

## Absorption Spectrum of Hexavalent Plutonium

R. H. Betts and B. G. Harvey

Citation: *The Journal of Chemical Physics* **16**, 1089 (1948); doi: 10.1063/1.1746735

View online: <http://dx.doi.org/10.1063/1.1746735>

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rate conditions are then applied, with replacement of  $y$  by  $y'$ , and lead to the equations:

$$\frac{c}{c_0} = \frac{e^{-T}[\varphi(T+t', rs) + I_0(2(rsT+rst')^{\frac{1}{2}})] - [\varphi(t', rs) + I_0(2(rst')^{\frac{1}{2}})]}{e^{-T}[\varphi(T+t', rs) + I_0(2(rsT+rst')^{\frac{1}{2}})] + \varphi(s, rT+rt') + [\varphi(rt', s) - \varphi(t', rs)]}, \quad (4)$$

$$\frac{p}{p_\infty} = \frac{e^{-T}[\varphi(T+t', rs)] - [\varphi(t', rs)]}{e^{-T}[\varphi(T+t', rs) + I_0(2(rsT+rst')^{\frac{1}{2}})] + \varphi(s, rT+rt') + [\varphi(rt', s) - \varphi(t', rs)]}, \quad (5)$$

where  $r$  and  $s$  remain as before, and  $t'_{ij}$  corresponds to the values of  $t_{ij}$  in Table I with  $y$  replaced by  $y'$ . Figure 1 presents typical elution curves as calculated from these equations, with  $r_{ij}$  and  $s_{ij}$  constant. At large  $T$  the equations become identical with those of Thomas,<sup>4</sup> as is indicated in the figure; for instance:

$$\frac{c}{c_0} = \frac{\varphi(rs, t')}{\varphi(rs, t') + I_0(2(rsT+rst')^{\frac{1}{2}}) + \varphi(rt', s)}. \quad (6)$$

As the new fluid front travels down the bed, the discontinuity in  $c/c_0$  decreases and rapidly becomes negligible; in actual practice, it may be obscured by diffusional effects even at small distances. For ion exchange, the above equations may be extended to regenerant concentrations other than  $c_0$  (i.e.,  $c_0'$ ) by replacing  $c_0$  by  $c_0'$  (except in the calculation of  $T$  which is a "memory" term); in this case a discontinuity is always encountered at the front. Figure 1 shows also how regeneration time is reduced by doubling the concentration level of regenerant.

The curve for  $p$  is continuous, but otherwise of the same general shape as for  $c$ ; its maximum represents a true equilibrium condition, at the time that net reaction at that particular cross section finally shifts from saturation to elution.

Where  $r=1$ , Eqs. (4) and (5) take on an especially simplified form:

$$\frac{c}{c_0} = e^{-(T+t'+rs)}[\varphi(T+t', rs) + I_0(2(rsT+rst')^{\frac{1}{2}})] - e^{-(t'+rs)}[\varphi(t', rs) + I_0(2(rst')^{\frac{1}{2}})], \quad (7)$$

$$\frac{p}{p_\infty} = e^{-(T+t'+rs)}[\varphi(T+t', rs)] - e^{-(t'+rs)}[\varphi(t', rs)]. \quad (8)$$

The two terms in each of the above equations represent pairs of values in the Furnas charts that are displaced along the  $t'$  scale by a value of  $T$ .

Saturation and elution equations have also been derived for cases involving more than one "memory" term. We are preparing tables of  $\varphi$  to facilitate exact evaluation of the above equations, and also are charting solutions of Eq. (1) for values of  $r$  other than unity. Complete derivations will be reported and applications discussed in a forthcoming paper.

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## Absorption Spectrum of Hexavalent Plutonium

R. H. BETTS AND B. G. HARVEY  
Atomic Energy Project, National Research Council,  
Chalk River, Ontario, Canada  
September 7, 1948

THE chemical similarity between uranium and plutonium now appears to be firmly established.<sup>1,2</sup> Recently, Kasha<sup>3</sup> has used this analogy to explain certain features of the absorption spectrum of  $\text{PuO}_2^{++}$  in 0.1*N* perchloric acid. Now the absorption spectrum of  $\text{UO}_2^{++}$  is well known;<sup>4</sup> it contains eleven regularly spaced bands in the region 3400–5000Å. These bands are believed to arise from symmetrical vibrations in the U–O bonds of

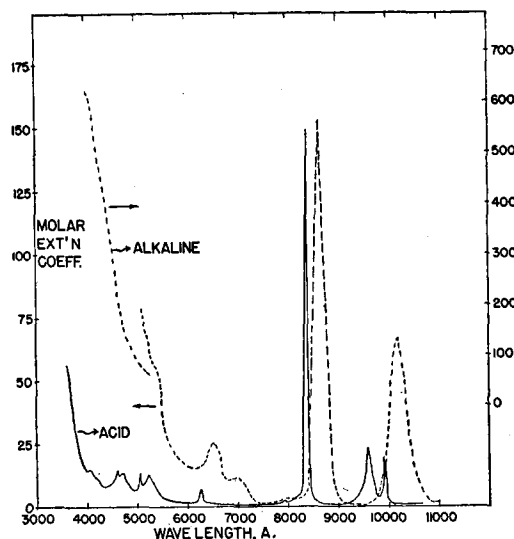


FIG. 1. Absorption spectrum of Pu(VI).

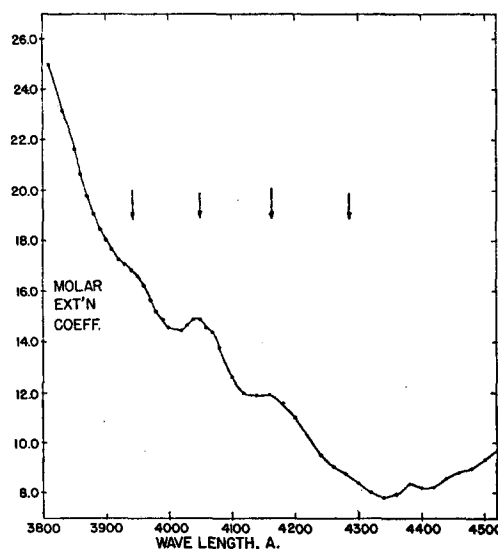


FIG. 2. Absorption spectrum of Pu(VI) in  $\text{HNO}_3$  solution.

the  $\text{UO}_2^{++}$  ion. Kasha found a series of four regularly spaced bands for  $\text{PuO}_2^{++}$  in the region 3900–4300Å, and ascribed them to symmetrical vibrations in the Pu–O bonds. In addition, an exceedingly sharp band at 8330Å was found, which was attributed to electronic transitions within the 5*f* electron shell. The  $\text{UO}_2^{++}$  spectrum has no corresponding sharp lines; this is to be expected, since uranium contains no 5*f* electrons in this valence state.<sup>2</sup>

We have measured the absorption spectrum of  $\text{PuO}_2^{++}$  in 0.9*N* nitric acid solution, using a Beckman quartz spectrophotometer. The spectrum over the region 3600–10,000Å is shown in Fig. 1. This result is very similar to that described for  $\text{PuO}_2^{++}$  in 0.1*N* perchloric acid.<sup>3</sup> That portion of the spectrum ascribed by Kasha to vibration is shown on an enlarged scale in Fig. 2. Four regularly spaced bands may be distinguished in the region 3900–4300Å (indicated by arrows). Starting from the ultraviolet end, the successive frequency intervals for these bands are 630, 670, and 670  $\text{cm}^{-1}$ , giving an average of 657  $\text{cm}^{-1}$ . This agrees within experimental error with the value of 708  $\text{cm}^{-1}$  found by Kasha.<sup>3</sup>

A qualitative comparison of the uranyl and plutonyl

spectra at higher *pH* values tends to confirm this distinction between the vibrational and electronic portions of the Pu(VI) spectrum. For U(VI), Sutton<sup>4</sup> has shown that as the *pH* is raised above 2.0, the banded structure gradually disappears, and is replaced by a region of more or less continuous absorption below 5000Å. We have determined the absorption spectrum of Pu(VI) in dilute ammonium hydroxide solution. (Ammonium plutonate is insoluble, in general, in dilute ammonium hydroxide solution, but we have found on occasion that a solution of Pu(VI) deepens to an orange color on addition of excess ammonia without the appearance of a precipitate.) The result is given in Fig. 1. The peak at 8330Å is broadened slightly, and shifted to longer wave-lengths, without a marked change in the extinction coefficient. However, the band structure has been replaced by a region of general absorption with much higher values of the extinction coefficients.

<sup>1</sup> Harvey, Heal, Maddock and Rowley, *J. Chem. Soc.* 1010 (1947).

<sup>2</sup> B. G. Harvey, *Nucleonics* 2, 30 (1948).

<sup>3</sup> M. Kasha, MDDC-591, U. S. Atomic Energy Commission, Oak Ridge, Tennessee (and references therein).

<sup>4</sup> J. Sutton, Report No. 1612, National Research Council of Canada, Ottawa, Canada.