THE PRESSURE-VOLUME-TEMPERATURE RELATIONSHIPS

OF PROPAME

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Thesis by

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Introduction:

To establish further the thermodynamic behavior of paraffin hydrocarbons, a study has been made on the naturally occurring substance propane, a material which has already been considered along these lines to no small extent (6)*. Data of the type presented in this paper are of considerable use in many fields and particularly in natural gasoline practice. It is hoped that this new and more exact knowledge of the behavior of propane Will prove of direct value not only to industry but also to those interested in the study of the thermodynamic properties of materials from the theoretical point of view.

The data presented include the pressure-volume-temperature relationships of propane and the corresponding compressibility factors. Also given is information concerning the two-phase boundary conditions, and the results from a special study in the vicinity of the critical point. The range covered in the work comprises that between 70°F and 520°F and the pressure interval from atmospheric pressure to· 3500 pounds per square inch.

Experimental Data:

The experimental data utilized in the derivation of the properties presented here come from three distinct and separate sources: the Chemical Engineering Laboratory of the California Institute of Technology; the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology; and the Laboratory of the Linde Air Products Company, Buffalo, New York.

* See literature citations at the close of the discussion.

The California Institute Laboratory, with which this writer has been associated, in its experimental work used propane obtained from the Phillips Petroleum Company. This propane was purified by fractionation in a glass column packed with glass rings of the type developed by Young (9). The work done at this laboratory on the propane was carried out on four separate experimental set ups, and led to the following quantities: pressurevolume-temperature relations, Joule-Thomson coefficients, specific heats at constant pressure, and latent heats of vaporization.

The pressure-volume-temperature work was done in the variable volume cell employed by Sage et al (7) in previous experimenta on hydrocarbons. A recent change in the apparatus has been the installation of a four- junction thermocouple of constantan and copper to control more accurately the temperature of the oil bath, and a multi-lead, single-junction couple of the same type to measure the temperature existing in the bomb. These calibrated thermocouples are accurate to two hundredths of a degree. Isotherms on r egion propane were run in the condensed liquid, and some distance into the twophase region at intervals of 30°F. In the critical area, isothermal runs separated by 5° were made in order to observe more closely the behavior existent in that region. Two runs, one at 190° and the other at 220°F, were also made on the superheated gas to serve as the basis of calculation of the volumes in the entire superheated region. (Adsorption of the superheated gas on the walls of the apparatus at temperatures lower than 190°F was found to be an important factor; hence, direct measurements of the volumetric relationships in that area could not be made.) For the condensed liquid work the temperature range from 70°F to 250°F was coverad, up to pressures of 3500 pounds per square inch.

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A recent publication in the series of articles on the subject, "Phase Equilibria in Hydrocarbon Systems" (4) , describes the Joule-Thomson apparatus employed at the California Institute Laboratory to obtain the data necessary for the determination of the Joule-Thomson coefficients of superheated gaseous propane. The values presented in that paper have been used in the calculations attendant on this work.

Another of the above-mentioned series of publications (S) outlines the adiabatic expansion equipment used to measure the specific heats at atmospheric pressure of gaseous propane. These, together with the Joule-Thomson coefficients, offer a means of calculation of \mathbb{G}_p^* throughout the superheated gas region as explained in reference (4).

The adiabatic colorimeter of Sage and Lacey (5) afforded a direct measurement of the latent heat of vaporization of propane in the temperature range 100° fo 160° . In addition, measurements were made on this apparatus to give the specific heat of the saturated liquid (5).

The data of the Massachusetts Institute of Technology (1) (Beattie and co-workers) gave the pressure-volume-temperature information for propane in the range of temperatures from the critical point to 527°F, and specific volumes from 0.036 to 0.36 cubic feet per pound. This work, however, extended down only to pressures in the neighborhood of 500 pounds per square inch. This same laboratory made a special study of the region in the immediate neighborhood of the critical point (2), and arrived at certain conclusions as to the values of the critical pressure, temperature, and volume of propane.

See Nomenclature.

Investigators at the Linde Air Products Company Laboratory (3) have determined the vapor pressure of propane up to $120°F$ as well as the latent heats of that substance up to 70°F.

Calculations:

The condensed liquid region of propane was established in the volumetric behavior on the basis of four sets of runs, made at the California Institute laboratory. These experimental values were plotted at constant temperature against pressure, smoothed, and then cross-plotted at constant pressure against temperature. The maximum deviation of the weret of the experimental points from the corresponding finally accepted values was not more than 0.2%. From these runs good vapor pressure data were also obtained, below 190°F. Figure 1 is a plot of volume against pressure for the condensed liquid.

The pressure-volume-temperature relationships in the superheated gas inaccuracy region had to be attacked indirectly because of the hadre of experimental data in that area, due to the difficulties mentioned above. However, use is made of the relationship $\left({\frac{{\partial H}}{{\partial p}}}\right)_T = -{\mathcal{A}} C_p$ employing the Joule-Thomson data already referred to (4) , and \int_{p}^{0} calculated from the recent values of \int_{p}^{0} at atmospheric pressure (8) and the Joule-Thomson coefficients by progressive approximate integration (4). $\left(\frac{\partial H}{\partial n}\right)$ as computed was smoothed against temperature and pressure and $\left(\frac{\partial P}{\partial n}\right)^T$ calculated from the relationship $\left(\frac{\partial z}{\partial T}\right)_P = -\left(\frac{\partial F}{\partial P}\right)_P$ $\frac{P}{bT^2}$. After plotting $\left(\frac{\partial z}{\partial T}\right)_P$ against both temperature and pressure to smooth, an integration was made. This was carried out employing the values of \geq (the compressibility factor), calculated at 220°F, from the volumetric isotherms previously mentioned, as a basis. These integrated

Figure 1. Volumetric Behavior in the Condensed Liquid Region.

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 \geq values, which were found to give a consistent set of data, are plotted in Figure 2. Hating these values of the compressibility factor it was then an easy matter to calculate the corresponding volumes from the primary definition of \geq (\geq = $\frac{PVM}{RT}$). The accuracy of these volumes and \geq , s naturally depends entirely upon the values of μ and C R \geq R employed in the early calculation as well as the validity of the two isotherms at 190°F and 220°F, vmich served as a basis for the integration. It is probable that the maximum . inaccuracy for the volumes and $\geq l$ in the superheated gas region is not more than 0.5%.

Since the overlapping of the data of Beattie, et al (1) , which extends down to the critical temperature $(206.3°)$, with that done at the California Institute, is only slight from the point of view of temperature, and, was, in addition, close to critical where the change of volume with pressure and temperature is great, some difficulty was encountered in fitting the two sets of data together. However, by suitable cross-plotting they were effectively joined and a smooth overall effect obtained. Values of **.z** were then calculated from these volumes, up to 2000 pounds per square inch, and plotted, $sine \geq a$ t pressure equal to zero is unity, these curves of \geq versus pressure at constant temperature were drawn to unity at zero pressure. This bridged the gap in the pressure range O to 500 pounds per square inch for temperatures above 220°F. wheme no data were available. These extrapolated values were assumed temporarily to be correct.

Values of $\left(\frac{dz}{dt}\right)_p$ for these curves of z against temperature were obtained graphically and smoothed. $\left(\frac{\partial H}{\partial p}\right)_T$ was then calculated from the relation:

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

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Above 1500 pounds per square inch and the critical temperature, and throughout the condensed liquid region. $\left(\frac{\partial V}{\partial T}\right)_P$ was obtained graphically. This quantity was smoothed and $\left(\frac{\partial H}{\partial p}\right)_{T}$ derived from the equation, $\left(\frac{\partial H}{\partial p}\right)_{T} = V - \left(\frac{\partial V}{\partial T}\right)_{P}$. These values of $\left(\frac{\partial H}{\partial p}\right)_m$ were then plotted with those obtained as above from $\left(\begin{matrix} 0 & \lambda & 0 \\ \lambda^T & \lambda^T & 0 \end{matrix}\right)$ and smoothed. The agreement of the two sets of data in the overlapping area is shown in Figure 3. To $\left(\frac{\partial H}{\partial p}\right)_m$ of the superheated gas region these smooth values were joined by a process of smoothing and cross-plotting putting the emphasis from the point of view of accuracy on the former. There was a somewhat marked change in the finally accepted values of $\left(\frac{dH}{\delta p}\right)_m$ at high temperatures and below 500 pounds per square inch as a result of this process. This could easily be traced to the original extrapolation of the high temperature curves of \geq versus pressure to zero pressure. Small errors, such as could be expected in the values of \geq from such a method, made for rather large discrepancies from accuracy of $\begin{pmatrix} \frac{\partial \mathbf{F}}{\partial T} \\ \frac{\partial T}{\partial T} \end{pmatrix}_p$ and, hence, $\begin{pmatrix} \frac{\partial H}{\partial D} \\ \frac{\partial H}{\partial T} \end{pmatrix}_p$ at these low pressures.

These smooth and now assumed correct values of $\left(\frac{\partial H}{\partial p}\right)_m$ from 220° to 520° and from 0 to 800 pounds per square inch were used in the calculation of new $\left(\frac{\partial P}{\partial T}\right)_D$ quantities for this region. An integration was carried out on these to obtain the corresponding $e^{\log n}$, using $e^{\log n}$ at 220° up to 500 pounds per square inch as a basis. Above that pressure z' at 310° were employed. r ef erence to a pressure of 800 pounds per square inch. These $_{\Lambda}$ values at 310°F were obtained by connecting the new values at 310°F below 500 pounds pressure with the previous values above 1000 pounds at 310°F. This procedure had the overall effect of establishing the lower pressure and all the way to 520@F and satisfactorily connecting it with the previously derived volumetric data in the superheated gas region.

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Figure 3. $\left(\frac{\partial \mathbb{H}}{\partial p}\right)_T$ in the High Temperature Region.

The next step was the calculation of e for pressures above 2000 pounds per square inch at temperatures above critical and for the condensed liquid region. The entire compressibility factor picture for propane could then be pieced together except for a small region around the critical point. A thorough smoothing and cross-plotting process having been gone through for the whole, with the above exception, it could then be said that volumes might be calculated with as much accuracy as could be expected from the corresponding \geq values. This was done and the volumes obtained are presented as final results in the tables. The accuracy from 250° to 520°F below 500 pounds per square inch is of the order of $0.5%$ and above 500 pounds per square inch of 0.2%.

The vapor pressures of propane, which were used in the calculations in the superheated gas region, were taken at low temperatures from the data of Dana and colleagues (3), above 70°F from a composite of the values indicated by four different sets of California Institute runs, and at the critical state and immediately adjacent thereto from the work at the Massachusetts Institute Laboratory (2). These three independent sets of data were plotted together and found to agree well as shown in Figure 4. Points were read off this curve at even temperatures and called for the moment P'. A mathematical method was then used to smooth these P1 points effectively. Tha relation $P = P_I - P'$, where P is the residual vapor pressure and log₁₀ P_I (P_I is the "ideal" vapor pressure at temperature t) equals $a - \frac{b}{m}$. Here the • *If* value of \mathbb{I} was taken as $5.\frac{172}{11}$, \mathbb{I} b¹¹ as 1788.132. The residual vapor pressures so calculated were plotted against temperature and smoothed, the smooth values being calculated back to give the finally accepted vapor pressures.

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Figure 4. Vapor Pressure Curve

AS mentioned previously the critical region is a difficult one to establish because of the fact that the change of volume with temperature and pressure is so great, being infinite at the critical point itself. However, advantage was taken of the fact that plots of pressure against temperature at constant volume are nearly straight lines. Curves of this the state nature were drawn for the area near, critical, using as their basis the published Massachusetts Institute data $(1,2)$, three sets of runs at the California Institute, and the established data at states farther removed from critical. The plot covered the range of pressure from 4oo to 14oo pounds per square inch and of temperature from 160° to 370°F. These curves were smoothed and values read from them . were accepted asfinal. Figure 5 shows the nature of the plot obtained. Corresponding \geq 'S were also calculated. Of much material aid in establishing the two phase boundaries in the vicinity of the critical point was a plot of the average density of the two phases against temperature which is very nearly a straight line function as shown in Figure 6. By this means a value of the critical volume of 7.199 cubic feet per pound was derived as compared to the value proposed by Beattie et al (2) of 7.093, who claimed one per cent accuracy. The critical pressure (617.4 pounds per square inch) and critical temperature (206.3ºF) of these investigations were accepted.

This procedure filled in all that remained unknown as to the volumetric behavior of propane. The accompanying tables present the data along with the corresponding values of the compressibility factor *2 .* Values for the two phase boundary conditions are given as well as vapor pressures. Figure 7 is a plot of the compressibility factor over the entire region studied. The volumetric behavior in the critical region is shown in Figure 8.

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Figure 6. Density of the Two-Phase Boundaries.

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Figure 7. Compressibility Factor-Pressure Diagram.

Figure 8. Specific Volume-Pressure Diagram **in the Vicinity of the Critical Point.**

Latent Heat of Vaporization:

The latent heat of vaporization for propane from 70°F to the critical temperature was calculated by making use of the Clapeyron equation: $\left(\frac{-\Delta V}{\Delta t}\right)_{\text{tot}}$ In addition, values of the latent heat, employing as a reference the Clapeyron value at 70°F, were computed by graphically integrating the expression: $AL = \int_{\tau}^{\tau} \left\{ \left[\left(\frac{\partial H}{\partial \rho} \right)_{\delta \rho, g,t} - \left(\frac{\partial H}{\partial \rho} \right)_{\delta \sigma, h g,t} \right] \left(\frac{\partial P}{\partial \tau} \right)_{\delta \sigma t} + \left(C_{\rho, \delta \sigma, g, g} - C_{\rho, \delta \sigma, k g, h g} \right) \right\} d\tau$ These two sets of latent heat values are plotted in Figure 9 along with the values of this quantity experimentally measured by the Linde Laboratory and the California Institute.

Summary:

The pressure-volume-temperature relations of propane have been established for the range of temperature from 70° to 520°T and of pressure from atmospheric pressure to 3500 pounds per square inch. The corresponding compressibility factors have been determined and a special study in the vicinity of the critical state has been made.

The accuracy of the tabulated values in the condensed liquid region is 0.1%; in the superheated gas area 0.5% ; and in the critical region, 0.5%. Above the critical temperature, the accuracy is 0.5% below 500 pounds per square inch pressure and 0.2% above that pressure. The vapor pressures are accurate to a probable 0.3 pound per square inch.

When published these data will be included with those for the enthalpy and entropy of propane under corresponding conditions which will be calculated by this writer.

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Figure 9. Latent Heat of Vaporization.

Acknowledgments:

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Nomenclature

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Literature Cited

- (1) Beattie, James A., Kay, William C., and Kaminsky, Joseph. J. Am. Chem. Soc., 59, 1589 (1937).
- (2) Beattie, James A., Poffenberger, Noland and Hallock, Canfield, J. Chem. Phys., *l,* 96 (1935).
- (3) Dana, L. I., Jenkins, A.C .• Burdick, J. N. and Timm, R. c., Refrigerating Eng., 12, 387 (1926)
- (4) Sage, B. H. 9 Kennedy, E. R., and Lacey, W. N., Ind. Eng. Chem., 28, 601 (1936).
- (5) Sage, B. H. and Lacey, W. N., Ibid., *£1..* 1484 (1935).
- (6) Sage, B. H., Schaafsma, J. G., and Lacey, W. N., Ibid., 26 , 1218 (1934), and literature cited
- (7) Sage, B. H., Webster, D. C., and Lacey, W. N., Ibid., 29, 658 (1937).
- (8) Sage, B. H., Webster, D. C., and Lacey, W. N., Ibid., 29, 1309 (1937).
- (9) Young, W. G., and Jasaitis, Z., J. Am. Chem. Soc., 58, 377 (1936).

TABLE I

SPECIFIC VOLUME OF PROPANE

Superheated Gas Region

Cu. ft. per lb.

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TABLE II

SPECIFIC VOLUME OF PROPANE

Condensed Liquid Region

Cu. ft. per lb.

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TABLE III

SPECIFIC VOLUME OF PROPANE

High Temperature Region

Cu. ft. per lb.

TABLE IV

COMPRESSIBILITY FACTOR OF PROPANE

Superheated **Gas Region**

TABLE **V**

COMPRESSIBILITY FACTOR OF PROPANE

High Temperature Region

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TABLE VI

PRESSURE-VOLUME-TEMPERATURE RELATIONS OF PROPANE IN CRITICAL REGION

Compressibility Factor Above

Pressure (1bs. per sq. in.) below

TWO-PHASE BOUNDARY RELATIONS OF PROPANE

VAPOR PRESSURE VALUES FOR PROPANE

TABLE IX

CRITICAL CONSTANTS OF PROPANE

