and Ritchie. At ordinary temperature the results are in agreement with the equation of Bodenstein and Unger, except that a small correction must be made for an inhibiting action by the hydrogen chloride formed. At temperatures below 172°K. the rate depends on the square root of the light absorbed instead of the first power. The temperature coefficient of the reaction has been determined both at ordinary and at low temperatures. The discussion includes a possible explanation for the change in the rate law as the temperature is lowered and some comments on the work of Norrish and Ritchie.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA, AND FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

# The Polymerization of Deutero-acetylene by Alpha-Rays[1]

BY S. C. LIND,[2] J. C. JUNGERS[3] AND C. H. SCHIFLETT[4]

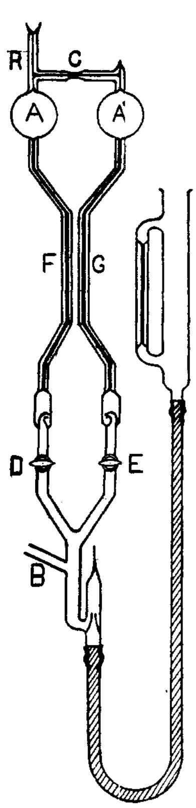

Fig. 1.

**Introduction.**—It is well known that acetylene under the influence of alpha-radiation from radon mixed with the gas polymerizes to a solid known as cuprene.[5] Preliminary experiments showed that a similar solid was obtained when deutero-acetylene was subjected to the rays. The $-M/N$ (the number of molecules of acetylene polymerized per ion pair) for ordinary acetylene is approximately twenty.[6] It was of interest, therefore, to know this value for deutero-acetylene. In this paper are reported the results of the direct determination of $-M/N$ and also the results of a more exact comparison of the reaction rates of the polymerization of heavy and light acetylene by a pressure differential method.

**Experimental Procedure.**—The direct determination of $-M/N$ for deutero-acetylene was made in the usual way[5,6] and found to agree[7] with the value previously obtained for ordinary acetylene within 5%. The following method was devised to permit of a more critical comparison of the rates of polymerization. Radon was introduced into A and A' (Fig. 1) through R, after which the system was sealed off at R. Care was taken to have reaction vessels A and A' as nearly the same volume as reasonably possible so that the radon might distribute itself equally between the two vessels. Several hours were then allowed to elapse, after which the connecting capillary was sealed at C. Deutero-acetylene was then introduced into A through B and D and ordinary acetylene into A' through B and E. For the purpose of this comparison it was important to adjust the pressure of $C_2H_2$ in A' quickly to equal within a few millimeters that of $C_2D_2$ in A so that the mercury levels in the parallel tubes at F and G could be read at one major setting of the leveling bulb and cathetometer. The reactions were then followed manometrically. The equality of distribution of radon between the two vessels, which was checked by gamma-ray comparison by shielding from the electroscope first one and then the other bulb with lead, was found to be satisfactory.

## Preparation of Acetylenes

**Preparation of Deutero-acetylene.**—Some difficulty has been experienced in the preparation of pure deutero-acetylene free from contamination with hydrogen (ordinary).[8] Accordingly, the following method was adopted. A (Fig. 2) is the vessel destined to receive the acetylene; B and D are traps. E is a small volume containing pure $D_2O$. C is the vessel containing calcium carbide. After the whole was carefully dried, the stopcocks were greased and put in place and the calcium carbide was dropped into

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[1] This work was supported in part by a grant from the Fluid Research Fund of the Graduate School of the University of Minnesota.

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[5] Mund and Koch, *Bull. soc. chim. Belg.*, **34**, 125 (1925); Lind and Bardwell, *Science*, **62**, 423 (1925).

[6] Lind, Bardwell and Perry, THIS JOURNAL, **48**, 1558 (1926); Mund and Koch, *J. Phys. Chem.*, **30**, 293 (1926).

[7] *Phys. Rev.*, **46**, 825 (1934).

[8] McKellar and Bradley, *Phys. Rev.*, **46**, 664 (1934).

the vessel C. The calcium carbide used was obtained from the Union Carbide Company and was brown-violet in color, showing it was unattacked by water which causes it to turn white. Only the central portion of a 200-cc. lump was used. The vessel is then sealed off at F. The apparatus was now carefully pumped out while the calcium carbide was heated at 400° for twenty-four hours. Water from E was then distilled into D surrounded by liquid air. The liquid air was then removed from D and both D and C were cooled to 0° with an ice-water bath while B was cooled by liquid air. This procedure maintains a very low pressure of acetylene and allows the water to distil slowly into contact with the calcium carbide. In order to make sure that all of the water had reacted with the calcium carbide it was distilled from B to D and back several times after which it was condensed in C, together with the acetylene, by means of liquid air. The gases were then condensed in B with liquid air and the acetylene distilled at the temperature of solid carbon dioxide-ether mixture and condensed in A.

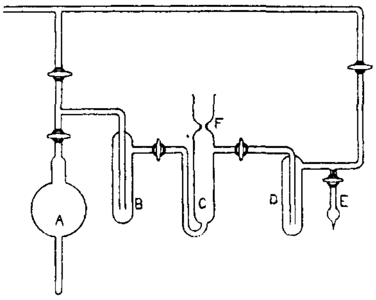

Fig. 2.

$D_2O$, provided by Professor H. S. Taylor, was of density $d_{20}$ 1.1059.

For the absence of hydrogen in the deutero-acetylene we had to rely on the purity of the calcium carbide and the precautions taken to extract traces of water which it might have

TABLE I

| Elapsed time | | | Total press. | | Stepwise press. change | | Stepwise | | $(k\mu/\lambda)'$ | | $-M/N$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| days | hrs. | min. | A | A' | A | A' | Diff. | % Diff. | A | A' | A | A' |
| Expt. 4 Vol. A 29.326 cm. (containing $C_2D_2$). Total $E_0$ 121.58 m. c. Vol. A' 29.173 cm. (containing $C_2H_2$) | | | | | | | | | | | | |
| 0 | 0 | 0 | 730.0 | 727.7 | ... | ... | ... | ... | .. | .. | .. | .. |
| 0 | 1 | 5 | 709.4 | 707.1 | 20.9 | 20.6 | +0.3 | +1.44 | 58.9 | 59.8 | 22.2 | 22.5 |
| 0 | 5 | 35 | 627.3 | 625.2 | 82.1 | 81.9 | + .2 | +0.24 | 61.3 | 62.9 | 23.1 | 23.6 |
| 0 | 8 | 0 | 591.8 | 589.9 | 35.5 | 35.3 | + .2 | + .56 | 53.4 | 54.7 | 20.2 | 20.6 |
| 0 | 17 | 30 | 475.3 | 474.2 | 116.5 | 115.7 | + .8 | + .69 | 55.0 | 56.2 | 20.6 | 21.0 |
| 0 | 23 | 45 | 421.0 | 418.8 | 54.3 | 55.4 | − .9 | −1.63 | 48.9 | 51.4 | 18.2 | 19.1 |
| 1 | 8 | 20 | 352.3 | 349.9 | 68.7 | 68.9 | − .2 | −0.29 | 55.7 | 57.6 | 20.7 | 21.3 |
| 1 | 16 | 5 | 302.4 | 299.7 | 49.9 | 50.2 | − .3 | −0.60 | 56.5 | 58.8 | 20.8 | 21.7 |
| 3 | 16 | 40 | 149.0 | 145.4 | 53.4 | 54.3 | − .9 | −1.65 | 50.7 | 53.2 | 18.4 | 19.4 |
| | | | | | | | | Weighted avs. | 53.1 | 55.5 | 19.6 | 20.4 |
| Expt. 5 Vol. A 30.91 cm. (containing $C_2D_2$). Total $E_0$ 123.48 m. c. Vol. A' 29.16 cm. (containing $C_2H_2$) | | | | | | | | | | | | |
| 0 | 0 | 0 | 725.9 | 728.9 | ... | ... | ... | ... | .. | .. | .. | .. |
| 0 | 5 | 44 | 626.4 | 630.3 | 99.5 | 98.6 | +0.9 | +0.90 | 54.8 | 57.1 | 21.4 | 21.4 |
| 0 | 6 | 57 | 608.6 | 612.8 | 17.8 | 17.5 | + .3 | +1.69 | 52.0 | 54.0 | 20.2 | 20.2 |
| 0 | 12 | 50 | 530.5 | 535.3 | 78.1 | 77.5 | + .6 | +0.77 | 53.3 | 55.5 | 20.7 | 20.8 |
| 0 | 20 | 17 | 449.5 | 454.4 | 81.0 | 80.9 | + .1 | +0.12 | 53.0 | 55.5 | 20.5 | 20.7 |
| 1 | 6 | 0 | 368.4 | 372.0 | 81.1 | 82.4 | −1.3 | −1.58 | 51.8 | 55.0 | 20.0 | 20.4 |
| 1 | 20 | 22 | 284.9 | 287.2 | 83.5 | 84.8 | −1.3 | −1.56 | 50.0 | 53.0 | 19.1 | 19.5 |
| 2 | 6 | 17 | 242.3 | 244.5 | 42.6 | 42.7 | −0.5 | −1.20 | 48.7 | 51.2 | 18.4 | 18.8 |
| 2 | 21 | 37 | 193.9 | 194.8 | 48.4 | 49.7 | − .9 | −1.80 | 48.9 | 52.8 | 18.4 | 19.2 |
| 3 | 21 | 37 | 144.6 | 144.9 | 49.3 | 49.9 | − .6 | −1.20 | 47.7 | 50.8 | 17.8 | 18.2 |
| | | | | | | | | Weighted avs. | 50.5 | 53.4 | 19.3 | 19.7 |
| Expt. 6 Vol. A 29.38 cm. (containing $C_2D_2$). Total $E_0$ 140 m. c. Vol. A' 29.37 cm. (containing $C_2H_2$) | | | | | | | | | | | | |
| 0 | 0 | 0 | 446.9 | 454.7 | ... | ... | ... | ... | .. | .. | .. | .. |
| 0 | 9 | 10 | 538.8 | 341.6 | 11.6 | 11.5 | +0.1 | +0.87 | 63.0 | 63.7 | 23.6 | 23.7 |
| 1 | 0 | 50 | 238.6 | 240.1 | 110.1 | 113.1 | −3.0 | −2.66 | 46.5 | 47.7 | 17.2 | 17.6 |
| 1 | 23 | 20 | 141.7 | 141.4 | 98.2 | 101.5 | −3.3 | −3.25 | 57.8 | 58.7 | 21.0 | 21.2 |
| 2 | 17 | 40 | 100.4 | 99.2 | 96.9 | 98.7 | −1.8 | −1.82 | 54.7 | 56.1 | 19.2 | 19.7 |
| 5 | 2 | 40 | 47.5 | 47.0 | 41.3 | 42.2 | −0.9 | −2.14 | 50.3 | 50.3 | 16.7 | 16.7 |
| | | | | | | | | Weighted avs. | 53.3 | 54.0 | 18.8 | 19.0 |

adsorbed.[9] It should be noted that water having reacted with calcium carbide and combined as calcium hydroxide cannot be driven out and made to react with uncombined calcium carbide. When vessel C was heated with stopcocks closed, a pressure of 12 cm. was built up and a brown product (probably due to polymerization) condensed on the cooler portions of the apparatus. When, however, the water was allowed to distil out into D it came over very quickly and quantitatively.

**Results.**—The average values of the ratio $-M/N$ from three preliminary experiments are given.

| | Vol. bulb, cc. | Diam., cm. | Millicuries Radon | $-M/N$ |
|---|---|---|---|---|
| Expt. 1 | 4.746 | 2.085 | 22.24 | 22.0 |
| Expt. 2 | 11.331 | 2.787 | 27.91 | 20.2 |
| Expt. 3 | 11.370 | 2.790 | 2.632 | 20.0 |

The average value reported by Lind, Bardwell and Perry,[6] using the same method of calculation (average path method) and the same constants, was 19.8.

In Table I are given the results of three of the differential comparisons.

## Conclusion

We conclude that the two rates are equal within the limits of experimental error. Since the chemical action under alpha-radiation is proportional to the ionization, several other factors may be assumed to be equal within these same limits: namely, the probability of ionization of the light and heavy acetylene molecules (which we may term their relative molecular ionization), their stopping power and probably their total ionization by a stream of electrons may also be assumed equal, which is of importance in the positive ray method of analysis of heavy hydrogen and its compounds.

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[9] Only a negligible quantity of gas could be produced in that way, confirming the purity of calcium carbide.

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON]

# Polymorphism in the FeS–S Solid Solutions. I. Thermal Study

BY HOWARD S. ROBERTS

The FeS–S solid solutions form a small portion of the system Cu–Fe–S investigated at the Geophysical Laboratory by Lombard and Merwin. Their work,[1] which was confined chiefly to the difficult problem of determining the compositions and fields of stability of the solid phases, raised several collateral questions of considerable interest.

In the case of solid solutions of S in FeS several kinds of evidence indicate that these solutions may exist in different polymorphic forms. Lombard and Merwin point out that a sharp break in magnetic properties of the series appears about midway of the sulfur content.

Thermal studies[2] by Rinne and Boeke show a thermal change in the compound FeS at 144°. Allen, Crenshaw, Johnston and Larsen[3] were able to crystallize pyrrhotite from solutions and obtained hexagonal crystals at 80° and orthorhombic crystals above 200°.

Ziegler,[4] in an investigation of the magnetic properties of pyrrhotite, found that its saturation magnetization decreased steadily as the temperature was raised, until 320° was reached, where it dropped suddenly to zero. He attributed this break in the curve to an allotropic transformation. At the same temperature Chevenard[5] observed a discontinuity in the coefficient of expansion; while in magnetite he found that the coefficient of expansion passed through a maximum near the Curie point but showed no discontinuity.

x-Ray powder spectra[6] of these solid solutions at room temperature are reported to form a continuous series from FeS to the sulfur-rich limit, giving no evidence of any abrupt change in structure.

At the beginning of this investigation a few x-ray powder photographs were made with the sul-

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[1] Summarized in Carnegie Institution of Washington Year Book, **25**, 62–69 (1926), and **30**, 82–84 (1931).

[2] Rinne and Boeke, *Z. anorg. allgem. Chem.*, **53**, 338 (1907).

[3] Allen, Crenshaw, Johnston and Larsen, *Am. J. Sci.*, **33**, 169 (1912).

[4] Ziegler, *Mitt. Phys. Ges. Zürich*, **17**, 1 (1915); abstracted in *Beiblätter Ann. Physik*, **40**, 61 (1916).

[5] Chevenard, *Compt. rend.*, **172**, 320 (1921).

[6] (a) Alsen, *Geol. För. Stockholm Förh.*, **47**, 19 (1925); (b) Hägg and Sucksdorff, *Z. physik. Chem.*, **B22**, 444 (1933); (c) Juza, Biltz and Meisel, *Z. anorg. allgem. Chem.*, **205**, 273 (1932).