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SOME PHYSICAL AND CHEMICAL PROPERTIES OF CURIUM

W. W. T. Crane

April 16, 1951

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ABSTRACT

SOME PHYSICAL AND CHEMICAL PROPERTIES OF CURIUM

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Improved methods of isolating curium are outlined. The absorption spectrum of Cm^{+3} is given as well as most of the prominent lines in the arc and spark spectra.

The method of production of curium metal is outlined and the density is reported as 7.

The molar magnetic susceptibility of CmF_3 has been found to be 24,000 ± 500 c.g.s. units in an environment of 296°K and 26,500 ± 700 c.g.s. units in the same environment when the sample was diluted with 90 percent LaF_3.

The susceptibility of CmF_3 is in agreement within experimental error of that expected theoretically for a $5f^7$ configuration.

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SOME PHYSICAL AND CHEMICAL PROPERTIES OF CURIUM

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INTRODUCTION

Curium (element 96) was first reported by G. T. Seaborg[1] in 1945. At this time only tracer quantities of curium were available. Using standard tracer techniques it was established that the most stable state of curium was its tripositive state.[2]

In 1947 sufficient curium became available for work to be performed on a microgram scale. At this time several micrograms of curium were isolated in the pure state by L. Werner and I. Perlman.[3]

Since that time larger amounts of curium have been prepared and improvements made in its separation. The currently separated curium has been used principally to establish that curium occupies the same position in the actinide series as gadolinium does in the lanthanide series.

The curium (Cm^{242}) was prepared as before by the transmutation of Am^{241} according to the following reactions:

$$Am^{241}(n,\gamma)Am^{242m}$$

$$Am^{242m} \xrightarrow{\beta^-} Cm^{242}$$

Cm^{242} is an alpha particle emitter of only 162 day half-life. This means that ten micrograms of curium emits 1.2×10^9 alpha particles per second. Therefore the problems of isolation of curium are those of working with intensely radioactive material, and the separation from americium and rare earth fission products which have closely allied

chemical properties.

The methods of separating curium from macroscopic amounts of americium and from rare earth fission products have been much improved in the past two years. One of the important new methods is that of Street and Seaborg[4] for separating actinide elements from lanthanide elements using cation exchange columns with concentrated hydrochloric acid as the eluting agent. In addition, the time for separation has been cut down from the order of a week to the order of a day by using adsorption columns maintained at an elevated temperature.[5]

CHEMICAL SEPARATION

The few milligrams of americium, irradiated as the oxide, was dissolved in nitric acid, 10 mg of lanthanum as the nitrate was added and the combined hydroxides precipitated with ammonia gas. The hydroxides were dissolved in 1 M HNO_3 and the trifluorides of lanthanum, americium, and curium were precipitated by making the solution 6 M in HF. The fluorides were then put back into 0.5 ml of 0.5 M HNO_3 solution by first metathesizing to the hydroxides with 10 M KOH at 85°C.

The substances in solution were added to the top of a column of Dowex-50 cation exchange resin 1 cm in diameter and 20 cm long. In then eluting with 12 M HCl the americium and curium came off in the third column volume while the rare earths remained considerably behind. The presence of americium and curium in the elution curve was detected by alpha particle analysis. The column used in this separation was larger than needed to hold the quantities of ions involved and was used in order to dilute the band of curium as it passed through the column. Otherwise the high density of alpha particles would cause sufficient concentration of water decomposition to produce active bubbling.

The solution containing the actinide element fraction was evaporated to dryness, taken up in 0.1 M HCl and placed on a similar cation exchange column. This time the column was maintained at 87°C and eluted with 0.25 M citrate solution at pH 3.5 as described by Thompson, Cunningham, and Seaborg.[6] In about 2 hours the curium and americium came off the column in the relation shown by the typical elution curve of Figure 1. The ordinate of the curve is alpha activity and since there is a 1000-fold difference in half-life, the americium is actually present in considerably larger quantities by weight than the curium. The activities of americium and curium were dissociated by using an alpha particle pulse analyzer which discriminates between different energies.

The curium represented by the first third of its elution peak is essentially pure. By assaying the activity with a Geiger counter as well as by spectrographic analysis, this curium fraction was shown to have less than one percent americium by weight. Other parts of the eluate containing appreciable amounts of curium were rerun through a column obtaining more pure curium, and this fractionation procedure was repeated once more.

The combined citrate solution of curium was adjusted to pH 1 and the curium was adsorbed on some fresh cation exchange resin by slurrying and this was placed on the top of another cation exchange column. The curium was again eluted with 12 M HCl, evaporated to dryness, and dissolved in 0.1 ml of 1 M HNO_3. (This second "HCl column" run was made for further purification and to place the curium in a solution from which it could be concentrated by evaporation.) This solution was transferred to a fluorothene microcone and pure CmF_3 was obtained by precipitating

in 6 M HF. The yield of curium in this separation was 90 percent.

Because of its high specific alpha activity, curium presents a problem in storage. It has been noted that glass vessels develop checks and cracks, and plastic vessels carbonize when exposed to concentrated forms of curium. The method used so far to store curium for more than a day or two is to evaporate the solution in s small platinum boat and to store there as the solid residue.

RADIATION CHARACTERISTICS

The most accurate value to date for the alpha energy of Cm^{242} is 6.08 mev. This 6.08 mev is a mean value for the energy of the alpha particle since approximately 30 percent of the alphas emitted are followed by a gamma ray of 43 kev as measured by G. D. O'Kelley[7] in a β^- ray spectrometer. This value has been confirmed by direct measurement of the difference in the alpha energies on an alpha ray spectrometer.[8] The short range group was found to be in 27 percent abundance. The 43 kev gamma ray is more than 90 percent converted. Since this is true, the principal photon emission of curium is the L x-rays of plutonium produced by the internal conversion of these gamma rays.

A sample of curium was prepared and given to G. Barton[9] for the measurement of the energies and abundancies of these L x-rays on a bent crystal x-ray spectrometer. The results are as follows:

Table 1

PLUTONIUM L X-RAYS FROM Cm^{242} DECAY

X-ray Designation	Energy	Relative Abundance
L_{α_1}	14.31 ± 0.01	100
L_{α_2}	14.14 ± 0.01	13
L_{β_1}	18.35 ± 0.02	91
L_{β_5}	17.91 ± 0.02	6
L_{β_2}	17.28 ± 0.02	28
L_{γ_1}	21.46 ± 0.04	23
L_{γ_6}	22.20 ± 0.04	4

ABSORPTION SPECTRUM

A previous measurement of the absorption spectrum of curium in solution was made with a Beckman spectrophotometer in which there was found no appreciable absorption in the visible region up to 10,000 A, but broad absorption in the ultraviolet region.[3] The absorption spectrum is among the properties desirable to compare with those of gadolinium, the corresponding lanthanide element with half-filled 4f shell. In the previous measurements with the spectrophotometer the absorption in the ultraviolet region could not be determined with satisfaction because of limitations of the instrument. As a result, with the new sample of curium, measurement was made in a special cell 1.5 mm wide and 1 cm deep using a Baird 3-meter grating spectrograph. The spectrograph measurements were made in conjunction with John Conway. The solution was 0.0013 M $Cm(ClO_4)_3$ in 0.2 M $HClO_4$, and the results are shown in

Figure 2 along with measurements of gadolinium taken by D. C. Stewart with a Beckman spectrophotometer using a hydrogen lamp. The similarity is marked since both curium and gadolinium absorption spectrums begin in the ultra violet region while all previous lanthanide and actinide elements have absorption spectrums in the visible region.

EMISSION SPECTRUM OF CURIUM

At the time of the first isolation of curium by Werner,[3] a sufficient amount was given to John Conway for spectrochemical analysis. The wave lengths of 54 lines was then measured. Since more curium has become available larger samples have made it possible to measure most of the prominent lines between 2516-5000 A.[10]

In this work one microgram samples were evaporated on 1/4 inch electrodes and sparked for 15 seconds using an applied Research Laboratory unit with .021 mfd and .36 mh at 100 volts.

For the arc lines one microgram samples were evaporated on 1/8 inch special spectrographic graphite and burned at 7 amperes DC for 15 seconds. The cyanogen bands were greatly reduced by the circulation of oxygen through the chamber during the arcing period.

The spectra were photographed in the first order on a Baird modified eagle mount spectrograph using a 25 micron slit. Eastman 103-O and 103F plates were used. The lines were measured with a Bausch and Lomb spectrum measuring magnifier. Copper lines were used as wave length standards in the spark and iron lines in the arc.

The results given in Table 2 are good to 0.2 A. The background and band structure limit the number of lines that can be observed in the arc spectra.

Table 2

WAVE LENGTHS OF THE PROMINENT LINES

IN THE EMISSION SPECTRUMS OF CURIUM

Wave Length	Intensity Spark	Wave Length	Intensity Spark
2516.0	2	2968.9	4
2562.3	1	2984.5	3
2585.8	2	2996.2	3
2616.8	2	2998.3	3
2617.2	3	2998.8	2
2625.4	2	3000.8	2
2628.2	2	3037.4	2
2636.2	3	3044.7	6
2651.1	4	3046.6	5
2653.7	4	3047.5	2
2677.0	1	3050.8	2
2693.8	1	3059.0	2
2704.8	1	3081.6	4
2707.1	1	3092.8	4
2710.1	1	3096.4	1
2725.6	2	3101.5	1
2727.7	3	3104.9	1
2736.8	3	3118.3	3
2748.0	1	3143.9	1
2773.5	2	3161.8	3
2792.0	1	3186.4	1
2796.2	1	3190.3	1
2796.4	1	3195.6	1
2811.5	5	3197.0	3
2817.4	4	3197.5	2
2821.5	4	3198.0	3
2833.7	4	3210.0	4
2862.2	2	3220.7	6
2862.8	2	3230.3	4
2872.0	3	3238.6	2
2882.3	1	3252.6	2
2888.1	1	3279.4	2
2909.1	2	3296.7	6
2913.1	4	3304.9	2
2929.0	2	3367.9	3
2933.2	3	3374.3	3
2934.9	3	3382.7	2
2935.4	3	3392.0	3
2944.5	2	3417.1	6
2953.0	3	3424.2	1
2955.6	2	3425.9	6

Wave Length	Intensity Spark	Wave Length	Intensity Spark
2957.5	4	3436.5	1
2961.8	2	3446.6	2
2963.0	2	3458.3	1
3461.7	7	3962.2	2
3473.5	7	3962.8	2
3492.9	2	3965.0	2
3498.9	5	3970.2	2
3503.7	3	3974.9	6
3518.5	2	3984.6	2
3546.1	5	3990.9	1
3550.3	3	4003.3	8
3567.4	5	4016.2	1
3585.6	3	4017.0	1
3591.9	2	4017.9	2
3619.9	2	4018.4	2
3639.9	1	4024.5	3
3643.5	1	4028.0	2
3670.4	2	4031.6	1
3691.7	3	4052.4	1
3692.5	3	4061.6	1
3697.3	2	4078.9	4
3708.8	1	4106.9	3
3709.6	1	4118.1	2
3723.3	3	4128.5	2
3732.3	3	4130.4	2
3738.2	3	4141.3	3
3739.3	4	4148.2	1
3750.5	3	4156.5	1
3763.6	4	4156.0	4
3767.3	3	4164.3	1
3778.2	4	4194.3	2
3788.0	1	4202.4	1
3799.5	3	4208.0	6
3842.1	3	4218.6	3
3846.9	2	4239.8	3
3903.9	7	4283.0	1
3908.2	6	4293.0	1
3936.6	5	4299.1	1
3941.5	1	4301.5	5
3942.1	1	4313.1	4
3947.9	3	4318.7	3
3948.8	2	4323.4	5
3953.3	1	4357.2	2
3957.5	1	4433.7	3
3960.8	2	4434.2	2
4435.3	2		
4442.0	3		

Wave Length	Intensity Spark	Wave Length	Intensity Arc
4446.5	1	3019.6	9
4455.2	2	3943.7	9
4546.9	1		
4570.1	2		
4608.3	2		
4632.1	1		
4665.4	2		
4670.4	2		
4681.8	2		
4722.8	4		
4761.6	1		
4873.8	3		
4880.5	3		
4905.6	4		
4906.3	1		
4925.5	3		
4989.9	1		

STABILITY OF THE TRIPOSITIVE STATE

Attempts to oxidize curium to a state higher than the tripositive state using tracer concentrations of curium have all failed.[2] In the light of the recent successes in oxidizing americium(III) to americium(VI) using macro concentrations of americium,[11] attempts were made to oxidize curium(III) under similar conditions. A solution of 0.1 M HNO_3 containing 0.004 M Am(III), 0.007 M La(III), and 0.0015 M Cm(III) was treated with ammonium peroxydisulfate for 2 hours at 85°C. The lanthanum was then precipitated as the fluoride as a means of removing all of the actinide ions that had not been oxidized to the hexapositive (fluoride soluble) state. Essentially all of the curium and americium were found in the precipitate showing that neither the curium nor the americium were oxidized. When the curium concentration was reduced 20-fold, other ions remaining the same, the americium became oxidized while the curium

remained unaffected. The inability to maintain a strong oxidizing potential in solutions 10^{-4} molar in curium must be related to reducing substances formed by the intense alpha radioactivity, probably hydrogen peroxide.

Similar attempts were made to produce curium(IV) and curium(V) without success. Oxidation was carried out with peroxydisulfate in phosphate solution to make use of the complexing action of phosphate for tetrapositive actinide ions in decreasing the (III)-(IV) potential. Zirconium phosphate was then precipitated to remove any tetrapositive curium. Over a range of acidities and curium concentrations, no oxidation could be detected. The oxidation to the pentapositive state was attempted using a method found applicable to americium and plutonium. If either of these actinide elements is treated with NaOCl in carbonate solution (40 percent K_2CO_3), oxidation takes place and an insoluble compound is found which can be proved to be the pentapositive state.[12] Under none of the conditions tried was there evidence for curium oxidation.

From these attempted oxidations it may be concluded that all of the potentials from curium(III) to higher oxidation states are either more negative than about -2 volts, or that the rates are too slow for concentrations of curium that will allow an oxidizing medium to exist.

Attempts to reduce curium to the dipositive state have also been attempted on the tracer scale. Barium metal in hydrochloric acid was used as the reducing agent, and cerium tracer was used to determine what percent of the tripositive ion was physically carried by the barium chloride precipitate and what was due to the actual reduction

of curium.

In this work no positive evidence was found that reduction occurred.

THE PREPARATION AND SOME PROPERTIES OF CURIUM METAL

Curium metal has been prepared by J. C. Wallman[13] on the microgram scale by reduction of curium trifluoride with barium metal vapor at 1275°C, using a vacuum furnace and double crucible system similar to that described by Fried and Davidson.[14]

Six successful reductions, which yielded bright metallic globules of metal ranging in mass from about 0.01 to 4 μg, have been made. The metal retained its bright appearance in the dry atmosphere of a nitrogen "dry box" for some hours, but gradually tarnished; and on standing for about 24 hours, it was rather badly corroded. Under the same conditions, samples of other actinide metals, such as americium or plutonium, have shown less evidence of reaction. The greater reactivity of curium probably is to be attributed to the radioactivity of the isotope Cm^{242} (equivalent to a power output of 1.2×10^{-4} watts/μg) which is sufficient to maintain the temperature of the sample substantially above that of its environment. Approximate calculations show that the steady-state temperatures of our samples probably were from 50 to 100°C above that of the surroundings.

The trifluoride used for the reductions was prepared by precipitating curium(III) in dilute nitric acid in a fluorothene microcone with an excess of hydrofluoric acid, washing the precipitate with dilute hydrofluoric acid, and drying the CmF_3 in platinum under a heat lamp.

Pieces of the dry fluoride were then transferred to the inner crucible for reduction. When the quantities of curium were relatively large (approximately 10 μg), the trifluoride was compacted in the bottom of the crucible by tamping with a quartz rod.

The conditions for reduction to usable metal were rather critical. Reduction at 1380°C left the metal as a thin film adhering to the wall of the crucible. Reduction at about 1250°C resulted in the formation of a cokey residue, indicating poor agglomeration of the metal. Reduction with barium vapor at 1275°C for 45 seconds followed by additional heating at 1100°C for 45 seconds and a final heating at 960°C for 20 seconds produced optimum results. In one such run on 12 μg of CmF_3, reduction yielded a single 4 μg spheroidal piece of metal. This piece was separated from the crucible intact and free of slag or other residues.

The volume of the piece was estimated by measurement with a filar micrometer under about 200 x magnification. The mass of the sample was determined by weighing with a torsion microgram balance, and the mass of curium was determined by radiometric assay for Cm^{242}. The results of the last two measurements (which constitute a specific activity determination) indicated that the curium metal was pure, within the limit of error of the measurements (± 5 percent).

From the mass and volume measurements the density of the metal was computed to be approximately 7. This is a surprisingly low value, and perhaps it is to be explained by the presence of a void in the piece of metal examined.

MAGENTIC SUSCEPTIBILITIES

Magnetic susceptibilities of many of the actinide ions have been measured by various workers.[15,16,17] The susceptibilities of these ions have in all cases been lower than the susceptibility of the corresponding lanthanide ion. This low value would seem to indicate that the molecular field constant in the Curie-Weiss law is larger than that found in the lanthanide series.

If one adopts the $5f^7$ configuration for Cm^{+3} in agreement with the actinide concept, and assumes that Russel-Saunders coupling provides a satisfactory description of the electron interaction, the term $N\alpha$ in the formula

$$\chi_m = \frac{Ng^2\beta^2S(S+1)}{3kT} + N\alpha$$

is zero. Thus the only temperature independent component in Cm^{+3} is that due to the Heisenberg exchange interaction. If the Heisenberg forces can be evaluated for curium they should be roughly the same for other actinide ions.

Early Apparatus

In a preliminary investigation of CmF_3 the susceptibility measurements were made by a modification of the Faraday method, using mainly the apparatus shown in Figure 3.

The sample, mounted in a thin quartz tube of about 1 mm id and 6 mm in length, was suspended by a thin quartz fiber attached to the free end of the beam of the balance. The construction and operation of balances of this kind have been described by Cunningham.[18] Sample and balance were surrounded by protecting tubes of pyrex glass as shown

in the figure. The front end of the horizontal 4 cm diameter tube was provided with an aluminum disk closure, with a central opening covered with a thin mica window through which the pointer attached to the free end of the balance could be observed with a microscope. The end closure was sealed to the tube with Gelva wax.

A stopcock ("A" of Figure 3) attached to the back permitted evacuation and the assembled apparatus was vacuum tight.

Temperature control was achieved by surrounding the vertical tube in which the sample was suspended by a small Dewar filled with a suitable refrigerant.

The microscope provided a magnification of about 200 diameters, and by the use of a filar micrometer it was possible to read the position of the pointer to about $\pm$ 0.3 μ. Since the sensitivity of the balance was about 1 cm/mg, this corresponded to a sensibility, or limit of precision of reading, of about $\pm$ 0.03 μg.

The microscope was attached to the arm of a simple rack-and-pinion manipulator for convenience in focusing and adjustment.

The susceptibility apparatus and microscope were mounted on a single heavy wooden frame, beneath which a 5 inch "alnico No. 5" permanent magnet could be slid in and out along a heavy brass track. The entire apparatus was placed in a box, provided with windows and glove ports, in which the experimental measurements could be made without undue risk of radioactive contamination.

The magnet was provided with pole pieces ("O" of Figure 3) specially cut to produce a region of pronounced but relatively constant field gradient. The product of field by field gradient in our experimental

region was about 3×10^5 (oersteds)^2/cm.

Later Apparatus

After the preliminary measurements had been completed, more exact values for the temperature dependence of CmF_3 were undertaken using the apparatus shown in Figure 4 and Figure 5.

The sample, mounted as before in a thin quartz tube about 1 mm in diameter and 4 mm in length, was suspended by a thin quartz fiber attached to a quartz torsion microgram balance similar to that described by Kirk, Craig, Gullberg, and Boyer.[19] One complete turn of the fiber corresponded to two micrograms; thus one half a degree corresponded to 10^{-4} micrograms which was the sensibility of the balance as used.

To make measurements at 77°K it was found that the balance must be in a vacuum of 10^{-5} mm to avoid condensation on the quartz fiber. This was accomplished by placing the balance in a dural case and running all movable controls through Wilson seals. The case was then attached to an oil diffusion pump and a duoseal fore pump. Since the case was all metal it was found that several hours pumping was necessary to attain a vacuum low enough for low temperature measurement.

At this low pressure damping of the balance became a problem. The difficulty was overcome by two methods. The first was by placing an aluminum foil on the counterweight side of the balance and placing this in a uniform magnetic field. The second was to place a micrometer scale in the optical system of the balance, thus allowing one to find the zero point while the beam was still oscillating.

The temperature control was achieved by surrounding the vertical tube in which the sample was suspended by a small Dewar filled with suitable refrigerant, or in the case of a high temperature a vessel with a tungsten heating coil was placed around the sample and suitable organic solvents were brought to their boiling point.

The dural case was mounted on a steel frame on which was swung the same magnet and pole pieces as used in the previous experiment, which could be swung in and out in a circular path. The entire apparatus was placed in a box, provided with windows and glove ports in which the experimental measurements could be made without undue risk of radioactive contamination.

Measurements

Our measurements are relative and depend upon previous calibration with sample of known susceptibility. We have used reagent grade $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$) for which we take χ to be 29.45×10^{-6} c.g.s. units at 298°K as our primary standard. A sample of spectroscopically pure gadolinium fluoride was used as a secondary standard. The gram susceptibility of this material was found to be 115×10^{-6} c.g.s. units at 296°K by comparison with ferrous ammonium sulfate. Gadolinium fluoride was used as a standard because it was stable at high vacuum and because the susceptibility of Gd^{+3} has recently been accurately measured by Sngden and Tailby.[20] Their value of 168.4×10^{-6} c.g.s. units at 293°K for the gram susceptibility is in very good agreement with 115×10^{-6} c.g.s. units for GdF_3 if one uses a molecular field constant of 19°.

Since the force exerted on a sample in an inhomogeneous magnetic field varies as the product H(dH)/(dx), a portion of the field in the experimental region was explored in preliminary measurements with gadolinium fluoride. A measure of HdH/dX with respect to the position of the magnet can be seen in Figure 6. In all subsequent measurements the position of the sample in the field was reproduced to within a few tenths of a millimeter as shown by observation with a cathetometer.

Gadolinium samples were weighed to within a few tenths of a percent on a torsion microgram balance similar to that described by Kirk, Craig, Gullberg, and Boyer. The samples of curium were assayed radiometrically to within ± 1 percent by alpha particle assay. Corrections for the diamagnetism of the quartz sample tubes were determined directly. Corrections for the diamagnetism of curium and gadolinium as well as the fluoride was made using $.48 \times 10^{-6}$ c.g.s. units for the gram susceptibility of the fluoride ion and 0.5×10^{-6} for the gadolinium and curium ions.

A summary of the experimental results is given in Tables 3 and 4.

Table 3

EARLY MAGNETIC SUSCEPTIBILITY MEASUREMENTS OF THE TRIFLUORIDES OF GADOLINIUM AND CURIUM

Sample	Wt of Sample μg	T °K	χ_M c.g.s. units x 10^{-6}	$\chi_M T$
GdF_3	95.8	295	24,800 ± 1000 (R is standard)	7.31
GdF_3	95.8	77	98,600 ± 2000	7.60
CmF_3	24	295*	19,000 ± 6000	5.60
CmF_3	31	295*	26,000 ± 5000	7.67
CmF_3	31	77*	58,000 ± 6000	4.46

*Temperature of the environment. The temperature of the sample may have been appreciably different. See discussion.

Table 4

MAGNETIC SUSCEPTIBILITIES OF THE TRIFLUORIDES OF GADOLINIUM AND CURIUM

Sample	Wt of Sample μg	T °K	χ_M c.g.s. units x 10^{-6}	$\chi_M(T + 19)$
GdF_3	53.4	77	80,000 ± 800	7.68
GdF_3	53.4	195	36,300 ± 300	7.77
GdF_3	53.4	296	24,600 ± 200	7.75
CmF_3	17.3	296*	24,100 ± 500	
10% CmF_3 90% LaF_3	350.	296	26,500 ± 700	

*Temperature of the environment. The temperature of the sample may have been appreciably different. See discussion.

Experimental Results

In the early work which was done using the cantilever balance system, many difficulties were encountered. The most difficult to overcome was the fact that the pressure in the system was about 10^{-1} mm, and at this pressure turbulence in the balance system during low temperature measurements is very bad. Condensation of moisture and CO_2 on the hangdown fiber also lead to difficulties.

Considering these difficulties the only conclusion one can draw from this early work is that the molecular field constant is less than 100°C.

When a pure sample of curium fluoride was placed on the more accurate balance a molar susceptibility of 24,000 x 10^{-6} ± 500 c.g.s. units was obtained for curium. When the balance was evacuated to 10^{-5} mm for temperature dependence work, the temperature of the sample

apparently increased to 800°C due to its intense radioactivity. This temperature was calculated from the reduction in the susceptibility of curium at high vacuum. The susceptibility returned to its original value when the pressure was returned to 1 atmosphere. An increase in temperature is not surprising since curium produced 1.2×10^{-3} watts/μgm and the only way that the heat could be dissipated is by radiation. Due to this difficulty the molecular field constant could not be measured directly.

Since both Van Vleck and Slater have shown that the Heisenberg interaction forces disappear when a paramagnetic sample is diluted with a diamagnetic substance; samples of curium were diluted with pure lanthanum and the susceptibility of curium measured. The difference in the susceptibility of pure curium fluoride and a mixture of 10 percent curium and 90 percent lanthanum fluoride being due to the Heisenberg exchange forces. The molar susceptibility of curium fluoride diluted with 90 percent lanthanum is $26,500 \pm 700 \times 10^{-6}$ c.g.s. units.

From this data one can only say that the molecular field constant for solid curium fluoride is less than 40°C. The reason that one is able to only set a maximum value is the uncertainty of the temperature of the sample at atmospheric pressure. If the equilibrium temperature of the sample of pure curium fluoride were above room temperature, then one would expect that the equilibrium temperature of the lanthanum diluted curium fluoride would be lower than the pure sample. This effect would cause the molecular field constant to appear larger than its true value.

DISCUSSION

In investigating the properties of the transuranium elements, preponderant evidence has been found that these elements are members of a second rare earth group.

The chemistry of the second rare earth series in their tripositive state is identical in properties with their analogy in the first rare earth series. Also, the absorption spectrums are similar through curium. This similarity is very striking in curium and gadolinium since all previous spectrums have pronounced absorption in the visible region.

The behavior of the tripositive actinides on resin columns also shows a behavior identical to their analogy in the first rare earth group.

After one considers all this evidence and then considers the magnetic susceptibility of this group of elements as shown in Figure 7 noticing the similarity of all the second rare earth group with those of the first rare earth group and above all notices the sharp rise of susceptibility at curium to a value nearly identical with the value found for gadolinium; there can be little doubt left that one is justified to call this second rare earth group the actinide series.

ACKNOWLEDGMENTS

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LIST OF ILLUSTRATIONS

1. Typical citrate elution curve for 0.25 M citrate at pH 3.5 and temperature of 87°C.

2. Left curve, absorption spectrum for gadolinium perchlorate at room temperature, 0.152 M $Gd(ClO_4)_3$ in 0.095 M $HClO_4$ against 0.55 M $HClO_4$. Right curve, absorption spectrum for Cm^{+3}, molar extinction versus wavelength ~0.1 M $HClO_4$.

3. Early magnetic susceptibility apparatus.

4. Magnetic susceptibility apparatus.

5. External view of magnetic susceptibility apparatus.

6. A measure of H(dH)/(dx) with respect to the magnet.

7. Magnetic susceptibilities of the rare earth groups.

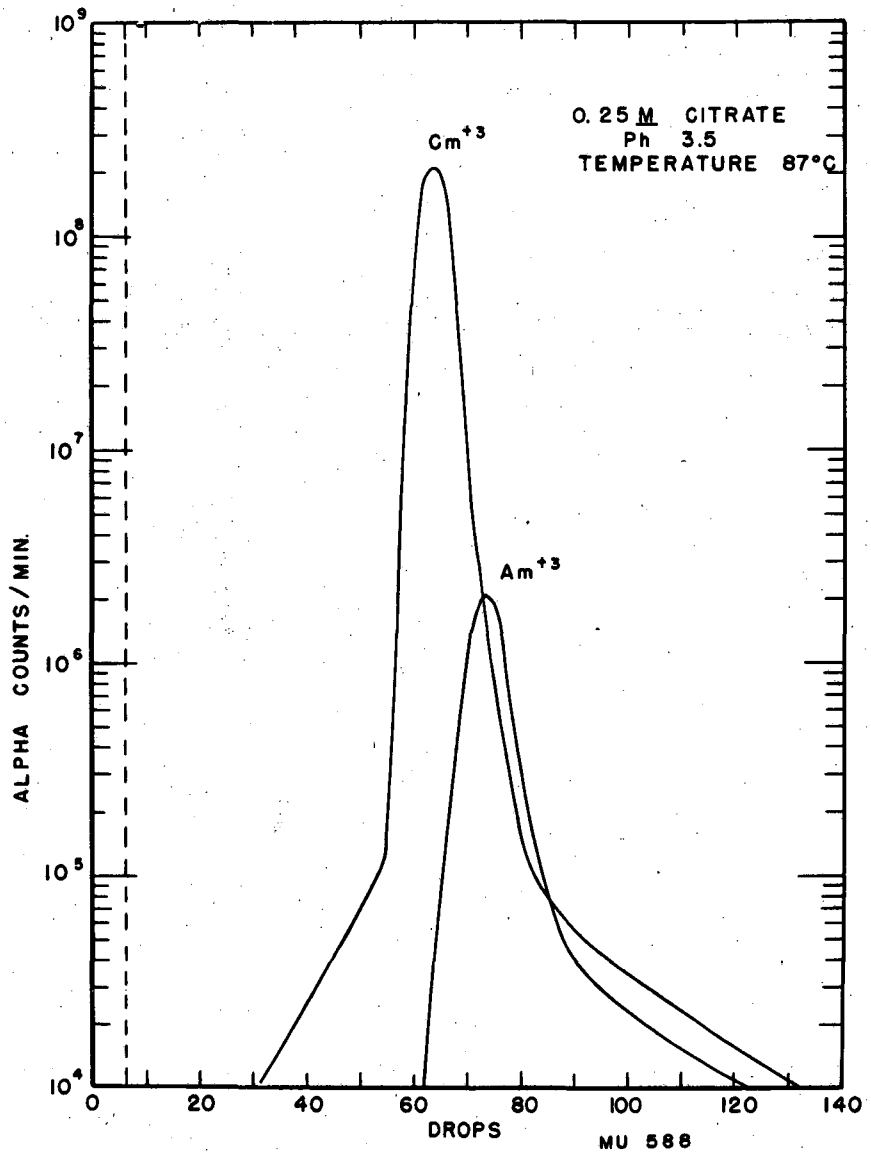

0.25 M CITRATE
Ph 3.5
TEMPERATURE 87°C
Cm+3
Am+3
ALPHA COUNTS / MIN.
10^9
10^8
10^7
10^6
10^5
10^4
0
20
40
60
80
100
120
140
DROPS
MU 588

Fig. 1

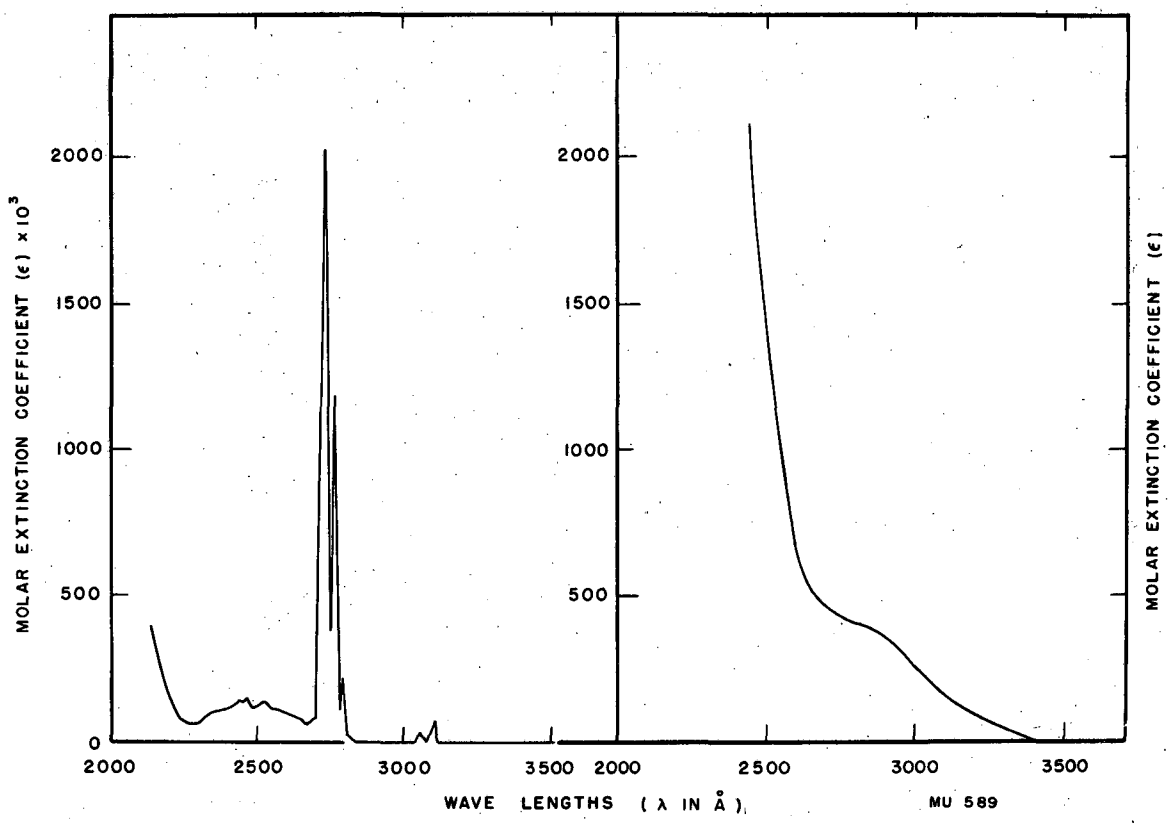

MOLAR EXTINCTION COEFFICIENT (ε) x 10³
2000
1500
1000
500
0
2000
2500
3000
3500
2000
2500
3000
3500
WAVE LENGTHS (λ IN Å)
MU 589
MOLAR EXTINCTION COEFFICIENT (ε)

Fig. 2

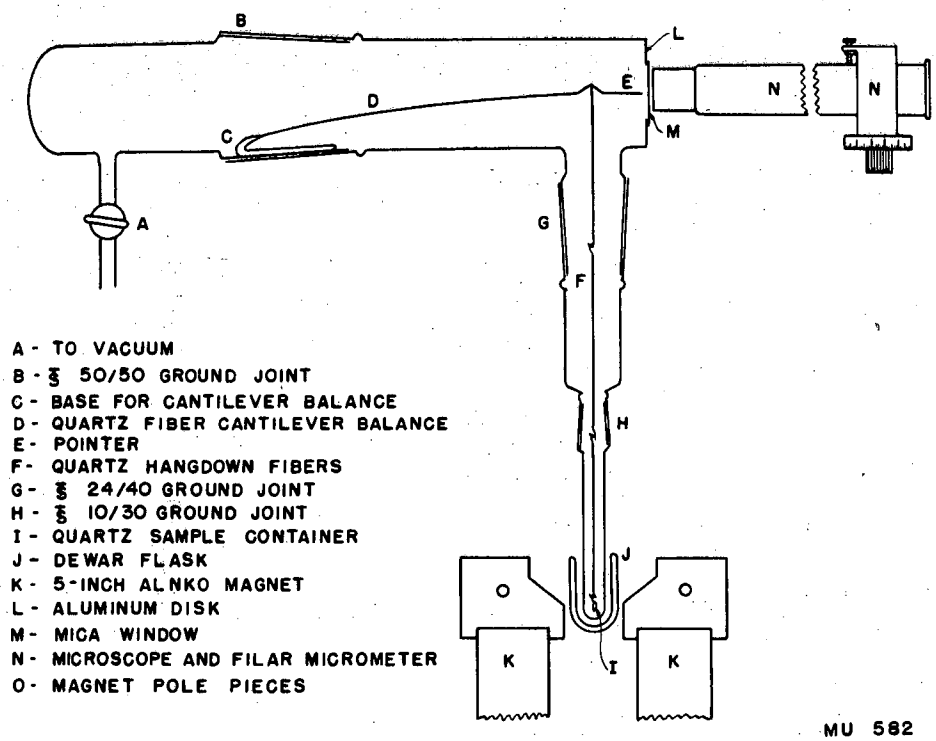
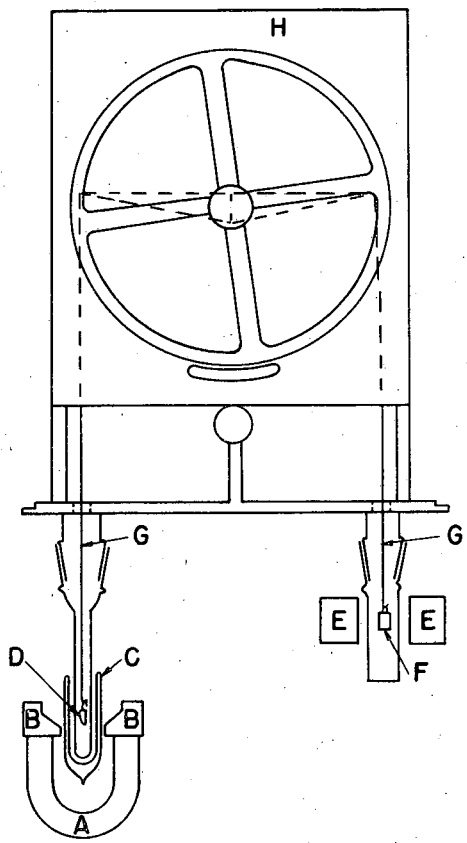

B
L
E
N
N
D
C
M
A
G
F
H
J
O
O
K
I
K
A - TO VACUUM
B - ₹ 50/50 GROUND JOINT
C - BASE FOR CANTILEVER BALANCE
D - QUARTZ FIBER CANTILEVER BALANCE
E - POINTER
F - QUARTZ HANGDOWN FIBERS
G - ₹ 24/40 GROUND JOINT
H - ₹ 10/30 GROUND JOINT
I - QUARTZ SAMPLE CONTAINER
J - DEWAR FLASK
K - 5-INCH ALNKO MAGNET
L - ALUMINUM DISK
M - MICA WINDOW
N - MICROSCOPE AND FILAR MICROMETER
O - MAGNET POLE PIECES
MU 582

Fig. 3



A - 5-INCH ALNICO MAGNET

B - MAGNET POLE PIECES

C - DEWAR FLASK

D - QUARTZ SAMPLE CONTAINER

E - MAGNET POLE PIECES FOR DAMPING THE BALANCE

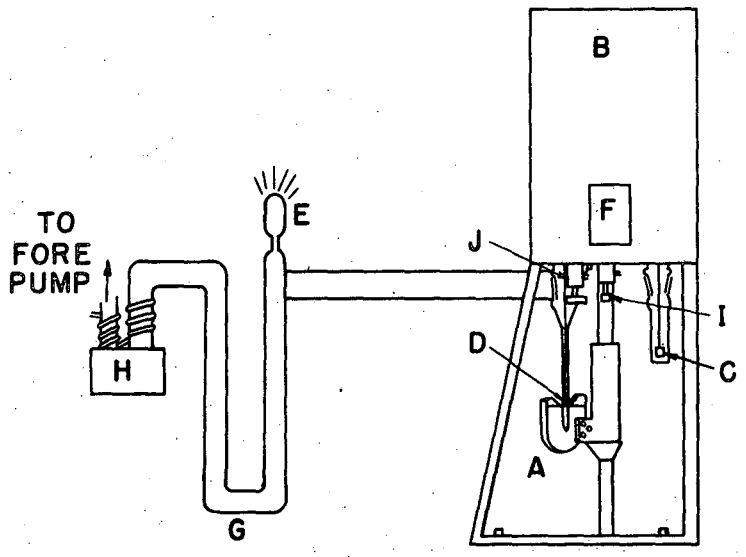
F - ALUMINUM FOIL FOR DAMPING THE BALANCE

G - QUARTZ FIBER TO BALANCE

H - KIRK, CRAIG, GULLBERG AND BOYER BALANCE

MU 1674

Fig. 4



A - 5 INCH MAGNET
B - DURAL VACUUM CASE
C - ALUMINUM COUNTER WEIGHT
D - SAMPLE
E - ION GAUGE
F - WINDOW TO VIEW BALANCE OPTICAL SYSTEM
G - COLD TRAP
H - OIL DIFFUSION PUMP
I - BEAM ARREST CONTROL THROUGH WILSON SEAL
J - TORSION CONTROL THROUGH WILSON SEAL

MU 1675

Fig. 5

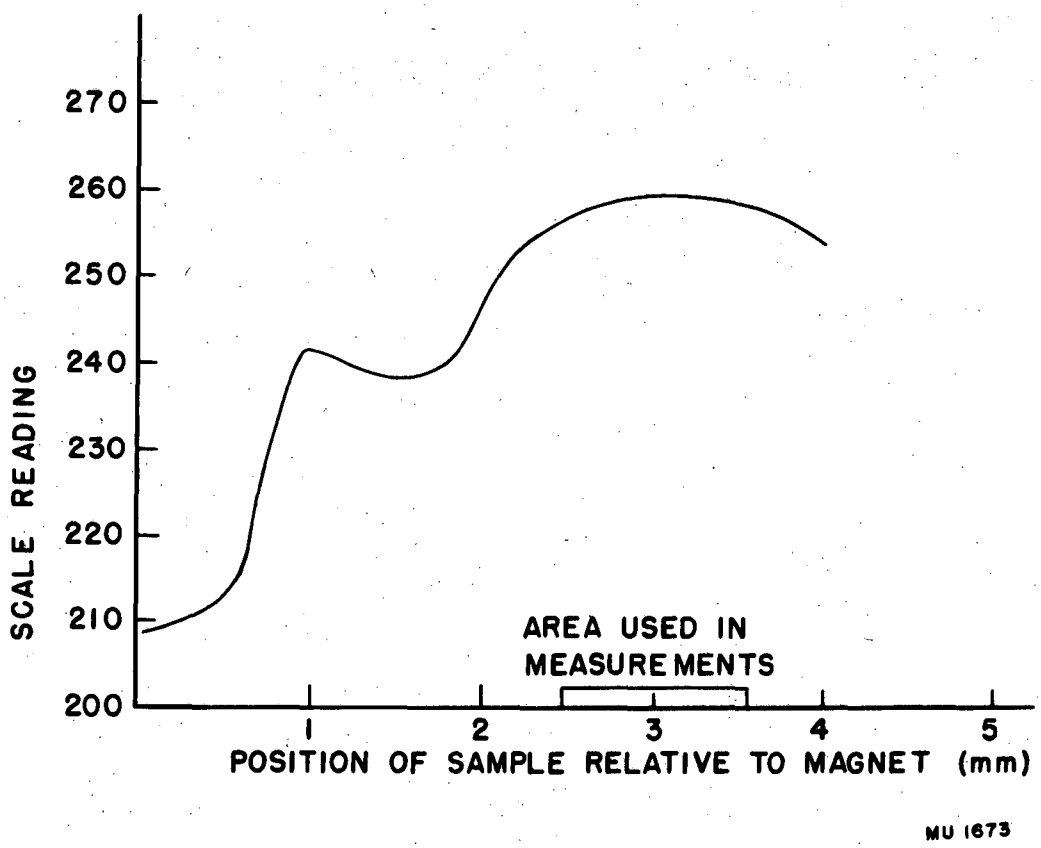

270
260
250
240
230
220
210
200
SCALE READING
AREA USED IN
MEASUREMENTS
1
2
3
4
5
POSITION OF SAMPLE RELATIVE TO MAGNET (mm)
MU 1673

Fig. 6

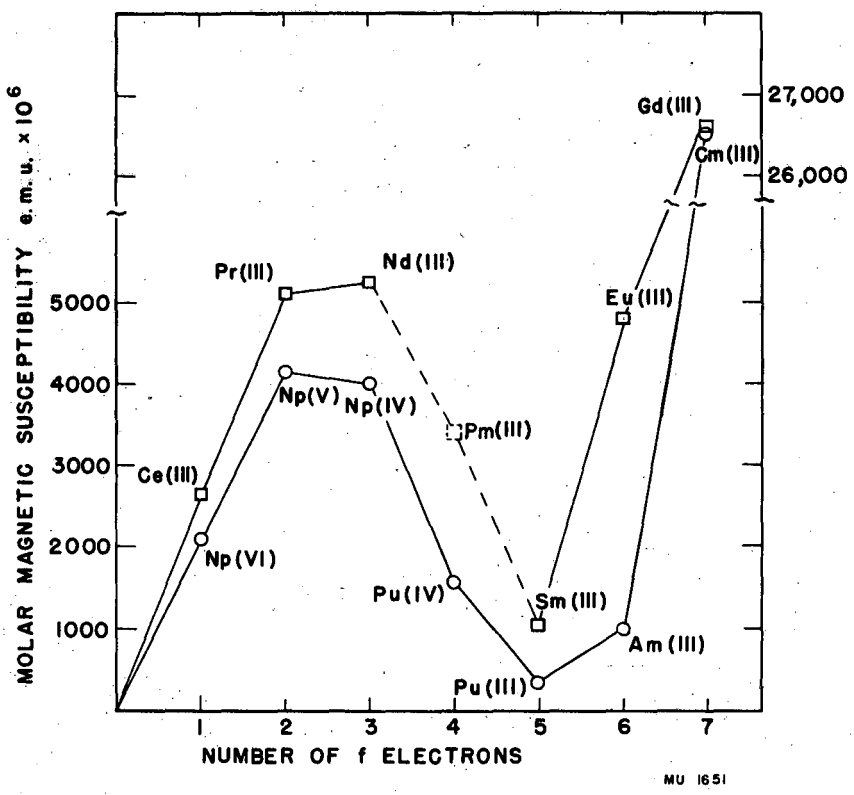

MOLAR MAGNETIC SUSCEPTIBILITY e.m.u. x 10^6
5000
4000
3000
2000
1000
27,000
26,000
Gd(III)
Cm(III)
Pr(III)
Nd(III)
Eu(III)
Np(V)
Np(IV)
Pm(III)
Ce(III)
Np(VI)
Pu(IV)
Sm(III)
Am(III)
Pu(III)
1
2
3
4
5
6
7
NUMBER OF f ELECTRONS
MU 1651

Fig. 7

DECLASSIFIED

CONFIDENTIAL