

Phase Behavior of Binary Carbon Dioxide-Paraffin Systems

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IN 1897 Kuenen reported the critical behavior of the binary carbon dioxide-ethane system (19, 20, 21). This system forms a minimum-boiling azeotrope and has a critical locus which is characteristic of this behavior as Figure 1 shows. The azeotrope persists up to the critical locus giving a critical azeotrope containing 27 mole % ethane. Since the carbon dioxide-ethane system forms a minimum-boiling azeotrope, one of the purposes of this investigation was to determine the effect on the critical behavior of substituting higher paraffin hydrocarbons for ethane. This study provides a basis for further examination of the equilibrium constants for carbon dioxide in complex hydrocarbon mixtures.

The binary systems studied are carbon dioxide-propane, carbon dioxide-butane, and carbon dioxide-pentane. Other binary carbon dioxide systems upon which critical data have been reported are listed in Table I.

The apparatus used to obtain the data was similar to that described by Katz and Kurata (12). It consisted primarily of an equilibrium cell with a glass window and suitable tubing and valve connections. Pressure was supplied by a hand pump, using mercury as the confining liquid, and was measured by a calibrated Bourdon gage. The cell was surrounded by an air bath which was agitated by a fan and heated by electric coils. The entire mechanism was mounted on a trunnion and rocked to ensure equilibrium, the mercury in the cell causing severe agitation of the liquid and vapor phases in the cell.

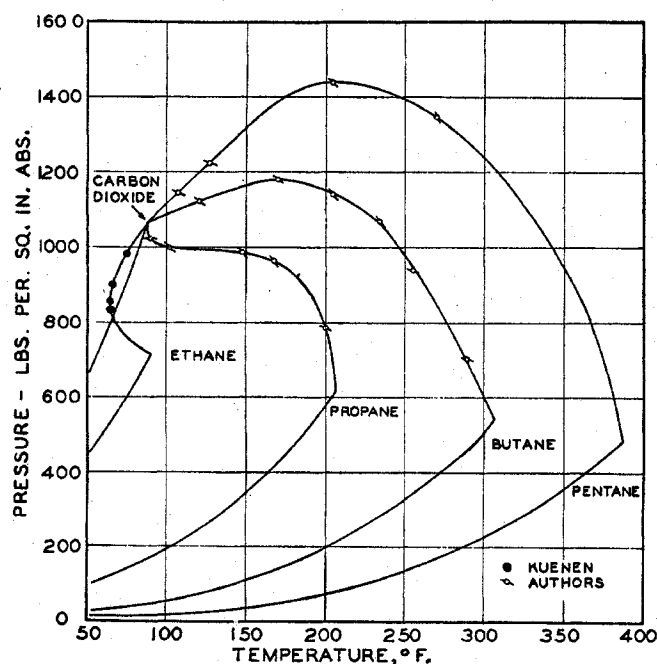


Figure 1. Critical Loci of Carbon Dioxide-Paraffin Systems

The vapor-liquid equilibria and critical loci of the binary carbon dioxide-propane, carbon dioxide-butane and carbon dioxide-pentane systems have been determined. The complete transition from the carbon dioxide-ethane system which forms constant-boiling mixtures to the carbon dioxide-pentane system which has normal behavior is shown. The experimental data are presented in both graphical and tabulated form.

The temperature was measured by a pair of calibrated copper-constantan thermocouples in series, embedded in the walls of the cell. The volume of the fluid in the cell was determined by a calibrated scale mounted beside the glass window.

The carbon dioxide used came from Pure Carbonic Incorporated and was stated to have a purity of 99.5%. Successive samples were completely absorbed in potassium hydroxide solution. The hydrocarbons were furnished through the courtesy of Phillips Petroleum Company. The propane was stated to have a purity of 99.9%; butane and pentane were 99.0% pure or better. The vapor pressures of the propane and butane checked those of the literature (4, 5, 10, 11, 22, 25, 27) to ± 5 pounds per square inch, which is within the accuracy of the apparatus. The vapor pressures of pentane were taken from the literature (3, 24, 26, 31).

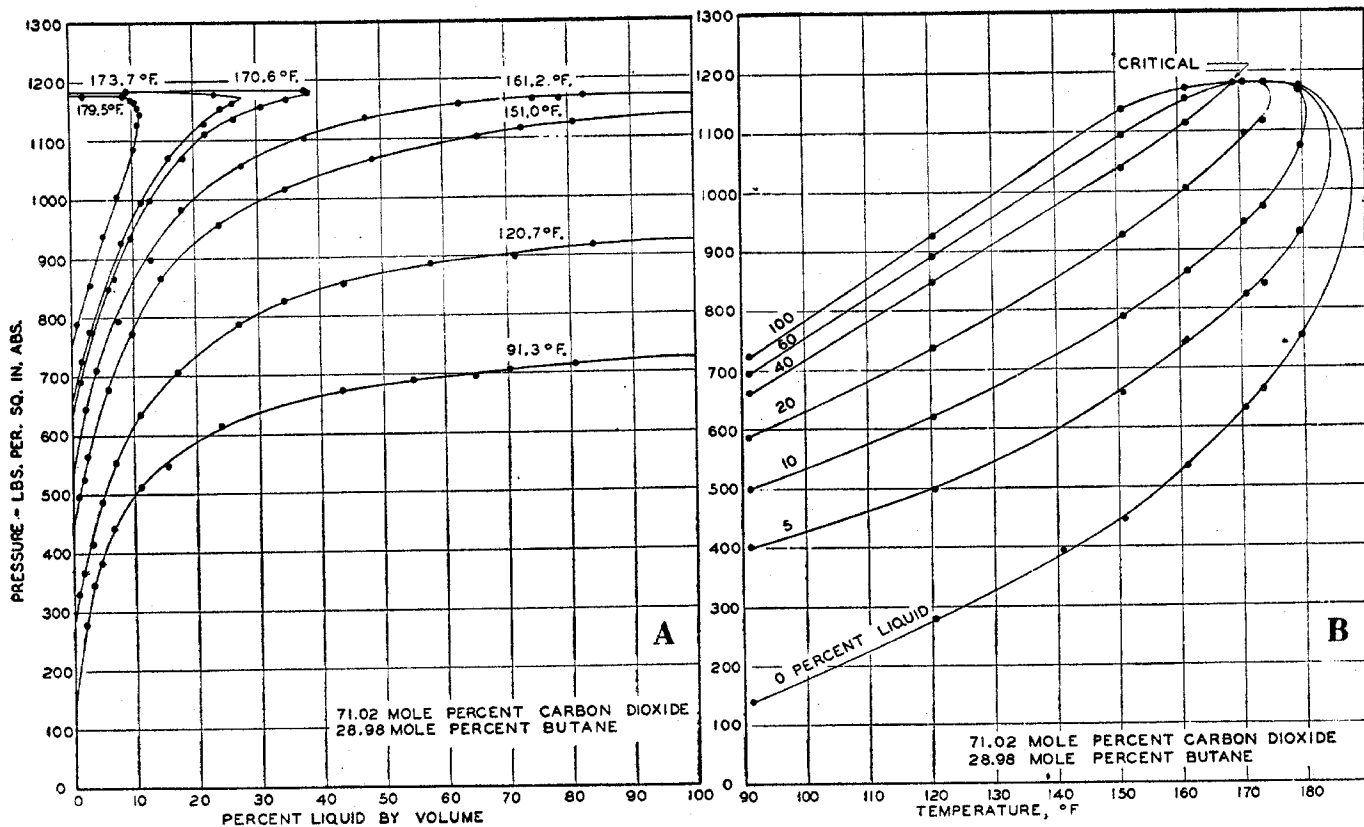
The gas mixtures were analyzed in an Orsat apparatus. The carbon dioxide was absorbed in a 35-40% solution of potassium hydroxide, and the hydrocarbon was determined by difference. The pentane gas mixtures were first diluted with a fixed volume of nitrogen before analysis to prevent the pentane from condensing after removal of the carbon dioxide. Most of the duplicate analyses checked within 0.2% and never differed more than 0.4%.

After the proper technique for taking data had been developed, the temperature of the cell was kept within $\pm 0.5^\circ$ F. of the value reported. Pressure observations were probably within ± 5 pounds per square inch of the true value.

The procedure for charging the cell was as follows: The cell was first evacuated, the lines were flushed out with hydrocarbon,

TABLE I. BINARY CARBON DIOXIDE MIXTURES

System	Investigators	Citation
CO ₂ -C ₂ H ₆	Kuenen	(19)
CO ₂ -air	Cailliet	(6)
	Van der Waals	(29)
CO ₂ -C ₂ H ₆	Kuenen	(19, 20)
CO ₂ -H ₂	Kuenen and Robson	(21)
CO ₂ -HCl	Vershafield	(23)
CO ₂ -CH ₃ Cl	Ansden	(8)
	Kuenen	(18, 20)
CO ₂ -N ₂	Caubet	(5)
CO ₂ -N ₂ O	Andrews	(1)
CO ₂ -C ₂ H ₅ NO ₂	Caubet	(8)
CO ₂ -O ₂	Kohnstamm and Reiders	(17)
CO ₂ -SO ₂	Keesom	(14, 15, 16)
	Caubet	(7)



↑ Figure 2

↓ Figure 3

Figure 4 →

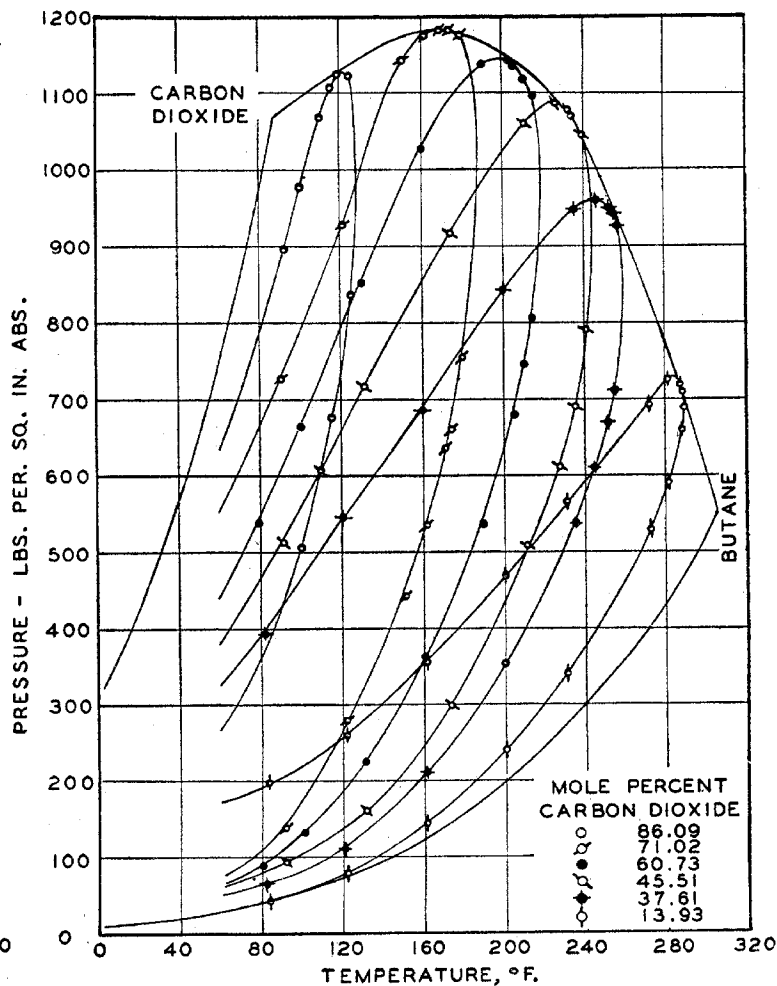
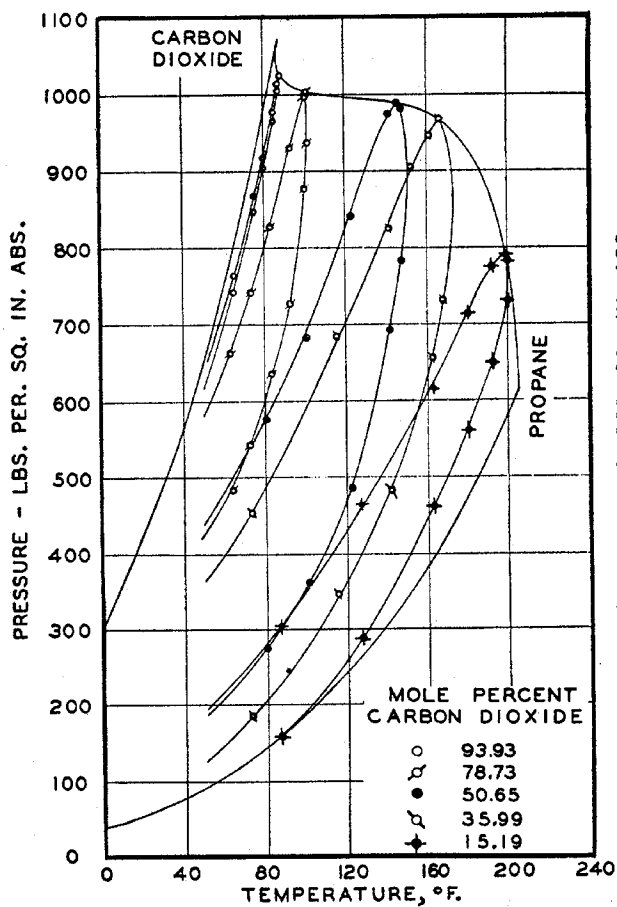


Figure 2. Isotherms and Phase Diagram of Carbon Dioxide-Butane System

Figure 3. Pressure-Temperature Diagram for Carbon Dioxide-Propane System

Figure 4. Pressure-Temperature Diagram for Carbon Dioxide-Butane System

and the cell was filled with liquid hydrocarbon which was allowed to boil off slowly. The cell was again filled with liquid hydrocarbon which was allowed to partially boil off. Carbon dioxide was then added.

The cell was maintained at a constant temperature by a thermostatically controlled air bath. The material charged into the cell was compressed to a single phase by means of the mercury and hand pump. The pressure was then gradually reduced in small increments into the two-phase region by withdrawing

mercury. Observations were made as to the amount of single phase or of vapor and liquid phase at each pressure. The cell was agitated vigorously before the volume and pressure readings were made. Special care was taken to select isotherms which cover retrograde regions as completely as possible.

Three binary systems were studied: carbon dioxide-propane, carbon dioxide-butane, and carbon dioxide-pentane. Six mixtures were studied in both the carbon dioxide-propane and carbon dioxide-butane systems; five mixtures were studied in the carbon dioxide-pentane system.

Figure 2A is a plot of isotherms as pressure against per cent by volume liquid for a mixture containing 71.02% carbon dioxide and 28.98% butane. This diagram and the usual observations provided the bubble and dew point data in Table II (page 851). In most cases the determination of the dew and bubble points by this method gave values which are believed to be correct within the experimental error. However, for some butane and pentane mixtures the dew point may be off as much as 20 pounds per square inch as a result of the rapid change of pressure with very small changes in temperature or per cent liquid by volume.

Figure 2B is a cross plot of 2A and shows the phase behavior of this mixture and the method for locating the critical temperature and pressure by plotting lines of constant per cent by volume liquid.

Figures 3, 4, and 5 show the pressure-temperature diagrams of the three series of binary mixtures. The critical loci for these systems were added to that of the carbon dioxide-ethane system in Figure 1.

The change in the temperature composition diagram as pressure is increased and the change in the pressure-composition diagram as temperature is increased for the systems reported are plotted in Figures 6, 8, and 9. These plots provide the vapor-liquid equilibrium data for the systems.

It is apparent from the critical locus of the carbon dioxide-propane system that the forces tending to form a minimum-boiling azeotrope, as in the carbon dioxide-ethane system, have not yet completely disappeared. This is shown by the sharp downward curvature of the critical locus at the carbon dioxide end of the curve. Thus, the carbon dioxide-propane locus is an intermediate stage between that of the constant-boiling azeotrope type of carbon dioxide-ethane system and the normal systems of carbon dioxide with butane or pentane.

The purpose of Kuenen in studying the carbon dioxide-ethane system was to test the van der Waals theory (30) of binary mixtures. The theory worked very well in predicting the critical temperatures and pressures of carbon dioxide-ethane mixtures (20), but when applied to the systems of carbon dioxide with propane, butane, and pentane, the method was obviously inadequate since many of the calculated critical points did not fall within the range of the coordinates of Figures 3, 4, and 5. The cause

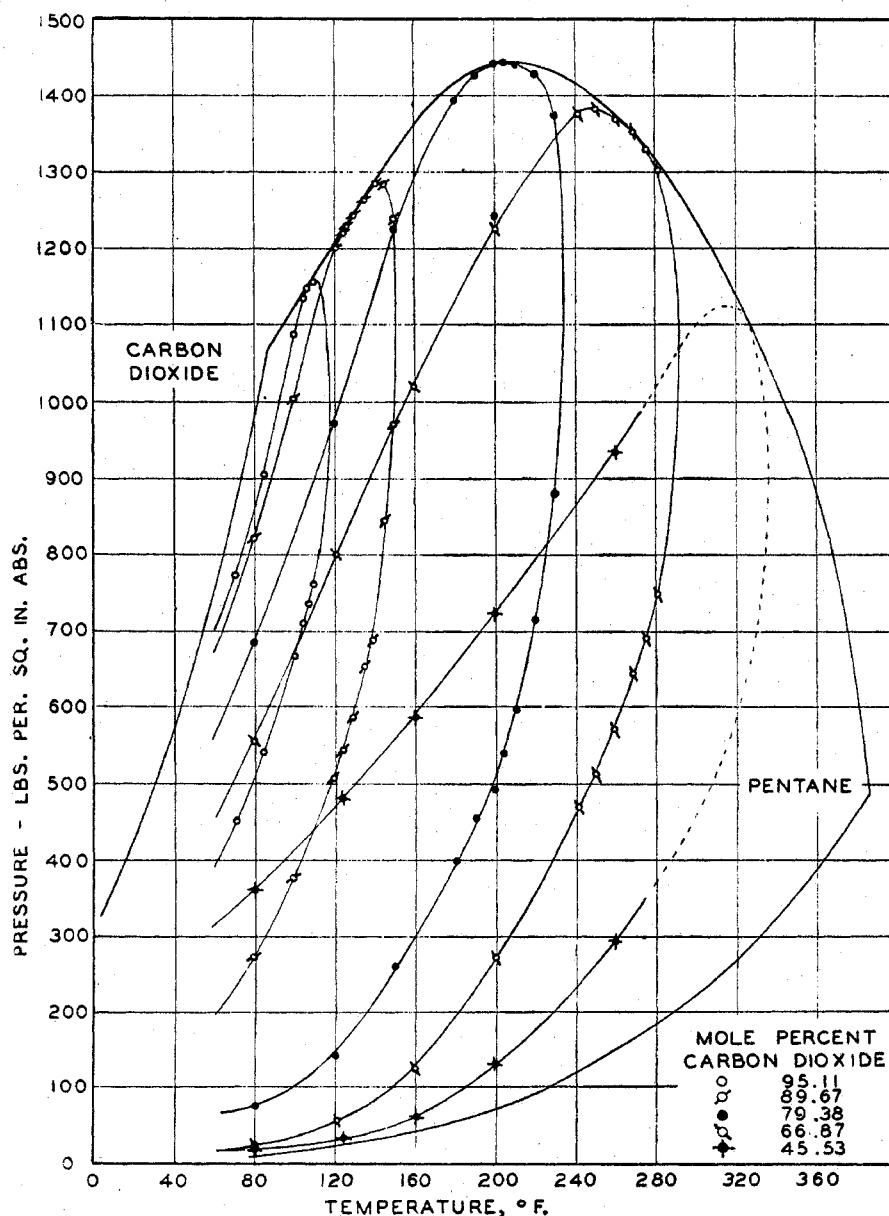


Figure 5. Pressure-Temperature Diagram for Carbon Dioxide-Pentane System

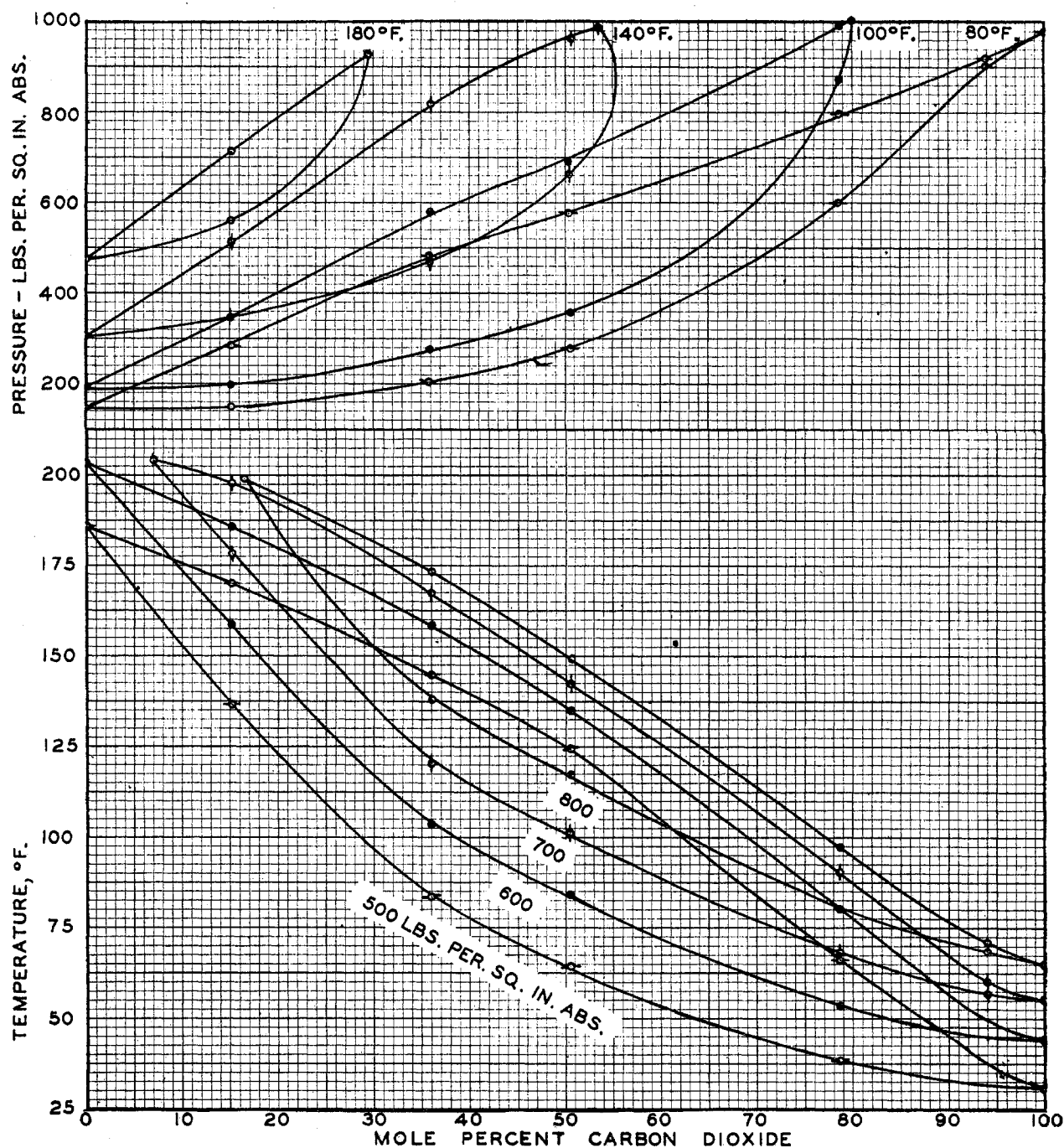


Figure 6. Vapor Equilibrium Data for Carbon Dioxide-Propane System

of this appears to be the great spread between the bubble and dew point curves of the latter mixtures. This spread increases as the vapor pressure curves of the two pure components become more divergent.

It seems that the farther apart the critical temperatures of the pure components are, the less will be the chance of forming critical azeotropic mixtures. This point is brought out in the binary carbon dioxide mixtures studied here.

Components with critical temperatures relatively close together, and those with critical pressures apart, are likely to form azeotropes but not necessarily, since the nature of the molecules and their bonds determine whether azeotropes are formed. The carbon dioxide-ethane system of Figure 7A (19, 20, 21), ethane-nitrous oxide system of Figure 7B (19, 20), carbon dioxide-

nitrous oxide system of Figure 7C (8), ethylene-acetylene system of Figure 7D (9, 13), and ethane-acetylene system of Figure 7E (19, 20) form azeotropes; the carbon dioxide-acetylene system of Figure 7C (15) and ethane-ethylene system of Figure 7F (23) do not form azeotropes. The acetylene-nitrous oxide system, which has not yet been determined, would be expected to form an azeotrope. The effect of the chemical bonds is most noticeable in Figures 7D and 7F for the ethylene-acetylene and ethylene-ethane systems. Although the relative positions of the critical points are the same for the two binary mixtures, the ethylene-acetylene system forms a critical azeotrope, whereas the ethylene-ethane system behaves in a normal manner. This difference is attributed to the nature of the acetylene molecule.

TABLE II. SUMMARY OF EXPERIMENTAL DATA

Compn., Mole %	Temp., ° F.	Pressure, Lb./Sq. In. Abs.	
		Bubble point	Dew point
CARBON DIOXIDE-PROPANE			
78.73 CO ₂ -21.27 C ₃ H ₈	63.1	661	484
	72.7	739	541
	83.7	825	635
	93.0	927	725
	100.6	996	876
	101.5	..	935, 1001.5
	101.4 (crit.)	1002	..
35.99 CO ₂ -64.01 C ₃ H ₈	72.4	452	182
	115.0	685	348
	141.8	824	483
	153.3	904	570
	162.0	944	655
	167.5	..	730, 967
	166.1 (crit.)	967	..
50.65 CO ₂ -49.35 C ₃ H ₈	80.1	575	275
	100.7	680	360
	122.7	837	485
	141.9	972	690
	147.8	..	982, 780
	146.9 (crit.)	986	..

15.19 CO ₂ -84.81 C ₃ H ₈	87.0	304	159
	127.7	464	288
	163.0	615	462
	180.3	712	580
	192.6	775	650
	200.1	..	783, 728
	199.4 (crit.)	790	..
96.01 CO ₂ -3.99 C ₃ H ₈	78.3	926	912
	84.0	994	979
	87.3	1031	1024
93.93 CO ₂ -6.07 C ₃ H ₈	64.8	763	740
	75.1	865	846
	80.0	915	903
	85.1	976	963
	87.3	1012	1003
	88.0	1018	1010
	88.2 (crit.)	1022	..
CARBON DIOXIDE-BUTANE			
45.51 CO ₂ -54.49 C ₄ H ₁₀	90.2	512	96
	131.0	715	162
	172.8	915	298
	210.2	1059	508
	226.7	1087	612
	234.8	..	1072, 689
	240.2	..	1046, 790
	233.5 (crit.)	1077	..

71.02 CO ₂ -28.98 C ₄ H ₁₀	91.3	725	140
	120.7	925	278
	151.0	1139	445
	161.2	1173	535
	170.6	..	1183, 632
	173.7	..	1183, 663
	179.5	..	1178, 754
	169.0 (crit.)	1181	..

86.09 CO ₂ -13.91 C ₄ H ₁₀	92.6	895	445
	99.9	976	505
	110.0	1066	609
	115.4	1104	675
	120.2	..	1124, 748
	125.0	..	1122, 835
	119.5 (crit.)	1122	..
60.73 CO ₂ -39.27 C ₄ H ₁₀	80.1	540	88
	100.2	665	133
	130.8	860	224
	160.5	1025	363
	190.0	1135	536
	200.5	1143	636
	205.3	..	1132, 679
	210.1	..	1115, 745
	215.0	..	1095, 804
	203.0 (crit.)	1140	..
37.61 CO ₂ -62.39 C ₄ H ₁₀	81.8	393	65
	120.2	545	111
	160.5	683	209
	200.0	840	352
	235.3	945	536
	245.0	959	609
	251.7	946	668
	255.2	..	925, 711
	254.0 (crit.)	940	..

13.93 CO ₂ -86.07 C ₄ H ₁₀	83.4	198	42
	121.0	269	77
	160.3	355	144
	200.0	469	240
	230.5	565	340
	272.2	690	527
	281.0	725	590
	288.1	719	659
	289.8	..	704, 688
	288.8 (crit.)	709	..

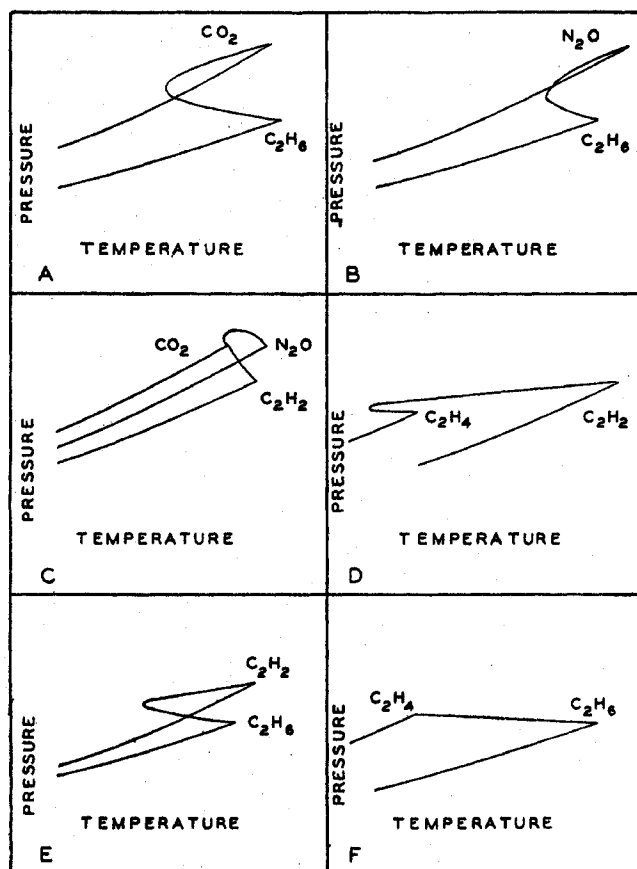


Figure 7. Critical Loci of Binary Systems

TABLE II (Continued)

Compn. Mole %	Temp. ° F.	Pressure, Lb./Sq. In. Abs.	
		Bubble point	Dew point
CARBON DIOXIDE-PENTANE			
95.11 CO ₂ -4.89 C ₅ H ₁₂	71.9	772	450
	85.3	904	541
	100.3	1086	668
	105.4	1184	710
	107.5	..	1150, 735
	110.0	..	1157, 760
	107.0 (crit.)	1148	..

89.67 CO ₂ -10.33 C ₅ H ₁₂	80.0	822	275
	100.0	1003	378
	120.0	1201	509
	125.0	1220	544
	129.9	..	1241, 586
	134.8	..	1264, 652
	140.3	..	1283, 688
	145.0	..	1283, 845
	150.3	..	1238, 972
	126.5 (crit.)	1228	..
79.38 CO ₂ -20.62 C ₅ H ₁₂	80.0	685	76
	120.0	970	145
	150.0	1225	260
	180.2	1391	400
	190.0	1429	455
	200.0	1441	490
	205.0	..	1441, 540
	210.1	..	1440, 597
	220.0	..	1431, 715
	229.9	..	1374, 880
*	203.5 (crit.)	1441	..
66.87 CO ₂ -33.13 C ₅ H ₁₂	79.8	555	24
	121.1	799	55
	160.2	1017	124
	200.0	1223	272
	241.5	1378	470
	250.6	1383	512
	259.9	1368	570
	268.8	1353	645
	275.3	..	1330, 689
	280.8	..	1304, 747
269.0 (crit.)	1352	..	
45.53 CO ₂ -54.47 C ₅ H ₁₂	80.2	360	20
	123.8	480	35
	160.2	585	60
	200.0	721	180
	260.1	934	293

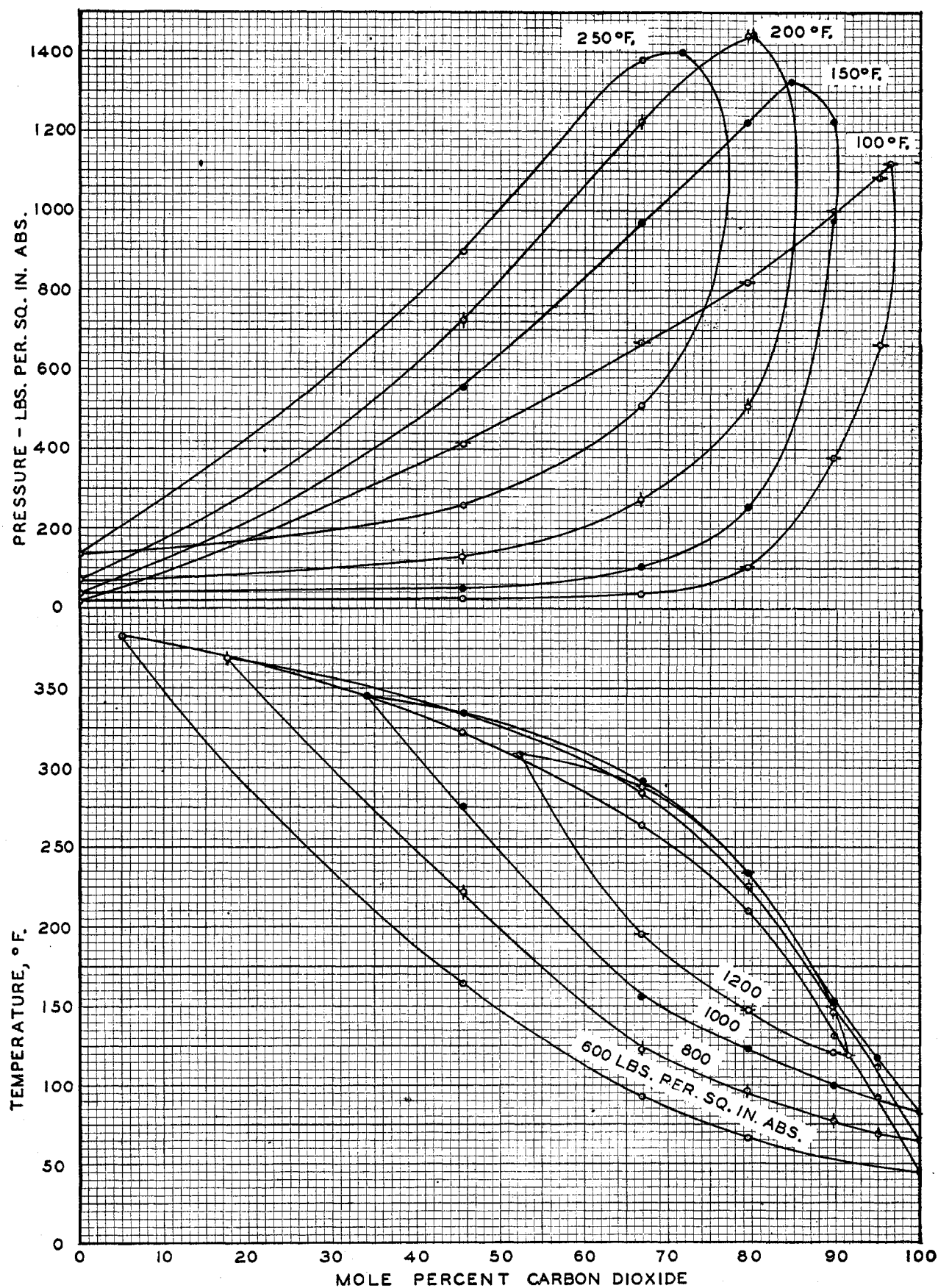


Figure 8. Vapor Equilibrium Data for Carbon Dioxide-Pentane System

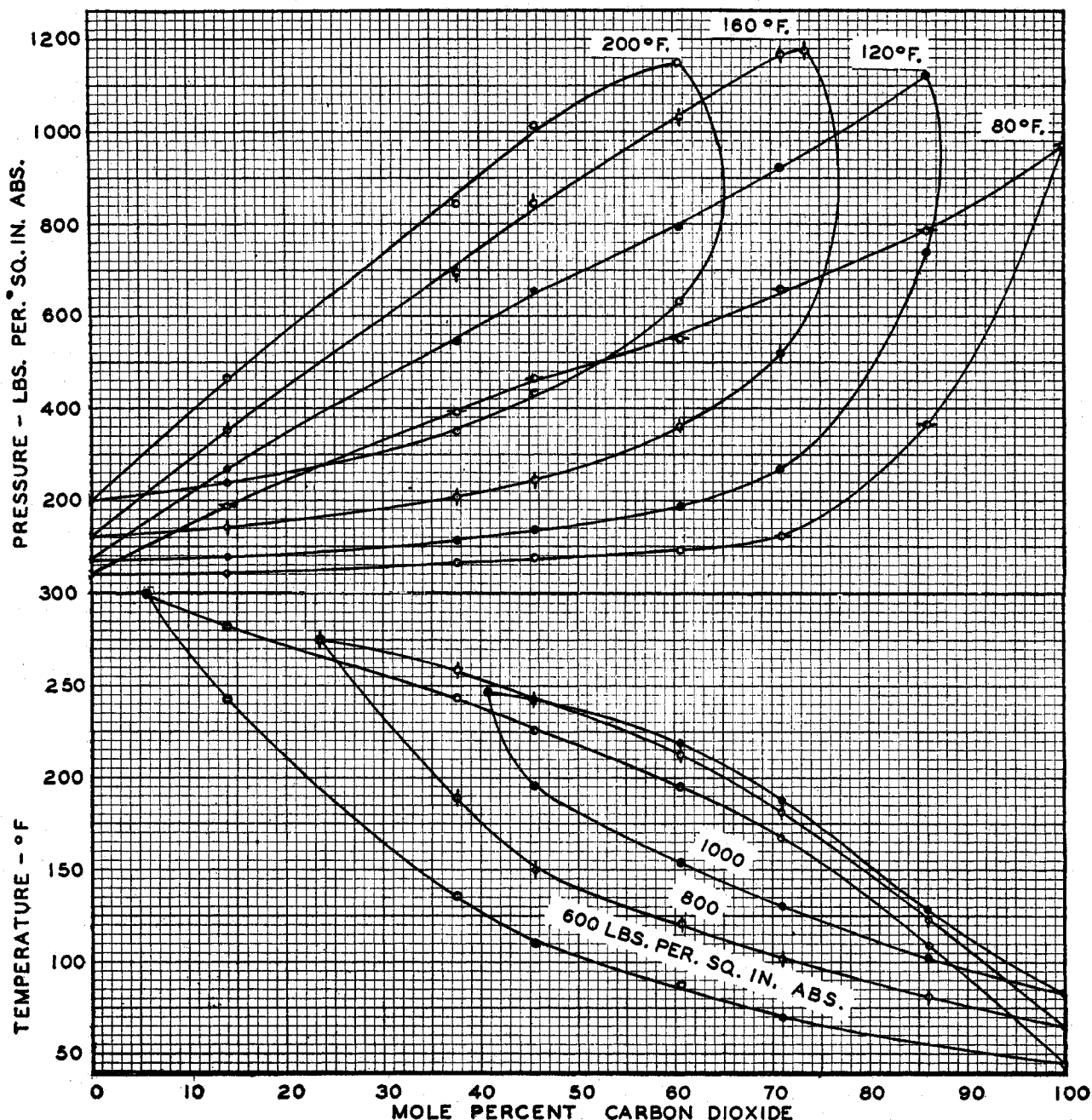


Figure 9. Vapor Equilibrium Data for Carbon Dioxide-Butane System

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