ACKNOWLEDGMENT

The support of the Petroleum Research Fund is acknowledged gratefully. The undergraduate authors (DEC, GRC, CMH, JPS, and JJS) wish to express their gratitude to the National Science Foundation and the Research Corporation for stipends received during the summer months.

LITERATURE CITED

(1) Campbell, A.N., Kartzmark, W.M., *Can. J. Chem.* **34**, 1405–7 (1956).
(2) Katzin, L.I., Ferraro, J.R., *J. Am. Chem. Soc.* **74**, 2752 (1952).
(3) Lloyd, E., Brown, C.B., Glynwyn, D., Bonnell, R., Jones, W.J., *J. Chem. Soc.* **1928**, p. 658.
(4) Ricci, J.E., "The Phase Rule and Heterogeneous Equilibrium," p. 343, Van Nostrand, New York, 1951.
(5) Schott, Hans, J. CHEM. ENG. DATA **6**, 324 (1961).
(6) Schott, Hans, Ph.D. Dissertation, University of Delaware, Newark, Del., 1958.

RECEIVED for review February 18, 1963. Accepted August 8, 1963.

Vapor-Liquid Equilibrium of the Methane–*n*-Butane–Carbon Dioxide System at Low Temperatures and Elevated Pressures

R. H. WANG[1] and J. J. McKETTA
The Univeristy of Texas, Austin, Texas

The effect of carbon dioxide on the vapor-liquid equilibrium of hydrocarbons at low temperatures and elevated pressures was studied. The temperature range was from −140 to 100° F., and the pressure range was from 400 to 1700 p.s.i.a. The experimental data are presented as the isotherms on pressure-composition plots and as isobars on temperature-composition plots. *K*-values are also presented.

CARBON DIOXIDE is found in varying percentages in many petroleum reservoir fluids. In recent years, the increasing interest in secondary recovery techniques has brought greater interest in the investigations of its presence. A knowledge of the effect of carbon dioxide on the vapor-liquid equilibrium of hydrocarbon systems would provide useful information.

Reliable data on the phase equilibrium relationship of ternary systems involving carbon dioxide and hydrocarbon at low temperatures are very scarce. Clark and Din (*1*), studied the carbon dioxide–ethane–ethylene system at low temperatures and at subatmospheric pressures.

EXPERIMENTAL

The equilibrium apparatus was essentially a windowed equilibrium cell contained in a constant temperature liquid bath. Circulation of the fluid in the cell was accomplished by a positive displacement magnetic pump which took vapor from the top of the cell, passed it through the pump, and coolers where the vapor was cooled to cell temperature, and injected into the bottom of the equilibrium cell to bubble through the liquid. Eight hours of circulation and two hours for phase separation were allowed before the phases were sampled for analyses.

The liquid bath consisted of a 10-gallon Dewar flask surrounded by vermiculite insulation all of which was enclosed in a metal box constructed of $\frac{1}{16}$-inch aluminum plate. Cell contents were viewed through slits cut in the box and insulation at positions corresponding to 1-inch wide unsilvered strips located on opposite sides of the Dewar.

Water was used as the liquid bath medium at 100° and 40° F. Freon Refrigerant-11 was used down to −140° F.

The temperature of the liquid bath was controlled using a precision temperature controller with a sensitivity of ±0.002° F. The temperature of the cell and the liquid bath was measured using three copper-constantan thermocouples. Pressures were read on Heise Bourdon tube gages which were calibrated, using a dead-weight gage, after each isotherm was completed. No change in calibration was noted during the entire project. Details of the equipment, operation, and analytical procedure are available (*3*).

Analytical. Each equilibrium phase was sampled for analysis. The vapor and liquid samples were withdrawn from the equilibrium cell into stainless steel, high pressure tubing connected to the cell proper. The pressure was carefully maintained in the equilibrium cell by adding mercury to the pressure control cylinder as the samples were withdrawn. Samples were analyzed using a Beckman GC-2 gas chromatograph, and occasional checks were made using a mass spectrometer. The analyses with these two methods never disagreed more than 0.10 mole %.

Materials Used. The methane and *n*-butane used in this work were Phillips Petroleum Co. research grade hydrocarbons with a 99.9 mole % minimum purity. The carbon dioxide was Matheson Co. bone dry grade with 99.8 mole % minimum purity.

[1]Present address: Harchem Division, Wallace & Tiernan Inc. Newark, N. J.

Table I. Experimental Binary Data of the Methane–*n*-Butane System at −140° F.

Compositions are in mole fractions

Pressure, P.S.I.A.	Vapor Phase		Liquid Phase	
	CH_4	n-C_4H_{10}	CH_4	n-C_4H_{10}
73	0.9732	0.0268	0.1579	0.8421
122	0.9924	0.0076	0.2652	0.7348
171	0.9945	0.0055	0.3582	0.6418
217	0.9868	0.0132	0.4601	0.5399
256	0.9925	0.0075	0.4913	0.5087
330	0.9942	0.0058	0.7037	0.2963
386	0.9901	0.0090	0.8241	0.1759
425	0.9942	0.0058	0.9086	0.0914
453	1.0000	...	1.0000	

Table II. Smoothed Binary Data and the *K*-Values of the Methane–*n*-Butane System at −140° F.

Pressure, P.S.I.A.	Methane			*n*-Butane		
	y	x	K	y	x	K
100	0.9964	0.223	4.468	0.0036	0.777	0.00463
150	0.9973	0.328	3.041	0.0027	0.672	0.00402
200	0.9977	0.428	2.331	0.0023	0.572	0.00402
300	0.9981	0.647	1.543	0.0019	0.353	0.00538
400	0.9980	0.873	1.143	0.0020	0.127	0.0157
453	1.000	1.000	1.000	0.000	0.000	...

Table III. Ternary Experimental Data

(All compositions are in mole fraction)

Run No.	Vapor Phase			Liquid Phase		
	CH_4	n-C_4H_{10}	CO_2	CH_4	n-C_4H_{10}	CO_2
		100° F.			400 p.s.i.a.	
271	0.824	0.176	...	0.122	0.878	...
272	0.6570	0.1787	0.1643	0.0936	0.8453	0.0611
273	0.5612	0.1784	0.2604	0.0858	0.8163	0.0979
274	0.4687	0.1727	0.3586	0.0665	0.8031	0.1304
275	0.3609	0.1780	0.4611	0.0495	0.7803	0.1702
276	0.1926	0.1782	0.6292	0.0332	0.7347	0.2321
277	0.1247	0.1800	0.6953	0.0221	0.7233	0.2546
278	...	0.1814	0.8186	...	0.6996	0.3004
		100° F.			800 p.s.i.a.	
281	0.877	0.123	...	0.254	0.746	...
282	0.7798	0.1202	0.1000	0.2336	0.6873	0.0791
283	0.7156	0.1100	0.1744	0.2045	0.6508	0.1447
284	0.5873	0.1062	0.3065	0.1861	0.5718	0.2421
285	0.4851	0.1053	0.4096	0.1517	0.5227	0.3256
286	0.3271	0.0977	0.5752	0.1002	0.4396	0.4602
287	0.1308	0.0892	0.7800	0.0433	0.3263	0.6304
288	...	0.0803	0.9197	...	0.2594	0.7406
		100° F.			1200 p.s.i.a.	
291	0.880	0.120	...	0.381	0.619	...
292	0.7887	0.1172	0.0941	0.3554	0.5572	0.0874
293	0.7008	0.1112	0.1880	0.3206	0.5102	0.1692
294	0.5498	0.1150	0.3352	0.2752	0.4246	0.3002
295	0.4603	0.1173	0.4224	0.2556	0.3700	0.3744
296	0.4383	0.1100	0.4517	0.2430	0.3549	0.4021
297	0.3817	0.1087	0.5096	0.2152	0.3287	0.4561
298	0.3282	0.1118	0.5600	0.1928	0.3052	0.5020
299	0.2191	0.1087	0.6722	0.1496	0.2496	0.6008
300	0.1478	0.1291	0.7231	0.1332	0.2003	0.6665
		100° F.			1700 p.s.i.a.	
391	0.844	0.156	...	0.599	0.441	...
392	0.7972	0.1566	0.0462	0.5562	0.4050	0.0388
393	0.7344	0.1589	0.1067	0.5426	0.3636	0.0938
394	0.6798	0.1714	0.1488	0.5308	0.3344	0.1348
395	0.6086	0.2014	0.1900	0.5337	0.2984	0.1679
		40° F.			400 p.s.i.a.	
301	0.928	0.072	...	0.159	0.841	...
302	0.8567	0.0635	0.0798	0.1484	0.8078	0.0438
303	0.7963	0.0635	0.1402	0.1310	0.7821	0.0869
304	0.6394	0.0706	0.2900	0.1002	0.7146	0.1852
305	0.5837	0.0739	0.3424	0.0904	0.6942	0.2154
306	0.4812	0.0688	0.4500	0.0698	0.6514	0.2788
307	0.3705	0.0778	0.5517	0.0509	0.5993	0.3498
308	0.2060	0.0748	0.7192	0.0289	0.5248	0.4463
309	0.0912	0.0790	0.8298	0.0157	0.4704	0.5139
310	...	0.0782	0.9218	...	0.4279	0.5721
		40° F.			800 p.s.i.a.	
311	0.945	0.055	...	0.296	0.704	...
312	0.8420	0.0598	0.0982	0.2801	0.6456	0.0743
313	0.7444	0.0560	0.1996	0.2607	0.5932	0.1461
314	0.6648	0.0604	0.2748	0.2480	0.5338	0.2182
315	0.5749	0.0504	0.3747	0.2292	0.4624	0.3084
316	0.5040	0.0638	0.4322	0.2070	0.3932	0.3998
317	0.4674	0.0474	0.4852	0.1886	0.3389	0.4725
318	0.3806	0.0623	0.5571	0.1740	0.2802	0.5458
319	0.2864	0.0736	0.6400	0.1723	0.2009	0.6268
320	0.2297	0.0954	0.6749	0.1845	0.1488	0.6667

(*Continued on page 32*)

Table III. Ternary Experimental Data *(Continued)*

(All compositions are in mole fraction)

Run No.	Vapor Phase			Liquid Phase		
	CH_4	n-C_4H_{10}	CO_2	CH_4	n-C_4H_{10}	CO_2
		40° F.			1200 p.s.i.a.	
321	0.942	0.058	...	0.426	0.574	...
322	0.8715	0.0503	0.0782	0.4383	0.4851	0.0762
323	0.8186	0.0502	0.1312	0.4273	0.4430	0.1297
324	0.7611	0.0489	0.1900	0.4309	0.3862	0.1829
325	0.6756	0.0506	0.2738	0.4288	0.3152	0.2560
326	0.6197	0.0526	0.3277	0.4208	0.2700	0.3092
327	0.5333	0.0767	0.3900	0.4152	0.2212	0.3636
328	0.4680	0.1042	0.4278	0.4145	0.1833	0.4022
		40° F.			1700 p.s.i.a.	
401	0.899	0.101	...	0.612	0.388	...
402	0.8542	0.1094	0.0364	0.6321	0.3376	0.0303
403	0.8100	0.1202	0.0698	0.6468	0.2921	0.0611
404	0.7562	0.1401	0.1037	0.6588	0.2459	0.0953
		−20° F.			400 p.s.i.a.	
341	0.973	0.027	...	0.194	0.806	...
342	0.9276	0.0247	0.0477	0.1777	0.7137	0.1086
343	0.8676	0.0226	0.1098	0.1511	0.5887	0.2602
344	0.8109	0.0212	0.1679	0.1483	0.4755	0.3762
345	0.6956	0.0198	0.2846	0.1204	0.3902	0.4894
346	0.6128	0.0208	0.3664	0.1100	0.3234	0.5666
347	0.5343	0.0136	0.4521	0.0755	0.2208	0.7037
348	0.4550	0.0113	0.5337	0.0692	0.0966	0.8342
349	0.2920	0.0102	0.6978	0.0992	0.0546	0.8462
		−20° F.			800 p.s.i.a.	
331	0.975	0.025	...	0.370	0.630	...
332	0.9495	0.0201	0.0304	0.3509	0.5779	0.0712
333	0.9223	0.0199	0.0578	0.3349	0.5289	0.1362
334	0.8765	0.0198	0.1037	0.3084	0.4321	0.2595
335	0.8288	0.0174	0.1538	0.2887	0.3411	0.3702
336	0.7920	0.0191	0.1889	0.2995	0.2312	0.4693
337	0.7498	0.0217	0.2285	0.2885	0.2012	0.5103
338	0.7238	0.0281	0.2481	0.2906	0.1439	0.5655
339	0.7005	0.0128	0.2867	0.3183	0.0913	0.5904
		−20° F.			1200 p.s.i.a.	
351	0.971	0.029	...	0.534	0.466	...
352	0.9056	0.0305	0.0639	0.5269	0.3897	0.0834
353	0.8486	0.0292	0.1222	0.5251	0.3241	0.1508
354	0.7980	0.0257	0.1763	0.5271	0.2595	0.2134
355	0.7374	0.0240	0.2386	0.5488	0.1717	0.2795
356	0.6762	0.0296	0.2932	0.5836	0.0966	0.3198
		−20° F.			1700 p.s.i.a.	
411	0.902	0.098	...	0.831	0.169	...
412	0.8868	0.1000	0.0132	0.8504	0.1282	0.0214
		−80° F.			400 p.s.i.a.	
371	0.990	0.010	...	0.335	0.665	...
372	0.9649	0.0097	0.0254	0.3253	0.6357	0.0393
373	0.9503	0.0096	0.0401	0.3217	0.6188	0.0595
374	0.9400	0.0037	0.0563	0.3181	0.6019	0.0800
375	0.9112	0.0085	0.0803	0.3068	0.5777	0.1155
376	0.8104	0.0084	0.1812	0.2802	0.4606	0.2592
377	0.7277	0.0123	0.2600	0.2700	0.3600	0.3700
378	0.5799	0.0198	0.4003	0.2801	0.1797	0.5402
379	0.5160	0.0204	0.4636	0.3011	0.0856	0.6133
		−80° F.			800 p.s.i.a.	
361	0.990	0.010	...	0.6700	0.3300	...
362	0.9698	0.0146	0.0156	0.6753	0.3055	0.0192
363	0.9570	0.0098	0.0332	0.6758	0.2835	0.0407
364	0.8760	0.0099	0.1141	0.6848	0.1855	0.1297
365	0.8275	0.0102	0.1623	0.6995	0.1209	0.1796
366	0.7988	0.0100	0.1912	0.7167	0.0811	0.2022
		−80° F.			1000 p.s.i.a.	
421	0.970	0.030	...	0.848	0.152	...
422	0.9582	0.0251	0.0167	0.8674	0.1103	0.0223
423	0.9433	0.0270	0.0297	0.8896	0.0742	0.0362
		−140° F.			400 p.s.i.a.	
381	0.996	0.004	...	0.850	0.150	...
382	0.9802	0.0031	0.0167	0.8389	0.1168	0.0443
383	0.9659	0.0042	0.0299	0.8455	0.0701	0.0844
384	0.9482	0.0056	0.0462	0.8737	0.0207	0.1056

RESULTS

The results of the methane–*n*-butane binary equilibrium mixtures from −80° to 220° F. were reported earlier (2). In Tables I and II the experimental and smoothed data and the *K*-values of the binary mixtures are shown at −140° F. The experimental equilibrium measurements for the ternary system, methane–*n*-butane–carbon dioxide, are shown in Table III. Table IV shows the ternary smoothed data and the *K*-values.

Typical plots, shown as isotherms on pressure-composition diagrams, and as isobars on temperature-composition

Table IV. Ternary Smoothed Data and the *K*-Values

Carbon Dioxide			Methane			*n*-Butane		
y	*x*	*K*	*y*	*x*	*K*	*y*	*x*	*K*
			100° F., 400 p.s.i.a.					
...	...	...	0.824	0.122	6.754	0.176	0.878	0.200
0.100	0.040	2.500	0.723	0.105	6.886	0.177	0.855	0.207
0.200	0.076	2.632	0.621	0.090	6.900	0.179	0.834	0.215
0.300	0.112	2.679	0.521	0.075	6.947	0.179	0.813	0.220
0.400	0.149	2.685	0.420	0.061	6.885	0.180	0.790	0.228
0.500	0.185	2.703	0.320	0.047	6.809	0.180	0.768	0.234
0.600	0.221	2.715	0.220	0.034	6.471	0.180	0.745	0.242
0.700	0.258	2.713	0.120	0.019	6.316	0.180	0.723	0.249
0.8186	0.3004	2.725	...	...	...	0.1814	0.6996	0.259
			100° F., 800 p.s.i.a.					
...	...	...	0.877	0.254	3.453	0.123	0.746	0.165
0.100	0.079	1.266	0.782	0.288	3.430	0.118	0.693	0.170
0.200	0.160	1.250	0.688	0.202	3.406	0.112	0.638	0.176
0.300	0.240	1.250	0.590	0.175	3.371	0.110	0.585	0.188
0.400	0.321	1.246	0.496	0.149	3.329	0.104	0.530	0.196
0.500	0.402	1.244	0.400	0.122	3.279	0.100	0.476	0.210
0.600	0.483	1.242	0.303	0.095	3.189	0.097	0.422	0.230
0.700	0.563	1.243	0.210	0.068	3.088	0.090	0.369	0.244
0.800	0.645	1.240	0.114	0.041	2.780	0.086	0.314	0.274
0.9197	0.7406	1.242	...	...	...	0.0803	0.2594	0.310
			100° F., 1200 p.s.i.a.					
...	...	...	0.880	0.381	2.310	0.120	0.619	0.194
0.100	0.093	1.075	0.783	0.350	2.237	0.117	0.557	0.210
0.200	0.182	1.099	0.687	0.318	2.160	0.113	0.500	0.226
0.300	0.272	1.103	0.587	0.284	2.067	0.113	0.444	0.255
0.400	0.361	1.108	0.490	0.251	1.952	0.110	0.388	0.284
0.500	0.451	1.109	0.390	0.217	1.797	0.110	0.332	0.331
0.600	0.542	1.107	0.289	0.183	1.579	0.111	0.275	0.404
0.700	0.631	1.109	0.184	0.145	1.269	0.116	0.224	0.518
			100° F., 1700 p.s.i.a.					
...	...	...	0.844	0.559	1.510	0.156	0.441	0.354
0.05	0.043	1.163	0.792	0.553	1.432	0.158	0.404	0.391
0.10	0.088	1.136	0.739	0.545	1.356	0.161	0.367	0.439
0.15	0.133	1.128	0.673	0.535	1.258	0.177	0.332	0.533
0.19	0.168	1.131	0.608	0.525	1.158	0.202	0.307	0.658
			40° F., 400 p.s.i.a.					
...	...	...	0.928	0.159	5.836	0.072	0.841	0.0856
0.100	0.057	1.754	0.832	0.141	5.901	0.068	0.802	0.0848
0.200	0.119	1.681	0.732	0.122	6.000	0.068	0.759	0.0899
0.300	0.183	1.639	0.631	0.102	6.186	0.609	0.715	0.0965
0.400	0.241	1.659	0.530	0.084	6.309	0.070	0.673	0.104
0.500	0.303	1.650	0.428	0.067	6.388	0.072	0.630	0.114
0.600	0.361	1.662	0.326	0.052	6.269	0.074	0.587	0.126
0.700	0.414	1.690	0.225	0.042	5.357	0.075	0.544	0.138
0.800	0.497	1.610	0.123	...	...	0.077	...	...
			40° F., 800 p.s.i.a.					
...	...	...	0.945	0.296	3.193	0.055	0.704	0.0781
0.100	0.076	1.316	0.841	0.275	3.058	0.059	0.649	0.0909
0.200	0.150	1.333	0.740	0.255	2.902	0.060	0.595	0.101
0.300	0.233	1.288	0.640	0.234	2.735	0.060	0.533	0.113
0.400	0.343	1.166	0.539	0.212	2.542	0.061	0.445	0.137
0.500	0.482	1.037	0.438	0.190	2.305	0.062	0.328	0.189
0.600	0.590	1.017	0.335	0.169	1.982	0.065	0.241	0.270
0.6749	0.6667	1.012	0.2297	0.1845	1.245	0.0954	0.1488	0.641
			40° F., 1200 p.s.i.a.					
...	...	...	0.942	0.426	2.211	0.058	0.574	0.101
0.100	0.096	1.042	0.850	0.425	2.000	0.050	0.479	0.104
0.200	0.191	1.047	0.757	0.424	1.785	0.043	0.385	0.112
0.300	0.284	1.056	0.651	0.421	1.546	0.049	0.295	0.166
0.4278	0.4022	1.064	0.4680	0.4145	1.129	0.1042	0.1833	0.568
			40° F., 1700 p.s.i.a.					
...	...	...	0.899	0.612	1.469	0.101	0.388	0.260
0.03	0.022	1.364	0.861	0.625	1.378	0.109	0.353	0.309
0.07	0.061	1.148	0.810	0.643	1.260	0.120	0.296	0.405
0.1037	0.0953	1.088	0.7562	0.6588	1.148	0.1401	0.2459	0.570

(*Continued on page 34*)

Table IV. Ternary Smoothed Data and the *K*-Values (*Continued*)

Carbon Dioxide			Methane			*n*-Butane		
y	*x*	*K*	*y*	*x*	*K*	*y*	*x*	*K*
			−20° F., 400 p.s.i.a.					
...	...	...	0.973	0.194	5.015	0.027	0.806	0.0335
0.100	0.256	0.391	0.878	0.162	5.420	0.022	0.582	0.0378
0.200	0.395	0.506	0.780	0.138	5.652	0.020	0.467	0.0428
0.300	0.508	0.591	0.682	0.107	6.374	0.018	0.385	0.0468
0.400	0.613	0.653	0.584	0.086	6.791	0.016	0.301	0.0532
0.500	0.707	0.707	0.486	0.074	6.568	0.014	0.219	0.0639
0.600	0.794	0.756	0.390	0.073	5.342	0.010	0.133	0.0752
0.6978	0.8462	0.825	0.2920	0.0992	2.944	0.0102	0.0546	0.187
			−20° F., 800 p.s.i.a.					
...	...	...	0.975	0.370	2.635	0.025	0.630	0.0397
0.100	0.243	0.412	0.881	0.310	2.842	0.019	0.447	0.0425
0.200	0.455	0.440	0.783	0.291	2.691	0.017	0.254	0.0669
0.2867	0.5904	0.486	0.7005	0.3183	2.201	0.0128	0.0913	0.140
			−20° F., 1200 p.s.i.a.					
...	...	...	0.971	0.534	1.818	0.029	0.466	0.0622
0.100	0.136	0.735	0.873	0.525	1.663	0.027	0.339	0.0796
0.200	0.233	0.858	0.778	0.532	1.462	0.022	0.235	0.0936
0.2932	0.3198	0.917	0.6762	0.5836	1.159	0.0296	0.0966	0.306
			−80° F., 400 p.s.i.a.					
...	...	...	0.990	0.335	2.955	0.010	0.675	0.0148
0.100	0.148	0.676	0.890	0.302	2.947	0.010	0.550	0.0182
0.200	0.290	0.690	0.789	0.278	2.838	0.011	0.432	0.0255
0.300	0.423	0.709	0.687	0.266	2.583	0.013	0.311	0.0418
0.400	0.544	0.735	0.585	0.275	2.127	0.015	0.181	0.0829
0.4636	0.6133	0.756	0.5160	0.3011	1.714	0.0204	0.0856	0.238
			−80° F., 800 p.s.i.a.					
...	...	...	0.990	0.670	1.478	0.010	0.330	0.0303
0.100	0.112	0.893	0.891	0.682	1.306	0.009	0.206	0.0437
0.1912	0.2022	0.946	0.7988	0.7167	1.115	0.010	0.0811	0.123
			−80° F., 1000 p.s.i.a.					
...	...	...	0.970	0.848	1.144	0.030	0.152	0.197
0.015	0.019	0.789	0.960	0.863	1.112	0.025	0.118	0.212
0.0297	0.0362	0.820	0.9433	0.8896	1.060	0.027	0.0742	0.364
			−140° F., 400 p.s.i.a.					
...	...	...	0.998	0.873	1.143	0.002	0.127	0.0157
0.010	0.030	0.333	0.984	0.844	1.166	0.006	0.126	0.0476
0.030	0.080	0.375	0.964	0.846	1.139	0.006	0.074	0.0811
0.0462	0.1056	0.437	0.9482	0.8737	1.085	0.0056	0.0207	0.271

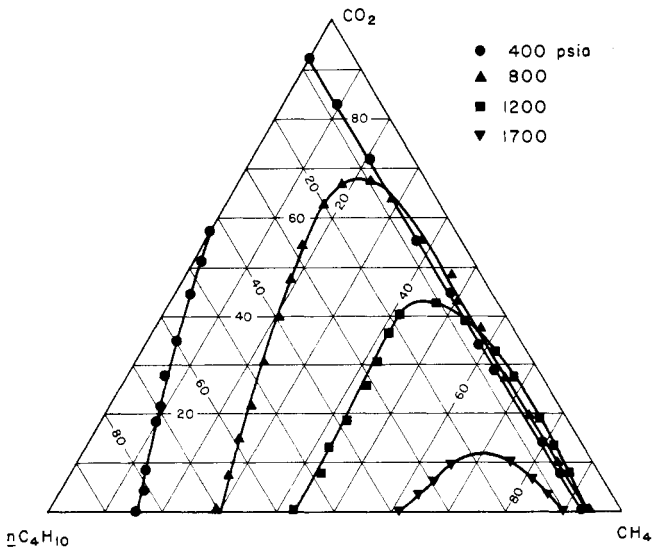

Figure 1. Pressure-composition diagram for methane–*n*-butane–carbon dioxide system at 40° F.

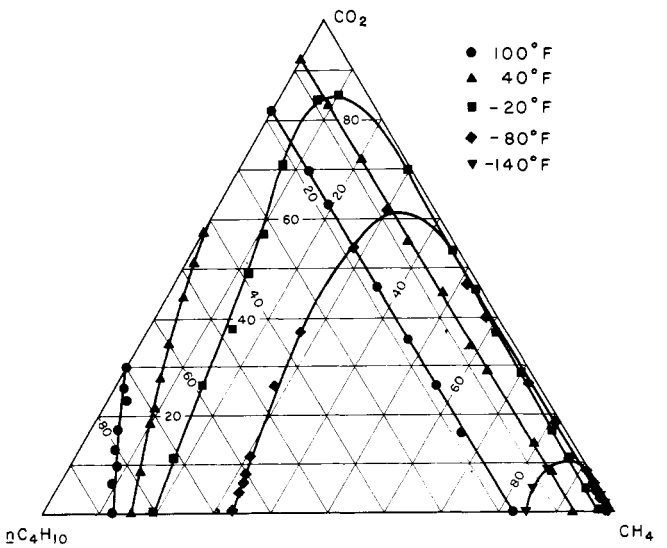

Figure 2. Temperature-composition diagram for methane–*n*-butane–carbon dioxide system at 400 p.s.i.a.

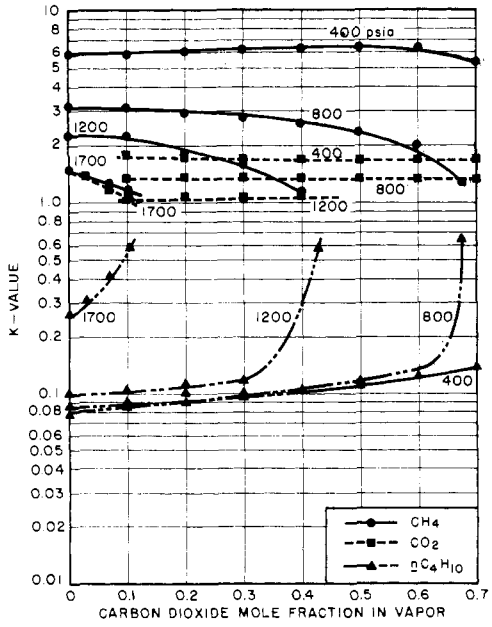

Figure 3. Effect of carbon dioxide on the *K*-values of the components at various pressures and at 40° F.

diagrams are shown in Figures 1 and 2. Figure 3 shows the effect of carbon dioxide on the *K*-values of each of the components.

The accuracy of the actual temperature measurements is within ±0.05° F. at 100° F. and ±0.5° F. at −140° F. The gage readings are accurate within 2 parts per 1000 parts (0.2%). The study shows that the actual analyses are reproducible to within ±0.1 mole %.

ACKNOWLEDGMENT

This work was carried out under a National Science Foundation Grant. The authors are grateful for this assistance.

LITERATURE CITED

(1) Clark, A.M., Din, F., *Discussions Faraday Soc.* **15**, 202 (1953).
(2) Roberts, L.R., Wang, R.H., Azarnoosh, A., McKetta, J.J., J. CHEM. ENG. DATA **7**, 484 (1962).
(3) Wang, R.H., "Vapor-Liquid Equilibrium of the Methane–*n*-Butane–Carbon Dioxide System at Low Temperatures," Ph.D. dissertation, University of Texas, Austin, Texas, 1963.

RECEIVED for review May 2, 1963. Accepted August 22, 1963.

Interaction in Nonelectrolyte Solutions

Solubility of Naphthalene in Some Mixed Solvents Containing Benzene

E. L. HERIC and CECIL D. POSEY
University of Georgia, Athens, Ga.

The solubility of napthalene has been determined in benzene and other solvents, and in solvent mixtures. The average uncertainty in the solubilities is 0.0005 mole fraction hapthalene in the binary systems and less than 0.001 mole fraction in the ternary systems. Ternary systems were investigated using the approaches of Guggenheim and Hildebrand. The average error in correlating predicted with experimental results is the same by either approach, 0.002 in mole fraction napthalene. Better correlation of ternary with binary behavior is obtained with Raoult entropy than with that of Flory-Huggins. Data obtained from binary solution studies are used to predict behavior in ternary systems.

CORRELATION of solution behavior with molecular parameters has been considered in some detail for binary systems of nonelectrolytes (*6–8, 16, 19*). A related problem is the prediction of behavior in multicomponent nonelectrolyte systems from that of the various component pairs. The present work describes a study of solute solubility in mixed solvent systems. The components considered—naphthalene, benzene, toluene, ethylbenzene, carbon tetrachloride, cyclohexane, *n*-hexane and *n*-hexadecane—are characterized by the absence of pronounced polarity.

EXPERIMENTAL

Reagents. Naphthalene used was Eastman (recrystallized from alcohol) and Baker (reagent grade). Since both had indistinguishable properties, which were unchanged upon further recrystallization, they were used as received.

All solvents were purified by distillation at a recovery rate of 1 ml. $min.^{-1}$ and the middle half of the starting material of each distillation was used. Each solvent was double-distilled except for ethylbenzene (single) and *n*-hexadecane (triple). Distillations, except that of *n*-hexadecane at 5mm., were conducted at atmospheric pressure