Phase Equilibria in Hydrocarbon Systems

VOLUMETRIC AND PHASE BEHAVIOR OF THE PROPANE-CARBON DIOXIDE SYSTEM

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Carbon dioxide is an important nonhydrocarbon component of petroleum. A study of the volumetric and phase behavior of binary mixtures of paraffin hydrocarbons and petroleum is of engineering value in predicting such characteristics for underground reservoirs.

The influence of pressure and temperature on four mixtures of propane and carbon dioxide was established experimentally at pressures up to 10,000 pounds per square inch, at eight temperatures between 40° and 460° F. In this temperature range the compositions of the coexisting liquid and gas phases were determined throughout the heterogeneous region. The results are presented in graphical and tabular form.

The present measurements of the phase behavior of the propane-carbon dioxide system are not in good agreement with earlier studies of this system. The influence of pressure and temperature upon the equilibrium ratios is similar to that encountered in other binary systems involving carbon dioxide and a hydrocarbon. The information presented, together with other available data, should permit the prediction of the partial volumetric and phase behavior of carbon dioxide in more complex systems.

KUENEN was perhaps the first to investigate the behavior of binary mixtures of paraffin hydrocarbons and carbon dioxide (3–5). These measurements indicated minimum boiling azeotropic characteristics for the ethane–carbon dioxide system. Poettmann and Katz (8) reviewed the literature relating to binary mixtures of carbon dioxide and hydrocarbons. In addition, they studied the phase behavior of mixtures of carbon dioxide with propane, n-butane, and n-pentane. Information on the volumetric behavior of binary mixtures of methane, ethane, and n-butane with carbon dioxide also is available (7, 9, 10). The present study relates to an experimental investigation of the volumetric and phase behavior of the propane–carbon dioxide system. Only fair agreement with the phase behavior of Poettmann and Katz (8) was realized except in the critical region where the two sets of data differed by less than the combined experimental uncertainties.

MATERIALS

The carbon dioxide was obtained by the thermal decomposition of recrystallized sodium bicarbonate. The gas was solidified at liquid air temperatures under a pressure of less than 0.002 inch of mercury. It was sublimed twice at a similar pressure and a product was saved from the central 80% portion of each sublimation. The purified carbon dioxide was stored in a stainless steel container which has been described (13). The vapor pressure of the carbon dioxide at a temperature corresponding to the ice point of water indicated a variation of less than 0.05 pound per square inch for a tenfold change in the total volume of the gas phase. The average two-phase pressure agreed with the measurements of Bridgeman (1) within 0.04%. It is doubtful if the purified carbon dioxide contained more than 0.0005 mole fraction impurity.

The propane was obtained from the Phillips Petroleum Co., which indicated that it contained less than 0.001 mole fraction of impurities. This hydrocarbon was fractionated in a column packed with glass rings at a reflux ratio of approximately 50 to 1. The central 80% portion of the overhead was withdrawn as product. The product from the distillation was condensed in a steel weighing bomb (13) at a pressure below 0.002 inch of mercury. As a result of varying the quality or fraction vaporized

from 0.1 to 0.9 at 100° F., the vapor pressure of the sample of propane utilized changed by less than 0.2 pound per square inch. It is believed that the propane used in this investigation contained less than 0.001 mole fraction of material other than propane.

APPARATUS AND PROCEDURE

The equipment and techniques employed in this study have been described (7, 13). In principle, the method involved the introduction of known quantities of propane and carbon dioxide into a stainless steel container whose effective volume was varied by the introduction or withdrawal of mercury. The temperature of the container which was controlled by immersion in an agitated oil bath was related to the international platinum scale by the use of a platinum resistance thermometer of the strain-free type. It is believed the temperature of the stainless steel container was known within 0.02° F. relative to the international platinum scale.

Attainment of equilibrium was hastened by mechanical agitation of the system and the volume occupied by the mixtures of propane and carbon dioxide was established with an uncertainty not larger than 0.2% except at molal volumes smaller than that at bubble point. In this region uncertainties as large as 0.3% may exist. The pressure was established by means of a special balance (13) which was calibrated against the vapor pressure of carbon dioxide at the ice point of water (1). The calibration of this instrument has changed by less than 0.05% in a 12-year period. It is believed that the pressures recorded are known within 0.1% or 0.3 pound per square inch, whichever is larger, throughout the entire range of investigation.

The bubble point states were determined for each of the four experimentally investigated mixtures with satisfactory accuracy. However, only a limited number of dew point states could be determined from the volumetric observations. In order to establish with greater certainty the relation of the composition of the dew point gas to pressure and temperature, samples were withdrawn at equilibrium under isobaric-isothermal conditions. Negligible changes in temperature and pressure were encountered during the withdrawal process. The composition of the gas sample obtained was determined gravimetrically by the use of

TABLE I. SAMPLE OF EXPERIMENTAL VOLUMETRIC DATA

100° F. Mole Fraction Propane = 0.5983

Pressure, Lb./Sq. Inch Absolute	Volume Cu. Ft./Lb. Mole	Compressibility Factor
Sample Weight 0.02829[a]		
157.7	34.211	0.89823
211.3	24.429	0.85938
282.5	17.070	0.80287
310.9	15.018	0.77737
333.5	13.527	0.75110
349.7	11.977	0.69731
396.1	8.5608	0.56455
Sample Weight 0.22011[a]		
504.7	4.1862	0.35175
540.0	3.2669	0.29370
579.3	2.3919	0.23069
596.1	2.0479	0.20324
606.9	1.8304	0.18496
614.7	1.6806	0.17200
621.6	1.5554	0.16097
628.7	1.4175	0.14836
697.1	1.3714	0.15917
1025.5	1.3168	0.22482
1974.6	1.2312	0.40477
3099.8	1.1748	0.60630
4142.4	1.1395	0.78584
5094.6	1.1138	0.94471
6143.0	1.0913	1.11610
7151.1	1.0719	1.27620
8179.2	1.0568	1.43912
9099.5	1.0452	1.58282
9579.1	1.0379	1.65520

[a] Sample weight expressed in pounds.

absorption tubes packed with Ascarite. To avoid adsorption of the propane, the Ascarite was conditioned with this hydrocarbon before use. Duplicate measurements were made at many of the states investigated and the average deviation of the duplicate measurements at the same state was 0.13%.

EXPERIMENTAL RESULTS

Four mixtures of propane and carbon dioxide were studied at 10 temperatures between 40° and 460° F. However, the measurements at 70° and 130° F. extended only to a pressure of 1500 pounds per square inch. A sample of the experimental results obtained is presented in Table I. A detailed record of these measurements is available (11). The experimental data were smoothed by appropriate residual graphical techniques to even values of pressure. The results of these graphical operations constitute Table II in which the molal volumes of the experimentally studied mixtures are recorded. In the calculations the molecular weights of carbon dioxide and propane were taken as 44.010 and 44.095, respectively. These quantities correspond to the atomic weights of carbon and hydrogen established for 1950. It is believed that the molal volume has been determined with a probable uncertainty of 0.2% throughout the entire range of conditions reported except for values below 1 cubic foot per pound mole where the uncertainty may be as much as 0.35%.

In order to establish in greater detail the behavior of this system at the boundaries of the heterogeneous regions near the critical state, the data of Poettmann and Katz (8) were utilized to establish the relationship of pressure to temperature at the critical state, and good agreement between such values and the less detailed measurements in this region was realized. Significant disagreement between the measurements of Poettmann and Katz and the present study was encountered in the relationships of bubble point and dew point pressures to composition. For this reason all of the data presented here are based upon the present measurements except for the variation in the critical pressure with temperature.

The data of Table II include states at pressures both above and below the heterogeneous region. Descriptions of states which exist in the two-phase region have been omitted from this table, since they can be obtained directly from information concerning the volumetric properties of the bubble point liquid and the dew point gas at the pressure and temperature of interest. In the detailed record of experimental data (11), the molal volume in the heterogeneous region is recorded.

Table III contains the experimentally measured compositions of the coexisting liquid and gas phase in the heterogeneous region. The duplicate determinations at each given state have been included. Table III does not include the bubble point and dew point states determined from the volumetric measurements, which are recorded in Table II. The properties of the coexisting gas and liquid phases constitute Table IV. The data have been smoothed with respect to temperature, pressure, and the mole fraction of propane. The molal volume of the bubble point liquid and dew point gas phases is presented for even values of pressure for five
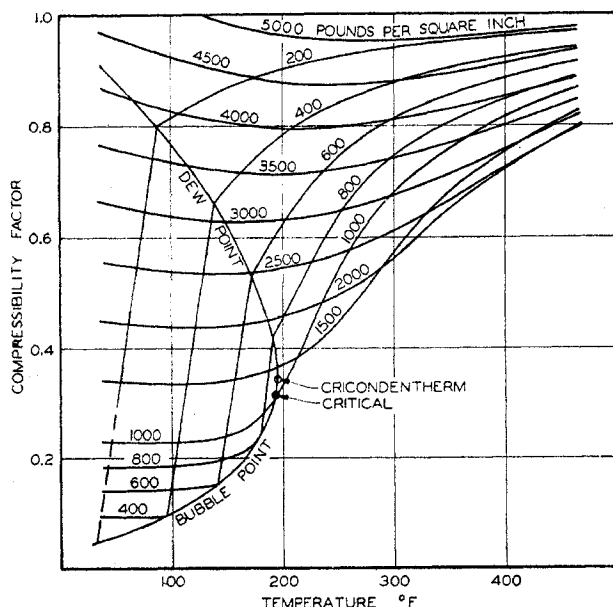

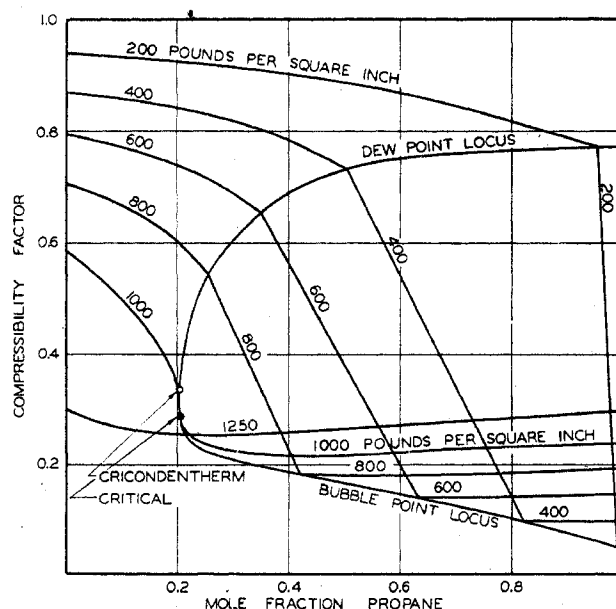Figure 1. Compressibility of a Mixture Containing 0.8038 Mole Fraction Propane

Figure 2. Effect of Composition on the Compressibility of the Propane–Carbon Dioxide System at 100° F.

TABLE II. VOLUMETRIC BEHAVIOR OF MIXTURES OF PROPANE AND CARBON DIOXIDE

Mole Fraction Propane, 40° F and 100° F

Pressure, Lb./Sq. Inch Absolute	40° F 0.2064	40° F 0.4116	40° F 0.5983	40° F 0.8038	100° F 0.2064	100° F 0.4116	100° F 0.5983	100° F 0.8038
Dew point	(356)[a] 11.66[b]	(193) 23.34	(134) 35.0	(99) 48.9	(964) 2.317	(501) 8.36	(327) 13.78	(239) 19.21
Bubble point	(499) 0.958	(415) 1.080	(335) 1.175	(223) 1.269	(1001) 1.650	(806) 1.351	(631) 1.384	(418) 1.439
200	23.73				27.76	27.01	26.03	24.48
400			1.171	1.262	12.58	11.66		
600	0.950	1.068	1.161	1.254	7.34			1.418
800	0.936	1.057	1.152	1.246	4.46		1.353	1.399
1,000	0.924	1.047	1.143	1.239		1.296	1.326	1.382
1,250	0.911	1.035	1.132	1.230	1.207	1.243	1.298	1.364
1,500	0.900	1.025	1.123	1.222	1.128	1.203	1.273	1.348
1,750	0.890	1.016	1.115	1.214	1.083	1.175	1.253	1.333
2,000	0.881	1.007	1.107	1.207	1.052	1.153	1.235	1.320
2,250	0.873	0.999	1.100	1.200	1.027	1.135	1.220	1.307
2,500	0.866	0.992	1.094	1.194	1.006	1.119	1.206	1.295
2,750	0.859	0.986	1.087	1.189	0.988	1.105	1.194	1.285
3,000	0.853	0.981	1.082	1.183	0.972	1.092	1.184	1.276
3,500	0.842	0.970	1.071	1.173	0.946	1.070	1.164	1.259
4,000	0.832	0.960	1.061	1.163	0.926	1.051	1.148*	1.245
4,500	0.823	0.951	1.052	1.154	0.910	1.035	1.134	1.232
5,000	0.816	0.944	1.044	1.146	0.897	1.021	1.121	1.220
6,000	0.801	0.929	1.029	1.131	0.872	0.998	1.099	1.201
7,000	0.789	0.916	1.016	1.118	0.853	0.977	1.081	1.184
8,000	0.778	0.904	1.006	1.106	0.836	0.961	1.064	1.169
9,000	0.768	0.894	0.997	1.097	0.823	0.947	1.050	1.156
10,000	0.759	0.885	0.988	1.089	0.810	0.935	1.037	1.145

Mole Fraction Propane, 160° F and 220° F

Pressure, Lb./Sq. Inch Absolute	160° F 0.2064	160° F 0.4116	160° F 0.5983	160° F 0.8038	220° F 0.2064	220° F 0.4116	220° F 0.5983	220° F 0.8038
Dew point	(974) 2.192	(828) 3.72		(511) 7.64				
Bubble point				(691) 1.824				
200	31.5	30.9	30.2	29.16	35.1	34.7	34.1	33.3
400	14.82	14.20	13.30	11.82	16.87	16.40	15.77	14.77
600	9.19	8.48	7.39		10.76	10.27	9.51	8.25
800	6.42	5.54	4.05	1.736	7.69	7.16	6.37	4.80
1,000	4.57	3.64	2.055	1.648	5.84	5.30	4.51	3.01
1,250	3.16	2.208	1.668	1.582	4.36	3.81	3.04	2.156
1,500	2.232	1.694	1.547	1.535	3.38	2.838	2.319	1.789
1,750	1.714	1.520	1.477	1.500	2.719	2.315	1.978	1.716
2,000	1.468	1.421	1.429	1.471	2.258	1.983	1.801	1.663
2,250	1.339	1.356	1.391	1.446	1.948	1.782	1.688	1.621
2,500	1.259	1.311	1.361	1.425	1.730	1.646	1.611	1.584
2,750	1.203	1.277	1.336	1.407	1.576	1.553	1.554	1.550
3,000	1.163	1.249	1.315	1.391	1.472	1.483	1.509	
3,500	1.104	1.203	1.282	1.363	1.339	1.390	1.439	1.493
4,000	1.059	1.169	1.255	1.340	1.246	1.324	1.388	1.451
4,500	1.024	1.141	1.231	1.321	1.182	1.274	1.351	1.421
5,000	0.999	1.116	1.211	1.304	1.136	1.234	1.320	1.397
6,000	0.961	1.079	1.177	1.274	1.071	1.176	1.267	1.357
7,000	0.931	1.049	1.148	1.249	1.022	1.133	1.226	1.326
8,000	0.906	1.025	1.125	1.228	0.984	1.097	1.194	1.299
9,000	0.885	1.005	1.106	1.210	0.953	1.071	1.170	1.274
10,000	0.866	0.988	1.089	1.194	0.928	1.049	1.149	1.252

Mole Fraction Propane, 280° F and 340° F

Pressure, Lb./Sq. Inch Absolute	280° F 0.2064	280° F 0.4116	280° F 0.5983	280° F 0.8038	340° F 0.2064	340° F 0.4116	340° F 0.5983	340° F 0.8038
200	38.6	38.2	37.7	37.1	42.0	41.7	41.34	40.8
400	18.78	18.40	17.00	17.16	20.60	20.29	19.89	19.32
600	12.17	11.78	11.24	10.46	13.46	13.15	12.74	12.15
800	8.84	8.46	7.90	7.06	9.90	9.59	9.17	8.55
1,000			5.92	5.02	7.76	7.46	7.04	6.41
1,250	5.24	4.86	4.38	3.60	6.04	5.75	5.36	4.78
1,500	4.19	3.85	3.39	2.741	4.91	4.64	4.29	3.78
1,750	3.46	3.16	2.781	2.339	4.11	3.86	3.55	3.13
2,000	2.943	2.689	2.392	2.115	3.52	3.31	3.05	2.710
2,250	2.561	2.350	2.145	1.978	3.09	2.901	2.686	2.437
2,500	2.268	2.107	1.973	1.882	2.749	2.597	2.429	2.253
2,750	2.041	1.934	1.848	1.809	2.484	2.363	2.241	2.122
3,000	1.869	1.809	1.757	1.753	2.271	2.176	2.093	2.020
3,500	1.641	1.640	1.641	1.667	1.953		1.894	1.875
4,000	1.485	1.523	1.558	1.601	1.739	1.748	1.759	1.776
4,500	1.377		1.490	1.552	1.592	1.628	1.660	1.699
5,000	1.301	1.378	1.438	1.514	1.484	1.539	1.586	1.641
6,000	1.195	1.290	1.366	1.451	1.334	1.412	1.481	1.552
7,000	1.122	1.228	1.314	1.403	1.238	1.328	1.406	1.491
8,000	1.072	1.180	1.271	1.366	1.168	1.269	1.352	1.443
9,000	1.032	1.144	1.235	1.334	1.112	1.219	1.309	1.402
10,000	0.999	1.114	1.207	1.303	1.070	1.178	1.271	1.368

Mole Fraction Propane, 400° F and 460° F

Pressure, Lb./Sq. Inch Absolute	400° F 0.2064	400° F 0.4116	400° F 0.5983	400° F 0.8038	460° F 0.2064	460° F 0.4116	460° F 0.5983	460° F 0.8038
200	45.4	45.2	44.8	44.3	48.8	48.6	48.3	47.9
400	22.39	22.12	21.78	21.31	24.16	23.91	23.64	23.24
600	14.72	14.44	14.11	13.64	15.95	15.71	15.44	15.05
800	10.88	10.62	10.28	9.81	11.84	11.61	11.35	10.97
1,000	8.59	8.33	8.01	7.54	9.38	9.16	8.91	8.54
1,250	6.76	6.52	6.22	5.76	7.41	7.22	6.99	6.63
1,500	5.54	5.32	5.05	4.63	6.10	5.94	5.73	5.39
1,750	4.67	4.48	4.24	3.87	5.18	5.04	4.84	4.54
2,000	4.02	3.86	3.65	3.35	4.51	4.37	4.20	3.92
2,250	3.55	3.40	3.22	2.968	3.99	3.87	3.71	3.46
2,500	3.17	3.05	2.896	2.691	3.58	3.47	3.33	3.13
2,750	2.872	2.768	2.643	2.489	3.25	3.16	3.03	2.868
3,000	2.636	2.540	2.444	2.337	2.976	2.906	2.800	2.673
3,500	2.263	2.209	2.161	2.120	2.558	2.522	2.459	2.387
4,000	2.002	1.993	1.980	1.979	2.259	2.248	2.219	2.192
4,500	1.816	1.834	1.850	1.872	2.039	2.054	2.048	2.054
5,000	1.680	1.716	1.746	1.788	1.870	1.901	1.921	1.949
6,000	1.484	1.551	1.611	1.671	1.636	1.692	1.743	1.798
7,000	1.356	1.442	1.512	1.589	1.479	1.557	1.621	1.688
8,000	1.266	1.361	1.440	1.531	1.373	1.463	1.531	1.609
9,000	1.199	1.302	1.388	1.481	1.293	1.389	1.465	1.549
10,000	1.149	1.252	1.346	1.438	1.231	1.327	1.408	1.498

[a] Figures in parentheses represent dew point or bubble point pressures expressed as pounds per square inch absolute.
[b] Volumes expressed in cubic feet per pound mole.

temperatures between 40° and 160° F. The data of Michels and Michels (6) and the results of another recent investigation (12) were employed to establish the behavior of pure carbon dioxide and propane. The equilibrium ratio, K, for each of the components is defined by the expression

$$K_k = \frac{Y_k}{X_k} \qquad (1)$$

in which Y_k is the mole fraction in the gas phase and X_k is the mole fraction in the liquid phase. Values of this quantity are included in Table IV. The bubble point and dew point pressures as determined by Poettmann and Katz (8) are compared with the present data in Table V. The disagreement appears to result from differences in the measured compositions of the mixtures investigated. The deviation of the bubble point and dew point data for each of the mixtures is systematic and good agreement can be realized by appropriate modification in composition. Since the presently established bubble point and dew point states based upon volumetric measurements agree well with directly measured compositions of the coexisting phases, the present values have been recorded in Table IV. The deviations presented in Table V are well beyond the estimated combined experimental uncertainty of the two sets of measurements. The agreement of the variations in pressure with temperature at the critical state is
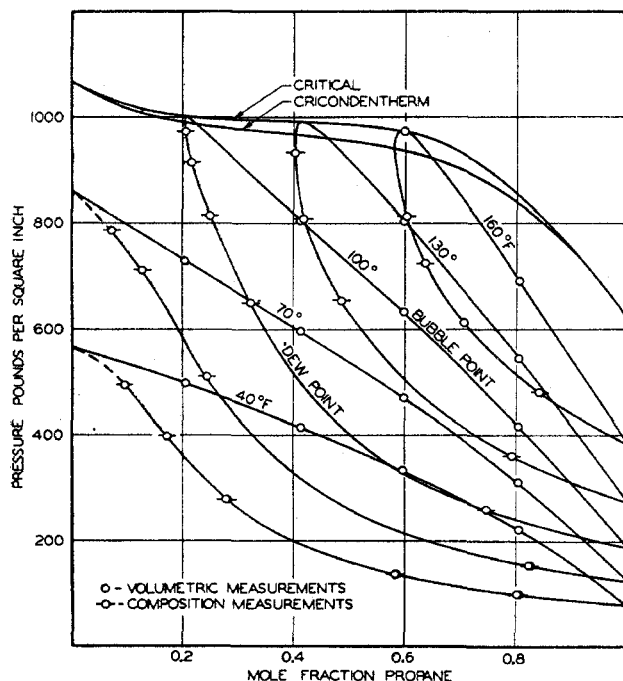
Figure 3. Pressure-Composition Diagram for the Propane–Carbon Dioxide System

good. However, marked differences in the composition corresponding to a particular critical temperature or pressure exist between the two sets of data. In the case of the n-butane–carbon dioxide system a similar lack of agreement was found (7) between the authors' measurements and those of Poettmann and Katz (8).

BEHAVIOR OF SYSTEM

In order to illustrate more fully the behavior of the propane–carbon dioxide system several figures are presented. The compressibility factor of a mixture containing 0.8038 mole fraction propane is shown as a function of temperature in Figure 1. This factor is defined as $Z = PV/RT$, where P is pressure, V is molal volume, T is thermodynamic temperature, and R the universal

TABLE III. EXPERIMENTAL COMPOSITIONS OF GAS PHASE IN HETEROGENEOUS MIXTURES OF PROPANE AND CARBON DIOXIDE

Pressure, Lb./Sq. Inch Absolute	Mole Fraction Propane	Pressure, Lb./Sq. Inch Absolute	Mole Fraction Propane	Pressure, Lb./Sq. Inch Absolute	Mole Fraction Propane
40° F.		100° F.		160° F.	
99.4	0.8005	260.5	0.7487	480.6	0.8418
	0.8065		0.7494		0.8401
138.5	0.5808	650.4	0.3214	613.0	0.7056
	0.5845		0.3217		0.7041
279.1	0.2789	814.2	0.2513	723.7	0.6347
	0.2803		0.2509		0.6370
399.8	0.1728	914.1	0.2160	813.4	0.6035
	0.1733		0.2161		0.6021
495.4	0.0953	973.9	0.2072		
	0.0949		0.2043		
70° F.		130° F.			
154.1	0.8216	360.5	0.7921		
	0.8258		0.7925		
512.2	0.2436	657.4	0.4857		
	0.2439		0.4854		
711.0	0.1276	808.6	0.4172		
	0.1277		0.4167		
788.2	0.0710	933.7	0.4013		
	0.0707		0.4005		

TABLE IV. PROPERTIES OF COEXISTING PHASES IN PROPANE–CARBON DIOXIDE SYSTEM

Pressure, Lb./Sq. Inch Absolute	Mole Fraction Propane		Volume Cu. Ft./Lb. Mole		Equilibrium Ratio	
	Gas	Liquid	Gas	Liquid	Propane	Carbon dioxide
—40° F.—						
79[a]	1.0000	1.0000	63.0	1.347	1.0000	...
100	0.7944	0.9753	48.3	1.338	0.8145	8.32
150	0.5324	0.9116	30.9	1.313	0.5840	5.29
200	0.3964	0.8398	22.43	1.284	0.4720	3.77
250	0.3136	0.7598	17.46	1.250	0.4127	2.858
300	0.2569	0.6684	14.20	1.209	0.3843	2.241
350	0.2124	0.5639	11.90	1.158	0.3768	1.806
400	0.1691	0.4468	10.16	1.099	0.379[b]	1.502
450	0.1312	0.3286	8.80	1.034	0.40	1.294
500	0.0898	0.2044	7.68	0.9571	0.44	1.144
550	0.0298	0.0599	6.64	0.8381	0.50	1.032
566.5[c]	0.0000	0.0000	6.27	0.7807	...	1.000
—70° F.—						
125[a]	1.0000	1.0000	38.5	1.412	1.0000	...
150	0.8382	0.9755	31.8	1.404	0.8593	6.60
200	0.6411	0.9258	23.33	1.386	0.6925	4.84
250	0.5188	0.8726	18.27	1.368	0.5945	3.78
300	0.4366	0.8166	14.89	1.348	0.5347	3.07
350	0.3765	0.7577	12.47	1.326	0.4969	2.573
400	0.3282	0.6952	10.64	1.302	0.4720	2.204
450	0.2852	0.6273	9.22	1.277	0.4544[b]	1.918
500	0.2482	0.5557	8.08	1.250	0.4469	1.692
550	0.2186	0.4822	7.14	1.221	0.4533	1.509
600	0.1908	0.4063	6.35	1.190	0.470	1.363
650	0.1632	0.3278	5.67	1.157	0.498	1.245
700	0.1327	0.2484	5.07	1.119	0.534	1.155
750	0.0989	0.1725	4.52	1.075	0.573	1.089
800	0.0583	0.0954	4.00	1.018	0.611	1.041
850	0.0126	0.0195	3.51	0.9427	0.64	1.007
860.9[c]	0.0000	0.0000	3.40	0.9233	...	1.000
—100° F.—						
188.7[a]	1.0000	1.0000	24.54	1.495	1.0000	...
200	0.9528	0.9919	23.12	1.493	0.9606	5.83
250	0.7719	0.9505	18.33	1.480	0.8121	4.61
300	0.6489	0.9074	15.12	1.468	0.7151	3.79
350	0.5630	0.8639	12.78	1.456	0.6518	3.21
400	0.5006	0.8201	10.99	1.444	0.6104	2.776
450	0.4519	0.7752	9.55	1.431	0.5830	2.439
500	0.4124	0.7291	8.38	1.418	0.5656	2.169
550	0.3787	0.6809	7.39	1.405	0.5562	1.947
600	0.3486	0.6307	6.55	1.392	0.5527	1.764
650	0.3219	0.5788	5.82	1.380	0.5562	1.610
700	0.2987	0.5265	5.17	1.368	0.5673	1.481
750	0.2762	0.4728	4.59	1.358	0.5842	1.373
800	0.2552	0.4186	4.04	1.351	0.6097	1.281
850	0.2353	0.3654	3.52	1.348	0.6440	1.205
900	0.2199	0.3139	2.992	1.351	0.7005	1.137
950	0.2092	0.2637	2.447	1.369	0.7933	1.074
1000	0.2027	0.2098	1.877	1.598	0.9662	1.009
1002.5[d]	0.205	0.205	1.708	1.708	1.0000	1.000
990[e]	0.202	...	2.014	...	...	...
—130° F.—						
273.5[a]	1.0000	1.0000	16.25	1.604	1.0000	...
300	0.9266	0.9824	14.82	1.599	0.9432	4.17
350	0.8127	0.9474	12.60	1.589	0.8578	3.56
400	0.7261	0.9118	10.90	1.581	0.7963	3.10
450	0.6575	0.8754	9.55	1.573	0.7511	2.749
500	0.6020	0.8382	8.44	1.567	0.7182	2.460
550	0.5574	0.8008	7.50	1.563	0.6960	2.222
600	0.5196	0.7624	6.68	1.560	0.6816	2.022
650	0.4876	0.7230	5.96	1.561	0.6742	1.850
700	0.4606	0.6829	5.31	1.565	0.6745	1.701
750	0.4381	0.6423	4.72	1.576	0.6821	1.571
800	0.4194	0.6004	4.17	1.595	0.6985	1.453
850	0.4104	0.5597	3.67	1.626	0.7332	1.339
900	0.4032	0.5160	3.19	1.677	0.7814	1.233
950	0.4020	0.4694	2.717	1.766	0.8564	1.127
992[d]	0.412	0.412	2.073	2.073	1.0000	1.000
969[e]	0.402	...	2.519	...	...	...
—160° F.—						
383.8[a]	1.0000	1.0000	10.70	1.761	1.0000	...
400	0.9685	0.9901	10.22	1.762	0.9782	3.18
450	0.8847	0.9591	8.92	1.766	0.9225	2.818
500	0.8168	0.9274	7.85	1.772	0.8807	2.523
550	0.7623	0.8957	6.95	1.781	0.8511	2.279
600	0.7160	0.8630	6.17	1.793	0.8297	2.073
650	0.6782	0.8302	5.50	1.808	0.8169	1.895
700	0.6487	0.7981	4.91	1.828	0.8128	1.740
750	0.6257	0.7662	4.40	1.850	0.8166	1.601
800	0.6070	0.7334	3.95	1.879	0.8277	1.474
850	0.5932	0.7002	3.55	1.915	0.8472	1.357
900	0.5838	0.6652	3.17	1.965	0.8776	1.243
950	0.5798	0.6265	2.736	2.046	0.9255	1.125
976[d]	0.593	0.593	2.270	2.270	1.0000	1.000
941[e]	0.579	...	2.831	...	...	...

[a] Vapor pressure of propane.
[b] Unusually large uncertainties exist in values at equilibrium ratios for propane at stages rich in carbon dioxide at 40° and 70° F.
[c] Vapor pressure of carbon dioxide.
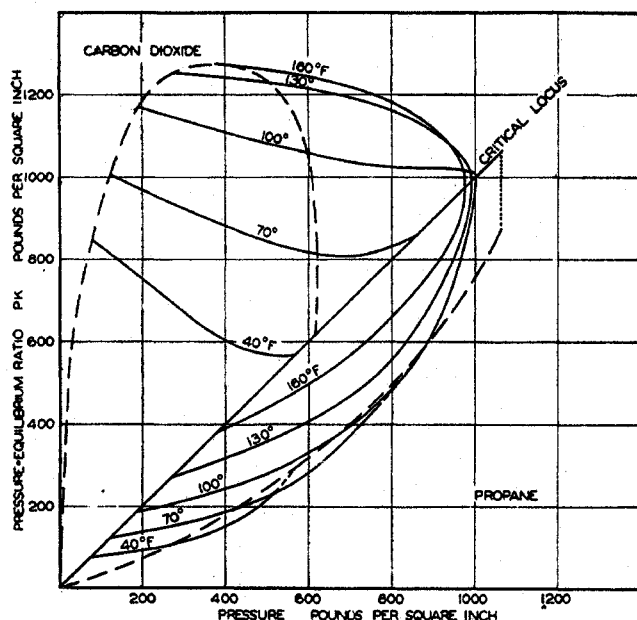[d] Critical.
[e] Cricondentherm.

Figure 4. Pressure–Equilibrium Ratio Products for Propane and Carbon Dioxide

Figure 5. Compressibility Factor–Temperature Diagram for the Propane–Carbon Dioxide System

gas constant. The data for the higher pressures have not been included in order to depict the behavior in the heterogeneous region with somewhat greater detail. The critical state for the mixture has been indicated on the phase boundary shown in Figure 1. At pressures above 875 pounds per square inch this mixture is homogeneous, whereas below this pressure the mixture is heterogeneous at temperatures below 195° F. The isobar at a pressure of 1000 pounds per square inch does not pass through the critical state, even though the compressibility factor is equal to that of the critical state at the same temperature. The effect of the mole fraction of propane upon the compressibility of the system at a temperature of 100° F. is shown in Figure 2. In this diagram the critical state is indicated and the cricondentherm, which might more properly be called maxcondentherm since it does not have the characteristics of a critical state, corresponds to the state at the boundary of the heterogeneous

TABLE V.   COMPARISON OF BUBBLE POINT AND DEW POINT
PRESSURES FROM DIFFERENT INVESTIGATIONS

Mole Fraction Propane	Temperature, ° F.	Dew Point		Bubble Point	
		Poettmann and Katz[a]	Authors	Poettmann and Katz[a]	Authors
0.0607	75.1	846[b]	854[b]	865[b]	878[b]
	80.0	903	908	915	933
	85.1	963	974	976	994
	87.3	1003	1003	1012	1021
0.2127	72.7	541	584	739	747
	83.7	635	690	825	844
	93.0	725	802	927	933
	100.6	876	949	996	1000
0.4935	80.1	275	307	575	604
	100.7	360	411	680	736
	122.7	485	566	837	878
	141.9	690	842	972	987
0.6401	115.0	348	575	685	670
	141.8	483	546	824	822
	153.3	570	641	904	893
	162.0	655	744	944	947
0.8481	127.7	288	321	464	475
	163.0	462	493	615	638
	180.3	560	614	712	742
	192.6	650	735	775	786

[a] See reference (8).
[b] Pressures expressed in pounds per square inch absolute.

region richest in carbon dioxide. Isobars for pressures below 188.7 pounds per square inch, which is the vapor pressure of propane, lie in the gaseous region throughout the entire composition interval. The isobars at compositions richer in propane than at bubble point are in the liquid phase. The experimental data already available for carbon dioxide (6) and propane (12) were used to establish the volumetric behavior of the system at the boundaries of the diagram.

The variation in the compositions of the coexisting phases with pressure at several temperatures is presented in Figure 3. The experimentally determined compositions of the dew point gas and the bubble point liquid are included on this diagram. The data are similar in appearance to many other hydrocarbon systems except at 40° and 70° F. At these temperatures there exists a reversal in curvature in the relationship of the composition of dew point gas to pressure. Such a situation was encountered at 100° F. in the case of the n-butane–carbon dioxide system (7). This type of behavior appears typical for systems made up of carbon dioxide and a paraffin hydrocarbon at temperatures up to slightly above the critical temperature of the hydrocarbon. A similar reversal in curvature of the isothermal pressure-composition relations at dew point was found by Poettmann and Katz (8) for such systems and by Caubet (2) for the carbon dioxide–sulfur dioxide system. The loci of the unique critical and cricondentherm states have been indicated in Figure 3, the data of Poettmann and Katz being used to aid in establishing these loci. The behavior is similar to that found for the n-butane–carbon dioxide system (7).

The product of the pressure and the equilibrium ratio is shown in Figure 4 as a function of pressure at the temperatures for which heterogeneous equilibrium was obtained. The behavior is similar to that found for other binary systems and the relatively complex behavior shown in Figure 3 at the lower temperatures and low mole fractions of propane did not result in any anomalous relation of the equilibrium ratio to pressure or temperature.

The compressibility factor of the dew point gas and bubble point liquid of the four mixtures investigated together with similar data for carbon dioxide (6) and propane (12) is presented as a function of temperature in Figure 5. The variation with temperature of the compressibility factor at the critical and cricondentherm states is shown.

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Action of Antifoaming Agents at Optimum Concentrations

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This work was done as part of an effort to find the mechanisms underlying the action of foam-inhibiting agents. For a comparison of the effects of different agents it was necessary to find the optimum concentration of each. On this basis the antifoaming effect was compared with the viscosity, the spreading coefficients, and the entering coefficients of each agent for each of two aqueous foaming solutions containing surface-active agents.

The sign of the spreading and entering coefficients is usually positive for a foam-inhibiting agent. No precise correlation exists between the magnitudes of the properties here reported, though usually a large positive spreading coefficient and a low viscosity are associated with more effective foam-inhibiting action.

Two distinct effects of foam inhibitors could be distinguished. With some, the agent promotes the rate of drainage of liquid from the foam films without much affecting the final thickness of the film at which its rupture takes place. This effect is believed to be the result of a decreased surface viscosity produced by the presence of the agent. Other agents cause the rupture of thick liquid films before drainage of liquid has thinned them to the breaking point. Many agents produce combinations of the two effects.

INDUSTRIAL chemists who use antifoaming agents have known for a long time that for most agents there is an optimum concentration, below which it is a less effective antifoam and above which it may actually serve to stabilize the foaming of the system. Hitherto in comparisons of antifoaming agents, a single concentration of each agent, usually 1% by volume, has been used as interest was chiefly in the existence or nonexistence of antifoaming effect, which, within wide limits, is not affected by variation of concentration of the agent. It is now established that for insoluble antifoaming agents the answer to that question depends on the sign of the initial spreading and entering coefficients (8, 10).

It now seems of interest to investigate the secondary effect of variation of concentration of the agent. This is of importance when comparisons are drawn between different agents as it is more logical to compare optimum effects, at a concentration for each agent that can be determined only by experiment, than to use the same concentration for each, imposed arbitrarily. By using a variety of agents it is also proposed to elucidate some factors that are of importance in the foam-inhibiting effect. In these experiments only systems that are limited to atmospheric conditions of pressure and temperature are dealt with, and hence any proposed factors or mechanisms of foam-inhibiting action are not held to apply to foams produced in steam generating systems. Gunderson and Denman (4) have found that use of organic foam inhibitors in steam generating foaming systems is primarily controlled by mechanisms other than those stressed in this paper or in preceding papers of this series.

MATERIALS AND METHODS

Two foaming systems were prepared. System A consisted of 0.50% by weight Nacconol NRSF (National Aniline Division, Allied Chemical and Dye Corp.) and 0.75% by weight sodium silicate solution, technical grade (Fisher Scientific Co.) dissolved in distilled water. System B consisted of 0.20% by weight Aerosol OT, 100% pure (American Cyanamid Co.), and 1.00% by weight glycerol, C.P., dissolved in distilled water.

Materials were selected, most of which are commercially available antifoaming agents in current use, as antifoaming agents for these foaming systems. There was little to be gained by using rigorously purified agents as it was not desired to establish effects caused by differences in structure, but to make a more fundamental inquiry—namely, greater precision in the description of the nature of the effect itself.

Foaming tests were made on each of the systems A and B alone and with different concentrations of each agent. The measurements were initial foam density, foam stability, viscosity, surface tension, and interfacial tension.

MEASUREMENT OF INITIAL FOAM DENSITY. Two hundred milliliters of sample are put in a 1-liter beaker and the twin blades of a Sunbeam Mixmaster are adjusted so as to come to within less than $1/16$ inch from the bottom of the beaker. The whipping is done at the top speed of the Mixmaster. After