and

$$\frac{[\mathrm{Ti}^{+4}]}{[\Sigma\ \mathrm{Ti}^{+4}]} = \frac{K_4}{K_4 + [\mathrm{C_2O_4}^{=}]^2} \qquad \mathrm{(VI)}$$

where [Σ Ti^{+3}] represents [Ti^{+3}] + [$Ti(C_2O_4)_2^-$], etc.

It is the ratio [Ti^{+3}]/[Ti^{+4}] which determines the standard potential (or polarographic half-wave potential) of reaction I. Dividing V by VI, one obtains

$$\frac{[\mathrm{Ti}^{+3}]}{[\mathrm{Ti}^{+4}]} = \frac{K_3}{K_4} \times \frac{K_4 + [\mathrm{C_2O_4}^{=}]^2}{K_3 + [\mathrm{C_2O_4}^{=}]^2} \times \frac{[\Sigma\ \mathrm{Ti}^{+3}]}{[\Sigma\ \mathrm{Ti}^{+4}]} \qquad \mathrm{(VII)}$$

If the square of the concentration of oxalate ion is large compared to the values of K_3 and K_4, the latter can be neglected in the center fraction of the right-hand side of equation VII, in which case the ratio is independent of the concentration of oxalate ion. If, however, the square of the concentration of oxalate ion is of the same order of magnitude as K_3 and/or K_4, then the ratio [Ti^{+3}]/[Ti^{+4}], and the corresponding potential, must be a function of the concentration of oxalate ion. The latter is a function of the concentration of oxalic acid in the present discussion at constant *p*H.

The positive shift of potential with increasing concentration of oxalic acid indicates that the numerator of equation VII increases less rapidly than the denominator; therefore, K_4 is larger than K_3. It is not possible to determine the values of K_3 and K_4 from the present data alone and no values have been reported in the literature.

The half-wave potential of this system extrapolated to 1 *M* oxalic acid and 0 *p*H is −0.25 v. *vs.* the saturated calomel electrode or 0 v. *vs.* the standard hydrogen electrode. The standard potential of the uncomplexed species is −0.04 v. *vs.* the standard hydrogen electrode[13] which is not measurable polarographically because of irreversible electrode reactions. This slight shift in potential of 0.04 v. indicates that the +3 and +4 complexes have dissociation constants of the same order of magnitude with the tervalent being slightly more stable, in agreement with the preceding paragraph.

The above discussion also resolves the discrepancy noted for the dependence of half-wave potential on *p*H. If the total oxalate concentration is maintained constant and the *p*H altered, two effects result. First, the potential is changed because hydrogen ions are involved in reaction I. Second, the concentration of oxalate ion is changed. The two effects are in opposite directions and qualitatively in accord with the observed facts.

An increase of *p*H of one unit will increase the concentration of oxalate ion 100-fold. Since the observed dependence of potential for the latter is 0.02 volt per tenfold increase, the observed discrepancy of 0.04 volt for the *p*H dependence is exactly accounted for.

Acknowledgment.—The author is indebted to Mr. C. E. Johnson for furnishing a solution of purified titanous chloride, and to Professor J. B. Ramsey for valuable discussion.

---

[13] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1943, p. 483.

LOS ANGELES 24, CALIFORNIA RECEIVED AUGUST 7, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA]

The Emission Spectrum of Curium[1]

BY JOHN G. CONWAY, MILTON F. MOORE AND W. W. T. CRANE

The wave lengths of the most prominent lines in the arc and spark spectra of curium have been measured. The region covered extended from 2516–5000 A. The wave lengths of the lines are given, together with a discussion of methods of spectrographic analysis of curium samples.

Introduction

In August of 1947 L. B. Werner[2] isolated a sufficient amount of curium to permit a spectrochemical analysis to be performed. At that time the wave lengths of 54 lines were measured and these assigned to curium.[3] More recently W. W. T. Crane isolated additional quantities of curium and a portion was made available for further wave length measurements.

The handling of active elements such as curium requires many special protective techniques and equipment. A controlled atmosphere chamber mounted in a gloved box and a filter system were developed and constructed (Fig. 1) to meet these requirements. The controlled atmosphere chamber is made air tight before sparking, so that during

TABLE I

WAVE LENGTHS OF CURIUM

Wave length	Intensity spark	Wave length	Intensity spark	Wave length	Intensity spark	Wave length	Intensity spark
2516.0	2	2727.7	3	2909.1	2	2998.8	2
2562.3	1	2736.8	3	2913.1	4	3000.8	2
2585.8	2	2748.0	1	2929.0	2	3037.4	2
2616.8	2	2773.5	2	2933.2	3	3044.7	6
2617.2	3	2792.0	1	2934.9	3	3046.6	5
2625.4	2	2796.2	1	2935.4	3	3047.5	2
2628.2	2	2796.4	1	2944.5	2	3050.8	2
2636.2	3	2811.5	5	2953.0	3	3059.0	2
2651.1	4	2817.4	4	2955.6	2	3081.6	4
2653.7	4	2821.5	4	2957.5	4	3092.8	4
2677.0	1	2833.7	4	2961.8	2	3096.4	1
2693.8	1	2862.2	2	2963.0	2	3101.5	1
2704.8	1	2862.8	2	2968.9	4	3104.9	1
2707.1	1	2872.0	3	2984.5	3	3118.3	3
2710.1	1	2882.3	1	2996.2	3	3143.9	1
2725.6	2	2888.1	1	2998.3	3	3161.8	3

---

[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] L. B. Werner, U. S. Atomic Energy Commission Declassified Document AECD-2729 (July, 1948).

[3] J. G. Conway and M. F. Moore, University of California Radiation Laboratory Report UCRL-78 (April, 1948).

TABLE I (*Continued*)

Wave length	Intensity spark	Wave length	Intensity spark	Wave length	Intensity spark	Wave length	Intensity spark
3186.4	1	3585.6^{a}	3	3962.2	2	4293.0	1
3190.3	1	3591.9^{a}	2	3962.8	2	4299.1	1
3195.6	1	3619.9	2	3965.0	2	4301.5	5
3197.0	3	3639.9	1	3970.2	2	4313.1	4
3197.5	2	3643.5	1	3974.9^{a}	6	4318.7	3
3198.0	3	3670.4^{a}	2	3984.6	2	4323.4^{a}	5
3210.0	4	3691.7	3	3990.9	1	4357.2	2
3220.7	6	3692.5^{a}	3	4003.3^{a}	8	4433.7	3
3230.3	4	3697.3	2	4016.2	1	4434.2	2
3238.6	2	3708.8	1	4017.0	1	4435.3	2
3252.6^{a}	2	3709.6	1	4017.9	2	4442.0	3
3279.4^{a}	2	3723.3	3	4018.4	2	4446.5	1
3296.7^{a}	6	3732.3	3	4024.5^{a}	3	4455.2	2
3304.9^{a}	2	3738.2^{a}	3	4028.0^{a}	2	4546.9	1
3367.9^{a}	3	3739.3^{a}	4	4031.6^{a}	1	4570.1	2
3374.3^{a}	3	3750.5	3	4052.4	1	4608.3	2
3382.7	2	3763.6	4	4061.6	1	4632.1	1
3392.0	3	3767.3	3	4078^{a}	4	4665.4	2
3417.1^{a}	6	3778.2^{a}	4	4106.9	3	4670.4	2
3424.2	1	3788.0	1	4118.1	2	4681.8	2
3425.9^{a}	6	3799.5	3	4128.5	2	4722.8	4
3436.5	1	3842.1	3	4130.4	2	4761.6	1
3446.6	2	3846.9^{a}	2	4141.3^{a}	3	4873.8	3
3458.3	1	3903.9	7	4148.2	1	4880.5	3
3461.7	7	3908.2	6	4156.5	1	4905.6	4
3473.5^{a}	7	3936.6^{a}	5	4156.0	4	4906.3	1
3492.9	2	3941.5	1	4164.3	1	4925.5	3
3498.9^{a}	5	3942.1	1	4194.3	2	4989.9	1
3503.7	3	3947.9	3	4202.4	1		arc
3518.5	2	3948.8	2	4208.0	6	3019.6	9
3546.1^{a}	5	3953.3	1	4218.6	3	3943.7	9
3550.3	3	3957.5	1	4239.8	3		
3567.4^{a}	5	3960.8^{a}	2	4283.0	1		

^{a} Lines also found in 1947 experiment.

sparking, no activity can escape into the gloved box. Activity created by the discharge during the sparking period is removed by continuously flushing air through the chamber and filter; then it is exhausted on the roof. The filter system is a six-foot train of loosely packed glass wool fibers connected to the chamber air outlet. The gloved boxes are maintained with a separate filter system under negative pressure at all times.

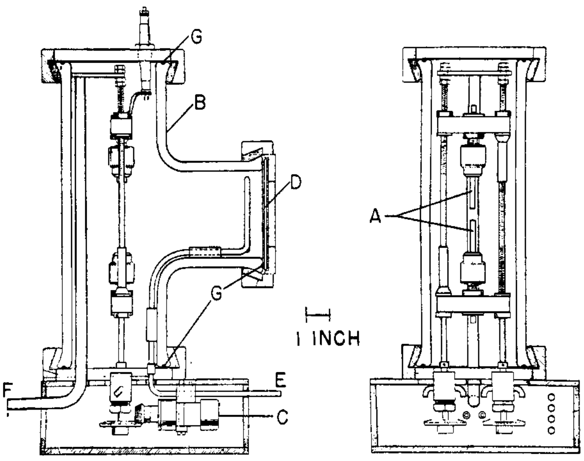

Fig. 1.—Controlled atmosphere chamber: A, copper electrodes held by Jacobs chucks; B, Pyrex glass pipe 4″ diameter; C, motors to adjust electrode separation (27 VDC); D, quartz window 5$^{1}/_{8}$″ diamter, $^{1}/_{4}$″ thick; E, air inlet; F, air outlet; G, "O" ring gaskets.

The curium was supplied in 0.1 *N* HCl solution. One-microgram aliquots were evaporated on 0.25″ copper electrodes[4a,4b] and sparked for 15 seconds using an Applied Research Laboratory unit with 0.021 mfd. and 0.36 mh. at 100 volts. For arcing one microgram, aliquots were evaporated on $^{1}/_{8}$″ special spectroscopic graphite and burned at 7 amperes d.c. 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 103-F 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.

Results

The wave lengths of curium lines as recorded in Table I are considered accurate to ±0.2 Å. Background and band structure limit the number of lines that can be observed in the arc spectra.

BERKELEY, CALIF. RECEIVED SEPTEMBER 15, 1950

---

[4] (a) M. Fred, N. H. Nachtrieb and F. S. Tomkins, *J. Optical Soc. Am.*, **37**, 279 (1947). (b) M. C. Bachelder, J. G. Conway, N. H. Nachtrieb and B. S. Wildi, U. S. Atomic Energy Commission Declassified Document MDDC-511 (December, 1946).