J. Chem. Eng. Data 1985, 30, 174-176

New Procedure for Vapor–Liquid Equilibria. Nitrogen + Carbon Dioxide, Methane + Freon 22, and Methane + Freon 12

Masahiro Yorizane, Shoshin Yoshimura, Hirokatsu Masuoka, Yoshimori Miyano,*† and Yukihiko Kakimoto

Department of Chemical Engineering, Hiroshima University, Higashihiroshima, 724 Japan

A new procedure to measure high-pressure vapor–liquid equilibria is proposed, in which both vapor- and liquid-phase samples are withdrawn without disturbing the equilibrium conditions. Vapor–liquid equilibrium data are reported for pressures approaching the critical pressures for the nitrogen–carbon dioxide system at 273.2, 293.2, and 298.2 K, and for the methane–Freon 22 (chlorodifluoromethane) system and the methane–Freon 12 (dichlorodifluoromethane) system both at 263.2, 273.2, and 298.2 K. Critical pressures and compositions at several temperatures were determined by means of a graphical method.

Introduction

Of the problems encountered in the measurement of vapor–liquid equilibria at elevated pressures, two are the most troublesome. They are the methods for agitating the system to facilitate the approach to equilibrium and for withdrawing the sample from the equilibrium phases without disturbing the equilibrium.

A static method or a circulation method is usually used for measuring high-pressure vapor–liquid equilibria. In general, with a static method it is difficult to withdraw a sample from the equilibrium phases without disturbing the equilibrium, and some special designs to withdraw a sample are needed (*1*, *2*). A circulation method (*3*–*5*) usually uses a pump to circulate gas and/or liquid to obtain the necessary mixing effect, and the pressure is slightly fluctuating.

In this paper, a gravitational circulation method, where gas and liquid are circulated by a gravitational force, is used to reduce the pressure fluctuation.

Experimental Apparatus

Figure 1 shows a schematic diagram of the experimental apparatus. This apparatus has two equilibrium cells, which are connected to each other at both top and bottom ends by means of flexible stainless steel tubes. One cell is fixed while the other is moved slowly up and down by means of a mechanical device. As a result of this up and down motion of the movable cell, liquid tends to flow from the cell which is at a higher elevation to the one at a lower elevation, while at the same time vapor tends to flow from the lower cell to the higher one to keep the pressures in the two cells equal. As a result of the vertical motion the vapor and the liquid are slowly mixed.

The two cells are of the same size (55-mm i.d., 63 mm in height, and 150 cm^3 in volume) and made of type 304 stainless steel. The sampling sections for vapor and liquid phases are located between the tubes which connect the cells to each other. Each sampling section has three valves: two of them are to isolate the sample, and the third, which is located between the other two, is a three-way valve and is used to withdraw the sample to the sample chamber. The design of the three-way valve is shown in Figure 2. The samples are isolated, and an entire sample is then expanded into the sample chambers at low pressure. The samples are analyzed by means of a gas chromatograph which is directly connected to the sample chambers. The conditions for analysis of the various mixtures are tabulated in Table I.

Table I. Conditions for Analysis

system	N_2–CO_2	CH_4–Freon 22	CH_4–Freon 12
carrier gas	H_2 (99.99%)	H_2 (99.99%)	H_2 (99.99%)
carrier gas flow rate, cm^3/min	100	100	100
detector temp, K	373	303	383
column packing	silica gel (80 mesh)	TCP (60–80 mesh)	Porapack Q (60–80 mesh)
column temp, K	368	273	373
column	3-m length, 3-mm i.d.	3-m length, 3-mm i.d.	3-m length, 3-mm i.d.
detector	TCD[a]		
gas chromatograph	Shimazu GC-4BPTF		
integrator	Takeda TR-2215A		

[a] Thermal conductivity detector.

A precise Bourdon gauge, which has been calibrated against a calibrated dead-weight balance, is used to measure pressure to a precision within ±0.5% of the measured values. The equilibrium temperature is measured by a standard mercury thermometer. The temperatures are accurate to within ±0.1 K. The equilibrium cell temperature did not fluctuate by more than 0.1 K during the determination of all the points on the isotherms at 263.2 and 273.2 K. At 293.2 and 298.2 K, the cell temperature did not fluctuate by more than 0.05 K.

Experimental Procedure

Initially the bath temperature was reduced below room temperature. After evacuation of the whole system, the high-boiling gas was introduced into the fixed cell, where it condensed until it filled the cell. Then the valves between the fixed cell and the movable cell were opened slowly and half of the liquid was allowed to flow from the fixed cell to the movable one, which was held at the same level. Then the solute gas was fed into the two cells. After the bath was adjusted to the experimental temperature, the movable cell was set in motion at a rate of 1 cycle per 10 min. This cycle time had previously been found suitable as a result of calculations and experiments conducted by using air and water. The vertical up and down motion of the cell was continued for 3–5 h until equilibrium was reached as observed by a constant system pressure. Then the vertical motion was stopped and the cells were brought to the same level. Vapor and liquid samples were isolated by closing both valves beside the three-way valves. Then the vapor- and liquid-phase samples were withdrawn to their respective sample chambers by opening the three-way valves. The pressures in

---

* Address correspondence to this author at the Department of Chemical Engineering, Hiroshima University, Higashihiroshima, 724 Japan.

† Department of Applied Chemistry, Okayama University of Science, 1-1 Ridai-cho, Okayama, 700 Japan.

0021-9568/85/1730-0174$01.50/0

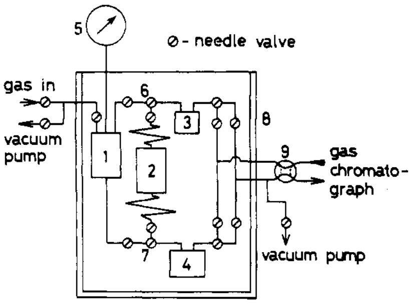

Figure 1. Schematic diagram of experimental apparatus: (1) fixed equilibrium cell, (2) movable equilibrium cell, (3) vapor-sample chamber, (4) liquid-sample chamber, (5) pressure gauge, (6) sampling section for vapor phase, (7) sampling section for liquid phase, (8) constant-temperature bath, (9) four-way glass cock.

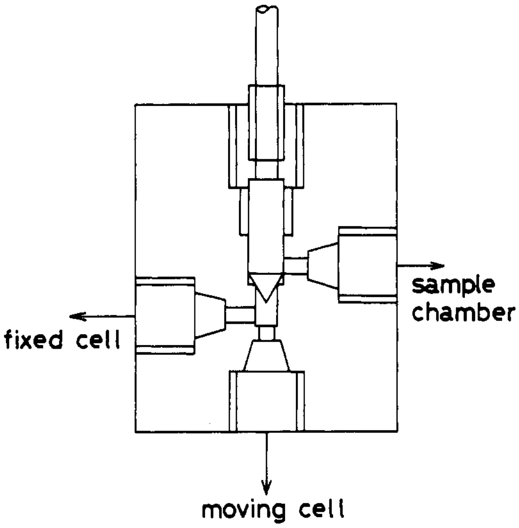

Figure 2. Details of three-way valve.

Table II. Experimental Vapor-Liquid Equilibrium Data for the Nitrogen-Carbon Dioxide System

	$[N_2]$, mole fraction			$[N_2]$, mole fraction	
press., MPa	vapor	liquid	press., MPa	vapor	liquid
273.2 K					
4.50	0.020	0.154	8.39	0.110	0.375
4.51	0.019	0.158	9.95	0.156	0.397
5.09	0.037	0.214	9.99	0.147	0.386
5.71	0.054	0.264	10.92	0.184	0.378
6.61	0.066	0.298	11.45	0.214	0.368
6.70	0.072	0.318	12.04	0.298^a	critical
7.83	0.105	0.356			
293.2 K					
6.59	0.021	0.067	8.53	0.077	0.143
6.60	0.021	0.066	8.86	0.093	0.142
7.56	0.050	0.117	8.91	0.093	0.145
7.59	0.049	0.118	9.26	0.102	0.145
8.31	0.068	0.138	9.32	0.111	0.147
8.33	0.070	0.139	9.37	0.114	0.149
8.35	0.070	0.140	9.55	0.118	0.150
8.37	0.070	0.140	9.60	0.123	0.148
8.43	0.073	0.139	9.79	0.140^a	critical
298.2 K					
7.40	0.026	0.058	8.17	0.050	0.088
7.41	0.027	0.057	8.51	0.067	0.098
8.14	0.053	0.084			

[a] Estimated values.

the sample chambers were observed to be from 0.01 to 0.03 MPa. For analysis the samples in the chambers were withdrawn to the analyzing sections and then brought to the gas chromatograph by means of hydrogen carrier gas.

Table III. Experimental Vapor-Liquid Equilibrium Data for the Methane-Freon 22 System

	$[CH_4]$, mole fraction			$[CH_4]$, mole fraction	
press., MPa	vapor	liquid	press., MPa	vapor	liquid
263.2 K					
1.12	0.051	0.617	8.86	0.480	0.852
2.03	0.096	0.775	9.25	0.510	0.850
3.21	0.172	0.843	9.80	0.540	0.844
3.99	0.195	0.859	10.21	0.601	0.819
5.02	0.276	0.881	10.48	0.631	0.760
8.00	0.434	0.880	10.67	0.712^a	critical
273.2 K					
3.18	0.147	0.806	8.83	0.458	0.838
4.11	0.195	0.830	9.82	0.537	0.828
4.98	0.239	0.847	10.27	0.580	0.818
6.67		0.853	11.08	0.711^a	critical
8.32	0.445	0.831			
298.2 K					
1.92	0.040	0.401	8.20	0.355	0.721
2.72	0.072	0.507	9.13	0.380	0.701
4.24	0.157	0.665	10.01	0.461	0.680
5.95	0.219	0.716	10.36	0.517	0.644
7.28	0.296	0.721	10.76	0.592^a	critical

[a] Estimated values.

Table IV. Experimental Vapor-Liquid Equilibrium Data for the Methane-Freon 12 System

	$[CH_4]$, mole fraction			$[CH_4]$, mole fraction	
press., MPa	vapor	liquid	press., MPa	vapor	liquid
263.2 K					
1.36	0.091	0.773	7.29	0.498	0.899
2.79	0.221	0.866	8.41	0.577	0.892
3.87	0.305	0.893	9.14	0.635	0.875
5.11	0.371	0.904	9.60	0.655	0.872
6.28	0.434	0.907	9.93	0.753^a	critical
273.2 K					
1.53	0.088	0.785	5.72	0.400	0.914
1.75	0.107	0.816	7.49	0.506	0.896
2.12	0.136	0.844	8.30	0.541	0.884
3.00	0.203	0.877	8.59	0.566	0.887
3.79	0.256	0.891	9.33	0.615	0.866
4.43	0.338	0.901	11.16	0.778^a	critical
298.2 K					
1.99	0.104	0.512	7.95	0.465	0.828
2.96	0.147	0.630	8.51	0.497	0.828
4.06	0.222	0.723	8.98	0.562	0.825
4.51	0.246	0.759	9.27	0.547	0.818
4.90	0.272	0.791	9.79	0.604	0.815
5.61	0.327	0.801	9.98	0.608	0.811
6.44	0.365	0.816	10.25	0.647	0.796
6.99	0.401	0.833	10.67	0.740^a	critical
7.40	0.431	0.829			

[a] Estimated values.

Materials

The specified purities of carbon dioxide, nitrogen, and methane were 99.99, 99.99, and 99.9 vol %, respectively, and those of both Freon 22 (chlorodifluoromethane) and Freon 12 (dichlorodifluoromethane) were 99.95 vol %.

Results and Discussion

Experimental vapor-liquid equilibrium data for the nitrogen-carbon dioxide system obtained at 273.2, 293.2, and 298.2 K, and for the methane-Freon 22 system and the methane-Freon 12 system both at 263.2, 273.2, and 298.2 K, are listed in Tables II-IV, respectively. Uncertainties in the phase compositions, due mainly to errors associated with sampling, are estimated to be ±0.005 in the mole fraction, although this may

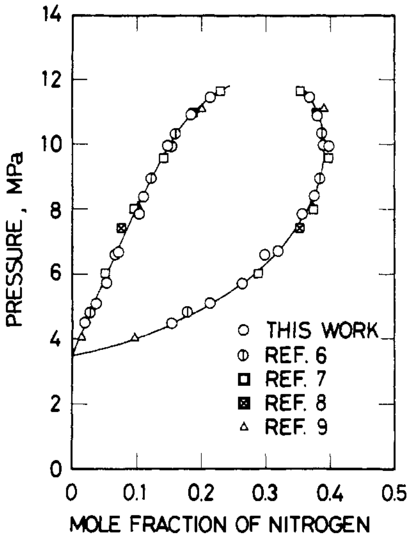

Figure 3. Comparison of experimental data with literature values for the nitrogen–carbon dioxide system at 273.2 K.

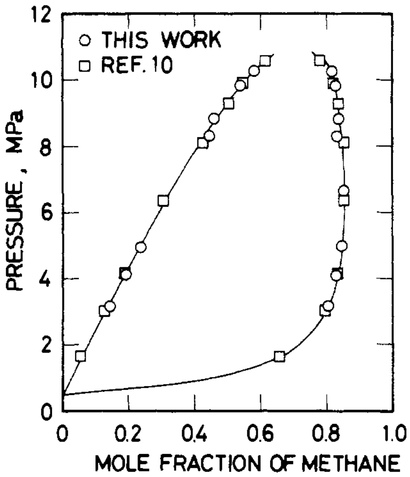

Figure 4. Comparison of experimental data with literature values for the methane–Freon 22 system at 273.2 K.

be as large as ±0.01 near the critical region. In these tables, the critical values were estimated by using a simple graphical method (rectilinear diameter method). Uncertainties in the estimated critical compositions and pressures are ±0.01 and ±0.15 MPa, respectively. Experimental data for the nitrogen–carbon dioxide system and the methane–Freon 22 system both at 273.2 K are compared with literature values (*6–10*) in Figures 3 and 4. From these comparisons it may be observed that the data of this work agree well with those from the literature.

Consistency tests for experimental data measured in this work were performed by using the enhancement factor method (*11*). The enhancement factor, E, is based on an increasing concentration of solvent in the vapor phase as a result of an increasing pressure. It is defined as

$$E = Py_2/P_2^s \tag{1}$$

where P is the total pressure, y_2 is the vapor-phase mole fraction of solvent, and P_2^s is the vapor pressure of pure solvent at the system temperature. If the concentrations in the vapor phase exhibited the ideal values, the enhancement factor would approach unity as P approached P_2^s. The results for the nitrogen–carbon dioxide system at 293.2 and 298.2 K using this method are shown in Figure 5. The enhancement factor did indeed approach unity as required for consistency. The enhancement factor tests for other systems indicated that the data for the other systems were also consistent.

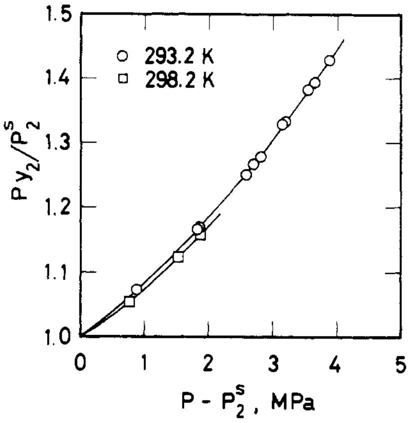

Figure 5. Enhancement factors for the nitrogen–carbon dioxide system at 293.2 and 298.2 K.

Conclusions

During the past three or four decades many investigators have measured high-pressure vapor–liquid equilibria using many different types of equipment. The apparatus described in this paper is considered to be simple and reliable and hence a useful improvement in equipment design. A minor defect of this apparatus is the length of time required to reach equilibrium, usually taking from 3 to 5 h. It may be possible to reduce the equilibration time by utilizing glass beads to fill a portion of the cell volume.

Acknowledgment

We acknowledge Ryoichi Kishimoto, who made the experimental measurements for this study.

Registry No. Methane, 74-82-8; Freon 22, 75-45-6; Freon 12, 75-71-8; nitrogen, 7727-37-9; carbon dioxide, 124-38-9.

Literature Cited

(1) Rogers, B. L.; Prausnitz, J. M. *Ind. Eng. Chem. Fundam.* **1970**, *9*, 174.
(2) Figuiere, P.; Hom, J. F., Laugier, S.; Renon, H.; Richon, D.; Szwarc, H. *AIChE J.* **1980**, *26*, 872.
(3) Toyama, A.; Chappelear, P. S.; Leland, T. W.; Kobayashi, R. *Adv. Cryog. Eng.* **1961**, *7*, 106.
(4) Hirata, M.; Suda, S.; Sagara, H. *Sekiyu Gakkaishi* **1966**, *9*, 717.
(5) Yorizane, M.; Sadamoto, S.; Yoshimura, S.; Masuoka, H.; Shiki, N.; Kimura, T.; Toyama, A. *Kagaku Kogaku* **1968**, *32*, 257.
(6) Muirbrook, N. K.; Prausnitz, J. M. *AIChE J.* **1965**, *11*, 1092.
(7) Zenner, G. H.; Dana, L. I. *Chem. Eng. Prog., Symp. Ser.* **1963**, *59*, 36.
(8) Kaminishi, G.; Toriumi, T. *Kogyo Kagaku Zasshi* **1966**, *69*, 175.
(9) Yorizane, M.; Yoshimura, S.; Masuoka, H. *Kagaku Kogaku* **1970**, *34*, 953.
(10) Nohka, J.; Sarashina, E.; Arai, Y.; Saito, S. *J. Chem. Eng. Jpn* **1973**, *6*, 10.
(11) Gunn, R. D.; McKetta, J. J.; Ata, N. *AIChE J.* **1974**, *20*, 347.

Received for review February 14, 1984. Accepted September 10, 1984. Financial support for this investigation was provided by a grant-in-aid for scientific research from the Ministry of Education of Japan.