High-Pressure Vapor–Liquid Equilibrium Data of the 10-Component System Hydrogen, Carbon Monoxide, Carbon Dioxide, Water, Methane, Ethane, Propane, Methanol, Ethanol, and 1-Propanol at 313.4 and 333.4 K

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Isothermal vapor-liquid equilibrium data for the system H_2 + CO + CO_2 + H_2O + CH_4 + C_2H_6 + C_3H_8 + CH_3OH + C_2H_5OH + n-C_3H_7OH were measured with a static type equilibrium apparatus at 313.4 and 333.4 K and in the 8–17-MPa pressure range.

Introduction

Production of C_1 to C_6 alcohols from syngas is one of the most promising developments in C_1 chemistry.

The reaction mechanism, which obeys a Schultz–Flory polymerization law, leads to simultaneous production of alcohols and hydrocarbons. The rate of heavier alcohols and hydrocarbons decreases with their increasing carbon number. A water–gas shift reaction occurs as a side reaction. Therefore, it is necessary to know the vapor–liquid equilibria of the H_2, CO, CO_2, CH_4, C_2H_6, C_3H_8, H_2O, CH_3OH, C_2H_5OH, and n-C_3H_7OH system for separation process design. In a previous publication, we reported vapor–liquid equilibrium data on CO_2–alcohols, CH_4–alcohols, and C_2H_6–alcohols (*1*).

In this work, we report isothermal high-pressure vapor–liquid equilibrium data for the H_2, CO, CO_2, CH_4, C_2H_6, C_3H_8, H_2O, CH_3OH, C_2H_5OH, and n-C_3H_7OH system in the 313–333 K temperature range.

Experimental Section

Apparatus. The experimental apparatus and the operation procedure used in this work have been reported previously (*1*). Briefly, the apparatus consists of a static type equilibrium cell enclosed in an air bath and an analysis section enclosed in another air bath. The former air bath is controlled to the desired equilibrium temperature within an accuracy ±0.1 K by a PID controller equipped with a Pt sensor. The temperature of the analysis section was kept at 423 K within an accuracy ±1 K and was high enough above the equilibrium temperature.

The equilibrium cell of about 500 cm^3 has three pairs of diametrically opposed windows of 12-mm outer diameter for viewing the liquid level. The equilibrium pressure was measured within an accuracy of ±0.02 MPa by both a Bourdon gauge (Model GP35, Nagano Keiki Seisakusho, Ltd.) and a $4^1/_2$ digital gauge (Model GC-11, Nagano). Equilibrium temperature was measured within an accuracy of ±0.2 K by a Pt resistance probe (Shimaden Model SD-10) with digital readout to 0.1 K.

Sampling and Analysis. The gas and liquid samples in the cell were vigorously stirred with a magnetic coupled stirrer and were recirculated through sampling valves with magnetic pumps. After over 8 h of agitation, gas and liquid samples were introduced to sampling valves, flashed into the analysis section, and homogenized. For each phase, double sampling loops in the analysis section provided for two samples to be simultaneously sent to two gas chromatographs (Shimadzu Model GC-8) equipped with TCD. One gas chromatograph contained a Polapak-N column for analyzing H_2, CO, CH_4, C_2H_6, and C_3H_8 and a molecular sieve-13X column for analyzing CO_2. The other gas chromatograph contained a polyethylene glycol-6000 column combined with a poly(phenyl ether) column for analyzing H_2O, CH_3OH, C_2H_5OH, and n-C_3H_7OH.

The accuracy of calibration curves for gas and liquid materials was within 1% and 3% respectively. Earlier work using the same apparatus to measure high-pressure phase equilibria in the alcohols containing binary systems leads us to believe that the reproducibility obtained in this apparatus is 0.5%.

Materials. The materials used in this experiment are given in Table I. The composition of gas and liquid samples is typical for a C_1 to C_6 alcohols process. Standardized gas mixtures blended by Nippon Sanso Co., Ltd., were used for the gas feed. The liquid feed was made from weighed quantities of the pure components. Besides the liquid being degassed in the cell, materials were used without further purification.

Table I. Feed Composition

Gas

component	concn, mol %
H_2	balance
CO	16.7
CO_2	2.44
methane	30.6
ethane	4.57
propane	1.84

Liquid

component	concn, mol %
water	18.0
methanol	64.8
ethanol	12.8
1-propanol	4.4

List of Liquid Materials

component	purity, %	supplier
methanol	99.6	Wako Pure Chem. Ind. Co., Ltd.
ethanol	99.5	Wako Pure Chem. Ind. Co., Ltd.
1-propanol	99.5	Wako Pure Chem. Ind. Co., Ltd.
water		(ion-exchanged water)

Results

We measured vapor–liquid equilibria for the 10-component system at 313.4 and 333.4 K and at pressures from 8 to 17 MPa. Liquid-phase separations were not observed in any of our experimental conditions. The results are shown in Table II.

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Table II. Vapor–Liquid Equilibria of the 10-Component System

P, MPa	phase	mole fraction H_2	 CO	 CO_2	 CH_4	 C_2H_6	 C_3H_8	 H_2O	 MeOH	 EtOH	 1-PrOH
					313.4 K						
8.10	V	0.4388	0.1674	0.0220	0.3107	0.0408	0.0159	0.0002	0.0035	0.0006	0.0001
	L	0.0051	0.0037	0.0051	0.0135	0.0060	0.0034	0.1616	0.6112	0.1370	0.0533
10.71	V	0.4502	0.1701	0.0192	0.3039	0.0384	0.0144	0.0002	0.0031	0.0005	0.0001
	L	0.0071	0.0049	0.0057	0.0170	0.0068	0.0039	0.1605	0.6054	0.1359	0.0527
12.43	V	0.4647	0.1725	0.0165	0.2956	0.0347	0.0122	0.0001	0.0030	0.0005	0.0001
	L	0.0087	0.0058	0.0055	0.0191	0.0069	0.0038	0.1526	0.6103	0.1362	0.0512
13.52	V	0.4586	0.1689	0.0179	0.2992	0.0379	0.0139	0.0001	0.0029	0.0005	0.0001
	L	0.0095	0.0062	0.0061	0.0205	0.0076	0.0042	0.1549	0.6047	0.1351	0.0511
15.01	V	0.4662	0.1708	0.0163	0.2943	0.0359	0.0132	0.0001	0.0027	0.0005	0.0001
	L	0.0107	0.0068	0.0060	0.0220	0.0077	0.0043	0.1533	0.6028	0.1351	0.0513
16.04	V	0.4630	0.1722	0.0167	0.2955	0.0358	0.0133	0.0001	0.0028	0.0005	0.0001
	L	0.0118	0.0076	0.0067	0.0239	0.0082	0.0045	0.1510	0.6016	0.1340	0.0507
17.19	C	0.4654	0.1711	0.0165	0.2946	0.0360	0.0130	0.0001	0.0027	0.0005	0.0001
	L	0.0123	0.0076	0.0065	0.0243	0.0082	0.0044	0.1539	0.5970	0.1343	0.0514
					333.4 K						
7.73	V	0.4321	0.1657	0.0215	0.3101	0.0426	0.0156	0.0004	0.0095	0.0021	0.0004
	L	0.0051	0.0032	0.0038	0.0120	0.0049	0.0025	0.1776	0.5979	0.1373	0.0556
10.29	V	0.4495	0.1681	0.0190	0.3003	0.0390	0.0137	0.0004	0.0079	0.0018	0.0004
	L	0.0073	0.0045	0.0042	0.0152	0.0055	0.0026	0.1765	0.5932	0.1366	0.0544
12.05	V	0.4773	0.1705	0.0150	0.2848	0.0316	0.0113	0.0004	0.0073	0.0016	0.0003
	L	0.0090	0.0055	0.0038	0.0164	0.0050	0.0019	0.1754	0.5960	0.1351	0.0518
13.87	V	0.4753	0.1707	0.0149	0.2864	0.0332	0.0110	0.0003	0.0065	0.0014	0.0030
	L	0.0104	0.0062	0.0042	0.0182	0.0056	0.0026	0.1757	0.5899	0.1339	0.0534
15.08	V	0.4793	0.1720	0.0144	0.2832	0.0309	0.0116	0.0003	0.0065	0.0014	0.0003
	L	0.0115	0.0068	0.0043	0.0197	0.0058	0.0020	0.1745	0.5906	0.1336	0.0514
17.42	V	0.4761	0.1722	0.0148	0.2847	0.0325	0.0117	0.0003	0.0061	0.0013	0.0003
	L	0.0133	0.0076	0.0048	0.0224	0.0065	0.0030	0.1740	0.5839	0.1321	0.0524

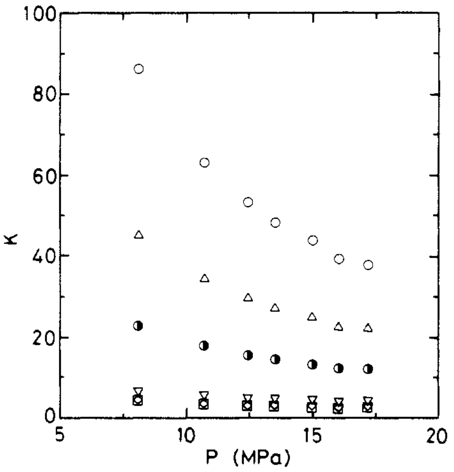

Figure 1. *K* values for the 10-component system at 313.4 K: ○, H_2; △, CO; □, CO_2; ◑, methane; ▽, ethane; ◇, propane.

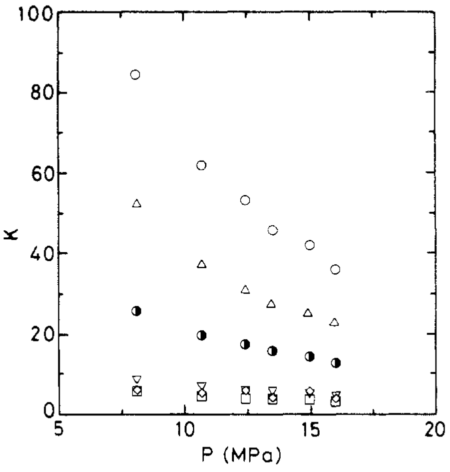

Figure 3. *K* values for the 10-component system at 333.4 K: ○, H_2; △, CO; □, CO_2; ◑, methane; ▽, ethane; ◇, propane.

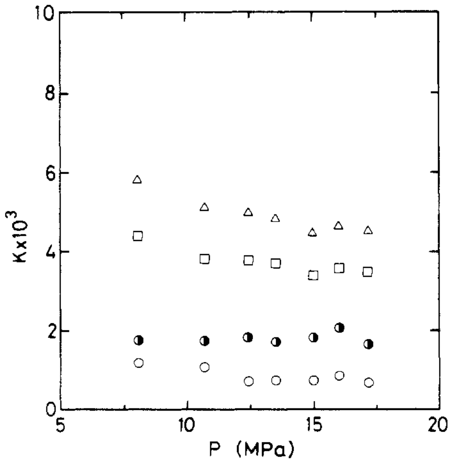

Figure 2. *K* values for the 10-component system at 313.4 K: ○, water; △, methanol; □, ethanol; ◑, 1-propanol.

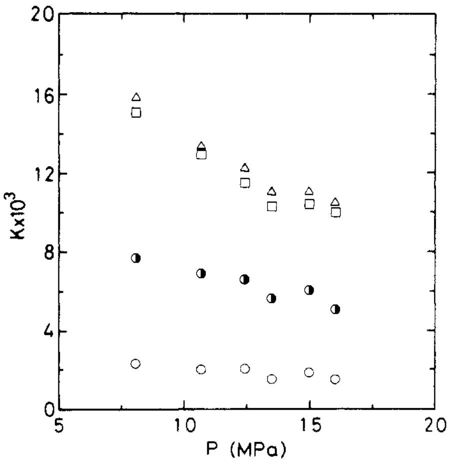

Figure 4. *K* values for the 10-component system at 333.4 K: ○, water; △, methanol; □, ethanol; ◑, 1-propanol.

The system has 10 degrees of freedom, and therefore, we represent the experimental results with equilibrium *K* values as shown in Figures 1-4. *K* values decreased with increasing pressures and tended to increase with increasing temperature except for H_2.

Literature Cited

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Thermodynamic Activities and Equilibrium Partial Pressures for Aqueous Sulfuric Acid Solutions

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Published room-temperature and azeotropic composition data for solutions together with recently published high-temperature *P–T–X* data and room-temperature values for the equilibrium vapor pressure of sulfur-bearing species over concentrated sulfuric acid–water solutions are evaluated critically for self-consistency. The adjusted data are used to calculate activity coefficients at 0 °C and at the normal azeotropic boiling temperature and to generate expressions for the partial molar heat capacities in H_2SO_4–H_2O solutions. These partial molar properties, calculated for temperatures between 25 and 320 °C and spanning the composition range from pure water to the azeotropic composition, are used as interpolation formulas for the calculation of basic thermodynamic parameters of H_2SO_4–H_2O solutions that are specifically needed for nucleation and precipitation phenomena involving vapors with a high sulfur oxide and/or sulfuric acid content.

(1) Introduction

It is generally recognized that the oxidation of sulfur dioxide to SO_3 and subsequent nucleation, in the presence of H_2O, of liquid droplets is the principal mechanism for the formation of sulfuric acid aerosol found in the atmosphere. Elaborate mechanisms have been postulated by which the heterogeneous or homogeneous nucleation of H_2SO_4 could take place under tropospheric or stratospheric conditions (*19*, *26*, *34*, *39*), and measurements of nucleation rates under such conditions have been reported (*5*, *9*, *30a*, *33*, *34*). Also, studies have been conducted of the formation of sulfuric acid aerosols in combustion processes where exhaust gases contain solid aerosol particles that may serve as catalysts for the oxidation of SO_2 and/or as nucleation sites for the condensation of sulfuric acid (*3*, *31*, *36*, *47*).

A quantitative interpretation of the conditions leading to the formation of sulfuric acid by nucleation and condensation requires knowledge of the thermodynamic properties of aqueous sulfuric acid solutions under the conditions of temperature and partial pressures at which the liquid phase is likely to form. Surprisingly, in light of the importance of sulfuric acid in industrial technology, such data are scarce and largely inconsistent. This problem has been recognized by authors who have tried to generalize the representation of thermodynamic properties of aqueous sulfuric acid solutions through correlations (*1*, *13*, *14*, *43*, *44*) and also by those who have attempted to use available data and data correlations to arrive at quantitative estimates of rates of formation of sulfuric acid in the atmosphere and in combustion processes. Specifically, the data required are liquid-phase activity coefficients and vapor pressures of the various species that are in equilibrium with aqueous solutions of sulfuric acid, for specified conditions of temperature and composition of the liquid phase. The inconsistencies in reported values of the vapor pressure of sulfuric acid and the lack of high-temperature heat capacity data have been the main obstacles in calculating accurate activity coefficients, vapor pressures, and degrees of supersaturation.

The measurement of activities and vapor pressures in solutions with compositions approaching pure sulfuric acid are extremely difficult. Even the vapor in equilibrium with "pure" sulfuric acid includes $H_2O(v)$ and $SO_3(v)$ as well as $H_2SO_4(v)$, and dissociation of H_2SO_4 into H_2 and SO_3, coupled with the very low vapor pressure of sulfuric acid near room temperature, complicates the measurement of the partial pressures of the various species. A relatively recent report (*6*) on the reasons for the failure of an attempted series of measurements in the sulfuric acid–water system at high acid concentrations dramatically illustrates such difficulties. Recent publications dealing with calculation of nucleation rates in the sulfuric acid–water system (*5*, *19*, *33*, *34*, *36*, *47*) most commonly use a value for the vapor pressure of pure sulfuric acid given by the correlation of Gmitro and Vermeulen (*13*) of 3.6×10^{-4} Torr (0.048 Pa), although it has been suggested that this value may be in error by several hundred percent (*43*), and more recently, the authors themselves have revised significantly their previous correlation (*44*). Another value in use, 10^{-6} Torr (1.3×10^{-4} Pa), is derived from estimations by LaMer et al. based on observed nucleation rates of aqueous sulfuric acid from the vapor phase (*9*, *30a*).

Such inconsistencies prevail not only among reported values of vapor pressures but also for azeotropic compositions, boiling points, and other thermodynamic parameters, as has been pointedly summarized by Myers in a recent article (*35*).

The purpose of the analysis reported here has been to reexamine the available thermodynamic data and to derive therefrom a framework of self-consistent values of basic thermodynamic parameters that may be used to calculate with some degree of consistency levels of supersaturation, dew points, and phase equilibria related to the precipitation of aqueous sulfuric acid droplets for various conditions of temperature, humidity, and partial pressure of SO_3.

(2) Thermodynamic Data for the H_2SO_4–H_2O System

Thermodynamic activities can be determined experimentally from several different properties of solutions. In the case of H_2O–H_2SO_4 solutions, properties such as vapor pressure, electromotive force, osmotic pressure, and freezing point depression have been used to determine the activities of one or the other component over various ranges of composition and temperature.

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