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VAPOR-LIQUID EQUILIBRIA IN THE SYSTEMS: CO_2-CO, CO_2-CO-H_2 AND CO_2-CH_4

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Vapor-liquid equilibria of the CO_2–CO, CO_2–CO–H_2 and CO_2–CH_4 systems were measured by the static method at −40 to 10°C. Also, for the CO_2–CH_4 system, orthobaric densities at dew and bubble points were determined by using a glass capillary tube at 10 and 20°C. And the *P-V-T* relations of homogeneous gas and liquid phases were also measured up to 200 atm.

Introduction

Few data on vapor-liquid equilibria at high pressures have been published, especially in the systems of liquefied gas and permanent gas. The authors have reported on the vapor-liquid equilibria containing ammonia[1)~5)] or carbon dioxide[6)] as a solvent. As a continuation, the CO_2–CO, CO_2–CO–H_2 and CO_2–CH_4 systems were further investigated. But similar measurements were performed by Donnelly *et al.*[7)] for the last system. These data may be very useful for the separation of carbon dioxide mixture by liquefaction.

CO_2-CO and CO_2-CO-H_2 Systems

Experimental Apparatus and Procedure

The schematic diagram of the experimental apparatus is illustrated in Fig. 1. The accuracies of temperature and pressure in this experiment were ±0.05°C and ±0.1 atm, respectively. To determine the compositions of vapor and liquid phases by the volumetric method, carbon dioxide was absorbed into a KOH solution and carbon monoxide into a cuprammonium solution.

The purities of carbon dioxide, carbon monoxide and hydrogen were more than 99.96 per cent, 99.8 per cent and 99.98 per cent respectively.

Experimental Results

The experimental results for the CO_2–CO system are shown in Fig. 2 and those for the CO_2–CO–

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2) G. Kaminishi and T. Toriumi, *ibid.*, **10**, 61 (1961)
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6) G. Kaminishi and T. Toriumi *ibid.*, **69**, 175 (1966)
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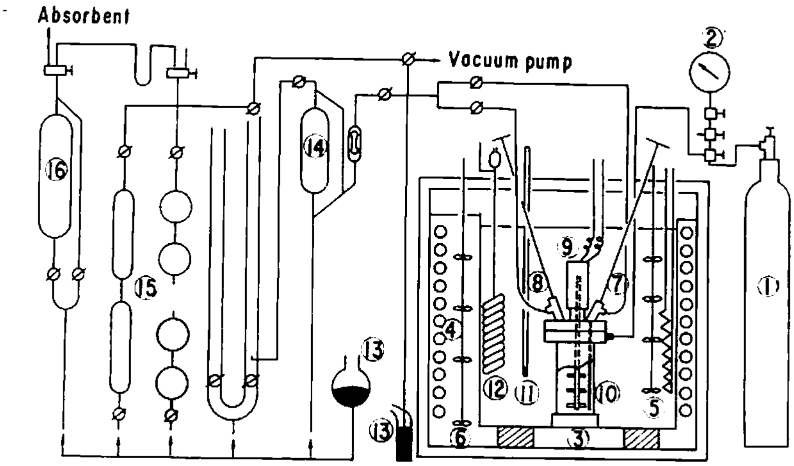

Fig. 1 Schematic diagram of the experimental apparatus (static method)
1: sample gas bomb, 2: pressure gauge, 3: methanol bath, 4: cooling tube, 5: heater, 6: stirrer, 7: liquid sample valve, 8: gas sample valve, 9: magnetic agitater, 10: equilibrium cell, 11: thermometer, 12: temperature regulator, 13: mercury, 14: Toepler pump, 15: burettes for measuring gas volume, 16: burettes for analyzing gas composition

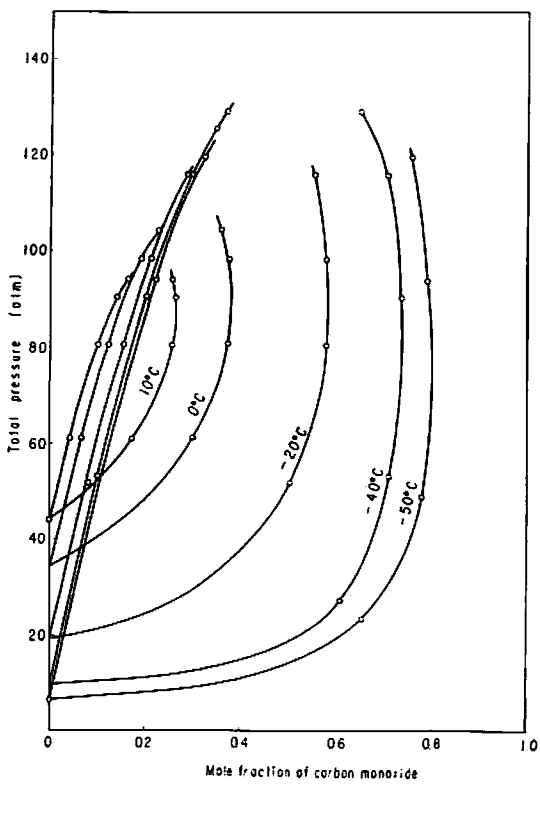

Fig. 2 P-X diagram for the CO_2-CO system

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H_2 system in Fig. 3. The equilibrium values of the binary CO_2-H_2 system in Fig. 3 are cited from the previous paper[6].

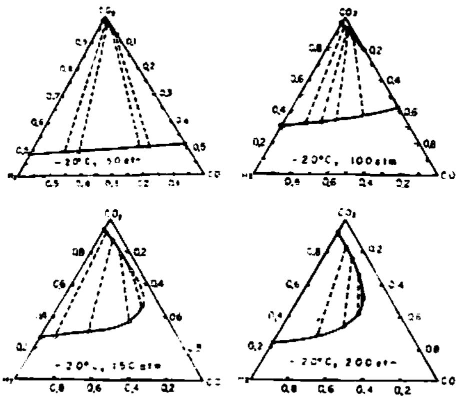

Fig. 3-a Vapor-liquid equilibria for the CO_2-CO-H_2 system at constant temperature

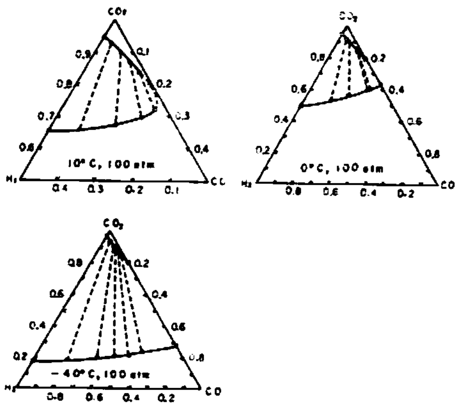

Fig. 3-b Vapor-liquid equilibria for the CO_2-CO-H_2 system at constant pressure

CO_2-CH_4 System

Vapor-liquid equilibria of the CO_2-CH_4 system were measured by the same method described in the above section. This system was further investigated by measuring dew and bubble points at 10 and 20°C. Orthobaric densities and the P-V-T relations of homogeneous gas and liquid phases were also measured. By using these data the partial molal volume, the activity coefficients and other properties concerning equilibrium can be evaluated*.

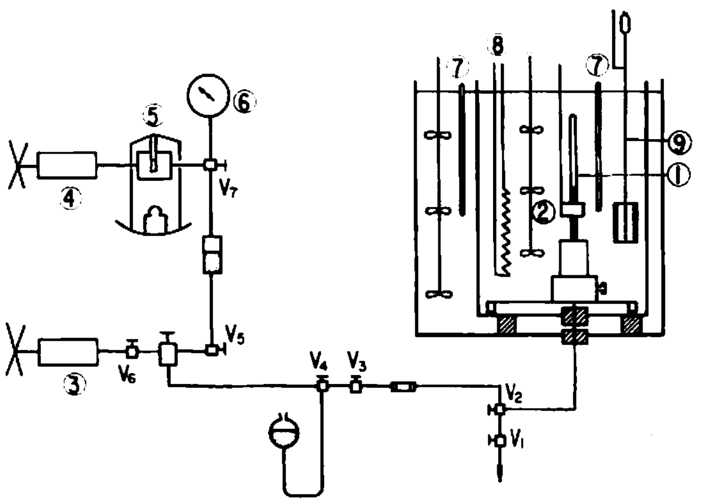

Fig. 4 Schematic diagram of the experimental apparatus (dew-bubble point method)
1: equilibrium cell
2: stirrer
3: mercury pump
4: oil pump
5: dead weight gauge
6: Bourdon gauge
7: thermometer
8: heater
9: temperature regulator

* Evaluated values will be published in a forthcoming paper.

Experimental Apparatus and Procedure

The experimental apparatus is shown in Fig. 4 and the details of the equilibrium cel in Fig. 5. The capillary has a 2.6 mm inner diameter and a 9 mm outer diameter; it is 300 mm in length and can be used up to 250 atm. A mixed gas, of which the composition and total mole were known, was compressed by mercury in this capillary and volume and phase changes were observed through a cathetometer. To examine this apparatus vapor pressure and saturated densities of vapor and liquid carbon dioxide were measured and compared with the data available in literature[8]. The maximum deviation from the literature value was less than 0.5 per cent. The purity of methane was more than 99.64 per cent.

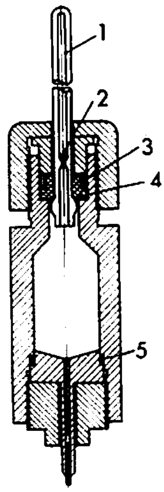

Fig. 5 Detail of the equilibrium cell
1: capillary tube
2: steel ball
3: steel collar
4: teflon gasket
5: teflon gasket

Experimental Results and Discussion

The composition-pressure diagram at constant temperature is shown in Fig. 6. In this figure ○ plots show the data by the static method and × plots the data by the dew-bubble point method. As shown in Fig. 6 they agree well. But discrepancies from the interpolated data by Donnelly *et al.*[7] are seen especially in the region near the critical point. Fig. 7 shows the relation between orthobaric density and pressure at 10°C. As shown in this figure the following equation, which is obtained by substituting temperature by pressure in Cailletet-Mathias' law, holds for a binary mixture.

$$\frac{d_g+d_l}{2}=d_c+a\left(1-\frac{p}{p_c}\right) \qquad (1)^{**}$$

Critical pressures and densities at 10°C and 20°C were determined graphically and summarized in Table 1.

Figs. 8 and 9 show the compressibility factor and the molal volume of homogeneous gas and liquid phases, respectively.

8) "International Critical Tables" vol. 3 (1928)

** In this equation the subscripts, g and l denote gas and liquid phases, and c critical point.

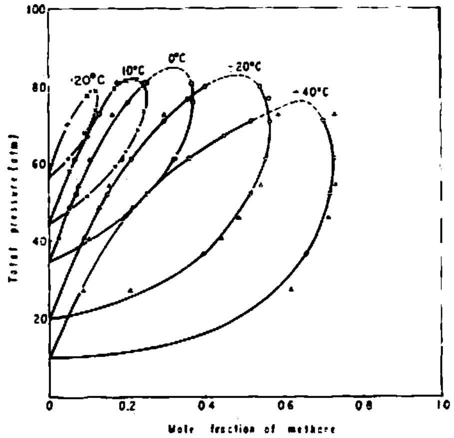

Fig. 6 P-X diagram for the CO_2-CH_4 system
Present work: ○ (static method), × (dew-bubble point method)
Donnelly *et al.*[7]: △

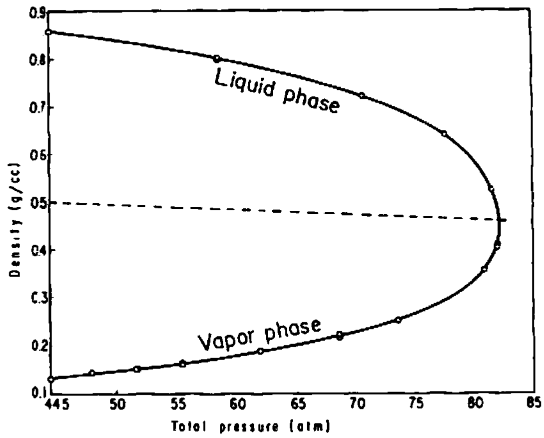

Fig. 7 Orthobaric density of for the CO_2-CH_4 system at 10°C

Table 1 Critical properties for the CO_2-CH_4 system

t (°C)	p_c (atm)	d_c (g/cm³)
10	82.2	0.464
20	79.2	0.466

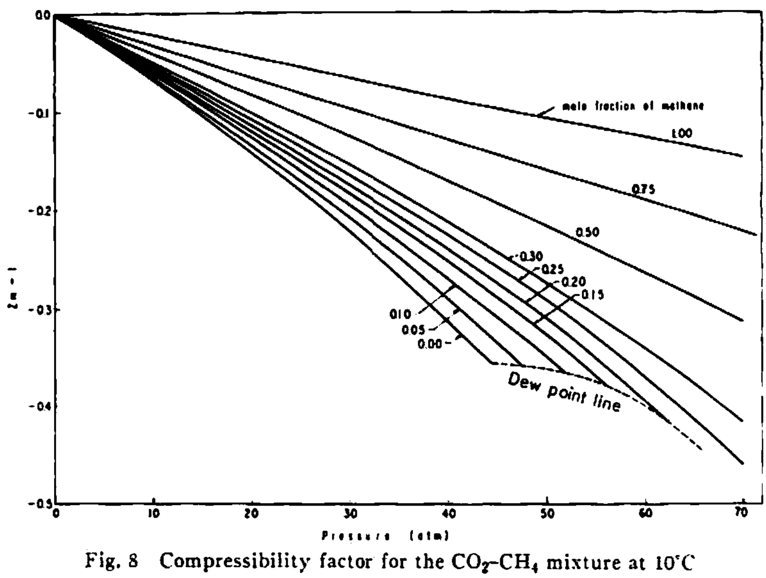

Fig. 8 Compressibility factor for the CO_2-CH_4 mixture at 10°C

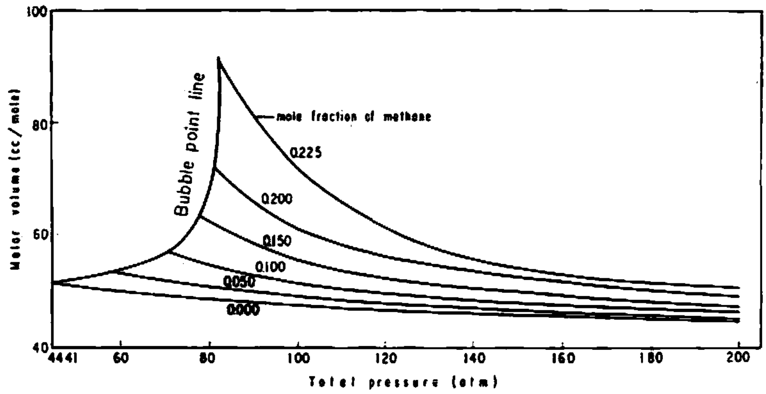

Fig. 9 Molal volume for the CO_2-CH_4 mixture at 10°C

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