2.   Small amounts of arsenic can be removed completely from large quantities of germanium in a single operation.   Relatively large quantities of arsenic require a retreatment of the precipitated sulfide to recover traces of occluded or co-precipitated germanium sulfide.

3.   Very small quantities of arsenic sulfide are shown to have marked coloring effect upon pure white germanium sulfide.   This coloring effect is quantitatively studied.

4.   Complete analysis of a selected sample of the mineral germanite is appended.

PHILADELPHIA, PENNSYLVANIA

THE PHOTOCHEMICAL POLYMERIZATION OF ACETYLENE

BY S. C. LIND AND ROBERT LIVINGSTON

Introduction

In an earlier paper[1] one of us pointed out the interest attaching to the comparison of the yields of chemical action per quantum and per ion pair in various reactions.   A few rough comparisons were possible with data existing in the literature, but it appeared preferable to select some suitable reactions which could be investigated photochemically and with alpha rays under the best experimental conditions.

The reactions that have been chosen are the polymerization of acetylene and of some of its simpler derivatives.   As expected, the alpha-ray reactions yielded readily to quantitative investigation and the results from six gaseous unsaturates have been recently published.[2]

The following deals with the photochemical yield in the polymerization of acetylene, of which a preliminary report has already been made.[3]

Acetylene polymerization has the advantage of being a direct reaction from gas to solid with no known side reactions or gaseous products.   The relatively high yield is favorable for manometric work.   In the photochemical reaction the one complication, the fogging of the window transmitting ultraviolet by deposition of the solid polymer, has been overcome by making measurements with a minimal amount of reaction, which is rendered possible by the employment of a very sensitive differential gage.

The photochemical condensation of acetylene, which was first reported by Berthelot and Gaudechon,[4] has been qualitatively studied by Bates

[1] Lind, *J. Phys. Chem.*, **32**, 575 (1923); "The Chemical Effects of Alpha Particles and Electrons," The Chemical Catalog Co., New York, **1928**, p. 215.

[2] G. B. Heisig, THIS JOURNAL, **53**, 3245 (1931).

[3] Lind and Livingston, *ibid.*, **52**, 4613 (1930).

[4] Berthelot and Gaudechon, *Compt. rend.*, **150**, 1169 (1910).

and Taylor[5] and by Reinke.[6]   It was demonstrated by these investigators that acetylene is polymerized to a yellowish inert solid, presumably cuprene, when it is exposed to the complete radiation of a quartz mercury arc. Reinke showed by the use of a glass filter that the reaction was not caused by light of wave length longer than 3000 Å.   Extreme purification had no appreciable effect on the course of the reaction.   In both of these investigations, the acetylene contained some mercury vapor, the latter two authors assuming that, since a "hot arc" was used, no resonance light which could be absorbed by the cold mercury vapor was produced.
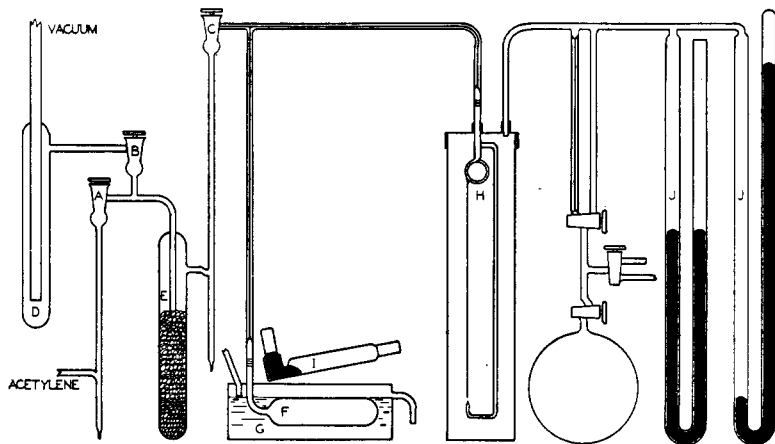

Fig. 1.—Apparatus.

Effect of Pressure and Temperature

Apparatus.—In the experiments presented in this paper, a hot arc was used and particular care was taken to prevent the contamination of the acetylene by mercury vapor.   The acetylene was taken from a commercial cylinder (solution in acetone). It was passed through a series of wash bottles containing sodium bisulfite solution, concentrated sulfuric acid saturated with potassium dichromate and sodium hydroxide solution.   In some of the experiments an extra bottle containing a solution of copper sulfate in sulfuric acid was included in the train.   The gas then passed through a column of glass wool, to remove spray, and was condensed with liquid air.   It was then fractionated at low temperature, to remove permanent gases, and was stored in a large flask over fused potassium hydroxide.

The reaction system, represented in Fig. 1, was isolated from the storage vessel by stopcock A.   The system was evacuated through stopcock B, which was only opened when the trap D was surrounded by liquid air.   A mercury diffusion pump was used and the apparatus was always evacuated to a pressure less than 10^{-4} mm. of mercury before the acetylene was admitted.[7]   Before being admitted to the reaction chamber an excess of acetylene was frozen, by means of liquid air, in trap E, which was filled with

[5] Bates and Taylor, THIS JOURNAL, **49**, 2438 (1927).

[6] Reinke, *Z. angew. Chem.*, **41**, 1144 (1928).

[7] In some of the earlier experiments, an oil pump only was used, and the system was flushed out with acetylene several times before beginning the experiment.

(dental) gold foil. The liquid air was then removed and the acetylene was allowed to evaporate into the reaction system until the desired pressure had been reached; stopcock C was then closed. Stopcocks A, B and C were lubricated with a mixture of ortho and metaphosphoric acids,[8] during the majority of the experiments; however, in several experiments ordinary vacuum stopcock grease was substituted without apparently affecting the results. The reaction vessel F is a quartz cylinder, 3.4 cm. in diameter and 15 cm. long, connected to the system by a graded seal. The temperature of the vessel was controlled by means of a flowing water-bath G. The pressure was measured with a quartz spiral manometer H,[9] which was used as a null instrument; it was connected to the system by a graded seal. The balancing pressure was measured with a mercury manometer which was read with an accurate cathetometer. The pressure readings were reproducible within 0.2 mm. The light source was a Cooper–Hewitt horizontal quartz mercury arc (I) operating at 42 volts and 4.2 amps. The arc was placed parallel to the reaction vessel and about 5 cm. above it.

The Reaction Product.—When acetylene is illuminated under these experimental conditions, the pressure decreases gradually and a yellowish solid, apparently cuprene, forms in the reaction vessel. The cuprene is largely deposited on the bottom of the vessel; however, a thin film forms on the upper surface, through which the light is entering. The experiments showed that this film does not affect the rate of the reaction appreciably until the pressure has been reduced by about 3 mm.; when the pressure has been reduced by 10 mm., the reaction rate falls to about a quarter of its initial value.

After two of the experiments, the gas was tested for hydrogen by condensing the acetylene with liquid air; if there was any residual pressure, it was less than 0.2 mm., the limit of sensitivity of the manometer. To determine whether ultraviolet light has any effect on cuprene, the reaction system was evacuated after one experiment, and the film of cuprene was exposed to the radiation of the arc for several hours. The solid did not change in color, nor was there any measurable pressure of gas produced. When heated in a vacuum, the cuprene darkened, but did not sublime. The deposit was easily and completely removed from the reaction vessel by admitting air to it and heating it with a hand torch.

Effect of Pressure.—Six experiments were performed at pressures ranging from 2.6 to 65.0 cm. These experiments are summarized in Table I. The values of the initial pressure and the average temperature are given in the first and second columns, respectively. The observed values of the initial rate, in centimeters per minute, are given in the third column.

To eliminate the uncertainties introduced by the film of cuprene, the values of the initial rate are based upon the first 2 mm. fall in pressure.

[8] Stephens, THIS JOURNAL, **52**, 635 (1930). The lubricant recommended by Boughton, *ibid.*, **52**, 2813 (1930), was also tried, but was found to have too high a vapor pressure for use in a vacuum system.

[9] Bodenstein and Dux, *Z. physik. Chem.*, **85**, 300 (1913).

P_0, cm.	t, °C.	V(measured)
64.5	11.0	0.042
43.5	13.5	.033
33.3	12.0	.032
8.8	13.0	.013
7.2	11.7	.013
2.7	11.4	.0035

To illustrate the type of pressure–time curve obtained, the detailed results of several experiments are plotted in Fig. 2. Since the temperature of the flowing water-bath sometimes varied by so much as 1.5°, it was necessary to correct the observed pressures to a constant (average) temperature, by means of the perfect gas laws. The volumes of the quartz spiral and the capillary corrections were sufficiently small to render the effect of fluctuations in room temperature negligible.
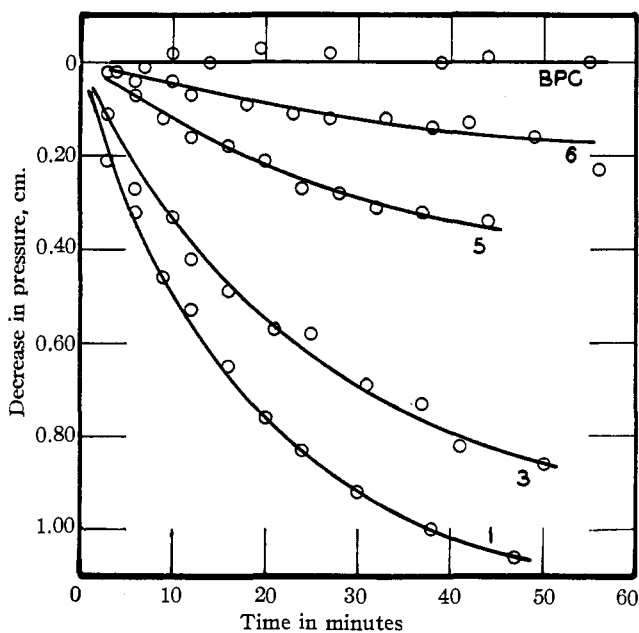

Fig. 2.—Rate of polymerization.

The data of Table I indicate that for the lower pressures the rate is practically proportional to the pressure, but at higher pressures it approaches a constant value. The simplest explanation of this result is that the rate is directly proportional to the intensity of the absorbed light, but is otherwise independent of the pressure of the acetylene. This may be demonstrated more definitely by combining the data of Table I with

the results of the absorption measurements which are given in Fig. 6. In order to use the absorption measurements for this purpose, it is necessary to assume (as a first approximation) that the energy distribution of the absorbable light produced by the optical system used in those experiments is the same as that of the horizontal arc used in the rate measurements. If this may be taken as true, the percentage of absorption in the two sets of experiments will, for any given pressure, differ by a constant multiplier, c.

$$\left(\frac{I_{abs.}}{I_0}\right)_{rate} = C \left(\frac{I_{abs.}}{I_0}\right)_{absorb.}$$

Since $(I_0)_{rate}$ was maintained constant

$$(I_{abs.})_{rate} = C' \left(\frac{I_{abs.}}{I_0}\right)_{absorb.}$$

Since we have already assumed that the rate is proportional to the intensity of the light absorbed

$$V = k \, (I_{abs.})_{rate}$$

we may write

$$V = kC' \left(\frac{I_{abs.}}{I_0}\right)_{absorb.}$$

or

$$\log V = \log (kC') + \log \left(\frac{I_{abs.}}{I_0}\right)_{absorb.}$$

This relation may be tested by plotting the logarithm of the rate against the pressure, and then plotting the logarithm of the percentage absorption against pressure on the same graph to the same scale. If the relation holds, the two curves will differ only by a constant factor in the logarithmic scale. In Fig. 3 a suitable constant factor has been added to each value of the logarithm of the percentage absorption to make the two curves coincide in the region of higher pressures. It is apparent that the results are in definite agreement with the prediction, and afford ample justification for the statement that the rate is proportional to the intensity of the light absorbed and is otherwise independent of the pressure of the acetylene. The small departure which is noticeable in the region of low pressures is very probably due to the difference in the light sources.

Effect of Temperature.—To determine the effect of temperature, two experiments were performed at 39° and at 10 cm. pressure. The initial rates of these experiments were 0.029 and 0.024. Using the average of these values and a 10-cm. value obtained by graphical interpolation of the 12° measurements, it may be shown that the 10° temperature coefficient

$$\log K_{10} = \frac{10}{39 - 12} \log \frac{V_{39}}{V_{12}}$$

has a value of 1.25. It is possible that this observed temperature coefficient may be due in part to the temperature coefficient of the absorption of light. However, an attempt to measure the temperature coefficient

of the absorption using a thermopile, galvanometer, and a light source which is described later in this paper, indicated that the absorption was practically constant over this temperature range. While this attempt to measure the temperature coefficient of the absorption was admittedly crude, it seems very probable that the value 1.25 is that of the temperature coefficient of the photochemical reaction itself. This is in interesting contrast with the radiochemical reaction, the ion pair yield of which is independent of the temperature from 0° to 100°.[10]
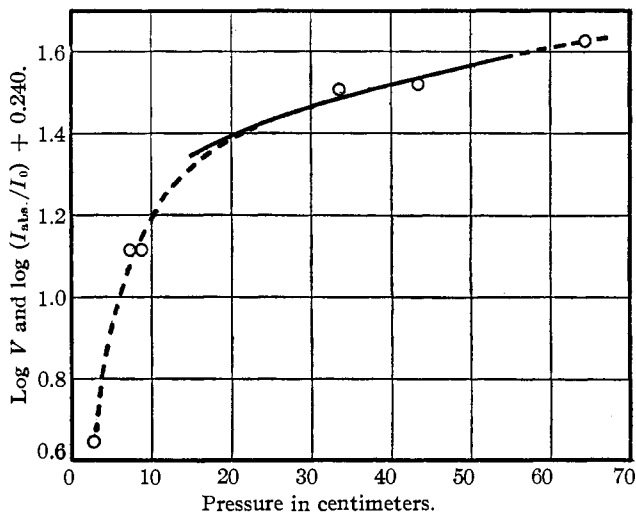

Fig. 3.—Reaction rate and the percentage absorption of light: ——, absorption; -O-O-, rate.

Photochemical Threshold.—Reinke showed that the light transmitted by a lead glass filter, having a sharp transmission limit at about 3000 Å., was not capable of causing the polymerization of acetylene. This work has been extended in the present investigation by using several of the Corning ultraviolet transmitting glasses. None of these, not even a new 4.8 mμ plate of the comparatively transparent blue-purple corex, was capable of transmitting an appreciable amount of photochemically active light. The experiments with blue-purple corex were performed with acetylene at 10 cm. pressure, both at 12 and 41°. The results of the measurements at 41° are represented by the points labeled BPC on Fig. 2. A series of spectrograms of the mercury arc taken with and without this filter indicates that an appreciable fraction of 2537 Å. is transmitted by it.[11] We may conclude from this that light of wave lengths equal to or

[10] See Mund and Koch, *J. Phys. Chem.*, **30**, 292 (1926); Lind and Bardwell, THIS JOURNAL, **48**, 1556 (1926).

[11] The data of Anderson, Fraser and Bird, *J. Optical Soc.*, **17**, 458 (1928), indicate that even an *aged* purple corex filter transmits 2% of λ2537 and 1% of λ2480 Å.

greater than λ2537 Å. are either not absorbed or are photochemically inefficient. This question will be discussed in a later section of this paper.[3]

Determination of the Quantum Yield

Apparatus.—Certain modifications of the apparatus, represented by Fig. 1, were necessary for the quantum yield measurements. A quartz cylinder with fused on plane ends was substituted for the reaction vessel used in the earlier experiments. It was 2.8 cm. in diameter and 4.7 cm. long.

It was necessary to use a light source of such a character that a measurable amount of the radiation would be absorbed by acetylene. A high pressure capillary arc of the type described by Langer and Meggers[12] was used. The arc consists of a thick-walled horizontal quartz capillary, 1.5 mm. inside diameter and 5 cm. long, connected to two vertical tubes open at the top. Constrictions were made in the vertical tubes about a centimeter above the points where they joined capillary, and close-fitting iron electrodes were introduced through these constrictions. The capillary and side tubes were filled with carefully purified mercury,[13] which was boiled in place to expel any trapped air. The arc was started by heating a point on the capillary with a blast lamp. As soon as the arc struck it was plunged into a copper tank through which distilled water was flowing. The capillary of the arc was placed directly behind a quartz window in the side of the tank. A diaphragm with a 1.5-mm. circular hole was fastened to the front face of the window. The arc was operated at 60 volts and 3.2 amperes. The intensity of the light, particularly of the shorter ultraviolet, is diminished fairly rapidly by a brownish film which forms on the inside of the capillary. However, this deposit can be easily and completely removed with dilute hydrofluoric acid.

The shorter ultraviolet radiation of the arc was isolated by means of a focal isolation apparatus.[14] This device utilizes the chromatic aberration of a quartz lens to separate the extreme ultraviolet from the visible and near ultraviolet. Two spherical fused quartz lenses were arranged to project a slightly converging beam of light through the reaction cell. The central part of the first lens was blocked out with a circular opaque screen, and a diaphragm was placed at its focus for λ2300 Å. to intercept all but the shorter wave lengths. A series of spectrograms indicated that the emergent light does not contain more than 2 or 3% of light of wave length greater than 2537 Å. and that the intensity of λ2537 Å. is considerably diminished relative to the shorter wave lengths. The system absorbs practically all light of wave lengths less than 2054 Å. The spherical aberration of the lenses makes it impossible to isolate a single line or even a narrow region; however, the elimination of the energy-rich long wave length part of the spectrum makes it possible to measure the amount of energy absorbed by the acetylene.

The energy measurements were made with a Moll surface thermopile fitted with a fluorite window, and a Leeds and Northrup high-sensitivity low resistance galvanometer. The galvanometer was mounted on a heavy concrete pillar, and deflections of a spot of light were observed on an opaque scale three meters distant from the galvanometer. The system was calibrated by means of a radiation standard lamp furnished by the Bureau of Standards, for which the total radiation in absolute units at two meters' distance in a given direction was known for various values of the current. When the calibrations were made, a shunt was used which reduced the deflections by a factor of 0.336. Following the explicit directions furnished with the lamp, the results summarized in the following table were obtained.

[12] Langer and Meggers, *Bur. Standards, J. Research,* **4,** 711 (1930).

[13] See Hulett, *Phys. Rev.,* **33,** 307 (1911).

[14] Compare Terenin, *Z. Physik,* **31,** 33 (1925); Andrews, *Gen. Electric Rev.,* 817 (1917); and Rubens and Wood, *Phil. Mag.,* **21,** 249 (1911).

TABLE II

CALIBRATION OF THE THERMOPILE AND GALVANOMETER

Amperes through filament[a]	$\dfrac{\text{Ergs}}{\text{Sq. mm. sec.}}$[b]	Average deflection	$\dfrac{\text{Ergs}}{\text{Sq. mm. sec.}}$ per mm. deflection
0.250	4.26	24.8	0.0172
.300	6.27	36.25	· .0173
.350	8.67	49.65	.0174

[a] The current was measured with an accurate ammeter kindly furnished by the Department of Electrical Engineering, University of Minnesota.   [b] Calibration of the Bureau of Standards for flux at two meters' distance from the lamp.

The deflections given in column three are the averages of a large number of observations.   A series of experiments demonstrated that practically all of the light falling into the thermopile horn is reflected onto the element. The inside diameter of the horn is 2.60 cm.; therefore, the sensitivity may be computed as $0.0173 \times (26.0/2)^2 \times = 9.19$ ergs/sec. per mm.   It was determined by experiment that the fluorite window absorbed or reflected approximately 10% of the incident radiation.   Applying this correction and the factor for the shunt the final value for the sensitivity is 3.39 ergs/ sec. per mm. deflection.   While the absorption by fluorite of light of the wave lengths transmitted by the focal isolation device is probably negligible, the reflection amounts to about 8%.[15]   It was determined experimentally that the second window of the quartz reaction vessel absorbs and reflects about 20% of the light incident upon it.   Therefore, a correction of about 30% must be applied when the intensity of the light passing through the reaction vessel is measured.   Applying this correction, the working value of the sensitivity is $3.39 \times 1.30 = 4.40$ ergs/sec. per mm. deflection.

In the final measurements of the quantum yield, a differential manometer was used which was sufficiently sensitive to measure a change in pressure of 0.15 to 0.3 mm. within 2 or 3%.   The apparatus consisted of a thin glass diaphragm, the motion of which changed the capacity of a small condenser, which was similar in principle to the device described by Dowling.[16]   The modified electrical circuit suggested by Olson and Hirst was used.[17]   However, instead of adjusting the resonance circuit until the primary circuit went out of oscillation, it proved more satisfactory to balance the changes in the manometer condenser with the precision variable condenser so as to keep the plate current of the tube in the oscillating circuit constant.   Since the highest sensitivity was not necessary in this work, a simplified diaphragm and condenser was used in place of that described by Olson and Hirst.   The upper surface of the diaphragm,

[15] "International Critical Tables," Vol. V, p. 257.

[16] Dowling, *Phil. Mag.*, **46**, 81 (1923).

[17] Olson and Hirst, THIS JOURNAL, **51**, 2378 (1930); see also Frank, Thesis, California, **1929**; and Gunn, *Phil. Mag.*, **48**, 224 (1924).

which was a 7.6-cm. No. 00 cover glass sealed to the end of the tube with red sealing wax, was silvered. A mica washer about 0.3 mm. thick (see detail M of Fig. 4) rested on the diaphragm and served to support a 7.6-cm. brass disk. Electrical contact was made with the silvered surface by means of a small piece of platinum foil, which slipped under the mica washer. A few drops of Duco cement served to hold the washer and brass plate in place.

The apparatus was used as a differential manometer. Both sides of the manometer were evacuated simultaneously, and the acetylene was then introduced at the desired pressure. After allowing some time for temperature and pressure equilibrium to be attained, the stopcock (a) was closed.
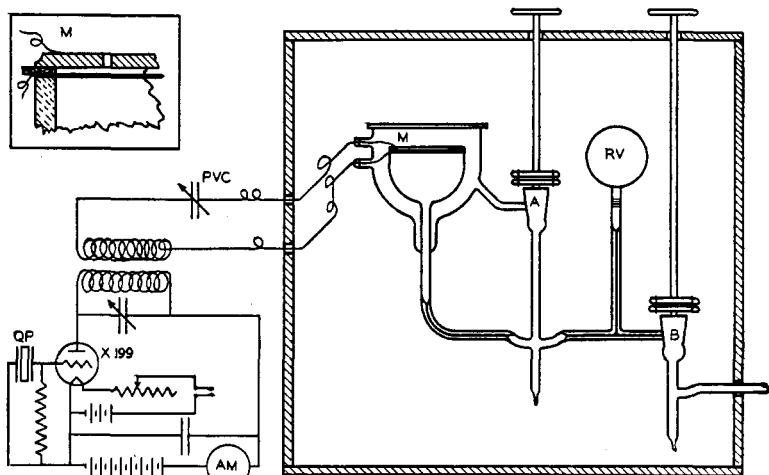

Fig. 4.—The reaction vessel and sensitive manometer.

As is indicated in Fig. 4, the manometer and reaction vessel were both inclosed in an air thermostat, and the stopcock was manipulated by means of a long rod which extended outside of the thermostat. It was found that temperature fluctuations were reduced to a minimum when the thermostat consisted simply of a large box containing a small electric fan. It was necessary to start the fan running at least an hour before beginning an experiment.

The differential manometer was compared to an accurately calibrated McLeod gage, at pressures ranging from 1.5 to 0.2 mm. A plot of the readings of the variable condenser against the differences in pressure gave a smooth curve passing through the origin. Three sets of comparisons were made: one before, one during and one after the quantum yield measurements. All of these results fitted the following semi-empirical equation within 1 or 2%

$$\Delta p = 7.00 \left(\frac{22.12}{C_2}\right)^2 \cdot \frac{\Delta C}{C_1}$$

$$= 3.425 \times 10^4 \cdot \frac{\Delta C}{C_2{}^2 C_1}$$

where C_1 and C_2 are, respectively, the initial and final readings of the variable condenser, and Δp is the pressure difference in millimeters. The equation corresponds roughly to a sensitivity of about 2.6×10^{-3} mm. per division of the condenser scale.

To determine the number of quanta corresponding to the energy absorbed by the acetylene, it is necessary to know the average wave length of the absorbed light. This was determined approximately by comparing a series of spectrograms of the light emerging from the reaction vessel, both when it was evacuated and when it contained acetylene. Since the beam of light was not homogeneous in respect to wave length, and since it could not all be focused on the slit of the spectrograph, a thin ground quartz plate was placed about 5 cm. in front of the slit to scatter the light. A small quartz spectrograph was used, and the spectrograms were taken on oiled process plates, prepared according to the directions of Lyman.[18] The absorption was appreciably only in the region between 2200 and 2050 Å., the lower limit of transmission of the apparatus. The average wave length of the absorbed light was estimated, somewhat arbitrarily, as 2150 Å. This result seems to be in good qualitative agreement with the measurements of Kistiakowsky[19] and of Stark and Lipp[20] on the absorption of ultraviolet light by acetylene. Kistiakowsky[19] found that a very faint series of bands appeared at wave lengths as great as 2400 Å. A more intense series was observed at approximately λ2290 Å. The occurrence of a continuous absorption, possibly due to residual traces of impurities, made it impossible for him to continue his measurements below λ2250 Å. He states, "It is, of course, not excluded that the bands here reported are also to be ascribed to impurities. On the other hand, every precaution exercised in purifying acetylene seemed not to affect them in the least." Stark and Lipp[20] report a series of bands beginning at λ2200 Å. and becoming increasingly intense with decreasing wave length. Herzberg[21] has recently reported that "acetylene has no absorption until λ2070 Å. at pressures up to 30 mm. and 20 cm. length of absorption tube." This statement is not necessarily contradictory to the results presented here, nor to the measurements of Kistiakowsky or of Stark and Lipp, all of which were performed at much higher pressures. As additional evidence that the absorption measurements presented here were not appreciably affected by the presence of impurities, the following results may be cited. In the experiments summarized in Table III the energy absorbed was measured at half-hour intervals during the course of the experiments (from three to four hours). In no case was any systematic trend in the

[18] Lyman, "Spectroscopy in the Extreme Ultraviolet," **1928**, p. 61.

[19] Kistiakowsky, *Phys. Rev.*, **37**, 276 (1931).

[20] Stark and Lipp, *Z. physik. Chem.*, **66**, 36 (1913).

[21] Herzberg, *Trans. Faraday Soc.*, **27**, 379 (1931).

percentage absorption evident, which indicated that the absorption was not due to a trace of a light-sensitive impurity.

Preliminary Experiments.—A few attempts were made to measure the quantum yield using the optical system described, and the quartz spiral manometer. The results of these determinations of the quantum yield are summarized in Table III.

TABLE III

QUANTUM YIELD DETERMINATIONS

P_0, mm.	t, °C.	P, mm.	Time in minutes	Quanta absorbed	Molecules reacted	M/m^a
587	27	1.0	220	2.3×10^{17}	1.3×10^{18}	5.6
435	27	1.4	180	2.4×10^{17}	1.8×10^{18}	7.5
410	22	1.2	210	2.25×10^{17}	1.5×10^{18}	6.7

[a] These values of the quantum yield are somewhat smaller than those upon which our earlier (preliminary) average value was based, since in the earlier computations the reflection errors were neglected and the average wave length was taken as 2300 Å.

Final Series of Measurements.—The final series of measurements were made with the differential manometer and with the light source which was
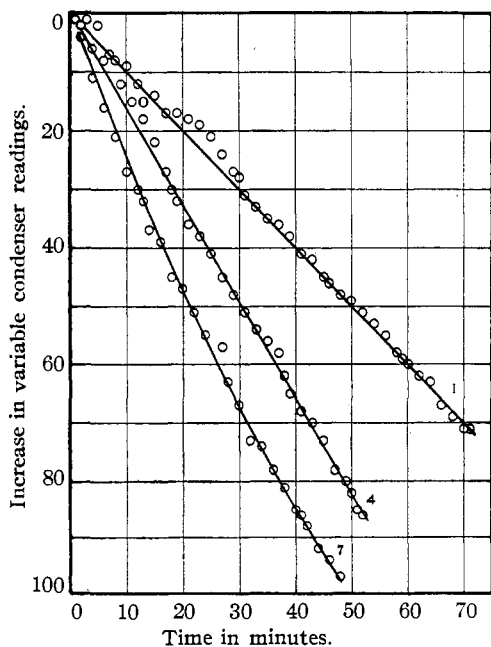

Fig. 5.—Rate of polymerization.

used in the preliminary measurements. The method of purification and introduction into the reaction system of the acetylene gas has been described. The total pressure of the acetylene was measured with the quartz spiral manometer. In order to reduce the effect of temperature and electrical fluctuations to a minimum, the thermostat fan was started several hours before each experiment and the oscillator was started at least an hour before the zero reading was taken. The acetylene was allowed to remain in the reaction system for about an hour before the manometer stopcock was closed. After each experiment this stopcock was opened in order that the zero point might be checked. In only one case (Experiment 4) did the zero point shift by more than 2 or 3 divisions.

To illustrate the type of pressure variation obtained, the detailed results of several experiments are plotted in Fig. 5. The readings of the

variable condenser are plotted against time in minutes.[22]   While the lag which occurred during the first few minutes of each experiment may possibly be due to an induction period, it seems more likely that it is caused by a Draper effect which is not quite sufficient to counterbalance the decrease in pressure due to the reaction.

During each of these experiments, the intensity of the transmitted light was determined at fifteen-minute intervals.   The time during which the shutter was down (about ninety seconds for each determination) was subtracted from the reaction time.   The percentage of absorption of light by acetylene, for these experimental conditions, was determined in a separate series of experiments.   This series of measurements is summarized in Fig. 6.   The percentage of the transmitted light absorbed is plotted against the pressure of the gas.   Since no difference was observed (in these experiments) when a newly cleaned arc was substituted for a badly discolored one, it is very probable that the brownish film was equally opaque to light of all wave lengths transmitted by the focal isolation device.

The results of the seven experiments of this series are summarized in Table IV.   The pressures listed in column two are the initial pressures of the

Fig. 6.—Absorption of light by acetylene as a function of pressure.

acetylene.   The total change in pressure in *millimeters* is given in column three and the corresponding decrease in the number of acetylene molecules in column seven.   The duration of the experiments, in minutes, is given in column four.   The average energy of the absorbed light and the corresponding total number of quanta absorbed are given in columns five and six, respectively.   The quantum yield is given in the last column.   These experiments were performed at average temperatures between 24 and 25°, with the exception of experiment 3, which was performed at 27°.

It is apparent that, within the limits of experimental error, the quantum

[22] It should be remembered that the intensity of the incident radiation decreased from 10 to 35% during each experiment.   The resulting decrease in rate is partly compensated for by the non-linear relation between pressure and condenser readings.
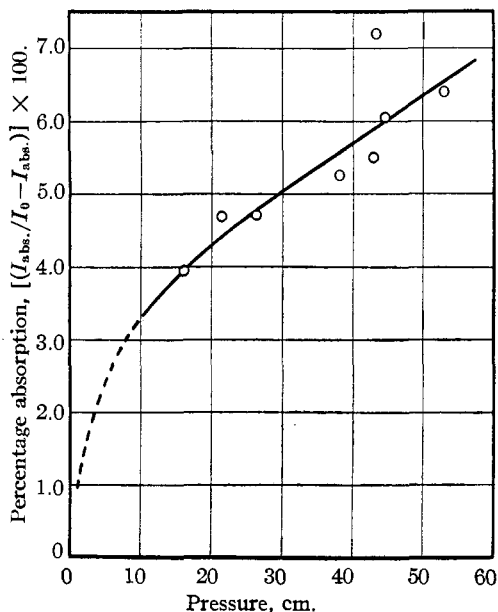
TABLE IV

DETERMINATION OF THE QUANTUM YIELD

No.	P, mm.	Mm.	t, minutes	Ergs per second	Quanta absorbed $\times 10^{-16}$	Molecules reacted $\times 10^{-17}$	M/q
1	217	0.218	72	116	5.50	5.55	10.1
2	235	.172	83	116	6.33	4.30	6.8
3	315	.234	54	162	5.75	5.95	10.3
4	319	.341	54	186	6.60	8.65	(13.1)
5	365	.312	80	151	7.95	7.65	9.6
6	395	.178	56	178	6.54	4.52	(6.9)
7	416	.253	52	202	6.90	6.42	9.3

Av. 9.2 ± 1.0

yield is not a function of either the pressure of the acetylene or of the intensity of the absorbed light. In computing the average value of the quantum yield, experiments 4 and 6 have been excluded; experiment 4 because the zero reading of the manometer condenser changed by 10 divisions during the experiment, experiment 6 because the arc was unsteady during the experiment. The average value of the other five experiments is 9.2. This value is probably correct (for the wave length and temperature used) within 10, or at most 15%, uncertainty. It is noteworthy that it is about half the yield per ion pair (9); that is, it is approximately equal to the average yield per ion.

In conclusion we wish to express our gratitude to Dr. Buchta, of the Department of Physics, for his helpful advice and hearty coöperation.

Summary

1. Acetylene is polymerized to a yellowish solid (resembling cuprene) when it is irradiated by ultraviolet light, in the absence of mercury vapor.

2. Light of $\lambda 2537$ Å., or longer, is not effective in producing the photochemical polymerization.

3. The rate of polymerization apparently depends only on the intensity of the absorbed light and is otherwise independent of the pressure of the acetylene.

4. It has been shown that the 10° temperature coefficient has a value of 1.25, when acetylene at 10 cm. pressure is exposed to the complete radiation of a quartz mercury arc.

5. The quantum yield of the polymerization, for an average wave length of 2150 Å., is 9.2 ± 1.5. This value appears to be independent of the pressure of the acetylene and of the intensity of the absorbed radiation.