous solid (54.80 per cent ThO_2) was found to be 11.88 per cent. This corresponds to 0.38 per cent N_2O_5 remaining in this solid. The theoretical composition for $\text{Th}(\text{NO}_3)_4$ is 55.01 per cent ThO_2 and 11.67 per cent nitrogen.

Further study of this reaction is contemplated.

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The System Cobaltous Chloride-Water-Tertiary Butyl Alcohol at 25°C -
Leonard I. Katzin and John R. Ferraro

The equilibrium solids found in the ternary system cobaltous-chloride-water-tertiary butyl alcohol, in addition to the hexahydrated, dihydrated, and monohydrated salts, which are well known, include cobaltous chloride tetrahydrate-dialcoholate. The anhydrous equilibrium solid probably is cobaltous chloride.

This ternary system is comparable in many ways with the salt-water-organic solvent systems reported previously for the salts uranyl nitrate,²¹ cobaltous nitrate,²² and cobaltous chloride.²³ Mixed solvates are found, and a high solubility, at maximum, of the salt in the organic phase is found. In the case of this system, the maximum solubility of cobaltous chloride in the organic phase is 9 mole per cent, as compared with 7 mole per cent in the saturated pure aqueous solution.

A region of immiscibility (two liquid phases) is found in part of the high-water region of the phase diagram. This behavior is attributable to the low solubility of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in the organic component.

Reflection Spectra of Some Solid Cobalt (II) Salts in the Visible Region -
Leonard I. Katzin and Elizabeth Gebert

There seems little reason to doubt any more that the "red" or "pink" solutions of cobaltous salts are associated with the six-coordinate condition, and the "blue" solutions with the four-coordinate condition.²⁴ The correlations of the colors of the cobalt halide solids are less obvious, in particular since intermediate colors are found, and in some instances two distinct color phases are known for the same analytical composition. Furthermore, the stoichiometry of the solid material does not correspond to the cobalt coordination number in the crystalline solid in cases other than the simple hexahydrate or analogous compounds. This consideration would not be important if crystal structures were known for all the relevant compounds. The authors have investigated the reflection spectra of a number of powdered solid cobalt (II) compounds and have found correlation with the solution spectra and with such crystal structure data as are available, which furnishes a basis for conclusions about the structures not yet determined crystallographically.

²¹L. I. Katzin and J. Sullivan, J. Phys. Colloid Chem. 55, 346 (1951).

²²L. I. Katzin and J. R. Ferraro, J. Am. Chem. Soc. 72, 5451 (1950).

²³L. I. Katzin and J. R. Ferraro, J. Am. Chem. Soc. 74, 2752 (1952).

²⁴L. I. Katzin and E. Gebert, J. Am. Chem. Soc. 72, 5464 (1950).

Hydrates and pyridinates of cobaltous nitrate and chloride, and dipyr-
idinium cobaltous tetrachloride, were prepared as previously described.^{22,23,25}
The first crop of crystals from an aqueous solution made with 11 g CsCl and
5 g cobaltous chloride hexahydrate gave Cs_2CoCl_4 with some 20 per cent of
 Cs_3CoCl_5 , while a second crop gave large crystals of the tricaesium form,^{26,27}
determined by cobalt analyses. Both of these solids were studied.

Powdered solid was distributed thinly and evenly as practical on the
gummed surface of transparent adhesive tape, which was then fastened to
white cardboard and mounted in the reflection spectrum attachment of the
Beckman Model DU spectrophotometer for measurement. A similar strip
of tape without cobalt salts added was used as the blank. Results of a num-
ber of such measurements are given in Figures 5, 6, and 7. It should be
pointed out that in the case of spectra with considerable intensity differences
between peaks and shallows (e.g., those in Figure 6) variations in sample op-
tical thickness over the area covered by the light beam result in exaggeration
of the heights of the minor peaks relative to the major, whose effective opti-
cal density is limited by the amount of "whiteness" seen by the light beam.
Preparations of different "thickness" will therefore give different promin-
ence to the minor peaks, and ratios of intensities between peaks cannot be
relied on. It is sufficient for the purposes of this paper, however, to be able
to compare the locations, shapes, and approximate relative intensities of the
peaks found.

The authors are indebted to Mr. John R. Ferraro for the necessary
cobalt analyses.

The substances whose reflection spectra are shown in Figure 5 are
unquestionably "red" salts. Typical blue forms may be expected to be salts
like Cs_3CoCl_5 , for which the existence of CoCl_4^- complex groups has been
demonstrated crystallographically,²⁷ and Cs_2CoCl_4 and $(\text{HPy})_2\text{CoCl}_4$, for which
the group may be assumed,^{25,28,29} and all of these are deep blue in color.
Measurements on the three compounds show (see Figure 6 for the spectra of
two of these compounds) that they are characterized by an intense peak cen-
tering at about $660 \text{ m}\mu$, with a series of less intense sharp peaks at shorter
wavelengths (about 532 , 452 and $410 \text{ m}\mu$), spectra which are very like that
of the CoCl_4^- complex in solution.^{24, 30, 31, 32} There are differences

²⁵L. I. Katzin, J. R. Ferraro and E. Gebert, J. Am. Chem. Soc. 72, 5471 (1950).

²⁶G. F. Campbell, Am. J. Sci. 48, 419 (1894).

²⁷H. M. Powell and A. F. Wells, J. Chem. Soc. 1935, 359.

²⁸F. Reitzenstein, Z. anorg. Chem. 18, 253 (1898).

²⁹E. G. V. Percival and W. Wardlaw, J. Chem. Soc. 1929, 1505.

³⁰W. R. Brode, Proc. Roy. Soc. (Lond.) 118A, 286 (1928).

³¹W. R. Brode and R. A. Morton, Proc. Roy. Soc. (Lond.) A120, 21 (1928).

³²A. V. Kiss and M. Gerndas, Z. phys. Chem. 180, 117 (1937).

Figure 5

Reflection Spectra of Solid Co(II) "Red" Compounds

The ordinates are arbitrary, the scale indicating differences for an optical density ratio of 10.

I	$\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{Py}$	V	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$
II	$\text{Co}(\text{NO}_3)_2 \cdot 2\text{Py}$	VI	$\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$
III	$\text{Co}(\text{NO}_3)_2 \cdot 3\text{Py}$	VII	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
IV	$\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	VIII	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{Py}$

Figure 6

Reflection Spectra of Solid Blue Co(II) Double Chlorides

The ordinates are arbitrary, the scale indicating differences for an optical density ratio of 10.

I and II preparations of Cs_2CoCl_4
III $(\text{HPy})_2\text{CoCl}_4$

Figure 7

Reflection Spectra of Some Violet and Blue CoCl_2 Compounds

The ordinates are arbitrary, the scale indicating differences for an optical density ratio of 10.

I	$\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (violet)	IV	$\text{CoCl}_2 \cdot \text{H}_2\text{O}$
II	$\text{CoCl}_2 \cdot 2\text{Py}$ (violet)	V	CoCl_2 (with CaSO_4)
III	$\text{CoCl}_2 \cdot 2\text{Py}$ (blue)		

between the spectrum of $(\text{HPy})_2\text{CoCl}_4$ and the caesium double salts, notably in the structure of the major peak, which may be ascribable to crystal structure effects. The particular curve for the pyridinium salt plotted (III, Figure 6) is intermediate between one from a "thinner" sample, which shows the 535 $\text{m}\mu$ peak at a lower intensity relative to the main peak, and a "thicker" preparation showing another peak at a about 455 $\text{m}\mu$, in correspondence to the spectra of the caesium salts. A plot of part of a "thick" preparation of a caesium double-salt (II of Figure 6) is given to show detail in the low-absorption region of the spectrum, while a "thinner" preparation (curve I) depicts better the relation of the major peak to the minor ones, and the structure of the major peak. The wavelengths of the minor peaks compare quite closely with the peaks for HCl solution found, for example, by Kiss and Gerendas.³²

The hydrates and pyridinates of cobaltous chloride with two or fewer of these groups per cobalt form an interesting series (Figure 7). The "violet" form of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (curve I) shows a principal peak centering at about 520 $\text{m}\mu$, with a secondary peak at about 625 $\text{m}\mu$ that masks the otherwise magenta or "red" color to a violet. The dipyridine "violet" form (curve II) shows a very similar spectrum, the major peak (with a suggestion of structure, as in the other pyridinates) coming at 525 $\text{m}\mu$, and the secondary peak at 625 $\text{m}\mu$. The "blue" form of the dipyridinate shows a markedly different spectrum (curve III), with the major absorption at 625 and 580 $\text{m}\mu$, and minor peaks suggested at about 510 and 480 $\text{m}\mu$. Comparison will show that this spectrum is very close to that of the compound in acetone solution,²⁴ which has been shown to be due to a 4-coordinate entity. Electron-diffraction determination of the crystal structure³³ of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ has shown the cobalt to be 6-coordinate, in agreement with the interpretation of the spectrum. The published studies of the structure of violet $\text{CoCl}_2 \cdot 2\text{Py}$ do not give a complete structure,³⁴ but allow an interpretation³⁵ of octahedral coordination. The structure of the blue form of the compound has not been deciphered but it is isomorphous with the corresponding bromide and iodide³⁴ for which only blue forms are known. The hypothesis that these are tetrahedral rather than octahedral cobalt structures, based on the correspondence of the spectra of the solid and the entity in solution, seems reasonable.

Cobaltous chloride monohydrate is a blue-violet solid, whose absorption parallels roughly that of the "violet" forms above, but combines the two peaks of the latter in a single broad absorption. The flat maximum in the absorption comes at about 560 $\text{m}\mu$. Anhydrous cobaltous chloride (in the presence of calcium sulfate, to maintain its anhydrous state) has a principal peak at about 600 $\text{m}\mu$, with a suggestion of structure in the region from 640 to 690 $\text{m}\mu$. A minor peak is indicated about 535 $\text{m}\mu$. The color is a very pale.

³³B. K. Vainshtein, Doklady Akad. Nauk S. S. S. R. 68, 301 (1949).

³⁴E. G. Cox, A. J. Shorter, W. Wardlaw and W. J. R. Way, J. Chem. Soc. 1937, 1556.

³⁵D. P. Mellor and C. D. Coryell, J. Am. Chem. Soc. 60, 1786 (1938).

blue, compared to the rich blue of the salts with the CoCl_4^- grouping. Crystallographic investigation has assigned the solid the CdCl_2 structure,³⁶ with the cobalt being 6-coordinate. It seems reasonable to conclude therefore, that the spectra of the anhydrous chloride and of the monohydrate represent further extension of the difference between the violet dihydrate or dipyridinate and the hexahydrated or hexapyridinated forms, and that the spectral shift leading to visual blueness may be ascribed to the mass effect of coordination predominately to chloride rather than oxygen or nitrogen. An analogous shift of spectrum to longer wavelengths is seen on comparing the spectra of solutions of cobalt chloride, bromide and iodide in the respective hydrogen halide acids.³¹

In the case of glasses, pigments, etc., in which cobalt is a minor component, it has already been proposed that the blue or red color of the substance is correlated with the 4-coordination or the 6-coordination of the basic lattice structure.^{37,38,39,40} In summary, therefore, one may say that the Co(II) solids which are red or pink certainly have 6-coordinate cobalt; the violet forms of the composition $\text{CoX}_2 \cdot 2\text{S}$ (X = halide, S = molecular base) are most probably all 6-coordinate also; and most of the blue forms are 4-coordinate. The exceptions to the last are blue solids in which 6-coordinate cobalt is attached predominately to heavy atoms, such as chloride or a heavier atom. In the case of the violet $\text{CoX}_2 \cdot 2\text{S}$ forms it does not seem very likely that the secondary long-wavelength peak signalizes the presence of two kinds of cobalt atoms in the solids, with some small proportion (perhaps just at the crystal surface) coordinated to only 4 groups. The more probable explanation is that the secondary peak represents a displacement of one of the peaklets not so well resolved in the hexapyridinate spectrum.

Separation of Cations by an Electrogravitational Method - George W. Murphy

Results on the application of this method to sodium-potassium mixtures were described in ANL-4873, where large separation factors were reported. Further work on this system was postponed in order to explore other binary mixtures of more practical interest. Three such systems have been investigated: lithium isotopes 6 and 7, cerium-thorium mixtures, and radium-barium mixtures.

Lithium isotopes - Operating conditions were similar to those reported for the sodium-potassium system. The triple (30 in., cell was attached to one of two reservoirs containing the mixture to be fractionated, and water passed slowly up through the assembly; the voltage applied to the electrodes was 0.5 volt and the current was reversed hourly.

³⁶L. Pauling, Proc. Natl. Acad. Sci. (Wash.) 15, 709 (1929).

³⁷R. Hill and O. H. Howell, Phil. Mag. (vi) 48, 833 (1924).

³⁸O. H. Howell, J. Chem. Soc. 1927, 2843.

³⁹W. A. Weyl, J. Appl. Phys. 17, 628 (1946).

⁴⁰J. E. Standworth, J. Soc. Glass Technol. 32, 224 (1948).

The first plan was carried out as follows: about 0.5 mole LiCl was contained in the large (500 ml) reservoir and an effluent from the top of the cell containing about 30 mg of Li was collected over a period of 239 hours. This head fraction solution, presumably enriched in the less mobile isotope, was evaporated to a convenient volume and introduced into the small (3 ml) reservoir attached to the cell in place of the larger one. This solution was refractionated, retaining only 0.5 mg as the head fraction for isotopic analysis.

The second plan called for the enrichment of the more mobile isotope in a reservoir sample by removing from it a large amount of material enriched in the less mobile isotope as effluent from the top. About 300 mg (as Li) of starting material was reduced to a final value of 2.3 mg in this manner over a period of 580 operating hours and subjected to isotopic analysis.

Isotopic analysis was based on the reaction between Li^6 and slow neutrons:

The samples were irradiated in the Argonne heavy-water pile, the tritiated water of the solution was reduced quantitatively by passage over hot zinc, and the resulting tritiated hydrogen was counted in an ionization chamber with the aid of a vibrating reed electrometer.⁴¹ None of the samples processed above showed isotopic fractionation within the estimated precision of 1.5 per cent. It was felt that at least a 5 per cent fractionation factor should have been obtained in order to offer promise for a practical lithium isotope separation method. Further efforts along this line have therefore been abandoned.

Cerium-thorium mixtures - This study offered an opportunity to investigate the applicability of the method to cations of higher valence. As in the preceding section, the results have not been encouraging, but for different reasons. The pH of the solution is not a critical factor when dealing with univalent cations, but when the valence is three or greater, too high a pH can cause precipitation of the hydroxide. Due to its extraordinarily high mobility, the hydrogen ion is rapidly stripped from the solution in the electrogravitational cell, which makes it impossible to maintain on a long-term basis a pH lower than 6 or 7, except by some artificial means. There is a further complication in the case of cerium, resulting from its tendency to oxidize and precipitate CeO_2 .

⁴¹The author is indebted to W. M. Manning for suggesting this method of analysis and to L. Kaplan, K. E. Wilzbach and A. R. Van Dyken for the apparatus and details of technique.

For separation tests, a radioactive tracer technique suggested by D. F. Peppard was employed. Cerium-thorium mixtures were spiked with beta-emitting Ce^{144} and alpha-emitting Th^{230} . A beta and alpha count on a sample thus yields on a relative basis the cerium-thorium ratio. A number of preliminary experiments were performed with unspiked solutions in an attempt to find conditions where precipitation in the cell would not interfere with the separation.

The results of this study can be summed up as follows: (1) at applied voltages (~ 0.5 volt) where satisfactory separation factors might be obtained, precipitation in the cell is excessive and renders the method unsatisfactory for continuous processing. (2) At voltages low enough to avoid precipitation in the cell (< 0.25 volt), the separation factor and production rate are both too low for the method to be of practical use. Further studies might be directed toward artificial means of maintaining the pH of the solution, but at present the demand for a new method of separating thorium and cerium seems insufficient to warrant work along this line.

Radium-barium mixtures - A solution containing tracer Ra^{226} with macroscopic quantities of barium chloride was studied using the short (9 in.) cell with the small reservoir attached. Operating conditions were similar to those reported above. Samples were removed from the top and bottom of the cell at intervals for analysis. The radium content was followed by alpha-assay; a detailed procedure was adopted in order to assure that the alpha-count was due to the radium decay and not to the daughters in the disintegration series. Total barium was determined conductometrically.

For reasons not fully understood, this mixture cannot be characterized by a definite separation factor. Instead there is evidence that the active material moved up the column in the form of bands. This is illustrated in the following table (Table 6) taken from the results on the second experiment (Run B-31). The separation factor is defined as the specific count ratio (i.e., count per unit quantity of BaCl_2) of top and bottom samples. Since the type of results obtained here (inversion of separation factors) had not been encountered before by this method, the results were analyzed in terms of several possible explanations. The details will be found in a project report to be issued. In particular, the possibility of spurious counts due to other radioactive materials was considered carefully but was rejected after several experimental tests.

A separation factor in the neighborhood of 6 is large enough to offer promise of a practical radium separation method. Further experimental work should involve macroscopic quantities of radium.

Table 6
SEPARATION FACTORS FOR RADIUM-BARIUM MIXTURE
(Run B-31)

Sample Collection	Separation Factor
1	0.90
2	0.73
3	6.2
4*	----
5*	----
6	4.1
7*	----
8	6.75
9	.78
10	.83
11	.80
12	.77

*Bottom sample not collected

Theoretical Studies on the Transference Cell - George W. Murphy

In developing theoretical approaches to the electrogravitational method of separating electrolytes described elsewhere in this report, certain basic concepts required clarification. The efforts of the author along this line have led to two methods of description of the transference cell which have considerably wider scope than the original aims called for. Both methods deal with electrode and ion transport processes as a single unit in cells where concentration gradients are present and current is flowing. The importance of time-independent or steady states in such cells is stressed. In contrast with currently accepted theories, results are expressed solely in terms of operational concepts.

The first method proposes an equivalent circuit model for the cell which is characterized by remarkable pictorial simplicity, despite the fact that phenomena occurring in the cell are commonly regarded as complex. The second analyzes the cell by the methods of the thermodynamics of the steady state, yielding a description of the system in the form of a pair of mathematical equations. A number of tests assure the consistency of both of these treatments with the known facts. The two approaches supplement and strengthen one another; together they offer promise of wide applicability.

Equivalent Circuit Model - The term "transference cell" refers to a system with two identical reversible electrodes in contact with an electrode reaction. By "reversible" is meant that the clearly specifiable reaction at one electrode occurs in exactly the reverse manner at the other, and that there is no activation or resistance over-potential at the electrodes. The applied or measured potential is always less than that required for decomposition of the solution; i.e., concentration gradients but no changes in composition are established in the cell as a result of passage of current. The familiar "concentration cell with transference" is a special case of the transference cell when there is a concentration gradient, but no external current. Also in the "transference cell" category is the inverse of the concentration cell with transference, i.e., a concentration gradient is generated in a cell through electrode and ion transport phenomena by application of a voltage from an external source. The same arrangement results when convection is eliminated from the electrogravitational process by operating with horizontal electrodes.⁴²

The silver - silver chloride electrode, chloride ion system is adopted for illustration. Three aspects of this cell are shown in Figure 8. In (a) the system is in equilibrium, with a uniform concentration and no external EMF. In (b) an external EMF has been applied, but changes in concentration have occurred near the electrodes only. This corresponds to a Hittorf transference experiment. Because of the density differences which arise, the cathode is situated at the bottom to avoid convection currents. In (c) the concentration difference between the top and bottom electrodes leads to an external EMF; this is a concentration cell with transference. The external battery of (b) has been replaced by a voltage measuring device. In (b) a substantial current passes, while in (c), for a measuring instrument of infinite sensitivity, no current passes at all.

It is evident that continued passage of current in (b), followed by removal of the external current source, leads to a concentration cell with transference (c). It has been shown^{43,44} that the steady-state concentration distribution reached after prolonged current passage, is linear for the ideal case. The postulated equivalent circuit of this cell is given by Figure 9a. The components R_+ and R_- are resistances ascribed to the cation and anion, respectively. The condenser is an energy-storage unit; the potential difference E_c across its plates is related to the process occurring in the cell by the equation

$$E_c = -\Delta G/F$$

where ΔG is the molar free energy change for the process

⁴²G. W. Murphy and D. Batzer, J. Electrochem. Soc., 99, 520 (1952).

⁴³H. J. S. Sand, Phil. Mag., (6), 1, 45 (1901).

⁴⁴T. R. Rosebrugh and W. L. Miller, J. Phys. Chem. 14, 816 (1910).

Figure 8

Cross-Section of the Transference Cell

Heavy black horizontal lines bounding upper and lower surfaces of cell represent Ag-AgCl electrodes; cross-hatching, insulating spacers; density of dots, concentration of electrolyte.

- (a) Cell in equilibrium, concentration uniform.
- (b) Cell with external applied potential difference (charging of cell).
- (c) Concentration cell with transference, EMF being measured with a potentiometer or high resistance voltmeter.

a.

b.

c.

Figure 9

Equivalent Circuit Corresponding to Cells of Figure 8

- (a) Basic circuit.
- (b) Charging with external source.
- (c) Self-discharge (free diffusion).

a.

b.

c.

F is the Faraday constant; C_a and C_o are the concentrations at the two electrodes. For an ideal transference cell,

$$E_c = -\frac{2RT}{F} \ln \frac{C_o}{C_a} .$$

Each of the three circuit elements of Figure 9a is non-linear; that is, the current through the resistances is not proportional to the applied potential difference, and the charge on the condenser is not proportional to the applied voltage, except for certain limiting conditions. For steady-state operation of the cell, suitable mathematical relations between EMF, current, and concentration are readily found.

In Figure 9b the current corresponding to Figure 8b is analyzed. The flow of negative charge through the right hand side is electrically equivalent to a positive charge flowing in the opposite direction. Thus, the current through the left is considered to be carried by the cation only, and the current through the right by the anion only. The current in the external circuit is the sum of these two.

The current during self-discharge of the cell is shown in Figure 9c. The internal current is equivalent to free diffusion of the salt, with the flux of positive ions equal to the flux of negative ions, as required by the electroneutrality condition. From the electrical circuit standpoint, this means that the current through the left must be equal to that through the right. A negligible current flows through the external circuit to actuate the measuring instrument.

A mathematical analysis based on this model leads directly to correct results for (a) the cell resistance, (b) the EMF of a concentration cell with transference, (c) the Nernst diffusion equation. In addition, equations for (d) the capacitance of the condenser, (e) current as a function of applied potential difference, and (f) concentration difference as a function of applied potential difference, are derived, none of which have been tested experimentally. Mixtures of electrolytes have been briefly considered. The concept of diffusion potential has been critically re-examined, and it is shown that the present model describes the characteristics of the cell in a far simpler manner than does this non-operational concept. Finally, it is shown on the basis of the model that EMF measurements on transference cells can yield thermodynamic properties of electrolytes directly, without auxiliary transference number data.

Thermodynamics of the Steady State⁴⁵ - According to the modern theory of the thermodynamics of the steady state, the phenomenological behavior of a flow system in which two forces are operative can be described by the equations

$$J_1 = L_{11}X_1 + L_{12}X_2$$

$$J_2 = L_{21}X_1 + L_{22}X_2$$

where the J 's are generalized flow vectors, the X 's are generalized force vectors, and the L 's are scalar proportionality factors having the nature of generalized conductances. The factors L_{12} and L_{21} are "coupling coefficients," representing the possible mutual coupling of the two flows. A basic theorem of this field, due to Onsager, states that

$$L_{12} = L_{21}$$

In applying this theory to a specific case, the choice of variables is of great importance. Previous applications to the transference cell are based on the selection of diffusion potential as one of the forces.⁴⁶ In the opinion of the author, this has not led to very useful results. The two forces selected in the present treatment are dE/dx , the cell potential gradient applied or measured, and $d\mu/dx$, the chemical potential gradient. (The same example is chosen as in the equivalent circuit treatment.) Both of these forces are operationally defined. As flow vectors, the electric current density I (amp cm^{-2}) and the flux J_+ of positive ion (equivalents $\text{cm}^{-2} \text{sec}^{-1}$), which is equal to the net flux J of electrolyte, are taken. The resulting equations are

$$I = L_{11}dE/dx + L_{12} d\mu/dx$$

$$-J_+ = L_{21}dE/dx + L_{22} d\mu/dx$$

The minus sign precedes J_+ in recognition of the convention that I represents a flow of electrons. When subjected to the same force, I and J_+ are in opposite directions. The remaining problem is to express the L 's in terms of familiar measurable quantities. It is readily shown that the evaluation of the L 's lead to the pair of equations

$$I = C \wedge \left[(dE/dx) + (t_+/F) (d\mu/dx) \right]$$

$$-J_+ = \frac{C \wedge t_+}{F} \left[(dE/dx) + (1/F) (d\mu/dx) \right]$$

⁴⁵General references: S. R. de Groot, Thermodynamics of Irreversible Processes (North-Holland Publishing Co., Amsterdam, 1951); K. G. Denbigh, The Thermodynamics of the Steady State (Methuen and Co., London, 1951).

⁴⁶S. R. de Groot, J. Phys. Rad. 8, 188, 193 (1947); K. G. Denbigh, loc. cit., p. 78.

where Λ is the equivalent conductance of the electrolytes, and t_+ is the cation transference number. The validity of these equations can be checked in several ways. For example, they lead to correct expressions for the EMF of a concentration cell with transference and for the diffusion of electrolytes (Nernst), and they satisfy the Onsager condition $L_{12} = L_{21}$. They are a compact and convenient quantitative description of the transference cell containing a binary 1-1 electrolyte. The general conclusions reached by the equivalent circuit approach are confirmed in the present treatment.

Isotope Effect in the Bromine Oxidation of Ethanol - Louis Kaplan

The oxidation of ethanol by bromine in dilute aqueous solution takes place according to the equations

On the basis of kinetic studies^{47,48} of these reactions the following three alternative mechanisms have been proposed⁴⁸ for the alcohol oxidation.

with reaction (1) the rate-determining step.

with (3) the rate-determining step.

with (6) as the rate-determining step.

⁴⁷Bugarszky, Z. physik. Chem. 38, 561 (1901); 71, 705 (1910).

⁴⁸Farkas et al., J. Am. Chem. Soc. 71, 2829 (1949).

Farkas *et al.*⁴⁸ appear to favor mechanism (a), which is supported by the existence of alkyl hypochlorites, which are known to break up into aldehyde and hydrochloric acid. Mechanism (c) is considered least probable, because no reactions analogous to (6), in which hydrogen is replaced by bromine in a reaction of the second order, are known to occur at room temperature.

The study of the hydrogen isotope effect for this reaction was carried out in order to further limit the possible mechanisms. Mechanisms (b) and (c), the rate-determining steps of which involve the rupture of a carbon-hydrogen bond, would be expected to show an isotope effect;⁴⁹ mechanism (a) should show little if any such effect.

Ethanol-1-t was prepared by the reduction of ethyl acetate with lithium aluminum hydride-t.⁵⁰ The absence of tritium in the methyl group was established by oxidation of a portion of the ethanol-1-t with neutral permanganate; the resulting acetic acid was free of tritium. That no methyl tritium was lost by exchange during the oxidation was proved by oxidizing ordinary ethanol in the presence of tritium water; the acetic acid was again tritium-free.

Aqueous solutions of ethanol-1-t (about 1 per cent by weight) were treated with varying amounts of bromine, and the reaction mixtures were kept at 37.5°C until the bromine was decolorized. After treatment with silver oxide to remove aldehyde and HBr, the ethanol was steam distilled. An aliquot from each reaction mixture was analyzed for residual ethanol by oxidation with excess dichromate in sulfuric acid solution, and back-titration of the excess with ferrous ion. The remaining ethanol was converted to the p-nitro-benzoate, which was then purified by recrystallization from pentene. Its specific activity was determined by combustion, conversion of the combustion water to hydrogen over heated zinc, followed by measurement of the ion current with a vibrating reed electrometer. The results are summarized in Table 7.

For the isotopic reactions

it can be readily shown that for incomplete reaction

$$\frac{\log (A)/(A)_0}{\log (A)/(A)_0} = \frac{k_2 + k_3}{k_1}$$

⁴⁹Westheimer and Nicolaides, J. Am. Chem. Soc. 71, 25 (1949).

⁵⁰Wilzbach and Kaplan, J. Am. Chem. Soc. 72, 5795 (1950).

Table 7

ISOTOPE EFFECT IN THE BROMINE OXIDATION OF ETHANOL

Run	Initial EtOH (mmoles)	Br ₂ (mmoles)	Final EtOH (mmoles)	Specific Activity (microcuries/mmole)	(k ₂ + k ₃)/k ₁
1	9.52	0*	9.25	12.34**	
2	9.52	9.1	4.95	16.15	0.568
3	9.52	14.5	2.40	22.00	0.571
4	19.04	33.3	2.87	26.85	0.582
5	9.52	9.7 *	5.13	15.95	0.562
					Mean 0.571

*Contained 35 mmoles HBr

**P-nitrobenzoate prepared directly from EtOH-1-t contained 12.23 microcuries/mmole

where (A') and (A) refer to the final concentrations of CH₃CHTOH and CH₃CH₂OH, respectively, and (A')₀ and (A)₀ refer to the corresponding initial concentrations. In terms of specific activities, this can be expressed as

$$\frac{k_2 + k_3}{k_1} = 1 + \frac{\log \left[\frac{(A')}{(A)} \frac{(A')_0}{(A)_0} \right]}{\log \frac{(A)}{(A)_0}}$$

where (A')/(A) is proportional to the specific activity, and (A)/(A)₀ corresponds to the fraction of ethanol not reacted. The value of (k₂ + k₃)/k₁ calculated for each experiment is included in Table 7. If it is assumed that k₁/k₂ = 2 (i.e., that the substitution of a C-T bond for a C-H bond does not affect the rate of rupture of an adjacent C-H bond), then k₂/k₃ = k_H/k_T = 7.

An isotope effect of this magnitude renders mechanism (a) highly improbable. Of the two remaining mechanisms, (c) is considered unlikely because of the objections mentioned above. Favoring mechanism (b), also, is the observation⁴⁸ that tribromide ion, Br₃⁻, is not an effective oxidizing agent for ethanol. Since (b) involves the removal of a negative hydride ion, it is not surprising that a negatively charged reactant would be ineffective. The observed isotope effect is considerably greater than that in some other reactions⁵¹ involving hydride transfer. This difference may, perhaps, be attributable to a low vibration frequency for the Br-H bond in Br₂ H⁻.

⁵¹Kaplan and Wilzbach, J. Am. Chem. Soc. 74, 6152 (1952).

Synthesis of Trimethyl Borate - R. Barnes, H. Diamond, and P. Fields

A proposed liquid scintillation counter⁵² for measuring fast neutrons, based on the $B^{10}(n,\alpha)Li^7$ reaction, requires a boron ester enriched in B^{10} . High efficiency thermal neutron liquid scintillation counters⁵³ also require the maximum density of B^{10} provided by boron esters. Of these esters, methyl borate is miscible with the fluorescent medium without quenching and has the highest boron density. The only available sources of B^{10} are boron trifluoride complexes. Boron trifluoride etherate, 78 per cent B^{10} , was chosen as the starting material because of availability, ease of handling, and the reactivity of boron trifluoride in this form. The reaction used for preparing methyl borate from this source is:

Since carbon-14 contributes to the background of the counter, care should be exercised to use sodium methyllate and methanol that are free of this isotope.

A two-liter three-necked flask was equipped with a two-foot Stedmann fractionating column, a thermometer, and a magnetic stirrer. The system was open to the atmosphere through a calcium chloride tube. The following procedure was used:

1. Nine moles of dry sodium methyllate were added slowly to 36 moles of anhydrous methanol with stirring. Continuous stirring prevented the formation of a hard cake by the partially dissolved sodium methyllate.
2. Three moles of boron trifluoride etherate were added dropwise, with stirring. The flask was equipped with an ice bath during this step. Ether vapors rising in the column served to trap and return any boron trifluoride liberated by the local heat at the site of reaction.
3. The ice bath was replaced with a Glas-col heating mantle and the mixture refluxed for 25 hours.
4. The column was fitted with a partial condensation-partial takeoff head with an adjustable cold finger, and the ether was distilled off at 36°C.
5. The azeotrope of methanol and methyl borate was collected at 55°C.

⁵²C. O. Muehlhause and G. E. Thomas, Jr., *Nucleonics*, 11, 44 (1953).

⁵³C. O. Muehlhause and G. E. Thomas, *Phys. Rev.* 85, 926, (1952).

6. The methanol-methyl borate azeotrope was treated with the minimum amount of concentrated sulfuric acid necessary to cause layering.⁵⁴ The upper layer, containing the methyl borate along with a small amount of methanol, was treated with acid several times more. The upper layer was then distilled and the excess methanol removed as the azeotrope at 55°C. The pure methyl borate was then collected at 67.5 to 68.5°C. The combined lower layers were then distilled and the methyl borate collected as the azeotrope at 55°C. The pot residue was discarded. The 55°C fractions were combined and treated again with concentrated sulfuric acid, and the upper layer again distilled as above. The over-all yield of the reaction and the separation was about 50 per cent.

Several other procedures were found to be unsuitable. Reactions in aqueous solutions involved extra steps and more elaborate equipment. Direct reaction of calcium fluoborate with magnesium methylate resulted in low yields. Attempts to carry the reaction in solvents other than methanol, i.e., kerosene and dibutyl ether, gave poor yields. In the separation of the methanol-methyl borate azeotrope, carbon disulfide was used to form a preferential azeotrope with methanol which would leave the methyl borate behind; but traces of carbon disulfide, which proved impossible to remove from the methyl borate, quenched the scintillations in the counter.

The authors are grateful to Anderson Laboratories, Inc., of Adrian, Michigan, for information concerning their process for the separation of the methanol-methyl borate azeotrope, which has been adopted here.

⁵⁴H. I. Schlesinger, H. C. Brown, D. L. Mayfield, and J. R. Gilbreath, Jour. Am. Chem. Soc. 75, 213 (1953).