

one might expect the formation of para-hydrogen as found in the decomposition of hydrogen iodide. Thus the absence of para-hydrogen formation can be regarded as excluding the step (10). Consequently the conclusion offers itself that, whichever the actual primary process may be, (7) or (8), the two atoms forming a hydrogen molecule must come from the same parent formaldehyde molecule. The state of affairs in the photolysis of methyl alcohol is exactly analogous.

As no detailed knowledge about the energy exchange during collisions in solids is yet available, one cannot decide between the primary reactions (7) and (8) on the basis of the present experiments. The suggestion that a dissipation of energy takes place at collisions within a solid, as

proposed for the reaction  $\text{H} + \text{HI}_{\text{solid}}$ , would favor mechanism (7) according to which no such dissipation of energy can occur.

### Summary

It is found that para-hydrogen is formed when irradiating solid hydrogen iodide at low temperatures. Two explanations are given and discussed: (a) the hydrogen primarily formed can be converted by the paramagnetic action of free iodine atoms; (b) the heat formed in the reaction  $\text{H} + \text{HI}_{\text{solid}} = \text{H}_2 + \text{I}$  is dissipated in the solid. In the photolysis of formaldehyde and methyl alcohol under the same conditions normal hydrogen is formed. This seems to indicate that the two hydrogen atoms forming a molecule are coming from the same formaldehyde or methyl alcohol molecule.

REHOVOTH, PALESTINE

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, THE HEBREW UNIVERSITY]

## The Catalytic Interaction of Acetylene and Hydrogen on Platinum

BY A. FARKAS AND L. FARKAS

In a series of communications the catalytic hydrogenation of ethylene,<sup>1</sup> benzene<sup>2</sup> and acetone<sup>3</sup> on platinum was investigated. In the first two examples, the hydrogenation consists of the addition of hydrogen to a double bond. In the case of acetone the reduction reaction can be

ditions, this reaction being chosen as representative of hydrogen addition to triple bonds.

### Experimental

The general experimental technique was similar to that previously described.<sup>1</sup> A platinized platinum foil (10 × 10 mm.) was used as the catalyst in a reaction vessel of 75 cc. volume. Hydrogen and acetylene were admitted to the reaction vessel through a U-tube kept at  $-80^\circ$ . Acetylene was prepared from calcium carbide and purified according to the usual method.<sup>4</sup>

#### Dependence of the Hydrogenation on Pressure.

In some experiments, first acetylene was admitted to a given pressure and then condensed in a thin side-tube. Subsequently hydrogen was introduced and then acetylene quickly evaporated, the reaction time being calculated from this moment. The progress of the reaction under these conditions is shown in Fig. 1 (expt. 16). The reasons for the sudden drop in the pressure in the first half minute

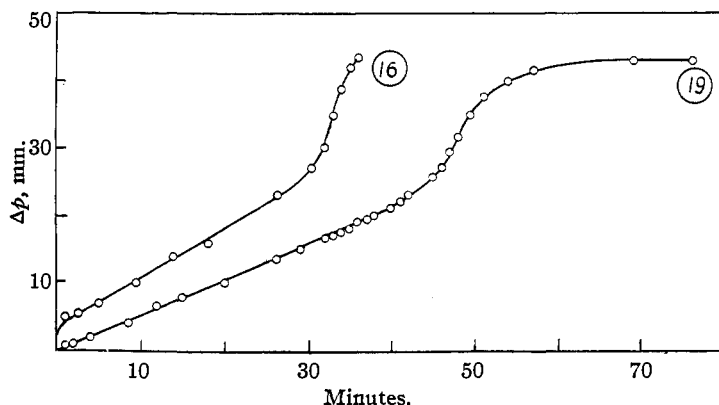


Fig. 1.—Hydrogenation of acetylene: expt. 16, 25 mm.  $\text{C}_2\text{H}_2$  + 60 mm.  $\text{H}_2$  at  $101^\circ$ ; expt. 19, 21 mm.  $\text{C}_2\text{H}_2$  + 49 mm.  $\text{H}_2$  at  $97^\circ$ .

envisaged as a similar type of process. In the present communication the hydrogenation of acetylene was investigated under similar con-

(1) Farkas and Farkas, *THIS JOURNAL*, **60**, 22 (1938).

(2) Farkas and Farkas, *Trans. Faraday Soc.*, **33**, 827 (1937).

(3) Farkas and Farkas, *THIS JOURNAL*, **61**, 1336 (1939).

(4) Farkas and Melville, "Experimental Methods in Gas Reactions," Macmillan and Co., Ltd., London, 1939, p. 167.

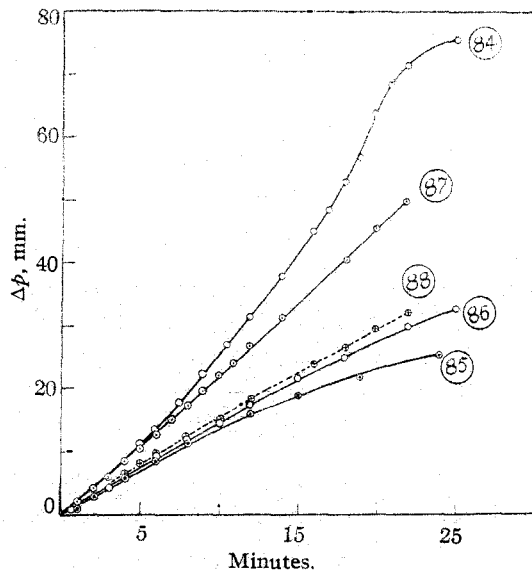


Fig. 2.—Hydrogenation of acetylene at 25°. Dependence on the hydrogen pressure: expt. 84, 40 mm.  $C_2H_2$  + 114 mm.  $H_2$ ; expt. 87, 39.5 mm.  $C_2H_2$  + 94.5 mm.  $H_2$ ; expt. 88, 41 mm.  $C_2H_2$  + 92 mm.  $D_2$ ; expt. 86, 40 mm.  $C_2H_2$  + 70 mm.  $H_2$ ; expt. 85, 40 mm.  $C_2H_2$  + 51.5 mm.  $H_2$ .

were that the pressure of the acetylene was rather low at the beginning of the evaporation, and that the reaction is strongly inhibited by the acetylene. If, however, the hydrogen was added to the acetylene directly without the latter being condensed, as in expt. 19, Fig. 1, the initial pressure drop is absent and the pressure decreases regularly. The sudden pressure drop in the thirtieth and fortieth minutes, respectively, will be referred to below.

The dependence of the hydrogenation on the hydrogen pressure is given in Fig. 2, and that of the acetylene pressure in Fig. 3. These results show that with increasing pressure of acetylene the rate of hydrogenation decreases, while it increases with the hydrogen pressure. The inhibition of the hydrogenation by acetylene is similar to, but more pronounced than, the inhibition of the hydrogenation of ethylene by ethylene.

In the course of the hydrogenation it has been observed repeatedly that at a certain stage the rate of hydrogenation increases rapidly. Examples of this behavior were given in Figs. 1, 2 and 3, expts. 16, 19, 84, 79 and 82. The rate of the hydrogenation in expts. 79 and 84, and in expts. 21 and 22

in which the catalyst was somewhat less active, is shown in dependence of time in Fig. 4. This acceleration is due to two causes: first, the reaction rate increases on account of the acetylene pressure being reduced, and, second, the hydrogenation of the ethylene, which occurs in the second half of the reaction, is much faster than the formation of ethylene. The moment when all acetylene is used up is marked by an arrow in Fig. 4. It will be noted that the sudden increase in the rate of hydrogenation coincides with this moment.

**Para-conversion and Hydrogenation.**—In order to gain some information on the relative adsorbabilities of hydrogen and acetylene, the rate of hydrogenation and the rate of the para-hydrogen conversion were measured simultaneously. It is interesting to note that from a few experiments with para-hydrogen the same conclusions could be drawn with regard to the composition of the adsorption layer as from the whole series of experiments in which the pressure of the reactants was varied systematically.

The rate of the para-hydrogen conversion in the

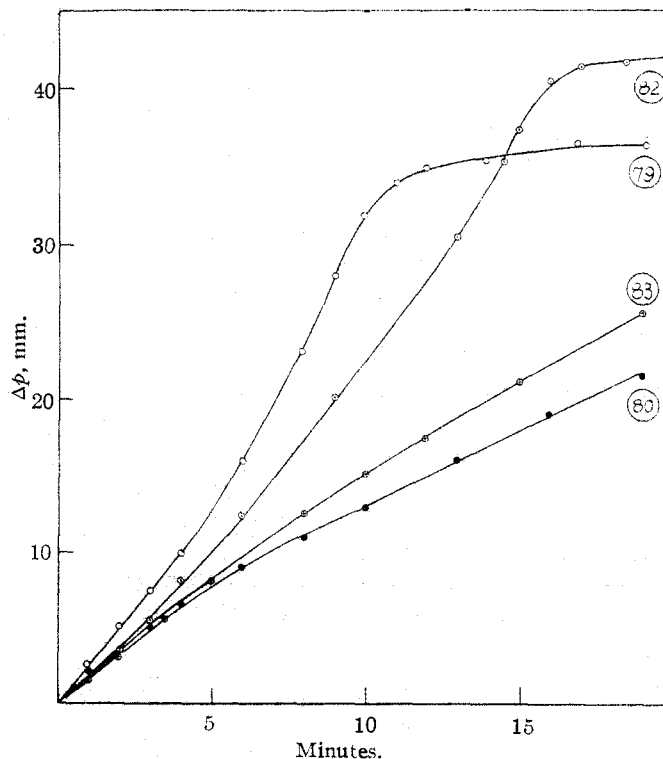


Fig. 3.—Hydrogenation of acetylene at 24°, dependence on the acetylene pressure. Expt. 79, 17.5 mm.  $C_2H_2$  + 72.5 mm.  $H_2$ ; expt. 82, 23.5 mm.  $C_2H_2$  + 72.5 mm.  $H_2$ ; expt. 83, 56 mm.  $C_2H_2$  + 72 mm.  $H_2$ ; expt. 80, 76 mm.  $C_2H_2$  + 71 mm.  $H_2$ .

TABLE I

No.	°C.	Reaction mixture	Rate of conversion, mm./min.	Rate of hydrogenation, mm./min.	Ratio $\frac{\text{Conversion}}{\text{Hydrogenation}}$
54	20	74 mm. <i>p</i> -H <sub>2</sub>	18.5	..	..
52	20	76 mm. <i>p</i> -H <sub>2</sub> + 19 mm. C <sub>2</sub> H <sub>4</sub>	6.7	0.83	8.1
53	20	73 mm. <i>p</i> -H <sub>2</sub> + 19 mm. C <sub>2</sub> H <sub>2</sub>	1.15	.21	5.5
9	22	27 mm. <i>p</i> -H <sub>2</sub> + 36 mm. C <sub>2</sub> H <sub>2</sub>	0.24	.084	2.8
27	88	27.5 mm. <i>p</i> -H <sub>2</sub> + 16.5 mm. C <sub>2</sub> H <sub>2</sub>	.089	.0065	7.3
33	20	88 mm. <i>p</i> -H <sub>2</sub> + 17 mm. C <sub>2</sub> H <sub>2</sub>	1.18	.22	5.4

absence and presence of acetylene or ethylene is shown in Fig. 5. As will be recognized from this

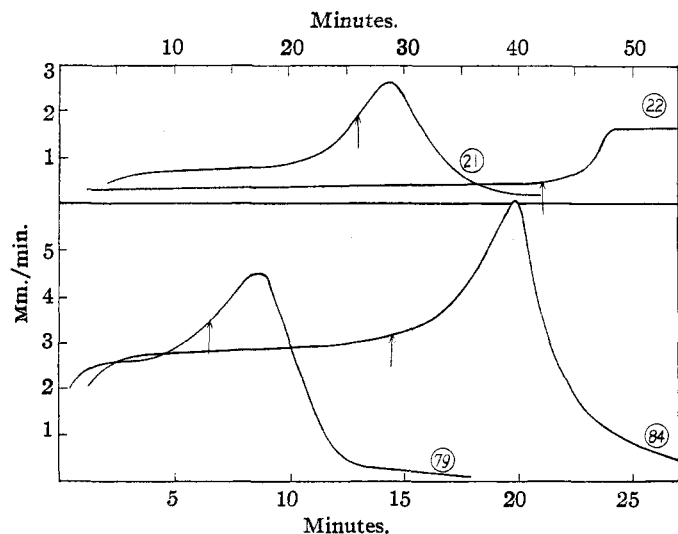


Fig. 4.—Rate of hydrogenation of acetylene—Expt. 21, 18 mm. C<sub>2</sub>H<sub>2</sub> + 102 mm. H<sub>2</sub> at 89°; expt. 22, 15 mm. C<sub>2</sub>H<sub>2</sub> + 55 mm. H<sub>2</sub> at 92°; expt. 79, 17.5 mm. C<sub>2</sub>H<sub>2</sub> + 72.5 mm. H<sub>2</sub> at 24°; expt. 84, 40 mm. C<sub>2</sub>H<sub>2</sub> + 114 mm. H<sub>2</sub> at 25°.

figure, by the addition of 19 mm. of acetylene to 73 mm. of para-hydrogen, the rate of conversion was reduced by a factor of 15, whereas the same amount of ethylene reduced the rate of para-conversion only by a factor 3. These results show that acetylene replaces the hydrogen to a great extent in the adsorption layer and is much more strongly adsorbed than ethylene.

The rates of the conversion and hydrogenation reactions and their ratio are given in Table I for catalysts in different states of activity.

The dependence of the hydrogenation on temperature could not be determined with great ac-

curacy on account of a gradual deactivation of the catalyst, especially at higher temperatures.

In Table II the first group of figures refers to the catalyst in a more active state, and the second group to a less active catalyst.

From these results an energy of activation of 12–17 kcal. can be calculated for the hydrogenation of acetylene. These figures are somewhat higher than the energy of activation for the hydrogenation of ethylene, which was found to be between 7 and 10 kcal. on the same catalyst and in the same temperature range.

**Hydrogenation with Deuterium.**—In Fig. 2, expts. 87 and 88 show the comparison of two hydrogenation experiments performed by hydrogen and deuterium. It will be recognized that the rate of hydrogenation by deuterium is about 1.5 smaller than that by hydrogen.

In hydrogenation experiments with deuterium the progress of the exchange reaction

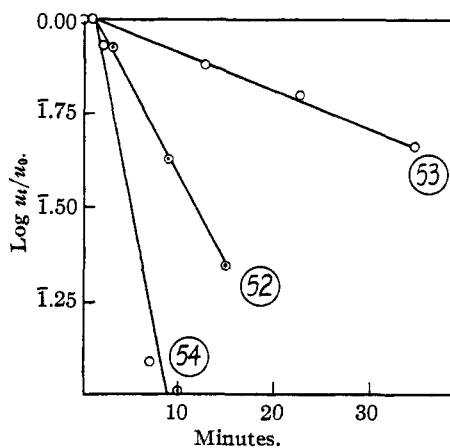


Fig. 5.—Conversion of para-hydrogen at 20°.  $u_0$  and  $u$  denote the excess concentration of parahydrogen relative to normal hydrogen at the time  $t = 0$  and  $t$ . Expt. 54, 74 mm. *p*-H<sub>2</sub>; expt. 52, 76 mm. *p*-H<sub>2</sub> + 19 mm. C<sub>2</sub>H<sub>4</sub>; expt. 53, 73 mm. *p*-H<sub>2</sub> + 19 mm. C<sub>2</sub>H<sub>2</sub>.

TABLE II

No.	°C.	C <sub>2</sub> H <sub>2</sub> , mm.	H <sub>2</sub> , mm.	Rate, mm./min.
55	15	30	72	0.29
58	47	31	78	2.0
57	57	31	76	3.9
64	72	30.5	78.5	0.13
63	98	30.5	78.5	.68
65	147	30.0	79.0	15.0

also was investigated and compared with the exchange of ethylene. The results indicate that the exchange of acetylene is very much slower than that of ethylene. For example (expts. 24 and 25), at 90° the D-content of 88 mm. of deuterium (initial D-content 99%) in a mixture with 38 mm. of acetylene decreased only by 1%, while all of the acetylene was hydrogenated to ethylene. On the other hand, in a mixture of 47 mm. of ethylene and 62 mm. of deuterium the D-content decreased by 34% when the hydrogenation was completed. Qualitatively the same results were obtained when the exchanges of acetylene and ethylene were compared in the same run. In these experiments a relatively rapid exchange was observed as soon as most of the acetylene was converted into ethylene.

### Discussion

The most striking feature of the hydrogenation of acetylene is the fact that the addition of two molecules of hydrogen occurs in two distinct steps. The acetylene is first converted to ethylene and the ethylene is only reduced further to ethane after all (or nearly all) of the hydrogen has been used up. This phenomenon, which is usually referred to as "selective hydrogenation" in organic chemistry, becomes manifest through the sudden change in the rate of hydrogenation as soon as all acetylene is used up.

The explanation for the selective hydrogenation is quite clear and already has been given.<sup>5</sup> It is due to the different absorbabilities of acetylene and of ethylene, but not to different rates of hydrogenation, though in the present case its occurrence can be ascertained kinetically by the sudden change of the reaction rate.

The strong adsorption of acetylene offers a ready explanation for the dependence of the rate of hydrogenation on the acetylene and hydrogen pressures also.

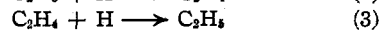
It is suggested that in the catalytic hydrogenation of ethylene the activation consists essentially of the dissociation of hydrogen.<sup>1</sup> This implies that the addition of hydrogen atoms to ethylene occurs with very little energy of activation. The experiments on the hydrogenation of acetylene by deuterium indicate that the same holds true for the hydrogenation of acetylene. The rates of hydrogenation by hydrogen and by deuterium differ by the same factor as was found for ethylene

and for the rate of dissociation of hydrogen and deuterium on a similar catalyst.

The relatively higher energy of activation can be accounted for as caused by the extensive displacement of hydrogen by acetylene in consequence of the latter being very strongly adsorbed.

Concerning the mechanism of the catalytic hydrogenation, complete accord has not yet been reached. These authors<sup>6</sup> have the opinion that hydrogenation consists of the simultaneous addition of two hydrogen atoms to unsaturated bonds while Horiuti and Polanyi<sup>7</sup> envisage the hydrogenation as the consecutive and independent addition of hydrogen atoms. Recently Twigg and Rideal<sup>8</sup> came to the same conclusion with regard to hydrogenation as the present authors, while they retain the mechanism suggested by Horiuti and Polanyi for explaining exchange reactions (see below).

If one considers the complete hydrogenation of acetylene under the assumption that one hydrogen atom is added after the other, the following steps are involved



Steps (1) and (3) represent the addition of hydrogen atoms to adsorbed molecules, while steps (2) and (4) involve the recombination of radicals with hydrogen atoms. This is an essential difference, as one would expect reactions (2) and (4) to proceed with less inertia than reactions (1) and (3), respectively. In other words, the *a priori* probability for a hydrogen atom to be added to the radicals  $\text{C}_2\text{H}_3$  or  $\text{C}_2\text{H}_5$  is larger than the probability of being added to the molecules  $\text{C}_2\text{H}_2$  or  $\text{C}_2\text{H}_4$ , respectively. This means that the addition of the second hydrogen atom to acetylene will follow very quickly the addition of the first, since through the addition of the first atom the inertia inherent in the hydrogenation reaction has been removed. The same holds *mutatis mutandis* for the addition of hydrogen atoms to ethylene also.

Thus it will be recognized that even if in the hydrogenation of acetylene or ethylene the hydrogen atoms are added in consecutive steps, in each case the second atom will be added at a larger speed than the first. Therefore, the addi-

(6) Farkas and Farkas, *ibid.*, **38**, 837 (1937).

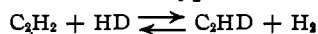
(7) Horiuti and Polanyi, *ibid.*, **30**, 1164 (1934).

(8) Twigg and Rideal, *Proc. Roy. Soc. (London)*, **171A**, 55 (1939).

(5) Farkas, *Trans. Faraday Soc.*, **35**, 906 (1939).

tion of the two hydrogen atoms can be regarded for practical purposes as occurring simultaneously.

The second kind of reaction which occurs in the interaction of acetylene and hydrogen is the exchange reaction of the type



Though this exchange reaction is not much in evidence in the interaction of hydrogen and acetylene, it will be recognized that its consideration will lead to some important conclusions with regard to the mechanism of the exchange reactions in general.

Two different mechanisms for the exchange reaction between unsaturated hydrocarbons and deuterium have been suggested. The so-called "dissociative" mechanism suggested by the present authors<sup>1,2,5,9</sup> consists of the detachment of hydrogen atoms from the hydrocarbon molecules followed by the recombination of the hydrocarbon radicals with deuterium atoms which in turn have been formed by the dissociation of deuterium molecules on the surface of the catalyst. The "associative" mechanism originally suggested by Horiuti and Polanyi<sup>7</sup> is closely connected with the atomic mechanism of hydrogenation and is based on a secondary decomposition of the half hydrogenated form. This mechanism is advocated also by Twigg and Rideal.<sup>8</sup>

As support for the associative mechanism usually the ease is referred to by which the unsaturated hydrocarbons exchange as compared with saturated compounds. This is true in the case of ethylene and ethane but by no means can be generalized. This is best seen in the example of the three compounds, acetylene, ethylene and ethane. In this system a sharp distinction between the rate of exchange of saturated and unsaturated compounds cannot be made since the rate of exchange of ethylene is much larger than either that of ethane or of acetylene.

While the small rate of exchange of ethane compared with that of ethylene is explained readily by the associative mechanism as being due to the saturated character of ethane, the difference in the rate of exchange of acetylene and of ethylene cannot be traced to the same reason as both compounds are unsaturated.

Therefore, in general it cannot be maintained that saturated and unsaturated hydrocarbons undergo exchange reactions with essentially dif-

ferent rates, the more so since ready exchange of saturated compounds also has been observed.<sup>10</sup> Consequently, there is no reason to assume different mechanisms for the exchange reactions of saturated and unsaturated hydrocarbons and it appears that the dissociative mechanism is applicable to both types of exchange reactions.

According to the dissociative mechanism, the rate of exchange depends on the adsorbability of the hydrocarbons, and on the ease with which hydrogen atoms are detached from the hydrocarbon molecule. Thus qualitatively one might suppose that while acetylene is adsorbed strongly when compared with ethane, the hydrogen atoms are detached so much less readily that the effect of the adsorbability is compensated. On the other hand, both adsorbability and dissociation rate are apparently in a favorable relation in the case of ethylene to induce a relatively rapid exchange.

In fact the state of affairs is more complicated, as the rate of exchange depends not only on the absolute concentration of the hydrocarbon, but also on its relation to the concentration of hydrogen on the surface of the catalyst. It seems, however, that a detailed discussion of the kinetics of exchange reactions from this point of view is premature.

### Summary

1. The catalytic hydrogenation of acetylene was investigated at pressures of 70–150 mm. and in the temperature range of 20–140° on a platinum catalyst. The rate of hydrogenation increases with increasing hydrogen pressure but is strongly reduced with increased acetylene pressure.

2. If the hydrogenation is carried out by para-hydrogen, the ortho-para conversion proceeds very much more slowly than in the absence of acetylene. The ratio of the rate of hydrogenation by hydrogen to that by deuterium is 1.5 at 20°.

3. The hydrogenation of acetylene proceeds in two distinct stages: first, all acetylene is reduced to ethylene and only then is ethylene hydrogenated to ethane. The start of the second step is indicated by a sudden increase in the rate of hydrogenation.

4. The catalytic exchange of hydrogen atoms between acetylene and molecular deuterium is very much slower than that between ethylene and deuterium under similar conditions.

5. The results indicate that acetylene is

(9) Farkas, Farkas and Rideal, *Proc. Roy. Soc. (London)*, **146A**, 630 (1934).

(10) Farkas and Farkas, *Nature*, **143**, 244 (1939); *Trans. Faraday Soc.*, **35**, 917 (1939).

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.

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY (NO. 713), AND FROM THE DEPARTMENT OF CHEMISTRY AT THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

## Evidence for Existence of a Selenium Iodide

BY JAMES D. McCULLOUGH<sup>1</sup>

Various attempts<sup>2</sup> 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  $\alpha$ -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

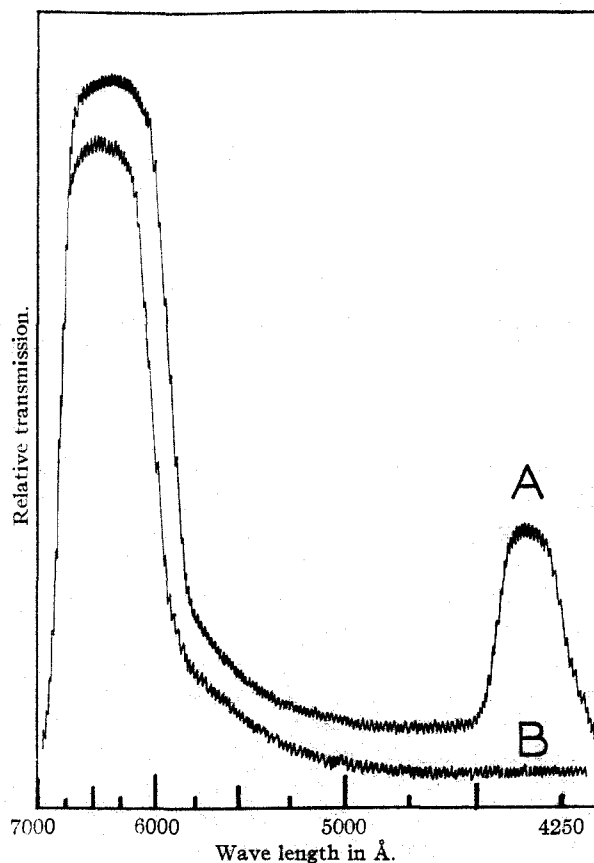


Fig. 1.—Reproduction of microphotometer records of absorption spectra of solutions of selenium and iodine in carbon bisulfide. Curve A is for the superimposed solutions before mixing, while curve B is for the solutions after mixing. Curve A has been displaced upward to reduce overlapping.

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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).