

In Table II the data are given from which the values of the equilibrium pressures were estimated. It will be noted that in most cases it was possible to approach the equilibrium from both sides.

Summary

The compounds formed between ammonia and

triphenyllead chloride have been investigated and their vapor pressures measured at -33.4° . Several compounds were detected, but the composition of only one was determined accurately. In this compound the number of moles of ammonia per mole of triphenyllead chloride cannot be expressed as the ratio of small whole numbers.

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The Standardization of Strong Oxidizing Agents with Potassium Iodide by the Acetone Method

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Lewis¹ attributes the low results obtained by us² in the standardization of potassium permanganate with pure potassium iodide by the acetone method of Berg³ to the use of too low an acidity. The acidity used in our work was 0.9 *N*, while Berg used 2.0–2.5 *N* with potassium iodate as the oxidant. According to his comments the most suitable acidity seems to vary with the oxidant which is being standardized. In order to determine whether our low results were caused by too low an acidity, we have extended our experiments over a range of varying concentrations of acid. The same sample of pure potassium iodide as described previously² was used. An accurately weighed amount of the pure iodide was dissolved in water, 50 ml. of acetone, water and varying amounts of 9 *M* sulfuric acid were added to make a volume of 200 ml. One tenth normal potassium permanganate, standardized by the accurate method previously described, was added from a weight buret to within about 1% of the end-point (40 to 50 ml.) and the titration was then finished with 0.01 *N* permanganate which was added from an ordinary buret. The results were found to be independent of the acidity when the initial sulfuric acid concentration lay between 0.5 and 4 *N*. The results were always low, but depended upon the speed with which the 0.01 *N* permanganate was added in the immediate vicinity of the end-point. When it was added at a rate of about ten seconds per drop the results were 1.0% low; on the other hand, if the permanganate was added

rapidly until the color change persisted for thirty seconds, the results were 0.2% low. The speed of addition of the permanganate up to 0.5% before the equivalence point did not affect the results. Apparently, the low results have to be attributed to the fact that part of the 0.01 *N* permanganate added in the immediate vicinity of the end-point reacts with the acetone and the iodoacetone and is withdrawn from reaction with iodide. If the titration was carried out and finished with 0.1 *N* permanganate, which was added either from a weight or a volume buret, the results were found to be close to the theoretical value but always slightly low. This is evident from the experiments reported in Table I which were carried out at varying acidity. In all these experiments 25 ml. of acetone was used in an initial volume of 100 ml.

TABLE I
STANDARDIZATION OF 0.1 *N* PERMANGANATE WITH POTASSIUM IODIDE BY BERG'S METHOD. THEORETICAL VOLUME OF PERMANGANATE 47.70 ML.

Initial normality of H ₂ SO ₄	0.25	0.5	1.0	2.0	3.0	4.0
0.1 <i>N</i> permanganate used	^a	47.69 ^b	47.68 ^b	47.67	47.62	47.63
Error, %		-0.02	-0.04	-0.06	-0.16	-0.14

^a Reaction velocity too small to allow titration.

^b Average of two to three titrations.

Under the specified conditions the titration yields excellent results, particularly when the initial acidity is between 0.5 and 2 *N* and the titration is carried out with 0.1 *N* permanganate. It was found that the amount of acetone in the initial volume of 100 ml. could be changed between 10 and 50 ml. without changing the results

(1) D. Lewis, *THIS JOURNAL*, **59**, 1401 (1937).

(2) I. M. Kolthoff, H. A. Laitinen and J. J. Lingane, *ibid.*, **59**, 429 (1937).

(3) R. Berg, *Z. anal. Chem.*, **69**, 369 (1926).

more than 0.05%. From the practical point of view the use of the following procedure for the standardization of 0.1 *N* permanganate is to be preferred over the standardization with sodium oxalate.

Procedure for the Standardization of 0.1 *N* Permanganate (and 0.1 *N* Ceric Sulfate).—Weigh out approximately 0.35 g. of pure potassium iodide, dissolve in 75 ml. of water, add 5 ml. of 18 *N* sulfuric acid, 3 drops of 0.025 *N* ferrous phenanthroline sulfate solution and 20 to 25 ml. of c. p. acetone. Mix and titrate with 0.1 *N* permanganate until the end-point color change from red to practically colorless persists for thirty seconds.

In his experiments, Lewis used a c. p. Mallinckrodt product of potassium iodide and found results which agreed within 0.1 to 0.2% with the normality obtained with sodium oxalate. Using our precise methods² we determine the purity of a c. p. Mallinckrodt product of potassium iodide. After drying at 250° we found a potassium iodide content of 99.94% as compared to 100.00% for our pure product. Thus, for most practical purposes the standardization can be made with the dried Mallinckrodt product.

A limitation of the method is that the procedure described gives low normalities in the standardization of 0.01 *N* permanganate. Under the most favorable conditions (fast titration close to the end-point), the results were found to be 0.8 to 1% low.

The experiments described above were repeated with ceric sulfate. The results obtained were strictly comparable with those obtained with permanganate. The procedure given for the standardization of 0.1 *N* permanganate gives equally good results in the standardization of 0.1 *N* ceric sulfate, but again yields 0.8 to 1% low results in the standardization of 0.01 *N* ceric sulfate.

A separate investigation has been made of the cause of the low results obtained in the slow titrations with 0.01 *N* permanganate in the vicinity of the end-point. In the following experiments 5 ml. of 0.1 *N* permanganate was added to a mixture of 25 ml. of c. p. acetone in 100 ml. of dilute sulfuric acid. After standing for fifteen minutes at room temperature, the excess of permanganate was determined by adding an excess of standard iodide and titrating with 0.1 *N* permanganate according to the procedure described above. From the results given in Table II it is evident that the amount of permanganate which has reacted is proportional to the acidity of the solution.

TABLE II

REACTION OF PERMANGANATE WITH ACETONE IN ACID MEDIUM AFTER FIFTEEN MINUTES

Sulfuric acid, <i>N</i>	0.5	1.0	2.0	3.0	4.0
MnO ₄ ⁻ reduced, %	17	34	70	98	100

Since the reduction of the permanganate may be attributed to impurities in the acetone, we have repeated the experiments with purified samples. The original c. p. sample was refluxed for several hours with an excess of permanganate and distilled. In other experiments the original sample was purified by making the sodium iodide addition compound from which the purified product

was obtained by distillation.⁴ The purified products behaved similarly to the original sample. Particularly immediately after addition of the permanganate the reaction velocity was found to be relatively great, the relative rate being greater with 0.01 *N* than with 0.1 *N* permanganate. A few figures given in Table III illustrate the behavior. The latter only partly accounts for the low results obtained in slowly titrating with 0.01 *N* permanganate near the end-point. Part of the error must be attributed to the fact that the presence of iodo-acetone increases the rate of reduction of permanganate. This rate was found to increase with increasing concentrations of iodoacetone.

The conditions under which the experiments of Table III were carried out were chosen so as to correspond closely to those in the neighborhood of the end-point in the titration. To a solution of 25 ml. of acetone in 140 ml. of 1.3 *N* sulfuric acid were added the indicated reagents and 2.90 ml. of permanganate. After various periods of standing at room temperature the amount of permanganate left was determined as described before.

TABLE III

RATE OF REACTION OF PERMANGANATE WITH ACETONE UNDER VARYING CONDITIONS

Concentration of Manganous sulfate, <i>M</i>	Iodo-acetone, <i>M</i>	Normality of permanganate	Permanganate reduced in % after			
			1	5	15	30 min.
		0.1	12 ^a		36 ^a	50 ^a
					32 ^a	44 ^a
0.0065	0.013	.1	22 ^a		85 ^a	90 ^a
		.01	36 ^a	50 ^b		
.0065	.013	.01	40 ^a	100 ^a		
			25 ^b	99 ^b		
.00065		.01	43 ^a	57 ^a		

^a Unpurified c. p. acetone. ^b Purified by the sodium iodide addition compound. ^c Purified by refluxing and distilling from neutral permanganate.

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Summary

1. A simple procedure is given for the standardization of 0.1 *N* permanganate and 0.1 *N* ceric sulfate by Berg's method using potassium iodide as a primary standard.

2. The method gives 0.8 to 1% low results in the standardization of 0.01 *N* solutions.

3. Low results are shown to be due to a reduction of the oxidizing agent by the acetone and the iodoacetone in the close neighborhood of the end-point.

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(4) K. Shipsey and E. A. Werner, *J. Chem. Soc.*, **103**, 1255 (1913); H. L. Lochte, W. A. Noyes and J. R. Bailey, *THIS JOURNAL*, **44**, 2563 (1922).