THE STATE DIAGRAM OF ACETYLENE.

By Ryo Kiyama, Tatsuya Ikegami and Kazuo Inoue.

Introduction.

Recently, acetylene chemistry under pressure is prospering, but the states of the diagrams of acetylene under pressure have not been reported in literatures, except Sameshima's[1] and Rimarski's[2] data under the conditions of low temperature and low pressure (0~25°C, 1~20 atm). The authors measured, therefore, the pressure-volume-temperature relation of acetylene under the conditions of higher temperature and higher pressure.

Experimental apparatus and procedure.

The volume change is observed under pressure at constant temperature in a transparent pressure proof capillary tube[3]. The whole and each part of the apparatus are shown in Figs. 1 and 2. A glass piezometer consists of the capillary
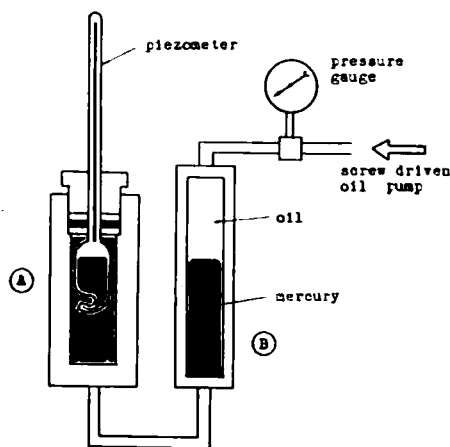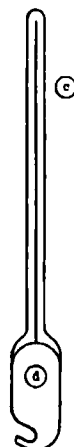

Fig. 1

Fig. 2

part c, about 35 cm in length and 1.0~1.2 mm in inner diameter, and the swelling part d set in a mercury pool of the steel bomb A. The one end of the capillary

1) J. Sameshima, *Bull. Chem. Soc., Japan*, 1, 41 (1926)
2) W. Rimarski, *Autogene Metallbearbeitung*, 26, 129 (1933)
3) R. Kiyama and K. Inoue, *This Journal*, 21, 73 (1951)

part is sealed and the volume per unit length is measured along the whole length. The measured volume of the gas sample less than the atmospheric pressure is sealed[1] with mercury. The mercury head appears in sight at the c part under pressure and observed by means of a telescope, and the volume change is measured. The c part is heated only in an air bath. An oil pump is adopted as the pressure generator. The mercury from the steel bomb B comes into A and presses the gas. The pressure measured by the Bourdon-type gauges made by Schäffer Budenberg G. m. b. H. Magdeburg Buckau, which maximum pressure are 100 and 300 kg/cm^2 and are graduated at 1/3 and 1 kg/cm^2 respectively.

Material.

Acetylene gas from carbide is purified through an ordinary refiner*, and bubbled through the solutions,—sodium hydroxide, dil. sulphuric acid, chromic acid, mercuric chloride in hydrochloric acid, alkaline sodium thiosulphate and conc. sodium hydroxide to remove carbon dioxide, sulphur and phosphor compounds and oxygen,—and finally dried with calcium chloride and phosphorus pentoxide.

The purity of acetylene gas is tested qualitatively with barium hydroxide, silver nitrate and mercuric chloride in hydrochloric acid, and it is confirmed that carbon dioxide, phosphor and sulphur compounds are not contained in the gas. Acetylene and oxygen, etc. are determined quantitatively by the absorption, acetylene with fuming sulphuric acid**, oxygen with alkaline pyrogallol solution, residual acetylene with alkaline K$_2$IHg solution and carbon monoxide with ammoniac cuprous chloride solution. The residual gases are considered to be nitrogen and small amounts of hydrogen, methane, etc. The analytical results are shown in Table 1.

Table 1
Volume of percentage

C$_2$H$_2$	O$_2$	CO	residual	total
99.3	0.0	0.1	0.6	100.0

Purification by the solidification of acetylene is not adopted, according to the report[5] the purity by solidification being 98.7∼99.4 percent with fuming sulphuric acid.

4) R. Kiyama and H. Kinoshita, *This Journal*, 19, 43 (1945)

* The refining materials are the solid form of a mixture of FeCl$_3$, HgCl$_2$, copper acetate and acid clay.

** C$_2$H$_2$ is almost absorbed with fuming H$_2$SO$_4$, but still unsatisfactorily.

5) E. W. Steacie and R. D. McDonald, *J. Chem. Phys.*, 4, 75 (1936)

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Experimental results.

1) The experimental results are shown graphically in the two groups of Figs. 3 and 4.

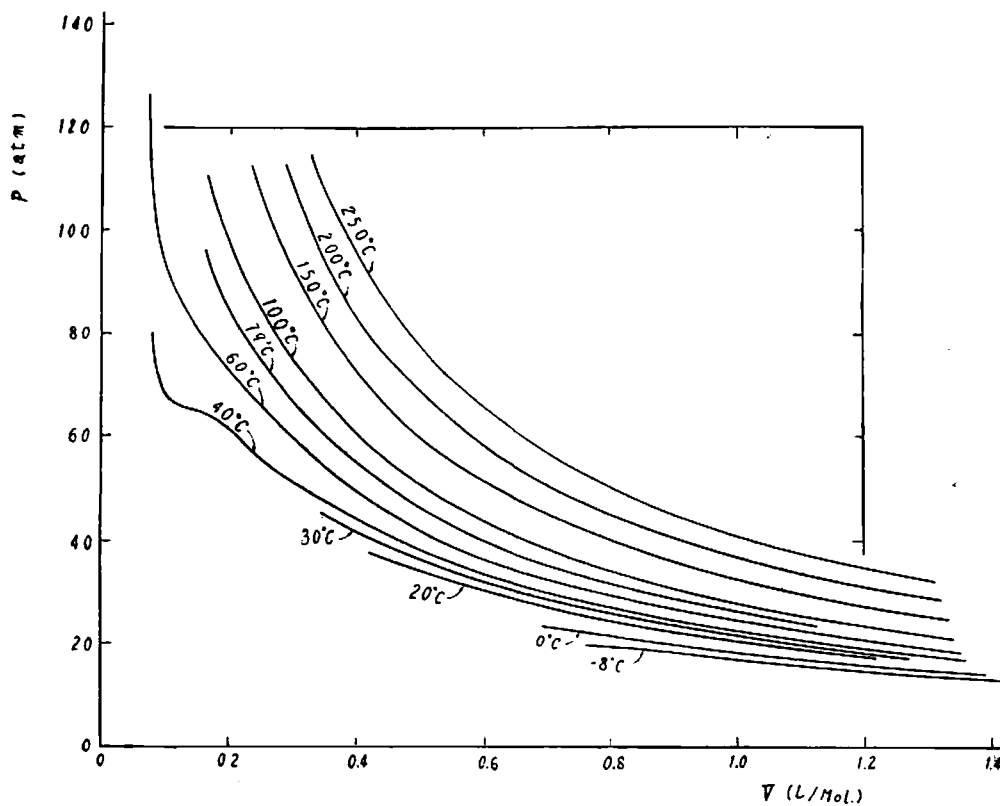Fig. 3 shows the pressure-volume (P-V) curves.
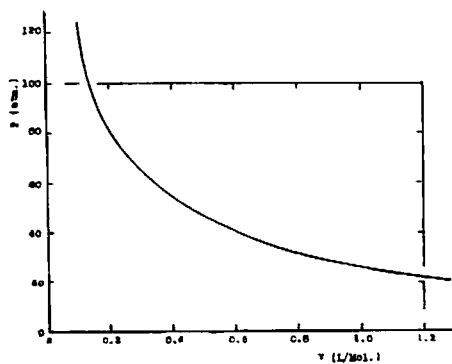

Fig. 3-1   P-V curves of acetylene.

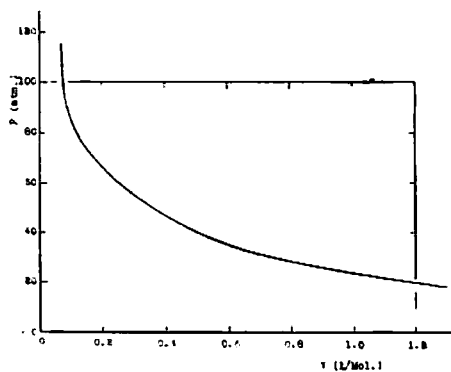Fig. 3-2   P-V curve of acetylene, 52°C

Fig. 3-3   P-V curve of acetylene, 72°C

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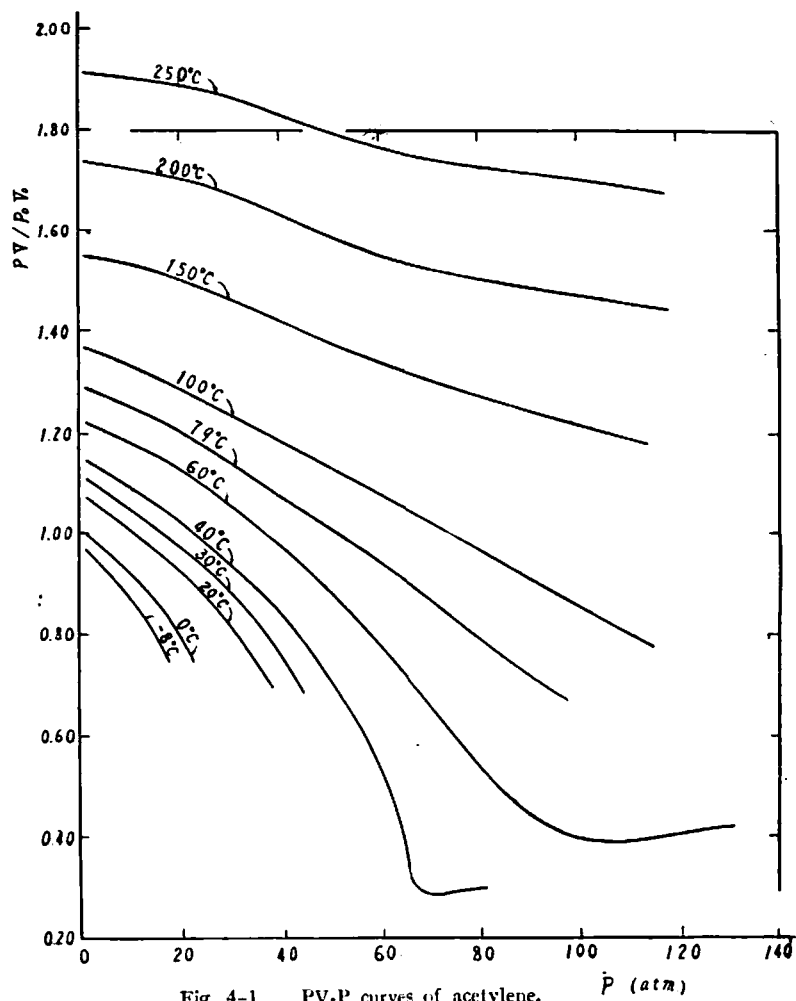Fig. 4 shows the pressure × volume-pressure (PV-P) curves.
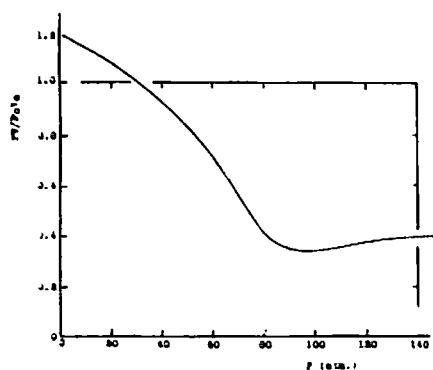

Fig. 4-1   PV-P curves of acetylene.
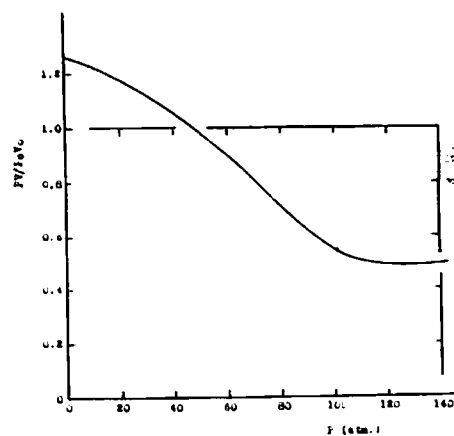

Fig. 4-2   PV-P curve of acetylene, 52°C

Fig. 4-3   PV-P curve of acetylene, 72°C

2) As the critical constants, 38.5°C, 64.0 atm are given[6].

Cosiderations.

1) Pressure measurements. The standard pressure gauges of Bourdon type tested with a dead weight tester are used in the experiments. The precision of the pressure gauges is 1/30 percent of their maximum pressures.

2) Temperature measurements. The temperatures are measured at the upper, middle, and lower points of the capillary part of the piezometer and the maximum fluctuation are 5/10, and 5/100°C at 80 and 100°C respectively. The temperatures of the middle point are recorded.

3) Volume measurements. The volume of the capillary part is calibrated by the weighing of a column of mercury which has previously been read to 1/20 mm with a cathetometer at every 1 cm. In the experiments, the height of the mercury head is read to 0.04 mm with a telescope. The observation errors are 2.0×10^{-4} and 1.4×10^{-4} cc for the capillaries of the piezometers of 1.2 and 1.0 mm inner diameter respectively.

4) Generally, the dissolution and chemical action of gases for the pressure transmitting liquid come into question. But, in the experiments, the authors do not take into consideration any physical and chemical actions between acetylene and mercury from the following reasons.

a) The change of the position of the mercury head is not observed at the constant temperature and pressure up to 250°C, 140 atm.

b) Any pressure creep is not found.

c) The values are found on the same curve, when the volume of the sample is changed and the measurement is repeated.

5) Condensation lines. Below the critical temperature, the pressure rise is not generally expected at condensation, but in the experiments is observed a small pressure rise.

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6) Ansdell, *Proc. Roy. Soc. London*, **29**, 209 (1879)
   D. McIntosh, *J. Phys. Chem.*, **11**, 306 (1907)
   MM. E. Cardoso and G. Baume, *Compt. rend.*, **151**. 141 (1910)
   O. Mass and C. H. Wright, *J. Am. Chem. Soc.*, **43**, 1098 (1921)
cf. The values of the critical constants of the above literatures are:
   $t_c=35.25$°C, $p_c=61.03$atm (Kuenen); $t_c=36.5$°C, $p_c=61.6$atm (McIntosh); $t_c=37.05$°C
   (Mathias); $t_c=37.05$°C, $p_c=68.0$atm(Ansdell); $t_c=35.5$°C, $p_c=61.6$atm (Cardoso, Baume);
   $t_c=36.5$°C(Mass, Wright).