

Title	Vapor-liquid equilibria in the systems : CO <sub>2</sub> -CO, CO <sub>2</sub> -CO-H <sub>2</sub> and CO <sub>2</sub> -CH <sub>4</sub> (The co-operative researches on the fundamental studies of the liquid phase reactions at high pressures)
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## VAPOR-LIQUID EQUILIBRIA IN THE SYSTEMS:



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Vapor-liquid equilibria of the  $\text{CO}_2\text{-CO}$ ,  $\text{CO}_2\text{-CO-H}_2$  and  $\text{CO}_2\text{-CH}_4$  systems were measured by the static method at  $-40$  to  $10^\circ\text{C}$ . Also, for the  $\text{CO}_2\text{-CH}_4$  system, orthobaric densities at dew and bubble points were determined by using a glass capillary tube at  $10$  and  $20^\circ\text{C}$ . And the  $P$ - $V$ - $T$  relations of homogeneous gas and liquid phases were also measured up to  $200\text{atm}$ .

## 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<sup>1)-5)</sup> or carbon dioxide<sup>6)</sup> as a solvent. As a continuation, the  $\text{CO}_2\text{-CO}$ ,  $\text{CO}_2\text{-CO-H}_2$  and  $\text{CO}_2\text{-CH}_4$  systems were further investigated. But similar measurements were performed by Donnelly *et al.*<sup>7)</sup> for the last system. These data may be very useful for the separation of carbon dioxide mixture by liquefaction.

 $\text{CO}_2\text{-CO}$  and  $\text{CO}_2\text{-CO-H}_2$  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  $\pm 0.05^\circ\text{C}$  and  $\pm 0.1\text{ atm}$ , 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  $\text{CO}_2\text{-CO}$  system are shown in Fig. 2 and those for the  $\text{CO}_2\text{-CO-}$

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- 1) G. Kaminishi and T. Toriumi, *Bull. Chem. Research Inst. of Non-Aqueous Solutions* (Tohoku University), **10**, 51 (1961)
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- 6) G. Kaminishi and T. Toriumi *ibid.*, **69**, 175 (1966)
- 7) H. G. Donnelly and D. L. Katz, *Ind. Eng. Chem.*, **46**, 511 (1954)

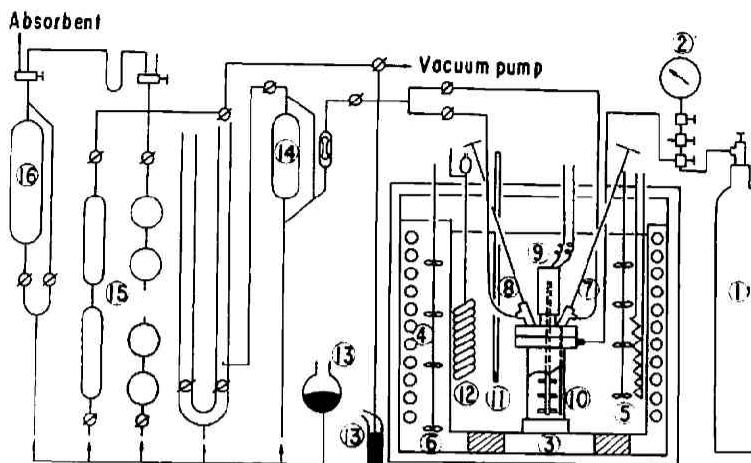


Fig. 1 Schematic diagram of the experimental apparatus (static method)  
 1: sample gas bomb, 2: pressure gauge, 3: methanol bath, 4: cooling tube, 5: heater, 6: stirrer, 7: liquid sample valve, 8: gas sample valve, 9: magnetic agitator, 10: equilibrium cell, 11: thermometer, 12: temperature regulator,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

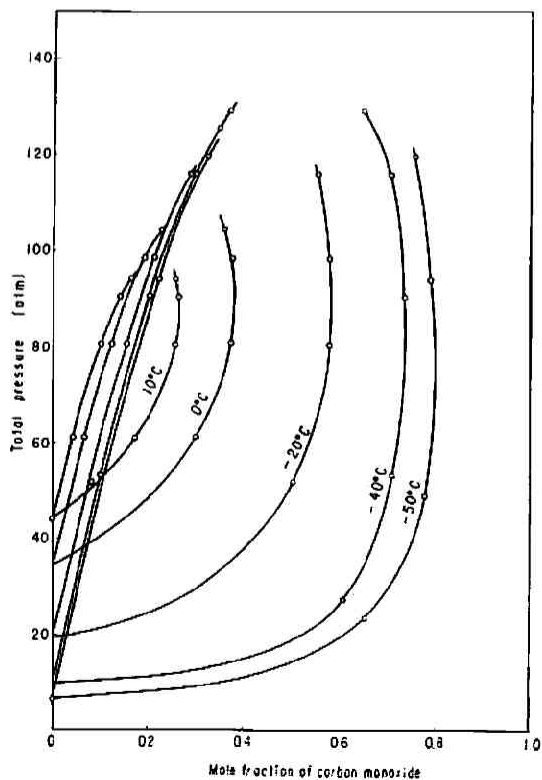


Fig. 2  $P$ - $X$  diagram for the  $\text{CO}_2$ - $\text{CO}$  system

$\text{H}_2$  system in Fig. 3. The equilibrium values of the binary  $\text{CO}_2\text{-H}_2$  system in Fig. 3 are cited from the previous paper<sup>6)</sup>.

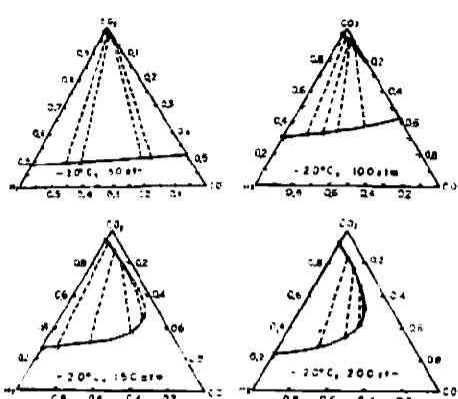


Fig. 3-a Vapor-liquid equilibria for the  $\text{CO}_2\text{-CO-H}_2$  system at constant temperature

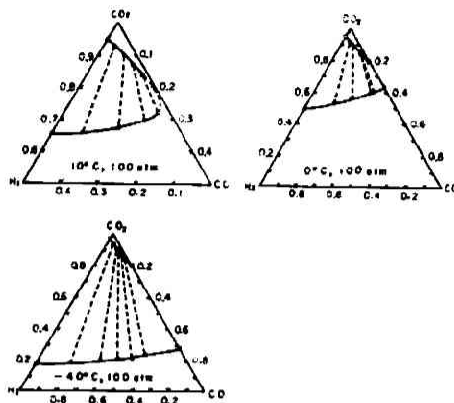


Fig. 3-b Vapor-liquid equilibria for the  $\text{CO}_2\text{-CO-H}_2$  system at constant pressure

$\text{CO}_2\text{-CH}_4$  System

Vapor-liquid equilibria of the  $\text{CO}_2\text{-CH}_4$  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  $P\text{-V-T}$  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\*.

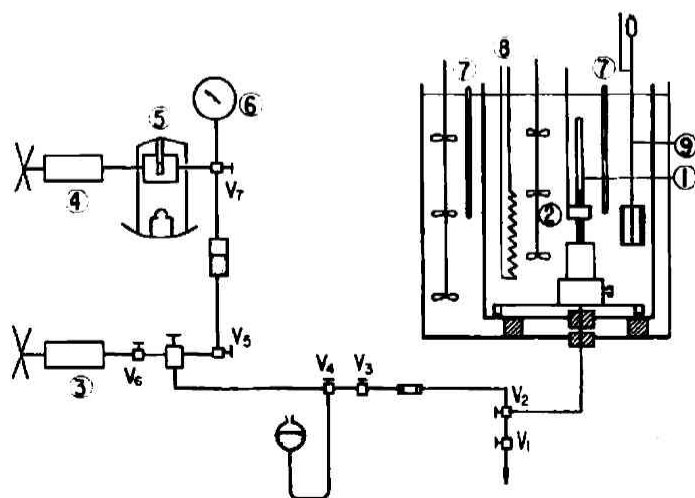


Fig. 4 Schematic diagram of the experimental apparatus (dew-bubble point method)  
 1: equilibrium cell  
 2: stirrer  
 3: mercury pump  
 4: oil pump  
 5: dead weight gauge  
 6: Bourdon gauge  
 7: thermometer  
 8: heater  
 9: temperature regulator

\* 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 cell in Fig. 5. The capillary has a 2.6mm inner diameter and a 9mm outer diameter; it is 300mm in length and can be used up to 250atm. 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<sup>8)</sup>. 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.

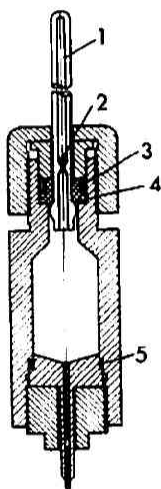


Fig. 5 Detail of the equilibrium cell

- 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 O 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.*<sup>7)</sup> 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.

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

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.

Vapor-Liquid Equilibria in the Systems:  $\text{CO}_2\text{-CO}$ ,  $\text{CO}_2\text{-CO-H}_2$  and  $\text{CO}_2\text{-CH}_4$

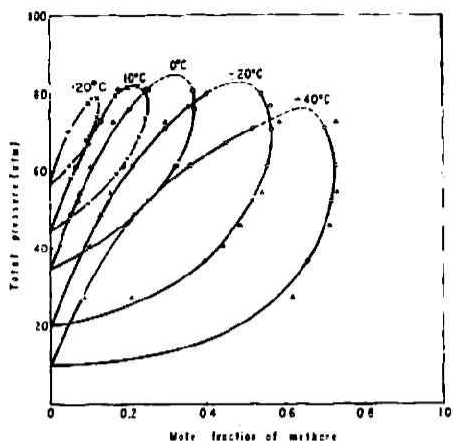


Fig. 6  $P$ - $X$  diagram for the  $\text{CO}_2\text{-CH}_4$  system

Present work: ○ (static method),  
 × (dew-bubble point method)  
 Donnelly *et al.*: △

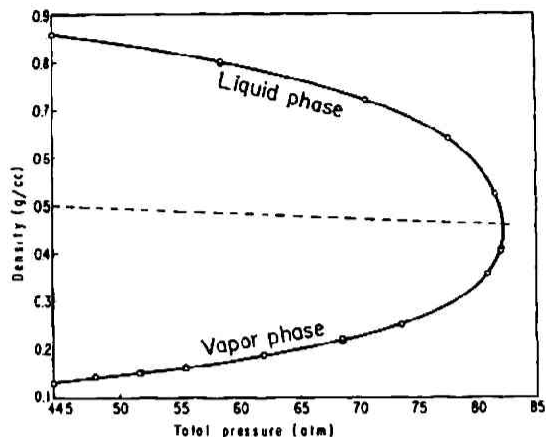


Fig. 7 Orthobaric density of for the  $\text{CO}_2\text{-CH}_4$  system at  $10^\circ\text{C}$

Table 1 Critical properties for the  $\text{CO}_2\text{-CH}_4$  system

$t$ ( $^\circ\text{C}$ )	$p_c$ (atm)	$d_c$ ( $\text{g}/\text{cm}^3$ )
10	82.2	0.464
20	79.2	0.466

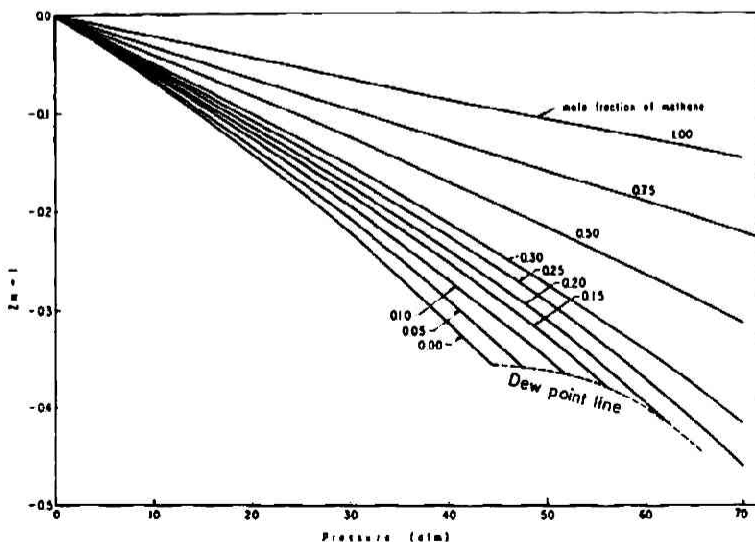
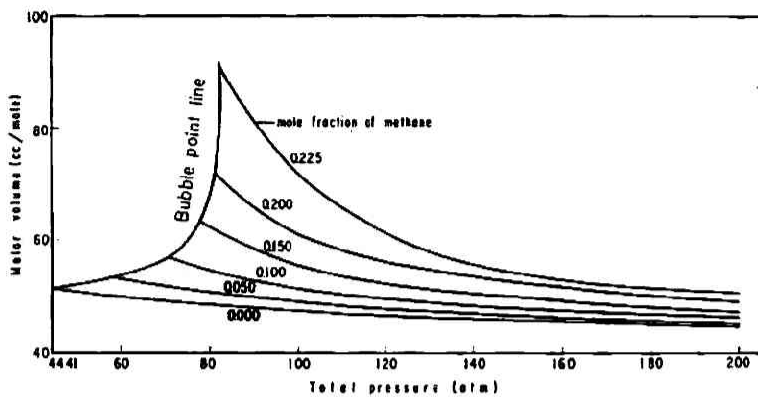


Fig. 8 Compressibility factor for the  $\text{CO}_2\text{-CH}_4$  mixture at  $10^\circ\text{C}$

Fig. 9 Molal volume for the  $\text{CO}_2\text{-CH}_4$  mixture at  $10^\circ\text{C}$ 

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