

strongly adsorbed on the surface of the catalyst and that acetylene can displace both hydrogen and ethylene in the adsorption layer. The

mechanisms of hydrogenation and exchange reactions are discussed.

JERUSALEM, PALESTINE

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Evidence for Existence of a Selenium Iodide

BY JAMES D. McCULLOUGH¹

Various attempts² have been made in an effort to detect compound formation between selenium and iodine, but in no case have these led to positive conclusions. During a recent study of the various crystalline forms of elementary selenium made by the author, it was observed that a color change occurred when selenium was added to a solution of iodine in carbon tetrachloride. Since selenium is not measurably soluble in carbon tetrachloride in any form, this change seemed significant. Accordingly the following experiments were carried out using carefully purified materials throughout.

Absorption Spectrum Studies.—Light from an incandescent bulb was passed through two similar glass absorption cells placed in series, one of which was filled with a solution containing 0.885 g. of iodine per 1000 g. of carbon bisulfide and the other with a solution containing 0.195 g. of crystalline α -monoclinic selenium per 1000 g. of the solvent. After preparing photographs with this arrangement, the solutions were mixed, the two cells filled with the resulting solution and a second set of absorption spectra prepared.

In Fig. 1, curve A is a reproduction of a microphotometer tracing of the absorption spectrum of the unmixed solutions while curve B is a similar record for the mixed solutions. Since the ordinates represent relative transmission, there is a new region of absorption from 4200 to 4500 Å. on mixing. Because of the care taken in purifying the selenium and iodine used, this must mean that a compound is formed which is responsible for the increased absorption.

The Selenium-Iodine Equilibrium.—Weighed quantities of iodine and carbon tetrachloride were

placed in glass-stoppered bottles with an excess of hexagonal selenium and shaken for twenty-four hours or longer in a thermostat at 25°. The solutions were then allowed to settle for at least ten minutes, after which samples of about 200 g. were removed by slowly forcing the solution in a closed system through a sintered glass filter into a weighed, glass-stoppered flask. After weighing

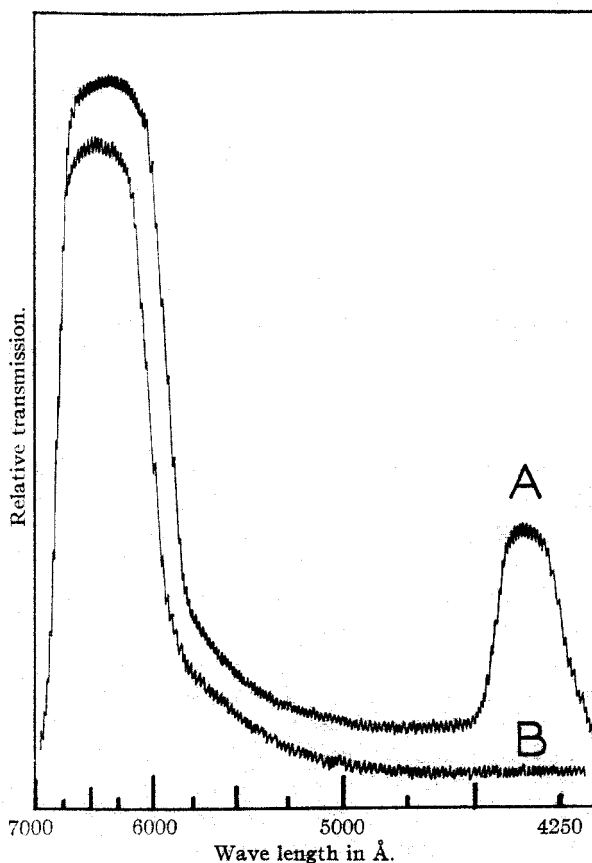


Fig. 1.—Reproduction of microphotometer records of absorption spectra of solutions of selenium and iodine in carbon bisulfide. Curve A is for the superimposed solutions before mixing, while curve B is for the solutions after mixing. Curve A has been displaced upward to reduce overlapping.

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(2) (a) F. Olivari, *Chem. Zentr.*, **100**, I, 83 (1910); (b) Beckmann and Hanslian, *Z. anorg. Chem.*, **80**, 221 (1913); (c) Beckmann and Faust, *ibid.*, **84**, 103 (1914); (d) Beckmann and Grünthal, *ibid.*, **84**, 97 (1914); (e) Pellini and Pedrina, "International Critical Tables," Vol. IV, p. 24; (f) R. Wright, *J. Chem. Soc.*, **107**, 1527 (1915); and (g) Beckmann and Platzmann, *Z. anorg. Chem.*, **102**, 215 (1918).

the sample, 100 ml. of 3 *N* sodium hydroxide solution was added, the mixture shaken and then transferred to a separatory funnel, where the shaking was continued for several minutes. By this process the selenium and iodine are both quite completely transferred to the aqueous layer, the selenium being oxidized mainly to selenite, with perhaps some selenate. After separating the two layers, the aqueous phase was saturated with sulfur dioxide and an equal volume of concentrated hydrochloric acid was added. More sulfur dioxide was then passed in and the solution was boiled to coagulate the elementary selenium, a process which required several hours. Near the end of the precipitation process a small quantity of hydrazine hydrochloride was added to precipitate any of the element left in the form of selenate. The selenium was collected in a sintered glass crucible, washed with water, then with alcohol, dried for several hours at 105° and then weighed.

The results of these experiments are shown in Table I. It is seen that there is a linear relationship between the quantity of selenium dissolved and the concentration of iodine. This is what would be expected for an equilibrium of the type:



This is evidence that the compound has two atoms of iodine per molecule but leaves the number of selenium atoms undetermined.

TABLE I
SELENIUM-IODINE EQUILIBRIUM IN CARBON
TETRACHLORIDE

Moles I ₂ per 1000 g. solvent	Gram atoms Se per 1000 g. solvent	Moles I ₂ G atoms Se
0.04236	0.00106	40.0
.05622	.00140	40.1
.07620	.00191	39.9

The author wishes to acknowledge his indebtedness to Dr. Arnold O. Beckman, in whose laboratory this work was done, for suggesting the study of selenium and for his interest in the problem.

Summary

1. Absorption spectra give strong evidence in favor of compound formation between selenium and iodine in carbon bisulfide.

2. Quantitative measurements of the equilibrium between selenium and iodine in carbon tetrachloride show the presence of a compound having the formula Se_nI_2 with *n* undetermined.

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Amperometric (Polarometric) Titrations. I. The Amperometric Titration of Lead with Dichromate or Chromate

BY I. M. KOLTHOFF AND YU-DJAI PAN

The classical methods of electrometric titrations are the potentiometric and conductometric titrations. In potentiometric titrations the potential of a suitable indicator electrode is measured during the titration and the end-point is characterized by a more or less pronounced change of the potential upon addition of a small amount of reagent. In conductometric titrations the electrical conductance of the titration mixture is measured during the titration and the end-point is found graphically as the point of intersection of the lines giving the changes of conductance before and after the equivalence point. To these two methods may be added another which we propose to call "amperometric titrations." In amperometric titrations the current which passes between two suitable electrodes at a constant applied e. m. f. is measured. Depending upon the conditions one or

both electrodes are placed in the titration medium. Quite generally, the end-point is found as the point of intersection of two lines giving the change of the current before and after the equivalence point.

The principle underlying amperometric titrations was mentioned as early as 1897 by Salomon¹ and later by Nernst and Merriam.² It is peculiar that these papers have escaped the attention of analytical chemists. It was shown by the above authors that the so-called "diffusion current"³ is proportional to the concentration of the electro-reduced substance. In a paper entitled "On a Galvanometric Titration Method"

(1) E. Salomon, *Z. physik. Chem.*, (a) **24**, 55 (1897); (b) **25**, 366 (1898); (c) *Z. Elektrochem.*, **4**, 71 (1897).

(2) W. Nernst and E. S. Merriam, *Z. physik. Chem.*, **53**, 235 (1905).

(3) For terminology compare I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1 (1939).