

STUDIES OF SOME PROPERTIES OF HYDROCARBONS

Thesis by

W. R. Mendenhall

In Partial Fulfillment

of the

Requirements for the Degree of

Master of Science

California Institute of Technology

Pasadena, California

1936

TABLE OF CONTENTS

		Page
Part I	Viscosity of Hydrocarbon Solutions	2
Part II	The Thermodynamic Properties of n-Butane	9
Part III	The Joule Thomson Coefficients of Iso-Butane	29
Symbols		37
Acknowledgments		38
Literature Cited		38

Part I

VISCOSITY OF HYDROCARBON SOLUTIONS

VISCOSITY OF HYDROCARBON SOLUTIONS
Solutions of Four Hydrocarbon Gases in a Crude Oil

BY
B. H. SAGE, W. R. MENDENHALL, AND W. N. LACEY
OF THE
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIF.

Reprinted from *Production Bulletin No. 216*
American Petroleum Institute
November 1935



Issued by Division of Production
American Petroleum Institute
1508 Gulf States Building
Dallas, Tex.

Price, 15 Cents

Viscosity of Hydrocarbon Solutions

Solutions of Four Hydrocarbon Gases in a Crude Oil

B. H. SAGE,* W. R. MENDENHALL,* AND W. N. LACEY *

In previous studies the viscosity of solutions of methane, ethane, propane, and *n*butane gases in a highly-refined hydrocarbon material, known as crystal oil, has been determined. It is the purpose of the present paper to report the results of similar studies when the same gases were dissolved in a crude oil. This work was a part of the investigation of the behavior of hydrocarbon mixtures being carried on as Research Project 37 of the American Petroleum Institute.

Materials Used

The crude oil used in this study was a blended sample produced from several zones in the Santa Fe Springs field in California. The sample, which has been used in other studies,^{1, 2, 5a} was kindly furnished by the Shell Oil Company, Los Angeles, Calif., together with an analysis made in the following manner: Three liters of the sample was placed in an iron still (9 in. in diameter by 10 in. high) equipped with a 2-in. diameter vertical pipe rising 4½ in. before the delivery or condenser tube branched off. Ice water and ice were used to cool the condenser tube. The crude was topped with fire alone until a still-head vapor temperature of 518 deg. F. (270 deg. C.) was reached. The distillation was then continued with the injection of steam until the residue in the retort had a Saybolt Furol viscosity of 120 sec. at 122 deg. F. The combined distillate was then charged to a "Badger-type" distillation column, consisting of a 3-liter electrically-heated pyrex distillation flask discharging vapors to a 1-in. diameter fractionating column 4 ft. long filled with glass beads nearly to the vapor outlet tube. The column was surrounded by an electrically-heated jacket. The overhead vapors passed to a glass spiral-tube condenser cooled with ice water. In this column the material was separated into gasoline, kerosine, and stove-oil fractions, the latter being the residue in the flask. Each of these fractions was then subjected to ASTM Engler distillations. The results of these distillations and various determinations upon the original oil and the several fractions are summarized in Table 1.

The methane used was obtained from natural gas by fractional-condensation and charcoal-adsorption methods previously described⁴ with the addition of a fractional condensation directly as solid at liquid-air tem-

perature and a pressure of 2 in. of mercury, absolute, to aid in removal of nitrogen and similar impurities. The resulting material gave an analysis in terms of mol percentages as follows: 99.5 per cent methane, 0.02 per cent ethane, and less than 0.5 per cent of nitrogen and similar gases. The ethane was prepared from a sample of crude ethane (approximately 90 per cent ethane) by fractional-condensation and charcoal-adsorption methods. The material used contained 0.5 per cent nitrogen and methane, 99.2 per cent ethane, and 0.3 per cent propane and higher hydrocarbons. The samples of propane and *n*butane were used as obtained from the Phillips Petroleum Company. Analyses of these two materials were furnished by that company. The former was 100.0 per cent propane, while the *n*butane sample contained 0.18 per cent *isobutane*, 99.14 per cent *n*butane, and 0.68 per cent *isopentane*.

Apparatus and Methods

The apparatus used for the measurement of the viscosity of the saturated solutions has been described by Sage and co-workers.^{3, 6} The viscometer consisted of an inclined tube, filled with the solution to be investigated, and a closely-fitting, spherical ball which was allowed to roll down the tube from one electrical contact to another. The roll time of the ball was determined by means of a chronograph. The temperature of the viscometer and contents was kept within 0.02 deg. F. of the desired value in an oil thermostat bath. Equilibrium between gas and liquid phases was attained by mechanical agitation and re-circulation of the liquid through the apparatus. The equilibrium pressure in the apparatus was measured by means of fluid-pressure scales having sensitivities of 0.1 lb. per sq. in. up to 300 lb. per sq. in., and of 1 lb. per sq. in. for higher pressures.

The sample of crude oil was placed in the apparatus, filling about two-thirds of the total volume. On account of the volatility of the oil, it was not feasible to remove the residual air from the apparatus by evacuation. The reported pressures represent, therefore, the increase of pressure due to addition of gas. The gas was added in a succession of quantities, the system being brought to equilibrium for measurements after each addition. The necessary values of the density of the saturated solutions were taken from previously-published data for the propane solutions⁵ and from as yet unpublished measurements by the authors for the other cases.

* California Institute of Technology, Pasadena, Calif.

^a Figures refer to bibliography on p. 7.

TABLE 1

Analysis of Crude-Oil Sample

Gravity, 34.8 deg. API
 Water and sediment, trace
 Sulfur, 0.39 per cent by weight
 Viscosity, Saybolt Universal, at 100 deg. F., 42 sec.; at 130 deg. F., 39 sec.

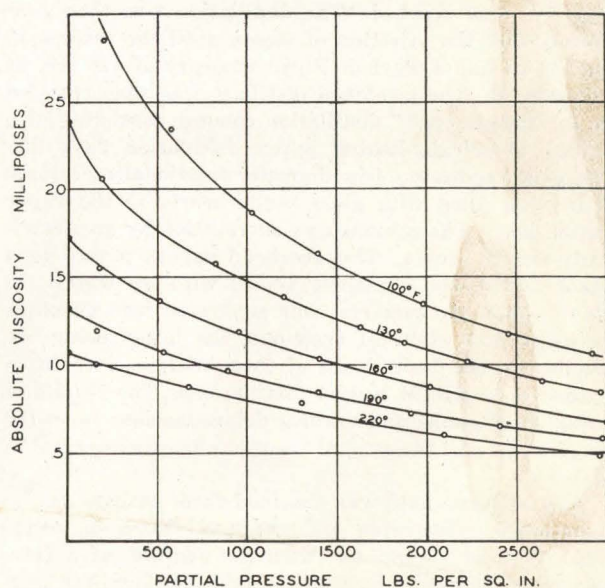
	Products				Loss
	Gasoline	Kerosine	Stove Oil	Residuum	
Per cent of charge (dry).....	37.37	6.83	18.20	36.20	1.40
Gravity, deg. API.....	53.2	38.6	33.3	17.3
Flash point (closed cup), deg. F.....	182	230+	230+
Viscosity, Saybolt Universal, at 100 deg. F., sec.....	42
Viscosity, Saybolt Furol, at 122 deg. F., sec.....	120
Absolute viscosity (at 68 deg. F.) centipoises.....	2.16
Sulfur, per cent by weight.....	0.047	0.125	0.33	0.79
Octane No., ASTM.....	59
Pour point, deg. F.....	85
<i>Distillation Summary, in Deg. C.</i>					
Initial boiling point.....	52	220	258	294
10-per-cent point.....	88	223	272
20-per-cent point.....	99	224	275
30-per-cent point.....	110	225	278
40-per-cent point.....	120	226	285
50-per-cent point.....	130	227	290
60-per-cent point.....	143	228	297
70-per-cent point.....	156	229	307
80-per-cent point.....	170	230	323
90-per-cent point.....	185	233	345
End point.....	205	242	387
Per cent over at 100 deg. C.....	20.5
Per cent over at 300 deg. C.....	64.0	1.0
Per cent recovered.....	98.0	98.0	98.0

Experimental Results

The viscosity of saturated solutions of methane in the crude oil was measured at five temperatures from 100 deg. F. to 220 deg. F. and for equilibrium pressures up to 3,000 lb. per sq. in. At the higher pressures, appreciable quantities of the more volatile constituents of the crude oil were transferred to the gas phase as a result of proximity to the critical state of the mixtures under these conditions. In order to render the results for different temperatures comparable to each other, the same amount of crude oil was used in each set of measurements.

The experimental results for the viscosity of the methane solutions, as a function of equilibrium pressure for the series of different temperatures, are shown in Fig. 1. The same data are re-plotted in Fig. 2 to show viscosity as a function of temperature for a series of different equilibrium pressures. Table 2 presents interpolated values of viscosity for convenient pressures at each of the temperatures at which measurements were made.

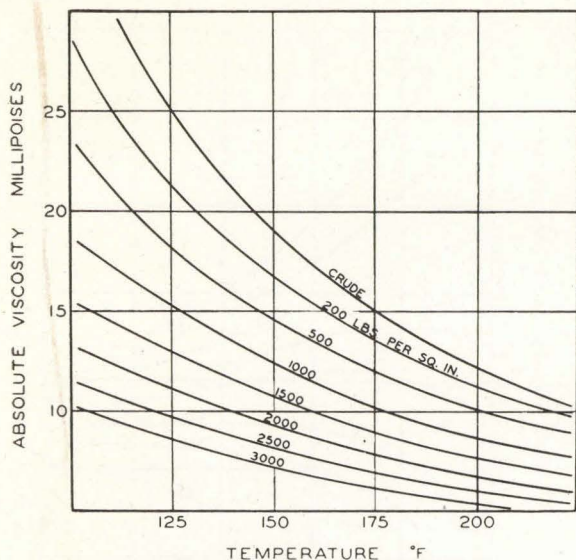
In the solutions of the three other gases—ethane, propane, and *n*butane—the maximum concentrations studied were limited by the appearance of a second



Experimental Results for Viscosity of the Methane Solutions.

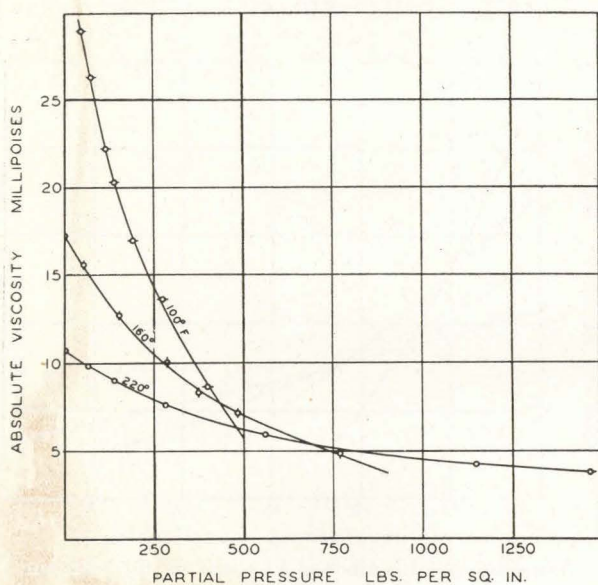
FIG. 1

liquid phase. This new phase, probably asphaltic in character, was semi-plastic, and prevented further measurements at higher concentrations. For these three



Viscosity of the Methane Solutions as Related to Temperature.

FIG. 2



Experimental Results for Viscosity of the Ethane Solutions.

FIG. 3

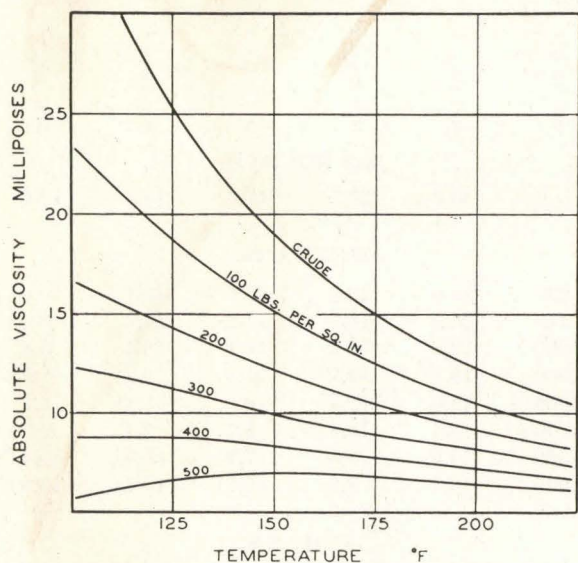
gases the large increase in volume of the liquid phase with increasing saturation pressures necessitated the withdrawal of portions of the liquid phase in the course of a set of measurements.

TABLE 2
Absolute Viscosities of Solutions in Millipoises

Partial Pressure of Solute (Lb. Per Sq. In.)	100 Deg. F.	130 Deg. F.	160 Deg. F.	190 Deg. F.	220 Deg. F.
	0	35.3	23.7	17.3	13.3
NO SOLUTE					
METHANE					
200	29.0	20.3	15.4	12.1	10.0
400	25.3	18.3	14.2	11.2	9.4
600	22.6	16.8	13.1	10.4	8.8
1,000	18.8	14.7	11.5	9.2	7.9
1,500	15.6	12.5	10.0	8.1	6.9
2,000	13.4	10.8	8.7	7.1	(6.1)
2,500	11.6	9.4	(7.7)	(6.3)	(5.4)
3,000	10.4	8.3	(6.7)	(5.7)	(4.9)
ETHANE					
100	23.5	17.9	14.1	11.3	9.4
200	16.7	13.9	11.5	9.7	8.4
300	12.3	11.0	9.5	8.5	7.5
400	8.8	8.8	8.1	7.5	6.8
500	(5.7)	6.8	7.0	6.6	6.2
600	(5.0)	6.1	(5.8)	(5.7)
800	(4.5)	(4.8)	(5.0)
1,000	(4.0)	(4.5)
1,250	(3.8)
PROPANE					
25	26.5	19.7	15.3	12.2	10.0
50	18.3	16.3	13.5	11.1	9.4
75	12.3	13.2	11.8	10.1	8.8
100	8.1	10.4	10.2	9.1	8.3
150	(6.3)	7.5	7.4	7.3
200	(3.5)	(5.5)	(6.1)	(6.5)
300	(3.8)	(5.1)
nBUTANE					
10	19.3	15.4	12.1	10.0
20	15.1	13.6	11.1	9.5
40	7.9	10.1	9.1	8.4
60	(6.9)	7.3	7.4
80	(3.9)	(5.7)	(6.4)
100	(4.1)	(5.4)
125	(4.3)

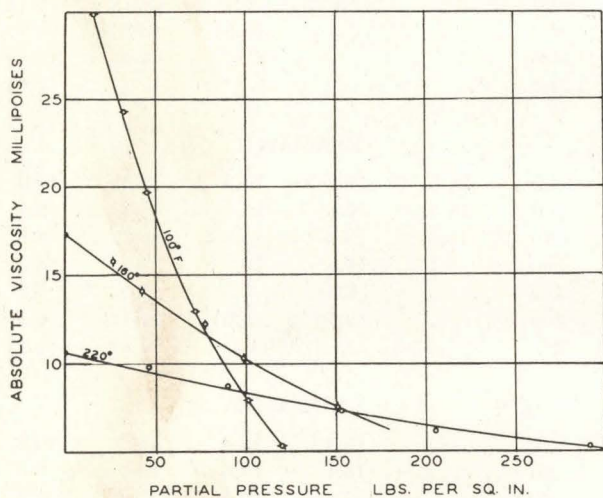
The experimental viscosity values for the ethane solutions, at three of the five temperatures studied, are shown in Fig. 3. Table 2 presents values for even pressures. The viscosity of these solutions is plotted as a function of temperature for a series of different pres-

tures in Fig. 4. The highest equilibrium pressure in the case of these ethane solutions was 1,600 lb. per sq. in. at 220 deg. F.



Viscosity of the Ethane Solutions as Related to Temperature.

FIG. 4



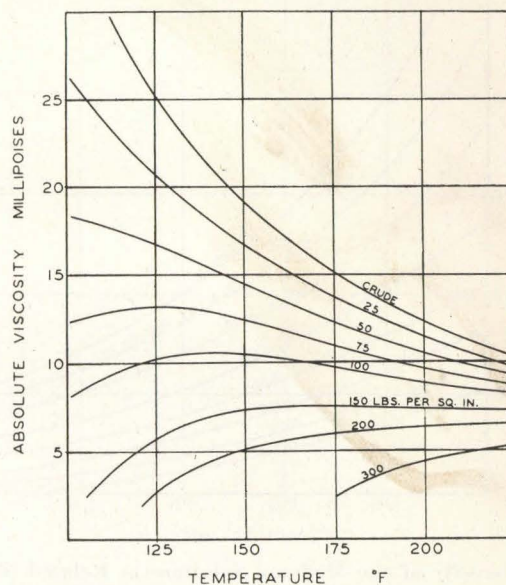
Experimental Results for Viscosity of the Propane Solutions.

FIG. 5

The corresponding values for propane solutions are given in Fig. 5 and 6 and in Table 2. The maximum pressure in this case was 400 lb. per sq. in. at 220 deg. F.

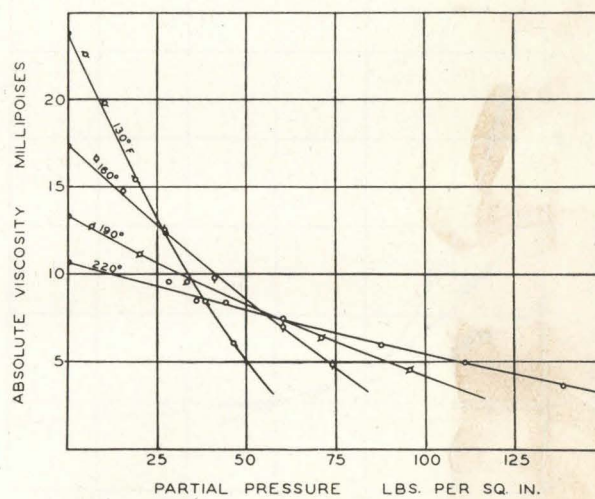
In the case of *n*butane solutions, only four temperatures from 130 deg. F. to 220 deg. F. were included in

the study, the vapor pressure of *n*butane at 100 deg. F. being too low to permit study at that temperature. The maximum pressure was 160 lb. per sq. in. at 220 deg. F.



Viscosity of the Propane Solutions as Related to Temperature.

FIG. 6

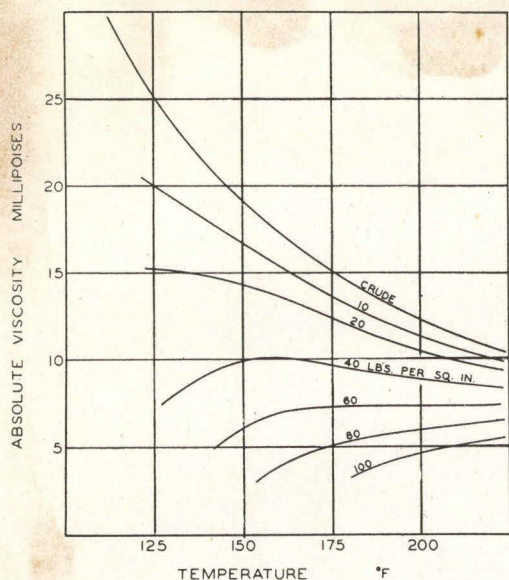


Experimental Results for Viscosity of the *n*Butane Solutions.

FIG. 7

Plots and a tabulation similar to those for the other cases will be found in Fig. 7 and 8 and in Table 2.

A comparison of the effect upon viscosity of dissolving separately each of the four gases in the crude oil is shown in Fig. 9, for equal equilibrium pressures at



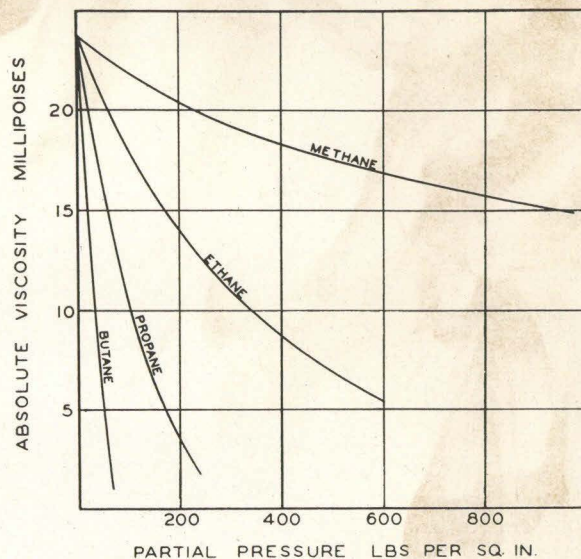
Viscosity of the *n*Butane Solutions as Related to Temperature.

FIG. 8

130 deg. F. The smaller decreases in viscosity for the gases of lower molecular weight are partly due to their smaller solubilities in the crude oil on the basis of equal saturation pressure. A corresponding comparison on the basis of equal concentrations of dissolved gas was not attempted on account of uncertainties in the compositions of the various solutions when as volatile a solvent as this crude oil is used in the presence of a gas phase.

Acknowledgments

The aid and encouragement of the American Petroleum Institute is much appreciated by the authors. The



Comparison of the Viscosity of Solutions of Different Gases in Santa Fe Springs Crude Oil at 130 Deg. F. on the Basis of Saturation Pressures.

FIG. 9

assistance of D. C. Webster in the preparation of the figures is gratefully acknowledged.

BIBLIOGRAPHY

- ¹ W. N. Lacey, *A.P.I. Production Bull. No. 210*, 16 (1932).
- ² W. N. Lacey, B. H. Sage, and C. W. Kircher, Jr., *Ind. Eng. Chem.*, **26**, 652 (1934).
- ³ B. H. Sage, *Ind. Eng. Chem. (Anal. Ed.)*, **5**, 261 (1933).
- ⁴ B. H. Sage, H. S. Backus, and W. N. Lacey, *Ind. Eng. Chem.*, **27**, 686 (1935).
- ⁵ B. H. Sage, W. N. Lacey, and J. G. Schaafsma, *Ind. Eng. Chem.*, **26**, 874 (1934).
- ⁶ B. H. Sage, J. E. Sherborne, and W. N. Lacey, *Ind. Eng. Chem.*, **27**, 954 (1935).

9

Part II

THE THERMODYNAMIC PROPERTIES OF N-BUTANE

THE THERMODYNAMIC PROPERTIES OF NORMAL BUTANE

Introduction

In recent developments of petroleum production and refining, the application of the thermodynamic properties of the oils and gases, and those of their components, to design problems is constantly increasing. The properties which are the most useful in such calculations are, besides the pressure-volume-temperature relations, the heat content, entropy, and fugacity. The P-V-T relations have been studied experimentally and the other quantities calculated for normal butane. Also values of the internal energy have been calculated, although they are not as useful as the heat content in engineering calculations. The range covered was from 20 to 3000 pounds per square inch absolute pressure, and from 70 to 220 degrees Fahrenheit.

In order to be able to calculate the thermodynamic properties of a substance, the necessary and sufficient data are the pressure-volume-temperature relations and one measurement of the change of internal energy with temperature throughout the range to be covered. Two sets of data were available from which the latter could be calculated, namely the specific heats at constant volume, and the Joule Thomson coefficients, both of which have been previously published (1,2). The pressure-volume-temperature relations have been studied and are here reported.

Apparatus and Procedure

The work was done as part of the American Petroleum Institute Research Project Number 37 and all of the apparatus and procedures have

been fully described in previously published papers (3,4,5). They will therefore only be briefly treated here.

The pressure-volume-temperature measurements were made in a variable volume cell. The pressures were measured by use of fluid pressure scales, the values below 300 pounds per square inch being good to 0.1 pound, those from 300 to 3000 pounds being good to 1 pound per square inch. The temperature was held constant at the desired value during a run by means of an oil bath, whose temperature was automatically controlled to within 0.01 degrees F. The temperatures chosen were 70, 100, 130, 160, 190, and 220° F. The volume of the sample under consideration was controlled by the addition or removal of mercury from the cell. The measurement of the volume was accomplished by locating accurately the top of the mercury with an electric contact. The contact was moved vertically by a carefully machined gear mechanism to which a counter was attached. The volume occupied by the sample could be then measured to within 0.0012 cubic inches after suitable calibration, which gave an accuracy of 0.1%.

A constant volume, adiabatic calorimeter was used for determining the specific heats. The apparatus consisted of a bomb (whose volume was about 160 cc) in which the sample was placed. The bomb was suspended in an evacuated space from a ring by three fine steel wires. The pressure in the vacuum chamber was maintained at approximately 10^{-4} millimeters of mercury by an oil diffusion pump, and was measured by a McLeod gauge. The vacuum space was surrounded by an oil bath, the temperature of which was kept within 0.02° of that of the surface of the bomb by a heater which was controlled automatically by a photo-electric circuit. This circuit consisted first of a thermocouple, one junction of which was on the surface of the bomb, the other in the oil bath. The electromotive

forces produced in the thermocouple deflected a galvanometer from which a light beam was reflected to a photo electric cell, the beam falling on the cell when the surface of the bomb and the oil bath were at the same temperature, and falling to one side when the temperatures were different. The cell, then, actuated relays which controlled the current to the bath heater. The oil in the bath was circulated so that temperature equilibrium in the bath was rapidly attained.

Around the oil bath there was an air thermostat, whose temperature was kept within 2°F of that of the oil bath manually, using electric heaters and a thermometer.

In order to assure equilibrium within the bomb, it was agitated by rocking an arm, attached rigidly to the ring supporting the bomb, by electromagnets external to the vacuum chamber. The temperature of the bomb, after equilibrium had been reached, was measured to an accuracy of 0.002°F . by means of a thermocouple, the cold junction of which was kept in a constantly agitated ice and water mixture, and the hot junction of which was in a well in the bomb. The electromotive forces produced were read by means of a potentiometer whose scale was divided into 10,000 divisions for a range of 5 millivolts, each reading being estimated to 0.10 of a division.

The procedure was to weigh a sample into the bomb, measure the temperature after equilibrium was established (as determined by no further change in the temperature for at least five minutes), add heat electrically for a period of time, agitate until equilibrium was again reached, and measure the new temperature. This process was then continued throughout the temperature range to be covered. The amount of heat added was measured by determining the current and voltage in the heater circuit and the length of the heating period. In this manner C_v as a function of temperature could be determined for a given sample throughout the whole

temperature range without removing the sample from the apparatus.

The Joule Thomson coefficients were determined, using the apparatus described by Sage and co-workers (5) and briefly treated elsewhere in this thesis.

The butane used in all this work was furnished by the Philgas Company, and was reported as being 99.21 percent n-butane, 0.18% iso-butane, and 0.61% iso-pentane.

Calculations

In the calculation of values of heat content, specific heats at constant pressure are more useful than at constant volume, consequently, the values obtained from the experimental measurements were converted to the constant pressure basis. The amount of gas phase present in the bomb was small in comparison to the amount of liquid phase, and therefore, the heat absorbed by it was a very small portion of the whole and did not need to be corrected for. The equations used for the other corrections

were
$$C_s = \frac{Q}{\Delta TM} - \frac{r_2 X_2 - r_1 X_1}{\Delta T} + \frac{r X}{T} \quad (1)$$

and
$$C_p = C_s + J \left(\frac{\partial V}{\partial T} \right)_p \cdot \frac{dP}{dT} \cdot T \quad (2)$$

(See list of symbols used for definitions of symbols) Equation (1) was used to correct for the amount of heat used in the vaporization of a portion of the liquid upon rise in temperature, after which equation (2) corrects the values from those of saturation to ones of constant pressure. These equations can be derived by consideration of appropriate cycles (6). Values of C_p calculated in this way have been published (1) and were used in the calculations described below.

Iso-baric changes of heat content can be calculated by integration of the equation

$$dH = C_p dT \tag{3}$$

and those of entropy by

$$dS = \frac{C_p}{T} dT \tag{4}$$

In these calculations, since it would be necessary to make measurements of the properties near absolute zero to be able to evaluate absolute values of heat content and entropy, the reference state was taken as 3000 pounds per square inch absolute pressure and 60° F. at which state the heat content and entropy were set equal to zero. The above integration was carried on along the 400 pound per square inch line. The values of heat content were then determined throughout the condensed by integration of the equation

$$dH = \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP \tag{5}$$

along the 60° F. isotherm from 3000 pounds to 400 pounds per square inch, adding this value to that obtained by the integration of equation (3), as above, and subsequent integration of equation (5) along the various isotherms from the 400 pound point. A similar calculation, using the results of the above integration of equation (4) and of the equation

$$dS = - \left(\frac{\partial V}{\partial T} \right)_P dP \tag{6}$$

gave the values of entropy for the condensed region.

By the addition of the heat of vaporization, or the entropy of vaporization, from the corresponding value at saturation obtained above, and continuing the same processes, one could complete the calculations throughout the superheated region also. However, by choosing a new reference point and using different methods of calculations for the values in the superheated region, a new set of saturation values could be obtained which should be different from each other by a constant value after the proper application of the values for the vaporization process had been used. This would render a check on the accuracy of

the calculations or values of the heat of vaporization. Such procedure was followed.

The new reference point was chosen as atmospheric pressure and 60° F., again the values being assumed to be zero at the reference point. Instead of using equation (5) for the heat content in this region, the equation

$$dH = -C_p \left(\frac{\partial T}{\partial P} \right) dP \quad 7$$

was used, since the values of the Joule Thomson coefficient, $\mu =$

$\left(\frac{\partial T}{\partial P} \right)_H$ were known. This was especially valuable since the values of $\left(\frac{\partial V}{\partial T} \right)_P$ for the superheated region were not considered to be as accurate as those of C_p and since the former were obtained by graphical differentiation of the isobars on the volume-temperature charts. For the same reason, use was made of the equation

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

for values of $\left(\frac{\partial V}{\partial T} \right)_P$ to be used in the integration of equation (5) in the superheated region.

For the quality, volume, and heat content lines on the temperature-entropy diagram, in the two phase region, the relations

$$x = \frac{V_m - V'}{V'' - V'}$$

$$S_m = S' + \frac{x r}{T}$$

and

$$h_m = h' + x r$$

were used.

By definition, $H = E + PV$, consequently the calculation of the values of internal energy entails only the subtraction of the PV product from the values of heat content as obtained above.

The fugacities were calculated by the proper integration of the expression

$$\ln f = \int_0^P z d \ln p$$

in which $z = \frac{PV}{RT}$

In this calculation, $\frac{dz}{dP}$ was considered to be constant below 10 pounds per square inch absolute pressure, and at zero pressure the fugacity was assumed equal to the pressure.

Results

Table I is the complete tabulation of the physical and thermodynamic properties of n-butane as obtained from the present work, except that the internal energies are not included, since they can be easily calculated from the tabulated values. Table II gives the properties of saturated liquid and gas for even pressures.

The pressure-volume-temperature relations are presented in the first three figures. Figure 1 is a plot of the isobars in the super heated region. The next figure shows specific gravity as a function of pressure for the series of temperatures. The deviations from a perfect gas are shown by the PV/RT chart vs. P chart in figure 3, since a perfect gas behavior would be represented by a straight, horizontal line. The triangle in the upper left hand corner represents a value taken from an atmospheric density measurement at 104°F. This furnishes a point obtained by a different method from the rest of the data and is a good check. The determination was made by weighing a sample in a bomb, withdrawing a definite volume, and then redetermining the weight. On Figure 3 the values for 70 degrees are not shown since they are not feasible to present on the same scale as the other values, due to the pressures being so low.

Values of heat content as a function of temperature at a series of pressures in the superheated region are shown as Figure 4. A similar diagram for the liquid region is not shown since the lines lie very close together and cross each other at the higher temperatures. On the temperature-entropy diagram. Figure 5. the values of pressure, volume, and

temperature are shown, as well as those of quality in the two phase region. A heat content-entropy diagram, or Mollier chart, was not included since interpolation on it would be very difficult, due to the position and slope of the lines. It should be noted, however, that the entropy of saturated gas is almost independent of heat content, which would make the Mollier chart very different from that of water.

The whole range of pressures was not included in the internal energy-pressure diagram, Figure 6, since beyond the range shown the values continue nearly linearly. As for the fugacity values, in the superheated region fugacity divided by pressure is shown plotted against pressure in Figure 7 while figure 8 depicts fugacity of the condensed liquid as a function of pressure for the series of temperatures.

Figure 9 is a representation of a relation followed by hydrocarbons, namely that if the reciprocal of the absolute temperature is plotted against the logarithm of the corresponding vapor pressure, the result is a line that is almost straight. Ordinarily this would indicate that the gas follows the perfect gas laws and that there is no change in the heat of vaporization with temperature. Butane follows neither of these stipulations, but the deviations from the perfect gas laws compensate for the change in the heat of vaporization, consequently the relation remains nearly linear. This relation has been used for hydrocarbons in general to extrapolate vapor pressures beyond the critical temperature for the use of Raoult's law in that region.

TABLE I

PHYSICAL AND THERMAL PROPERTIES OF NORMAL BUTANE

p ^a	v	70° (31.67)			100° (52.81)			Superheated Gas and Condensed Liquid Regions						190° (178.5)			220° (249.2)							
		f/p	h	s	v	f/p	h	s	v	f/p	h	s	v	f/p	h	s	v	f/p	h	s				
Satd. vapor	2.707	0.9453	152.01	0.3165	1.6988	0.9183	161.32	0.3175	1.1079	0.8882	170.34	0.3194	0.7419	0.8618	178.91	0.3222	0.5051	0.8308	186.97	0.3249	0.3444	0.8010	194.41	0.3273
Satd. liquid	0.02777	0.9453	-3.35	0.0220	0.02861	0.9183	14.14	0.0538	0.02962	0.8882	32.71	0.0858	0.03080	0.8618	52.40	0.1181	0.03230	0.8308	73.38	0.1506	0.03443	0.8010	95.61	0.1833
20	4.7059	0.970	153.59	0.3341	5.0173	0.9755	165.20	0.3554	5.3114	0.9790	177.15	0.3762	5.6112	0.9835	189.47	0.3965	5.9153	0.9880	202.19	0.4166	6.2202	0.9925	215.31	0.4363
40	-	-	-	-	2.3722	0.9443	163.01	0.3291	2.5649	0.9545	175.31	0.3504	2.7386	0.9645	187.86	0.3713	2.9023	0.9743	200.84	0.3890	3.0681	0.9840	214.19	0.4117
60	-	-	-	-	-	-	-	-	1.6286	0.9250	173.16	0.3338	1.7689	0.9433	186.07	0.3553	1.8875	0.9575	199.34	0.3764	2.0059	0.9736	212.95	0.3964
80	-	-	-	-	-	-	-	-	1.1526	0.8925	170.68	0.3209	1.2706	0.9196	184.07	0.3432	1.3764	0.9386	197.67	0.3646	1.4646	0.9584	211.60	0.3851
100	-	-	-	-	-	-	-	-	-	-	-	-	0.9766	0.8945	181.85	0.3329	1.0642	0.9181	195.85	0.3549	1.1435	0.9423	210.12	0.3759
125	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.8125	0.8912	193.34	0.3444	0.8802	0.9208	208.10	0.3661
150	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.6428	0.8633	190.55	0.3350	0.7036	0.8973	205.86	0.3575
175	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.5194	0.8348	187.44	0.3261	0.5768	0.8731	203.40	0.3495
200	0.02768	0.1573	-2.92	0.0211	0.02851	0.2525	14.45	0.0530	0.02948	0.3787	32.89	0.0850	0.03066	0.5443	52.45	0.1174	0.03224	0.7459	73.35	0.1504	0.4799	0.8485	200.67	0.3419
225	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.4043	0.8231	197.65	0.3345
400	0.02759	0.0833	-2.39	0.0202	0.02837	0.1334	14.90	0.0519	0.02928	0.1999	33.23	0.0838	0.03037	0.2871	52.61	0.1159	0.03179	0.3933	73.12	0.1482	0.03382	0.5197	94.98	0.1809
600	0.02750	0.0590	-1.84	0.0193	0.02823	0.0940	15.37	0.0509	0.02911	0.1406	33.60	0.0826	0.03012	0.2019	52.82	0.1144	0.03142	0.2764	73.01	0.1463	0.03328	0.3656	94.35	0.1782
800	0.02740	0.0470	-1.27	0.0185	0.02810	0.0744	15.88	0.0499	0.02895	0.1112	34.01	0.0814	0.02992	0.1594	53.09	0.1130	0.03110	0.2184	73.00	0.1445	0.03278	0.2890	93.91	0.1757
1000	0.02730	0.0394	-0.70	0.0176	0.02799	0.0629	16.40	0.0490	0.02879	0.0939	34.45	0.0808	0.02972	0.1344	53.40	0.1118	0.03084	0.1841	73.08	0.1428	0.03238	0.2436	93.60	0.1735
1250	0.02718	0.0338	0.03	0.0166	0.02784	0.0538	17.07	0.0479	0.02861	0.0819	35.04	0.0791	0.02948	0.1147	53.84	0.1103	0.03052	0.1569	73.27	0.1409	0.03191	0.2077	93.36	0.1710
1500	0.02707	0.0302	0.769	0.0157	0.02772	0.0480	17.76	0.0468	0.02845	0.0714	35.64	0.0779	0.02928	0.1020	54.33	0.1088	0.03026	0.1393	73.55	0.1392	0.03152	0.1844	93.25	0.1687
1750	0.02698	0.0277	1.51	0.0147	0.02760	0.0440	18.47	0.0458	0.02829	0.0653	36.31	0.0768	0.02906	0.0931	54.86	0.1075	0.02999	0.1272	73.89	0.1375	0.03118	0.1682	93.23	0.1665
2000	0.02687	0.0260	2.27	0.0138	0.02748	0.0411	19.20	0.0448	0.02813	0.0610	36.98	0.0757	0.02888	0.0869	55.42	0.1063	0.02976	0.1184	74.29	0.1360	0.03089	0.1566	93.29	0.1645
2250	0.02679	0.0248	3.03	0.0129	0.02738	0.0391	19.94	0.0439	0.02800	0.0578	37.67	0.0747	0.02871	0.0822	56.02	0.1051	0.02954	0.1118	74.73	0.1346	0.03060	0.1480	93.42	0.1626
2500	0.02670	0.0239	3.81	0.0121	0.02728	0.0376	20.69	0.0429	0.02788	0.0555	38.37	0.0737	0.02856	0.0788	56.55	0.1040	0.02934	0.1072	75.20	0.1332	0.03034	0.1416	93.59	0.1608
2750	0.02661	0.0232	4.59	0.0111	0.02718	0.0365	21.45	0.0421	0.02777	0.0538	39.10	0.0727	0.02840	0.0762	57.31	0.1029	0.02913	0.1036	75.70	0.1319	0.03009	0.1367	93.80	0.1590
3000	0.02655	0.0228	5.38	0.0103	0.02709	0.0357	22.21	0.0412	0.02766	0.0525	39.84	0.0718	0.02827	0.0743	57.98	0.1019	0.02898	0.1009	76.22	0.1306	0.02989	0.1330	94.05	0.1573

^a p pressure lb. per sq. in. abs.; v specific volume, cu. ft. per lb.; f fugacity, lb. per sq. in.; h heat content, B.t.u. per lb.; s entropy, B.t.u. per lb. per ° F. abs.

TABLE II

PHYSICAL AND THERMAL PROPERTIES OF N-BUTANE

Saturated Liquid and Saturated Gas

p	t ^a	f/p	Saturated Gas			Saturated Liquid		
			v	h	s	v	h	s
20	44.30	-	-	-	-	0.02715	-	-
40	82.85	0.9338	2.2069	156.1	0.3158	0.02812	4.2	0.0353
60	108.25	0.9100	1.5051	163.8	0.3175	0.02887	19.1	0.0623
80	127.77	0.8910	1.1427	169.6	0.3190	0.02953	31.2	0.0835
100	143.67	0.8759	0.9183	174.2	0.3207	0.03013	41.6	0.1008
125	160.83	0.8602	0.7340	179.1	0.3224	0.03084	52.9	0.1192
150	175.44	0.8459	0.6081	183.1	0.3236	0.03151	62.9	0.1343
175	188.33	0.8323	0.5161	186.5	0.3247	0.03220	72.2	0.1487
200	199.93	0.8205	0.4455	189.5	0.3256	0.03292	80.5	0.1612
225	210.53	0.8101	0.3894	192.1	0.3265	0.03366	88.5	0.1729
250	220.28	0.8008	0.3433	194.4	0.3274	0.03443	95.8	0.1838

^a t temperature in °F.; other units as in Table I.

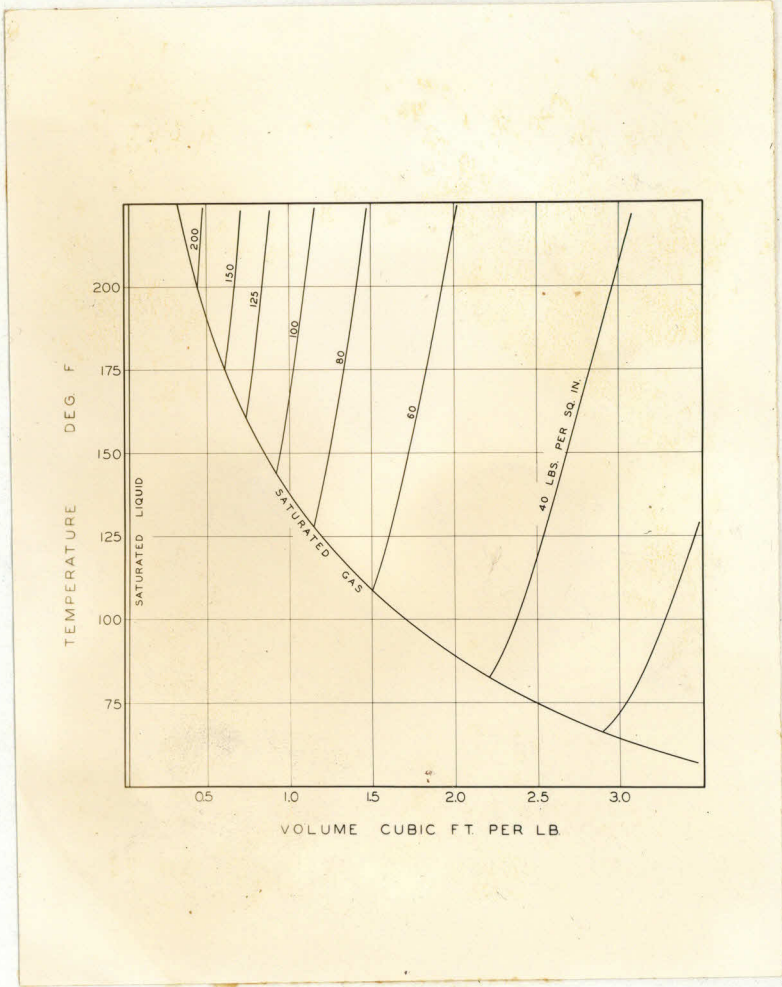


Figure 1. Specific Volume of Superheated Gas

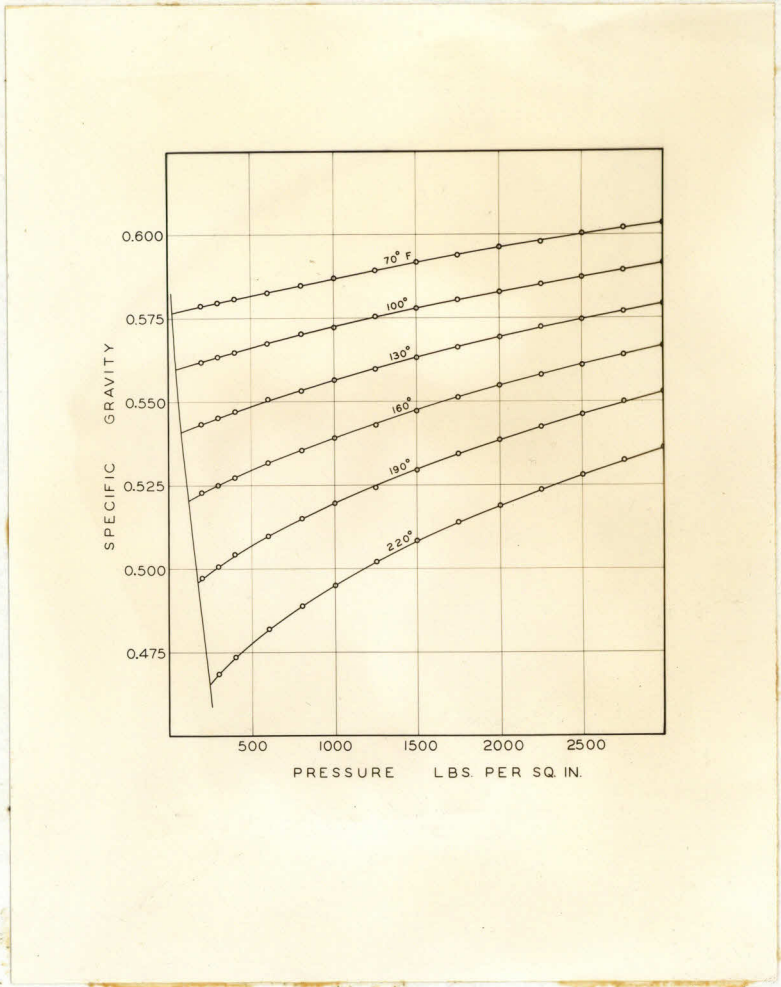


Figure 2. Specific Gravity of Condensed Liquid

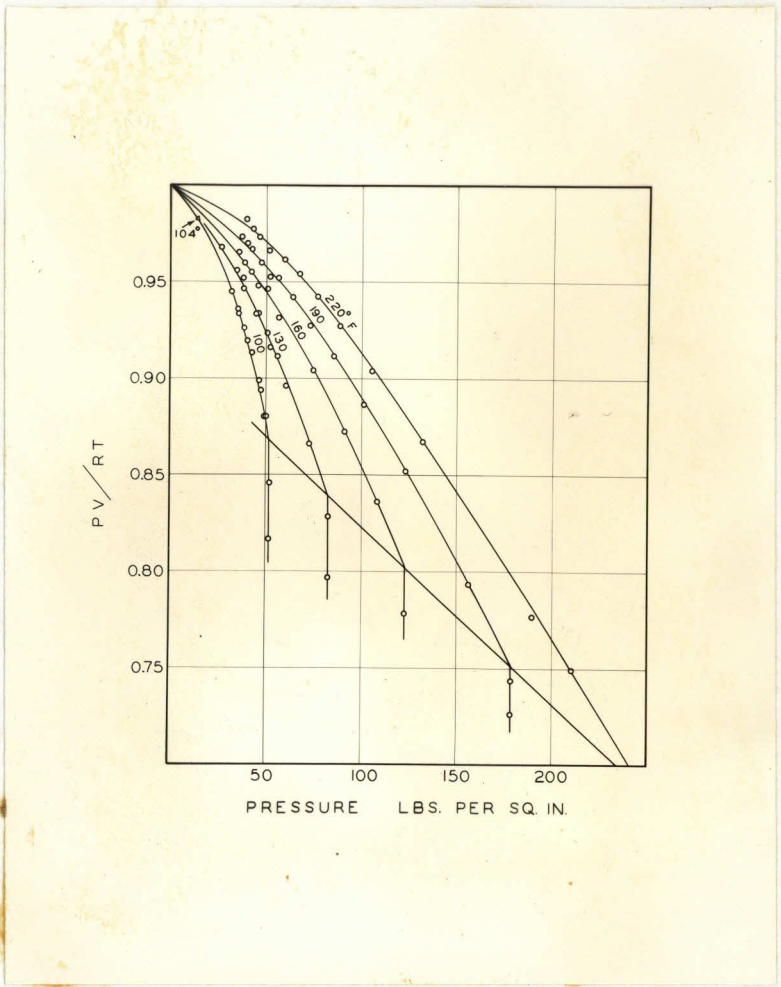


Figure 3. Compressibility of Superheated Gas

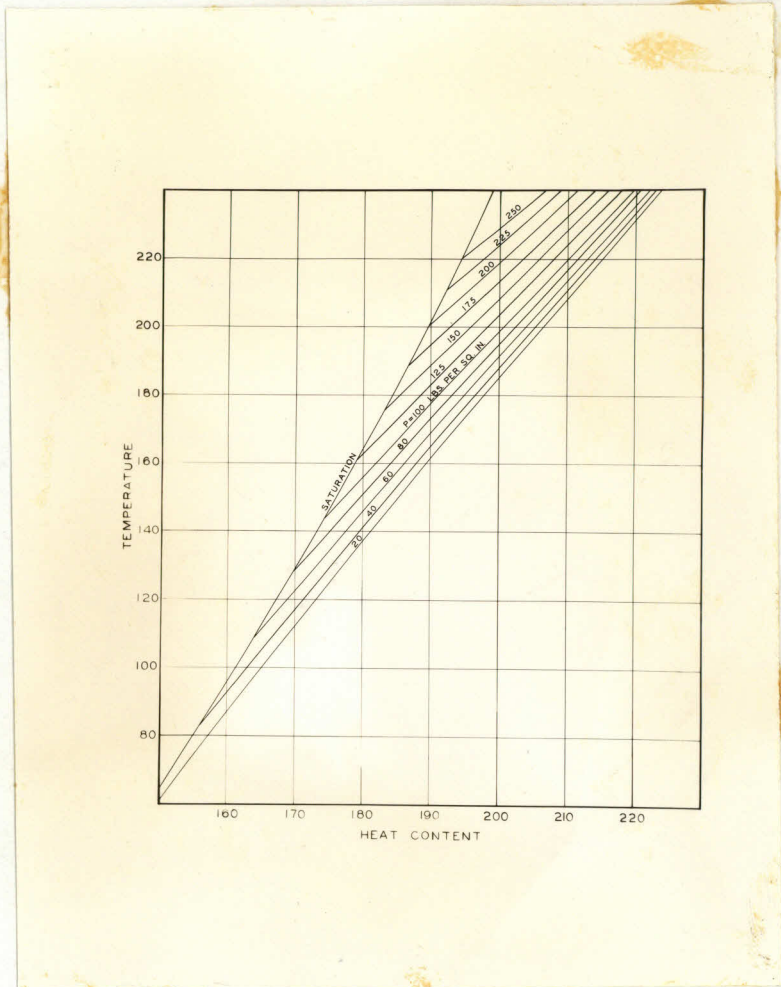


Figure 4. Heat Content Temperature Diagram

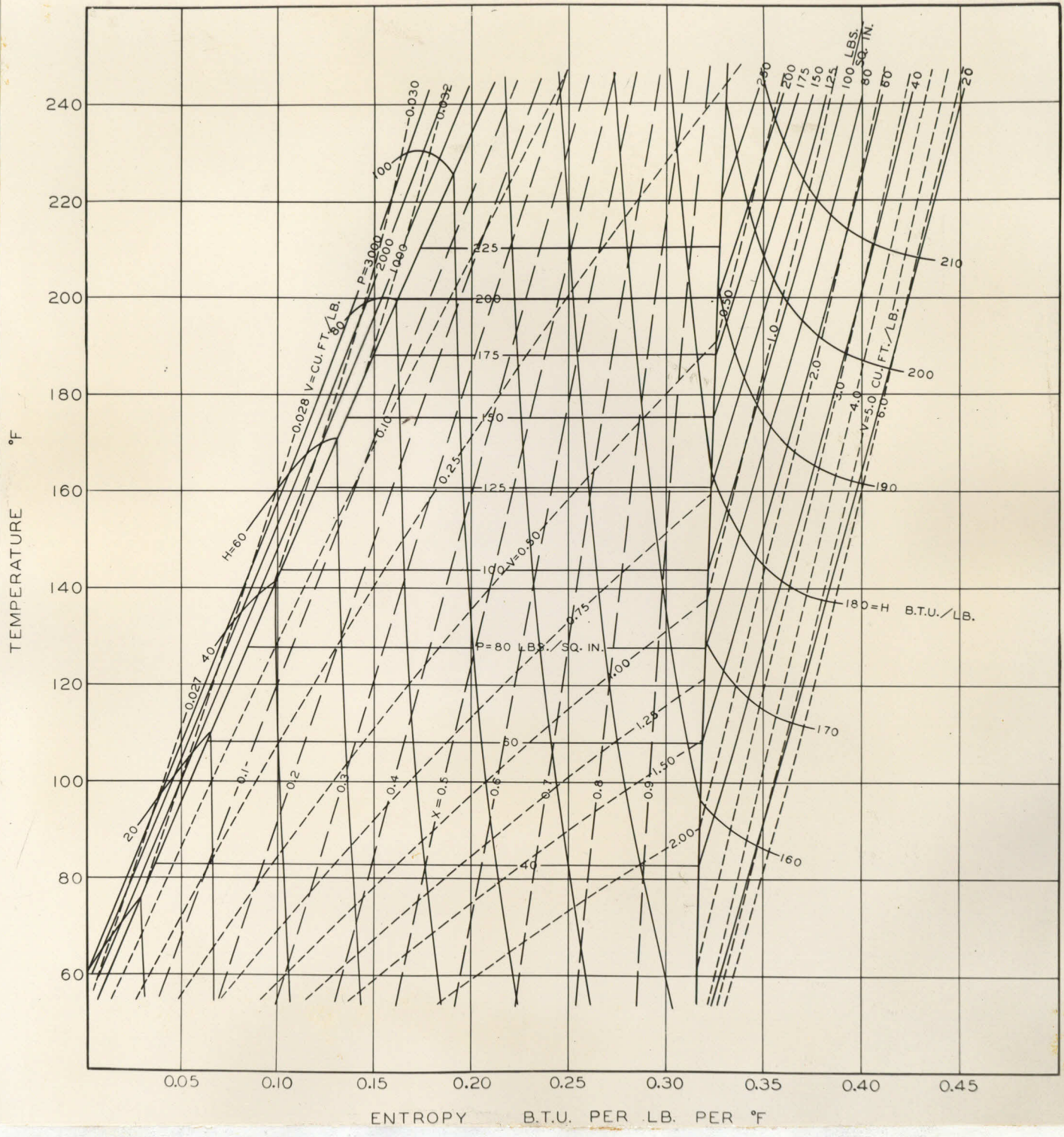


Figure 5.

Temperature Entropy Diagram

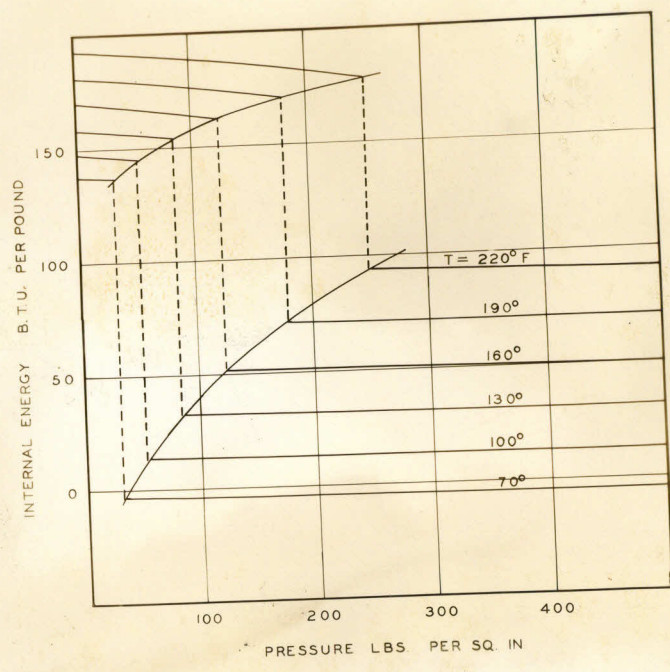


Figure 6. Internal Energy Pressure Diagram

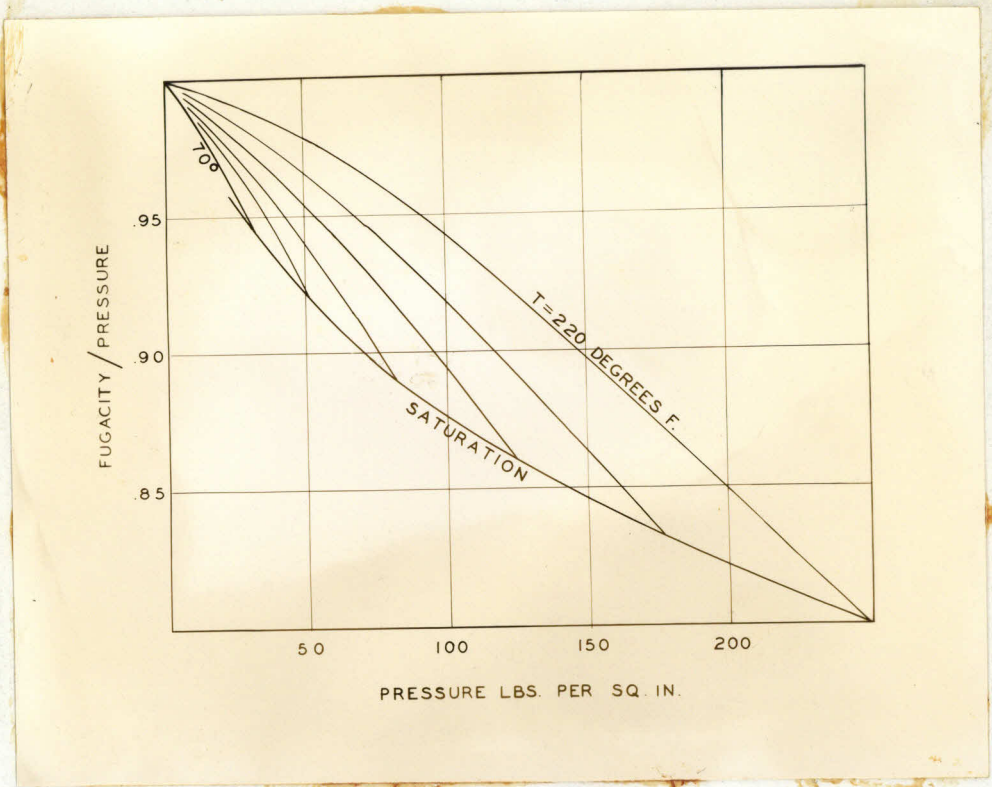


Figure 7. Fugacity of Superheated Gas

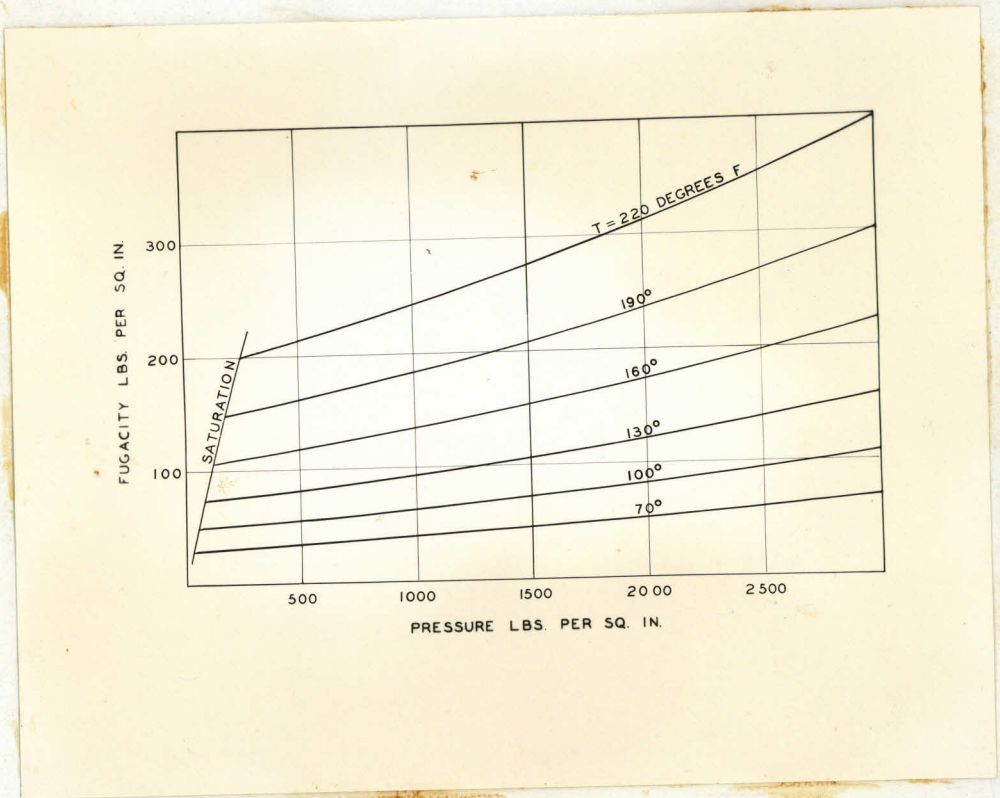


Figure 8. Fugacity of Condensed Liquid

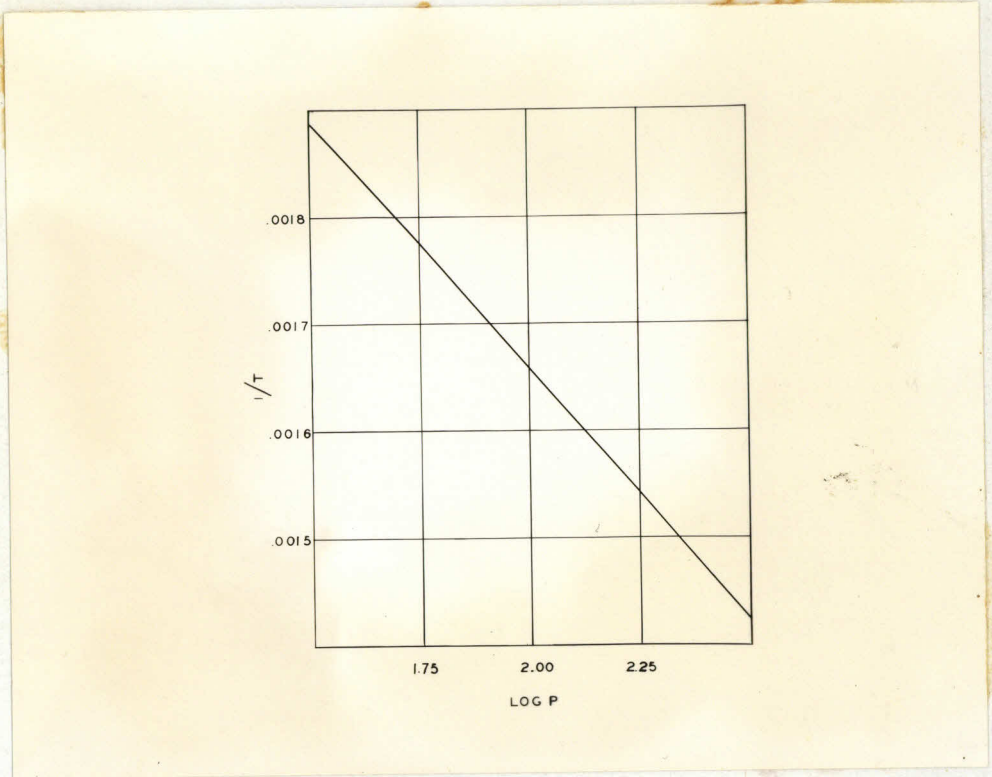


Figure 9. Vapor Pressure of Normal Butane

Part III

THE JOULE THOMSON COEFFICIENTS OF ISO-BUTANE

THE JOULE-THOMSON COEFFICIENTS OF ISO-BUTANE

Introduction

The Joule-Thomson coefficient, μ , of a substance is defined as the rate of change of temperature with pressure when a change of state of the substance takes place under conditions of constant heat content. The coefficient is of value in obtaining the change in internal energy with pressure, which is one of the necessary pieces of data needed to enable one to calculate the thermodynamic properties of a substance, as was mentioned in part two of this thesis. The coefficients of iso-butane were measured at temperatures ranging from 70 to 220 °F. at 30 degree intervals, the pressures being varied from atmospheric to within ten pounds per square inch of the vapor pressure at the temperature in question.

The iso-butane used in these determinations was furnished by the Philgas Company. Their analysis shows 0.00 percent propane, 100.00 percent iso-butane, and an unmeasurable trace of n-butane.

Apparatus and Procedure

Since it has been done elsewhere, (5), the apparatus will only be described briefly here. It consisted of a porous alundum thimble, through which the gas was forced to flow. A cam pump was used to maintain the flow, by-pass valves and pipes being included to facilitate the maintenance of constant flow. After the gas had passed through the thimble, it was recirculated through the system, which effected a great saving in the amount of gas necessary for a determination. A magnetic valve, operated through relays by a mercury manometer, kept the pressure differential across the thimble constant to within 0.5 percent. In order that the temperature of the manometer would not change with the temperature of the bath or room, and that the gas in the apparatus would not condense in the

manometer, the latter was enclosed in a steam jacket, so that its temperature was always 212 °F. The pressure differential which the steam-jacketed manometer maintained was calibrated by the use of another manometer, parallel to the first, whose differential could be measured by an especially designed vertical component cathetometer. The differential was determined by the height which one arm of the steam-jacketed manometer reached before it touched an electric contact, closing a circuit which, in turn, closed the magnetic valve.

The pump, magnetic valve, and cell containing the thimble were immersed in an oil bath, whose temperature was held at the desired value, with an absolute accuracy of 0.02 °F., by a control whose drift was less than 0.002°F. per hour. Between the magnetic valve and the thimble was a conditioning coil, (also immersed in the oil bath) which was about twelve feet long. The temperature difference across the thimble was measured by a three junction differential thermocouple, there being three junctions on each side of the thimble. A three junction thermocouple, the thermocouple being in series, was used so that the electromotive forces produced would be measurable with a greater degree of accuracy than would be possible with the small electromotive forces which would be produced by one thermocouple. The electromotive forces were measured by a potentiometer whose scale was divided into 10,000 divisions for a range of 0.5 millivolts, being read to the nearest division. The total pressure on the system was determined by a fluid pressure scale whose accuracy was 0.1 pound per square inch in 300 pounds per square inch.

Before any gas was added to the system it was evacuated to an absolute pressure of approximately 4 millimeters of mercury, then purged twice with the gas, re-evacuating each time. With the oil bath regulating at the desired temperature, gas was added until the pressure reached the

value chosen, the cam pump started, and then the by-pass valves set so that just enough gas was flowing through the magnetic valve to keep it rhythmically opening and closing, as could be determined by watching a lamp in series with the exciting electric circuit of the valve. As much as half an hour was sometimes needed before the temperature differential would become constant. It was found that equilibrium was reached much sooner when the amount of gas in the apparatus was increased from determination to determination than when it was decreased. Also, as soon as saturation was approached, the values dropped below that which would be expected (probably due to small droplets of liquid appearing in the gas), and, consequently, no values could be measured at pressures closer than 10 pounds per square inch to the vapor pressure at the temperature under consideration.

Traces of impurity, such as oil from leaks into the system from its surrounding bath, or from the grease used on the cam pump, caused much trouble, necessitating frequent, thorough cleaning of the apparatus. Such impurities would often condense in the thimble and then would have to be removed, either by burning them out or by replacing the thimble entirely.

Besides the errors due to impurities, the small drift in bath temperature was enough to be a fruitful source of error. With a three junction thermocouple, the temperature measurements were not hard to obtain within satisfactory accuracy. The maintenance of the pressure differential was more difficult. A differential of slightly under one pound per square inch was used throughout the determinations, the value changing slightly from time to time. Frequent calibrations were made to eliminate an error in this value. However, the by-pass valve adjustments were very delicate and had to be continually watched. Mechanical difficulties were encountered in the magnetic valve, due to the close fit between the moving

part and the side walls. In spite of these difficulties, the accuracy of the values as a whole is believed to be about one and one half percent.

Calculations and Results

The scale divisions on the potentiometer per degree Fahrenheit were determined by calibration of the wires used in the thermocouple circuits. These values, when divided into the potentiometer reading, yielded the temperature difference between the inside and outside of the thimble. The temperature differential was then divided by the pressure differential, giving the Joule-Thomson coefficient.

The coefficients have been calculated by the above method and are tabulated in Table I. They are shown plotted against pressure in Figure 1, showing the experimental points. Figure 2 shows them interpolated against temperature.

In general, the curvature of the lines in Figure 1 is somewhat greater than that of similar curves for the other hydrocarbon gases which have been studied and reported. It is of the same general shape as would be expected for gases in the region in which this work was done, namely that of low reduced pressure and temperature, where a reduced value consists of the actual value divided by the critical value. At higher temperatures, the slope of the line would be expected to become less until finally, not far below critical temperature it would change in sign. Above critical temperature, the slope would be negative, and the lines become nearly linear at still higher temperatures. The above remarks pertain only to the gas. For the corresponding liquid values at the low temperatures, the lines on a similar μ vs. P plot would be straight and horizontal. However, as the temperature rises, they show an ever increasing negative slope and curvature, until the critical temperature is reached.

TABLE I

JOULE-THOMSON COEFFICIENTS OF GASEOUS ISO-BUTANE

Abs. Pressure, Lb./Sq. In.	, ° F. per Lb. per Sq. In.					
	70°F	100°F	130°F	160°F	190°F	220°F
Satd. Gas	0.3544	0.3090	0.2748	0.2488	0.2321	0.2215
0	0.1503	0.1312	0.1118	0.0928	0.0738	0.0544
20	0.2298	0.1830	0.1468	0.1187	0.0972	0.0791
40	0.3260	0.2330	0.1799	0.1460	0.1216	0.1008
60	-	0.2790	0.2110	0.1727	0.1421	0.1185
80	-	-	0.2385	0.1942	0.1600	0.1325
100	-	-	0.2635	0.2115	0.1760	0.1469
125	-	-	-	0.2290	0.1919	0.1612
150	-	-	-	0.2439	0.2055	0.1735
175	-	-	-	-	0.2160	0.1830
200	-	-	-	-	0.2242	0.1925
250	-	-	-	-	-	0.2076

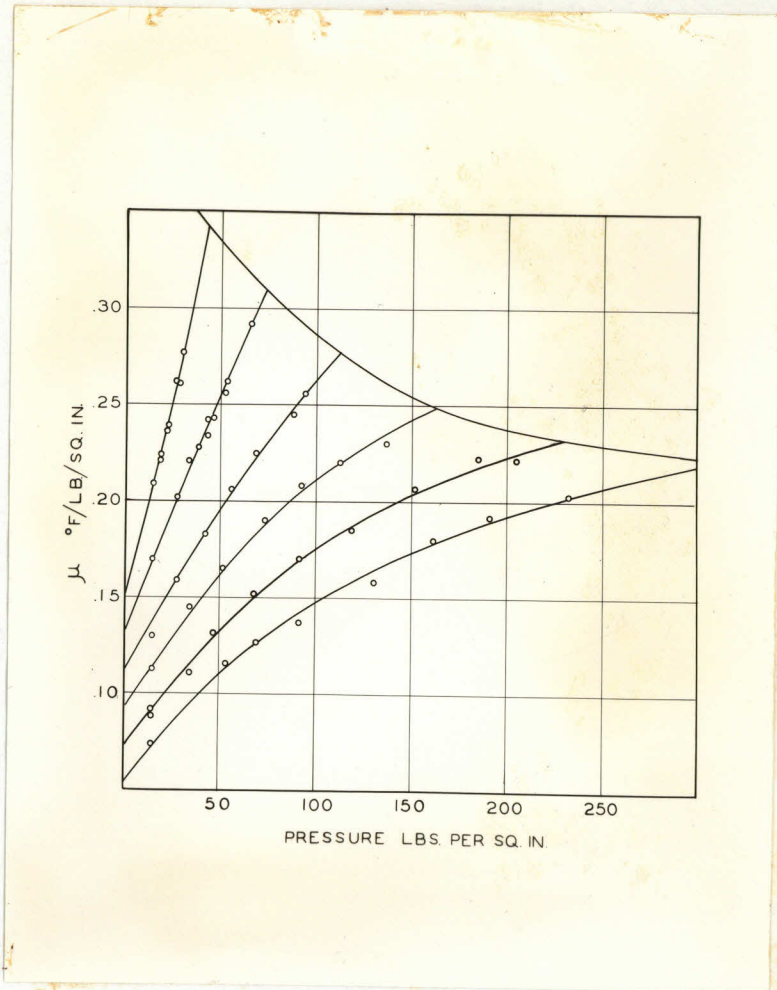


Figure 1.

Experimental Values of
Joule Thomson Coefficients

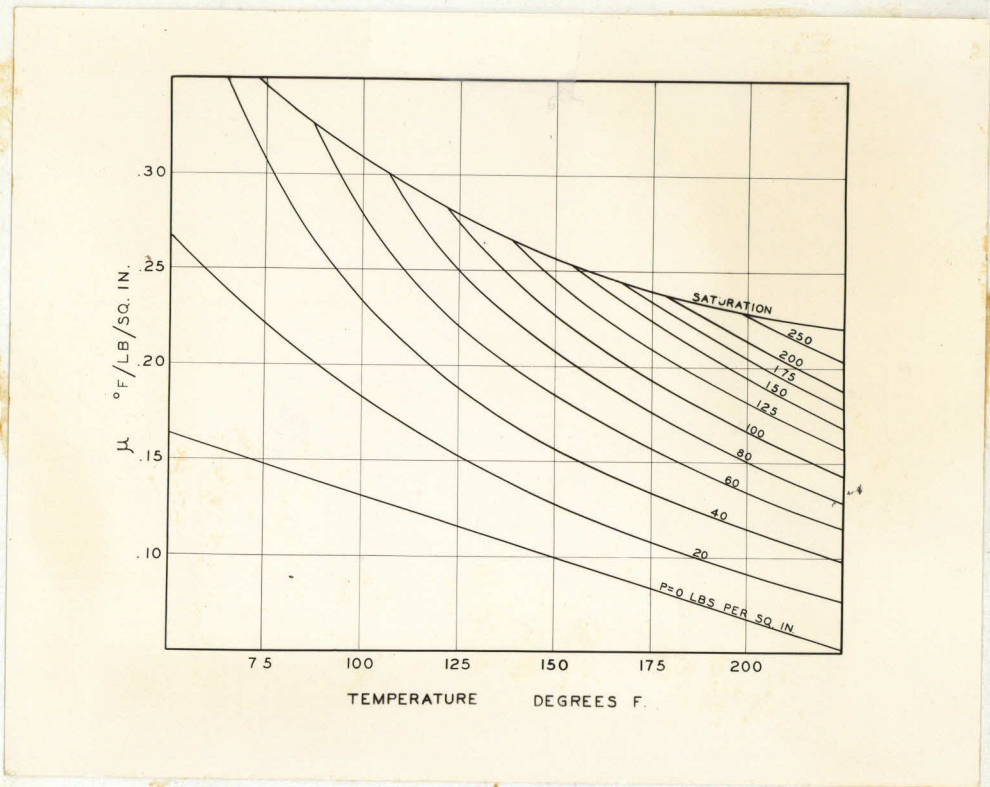


Figure 2. Effect of Temperature on Joule Thomson Coefficients

Symbols

C_p	-	Specific Heat at constant pressure
C_s	-	Specific Heat at saturation conditions
C_v	-	Specific Heat at constant volume
f	-	Fugacity
H	-	Heat Content
J	-	Mechanical equivalent of heat
M	-	Molecular weight
P	-	Pressure
Q	-	Heat absorbed
R	-	Gas constant
r	-	Heat of vaporization
S	-	Entropy
T	-	Temperature
V	-	Volume
x	-	Quality
	-	Joule Thomson coefficient

Acknowledgements

Thanks are due for the assistance of J. E. Sherborne, H. S. Backus, and E. R. Kennedy in carrying out the experimental work of the butane study. D. C. Webster assisted in the drafting. The work was made possible through the financial assistance of the American Petroleum Institute.

The advice and criticism of Drs. W. N. Lacey and E. H. Sage, as well as their patient and untiring efforts while leading the author through the theoretical background and experimental difficulties, was invaluable.

Literature Cited

- (1) Sage, B. H., Backus, H. S., and Vermeulen, T., Ind. Eng. Chem., 28, 489 (1936)
- (2) Kennedy, E. R., C. I. T. Thesis, 1936
also to be published in June, 1936, Ind. Eng. Chem., 28, 0000
- (3) Sage, B. H., Schaafsma, J. G., and Lacey, W. N., Ind. Eng. Chem., 26, 1218 (1934)
- (4) Sage, B. H., and Lacey, W. N., Ind. Eng. Chem., 27, 1484, (1935)
- (5) Sage, B. H., Kennedy, E. R., and Lacey, W. N., Ind. Eng. Chem., 28, 601 (1936)
- (6) Osborne, N. S., and Van Dusen, M. S., Bur. Standards, Bull. 14, 397 (1918)