

CALORIMETRIC MEASUREMENT OF LATENT HEATS OF VAPORIZATION  
OF PROPANE AND NORMAL PENTANE AND SOME THERMODYNAMIC PROPERTIES  
OF NORMAL PENTANE

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ABSTRACT

Measurements of the latent heat of vaporization of propane and normal pentane were made with an adiabatic bomb calorimeter. The temperature, <sup>range</sup> for propane was from 103.4° F. to 163.2° F. Normal pentane measurements were from 103.7 to 200° Fahrenheit. A description of the apparatus and the method of calculation will be found in Part 1 of this paper.

In the second section of this paper some of the thermodynamic properties of n-pentane in the superheated gas region were calculated. Included in this section are tabulated values of entropy, enthalpy, residual volume, and heat capacity.

## I. LATENT HEATS OF VAPORIZATION

Latent heat of vaporization may be defined as the energy required to convert a unit mass of material from saturated liquid to saturated gas at the same pressure and temperature.

The use of latent heats of vaporization is widespread in industries in which materials are distilled or condensed. The accurate determination of latent heats of hydrocarbons is particularly important in the petroleum industry. Here the heat required for fractionating columns and the design of condenser equipment are based on latent heats.

There are three methods commonly used in the evaluation of latent heats. If the P. V. T. relations of a certain material are known, the latent heat may be calculated from an application of the First and Second Laws of Thermodynamics known as the Clapeyron equation.

$$L = T \left( \frac{dP}{dT} \right) (V_d - V_b) * \quad (1)$$

This method is particularly accurate for vapor pressure greater than 100 pounds per sq. in. Above this pressure reliable vapor pressures may be obtained whereas, at lower pressures, adsorption on the walls of the pressure measuring device often cause errors in the experimental measurements. It is to be expected, then, that at the lower

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\*A definition of symbols will be found at the end of this thesis.

temperatures the latent heat values determined from the Claperon equation will usually be somewhat lower than the actual latent heats.

A second method of relating latent heat of vaporization to temperature involves the heat capacities of saturated gas and liquid, the change in pressure with temperature in the two phase region, and  $\left(\frac{dH}{dP}\right)_T$  for both saturated gas and liquid.

$$L = L_0 + \int_{T_0}^T [C_{P,d} - C_{P,b} + \left\{ \left(\frac{dH}{dP}\right)_{T,d} - \left(\frac{dH}{dP}\right)_{T,b} \right\} \left(\frac{dP}{dT}\right)_b] dT \quad (2)$$

If the latent heat of vaporization is known at one temperature it may be calculated for any other temperature by means of this equation. Results are more accurate in the lower temperature range when this method is used because, at lower temperatures, heat capacities vary less with temperature, and lower  $\left(\frac{dP}{dT}\right)$  values make the other terms of the equation less important. At higher temperatures all quantities involved change more rapidly with temperature, and the possibility of error will be greater. Since  $\left(\frac{dH}{dP}\right)_T$  is derived from heat capacity, an error in heat capacity may introduce an accumulative error into the evaluation. Therefore, the accuracy of latent heat values determined by this method will be limited by the accuracy of the heat capacity data.

Latent heats may also be determined experimentally. Basically, the method consists of the addition of a known amount of energy to a liquid in a suitable container and of the measurement of the amount of liquid vaporized at constant pressure and temperature. By considering the various energy

losses from the system the latent heat of vaporization can be evaluated from the following general equation:

$$L = \frac{(Q + Q' + Q'' + Q''')}{W' \left( \frac{V_d}{V_d - V_b} \right)} \quad (3)$$

$Q$  is the known amount of energy added to the system.

$Q'$ ,  $Q''$  and  $Q'''$  are respectively, the thermal leakage loss, the superheat correction, and the heat capacity correction.

$W' \left( \frac{V_d}{V_d - V_b} \right)$  is the mass of material vaporized. All of these terms will be discussed further in part (e) of this section.

Latent heats determined experimentally may be expected to be less accurate at higher temperatures because the volume correction becomes increasingly important as the critical temperature is approached.

The best previous work on latent heat of vaporization has been done by the Linde Laboratory (1)\* and the Bureau of Standards (2).

#### (a) Theoretical considerations

As a means of extrapolating latent heat curves beyond the temperature range covered by the experimental points it is well to understand the behavior commonly expected throughout the desired range. This behavior can be predicted to a certain extent by a consideration of the Clapeyron equation. At low temperatures the volume of the saturated gas will be very large in comparison to the volume of the saturated liquid, and the latter may be neglected with slight error. Also, at low temperatures it may be expected that the gas will closely approximate perfect gas behavior. Thus, from

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\* References to literature cited will be found on page 33.

the Clapeyron equation results the following:

$$L = T \left( \frac{dP}{dT} \right)_s V_d = \frac{bT^2}{dT} \frac{dP}{P} = -b \frac{d \ln P}{d \left( \frac{1}{T} \right)} \quad (4)$$

The slope of the logarithm of vapor pressure against reciprocal temperature has been found experimentally to be approximately constant under these conditions. Therefore L will approach asymptotically to a limiting maximum value.

When the gas approaches the critical temperature, the difference between the volumes of the saturated gas and the saturated liquid grows rapidly smaller and at the critical temperature it is zero. At the critical temperature L is also zero.

#### (b) Materials

The sample of n-Pentane used in determining latent heats of vaporization was obtained from the Phillips Petroleum Company. Their special analysis showed it to contain 99.3% of n-pentane and 0.7% of isopentane.

The propane used in this study was obtained from the Philgas Company, Bartlesville, Oklahoma. Their analysis showed it to be pure propane, containing neither ethane nor isobutane in appreciable amounts.

#### (c) Apparatus

The adiabatic bomb calorimeter used in carrying out the majority of the determinations of latent heats of vaporization was similar to that described by Vermeulen (3). Some changes were made, however, that are important enough to justify their description.

All thermocouples used were enclosed in copper tubing to prevent excessive wear and possible physical damage. The tubing

containing these thermocouples led to a central wiring box. Here the thermocouples were soldered to number 18 B.&S. gage copper wire. This larger wire was enclosed in conduit and carried by this means directly to a potentiometer switch board. Here, the two junctions of any thermocouple could be plugged into any of the three potentiometers installed on the board. The plugs were also arranged so that any potentiometer could be used in conjunction with any of the four galvanometers on the board. Any potentiometer could be connected to either of the other two, and this served as a valuable means of checking each instrument for accuracy of standard cell setting. The agitator described by Vermeulen was not used because early experiments showed that agitation was not needed to secure equilibrium in the bomb.

With the idea of investigating the heat of mixing of various hydrocarbons at a later date, a new bomb assembly was designed and installed after a portion of the latent heat measurements had been completed.

This new bomb was of a steel alloy with a yield point of 120,000 pounds per square inch. The outside overall height of the bomb was 6 inches and the center diameter was  $3\frac{3}{8}$  inches. It consisted of two hemispherical pieces threaded and sweated onto a cylindrical center section. The inside volume of the bomb was approximately 15.2 cubic inches, after allowing for space occupied by the heater. The heater consisted of insulated no. 36 B. & S. gage constantan wire within 0.06 inch steel tubing. The heater leads were brought out through two openings in the bottom of the bomb, and the steel tubing was

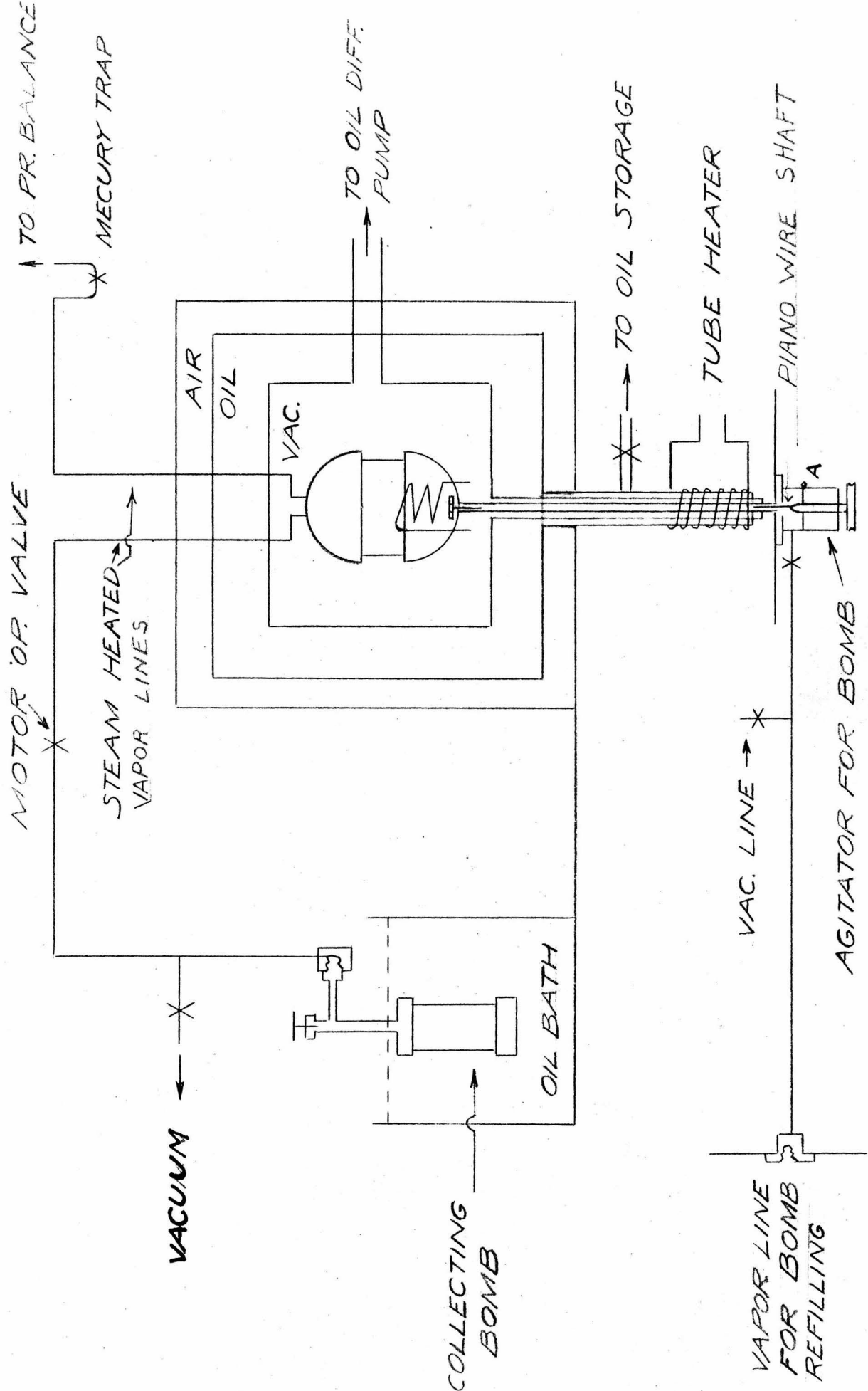


Figure 1. Calorimeter Assembly



soldered to the bomb at this point. The parts of the bomb were machined by the Fred C. Henson Company and heat treated by Dr. D. S. Clark of the California Institute.

A schematic diagram of the apparatus is shown by **Figure I**. Into the top of the bomb a threaded nut was sweated. This nut had two openings through which the vapors were led to a pressure balance and to the vapor intake by means of steam-heated  $\frac{1}{8}$  inch copper tubing. The agitator consisted of a small centrifugal impeller mounted on ball bearings in the bottom of the bomb. The shaft of this impeller was made of 0.020 inch piano-wire enclosed in 0.06 inch steel tubing, one end of which was soldered to the bomb. These two concentric pieces extended from the bottom of the bomb through the oil bath and through the floor of the air thermostat to a flat machined piece (A) mounted on a wooden support directly below the bomb. Here the 0.06 inch tubing was soldered, and the piano-wire extended through a packing gland to a drive pulley. Into the space in the machined piece between the sealed tubing and the packing gland an additional vapor line was sealed. This vapor line was used for filling the bomb with liquid, and it was so arranged that it could be evacuated before the liquid was admitted. The pulley connected to the piano-wire drive shaft was driven by a  $\frac{1}{8}$  horsepower motor, connected to the drive pulley by means of a belt and other pulleys which served to reduce the rotating speed of the agitator.

A third tube made of  $\frac{3}{8}$  inch brass surrounded the two tubes mentioned above. One end of this was sealed to the calorimeter

vacuum jacket and the other to the 0.06 inch steel tubing about three inches from the machined piece A (Figure I.). This tube was kept evacuated during operations and served to reduce heat loss from the inside tubes. To minimize still further the heat loss, the vacuum tube was surrounded by another tube of  $\frac{3}{4}$  inch brass. One end of this tube was soldered to the oil bath container, and the other was sealed off by soldering to the outside of the vacuum tube. There was an outlet from this tube leading to an oil-storage tank. This outer tube was wrapped with a thin layer of asbestos paper over which a heater was placed. The heater was covered with another layer of asbestos paper and, finally, with a layer of asbestos rope. During a determination this tube was kept at the same temperature as the main oil bath by means of the heater, a differential thermocouple indicating any temperature difference between the two. The heater was operated on 110 volt alternating current with suitable resistance in series, and the amount of energy added was controlled manually.

All other parts of the apparatus were very nearly as described by Vermeulen (I).

#### (d) Method of Operation

In making a determination of latent heat of vaporization a sample was placed in the bomb, and the space inside the jacket was evacuated. The bomb and the jacket were brought to the desired temperature. As soon as equilibrium between the bomb and the jacket had been reached, this equilibrium

was indicated by a zero reading on the differential thermocouple between the two, current was passed through the heater element inside the bomb for a period of from 10 to 20 minutes. During this period the vapor distilled off at constant temperature was collected in a tared collecting bomb immersed in an oil bath controlled by a mercury regulator. The temperature of the distilling vapor was controlled by regulating the amount flowing through a motor-operated valve in the vapor line and to a certain extent by adjustment of the temperature of the oil bath, in which the collecting bomb was immersed, so that the pressure drop from the main bomb to the collecting bomb was small.

At the end of the vaporization period the heater current was shut off, and the contents of the bomb were allowed to come to equilibrium. The equilibrium temperature of the bomb was recorded. In order to correct for heat loss, readings of the differential thermocouple between the bomb and the jacket were recorded every 30 seconds. This thermocouple was also used as a guide in the adjustment of the motor-operated valve. Temperatures of the bomb, of the vapor line, and of the oil bath surrounding the vacuum jacket were also recorded at intervals. At the termination of a run the collecting bomb was again weighed to determine the amount of liquid evaporated. If the final temperature of the bomb was not the same as the temperature at the beginning of the run, a heat capacity determination was made in order to permit correction for this. Usually the final temperature was within

0.04 ° F. of the initial temperature.

(e) Method of Calculation

To calculate the latent heat of vaporization an energy balance is required. The energy supplied to the bomb by the heater may be dissipated in several ways. The greatest proportion of this supplied energy is, of course, used for the actual vaporization of the liquid. Energy may also be carried out as superheat in the vapor; as heat loss to the jacket by conduction, radiation, and convection; or it may serve to make the final temperature of the bomb different than the initial temperature. These possibilities must be considered if precision results are expected.

Thermocouples in the bomb and on the vapor line just outside the bomb showed that if there was sufficient liquid in the bomb to cover the heating coil, no superheat was apparent. If the liquid did not cover the heater, the superheat was very marked and was indicated by a rapid rise in outlet vapor temperature and a fall in the temperature of the liquid in the bomb. This superheat occurred at infrequent intervals, and it was felt that, rather than correct for superheat with the possibility of error in the correction and in the determination of the average temperature of vaporization, more satisfactory results would be obtained if more liquid were added and the determinations were repeated. Therefore, for all measurements taken superheat was negligible.

Even slight changes in the temperature of the bomb relative to the vacuum jacket gave appreciable heat loss. To

calculate this heat loss a calibration curve was established by adding a known amount of energy to the bomb with the temperature of the vacuum jacket remaining constant. The rise in temperature of the bomb as measured by the differential thermocouple was recorded. As the bomb cooled the reading of this differential thermocouple was recorded against time. From this record of time vs. temperature difference the cooling curve shown as Figure 2 was plotted. It was found that the rate of cooling was approximately proportional to the temperature difference between the bomb and jacket.

$$\left(\frac{dM}{d\theta}\right) = KM \quad (5)$$

The constant, K, was found from the slope of the cooling curve to be 0.000299 seconds<sup>-1</sup>. Energy added to the bomb per microvolt change in potentiometer reading =  $\frac{E}{M'}$

- Q' = Heat loss per pound =  $\frac{EKMO}{M'W'}$  B. T. U. (6)
- M = Microvolt bomb-jacket differential reading
- M' = Rise in temp. of bomb upon addition of energy as measured in microvolts by the potentiometer
- E = Energy added to the bomb in B. T. U.
- W' = Pounds of liquid collected in the receiving bomb
- θ = Total time of a determination in seconds.

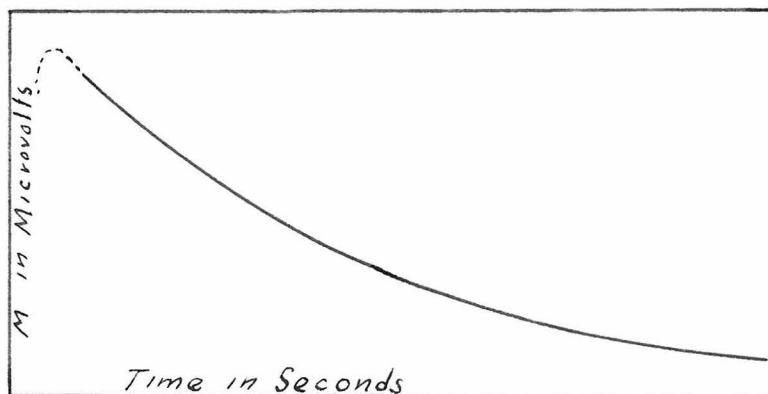


Figure 2. Calibration cooling curve

If the bomb temperature at the end of the determination was different than at the beginning, an additional correction was necessary. This correction will be called the heat capacity correction in further discussion. To calculate it, a known amount of electrical energy was added to the bomb, and the rise in temperature of the bomb was recorded. After this temperature rise was corrected for heat loss, the energy required per unit increase in temperature could be calculated. This value was multiplied by the difference in temperature between initial and final conditions to give the desired correction.

The accurate determination of energy supplied to the bomb was of utmost importance in determining the latent heat of vaporization. Figure 3 shows the electrical circuit used. The e. m. f. drops across resistances  $R_1$  and  $R_2$  were measured against time during a determination. The integrated averages of these values were used to determine  $E_H$  and  $I_H$ .

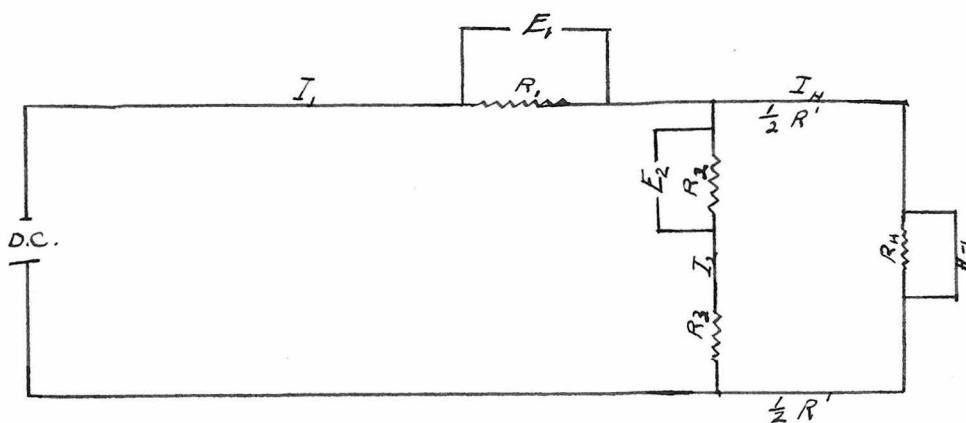


Figure 3. Electrical Circuit for Calorimeter Bomb Heater

Calculation of  $I_H$  and  $E_H$ :

$$R_1 = 2.4287 \text{ ohms}; \quad \frac{R_3}{R_2} = 10.40156, \quad R_2 = 559.208 \text{ ohms}$$

$R'$  = Lead wire resistance = .335 ohms.

$$I_{\text{Heater}} = \frac{A_v E_1}{R_1} - \frac{A_v E_2}{R_2} = .411745 \times \frac{1}{\theta} \int_0^{\theta} E_1 d\theta - .0017883 \times \frac{1}{\theta} \int_0^{\theta} E_2 d\theta$$

$$E_H = 11.40156 \times \frac{1}{\theta} \int_0^{\theta} E_2 d\theta - \frac{.335}{2.4287} \times \frac{1}{\theta} \int_0^{\theta} E_1 d\theta$$

$$E_H = 11.40156 \times \frac{1}{\theta} \int_0^{\theta} E_2 d\theta - 0.138037 \times \frac{1}{\theta} \int_0^{\theta} E_1 d\theta$$

Calculation of Volume Correction:

If the hydrocarbon under investigation is held at constant volume, not all of the material vaporized is removed across the boundary of the system. A volume just equal to that of the liquid vaporized is now filled with an additional quantity of gas. The experimental value must be corrected as shown in the equation:

$$L = \frac{Q + Q' + Q'' + Q'''}{W} \quad \frac{Q + Q' + Q'' + Q'''}{W' \left( \frac{V_d}{V_d - V_b} \right)} \quad \left( \frac{Q + Q' + Q'' + Q'''}{W'} \right) \frac{V_d - V_b}{V_d} \quad (3)$$

By substitution of the proper values into Equation 3 the final calculation of latent heat of vaporization is as follows:

$$Q = \frac{E_H I_H \theta' (0.00094866)}{W'}; \quad Q' = \frac{EK M \theta}{M' W'}; \quad Q'' = \text{Superheat} = 0$$

$$L = \left( \frac{E_H I_H \theta' (0.00094866) + EK M \theta}{W'} + Q'' \right) \frac{V_d - V_b}{V_d} \quad (7)$$

Symbols defined:

0.00094866 = Factor to convert from watt seconds to B. T. U.

$\theta'$  = Time of energy input to the bomb (seconds)

$Q$  = Total energy " " " " (B.T.U.)

$W$  = Total weight of liquid vaporized (pounds)

$W'$  = Weight of vapor collected in the weighing bomb (pounds)

$E_H$  = Bomb heater voltage

$I_H$  = " " current

(f) Correlation of the Data

Fourteen measurements of L were made for normal pentane. Of these values thirteen did not vary from the mean by more than 0.5% and in most instances by much less than this. The other value differed by nearly 2% and it was discarded. Values of L for pentane are shown in Table I. Figure (4) shows a comparison of experimental data with values reported by Young (4) and with values calculated in this laboratory from pressure-volume-temperature data by means of the Clapeyron equation. Young's values are intermediate between the experimental and the calculated values although, even at the lower temperatures, the maximum variation is not more than 1.5%. It is believed that the experimental <sup>latent heat</sup> values are more trustworthy at these lower temperatures. Experimental P-V-T relations are difficult to obtain accurately in this temperature range, while experimental latent heats of vaporization are obtained with greater precision because the lower vapor pressures encountered permit more favorable operating conditions and because volume corrections are not so important. Using heat capacity and Joule-Thomson data Equation (2) on page 3 was evaluated taking for  $L_0$  the experimental value at 104° F. This value was used because of the general consistency of experimental measurements in this temperature range. The values of L calculated from this equation throughout the entire experimental temperature range were within 0.5% of the curve based upon the directly measured values. To avoid confusion in interpreting the other curves these results were not shown in Figure 4. The good agreement of experimental data with latent heats obtained from other sources indicates



an absolute accuracy of nearly 0.3%.

Figure (5) shows a plot of  $L$  as a function of temperature for propane. The agreement here is not all that could be desired. On the same figure are values from the Clapeyron equation, from the experiments of the Linde Laboratories (1), and from the integrated equation mentioned above. The experimental values seem to fit the points reported by Dana much better than do the values from the Clapeyron equation. However, the values calculated from the Clapeyron equation are almost the same as previously reported values (5) calculated using entirely independent P-V-T data. The results obtained by integration of Equation (2), taking for  $L_0$  a value derived from the Clapeyron equation, agree very well with the Clapeyron equation values, but these would agree equally well if a value of  $L_0$  had been taken from the experimental curve. Until additional measurements can be made, it will be difficult to ascertain which values are correct. Experimental values for propane are tabulated in Table 2.

Table 1.

## Latent Heat of Vaporization of Normal Pentane

Temperature F	Calculated Energy B.T.U. #	Heat Capacity Correction B.T.U. #	Heat Loss Correction B.T.U. #	Calculated Energy Plus Correction	$\frac{V_d - V_b}{V_d}$	Heat of Vaporization B.T.U. #
104.3	154.38	-.2432	-.1460	153.99	.9944	153.14
103.7	153.69	-.0630	.2376	153.86	.9945	153.03
111.5	152.93	.0891	.0590	153.08	.9936	152.10
114.4	151.43	.7678	-.2297	151.97	.9933	150.96
120.5	150.96	.4785	-.2862	151.15	.9925	150.03
122.4	150.37	-.0330	-.1798	150.29	.9923	149.14
127.8	148.34	3.2798	-1.1842	150.43	.9916	149.17
131.0	151.10	-1.4355	-.1409	149.53		148.15
149.0	146.38	-.1070	-1.2030	145.07	.9882	143.36
154.3	144.07	.4950	.2340	144.80	.9872	142.94
179.5	140.34	.8360	.4750	141.65	.9810	138.97
180.4	137.10	.9734	.6940	138.77	.9807	136.10
180.5	138.43	1.0440	.2650	139.74	.9807	137.06
200.0	128.18	4.3180	1.6360	134.13	.9753	130.82

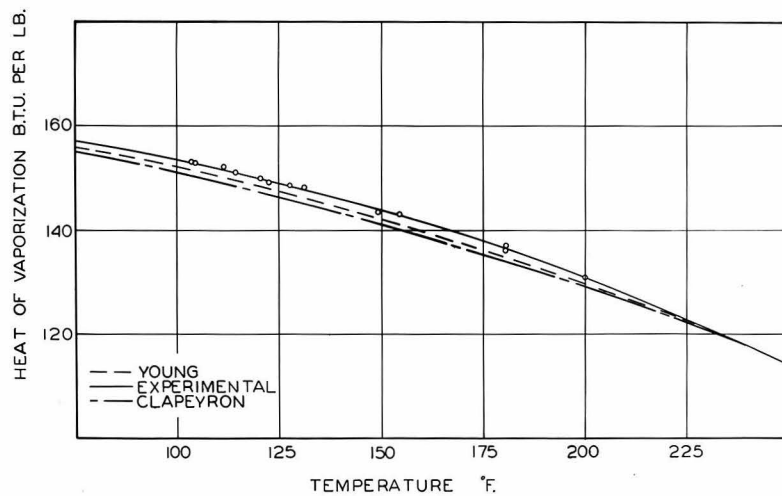


Figure 4. Latent heat of vaporization of n-pentane

Table II  
Latent Heat of Vaporization of Propane

Temperature °F.	Calculated Energy* B.T.U./#	Heat Loss Correction B.T.U./#	Calculated Energy Plus Correction	$\frac{V_d - V_b}{V_d}$	Heat of Vaporization B.T.U./#
103.4	140.47	1.7756	142.24	0.9346	132.94
103.7	141.44	1.0996	142.54	0.9342	133.16
109.5	138.49	1.9663	140.45	0.9281	130.34
109.8	143.62	-1.1385	142.48	0.9278	132.20
110.0	142.53	-0.2594	142.27	0.9276	132.20
110.1	141.10	-1.4084	139.69	0.9276	129.58
110.6	145.33	-1.2562	144.08	0.9270	133.56
114.4	139.66	-0.3975	139.27	0.9227	128.50
130.7	132.94	0.2064	133.14	0.9000	119.84
130.9	133.89	-1.3886	132.50	0.9000	119.26
144.4	125.93	-0.0916	125.84	0.8758	110.21
144.5	126.55	-0.1900	126.36	0.8758	110.67
161.6	108.85	4.0540	112.90	0.8310	93.82
162.0	120.11	-0.1951	119.92	0.8302	99.56
163.2	119.57	0.1823	119.75	0.8299	99.386

\* The heat capacity correction is included in the calculated energy term.

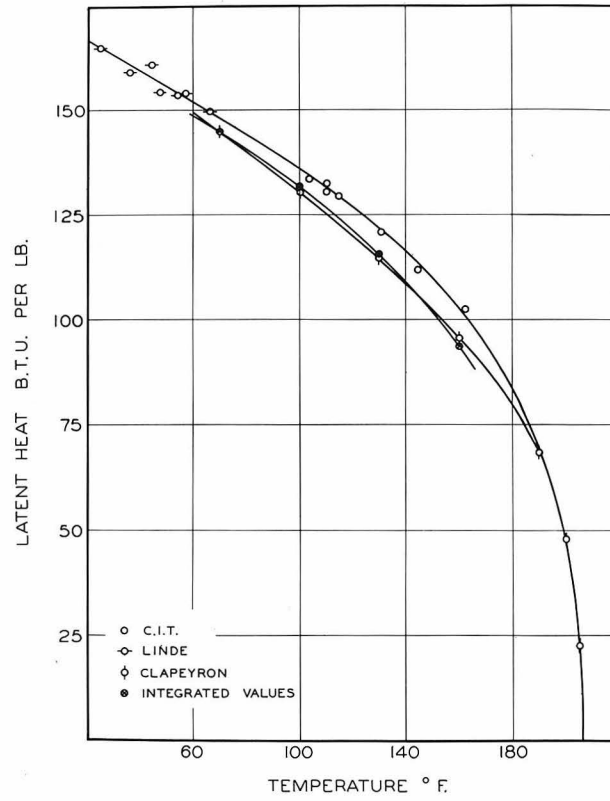


Figure 5. Latent heat of vaporization of propane

## II. SOME THERMODYNAMIC CALCULATIONS FOR n-PENTANE

A knowledge of the Joule-Thomson coefficient as a function of state and of the isobaric heat capacity as a function of temperature for a single pressure is sufficient to determine completely the heat capacity throughout the pressure range for which Joule-Thomson data are available. The method employed in such calculations is based upon the progressive graphical integration of the following general thermodynamic relation.

$$-\left(\frac{\partial C_P}{\partial P}\right)_T = \mu \left(\frac{\partial C_P}{\partial T}\right)_P + C_P \left(\frac{\partial \mu}{\partial T}\right)_P \quad (8)$$

Data for the isobaric heat capacity of n-pentane have recently been published (6). These values together with Joule-Thomson data (7) have been used to calculate the heat capacity throughout the superheated region. The heat capacity as a function of pressure and temperature is shown in Table 3 and is graphically recorded in Figure 5. Previous values of heat capacity have been reported (7) based upon estimated values of  $C_p$  at atmospheric pressure. Later experimental work (6) showed that these values were about 1% in error. Using the latest atmospheric heat capacity data, the values of heat capacity in the superheated gas region are slightly greater than those previously reported. It is believed that the accuracy of the present values is 0.5%.

From the isobaric heat capacity and the Joule-Thomson coefficient, the isothermal change in enthalpy with pressure

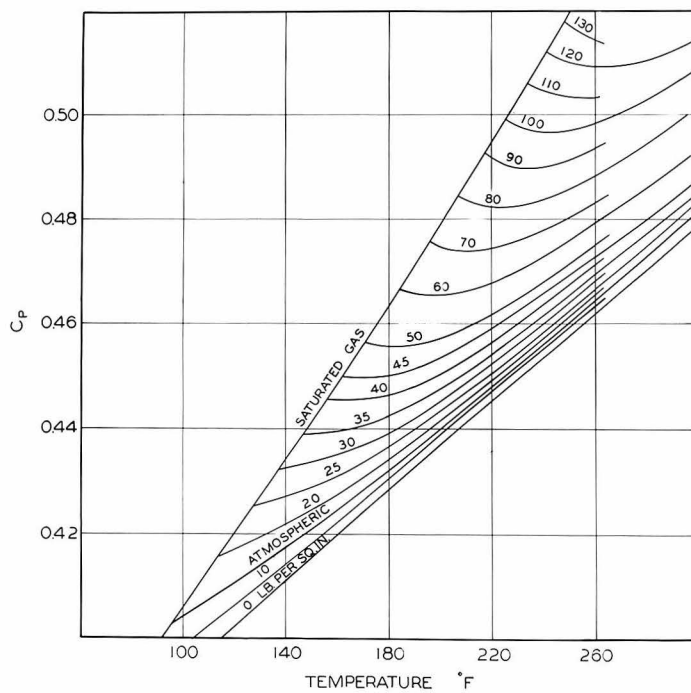


Figure 6. Heat Capacity at constant pressure  
for n-Pentane ( $C_p$  is expressed in B.T.U.  
per pound.)

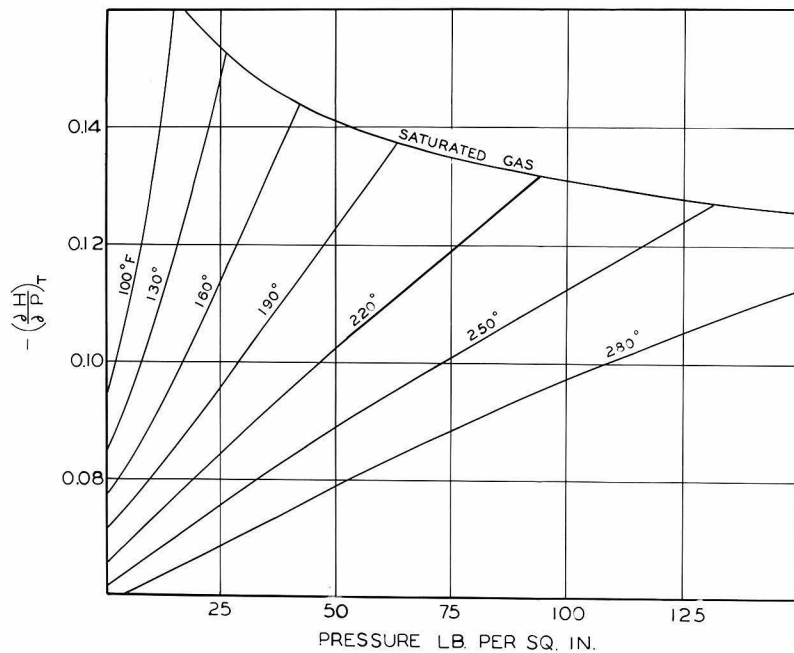


Figure 7. Isothermal change in enthalpy with pressure.

n-Pentane



may be calculated by means of the general thermodynamic relation: 
$$\left(\frac{\partial H}{\partial P}\right)_T = -v C_p \quad (9)$$

These values are shown in Figure 7.

The compressibility factor  $z$  may be defined as the ratio  $\frac{PV}{bT}$ . The isobaric change in this quantity with temperature may be calculated from the following equation:

$$\left(\frac{\partial z}{\partial T}\right)_P = -\left(\frac{\partial H}{\partial P}\right)_T \frac{P}{bT^2} \quad (10)$$

Values of  $z$  were determined from the above expression by graphical integration using values of  $z$  at 220° F. (8) as reference points.

Residual volume may be defined as the difference between the perfect gas volume and the actual gas volume for any given pressure and temperature. Residual volumes were calculated from the simple relation:

$$v = \frac{(1-z)bT}{P} \quad (11)$$

The results are shown in Figure 8 and Table 4. It was found that these values were slightly lower than those previously reported (8). This would be expected since the heat capacity data from which  $\left(\frac{\partial H}{\partial P}\right)_T$  was calculated were found to be slightly higher than the earlier ones.

From these primary data the variations in enthalpy and entropy with pressure and temperature have been calculated for the superheated gas. Both entropy and enthalpy were arbitrarily taken as zero for the saturated liquid at 60° F. The method of calculating these values has already been described (9,10). Calculated values of entropy differ from previous

values (8) by as much as 7% at the higher temperatures.

The improved experimental data on latent heat of vaporization and atmospheric heat capacity are believed to be sufficient to account for the difference.

Tabulated and graphical values of entropy are shown by Table 6 and Figure 10. Values for enthalpy are shown by Table 5 and Figure 9.

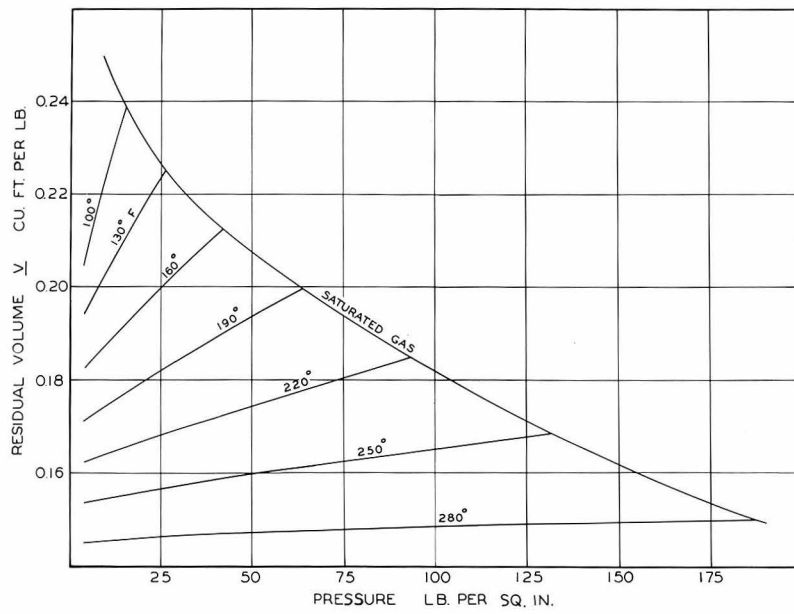


Figure 8. Residual Volume

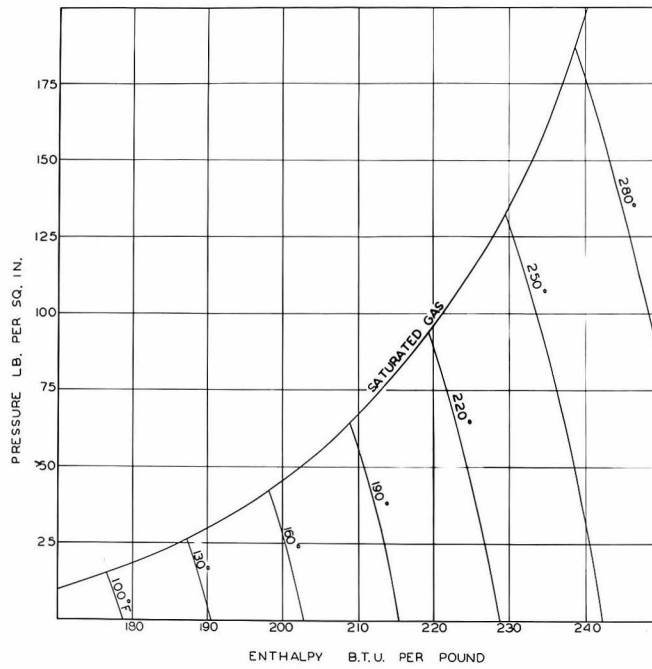


Figure 9. Effect of pressure on Enthalpy at constant temperature

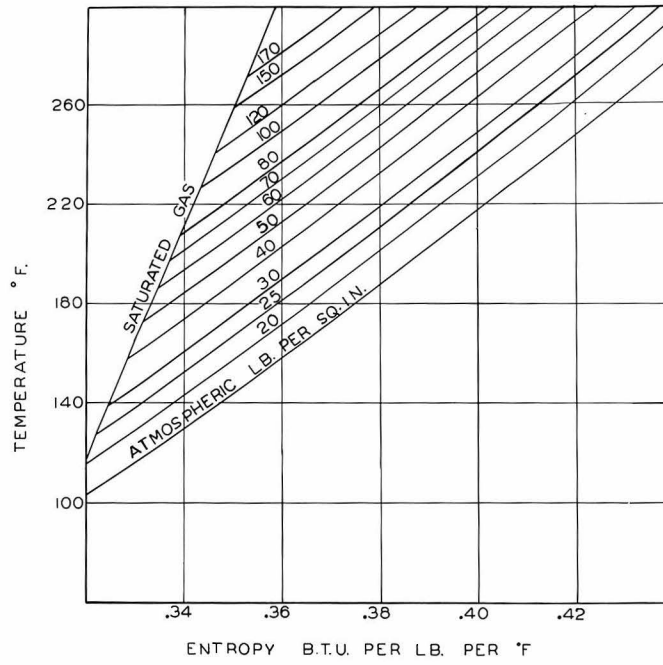


Figure 10. Effect of Temperature on Entropy

Table III  
 Values of  $C_p$  from Smoothed Curves (B.T.U. per pound)

Pressure #/sq. in.	Saturated Gas	130	160	190	220	250*
0		.4065	.4196	.4325	.4455	.4578
10	.3900	.4100	.4221	.4344	.4470	.4593
14.696	.4033	.4138	.4245	.4360	.4479	.4603
20	.4150	.4192	.4274	.4378	.4491	.4614
25	.4242	.4256	.4308	.4398	.4506	.4627
30	.4321		.4350	.4419	.4523	.4641
35	.4392		.4394	.4447	.4543	.4657
40	.4456		.4456	.4479	.4566	.4674
45	.4512			.4514	.4590	.4693
50	.4568			.4559	.4618	.4713
60	.4668			.4658	.4678	.4756
70	.4762				.4744	.4805
80	.4846				.4824	.4857
90	.4924				.4914	.4913
100	.4993					.4972
110	.5060					.5036
120	.5120					.5103
130	.5180					.5174
Saturation		.4268	.4484	.4750	.4950	.5194

\* Extrapolated values.

Table IV.  
Residual Volume  
Cu. ft./#

Pressure #/sq. in.	Saturated Gas	130	160	190	220	250	280
10	.247	.203	.187	.174	.163	.155	.147
14.696		.210	.192	.177	.165	.155	.146
20	.232	.217	.195	.179	.166	.156	.146
25		.223	.199	.181	.167	.156	.146
30	.221		.202	.184	.169	.157	.146
35			.207	.186	.170	.158	.146
40	.214		.211	.188	.172	.158	.147
45				.191	.173	.159	.147
50	.208			.193	.174	.160	.147
60	.201			.197	.176	.160	.147
70	.196				.179	.162	.148
80	.191				.181	.163	.148
90	.186				.184	.164	.148
100	.182					.164	.148
110						.165	.149
120						.166	.149
130						.168	.149
150							.149
170							.149
Saturation		.225	.213	.199	.185	.168	.150

Table V  
Enthalpy  
B.T.U./#

Pressure #/sq. in.	130	160	190	220	250	280
14.696	188.8	201.4	214.3	227.6	241.2	255.2
20	188.2	200.9	213.9	227.2	240.8	254.9
25	187.5	200.4	213.4	226.8	240.5	254.5
30		199.8	212.9	226.3	240.1	254.2
35		199.1	212.4	225.9	239.7	253.8
40		198.5	211.8	225.4	239.3	253.5
45			211.3	224.9	238.9	253.1
50			210.7	224.4	238.4	252.7
60			209.4	223.4	237.5	251.9
70				222.2	236.5	251.0
80				221.1	235.5	250.2
90				219.8	234.5	249.2
100					233.4	248.3
110					232.2	247.3
120					231.0	246.3
130					229.8	245.2
150						243.0
170						240.7
Saturation	187.3	198.1	208.8	219.3	229.5	238.6



Table VI  
Entropy  
B.T.U./#/F

Pressure #/sq. in.	130	160	190	220	250	280
14.696	.3403	.3311	.3815	.4014	.4210	.4403
25	.3241	.3453	.3660	.3860	.4057	.4251
30		.3397	.3605	.3806	.4004	.4198
40		.3302	.3514	.3718	.3917	.4113
50			.3440	.3647	.3848	.4045
60			.3376	.3587	.3789	.3987
70				.3532	.3737	.3937
80				.3484	.3691	.3893
90				.3438	.3648	.3851
100					.3607	.3813
110					.3569	.3777
120					.3532	.3743
130					.3495	.3711
150						.3650
170						.3592
Saturation	.3226	.3287	.3353	.3419	.3484	.3546

LITERATURE CITED

- (1) Dana, Jenkins, Burdick and Timm, Ref. Eng. 12,387(1926)
- (2) Osborne and Van Dusen, Bur. Stan. Bull.,  
14 439 (Sci. Paper No. 315) (1918)
- (3) Vermeulen, T., M.S. Thesis in Chemical Engineering,  
C.I.T. (1937)
- (4) Young, S., Sci. Proc. Roy. Dublin Soc. 12, 374(1910)
- (5) Sage, Schaafsma, and Lacey, Ind. Eng. Chem.  
26, 1218 (1934)
- (6) Sage, B. H., Webster, D. C. and Lacey, W.N., Ibid,  
29, 1309 (1937)
- (7) Kennedy, E. R., Sage, B. H. and Lacey, W. N. Ibid,  
28, 718 (1936)
- (8) Sage, B. H., Schaafsma, J. G., and Lacey, W. N., Ibid,  
27, 48 (1935)
- (9) Sage, B. H., Webster, D.C. and Lacey, W.N., Ibid,  
26, 1213 (1934)
- (10) Ibid, 29, 1188 (1937)

A definition of symbols not previously defined:

$b$  = Gas constant = 10.715 cubic feet/square in.  $\times$   $^{\circ}$ R.

$b$  (when used as a subscript) refers to bubble point conditions

$C_p$  = Heat Capacity (B.T.U. per pound)

$d$  (when used as a subscript) refers to dew point conditions

$H$  = Enthalpy (B.T.U. per pound)

$L$  = Latent heat of vaporization (B.T.U. per pound)

$P$  = Pressure (pounds per square inch)

$\mu$  = Joule-Thomson coefficient =  $\left(\frac{dT}{dP}\right)$

$T$  = Absolute temperature (degrees Rankin)

$V$  = Volume (cubic feet per pound)

$\underline{V}$  = Residual volume (cubic feet per pound)

$Z$  = Compressibility factor =  $\frac{bT}{PV}$

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