

CALORIMETRIC MEASUREMENTS OF SOME HYDROCARBONS

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# Phase Equilibria in Hydrocarbon Systems

## XII. Specific Heats of Some Mixtures of Propane, *n*-Butane, and *n*-Pentane<sup>1</sup>

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 COMPOSITION and temperature have a much larger effect upon the specific heats of hydrocarbon mixtures of low molecular weight than they do upon those with a large number of carbon atoms in the molecule. A great many more experimental measurements have been made for hydrocarbon mixtures of high average molecular weight than for more volatile ones. Because of the lack of suitable information in this region, a study was undertaken to determine the variation of specific heat with composition and temperature for liquid mixtures in the three two-component systems containing propane, *n*-butane, and *n*-pentane. The work also includes the specific heat of *n*-pentane and of a series of liquid mixtures of propane and a highly refined water-white oil (average molecular weight, 337) called "crystal oil." The specific heat measurements were made throughout the temperature interval from 70° to 220° F.

The specific heat measurements reported in this paper were made at constant volume in the calorimeter previously described (1). After determining experimentally the specific heat at constant volume in the two-phase region, we can then calculate the specific heats at constant volume and constant pressure at any temperature within the range studied and for any pressure for which the pressure-volume-temperature relations for the substance in question are known.

In brief, the method consisted first of introducing a sample of fixed composition into a light-weight steel bomb, adding known amounts of electrical energy, and measuring the rise in temperature of the bomb and contents by the use of thermocouples. Heat loss from the bomb was prevented by surrounding it with a vacuum jacket and maintaining the jacket at the same temperature as the surface of the bomb. The specific heat measurements are considered trustworthy to

<sup>1</sup> Previous articles in this series appeared during 1934 and 1935, and in January and February, 1936.

within 1.5 per cent. The directly measured values of specific heat are under constant volume conditions in the two-phase region. These values are not as useful as are values of the specific heat at constant pressure for condensed liquid adjacent to the bubble point, although the difference between the two quantities may be rather small. The calculations which must be utilized to convert the specific heat in the two-phase region to the specific heat at constant pressure for condensed liquid adjacent to the bubble point are based upon a knowledge of the pressure-volume-temperature relations of the material. To obtain these values for all the systems involved would require a rather extended experimental program. If, however, the mixtures follow the laws of ideal solutions within the accuracy required for the evaluation of the correction terms, the experimental work is greatly reduced. In order to check the agreement of these two-component mixtures with the laws of ideal solutions, a study was made of the pressure-volume-temperature relations of a mixture of propane and pentane. This study was restricted to the condensed region and part of the two-phase region. The methods and apparatus used for this work have already been described (2, 6). Briefly, the method consisted in isothermally changing the volume of a steel chamber con-

taining a known amount of the sample by addition or withdrawal of mercury. The change in equilibrium pressure with change in volume was thus determined. An agitator was provided within the chamber to insure equilibrium.

### Pressure-Volume-Temperature Measurements

In the pressure-volume-temperature measurements the following precision was attained: mass of sample, 0.1 per cent; volume of sample, 0.1 per cent; pressure, 0.1 pound per square inch from atmospheric pressure to 300 pounds per square inch, and 1 pound per square inch from 300 to 3000 pounds per square inch; temperatures, 0.02° F.

The materials used in this work were used in other studies (1, 5, 6). The Philgas Company, from which the samples of propane, *n*-butane, and *n*-pentane were obtained, submitted the following special analyses, expressed in mole per cent: propane, 100.0; *n*-butane, 99.21 with 0.18 isobutane and

The specific heats at constant pressure for a number of two-component mixtures consisting of propane, *n*-butane, and *n*-pentane are reported for the condensed liquid adjacent to bubble point. In order to demonstrate that the behavior of such mixtures was sufficiently close to that of ideal solutions for the purposes of the specific heat calculations, a study of the thermodynamic properties of a mixture of propane and *n*-pentane was made, and the results are reported.



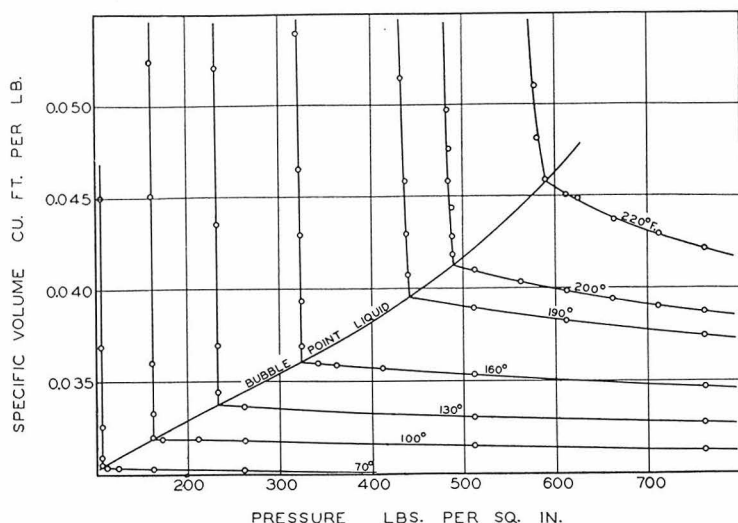


FIGURE 1. SPECIFIC VOLUMES FOR A MIXTURE CONTAINING 79.41 MASS PER CENT PROPANE AND 20.59 MASS PER CENT *n*-PENTANE

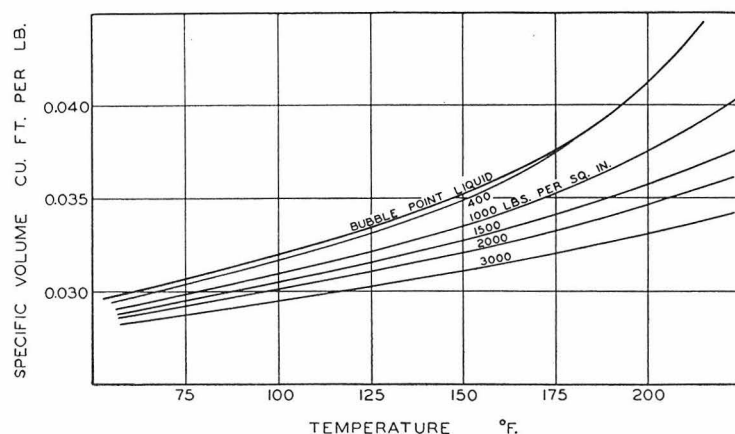


FIGURE 2. SPECIFIC VOLUME OF THE PROPANE-PENTANE MIXTURE AS A FUNCTION OF TEMPERATURE

0.61 isopentane; *n*-pentane, 99.3 with 0.7 isopentane. The compositions of mixtures discussed hereafter are given in terms of the proportions of these three samples, referred to as propane, *n*-butane, and *n*-pentane.

The mixture chosen for the pressure-volume-temperature work was composed of 79.41 mass per cent propane and 20.59 mass per cent *n*-pentane. This mixture was chosen as representing the mixture of those studied which would be expected to deviate most widely from the laws of ideal solutions; it was composed of the two constituents of most widely divergent properties and with the maximum concentration of the constituent nearest to its critical state. The study included the effect of pressure upon volume at seven temperatures spaced between 70° and 220° F. In each case the volume of the system was increased to about three times its volume at bubble point. Figure 1 shows the results of these measurements in the vicinity of the bubble point. The much larger decrease in pressure with increase in volume in the two-phase region for the higher temperatures is apparent. The rapid increase in compressibility of the liquid as bubble-point pressure is approached at the higher temperatures can be clearly seen. Figure 2 shows the isobaric variation in volume of the liquid with temperature; the rapid increase in thermal expansion with temperature at the bubble

point is striking. At the higher pressures, temperature has a much smaller effect upon the thermal expansion.

The principal interest in this pressure-volume-temperature work is a comparison of the actual measurements with those predicted from the laws of ideal solutions. One of the assumptions which must be validated before these laws are applicable is that of additive volumes. Figure 3 shows the percentage deviation of the volumes predicted by the laws of ideal solutions from the experimental volumes as a function of temperature for a series of pressures. This percentage deviation was obtained from the expression:

$$\text{Per cent deviation} = \frac{(0.7941V_3 + 0.2059V_5 - V)(100)}{V}$$

where  $V_3$ ,  $V_5$ ,  $V$  = specific volumes of propane, pentane, and the mixture, respectively

The deviation from additivity is negligible at the lower temperatures, but as the critical temperature of propane is approached the deviation becomes appreciable.

It is also apparent from Figure 3 that the assumption of additive volumes is much more closely followed at the higher pressures than at pressures in the neighborhood of the bubble point. However, in all cases the deviation is small except near the critical temperature and pressure of propane, where deviations of over 100 per cent are encountered.

Another interesting correlation which the data permit is a comparison of the observed bubble point with that predicted from Raoult's law and from the laws of ideal solutions. In the following table the experimentally determined bubble-point pressures (in pounds per square inch absolute) for a series of temperatures are shown for comparison with similar values based upon ideal solutions and upon Raoult's law:

	70° F.	100° F.	130° F.	160° F.	190° F.	220° F.
Exptl.	106.4	162.0	231.5	322	441	590
Ideal soln.	107.9	162.7	234.3	334	455	600
Raoult's law	109.8	165.8	239.8	333	459	600

In each case the agreement is satisfactory at the lower temperatures but becomes poor at higher temperatures, approaching the critical temperature of propane.

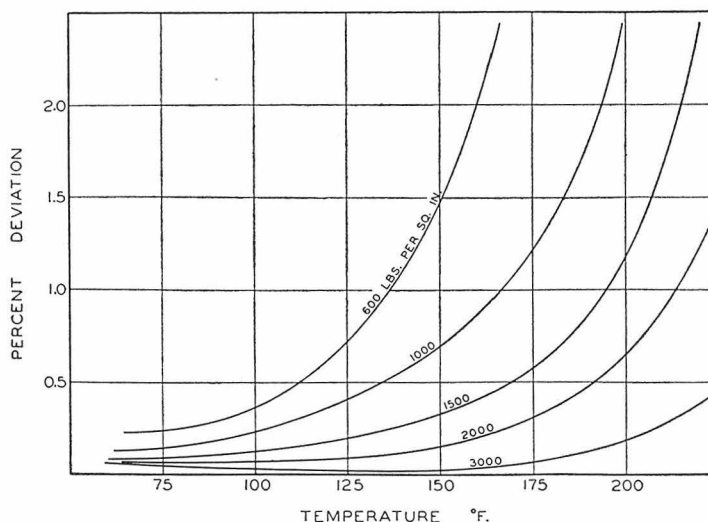


FIGURE 3. DEVIATION FROM EXPERIMENTAL VALUES OF SPECIFIC VOLUMES OF THE PROPANE-PENTANE MIXTURE CALCULATED FOR IDEAL SOLUTION

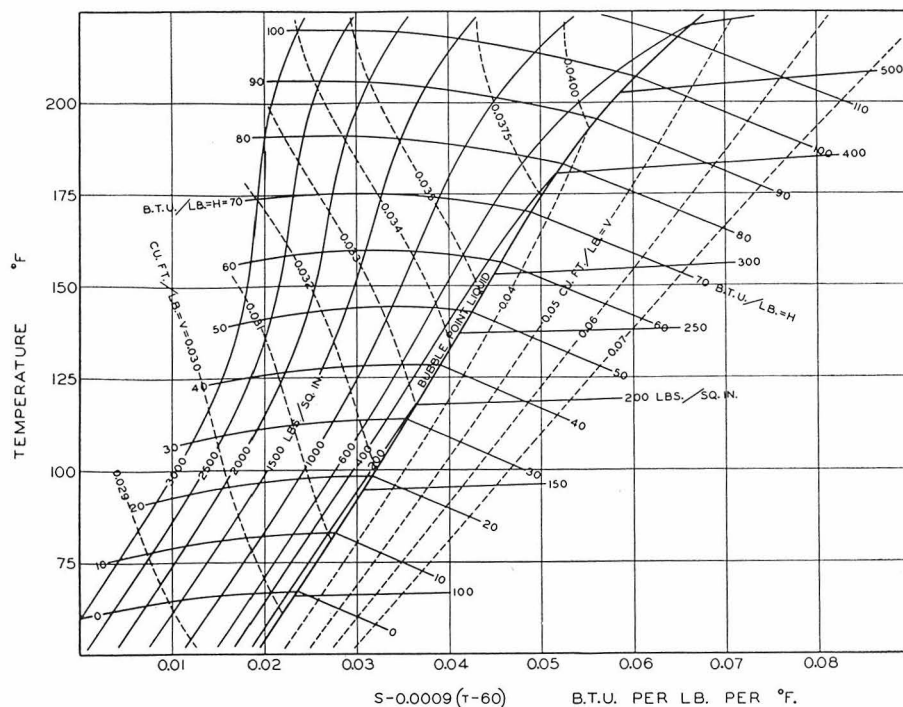


FIGURE 4. TEMPERATURE-ENTROPY DIAGRAM FOR THE PROPANE-PENTANE MIXTURE

Still another assumption which must be fulfilled by an ideal solution is the additivity of the heat contents. In other words, there must be no change in internal energy upon mixing. Experimental verification of this assumption is not easy, since high precision in the determination of specific heat is laborious and difficult of attainment. For this reason a comparison of this nature was not attempted, although the specific heat data indicate agreement within the limits of their accuracy, as will be shown later.

The pressure-volume-temperature data along with the specific heat data to be discussed later furnish sufficient information to determine the thermodynamic properties of this mixture throughout the pressure and temperature range investigated. The methods of calculation used have already been described in detail (6). However, because of the small change in pressure with increase in volume in the two-phase region, a modification of the previous procedure had to be used. In the two-phase region, volume was used as the independent variable instead of pressure. The isothermal changes in internal energy with volume were determined by graphical integration of the expression:

$$\left(\frac{\delta E}{\delta V}\right)_T = T \left(\frac{\delta P}{\delta T}\right)_V - P$$

The changes in internal energy with temperature were determined by graphical integration of the following expression:

$$\left(\frac{\delta E}{\delta T}\right)_V = C_V$$

Heat contents were determined from the internal energy values by use of the relation:

$$H = E + pv$$

In the two-phase region the isothermal changes in entropy were determined by graphical integration of the expression:

$$\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V$$

The changes in entropy with temperature were determined by integration of the equation:

$$\left(\frac{\delta S}{\delta T}\right)_V = \frac{C_V}{T}$$

The determination of the effect of pressure upon heat content and entropy in the condensed region was carried out in exactly the same manner as previously described (6).

The results of the calculations for the two-phase region are shown in Table I; the pressure, heat content, and entropy are given as functions of the total volume of the system for a series of temperatures. Table II presents the specific volumes, heat contents, and entropy as functions of pressure for the condensed region at the same series of temperatures.

The temperature-entropy plane offers the best method of presenting the thermodynamic data in graphical form. Because of the small isothermal changes in entropy as compared to the changes with temperature, a function of entropy is used in Figure 4 in order to show these isothermal variations on a better scale. The use of this function is based upon a device to exaggerate graphically the small isothermal changes and still allow plotting on a reasonable scale the larger changes in entropy with change of temperature. For this purpose the values shown are merely differences, at constant temperature, between the entropy and the function  $0.0009(t - 60)$ , where  $t$  is the temperature in  $^{\circ}\text{F}$ . To obtain the value of the entropy for a given state, the value of the abscissa is read from Figure 4 and the quantity  $0.0009(t - 60)$  for the temperature in question is added to it. The inversion of the Joule-Thomson coefficient in the condensed region at the higher temperatures is evident from the shape of the lines of constant heat content. The large positive Joule-Thomson coefficient in the two-phase region is in agreement with that expected from the values for propane and pentane. The behavior is in distinct contrast to that found for mixtures of crude oil and natural gas (3). In such mixtures the Joule-Thomson coefficients were small and inverted in the two-phase region. The inversion of curvature of the constant-pressure lines in the con-

TABLE I. PROPERTIES IN THE TWO-PHASE REGION FOR PROPANE-PENTANE MIXTURE CONTAINING 79.41 MASS PER CENT PROPANE

$v^a$	70° F.			100° F.			130° F.			160° F.			190° F.			220° F.			
	$p$	$h$	$s$	$p$	$h$	$s$	$p$	$h$	$s$	$p$	$h$	$s$	$p$	$h$	$s$	$p$	$h$	$s$	
0.035	106.3	2.67	0.03472	160.8	21.84	0.06927	232.6	41.75	0.10309										
0.040	106.1	3.48	0.03623	160.5	22.92	0.07121	232.0	43.21	0.10558	323.1	64.22	0.13919	440.7	85.77	0.17177	...	...	...	...
0.045	105.9	4.27	0.03773	160.2	24.00	0.07314	231.4	44.66	0.10805	321.7	66.18	0.14237	437.5	88.47	0.17597	...	...	...	...
0.050	105.7	5.07	0.03923	159.9	25.07	0.07506	230.9	46.10	0.11049	320.3	68.11	0.14551	434.4	91.12	0.18009	483	114.3	0.21440	
0.055	105.5	5.87	0.04073	159.6	26.14	0.07696	230.4	47.52	0.11291	319.0	70.02	0.14861	431.5	93.72	0.18413	475	117.62	0.21965	
0.060	105.3	6.65	0.04222	159.3	27.20	0.07886	229.9	48.93	0.11530	317.6	71.90	0.15167	428.7	96.25	0.18808	468	121.00	0.22473	
0.065	105.2	7.45	0.04371	159.1	28.25	0.08075	229.4	50.32	0.11768	316.3	73.75	0.15468	426.1	98.74	0.19195	462	124.26	0.22963	
0.070	105.1	8.23	0.04519	159.0	29.30	0.08262	229.0	51.70	0.12002	315.1	75.58	0.15765	423.6	101.16	0.19573	457	127.42	0.23437	

<sup>a</sup>  $v$  = specific volume, cu. ft./lb.;  $p$  = pressure, lb./sq. in. abs.;  $h$  = heat content, B. t. u./lb.;  $s$  = entropy, B. t. u./lb./ $^{\circ}\text{F}$ . abs.

TABLE II. PROPERTIES IN CONDENSED REGION FOR PROPANE-PENTANE MIXTURE CONTAINING 79.41 MASS PER CENT PROPANE

$p^a$	70° F.			100° F.			130° F.			160° F.			190° F.			220° F.		
	<i>v</i>	<i>h</i>	<i>s</i>	<i>v</i>	<i>h</i>	<i>s</i>	<i>v</i>	<i>h</i>	<i>s</i>	<i>v</i>	<i>h</i>	<i>s</i>	<i>v</i>	<i>h</i>	<i>s</i>	<i>v</i>	<i>h</i>	<i>s</i>
Satd.	0.03042	1.94	0.03333	0.03199	21.19	0.06810	0.03377	41.38	0.10248	0.03606	62.64	0.13665	0.03958	85.54	0.17141	0.04580	111.95	0.2098
200	0.03033	1.97	0.03239	0.03194	21.19	0.06770												
400	0.03015	2.08	0.03047	0.03166	21.22	0.06566	0.03342	41.20	0.10040	0.03576	62.29	0.13526						
600	0.02995	(2.31)	0.02865	0.03140	21.28	0.06375	0.03302	41.09	0.09812	0.03511	61.59	0.13201	0.03836	84.07	0.16729	0.04548	111.71	0.20938
800	0.02979	2.42	0.02691	0.03118	21.43	0.06195	0.03268	41.06	0.09601	0.03458	61.11	0.12915	0.03730	82.64	0.16291	0.04165	107.99	0.20176
1000	0.02964	2.65	0.02526	0.03097	21.63	0.06024	0.03239	41.11	0.09405	0.03413	60.81	0.12658	0.03650	81.57	0.15919	0.03987	105.65	0.19607
1250	0.02946	2.98	0.02329	0.03072	21.92	0.05821	0.03205	41.25	0.09178	0.03365	60.61	0.12369	0.03572	80.64	0.15519	0.03830	103.67	0.19050
1500	0.02930	3.36	0.02142	0.03050	22.27	0.05630	0.03176	41.49	0.08967	0.03322	60.55	0.12107	0.03507	80.03	0.15173	0.03730	102.33	0.18598
1750	0.02915	3.77	0.01964	0.03029	22.66	0.05447	0.03148	41.78	0.08769	0.03284	60.60	0.11867	0.03452	79.65	0.14869	0.03658	101.41	0.18212
2000	0.02902	4.22	0.01793	0.03011	23.08	0.05274	0.03123	42.13	0.08583	0.03250	60.73	0.11644	0.03406	79.44	0.14595	0.03591	100.76	0.17872
2250	0.02888	4.69	0.01629	0.02994	23.54	0.05108	0.03101	42.53	0.08405	0.03221	60.94	0.11437	0.03366	79.38	0.14343	0.03535	100.32	0.17564
2500	0.02876	5.19	0.01471	0.02977	24.02	0.04948	0.03080	42.97	0.08236	0.03192	61.23	0.11243	0.03330	79.41	0.14110	0.03486	100.02	0.17280
2750	0.02866	5.72	0.01320	0.02963	24.53	0.04794	0.03061	43.44	0.08075	0.03167	61.56	0.11059	0.03298	79.53	0.13892	0.03443	99.82	0.17015
3000	0.02857	6.27	0.01175	0.02948	25.07	0.04637	0.03041	43.94	0.07921	0.03144	61.95	0.10886	0.03267	79.71	0.13687	0.03403	99.72	0.16767
Satd. pressure	106.4			162.0			231.5			322			441			590		

<sup>a</sup> The letters indicate the same properties as those in Table I.

densified region of Figure 4 is due to the fact that the rapid increase in the specific heat at constant pressure outweighs the effect of pressure upon the isothermal change in specific heat. This latter effect causes the lines of constant higher pressures to recede from the bubble point line as the temperature is increased.

### Specific Heat Measurements

From the pressure-volume-temperature study upon the mixture discussed, the authors consider that the deviation from the behavior of ideal solutions in the case of the other more favorable mixtures would be small enough to permit calculation of the required specific heat conversions. These corrections to the specific heat at constant volume in the two-phase region are applied in two steps. First the change in specific heat at constant volume with volume must be evaluated over the range from the volume at which the specific heat measurements were made to the volume at bubble point. This change was determined by graphical integration of the following expression:

$$\left(\frac{\delta C_v}{\delta V}\right)_T = T \left(\frac{\delta^2 P}{\delta T^2}\right)_V$$

The change from specific heat at constant volume at the two-phase side of bubble point to the specific heat at constant pressure on the condensed side of bubble point must also be determined. This was done by evaluation of the following expression:

$$C'_{p_B} = C''_{v_B} + T \left(\frac{\delta P}{\delta T}\right)_{v_B} \left(\frac{dV}{dT}\right)_B + T \left(\frac{\delta V}{\delta T}\right)_{p_B} \left(\frac{dP}{dT}\right)_B$$

It should be realized that there is an abrupt discontinuity in  $C_p$  in passing from one side of the bubble point condition to the other. That is, the value of  $C_p$  for condensed liquid very close to the bubble point is definitely different from that for the liquid in equilibrium with an infinitesimal amount of gas phase, even though the two states are almost identical. The values of  $C_p$  in these two conditions would be denoted by  $C'_{p_B}$  and  $C''_{p_B}$ , in which the subscript  $B$  refers to bubble point and the superscripts ' and '' indicate the presence of one or two phases, respectively.

The two correction calculations indicated were carried out for each experimental point, and the values of specific heat at constant pressure,  $C'_{p_B}$ , obtained. With the exception of mixtures with more than 70 mass per cent propane, the two corrections together were not more than 2 per cent of the specific heat.

The lowest curve in Figure 5 shows the results of the experimental work done on  $n$ -pentane. These values for the specific heat at constant pressure of the saturated liquid are distinctly lower than the values previously reported ( $\delta$ ) for the specific heat at a constant pressure of 1000 pounds per square inch. The earlier values were determined by the adiabatic expansion method ( $\epsilon$ ) which becomes unreliable when the thermal expansion is small. The values of  $(\delta T/\delta P)$ , which were used in these earlier determinations were checked

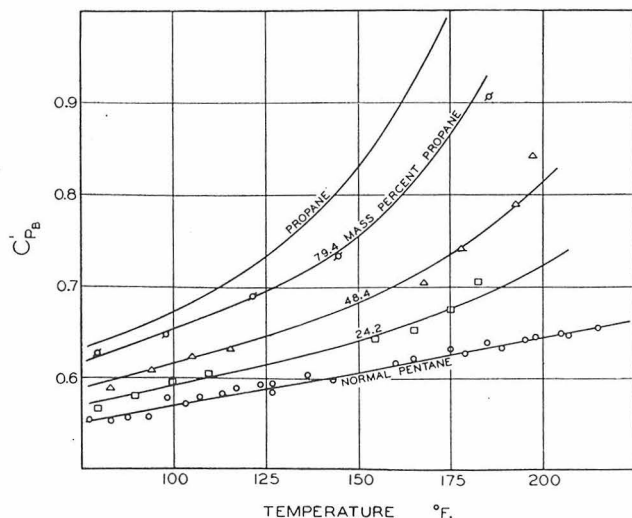


FIGURE 5. SPECIFIC HEAT AT CONSTANT PRESSURE FOR CONDENSED MIXTURE OF PROPANE AND  $n$ -PENTANE ADJACENT TO BUBBLE POINT

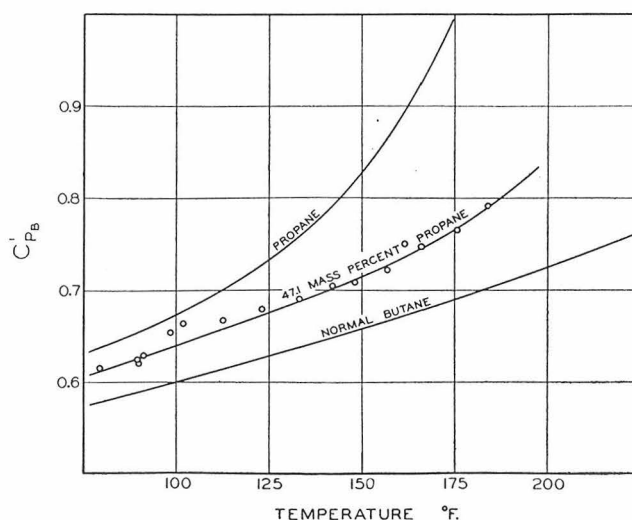


FIGURE 6. SPECIFIC HEAT AT CONSTANT PRESSURE OF PROPANE- $n$ -BUTANE SYSTEM FOR CONDENSED LIQUID ADJACENT TO BUBBLE POINT

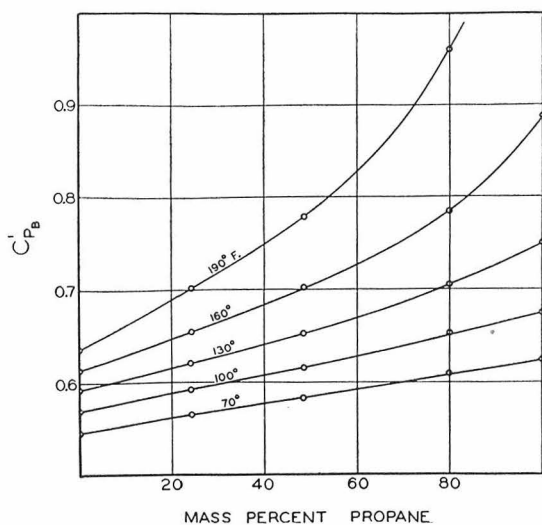


FIGURE 7. SPECIFIC HEAT AT CONSTANT PRESSURE OF MIXTURES OF PROPANE AND *n*-PENTANE FOR CONDENSED LIQUID ADJACENT TO BUBBLE POINT

with the present apparatus with higher precision and were found in satisfactory agreement. This indicates that the discrepancy in the earlier reported specific heats was due to uncertainty in the isobaric thermal expansion at 1000 pounds per square inch.

The results of these experimental studies for the two-component systems propane with *n*-pentane and propane with *n*-butane are shown in Figures 5 and 6. At the lower temperatures the agreement of the curves drawn through the experimental points for the mixtures is within experimental error of that predicted from the laws of ideal solutions. However, in the case of mixtures of propane and pentane at the higher temperatures, this is not the case. Figure 7 shows the isothermal change in specific heat as a function of the composition at a series of temperatures for mixtures of propane and *n*-pentane. The points plotted in this figure were read from the curves shown in Figure 5. As can be seen from the straight-line relationship throughout the composition range at 70° and 100° F., these solutions have little or no change in internal energy upon mixing. At the higher temperatures the curvature becomes marked, showing that the heat contents are not additive in this region and hence the solutions do not follow the laws of ideal solutions accurately at these temperatures and pressures.

In the case of mixtures of *n*-butane and *n*-pentane, the specific heats of the pure components differ by an amount small enough so that the magnitude of the experimental error of the present work renders results from the mixtures inconclusive. However, determinations made upon three mixtures indicated accord with the behavior of ideal solutions within the experimental error.

To gain further insight into the behavior of propane in solutions as its critical temperature is approached, another set of specific heat measurements was made on mixtures of propane and crystal oil. In order to make the necessary specific heat conversions, the pressure-volume-temperature data already published for these mixtures (4) were used. The corrections were applied in the same manner as was described earlier. Figure 8 shows the experimental points for several mixtures of propane in crystal oil as a function of temperature. The curve shown for crystal oil was taken from published data (2). Figure 9 shows the isothermal change in specific heat at constant pressure for the condensed liquid at the bubble point as a function of composition for a series of temperatures. The points plotted in this figure were read from the curves shown in Figure 8. In this case the divergence

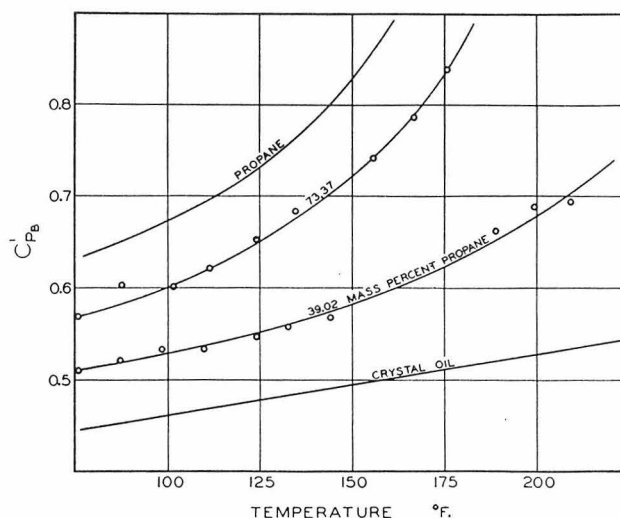


FIGURE 8. SPECIFIC HEAT AT CONSTANT PRESSURE OF PROPANE-CRYSTAL OIL SYSTEM FOR CONDENSED LIQUID ADJACENT TO BUBBLE POINT

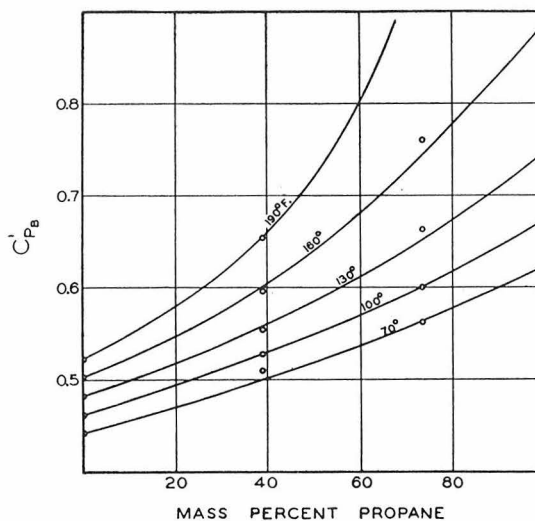


FIGURE 9. SPECIFIC HEAT AT CONSTANT PRESSURE IN PROPANE-CRYSTAL OIL SYSTEM FOR CONDENSED LIQUID ADJACENT TO BUBBLE POINT AS A FUNCTION OF COMPOSITION

from the straight line is apparent even at the lower temperatures but is marked only at the higher concentration of propane. At the higher temperatures, however, the curvature of the isotherms is appreciable at all concentrations, and the divergence from ideal solutions would be expected to be large.

#### Acknowledgment

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#### Literature Cited

- (1) Sage, B. H., and Lacey, W. N., *IND. ENG. CHEM.*, **27**, 1484 (1935).
- (2) *Ibid.*, **28**, 106 (1936).
- (3) *Ibid.*, **28**, 249 (1936).
- (4) Sage, B. H., Lacey, W. N., and Schaafsma, J. G., *Ibid.*, **26**, 874 (1934).
- (5) *Ibid.*, **27**, 48 (1935).
- (6) Sage, B. H., Schaafsma, J. G., and Lacey, W. N., *Ibid.*, **26**, 1218 (1934).

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## II. SPECIFIC HEATS OF LIQUID HYDROCARBONS

### a. Theoretical Considerations

Numerical data for specific heats of the pure normal alkanes are necessary in a tabulation of the thermodynamic properties of these compounds. The functions of state most used in engineering calculations are pressure, volume, temperature, entropy and enthalpy. During any process in which a material undergoes a change in temperature, the heat absorbed can not be calculated from P-V-T data alone.

Thermal values for any change in state may be calculated, with the aid of the physical data, once the thermal quantities have been obtained for some one process (for instance, a change at constant volume). The heat quantities used in isothermal changes of state are calculated by integration of one of the Second Law relations:

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

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

The isobaric specific heat applies directly in many problems, and is the value most frequently tabulated; but it is difficult to measure calorimetrically, either in a system of constant mass or under conditions of steady-state flow. The isentropic process or method of adiabatic expansion is best applied to gases near atmospheric pressure, where the thermal expansion is large. For liquids, a large pressure drop is necessary for reliable values. This method makes use of the relation<sup>1</sup>:

$$\left(\frac{\partial T}{\partial p}\right)_s = \frac{T}{C_p} \left(\frac{\partial v}{\partial T}\right)_p$$

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<sup>1</sup> Lewis and Randall, Thermodynamics, p.137.

Joule-Thomson coefficients for the liquid state are too small to be determined satisfactorily by experimental methods. Measurements on gases have been made by investigators on this research project (A.P.I. 37) with gratifying accuracy. From these data the specific heat is calculated by the equation<sup>1</sup>:

$$\mu C_p = \left(\frac{\partial T}{\partial p}\right)_H \left(\frac{\partial H}{\partial T}\right)_p = - \left(\frac{\partial H}{\partial p}\right)_T = T \left(\frac{\partial v}{\partial T}\right)_p - v$$

Liquid specific heats are probably best obtained by measurements in an adiabatic calorimeter. The author has carried on an investigation, begun by Sage<sup>2</sup> and Backus<sup>3</sup>, of values of the isochoric specific heats of a number of pure compounds and mixtures of known composition. Accepted experimental points have not differed from the mean by more than 2 percent<sup>4</sup>. As a result of correlations of the data for the different materials studied, curves have been located for which the maximum relative error is about 0.5 percent. Agreement of our values with those of two other investigations, carried on by Parks and Huffman at Stanford University and Dana of the Linde Air Products laboratories, indicates that our absolute error is less than 1 percent.

The apparatus used has been described by Sage and Lacey and will be reviewed in the next section. The liquid to be investigated is at its own vapor pressure, a small amount of the gas phase being always present. Experimental values have been converted so as to apply to the condensed liquid at a constant pressure equal to that of saturation. The reported values apply, well within experimental accuracy, over a pressure range of 100 pounds per square inch. It is believed that the data for this region adjacent to bubble point are more directly useful than values at

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<sup>1</sup> Lewis and Randall, Thermodynamics, pp.68, 133.

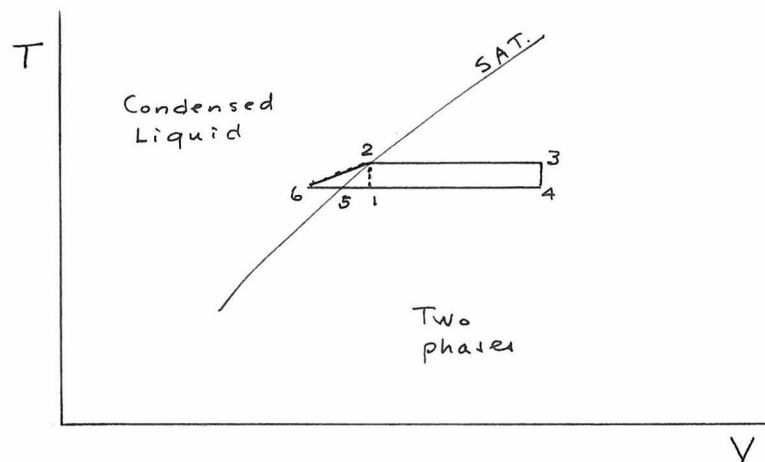
<sup>2</sup> Sage, B.H. and Lacey, W.N., Ind.Eng.Chem., 27, 1484 (1935).

<sup>3</sup> Backus, H.S., M. S. Thesis in Chemical Engineering, C.I.T., 1935.

<sup>4</sup> For measurements on n-pentane, the 25 points used in plotting the curve deviated by less than 1 percent. Only two points were rejected.

some constant higher pressure which might be taken as an arbitrary basis. Too, additional correction terms would increase the probably error of the results.

From the two-phase constant volume specific heats, the isobaric values for condensed liquid at bubble point are calculated with the use of P-V-T data by means of equations given in the foregoing article. The derivation of these equations is included here to indicate the physical significance of the various terms. A five-step cycle is used, giving results identical with those obtained through purely mathematical analyses. In the accompanying figure,  $T_2$  is only infinitesimally higher than  $T_1$ , while  $V_{3,4}''$  (double-primed denotes two phases) differs from  $V_B$  (at bubble point) by a finite amount.



Three relations are used in evaluating the enthalpy changes for the different steps:

$$dH = T ds + v dp$$

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

$$L_v = T \left(\frac{dp}{dT}\right)_s (v_D - v_B)$$

In the Clapeyron equation for the "latent" heat of vaporization, subscript D refers to the state of the saturated gas, or dew point. The changes in enthalpy or heat content are given as follows. (Subscript M denotes an average value over the temperature change; i.e., the value at  $T + \frac{dT}{2}$ ).

$\underline{x}$  is the quality, or the fraction of the total material that is in the gas phase.)

$$\begin{aligned}
 H_2 - H_6 &= c_{PB}' dT \\
 H_3 - H_2 &= L_2 x_3 = \left(\frac{dp}{dT}\right)_2^B (v'' - v_2^B) T_2 \\
 &= \left\{ \left(\frac{dp}{dT}\right)_1^B + \left(\frac{d^2p}{dT^2}\right)_M^B dT \right\} \left\{ v'' - v_1^B - dv^B \right\} \left\{ T_1 + dT \right\} \\
 &= - \left(\frac{dp}{dT}\right)_1^B (v_1^B - v'') T_1 + \left(\frac{d^2p}{dT^2}\right)_M^B (v_1^B - v'') dT \\
 &\quad + T_1 \left(\frac{\partial p}{\partial T}\right)_{v_1}^B \left(\frac{dv}{dT}\right)^B dT + \left(\frac{dp}{dT}\right)_1^B (v_1^B - v'') dT \\
 H_4 - H_3 &= -c_v'' dT - v'' dp = -c_v'' dT - v'' \left(\frac{dp}{dT}\right)_M^B dT \\
 H_1 - H_4 &= -L_1 x_4 = \left(\frac{dp}{dT}\right)_1^B (v_1^B - v'') T_1 \\
 H_6 - H_1 &= v_1^B \left(\frac{dp}{dT}\right)_1^B dT - T_1 \left(\frac{\partial v}{\partial T}\right)_P \left(\frac{dp}{dT}\right)_1^B dT
 \end{aligned}$$

Second-order infinitesimals are of course neglected throughout. Adding, equating to zero; and dividing by  $dT$ , there is obtained the expression:

$$c_{PB}' - c_v'' = \left(\frac{d^2p}{dT^2}\right)_B T (v_B - v'') + T \left(\frac{dp}{dT}\right)_B \left(\frac{dv}{dT}\right)_B + T \left(\frac{dp}{dT}\right)_B \left(\frac{\partial v}{\partial T}\right)_{PB}'$$

The derivatives of the pressure may be written as partials at constant  $V_B^H$ , without changing their values; this gives a symmetrical form to the two similar terms. A correction of this form is identical with that derived by the Bureau of Standards<sup>1</sup> for the work on ammonia, and used by the Linde laboratories in their study of the lighter paraffins at low temperature. The saturation specific heat at bubble point is calculated as an intermediate step.

$$\begin{aligned}
 c_B &= \frac{Q}{(\Delta T)_M} - \frac{L_2 x_2 - L_1 x_1}{\Delta T} + \frac{Lx}{T} \\
 c_{PB}' &= c_B + T \left(\frac{dp}{dT}\right)_B \left(\frac{\partial v}{\partial T}\right)_{PB}'
 \end{aligned}$$

<sup>1</sup> Osborne and Van Dusen, Bur. Stds. Bull., 14, 397 (1918).



This derivation is rigorous only for a pure compound. A similar treatment could be applied to a multi-component system, taking into account the change in pressure during the isothermal vaporization; but it would be impracticable to obtain physical data for every mixture investigated. For ideal solutions the partial enthalpies are equal to the enthalpies of the respective components in the pure state. Addition of the correction terms for the pure substances should provide a fairly good basis for conversion even if the assumption of ideality is widely in error; and it turns out, both from the physical measurements on the pentane-propane mixture and from the specific heat data obtained, that most mixtures of normal hydrocarbons are closely ideal.

The "specific heat" for any particular type of process is a function of the state of the system. Values may be determined for every process which satisfies either an actual or an empirical physical relation<sup>1</sup>. Thus, two paths not included in the cycle are shown in the figure:  ${}_5Q_2 = C_{V_B}''$ , is the isochoric specific heat of the two-phase mixture adjacent to bubble point.  ${}_1Q_2 = C_B$  is the specific heat for liquid under a changing volume equal to the bubble-point values at each temperature; the saturation specific heats  $C_S$  may be calculated for a mixture of any constant quality. The three terms in the conversion equation provide a step-wise correction, in their respective order, to  $C_{V_B}''$ , to  $C_B$ , and to  $C_{P_B}'$ .

#### b. Experimental Methods

The adiabatic calorimeter used for specific heat measurements was not designed or installed by the author, whose principal construction work on the equipment has been in maintenance repairs. But it is felt that a short description of the assembly has its place here.

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<sup>1</sup> "Specific heat" data in the literature are often of limited application in those cases where the authors have failed to report specifically the process on which the values are based.

In any accurate calorimetric method, heating due to other sources than that measured must be eliminated as completely as possible. The bomb upon which measurements were made was placed in a chromium-plated brass jacket so constructed as to minimize the three types of heat transmission. Conduction could take place only along the fine steel wires (Number 36, A.W.G.) by which the bomb was supported in a ring resting upon trunnions. Convection and conduction through the space between bomb and jacket were prevented by evacuation of the chamber to a pressure between  $10^{-4}$  and  $10^{-5}$  millimeters of mercury by means of a Cenco Hyvac pump and a diffusion pump using Apiezon-B oil.

Radiation was largely eliminated by polishing the two metallic surfaces and by maintaining the oil bath surrounding the brass jacket at a temperature within  $0.02^{\circ}\text{F}$ . of that of the bomb<sup>1</sup>. The differential thermocouple used had one junction on the surface of the bomb and the other in the oil bath outside of the jacket. A light beam, deflected by the mirror of a high-sensitivity galvanometer in series with the couple, operated a photo-electric cell; this in turn operated a relay on one of the heater circuits in the oil bath. The quantities of continuous and control heat were adjusted manually by means of rheostats. A thermostated air bath, surrounding the oil bath, was enclosed by double walls of an insulating wallboard. The front panel was removable, and included a window of two panes of glass with dead air space between them.

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<sup>1</sup> The fluctuations of oil bath temperature due to opening and closing of the control heater circuit are largely damped out by the brass jacket, the inner surface of the latter remaining at much more nearly constant temperature than the value stated.

"In order to insure both thermal and phase equilibrium within the bomb<sup>1</sup>, the latter 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 outside the jacket." The construction and operation of the magnetic clutch are indicated in Figures 1, 2 and 8.

The original bomb could not be used for measurements at high temperatures on the more volatile mixtures because it had not been designed for pressures greater than 1000 pounds per square inch. It became necessary to build a new bomb, very similar in general design and in its dimensions, weight, and heat capacity, but designed to withstand an internal pressure of 3000 pounds per square inch. The new bomb was formed from a solid piece of alloy tool steel (Seminole). After heat treatment by Dr. D. S. Clark of the California Institute, this material had a yield strength of 200,000 pounds per square inch. Fred C. Henson Company machined this roughly to shape, then ground it accurately to a thickness, for the side wall, of 0.040 inch, and for the end walls, of 0.045 inch. Both bombs were 2 inches in diameter and 4 inches in body length<sup>2</sup>. They were fitted with diaphragm valves, which could be removed for filling with liquid.

The ends were threaded and sweated on to the central cylinder. A thermocouple well and two stainless steel tubes for the heater leads were soldered into the bomb wall. Subsequent use of the bomb showed that these soldered joints were the weakest points. After continued use, the solder would rupture at pressures of from 1000 to 2000 pounds per square inch;

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<sup>1</sup> The quotations are from the article by Sage and Lacey, *Ind. Eng. Chem.*, 27, 1484 (1935).

<sup>2</sup> The volumes of both bombs were thus about 10 cubic inches or 160 cubic centimeters.

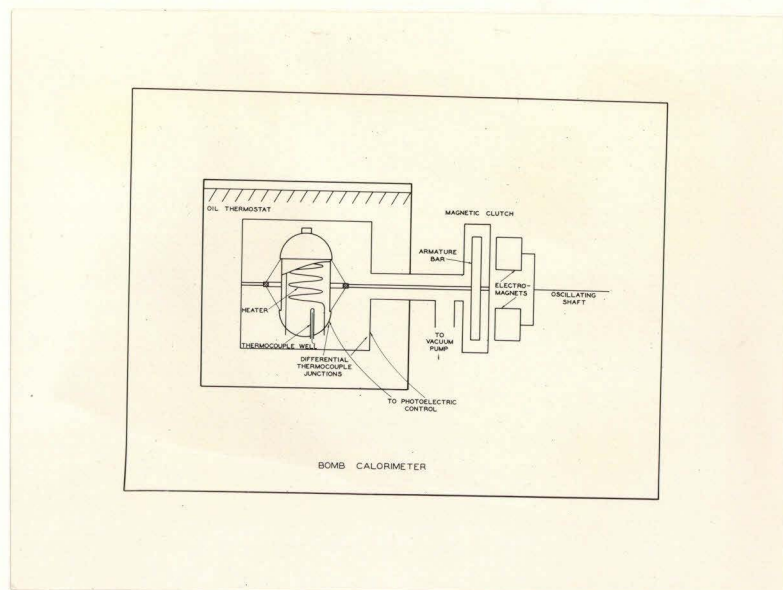


Figure 1. Bomb Calorimeter

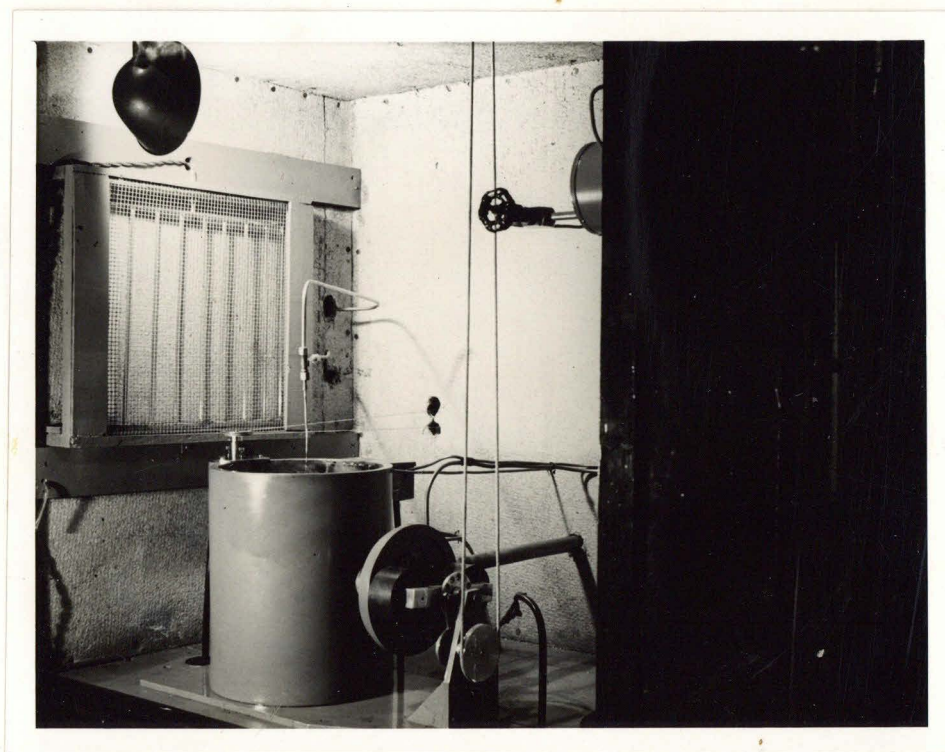


Figure 2. Bomb Calorimeter

this occurred because its elasticity under increased temperature and pressure is small compared to that of steel.

The heat capacity of each of the bombs was determined by filling it with hydrogen at a pressure near atmospheric, and measuring current input and temperature rise in the usual way. For most of the materials studied, this was about 40 percent of the total heat capacity. The bomb-well thermocouple was calibrated by recording the observed voltage and the temperature of the oil bath when the control galvanometer indicated no difference between bomb and bath. This temperature was obtained on a calibrated mercury-in-glass thermometer on which all readings are believed accurate to  $0.02^{\circ}\text{F}$ . The quotient of temperature by potentiometer scale reading was plotted against the scale reading itself, and a smooth calibration curve was drawn which established an accuracy of the temperature differences observed of within  $0.005^{\circ}\text{F}$ . From voltage readings which indicated the voltage and current of the bomb heater circuit, the electrical heat was calculated. These were taken at frequent intervals during each run, and any variations were integrated against the time.

To quote again from Sage and Lacey, "In making a determination with the calorimeter, a sample was placed in the bomb, the weight of materials added being ascertained by weighing the bomb." The apparatus was assembled, and the jacket space was evacuated. Before each run the temperature of the sample was determined, "readings being repeated at 5-minute intervals until found constant. Current was passed through the heater element inside the bomb for about 20 minutes, (measured to within about 0.3 second). About 6 to 8 minutes after stopping the current, temperature readings were again taken until a constant value was obtained". The amounts of heat energy added as a result of agitation, or transferred because of heat leakage to or from the jacket, were found to be entirely negligible.



Five normal hydrocarbons and nine binary mixtures were measured thermally by the author. Previous work had been done on ethane, propane and butane by Backus and by J. E. Sherborne<sup>1</sup>, but uncertainty in their values was reduced by the new measurements and by correlation of the data for the pure compounds.

Data for ethane, obtained with the new bomb, are shown in Figure 3. The experimental values do not agree as accurately as our other calorimetric measurements because of the large specific volume of the material over the temperature range investigated, the less rapid attainment of equilibrium by the gas, and the smaller temperature increment required because of the more rapid change in value. For the specific volume shown, the heat capacity of the bomb amounted to 50 to 70 percent of the total. Confirmatory runs were made upon ethane for three other volumes. These data were not used directly and are not shown in the figure, but they were of value in locating and shaping the curve of Figure 3. The specific volume of 0.0764 cubic feet per pound was used in this curve because it approaches the value for the critical state<sup>2</sup>. In the critical region,  $C_p$  is of little use because it is very large. The isochoric specific heat which has been measured was used directly in calculating the thermodynamic properties of ethane. The discontinuity shown on the plot was calculated by means of the expression:

$$C'_{v_D} - C''_{v_D} = T \left( \frac{\partial p}{\partial T} \right)''_{v_D} \left( \frac{dv}{dT} \right)_D - T \left( \frac{\partial p}{\partial T} \right)'_{v_D} \left( \frac{dv}{dT} \right)_D$$

<sup>1</sup> Other measurements have been made with this calorimeter by W.R. Mendenhall upon isobutane and of three additional binary mixtures; by Backus on mixtures of crystal oil with propane and butane, and on several crude oils; and by J. A. Davies (M.S. Thesis in Chemical Engineering, C.I.T., 1936) upon ethane-crystal oil mixtures.

<sup>2</sup> The critical constants of ethane have been determined by this laboratory to be 718.1 pounds per square inch and 0.07553 cubic feet per pound at 90.6°F.

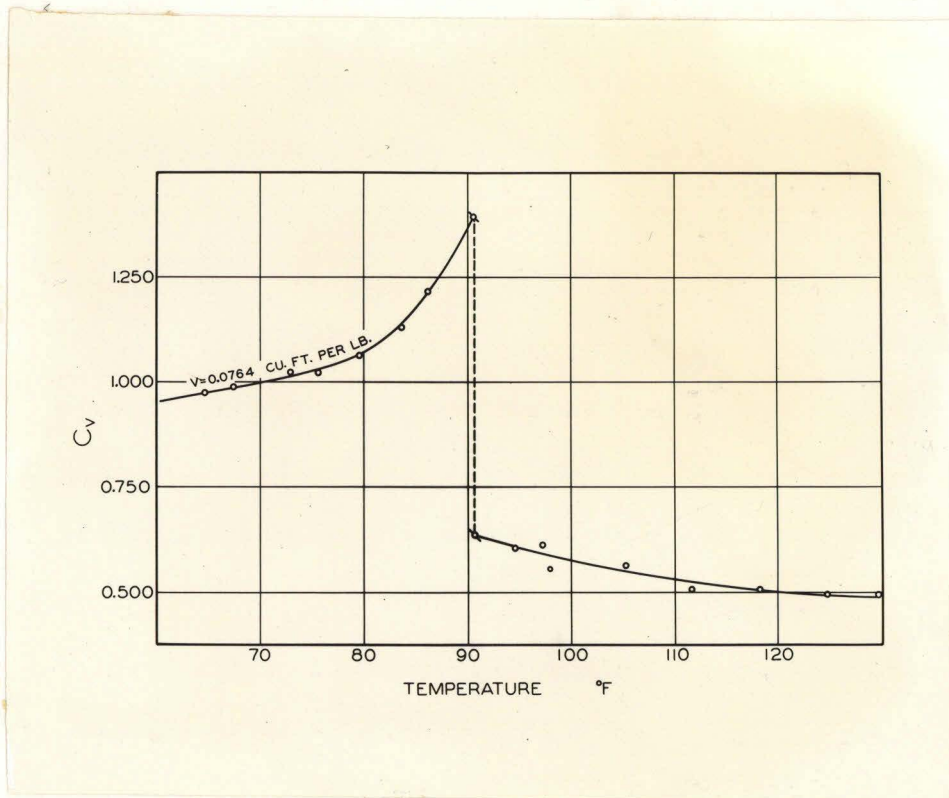
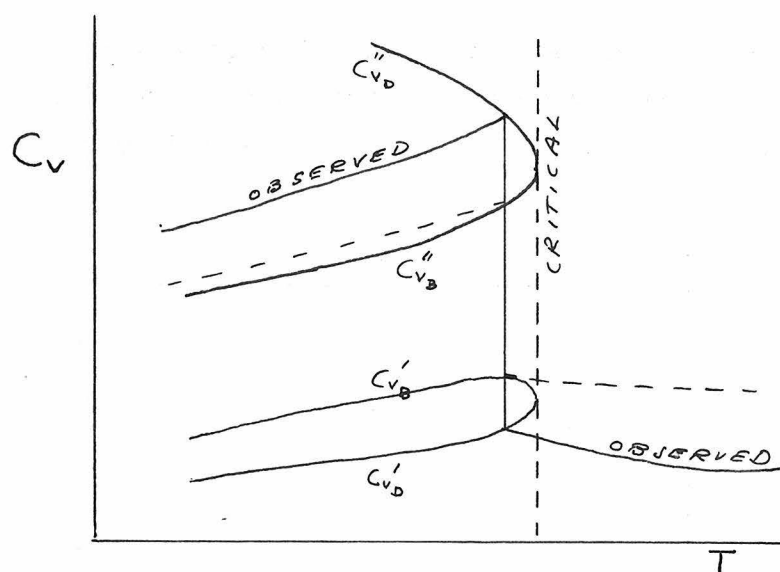


Figure 3. Specific Heat of Ethane in the Critical Region at a Constant Volume near the Critical Volume.

The temperature was located by reference to the P-V-T data, and was found to be 90.5°F. At this point the liquid phase disappears completely, and the specific volume is equal to the specific volume tabulated for the saturated gas. Because essentially the vaporization process has been completed, it is expected that the single-phase specific heat will be smaller than that for the two phases. This is substantiated by the equation above<sup>1</sup>. The experimental values dropped rapidly in this region and confirmed the temperature and discontinuity calculated. It should be noted that a break in the curve might also occur at the same temperature for another value of specific volume at which point saturated liquid would completely fill the bomb after having expanded to take up the volume previously occupied by gas. These relations may be indicated graphically:



Curves for the isobaric specific heats of propane, n-butane, and n-pentane have been published by Sage and Lacey, and in the foregoing reprint. If the experimental data alone are used as a basis, the shape assigned to the curves is somewhat arbitrary. A plot of the nature of Figure 5, correlating values for the homologs of the paraffin series, indicates the true curvature rather closely. The curves shown in Figure 4 were plotted on the basis of this correlation and fit the experimental

<sup>1</sup> The pressure derivative along saturation is greater than that at constant volume for the superheated gas. The thermal expansion for the saturated vapor is negative.



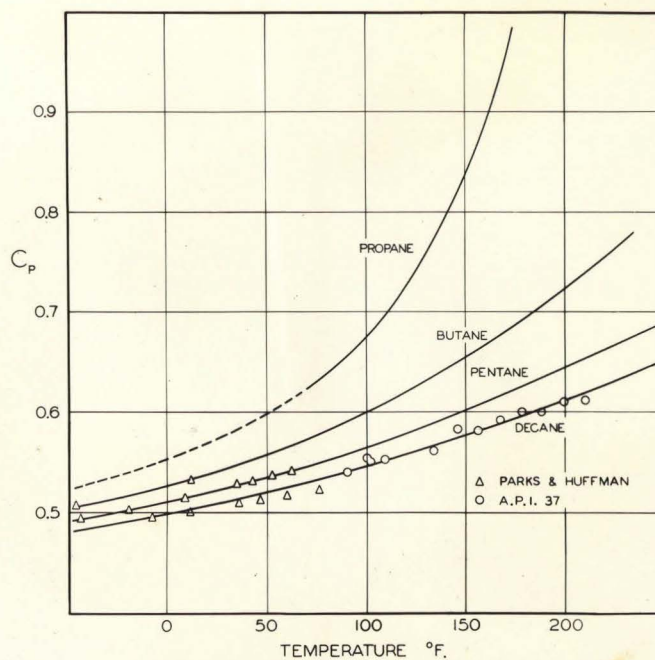


Figure 4. Isobaric Specific Heat for Condensed Liquid adjacent to Bubble Point. Dotted curve for Propane shows values predicted from Figure 5. Values are for straight-chain hydrocarbons.

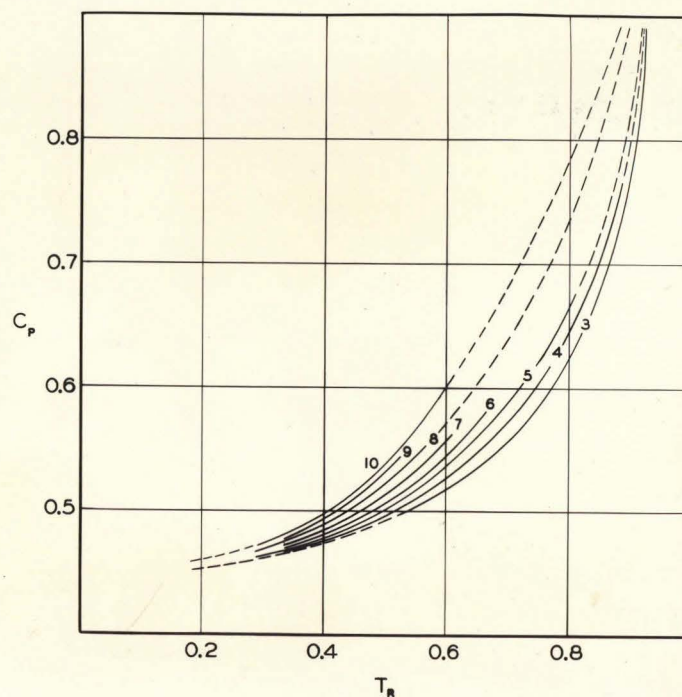


Figure 5. Isobaric Specific Heat for Condensed Liquid for Normal Alkanes of from 3 to 10 Carbon atoms.

points well. The smoothed values tabulated in section IIc likewise show this curvature.

Low-temperature specific heat determinations have been made on propane and butane by Dana and co-workers<sup>1</sup>, and on all the normal alkanes of four to twelve carbon atoms by Parks, Huffman and co-workers<sup>2</sup>. The agreement between Dana's values and ours is shown in Figure 8 of the paper by Sage and Lacey. The data of Parks and Huffman are plotted in Figure 4 of this thesis, showing excellent agreement for butane and pentane. The deviation for values of decane is about equal to the sum of the experimental uncertainties (2 percent), indicating that the true values probably fall between the two sets of data. This fact has influenced the location of the curves for decane.

Data for the mixtures of propane with butane and with pentane are published in the reprint. For three mixtures of butane and pentane and two mixtures of pentane and decane, the experimental values did not indicate that the solutions were ideal. The agreement with theory in the case of mixtures of propane with pentane and with crystal oil indicates that the deviation in the other mixtures investigated is probably due to experimental inaccuracy.

### c. Correlation of the Data

Each member of the homologous series of normal aliphatic hydrocarbons differs from the next in its physical properties by an increment which is some progressive function of the size of the molecule. The properties of a mixture of two widely separated components always fit into the series fairly near the point represented by the "molar" weight of the mixture. The isobaric specific heat of the bubble-point liquid shows this characteristic gradation, both when plotted against temperature (Figure 4) and when

<sup>1</sup> Dana, Jenkins, Burdick and Timm, Ref. Eng., 12, 387 (1926).

<sup>2</sup> (For heptane) Parks, Huffman and Thomas, J.A.C.S., 52, 1032 (1930); for pentane) Parks and Huffman, J.A.C.S., 52, 4381 (1930); (for all others) Huffman, Parks and Barmore, J.A.C.S., 53, 3876 (1931).

shown on a reduced temperature<sup>1</sup> plot (Figure 5). Ideal solutions may be assumed without loss of accuracy as compared to the experimental specific heat data available.

Correlations of data consist of generalizations which allow the prediction of behavior from a minimum of information. In the preceding section, there was mentioned the use of Figure 5 in approximating the true curvature for the plots of Figure 4. This section will describe two bases for prediction of specific heat values, by means of the Theory of Corresponding States and by use of an empirical equation derived by the author to fit the curves drawn through the experimental data obtained.

In its most literal interpretation, the Theory of Corresponding States establishes the reduced temperature and pressure scales as coordinates upon which the specific or molal values of a certain property for all members of a homologous series may be shown by a single line. Reference to Figure 5 shows that strict application of the theory is inadmissible. At the same time predictions can be made of the isobaric specific<sup>heat</sup> throughout the range of composition and temperature shown, to an accuracy of within 3 percent, by extrapolation of the experimental values on the basis of this theory. The solid lines have been fitted to the actual data; the broken lines are extrapolated.

Ordinarily, the theory applies best in the critical region. For these curves the accuracy of extrapolation is not improved because  $C_p$  becomes infinite at the critical point. This is shown thermodynamically by reference to the First Law expression:

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p = \left( \frac{\partial E}{\partial T} \right)_p + P \left( \frac{\partial v}{\partial T} \right)_p$$

---

<sup>1</sup> The reduced temperature is obtained by dividing the absolute temperature by the absolute value of the critical temperature. The values of the critical temperature for the series through octane were taken from the International Critical Tables (3, 248). For nonane and decane, the temperatures were estimated from charts by Warren K. Lewis to be respectively, 597°K. (616°F.) and 625°K. (665°F.).

The critical point is the upper limit of the two-phase region, throughout which the thermal expansion is infinite. The critical isobar on the temperature-volume plane thus becomes tangent to the dome.

Previous to the initiation of this research project, little experimental work had been done on the range of materials and at the temperatures shown in Figure 4. Empirical equations<sup>1</sup> for heavier oils do not apply by better than 10 percent to this region.

An equation for the range from 3 to 10 carbon atoms and from 60°F. to 160°F. has been derived empirically. It includes linear and quadratic terms in  $t$  to account for the curvatures, and a power function of the molecular weight to explain the separation of the curves. While the function used is arbitrary<sup>2</sup>, it is improbable that this number of parameters can be used in a more satisfactory form than that obtained. The expression takes the following form:

$$C'_{p_s} = 0.490 + 0.0006t + M^{-4} (380,000 + 66(t-60)^2)$$

$M$  is the molecular weight of the compound or mixture. The average deviation<sup>3</sup> from smoothed experimental curves is 1 percent, the maximum deviation about twice that amount. This equation may be extrapolated back linearly from 60°F. to 0°F. with about the same accuracy, the quadratic term being omitted.

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<sup>1</sup> Bureau of Standards, Misc. Publ., 97, 26 (1929). Also Fortsch and Whitman, Ind. Eng. Chem., 18, 795 (1926).

These expressions cover a wide range of materials, both paraffins and naphthalenes, with an average deviation of 2 percent over the temperature range from 50°F. to 430°F. Specific heat is given as a linear function of the temperature, and the composition variable used is the specific gravity at 60°F.

<sup>2</sup> It is entirely possible that future developments in the structural theories of matter will lead to the derivation of such correlative equations, leaving only the coefficients to be determined experimentally.

<sup>3</sup> The calculated points are compared with the most reliable values in the table on page 17.

## ISOBARIC SPECIFIC HEATS OF NORMAL ALIPHATIC HYDROCARBONS

For Condensed Liquid Adjacent to Bubble Point

Smoothed experimental data are shown.

Parenthetical values are calculated from the equation:

$$C_{PB} = 0.490 + 0.0006t + M^{-4} (380,000 + 66 (t-60)^2)$$

PURE COMPOUNDS						
	70°	100°	130°	160°	190° <sup>a</sup>	220° <sup>a</sup>
Propane	.624 (.635)	.674 (.680)	.750 (.757)	.888 (.867)		
Butane	.572 (.567)	.600 (.593)	.632 (.630)	.668 (.678)	.709 (.736)	.756 (.804)
Pentane	.546 (.546)	.565 (.568)	.587 (.594)	.610 (.624)	.636 (.659)	.660 (.697)
Decane	.530 (.533)	.546 (.551)	.564 (.569)	.583 (.587)	.604 (.605)	.627 (.623)
SOLUTIONS						
Propane-Butane						
47.1% C <sub>3</sub> H <sub>8</sub> (by weight)	.598 (.591)	.640 (.624)	.682 (.676)	.734 (.745)	.809 (.833)	.906 (.939)
Propane-Pentane						
24.2% C <sub>3</sub> H <sub>8</sub>	.565 (.557)	.592 (.582)	.620 (.614)	.654 (.654)	.702 (.702)	
48.4%	.583 (.574)	.616 (.602)	.653 (.644)	.702 (.698)	.778 (.765)	
79.1%	.609 (.605)	.654 (.642)	.705 (.701)	.792 (.783)	.961 (.887) <sup>b</sup>	

<sup>a</sup> The empirical equation of fit was derived only for temperatures of 160°F. and below.

<sup>b</sup> The difference between the experimental and calculated values for this point is due mainly to deviation from ideal solution. Refer to Figure 7 in the reprint.

The exponent of the molecular weight was found more accurately to be  $3.50 + 0.0002 (t - 85)^2$ . This was rejected as too unwieldy for such a correlation as is desired. Use of this exponent would require recalculation of the coefficients of  $\underline{M}$  and the quadratic in  $\underline{t}$ .

Specific heat data for the more volatile liquids in the series of normal aliphatic hydrocarbons are now known with reasonable accuracy throughout a wide temperature range. Further experimental work in this field may be most advantageously directed toward the development of more accurate experimental methods.

### III. HEAT OF VAPORIZATION OF ISOBUTANE

#### a. Theoretical Considerations

Accurate pressure-volume-temperature data are the most usual source of values of the latent heat of vaporization. These may be calculated by an application of the Second Law of Thermodynamics to give the relation known as the Clapeyron equation:

$$L_v = T \left( \frac{dp}{dT} \right)_B (v_D - v_B)$$

Calorimetric measurement of the heat of vaporization provides a serviceable check upon the physical data. Frequently the volume of the saturated vapor can not be accurately obtained from the measurements in a compression tube because of adsorption effects and the difficulty of attaining complete equilibrium. In such cases an independent determination of the heat of vaporization is of use in calculating the enthalpy, entropy and specific volume for the dew-point gas.

In the limiting case of very small vapor pressures, the dew-point volume approaches infinity. The volume of the bubble-point liquid is then negligible. Perfect gas laws may be assumed, with the introduction of the specific gas constant  $b$ . Thus, in the limiting case,

$$L_v \approx T \left( \frac{dp}{dT} \right)_B v_D = \frac{bT^2}{p_B} \frac{dp_0}{dT} = -b \frac{d \ln p_B}{d \left( \frac{1}{T} \right)}$$

Experimentally the slope of the logarithm of vapor pressure against reciprocal absolute temperature has been found to be nearly constant under these conditions. Thus  $L_v$  will approach asymptotically to a limiting maximum value as the temperature is decreased. As the temperature increases, the latent heat becomes appreciably smaller because of the contribution of the liquid volume, and the deviations of the vapor from a perfect gas.

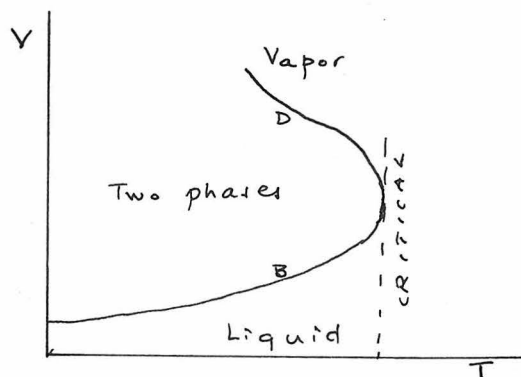


At the critical point the phase boundary has disappeared, the specific volumes of gas and liquid are identical, and the heat of vaporization must vanish. The slope of the latent heat plot near the critical temperature may be evaluated in terms of the physical properties and is found to have very large negative values:

$$L_v = H_D - H_B = E_D - E_B + p(v_D - v_B)$$

$$\frac{\partial L_v}{\partial T} = (c_{v_D}' - c_{v_B}') + \frac{dp}{dT}(v_D - v_B) + p\left(\frac{\partial v_D}{\partial T} - \frac{\partial v_B}{\partial T}\right)$$

Of these three difference terms, the first two vanish at the critical point. The thermal expansion of the dew-point vapor becomes negatively infinite, while that of the bubble-point liquid goes to infinity in the positive direction. These are the slopes along the saturation curve on the volume-



temperature plane. This knowledge of the behavior of the heat of vaporization at low temperatures and in the critical region is of use in fitting a curve to the experimental data.

Essentially, the experimental determination of latent heats of vaporization consists in maintaining isothermal conditions, adding a measured amount of electrical energy, and weighing the quantity of material which has vaporized. If the hydrocarbon under investigation is held in a constant volume, not all of the material vaporized is removed from the boundary of the system. A volume just equal to that of the liquid which has evaporated is now filled with an additional quantity of gas. The experimental values



must therefore be corrected as shown in the equation:

$$L_v = \frac{Q}{\Delta M \left( \frac{v_D}{v_D - v_B} \right)} = \frac{Q}{\Delta M} \left( \frac{1}{1 + \frac{v_B}{v_D - v_B}} \right)$$

An additional correction must be applied to the quantity of heat measured if the temperatures at the beginning and end of the run are not identical. From the observed input, the product of the temperature rise by the average heat capacity of bomb and contents must be subtracted.

The best recent experimental determinations of latent heats of vaporization have been made at the Bureau of Standards<sup>1</sup> and the Linde laboratories.<sup>2</sup> The latter investigation was made at temperatures between 0°F. and 50°F. and included the two butanes, on which measurements have been made in this investigation. The values of Dana and co-workers have been of assistance in shaping our curves, and will be shown along with our points on the plots of the next section.

#### b. Experimental Methods

The calorimeter described in part II, used for specific heat measurements, was converted into an instrument suitable for the measurement of heats of vaporization. The extent of the auxiliary equipment installed may be seen by comparing Figure 6 with Figure 1. A vapor line was sealed into the bomb, brought out through the wall of the vacuum jacket and through a motor-operated valve to a manifold which could be opened to a receiving bomb thermostated by an oil bath. One arm from the line between the bomb and the valve led to a mercury trap, which was connected by an oil line to the laboratory's pressure balances<sup>3</sup>.

<sup>1</sup> Osborne and Van Dusen, Bur. Stan. Bull., 14, 439 (Sci. Paper No. 315) (1918).

<sup>2</sup> Dana, Jenkins, Burdick and Timm, Ref. Eng., 12, 387 (1926).

<sup>3</sup> Pressure readings could have been taken to supplement the temperature readings. Actually they were made only when testing the assembly for leaks by filling with air at pressures around 400 pounds per square inch. Pressure measurements will be more necessary in case this calorimeter is adapted for investigation of heats of solution.

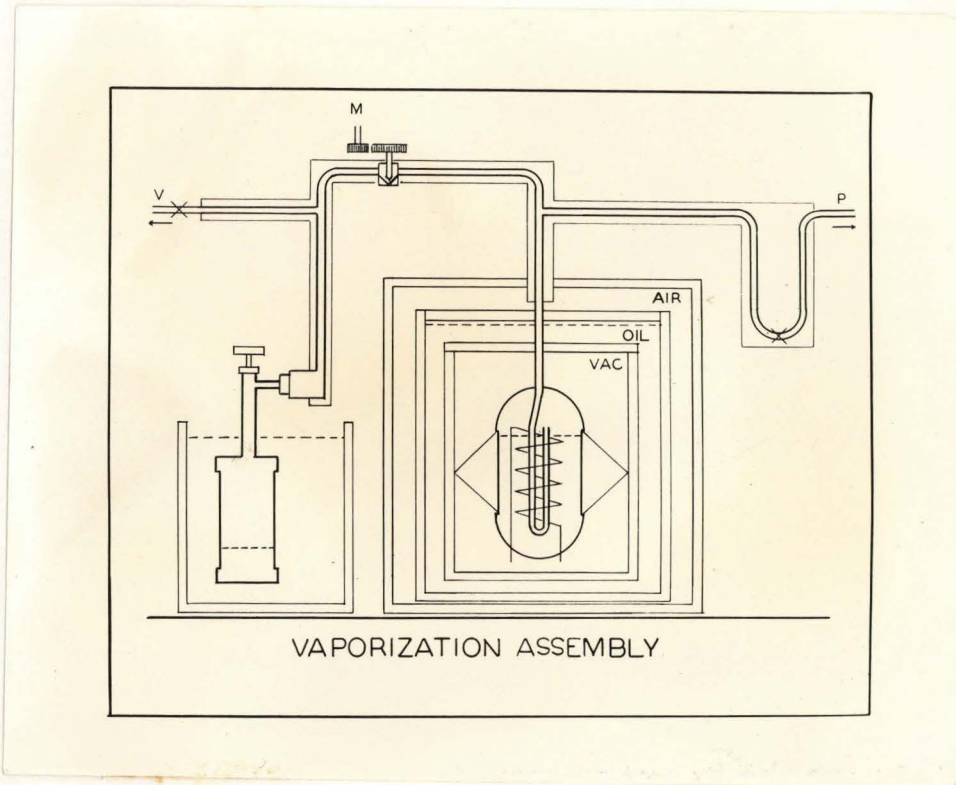


Figure 6.

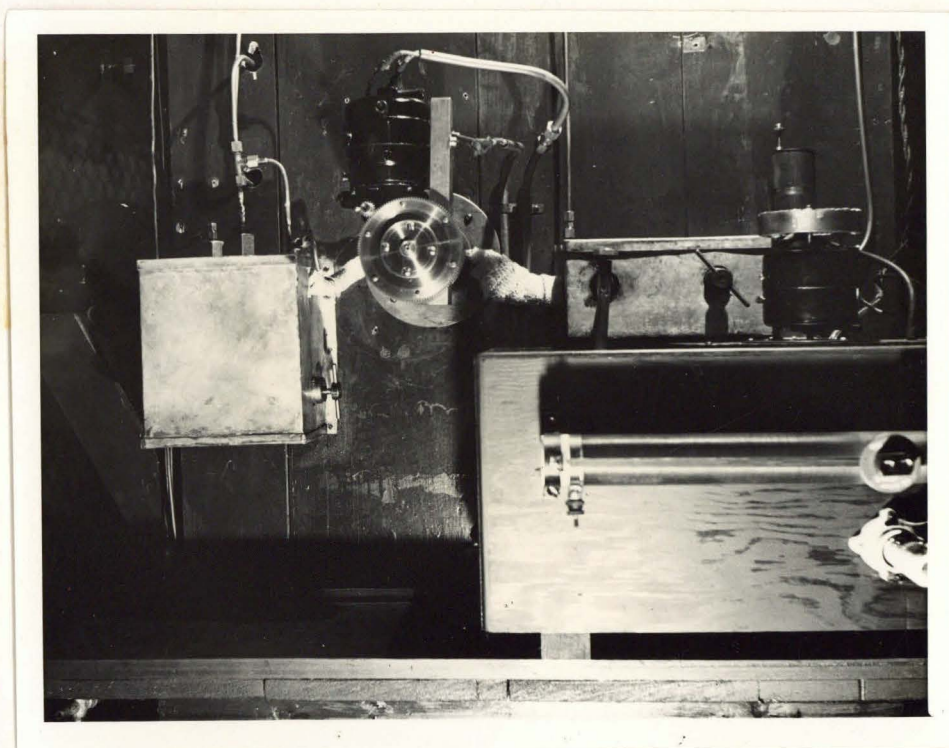


Figure 7. Condensation Assembly.

The steam-jacketed vapor line comes down at the left to the pressure trap. Steam outlet lines are also shown. A lagged vapor line goes to the right, leading through the throttling valve, which is also jacketed. The valve is operated by the direct-current motor, the spur gears, and a friction clutch. A long-necked weighing bomb is attached by a standard fitting, its temperature being controlled by the thermostated condenser bath. The valve opening to vacuum is shown between the receiving bomb and the agitator motor for the bath. Behind the motor is the mercury agitator, enclosed in a brass jacket.

The bomb installed was the one previously used for low-pressure specific heat measurements. The diaphragm valve was removed from the top of the bomb. A 1/16 inch tube of stainless steel was doubled, the two arms were soldered together, and the tube was sealed into a fitting which was threaded into the top of the bomb. The tube was soldered onto the end of a 1/8 inch copper tube, around which was fitted a 1/4 inch copper tube; saturated steam at about 280°F. was introduced into the outer line to prevent condensation of the vapor. The trap, the motor-operated valve and connecting lines on the outside wall were also heated with steam, as is indicated by diagrammatic jacketing in Figure 6.

Control of the rate of flow was needed to maintain isothermal conditions within the bomb, electric heat being added at a constant measured rate. The temperature of the bomb and the differential temperature between the bomb surface and the oil bath were shown by light beams reflected from high-sensitivity galvanometers onto ground-glass millimeter scales. Vapor flow was regulated by variation of the opening of the throttling valve, by means of a two-way switch installed on the potentiometer bench in front of these scales. The pressure differential had to be adjusted carefully, and was established by manual adjustment of a mercury regulator which thermostated the oil bath condenser surrounding the receiving bomb. The difference in temperature between the calorimeter jacket and the condenser bath was measured by a thermocouple and was indicated by an additional galvanometer beam on the control bench.

The throttling valve was operated by a 100-volt direct current motor rated at about 40 watts. The direction of the motor (and of the current) was governed by means of two relays actuated by two separate 110-volt alternating current circuits either of which could be closed by the switch on the control bench. The motor was connected by the spur gears shown in Figure 7 to a friction clutch on the valve stem.



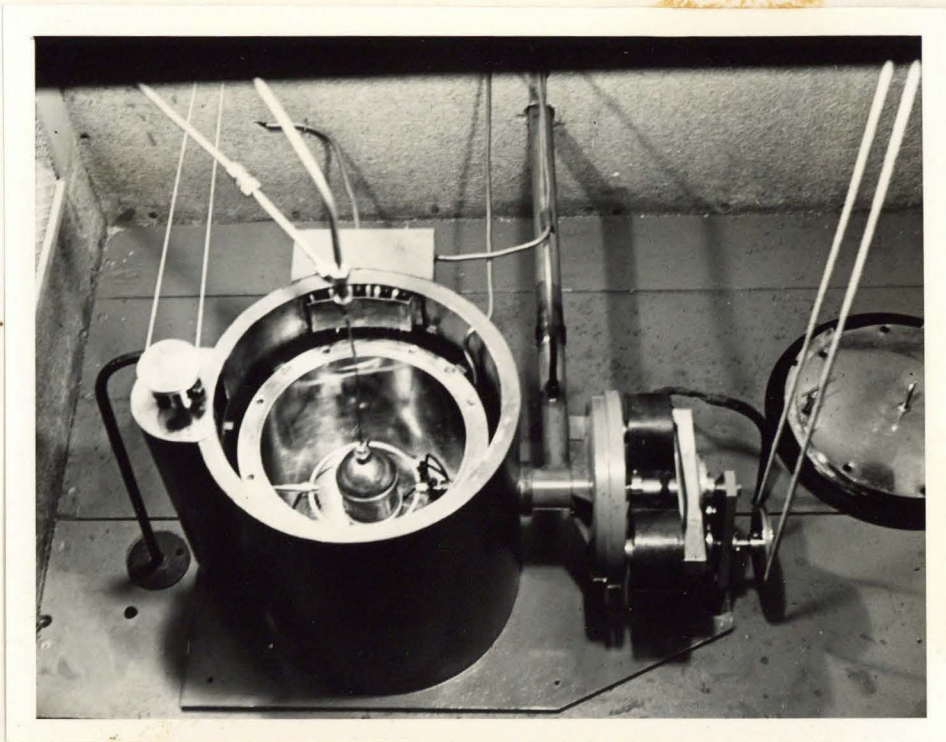


Figure 8. Calorimeter, showing bomb and steam-jacketed vapor line.

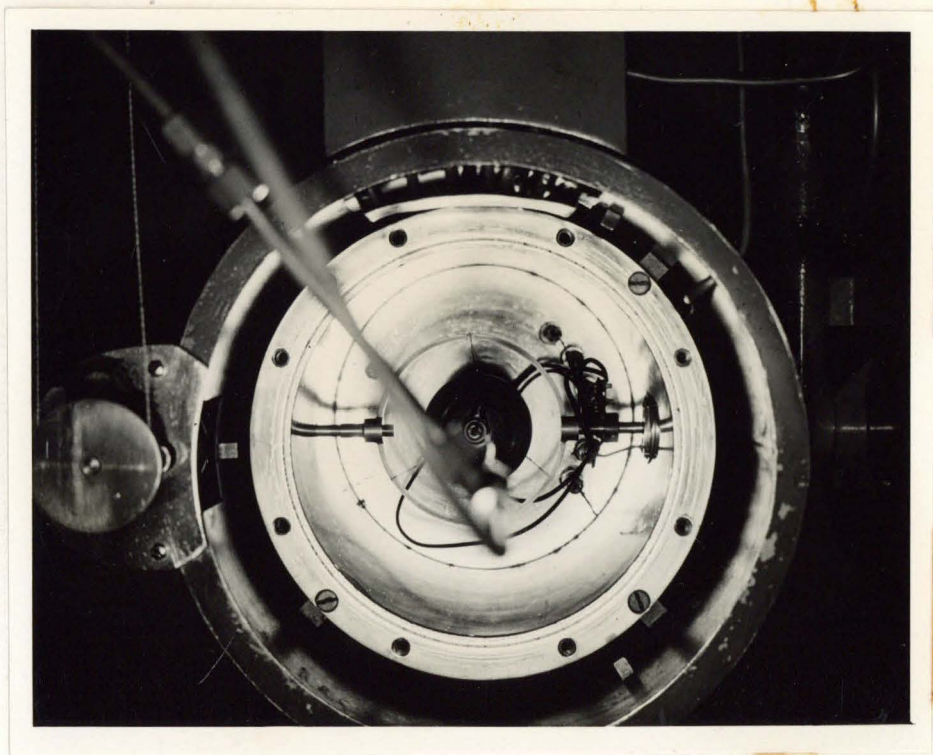


Figure 9. Interior of the Calorimeter. Leads to heater and thermocouples are shown.

The outlet tube from the bomb led from the vapor space through the liquid in order to avoid entrainment of liquid and superheating of the vapor before leaving the bomb. Liquid which might have been condensed in the bend of this tube was removed by making a short run to vacuum before each vaporization measurement. The amount of superheating was found to be negligible on a trial run in which the bomb thermocouple was removed from the well and was mounted on the outlet tube just above the bomb; fluctuations in its temperature were compared with those of the bomb surface relative to that of the jacket<sup>1</sup> and were found to vary not more than 0.01°F. from the bomb temperature. The variation in the bomb temperature was therefore recorded for each run as a measure of the superheating. Maximum deviation during accepted runs was less than 0.1°F., and integrated averages were around 0.03°F., a difference too small to require correction of the heat content of the vapor.

Leaks through soldered joints and valve packing presented a major difficulty in putting the apparatus into operation. These could be detected by a continued drop in the observed bomb temperature of the order of 0.01°F. per minute. Since on experimental runs heat was added for 20 to 30 minutes, it was impossible to compensate or correct accurately for any loss of material. Finally all leaks were found and sealed.

### c. Data Obtained

After numerous experimental difficulties had been overcome and the apparatus was in the form described above, four runs were made upon normal butane. The agreement with the values obtained by calculation from physical data is evident from Figure 10. Points obtained by Dana and co-workers are also shown. Because of the good agreement, and because the remaining data for n-butane were ready for publication, no additional work was done on this compound.

Twenty measurements were then made on isobutane, thirteen of these

<sup>1</sup> The oil bath surrounding the jacket was maintained at constant temperature by means of a potentiometer circuit operated by a thermocouple between the

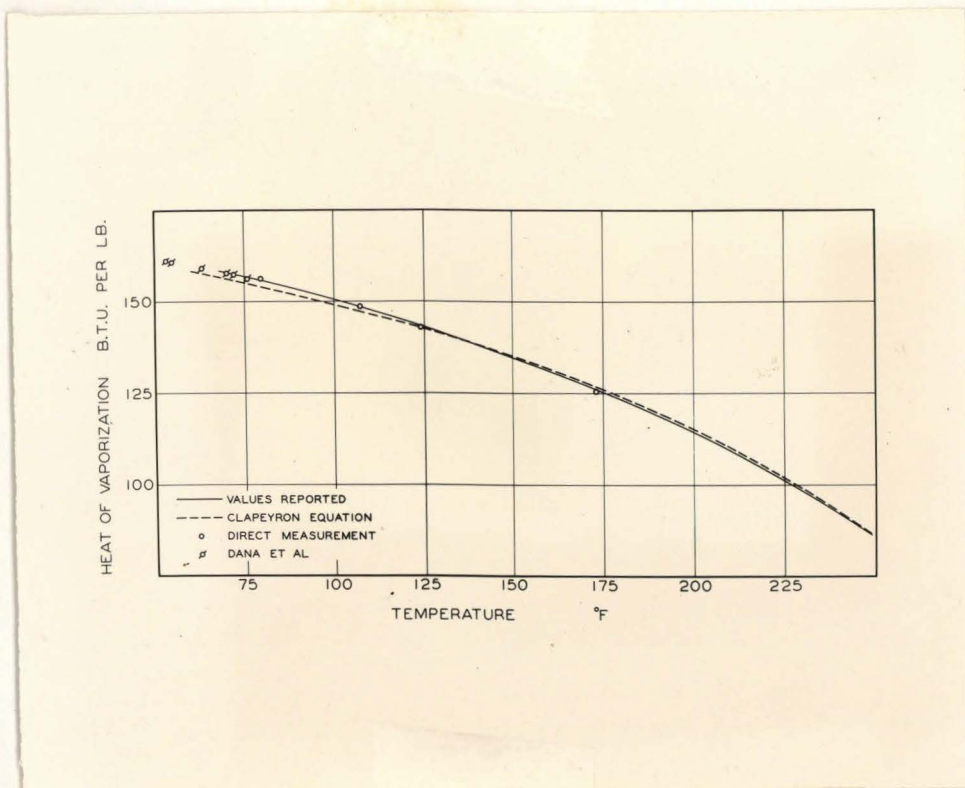


Figure 10. Latent Heat of Vaporization of Normal Butane.

points giving the agreement shown on the large-scale plot of Figure 12. The points rejected were in most cases known from observed experimental conditions not to be trustworthy. The shape of the curve plotted was obtained by reference to the critical behavior and to Dana's points, as shown in Figure 11. Relative accuracy of the plotted curve is within 0.3 percent, and the probable absolute deviation is not greatly in excess of this amount.

In the case of isobutane, the latent heat measurements were much more reliable than the values calculated from the physical data, and indicated errors of several percent in the latter.

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<sup>1</sup> (p.26)

oil and an ice bath, actuating the photo-electric circuit for control of the heat added to the oil bath. Small fluctuations in the bomb temperature made the differential temperature unsuitable for control.



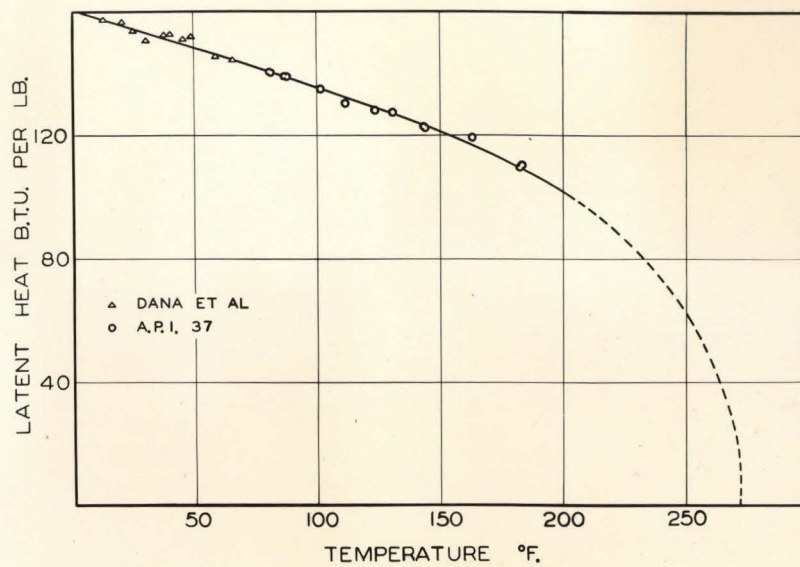


Figure 11. Latent Heat of Vaporization of Isobutane.

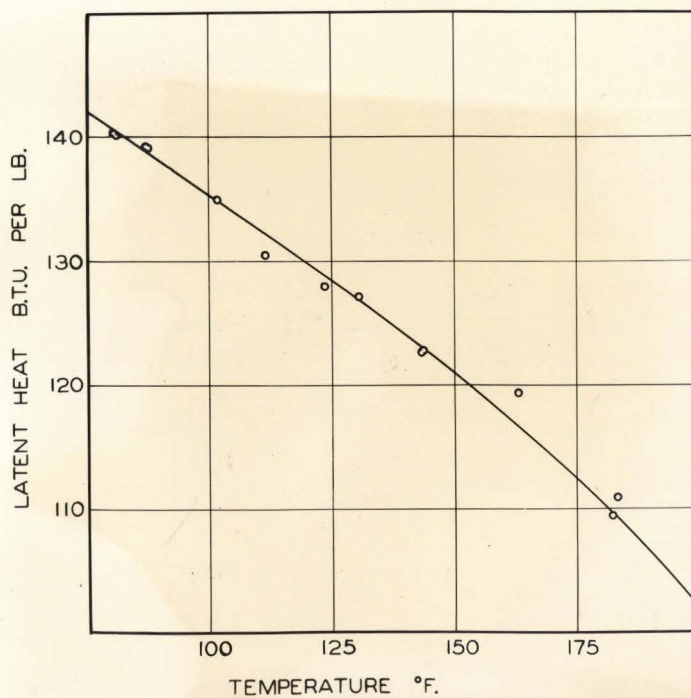


Figure 12. Latent Heat of Vaporization of Isobutane.

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