

discolored instantaneously. When a mixture of ethanol and acetone is used as a solvent, the rate of discoloration of the permanganate solution increases with the increase of alcohol concentration. Ethanol *per se* in the absence of olefins does not discolor the permanganate solution even after five minutes of standing. Methanol and 2-propanol act in a similar fashion as ethanol.

It was found that the addition of only a small amount of water to acetone increases the rate of discoloration when tested for unsaturation. A 5% solution of water in acetone seems to be a suitable solvent for the unsaturation test.

The procedure used for testing the various compounds was essentially as follows: One drop of a 2% aqueous solution of potassium permanganate was added to 0.1 cc. (0.1 g. if solid) of the compound dissolved in 2 cc. of the investigated solvent. Test was indicated as positive (+) when the color of the potassium permanganate changed within five seconds after the addition of the permanganate. If the potassium permanganate color persisted for longer than five minutes, the test was reported to be negative (-). The length

of time required to discolorize the permanganate is expressed in seconds.

The tables summarize the results obtained.

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Hydrolytic Titrations of Lead with Potassium Cyanide

BY LOUIS MEITES

In the course of a study of hydrolytic titrations of various divalent cations with potassium cyanide, it was found that the atypical behavior of plumbous ion was of particular interest. It is well known that most such titrations are characterized by a continuous rise in *pH* on addition of cyanide, with sharp increases at points corresponding to quantitative formation of insoluble compounds, such as $M(CN)_2$, or complex ions, such as $M(CN)_4^-$.

Titration of an aqueous solution of lead nitrate, however, gives, after an ill-defined end-point at about 1.5 mole of cyanide per mole of lead, a sharp downward break in *pH* at a mole ratio of about 1.8. This break is of the order of 0.25 *pH* unit, and it is followed by a steady rise in *pH* as the titration is continued, with no clear indication of any further end-point to a mole ratio of at least eight.

In 50% ethanol a pronounced end-point (taken as the point of maximum slope) is observed at a mole ratio of 1.002 ± 0.004 , and it is followed by, first, a downward break similar to that found in aqueous medium, and then, at a mole ratio of 1.50 ± 0.01 , a second sharp end-point.

The insoluble products of the reactions in 50% ethanol were isolated by titrating 500-ml. portions of an 0.05 *M* solution of lead nitrate with standard potassium cyanide until the previously determined *pH* values at the respective end-points, as measured with a Beckman glass electrode *pH* meter, had been exactly reached. The products were filtered off, washed with 50% ethanol and ether, and air-dried. They were analyzed by decomposition in platinum over a very low flame, followed by ignition at a dull red heat, and both gave light yellow plumbous oxide apparently uncontaminated by any trace of a red higher oxide. The compound formed at the first end-point evolved much nitrogen dioxide during its decomposition. Found: PbO , 78.1, 78.2; calculated for $Pb(OH)(NO_2)$, 77.99%. The other compound gave off only a faint odor of cyanogen. Found: PbO , 87.4, 87.3; calculated for $Pb(OH)(CN) \cdot Pb(CN)_2$, 87.62%. This substance has not previously been described in the literature.

The reactions taking place during this titration may, therefore, be represented by the equations

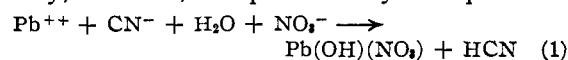


TABLE I

COMPARISON OF ETHANOL WITH ACETONE IN PERMANGANATE TEST FOR UNSATURATION

Compounds tested	Solvents	
	Ethanol	Acetone
Amylenes	+	15 sec. (-) ^a
Octene	+	-
Butadiene	+	45 sec.
Cyclohexene	+	-
α -Pinene	+	-
3-Methylcyclohexene	+	-
1,1,3-Trimethyl-x-cyclohexene	+	30 sec. (-) ^a
β -Pinene	+	-
Dihydrolimonene	+	-
Limonene	+	-
Terpineol	+	180 sec.
Allyl alcohol	+	20 sec.
Cholesterol	-	-
Ergosterol	20	-
Mesityl oxide	+	+
Isophorone	+	20 sec.
Acetylacetone	20	240 sec.
Crotonic acid	+	10 sec.
Crotonaldehyde	+	+
Cholesteryl acetate	-	-
Dihydropyran	+	30 sec.

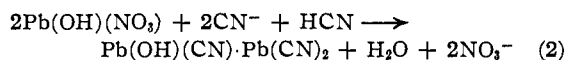
^a Test after redistillation of the hydrocarbons.

TABLE II

EFFECT OF MIXTURES OF ETHANOL/ACETONE ON RATE OF PERMANGANATE TEST OF OLEFINS

Alcohol concentration, vol. % Compounds tested	Time in seconds for color change					
	100	80	60	40	20	0
Limonene	0	5	15	30	60	>300
Cyclohexene	0	5	15	40	120	>300
Methylcyclohexene	0	10	30	90	240	>300

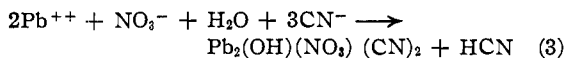
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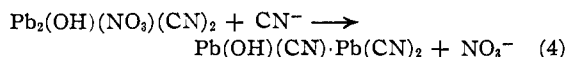
The sudden decrease in $p\text{H}$ between the two end-points is accounted for by the assumption that the concentration of cyanide ion must reach a certain value before reaction (2) is initiated, but that, once started, it progresses to a point at which most of the free cyanide ion has been removed.

The products formed during the titration in aqueous medium were prepared by adding known volumes of standard potassium cyanide to known volumes of standard lead nitrate solution, filtering, and air-drying. They were analyzed as described above. Addition of 1.50 mole of cyanide per mole of lead gave another new compound. Found: PbO , 81.8, 81.8; calculated for $\text{Pb}_2(\text{OH})(\text{NO}_3)(\text{CN})_2$, 81.85%. This compound evolved nitrogen dioxide during its decomposition. The substance formed at a mole ratio of 2.00 (*i.e.*, after the downward break) was again the hydroxytricyanide described above.

Consequently, the stoichiometry of the reactions in aqueous medium is described by the equations



and



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The Structure of Uranium Hydride

BY LINUS PAULING AND FRED J. EWING

R. E. Rundle¹ has recently reported the results of an X-ray investigation of uranium hydride, UH_3 . He found that there are eight molecules of this substance in the unit cube, with $a_0 = 6.631 \text{ \AA}$., and that the uranium atoms have the β -tungsten arrangement, with two UI at 000 and $1/2 \ 1/2 \ 1/2$ and six UII at $1/2 \ 1/4 \ 0$, etc. He suggested that each uranium I atom is surrounded by twelve hydrogen atoms, on the lines connecting the UI atom with the twelve surrounding UII atoms, and that there are half-bonds between hydrogen and each of the two uranium atoms ligated to it.

In this note we point out that consideration of the interatomic distances supports this proposal, and, moreover, leads to the conclusion that uranium hydride contains a new form of uranium, with small valence, similar to the low-valent forms of chromium and manganese previously reported.²

A hydrogen atom in a metallic hydride may be at the center of a tetrahedron of metal atoms, or

of an octahedron of metal atoms.³ In zirconium hydride, ZrH , for example, the zirconium atoms are in a cubic closest packed arrangement, and it seems likely from consideration of the interatomic distances that the hydrogen atoms occupy tetrahedral positions, corresponding to the sphalerite structure. The single-bond radius of hydrogen is then calculated from the zirconium-hydrogen distance 2.06 \AA ., with use of the zirconium single-bond radius 1.454 \AA . and the correction 0.36 \AA . for bond-number $1/4$, to be 0.25 \AA . In palladium hydride, PdH_x , the tetrahedral positions are too small for hydrogen atoms, which instead occupy octahedral positions; the palladium-hydrogen distance 2.03 \AA ., with palladium single-bond radius 1.28 \AA . and correction 0.47 \AA . for bond-number $1/6$, then leads to 0.28 \AA . for the hydrogen radius. This radius lies between 0.25 and 0.32 \AA in most metallic hydrides, in good agreement with the range of values for non-metallic hydrides, 0.28 to 0.32 \AA .⁴

In uranium hydride the U-H distance of 1.85 \AA . (assuming the hydrogen to be midway between UI and UII) is approximately equal to that predicted, namely, the single-bond radius of uranium, 1.42 , plus the radius of hydrogen, 0.27 , plus the correction for bond number $1/2$, 0.18 , a total of 1.87 \AA . There is no satisfactory position in the uranium hydride structure for hydrogen with coordination number larger than two. In UH_3 each UI atom forms twelve bonds with bond number $1/2$ with the surrounding hydrogen atoms, corresponding to a valence of six for uranium I. Each UII forms four such bonds with four surrounding hydrogen atoms, and also forms two bonds with adjacent UII atoms, at 3.316 \AA ., the calculated bond-number for these bonds being 0.16 . This leads for uranium II to the value 2.3 for the valence. No form of uranium metal or intermetallic compound of uranium has been reported so far in which uranium has this low valence, but a low-valent form of chromium and one of manganese have already been reported, so that a similar form for uranium is not entirely unexpected.

It is interesting to point out that the Brillouin-zone treatment of the β -tungsten structure provides some basis of understanding of the stability of this structure for both β -tungsten and uranium hydride. The first expected Brillouin zones correspond to the strong reflections $\{210\}$ and $\{211\}$, which lead to about 16 electrons per unit cube. There then occurs another Brillouin polyhedron, bounded by the strong reflections $\{222\}$, $\{320\}$, and $\{400\}$. (A fourth strongly reflecting form, $\{321\}$, does not further truncate this polyhedron.) The content of this polyhedron is 53.5 electrons

(3) G. Hägg, *Z. physik. Chem.*, **B11**, 433 (1930); **B12**, 33 (1931). Hägg's assignment of the hydrogen atoms to these positions was based on the assumption that the effective radius of hydrogen in metallic hydrides is about the same as in non-metallic hydride molecules.

(4) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1940, p. 168.

(1) R. E. Rundle, *THIS JOURNAL*, **69**, 1719 (1947).

(2) L. Pauling, *ibid.*, **69**, 542 (1947).