ON THE ACTION OF LIGHT UPON THE DISSOLUTION OF AMORPHOUS SELENIUM IN CARBON BISULPHIDE.

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The solubility of red amorphous selenium in carbon bisulphide and the action of light on it have been measured by several investigators.⁽¹⁾ Their results, however, are qualitative in nature. The present work was undertaken in order to determine these systematically and more accurately, for studies of this sort are valuable for the light they throw upon the dissolution of some materials sensitive to light.

Experimental. Red amorphous selenium was prepared by reducing selenium dioxide with sulphur dioxide in aqueous solution acidified with hydrochloric acid. The selenium dioxide was obtained by dissolving vitrious selenium of Merck in dilute nitric acid and purifying by repeated sublimation at about 300°C. in the atmosphere of nitrogen dioxide in a glass tube. Carbon bisulphide was carefully purified by the ordinary method.

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(1) E. Mitscherlich, *Sitzber. Akad. Wien*, **1855**, 409; *J. prak. Chem.*, (1), **66** (1855), 257. C. F. Rammersberg, *Ber.*, **7** (1874), 667. R. Saunders, *J. Phys. Chem.*, **4** (1900), 455. G. Briegleb, *Z. physik. Chem.*, (A), **144** (1929), 340; *Naturwiss.*, **17** (1929), 51.

In every experiment, 250 c.c. of carbon bisulphide and 1 g. of red amorphous selenium were employed. Carbon bisulphide was previously kept in a reaction vessel at the required temperature, with which selenium was then mixed. The time at which the two components were mixed was taken as the initial point of dissolution. After mixing them, portions, each nearly 25 c.c., of the solution were withdrawn at proper time intervals and their compositions were determined.

For the light source, an electric lamp of 100 volts and 400 watts was employed, and the reaction vessel was illuminated from its bottom. The experiments were carried out at 33°, 25°, 0.5°, −9°, and about −60°.

(1) *The results at 33°C.* In the dark, the dissolved amount of selenium first increased rapidly and reached its maximum after about 2 hours. After that time, it decreased slowly, and in about 10 hours it seemed to reach a constant value. Previous to the time when the maximum was observed, a quantity of red monoclinic crystals was found to deposit on the bottom of the vessel, and after that time the residue was observed to consist entirely of red monoclinic crystals.

In the case of exposing to light, similar behaviours as in the dark were observed, but the rate of dissolution increased remarkably. The constant dissolved amount which was to be reached finally, seemed to coincide with that in the dark. The experimental results are shown in Table 1 and Fig. 1. The dissolved amounts are given in mg. Se per 100 g. CS_2.

Table 1.

Temp. °C.		Time (hours)									
		1	2	3	4	5	6	8	10	26	28
33	(D)	67.0	98.1	98.9	93.6	87.4	83.1	72.8	70.0	66.5	69.0
	(L)	99.5	99.2	—	79.4	—	71.6	68.8	67.2	60.5	60.1
25	(D)	17.4	33.8	—	63.9	—	65.9	59.9	56.5	—	48.0
	(L)	50.4	63.2	—	58.4	—	55.2	48.0	44.5	44.9	45.4
0.5	(D)	—	0.9	—	0.7	—	1.0	1.8	4.4	—	—
	(L)	21.6	24.3	—	28.3	—	26.9	26.4	25.5	—	—
−9	(D)	—	0.6	—	0.8	—	1.0	0.8	—	—	—
	(L)	17.4	22.4	—	23.4	—	18.6	18.3	—	—	—

(D) and (L) show the results in the dark and in exposure to light respectively.

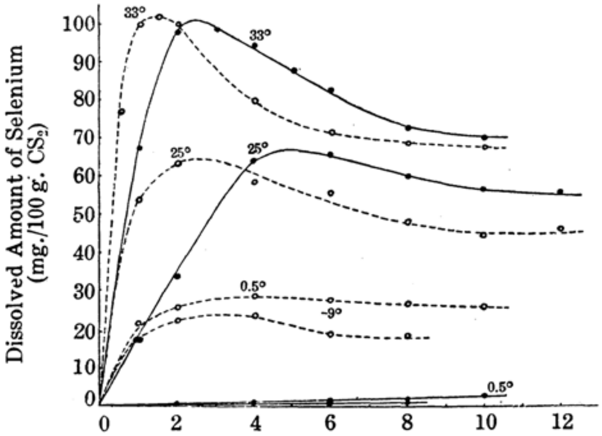

Fig. 1.

(2) *The results at 25°C.* In this case similar behaviours of dissolution were observed; the dissolved amount of selenium had a maximum value, and after a long time it seemed to reach a constant value smaller than that at 33°C. The red monoclinic crystals were also found depositing about the time of the maximum dissolution. However, the dissolved amount at each time was far smaller than that at 33°C., and both the time needed to reach the maximum and that to the final constant value were longer in this case than at 33°C. Light exerted more remarkable influence upon the rate of dissolution.

(3) *The results at 0.5°C. and −9°C.* In the dark, the dissolved amount of selenium was quite small and the rate of dissolution was so slow at these temperatures that the maximum dissolution was not reached within 10 hours. The action of light on the rate of dissolution was found to be very strong as will be seen from Table 1 and Fig. 1. At these temperatures red monoclinic crystals were found only in a trace and barely after exposure to light for about 6 hours, but not in the dark.

(4) *The results at about −60°C.* In the dark, the dissolution of selenium was not observed at all. By exposure to light, it was dissolved slightly.

Discussion of Results. G. Briegleb(1) has confirmed the constitutions of the several modifications of selenium and interpreted their transformation in solution by a diagram for pseudo ternary solution. According to him, the red amorphous selenium is pure Se_2, the monoclinic one is mixed crystals of varying compositions of Se_1 and Se_2, the latter predominating in amount, and the amorphous one is transformed into the monoclinic through the equilibrium $2\,Se_1 \rightleftarrows Se_2$ in solution, after being dissolved in carbon bisulphide.

The results obtained by the present writers seem undoubtedly in some degree to give a strong evidence in favour of the consideration of Briegleb. The above-mentioned fact that the dissolved amount of selenium has a maximum value, is in a good agreement with his view, for, according to it, the deposition of the monoclinic selenium from the solution and the dissolution of the amorphous one must compensate each other after a certain time, and then, the former would predominate over the latter in rate. When all of amorphous selenium was transformed into the monoclinic one, the dissolved amount would reach a constant value corresponding to the solubility of the latter, as was the case in every experiment mentioned above except those at lower temperatures. In order to ascertain this again, the solubility of monoclinic selenium was measured in the dark. The samples used for this purpose were prepared by deposition from solutions of amorphous selenium in carbon bisulphide at the respective temperatures at which their solubilities were to be measured. The experimental results are given in Table 2 (No. 1 and No. 3). The results indicate that monoclinic selenium has a definite solubility at each temperature and that, in favour of the consideration just mentioned above, the values of it coincide with those of the constant dissolved amounts given in Table 1, which were to be reached after a long time at the respective temperatures.

Table 2.

Temp. °C.	No.		Time (hours)				
			1	2	4	6	8
33	1	(D)	42.6	53.0	62.1	64.4	65.0
	2	(L)	40.5	53.1	61.5	64.9	67.5
25	3	(D)	32.9	42.4	46.1	44.9	45.7
	4	(L)	32.8	41.2	46.2	45.9	45.2

The transformation between the two modifications may also be considered to be due to some catalytic action of the solvent, but, the evidence of this cannot be shown in the present experiments.

Light seems to cause the increase in the rate of dissolution only. But, it cannot be decided from the results mentioned above, whether light acts on any one or both of the two modifications. In order to determine this, the following experiments were carried out. (1) The dissolved amounts of the samples of the monoclinic selenium the same with those used in No. 1 and No. 3 in Table 2 were measured at 33°C. and 25°C. and in exposure to light. The results obtained indicate no action of light on the monoclinic selenium as is shown in Table 2 (No. 2 and No. 4). (2) The dissolved amounts were measured with the mixtures the same with those employed in the experiment at 0.5°C. in Table 1 in the light and in the dark and at 0.5°C. By these experiments, it was found that the dissolved amount was suddenly decreased when the light was cut off, but increased again on exposure to light so as to reach the value which would be reached if the mixture were exposed to light

Table 3.

No.	Time (hours)										
	1	2	3	4	5	6	7	7.5	8	8.5	10
	(L)				(D)						
1	21.8	25.8	—	27.3	—	21.1	—	—	19.6	—	18.8
	(L)	(D)									
2	23.5	25.9	23.9	—	19.0	—	18.0	—	—	—	—
	(L)				(D)				(L)		
3	23.2	—	—	29.3	24.3	—	—	18.6	—	24.0	27.1

Table 4.

Time (hours)									
0.5	1	1.5	2	3	4	5	6	8	
—	99.5	—	99.2	—	79.4	—	71.6	68.8	[From Table 1, 33°C. (L).]
(L)			(D)				(L)		
76.8	—	101.6	—	88.4	—	74.5	71.6	69.0	

throughout the time (Table 3). These behaviours can well be interpreted by assuming that light causes an increase in the rate of dissolution of the amorphous selenium alone, for, as has been already mentioned, at such a temperature as low as 0.5°C. some of the amorphous selenium remained unaltered for a fairly long time because of its slow transformation into the monoclinic modification. (3) Similar experiments were made at 33°C. These showed that the dissolved amounts in the light coincide with those in the dark at each time after the illumination of about 2 hours, as seen from Table 4. Since, in this case, the amorphous selenium was all found to transform into the monoclinic modification in a short time, the residue being all the monoclinic, it is a matter of course that the dissolved amount remains the same in the light and in the dark, provided the monoclinic modification does not suffer the action of light.

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