portional to the absolute temperature. While there might be some minor corrections to apply, these could be experimentally determined by observations on substances of known melting point.

BERKELEY, CALIFORNIA.

THE RELATIVE STABILITY OF PRIMARY CADMIUM POTASSIUM IODIDE AND ITS APPLICATION IN THE DETERMINATION OF OZONE.[1]

BY CHARLES BASKERVILLE AND W. J. CROZIER.

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Of the several methods which have been proposed for the determination of ozone, that of Schönbein, which consists in estimating the iodine liberated from metallic iodides, has been quite generally employed, although it is open to a number of serious objections. It is well known that when acid potassium iodide solution is employed, the potassium iodide-starch reaction is neither a qualitative nor a quantitative indication of the presence or amount of ozone; and that various agencies influence the liberation of iodine from the acidified potassium iodide solution, while chlorine, bromine and nitrites (frequently found in the air) also give the reaction. These influences, of an order of magnitude safely disregarded in other analytical work, must be dealt with. With regard to the reliability of neutral metallic iodide solutions, Lechner[2] maintained that unsatisfactory results were obtained when determining ozone with the aid of neutral potassium iodide solutions, as large quantities of iodine vapor were liberated. This is directly contrary to the results obtained by Ladenburg and Quasig,[3] who found that neutral solutions only give correct results, and that acid solutions give no sharp end-point and the results are too high.[4] They obtained good results, but used, apparently, only ozone of a high state of purity.

Baskerville and Hamor[5] have pointed out the objections to which potassium iodide is open as a reagent for hydrogen dioxide, and the authors have found that as a test for ozone, potassium iodide is subject to the same limitations, and, generally, even to a greater degree. Baskerville and Hamor found that since primary cadmium potassium iodide ($CdKI_3.H_2O$) is unaffected by the presence of any likely amounts of acids in ethyl ether, and is much more stable in light than potassium iodide in solutions of comparable strength, its use is preferable for the detection of peroxidized compounds in ether. The authors have extended the observa-

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[1] Read before the Eighth International Congress of Applied Chemistry, New York, Sept., 1912.

[2] *Z. Elektrochem.*, 17, 412.

[3] *Ber.*, 34, 1184 (1901).

[4] Our experiments would tend to confirm these findings.

[5] *J. Ind. Eng. Chem.*, 3, No. 6 (1911).

tions on the stability of cadmium potassium iodide and have employed it as a reagent for the quantitative determination of ozone.

1. The Comparative Stability of Potassium Iodide and Cadmium Potassium Iodide.

The cadmium potassium iodide used in the experiments which follow was found to possess the following composition:

	Water.	Cadmium.
Calculated for $CdKI_3.H_2O$	3.27%	21.17%
Found	3.36	20.98

It was free from foreign metals, sulfuric acid, and hydriodic acid, and was soluble in about 0.95 part of water at 15°. The potassium iodide used was also found to be pure.

The statement is made in the literature[1] that solid cadmium potassium iodide assumes a slight yellow color on standing. In the experiments made by the authors on this point, the salt was from two different lots: (*a*) Some which, after purification, had been standing for five years in a museum case, freely exposed to diffused light during most of every day. This sample possessed no yellowish tinge whatsoever, nor was there present any detectable free iodine. (*b*) Samples of a fresh lot of "cadmium and potassium iodide Merck." These were exposed to direct sunlight for periods ranging up to 25 days, and analysis showed that no decomposition occurred. We are therefore inclined to believe that pure primary cadmium potassium iodide uncontaminated with cadmium iodide, potassium iodide or water in excess, will not become colored upon storage.

The next experiments were made on the rate of the decomposition of stock solutions of potassium iodide and cadmium potassium iodide under laboratory conditions. Tenth-normal solutions were kept in the ordinary diffused light of the laboratory for two months, at the end of which time the following comparative results were obtained in grams of iodine:

Potassium iodide.	Cadmium potassium iodide.
0.00053	0.00046

A series of experiments was then made on the relative stability of cadmium potassium iodide toward various reagents.[2] A 10% solution was prepared and the following tests were made with 2 cc. quantities, the exposures being to diffused daylight during the daytime:

1. With 2 cc. of hydrochloric acid (density 1.20), no perceptible reaction occurred until after 30 hours.
2. With 2 cc. of sulfuric acid (density 1.84), a yellow coloration resulted at once.
3. With 2 cc. of 10% sulfuric acid, after two days, the reaction was as strong as in 6.
4. With 2 cc. of concentrated nitric acid, the reaction was immediate.
5. With 2 cc. of 1 : 10 nitric acid, a reaction resulted.

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[1] E. g., by Abegg and by Merck (**1907** *Index*, p. 110).

[2] The results recorded are at least the result of duplicate experiments.

6. With 2 cc. of 1 : 50 nitric acid, a reaction occurred after 40 hours.

7. Nitrogen tetroxide was found to give a prompt reaction, being apparently the same as in the case of potassium iodide.

8. An equal volume of 99.5% acetic acid gave no separation of iodine even after 5 days.

9. With 10 cc. of dilute hydrochloric acid, a slight reduction was noted after 3 days. A 10% potassium iodide solution treated in the same way gave a strong reaction over night.

10. Two small flasks were one-third filled with (A_1) 10% potassium iodide and (B_1) 10% cadmium potassium iodide, and then exposed to diffused sunlight. After 3 days, there was a faint yellow coloration in A_1, but no separation of iodine in B_1. Titration gave the following results:

		A_1.	B_1.
After 3 days	Cc. 0.01 *N* $Na_2S_2O_3$ per 10 cc. soln.	0.16	None
After 7 days	" " " "	0.70	0.15

11. As in No. 10, except that to each 0.10 cc. hydrochloric acid (density 1.20) was added. After 2 days, the liquids were withdrawn and the free iodine determined.

	A_2. (10% KI.)	B_2. (10% $CdKI_3$.)
Cc. 0.01 *N* $Na_2S_2O_3$ per 10 cc. soln.	1.25	0.19

12. One cc. of 0.25 *N* hydrochloric acid was added to 10 cc. each of potassium iodide and cadmium potassium iodide in 10% solution, and the solutions were then placed in the sunlight. After 4 days exposure, the results were:

	A_3. (10% KI.)	B_3. (10% $CdKI_3$.)
Cc. 0.01 *N* $Na_2S_2O_3$ per 10 cc. soln.	19.91	1.88

13. Replacing the hydrochloric acid with 99.5% acetic acid, the following results were obtained after 4 days exposure:

	A_4. (10% KI.)	B_4. (10% $CdKI_3$.)
Cc. 0.01 *N* $Na_2S_2O_3$ per 10 cc. soln.	9.63	2.12

14. Following the same procedure, except that an equal volume of 0.125 *N* hydrochloric acid was added in each case, the results were after 5 days:

	A_5. (10% KI.)	B_5. (10% $CdKI_3$.)
Cc. 0.01 *N* $Na_2S_2O_3$ per 10 cc. soln.	33.22	14.20

The above experimental results demonstrate the comparatively high stability of cadmium potassium iodide—a fact which would seem to be of importance in the selection of a reagent for the determination of ozone, especially since we have found that the compound is a sufficiently sensitive reagent for the detection of nascent oxygen. It has been shown that in diffused sunlight the action of mineral acids on cadmium potassium iodide is of the following order: nitric acid reacts rapidly, while sulfuric and hydrochloric acids react much more slowly, although sulfuric acid reacts with greater velocity. No attempt was made to maintain the oxygen concentration constant, but all the experiments were run under identical conditions, and thus the relative stability of the solutions experimented with are on a comparative basis. Since Schwezoff[1] has shown that equivalent quantities of sodium, potassium and cadmium iodides under

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[1] *J. Russ. phys. chem. soc.*, 42, 219 (1910).

similar conditions evolve equal quantities of iodine, this point was not determined.

Some experiments were also made on the chemical action of ultraviolet light upon cadmium potassium iodide and potassium iodide solutions; 100 cc. portions of the solutions and 10 cc. of starch solution were exposed to the rays from a Cooper-Hewitt quartz lamp in porcelain vessels, with the following results:

Concentration of solutions run side by side.	Results with potassium iodide.	Results with cadmium potassium iodide.
Saturated	After an exposure of 5 minutes, 1.0 cc. 0.1 *N* $Na_2S_2O_3$ required	Negative even after 40 minutes
0.1 *N*	Traces of iodine in 20 to 30 seconds. In 5 minutes, 0.05 cc. 0.1 *N* $Na_2S_2O_3$ required	Traces of iodine in 3 minutes when the lamp was started with the experiment; titratable amount of iodine in 10 minutes, 0.03 cc. $Na_2S_2O_3$. When the experiment was started after the lamp had been running 30 minutes, a faint reaction was noted in 30 seconds and 0.04 cc. $Na_2S_2O_3$ were required after 5 minutes
0.01 *N*	Traces of iodine in 30 seconds	Traces of iodine in 30 seconds. No difference from KI
0.001 *N*	No coloration with starch solution even after 25 minutes	No coloration even after 1$^1/_2$ hours

These results showed that 0.1 *N* and 0.01 *N* cadmium potassium iodide is fully as delicate a reagent for hydrogen dioxide and ozone as are solutions of the same strength of potassium iodide. Our results on potassium iodide solutions present differences with those of Ross,[1] but this is probably to be ascribed to the difference in the form of lamp and to the natural variability of such results. Ross found that ultraviolet light alone probably liberated a very small amount of iodine from potassium iodide; his observations are, in our opinion, to be ascribed to the formation of hydrogen dioxide.

2. The Employment of Cadmium Potassium Iodide as a Reagent in the Estimation of Ozone.

In the first experiments the air to be ozonized was taken from a water gasometer and passed through the system including an ozonizer and a Meyer bulb apparatus, the latter being connected with the ozonizing apparatus by means of a ground glass joint. The type of ozonizer employed was not very efficient, as is shown by the results obtained:[2]

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[1] THIS JOURNAL, **28**, 786; *Chem. News*, **94**, 245.

[2] All analytical results are the average of a series of runs; in no case were other than duplicate analyses made, and these invariably checked satisfactorily.

	With neutral 0.1 *N* KI.	With neutral 0.1 *N* $CdKI_3$.
Mg. ozone per liter..........	0.36	0.33
	With acid (HCl) 0.1 *N* KI.	With acid 0.1 *N* $CdKI_3$.
Mg. ozone per liter..........	0.42	0.34

It will be seen that the results with acidified potassium iodide were high, while those obtained in using cadmium potassium iodide, although slightly lower than those found by using neutral potassium iodide, were about the same whether neutral or acid 0.1 *N* solutions were used. Alkalin solutions were found to be unreliable, as the end-point is difficult to determin and a precipitate results in the case of cadmium potassium iodide.

In further experiments, a different type of "silent discharge" ozonizer was used; this, operated on a storage battery circuit at 22–23 volts, gave much more satisfactory yields of ozone. In the runs which were made, the ozone was absorbed, except where noted to the contrary, and the iodine liberated by agitation of the absorbent with the iodide solution was then determined by titration with standard sodium thiosulfate solution.

1. One-half liter of air was ozonized and turpentine (157° to 165° C.) was used as the absorbent. The amount of iodine liberated from neutral 0.1 *N* potassium iodide was then determined. Cc. of 0.1 *N* $Na_2S_2O_3$ required = 29.48 = 140.1 mg. ozone.

2. Run under the same conditions. Cc. of 0.1 *N* $Na_2S_2O_3$ = 29.70 = 143.2 mg. ozone.

3. Run under the same conditions. Cc. of 0.1 *N* $Na_2S_2O_3$ = 29.71 = 143.2 mg. ozone. In Nos. 2 and 3, 20 minutes were found to be sufficient.

4. Run under the same conditions, but using neutral 0.1 *N* cadmium potassium iodide solution. Cc. of 0.1 *N* $Na_2S_2O_3$ = 25.5.

5. As in No. 4. Cc. of 0.1 *N* $Na_2S_2O_3$ = 25.5.

6. As in No. 4. Cc. of 0.1 *N* $Na_2S_2O_3$ = 25.6.

7. As in No. 1, but adding 10% of 0.05 *N* hydrochloric acid to the potassium iodide solution. Cc. of 0.1 *N* $Na_2S_2O_3$ = 34.8 and 34.75.

8. As in No. 4, but adding 10% of 0.05 *N* hydrochloric acid to the cadmium potassium iodide solution. Cc. of 0.1 *N* $Na_2S_2O_3$ = 27.21 and 27.20.

In other experiments, alkaline iodide solutions were found to be totally unsatisfactory; vegetable oils were found to be unsuitable for the absorption of ozone; and the use of anesthetic ethyl ether gave low results (20 and 18.5 cc. 0.1 *N* $Na_2S_2O_3$ when used as in No. 4) and a slow evolution of iodine from acid or neutral solutions. A higher turpentine fraction (165° to 185°) than that used before gave accurate results, but a longer time was required to complete a run.

It is shown that acidified potassium iodide solutions always give high results, and that the results obtained by the use of both neutral and acid 0.1 *N* cadmium potassium iodide solutions are lower than those by means of neutral potassium iodide solutions, a result attributable to the greater stability of the cadmium potassium iodide towards light and certain likely contaminants of ozonized air. We believe that cadmium potassium iodide solution acidified with hydrochloric acid is a more reliable reagent than potassium iodide in neutral solution; its employment is only necessary, however, when absorption of the ozone in turpentine is the method followed. In the method of Schönbein, as used by Ladenburg and Quasig, either neutral or acid solutions of cadmium potassium iodide may be used; sharp end-points are obtained and the results are not too high.

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THE HEAT OF COMBUSTION OF ETHYLBENZENE.

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Sometime ago, together with Professor T. W. Richards, the writer carried out a comparison of the differences which exist between the heats of combustion of a number of isomeric substances, especially several of the octanes and the three xylenes.[1] In connection with the xylenes it was desirable to study the isomeric compound, ethylbenzene, and indeed, preliminary work was started at that time but lack of time prevented its completion. Facilities for further work with the calorimetric bomb have only recently become available. This paper presents the results of the completed study of ethylbenzene.

The preliminary work showed that it was difficult to free commercial samples of this compound completely from organic bromides. The sample used in these experiments was prepared by the Fittig synthesis from bromoethane and bromobenzene, with the former in excess in the hope of eliminating more completely the bromobenzene, whose boiling point is not far removed from that of ethylbenzene. The crude product after one distillation was fractionated seven times with the help of a long fractionating column. The sixth fraction (44 grams) boiled between 135.5–136.4° (745.5 mm.). This portion was distilled again, 7 grams coming over between 135.5–135.8° and 35 grams between 135.9–136.1°. The determinations later showed that these two fractions were identical in so far as thermochemical means could decide.

The bomb used in this work was one made by Professor S. W. Parr of this laboratory from a special alloy of nickel, copper, and chromium.[2] This alloy is so resistant to the attack of acids that it is proposed to use bombs made of it as substitutes for those with the expensive platinum linings. Analyses of the washings from eight runs showed that the amounts of metal dissolved in an average determination were 0.2 mg. of copper and 0.8 mg. of nickel.[3] The heat of formation of the nitrates

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[1] THIS JOURNAL, 31, 268 (1910).

[2] See *Proc. Eighth Intern. Congr. Appl. Chem.* where there is a full description of this bomb.

[3] A fuller description of the behavior of this bomb under actual working conditions has been given in the *Proc. Eighth Intern. Congr. Appl. Chem.*