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THE SOLUBILITIES OF COMPRESSED ACETYLENE GAS IN LIQUIDS, I

The Solubility of Compressed Acetylene Gas in Water

BY HIROYUKI HIRAOKA

Introduction

The measurements of the solubility of compressed acetylene gas in acetone were performed early by M. P. E. Berthelot and P. M. E. Vieulle* and W. Siller* and recently by P. Hölemann and R. Hasselmann¹⁾. The measurements of its solubility in other liquids, however, have not been done yet. Now then, in this experiment, the solubility of compressed acetylene gas in water is measured in the range of pressure from 5 to 40 kg/cm² and that of temperature from 1 to 30°C, using the bubbling method. There is a plan to extend this study over other liquids.

Apparatus and Method

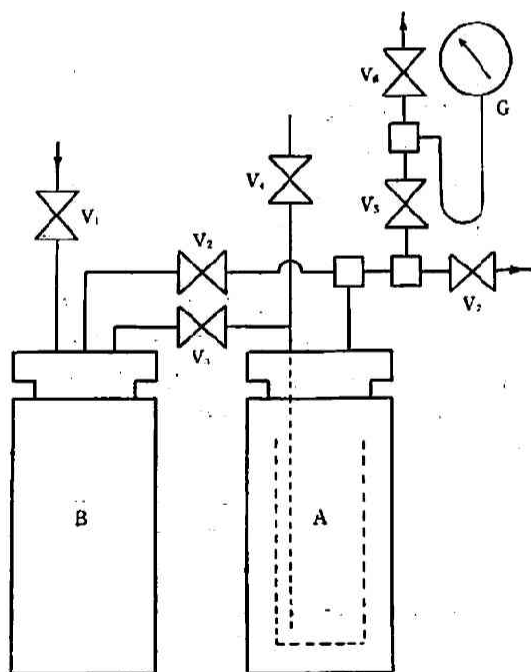


Fig. 1

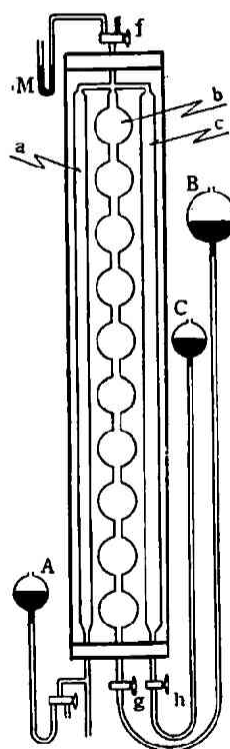


Fig. 2

* cf. 1)

1) P. Hölemann und R. Hasselmann, *Chem. Ing. Tech.*, 25, 466 (1953)

The experimental apparatus consists of the parts of the high pressure cylinders and the liquid phase analyser shown in Figs. 1 and 2, respectively. In Fig. 1, a glass vessel of about 400cc, in which water is filled to one third capacity at the start of each run, is inserted into a cylinder A. The end of the pipe (1mm in inner diameter) shown by a dotted line in the cylinder, is about 2cm apart from the bottom of the glass vessel. A large cylinder B of about 300cc capacity is used as a reservoir to keep the pressure fluctuation as small as possible during the sampling and also in the course of the bubbling procedure, and moreover serves to make the temperature of the inlet gas that of the thermostat previously. A, B and their pipe lines between them are below the level of the water in the thermostat, which is held at constant temperature within $\pm 1/20^\circ\text{C}$. V's are high pressure valves and G is a Bourdon type gauge by which pressure can be read accurately within the error of 1 % of the pressure used. The samples are taken out through V_4 , which is connected to the apparatus of the liquid phase analyser shown in Fig. 2. In Fig. 2, a is a liquid burette graduated to 0.05cc, b a gas burette, each bulb of which having 35cc capacity and c also a gas burette graduated to 0.1cc. A, B and C are mercury reservoirs belonging to a, b and c, respectively. M is a manometer, by means of which the pressure in the burettes is kept at the barometric one. All the burettes are held in the water jacket and kept at constant temperature by circulating water.

The purity of acetylene gas is from 99.5 to 99.6% and the water used as a solvent is free from the carbon dioxide dissolved in a distilled water.

The procedures to establish the equilibrium from both sides of the high pressure and the low pressure are the same as adopted by R. Wiebe et al.²⁾ to bring about the equilibrium and from the results obtained no difference is found between the two approaches.

The experiment is conducted in the following manner. Acetylene gas is introduced into the part of high pressure through V_1 to replace the air in it, and compressed to a nearly desired pressure, then all valves except V_2 are closed. After keeping the thermostat at the desired temperature, the gas is bubbled at the rate of about 2 litres per minute. On carrying out the bubbling procedure, V_3 is opened and V_2 is closed. Then the compressed gas is led into the apparatus through V_1 and is allowed to expand to the atmosphere through V_7 , so as to keep the pressure at a required level, which is several to ten per cent higher or lower than a desired pressure, using the pressure gauge of the compressor. After this procedure V_7 is closed, V_5 opened and the gas allowed to escape through V_6 to keep a desired pressure by means of the gauge G. After the bubbling procedure is finished, V_2 is opened and V_1 , V_3 and V_6 are closed. If the pressure change is recognized standing at rest for several hours, the gas is bubbled again at a desired pressure, because the system is not in equilibrium.

2) V. L. Gaddy, R. Wiebe and C. Heins, *Ind. Eng. Chem.*, 24, 823 (1932); *J. Am. Chem. Soc.*, 55, 947 (1933)

After equilibrium is established, the liquid phase analysis is carried on in the following procedure. First, V_4 is slightly opened in order to replace the gas in the pipe between V_3 and V_4 with the saturated solution. Then both heads of the mercury columns of manometer being balanced, the cock f is closed. As V_4 is slightly released, the cock g or h is opened and the bulk of gas separated from the water is collected in the gas burettes, nearly at the barometric pressure by the mercury reservoir B or C. After a certain quantity of the sample is taken out, V_4 is closed and the pressure in the burettes is kept correctly at the barometric one. The quantity of the liquid samples taken out is 3 or 5 cc. After standing for a long time in order to reach the equilibrium at the temperature of the water jacket and the barometric pressure, the liquid and the gas are measured in the burettes of the liquid and gas, respectively. The pressure drop in the high pressure apparatus due to the sampling is recovered so rapidly that the pressure fall would not give the measurable influence on the equilibrium in the apparatus. The pressure fall observed is within 1% of the total pressure. According to the above mentioned procedure, the next sampling is performed in succession. The results of these measurements are reproducible at each temperature and pressure.

Results

The results expressed as the number of cc of acetylene (S. T. P.) contained in 1 g of water, which is denoted by γ hereafter, are given in Table 1. In Fig. 3 the number of cc of the gas (S. T. P.) per gram of water is plotted against the total pressure or

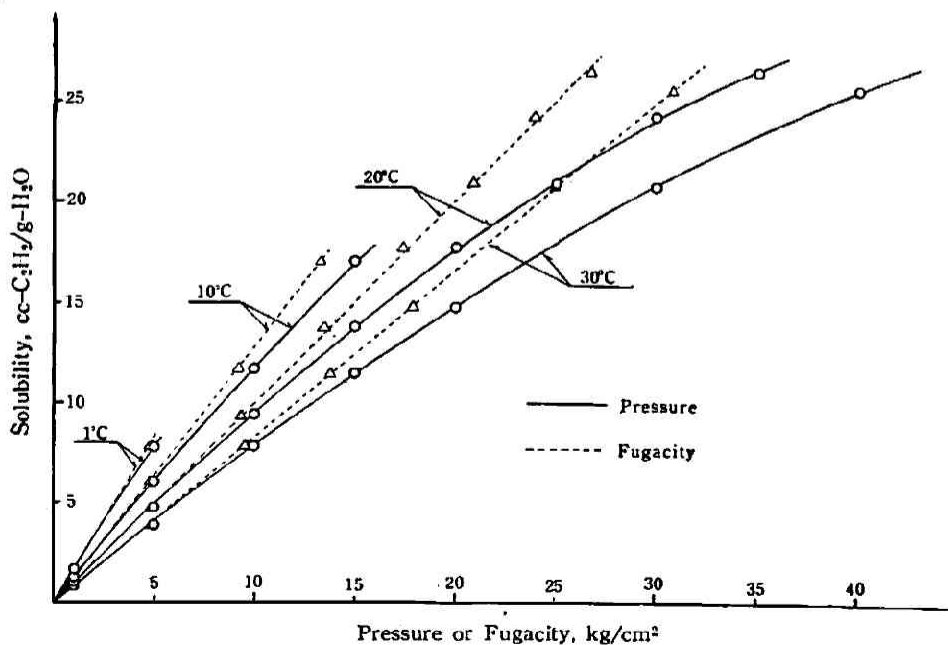


Fig. 3

Table 1 The solubility of acetylene in water
(cc-C₂H₂/g-H₂O)

Temp. °C Press. kg/cm ²	1	10	20	30
5	7.82	6.07	4.81	3.88
10		11.7	9.40	7.83
15		17.0	13.8	11.5
20			17.7	14.8
25			20.9	—
30			24.2	20.7
35			26.5	—
40				25.6

Table 2 The absorption coefficient of acetylene
in water (cc-C₂H₂/cc-H₂O/kg/cm²)

Temp. °C Press. kg/cm ²	1	10	20	30
1.033*	1.63	1.27	1.00	0.81
5	1.64	1.26	0.992	0.795
10		1.27	1.00	0.824
15		1.29	1.02	0.833
20			1.02	0.826
25			1.01	—
30			1.01	0.831
35			1.00	—
40				0.831

* The values of L. W. Winkler

the fugacity of the acetylene. In order to correct for the gas quantity dissolved in the liquid burette, the values of L. W. Winkler³⁾ are added to the amounts obtained from the gas burettes. The total pressure is assumed to be equal to the partial pressure of the acetylene gas in the high pressure apparatus, because the vapor pressure of water is negligible compared with the partial pressure of acetylene, while the vapor pressure of water in the burettes is taken into account, as it is not to be neglected with the barometric pressure. In Table 2 the absorption coefficients of acetylene in water defined by equation (1) are given,

$$\alpha = \frac{V_0}{f \cdot V_L} \quad (\text{cc-C}_2\text{H}_2/\text{cc-H}_2\text{O/kg/cm}^2) \quad (1)$$

where f is the fugacity of acetylene gas and V_0 is the number of cc of the gas (S.T.P.) dissolved in V_L cc of the liquid and in the values of Table 2 the density of the water

3) L. W. Winkler, *Landolt-Börnstein*, 1, 767; *Int. Crit. Table*, 3, 260

is assumed to be 1.00g. It is noticed from Table 2 that the absorption coefficient is constant at each temperature.

Table 3 The fugacity of acetylene
(kg/cm²)

Temp. °C Press. kg/cm ²	0	10	20	30
5	4.76	4.82	4.85	4.88
10	9.05	9.24	9.36	9.50
15	12.89	13.26	13.53	13.81
20	16.24	16.88	17.34	17.83
25		20.10	20.82	21.53
30		22.89	23.94	24.92
35			26.70	28.01
40			29.10	30.78
45				33.21

The fugacity of acetylene gas is calculated by graphical integration using the state diagram measured by R. Kiyama et al.⁴⁾ and equation (2),

$$\ln \frac{f}{P} = - \int_0^P \frac{1-Z}{P} dP, \quad Z = \frac{PV}{RT} \quad (2)$$

where f , P , V , T and R are fugacity, pressure, volume, absolute temperature and gas constant, respectively. The values of the fugacities calculated from the diagram of R. H. Newton⁵⁾ are about 2% lower than those given in Table 3.

From Fig. 3 or Table 2, equation (3) is derived,

$$\gamma = K \cdot f \quad (\text{cc-C}_2\text{H}_2/\text{g-H}_2\text{O}) \quad (3)$$

where K is constant, and numerically equal to α in this experiment.

In Tables 1 and 2, and Fig. 3 the data above 5kg/cm² at 1°C and 15kg/cm² at 10°C are not given, because the measurement is not to be performed owing to the abnormal phenomena described below, which take place above 7kg/cm² at 1°C and 20kg/cm² at 10°C. That is to say, under these conditions the circulation of the gas is frequently interrupted. From the gradual decrease of the pressure at rest after the bubbling procedure, it may be assumed that the equilibrium is not established. In the case above mentioned a small quantity of the water evolves a large quantity of the gas which is unable to be measured by the present apparatus. So, it should be considered that some substance, maybe acetylene hydrate*, is formed at these temperatures and pressures, and the solution becomes high viscous due to this substance.

4) R. Kiyama, T. Ikegami and K. Inoue, *This Journal*, 21, 58 (1951)

5) R. H. Newton, *Ind. Eng. Chem.*, 27, 302 (1935)

* The details of this hydrate will be reported.

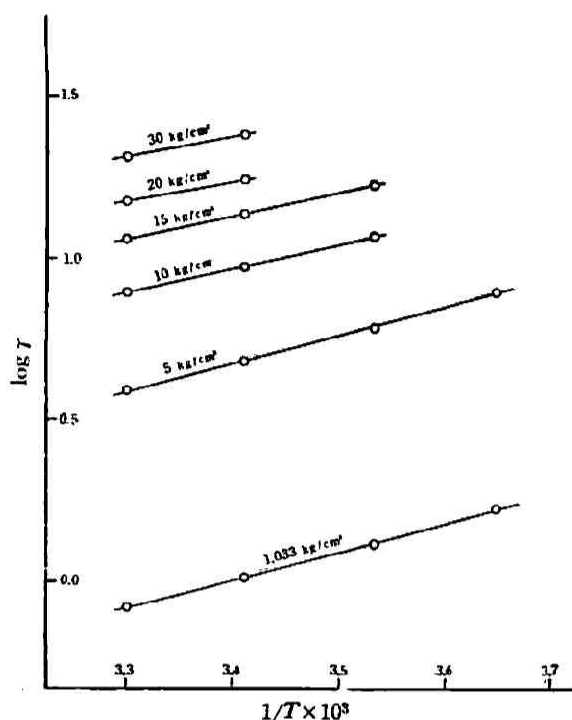


Fig. 4

Table 4 The heat of solution (Kcal/mole)

Pressure, kg/cm ²	Q
1.033	3.96
5	3.96
10	3.44
15	3.35
20	3.28
30	2.80

If the heat of solution is expressed by Q and assumed to be constant at a given pressure in the temperature range of this experiment, the relation between Q and absolute temperature T , is thermodynamically given by equation (4), which holds for the present acetylene water solution from equation (3),

$$\ln \gamma = \frac{Q}{RT} + C, \quad (4)$$

where Q is positive in the case of exothermic dissolution and C constant. A plot of values of the logarithm of the solubility as a function of the reciprocal of absolute temperature is given in Fig. 4, and the values of the heat of the solution calculated, using equation (4), are given in Table 4. As will be seen from Fig. 4, straight lines are obtained for any pressures and the heat of solution is decreased with the increase of pressure.

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