

the solution during deëmanation; use of an automatic regulator to maintain constant pressure in the ionization chamber during measurements; maintenance of optimum pressure gradient along air-current line through the measuring apparatus, thus assuring minimum error on account of pressure variations, and maximum speed of measurement; protection of the insulation of the electroscope by means of a current of dry air. Analyses by this method gave results agreeing very well with results obtained by gravimetric methods, and required much less time for each determination.

In concluding, the writer wishes to express his sincere appreciation of the valuable criticisms of Dr. Herbert N. McCoy at whose suggestion this research was taken up.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY.]

THE HEAT OF FORMATION OF SILVER IODIDE.

BY HUGH STOTT TAYLOR AND WILLIAM THEODORE ANDERSON, JR.

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A discrepancy, amounting to 600 calories, exists between the determinations of the heat of formation of silver iodide as measured by Jones and Hartmann¹ using electrometric methods and the calorimetric determinations of Braune and Koref.² The values obtained are 14,565 and 15,100 calories respectively, so that the divergence represents a difference of some 4% which is much greater than would be anticipated from the reproducibility of either set of experimental measurements. Certain electrometric determinations by Taylor³ and Perrott, involving the iodides of silver, lead and cadmium, have shown agreement with the calorimetric data of Braune and Koref and favor the adoption of the higher value for the heat of formation of silver iodide.⁴

¹ Jones and Hartmann, *THIS JOURNAL*, **37**, 752 (1915).

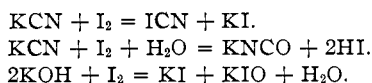
² Braune and Koref, *Z. anorg. Chem.*, **87**, 175 (1914).

³ Taylor, *THIS JOURNAL*, **38**, 2295 (1916); Taylor and Perrott, *ibid.*, **43**, 484 (1921).

⁴ Since the communication of the present paper an article by O. Gerth has appeared in *Z. Elektrochem.*, **27**, 287 (1921), in which new electrometric measurements of the free energy and heat of formation of silver iodide have been made. By substituting a direct experimental method in place of a calculation of liquid junction potentials in the silver|silver iodide|iodine cells, Gerth has demonstrated that it is in the calculation of such liquid junction potentials that the discrepancy above mentioned has arisen. The value obtained by Gerth for the heat of formation of silver iodide is 15158 calories, in good agreement with the value of 15150 calories obtained by one of us (H. S. T.) at an earlier date. The present communication confirms the correctness of these results and of the earlier calorimetric measurements of Braune and Koref.

The calorimetric data of Braune and Koref were obtained by measurement of the heat evolution (*a*) when iodine reacted with silver suspended in potassium cyanide solution; (*b*) when silver iodide dissolved in a similar solution. The difference between the two heat effects was taken to be the heat of formation of silver iodide. A 3 *N* solution of potassium cyanide was employed in the determinations.

Objection to the calorimetric procedure may be urged, owing to the possibility that the iodine may have entered into side reactions with the potassium cyanide solution. Some such possibilities may be illustrated by means of the equations,



If such side reactions occurred, the desired heat of formation would not be obtained unless the presence of metallic silver caused the reduction of all these oxidized compounds. Only in that case would the solution obtained be identical with that resulting from the interaction of silver iodide and potassium cyanide, as in the second part of the calorimetric measurement.

The nature and extent of the various possible side reactions must manifestly depend in part on the concentration of potassium cyanide solution employed in the determination, as well as upon the relative proportions of iodine and potassium cyanide present together during the course of the experiment. With this in mind, a repetition of the calorimetric experiments of Braune and Koref has been undertaken, using, instead of the 3 *N* cyanide solution employed by them, a 1 *N* solution. The modifying effect of dilution made itself at once apparent in the lower values obtained for the heat of solution of silver iodide. This result was to be anticipated, as, in the more dilute solution, complex formation and double decomposition would occur to a less degree. The heat effects obtained from the interaction of the silver and the iodine were, however, also correspondingly lower and, as the subjoined table shows, the net thermal effect obtained for the heat of formation of silver iodide in the more dilute solution is almost exactly that previously obtained by Braune and Koref using the stronger solution of potassium cyanide. We regard this as strong proof of the correctness of the calorimetric determination of the required heat of formation.

Experimental.

Apparatus.—The apparatus used has been recently described by Taylor and Perrott⁵ and does not therefore need to be discussed here. The method employed was essentially the same. Instead of measuring the current employed in the electrical heating of the solution for calibration purposes

⁵ Taylor and Perrott, *THIS JOURNAL*, 43, 491 (1921).

by means of a coulometer, a measurement of the time of heating was made as well as the voltage drop over a resistance functioning as a heating element. The calibration of this resistance in terms of heating element and lead wires was carefully checked. The total resistance of the heater and leads was 10.35 ohms. The resistance of the heating element alone was 10.17 ohms. The temperature rise of the calorimeter system due to the interaction of a given weight of iodine with silver suspended in the potassium cyanide solution having been observed, the rise in temperature due to the introduction of a measured amount of electrical energy was then determined. This was followed by a measurement of the temperature rise from the solution of a given weight of silver iodide and this by a second measurement of the heat rise due to electrical energy. Thereafter the experiments were conducted in the order indicated in the table. The experiments were conducted at room temperature.

Materials.—Finely divided silver was prepared by igniting powdered silver oxide at 400° for several hours. This latter was obtained from high grade silver nitrate by precipitation with alkali followed by a thorough washing to remove excess of alkali and salts.

Resublimed iodine of high grade was used. It was finely powdered in a mortar before use.

The silver iodide employed was obtained by precipitation from solutions of high grade silver nitrate and potassium iodide. It was washed free from soluble salts and with ammonia to remove any possible chloride. The material was dried and used in the amorphous form thus obtained.

Very high grade imported potassium cyanide was employed, 800 cc. of a 1 *N* solution being used in the experiments.

The following table gives the experimental results obtained and the calculated values for the heats of the several reactions.

Expt.	Iodine G.	Rise in temp. °C.	Volts.	Time. Sec.	Rise on heating. °C.	Heat of reaction per mol. iodide, cal.
	3.127	0.710	8.30	480	0.849	25,500
2	2.359	0.533	8.10	300	0.506	25,290
4	2.740	0.695	8.10	360	0.681	25,370
7	3.467	0.877	8.10	360	0.677	25,455
8	1.586	0.393	10.52	120	0.375	25,310
					Mean	25,385
	AgI. G.					
3	5.336	0.276	8.10	180	0.319	10,215
5	6.077	0.323	8.10	180	0.328	10,200
6	7.131	0.380	8.10	180	0.330	10,340
					Mean	10,251

The difference in value of the two mean heat effects with iodine and silver iodide gives the desired heat of reaction $\text{Ag} + \text{I} = \text{AgI} + (25385 - 10251)$ calories; whence $Q = 15,134$ calories. In 3 *N* potassium cyanide solution the value obtained by Braune and Koref was 15,100 calories. Since

the latter used crystallized silver iodide it is evident that the divergence between the two is within the error of the measurement.

Summary.

A repetition of Braune and Koref's calorimetric measurement of the heat of formation of silver iodide using 1 *N* potassium cyanide instead of 3 *N* solution as solvent for silver iodide has been made. Their result, a value of 15,100 calories per mole of silver iodide, has been confirmed.

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[CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC CHEMISTRY, COLUMBIA UNIVERSITY, No. 373.]

THE CATALYTIC INFLUENCE OF FOREIGN OXIDES ON THE DECOMPOSITION OF SILVER OXIDE, MERCURIC OXIDE AND BARIUM PEROXIDE.¹

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Introduction.

The results obtained by previous investigators on the decomposition of substances liberating oxygen are, for the most part, very indefinite and unsatisfactory. Particular reference may be made to the extensive work done on the decomposition of *potassium chlorate* under the catalytic influence of metallic oxides.² The decomposition temperatures recorded for *simple oxides* also vary widely.

	°C.		°C.		°C.
Ag ₂ O	250-350	BaO ₂	450-825	CrO ₃	180-320
HgO	175-660	MnO ₂	210-560	CuO	800-1200

The data for *mixtures of oxides* are, in general, still more divergent. It is often impossible to correlate the results of different observers, either because the relative amounts of the components are not specified at all or because mention is made in such a way as to leave it quite uncertain whether volume, weight or molecular composition units were employed.

The present investigation is an attempt to obtain systematic data on the dissociation equilibria of silver oxide, mercuric oxide and barium peroxide, as affected by the presence of other oxides. The choice of these three oxides as experimental material was made on account of their ease of preparation and their conveniently low decomposition temperatures. It was anticipated that the results would prove of interest not only with respect to the mechanism of the reactions actually studied, but

¹ Condensation of a thesis submitted by Francis J. Fuchs in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, May 1920.

² See Sodeau, *J. Chem. Soc.*, **81**, 1067 (1902).