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Laboratory for Nuclear Science

PROGRESS REPORT

February 28, 1958

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This is the fifty-second progress report of the Laboratory for Nuclear Science at the Massachusetts Institute of Technology. Progress during the period December 1, 1957 through February 28, 1958 is recorded.

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CHEMISTRY OF THE FISSION ELEMENTS GROUP

I. Chemistry of the Fission Elements

A. Studies of Irreversible Electrochemical Reactions

Studies involving carbon tetrachloride, dibromacetic acid and p-dinitrobenzene have clearly demonstrated the effect on the half-wave potential of certain ions in the electrical double layer. Each of the above substances has at least two polarographic waves and, by control of the pH and the alcohol content of the solution, the electrocapillary maximum can be made to fall between the two reductions. Capillary-active ions like thiocyanate retarded the first wave, while tetramethylammonium ions accelerated the second wave for carbon tetrachloride and dibromoacetic acid. In contrast, the first wave for p-dinitrobenzene was unaffected by thiocyanate and the second only slightly so by the tetramethylammonium ion. This may indicate that the p-dinitrobenzene is reduced via a more nearly reversible reaction.

Another interesting difference in behavior was discovered with respect to the effect of calcium ion. The presence of calcium had virtually no effect on the reductions of the halogen-containing compounds or the first wave of the nitro compound. However, it greatly facilitated the second reduction of the nitro compound. Because calcium also aids the reduction of nitrate ion, a more specific mechanism may be involved which is not associated with charge alone.

Gelatin has been found to produce a cathodic shift for all waves in alkaline medium except the first one for p-dinitrobenzene. In acidic solutions, however, it sometimes produces an anodic shift, probably as a result of its positive charge. (L. E. I. Hummelstedt)

In order to be able to interpret more clearly the effects brought about by changing the solvent, attempts are being made to estimate changes in junction potential. The junction potentials are being measured by means of several different electrode systems, including a palladium-hydrogen electrode which has not as yet been extensively studied by others.

The palladium-palladium black electrode is being compared with a standard hydrogen electrode in a variety of solutions. In addition to exhibiting a constant difference in potential from its platinum counterpart, the palladium electrode appears to be more readily polarized, especially in solutions containing substantial percentages of ethyl alcohol. (R. F. Breese)

B. Application of Ion-Exchange Membranes

A study is being initiated to explore possible analytical applications of ion-exchange membranes. The effects of different experimental conditions on the reproducibility with which the ions can be transported through the membrane will be examined first. (R. B. Hanselman)

C. Luminescence of Chelates

In an attempt to evaluate the effect of changes in structure on the fluorescence spectrum, zinc derivatives of 5-nitroso 8-quinolinol and 8-quinolinol-5-sulfonic acid have been prepared. Analyses of these substances are being made to check their compositions following which fluorescence spectra and quantum yields will be determined. (O. Popovych)

A similar study of dihydroxynaphthols is being initiated, except that the emphasis will be on the phosphorescence properties. The parent organic molecules will be studied before making any derivatives. (R. E. Griswold)

D. Gas Chromatography

Selectivity studies in gas chromatography have been largely confined to the use of different liquids supported on inert solids. The present study is being started in order to evaluate systematically whether or not the properties of different adsorbents can be combined effectively with those of the partitioning liquid. (J. J. Duffield)

Work on the use of gas chromatography for the determination of the composition of polymeric materials was abandoned when it was learned that an extensive program of investigation along these lines had been carried out in an industrial laboratory. Attention has been turned to the study of the retention time of gases in adsorption chromatography. Experiments with a number of the fixed gases have indicated a linear relationship between the logarithm of retention time and the constant "b" in the Van der Waal's equation for the carrier gas. Attempts will be made to see if a similar relationship holds for more complex molecules at higher temperatures. (T. J. Healy)

E. Flame Photometry

Factorial studies of the mutual interference of lithium, sodium and potassium as chlorides in the hydrogen flame have been undertaken. The work to date has been mainly concerned with the measurement of 5 to 10 parts per million levels of sodium in the presence of 10 to 20 times as much lithium and/or potassium. At these levels mutual interferences have been found to be quite small and the experiment is being continued with higher levels of sodium and higher ratios of extraneous alkali to sodium. Instrumental variables which may affect the results, in particular, the effect of wavelength scanning rate upon peak height, are being studied. (W. H. Foster)

F. Millicoulometry

It has been shown that internal silver-silver chloride electrodes may lead to errors of 50 to 100% when the chloride concentrations employed are greater than a few tenths molar. This effect is not compensated by the running of blanks or the subtraction of residual currents. Satisfactory results have been obtained with cadmium over a wide range of chloride concentrations if the anode is separated from the electrolysis cell by a sintered glass disc and a salt bridge. Studies on the reduction of chromic salts to divalent chromium have been complicated by the complexity of the reactions involved, the simultaneous discharge of hydrogen ions, and the extreme sensitivity

of divalent chromium compounds to traces of oxygen. (B. Miller)

G. Fused Salt Systems

The use of molten salt systems as solvents for analytical operations is being studied. Equipment has been built for operations with temperatures up to about 900°C. Experience is being gathered in the use of the potassium chloride-sodium chloride eutectic mixture as a solvent. Exploratory polarographic investigations are being made to select the most favorable systems for electrochemical investigation. The major difficulty to date has been the destructive action upon the Vycor apparatus. (D. L. Maricle)

H. Silicon Carbide Indicator Electrodes

The behavior of silicon carbide electrodes was investigated for two cases where they might possess advantages over platinum electrodes. Silicon carbide is exceptionally stable to oxidation, even at high temperatures and it was hoped that a silicon carbide electrode would not be subject to potential drift found with platinum electrodes on oxidizing solutions. In dichromate and ceric solutions, silicon carbide electrodes showed a potential drift with time of the same order of magnitude as platinum electrodes. The potential drift was not affected by pretreatment in HNO_3 , HF , Ce(IV) or Fe(II) solutions. The possibility of using silicon carbide electrodes in strongly reducing solutions where platinum is not usable was also investigated. Surprisingly, silicon carbide exhibits a more oxidizing potential in Cr(II) solutions than platinum. This behavior is believed due to the formation of a stable intermediate silicon oxide coating (possibly SiO) on the electrode surface by reduction of an SiO_2 layer originally present. The potentials assumed by silicon carbide in reducing solutions are not reproducible and the electrode cannot be used as an end point indicator in Cr(II) titrations with satisfactory precision. The electrode is not pH sensitive in contrast with an oxidized Pt electrode. The resistance of silicon carbide electrodes ranges upward from 1 meg ohm precluding their use in voltammetry. The purity of the electrode does not affect its behavior--pure transparent SiC and commercial carborundum gave very similar potentials. The silicon carbide electrode does not seem to possess any advantage over platinum electrodes in potentiometric measurements. This project will not be continued. (Ann E. Baker)

I. Voltammetry of Thin Layers of Solution

An investigation of voltammetry using thin layers of solution has been started. Equations have been derived relating electrolysis current to time, potential, solution layer thickness, the diffusion coefficient and concentration of the electroactive species in solution. Because of the large ratio of electrode area to solution volume, this technique should possess high sensitivity and be applicable to analysis in the submicrogram region. An electrolysis cell suitable for the reduction or oxidation of a material present as a spot on a paper chromatogram has been constructed. Current potential curves for spots containing Pb, Tl and Cd have been obtained. In all cases, currents were lower by several orders of magnitude than predicted by theory, assuming the metal ion is free to diffuse in the paper after it is saturated with a KCl solution. The low currents are chiefly

due to adsorption of the metal ion by the paper. Various complexing agents are currently being investigated in an attempt to desorb the ions. Residual currents are large as a result of incomplete removal of O_2 . Equilibrium of the paper with a stream of N_2 is only partially effective in removing O_2 . Sodium sulfite reduces the O_2 to a negligible level but cannot be used in acid solution. In addition to the analysis of paper chromatograms we also plan to adapt the method to the electrolysis of small volumes of solutions adsorbed in spectrographic graphite electrodes.

(R. B. Hanselman)

ADDRESSES

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D. N. Hume

L. B. Rogers

NUCLEAR CHEMISTRY (INORGANIC) GROUP

I. Physico-Chemical Studies

A. Effects of Diffusion and Flow through Charged Membranes

Measurements were continued on the bi-ionic cell Ag, AgCl, HCl(0.002M), cation exchange membrane, NaCl(0.002M), AgCl, Ag in a lucite cell with channel 5 mm long, 1 mm wide, and about 1 mm deep, directly opposite each other on the two sides of the membrane. The membrane was usually two thicknesses of Rohm and Haas Amberplex C-1 of about 10×15 mm cross-section. The edges of the membrane were heated by passing along a copper super-heated-stem pipe to reduce lateral loss of solution. At the start of a series of runs, each membrane was equilibrated with the solution which would be in contact with it. In many of the experiments, manometers were attached to each side of the cell, which could otherwise be isolated by stop-cocks above and below the cell. The rates of flow on the two sides were made very nearly the same. Flow was measured in ml/minute. This is approximately the average linear rate of flow in meters per minute through the channels past the membranes.

From 4 to 115 ml/min, the electromotive force appears to decrease linearly with the rate of flow about 0.01 millivolt per ml/min. The value extrapolated to zero rate of flow is about that calculated for a liquid junction within the membrane, which is 34.7 mv if the solutions are pure and have the same concentration. When the flow is stopped, the electromotive force drops about 4-5 mv in 5-15 minutes and then increases to a maximum in a few hours. The subsequent slow decrease appears to be linear, but is probably exponential. The value extrapolated to zero time appears to be the same as the value for flow extrapolated to zero flow rate. The final slow change apparently corresponds to the regular shift from a concentration gradient within the membrane to one in the aqueous solution, which should be a drop of about 3.5 mv.

The rapid drop at the start is associated with the rapid diffusion of ions and water through the membrane. The bulk flow is from HCl to NaCl. The linear flow rate is 0.1 to 1 mm/hour and the pressure developed has been as great as 9.4 cm water, which is nearly ten per cent of the total osmotic pressure of either solution. This flow continues even after the electromotive force has passed through the maximum. The initial change is apparently caused by the concentration of total chloride in the solution at the hydrogen surface of the membrane being less than the average concentration while that at the sodium surface is greater. There are still some irregularities which need further experimentation. (G. Scatchard, R. L. Yoest)

B. Distribution of Hydrochloric Acid Between a Cation Exchanger and Dilute Aqueous Solution

Measurements of the distribution of an electrolyte between an ion-exchange resin and water have indicated that the activity coefficients within the resin behave essentially as in aqueous solutions of simple ions, except that they decrease very rapidly when the mean activity is small. The earlier results were thought to have been caused by experimental error until Kraus and Moore¹ found that the concentration of hydrogen ion in a very dilute aqueous solution of hydrochloric acid is actually less than that within a polystyrene trimethyl ammonium anion-exchange resin (Dowex 1) in equilibrium with it. Their results might be explained by hydrolysis or by the presence of a few weakly acidic sites in the resin.

We therefore measured the distribution of HCl between water and a sulfonated polystyrene cation-exchange resin (Dowex 50). Hydrolysis is impossible in this case and a weak chloride is much less probable than a weak acid. We made three pairs of duplicate measurements in which the concentration of the aqueous hydrochloric acid was varied from about 0.2 M to about 0.0002 M in steps. All of the HCl removed was determined by acid-base titration, and in the last pair also by electrometric chloride-silver titration. The checks were excellent.

Some approximate values of the concentrations of the chloride ion and the mean activity coefficients of HCl in the resin, as functions of the mean activity of HCl are:

TABLE 2.I

Distribution of HCl between Dowex 50 and Water

$a_{\pm}$	M_{Cl}^{R}	$\gamma_{\pm}^{\text{R}}$	$D_{\text{Cl}}^{\text{W}}/\gamma_{\pm}^{\text{W}}$
0.2	0.02	0.7	0.1
0.02	0.002	0.3	0.1
0.002	0.0006	0.04	0.3
0.0002	0.0003	0.007	1.5

The concentration of hydrogen ion in the resin M_{H}^{R} is 4.6 M at all dilutions. In spite of the fact that there is only about one per cent change in the electrolyte concentration in the resin, the mean activity coefficient varies about a hundred fold.

Another way of describing the anomaly is the distribution coefficient, corrected for the activity coefficients in the aqueous phase, $D_{\text{Cl}}^{\text{W}}/\gamma_{\pm}^{\text{W}} = M_{\text{Cl}}^{\text{R}}/a_{\pm}^{\text{R}}$, which in dilute solution should be proportional to the mean activity. If there is retention of the aqueous phase, the distribution coefficient should approach a horizontal asymptote corresponding to the ratio of retained water to the total water. If there are sites at which anions are bound in a cation exchanger, the distribution coefficient should pass through a minimum. Our results seem to be near the minimum with our most concentrated solutions. In the most dilute solution, as in the experiments of Kraus and Moore¹, the chloride ion concentration is greater in the resin than in the aqueous solution.

We measured the water content of the resin only in the most dilute solution with high speed centrifugation, and have assumed that it is independent of the concentration of HCl. We should expect the error in the assumption to be nearly linear in the mean activity of hydrochloric acid and to be less than half per cent in our most concentrated solutions. There are some measurements², however, which indicate a much more rapid change in dilute solutions with a maximum error of about three per cent. The uncertainty of the water content is probably the greatest uncertainty of our measurements. (N. J. Anderson, and U. Schödel)

C. Activity of Water in Dilute Polyelectrolytes

The procurement and testing of parts and their assembly in the apparatus described in the last annual report (May 1957) are progressing. (G. Scatchard, F. G. Satkiewicz, G. Wilson and R. L. Yoest)

D. Water Content of Ion Exchangers

The greatest uncertainty in the measurement of the concentration of invading electrolyte in an ion-exchange resin comes from uncertainty as to the water content of the resin (see B). The greatest uncertainty in the measurement of distribution coefficients of the counter-ions come from the uncertainties in the content of water and of invading electrolyte. We are starting the study of the water content by determining its change with external concentration of electrolyte by measuring microphotographically the diameter of individual beads. (D. H. Freeman)

E. KCl Uptake by Anion-Exchange Resins

A detailed knowledge of electrolyte uptake by ion-exchange resins is important to the understanding of ionic interactions within the exchanger phase, and to other fields such as the determination of ion-ligand complex formation constants from anion-exchange measurements.

To date, little work has been reported on electrolyte uptake, particularly for dilute aqueous concentrations. The measurements which have been given show that very small amounts of potassium and hydrogen ions are very strongly adsorbed by anion-exchange resins. This sorption gives rise to very small activity coefficients for invading species from dilute solution, and is not in keeping with what must be expected if we are to consider the exchanger phase as a concentrated electrolyte solution of charged exchanger functional groups and oppositely charged exchangeable ions.

The present work³ resolves this difficulty into two parts, one pertaining to measurement problems and the other to characterization of variations in the behavior of different batches of the same resin. Strong-base anion-exchangers, Dowex 1 and Dowex 2, have been employed in these studies and in a number of cases, electrolyte uptake was found to be much more in keeping with what is ordinarily expected than earlier measurements would indicate.

The present measurement of electrolyte uptake was made by a procedure similar to that of Pepper, Reichenberg, and Hale⁴. Resin-chloride samples were batch-wise equilibrated with

KCl solutions containing 12-hr K^{42} . Following equilibration the resin was centrifuged to constant weight at 1000 G for fifteen minutes. Radioactivity of weighed resin samples and aliquots of solution were determined by well-type scintillation counting. A correction for solution retained by the centrifuged resin was applied by finding the amount of retention which occurs with glass beads under identical conditions. As will be shown later, this correction is probably lower than the retention which actually occurs with centrifuged resin. This possible difficulty has led to the expression of experimental results in terms of a simple distribution coefficient which is directly related to retention error.

The activity relation¹ which applies at equilibrium is given as:

$$m_K^r m_{Cl}^r (\gamma^r)^2 = (m_{KCl}^w)^2 (\gamma^w)^2 \quad (1)$$

where m is moles per kg of water, m^r is moles per kg of imbibed resin water, and γ is the mean ionic molal activity coefficient.

The distribution coefficient for electrolyte distributed in resin and aqueous phases is defined as:

$$D = \frac{m_K^r}{m_{KCl}^w} \quad (2)$$

The occurrence of retention error would give rise to an apparent value of D given by D' where:

$$D' = D + r \quad (3)$$

in which r is gms of retained solution per gm of imbibed resin water.

By rearranging (1), the true distribution coefficient should obey the law:

$$D = \left(\frac{\gamma^w}{\gamma^r} \right)^2 \frac{m_{KCl}^w}{m_{Cl}^r} \quad (4)$$

With decreasing concentration m_{Cl}^r is known to become constant (approaching the concentration of the exchange groups), the aqueous electrolyte activity coefficient approaches unity, and the activity coefficient of the invasion electrolyte should approach a finite limit. The limit is expected from the behavior of strong aqueous electrolyte mixtures at constant ionic strength to be:

$$\log \gamma_{HCl} = A + Bm_{HCl} \quad (4a)$$

for HCl in the presence of NaCl⁵. This rule should apply to the case of low invasion. (It is probably a good approximation up to rather high invasion*.) Thus, the limiting behavior of the distribution coefficient is given by:

$$D = k_0 m_{KCl}^w \quad (5)$$

* G. Scatchard, private communication.

with k_0 given as:

$$k_0 = \lim_{\substack{w \\ m_K \rightarrow 0}} \left[\left(\frac{\gamma^w}{\gamma^r} \right)^2 \frac{1}{m_{Cl}^r} \right] \quad (5a)$$

The values of D obtained by Kraus and Moore¹ in their study of HCl uptake by Dowex 1 were found to increase with decreasing aqueous HCl concentration. This differs from and is opposite to the behavior predicted by Equation 5. The authors offered the explanation that a small amount of tertiary amine, less than 0.3% of the exchange capacity of the resin, could account for this strong HCl adsorption effect. The same behavior of HCl was found by Gottlieb and Gregor⁶ in their study of electrolyte uptake by Dowex 2. This may also be caused by small amounts of tertiary amine in the Dowex 2 resin. In their measurements of several potassium salts with Dowex 2, a behavior very similar to that of HCl was found. This adsorption must be explained by something entirely different from the proposed explanation for HCl adsorption since potassium ion-amine interactions must be very weak, if not negligible.

The uptake of KCl, studied by Gottlieb and Gregor⁶ down to 0.01 molal, was measured in the present study, extending the range of the measurements to 10^{-6} molal. The results shown in Figure 2.1 are comparable with the earlier work over the same range studied. The measurement at 10^{-6} molal appears out of line with the general trend, and this lower value of D' suggests the possibility of cation-exchange being responsible for the strong adsorption of potassium ion. At 10^{-6} molal, the concentration ratio of hydronium ions relative to potassium is about ten per cent. Supposing the existence of an acidic hydrogen H attached to the exchanger matrix Z , an equilibrium such as:

would cause lesser K^+ sorption effects as the H^+ concentration becomes appreciable. These effects could be stopped altogether if the H were to be replaced by a non-ionizing group. To this end the resin was acetylated by successive treatment with acetic anhydride and acetyl chloride. In repeated measurements at 10^{-4} molal KCl, the value of D' was found to be four-fold less than that measured before resin acetylation. This result supports the argument that a small number of cation-exchange groups, (less than 0.1% of the anion-exchange capacity has been calculated) are responsible for the excessive sorption of potassium in the region of dilute aqueous concentration.

Electrolyte uptake by several other production batches of Dowex 2 was also studied. In one of these batches, strong cation adsorption was again observed in dilute solution. In two other batches, however, quite a different behavior was found; this is shown by Figure 2.2 for one of these samples. Correspondence with the manufacturer of the Dowex resins (Dow Chemical Company, Midland, Michigan) yielded the information that corresponding batches of resin which show strong cation adsorption in dilute solution had received a significantly higher temperature of amination, the final synthetic step in their manufacture. It appears likely, therefore, that under the

DOWEX 2, Lot 1278

Figure 2.1

KCl distribution on Dowex 2, Lot 1278;
(excessive cation sorption due to resin degradation).

DOWEX 2 x 7.5, Lot 749

Figure 2.2

Normal KCl distribution on Dowex 2, Lot 749.

DOWEX 1 x7.5, Lot 4307 - 43

Figure 2.3

Normal KCl distribution on Dowex 1, Lot 4054-19.

more strenuous conditions for amination, Dowex 2 undergoes a slight decomposition involving the formation of a very small but highly detectable capacity for cation-exchange.

In the determination of KCl uptake by Dowex 1, results similar to those obtained in the last batch of Dowex 2 were found and are shown in Figure 2.3. This weaker adsorption provides a primary criterion by which "abnormal" potassium sorption, i.e. Figure 2.1, can be defined. It is important to question to what extent the other results are "normal".

A constant value of D below 0.01 molal KCl conflicts with the ideal behavior described by Equation 5. It also conflicts with a capacity of the anion-exchanger for cation-exchange, the case for partial saturation of these sites is exemplified by Figure 2.1. A constant ratio of internal to external electrolyte concentrations is explainable if the resin had holes like a sponge, although this contradicts the picture of a resinous exchanger being microscopically continuous. The opposite explanation, i.e., the existence of patches of solution outside of the bead, is probably much closer to the correct explanation. Thus, a constant error of retention (r), as found in Eq. 3, must give rise to a constant apparent value of D for the case of an ideal resin described by Eq. 5. Since a correction for retention by equivalent volumes of glass beads has been already made, to designate the constant value of D' as due to an insufficient retention correction would imply more effective capillary forces between resin particles than those between glass beads. This may be related to a higher density of ionic groups for the resin as opposed to glass surfaces which

could be accentuated by a flattening of the bead-bead contact under the stress of centrifugation. To summarize, electrolyte uptake measurements on Dowex 1 and Dowex 2 fall into two classes. Certain batches of Dowex 2 show excessive adsorption of electrolyte from dilute solution, and other batches of both Dowex 1 and Dowex 2 show a constant value of the distribution coefficient at varying concentrations of dilute solution. Some experimental evidence was found to identify the source of excessive adsorption as due to a relatively small capacity for cation exchange within the anion exchanger. The finding of a constant value of the distribution coefficient at various dilute concentrations probably represents error due to an insufficient retention correction as measured from glass beads. (D. H. Freeman)

F. Determination of Ion-Exchange Phase Properties from Freezing Point Measurements

Cation exchange resin samples (Dowex 50, X10, 20-50 mesh) were equilibrated with HCl solutions of 9, 3, 1, and 0.1N and with demineralized water. After equilibration, the aqueous solutions were decanted from beads of resin and the equilibrium aqueous concentration determined titrimetrically.

The wet resin was then transferred to a Buechner funnel and suction applied for a few minutes to remove the excess solution on the surface of the resin beads. The resin was then placed on a pad of filter paper and blotted with another pad until free-flowing. Two small portions of the resin (about 1 gram) were then taken for determination of the total acid content of the resin (invasion electrolyte) and of total weight of solution in the resin (for determination of total water content).

The invasion acid content was determined by titrating a sodium chloride solution that had been passed through a weighed amount of resin in a small column or by titrating the resin directly with 0.1N NaOH. The two methods gave comparable results, with the direct titration being the faster. Since the equilibrium between resin and base is attained relatively slowly, a Beckman Model G pH meter was adapted to control a solenoid-operated buret and maintain the pH of the solution at about 7 up to equivalent point. It was felt that this method was preferable to adding an excess of base and back titrating in that errors due to invasion of base should be minimized.

The amount of solution inside the resin beads was determined by drying the resin at 105°C for 24 hours in a gravity-convection oven. It was found that this was the optimum length of time to obtain a constant dry weight of resin.

Two-gram portions of the same blotted resin were slowly cooled over a period of two hours in a vacuum-jacketed glass tube in a dry ice-acetone bath. A Wenner potentiometer reading to microvolts was used to obtain EMF-temperature of a copper-constantin thermo-couple buried in the resin sample. Readings were recorded at one minute intervals.

From a plot of EMF (temperature) vs. time during cooling (see Figure 2.4), the transition temperature (break in curve) at which the resin-phase electrolyte solution began to freeze out was determined. At lower concentrations it was more difficult to discern the break; hence the

Figure 2.4

Electromotive force-time values obtained during cooling of Dowex 50 samples after equilibration with 1M HCl and with water.

Figure 2.5

Freezing-point depression of aqueous HCl solutions vs. concentration of HCl.

value for 0.1 M HCl was obtained only on the warming curve. No transitions were seen in a number of runs at zero molar HCl (demineralized H₂O).

The temperature of the transition may be correlated with the effective HCl concentration if it is assumed that the freezing corresponds to that of the invasion HCl solutions, and that the resin does not participate. The HCl-H₂O phase diagram⁷ given in Figure 2.5, is then used to arrive at the effective concentrations listed below in Table 2.II.

TABLE 2.II
Equilibrium Concentrations of HCl in the Resin and Solution Phases

<u>External HCl Concentration</u>	<u>Temperature of Break in Cooling Curve</u>	<u>"Effective" HCl Concentration in Resin</u>
8.74 M	-47.6°C	9.8
3.09	-20.0	3.7
1.01	-17.8	3.5
0.102	-15.2	3.2
0.000	—	No transition observed

The authors are grateful to Prof. C. C. Stephenson for the use of the potentiometer and vacuum apparatus used in this work and to Mr. R. Lundell for his aid in making the freezing point determinations. (K. Kreiselmaier and L. Leifer)

G. The Dissociation and Extraction of Mineral Acids in Bis(2-chloroethyl) Ether

The thermodynamic acid dissociation constants K_{th} of HClO₄, HCl, HNO₃, HBr, and HGaCl₄ in water-saturated bis(2-chloroethyl) ether, as obtained from conductimetric measurements, are 1.1×10^{-4} , 5×10^{-8} , approximately 1×10^{-7} , and $\sim 1 \times 10^{-4}$ respectively. These constants are expressed in moles⁻¹ liters⁻¹ and the last two, i.e. for HBr and HGaCl₄, are estimated values based on special interpretation of the conductance-concentration curves with estimated anion mobilities. Figure 2.6 shows on double logarithmic scale the experimental conductivities in mho-cm² as a function of the acid concentration C in the organic phase, the various acids being designated on the figure.

The determination of K_{th} from conductimetric measurements is a theoretically well established procedure, but it is restricted to weak acids and to solvents of relatively high basicity and dielectric constant. It seems to be the only direct approach to the determination of the strength of mineral acids in bis(2-chloroethyl) ether. The conductance-concentration data were evaluated in terms of Debye-Huckel and Onsager ionic interaction theories⁸ modified by Bjerrum and Fuoss and Shedlovsky⁹ for application to weak electrolytes.

The theoretical basis of the procedure used can be summarized by the following set of equations:

$$K_{th} = \frac{c \alpha^2 f^2}{1 - \alpha} \quad (7)$$

Figure 2.6

Distribution of inorganic acids between bis(2-chloroethyl) ether and aqueous phases.

Figure 2.7

Concentration-dependence of the equivalent conductivity of some inorganic acids in wet bis(2-chloroethyl) ether.

$$\log f = -A\sqrt{\alpha c} \quad (8)$$

$$S(Z) = 1 + Z + Z^2/2 \quad (9)$$

$$Z = \frac{a\Lambda_0 + b}{\Lambda_0^{3/2}} \sqrt{\Lambda c} \quad (10)$$

$$\frac{1}{\Lambda S(Z)} = \frac{1}{\Lambda_0} + \frac{c\Lambda S(Z)f^2}{K_{th}\Lambda_0^2} \quad (11)$$

$$\alpha = \frac{\Lambda S(Z)}{\Lambda_0} = 1 - \frac{1}{K_{th}\Lambda_0^2} [c\Lambda^2 S^2(Z)f^2] \quad (12)$$

where c is the total acid molarity in the ether; α , the degree of dissociation; f , the molar mean ionic activity coefficient; Λ and Λ_0 , the equivalent conductances at a given concentration and at infinite dilution respectively; a and b the Onsager coefficients⁸; and A , the Debye-Huckel coefficient.⁹ Actually the background conductivity κ_0 of the solvent had to be taken as a parameter as it increased during the course of each experiment. The working out of the equations involves successive approximations for κ_0 , α , and f until the K_{th} values are stable.

The determination of Λ_0 from the experimental results by the extrapolation method of Fuoss and Shedlovsky¹⁰ was possible only for the case of HClO_4 . The fact that the Λ_0 values of mineral acids, as far as they have been measured in different solvents, differ less than 5% from each other in a particular system, led us to make the approximation that the experimental value $\Lambda_0 = 50 \text{ mho-cm}^2 \text{ mole}^{-1}$ for HClO_4 is a good approximation for all the other acids. Then for each experimental point, K_{th} was calculated by Eq. (7). An average of some 15 experimental points was considered in the case of each acid.

The extraction of dilute mineral acids from about 1 M in water into the ether phase increases in the order: H_2SO_4 , HCl , HBr , HClO_4 , HNO_3 . The ratios of the acid concentration in the ether phase to that in the aqueous phase were in the range 10^{-6} to 10^{-3} , increasing with increasing acid concentration. Figure 2.7 shows a plot of the equilibrium molar concentrations of the acids in the organic phase vs. the aqueous phase.

A commercial AC Wheatstone bridge equipped with a cathode-ray tube indicator and operating at 0.4, 1, and 5 Kc was used for conductimetric measurements. The bridge indicator was of sufficient sensitivity to be used for determinations of small amounts of acid by conductimetric microtitration to the resistance minimum. Since the investigated systems were air- and light-sensitive, all the transfer and measuring operations were carried out under the atmosphere of prepurified nitrogen. All the measurements were done at 25°C.

A possible platinum catalyzed self-decomposition of the ether was suspected, but measurements did not indicate any dissimilarities between gold-plated and platinum electrodes. These results are more extensive and more reliable than those given in earlier reports¹¹, and are being

prepared for publication. The results for HCl and HBr have been given separately¹². (E. Rudzitis and J. W. Irvine, Jr.)

H. Correlation of Overlap Integrals and Structure

General formulae and tables of values for two center overlap integrals with atomic orbitals of principal quantum number 4 have been computed. The general method is described in a recent paper.¹³ There has been deposited in the Library of Congress¹⁴, the general formulae and tables of values of the following overlap integrals: $S(2s-4s)$; $S(3s-4s)$; $S(2s-4p_{\sigma})$; $S(2p_{\sigma}-4s)$; $S(3s-4p_{\sigma})$; $S(3p_{\sigma}-4s)$; $S(2p_{\sigma}-4p_{\sigma})$; $S(3p_{\sigma}-4p_{\sigma})$; $S(2s-4d_{\sigma})$; $S(2p_{\sigma}-4d_{\sigma})$; $S(3p_{\sigma}-4d_{\sigma})$; $S(3p_{\pi}-4d_{\pi})$. Each table covers the following values of the parameters: $p = 1 - 9$, $t = -0.75, -0.50, -0.25, 0.00, +0.25, +0.50, \text{ and } +0.75$, based on the terminology of Mulliken et al¹⁵. (L. Leifer, J. R. Leto, and F. A. Cotton)

II. Solvent-Extraction Studies

A. Solvent Extraction of Indium Halides in Bis(2-Chloroethyl) Ether

A major portion of the study of the distribution behavior of InBr_3 and InCl_3 in HBr and HCl has been completed.

Equal volumes of a standardized aqueous phase containing radioactive tracer indium and freshly purified bis(2-chloroethyl) ether were shaken vigorously for 15 minutes in a specially constructed apparatus designed to maintain a temperature of $25.0^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$. Immediately upon removal from this apparatus the samples were centrifuged for approximately one minute to ensure phase separation before analysis. E , the distribution coefficient, was obtained directly by comparing the γ activities of equi-volumar aliquots of each phase.

The change in acid concentration in both aqueous and organic phases after equilibration of initially equal volumes of acid and ether was measured as a function of initial acid concentration, as was the change in phase volumes upon equilibration.¹⁶

Metallic indium, 99.97+% pure was dissolved in water saturated with HCl gas constantly bubbled through the solution. Traces of FeCl_3 were removed by an extraction procedure.

Specially purified In-free CdO was prepared by our extraction technique and bombarded with 16-Mev deuterons in the M.I.T. cyclotron for periods up to five hours. The 2.8-day In^{111} with some 48-day In^{114} was removed from the gross material by solvent extraction and purified without the aid of added carrier.

By far the most difficult portion of this work concerned the establishment of the validity of these measurements through their reproducibility.^{17, 18} Very early in this study it was found that duplicate samples often produced widely divergent results, while runs performed at different times were seldom comparable. Experiments performed with different batches of solvent were widely

divergent; a situation only slightly improved by prewashing the solvent and simple distillation at reduced pressure.

Any lack of agreement between successive batches of ether was most pronounced at the lowest In concentrations and it was impossible to detect any differences in the physical or chemical properties of batches that were quite different in extraction behavior. It was necessary to evaluate the condition and purity of the solvent by using it as the second phase in the extraction of carrier-free In from standard aqueous HCl. Studies over a period of several months showed that aging of the ether under various conditions invariably resulted in a decrease of the standard distribution coefficient while procedures designed for purification produced somewhat higher extraction. The ether was found to be sensitive to air oxidation, light, and thermal decomposition and hydrolysis under the normal conditions encountered in its handling. In addition, the immeasurably small concentrations of impurities sufficient to produce a marked change in the distribution of carrier-free indium were found to be auto-catalytic in regard to further decomposition. No detailed effort was made to identify the decomposition products, as the main concern was with their removal. However, the hypothesis that the offending material is a decomposition product of bis(2-chloroethyl) peroxide, and is a volatile, extractable organic acid is consistent with the information available.

As a result of somewhat extensive testing, the following procedure was developed. The ether as obtained from the manufacturer was passed through a 20-cm column of activated alumina to remove water and any stabilizer present. The effluent was then distilled at reduced pressure, under dry nitrogen through a 1-m vacuum-jacketed column, packed with pyrex helices. At the receiver end of the still the distillate was forced to run through a 10-cm column of alumina before collection. This latter column was designed to remove any polar impurities formed as a result of thermal decomposition which might have an autocatalytic effect. After passing through this system the ether was stored in black glass bottles through which a continuous stream of dry nitrogen was bubbled. Ether purified in this way gave the highest and most consistent distribution coefficients. The internal precision of measurements with this ether was 1% and the variation from batch to batch was approximately the same. All measurements reported as part of the extraction study were made with ether subjected to this treatment or its equivalent. Ether stored for more than 48 hours was discarded and an effort was made to limit storage to 24 hours.

The distribution coefficients, $E(\text{org/aq})$ for In(III) in HCl and HBr were measured both as a function of aqueous acid concentration and aqueous metal concentration. The initial acid concentration ranged from 0.25 M to the most concentrated aqueous solutions obtainable at room temperature and pressure. The initial In concentration was increased from carrier-free through nominal concentrations ranging from 10^{-8} M to 10^{-1} M in In.

It was found that E is a very strong function of the acid concentration, increasing approximately one million-fold across the acid range studied. The distribution coefficient is independent of In concentration from carrier-free up to a reasonably large concentration and then falls rapidly with further increases in concentration. The type of behavior is common to several similar

systems.¹⁸⁻²⁰ Several interpretations have been advanced,²⁰⁻²³ the most comprehensive, due to A. M. Poskanzer²⁴ will be used in this study.

The raw data must be corrected to describe the system at equilibrium. The most obvious corrections involve the changes from initial to equilibrium concentrations after the equilibration of equal volumes of each phase. These corrections arise both from the extraction of a given component and the phase volume changes due to mutual solubility. The aqueous phase volume increase was determined by titration.¹⁶ The equilibrium molar aqueous metal concentration C_M is calculated from the following stoichiometric equation, valid for the case of initially equal phase volumes:

$$C_M = C_O \frac{1}{(E+1) - \frac{\Delta V}{V_O} (E-1)} \quad (13)$$

where C_O is the initial aqueous metal concentration and $\frac{\Delta V}{V_O}$ the fractional aqueous phase volume increase.

The initial molality of each acid solution was calculated from the molarity as determined by direct titration, using literature density data²⁵.

When a solution of initial molality m_i is equilibrated with ether the molality changes due to both the extraction of acid and the extraction of water into the ether. The exact stoichiometric relation is:

$$m_i - m_E = \frac{(1 - \frac{\Delta V}{V_O})}{\rho_i f_i} (N_\beta - m_E \rho_\beta f_\beta) \quad (14)$$

where m_i is initial molality of aqueous phase, m_E its equilibrium molality; $\frac{\Delta V}{V_O}$ the fractional volume change, N_β the equilibrium acid molarity in the ether phase; ρ_i the initial density of aqueous phase, ρ_β the equilibrium density of organic phase, f_i the fraction of water in initial aqueous phase, and f_β the fraction of water in equilibrium organic phase.

As the total correction $m_i - m_E$ is small, m_E in the second term may be replaced by m_i and ρ_β may be replaced by the density of pure bis(2-chloroethyl) ether with f_β taken from the work of Horne.²⁶

The activities of both acids were obtained from the molal activity coefficients of the pure acids²⁵ and the equilibrium molality. A correction from the activity coefficient γ in pure water to the activity coefficient γ' in water saturated with ether should be considered. Poskanzer²⁴ has shown that this is of the form:

$$\gamma' = \gamma e^{-Bm_\beta} \quad (15)$$

where m_β is the molality of the ether in the aqueous phase. The constant B is difficult to evaluate precisely; he gives²⁴ $B = 0.059$ for HCl which introduces a maximum correction of -4% at 12N HCl, which was neglected.

Recalling the treatment²⁴ of Section IV-A above, the formation of the In complexes in both phases can be considered as:

where L^- is the ligand Cl^- or Br^- , and any complex is uniquely described by the parameters m , h , and z . The underlined symbols refer to the organic phase.

The experiments carried out fall in the Poskanzer category Type B - One Main Electrolyte. For experiments of this nature involving only a complexing acid and a conjugate metal salt in contact with a suitable organic phase, we have relationships, subject to the following conditions:

Case I - The hydrogen ions in the organic phase are due to the ionization of extracted HL.

$$\left(\frac{\partial \ln E}{\partial \ln C_M} \right)_{[\text{HL}]} = \frac{\overline{m}}{m} - 1 \quad (17)$$

$$\left(\frac{\partial \ln E}{\partial \ln [\text{HL}]} \right)_{C_M} = \overline{h} - 0.5 \overline{z} - \frac{\overline{m}}{m} (\overline{h} - 0.5 \overline{z}) \quad (18)$$

Case III - The hydrogen ions in the organic phase are due to the ionization of an acidic metal-containing species such as HZ, where Z^- may be any metal-containing anion.

$$\left(\frac{\partial \ln E}{\partial \ln C_M} \right)_{[\text{HL}]} = \frac{\overline{m}}{(1 - \overline{z})\overline{m}} - 1 \quad (19)$$

$$\left(\frac{\partial \ln E}{\partial \ln [\text{HL}]} \right)_{C_M} = \frac{1}{1 - \overline{z}} \left[\overline{h} - \overline{z} - \frac{\overline{m}}{m} (\overline{h} - 0.5 \overline{z}) \right] \quad (20)$$

It is evident from the relatively high extraction of HCl and HBr into bis(2-chloroethyl) ether that Case I should be valid for both these acids at low metal concentrations; certainly in the region of carrier-free concentrations. Case III is expected to be valid at high metal concentrations^{20, 22} as shown also from conductimetric studies in Section III-C above.

From the general shape of the curves^{18, 20, 24} showing E as a function of metal concentration at constant acidity the high plateau at low metal concentrations is regarded as the condition of Case I, with $\overline{m} = m = 1$. In this region of very low metal concentration polymerization is discounted.^{20, 22, 27} The rapid decrease of E at higher metal concentrations has been attributed by others²¹ to polymerization of the metal containing species; but as the slope of the curve demands higher polymers in the aqueous (higher dielectric) phase, this hypothesis is a weak one. In addition, direct ultracentrifugal experiments²⁷ with In and other metals which exhibit similar behavior in HCl have failed to show the existence of any significant concentration of polymer in the aqueous phase.

If it is postulated that this decrease is due instead to the increased contribution of hydrogen ion in the organic phase from the ionization of an extracted metal species HZ, several interesting conclusions may be drawn through the satisfaction of the conditions of Case III.

Several values of $\bar{z}$ have been calculated from equation (19). They exhibit a definite regularity, giving reasonable values for the average charge in the organic phase which reinforce the hypothesis that the extracted species is HZ and its acid ionization products, H^+ and Z^- .

In HCl at $C_M = 10^{-2}$, $\bar{z}$ varies from -0.83 to -0.50 over the acid range 3M to 11M (equilibrium). In the region 3M to 7.5M, $\bar{z}$ is constant within experimental error at -0.8 ; indicating 80% ionization of HZ.

From equation (20) we gain considerable information about the identity of the anion Z^- and are able to estimate $\bar{h}$. This equation may not be solved uniquely, for it is necessary to postulate a species, solve the equation, and judge the validity of the hypothetical species from the results thus obtained and other pertinent information.

For example, at $10^{-2}M$ $InCl_3$ and 5.04 M HCl it is found, following equation (20) that

$$\left(\frac{\partial \ln E}{\partial \ln [HL]} \right)_{C_M} = 1.01 \quad (21)$$

$$\bar{h} - z - \bar{h} + 0.5 z = 1.83 \quad (22)$$

It is informative²⁴ to define $\bar{n}$, the average number of ligands, including hydrogen, per metal atom in the aqueous phase and to evaluate it under these hypothetical conditions.

$$\bar{n} = 3 - (\bar{z} - 2\bar{h}) \quad (23)$$

Treating*the body of data for 5.0 M HCl, we make three alternative postulates.

Postulate A: Z^- is ML_4^- .

($InCl_4^-$ in the organic phase.) Then $\bar{h} - \bar{z}$ is 1, and $\bar{n}$ is 1.35. This value of $\bar{n}$ indicates very little coordination in the aqueous phase, the major aqueous species probably being $InCl^{++}$ and some $InCl_2^+$. This is not in agreement with formation constants^{28, 29} for indium chloride which indicate much higher coordination.

Postulate B: Z^- is HML_5^- .

($HInCl_5^-$ in the organic phase.) Then $\bar{h} - \bar{z}$ is 2, and $\bar{n}$ is 3.35, indicating for the aqueous phase mixtures of $InCl_3$ and $InCl_4^-$ consistent with the information^{28, 29} available concerning the aqueous phase species at this concentration.

Postulate C: Z^- is $H_2ML_6^-$.

($H_2InCl_6^-$ in the organic phase.) Then $\bar{h} - \bar{z}$ is 3, and $\bar{n}$ is 5.35, with the most prominent aqueous species being $InCl_5^{--}$ and $InCl_6^{---}$ or $HInCl_4$ and $HInCl_5^-$. This conclusion is not in

*There have been some revisions in the numerical evaluations of slopes; as a consequence the following analyses are only qualitatively correct.

agreement with anion-exchange conclusion of Marcus²⁹, but may be structurally attractive.

While these sample calculations are not conclusive alone, our experimental curves may be analyzed at several points under Case I or Case III conditions with more decisive conclusions. The most striking fact concerning this sample calculation is the failure of Hypothesis A, in direct contradiction to what had been anticipated from analogy^{18, 19, 20, 22} with Fe(III), Ga(III), and Au(III).

In HBr at $C_M = 10^{-3}$, $\bar{z}$ varies from -1.0 to -0.55 over the range 1 M to 8 M HBr. In the region 3 M to 7 M it is within experimental error -0.60, indicating 60% ionization of HZ in the organic phase. The decrease in $\bar{z}$ at low acid concentrations is consistent with the extremely low concentration of HBr in the organic phase.

Treating this information in the manner described above, for 3 - 7 M HBr, we find the following:

Postulate A: $Z^- = ML_4^-$.

($InBr_4^-$ in the organic phase.) Then $\bar{n}$ is 0.0, and $\bar{z}$ is 3.0, indicating no complexing in the aqueous phase, so that the only species is In^{+++} . This is obviously not consistent with what is known about the system.²⁸

Postulate B: $Z^- = HML_5^-$.

($HInBr_5^-$ in the organic phase.) Then $\bar{n}$ is 2.0, which indicates that $InBr_2^+$ is the most probable aqueous species. Bromide complex formation²⁸ is very probably greater at these acid concentrations.

Postulate C: $Z^- = H_2ML_6^-$.

($H_2InBr_6^-$ in the organic phase.) Then $\bar{n}$ is 4.0, indicating $InBr_4^-$ is the major aqueous species.

The results of Postulate C for HBr are in excellent agreement with the recent spectrophotometric study of Burns and Hume which shows that $InBr_4^-$ is the predominant species in aqueous HBr above 4 M.³⁰

The above interpretations are based on calculations for only one region of HL concentration. These calculations are being made over the entire available concentration range.

The present calculations and arguments seem good for Postulate C for In(III)-HBr, and although they give a different structural picture for In(III)-HCl, they seem acceptable here. Postulates C rest on analogous complexes in the organic phase, H_3ML_6 which has largely lost one proton by acid ionization. This is an unconventional formula compared to Fe(III), Ga(III), Au(III), and Tl(III). Woodward and Bill³¹ studied Raman spectra to exclude the form $InBr_4^-$ for the aqueous phase in about 5 M HBr, which our postulate C requires and which Burns and Hume support.

It should be recalled that different postulates for HCl and HBr may be required. From the same postulate, considerably different conclusions flow for the nature of the aqueous phase.

This is a consequence of the rather large differences in E and its HL dependence for the two acids, as well as of the differences in extractability of the complex formers HL.

In addition, it should be possible to check the various hypotheses in the organic phase by the direct titration of total acid in the case of HBr, where acid extraction is very low and metal extraction is relatively high. Direct verification of these hypotheses in HCl does not seem feasible at this time. The results of the more comprehensive analyses will be reported shortly.

(R. J. Dietz, Jr., and J. W. Irvine, Jr.)

III. Ion Exchange Studies

A. Liquid Anion Exchangers: The Extraction of Zn and Ag from Chloride Solutions by Dioctylamine Salts

Partly esterfied polybasic acids in inert organic solvents, such as dihexylphosphate HP in mineral oil, extract cations from aqueous electrolyte solutions by a process that can be considered as cation exchange:

Correspondingly substituted amines such as dioctylamine R in trichloroethylene show extractability for anionic metal complexes very analogous to anion exchange:

The name "liquid anion exchanger" is applied to this process.

Extensive study has been made of the physico-chemical variables involved in the extraction of tracer Zn and Ag from HCl solutions, to compare the results with the conventional resin anion exchangers³²⁻³⁵, such as Dowex 1, polystyrene methylene (trimethyl) ammonium chloride. What follows is a summary of an invited paper³⁶ for Zeitschrift Für Physikalische Chemie; figures are taken from the manuscript, with German concentration conventions. Part of this work was done on the Phoenix Project, University of Michigan.

The liquid anion exchangers extract metal anion complexes from aqueous solutions with high selectivity anionic complexes. The extraction curves (distribution coefficient D versus activity $a = (\text{Cl}^-) \gamma_{\pm}$ of complex-forming agent) have the same general form and the same type of charge with different cations as is observed with solid anion exchangers. In Figure 2.8 the extraction of tracer Zn from solutions of CaCl, HCl, and LiCl by a solution of 10% methyldioctylamine in trichloroethylene is shown in a log-log plot. This is to be compared with Figure 2.9, which gives similar curves for the absorption of tracer Zn by a solid anion exchanger (Dowex 1, 4% cross linked) from chloride solution.

Figure 2.8

Extraction of tracer Zn from solutions of CsCl, HCl, and LiCl by a liquid anion exchanger (10% methyldioctylamine in trichloroethylene).

Figure 2.9

Absorption of tracer Zn from solutions of CsCl, HCl, and LiCl by a solid anion exchanger (Dowex 1, 4% cross-linked).

Figure 2.10

Liquid anion exchange: dependence of the extraction coefficient of Zn upon the concentration of the active group (amine) in the organic phase.

It is difficult to study the effect of the concentration of the active groups of the ion exchanger on the absorption of ions from aqueous solutions. This can however be very easily done with the liquid ion exchangers, because by simple dilution of the organic phase their concentration can be varied over a wide range. Figure 2.10 represents the dependence of the extraction coefficient of Zn on the concentration of the amine in the organic phase. It is obvious that in the double log scale all the curves are parallel and have a slope of 2, indicating that D increases as the square of the amine concentration. This proves that for the absorption of one Zn atom two amino groups are necessary and the absorbed complex probably has the form $(\text{RH})_2 \text{ZnCl}_4$ (RH^+ stands for the substituted ammonium ion). This curve also shows that the cation effect is independent of the concentrations in the organic phase and must have its cause in the aqueous solution. The slope of 2 at low Cl^- activity in Figures 2.8 and 2.9 suggests that the step leading to the absorption or extraction of Zn can be described³² by:

The desorption which occurs at higher Cl^- concentrations is given by:

Therefore at higher Cl^- concentrations the curve should have the slope -2 . This is seen in Figure 2.9 with CsCl as supporting electrolyte only, large deviations being obvious with HCl and LiCl .

Figure 2.11 shows the extraction of Ag from chloride solutions as a function of the Cl^- activity; Figure 2.12 gives the dependence of the distribution coefficient on the amine concentration.

Figure 2.11

Liquid anion exchange: extraction of Ag from chloride solutions as a function of the chloride ion activity.

Figure 2.12

Liquid anion exchange: extraction of Ag from chloride solutions as a function of the active group (amine) concentration.

Figure 2.13

Liquid anion exchange: extraction of bromide ion from chloride solutions as a function of the chloride ion activity.

Figure 2.14

Liquid anion exchange: extraction of bromide ion from chloride solutions as a function of the active group (amine) concentration.

The analysis of the slopes suggests that the complex absorbed is R_2AgCl_3 and that the desorption is given by:

The absorption or extraction of Br^- by the anion exchanger can occur only by the formation of the ammonium bromide in the exchange phase RBr and its exchange by Cl^- ions must be described by:

Therefore slopes of -1 and $+1$ have to be expected for the curves $\log D$ versus $\log Cl$ and $\log D$ versus $\log$ amine concentration, as is seen in Figure 2.14 for $CsCl$, HCl , and $LiCl$, and as in Figure 2.13 for HCl . Again the $LiCl$ and HCl curves show considerable deviations from the expected slope. Obviously only $CsCl$ can be considered as an ideal supporting electrolyte. Further details and more complete analysis of the data are given elsewhere.³⁶ (U. Schindewolf)

B. Chemical Specificity in Cation Exchange: Charge and Radius Effects with Polyammino Cobaltic Complexes

Ion-exchange resins provide a powerful general method for the separation of similar materials, on the tracer or macro level of concentration, and one which is well suited for separating constituents in low-grade ores, exhausted fuel materials, and radionuclide mixtures.³⁵⁻³⁸ There are, however, few sound bases for predicting chemical specificity, and consequently for predicting its variation with ion-exchange column operating conditions such as nature of complexing agent in the eluant, nature of displacing ions, degree of loading, and rate of elution. The present investigation is directed towards studying the structural implications for cation-exchange equilibria of the ionic charge, radius and composition. The study is based on comparisons among the structures of the partially substituted ammino complexes of cobalt(III) and of other transition metals. A preliminary study of this type has been reported by Bench, Weisblatt, and Winget³⁹ without detailed controls and cross comparisons.

Extensive studies have been made on the system $Co(NH_3)_6^{3+} - La^{3+}$ with the sulfonated polystyrene exchanger Dowex 50, 8% cross linked. This serves as the reference system. The ion-exchange equilibrium has been approached from both sides, carrying out analyses with a scintillation counter and 5.3-yr Co^{60} and 40.2-hr La^{140} tracers. The stoichiometric nature of the ion-exchange process has been checked and the rate of approach to equilibrium noted. The logarithm of the equilibrium quotient $\log K_1$ for the process:

(where R is one equivalent of exchanger) falls nearly linearly from 2.2 to 1.4, as shown in the lower curve of Figure 2.15, as the cation mole fraction of $Co(NH_3)_6^{3+}$ in the resin phase changes from 0 to 1, when the solution ionic strength is kept at 0.2. Equilibrium is reached in about ten hours at $25.0^\circ C$, and a subsequent small drift is ascribed to slow aquation of the complex.

Corresponding studies on the system $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}\text{La}^{3+}$ give for the process:

values of $\log K_2$ falling from 3.3 to 2.4 as the mole fraction of $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ changes from 0 to 1 (compare the upper curve of Figure 2.15). The comparative affinities of the resin for $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ may be represented by $K_1/K_2^{1/2}$ referring to equal resin demand per cobalt complex. Thus it is seen that the tripositive complex has about three times the resin affinity of the dipositive complex. A larger difference was anticipated^{35, 38}. The fact that the affinity of $\text{Co}(\text{NH}_3)_6^{3+}$ is about sixty times that of La^{3+} suggests substantial hydration of the latter ion.

Figure 2.15

Ion exchange equilibria between hexammino-cobalt(III) and chloro-pentammino-cobalt(II) ions in respect to lanthanum ions in Dowex 50 NaR.

Further information on analogous ion-exchange equilibria will be reported from studies on $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$, $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^{1+}$, the ethylenediamine complex Coen_3^{3+} , $\text{Cr}(\text{NH}_3)_6^{3+}$, Cren_3^{3+} , $\text{Cu}(\text{NH}_3)_4^{2+}$, referred to La^{3+} , Ba^{2+} , and Na^+ , to discriminate among effects of charge, radius, and composition, including hydration. (B. Baysal)

IV. General Nuclear Chemistry

A. Determination of K in Rocks by Neutron Activation*

For a wide variety of common rocks and minerals virtually all of the radioactivity induced by a short thermal neutron irradiation is due to Na and K. The active species are 15-hr Na^{24} ($E_\beta = 1.4$ Mev, $E_\gamma = 2.75, 1.37$ Mev) and 12.5-hr K^{42} ($E_\beta = 3.5$ Mev, with $E_\gamma = 1.5$ Mev present in 10% of the decays). By selective β and γ counting the amounts of each active species can be measured separately. It is then possible to determine Na and K in many rocks by pile neutron irradiation of samples and standards followed by counting of the induced radioactivity without prior chemical processing.⁴⁰ A test experiment for the determination of potassium in granite, diabase, shale, clay, feldspar, biotite, muscovite, and lepidolite using a K_2CO_3 reference standard gave potassium contents with a few per cent accuracy by selective β -counting with an end-window proportional counter and Al absorbers. (Table 2.III).

Each sample of known K content (rated K_2O) was analyzed in quadruplicate by irradiating 20-mg portions sealed in Scotch Tape and Pliofilm in the Brookhaven Reactor for 15 min at a flux of about 10^{12} nn/cm²sec. They were counted without unwrapping 42 and 54 hours after irradiation in a proportional counter with 4 Al absorbers, and the averages of the four specimens of each for each set of counting data are presented in columns "A.M." and "P.M." of Table 2.III; the average of these is in the last column.

TABLE 2.III

Typical Radiochemical Activation Analyses for K in Geologic Materials

Sample(a)	Wt. % K_2O (rated)	Neutron Act. Anal.		
		A.M.	P.M.	Avg.
1. Diabase W1	0.63	0.5	---	0.5
2. Granite G1	5.4	5.34	5.12	5.2
3. Granite Haplo (synthetic)	5.7	5.44	5.35	5.4
4. Feldspar NBS No. 70	12.58	14.00	12.62	13.3
5. Plastic clay NBS No. 98	3.17	3.40	3.39	3.4
6. Shale composite (Feiss)	3.6	3.64	3.41	3.5
7. Biotite Goldich No. 13	6.9, 7.1	6.99	7.08	7.0
8. Biotite Sudbury Norite	7.95	8.46	8.32	8.4
9. Biotite Sudbury Murray Granite	8.5, 9.1	8.30	9.00	8.6
10. Muscovite Lithonia Gneiss, Georgia	9.2	8.75	10.00	9.4
11. Lepidolite Bikita Quarry	8.8, 9.7	9.10	8.58	8.8
12. Feldspar Meat Cove, N.S.	5.1	5.27	4.70	5.0

(a) The reliability of the rated K_2O contents of these samples is greatest for samples 1 - 7.

The principal source of error is believed to be in the counting, as can be seen by comparing the two columns "A.M." and "P.M." which are two separate countings of the same quadruplicate sets of samples. It was particularly difficult to obtain reproducible counting data when counting the sample through 1700 mg/cm^2 of Al to determine the gamma-ray contribution of Na^{24} to the total counting rate. Improved counting techniques should lead to much more accurate K determinations, and the method should be rapid and relatively independent from chemical contamination.

Part of this work was submitted in partial fulfillment of the requirements for the S. B. degree of M. Goldstein, Department of Geology and Geophysics, M.I.T., June 1957. Grateful acknowledgement is due Dr. H. L. Finston of the Brookhaven National Laboratory for use of laboratory facilities, and Professor P. M. Hurley of the Department of Geology and Geophysics, M.I.T., for providing the samples. (J. W. Winchester and M.I. Goldstein)

B. Search for Isomerism in Br^{78}

In "Nuclear Level Schemes"⁴¹, the cumulative information on Br^{78} has been interpreted to give the decay scheme shown in Figure 2.16. The case for isomeric transition rests largely on observation⁴² of the K_α x-rays of bromine in the decay of 6.4-min Br. Failure to observe the decay of ground-state Br^{78} requires that its half-period be appreciably under 6 min, so that Br^{78} rapidly attains secular equilibrium with $\text{Br}^{78\text{m}}$. On the other hand, theoretical considerations suggest that ground-state Br^{78} should have a half-period of 100 sec for $\log ft = 4.0$, with this as a rough lower limit.

Figure 2.16

Postulated nuclear level scheme of Br^{78} .

* This investigation was carried out in collaboration with Contract AT(30-1)-1381, Department of Geology and Geophysics, M.I.T., Professor P. M. Hurley, project leader, and is also discussed in his progress report.

Investigations are under way to clarify the situation. A "positron counter" has been built. This consists of two scintillation counters at 180° from the sample holder, each of which sends pulses through an amplifier to a discriminator set at 0.51 Mev and thence to a coincidence circuit, and scaler. In this way, only back-to-back 0.51-Mev coincidental gamma rays (annihilation radiation) are counted. When fast counting is required, the output from the last flip-flop on the coincidence scaler is sent to a motorized tape punch which automatically records the activity and time.

The M.I.T. Linear Electron Accelerator has been used to induce (γ, n) reactions in carbon tetrabromide. The electron energy is peaked around 16 Mev. The only activities induced by 16-Mev γ irradiation of CBr_4 should be $\text{Br}^{78\text{m}}$, Br^{78} , 4.5-hr $\text{Br}^{80\text{m}}$, and 18-min Br^{80} . Of these, the latter two would not have high activity when observed in a positron counter because only about 3% of the 18-min Br^{80} decay goes via β^+ emission⁴¹ and its half-period is relatively long. Therefore the only substantial activity we should observe is that due to the Br^{78} pair. If Br^{78} is produced in two states by γ irradiation, the shape of the decay curve will depend on the relative cross-sections for production of the two isomers, the half-life of the unknown ground state, and the length of the bombardment. It is apparent, then, that if one varies the length of bombardment and/or the energy of the electron beam for different runs, at least some of the runs should give evidence of decay of the lower state isomer, regardless of the extent to which it may be formed directly or grown in from the parent. Figure 2.17 illustrates this effect, using 15 sec and 1 min bombardments,

Figure 2.17

Calculated $\text{Br}^{78} \beta^+$ decay following (γ, n) activation of Br^{79} .

in the case where the cross-sections for production of the two isomers are assumed equal (which is a reasonable case) and where the lower state isomer is assumed to have a half-period of 1 min. Similar curves have been calculated for other cross-section ratios and for lower state half-lives between 1 sec and 5 min. In Fig. 2.17, a is the decay of the directly formed Br^{78} , b is the growth and decay of Br^{78} formed by isomeric transition of 6.4-min $\text{Br}^{78\text{m}}$, and c is the sum of curves a and b, all based on the assumed half-period of 1 min for Br^{78} , and equal cross-section for the formation of $\text{Br}^{78\text{m}}$ and Br^{78} . Subscript 1 refers to bombardment time $T = 15$ sec, and subscript 2 refers to $T = 1$ min. Curves for other assumed Br^{78} half-periods or other cross-section ratios would be comparable.

Figure 2.18

Experimental $\text{Br}^{78} \beta^+$ decay following (γ, n) activation of Br^{79} .

It turns out, however, that bombardments of 15 sec and 1 min duration both give pure 6.4-min decay; the first few minutes of the decay curves from these experiments are shown in Figure 2.18. The statistical error is about 7%, but the results are definite enough to exclude any reasonable possibility of the formation of a lower state Br^{78} of half-life between a few seconds and somewhat more than a minute, if it is formed in the bombardment with a probability comparable to the probability of formation of the excited state (6.4m Br^{78}).

Production of Br^{78} ground state was also tried by the $(n, 2n)$ reaction on natural bromine at the M.I.T. cyclotron, with β and γ counting to search for initial fast decay of independently formed ground-state Br^{78} or growth of this from excess of 6.4-min $\text{Br}^{78\text{m}}$. The results were less decisive but gave no good evidence for the existence of isomerism.

On the basis of these experiments, it is suspected that Br^{78} does not exist in isomeric states. Further decay observations are being carried out, but more decisive evidence will come from x-ray observations. Special thanks are due to Mr. Frank R. Paolini, Dr. William Bertozzi, and Dr. C. Philip Sargent for indispensable assistance. (W. R. Pierson, and C. D. Coryell)

C. Deuteron Reactions on Sr and Rb†

The feasibility of determining the relative amounts of Sr^{86} , Sr^{87} , and Rb^{85} in silicate materials by 15-Mev deuteron bombardment is being studied. Such information may lead to a method for age determination of minerals.

Deuteron bombardment of Sr and Rb produce Y and Sr activities according to the following reactions.

82.7% $\text{Sr}^{88}(\text{d}, 2\text{n})\text{Y}^{88}\beta^+$, EC, 105 day, $E_\gamma = 1.85$ Mev, other

7.0% $\text{Sr}^{87}(\text{d}, \text{n})\text{Y}^{88}$ "

$\text{Sr}^{87}(\text{d}, 2\text{n})\text{Y}^{87}$ IT, 14 hr $E_\gamma = 0.38$

β^+ , EC, 80 hr $E_\gamma = 0.51$, 0.48 others

9.8% $\text{Sr}^{86}(\text{d}, \text{n})\text{Y}^{87}$ "

$\text{Sr}^{86}(\text{d}, 2\text{n})\text{Y}^{86}\beta^+$, EC, 15 hr, $E_\gamma = 1.93$, others

0.55% $\text{Sr}^{84}(\text{d}, \text{n})\text{Y}^{85}$ 5 hr $\beta^+ ? \gamma ?$

$\text{Sr}^{84}(\text{d}, 2\text{n})\text{Y}^{84}\beta^+$, EC, 3.7 hr $E_\gamma = 0.51$, other

72.2% $\text{Rb}^{85}(\text{d}, 2\text{n})\text{Sr}^{85}$ IT, EC, 70 min, $E_\gamma = 0.23$, others

EC 64 day, $E_\gamma = 0.513$ delayed

$\text{Sr}^{84}(\text{d}, \text{p})\text{Sr}^{85}$ "

† This investigation was carried out in collaboration with Contract AT(30-1)-1381, Department of Geology & Geophysics, M.I.T., Professor P. M. Hurley, Project leader, and is also discussed in his Progress Report.

By measuring the relative amounts of the species Y^{88} , Y^{87} , Y^{86} , and Sr^{85} produced in a thick or thin target by deuteron bombardment, the relative amounts of Rb, normal Sr, and radiogenic Sr^{87} in the sample can be computed.

Preliminary experiments have been begun to measure the relative yields of these isotopes. A thin target of $SrCO_3$ (about 1 mg/cm^2) wrapped in Al foil was irradiated for 15 min with 15-Mev deuterons at 20 μamp in the M.I.T. cyclotron, the sample and Al foil were dissolved in HCl, 10 mg of Y carrier was added, and $Y(OH)_3$ was precipitated with NaOH. After purification by reprecipitation and washing, the total gamma activity of the Y fraction above 1.5 Mev was measured with an integral discriminator well-crystal scintillation counter. A decay curve was resolved into components of 15.0 hours over 3 half-lives and long (105 day). The ratio of 15.0 hr to long-lived activities at end of irradiation was 25.8. Assuming equal counting efficiencies for the two γ rays and one γ ray per decay in each case, it appears that the cross section for the reaction $Sr^{86}(d, 2n)Y^{86}$ is 1.3 times as great as the cross section for $Sr^{88}(d, 2n)Y^{88}$. The contribution of the reaction $Sr^{87}(d, n)Y^{88}$ has been neglected in this calculation, but will be taken into account with isotopically enriched materials. (J. Crocket*, J. W. Winchester, and K. Gowan*)

D. Determination of Nb by α -particle Activation†

Experiments are being carried out to test the feasibility of determining Nb in silicate materials by activation by cyclotron α particles (30 Mev). Nb is difficult to determine by ordinary chemical means and cannot be determined by neutron activation except in special samples. Irradiation by α particles followed by separation and counting of induced Tc activities could lead for Nb determination to a sensitivity of better than 1 ppm. The following reactions are important on the monoisotopic element:

It has been found that bombardment of a thick target (5 mg/cm^2 of Nb metal foil) gives predominantly the (α, n) reaction. However, bombardment of a thin target of finely divided Nb_2O_5 gives (α, n) and $(\alpha, 2n)$ reactions, and the cross section of the second is about 20 times greater than that of the first. A stacked foil experiment to determine an excitation curve for 30 Mev α particles on Nb metal is now in progress.

* Graduate students in the Department of Geology and Geophysics.

† This investigation was carried out in collaboration with Contract AT(30-1)-1381, Department of Geology and Geophysics, M.I.T., Professor P. M. Hurley, project leader, and is also discussed in his progress report.

Tracer Tc^{96} has been prepared by bombarding Nb metal, dissolving in hot H_2SO_4 , oxidizing with $\text{Na}_2\text{S}_2\text{O}_8$, and extracting the Tc with tetraphenylarsonium chloride $\phi_4\text{AsCl}$ in chloroform at pH 10.

A procedure for removing Tc from silicate rocks based on the extraction of $\phi_4\text{AsTcO}_4$ into organic media is being studied and looks promising.

Construction of a special sample holder for α -activation analysis is planned to permit equal bombardment of several samples on it. (Audrey Buryn* and J. W. Winchester)

E. A Radiochemical Study of Technetium in Fission

Work on a fast separation of technetium from the fission products is continuing. Present effort involves the solvent extraction of TcO_4^- into chloroform as the tetraphenyl arsonium salt. Low chloride and nitrate concentrations are found to enhance greatly the distribution coefficient of $\phi_4\text{AsTcO}_4$, so the work has been carried out in a sulfate medium. With a fast separation, it is hoped that Tc^{103} and Tc^{104} may be isolated from the fission products. Flegen^{43, 44} reports 1.2-min Tc^{103} and 3.8-min and 118-min Tc^{104} isomers. (J. T. Wasson)

F. Radiochemical Study of 6.7-hr I^{135}

An attempt at isolating I^{135} free from other fission products and interfering I activities has been made. This was done by using the method of Edwards⁴⁵ et al. for fast Se separation, but separating Te instead of Se. It is found that Te fission products exchange rapidly with freshly precipitated Te metal⁴⁶, providing a rapid one-step separation from the other fission products. The reported half-period of Te^{135} is < 2 min, and by quickly separating I^{135} from the Te, it is hoped to obtain I^{135} in a form in which a detailed scintillation-spectroscopy study may be made. (J. T. Wasson)

G. Gamma Rays of Short-lived Cs and Ba Fission Products

A scintillation-spectroscopy study of short-lived Cs in the fission products has been undertaken. The fast chemical separation following fission is that developed by Fix⁴⁷, who also reported γ radiation of greater than 0.7 Mev associated with 9.5-min Cs^{139} . Radiations were identified with the aid of an RCL256-channel analyzer at the Laboratory for Nuclear Science Data Center, supported by the Air Force. The detector consisted of a large (3" by 3") sodium iodide crystal. The work to date shows a γ ray of energy 1.28 Mev which seems to belong to Cs^{139} , and a γ of energy 0.86 Mev which decays with a half-period comparable with that of 85m Ba^{139} . Previously unreported γ rays of 32 min Cs^{138} are also suggested in the preliminary work. Coincidence studies are planned for the immediate future. (J. T. Wasson)

* Senior in the Department of Physics, M.I.T.

V. Fission Radiochemistry

A. Cd and In Fission Products in the Mass Region 117-119

In order to increase our understanding of the fission process, a study of the mass yields of nuclides in the fission-valley region formed in the bombardment of U^{238} with low energy particles has been undertaken. Natural U foil was bombarded with 14-Mev deuterons produced at the MIT Cyclotron, and with neutrons produced by the reaction of such deuterons on Be. Cadmium was separated from a basic solution containing hydroxylamine, tartrate, and cyanide into a chloroform solution of dithizone⁴⁸. In order to determine the cadmium yields quantitatively, Cd was precipitated with tetraphenylarsonium chloride and the excess of the reagent titrated potentiometrically with I_2 . Indium was milked from the cadmium by extraction with HBr into bis(2-chloroethyl ether) or by precipitation, carrier free, with NH_4OH .⁴⁸

In the course of this work, several new isotopes have been found. Beta rays of greater than 2 Mev, and a prominent γ ray of 0.8 Mev, are associated with the decay of a 3-min isomer of Cd^{119} . A 10-min isomer of Cd^{119} is detectable in neutron fission.⁴⁹ Both these nuclides decay⁵⁰ to 18-min In^{119} . There is some evidence indicating the existence of a 2-min isomer of In^{119} . The 118 mass chain is characterized by 50-min Cd^{118} decaying to 5-sec In^{118} , which exhibits a 4.5-Mev beta ray. The data in this region are in reasonable agreement with those of Knight and co-workers⁵¹. New decay data are also being sought for Cd^{117} and In^{117} isomers. Fission yields of the Cd isotopes formed in deuteron fission are being measured. (C. E. Gleit)

B. Charge Distribution in the Deuteron Fission of U^{235}

Previous studies⁵² on the deuteron fission of natural uranium (U^{238}), involving detailed analysis of the yield-mass curve and the measurement of the independent yields of six shielded nuclides, provide several arguments that the main path (0.8 ± 0.2) for fission involves capture of the deuteron, with (d, pf), stripping followed by fission, as a minor path. Confirmation of this conclusion has been provided by coincidence measurements⁵³ of Northrop and Stokes, who report the fractional yield of about 0.04 for the $U^{238}(d, pf)$ path, and a higher value (~ 0.15) for the $U^{235}(d, pf)$ path.

Work has been initiated on the yield-mass curve for the deuteron fission of U^{235} , and on the independent fission yield of shielded nuclides, which run higher here than in the U^{238} work. Enriched U^{235} ($\sim 95\%$) has been furnished by the New York Office of the Atomic Energy Commission. Table 2.IV shows the preliminary results for cumulative fission yields, referred to $Ba^{140} = 1.00$. Relative yields for six species (Mo and Ru) in the mass region 99-106 have been reported earlier⁵⁴, and a rough yield-mass curve indicated by Lessler⁵⁵ with 0.72 for Sr^{89} . Further work is in progress to define the yield-mass curve with higher precision, and to characterize in detail the charge-distribution pattern and the role of deuteron involvement in the fission process.

TABLE 2.IV

Cumulative Fission Yields in the Deuteron Fission of U²³⁵

Species	Cumulative Yield	Shielded Species	Independent Yield
51-day Sr ⁸⁹	0.65	18.6-day Rb ⁸⁶	1.5×10^{-3}
8.0-day I ¹³¹	0.82	13.0-day Cs ¹³⁶	0.19
77-hr Te ¹³²	0.66	12.8-day Ba ¹⁴⁰	(1.00)
30-yr Cs ¹³⁷	1.39		
12.8-day Ba ¹⁴⁰	(1.00)		

(P. del Marmol and C. D. Coryell)

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NUCLEAR CHEMISTRY (ORGANIC) GROUP

I. The Methanolysis of Triphenylmethyl Chloride In Benzene Solution

Excellent checks of the rate constants observed by E. E. Pegues¹ have been obtained using 0.08-0.12 M trityl chloride, 0.0005-0.0023 M tritium-labeled methanol and 0.01-0.10 M pyridine at 25°. In the runs using pyridine less than equivalent to trityl chloride, extra pyridine was added to the water to prevent its becoming acidic during extraction, a precaution not observed previously. The measured rates were found to be still practically independent of pyridine concentration.
(Y. Okamoto)

II. Mechanism of the Cannizzaro Reaction

A constant-temperature oil bath regulated to control at 100° has been set up and is operating satisfactorily. All preliminary arrangements have been completed for the first set of kinetic measurements which will be made with benzaldehyde-p-t.

Meanwhile, synthesis of an additional quantity of benzaldehyde-p-t is well under way. The photochlorination step has been completed and fractionation of the side-chain chlorides is in progress. This will be followed by hydrolysis of the benzal chloride fraction to benzaldehyde-p-t. Work is being initiated for preparation of a supply of benzyl-p-t benzoate-p-t. (A. L. Powell)

III. Comparison of Scintillation Counting Efficiencies of Different Compounds

Samples of known specific activity (from ionization chamber counting) of CH₂TOH, CH₃OT, HOT, CH₂TOCH₃, C₆H₅T and TC₆H₄CHO were compared by scintillation counting in toluene solution and toluene containing 15% methanol. In toluene the counting rates dropped 10-20% over a period of weeks, apparently due to adsorption on the walls of the counting bottles. With 15% methanol there was no such change in counting rates. The relative efficiencies in the latter solvent were benzene > benzaldehyde > water $\cong$ methanol (either kind) $\cong$ dimethyl ether, with the efficiency of the benzene 35% greater than that of the dimethyl ether. Since this is such a small range, an attempt was made to nullify the difference by counting in methanol solution. However, the efficiency was then so low for all the compounds that the readings were barely above background.

(K. H. Lohmann)

IV. Relative Reactivity of Different Leaving Groups in Polar Displacement Reactions

Rate constants have been determined for reactions of trimethylsulfonium perchlorate and methyl fluoride with methoxide ion in methanol. A method has been perfected for separating 10^{10} parts of radioactive methanol from one part of radioactive dimethyl ether by shaking with magnesium perchlorate saturated with dimethyl ether in petroleum ether. (K. H. Lohmann)

V. Relative Reactivity of Nucleophilic Reagents in Weakly Polar Solvents

Most of the previous studies of relative reactivity of different nucleophilic reagents have been in water or part-aqueous solvents like 50% acetone. Reactivities will be determined in benzene for comparison with the previous data. Methyl benzenesulfonate, containing tritium in the ring, will be allowed to react with various quaternary ammonium salts at 25° . Aliquot samples will be extracted with water and benzenesulfonate ion determined in the water extracts by scintillation counting. Methods for synthesis of tritiated methyl benzenesulfonate are now being investigated. (S. Weininger)

VI. Anion- and Cation-Solvating Power of Different Solvents

For correlating solvolytic reaction rates quantitatively, it would be helpful if independent measures of anion and cation solvating power of the different solvents could be obtained. An attempt will be made to obtain such measures from solubility measurements of sparingly soluble strong electrolytes in different solvents. Light and heavy (deuterated) solvents will be included in these studies. (E. R. Thornton)

VII. Mechanism of Proton Exchange Between Alcohols

The change of the shape of the doublet hydroxyl peak of isopropyl alcohol in the nuclear magnetic resonance spectrum is being used to measure the exchange rate. n-Butylamine proves to be a much more powerful catalyst for exchange than is water. However it is proving difficult to obtain accurately reproducible rates. (A. S. Rosenberg)

VIII. Hydrolysis of Benzoyl Chlorides
in Light and Heavy Water

The isotope effect is being determined in the hydrolysis of benzoyl and p-methyl- and p-nitrobenzoyl chlorides in light and heavy aqueous dioxane containing 9, 27 and 50% water at 25° by a conductivity method. A suitable thermostat bath constant to $\pm 0.002^\circ$ has been constructed and conductivity calibration curves are being determined with known mixtures.

IX. Stereospecificity of Free Radical Chain Reactions

The stereospecificity in the chain-carrying step for bromination by N-bromosuccinimide in which a carbon-hydrogen bond is broken has been examined with threo-1-bromo-2-deutero-1, 2-diphenylethane of deuterium content 1.00 g. atom D per mole. (For preparation, see previous L.N.S. Progress Report: for November 1957.) Reaction of this bromide with N-bromosuccinimide in carbon tetrachloride afforded meso- α, α' -dibromobibenzyl containing 0.978 g. atom D per mole (97.8% retention of D). From the data for this system and for the related erythro isomer reported earlier may be calculated the stereospecificity and the isotope effect for the carbon-hydrogen rupture by succinimide radical: stereospecificity (ease of removal of H₁ over ease of removal of H₂) ≥ 9.5 ; isotope effect (ease of removal of H₁ over ease of removal of D at position 1) = 4.8.

(G. Maciel)

As part of the program for the elucidation of the factors controlling the stereochemistry of free radical reactions, α -cyanobibenzyl has been prepared and subjected to brominating conditions with N-bromosuccinimide. Bromination occurs more slowly than with the α -bromo compound and affords a mixture of the two α -bromo- α' -cyanobibenzyls. Analysis of the mixture, utilizing stereospecific elimination reactions is in progress. (Paul Zanet)

X. Investigation of "Oxygen Extrusion" Reactions

The kinetics of decomposition of phthaloyl peroxide in carbon tetrachloride has been examined at 80° and 100°. Decomposition obeys first order kinetics: $k_{79.92^\circ\text{C}}$, $5.36 \pm 0.18 \times 10^{-7} \text{ sec}^{-1}$; $k_{100.39^\circ\text{C}}$, $5.15 \pm 0.09 \times 10^{-6} \text{ sec}^{-1}$; ΔH^* , 28.1 kcal/mole; ΔS^* , -7.8 e. u. The principal

product of decomposition is phthalic anhydride. The nature of this decomposition reaction and its relationship to decomposition of peracids will be examined utilizing oxygen-18. (F. D. Greene, II)

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PUBLICATIONS

C. G. Swain and E. E. Pegues, "The Mechanism of Methanolysis of Triphenylmethyl Chloride in Benzene Solution", J. Am. Chem. Soc., 80, 812 (1958).

C. G. Swain

F. D. Greene, II

COSMIC RAY GROUP

I. Multiplate Cloud Chamber Analysis

Measurements on the pictures taken with the large M.I.T. cloud chamber at the Brookhaven National Laboratory have been completed. These measurements have been processed, using an I.B.M. 650 computer, and a second machine program for the angular correlations in the production and decay of strange particles has also been used. Hence, final results will be forthcoming shortly on the cross sections for strange particle production, on the branching ratio for neutral decays of the θ^0 and Λ^0 , and on the angular correlations which give information concerning particle spins and parity non-conservation in the strange particle decays. Results available now on $\bar{\theta}$ interactions and on the lifetimes of the Λ^0 and the θ^0 , are presented below.

The neutral K meson, or θ^0 , is believed to be a mixture of two particles, the short-lived θ_1^0 , and the long-lived θ_2^0 . After the θ_1^0 component has died out and only the θ_2^0 is left, this θ_2^0 then consists of a mixture of the non-interacting, positive strangeness θ^0 and the strongly interacting, negative strangeness $\bar{\theta}^0$. When a θ_2^0 traverses the iron plates of our cloud chamber, its $\bar{\theta}^0$ component can interact, and if this interaction is with a single nucleon a hyperon and a π meson are produced ($\bar{\theta}^0 + \eta \rightarrow \gamma + \pi$). In an ideal case, then, the presence of a θ_2^0 can be detected because its point of production is marked by both the interaction of an incoming π meson in a plate of the chamber and by the associated production of a hyperon, and its interaction at some distance from the point of production is marked by the appearance of another hyperon and a π meson.

We have observed eleven cases in which a strange particle is produced by a neutral particle. Of these eleven, not more than one could have been caused by a high-energy neutron. Further support that these are θ_2^0 interactions comes from the determination that in ten of the cases, the decaying interaction product is definitely a hyperon. In one case the momentum of the particle is too high (~ 1 Bev/c) to allow a clear distinction between a Λ^0 and a θ^0 . In addition, the other expected reaction product, a π meson, is observed in at least half the cases. In four cases a charged π is seen, and in another case an associated shower is found, indicating a π^0 . Four of the remaining six events could have a charged π among the reaction products, but these cannot be identified definitely. Considering the large probability for the absorption of a π meson in an iron nucleus, the eleven events are all consistent with the reaction with a single nucleon, $\theta_2^0 + \eta \rightarrow \gamma + \pi$. Since this reaction is just like that of the K^- , this shows that the θ_2^0 must have a negative strangeness ($\bar{\theta}^0$) component.

In only three of the eleven cases is another strange particle seen which could have been produced in association with the θ_2^0 . However, from the number of associated productions we observe involving θ_1^0 's, we expect to see associated productions involving θ_2^0 's only 38% of the time.

This result is then also consistent with our sample being almost entirely θ_2^0 interactions.

In the eleven interactions, we have five cases of a Λ^0 , four of a $\Sigma^+ \rightarrow n + \pi^+$, one of $\Sigma^+ \rightarrow p + \pi^+$, and one of Λ^0 , or θ^0 . If the last is a Λ^0 , and if Σ^0 's are produced half as often as charged Σ 's, then putting in the inverse probabilities for the observation of the particles gives the number of Σ 's as ~ 5 times the number of Λ^0 's. This is consistent with charge independence combined with the experimental results for K^- absorption in liquid hydrogen. The result, however, suffers from the smallness of the sample.

The average number of plates a θ_2^0 traverses before interacting is a function of the extremely small mass difference, Δm , between the θ_1^0 and the θ_2^0 . Since the interaction distance depends also on the energy and angular distribution of the θ_2^0 's at production, we have calculated for each θ_1^0 seen in the chamber the probability that it would have produced an interaction had it been a θ_2^0 instead of a θ_1^0 . This calculation uses the known lifetimes of the θ_1^0 and θ_2^0 , the mean free paths for interaction of the K^+ and K^- , and the mass difference Δm . The values of Δm used were zero, the lifetime width $\hbar/\tau$ (where $\tau = 1 \times 10^{-10}$ sec.), and $\hbar/2\tau$. Normalizing to the total number of θ^0 's produced in the chamber, we obtain as a function of Δm , the total number of θ interactions expected, and their spatial distribution. Comparison of this semi-empirical calculation with the experimental observations shows that (1) both the total number of interactions and their distribution agree with the particle mixture theory, and (2) the agreement is much better for a mass difference of $\Delta m \approx \hbar/\tau$, than it is with $\Delta m \approx 0$.

The results of the life-time measurements are:

$$\tau_{\Lambda^0} = (2.4 \pm 0.2) \times 10^{-10} \text{ sec.}$$

$$\tau_{\theta^0} = (1.0 \pm 0.1) \times 10^{-10} \text{ sec.}$$

The latter is in agreement with essentially all recent measurements, but the former is somewhat lower than most determinations, although in agreement with the most recent result at Columbia. A decay curve for the Λ^0 shows a single exponential out to at least three mean lives, indicating that the Λ^0 is a single particle, and that there is no parity mixture. (E. Boldt, H. Bradt, H. S. Bridge, D. O. Caldwell, Y. Pal, and B. Rossi)

II. High-Counting Rate Monitor

The high-counting rate meson monitor has been brought to essentially its final form: three telescopes whose outputs are added and fed into one integrator circuit which will record the number of counts in each 30-second interval; in addition one of the telescopes is monitored independently by another integrator circuit. The absolute time is known to within 2 or 3 seconds; the number of counts per interval is known to an accuracy comparable with the statistics (1000 counts per second). Meteorologic effects are not large, since the meson component is relatively insensitive.

Figure 4.1

Cutaway view of a scintillator telescope unit.

Figure 4.2

Block diagram of electronic apparatus.

Figure 4.1 shows a view of one telescope; however, two 5" phototubes are now used in each box. Figure 4.2 is a block diagram of the apparatus. The coefficients for atmospheric pressure, and atmosphere height were obtained by standard regression methods, for two months of operation during 1957. The pressure coefficient found was $(-5.75 \pm 1.36)\%/in. Hg$, in agreement with the usual experience; the results on the other quantity were not significant, presumably because the observation interval was too short, and the nearest radiosonde station was 100 miles away (although an attempt was made to overcome the latter difficulty by interpolating between two or three stations). Figure 4.3 shows the average counting rate at 10 a.m. and 10 p.m. during May 1957,

Figure 4.3

Twice daily counting rates, corrected for atmospheric effects, during May 1957.

after correcting for meteorological effects (Olbert's¹ coefficient was used for the height correction). No reasonable assumption on the height correction can remove the general trend of the data; it is presumably real, corresponding to the slow changes of magnetic environment of the earth which are observed in much accentuated form with neutron monitors. Figure 4.4 shows a typical "Forbush decrease" which was observed on August 29, 1957. Figure 4.5 shows a very interesting rapid decrease which was observed on the night of February tenth, in connection with a large auroral display and magnetic storm.

The record (Figure 4.5) shows that a small decrease began at about 0100 Universal (Greenwich) Time on 11 February 1958, and the intensity had dropped 0.5% by 0240 U.T. At 0245 ± 5 U.T. the sharp drop began; the intensity dropped 2.1% in about one hour, leveling off at 0340 ± 5 U.T. The intensity remained at this level for a few hours (Table 4.I), then rose gradually to its pre-drop value, the total time from the drop being about 14 hours. The magnetic storm began with a "sudden commencement" at 0121 U.T.², and the aurora began a few minutes later. Presumably the three phenomena correspond to the arrival of ionized gas emitted from the

sun during the previous day, but the solar activity of that day was so great that it does not seem possible to identify the specific event that was responsible.

Figure 4.4

A typical Forbush type cosmic ray decrease, recorded on and after August 29, 1957.

Figure 4.5

Rapid decrease observed in connection with magnetic storm.

TABLE 4.I

Counting rate averaged over 8-minute intervals.
The standard deviation of each entry is ± 1.2 counts per second.

<u>Universal Time</u>	<u>Counts per Second</u>	<u>Universal Time</u>	<u>Counts per Second</u>
0002	639.3	0250	634.3
0010	640.0	0258	630.3
0018	640.5	0306	631.5
0026	639.3	0314	629.9
0034	641.8	0322	626.2
0042	640.0	0330	627.4
0050	640.5	0338	621.3
0058	642.9	0346	624.3
0106	638.0	0354	621.6
0114	639.7	0402	623.7
0122	637.7	0410	624.0
0130	634.8	0418	624.1
0138	637.1	0426	620.9
0146	638.1	0434	622.8
0154	637.7	0442	621.7
0202	637.4	0450	623.6
0210	632.7	0448	625.6
0218	637.4		
0226	636.6	0800	625.6
0234	638.8		
0242	637.5	1100	632.4
		1430	633.1
		1700	638.7

The event reported here resembles previously-reported "Forbush" decreases, except that the scale time is shorter. Theories of these decreases³⁻⁵ generally assume the arrival of solar gas clouds carrying magnetic fields which somehow exclude a fraction of the cosmic rays from the vicinity of the earth. The median energy of the primaries of the mesons recorded by our apparatus is about 10 Bev; the gyration radius of a 10-Bev proton in a field of B gauss is $3.3 \times 10^7 B^{-1}$ cm; and the minimum time in which a magnetic cloud of velocity v carrying a field B could make its effects felt is greater than $3.3 \times 10^7 (B v)^{-1}$ sec. This implies, for a typical gas-cloud velocity of 2000 km sec⁻¹, and a one-hour decrease a model-independent lower limit for B of

5×10^{-5} gauss. The actual lower limit depends on the model assumed; in the diffusion model³, for example, fields from two to three orders of magnitude greater than this would be required; in the gravitational-capture model the capture time is longer than one hour, and a more detailed calculation would be required to see whether the model could reproduce the effects reported. The model proposed by Cocconi et al. envisions an elongated tongue-shaped magnetic field drawn out from the sun by the outburst of gas, and remaining well-organized out to the earth's orbit. The decrease would then correspond to the tip of this tongue passing over the earth. The three models should give quite different predictions for the anisotropy of the cosmic-ray decreases. It would be very useful to have high-resolution records of these events from different parts of the world. We have submitted an account of this event for publication.

A search has been made for possible intensity increases connected with four solar flares of importance 3 or 3+; no evidence for an increase as large as a few tenths of a percent could be found. (R. A. R. Palmeira, R. G. D'Arcy, and R. W. Williams)

III. Large Air Shower Experiment

The entire catalogue of shower events is being scanned and a group of large events is being selected for re-analysis in order to obtain final results for the experiment based on a uniform procedure of analysis and having a greater statistical accuracy. (G. Clark, W. Kraushaar, J. Linsley, B. Rossi, and F. Scherb)

IV. India Air Shower Experiment

The new program for the I.B.M. 704 Computer is now being used to process the data on air shower arrival directions obtained at Kodaikanal, S. India. All the data for the approximately 40,000 events recorded during operation of the equipment with large scintillators has been received from S. India, and the computations are nearly complete. In addition, data from about 20,000 events recorded with small scintillators has been received. The latter data will give arrival direction information for showers which have a greater average size than the former group.

Another computer program has been written to carry out the statistical analysis of the computed arrival directions. This program is now being tested and will shortly be used to tabulate the results on the distribution of celestial arrival directions. (E. Chitnis and G. Clark)

V. Polarization of Cosmic-Ray μ -Mesons

The polarization of cosmic-ray μ -mesons depends on 1) the dynamics of the decay processes which give rise to the μ mesons (e.g., $\pi \rightarrow \mu + \nu$, $K_{\mu 2} \rightarrow \mu + \nu$), - and 2) the production

spectra of the parent particles⁶. The observed polarization⁷ is consistent with the theoretical prediction⁶ based on the assumption that low energy μ -mesons at sea-level come from the decay of μ -mesons. The μ -mesons which stop in a thin absorber at sea-level are those which arise from parent particles produced in nuclear disintegrations initiated by nuclear active particles with energies of the order of 10 Bev so that the apparent predominance of π -mesons among the parents of the observed μ -mesons is in accordance with observations of nuclear interactions at bevatron energies. Little evidence is available on the relative frequency of π and K-meson production at energies above the region of 10 Bev. Since the expected polarization of cosmic-ray μ -mesons which come from K-meson decays is much greater than from π -meson decays, it appears that a measurement of polarization as a function of depth underground may indicate the dependence on energy of the relative production frequency of π - and K-mesons.

μ -mesons which stop at a depth of 10^4 g cm^{-2} underground arise from parent particles produced in nuclear interactions of the order of 100 Bev. The differential range spectrum at 10^4 g cm^{-2} is reduced by a factor of about 10^2 under its value at sea-level, so that at 10^4 g cm^{-2} an absorber of roughly 100 times greater area than at sea-level must be used in order to accomplish a measurement of polarization in a time comparable to that required at sea-level. An apparatus with scintillation counters and an absorber area of 10 m^2 is now under construction. It will be built in four units, each of area 2.5 m^2 , and the first of these is nearing completion. The electronic apparatus is designed to measure the downward flux of decay electrons from μ -mesons stopping in a brass absorber. The measurement will be made alternately with and without a magnetic field on the absorber as in the previous smaller experiment. (G. Clark, and S. Saunders)

VI. Computation of Extensive Air Showers

The programming of the theoretical results on the extensive air showers is being continued. As mentioned in the preceding Progress Report (L.N.S. Quarterly Progress Report for November 30, 1957), this processing is meant as preparation for the numerical computations on the 704 I.B.M. computer. (S. Olbert, and D. Scott)

VII. Energy Flow in Air Showers

Two experiments on the absorption of the shower front have been undertaken at the Agassiz site: In the first, the energy detected by a stack of four scintillators has been recorded for a group of showers. The second experiment has been recently completed: here lead sheets were sandwiched above the scintillators. The results are now being analyzed. (T. L. Cline)

VIII. Volcano Ranch Air Shower Experiment

Production of the plastic scintillator discs is about 80 per cent complete. The steel cans to enclose the plastics have been delivered. So have the photomultiplier tubes. The preamplifiers and associated electronic equipment have been built and given extensive tests. A trial cable has been laid at the Agassiz site extending 7,000 feet from the headquarters building. Favorable results were obtained, so the balance of cable for the full experiment has been ordered. Work on the main part of the electronic equipment to be located at the central building is proceeding at a satisfactory rate.

Negotiations for land on which to locate the experiment seem to be near completion. A government permit for use of parts of the tract and a private lease for the remainder are ready for signatures. One of us intends to travel to New Mexico before the end of February to expedite the agreements. (J. Linsley and L. Scarsi)

IX. High-Energy Cosmic Gamma Rays

In addition to the low-energy γ -rays mentioned in the previous paragraphs, there exists the possibility that γ -rays of energy 50 Mev and over may be incident upon the atmosphere. Gamma rays in this energy region would arise from the decay of the neutral π -mesons, and so there is a potential source of γ -rays from wherever moderately energetic nuclear interactions are taking place, and wherever there is the annihilation of matter and anti-matter.

The design of this experiment is in a preliminary state. We expect to utilize a plastic scintillation counter in anticoincidence, followed by a converter and a coincidence telescope. The coincidence telescope, which will probably involve one scintillation counter and one Cerenkov counter, will detect the electron pairs formed in the converter.

This too will be a balloon-borne experiment, and it will be necessary to scan the sky in much the same way as discussed above for the low-energy γ -rays. (T. L. Cline, and W. L. Kraushaar)

X. Low-Energy Cosmic Gamma Rays

An experiment designed to survey the flux, energy and arrival directions of low energy (.3 - 3 Mev) cosmic γ -rays is under construction. We have speculated that such γ -rays might arise from processes such as

- 1) Decay of nuclei excited in stellar atmospheres;
- 2) Annihilation of positrons in stellar atmospheres;
- 3) Bremsstrahlung of high-energy particles;

- 4) Synchrotron radiation;
- 5) Annihilation of anti-matter in colliding galaxies.

Processes 1), 2), and 5) may show characteristic line spectra.

The principle experimental requirements that we have set and satisfied with a proposed balloon-borne apparatus are:

- 1) Determination of γ -ray energy to about 15%;
- 2) Elimination of charged-particle background;
- 3) Evaluation of locally produced γ -rays;
- 4) Determination of arrival direction with an angular resolution such that the most likely high-intensity source: the sun, is within the operation for about 10% of the flight time.

We have arranged the apparatus so that a large (2" $\times$ 3" diameter) Cesium Iodide crystal is enclosed in plastic scintillation material. This assembly is viewed by a single photomultiplier, and the circuitry is such that only those events which occur within the Cs I are recorded. The plastic, in effect, is in anti-coincidence with the Cs I, and this serves to eliminate easily and reliably the charged particle background. The scintillator and photomultiplier are enclosed in a heavy lead collimator, and the entire assembly sweeps automatically through the upper hemisphere. The pulses will be displayed on a miniature cathode ray tube and photographed, together with a clock, plumb bob and compass on 16 mm film.

It is expected, of course, that the apparatus will be recovered following the flight. Recovery, in recent years, has become virtually certain thanks to radar and aircraft tracking procedures. (W. Kraushaar and G. Clark)

XI. A Search for Long-Lived Particles in the Cosmic Ray Flux at Sea Level

References to the possible existence of a particle with mass ~ 550 me can be found in early literature^{8, 9, 10} dealing with the mass spectrum of the cosmic ray flux. Insufficient statistics and lack of reliability in the data, though, prevented any sort of positive identification. However, the report of Alikhanian et al¹¹ lends much support to the other evidence that there is an unstable particle intermediate in mass between the π and the K mesons. Also, the events reported by Alikhanian et al indicate that the lifetime may be comparable or longer than that of the μ meson. The reported large abundance (i.e. about 1 in 200 μ mesons) and complete lack of local production lead to this contention.

If the 550 me particle exists, with a lifetime longer than that of the μ meson, and has a range spectrum similar to it, then observations at sea level should detect an enhanced relative abundance of such particles. This hypothesis forms the basis for the investigation reported here.

In particular, this measurement did not attempt to make a direct mass selection, but rather to search for all decay modes consistent with a 550 me particle and exhibiting a lifetime greater than one microsecond.

The following general decay schemes were investigated:

Experiment No. 1) $550 \text{ me} \rightarrow \text{light meson} + Q + \dots$

where: $Q > 5 \text{ Mev}$

Experiment No. 2) $550 \text{ me} \rightarrow \pi^0 \text{ and/or } \gamma \text{ and/or } e^\pm + Q + \dots$

where: detectable energy released was greater than

80 Mev (e.g. there is 135 Mev from the π^0 decay).

Experiment No. 1): In the first experiment, an organic plastic scintillator of 55 kg mass was used as the stopping medium and as the main detector. The low efficiency of this scintillator (p-terphenyl in polystyrene) for γ -ray detection made it suitable only for the detection of charged decay products. Hence, it was used only for that part of this investigation which was concerned with the decay scheme that yields a light meson among the products.

The detector arrangement used is outlined in Figure 4.5a. A and C are slabs of the same material as is used for the main detector (B); and all are associated with 5" Dumont photomultiplier tubes (6364) as light detecting devices. A block diagram of the electronic apparatus is shown in Figure 4.7, and its operation may be described as follows:

The signal from B, (a coincidence between the discriminator outputs following the two phototubes B_1 and B_2 viewing the main detector), was used in connection with A and C (via ABC) to select particles arriving from above, and stopping in B. For this purpose, the energy release in B was required to exceed 10 Mev. The pulse (ABC), indicating a stopping particle, was fed to a trigger circuit which, after an intrinsic 20 microsecond delay, initiated a train of gates in the main five-channel delay coincidence discriminator, that extended to 36.6 milliseconds. An independent delayed coincidence circuit was also triggered by this signal (ABC) in order to monitor μ mesons stopping in B under the same operating conditions. Any delayed pulse ($B_1 + B_2$), arriving 4 to 14 microseconds after the primary particle stopped, was recorded by this monitor as a μ -meson.

The "event" signal for the main delay coincidence discriminator was arranged to indicate a decay of the first kind (i.e., Experiment No. 1). For this purpose the signals from B (B_1 and B_2) were fed through pulse height discriminators set at approximately a 5-Mev level, put in coincidence with one another, and in anticoincidence with A and the surrounding Geiger trays. In turn, these ($B_1 B_2 \bar{A} \bar{G}$) pulses were fed to a fast delay discriminator that gave an "event" pulse upon a delayed coincidence (4-10 microseconds) in any one of three successive independent time channels. These channels were separately monitored to check the lifetime of the ($\mu^\pm \rightarrow e^\pm$) signatures that defined the delayed events.

Figure 4.5a

The detector arrangement for experiment No. 1.

Figure 4.6

The detector arrangement for experiment No. 2.

Figure 4.7

Block diagram of electronic apparatus for experiment No. 1.

Figure 4.8

Block diagram of electronic apparatus for experiment No. 2.

Figure 4.9

Delayed events that correspond to the release of a charged light meson with more than 5 Mev energy.

Figure 4.10

Delayed events that correspond to the release of more than 80 Mev energy.

The channel widths for the main five-channel delay coincidence discriminator were set at the following values (in milliseconds):

I	II	III	IV	V
2.3	2.3	4.6	9.1	18.3

The lengths of the individual gates were set by a composite system which included an oscillator in association with a binary scaling circuit. The timing pulses were derived from successive stages of the latter, and hence provided accurate channel width ratios. In this arrangement, the overall length was fixed by the oscillator frequency.

The energy calibration of the pulse height discriminators was made with the electron spectrum from the muon decay as a reference. The spectrum was calculated theoretically using .66 for the value of the Michel parameter.

The results for 120 hours of data collection, under the conditions of Experiment No. 1, are presented in Figure 4.10 for the interval from 20 microseconds to 36.6 milliseconds. (The interval between 1 and 9 microseconds was investigated in a separate study, which will be described in connection with Experiment No. 2.)

The number of delayed events in the different channels does not deviate significantly from the expected number of background events, which were monitored continuously. The background was due mainly to μ -mesons arriving from outside, which were detected as delayed events due to inefficiencies in the Geiger detector anticoincidence arrangement.

If a particle satisfying the requirements of Experiment No. 1 exists, then the abundance relative to μ -mesons, at sea level, is given as follows:

<u>Lifetime Limits</u>	<u>1 μ sec *</u> <u>-10 μ sec</u>	<u>10 μ sec</u> <u>-1 millisecc</u>	<u>1 millisecc</u> <u>-5 millisecc</u>	<u>5 millisecc</u> <u>-20 millisecc</u>
Relative Abundance (Percentage)	< 0.05 %*	< 0.05 %	< 0.15 %	< 0.6 %

* This particular result, unlike the others quoted above, was obtained using the arrangement shown in Figure 4.6 (see discussion for Experiment No. 2).

Experiment No. 2:

As previously mentioned, the main detector used for Experiment No. 1, and the associated electronic selection requirements, were not suitable for detecting γ rays, π^0 mesons or electrons as decay products. Therefore, another scheme, employing a 25 kg. sodium iodide crystal instead of the plastic scintillator for the main detector, was used to cover these possibilities. This crystal was viewed by a single 14-stage photomultiplier tube (RCA 7046). The physical arrangement of the equipment (see Figure 4.6) remained essentially the same as used for Experiment No. 1, except for the addition of a 2" layer of lead between detectors B and A.

The discriminator level for B was chosen, in this experiment, to correspond to an 80-Mev energy release. A neutral pion produced in the decay would often release more than this amount of detectable energy via conversion of the associated γ rays, whatever the "Q" value of the long-lived decay process. Such delayed energetic events satisfying the anti-coincidence requirement ($\overline{BAG}$), were fed directly to the main delay coincidence discriminator, which was triggered by the occurrence of a particle stopping in B (via: $\overline{ABC}$), as previously described.

To increase the time resolution, and detect delayed events as soon as 1μ second after the occurrence of a particle stopping in B, a fast anti-coincidence circuit was now used in association with A (see Figure 4.8) before taking a slower anti-coincidence with the Geiger detectors. The interval from 1 to 9μ seconds was investigated by displaying the signals from the main detector on an oscilloscope, after 8μ seconds of delay line (RG-176/ μ). This was done whenever a delayed energetic event, satisfying $\overline{BAG}$, occurred within 1 to 9μ seconds after an incoming particle stopped in the NaI crystal. The "electron" pulses from μ mesons stopping in the crystal were rejected, in this instance, by the high energy (80 Mev) bias for B. However, the "electron" pulses from such stopping μ mesons were monitored, as in the previously described experiment, by a completely independent system.

A block diagram of the electronic arrangement used in this experiment can be seen in Figure 4.8. The results for 119 hours of data collection are presented in Figure 4.10 for the interval from 30 microseconds to 36.6 milliseconds. The data for the interval from one to nine microseconds consists of one energetic delayed event, which is consistent with the background.

If a particle satisfying the requirements of Experiment No. 2 exists, then the abundance relative to μ mesons, at sea level, is given as follows:

Lifetime Limits	$1 \mu \text{ sec}$ $-10 \mu \text{ sec}$	$1 \mu \text{ sec}$ -1 millisecc	1 millisecc -5 millisecc	5 millisecc -20 millisecc
Relative Abundance	$< 0.01 \%$	$< 0.06 \%$	$< 0.2 \%$	$< 0.5 \%$

The number of μ mesons detected by the monitor in this case corresponds only to positive particles, since the negative μ mesons are absorbed by the NaI before they can decay. Hence, in order to compare these results with those of Experiment No. 1, the stated relative abundance is, in each case, referred to the total number of mesons of both signs stopping in the NaI crystal, rather than the observed number.

An independent measurement was performed, in association with this part of the experiment, to observe charged light mesons as decay products (Experiment No. 1), beginning 1 microsecond after the occurrence of a particle stopping in B, and extending to 9 microseconds. This was accomplished by using a CRO in exactly the manner just described, except that, for this case, a very low energy requirement was placed on B, as used for $\overline{BAG}$. This modification rendered as acceptable most of the "electron" pulses from μ mesons arising from possible low "Q" 550 Me

decay processes. With this arrangement, the sequence of pulses (stopping - μ - e) for any decay (1 - 9 microseconds) yielding a light meson, would be seen on the oscilloscope. Only one such event in over 3×10^3 CRO photographed μ -meson decays was observed; which is a number consistent with background events due to chance coincidence. These results are included in the tabulation presented for Experiment No. 1. (E. Boldt, J. Hersil, Y. Pal, and J. Russell)

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B. Rossi

HIGH ENERGY ACCELERATOR PHYSICS GROUP

I. Synchrotron Operation and Maintenance

The operation of the machine has been relatively steady, operating for about 75% of around the clock operation. The majority of running time has been operation at 140 Mev to do the low-energy nuclear Compton effect. At this energy we have run between 10 and 12 pulses per second, with an average intensity in the collimated beam of 1.5×10^8 equivalent quanta per second. The intensity in the uncollimated beam is twenty times this.

The beam intensity is much steadier and more reliable with 1 Mev injection than it had been with the previous 70 kilovolt gun. Occasionally the synchrotron runs for hours with no attention. By the same token no combination of variables has increased the peak intensity much above 2×10^8 equivalent quanta per second. The present Van de Graaff filaments are capable of a current of 200 μ amps, and the resulting beam increases up to this emission; beyond this, greater emission does not increase the beam intensity. We measured the beam intensity in the center of the Van de Graaff beam and found, as might be expected, that this was just correlated with the synchrotron beam. We are making further attempts to improve the beam optics.

A general program has been initiated to improve the operating reliability of the machine; chronic trouble spots are being redesigned or replaced. One of the weakest points has been the r.f. system which operates at a marginal power level. Since we are coming to the end of our supply of surplus transmitter tubes we plan to design and build an oscillator, power amplifier system employing current tubes. (G. Davidson, P. D. Luckey, W. Lobar, L. S. Osborne, C. J. Strumski, and R. M. Weinstein)

II. Synchrotron Research

A. Capture of π^- Mesons in Complex Nuclei

Instrumentation has been constructed and tested for the purpose of measuring the pairs of nucleons emitted when π^- mesons are captured at rest. The neutron detectors consist of liquid scintillator (11-1/4" diameter by 8" deep) viewed by an R.C.A. 7046 photomultiplier tube (4-1/2" photocathode - 14 stage). With the anode fed into the grid of a 404A, saturated pulses are obtained from 500 Kev X-rays despite reflections being minimized in order to obtain short pulse times. (S. Ozaki, E. C. Loh, A. Wattenberg, and R. M. Weinstein)

B. Persistence of Circular Polarization in an Electromagnetic Shower

The stability of the detecting equipment and the functioning of the analyzing magnet have been found to be satisfactory. A check measurement of the effect of inverting the direction of the magnetic field has been made using the bremsstrahlung from Sr^{90} . The results of our measurements lay between the experimental values of Goldhaber et al¹ and the theoretical values.

(R. Miller, A. Wattenberg, and R. M. Weinstein)

C. One-Quantum Annihilation of Positrons

An initial run has been made using lead and aluminum targets, and using 3 mc Na^{22} as a source.

Some background calculations have been checked experimentally. The counting rate in the gamma counter is as calculated. However, the counting rate in the X-ray counter, due to gammas from the Na^{22} source interacting in the lead shielding and producing lead X-rays, is equal to about twice the counting rate due to lead X-rays actually produced at the lead target (i.e. the "signal" X-rays). This leads to a chance counting rate three times higher than expected and, as a result, the signal is masked. The lead X-ray counting rate, due to source gammas, will be lowered by covering the lead shielding with a thin coating of tin. The tin has a high enough Z to effectively cut the lead X-ray intensity, but too low a Z to have tin X-rays detected by the X-ray counter.

(A. Sadoff, L. Sodickson, and R. M. Weinstein)

D. Gas Scintillation Counters

Measurements are in progress on a gas scintillation beta spectrometer.

A high pressure (10 atmospheres) counter has been built for the purpose of observing the relativistic rise of dE/dx for 10 and 100 Mev electrons. (W. Lobar, L. Q. Niemela, and R. M. Weinstein)

E. Compton Scattering

Many electronic, liquid hydrogen target and synchrotron troubles. Hence no progress. (L. G. Hyman, R. Ely, D. H. Frisch, and M. A. Wahlig)

F. Scattering of Polarized Protons in Nuclear Emulsions

A new technique for measuring the right-left asymmetry in the scattering of polarized protons by the nuclei in emulsions is being investigated. This technique consists in a careful comparison of the angular dispersion of a polarized proton beam as it enters the emulsion and after it has passed through a certain length of material. The polarization effects manifest themselves through the introduction of an asymmetry in the beam angular distribution as a result of asymmetric scattering through small angles. Preliminary results indicate that the effects are observable and significant. (B. Maglich and B. T. Feld)

G. Nucleon-Nucleon Scattering on the "Atomic Model"

The interaction between two nucleons is being derived on the assumption that each nucleon may be regarded as a core surrounded by a $p_{1/2}$ pion cloud. The interaction between the core and pion is chosen so as to reproduce the ground state and "isobar" nucleon properties. The computation is analogous to the Heitler-London method for computing the potential between hydrogen atoms. (G. Costa, and B. T. Feld)

III. Nuclear Emulsions

A. Sea Level Mass Spectrum of Cosmic Radiation

Scanning is continuing satisfactorily of the sea level mass spectrum of cosmic radiation. (G. G. Fazio, D. M. Ritson, and R. A. Schluter)

B. High Intensity Pulsed Magnet

The apparatus ^{2,3} will be rebuilt for use in an experiment to measure the magnetic moment of the lambda hyperon. This experiment is described elsewhere in this report.

IV. Berkeley-Brookhaven Counter Group

The breakdown of the Brookhaven machine stopped the K^+ -total absorption experiment temporarily, but we have been scheduled for a run on the Berkeley Bevatron in the latter part of this summer. We are at present designing the experiment based on the differential Cerenkov detectors previously described.⁴ (C. Burrowes, D. O. Caldwell, D. H. Frisch, D. A. Hill, D. M. Ritson, and R. A. Schluter)

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P. D. Luckey, "A Differential Cerenkov Counter", given at the Scintillation Conference in Washington, D. C., January 1958.

B. T. Feld

BUBBLE CHAMBER GROUP

The scanning of the Cornell film, in order to determine π -pair production by γ rays at threshold, is continuing. This should be completed in the next few months. We have developed new heavy liquids to be used in bubble chambers and at present we have achieved radiation lengths of the order of 6 centimeters. (A. Brenner, P. D. Luckey, I. A. Pless, A. Tuchman, R. Williams, and R. Yamamoto)

I. A. Pless

R. W. Williams

LINEAR ACCELERATOR GROUP

Work has continued toward increasing the short-pulse current output of the Linac. The tungsten filament previously used in the Van de Graaff injector has been replaced by an indirectly heated metal capillary cathode obtained from Siemens and Halske Aktiengesellschaft. This cathode has been used for several weeks in a vacuum of about 5×10^{-6} mm Hg with no sign of fatigue. Several times the cathode has been exposed to the atmosphere and then reactivated. The emission is about 600 ma from the 3 mm diameter cathode. The cathode requires about 7 watts of heating power.

Using this cathode, pulses a few millimicroseconds wide and 200 ma in amplitude have been obtained from the Van de Graaff. It is expected that an axial magnetic field to help overcome space-charge divergence and a larger diameter cathode will further increase the available current.

The Van de Graaff beam has been used to calibrate the beam detector of the C.E.A.
(W. Bertozzi, P. T. Demos, F. R. Paolini, and C. P. Sargent)

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W. Bertozzi, "Photoneutron Energy Spectra", University of Washington, Seattle, Washington, January 13, 1958.

C. P. Sargent, "Photoneutrons", M.I.T. Physics Colloquium, Cambridge, Mass., February 20, 1958.

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P. T. Demos

ROCKEFELLER GENERATOR GROUP

The work of the Rockefeller Generator Group during the quarter November 1957 - February 1958 was concerned with the following items.

Generator

(1) The routine belt changing maintenance was carried out. The entire accelerating stack was disassembled, cleaned, and reassembled again with a new belt. The performance of the machine was improved as a consequence, and reliable operation at 4 Mev is now possible.

(2) Testing and modification of the pulsed terminal head described in the LNS Quarterly Progress Report for August 31, 1957 was continued. (L. E. Beghian, G. H. Kegel, M. K. Salomaa, and R. P. Scharenberg)

Low-Energy Neutron Counter

Construction of the counter system described in the L.N.S. August - November 1957 Report was commenced and completed. The instrument is ready for preliminary tests. (L. E. Beghian, A. Cade, R. P. Scharenberg, and M. Wachter)

Positron Polarization Experiments

The work described in the L.N.S. Report for August - November 1957 was continued. A thin lens beta spectrometer was installed to select positrons emitted from the source and thus reduce the background effects of scattered radiation.

Tests were carried out to determine the source strength of Al^{26} which could be generated by the $\text{Mg}^{25}(\text{d}, \text{n})\text{Al}^{26}$ reactions. Sources of 1 - 3 mc were obtained. (M. Deutsch, L. E. Beghian, B. Gittelman, and R. P. Scharenberg)

Gadolinium Decoupling Experiment

Reference is made to the L.N.S. Annual Progress Report for May 1957. In order to test the hypothesis that the gamma-ray angular distributions follow coulomb excitation of the Gd^{+3} in a liquid environment are perturbed by a magnetic hyperfine interaction work on a decoupling experiment has been undertaken.

Rockefeller Generator Group

A magnetic field of sufficient strength placed in the beam direction can precess a free Gd^{+3} electron shell fast enough to average out the internal fields responsible for the perturbation of the gamma ray angular distribution. A small decoupling magnet capable of supplying 2,000 gauss has been designed. (R. P. Scharenberg, and H. Helmkin)

W. W. Buechner

M. Deutsch

ONR GENERATOR GROUP

I. Development Work on ONR Generator

During this quarter, a considerable portion of our effort has been directed towards making various changes and improvements in the accelerator. In an attempt to improve the voltage and current output, the thyrites that had been used to distribute the voltage along the first six feet of the column were replaced by resistors. The total column resistance is now approximately 150,000 megohms. At the time this change was made, the old belt was replaced by one of a new type. The first test runs with the new belt revealed an appreciable amount of frictional charging on the belt spacers at various places in the column. After a more careful alignment procedure and after cleaning the Formvar from the old belt off the belt spacers and the pulleys, these frictional charging difficulties seemed to have been largely overcome.

A difficulty of a different sort was encountered when a beam was obtained in the acceleration tube. It was observed that the voltage on the intermediate equipotential shell, which is supposed to be at two-thirds of the terminal voltage, dropped rapidly with increasing beam current. We believe that this drop is caused by a larger x-ray produced ion current in the volume between the shell and the tank than in that between the terminal and the shell. The top of the tube and the ion source have now been shielded with 1 to 2 inches of lead. We have also mounted a movable collector screen in the column plane connected to the intermediate shell. The position of this screen can be controlled from the panel so that a portion of the belt charge can be removed and placed on the equipotential shell.

II. Multiple-gap, Broad-range Spectrograph

Orders have been placed for some of the major parts of the multiple-gap spectrograph. The large vacuum tank is scheduled for delivery in April. The machine work on the tank flanges and those parts of the spectrograph supporting structure that could be done at M.I.T. is essentially completed.

An extensive survey of the availability and cost of low-carbon magnetic iron has been made. Bids have been received from a number of sources. The most satisfactory solution will be to have the iron cast at the Boston Naval Shipyard, and a request for permission to expend \$15,000 for this purpose has been sent to the OSR. Magnetic measurements on test samples cast at the Navy Yard gave very satisfactory results.

The design of the copper coils has been changed because it appears to be possible to obtain square hollow conductors with the cross section we require. The coil drawings will be sent out for

bids to three experienced companies in the near future. The coils will be electrically series connected, but there will be four parallel paths for cooling water.

The magnetic tests mentioned above gave, for the particular iron we plan to use, a quite high permeability for field strengths up to 15,000 gauss. Thus, it seems wise to design the power supply for the magnet such that it can operate at these high field strengths. Twelve hundred amperes at 60 volts will be required to reach 15,000 gauss, and a bid on a complete selenium-rectifier power supply to which we can adapt our stabilizing system has been received.

A new idea has been advanced by which the solid angle of collection of a homogeneous field narrow-gap spectrograph can be increased. A single quadrupole magnetic lens is placed quite close to the source of particles. This acts as a concave lens in the median plane of the spectrograph and forms a virtual image of the source at about the lens entrance. In the other direction, it acts as a convex lens and forms a real image on the recorder after the particles have passed through the main magnet. The lens and the main magnet together form a stigmatic image on the recorder. The solid angle that can be obtained with a 1-1/2" air gap and a 50-cm radius of curvature is of the order of 10^{-2} steradians. It has been decided to include such an air gap in multiple-gap spectrograph design at an angle of 45 degrees. This gap will be in the previously unused quarter of the core. The quadrupole lens and scintillation counter recorder can then be added when the need arises.

The floor in the target room has its weakest point exactly where we want to locate the new spectrograph. Some reinforcement is necessary, and the solution we favor is to build a steel structure on top of the floor so as to distribute the load to nearby supporting caissons.

III. $K^{41}(p, p')K^{41}$

A target of enriched $K^{41}I$ on a Formvar backing has been bombarded with 6.5-Mev protons, and the spectrum of protons elastically and inelastically scattered through an angle of 90 degrees has been observed. The data indicate levels in K^{41} at approximately 0.98, 1.30, 1.56, 1.58, 1.68, 1.70, 2.14, and 2.17 Mev. Whether a level at 0.72 Mev¹ exists or not could not be determined from our present data because the region of interest in the proton spectrum was obscured by the intense peak of protons elastically scattered from C^{12} . There appears to be a considerable amount of sodium contamination in the target. The elastically scattered group and four inelastically scattered groups from known levels in Na^{23} have been observed. (H. A. Enge, W. H. Moore, and J. W. Kelley)

IV. (d, p) Reactions of the Nickel Isotopes: Ni^{58} and Ni^{60}

The experimental data mentioned in the November 15, 1957 Progress Report have been analyzed up to an excitation energy of 4.0 Mev for Ni^{59} and 3.5 Mev for Ni^{61} . The ground-state Q-value of the reaction $Ni^{58}(d, p)Ni^{59}$ is determined to be $Q_0 = 6.779 \pm 0.008$ Mev and of the reaction

$\text{Ni}^{60}(\text{d}, \text{p})\text{Ni}^{61}$ to be $Q_0 = 5.598 \pm 0.008$ Mev. Table 9.I gives the excited states, as analyzed thus far, for both reactions.

TABLE 9.I
Excited States of Ni^{59} and Ni^{61}

$\text{Ni}^{58}(\text{d}, \text{p})\text{Ni}^{59}$

$Q_0 = 6.779 \pm 0.008$

<u>Level</u>	<u>Ex (Mev)</u>	<u>Level</u>	<u>Ex (Mev)</u>
1	0.341 ± 0.008	28	3.307 ± 0.010
2	0.466 ± 0.008	29	3.319 ± 0.010
3	0.880 ± 0.008	30	3.352 ± 0.010
4	1.193 ± 0.008	31	3.37
5	1.309 ± 0.008	32	3.383 ± 0.010
6	1.344 ± 0.008	33	3.421 ± 0.010
7	1.683 ± 0.008	34	3.457 ± 0.010
8	1.736 ± 0.008	35	3.541 ± 0.010
9	1.747 ± 0.008	36	3.569 ± 0.010
10	1.774 ± 0.008	37	3.597 ± 0.010
11	1.952 ± 0.008	38	3.640 ± 0.010
12	2.416 ± 0.008	39	3.693 ± 0.010
13	2.424 ± 0.008	40	3.725 ± 0.010
14	2.531 ± 0.008	41	3.741 ± 0.010
15	2.542 ± 0.008	42	3.788 ± 0.010
16	2.630 ± 0.008	43	3.809 ± 0.010
17	2.68	44	3.862 ± 0.010
18	2.69	45	3.903 ± 0.010
19	2.70	46	3.941 ± 0.010
20	2.72	47	4.00
21	2.898 ± 0.010	48	4.012 ± 0.010
22	3.033 ± 0.010	49	4.033 ± 0.010
23	3.058 ± 0.010	50	4.084 ± 0.010
24	3.133 ± 0.010	51	4.116 ± 0.010
25	3.17	52	4.130 ± 0.010
26	3.183 ± 0.010	53	4.149 ± 0.010
27	3.193 ± 0.010		

Table 9.I (Continued)

Excited States of Ni⁵⁹ and Ni⁶¹

Ni⁶⁰(d, p)Ni⁶¹

$$Q_0 = 5.598 \pm 0.008$$

<u>Level</u>	<u>Ex (Mev)</u>	<u>Level</u>	<u>Ex (Mev)</u>
1	0.068 ± 0.008	19	2.474 ± 0.008
2	0.284 ± 0.008	20	2.536 ± 0.008
3	0.659 ± 0.008	21	2.599 ± 0.008
4	0.915 ± 0.008	22	2.645 ± 0.008
5	1.104 ± 0.008	23	2.704 ± 0.008
6	1.137 ± 0.008	24	2.770 ± 0.008
7	1.189 ± 0.008	25	2.801 ± 0.008
8	1.460 ± 0.008	26	2.869 ± 0.008
9	1.616 ± 0.008	27	2.889 ± 0.010
10	1.735 ± 0.008	28	2.906 ± 0.010
11	1.811 ± 0.008	29	3.05
12	1.994 ± 0.008	30	3.069 ± 0.010
13	2.007 ± 0.008	31	3.112 ± 0.010
14	2.023 ± 0.008	32	3.136 ± 0.010
15	2.127 ± 0.008	33	3.239 ± 0.010
16	2.41	34	3.294 ± 0.010
17	2.43	35	3.365 ± 0.010
18	2.44	36	3.502 ± 0.010

(C. H. Paris)

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C. H. Paris and W. W. Buechner, "(d, p) Reactions of the Nickel Isotopes Ni^{58} and Ni^{60} ", Bull. Am. Phys. Soc., Ser. II, 3, No. 1, 38 (1958).

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W. W. Buechner

RADIOACTIVITY GROUP

The measurement of the positron helicity¹ in the ground state β decay of Cu^{62} ($\log ft = 5.15$) has made it worthwhile to check the nature of the beta transition. The ground state of Ni^{62} has spin 0^+ since it is an even even nuclei. Among the many γ rays reported in the decay spectrum of Cu^{62} is the $E_\gamma = 1.17$ Mev which goes from the first excited level of Ni^{62} to the ground state. This first excited state has a spin $2^+ (2)$. If there are β decays directly to this state, it would indicate that the ground state of Cu^{62} has spin 1^+ showing that the interaction is Gamow-Teller.

We have looked for the betas in coincidence with the 1.17-Mev γ ray. A 5 μcuries β source of Zn^{62} in equilibrium with Cu^{62} was evaporated on 1 mil mylar film and mounted in a thin lens β spectrometer.

The coincidence to β single rates at positron energies of 0.5, 1 and 1.5 Mev were respectively:

$$\begin{aligned}(72.3 \pm 3) \times 10^{-6} \\ (26.0 \pm 1.7) \times 10^{-6} \\ (9.15 \pm 0.89) \times 10^{-6}\end{aligned}$$

The γ counter efficiency for the 1.26-Mev from Na^{22} was measured to be 1.06×10^{-2} .

After correcting for the shape of the 1.7-Mev beta spectrum compared to the 2.9-Mev spectrum going to the ground state, we find an abundance for the transition:

$$\begin{cases} (2.5 \pm 0.1) \times 10^{-3} \\ (1.63 \pm 0.1) \times 10^{-3} \\ (2.1 \pm 0.2) \times 10^{-2} \end{cases}$$

(The errors shown are the statistical ones only.) The fact that the abundance is roughly the same at the three energies indicates that the first excited state is populated directly in $0.2 \pm 0.05\%$ of the decay of Cu^{62} . Thus we conclude the ground state of Cu^{62} is 1^+ and the ground state transition is a pure Gamow-Teller interaction. (Monique Crut and B. Gittelman)

A cryostat for adiabatic demagnetization has been constructed. The present plans are to observe the anisotropy in the angular distribution of the gamma rays emitted by polarized radioactive nuclei, using the Gorter-Rose method of polarization.^{2,3}

Attempts were made to measure the warm-up times of the cooling salt (Cerium-magnesium nitrate); further refinements will be necessary for the observation of the gamma-anisotropy of the Co^{60} nuclei (approximately 35 μc of Co^{60} in 11 gr. Ce-Mg nitrate). Experimental arrangements similar to the ones described by E. Ambler et al.⁴ and C. S. Wu et al.⁵ are used at present.⁶

After these preliminary experiments, plans are to measure the matrix elements of β decay of Co^{58} , by observing the angular distribution of the succeeding γ ray in Fe^{58} , using the same method as above (cf. experiments by Griffing and Wheatley,⁷ using the Bleaney method of alignment). (R. W. Bauer and M. Deutsch)

A polarization detector for measuring the degree of circular polarization of γ rays in the 700 kev range has been constructed and calibrated. The apparatus, which makes use of the polarization sensitivity of the Klein Nishina differential scattering cross section, is similar in operation to that described by H. A. Tolhoek et al.^{8, 9}

It is planned to use this apparatus in conjunction with fast coincidence counters for an investigation of polarization-angular correlation in radioactive decay. (R. F. Stiening)

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R. D. Evans

CYCLOTRON GROUP

I. Proton Polarization

A large portion of our previous experiments were of no value because of a high background. We have found that the cause of this background is residual deuterium in the cyclotron and requires of the order of one week to be flushed from the machine. (C. W. Darden III)

II. Time-of-Flight

We have recently been considering the modification of the time-of-flight apparatus to the problem of particle mass identification. The basic scheme is to measure both the velocity of the particle and its energy by the use of a NaI(Tl) counter. With an adequate length drift tube it may be possible to better the usual proportional counter identification schemes. (P. R. Klein and N. Cindro)

III. Inelastic α -Particle Scattering

A series of elements have been studied and preliminary measurements show that the inelastically scattered alpha-particle spectra are similar to inelastic proton spectra, and show structure which seems to be similar for all nuclei. This structure indicates an anomalously large cross-section at excitation energies of 2-3 Mev. In addition, we have observed structure at higher excitation energies for intermediate and light nuclei. (D. R. Sweetman and N. S. Wall)

In the various other experiments previously reported on, there has been no significant progress.

M. Deutsch

THEORETICAL GROUP

I. Optical Model and its Justification

A review article for the Annual Reviews of Nuclear Science is just about completed. Besides a historical introduction, it contains (1) a derivation of the existence of a generalized optical potential together with a discussion of the effect of the non-locality; (2) a review of the Lax-Wilson multiple scattering approximation which is valid at high energies; (3) a review of the various attempts at low energies including those of Lane, Thomas and Wigner; C. Bloch; and papers from the University of Birmingham; (4) a review of the empirical data. (H. Feshbach)

II. A Unified Theory of Nuclear Reactions

A formalism has been developed which at one and the same time gives (1) the Breit-Wigner resonances, (2) the optical model, (3) the direct and compound nuclear inelastic scattering, (4) forms a natural basis for the application of statistical theory. The effect of the hard core can be taken into account, at least formally, by either introducing appropriate polarization factors or by using a modification of the Watson formalism due to Kerman. The effects of the identity of particles are difficult in only one respect: in that in the phenomenon of exchange scattering it is shown that the structure of the formalism is nevertheless maintained, and that the general results still hold, but that the connection to nucleon-nucleon forces becomes obscure. (H. Feshbach)

III. A Wave Equation for a Particle of Maximum Spin One

A general, first-order, linear, relativistic wave equation for a particle of arbitrary half-integral maximum spin is presented. The structure of the general theory is described briefly, while its specialization to a particle of maximum spin one is treated at greater length. The special theory describes not only the simple scalar, pseudoscalar, vector, and axial-vector mesons, but also composite "particles" possessing S, P, V, and A components, all components differing in rest mass. The restriction to a unique rest mass allows the wave function to satisfy the Klein-Gordon equation. The restriction to positive-definite energy density eliminates all composite particles except for the S-P, the S-A, and the P-V. The theory is invariant under the extended Lorentz group, charge conjugation, and Hermitian conjugation. (H. Feshbach and W. H. Nichols)

IV. Many-Body Problem

The general problem of calculating the properties of a bound state of very many particles (nuclear saturation, liquid formation) is being studied. (K. Huang and F. E. Low)

V. Current Operator

An integral representation for the current density of an elementary particle would be an extremely useful tool for the analysis of experiments; it would also be of considerable theoretical interest. Such a representation has been conjectured to exist, but so far has not been proved. A program which it is hoped will lead to a proof is being followed. (F. E. Low)

VI. Exchange in Scattering

A method has been developed to replace the symmetrization problem in nucleon-nucleus scattering by a pseudopotential. (F. E. Low)

VII. Collective Model of the Nucleus

A. Moment of Inertia of Rotational States

The canonical form¹ of the nuclear Hamiltonian has been used to apply the method of Bohr and Mottelson² to determine the moment of inertia of rotational states. In this method, the existence of a rotational spectrum is assumed and three Euler angles $\theta_s(x_i, p_i)$ are to be found, which define a body-fixed coordinate system (P, Q, R) in terms of the space-fixed coordinate system (α, β, γ) . Let $R_{P\alpha}(\theta_s)$ be the rotation matrix which transforms the one into the other and let $\vec{J}$ be the total angular momentum. Then the relations

$$J_P = \sum_{\alpha} R_{P\alpha} J_{\alpha} \quad [J_P, R_{Q\alpha}] = -iR_{R\alpha}$$

hold; the principal moments of inertia $\mathcal{J}_R$ are then defined by

$$\sum_{\gamma} i [H, R_{P\gamma}] R_{Q\gamma} = \frac{1}{\mathcal{J}_R} J_R \quad (1)$$

In the canonical form¹ a particular body-fixed system (ABC) is already introduced through Euler angles $\theta'_s(x_i)$. Writing

$$R_{P\alpha}(\theta) = \sum_A R_{PA}(\theta'') R_{A\alpha}(\theta') \quad (2)$$

and using the canonical Hamiltonian

$$H = H_\gamma + \frac{1}{2} \sum_A \frac{1}{\mathcal{J}(0)} (J_A - J'_A)^2 \quad (3)$$

leads to an equation for $\mathcal{J}_R$. Assuming θ'' to be a small angle, one gets a familiar result:

$$\langle n | \mathcal{J}_R^{-1} | n \rangle = \frac{1}{\mathcal{J}(0)} \left(1 - \frac{2}{\mathcal{J}(0)} \sum_k \frac{|\langle n | J_R | k \rangle|^2}{(E_k^0 - E_n^0)} \right) \quad (4)$$

$|n\rangle, |k\rangle$ being eigenstates of $H_0 + \sum_A \frac{1}{2\mathcal{J}(0)} L_A^2$

This result is unsatisfactory yet, but a variational technique is now being tried out which should be more adequate. Canonical transformations of (3) have been tried too, but it has been found difficult to go beyond an approximation that leads to (4) again. (F. Villars)

B. Investigation of the Peierls Formula³ for the Moment of Inertia

The Peierls-Yoccoz formula

$$\frac{1}{\mathcal{J}} = \frac{\langle HJ^2 \rangle - \langle H \rangle \langle J^2 \rangle}{\langle J^2 \rangle^2}$$

(in which $\langle \rangle$ refers to expectation values with respect to an independent particle state in a spheroidal well) is being investigated; particular attention is being paid to the possibility of making a general statement about the dependence of $\mathcal{J}$ on the deformation of the well. We hope to achieve this by singling out the relevant intermediate states $|n\rangle$ in

$$\langle HJ^2 \rangle = \sum_n \langle 0 | H | n \rangle \langle n | J^2 | 0 \rangle.$$

(A. Steiger and F. Villars)

C. Magnetic Moments

The value of the collective g-factor g_c in the magnetic moment formula for strongly deformed nuclei

$$\mu = g_c I + (g_r - g_c) \frac{K^2}{I+1}$$

is intimately connected with the deviation of the moment of inertia from the "hydrodynamic" value $\mathcal{J}(0)$ (eq. (3)).

It has been shown that the Hamiltonian (3) leads to $g_c = Z/A$ in lowest approximation; the corrections due to the "Coriolis coupling" $\sum_A \frac{1}{\mathcal{J}(0)} J_A J'_A$ are now being investigated. No further

progress has been made in the previously reported calculation of g_C through the Peierls model, which leads to $g_C = \frac{\langle \vec{M} \cdot \vec{J} \rangle}{J^2}$. (F. Villars)

VIII. Imperfect Bose-Einstein Gas

This work is a continuation of that reported in the preceding quarter. We have followed the suggestion then made that the portion of H giving rise to non-vanishing matrix elements for the chosen form of the trial function be extracted. An evaluation of the expectation value of this portion of H has been carried out. Minimization with respect to the amplitudes have been performed yielding a coupled set of recursion relations for the amplitudes. Work is now in progress attempting to solve these recursion relations by transforming them into the equivalent differential equations. (M. H. Friedman)

IX. Nucleon-Nucleus Scattering

The problem of scattering of high-energy nucleons from nuclei has been considered. It has been found that a simplification of the scattering formalism can be achieved by making explicit use of the antisymmetry of nuclear wave functions. The formalism has been developed and calculations of elastic and inelastic scattering are in progress. (A. K. Kerman, H. McManus, and R. M. Thaler)

X. A Parity-Conserving Interaction for K-Pion Decay

A specific interaction Lagrangian is proposed which, to the first approximation in a perturbation expansion, accounts for the lifetimes and branching ratios in $K-\pi$ decays. Since parity is rigorously conserved, the K -meson is described as a parity doublet. The total Lagrangian is invariant under charge conjugation and time reflection. The strong interaction, of the form $g_S \bar{\psi} \gamma_5 \psi \chi_K \chi_\pi$, is a scalar in isotopic space and is invariant under parity conjugation (in order to have scalar and pseudoscalar K masses equal). The weak interaction, of the form $g_W (\sigma + \alpha \sigma_0) \chi_K \chi_\pi$, allows a change in total isotopic spin of $1/2$ or $3/2$. The final-state pions are considered to be in plane-wave states. The following dimensionless constants are obtained: $g_S = 1.6$; $g_W = 5 \times 10^{-8}$; $\alpha = -0.16$. No account is taken of any of the K -decay modes involving neutrinos, nor of the production or scattering properties of the K -particles. (W. H. Nichols)

XI. Optical Model Analysis of Neutron-Nucleus Scattering at Intermediate Energies

The problem is the interpretation of intermediate- and high-energy neutron-nucleus scattering in terms of the optical model (complex potential) parameters. From the scattering data, one hopes to obtain the (complex) potential depth, the potential radius, the spin-orbit strength, and some information as to the shape of the potential well. My thesis develops a short wavelength, small-angle approximation similar to that of Shapiro⁴ and Schiff⁵, but less restricted in regard to potential magnitude and shape. This approximation groups the theoretical parameters as to allow one to calculate, once and for all, "all possible cases" of short wavelength scattering by a particular potential well shape, with as little work as would be required to analyze just a few cases exactly. The results can be plotted in terms of appropriate combinations of the experimental parameters: total cross section, zero-angle differential cross section, width of the forward diffraction maxima⁶ and small angle polarization. These plots allow direct and immediate interpretation of all data. (J. Riese)

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V. F. Weisskopf

APPENDIX

PERSONNEL LISTING BY PROJECTS

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