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THE STATE DIAGRAMS OF FORMALDEHYDE AND FORMALDEHYDE-ACETYLENE MIXTURES.

By RYO KIYAMA and HIROSHI TERANISHI.

Introduction.

The state diagram of formaldehyde has not been reported in literatures, because of the difficulties due to the remarkable tendency of polymerization of the gas, except M. Trautz and E. Ufer's report⁽¹⁾ which states that the gas obeys the ideal gas law at pressures 568 ~ 672 mm Hg and temperatures 82 ~ 120°C. The authors measured, therefore, the pressure-volume-temperature relations of formaldehyde and its mixtures with acetylene under the conditions of pressures 2 ~ 30 atm and temperatures 120 ~ 200°C.

Experimental Apparatus and Procedure.

The volume change is observed under pressure at constant temperature in a transparent pressure proof capillary glass tube (piezometer)⁽²⁾. The capillary part of the piezometer is about 35 cm in length and 0.2 cm in inner diameter. The gas sample, which has been taken in a gas burette at room temperature and about 20 mm Hg pressure* and whose quantity has been precisely measured, is sealed with mercury in the piezometer⁽³⁾. Then the formaldehyde gas polymerizes rapidly as the pressure in the piezometer rises and approaches to 1 atm. To prevent the polymerization, the piezometer is previously heated at temperatures above 120°C in an air bath. In the case of mixtures of formaldehyde and acetylene, acetylene is sealed first and then formaldehyde in the same way, and the two gases are mixed in the piezometer. The piezometer, filled with the sample gas, is set in the pressure transmitting apparatus⁽⁴⁾, being carefully kept above 120°C. The pressure is measured by the Bourdon-type gauge made by Schäffer Budenberg G. m. b. H. Magdeburg Bucken, whose maximum pressure is 33 kg/cm². The gauge has been graduated at 1/10 kg/cm² and tested by means of a dead weight tester.

Materials.

Although paraformaldehyde, when heated above 120°C, depolymerizes into formaldehyde gas and water, the monomeric formaldehyde gas (CH₂O) which has 50

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- (1) M. Trautz and E. Ufer, *J. prakt. Chem.*, **113**, 105 (1926)
 - (2) R. Kiyama, T. Ikegami, and K. Inoue, *This journal*, **21**, 58 (1951)
 - (3) R. Kiyama and H. Kinoshita, " " **19**, 43 (1945)
 - (4) R. Kiyama and K. Inoue, " " **21**, 73 (1951)

* In the preliminary test, it was confirmed that the pure, dry formaldehyde gas, having 30 mm Hg pressure or below did not polymerize for several hours at room temperature.

mm Hg pressure or above is unstable, and polymerizes at room temperature or below especially rapidly when even a trace of water or oxygen is contained. Chemical drying agents, P_2O_5 and $CaCl_2$ etc., can not be used for removing the moisture from the formaldehyde gas; because they catalyse the polymerization. However, liquid formaldehyde (B.P. $-19^\circ C$) is comparatively stable and does not react with ice⁽⁵⁾. So in this work, the monomeric formaldehyde and water obtained by heating dry paraformaldehyde in vacuum to $120 \sim 150^\circ C$ in an oil bath, are cooled and fractionated to liquid formaldehyde and ice by the three traps which have been previously cooled by solid carbon dioxide and methanol. The sample gas is prepared by slow vaporization of the pure liquid formaldehyde collected in the last trap.^(5, 6, 7) The liquid formaldehyde is prepared at each experiment.

The preparation and purification of acetylene were reported in the previous paper.⁽²⁾

Results.

(1) The results of the measurements of the P-V-T relations of formaldehyde

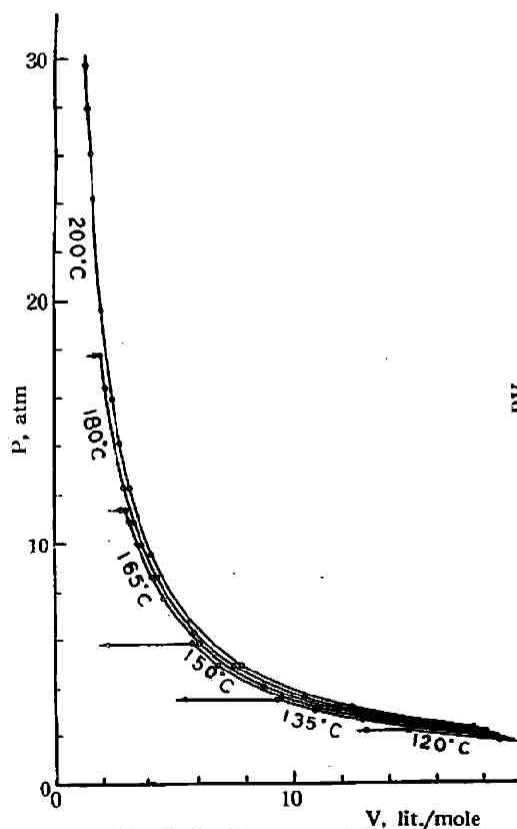


Fig. 1 P~V curves of formaldehyde.

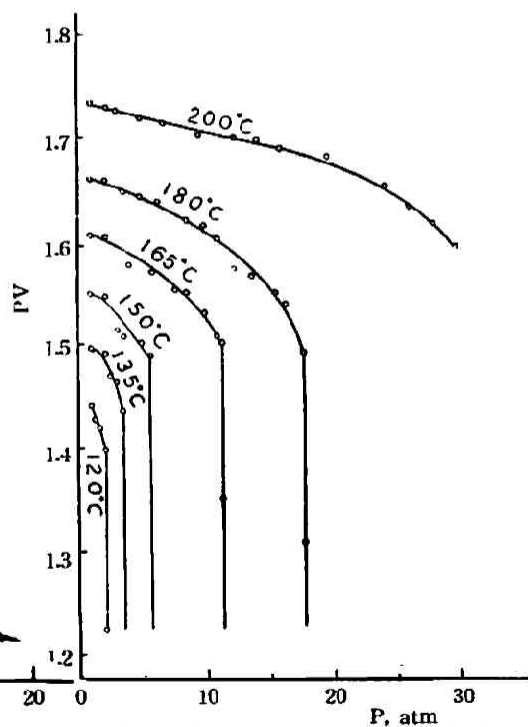


Fig. 2 PV~P curves of formaldehyde.

(5) J. F. Walker, *J. Am. Chem. Soc.*, 55, 2821 (1933)

(6) " " *FORMALDEHYDE*", Reinhold Publishing Corporation, N. Y. (1944)

(7) R. Spence and W. Wild, *J. Chem. Soc.*, 338 (1935)

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at 120°, 135°, 150°, 165°, 180°, and 200° C are shown in Figs. 1 and 2. Summarizing these results, we assume that the sample gases under 1 atm obey the ideal gas law at the experimental temperatures. P is the pressure in atmosphere unit converted from kg/cm^2 , V is the volume in litre/mole unit, and P_0V_0 (the value at the

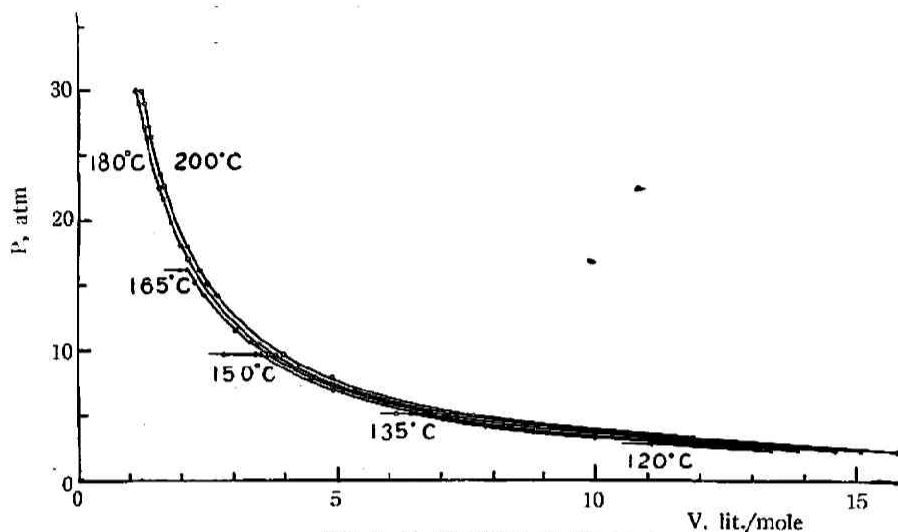


Fig. 3 P - V curves of mixture.
($\text{C}_2\text{H}_2 : \text{CH}_2\text{O} = 1 : 2$)

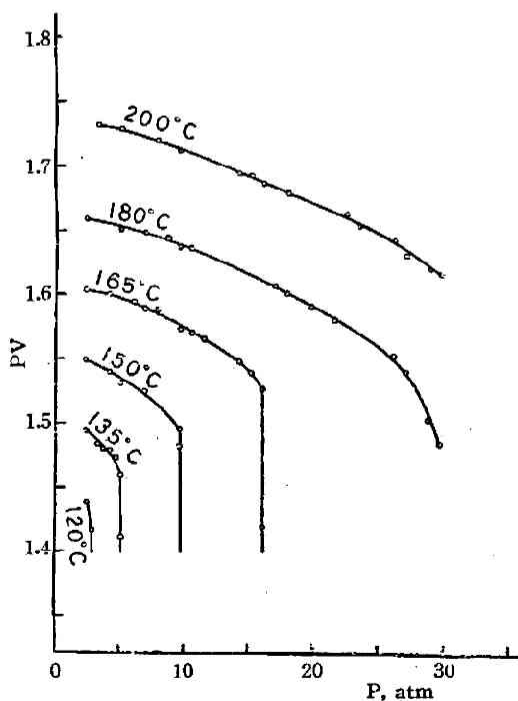


Fig. 4 PV - P curves of mixture.
($\text{C}_2\text{H}_2 : \text{CH}_2\text{O} = 1 : 2$)

standard state) is taken as an unit of PV . On the runs at temperatures 120°, 135°, 150°, 165°, and 180° C, the existence of the liquid is observed at the pressures 2.10, 3.44, 5.80, 11.34, and 17.74 atm respectively, but at 200° C the liquid is not observed up to 30 atm. On the run at 250° C, the gas volume at a constant pressure decreases slowly and after several hours a brown coloured product is observed on the inner wall of the piezometer, and the gas volume is not completely restored to the initial when pressure returns to 1 atm. On the run at 100° C, the gas volume decreases slowly at 1.24 atm and the white coloured polymer is produced on the inner wall of the piezometer.

(2) The results of the measurements of the P - V - T relations on the

mixture, having the mole ratio of $C_2H_2 : CH_2O = 1 : 2$, at 120° , 135° , 150° , 165° , 180° , and 200° C are shown in Figs. 3 and 4. On the runs at 120° , 135° , 150° , and 165° C, the existence of liquid is observed at the pressures 2.87, 5.15, 9.66, and 16.12 atm respectively, but at 180° C liquid is not observed up to 29.74 atm.

(3) The results of the measurements on the mixtures, having the mole ratios of $C_2H_2 : CH_2O = 1 : 0.1$, $1 : 0.5$, and $1 : 1$ at 150° C are shown in Fig. 5. In Fig. 5, the

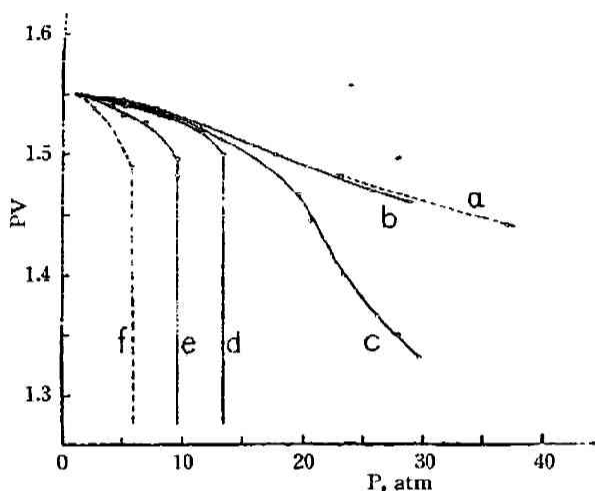


Fig. 5 PV~P curves at 150° C.

- a ... Acetylene (C_2H_2)
- b ... $C_2H_2 : CH_2O = 1 : 0.1$
- c ... " " 1 : 0.5
- d ... " " 1 : 1
- e ... " " 1 : 2
- f ... Formaldehyde (CH_2O)

a and f curves are the PV~P curve of pure acetylene⁽²⁾ and that of formaldehyde respectively. On the run of $C_2H_2 : CH_2O = 1 : 1$, the gas mixture is liquefied at 13.42 atm, and of $C_2H_2 : CH_2O = 1 : 0.5$, fine liquid droplets are observed at 26.13 atm, but the mixture does not separate into liquid phase and gas phase up to 29.72 atm and its PV~P curve shows no discrete point corresponding to the liquefying region. On the run of $C_2H_2 : CH_2O = 1 : 0.1$, the mixture is in a gaseous state up to 29.06 atm.

Considerations.

(1) Pressure measurements.

The standard pressure gauge of Bourdon type is used in the experiments. It is graduated at $1/10$ kg/cm² and its precision is ± 0.01 kg/cm² and is $1/30$ per cent of its maximum pressure.

(2) Temperature measurements. Each experimental temperature is kept constant within the fluctuation of $\pm 0.2^\circ$ C by the air bath and is measured at the middle point of the capillary part of the piezometer by a thermometer graduated at $1/10^\circ$ C.

(3) Volume measurements. The volume of the capillary part of the piezometer is calibrated by weighing a column of mercury whose length has previously been read to $1/20$ mm by means of a cathetometer at every 1 cm. In the experiments, the height of the mercury head is read in accuracy of ± 0.04 mm by means of a telescope, using a scale graduated at every 0.4 mm. The maximum observation error is 2.4×10^{-4} cc.

(4) As the critical temperature of acetylene is 38.5° C⁽²⁾ and that of formaldehyde seems to be above 180° C, the liquid observed at the above experiments on the mixtures will be formaldehyde. On every run at temperatures $120^\circ \sim 200^\circ$ C, the P~V

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relations show good coincidence between the both cases of increasing and decreasing pressure. And so neither irreversible polymerization of formaldehyde nor a chemical reaction between the components of the mixtures would occur under these conditions.

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