

THE THERMODYNAMIC PROPERTIES OF AN ETHANE CRYSTAL
OIL MIXTURE

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Introduction

This study of the thermal properties of an ethane-crystal oil system was made as a part of an extended research plan being carried out by the American Petroleum Institute Research Project Number 37. These studies are being made at the California Institute of Technology in order to gain an extensive knowledge of the behavior of hydrocarbons and their mixtures. This accumulation of knowledge will be used by petroleum technologists in the solution of their complicated flow and under ground reservoir problems. The experimental work presented in this paper covers the pressure-volume-temperature relationships and the specific heat at constant volume measurements for a series of ethane-crystal oil mixtures. From this work the entropy, heat content, internal energy, and free energy are calculated for a mixture containing 26.32 percent by mass of ethane. The pressure range is from 400 to 3000 pounds per square inch absolute, and the temperature range from 70°F. to 320°F.

Materials

The crystal oil, a water-white highly refined oil consisting mainly of naphthenic ringed hydrocarbons, was obtained from the Union Oil Company. It had a specific gravity of 0.8663 at 100°F., a viscosity of 284 millipoises measured at 100°F., and an average molecular weight of

337 as obtained by the freezing point lowering method using several different solvents (1). There were two different samples of ethane used for the experimental work. The ethane used in the specific heat measurements was crude ethane obtained from the Carbide and Carbon Chemicals Corp. and showed the following analysis:

ethane	98%
impurities -	2%

This ethane could be used directly for specific heat measurements since small amounts of impurities do not measurably affect them. However, with the pressure-volume-temperature measurements in order to get a bubble-point curve to coincide with the dew point curve, a specially designed ethane purifying apparatus had to be built. The method employed was to fractionate the ethane in a glass ring packed column one half inch in diameter and four feet long. Suitable reflux was obtained by a regenerative cooling cycle similar to the Linde cycle used in the production of liquid air. The middle fraction from the overhead of the column was condensed at liquid air temperature at a pressure less than 0.003 inches of mercury. The ethane that was ultimately obtained had a dew point-bubble-point difference of 0.1 pounds per square inch at 85°F.

Apparatus

To obtain the thermodynamic properties, two different types of measurements were made. One type consisted of the pressure-volume-temperature measurements. These were made by J. E. Sherborne with the Variable Volume apparatus (2). The other type consisted of measurements of specific heat at constant volume. The apparatus used for this work was an adiabatic calorimeter shown in Figure 1 (3). It consists of a bomb, in which the sample is placed, which was machined from a solid

bar of an alloy steel having a yield point of over 120,000 pounds per square inch. The walls were made as thin as possible, 0.02 inches thick, so that the total weight and, hence, the heat capacity, of the bomb would be small in comparison with that of the sample. The thin wall made it possible to attain thermal equilibrium a little more quickly. The bomb was chromium coated inside to prevent corrosion by the hydrocarbons and chromium plated on the outside to cut down heat loss from it due to radiation. Within the bomb was a heating coil, P, of #36 constantin wire incased in a stainless steel tube, 0.030 inches in diameter, soldered through the wall of the bomb. Also soldered through the wall of the bomb was another hollow steel tube sealed at the end in the bomb which served as the well for the thermocouple junction used to measure the temperatures in the bomb. The maximum working pressure of the bomb was 1500 pounds per square inch.

The bomb, B (figure 2), was suspended in a ring, A, by means of #36 B and S gauge wires. The ring in turn was supported upon trunnions, D and E, within the jacket, K. The space between the bomb and the jacket was evacuated to a pressure of about 10^{-5} mm. of mercury by an oil diffusion pump connected to an oil cam fore-pump. To avoid heat transfer from the bomb by radiation, the jacket was chromium plated on the inside and was submerged in an oil bath, F, whose temperature was automatically maintained within 0.02°F. of that of the bomb. This control was accomplished by the use of a photoelectric relay actuated by the light beam from the mirror of a high sensitivity galvanometer connected in series with a thermocouple, one junction of which was on the inner surface of the bomb. Thus, when the jacket got colder than the bomb, the light would rotate away from the photoelectric cell closing a relay which closed the circuit to the heating coils in the oil bath. In order to insure both thermal and phase equilibrium (the latter being the slower of attainment) within the bomb, it was oscillated about the axis of the trunnions. To accomplish

this movement without a stuffing box through the vacuum jacket wall, an iron bar was mounted on the shaft inside the jacket. This bar served to oscillate the bomb by following the movement of the electromagnet, G. outside the jacket. The jacket was placed in an air bath which was kept at the same temperature by a mercury thermostat. A differential thermocouple circuit in which there was a galvanometer was placed between the air bath and the oil bath to indicate the relative temperature of the air bath. It was found that when the apparatus was in operation and the bomb was at a temperature of 160°F ., its temperature would change less than 0.03°F . per hour because of heat leakage to and from the jacket by any means.

The temperature of the system was measured with the aid of a thermocouple and a high sensitivity potentiometer capable of reading to 0.002°F .. The cold junction of the thermocouple was placed in a vacuum jacketed ice bath. The bath was kept agitated by means of a glass propeller placed in the bath and rotated by a motor. The amount of electrical energy added to the bomb upon heating was measured by means of another potentiometer of much lower sensitivity. The current input was obtained by measuring the electromotive force across a shunt around the heating coil in the bomb. To insure no change in the resistance of the heating circuit when the heating was begun, the circuit was kept closed all the time except that directly connected to the heating coils. Since the leads to the coils were very short in length, this fact did not introduce an appreciable error.

Experimental Method

The experimental method employed in the pressure-volume-temperature work has been described elsewhere (2). Preliminary to the

experimental work on the specific heats at constant volume the precision thermocouple system was calibrated against a standard thermometer placed in the oil bath. Since the oil bath was at the same temperature as the bomb, the thermometer read the true temperature. The thermometer could only be read to $0.01^{\circ}\text{C}.$, and this accuracy is not nearly good enough for this work. The temperature also would vary about a $0.1^{\circ}\text{C}.$ with the control heater in the oil bath. An average value was taken for each reading, and this divided by the potentiometer scale reading was plotted against potentiometer scale reading. Even though there were many inaccuracies in reading the thermometer, nevertheless, due to the averaging process, a very smooth and reproducible calibration curve was obtained. This method of plotting made it possible to read the temperatures very accurately, and it is thought that they could be read to within $0.002^{\circ}\text{F}.$ However, because of heat loss and non-attainment of equilibrium, the actual temperature of the bomb could only be obtained to within $.01^{\circ}\text{F}.$ The heat capacity of the bomb was determined by running a specific heat measurement, as described below, when it contained hydrogen to serve as the heat transmission medium.

A specific heat determination was begun by first evacuating the bomb and accurately weighing it to 5 milligrams. The bomb was weighed again after the crystal oil had been added and the air pumped off. After the ethane was added, the bomb was weighed once more. From this procedure the total weight of the hydrocarbons, the composition, and the weight of the bomb itself was obtained. The bomb was then placed in the jacket which was closed and evacuated. When the apparatus had come to equilibrium, the initial temperature was taken with the potentiometer. For each temperature several readings were always taken to insure that the bomb was at equilibrium. The heating period was then begun and lasted for twenty minutes. The time being kept by a revolution counter connected to an electric clock mechanism. During the heating period and the subsequent fifteen

minute period of attaining equilibrium, before the temperature readings were made, the bomb was agitated. This agitation of the bomb did not measurably affect the temperature of it as practically all the energy used up was lost in the bearings and the magnetic clutch, hence, no correction had to be made. During the heating several readings of the current and voltage input were taken and recorded. At the end of the twenty minute period the heating was stopped, and the system was allowed to come to thermal and phase equilibrium for fifteen minutes. Temperature recordings were made again, and the procedure repeated until 320°F. was attained. The temperature at the start was usually around 65°F. and about 10°F. intervals were made. The specific heats so obtained, after subtracting the specific heat of the bomb, were plotted, and a smooth curve drawn through them. Since these specific heats varied nearly linearly with temperature, there was no appreciable error introduced by taking specific heats as equal to $\frac{\Delta Q}{m \Delta T}$ instead of equal to the rigorous expression $\frac{dQ}{m dT}$. As the temperature of the bomb was kept equal to the temperature of the oil bath there was no error introduced by heat loss that was measurable. The most important source of error usually present was the non-attainment of equilibrium. The limiting factor of the accuracy was the heat losses which were reduced as far as possible. The temperature factor was good to about 1/3%, since it was the difference in temperatures that were used in the calculation of specific heats and not the actual temperatures which were good to 0.01°F. The values of specific heat at constant volume obtained had an error of a little less than 1%.

Experimental Results and Calculations

The experimental values of the pressure-volume-temperature work for 49.31 mass percent of ethane mixture are given in Figure 3. In the 26.32 mass percent of ethane mixture there are no abnormalities apparent, and is, therefore, not shown.

For this composition, the isotherms in the two phase region do not show so pronounced a curvature near the bubble point as they do for the higher mass percents. This phenomenon makes the determination of the bubble point difficult. This rapid change in the curvature at 85°F. may be explained by the fact that crystal oil is not a pure substance but a complicated mixture which is above the critical points of some of the constituents and that 85°F. is near the critical temperature of ethane itself. Hence, there is not a clear-cut bubble point. Another striking feature of this system is the maximum bubble point pressure or minimum boiling point exhibited by it. In Figure 4, bubble point pressures are plotted against composition. At 85°F. the bubble point pressure is seen to be about 1000 pounds per square inch at 60 mass percent, but at this temperature the vapor pressure of pure ethane is only around 720 pounds per square inch. The appearance of maximum and minimum boiling mixtures in hydrocarbons makes the task of correlating known data for application to petroleum mixtures doubly hard. It is an interesting fact that the change in volume with composition is nearly constant along an isobar since the system at 160°F. is above the critical point of one of the components. This is shown in Figure 5. In Figure 6, composition against pressure is plotted. It is of interest to note that the change in specific gravities with temperature invert in the high pressure region. In this region in contradistinction to the usual case, the specific gravities increase with increase in temperature, as is shown in Figure 7.

The experimental work of the specific heats at constant volume consisted of measurements for a series of mixtures ranging from pure crystal oil to 30 mass percent ethane. Values at higher percentages of ethane would have been advisable to obtain, but the bomb used could not withstand the pressures that would have been encountered. Experimental specific heats at constant volume for 47 mass percent and 30 mass percent

ethane are shown in Figure 8. It is seen that at some composition between the two the specific heats begin to decrease with increase in temperature instead of increasing. This phenomenon is common in pure compounds near the critical region, but this example is the first one to the author's knowledge that exhibits it for a mixture, although it was to be expected. This fact of decreasing specific heats with increasing temperature will make the task of correlating much more difficult.

To get these experimental data on a comparable basis so that the thermodynamic properties might be more easily calculated, they had to be reduced to the same specific volume (a specific volume of 0.035 cubic feet per pound was chosen) and interpolated to the required composition. To do this the following equation was used:

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T \left(\frac{\partial^2 p}{\partial T^2}\right)_v \quad (4)$$

The $\left(\frac{\partial^2 p}{\partial T^2}\right)_v$ term was obtained by taking slopes of the isochores plotted in Figure 9, and plotting them against temperature and taking slopes again. The change of specific heat with volume was obtained by graphically integrating the right hand member of the above equation with respect to volume. The result of this procedure is shown in Figure 10. The inversion of the specific heat change with temperature is clearly seen. As with all these curves and with the tabulated data, the points were smoothed against the various quantities such as pressure, temperature, and volume.

The change in entropy with pressure in the condensed region was obtained by the graphical integration of the equation:

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$$

In the two phase region the term $\left(\frac{\partial v}{\partial T}\right)_p$ becomes very large near the bubble point, and the resulting integration would be inaccurate. Hence, the following equation is used:

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$$

This expression gives the change of entropy with volume and, therefore,

the entropy had to be plotted against volume and the values read off at the volumes corresponding to the standard pressures used in the tabulation.

$\left(\frac{\partial v}{\partial T}\right)_P$ was obtained from the slopes of the isobars plotted in Figure 11.

This procedure gave the evaluation of isothermal entropy changes but not the change with temperatures. To get the change of entropy with temperature the following expression was integrated:

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{C_v}{T}$$

The volume used for this integration was 0.035 cubic feet per pound to which all the experimental specific heats had been reduced as described above and which is in the two phase region. In evaluating both the entropy and heat content the value at 60°F. and 3000 pounds per square inch were arbitrarily taken as zero.

In the condensed region the following expression for the calculation of the heat content was used:

$$\left(\frac{\partial h}{\partial P}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_P$$

This was accomplished by plotting the second term against pressure and integrating graphically. However, this equation could not be used in the two phase region, and the internal energy was evaluated first in this region. The expression used was:

$$\left(\frac{\partial E}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P$$

The internal energies at the standard pressures were obtained in a similar manner to that used for the entropies. The heat contents are obtained from the internal energies by the equation:

$$h = E + Pv$$

Also the internal energies in the condensed region were obtained from the above equation. The change in both the heat contents and internal energies with temperature were obtained from:

$$\left(\frac{\partial E}{\partial T}\right)_v = C_v$$

The free energy values were calculated by the following expression:

$$-F = Ts - h$$

All these thermodynamic properties are tabulated in Table 1.

In Figure 12 is shown a plot of temperature against a function of entropy. Such a function had to be used instead of entropy itself because the change in entropy with temperature at constant pressure is nearly the same for all pressures throughout the range, and the isothermal change in entropy is very small. This means that the temperature-entropy plot would have the lines congested in one long narrow band across the graph. Figure 13, in which the heat contents are plotted against pressures, shows an interesting fact that the heat contents change quite fast with pressure at the lower temperatures. At the higher temperatures the change is not nearly as great, and the discontinuity at the bubble point is not so sudden. At higher temperatures above the critical point there would be no discontinuity and the heat content would decrease with increase in pressure. The slopes in the condensed region are seen to be getting smaller as the temperature is increased. The internal energy against pressure has the same characteristics as the heat content-pressure diagram. This is apparent in Figure 14. The free energies against pressure show an interesting fact in that along the bubble point curve there is a minimum free energy which occurs at about 70°F. At low pressures the graph, Figure 15, indicates that the negative free energies will be nearly infinite. The isotherms for the higher temperatures clearly show that the unstable phase has the greater free energy, which is what theory would indicate, for if the lines are extrapolated across the bubble point, they will lie above the line for the stable phase. This is shown in Figure 15.

SYMBOLS

C_v	-	Specific heat at constant volume
E	-	Internal energy, B. T. U. Per lb.
F	-	Free energy, B. T. U. per lb.
h	-	Heat content, B. T. U. per lb.
m	-	Mass, lbs.
p	-	Pressure, lbs per sq. in.
Q	-	Heat input, B. T. U.
s	-	Entropy, B. T. U. per lb. per °F.
T	-	Temperature, degree Rankine
v	-	Specific volume, cu. ft. per lb.

Acknowledgments

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References

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27, 686 (1935)
- (2) Sage, B. H., Schaafsma, J. G., Lacey, W. W. Ibid, 26, 1218 (1934)
- (3) Sage, B. H. , and Lacey, W. W. Ibid, 27, 1484 (1935)
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Table I

Physical and Thermodynamic Properties of a Mixture
of 26.32 Mass Percent Ethane with Crystal Oil

Temp. °F.	Abs. Pressure Lb./Sq. In.	v	h	s	E	- F
70.0	Bubble Point	0.02260	-1.97	0.01582	-4.09	10.35
(506)	400	0.0586	12.67	0.04489	8.33	11.11
	500	0.02426	-1.03	0.01759	-3.28	10.35
	600	0.02257	-1.72	0.01556	-4.23	9.96
	800	0.02251	-1.18	0.01499	-4.52	9.13
	1000	0.02246	-0.64	0.01444	-4.80	8.29
	1250	0.02239	0.04	0.01377	-5.14	7.26
	1500	0.02233	0.73	0.01311	-5.48	6.22
	1750	0.02227	1.42	0.01247	-5.80	5.19
	2000	0.02221	2.12	0.01184	-6.11	4.15
	2250	0.02215	2.82	0.01123	-6.41	3.13
	2500	0.02209	3.53	0.01064	-6.70	2.11
	2750	0.02205	4.24	0.01005	-6.99	1.08
	3000	0.02199	4.96	0.00947	-7.26	0.06
100.0	Bubble Point	0.02303	13.72	0.04311	10.66	10.42
(716)	400	0.0852	35.24	0.08598	28.93	12.90
	500	0.05689	29.30	0.07309	24.04	11.61
	600	0.03750	22.46	0.05972	18.29	10.97
	800	0.02300	13.93	0.04285	10.52	10.06
	1000	0.02293	14.43	0.04222	10.18	9.21
	1250	0.02285	15.06	0.04147	9.77	8.15
	1500	0.02277	15.71	0.04073	9.38	7.09
	1750	0.02269	16.36	0.04002	9.01	6.04

Temp. °F.	Abs. Pressure Lb./Sq. In.	v	h	s	E	- F
2000		0.02263	17.02	0.03933	8.64	5.00
2250		0.02256	17.69	0.03865	8.29	3.95
2500		0.02250	18.36	0.03798	7.94	2.90
2750		0.02244	19.03	0.03733	7.61	1.86
3000		0.02238	19.72	0.03669	7.28	0.82
130.0	Bubble Point	0.02347	30.01	0.06931	25.72	10.87
(988)	400	0.1029	--	--	--	--
	500	0.0744	50.02	0.10963	43.14	14.64
	600	0.05585	45.98	0.10067	39.77	13.40
	800	0.03350	37.31	0.08330	32.35	11.82
	1000	0.02346	30.04	0.06926	25.70	10.81
	1250	0.02337	30.61	0.06839	25.20	9.73
	1500	0.02328	31.20	0.06756	24.73	8.65
	1750	0.02319	31.80	0.06675	24.29	7.57
	2000	0.02310	32.41	0.06596	23.85	6.49
	2250	0.02302	33.03	0.06520	23.44	5.43
	2500	0.02294	33.66	0.06446	23.04	4.36
	2750	0.02288	34.30	0.06374	22.64	3.30
	3000	0.02281	34.94	0.06304	22.27	2.24
160.0	Bubble Point	0.02394	46.78	0.09486	40.97	12.02
(1310)	400	0.1167	--	--	--	--
	500	0.0880	68.63	0.14033	60.48	18.35
	600	0.06858	65.54	0.13304	57.92	16.92
	800	0.04509	59.34	0.11969	52.66	14.85

Temp. °F.	Abs. Pressure Lb./Sq. In.	v	h	s	E	- F
1000		0.03225	53.29	0.10774	47.32	13.49
1250		0.02487	47.71	0.09654	41.95	12.13
1500		0.02385	47.17	0.09414	40.55	11.18
1750		0.02374	47.71	0.09322	40.01	10.07
2000		0.02364	48.26	0.09235	39.50	8.98
2250		0.02354	48.83	0.09151	39.02	7.89
2500		0.02346	49.41	0.09069	38.55	6.80
2750		0.02337	50.00	0.08990	38.10	5.72
3000		0.02329	50.60	0.08912	37.66	4.64
190.0	Bubble Point (1626)	0.02443	63.91	0.11961	56.56	13.81
400		0.1283	--	--	--	--
500		0.0992	--	--	--	--
600		0.0790	83.78	0.16169	75.00	21.29
800		0.05439	78.85	0.15039	70.79	18.87
1000		0.04046	74.12	0.14056	66.62	17.22
1250		0.03074	69.00	0.13020	61.89	15.60
1500		0.02578	65.20	0.12256	58.04	14.44
1750		0.02436	64.14	0.11907	56.24	13.24
2000		0.02423	64.61	0.11807	55.60	12.11
2250		0.02411	65.12	0.11712	55.07	11.00
2500		0.02401	65.64	0.11622	54.53	9.88
2750		0.02391	66.18	0.11535	54.01	8.77
3000		0.02381	66.74	0.11450	53.51	7.67

Temp. °F.	Abs. Pressure Lb./Sq. In.	v	h	s	E	- F
220.0	Bubble Point	0.02495	80.97	0.14355	72.10	16.62
(1920)	400	--	--	--	--	--
	500	0.1090	--	--	--	--
	600	0.0883	101.48	0.18765	91.67	26.09
	800	0.06226	97.34	0.17780	88.12	23.53
	1000	0.04638	93.32	0.16915	84.54	21.67
	1250	0.03626	88.57	0.15963	80.19	19.94
	1500	0.02995	85.11	0.15217	76.79	18.33
	1750	0.02646	82.52	0.14644	73.94	17.03
	2000	0.02489	81.09	0.14319	71.87	16.25
	2250	0.02474	81.51	0.14212	71.20	15.10
	2500	0.02460	81.97	0.14111	70.59	13.96
	2750	0.02446	82.46	0.14015	70.00	12.82
	3000	0.02434	82.96	0.13922	69.43	11.69

Note: Numbers in parentheses are bubble point pressures.

Specific Heat at Constant Volume

v = 0.035 cu. ft. per lb.

Temp. °F.	70°	100°	130°	160°	190°	220°
C _v	0.535	0.530	0.525	0.520	0.514	0.509

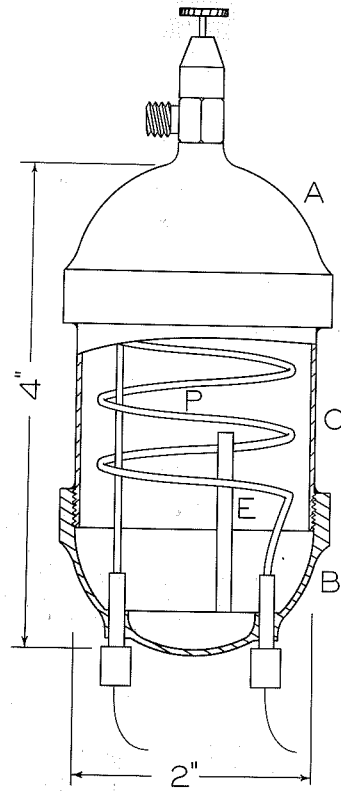


Figure 1.

Calorimeter Bomb

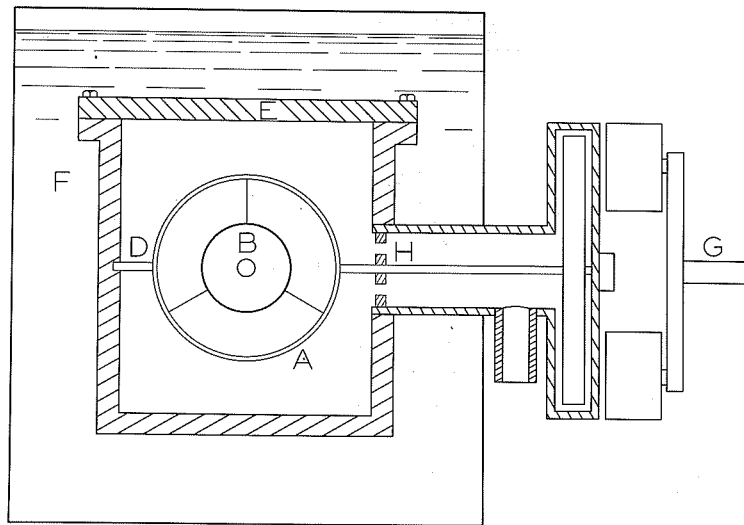


Figure 2.

Calorimeter Assembly

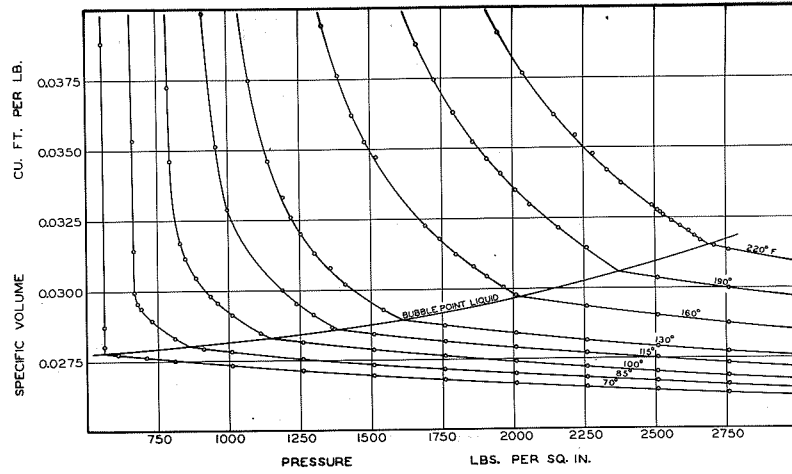


Figure 3. Experimental Pressures Volume Curves
for 49.81 Mass Percent Ethane Mixture

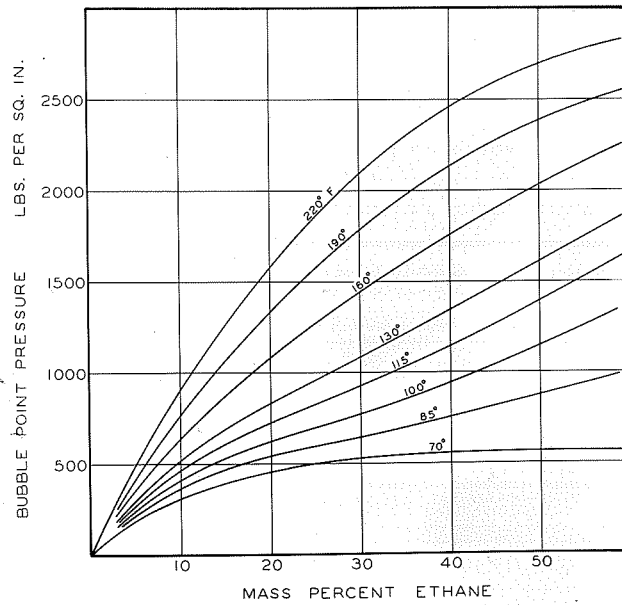


Figure 4. Variation of Bubble Point Pressures
With Composition

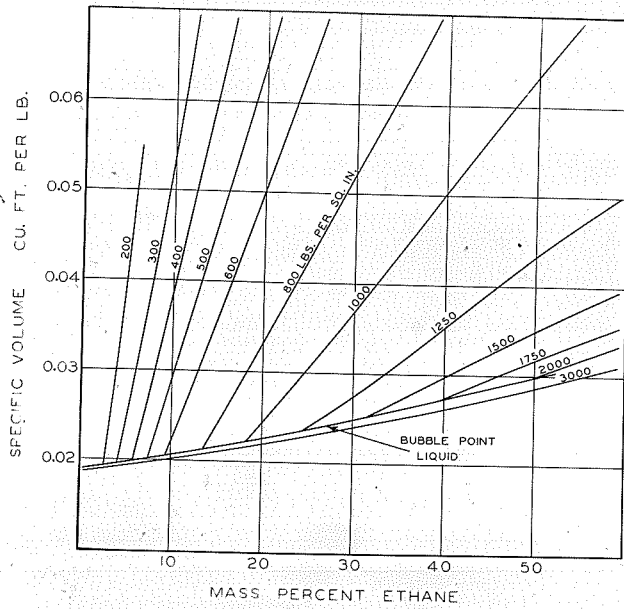


Figure 5. Variation of Specific Volume
with Composition Near Bubble Point at 160°F.

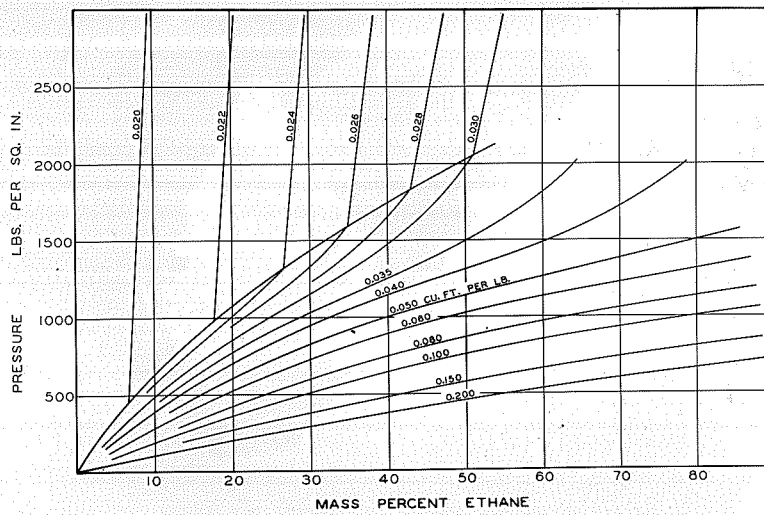


Figure 6. Variation of Pressure with Composition
Near Bubble Point at 160°F.

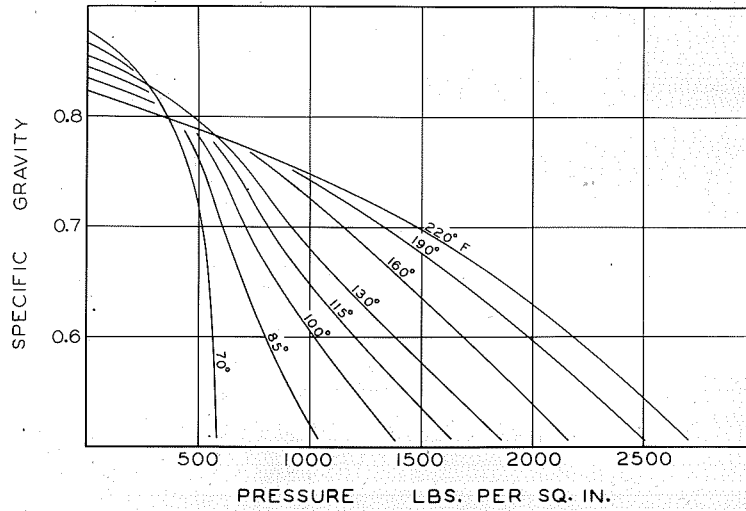


Figure 7. Bubble Point Specific Gravity

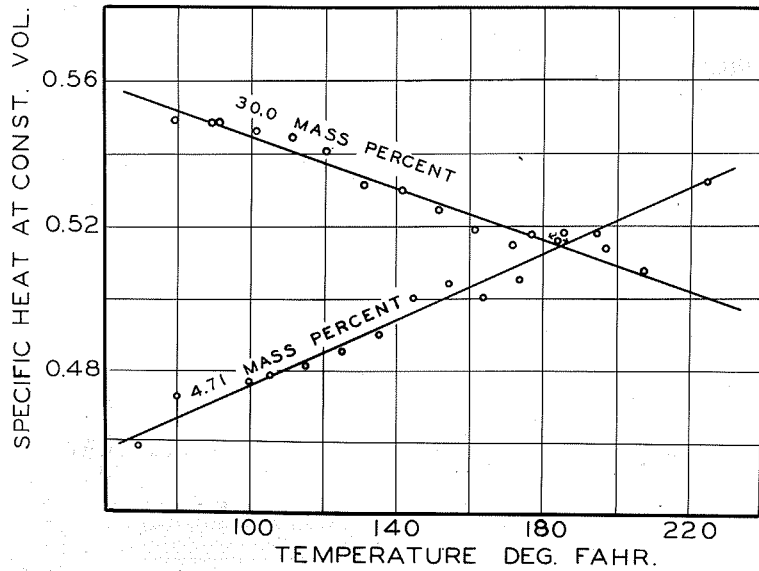


Figure 8. Experimental Specific Heat at Constant Volume for Two Different Mixtures

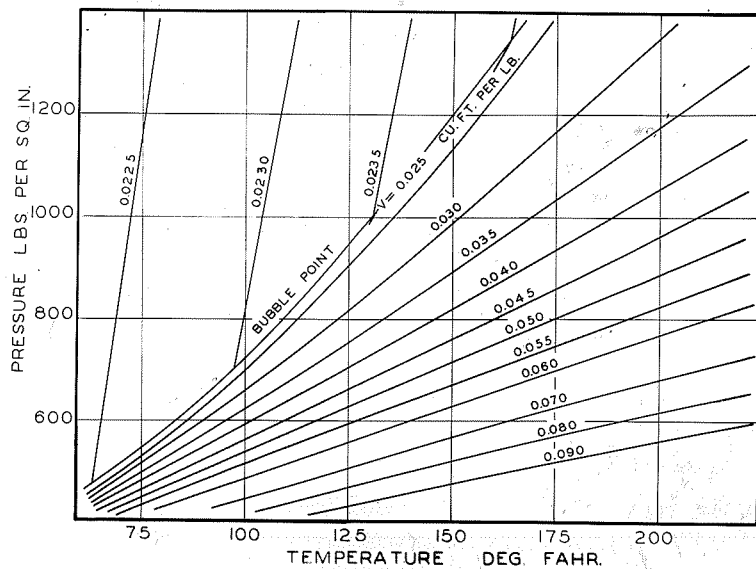


Figure 9. Variation of Pressure With Temperature

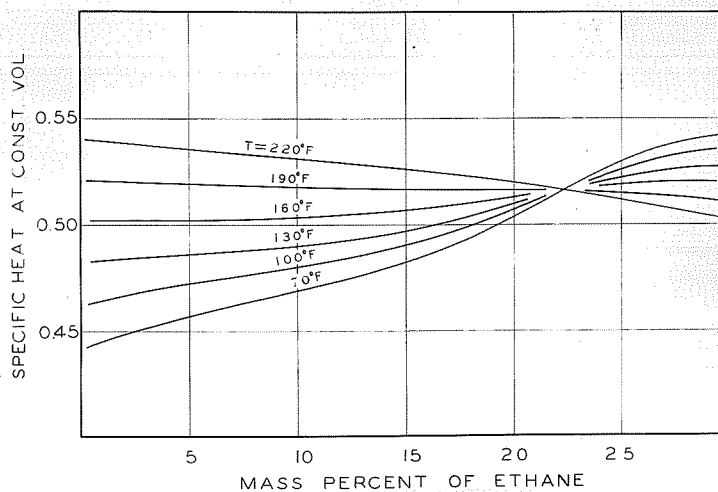


Figure 10. Specific Heat at a Constant Volume of .035 Cu. Ft. Per Lb. as a Function of Composition

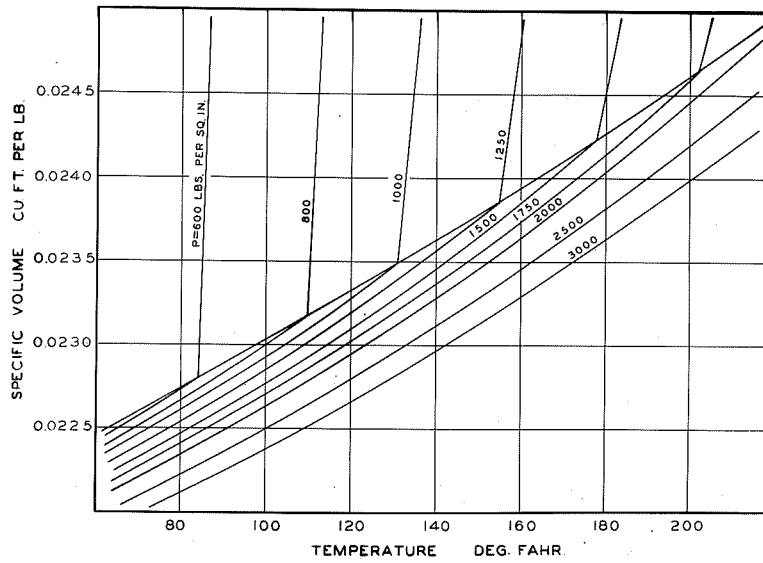
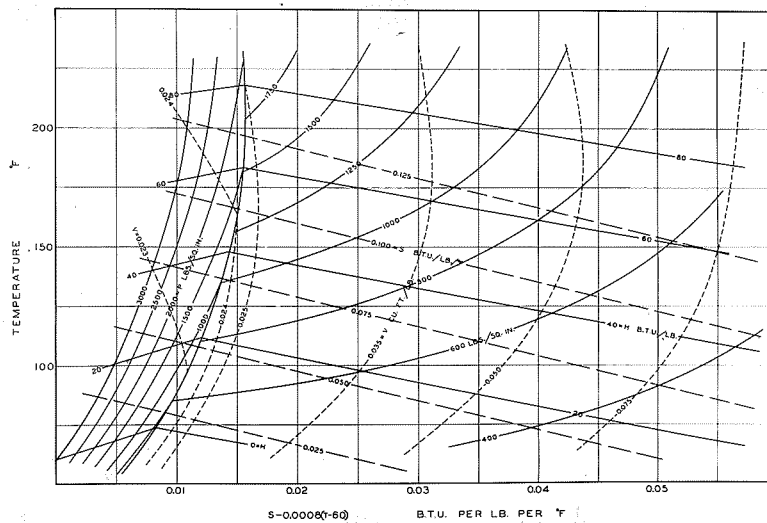


Figure 11. Variation of Specific Volume With Temperature for 26.32 Mass Percent Ethane Mixture



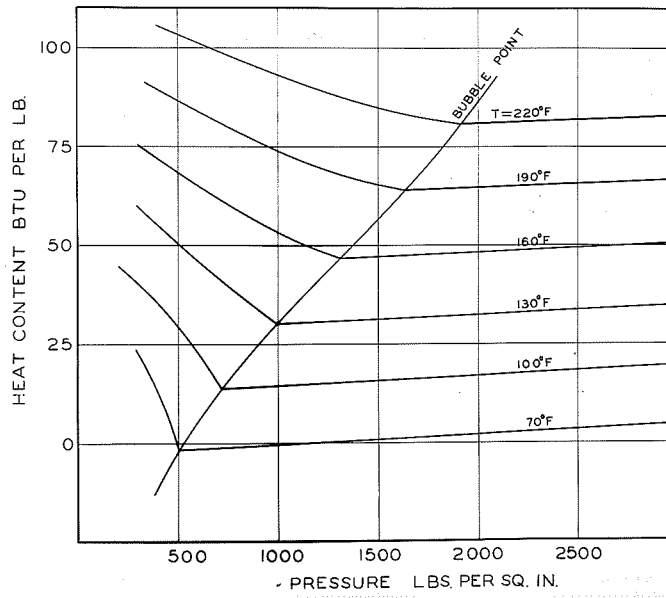


Figure 13. Heat Content-Pressure Diagram For
26.32 Mass Percent Ethane Mixture

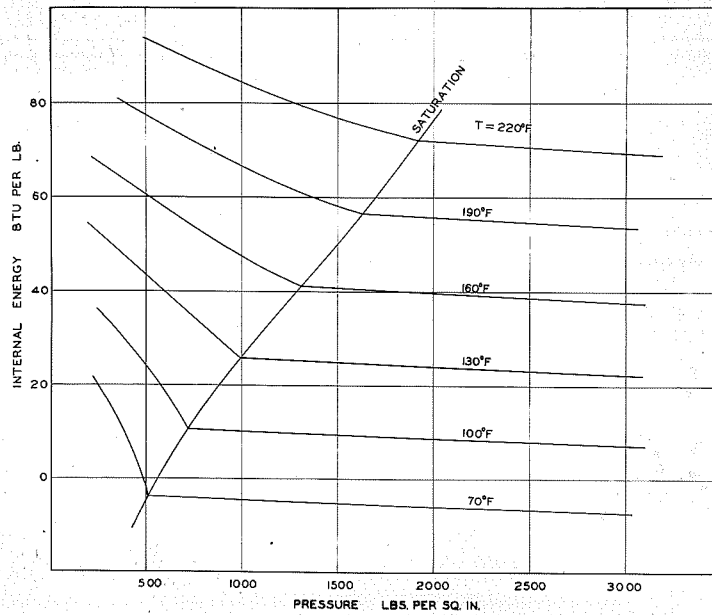


Figure 14. Internal Energy-Pressure Diagram For
26.32 Mass Percent Ethane Mixture

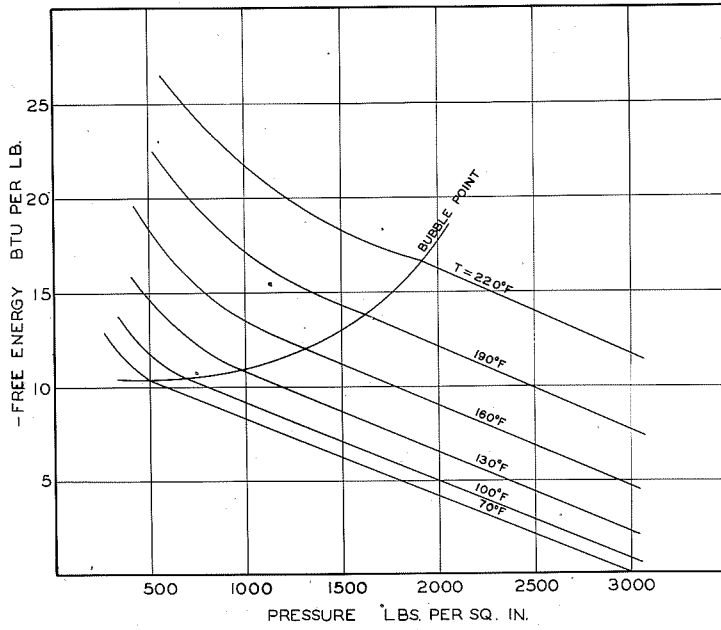


Figure 15. Free Energy-Pressure Diagram for
26.32 Mass Percent Ethane Mixture