# SOME THERMODYNAMIC PROPERTIES OF HYDROCARBON MIXTURES

Thesis by

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# PART I.

## JOULE-THOMSON COEFFICIENTS OF TWO GASEOUS HYDROCARBON MIXTURES

# CALCULATION OF THE THERMODYNAMIC PROPERTIES OF GASES FROM THEIR JOULE-THOMSON COEFFICIENTS

The rapid development of the petroleum industry in recent years has made it necessary to secure more information than is now available concerning the thermodynamic properties of hydrocarbons. Many investigations have been undertaken with this viewpoint in mind. As a result, several of the more important binary hydrocarbon systems have been studied in considerable detail, and their properties are now well established. However, a major part of this work has been confined to the liquid and two-phase regions where data on the volumetric and phase behavior of the systems could be determined with accuracy by the direct measurement of volume as a function of pressure and temperature.

In the gaseous regions, especially at low pressures, accurate volumetric data are very difficult to obtain by direct measurement. This is perhaps due in part to the adsorption of gas by the walls of the container. Another factor contributing to the difficulty is the fact that under isothermal conditions small changes in pressure cause relatively large changes in volume. This necessitates smaller samples and also limits the pressure range under which any one sample may be investigated.

Because of these difficulties, it is desirable to have at hand some means of checking the volumetric data obtained by direct measurement in a manner as nearly independent as possible. The Joule-Thomson coefficient may be made to serve this purpose admirably, because in conjunction with a limited amount of specific heat data it affords a means of calculating the change in volume of a gas with temperature under isobaric conditions. This fact, coupled with the added advantage that it is most easily determined experimentally in regions of moderately low pressure, makes it a useful derivative for the evaluation of thermodynamic properties of gases.

In addition to the above use, it also finds utility in the evaluation of many properties other than volume. For example, it may be used to advantage in calculating the change in isobaric heat capacity with pressure. It may also be used for determining the latent heat of pressure variation, $\ell_p$, and the isothermal enthalpy-pressure coefficient $(\partial H/\partial P)_T$ *.

It is the purpose of this section to indicate in what manner one may apply the Joule-Thomson coefficient for the evaluation of many of these useful quantities.

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* Nomenclature for this section will be found on page 12. In this connection, it should be pointed out that some of the relations derived in this thesis are dimensionally incorrect without the application of proper conversion factors. For the sake of simplification of writing, these factors have been omitted from the equations. These must be supplied if numerical calculations are to be made.

## Calculation of Changes in Isobaric Heat Capacity with Pressure

As indicated previously, one of the calculations which can be made with the aid of the Joule-Thomson coefficient is the change in isobaric heat capacity with respect to pressure at constant temperature.

For any system of constant composition the enthalpy measured above any arbitrarily selected datum may be expressed as a function of the pressure and temperature, thus:

$$H = f(P, T) \tag{1}$$

Differentiation of Equation 1 results in the relation:

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT \tag{2}$$

If dH = 0, Equation 2 may be written as:

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{C_P} \tag{3}$$

where $\mu$ designates the Joule-Thomson coefficient.

Since dH is an exact differential and since $(\partial H/\partial P)_T$ and $(\partial H/\partial T)_P$ are both continuous functions in any single phase region, it follows that the reciprocity law will hold; namely, that:

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right]_P = \left[\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial T}\right)_P\right]_T = \left(\frac{\partial C_P}{\partial P}\right)_T \tag{4}$$

Combining Equations 3 and 4 yields the important relation:

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -\left(\frac{\partial \mu C_P}{\partial T}\right)_P \tag{5}$$

From the relation expressed by Equation 5, it is possible to calculate the value of $C_p$ at any pressure and temperature within the region in which the Joule-Thomson coefficient is known, provided data on the isobaric heat capacity at a single pressure throughout the temperature range are available. If the value of the isobaric heat capacity at some pressure $P_0$ be designated as $C_{p_0}$, its value at any other pressure but at the same temperature may be ascertained by the integration of the equation:

$$C_P = C_{P_0} - \int_{P_0}^{P} \left(\frac{\partial \mu C_P}{\partial T}\right)_P dP \tag{6}$$

Since $C_p$ appears on both sides of this equation, and since the values of $\mu$ are usually not expressed as a mathematical function of the pressure, it becomes necessary to solve Equation 5 by graphical methods. This may be done by starting at $P_0$ where both $C_{p_0}$ and $\mu$ are known and extending the solution of Equation 6 by successive approximation to the desired pressure in such a manner that Equation 5 is satisfied at all intermediate pressures.

In regions where $\mu$ is changing rapidly with temperature and pressure the solution of Equation 6 becomes exceedingly difficult so that its utility is limited in a large degree to those regions in which the variation of $\mu$ with pressure and temperature is not abrupt. These regions are usually at low pressures, and at temperatures well above the critical.

Making use of the values of $C_p$ as calculated in the above manner, one is in a position to solve Equation 3 for the isothermal enthalpy-pressure coefficient.

$$\left(\frac{\partial H}{\partial P}\right)_T = -\mu C_p \tag{7}$$

## Evaluation of the Change in Compressibility Factor With Temperature

The compressibility factor for any gas may be defined by the equation:

$$Z = \frac{PV}{bT} \tag{8}$$

For a perfect gas the value of Z is unity at all pressures and temperatures;but for an imperfect gas its value is in general different from unity except in the limit as the pressure approaches zero. If Equation 8 be differentiated with respect to temperature, holding the pressure constant, it becomes:

$$\left(\frac{\partial Z}{\partial T}\right)_P = \frac{P}{bT^2}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] \tag{9}$$

In order to express Equation 9 in terms of the Joule-Thomson coefficient and isobaric heat capacity, recourse may be made to the reciprocity relation which must hold for the differential entropy.

Thus, for the equation:

$$dS = \frac{dH - VdP}{T} = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP + \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P dT \qquad (10)$$

the reciprocity relation is:

$$\left\{\frac{\partial}{\partial T}\frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]\right\}_P = \left\{\frac{\partial}{\partial P}\ \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P\right\}_T \qquad (11)$$

Performing the partial differentiation indicated and making use of the relations expressed by Equations 4 and 7, one obtains:

$$T\left(\frac{\partial V}{\partial T}\right)_P - V = \mu C_P \qquad (12)$$

Substitution of this relation into Equation 9 gives an equation expressing the change in compressibility factor with temperature when holding the pressure constant:

$$\left(\frac{\partial Z}{\partial T}\right)_P = \frac{P\mu C_P}{bT^2} \qquad (13)$$

Examination of Equation 13 shows that it is possible to calculate the change in compressibility factor with respect to temperature throughout the entire range of pressure and temperature for which values of $\mu$ and $C_p$ are known. If the value of Z be otherwise determined at some temperature $T_0$ throughout the pressure range, the absolute value of Z may be calculated over the entire range of both temperature and pressure by integration of the equation:

$$Z = Z_0 + \int_{T_0}^{T} \frac{P\mu C_p}{bT^2}\, dT \tag{14}$$

This equation can be solved graphically without difficulty and therefore offers a convenient method of determining compressibility factors when only a limited amount of pressure-volume-temperature data is available. If suitable pressure-volume-temperature data are available, they may be used as an effective check on the accuracy of these data as indicated previously.

## Determination of the Latent Heat of Pressure Variation

Another important property which can be evaluated from a knowledge of the Joule-Thomson coefficient together with the isobaric heat capacity and compressibility factor is the latent heat of pressure variation (1). This quantity is defined by the term $\ell_p$ in the equation:

$$q = C_p\, dT + \ell_p\, dP \tag{15}$$

From the second law, q may be replaced by T ds for any reversible process so that Equation 10 may be combined with Equation 15 to give:

$$\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] dP + \left(\frac{\partial H}{\partial T}\right)_P dT = C_p\, dT + \ell_p\, dP \tag{16}$$

Replacing $(\partial H/\partial P)_T$ with $-\mu C_p$ and $(\partial H/\partial T)_P$ with $C_p$, Equation 16 reduces to:

$$\ell_p = -(\mu C_p + V) = -\mu C_p - \frac{ZbT}{P} \tag{17}$$

The term $\ell_p$ is a state function of the same general character as $C_p$. It is very useful in evaluating heat interchanges between the system and surroundings when the thermodynamic path is known.

## A Method of Determining $C_{p_o}$

An ingenious method of determining the absolute value of the isobaric heat capacity of gases has been developed by Eucken (1). This method, which requires a knowledge of the Joule-Thomson coefficient, has also been applied by other investigators (3) with considerable success. If in Equation 10 $(\partial H/\partial P)_T$ be replaced with $-\mu C_p$ and $(\partial H/\partial T)_P$ be replaced with $C_p$, one obtains the relation:

$$T\,dS = -(\mu C_p + V) + C_p\,dT \qquad (18)$$

If the entropy is held constant, this equation may be written as:

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\mu C_p + V}{C_p} \qquad (19)$$

from which

$$C_p = \frac{V}{\left(\frac{\partial T}{\partial P}\right)_S - \mu} \qquad (20)$$

Equation 20 is very valuable for establishing the value of $C_p$ as a function of the temperature at some particular pressure. The values of $C_p$ thus obtained may be used as the absolute values of heat capacity $C_{p_o}$ in Equation 6. Because of the experimental difficulties, it is usually not employed at pressures greatly exceeding atmospheric.

The actual evaluation of $C_p$ from experimental data is somewhat difficult, because over a finite temperature drop $(\Delta T/\Delta P)_S \neq (\partial T/\partial P)_S$. Sage and Lacey (3) have worked out a method by which $C_p$ can be obtained quite accurately if it is assumed that $(\partial C_p/\partial P)_S$, $(\partial \mu/\partial P)_S$, and $(\partial Z/\partial P)_S$ may be considered constant in the range in which the expansion occurs. If this is the case, average values of $\mu$, $C_p$, and Z may be used in Equation 11. Since the measurement of $(\partial T/\partial P)_S$ represents a finite temperature difference for a finite isentropic expansion, we may write:

$$\Delta T = T_2 - T_1 = \int_{P_1}^{P_2} \left(\frac{\partial T}{\partial P}\right)_S dP \tag{21}$$

Assuming that $(\partial Z/\partial P)_T$ is constant at low pressures, the value of V can readily be obtained as a function of the pressure at any one temperature by the relation:

$$V = \left[1 + \int_0^P \left(\frac{\partial Z}{\partial P}\right)_T dP\right]\frac{bT}{P} \tag{22}$$

Substitution of $(\partial T/\partial P)_S$ in terms of $\mu$, $C_p$, and V into Equation 21 gives:

$$T_2 - T_1 = \int_{P_1}^{P_2} \left(\frac{V}{C_p} + \mu\right) dP \tag{23}$$

The values of $\mu$, $C_p$, and V in this expression must be evaluated along the isentropic path because they are functions of the temperature as well as the pressure. Since $\mu$ and $C_p$ will change only slightly over the temperature and pressure range involved in the finite expansion, average values may be taken, giving upon substitution of Equation 13 into Equation 14:

$$T_2 - T_1 = \int_{P_1}^{P_2} \left\{ \frac{\left[ 1 + \int_0^P \left(\frac{\partial Z}{\partial P}\right)_{T_m} dP \right] \frac{bT_m}{P}}{C_{P_m}} + \mu_m \right\} dP \qquad (24)$$

where the subscript m indicates that the mean value is assumed. Integrating the inner portion of the equation, it becomes:

$$T_2 - T_1 = \int_{P_1}^{P_2} \left[ \frac{bT_m}{PC_{P_m}} + \frac{bT_m}{C_{P_m}} \left(\frac{\partial Z}{\partial P}\right)_T + \mu_m \right] dP \qquad (25)$$

from which

$$T_2 - T_1 = \frac{bT_m}{C_{P_m}} \log_e \frac{P_2}{P_1} + \frac{bT_m}{C_{P_m}} \left(\frac{\partial Z}{\partial P}\right)_{T_m} (P_2 - P_1) + \mu_m (P_2 - P_1) \qquad (26)$$

Solving for $C_{p_m}$ then gives:

$$C_{P_m} = \frac{bT_m \log_e \frac{P_1}{P_2} + bT_m \left(\frac{\partial Z}{\partial P}\right)_{T_m} (P_1 - P_2)}{T_1 - T_2 - \mu (P_1 - P_2)} \qquad (27)$$

Equation 27 permits the approximate evaluation of $C_p$ at the mean temperature and pressure of the expansion but does not offer an exact means of evaluating it.

## Conclusion

In the foregoing discussion, only the most fundamental relations connecting the Joule-Thomson coefficient to other thermodynamic quantities have been discussed. Many other useful relations may be derived, but it is believed that the ones presented offer the greatest utility when it is desired to establish the thermodynamic properties of a gas of constant composition with respect to pressure and temperature. It should be realized that these methods do not offer a means of evaluating the change in such properties as enthalpy, internal energy, and entropy with composition. They are therefore primarily of value only in evaluating changes with respect to pressure and temperature and must be supplemented with other data if values of enthalpy, internal energy, and entropy are to be evaluated as functions of the composition.

## NOMENCLATURE

| | |
|---|---|
| b | Specific gas constant (10.715/M) cubic feet per square inch per °F. |
| $C_p$ | Isobaric heat capacity, Btu. per lb. per °F. |
| H | Specific enthalpy, Btu. per lb.. |
| p | Latent heat of pressure variation, Btu. per lb., per lb.. per square inch. |
| M | Molecular weight. |
| P | Pressure, lbs. per square inch absolute. |
| q | Heat effect associated with an infinitesimal change in state, Btu. per lb.. |
| S | Specific entropy, Btu. per °F. absolute per lb.. |
| T | Absolute temperature, °F. absolute. |
| V | Specific volume, cubic feet per lb.. |
| Z | Compressibility factor $(P\ V/b\ T)$. |
| $\mu$ | Joule-Thomson coefficient $(\partial T/\partial P)_H$, °F. per lb. per square inch. |

Subscript m refers to arithmatic mean value.

Subscripts 1, 2, ... refer to states of the system.

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2. Roy W. Goranson, "Thermodynamics in Multicomponent Systems", Carnegie Institution of Washington, 10, (1930).

3. Sage, Webster, and Lacey, Ind. Eng. Chem., 29, 1309 (1937).

# THE POROUS THIMBLE METHOD OF DETERMINATION OF THE JOULE-THOMSON COEFFICIENT

Because of the fact that the Joule-Thomson coefficient may be used to advantage in the calculation of certain thermodynamic properties, it is essential that an accurate experimental method of determination be available. From the definition of the Joule-Thomson coefficient, it is apparent that some type of apparatus must be employed which will permit the gas to decrease in pressure without undergoing a change in enthalpy. At the same time, some means of measuring the decrease in pressure as well as the change in temperature must be provided.

The most widely used method of securing the isenthalpic change in pressure is to allow the gas to flow through a porous thimble in such a manner that the pressure and temperature may be measured on either side of the thimble. This method, if properly used, permits a very accurate determination of the Joule-Thomson effect. However, it should be recognized that the method is not absolutely correct because of certain physical limitations which cannot be entirely overcome by any known refinements.

## Effect of Changes in Velocity On the Accuracy of Measurement

In Figure 1 is shown a schematic diagram of a typical porous thimble of the type which might be used for this purpose. The gas enters the thimble from the outside and flows through the porous

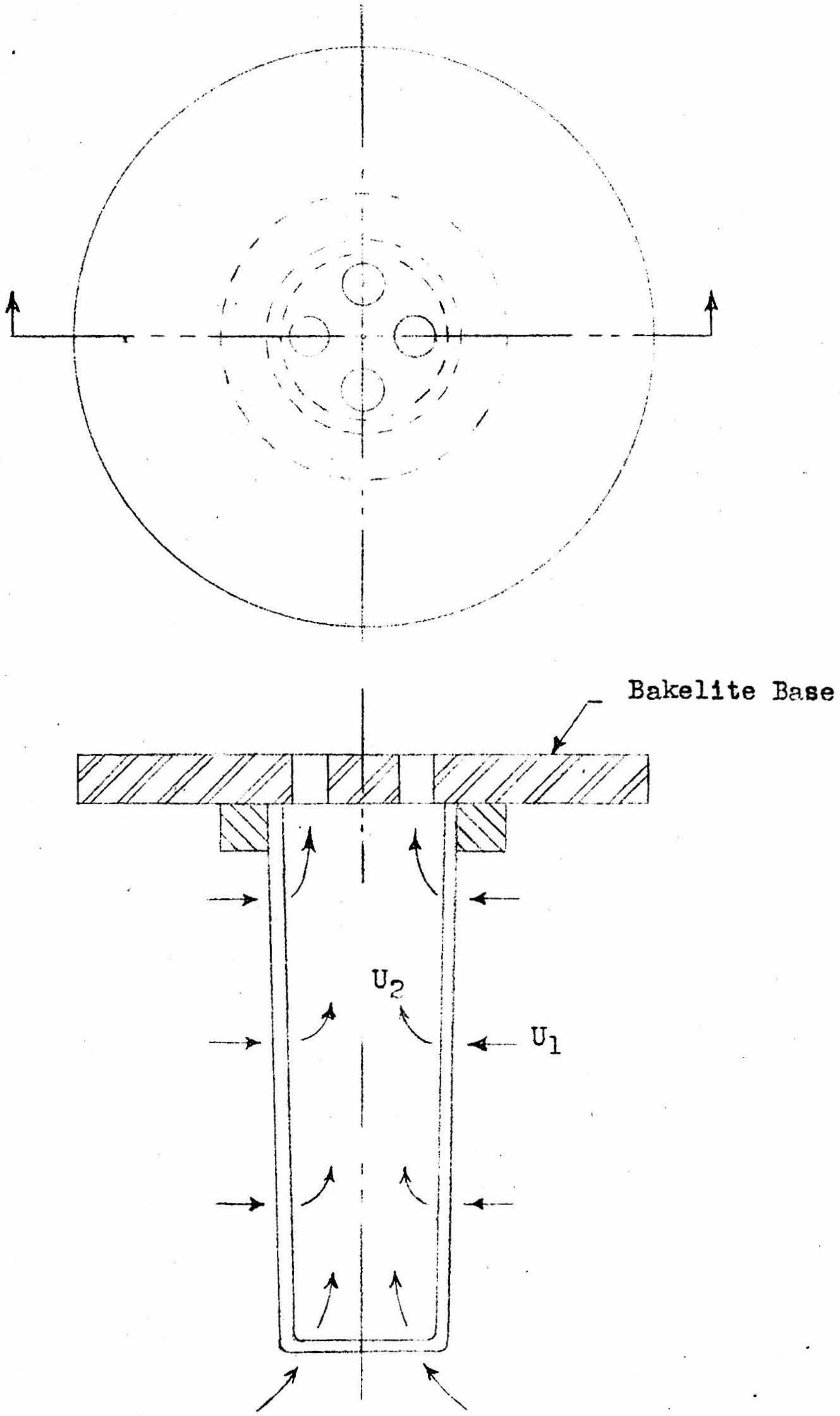

Figure 1. Diagram of Porous Thimble Showing Direction of Flow

thimble at a steady rate without the addition of external heat. From the law of conservation of energy an equation for a unit weight of gas may be written between any two sections perpendicular to the direction of flow as follows:

$$h_1 + E_1 + P_1 V_1 + \frac{U_1^2}{2g} + Q_{1-2} - W_{1-2} = h_2 + E_2 + P_2 V_2 + \frac{U_2^2}{2g} \qquad (28)^*$$

If it is assumed that the elevations of sections 1 and 2 are substantially equal and that $Q_{1-2}$ and $W_{1-2}$ are each equal to zero, Equation 28 may be written as:

$$H_1 + \frac{U_1^2}{2g} = H_2 + \frac{U_2^2}{2g} \qquad (29)$$

where H1 and $H_2$ are the specific enthalpies of the gas and $(U_1^2/2\ g)$ and $(U_2^2/2\ g)$ are the energies possessed by the molecules of the gas as a result of their group movement normal to the section at sections 1 and 2, respectively.

Equation 29 may also be written in the form:

$$\Delta H = \frac{1}{2g}\left(U_1^2 - U_2^2\right) \qquad (30)$$

For small finite changes in enthalpy, Equation 2, page 3, may be written as:

$$\Delta H = \left(\frac{\partial H}{\partial T}\right)_P \Delta T + \left(\frac{\partial H}{\partial P}\right)_T \Delta P \qquad (31)$$

Solving for $(\Delta T/\Delta P)$ gives:

$$\frac{\Delta T}{\Delta P} = \frac{\frac{\Delta H}{\Delta P} - \left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} \qquad (32)$$

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*Nomenclature for this section will be found on page 21.

which upon substitution of $-\mu C_p$ for $(\partial H/\partial P)_T$ and $C_p$ for $(\partial H/\partial T)_P$ reduces to the relation:

$$\mu = \frac{\Delta T}{\Delta P} - \frac{1}{C_p}\frac{\Delta H}{\Delta P} \tag{33}$$

In any porous thimble experiment, the term $(\Delta T/\Delta P)$ rather than $(\partial T/\partial P)_H$ must of necessity be measured. For this reason, it may be found necessary when appreciable changes in velocity occur to write for the Joule-Thomson coefficient:

$$\mu = \frac{\Delta T}{\Delta P} + \frac{1}{C_p}\frac{U_2^2 - U_1^2}{2g\,\Delta P} \tag{34}$$

If $(\Delta T/\Delta P)$ is a very small quantity, and the changes in velocity are large, the second term of Equation 34 may be of sufficient magnitude to affect the results appreciably. In cases where relatively large pressure differentials are being used to measure the Joule-Thomson effect in regions of high temperature and low pressure, this might easily be the case. Equation 34 offers a direct means of estimating the errors which might be involved in neglecting the effect of changes in velocity of the gas.

In the experimental work reported in this thesis, the term $(U_2^2 - U_1^2/2g\,\Delta P)$ was sufficiently small that it could be neglected without in any case introducing an error of more than a few hundredths of one per cent. For example, in measuring the Joule-Thomson coefficient of methane at a temperature of 220°F., the maximum velocity encountered on the downstream side of the porous thimble* was esti-

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* A detailed description of the apparatus employed for the measurement of the Joule-Thomson coefficient of methane will be found on page 23 of this thesis.

mated to be less than 2 feet per second with a pressure differential of approximately 13 pounds per sq. in. abs.. If it is assumed for purposes of approximation that the velocity of the gas on the upstream side of the thimble is zero, and that the specific heat of methane is 0.5 B.t.u. per lb. per °F., the second term of Equation 34 is numerically equal to:

$$\frac{1}{0.5} \cdot \frac{2^2}{778.64.34.13} = 0.0000123 \text{ °F. per pound per sq. in.}$$

Assuming the Joule-Thomson coefficient to be 0.02 °F. per lb. per sq. in., the error introduced by neglecting the effect of change in velocity would be only 0.06 per cent. Since this error was well within the experimental uncertainty involved in the measurements, the effects of any change of velocity could safely be neglected.

## Effect of Heat Transfer

Equation 34 is based upon the assumption that no energy is added to the gas in the form of heat between sections 1 and 2. If a quantity of heat $Q_{1-2}$ is added between the two sections, Equation 34 becomes:

$$\mu = \frac{\Delta T}{\Delta P} + \frac{1}{C_p} \frac{U_2^2 - U_1^2}{2g\,\Delta P} + \frac{Q_{1-2}}{C_p \Delta P} \qquad (35)$$

In most well designed apparatus the term $Q_{1-2}$ is so small that it can be entirely neglected. In the apparatus used for the determination of the coefficients reported in this thesis, the heat transferred to the gas from the surroundings was reduced to a negligible amount by the use of a double radiation shield around the thimble on upstream side, and a single radiation shield on the downstream side. The thimble itself was insulated from the surroundings by means of a bakelite base approximately one-fourth inch in thickness. The temperature difference was measured by means of a three-junction multilead copper-constantan thermocouple having alternate junctions fastened with Glyptal lacquer to aluminum foil radiation shields on either side of the thimble. These shields were placed sufficiently close to the thimble to give little time or opportunity for heat transfer between the gas and surroundings during its flow from one shield to the other. If the quantity of heat added during the process is not negligible, Equation 35 should be used for calculating $\mu$ from the experimental data.

Another factor which must not be overlooked is the fact that Equation 35 assumes that no heat interchange takes place between opposite surfaces of the porous thimble as a consequence of the temperature gradient established as a result of the Joule-Thomson effect of the gas flowing through the thimble. If the mass velocity of flow through the thimble is of insufficient magnitude to maintain the correct temperature difference, the readings obtained by this method will be too small. This means that the term $(\Delta T/\Delta P)$ in Equation 35 will not be as great as it should be, and that a correction must therefore be applied. This problem was investigated by Kennedy, Sage and Lacey (1) using the same apparatus as was used for the measurements reported in this thesis. Their investigation indicated that the effect was negligible, even for mass velocities much lower than any encountered during the experimental work here reported.

# NOMENCLATURE

| | |
|---|---|
| $C_p$ | Isobaric heat capacity, B.t.u. per lb. per °F. |
| E | Specific internal energy, B.t.u. per lb.. |
| g | Gravitational constant, 32.2 ft. per second per second. |
| H | Specific enthalpy, B.t.u. per lb. |
| h | Elevation above a given arbitrary datum, feet. |
| P | Pressure, lbs. per square inch absolute. |
| Q | Energy added to flowing fluid, B.t.u. per lb. |
| T | Absolute temperature, °F. absolute. |
| U | Velocity of flow, feet per second. |
| V | Specific volume, cubic feet per lb. |
| W | Work done by the flowing fluid on the surroundings, B.t.u. per lb. |

Subscripts 1 and 2 refer to sections 1 and 2 in Figure 1.

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# Phase Equilibria in Hydrocarbon Systems

## Joule-Thomson Coefficient of Methane[1]

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**The Joule-Thomson coefficient for gaseous methane was determined at temperatures from 70° to 220° F. and for pressures from atmospheric to 1,500 pounds per square inch. A comparison of volumetric data derived from these measurements with directly measured values has been included. The experimental results have been presented in tabular and graphical form.**

AN INDUSTRIAL need for accurate thermodynamic data relating to the lighter paraffin hydrocarbons has been increasing. The Joule-Thomson coefficient is a useful property in this connection, especially at pressures below 1,000 pounds per square inch. There is no experimental information known to the authors pertaining to such coefficients for methane. The present paper deals with an experimental investigation of the Joule-Thomson coefficient for methane at temperatures from 70° to 220° F. and at pressures from atmospheric to 1,500 pounds per square inch. This range of pressures and temperatures covers the major portion of the conditions encountered in petroleum production practice within which the Joule-Thomson coefficient is of outstanding value in ascertaining the volumetric and thermodynamic properties of methane.

The pressure-volume-temperature relations of a gas, taken in conjunction with the isobaric heat capacity at a single pressure throughout the temperature range in question, suffices to ascertain the Joule-Thomson coefficient as a function of state. However, high accuracy is required in the pressure-volume-temperature relations in order to ascertain the Joule-Thomson coefficient with even a reasonable degree of precision, especially at the lower pressures. The pressure-volume-temperature data of Kvalnes and Gaddy (*11*) and of Keyes and Burks (*9*) have been employed for this purpose. Perry and Herrmann (*12*) employed the Beattie-Bridgeman equation of state (*1*) with constants obtained from the data of Keyes and Burks to derive Joule-Thomson coefficients for methane over a wide range of pressures and temperatures. Edmister (*5*) calculated values of the Joule-Thomson coefficient for methane, employing residual methods (*4*) instead of an equation of state and using the data of Kvalnes and Gaddy (*11*). Edmister also presented a comparison of the results obtained by these two methods of calculation, and the agreement was not particularly good.

Eucken and Parts (*7*) measured the isobaric heat capacity of methane at atmospheric pressure from 65° to 400° F. Vold (*16*) recently calculated the isobaric heat capacity at infinite dilution from spectroscopic data. These latter values appear to be the best information available concerning the heat capacity of methane.

### Method

The information presented here was obtained by the direct determination of a change in temperature resulting from a change in pressure under conditions of constant enthalpy. The Joule-Thomson coefficient may be defined by the following thermodynamic relation:

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H \tag{1}$$

If it is assumed that $(\partial\mu/\partial T)_P$ and $(\partial\mu/\partial P)_T$ are constants over the range of pressure and temperature involved in a single measurement, Equation 1 may be rewritten as follows:

$$\mu = \left(\frac{\Delta T}{\Delta P}\right)_H \tag{2}$$

Under these conditions the measurement of the change in temperature resulting from a finite change in pressure under conditions of constant enthalpy suffices for a direct evaluation of the Joule-Thomson coefficient as a function of state as long as the changes in pressure and temperature are sufficiently small that the foregoing assumptions do not introduce appreciable uncertainty.

### Apparatus

A diagram of the apparatus as employed for these measurements is presented in Figure 1. It was a modification of the apparatus used in an earlier investigation of the Joule-Thomson coefficients of propane (*14*):

> The methane from supply tank *A* was introduced into the inlet of a special plunger-type compressor, *B*. The gas from the outlet of the compressor was passed through an oil separator and

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[1] This is the twenty-third paper in this series. Previous articles appeared in INDUSTRIAL AND ENGINEERING CHEMISTRY in 1934, 1935, 1936, 1937, and 1938.

then through calcium chloride and sodium hydroxide in chamber *C* in order to remove water and carbon dioxide, respectively. Chamber *C* also served as a small receiver for the compressor and helped to damp out the minor oscillations in pressure which otherwise existed. The gas then passed through a preliminary conditioning coil, *D*, located in the oil thermostat bath, *N*, which contained the other parts of the apparatus. The flow of gas from this conditioning coil was controlled manually by means of throttle valve *E*, and the minor changes in gas rate were taken care of automatically by means of magnetic valve *F*. The gas then passed through conditioning coil *G* where it was brought to thermal equilibrium with the thermostat. This conditioning coil was placed in a small buffer chamber within oil bath *N*.

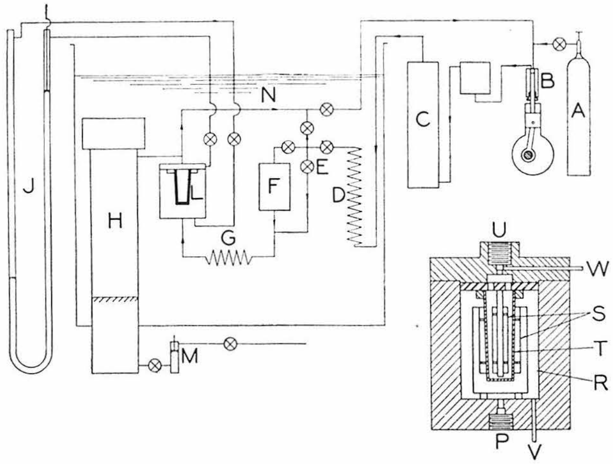

FIGURE 1. DIAGRAM OF APPARATUS

The gas was then allowed to pass through a porous radial-flow thimble within chamber *L* from which it returned to the compressor for recycling. A second receiver, *H*, was installed on the low-pressure side of the porous thimble in order to reduce any fluctuations in pressure.

The change in pressure due to the flow of gas through the porous thimble was measured by means of the mercury-in-steel manometer, *J*. The position of the mercury within the manometer was ascertained by means of an electrical contact, indicated in the right-hand arm of manometer *J*, which was connected through a suitable relay to a signal light. This contact also controlled magnetic valve *F* in order to maintain automatically a constant-pressure differential across the porous thimble in chamber *L*.

The absolute pressure existing within the apparatus was measured by means of a fluid-pressure balance which was connected to the apparatus through a mercury-oil interface at *M*. The pressure balance used in this investigation was calibrated against the vapor pressure of carbon dioxide at the freezing point of water; a value of 505.56 pounds per square inch (*2*) was taken as the vapor pressure of carbon dioxide at this temperature. The temperature of the gas entering the porous thimble was ascertained by means of a thermocouple placed within the buffer thermostat surrounding the final conditioning coil, *G*. This thermocouple was calibrated in place against mercury-in-glass thermometers which were recently calibrated by the National Bureau of Standards. The temperature of the bath was maintained nearly constant by means of a mercury-in-glass regulator placed within the agitated oil bath, *N*. Exploration with a thermocouple of low heat capacity indicated that the maximum temperature variation with time within the buffer chamber was less than 0.001° F. in any particular cycle of operation of the regulator. The temperature drift of the main thermostat was less than 0.003° F. per hour if no manual compensation was employed. Such compensation reduced the drift in temperature with time to a negligible value throughout the course of any given set of measurements.

A schematic diagram of the arrangement of the interior of chamber *L* is included as a part of Figure 1. The gas entered the bottom of the cell at *P*. It flowed upward around shield *R* and passed the secondary radiation shield, *S*, to which one set of differential thermocouple junctions was attached with Glyptal lacquer. The gas then flowed through thimble *T* and passed the inner secondary radiation shield, *S*, to which the other junctions of the differential thermocouples were attached. The gas passed out of the chamber through connection *U*. Manometer *J* was connected to the apparatus at points *V* and *W*. The arrangement of the inlet and outlet passages was such that negligible changes in pressure occurred between these manometer connections and the inner and outer surfaces of the thimble itself. The difference in pressure indicated by the manometer corresponded therefore, within small limits, to the actual change in pressure which occurred across the porous thimble. With the small changes in pressure employed throughout the investigation, the changes in velocity during the passage of the gas across the thimble were entirely negligible in so far as transfers of energy were concerned. The maximum velocity encountered in any part of chamber *L*, except in the pores of the thimble itself, was 2 feet per second. The total kinetic energy of the gas at this velocity amounted only to 0.00008 B. t. u. per pound, which would correspond to a temperature change of only 0.0002° F. Therefore, any minor changes in velocity between the entering and exit gas would have a neglible effect upon the resulting measurement of temperature or pressure difference. The same is true of changes in elevation.

The change in temperature of the gas resulting from its flow through the porous thimble was ascertained by a three-junction copper-constantan thermocouple. The junctions of this couple were attached to the inner and outer secondary radiation shields, *S*, by means of Glyptal lacquer. These shields were constructed of 0.004-inch aluminum foil and were mounted upon thin Micarta rings. This arrangement permitted the rapid attainment of thermal equilibrium between the gas and the thermocouples without increasing the heat capacity of the system unduly.

In operation, thermostat bath *N* was brought to the temperature of the investigation, and the entire contents of the bath were allowed to come to thermal equilibrium. The pressure within the system was then built up to the desired value by the admission of gas from supply tank *A*. Circulation of the gas was started at such a rate that a pressure change of approximately 12 pounds per square inch was obtained across porous thimble *T*. This constant pressure difference was maintained by means of magnetic valve *F*, and the resulting change in temperature for the particular state in question was ascertained by measurement of the electromotive force developed by the three-junction thermocouple described. The electromotive force was determined by means of a White potentiometer with a range of 10,000 microvolts. The uncertainty in this electromotive force measurement corresponded to not more than 0.0004° F. However, minor fluctuations in pressure within the apparatus reduced the precision of the temperature difference measurement to approximately 0.001° F.

After the change in temperature resulting from the measured change in pressure had been ascertained at a particular state, additional gas was introduced and the measurement repeated at

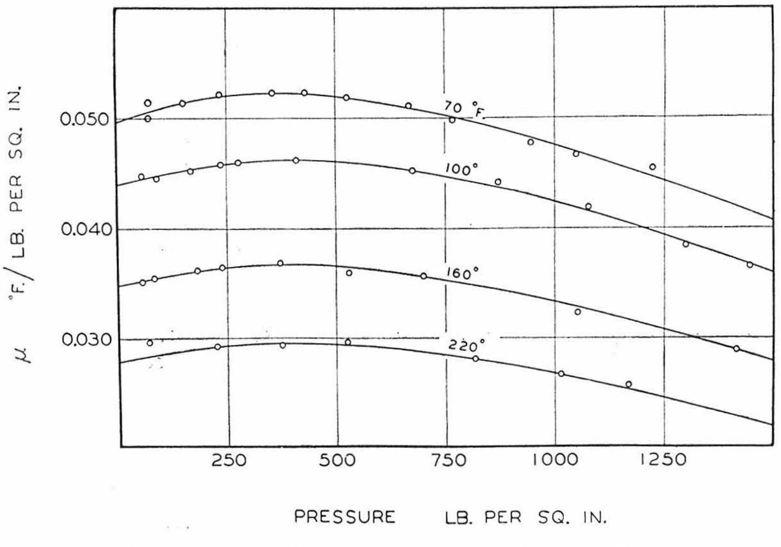

FIGURE 2. EXPERIMENTAL RESULTS FOR JOULE-THOMSON COEFFICIENT OF GASEOUS METHANE

a higher pressure. This process was continued until the entire range of pressures at a particular temperature had been investigated. At the conclusion of this set of measurements at a given temperature, the pressure was again decreased and a check value determined at a pressure not greatly different from atmospheric. A set of measurements of this nature was made at four temperatures between 70° and 220° F. The mean temperature and pressure existing within the thimble were employed in describing the state at which the measurement was made.

## Calibration

The primary measurements involved in the work were of values of the change in pressure and temperature due to the flow of the gas through the thimble. The former was ascertained by direct calibration of the mercury-in-steel manometer, *J*, against a mercury-in-glass manometer. The differences in mercury heights in the glass manometer were ascertained by means of a vertical-component cathetometer. The use of this device permitted the determination of the difference in mercury heights corresponding to a given location of the contact in the steel manometer with an uncertainty of not more than 0.1 per cent at the pressure differences that were employed for this work. The effect of pressure upon the calibration of the manometer was ascertained by a calculation of the deformation of the steel parts of the manometer and the change in volume of the mercury due to the maximum pressure encountered in these measurements. These calculations indicated a probable maximum change in the calibration of the manometer, due to a change of pressure from atmospheric to 1,500 pounds per square inch, of approximately 0.2 per cent. The manometer was incased in a metal jacket and its temperature was ascertained by means of a mercury-in-glass thermometer. Proper corrections were made to the indicated pressure difference to take into account the effect of small temperature changes upon the calibration of the manometer.

The three-junction thermocouple used in measuring the temperature change of the gas was calibrated throughout the temperature range against recently standardized mercury-in-glass thermometers. The calibration was made with sufficient precision so that the results were considered trustworthy within 0.2 per cent except at the highest temperature where uncertainties as large as 0.4 per cent were encountered.

In order that these measurements of the change in temperature due to a change in pressure might be made under conditions of constant enthalpy, it was necessary that no energy be lost from the thimble in the form of heat and that the changes in velocity and elevation between the two sides of the thimble be of negligible magnitude in so far as energy utilization was concerned. As was mentioned earlier, the changes in elevation and velocity were entirely negligible throughout all of the ranges of pressure and temperature covered in the present investigation. An estimation of the energy loss from the thimble due to temperature gradients to its surroundings indicated that this was also of negligible magnitude. However as an over-all check, the Joule-Thomson coefficient of air was determined at 100° F. The air used for this purpose was taken from the laboratory, and the carbon dioxide and water vapor were removed at the pressure of the measurement by means of the calcium chloride and sodium hydroxide in container *C* of Figure 1. A comparison of these results with those obtained by Roebuck (*13*) indicated a satisfactory agreement, except at the lowest pressures, in the neighborhood of atmospheric pressure. This agreement indicated that no systematic errors of large magnitude were involved in the operation of the apparatus.

## Precision of Measurement

It is difficult to estimate the over-all absolute accuracy of measurement that is attained in an investigation of this nature. The change in pressure across the porous thimble was determined with an error of not more than 0.3 per cent throughout the entire range of pressures and temperatures. The change in temperature was determined with an uncertainty of not more than 1 per cent after due allowance had been made for the fluctuations in pressure and temperature that resulted from slight irregularities in the control of the flow of gas through the apparatus. The temperature of the gas entering the porous thimble was known within 0.1° F. in relation to the international platinum scale. The pressure of the gas leaving the thimble was known with an uncertainty of not more than 2 pounds per square inch throughout the pressure range of this investigation and was determined with much greater accuracy at pressures below 200 pounds per square inch. The precision of the individual measurements and the consistency of results indicated a probable over-all error in measurement of not more than 1.5 per cent, but it is believed that systematic uncertainties may be involved which may decrease the absolute accuracy to some extent. For this reason it is believed that the values of the Joule-Thomson coefficient reported in the present paper may not be trustworthy to better than 3 per cent.

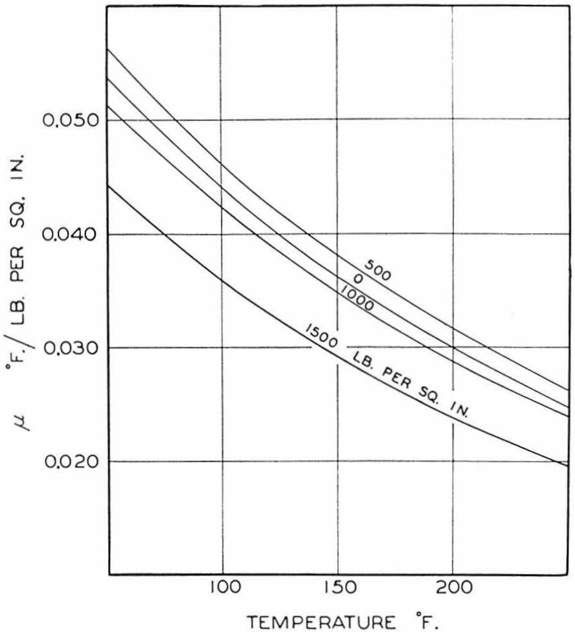

FIGURE 3. EFFECT OF TEMPERATURE UPON THE JOULE-THOMSON COEFFICIENT FOR METHANE

## Materials

The methane used in this investigation was obtained from the Buttonwillow Field in California and originally contained 0.1 per cent ethane or heavier hydrocarbons, and 0.3 per cent carbon dioxide. Careful combustion analyses have indicated that gas from this field contains a negligible amount of nitrogen or other gases of similar nature. The calcium chloride and sodium hydroxide in chamber *C* (Figure 1) removed the water and carbon dioxide in the gas at the pressure of the measurement. It is believed that the gas upon which the measurements were made contained less than 0.2 per cent of material other than methane. This degree of purity is adequate for measurements of this nature, and the impurities should not introduce any appreciable uncertainty in the measurements reported.

Table I. Joule-Thomson Coefficients and Isobaric Heat Capacities for Methane[a]

| | 70° F. | | 100° F. | | 130° F. | | 160° F. | | 190° F. | | 220° F. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $P$ | $\mu$ | $C_P$ | $\mu$ | $C_P$ | $\mu$ | $C_P$ | $\mu$ | $C_P$ | $\mu$ | $C_P$ | $\mu$ | $C_P$ |
| 0 | 0.0496 | 0.5302 | 0.0440 | 0.5400 | 0.0390 | 0.5505 | 0.0347 | 0.5620 | 0.0310 | 0.5748 | 0.0278 | 0.5880 |
| 250 | 0.0520 | 0.5545 | 0.0459 | 0.5613 | 0.0408 | 0.5692 | 0.0365 | 0.5782 | 0.0327 | 0.5888 | 0.0293 | 0.6005 |
| 500 | 0.0520 | 0.5810 | 0.0461 | 0.5845 | 0.0409 | 0.5893 | 0.0366 | 0.5958 | 0.0328 | 0.6040 | 0.0295 | 0.6137 |
| 750 | 0.0502 | 0.6100 | 0.0447 | 0.6095 | 0.0397 | 0.6107 | 0.0355 | 0.6140 | 0.0317 | 0.6200 | 0.0285 | 0.6279 |
| 1,000 | 0.0477 | 0.6410 | 0.0424 | 0.6359 | 0.0375 | 0.6332 | 0.0333 | 0.6333 | 0.0298 | 0.6364 | 0.0268 | 0.6423 |
| 1,250 | 0.0443 | 0.6728 | 0.0394 | 0.6638 | 0.0348 | 0.6571 | 0.0308 | 0.6534 | 0.0273 | 0.6538 | 0.0244 | 0.6570 |
| 1,500 | 0.0407 | 0.7073 | 0.0360 | 0.6917 | 0.0316 | 0.6800 | 0.0280 | 0.6723 | 0.0248 | 0.6703 | 0.0220 | 0.6720 |

[a] $P$ = pressure, lb./sq. in. abs.; $\mu$ = Joule-Thomson coefficient, ° F./lb./sq. in.; $C_P$ = isobaric heat capacity, B. t. u./lb./° F.

## Results

The experimental results are presented in Figure 2. These data indicate a maximum in the Joule-Thomson coefficient at any given temperature. This type of behavior is in accord with that found by Davis (*3*) and Kleinschmidt (*10*) for water at higher temperatures. At the higher pressures the Joule-Thomson coefficient decreases with an increase in pressure, and this effect is more pronounced at the lower temperatures. These data indicate a finite value for the Joule-Thomson coefficient at infinite dilution which is in accord with the kinetic theory and has been substantiated by several earlier investigations (*3, 8, 10*).

The effect of temperature upon the Joule-Thomson coefficient at several pressures is indicated in Figure 3. In general, the effect of temperature is not greatly different for the various pressures covered in this investigation. These data indicate a decrease in $-(\partial\mu/\partial T)_P$ with an increase in temperature.

Figure 4 presents a comparison of the present experimental measurements with the values obtained by Edmister (*5*) and by Perry and Herrmann (*12*) from pressure-volume-temperature measurements. The values calculated by Edmister are in satisfactory agreement with the present measurements except at the lower pressures where appreciable divergence occurs. The values calculated by Perry and Herrmann are consistently lower than the experimental values except at pressures in the vicinity of atmospheric. The digression of the values calculated by Edmister from the experimental measurements at the lower pressures is not surprising since it becomes increasingly difficult to determine Joule-Thomson coefficients accurately from specific heat and pressure-volume-temperature data as the pressure is decreased. Some of the differences may be explained by the use of earlier specific heat data which are not in particularly good agreement with more recent spectroscopic values. In general, the agreement is considered satisfactory since calculated Joule-Thomson coefficients are extremely sensitive to minor uncertainties in the pressure-volume-temperature relations upon which they are based.

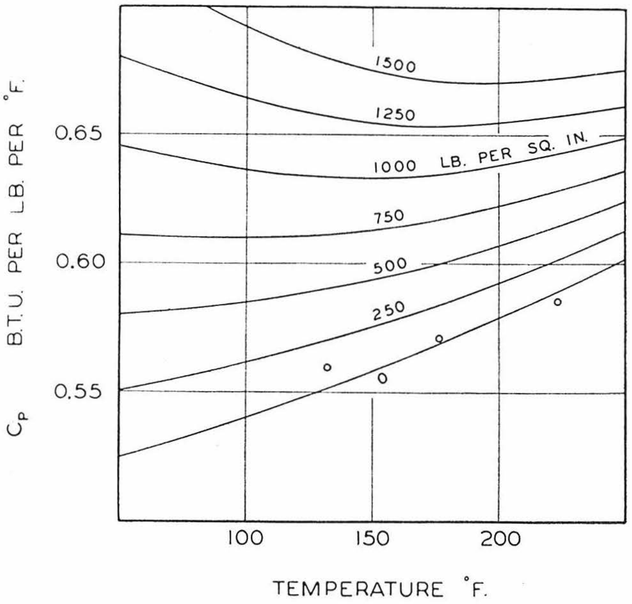

Figure 5. Isobaric Heat Capacity for Gaseous Methane

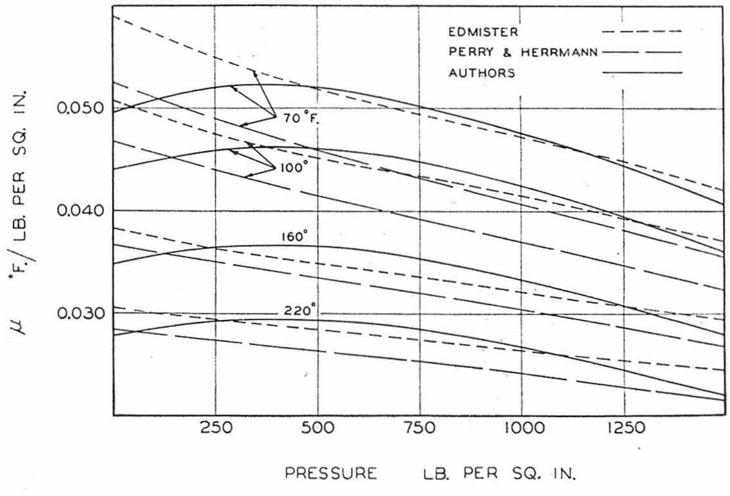

Figure 4. Comparison of the Joule-Thomson Coefficients Obtained by Various Investigators

The experimental Joule-Thomson coefficients are recorded in Table I as a function of pressure for six temperatures between 70° and 220° F. These tabulated values do not differ more than one per cent from any of the experimentally determined values and therefore represent the data well within its precision of measurement.

## Derived Quantities

The Joule-Thomson coefficient is useful in an evaluation of the isothermal change in the isobaric heat capacity with change in pressure. This quantity is rather sensitive to minor uncertainties in pressure-volume-temperature relations when based upon them. The Joule-Thomson coefficient is related to the isothermal change in the isobaric heat capacity by means of the following equation:

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -\mu\left(\frac{\partial C_P}{\partial T}\right)_P - C_P\left(\frac{\partial \mu}{\partial T}\right)_P = -\left(\frac{\partial \mu C_P}{\partial T}\right)_P \quad (3)$$

Values of the isobaric heat capacity as a function of temperature at some one pressure are necessary to solve Equation 3 by trial in order to obtain values of $C_P$ as a function of state. The spectroscopic values for infinite dilution recently re-

TABLE II. ISOTHERMAL CHANGES IN ENTHALPY FOR METHANE

| P, Lb./Sq. In. Abs. | Enthalpy, B. T. U. per Pound: 70° F. Edmister | 70° F. Authors | 100° F. Edmister | 100° F. Authors | 130° F. Edmister | 130° F. Authors | 160° F. Edmister | 160° F. Authors | 190° F. Edmister | 190° F. Authors | 220° F. Edmister | 220° F. Authors |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 500 | 14.31 | 15.17 | 12.83 | 13.38 | 11.54 | 12.20 | 10.42 | 11.23 | 9.55 | 10.19 | 8.74 | 9.41 |
| 1000 | 29.59 | 30.04 | 26.41 | 26.61 | 23.62 | 24.09 | 21.26 | 21.85 | 19.34 | 20.06 | 17.66 | 18.26 |
| 1500 | 44.49 | 44.60 | 39.44 | 39.29 | 34.99 | 35.19 | 31.29 | 31.34 | 28.25 | 28.88 | 25.66 | 26.39 |

TABLE III. COMPRESSIBILITY FACTORS FOR METHANE

| P, Lb./Sq. In. Abs. | 70° F. K. & G.[a] | 70° F. Authors | 100° F. K. & G. | 100° F. Authors | 130° F. K. & G. | 130° F. Authors | 160° F. K. & G. | 160° F. Authors | 190° F. K. & G. | 190° F. Authors | 220° F. K. & G. | 220° F. Authors |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| 200 | 0.975 | 0.976 | 0.980 | 0.980 | 0.984 | 0.984 | 0.986 | 0.987 | 0.988 | 0.989 | 0.991 | 0.991 |
| 400 | 0.950 | 0.951 | 0.961 | 0.960 | 0.968 | 0.968 | 0.974 | 0.974 | 0.978 | 0.979 | 0.983 | 0.983 |
| 600 | 0.926 | 0.927 | 0.942 | 0.941 | 0.953 | 0.952 | 0.962 | 0.961 | 0.969 | 0.969 | 0.975 | 0.975 |
| 800 | 0.904 | 0.904 | 0.924 | 0.923 | 0.939 | 0.938 | 0.951 | 0.950 | 0.960 | 0.960 | 0.968 | 0.968 |
| 1000 | 0.884 | 0.883 | 0.908 | 0.907 | 0.926 | 0.925 | 0.941 | 0.940 | 0.953 | 0.952 | 0.962 | 0.962 |
| 1250 | 0.861 | 0.861 | 0.891 | 0.890 | 0.913 | 0.912 | 0.931 | 0.930 | 0.945 | 0.944 | 0.956 | 0.956 |
| 1500 | 0.840 | 0.844 | 0.861 | 0.861 | 0.876 | 0.877 | 0.923 | 0.923 | 0.939 | 0.939 | 0.952 | 0.952 |

[a] Kvalnes and Gaddy (*11*).

ported by Vold (*16*) were employed by the authors in this connection. The isobaric heat capacity based upon these data is presented in Figure 5 as a function of temperature for several pressures. The circled experimental points shown for infinite dilution were taken from recent experimental measurements of the isobaric heat capacity of methane (*15*). It is believed that the trial solution of Equation 3 was carried out with sufficient precision to avoid significant errors from this source in the evaluation of the isobaric heat capacity as a function of state.

The values of isobaric heat capacity reported by Edmister were based in part upon the heat capacities at atmospheric pressure determined by Eucken and Parts (*7*) which are not in satisfactory agreement with the spectroscopic values of Vold (*16*). The latter values were employed in the present calculations. The discrepancy between these two sets of atmospheric heat capacity values explains for the most part the differences between the present values and those reported by Edmister. It is believed that the values of heat capacity which are recorded in a part of Table I are known with an uncertainty of not more than one per cent except that they are subject to possible later modifications of the spectroscopic value of the heat capacity at infinite dilution. This degree of accuracy is due primarily to the relatively small change in heat capacity with pressure. On this account only relatively low accuracy in ascertaining the change in heat capacity with pressure is required in order to establish the heat capacity at a particular state with the accuracy cited.

From a knowledge of the isobaric heat capacity and the Joule-Thomson coefficient, the isothermal enthalpy-pressure coefficient $(\partial H/\partial P)_T$ may be ascertained from the following general thermodynamic relation:

$$\left(\frac{\partial H}{\partial P}\right)_T = -\mu C_P \qquad (4)$$

The results of such a calculation are presented in a part of Table I along with values of the Joule-Thomson coefficient and the isobaric heat capacity.

These values of the isothermal enthalpy-pressure coefficient permit comparison of the present data with those determined by other investigators. The enthalpy at a given pressure may be ascertained by integrating the following expression graphically:

$$H_A = H_0 + \int_0^{P_A} \left(\frac{\partial H}{\partial P}\right)_T dP \qquad (5)$$

where $H_0$ = enthalpy at infinite dilution.

The results of this integration from infinite dilution to the pressure in question are presented in Table II, together with the values obtained by Edmister (*6*) in a generalization of the thermodynamic properties of the hydrocarbons based in part upon the law of corresponding states. These data agree satisfactorily at 1,500 pounds per square inch but show appreciable divergencies at the lower pressures. This indicates that the average value of the isothermal enthalpy-pressure coefficient as determined by the above-mentioned generalization over the range from 0 to 1,500 pounds per square inch was in agreement with the present measurement. However, a significant deviation in the detailed relation of this coefficient to pressure, as predicted from the two sources of information, was indicated by the disagreement of the values at the lower pressures.

Joule-Thomson coefficients in conjunction with specific heat data afford a satisfactory basis for determining the volumetric behavior of a gas as a function of temperature. One relation which can be used for the purpose is given in Equation 6:

$$\left(\frac{\partial Z}{\partial T}\right)_P = -\frac{P}{bT^2}\left(\frac{\partial H}{\partial P}\right)_T \qquad (6)$$

In order to determine the value of the compressibility factor, $Z$, as a function of temperature, it is necessary to have information concerning the value of $Z$ at one temperature at the pressure in question. Upon this basis the compressibility factor may be ascertained as a function of temperature by integration of the following equation:

$$Z_B = Z_A - \int_{T_A}^{T_B} \frac{P}{bT^2}\left(\frac{\partial H}{\partial P}\right)_T dT \qquad (7)$$

For present purposes the measurements by Kvalnes and Gaddy (*11*) at 212° F. were taken as a reference basis. From these data the values of the compressibility factor were calculated at other temperatures by means of Equation 7, and the values are recorded in Table III. Values at these temperatures interpolated directly from the measurements of Kvalnes and Gaddy were also included for comparison. The agreement is good throughout the range of temperatures and pressures covered by this investigation. This agreement emphasizes the fact that an extraordinarily high accuracy is required in the pressure-volume-temperature relations when used to establish values of the isothermal enthalpy-pressure coefficient at relatively low pressures. Although the volume-temperature relations of methane based upon the measurements of Kvalnes and Gaddy are in excellent agreement with values computed from the authors' data, the isothermal enthalpy-pressure coefficients computed from the same source are in disagreement by almost 10 per cent from the values based upon the Joule-Thomson coefficients reported in this paper.

## Acknowledgment

This investigation was carried out as a part of a general program of research being conducted by Research Project 37 of the American Petroleum Institute. The financial assistance and cooperation of the institute which made this work possible are acknowledged. The Southern California Gas Company furnished the supply of methane used in this study.

## Nomenclature

$C_P$ = isobaric heat capacity, B. t. u./lb./° F.
$T$ = temperature, ° F. abs.
$P$ = pressure, lb./sq. in. abs.
$H$ = enthalpy, B. t. u./lb.
$\mu$ = Joule-Thomson coefficient, ° F./lb./sq. in.
$b$ = specific gas constant (per lb.)
$Z$ = compressibility factor ($PV/bT$)

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# PHASE EQUILIBRIA IN HYDROCARBON SYSTEMS

# JOULE-THOMSON COEFFICIENT OF GASEOUS MIXTURES OF METHANE AND ETHANE*

By

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## Abstract

Joule-Thomson coefficients for three mixtures of methane and ethane were determined experimentally at pressures from 40 to 1500 pounds per square inch absolute at four temperatures between 70° and 220° F.. From these and other published data the isobaric heat capacity of the mixtures under these conditions was calculated. The experimental and calculated results are presented in tabular form.

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There does not appear to be experimental information available relating to the Joule-Thomson coefficient of any gaseous binary hydrocarbon mixtures in the range of pressures and temperatures that are commonly encountered in production practice. This coefficient is useful in establishing the thermodynamic behavior of

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* This article has been accepted for publication by the Editors of "Industrial and Engineering Chemistry".

gaseous mixtures, especially at pressures below 1000 pounds per square inch. The present investigation involved the measurement of the Joule-Thomson coefficient of three mixtures of methane and ethane at four temperatures between 70° and 220° F. and at pressures from 40 to 1500 pounds per square inch. Although the range of pressures does not include many of the conditions encountered in petroleum production practice, it does cover the majority of the conditions in which the Joule-Thomson coefficient is especially useful in ascertaining the thermodynamic behavior of gaseous systems of constant composition.

Perry and Herrmann (11) computed the Joule-Thomson coefficient of mixtures of methane and nitrogen employing the Beattie-Bridgeman equation of state (2,3). The constants of this equation were obtained by the method proposed by Beattie (1) for the methane-nitrogen system. These appear to be the only Joule-Thomson coefficients for binary systems containing a paraffin hydrocarbon that are available. Pattee and Brown (10) determined throttling curves for a "painter's naphtha". Values of the Joule-Thomson coefficient for a natural gas have been reported (14).

Recently experimental data have appeared relating to the Joule-Thomson coefficient of methane (6) which are in good agreement with existing pressure-volume-temperature data (9). The isobaric heat capacity of methane at infinite dilution has been calculated from spectroscopic data by Vold (16). The Joule-Thomson coefficients of ethane have been experimentally investigated (15) at pressures up to 600 pounds per square inch throughout the temperature range from 70° to 220° F.. Eucken and Parts (8) have measured the isobaric heat capacity of ethane at atmospheric pressure. These latter measurements are in reasonable agreement with the values calculated by Beeck (5).

## Materials

The methane employed in this study was obtained from the Buttonwillow Field in California and contained 0.05 mole per cent ethane or heavier hydrocarbons and 0.3 mole per cent carbon dioxide. Before use in the apparatus the gas was circulated through a chamber containing calcium chloride and sodium hydroxide to remove water and carbon dioxide, respectively. It is believed that the methane as utilized in the measurements contained less than 0.2 mole per cent of impurities.

The ethane used was obtained from the Carbide and Carbon Chemicals Corporation and a low temperature fractionation analysis indicated that it contained 0.8 mole per cent propane and 0.7 mole per cent ethylene and air. This analysis was further substantiated by the excellent agreement of the atmospheric density calculated from it with the experimentally measured value. This material was used in the experimental study without further purification except drying at elevated pressures over calcium chloride. It is believed that the impurities present in the methane and ethane are sufficiently small to introduce no significant uncertainty in the measurements reported.

## Method

The experimental information presented in this paper was obtained by measurement of the change in temperature resulting from a small change in pressure under conditions of constant enthalpy. If the change in pressure is sufficiently small that the quantities $(\partial\mu/\partial T)_P$ and $(\partial\mu/\partial P)_T$ may be considered to be constants during the change, this measurement affords a direct evaluation of the Joule-Thomson coefficient as indicated in the following expression:

$$\left(\frac{\Delta T}{\Delta P}\right)_H = \left(\frac{\partial T}{\partial P}\right)_H = \mu \qquad (1)$$

The use of relatively small changes in pressure (12 pounds per square inch in the case of the present measurements) permits the direct evaluation of the Joule-Thomson coefficients as a function of state and avoids the necessity of differentiating throttling curves.

The apparatus that was employed in the present investigation has been described (6,13) in detail. In principle, it consisted of a porous thimble through which the gas was allowed to flow radially under carefully controlled conditions. The change in pressure was measured by means of a mercury-in-steel manometer connected to the gas spaces on each side of the porous thimble.

The resulting temperature change was determined by a three-junction, three-wire copper-constantan thermocouple which was attached to aluminum shields in the gas spaces on each side of the porous thimble. The chamber containing the porous thimble was immersed in an oil bath whose temperature did not drift more than 0.002° F. per hour. The gas was circulated through the thimble by means of a special plunger-type compressor which was operated with a minimum of lubrication. Castor oil was employed for this purpose because of the smaller solubility of methane and ethane in this oil than in a mineral lubricating oil.

The mixtures of methane and ethane were prepared in a separate container at approximately the desired composition. The gas was then introduced into the apparatus and samples were withdrawn for analysis at intervals during the course of a set of measurements at a particular temperature. The composition of the gas was determined by its density near atmospheric pressure at 32.00° F.. The density was determined by weighing an evacuated glass bulb of approximately 0.02 cubic foot capacity against a nearly identical tare and determining the increase in weight due to filling the bulb with the gas in question to an accurately measured pressure at 32.00° F.. The pressure existing within the bulb was ascertained by means of a mercury-in-glass manometer. The difference in mercury height in the manometer was determined by a vertical-component cathetometer with an uncertainty of not more than one part in five thousand. It is believed that the density of the gas samples was determined with an error of not more than 0.2 per cent. The density of the methane and ethane used in making up the gas mixtures was also determined and found to be in satisfactory agreement in the two cases with values based upon measurements of Kvalnes and Gaddy (9) and Beattie and coworkers (4), respectively. It was necessary, however, to correct the measured density of the sample of ethane for the small amount of impurities present in order to obtain satisfactory agreement with Beattie's measurements. It is believed that the composition of the mixtures was established with an uncertainty of not more than 0.4 per cent by the use of the additive volume relationship and the measured density. As a check on this method, the composition of one mixture was determined by means of a low temperature fractionation analysis and was found to be in satisfactory agreement with the composition calculated from the density measurements. No measurement change in the composition of the gas in the apparatus occurred due to the selective solubility of the methane and ethane in the small amount of castor oil used in the lubrication of the compressor.

It is believed that the change in temperature due to the flow of gas through the porous thimble was established within 0.001° F.. The change in pressure was determined with an uncertainty of not more than 0.2 per cent. However, due to fluctuations in the conditions of flow and the periodic variation of bath temperature, there may be an absolute uncertainty of measurement as great as 1.5 per cent in the final smoothed experimental results.

## Results

The experimental results obtained for a mixture containing 55.5 weight per cent (40.0 mole per cent) ethane are presented in Figure 1. These data indicate a maximum in the Joule-Thomson coefficient similar to that found for methane. In this instance, however, the maximum occurs at a somewhat higher pressure and is followed by a much more rapid decrease in the coefficient with an increase in pressure at the lower temperature.

Figure 2 indicates the variation in the Joule-Thomson coefficient with temperature for the above-mentioned mixture of methane and ethane. At the higher pressures and lower temperatures, There is a decrease in the coefficient with a decrease in temperature. This behavior is in agreement with that found by Roebuck (12) for air and Burnett (7) for carbon dioxide. The rapid changes in the Joule-Thomson coefficient with environment at the lower temperatures and higher pressures increase the experimental uncertainty somewhat and it is believed that the coefficients at pressures above 1000 pounds per square inch for temperatures below 130° F. in the case of this mixture containing 55.5 weight per cent (40.0 mole per cent) ethane may involve an absolute uncertainty as large as 2 per cent.

In general, the experimental results for the two other mixtures containing 36.7 and 83.8 weight per cent (23.6 and 73.3 per cent) ethane are similar to those depicted in Figures 1 and 2 except that the maximum in the relationship of the Joule-Thomson coefficient to pressure occurs at a progressively lower pressure as the mole fraction of ethane is decreased and there is no maximum in the Joule-Thomson coefficient relation to temperature in the case of the mixture containing 36.7 weight per cent ethane. The detailed experimental results are recorded in Table I. together with the corresponding smoothed values and the percentage deviation of each of the individual measurements. The average deviation of all of the experimental values from the smoothed data was 0.61 per cent. This deviation is well within the estimated absolute uncertainty of 1.5 per cent. Smoothed values of the Joule-Thomson coefficient are recorded at even pressures, temperatures, and compositions in a part of Table II.

For convenience values of the Joule-Thomson coefficient for ethane have been included in Table II. These data are based upon experimental measurements (15) at pressures below 600 pounds per square inch and upon calorimetric heat capacity data and pressure-volume-temperature measurements (15) at the higher pressures.

The variation in the Joule-Thomson coefficient with composition for several pressures at a temperature of 100° F. is depicted in Figure 3. The values corresponding to pure methane were taken from recently published (6) experimental measurements. The consistency of these various sets of data is satisfactory. The effect of composition at other temperatures is similar to that shown in Figure 3, except that the magnitude of the variation is somewhat smaller at the higher temperatures, and there is no decrease in the Joule-Thomson coefficient with an increase in the mole fraction of ethane as is indicated in Figure 3 at the higher pressures.

## Isobaric Heat Capacity

The change in the isobaric heat capacity with pressure may be evaluated to advantage by use of the Joule-Thomson coefficient. The methods employed for this purpose have already been described (6) and involve the solution of the following equation:

$$\left(\frac{\partial C_P}{\partial P}\right)_{T,n} = -\left(\frac{\partial \mu C_P}{\partial T}\right)_{P,n} \qquad (2)$$

A knowledge of the isobaric heat capacity at one pressure as a function of temperature is required in order to establish the value of this quantity at other pressures from Equation 2. The measurements of Vold (16) for methane together with the experimentally determined values of Eucken and Parts (8) for ethane have been employed in the evaluation of the isobaric heat capacity of the mixtures of methane and ethane at infinite dilution. The heat capacity of the mixtures at infinite dilution may be evaluated from the heat capacity of the components by means of the following equation:

$$C_p = n_1 C_{p_1} + (1 - n_1) C_{p_2} \tag{3}$$

Smoothed values of the isobaric heat capacity at a series of pressures, temperatures, and compositions are recorded in a part of Table II. It is believed that the isobaric heat capacity at pressures below 1000 pounds per square inch has been established with an uncertainty of not more than 1 per cent except for possible uncertainty in the values chosen for the heat capacity at infinite dilution. At pressures above 1000 pounds per square inch the uncertainty in the evaluation of $(\partial C_p/\partial P)_{T,n}$ becomes somewhat greater. This is reflected in less accurate values of the isobaric heat capacity at the higher pressures where errors as large as 3 per cent may be encountered.

The variation in the isobaric heat capacity with temperature at several pressures is presented in Figure 4 for a mixture containing 65.2 weight per cent (50.0 mole per cent) ethane. The rather complicated behavior indicated is to be expected since the mixture is not far above its cricondentherm at the lower temperatures included in Figure 4. The effect of composition upon the isobaric heat capacity of the methane-ethane system at 100° F. is depicted in Figure 5. In this figure values of the isobaric heat capacity for pure methane and ethane were taken from recent publications (6, 15) relating to the Joule-Thomson coefficients and thermodynamic properties of the two substances. The values of the isobaric heat capacity for ethane at the higher pressures involve a somewhat larger uncertainty than exists in the other values. However, the consistency of the data is considered satisfactory since the proximity of the critical state of ethane at the lower temperatures makes the accurate experimental evaluation of the isobaric heat capacity for ethane in this region difficult.

A knowledge of the isobaric heat capacity and the Joule-Thomson coefficient is sufficient to determine the isothermal enthalpy-pressure coefficient as indicated in the following expression:

$$\left(\frac{\partial H}{\partial P}\right)_{T,n} = -\mu C_P \qquad (4)$$

Values of the isothermal enthalpy-pressure coefficient are presented in Figure 6 as a function of composition for several pressures at a temperature of 160° F.. These data indicate a progressive increase in the enthalpy-pressure coefficient with an increase in the weight fraction of ethane at the lower pressures. The rapid change in this derivative at compositions in the vicinity of pure ethane for a temperature of 160° F. is to be expected since the isothermal enthalpy-pressure coefficient is infinite at the critical state.

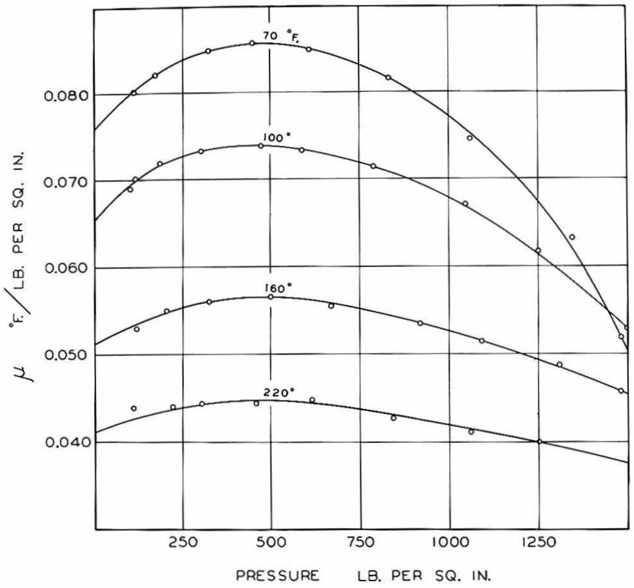

Figure 1. Joule-Thomson Coefficient for a Mixture of Methane and Ethane Containing 55.5 weight per cent Ethane.

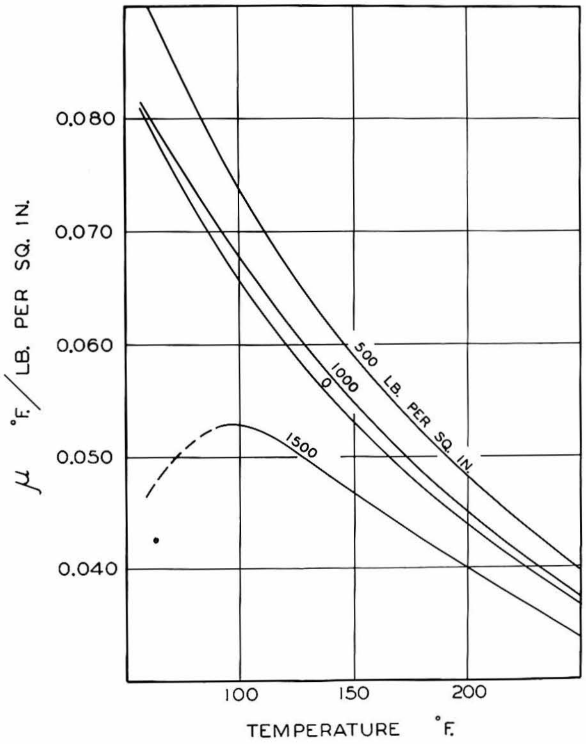

Figure 2. Effect of Temperature upon the Joule-Thomson Coefficient of a Mixture Containing 55.5 weight per cent Ethane.

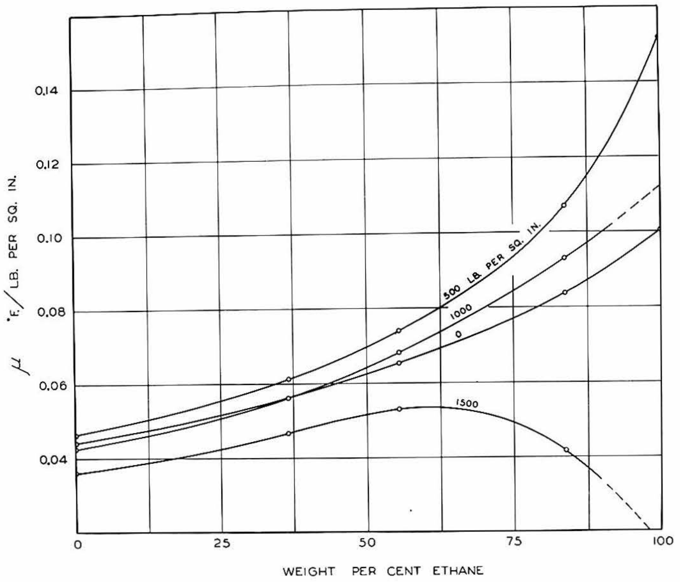

Figure 3. Effect of Composition upon The Joule-Thomson Coefficient at 100° F.

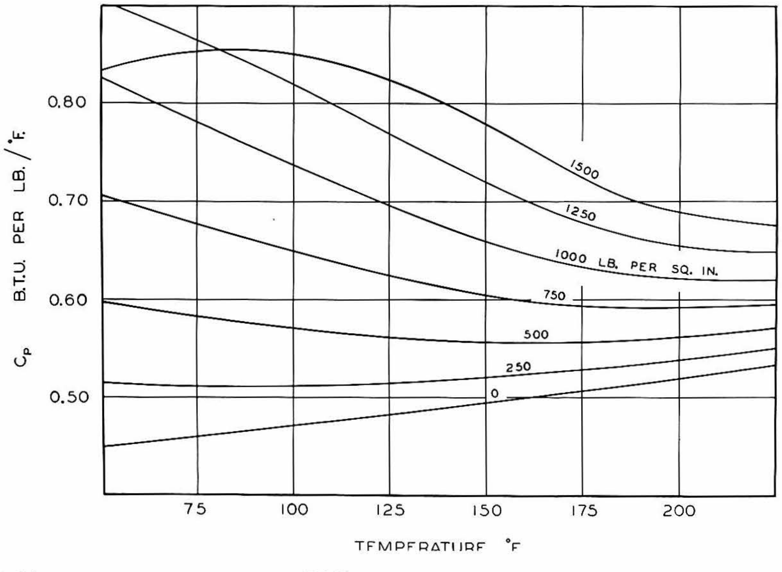

Figure 4. Heat Capacity for a Mixture Containing 65.2 weight per cent Ethane.

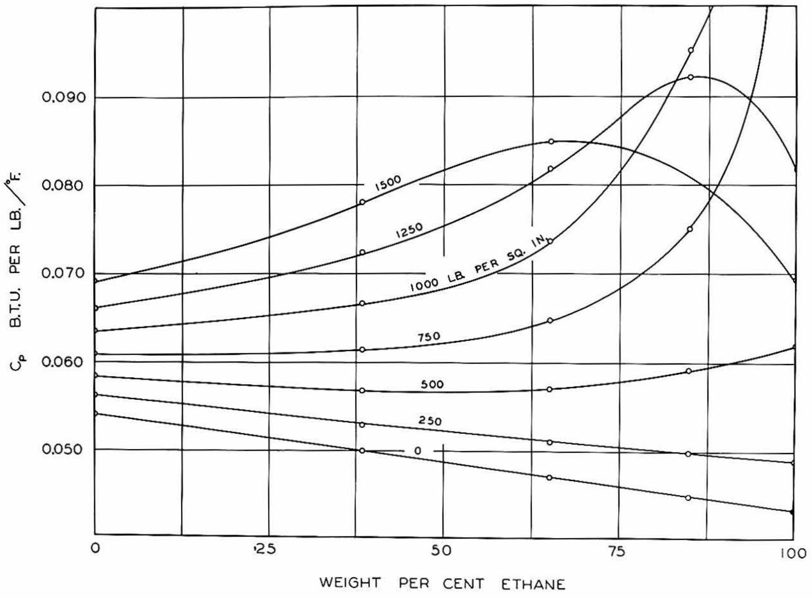

Figure 5. Effect of Composition upon the Isobaric Heat Capacity at 100° F.

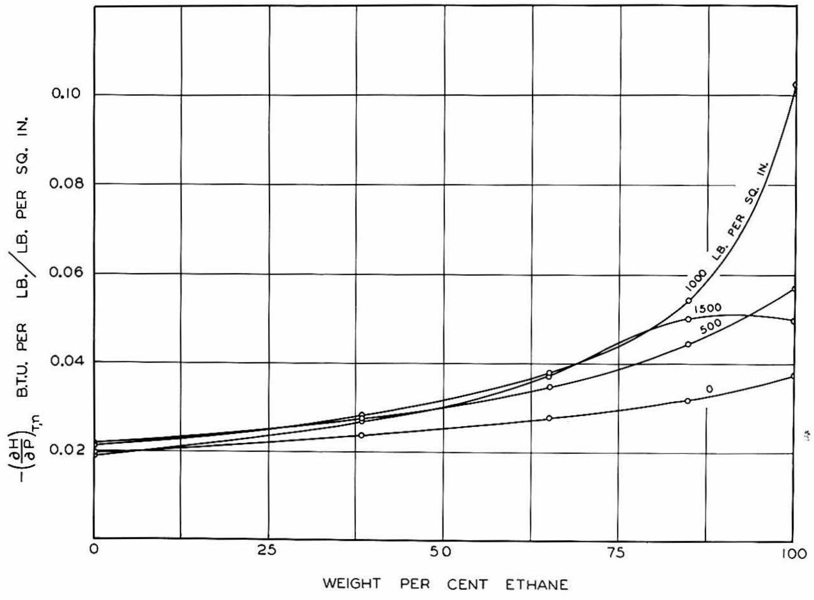

Figure 6. Effect of Composition upon the Isothermal Enthalpy-Pressure Coefficient at 160° F.

TABLE I. JOULE-THOMSON COEFFICIENT OF THE METHANE-ETHANE SYSTEM

| Temp. °F. | 36.7 Weight Per Cent Ethane (23.6 Mole Per Cent) | | | | 55.5 Weight Per Cent Ethane (40.0 Mole Per Cent) | | | | 83.8 Weight Per Cent Ethane (73.3 Mole Per Cent) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pressure Lb/Sq.In. | Experimental | Smoothed | Deviation Per Cent | Pressure Lb/Sq.In. | Experimental | Smoothed | Deviation Per Cent | Pressure Lb/Sq.In. | Experimental | Smoothed | Deviation Per Cent |
| 70 | 110.5 | 0.0670[a] | 0.0676[a] | -1.0 | 113.0 | 0.0802[a] | 0.0803[a] | -0.2 | 62.5 | 0.1061[a] | 0.1061[a] | 0.0 |
| | 195.5 | 0.0692 | 0.0692 | 0.0 | 173.0 | 0.0822 | 0.0822 | 0.0 | 126.7 | 0.1124 | 0.1118 | 1.0 |
| | 311.8 | 0.0702 | 0.0702 | 0.0 | 326 | 0.0848 | 0.0848 | 0.0 | 264 | 0.1191 | 0.1200 | -0.7 |
| | 463.0 | 0.0700 | 0.0700 | 0.0 | 450 | 0.0857 | 0.0857 | 0.0 | 415 | 0.1239 | 0.1248 | -0.7 |
| | 793.5 | 0.0672 | 0.0672 | 0.0 | 610 | 0.0849 | 0.0851 | -0.2 | 575 | 0.1274 | 0.1267 | -0.6 |
| | 1052.0 | 0.0627 | 0.0623 | 0.6 | 833 | 0.0816 | 0.0816 | 0.0 | 712 | 0.1260 | 0.1257 | 0.2 |
| | 1259 | 0.0576 | 0.0576 | 0.0 | 1060 | 0.0746 | 0.0746 | 0.0 | 952 | 0.0952 | - - | - - |
| | - - | - - | - - | - - | 1347 | 0.0632 | 0.0632 | 0.0 | 1062 | 0.0680 | - - | - - |
| | - - | - - | - - | - - | 1482 | 0.0519 | 0.0519 | 0.0 | - - | - - | - - | - - |
| 100 | 88.0 | 0.0583 | 0.0583 | 0.0 | 103.1 | 0.0689 | 0.0695 | -0.8 | 59.3 | 0.0892 | 0.0892 | 0.0 |
| | 171.2 | 0.0597 | 0.0596 | 0.1 | 117.2 | 0.0701 | 0.0699 | 0.3 | 164.0 | 0.0973 | 0.0970 | 0.3 |
| | 288 | 0.0609 | 0.0608 | 0.1 | 187.3 | 0.0719 | 0.0716 | 0.4 | 200 | 0.0986 | 0.0990 | -0.4 |
| | 437 | 0.0612 | 0.0612 | 0.0 | 305.8 | 0.0733 | 0.0733 | 0.0 | 328 | 0.1039 | 0.1039 | 0.0 |
| | 567 | 0.0607 | 0.0607 | 0.0 | 475 | 0.0738 | 0.0739 | -0.1 | 454 | 0.1058 | 0.1064 | -0.6 |
| | 762 | 0.0588 | 0.0590 | -0.3 | 588 | 0.0733 | 0.0734 | -0.2 | 637 | 0.1068 | 0.1070 | -0.2 |
| | 997 | 0.0560 | 0.0560 | 0.0 | 789 | 0.0715 | 0.0715 | 0.0 | 856 | 0.1036 | 0.1036 | 0.0 |
| | 1264 | 0.0521 | 0.0514 | 1.3 | 1047 | 0.0671 | 0.0669 | 0.3 | 964 | 0.0968 | 0.0964 | 0.4 |
| | 1492 | 0.0468 | 0.0468 | 0.0 | 1250 | 0.0617 | 0.0614 | 0.5 | 1202 | 0.0723 | 0.0724 | -0.1 |
| | - - | - - | - - | - - | 1498 | 0.0529 | 0.0529 | 0.0 | 1437 | 0.0479 | 0.0479 | 0.0 |
| 160 | 93.7 | 0.0434 | 0.0452 | -4.0 | 119.4 | 0.0529 | 0.0534 | -1.0 | 54.0 | 0.0678 | 0.0682 | -0.6 |
| | 211.3 | 0.0457 | 0.0464 | -1.5 | 205.0 | 0.0549 | 0.0547 | 0.4 | 206 | 0.0747 | 0.0738 | 1.2 |
| | 347.5 | 0.0468 | 0.0472 | -0.9 | 326.0 | 0.0560 | 0.0560 | -0.1 | 339 | 0.0767 | 0.0767 | 0.0 |
| | 554.2 | 0.0467 | 0.0476 | -1.7 | 500 | 0.0565 | 0.0566 | -0.1 | 529 | 0.0784 | 0.0784 | 0.1 |
| | 781.3 | 0.0466 | 0.0466 | 0.0 | 670 | 0.0555 | 0.0558 | -0.7 | 702 | 0.0781 | 0.0784 | -0.4 |
| | 996.4 | 0.0466 | 0.0448 | 4.1 | 918 | 0.0534 | 0.0535 | -0.2 | 932 | 0.0770 | 0.0762 | 1.1 |
| | 1275 | 0.0424 | 0.0414 | 2.4 | 1092 | 0.0515 | 0.0515 | -0.1 | 1046 | 0.0739 | 0.0739 | 0.0 |
| | 1508 | 0.0382 | 0.0382 | 0.0 | 1309 | 0.0487 | 0.0485 | 0.4 | 1262 | 0.0673 | 0.0673 | 0.0 |
| | - - | - - | - - | - - | 1482 | 0.0457 | 0.0457 | 0.0 | 1465 | 0.0580 | 0.0580 | 0.0 |
| 220 | 113.0 | 0.0359 | 0.0365 | -1.8 | 127.8 | 0.0442 | 0.0429 | 3.0 | 93.0 | 0.0568 | 0.0548 | 3.6 |
| | 129.9 | 0.0359 | 0.0366 | -2.1 | 222.0 | 0.0440 | 0.0437 | 0.7 | 218.3 | 0.0585 | 0.0576 | 1.6 |
| | 153.3 | 0.0364 | 0.0368 | -1.2 | 306.0 | 0.0443 | 0.0443 | 0.0 | 413 | 0.0598 | 0.0600 | -0.3 |
| | 167.0 | 0.0365 | 0.0369 | -1.0 | 459.0 | 0.0443 | 0.0448 | -1.1 | 613 | 0.0600 | 0.0607 | -1.1 |
| | 178.0 | 0.0370 | 0.0370 | 0.0 | 617.0 | 0.0448 | 0.0444 | -0.8 | 872 | 0.0599 | 0.0598 | 0.2 |
| | 315.2 | 0.0377 | 0.0377 | 0.0 | 843 | 0.0427 | 0.0431 | -1.0 | 1062 | 0.0586 | 0.0581 | 0.9 |
| | 323.0 | 0.0380 | 0.0377 | 0.7 | 1060 | 0.0411 | 0.0415 | -1.1 | 1247 | 0.0560 | 0.0554 | 1.1 |
| | 507 | 0.0376 | 0.0379 | -0.7 | 1252 | 0.0400 | 0.0400 | 0.0 | 1484 | 0.0611 | 0.0611 | 0.0 |
| | 763 | 0.0367 | 0.0369 | -0.5 | - - | - - | - - | - - | - - | - - | - - | - - |
| | 1026 | 0.0356 | 0.0353 | 0.7 | - - | - - | - - | - - | - - | - - | - - | - - |
| | 1292 | 0.0334 | 0.0333 | 0.3 | - - | - - | - - | - - | - - | - - | - - | - - |
| | 1544 | 0.0313 | 0.0313 | 0.0 | - - | - - | - - | - - | - - | - - | - - | - - |

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[a] Joule-Thomson Coefficient, °F. Per pound per square inch.

TABLE II. JOULE-THOMSON COEFFICIENT AND ISOBARIC HEAT CAPACITY OF THE METHANE-ETHANE SYSTEM

| Temp. °F. | Pressure Lb/sq.in. | Per Cent Ethane as Follows | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 38.4 Weight %<br>25.0 Mole % | | 65.2 Weight %<br>50.0 Mole % | | 84.9 Weight %<br>75.0 Mole % | | 100.0 Weight %<br>100.0 Mole % | |
| | | $\mu$ | $C_p$ | $\mu$ | $C_p$ | $\mu$ | $C_p$ | $\mu$ | $C_p$ |
| 70 | 0 | 0.0658[a] | 0.4867[b] | 0.0824 | 0.4564 | 0.0988 | 0.4341 | 0.115 | 0.4170 |
| | 250 | 0.0710 | 0.5267 | 0.0936 | 0.5109 | 0.1210 | 0.5010 | 0.149 | 0.484 |
| | 500 | 0.0713 | 0.5767 | 0.0961 | 0.5873 | 0.1296 | 0.6352 | 0.190 | 0.765 |
| | 750 | 0.0690 | 0.6368 | 0.0940 | 0.6823 | 0.1260 | 0.8847 | - - | - - |
| | 1000 | 0.0645 | 0.7061 | 0.0851 | 0.7892 | 0.0756 | - - | - - | - - |
| | 1250 | 0.0585 | 0.7806 | 0.0688 | 0.8739 | 0.0370 | - - | - - | - - |
| | 1500 | 0.0510 | 0.8506 | 0.0418 | 0.8490 | - - | - - | - - | - - |
| 100 | 0 | 0.0568 | 0.4989 | 0.0704 | 0.4702 | 0.0849 | 0.4492 | 0.102 | 0.4330 |
| | 250 | 0.0618 | 0.5294 | 0.0804 | 0.5108 | 0.1026 | 0.4987 | 0.127 | 0.489 |
| | 500 | 0.0622 | 0.5681 | 0.0826 | 0.5708 | 0.1092 | 0.5925 | 0.152 | 0.620 |
| | 750 | 0.0602 | 0.6146 | 0.0810 | 0.6480 | 0.1080 | 0.7515 | - - | - - |
| | 1000 | 0.0569 | 0.6676 | 0.0751 | 0.7372 | 0.0944 | 0.9530 | - - | - - |
| | 1250 | 0.0525 | 0.7244 | 0.0651 | 0.8191 | 0.0670 | - - | - - | - - |
| | 1500 | 0.0472 | 0.7804 | 0.0535 | 0.8495 | 0.0400 | - - | - - | - - |
| 130 | 0 | 0.0503 | 0.5116 | 0.0621 | 0.4845 | 0.0747 | 0.4646 | 0.0903 | 0.4493 |
| | 250 | 0.0541 | 0.5348 | 0.0695 | 0.5145 | 0.0878 | 0.5019 | 0.108 | 0.497 |
| | 500 | 0.0545 | 0.5646 | 0.0715 | 0.5595 | 0.0926 | 0.5661 | 0.124 | 0.585 |
| | 750 | 0.0531 | 0.5994 | 0.0702 | 0.6185 | 0.0923 | 0.6656 | 0.122 | 0.869 |
| | 1000 | 0.0505 | 0.6384 | 0.0660 | 0.6894 | 0.0864 | 0.8121 | 0.0968 | - - |
| | 1250 | 0.0470 | 0.6801 | 0.0598 | 0.7619 | 0.0705 | 0.9569 | 0.0654 | - - |
| | 1500 | 0.0430 | 0.7228 | 0.0523 | 0.8168 | 0.0550 | - - | 0.0310 | - - |
| 160 | 0 | 0.0450 | 0.5249 | 0.0554 | 0.4990 | 0.0664 | 0.4799 | 0.0805 | 0.4653 |
| | 250 | 0.0478 | 0.5440 | 0.0608 | 0.5226 | 0.0759 | 0.5097 | 0.0931 | 0.506 |
| | 500 | 0.0484 | 0.5667 | 0.0625 | 0.5550 | 0.0796 | 0.5564 | 0.104 | 0.575 |
| | 750 | 0.0474 | 0.5930 | 0.0614 | 0.5961 | 0.0796 | 0.6224 | 0.109 | 0.706 |
| | 1000 | 0.0452 | 0.6221 | 0.0584 | 0.6459 | 0.0758 | 0.7119 | 0.103 | 0.993 |
| | 1250 | 0.0421 | 0.6530 | 0.0543 | 0.7012 | 0.0684 | 0.8144 | 0.0791 | 1.358 |
| | 1500 | 0.0389 | 0.6848 | 0.0490 | 0.7546 | 0.0568 | 0.8979 | 0.0423 | 1.178 |
| 190 | 0 | 0.0401 | 0.5388 | 0.0496 | 0.5139 | 0.0591 | 0.4956 | 0.0718 | 0.4816 |
| | 250 | 0.0426 | 0.5555 | 0.0540 | 0.5342 | 0.0664 | 0.5214 | 0.0806 | 0.519 |
| | 500 | 0.0436 | 0.5743 | 0.0553 | 0.5594 | 0.0694 | 0.5569 | 0.0871 | 0.579 |
| | 750 | 0.0423 | 0.5950 | 0.0544 | 0.5894 | 0.0696 | 0.6026 | 0.0876 | 0.671 |
| | 1000 | 0.0404 | 0.6175 | 0.0520 | 0.6237 | 0.0670 | 0.6601 | 0.0820 | 0.817 |
| | 1250 | 0.0379 | 0.6410 | 0.0492 | 0.6616 | 0.0628 | 0.7271 | 0.0709 | 1.108 |
| | 1500 | 0.0353 | 0.6649 | 0.0452 | 0.6995 | 0.0546 | 0.7941 | 0.0525 | 1.118 |
| 220 | 0 | 0.0358 | 0.5534 | 0.0442 | 0.5292 | 0.0525 | 0.5115 | 0.0610 | 0.4979 |
| | 250 | 0.0380 | 0.5682 | 0.0480 | 0.5476 | 0.0584 | 0.5340 | 0.0700 | 0.534 |
| | 500 | 0.0395 | 0.5839 | 0.0492 | 0.5689 | 0.0610 | 0.5618 | 0.0730 | 0.588 |
| | 750 | 0.0378 | 0.6004 | 0.0482 | 0.5930 | 0.0614 | 0.5968 | 0.0718 | 0.665 |
| | 1000 | 0.0361 | 0.6177 | 0.0464 | 0.6198 | 0.0596 | 0.6398 | 0.0665 | 0.795 |
| | 1250 | 0.0341 | 0.6354 | 0.0441 | 0.6490 | 0.0560 | 0.6880 | 0.0586 | 0.933 |
| | 1500 | 0.0320 | 0.6537 | 0.0413 | 0.6783 | 0.0502 | 0.7380 | 0.0489 | 1.070 |

[a] Joule-Thomson coefficient, °F./ pound per square inch.

[b] Isobaric heat capacity, B.t.u. per pound / °F.

# ACKNOWLEDGMENT

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# NOMENCLATURE

$C_p$ = Isobaric heat capacity, B.t.u./lb./°F.

T = Temperature, ° F. abs.

P = Pressure, lb./sq. in. abs.

H = Enthalpy, B.t.u./lb.

$\mu$ = Joule-Thomson coefficient, °F./lb./sq. in.

$n_1$ = Weight fraction of component 1.

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# PHASE EQUILIBRIA IN HYDROCARBON SYSTEMS

# JOULE-THOMSON COEFFICIENTS FOR GASEOUS MIXTURES OF METHANE AND n-BUTANE*

By

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## Abstract

Joule-Thomson coefficients for five mixtures of methane and n-butane were determined experimentally for five temperatures between 70° and 310° F. at pressures between 50 and 1500 pounds per square inch absolute. From these data together with the isobaric heat capacity at infinite attenuation the heat capacities of several mixtures were calculated as functions of pressure and temperature. The results are presented in graphical and tabular form.

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The Joule-Thomson coefficient is of utility in the evaluation of the thermodynamic behavior of gaseous mixtures. This coefficient is especially useful at pressures below 1000 pounds per square inch. The present investigation involves the measurement

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of the Joule-Thomson coefficients of five mixtures of methane and n-butane at five temperatures between 70° and 310° F.. Results were obtained at pressures between 50 and 1500 pounds per square inch. These data permit the estimation of the Joule-Thomson coefficient for the methane-n-butane system throughout the gaseous region in the range of pressures where this coefficient is of greatest utility in the evaluation of the thermodynamic behavior of the system.

The Joule-Thomson coefficient for methane was measured recently (2) and is in good agreement with existing pressure-volume-temperature measurements (5). Perry and Herrmann (6) calculated the coefficient for methane by the use of the Beattie-Bridgeman equation of state (1) and these values are also in reasonable agreement with the experimental measurements (2). The isobaric heat capacity of methane at infinite attenuation,as calculated by Vold (10) from spectroscopic data, is in good agreement with values determined directly (8). The Joule-Thomson coefficient for n-butane has been measured experimentally (4) and the results are in satisfactory agreement with published volumetric data (8). The heat capacity of gaseous n-butane at atmospheric pressure was determined at temperatures between 100° and 340° F. (9).

These data for methane and n-butane taken together with the Joule-Thomson coefficients reported in this paper permit the establishment of the Joule-Thomson coefficients and the isobaric heat capacities for the methane-n-butane system in the gaseous region at pressures below 1500 pounds per square inch in the temperature interval between 70° and 310° F..

## Materials

The methane used in this investigation was obtained from the Buttonwillow Field in California. After the removal of water and carbon dioxide by contact with magnesium perchlorate and granular potassium hydroxide, respectively, the methane contained less than 0.08 mole per cent of impurities. The n-butane was obtained from the Philgas Division of the Phillips Petroleum Company and their special analysis indicated that this sample contained 99.8 mole per cent isobutane.

## Method

The Joule-Thomson coefficients reported in this paper were obtained by the direct measurement of the change in temperature resulting from a small change in pressure under such conditions that the enthalpy of the gas remained constant. A sufficiently small change in pressure (12 pounds per square inch) was employed throughout this investigation that the Joule-Thomson coefficient may be evaluated directly from the measured finite changes in temperature and pressure as indicated in the following equation:

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \left(\frac{\Delta T}{\Delta P}\right)_H \qquad (1)$$

The apparatus employed in this investigation was recently described (2). In principle, the method consisted of measuring the change in temperature resulting from the flow of the gaseous mixture through a porous thimble under carefully controlled conditions. The change in temperature was measured by means of a multi-lead, three junction, copper-constantan thermocouple which was mounted upon suitable supports on the inside and outside of the thimble. The change in pressure was measured by means of a mercury-in-steel manometer connected to the inlet and outlet of the porous thimble chamber. The entire thimble chamber assembly was immersed in an oil bath whose average temperature did not change by more than 0.002° F. per hour. A specially constructed plunger-type compressor was employed to circulate the gas through the apparatus. The tubing connecting the compressor and the apparatus was steam jacketed at a temperature in excess of 250° F.. From information as yet unpublished, it was established that at this temperature no condensation would occur with any of the mixtures investigated.

The temperature of the oil bath was ascertained by means of a multi-lead copper-constantan thermocouple used in conjunction with a White potentiometer and an agitated ice bath. The thermocouple was calibrated in place by comparison with a strain-free platinum resistance thermometer which had recently been standardized by the U. S. Bureau of Standards. It is believed that the temperature of the gas entering the porous thimble was known in any case with an uncertainty of not more than 0.1° F. relative to the international temperature scale. The three-junction multi-lead thermocouple employed in the measurement of the change in temperature of the gas during its flow through the porous thimble was calibrated by the use of the same platinum resistance thermometer. It is believed that the differential thermocouple was calibrated with sufficient precision to establish the change in temperature of the gas with an uncertainty in any measurement of not more than 0.3 per cent. The mercury-in-steel manometer was calibrated at low pressures by direct comparison with a mercury-in-glass manometer (0.4 inch inside diameter). The differences of mercury height in the latter were established by means of a vertical-component cathetometer with an uncertainty in individual measurement of not more than 0.005 inch in a length greater than 24 inches.

Adequate supplies of mixtures of methane and n-butane were made up in steel containers at approximately the compositions desired for investigation. These containers were heated to a temperature in excess of 270° F. and were agitated for an extended period at this temperature in order to insure uniformity of the sample. All of the connecting tubing betweenthese containers and the circulating system of the apparatus was steam jacketed to avoid condensation of n-butane. In the course of a set of measurements at a particular temperature at least two samples were withdrawn from the circulating system for analysis, in order to ascertain any changes in composition which might occur. The compositions of the samples were determined by means of gas density measurements at a temperature of 100° F.. These densities were determined gravimetrically and sufficient care was exercised to permit the estimation of the mole fraction of n-butane in any of the mixtures with an uncertainty of not more than 0.003. The volumetric data for methane (4) and n-butane (8), together with unpublished experimental information concerning the volumetric behavior of gaseous mixtures of methane and n-butane, were employed in the estimation of the composition of the samples from the density measured at atmospheric pressure. Analyses of the material in the apparatus were made during the course of a given set of measurements, the samples being taken at different operating pressures. The results indicated changes in the mole fraction of n-butane of more than 0.005in two out of seventeen cases. This probably resulted from some absorption of n-butane by the castor oil used in the lubrication of the compressor. In the other measurements these changes were much smaller and were neglected. These variations in composition necessitated in the two cases detailed interpolation of the individual isotherms, and in certain instances of the individual experimental points, in order to present the results at even compositions.

In measurements of this nature it is difficult to ascertain with accuracy the absolute uncertainty involved in the final results. However, it is believed that the composition of the system, the pressure, the temperature of measurement, and the change in temperature resulting from the measured change in pressure were established with sufficient accuracy that the resulting Joule-Thomson coefficients are known with an uncertainty which does not exceed 2.5 per cent for any of the conditions reported in this investigation.

## Results

A typical set of measurements for a mixture containing 34.2 weight per cent n-butane is presented in Figure 1. The curves do not differ greatly in appearance from those for mixtures of methane and ethane, except that the maximum in the isothermal relationship of the Joule-Thomson coefficient to pressure is somewhat more pronounced in this case. In this instance the changes in composition with temperature and pressure that were encountered in the experimental study were sufficiently small (0.003 weight fraction) that they have been neglected in the presentation of the data. Many of the experimental points shown were obtained from different sets of measurements made at the same temperature. Figure 2 presents similar information for a number of mixtures containing smaller concentrations of n-butane. In those cases the change in composition from one temperature to another was significant as has been indicated on the curves. The experimental points shown were taken both upon increase and decrease of pressure in the system and the analyses taken at each temperature indicated that for these mixtures, the changes in composition of the system with pressure were insignificant.

The variation in the Joule-Thomson coefficient with composition for a series of temperatures at a pressure of 1000 pounds per square inch is depicted in Figure 3. These data indicate a progressive increase in the coefficient with an increase in the concentration of n-butane at the lower pressures. However, at the higher pressures the coefficient reaches a maximum and decreases with a further increase in the concentration of n-butane. These curves for the higher pressures cannot be extended to states in the vicinity of pure n-butane because of the separation of a liquid phase. The boundary between the single- and two-phase regions for this system has been established from dew point measurements which are as yet unpublished.

Due to the number of different compositions investigated it was not feasible to tabulate the experimental results directly. They were interpolated graphically to even values of pressure and composition and are recorded in a part of Table I. It is believed that no uncertainties greater than 0.3 per cent result from these interpolations. From a consideration of the precision of measurement attained in establishing the pertinent quantities involved in ascertaining these Joule-Thomson coefficients, it is probable that no uncertainties greater than 3 per cent are involved in the recorded values.

By methods which have been outlined in detail (3) it is possible to compute the isobaric heat capacity as a function of state from the heat capacity at infinite attenuation and the recorded values of the Joule-Thomson coefficient. The heat capacity at infinite attenuation was established from published data for methane (10) and n-butane (9) by use of the concept of ideal solutions which applies with accuracy to gaseous solutions at infinite attenuation. The results of this calculation are recorded in Table I. The isobaric heat capacity is presented in Figure 4 as a function of composition for several pressures at a temperature of 250° F.. These results indicate a progressive increase in the isothermal coefficient relating isobaric heat capacity to pressure with an increase in the concentration of n-butane. The linear relationship for states corresponding to infinite attenuation results from the assumption of ideal solutions under these circumstances.

The change in the compressibility factor ( $Z$ = PV/bT) with temperature may be ascertained from the Joule-Thomson coefficient and the isobaric heat capacity by means of the following general thermodynamic relationship:

$$\left(\frac{\partial Z}{\partial T}\right)_P = \frac{P\mu C_P}{bT^2} \tag{2}$$

Integration of Equation 2 permits the establishment of the volumetric behavior from a knowledge of the volume as a function of pressure at a single temperature. In Table II is presented a comparison of experimentally determined compressibility factors for several mixtures of methane and n-butane with those determined from the information recorded in Table I. In calculating the values from the Joule-Thomson coefficient, the compressibility factors at a temperature of 250° F. have been taken equal to those determined experimentally. The agreement between the two sets of values is not as good as was found in the case of the methane-ethane system (7). In the present instance, discrepancies as large as two per cent were encountered at the lower temperatures for the mixtures containing a large amount of n-butane. This was probably due to errors in the pressure-volume-temperature data that are likely to occur in these measurements at states in the vicinity of dew point. In general, the Joule-Thomson values are to be preferred at pressures below 1000 pounds per square inch but it is the authors' belief that the directly measured values should be given greater weight at the higher pressures. This comparison has not been extended to all of the conditions covered by the present investigation of the Joule-Thomson coefficient. This omission was made necessary by the difficulty encountered in establishing (3) the isobaric heat capacity in these regions from the Joule-Thomson coefficient.

For some purposes the isothermal enthalpy-pressure coefficient is of value and it can be obtained from the product of the isobaric heat capacity and the Joule-Thomson coefficient as recorded in

Table I. Figure 5 presents this isothermal enthalpy-pressure coefficient as a function of composition for a series of pressures at a temperature of 250° F.. The results indicate a progressive increase in this coefficient with an increase in the concentration of n-butane.

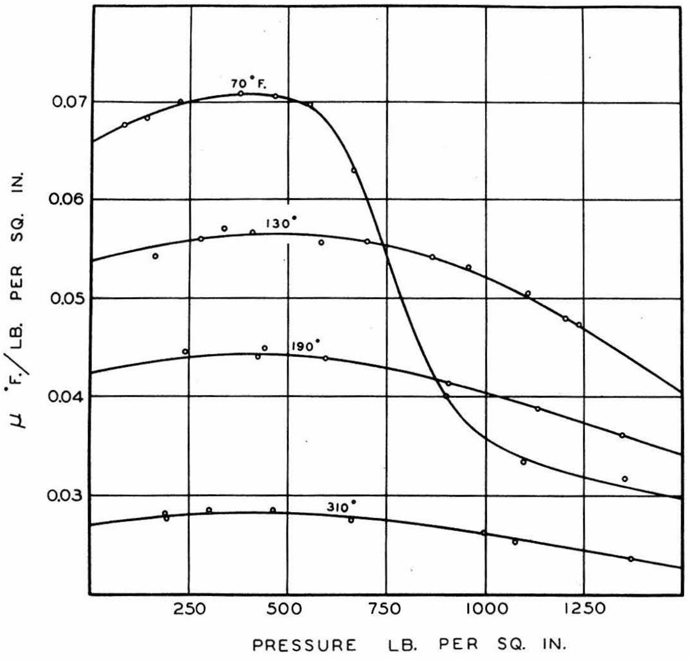

Figure 1. Joule-Thomson Coefficients for a Gaseous Mixture of Methane and n-Butane Containing 34.2 Weight Per Cent n-Butane

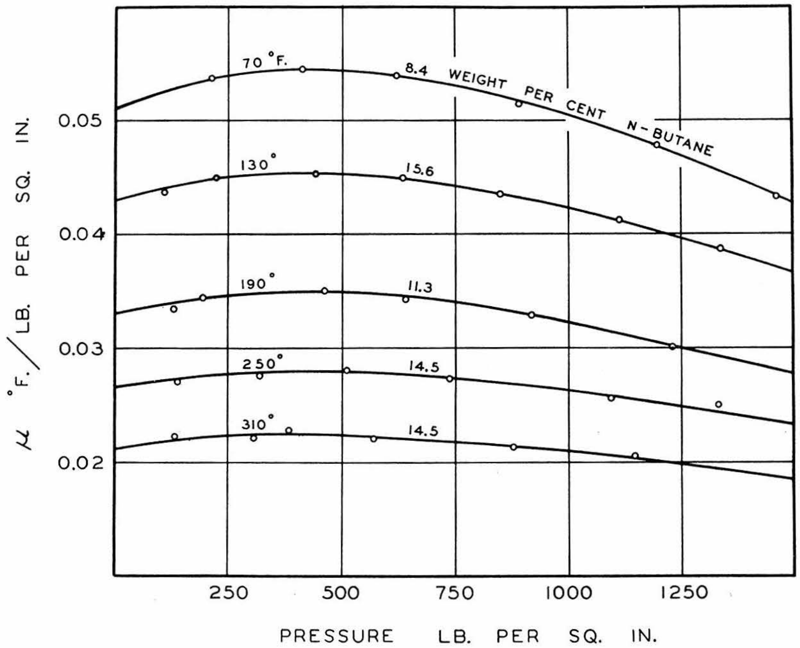

Figure 2. Joule-Thomson Coefficients for Gaseous Mixtures of Methane and n-Butane.

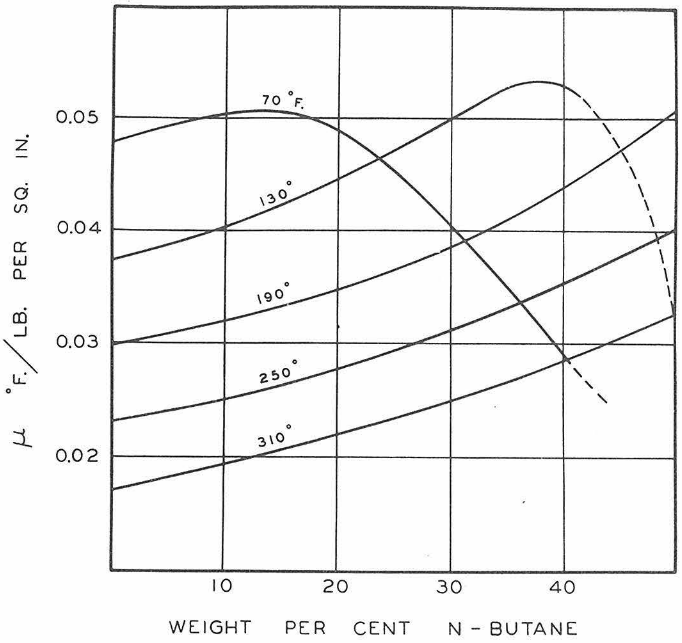

Figure 3. The Effect of Composition upon the Joule-Thomson Coefficients of Gaseous Mixtures of Methane and n-Butane at 1000 pounds per square inch.

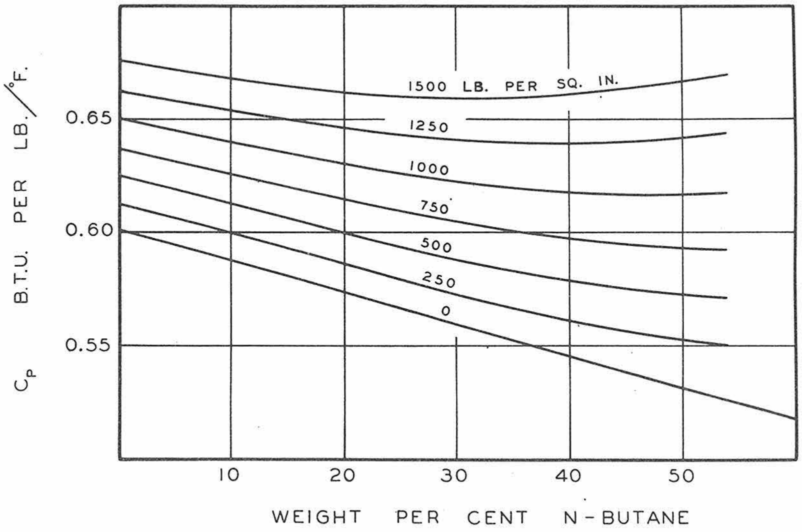

Figure 4. Isobaric Heat Capacities of Gaseous Mixtures of Methane and n-Butane at 250° F.

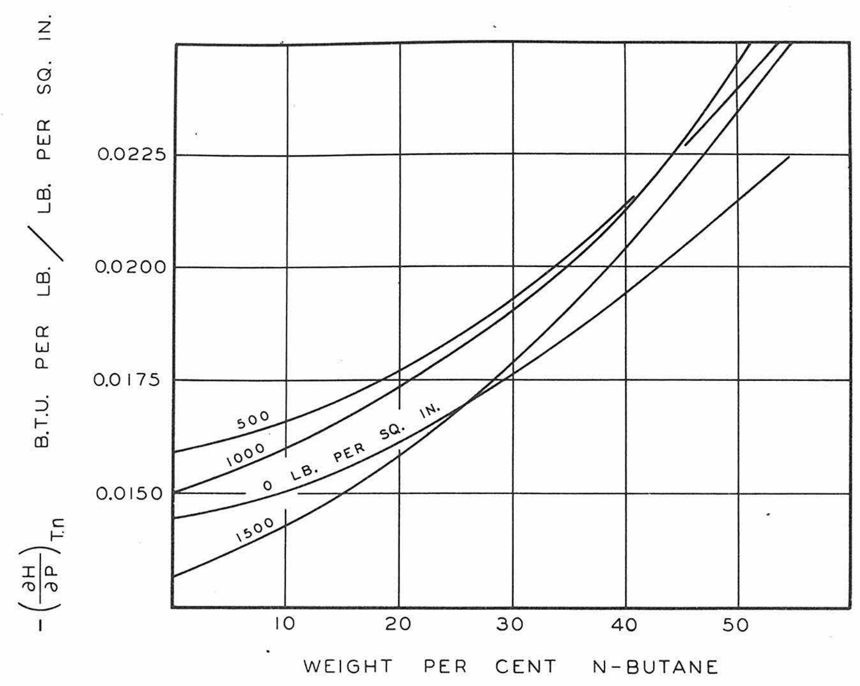

**Figure 5.** Isothermal Enthalpy-Pressure Coefficients for Gaseous Mixtures of Methane and n-Butane at 250° F.

TABLE I. JOULE-THOMSON COEFFICIENTS AND ISOBARIC HEAT CAPACITIES FOR GASEOUS MIXTURES OF METHANE AND n-BUTANE

| Temp. °F. | Absolute Pressure Lb/sq.in. | Weight Per Cent n-Butane as Follows | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 10.0 | | 20.0 | | 30.0 | | 40.0 | | 50.0 | |
| | | $\mu$ | $c_p$ | $\mu$ | $c_p$ | $\mu$ | $c_p$ | $\mu$ | $c_p$ | $\mu$ | $c_p$ |
| 70 | 0 | 0.0519[a] | 0.5160[b] | 0.0566 | 0.5018 | 0.0634 | 0.4875 | 0.0752 | 0.4733 | - - | 0.4591 |
| | 250 | 0.0546 | 0.5398 | 0.0594 | 0.5266 | 0.0668 | 0.5154 | 0.0778 | 0.5064 | - - | 0.5003 |
| | 500 | 0.0549 | 0.5684 | 0.0599 | 0.5580 | 0.0671 | 0.5501 | 0.0782 | 0.5447 | - - | - - |
| | 750 | 0.0535 | 0.5995 | 0.0574 | 0.5909 | 0.0616 | 0.5842 | 0.0666 | 0.5795 | - - | - - |
| | 1000 | 0.0505 | - - | 0.0524 | - - | - - | - - | - - | - - | - - | - - |
| | 1250 | 0.0464 | - - | 0.0452 | - - | - - | - - | - - | - - | - - | - - |
| | 1500 | 0.0414 | - - | 0.0360 | - - | - - | - - | - - | - - | - - | - - |
| 130 | 0 | 0.0411 | 0.5367 | 0.0450 | 0.5229 | 0.0506 | 0.5091 | 0.0589 | 0.4953 | 0.0705 | 0.4815 |
| | 250 | 0.0429 | 0.5550 | 0.0469 | 0.5429 | 0.0527 | 0.5319 | 0.0612 | 0.5222 | 0.0746 | 0.5150 |
| | 500 | 0.0433 | 0.5755 | 0.0473 | 0.5659 | 0.0531 | 0.5587 | 0.0615 | 0.5536 | 0.0732 | - - |
| | 750 | 0.0422 | 0.5980 | 0.0460 | 0.5907 | 0.0520 | 0.5861 | 0.0585 | 0.5854 | 0.0501 | - - |
| | 1000 | 0.0403 | 0.6220 | 0.0440 | 0.6149 | 0.0494 | 0.6100 | 0.0530 | 0.6061 | 0.0320 | - - |
| | 1250 | 0.0377 | 0.6471 | 0.0413 | 0.6350 | 0.0454 | - - | 0.0446 | - - | 0.0224 | - - |
| | 1500 | 0.0346 | - - | 0.0382 | - - | 0.0400 | - - | 0.0340 | - - | 0.0212 | - - |
| 190 | 0 | 0.0328 | 0.5610 | 0.0356 | 0.5472 | 0.0399 | 0.5334 | 0.0455 | 0.5196 | 0.0520 | 0.5058 |
| | 250 | 0.0342 | 0.5761 | 0.0369 | 0.5633 | 0.0414 | 0.5519 | 0.0466 | 0.5406 | 0.0534 | 0.5318 |
| | 500 | 0.0345 | 0.5924 | 0.0373 | 0.5812 | 0.0417 | 0.5726 | 0.0470 | 0.5647 | 0.0536 | 0.5599 |
| | 750 | 0.0336 | 0.6095 | 0.0365 | 0.6004 | 0.0408 | 0.5940 | 0.0461 | 0.5911 | 0.0525 | - - |
| | 1000 | 0.0320 | 0.6273 | 0.0348 | 0.6195 | 0.0385 | 0.6169 | 0.0439 | 0.6176 | 0.0506 | - - |
| | 1250 | 0.0296 | 0.6454 | 0.0324 | 0.6403 | 0.0358 | - - | 0.0430 | - - | 0.0478 | - - |
| | 1500 | 0.0271 | 0.6628 | 0.0296 | 0.6580 | 0.0327 | - - | 0.0396 | - - | 0.0442 | - - |
| 250 | 0 | 0.0256 | 0.5873 | 0.0282 | 0.5734 | 0.0315 | 0.5594 | 0.0357 | 0.5454 | 0.0404 | 0.5315 |
| | 250 | 0.0269 | 0.5998 | 0.0292 | 0.5863 | 0.0326 | 0.5730 | 0.0366 | 0.5609 | 0.0416 | 0.5520 |
| | 500 | 0.0271 | 0.6127 | 0.0296 | 0.6001 | 0.0328 | 0.5881 | 0.0370 | 0.5781 | 0.0418 | 0.5717 |
| | 750 | 0.0263 | 0.6260 | 0.0289 | 0.6147 | 0.0320 | 0.6044 | 0.0362 | 0.5969 | 0.0412 | 0.5936 |
| | 1000 | 0.0250 | 0.6400 | 0.0276 | 0.6298 | 0.0309 | 0.6220 | 0.0350 | 0.6170 | 0.0398 | - - |
| | 1250 | 0.0233 | 0.6530 | 0.0259 | 0.6460 | 0.0290 | 0.6411 | 0.0333 | 0.6382 | 0.0378 | - - |
| | 1500 | 0.0214 | 0.6670 | 0.0239 | 0.6613 | 0.0271 | 0.6594 | 0.0309 | 0.6606 | 0.0353 | - - |
| 310 | 0 | 0.0198 | 0.6151 | 0.0226 | 0.6008 | 0.0256 | 0.5865 | 0.0290 | 0.5722 | 0.0328 | 0.5579 |
| | 250 | 0.0208 | 0.6252 | 0.0234 | 0.6112 | 0.0266 | 0.5965 | 0.0300 | 0.5832 | 0.0340 | 0.5724 |
| | 500 | 0.0210 | 0.6360 | 0.0236 | 0.6221 | 0.0268 | 0.6085 | 0.0303 | 0.5951 | 0.0343 | 0.5825 |
| | 750 | 0.0203 | 0.6470 | 0.0230 | 0.6336 | 0.0261 | 0.6203 | 0.0294 | 0.6081 | 0.0334 | 0.5990 |
| | 1000 | 0.0193 | 0.6581 | 0.0218 | 0.6456 | 0.0249 | 0.6328 | 0.0284 | 0.6224 | 0.0324 | 0.6142 |
| | 1250 | 0.0182 | 0.6692 | 0.0206 | 0.6580 | 0.0234 | 0.6471 | 0.0266 | 0.6378 | 0.0305 | 0.6294 |
| | 1500 | 0.0170 | 0.6813 | 0.0192 | 0.6702 | 0.0218 | 0.6616 | 0.0245 | 0.6544 | 0.0282 | 0.6495 |

[a] Joule-Thomson coefficient, ° F./ pound per square inch.

[b] Isobaric heat capacity, B.t.u. per pound / ° F.

TABLE II. COMPARISON OF EXPERIMENTAL COMPRESSIBILITY FACTORS WITH THOSE BASED UPON JOULE-THOMSON MEASUREMENTS

| Temp. ° F. | Absolute Pressure Lb/sq.in. | Weight Per Cent n-Butane as Follows 10.0 | | 20.0 | | 30.0 | | 40.0 | |
|---|---|---|---|---|---|---|---|---|---|
| | | Exp. | J-T | Exp. | J-T | Exp. | J-T | Exp. | J-T |
| 70 | 0 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | 250 | 0.9560 | 0.9629 | 0.9425 | 0.9532 | 0.9281 | 0.9406 | 0.9071 | 0.9254 |
| | 500 | 0.9172 | 0.9257 | 0.8961 | 0.9099 | 0.8699 | 0.8850 | 0.8322 | 0.8530 |
| | 750 | 0.8831 | 0.8922 | 0.8570 | 0.8651 | 0.8280 | 0.8362 | 0.7815 | 0.7918 |
| | 1000 | 0.8529 | - - | 0.8200 | - - | 0.7803 | - - | 0.7273 | - - |
| | 1250 | 0.8268 | - - | 0.7886 | - - | 0.7443 | - - | 0.6889 | - - |
| | 1500 | 0.8045 | - - | 0.7632 | - - | 0.7142 | - - | 0.6583 | - - |
| 100 | 0 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | 250 | 0.9647 | 0.9690 | 0.9525 | 0.9603 | 0.9377 | 0.9492 | 0.9194 | 0.9361 |
| | 500 | 0.9334 | 0.9388 | 0.9137 | 0.9250 | 0.8916 | 0.9034 | 0.8560 | 0.8763 |
| | 750 | 0.9042 | 0.9123 | 0.8789 | 0.8902 | 0.8504 | 0.8634 | 0.8107 | 0.8245 |
| | 1000 | 0.8800 | 0.8867 | 0.8509 | 0.8601 | 0.8153 | 0 - - | 0.7735 | - - |
| | 1250 | 0.8584 | 0.8663 | 0.8246 | - - | 0.7862 | - - | 0.7413 | - - |
| | 1500 | 0.8396 | - - | 0.8021 | - - | 0.7613 | - - | 0.7138 | - - |
| 130 | 0 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | 250 | 0.9724 | 0.9740 | 0.9640 | 0.9661 | 0.9478 | 0.9561 | 0.9319 | 0.9449 |
| | 500 | 0.9454 | 0.9493 | 0.9282 | 0.9372 | 0.9067 | 0.9181 | 0.8793 | 0.8951 |
| | 750 | 0.9227 | 0.9282 | 0.9000 | 0.9092 | 0.8727 | 0.8859 | 0.8388 | 0.8521 |
| | 1000 | 0.9021 | 0.9079 | 0.8754 | 0.8852 | 0.8441 | 0.8549 | 0.8061 | 0.8144 |
| | 1250 | 0.8844 | 0.8922 | 0.8543 | 0.8645 | 0.8209 | - - | 0.7786 | - - |
| | 1500 | 0.8695 | - - | 0.8367 | - - | 0.8012 | - - | 0.7568 | - - |
| 160 | 0 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | 250 | 0.9761 | 0.9780 | 0.9670 | 0.9707 | 0.9550 | 0.9618 | 0.9395 | 0.9519 |
| | 500 | 0.9545 | 0.9578 | 0.9384 | 0.9471 | 0.9211 | 0.9301 | 0.8979 | 0.9101 |
| | 750 | 0.9330 | 0.9411 | 0.9132 | 0.9241 | 0.8931 | 0.9043 | 0.8620 | 0.8750 |
| | 1000 | 0.9195 | 0.9249 | 0.8960 | 0.9050 | 0.8699 | 0.8791 | 0.8362 | 0.8435 |
| | 1250 | 0.9060 | 0.9127 | 0.8790 | 0.8884 | 0.8492 | 0 - - | 0.8130 | - - |
| | 1500 | 0.8950 | 0.9026 | 0.8655 | 0.8751 | 0.8323 | - - | 0.7944 | - - |
| 190 | 0 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | 250 | 0.9790 | 0.9814 | 0.9720 | 0.9746 | 0.9638 | 0.9664 | 0.9518 | 0.9576 |
| | 500 | 0.9623 | 0.9647 | 0.9488 | 0.9550 | 0.9332 | 0.9398 | 0.9128 | 0.9221 |
| | 750 | 0.9458 | 0.9516 | 0.9288 | 0.9363 | 0.9100 | 0.9192 | 0.8845 | 0.8934 |
| | 1000 | 0.9340 | 0.9387 | 0.9149 | 0.9210 | 0.8912 | 0.8985 | 0.8613 | 0.8678 |
| | 1250 | 0.9231 | 0.9292 | 0.9004 | 0.9078 | 0.8753 | 0.8824 | 0.8418 | - - |
| | 1500 | 0.9144 | 0.9212 | 0.8897 | 0.8972 | 0.8619 | 0.8695 | 0.8259 | - - |
| 220 | 0 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | 250 | 0.9833 | 0.9841 | 0.9768 | 0.9777 | 0.9680 | 0.9703 | 0.9574 | 0.9622 |
| | 500 | 0.9694 | 0.9705 | 0.9581 | 0.9616 | 0.9443 | 0.9477 | 0.9261 | 0.9318 |
| | 750 | 0.9570 | 0.9602 | 0.9433 | 0.9464 | 0.9260 | 0.9312 | 0.9024 | 0.9084 |
| | 1000 | 0.9471 | 0.9500 | 0.9310 | 0.9342 | 0.9112 | 0.9143 | 0.8838 | 0.8876 |
| | 1250 | 0.9380 | 0.9426 | 0.9196 | 0.9235 | 0.8977 | 0.9015 | 0.8668 | 0.8696 |
| | 1500 | 0.9306 | 0.9362 | 0.9101 | 0.9152 | 0.8865 | 0.8910 | 0.8531 | 018611 |
| 250 | 0 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | 250 | 0.9864 | 0.9864[a] | 0.9804 | 0.9804 | 0.9734 | 0.9734 | 0.9660 | 0.9660 |
| | 500 | 0.9752 | 0.9752 | 0.9671 | 0.9671 | 0.9542 | 0.9542 | 0.9398 | 0.9398 |
| | 750 | 0.9673 | 0.9673 | 0.9553 | 0.9553 | 0.9410 | 0.9410 | 0.9205 | 0.9205 |
| | 1000 | 0.9591 | 0.9591 | 0.9450 | 0.9450 | 0.9273 | 0.9273 | 0.9036 | 0.9036 |
| | 1250 | 0.9534 | 0.9534 | 0.9365 | 0.9365 | 0.9172 | 0.9172 | 0.8895 | 0.8895 |
| | 1500 | 0.9485 | 0.9485 | 0.9298 | 0.9298 | 0.9091 | 0.9091 | 0.8780 | 0.8780 |

[a] Joule-Thomson values were taken equal to the experimental values at 250° F.

## ACKNOWLEDGMENT

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# NOMENCLATURE

| | |
|---|---|
| $T$ | Temperature, °F. abs. (°R). |
| $P$ | Pressure, lb./sq.in.abs. |
| $V$ | Specific volume, cu.ft./lb. |
| $Z$ | Compressibility factor ( $Z = PV/bT$ ). |
| $C_P$ | Isobaric heat capacity, B.t.u./lb./°F. |
| $\mu$ | Joule-Thomson coefficient, °F./lb./sq.in. |
| $b$ | Specific gas constant (per lb.). |

# PART II.

## CHANGE IN PARTIAL ENTHALPY ASSOCIATED WITH THE SOLUTION OF A GASEOUS SOLUTE IN A LIQUID SOLVENT

# CHANGE IN PARTIAL ENTHALPY ASSOCIATED WITH THE SOLUTION OF A GASEOUS SOLUTE IN A LIQUID SOLVENT

## Abstract

The change in partial enthalpy associated with the solution of a gaseous solute in a liquid solvent has been discussed from a theoretical standpoint. A method of measuring this quantity experimentally by means of an adiabatic calorimeter is described. Preliminary results obtained by the use of this experimental method when applied to the propane-crystal oil system are included. These are compared to those which would be predicted on the assumption that the system follows the law of ideal solutions.

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In connection with many industrial processes a knowledge of the change in partial enthalpy of a component as a consequence of its solution in another is of importance. In cases where the components are both mutually soluble liquids, this change is usually small because no change in phase of either of the components is involved. If, however, a gaseous component is dissolved in a liquid component, there may be an appreciable amount of energy liberated during the process, because of the change of phase which takes place.

There are two possible methods of obtaining the change in partial enthalpy associated with such a process. One method of approach is to calculate the change in partial enthalpy of the component under-going a change in phase by employing detailed volumetric and phase equilibrium data. The other is to measure this change in partial enthalpy by means of a calorimeter. The purpose of this portion of the thesis is to present the equations required in each case, and to describe an adiabatic calorimeter which may be used for an experimental determination. The results obtained with this calorimeter when applied to the propane-crystal oil system will be presented together with a comparison of the values which one would predict if the system followed the behavior of an ideal solution.

## Phase Equilibrium Method

By proper application of the chemical potential (Lewis' free energy) as a criterion for equilibrium between phases, it is possible to obtain an expression for the change in partial enthalpy of a component in a binary system when it undergoes a change in phase. The chemical potential of a system may be expressed by the equation:*

$$\underline{F} = \underline{E} - T\,\underline{S} + P\,\underline{V} \tag{1}$$

The function $\underline{F}$ in Equation 1 has the property that, for an isolated system under conditions of constant pressure, temperature

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* Nomenclature for this section will be found on page 100.

and total mass of the system it can of itself only decrease. This being the case, it has the nature of a potential function which will permit the system, under the imposed conditions, to be in equilibrium only when it has reached its minimum value. For a system of more than one phase, the chemical potential of each of the phases may be considered additive. Thus, for the case of a system composed of a liquid phase and a gas phase, one may write:

$$\underline{F} \overset{=}{+} \underline{F}_L + \underline{F}_g \tag{2}$$

where $\underline{F}_L$ and $\underline{F}_g$ are the chemical potentials of the liquid and gas phases, respectively. If a process is now visualized by which a very small quantity of one of the components of an n-component system, say component k, is transferred from the liquid phase to the gas phase under conditions of equilibrium, the following expression must hold:

$$dF = \left(\frac{\partial F_L}{\partial m_{KL}}\right)_{P,T,m_i} dm_{KL} + \left(\frac{\partial F_g}{\partial m_{Kg}}\right)_{P,T,m_i} dm_{Kg} \tag{3}$$

Since $dm_{kg} = - dm_{kL}$, this equation may be written as:

$$\left(\frac{\partial F_L}{\partial m_{KL}}\right)_{P,T,m_i} = \left(\frac{\partial F_g}{\partial m_{Kg}}\right) \tag{4}$$

For the purpose of simplification of writing, the terms $(\partial \underline{F}_L / \partial m_{kL})_{p,T,mi}$ and $(\partial \underline{F}_g / \partial m_{kg})_{p,T,mi}$ may be replaced by the terms $\overline{F}_{kL}$ and $\overline{F}_{kg}$, respectively, giving in place of Equation 4, the relation:

$$\bar{F}_{kL} = \bar{F}_{kg} \tag{5}$$

Equation 5 expresses the fundamental condition for the equilibrium of component k in the co-existing liquid and gas phases. If the system be permitted to move from one equilibrium state to another equilibrium state separated from the first by only an infinitesimal amount, the following equation will also hold as a consequence of Equation 5:

$$d\,\bar{F}_{kL} = d\,\bar{F}_{kg} \tag{6}$$

Since $\bar{F}_k$ is solely a function of the pressure, temperature, and composition of the phase in which it exists, one may write in place of Equation 6:

$$\left(\frac{\partial \bar{F}_{KL}}{\partial P}\right)_{T,\underline{x}} dP + \left(\frac{\partial \bar{F}_{KL}}{\partial T}\right)_{P,\underline{x}} dT + \sum_{\nu=1}^{\nu=n-1} \left(\frac{\partial \bar{F}_{KL}}{\partial \underline{x}_\nu}\right)_{P,T} d\underline{x}_\nu = \left(\frac{\partial \bar{F}_{Kg}}{\partial P}\right)_{T,\underline{y}} dP + \left(\frac{\partial \bar{F}_{Kg}}{\partial T}\right)_{P,\underline{y}} dT + \sum_{\nu=1}^{\nu=n-1} \left(\frac{\partial \bar{F}_{Kg}}{\partial \underline{y}_\nu}\right)_{P,T} d\underline{y}_\nu \tag{7}$$

In the discussion which follows only binary systems will be considered. In this case the number of components will be equal to two so that Equation 7 reduces to the form:

$$\left(\frac{\partial \bar{F}_{KL}}{\partial P}\right)_{T,\underline{x}_K} dP + \left(\frac{\partial \bar{F}_{KL}}{\partial T}\right)_{P,\underline{x}_K} dT + \left(\frac{\partial \bar{F}_{KL}}{\partial \underline{x}_K}\right)_{P,T} d\underline{x}_K = \left(\frac{\partial \bar{F}_{Kg}}{\partial P}\right)_{T,\underline{y}_K} dP + \left(\frac{\partial \bar{F}_{Kg}}{\partial T}\right)_{P,\underline{y}_K} dT + \left(\frac{\partial \bar{F}_{Kg}}{\partial \underline{y}_K}\right)_{P,T} d\underline{y}_K \tag{8}$$

Making use of the fundamental relations (3) that:

$$\left(\frac{\partial \bar{F}_{KL}}{\partial T}\right)_{P,\underline{x}_K} = \frac{\bar{F}_{KL} - \bar{H}_{KL}}{T} \tag{9}$$

$$\left(\frac{\partial \bar{F}_{Kg}}{\partial T}\right)_{P,\underline{y}_K} = \frac{\bar{F}_{Kg} - \bar{H}_{Kg}}{T} \qquad (10)$$

$$\left(\frac{\partial \bar{F}_{KL}}{\partial P}\right)_{T,\underline{x}_K} = \bar{V}_{KL} \qquad (11)$$

$$\left(\frac{\partial \bar{F}_{Kg}}{\partial P}\right)_{T,\underline{y}_K} = \bar{V}_{Kg} \qquad (12)$$

one may write for Equation 8:

$$\bar{V}_{KL}\, dP + \frac{\bar{F}_{KL} - \bar{H}_{KL}}{T}\, dT + \left(\frac{\partial \bar{F}_{KL}}{\partial \underline{x}_K}\right)_{P,T} d\underline{x}_K = \bar{V}_{Kg}\, dP + \frac{\bar{F}_{Kg} - \bar{H}_{Kg}}{T}\, dT + \left(\frac{\partial \bar{F}_{Kg}}{\partial \underline{y}_K}\right)_{P,T} d\underline{y}_K \qquad (13)$$

Solving this equation for the differential of pressure with respect to temperature under equilibrium conditions, and recalling from Equation 5 that $\bar{F}_{kL} = \bar{F}_{kg}$, one obtains:

$$\left(\frac{dT}{dP}\right)'' = \frac{\bar{H}_{Kg} - \bar{H}_{KL}}{T(\bar{V}_{Kg} - \bar{V}_{KL})} + \frac{1}{\bar{V}_{Kg} - \bar{V}_{KL}} \left[\left(\frac{\partial \bar{F}_{KL}}{\partial \underline{x}_K}\right)_{P,T} \left(\frac{d\underline{x}_K}{\partial T}\right)'' - \left(\frac{\partial F_{Kg}}{\partial \underline{y}_K}\right)_{P,T} \left(\frac{d\underline{y}_K}{dT}\right)''\right] \qquad (14)$$

where the double prime symbols indicate that the derivatives are taken along the path of equilibrium between the liquid and gas phases.

In general it is impossible in a binary system composed of two phases, to move from one state to another under conditions of equilibrium in such a manner that d $\underline{x}$k and d $\underline{y}$k will both remain equal to zero. However, it is possible to move in such a manner that either $\underline{x}$k or $\underline{y}$k , but not both, will remain constant. If the variation of pressure with respect to temperature be obtained under conditions of equilibrium when the system is constrained to move along a path for which d $\underline{x}_k$ is zero, the following equation will result:

$$\left(\frac{dP}{dT}\right)'' = \frac{\bar{H}_{kg} - \bar{H}_{kL}}{T(\bar{V}_{kg} - \bar{V}_{kL})} - \frac{1}{\bar{V}_{kg} - \bar{V}_{kL}} \left(\frac{\partial \bar{F}_{kg}}{\partial \underline{y}_k}\right)_{P,T} \left(\frac{d\underline{y}_k}{dT}\right)''_{\underline{x}_L} \qquad (15)$$

From which:

$$\bar{H}_{kg} - \bar{H}_{kL} = T(\bar{V}_{kg} - \bar{V}_{kL})\left(\frac{dP}{dT}\right)''_{\underline{x}_k} + T\left(\frac{\partial \bar{F}_{kg}}{\partial \underline{y}_k}\right)_{P,T}\left(\frac{d\underline{y}_k}{dT}\right)''_{\underline{x}_k} \qquad (16)$$

By using phase equilibrium data, it is possible to obtain $(d\,P\,/\,d\,T)''_{\underline{x}k}$ and $(d\,\underline{y}k\,/\,d\,T)''_{\underline{x}k}$. From information concerning the change in chemical potential of gases at infinite attenuation, together with pressure-volume-temperature data for the gases involved, $(\partial\,\bar{F}_{kg}/\partial\,\underline{y}_k)$ can be obtained. This permits the evaluation of $\bar{H}_{kg} - \bar{H}_{kL}$. If Equation 12 be integrated from a pressure $p_o$ to the pressure p , one obtains the relation:

$$\bar{F}_{kg} = \int_{P_o}^{P} \bar{V}_{kg}\,dP + \bar{F}_{k_o} \qquad (17)$$

where $\bar{F}_{k_o}$ is the value of the partial chemical potential of component k at the pressure $p_o$. By choosing $p_o = \lim p \rightarrow 0$ the value of $\bar{F}_{k_o}$ may be taken (1) as equal to:

$$\bar{F}_{k_o} = b_k T \ln \underline{y}_k + F_{k_o} \qquad (18)$$

where $F_{k_o}$ is the chemical potential of the pure component k at the pressure $p_o$ and at the temperature T. Substitution of this quantity in Equation 17 and differentiating with respect to $\underline{y}_k$, holding the pressure and temperature constant, results in the relation:

$$\left(\frac{\partial \bar{F}_{kg}}{\partial \underline{y}_k}\right)_{P,T} = \int_{P_o}^{P} \left(\frac{\partial \bar{V}_k}{\partial \underline{y}_k}\right)_{P,T} dP + \frac{b_k T}{\underline{y}_k} \qquad (19)$$

When this expression is substituted in Equation 16, it reduces to an equation which can be solved directly from volumetric and phase equilibrium data.

$$\bar{H}_{kg} - \bar{H}_{kL} = T(\bar{V}_{kg} - \bar{V}_{kL})\left(\frac{dP}{dT}\right)''_{\underline{x}_k} + \left[T\int_{P_o}^{P}\left(\frac{\partial V_{kg}}{\partial \underline{y}_k}\right)_{P,T} dP + \frac{b_k T^2}{\underline{y}_k}\right]\left(\frac{d\underline{y}_k}{d\underline{x}_k}\right)''_{\underline{y}_k} \qquad (20)$$

Having determined $\bar{H}_{kg} - \bar{H}_{kL}$ by the use of Equation 20, one is then in a position to evaluate $(\partial \bar{F}_{kL} / \partial \underline{x}_k)_{p,T}$. This may be done by moving the system along a path of equilibrium between phases, when constrained to the condition that d $\underline{y}_k = 0$. Then from Equation 14:

$$\left(\frac{\partial \bar{F}_{kL}}{\partial \underline{x}_k}\right)_{P,T} = \left[\left(\frac{dP}{dT}\right)''_{\underline{y}_k}(\bar{V}_{kg} - V_{kL}) - \frac{\bar{H}_{kg} - \bar{H}_{kL}}{T}\right]\left(\frac{dT}{d\underline{x}_k}\right)''_{\underline{y}_k} \qquad (21)$$

With the aid of the above equations it is clear that one is able to evaluate all of the thermodynamic properties of the liquid and gas phases of a binary system, provided there is available sufficient detailed information regarding the isobaric heat capacity as well as the pressure, volume, and temperature relations throughout the liquid, gas, and two-phase regions. This evaluation would, of course, involve the assumption that the partial chemical potential of the gaseous component k at infinite attenuation is expressed by Equation 18.

For the special case in which the solvent may be considered non-volatile the term $(d\,\underline{y}_k / d\,T)''_{\underline{x}_k}$ will always be equal to zero. This will be true because under these conditions the gas phase will be composed entirely of component k. Equation 15 may then be written in the form:

$$\bar{H}_{kg} - H_{kL} = T(\bar{V}_{kg} - \bar{V}_{kL})\left(\frac{dP}{dT}\right)''_{\underline{x}_k} \qquad (22)$$

An example of this special case is the propane-crystal oil system in which the crystal oil is treated as a non-volatile component. This system, which was experimentally investigated, will be considered later in more detail.

## Calorimetric Method

The calorimetric method of determination of the change in partial enthalpy of a gaseous component undergoing a change in phase is one which is based upon the direct measurement of the energy quantities associated with such a process. In general the method is one of providing a means by which the energy transformations involved may be measured experimentally with a high degree of precision.

For the purpose of deriving the relations involved in a determination of this nature, one may assume the apparatus to consist of a calorimeter bomb of known heat capacity in which the process of solution is allowed to take place. This bomb will be assumed to be provided with a small inlet through which the gaseous components to be dissolved may be added at a known rate. It will also be assumed that there is available equipment for measuring accurately the pressure and temperature of the contents as a function of the time, as well as apparatus for securing agitation of the contents in order to make certain that equilibrium is attained when needed. In addition to the above factors, means must be provided for measuring the temperature of the incoming gaseous component as a function of the time and also for determining the total energy interchange between the calorimeter and surroundings as a result of temperature gfadients which might exist.

Assuming that a calorimeter of this nature is available, one may proceed with the thermodynamic analysis of the problem. In making this analysis, the system will be defined arbitrarily as the material which is included within the confines of the outer surface of the calorimeter bomb. It will, therefore, consist of the liquid and gas phases within the bomb as well as the bomb itself. In selecting this boundary it should be recognized that the treatment must follow that of a system of variable weight, formations involved may be measured experimentally with a high degree of precision.

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The analysis of the problem will be based on the assumption that the system is binary. In this connection, component 1 will be defined as the gaseous solute; while component 2 will be defined as the liquid solvent.

Because of the nature of the process involved, in this type of measurement, it is usually more feasible to calculate the change in partial internal energy with change in phase, rather than the corresponding change in partial enthalpy. For this reason the former quantity will first be evaluated. The latter may then be determined by means of the equation:

$$\bar{H}_{1g} - \bar{H}_{1L} = \bar{E}_{1g} - \bar{E}_{1L} + P(\bar{V}_{1g} - \bar{V}_{1L}) \qquad (23)$$

For a homogeneous binary system of variable weight and composition under-going a change in state from A to B, the first law may be written as (2):

$$\underline{E}_B - \underline{E}_A = \int_{T_A, P_A, m_{1A}, m_{2A}}^{T_B, P_B, m_{1B}, m_{2B}} (m_1 + m_2)\left\{\left[C_P - P\left(\frac{\partial V}{\partial T}\right)_P\right]dT + \left[\ell_P - P\left(\frac{\partial V}{\partial P}\right)_T\right]dP\right\} + \bar{E}_1 dm_1 + \bar{E}_2 dm_2 \qquad (24)$$

where $C_p$, $\ell_p$, $\bar{E}_1$ and $\bar{E}_2$ are all state functions depending upon only the pressure, temperature and composition of the system. The value of $\underline{E}_B - \underline{E}_A$ is independent of the path by which the state change is accomplished. The line integral, as written above, serves only as a means of evaluating the change in internal energy when employing the particular path by which the change is accomplished. It should be recognized that Equation 1 applies only to a homogeneous phase in which the pressure and temperature are uniform throughout.

As a consequence of the first law, one may also evaluate the change in internal energy between states A and B for any system, whether homogeneous or not, by means of the equation:

$$E_B - E_A = Q_{A-B} + W_{A-B} + \int_{m_{1A}, m_{2A}}^{m_{1B}, m_{2B}} E_1 \, dm_1 + E_2 \, dm_2 \tag{25}$$

where $Q_{A-B}$ represents the energy transferred to the system from the surroundings as a consequence of a temperature gradient, and $W_{A-B}$ represents the mechanical work done on the system as a consequence of the action of a force through a distance. The last term of Equation 11 represents the energy added to the system as a consequence of the internal energy possessed by the components being added. In this equation it has been assumed that these components are added in the pure state.

Combining Equations 24 and 25, results in the relation:

$$Q_{A-B} + W_{A-B} + \int_{m_{1A}, m_{2A}}^{m_{1B}, m_{2B}} E_1 \, dm_1 + E_2 \, dm_2$$

$$= \int_{T_A, P_A, m_{1A}, m_{2A}}^{T_B, P_B, m_{1B}, m_{2B}} (m_1 + m_2) \Big\{ \Big[ C_P - P\left(\frac{\partial V}{\partial T}\right)_P \Big] dT + \Big[ \ell_P - P\left(\frac{\partial V}{\partial P}\right)_T dP \Big\} + \bar{E}_1 \, dm_1 + \bar{E}_2 \, dm_2 \tag{26}$$

Before Equation 26 may be properly applied to a calorimeter having more than one phase present, it is necessary to divide the system into three separate parts; namely, the liquid phase, the gas phase, and the calorimeter bomb itself. In this case, Equation 26 may be written in the following differential form for the purpose of simplification of writing:

$$
\begin{aligned}
q + w + E_{1g}dm_1 + E_{2g}dm_2 = {} & (m_{1g} + m_{2g})\left[C_{Pg} - P\left(\frac{\partial V_g}{\partial T}\right)_P\right]dT + (m_{1g} + m_{2g})\left[\ell_{Pg} - P\left(\frac{\partial V_g}{\partial P}\right)_T\right]dP \\
& + (m_{1L} + m_{2L})\left[C_{PL} - P\left(\frac{\partial V_L}{\partial T}\right)_P\right]dT + (m_{1L} + m_{2L})\left[\ell_{PL} - P\left(\frac{\partial V_L}{\partial P}\right)_T\right]dP \qquad (27) \\
& + \bar{E}_{1g}\,dm_{1g} + \bar{E}_{2g}\,dm_{2g} + \bar{E}_{1L}\,dm_{1L} + \bar{E}_{2L}\,dm_{2L} + C_B\,dT
\end{aligned}
$$

In writing Equation 27, it has been assumed that the change in internal energy of the calorimeter bomb itself is equal to its specific heat at constant pressure multiplied by its change in temperature.

In order to apply Equation 4 to best advantage, it is well to express all variables as a function of some particular parameter which is convenient to measure and which will further simplify the calculations. Since for any actual determination the pressure, temperature, and physical properties of the phases are recorded as functions of the time, this latter quantity is an excellent parameter to choose. If the rates at which components 1 and 2 are added to the system in the gaseous state be designated as

($d\,m_1$ / $d\,\Theta$) and ($d\,m_2$ / $d\,\Theta$), respectively, the change in weight of the individual components of the gas phase in the calorimeter with respect to time will be given by the expressions:

$$\frac{dm_{1g}}{d\theta} = \frac{dm_1}{d\theta} - \frac{dm_{1L}}{d\theta} \tag{28}$$

and

$$\frac{dm_{2g}}{d\theta} = \frac{dm_2}{d\theta} - \frac{dm_{2L}}{d\theta} \tag{29}$$

where the terms ($d\,m_{1L}$ / $d\,\Theta$) and ($d\,m_{2L}$ / $d\,\Theta$) represent the rates at which components 1 and 2 are entering the liquid phase from the gas phase at the liquid-gas interface. Substitution of the above quantities into Equation 27 gives:

$$\begin{aligned} & q - w + E_1 \frac{dm_1}{d\theta} d\theta + E_2 \frac{dm_2}{d\theta} d\theta \\ & = \Bigg\{ (m_{1g} + m_{2g}) \left[ C_{Pg} - P\left(\frac{\partial V_g}{\partial T}\right)_P \right] \frac{dT}{d\theta} + (m_{1g} + m_{2g}) \left[ \ell_{Pg} - P\left(\frac{\partial V_g}{\partial P}\right)_T \right] \frac{dP}{d\theta} \\ & \quad + (m_{1L} + m_{2L}) \left[ C_{PL} - P\left(\frac{\partial V_L}{\partial T}\right)_P \right] \frac{dT}{d\theta} + (m_{1L} + m_{2L}) \left[ \ell_{PL} - P\left(\frac{\partial V_L}{\partial P}\right)_T \right] \frac{dP}{d\theta} \\ & \quad + \bar{E}_{1g} \frac{dm_{1g}}{d\theta} + \bar{E}_{2g} \frac{dm_{2g}}{d\theta} + (\bar{E}_{1L} - \bar{E}_{1g}) \frac{dm_{1L}}{d\theta} + (\bar{E}_{2L} - \bar{E}_{2g}) \frac{dm_{2L}}{d\theta} + C_B \frac{dT}{d\theta} \Bigg\} d\theta \end{aligned} \tag{30}$$

Solving this equation for ($\bar{E}_{1g} - \bar{E}_{1L}$) ($d\,m_{1L}$ / $d\,\Theta$) $d\,\Theta$ and integrating, gives the general relation for the change in partial internal energy of component 1 in a binary system when undergoing a change in phase in the calorimeter:

$$\begin{aligned}\int_{\theta_A}^{\theta_B} (\bar{E}_{1g} - \bar{E}_{1L}) \frac{dm_{1L}}{d\theta} = {} & -Q_{A-B} - W_{A-B} + \int_{\theta_A}^{\theta_B} \Bigg\{ (\bar{E}_{1g} - \bar{E}_1) \frac{dm_1}{d\theta} \\ & + (\bar{E}_{2g} - E_2) \frac{dm_2}{d\theta} + (\bar{E}_{2L} - \bar{E}_{2g}) \frac{dm_{2L}}{d\theta} + (m_{1g} + m_{2g}) \left[ c_{Pg} - P\left(\frac{\partial V_g}{\partial T}\right)_P \right] \frac{dT}{d\theta} \\ & + (m_{1g} + m_{2g}) \left[ \ell_{Pg} - P\left(\frac{\partial V_g}{\partial P}\right)_T \right] \frac{dP}{d\theta} + (m_{1L} + m_{2L}) \left[ c_{PL} - P\left(\frac{\partial V_L}{\partial T}\right)_P \right] \frac{dT}{d\theta} \\ & + (m_{1L} + m_{2L}) \left[ \ell_{P_L} - P\left(\frac{\partial V_L}{\partial P}\right)_T \right] \frac{dP}{d\theta} + C_B \frac{dT}{d\theta} \Bigg\} d\theta \end{aligned} \tag{31}$$

Equation 31 is complex and can be greatly simplified for actual calculation by neglecting terms which are too small to be of consequence. In case the liquid solvent has a sufficiently low vapor pressure that it does not appear in the gas phase in measurable quantities, all terms involving the mass of component 2 in the gas phase may be omitted. Also the omission of the latent heat of pressure variation and of all volume derivatives in the liquid phase still further simplifies the equation without introducing significant inaccuracies. Making these simplifications and assuming that the weight of component 2 in the liquid phase remains constant, Equation 31 reduces to the form:

$$\begin{aligned}\int_{\theta_A}^{\theta_B} (\bar{E}_{1g} - \bar{E}_{1L}) \frac{dm_{1L}}{d\theta} = {} & -Q_{A-B} - W_{A-B} + \int_{\theta_A}^{\theta_B} \Bigg\{ (\bar{E}_{1g} - E_1) \frac{dm_1}{d\theta} \\ & + m_{1g} \left[ c_{P1g} - P\left(\frac{\partial V_{1g}}{\partial T}\right)_P \right] \frac{dT}{d\theta} + m_{1g} \left[ \ell_{P1g} - P\left(\frac{\partial V_{1g}}{\partial P}\right)_T \right] \frac{dP}{d\theta} \\ & + (m_{1L} + m_{2L}) C_{PL} \frac{dT}{d\theta} + C_B \frac{dT}{d\theta} \Bigg\} d\theta \end{aligned} \tag{32}$$

Equation 32 is applicable to all cases where the solvent may be considered non-volatile and where the pure component 1 is added to or withdrawn from the system in the form of a gas. Since the left-hand term of Equation 32 must be integrated along a path in which pressure and temperature are changing, it is impossible to obtain $(\overline{E}_{1g} - \overline{E}_{1L})$ at any one pressure and temperature without a knowledge of its variation with respect to these variables. If the variation with respect to pressure and temperature is not too large, one may assume as a first approximation that within the range of measurement the integral may be represented satisfactorily by the relation $(\overline{E}_{1g} - \overline{E}_{1L}) \Delta m_{1L}$. The result obtained would then apply to the mean temperature and pressure of the measurement. Following this method the values of $(\overline{E}_{1g} - \overline{E}_{1L})$ can be calculated from experimental data for several pressures and temperatures and the deviations of $(\overline{E}_{1g} - \overline{E}_{1L})$ with respect to these variables determined. These deviations may then be used in conjunction with Equation 32 for calculating the correct value of $(\overline{E}_{1g} - \overline{E}_{1L})$ at the initial pressure and temperature of the measurement.

## Experimental Investigation of the Propane-Crystal Oil System

In order to investigate the applicability of the calorimetric method for the determination of the change in partial enthalpy a number of runs were made on the propane-crystal oil system. For this work the adiabatic calorimeter shown diagrammatically in Figures 1 and 2 was used. It consisted essentially of a polished calorimeter bomb A mounted inside an evacuated and highly polished chromium-plated metal jacket B. Leading out of the top of the calorimeter bomb were two small stainless steel lines approximately .02 inch in inside diameter. One of these lines was connected to a small mercury-oil trap M, through which the pressure in the apparatus could be transmitted to a fluid pressure balance N for measurement. The other passed through a motor-operated valve H into the evaporator bomb J, which contained the pure propane to be admitted into the calorimeter bomb in the form of a gas. These lines were each surrounded by a steam-heated jacket for the purpose of preventing condensation of any of the gas in the lines during operation.

Leading out of the lower end of the calorimeter bomb was a long tube Q, .125 inch in inside diameter, through which was inserted a stirring shaft attached to an agitator Y located within the bomb. A packing gland R was placed at the lower end of this tube in order to prevent the escape of any liquid at that point.

Inside the calorimeter bomb was located an electric heating coil P which could be used for supplying a measured quantity of heat to the contents of the bomb. This heater was constructed of approximately three feet of number 36 constantan wire enclosed within a small stainless steel tube approximately .03 inch in

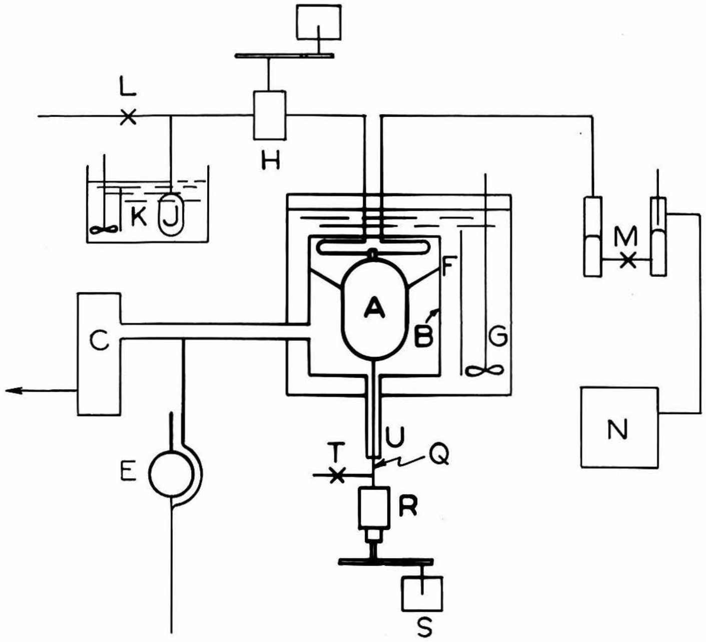

Figure 1. Diagram Showing General Arrangement of Calorimeter Equipment.

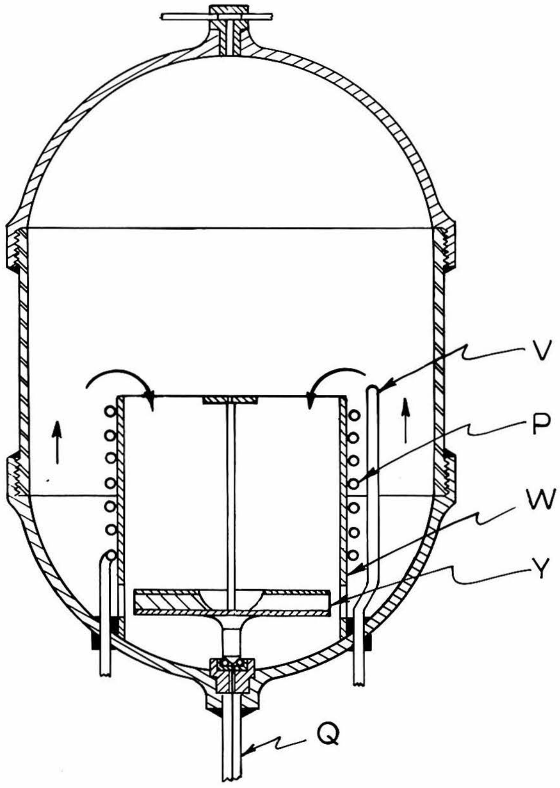

Figure 2. Diagram Showing Details of Calorimeter Bomb.

diameter. The construction was such that all of the constantan wire was located within the calorimeter bomb. The leads from the bomb were relatively large, being made of number 28 B and S gauge copper wire. During operation, the voltage impressed upon the heater was measured at a point just outside the bomb by means of a Leeds & Northrup Type K-2 potentiometer operating in conjunction with a volt box having a resistance of $10^4$ ohms. The current flowing through the heater was established with the same instrument by measuring the voltage across a standardized resistance connected in series with the heater. Also located within the bomb was a multi-lead, copper-constantan thermocouple junction. This was so placed inside the tube V as to permit as nearly as possible the determination of the average temperature of the liquid contents of the bomb.

Surrounding the jacket B was an oil thermostat G which could be automatically controlled by means of a galvanometer and photo-electric cell arrangement operating in conjunction with thermocouples placed within the bath. This arrangement was connected so as to permit either isothermal, or adiabatic control of the bath. In the latter case, the temperature of the bath was maintained at a value such that the temperature differential between the bomb and the jacket was as nearly zero as possible at all times. This was accomplished by connecting the galvanometer to a two-junction, three-wire copper-constantan differential thermocouple having alternate junctions located in the oil bath and on the outer surface of the calorimeter bomb. In the former case, the galvanometer was connected to a potentiometer and battery circuit whose e.m.f. was opposed by that of a three-wire copper-constantan thermocouple having its hot junction in the oil bath and its cold junction in an agitated ice bath.

The calorimeter bomb itself was supported inside the jacket B by means of small wires of low thermal conductivity, in order to reduce heat interchanges between it and the surroundings to a minimum. The evaporator J was placed in an oil thermostat K in which the temperature could be controlled by means of a mercury-in-glass regulator. In this manner the vapor pressure of the liquid contents of the evaporator was kept at a constant value which was sufficiently high to permit the material to flow as a gas into the calorimeter bomb under the desired pressure. The rate of flow could be controlled by means of the motor-operated valve H.

During a run the temperature of the contents of the calorimeter bomb, as well as that of the entering gas, was ascertained as a function of the time. For this purpose three-wire copper-constantan thermocouples were used. One couple was located within the liquid-filled portion of the bomb, while the other was located at a point slightly in advance of the position where the tube carrying the gas from the evaporator bomb joined the calorimeter bomb. A four-junction three-wire, copper-constantan differential thermocouple having alternate junctions on the surface of the calorimeter bomb and on the surface of the jacket B was also provided. This permitted the difference in temperature between the bomb and the jacket to be measured as a function of the time so that any energy interchange obtained as a consequence of such a temperature difference could be evaluated. Another differential thermocouple was provided for the measurement of the temperature difference between the oil bath surrounding the jacket B, and the lower end of the tube through which the stirring shaft passed. This permitted the evaluation of any energy loss which might result from temperature gradients along the tube Q.

## Calibration of Apparatus

Before any actual measurements were undertaken, it was necessary to perform certain preliminary calibration tests on the equipment. These tests were made for the purpose of obtaining the following fundamental data:

(1) The relationship between the various thermocouple readings and the international platinum temperature scale.

(2) The heat capacity of the calorimeter bomb as a function of the temperature.

(3) A constant K for evaluating the energy interchanges between the calorimeter bomb and the surroundings as a result of temperature gradients.

The first of the above calibrations was made by comparing the readings obtained from the oil bath and calorimeter bomb thermocouples with those of a platinum resistance thermometer which had been calibrated shortly before by the United States Bureau of Standards. This comparison taken at several temperatures gave the desired relationship between the readings of these thermocouples and the international platinum temperature scale.

The second quantity determined was the heat capacity of the calorimeter bomb as a function of its temperature. If it is assumed that the heat capacity of the calorimeter bomb exhibits a linear relation with respect to temperature, two determinations, each at a different temperature, are sufficient. The method of evaluating the heat capacity of the calorimeter bomb at any one temperature consisted in introducing into the bomb a known weight of crystal oil and then measuring the rise in temperature of the bomb and contents as a consequence of the addition of a measured quantity of electrical energy. During the addition of heat the losses were kept to a minimum by maintaining the temperature differential between the bomb and the jacket as near zero as possible. From these data the heat capacity of the calorimeter bomb and contents was calculated for the average temperature of the determination. Following this, a known weight of the crystal oil was removed from the bomb and a second determination between the same temperature intervals was made in an identical manner. This resulted in a heat capacity for the bomb and contents which differed from the first only by the heat capacity of the oil removed. From these two determinations, it was possible to eliminate the heat capacity of the oil and to obtain that of the calorimeter bomb alone. By making two such sets of measurements, each at a different temperature, the heat capacity of the bomb as a function of the temperature was established.

The constant K was evaluated by maintaining the temperature of the oil bath at a constant value while heating the calorimeter bomb to a temperature considerably above that of the bath and then allowing it to cool gradually as a result of the energy which it has lost to the surroundings. During the cooling process, the temperature of the bomb and its contents, together with that of the differential temperature between the bomb and jacket, was taken as a function of the time. Since the temperature differential between the bomb and jacket waa measured in microvolts, it was convenient to express the constant K in joules per microvolt differential per second. That this might be done to best advantage, it was also found desirable to express the change in temperature of the bomb and contents in microvolts directly as measured. A typical cooling curve obtained in the manner outlined is presented in Figure 3.

For the cooling process the following equations may be assumed to hold:

$$\frac{dQ}{d\theta} = -\left(C_B + m_{co} C_{co}\right) \frac{d\xi_B}{d\theta} \tag{33}$$

and

$$\frac{dQ}{d\theta} = -K\,\xi_D \tag{34}$$

Combining Equations 33 and 34 gives the relation:

$$K \xi_D = (C_B + C_{co} m_{co}) \frac{d\xi_B}{d\theta} \tag{35}$$

Assuming that for the particular run in question may be expressed as some function of the time θ multiplied by , one may write that:

$$\xi_D = f(\theta)\, \xi_B \tag{36}$$

Substitution of this relation in Equation 35 results in the expression:

$$K\, f(\theta)\, \xi_B = (C_B + m_{co} C_{co}) \frac{d\xi_B}{d\theta} \tag{37}$$

which upon integrating and solving for K gives:

$$K = \frac{\displaystyle\int_{\xi_{B_0}}^{\xi_B} (C_B + m_{co} C_{co}) \frac{d\xi_B}{\xi_B}}{\displaystyle\int_{\theta_0}^{\theta} f(\theta)\, d\theta} \tag{38}$$

This equation may be solved for K over any desired interval of the cooling curve as well as over the entire cooling curve. If the value of K obtained over each of these intervals is found to be substantially the same, it indicates that the assumptions underlying Equations 1, 2, and 4 are correct and that the equations are therefore valid. The results of measurements carried out on the apparatus described indicated that over any interval selected the value of K always remained within one per cent of the mean value.

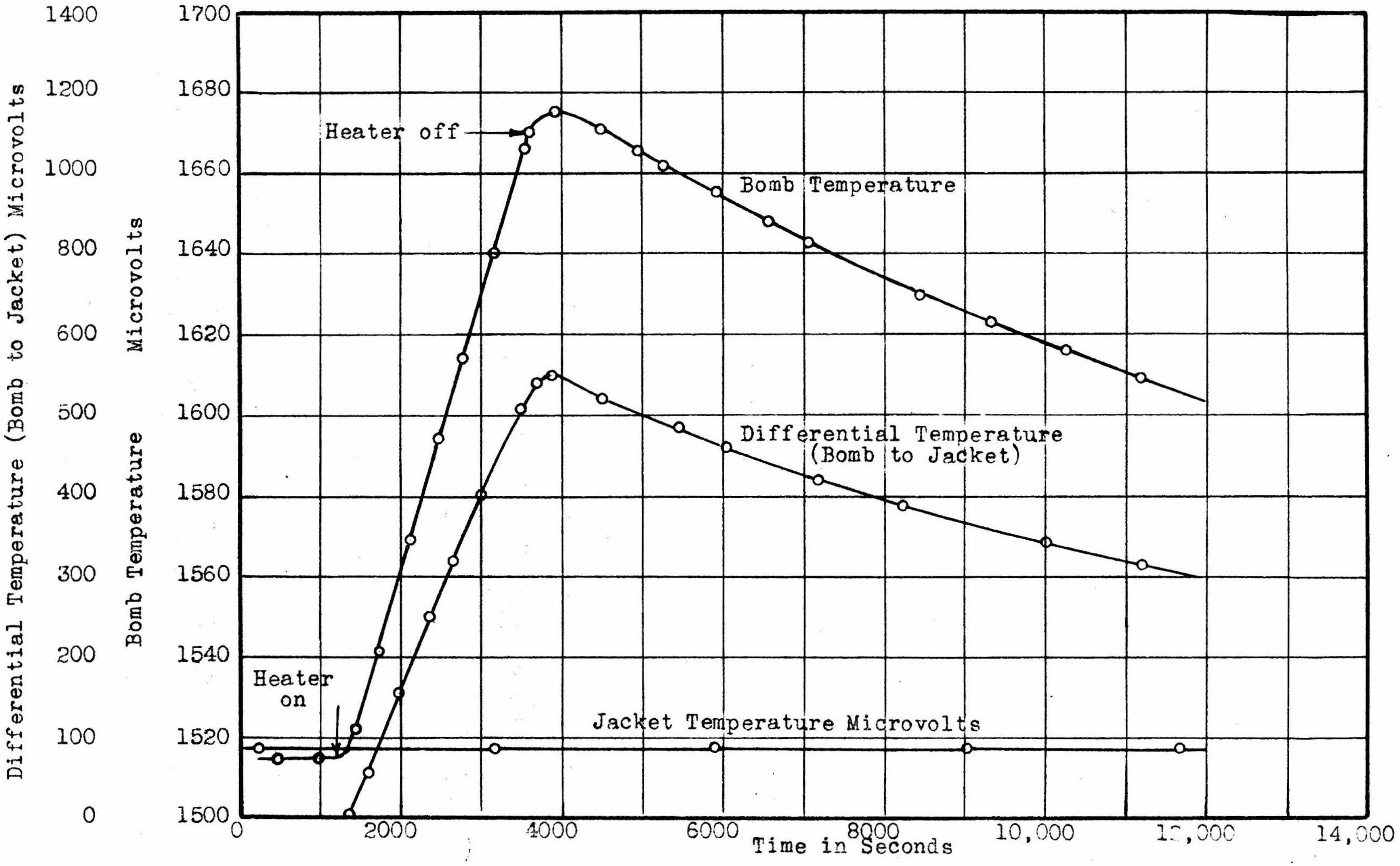

Figure 3. Cooling Curves for Determination of K.

## Experimental Method

The change in partial internal energy of one component under-going solution in another is a quantity which depends only upon the pressure, temperature, and composition of the phases in which the process is taking place. This being the case, the experimental aim should be to obtain values of this quantity as a function of the pressure, temperature, and composition of the phases involved. This is difficult to do because of the limitations imposed by the experimental requirements. For example, if two phases of a binary mixture exist together in a calorimeter, the composition of one of the phases cannot under-go an equilibrium change without necessitating a change in either the temperature or pressure of the system. This means that any calorimetric measurement of the change in partial internal energy must involve changes in either the pressure or temperature of the system if equilibrium is to exist at the beginning and end of the run. Also from the experimental requirements it is clear that before any portion of the gas phase can be induced to dissolve in the liquid phase, it is necessary that the gas pressure exceed the bubble point pressure of the liquid at the temperature and composition at which it exists. This limitation prevents the possibility of obtaining perfect equilibrium between the gas and liquid phase throughout a run. Because of the limitations listed above, any calorimetric determination of the change in partial internal energy of a gaseous component dissolving in a liquid phase must be corrected for changes in pressure, temperature, and composition, or else average values must be assumed.

With these facts in mind, a method of operation of the calorimeter was devised so as to permit the necessary changes in temperature and pressure to occur in such a manner that they could be followed as a function of the time. To do this the calorimeter bomb and contents were brought to a constant temperature equal to that of the jacket surrounding the bomb. The agitator was then turned on for a sufficient period of time to insure equilibrium between phases, after which the pressure and temperature of the contents of the bomb were recorded. This information was sufficient to establish the state of the system at the start of the run. With the agitator turned off, the valve H̲ was opened and gas from the evaporator J̲ was allowed to flow into the calorimeter bomb until the pressure was at a value considerably above that corresponding to the bubble point pressure of the liquid contents of the bomb. When this pressure had been reached, the agitator was turned on again and the gas from the evaporator J̲ immediately began entering into solution causing a rapid drop in pressure, and a sudden rise in temperature of the contents of the bomb. At this point the motor-operated valve H̲ was brought into play and adjusted manually throughout the remainder of the run so as to maintain the pressure in the calorimeter bomb as nearly constant as possible. Readings of this pressure were recorded at regular intervals. As the run progressed the temperatures of both the contents of the calorimeter bomb and of the gas entering the bomb were observed as functions of the time. These readings were taken using a White double potentiometer that could be read with an accuracy of approximately .05 microvolt, which corresponded to a temperature of approximately .0025 °F.. The difference in temperature between the bomb and jacket was also read on the White potentiometer and was recorded at regular intervals. This difference was kept as low as possible by placing the oil bath on adiabatic control so that it might keep the jacket B at a temperature as close to that of the calorimeter bomb as the control system would permit.

As the run progressed the rate of solution of gas into the liquid phase decreased until a point was reached at which no more gas would enter into solution. This point represented a state of equilibrium between the liquid and gas phases. As soon as this point was reached the agitator was turned off and the bomb and contents were allowed to come to complete thermal equilibrium before final readings of the pressure and temperature of the contents of the bomb were recorded. These last readings served to establish the final state of the system.

In addition to the above quantities, the total weight of gas entering the calorimeter bomb during the run was determined by weighing the evaporator bomb J at the beginning and end of the run. The exact time of agitation was also recorded by means of a chronometer so that any energy added from this source might be evaluated. This was done by running a separate agitator test on the bomb and contents for the purpose of evaluating the quantity of energy added by the agitator per unit time under the same conditions as those obtaining during the test.

The weight of gas dissolving in the liquid phase as a function of the time could be estimated very closely by assuming that the rise in temperature of the bomb is proportional to the quantity of material entering into solution. If this is the case, one may write:

$$\frac{dm_{1L}}{d\theta} = k\,\frac{d\xi_B}{d\theta} \tag{39}$$

This expression may then be integrated over the time interval during which gas was added to give the relation:

$$\Delta m_{1L} = k\int_{\theta_A}^{\theta} \frac{d\xi_B}{d\theta}\,d\theta \tag{40}$$

Since the total weight of gas added to the system during a run was carefully measured, the value of $\Delta m_{1L}$ for a complete run could be calculated from a knowledge of the pressure and temperature of the contents of the calorimeter bomb at the beginning and end of the run, together with the known volumes occupied by the liquid and gas phases. This calculation requires a knowledge of the specific volume of the liquid and gas phases as a function of pressure, temperature, and composition. If the volume occupied by the gas phase is small, the accuracy with which these data need be known is not great. Using a value of $m_{1L}$ as calculated from the measured quantity of gas entering the bomb, one is in a position to evaluate the constant by means of the equation:

$$k = \frac{\Delta m_{1L}}{\Delta \xi_B} \tag{41}$$

where $\Delta m_{1L}$ is the total weight of gas which has gone into solution during a run, and $\Delta \xi_B$ is the total rise in temperature of the bomb during the run.

Following this procedure, the weight which has gone into solution at any time may be calculated using Equation 41 together with $k$, as determined above. It should be recognized that this method is not exact, because it does not take into account the changes in heat capacity of the bomb and contents as a function of the time. It also neglects the effect of a time lag, and assumes that the heat evolved per unit weight of gas entering into solution is independent of the pressure, temperature, and composition, throughout the run. Since the value of $m_{1L}$ when expressed as a function of the time is used only in second order corrections when calculating the final result, Equation 41 is believed to be sufficiently accurate for the purpose intended.

In order to indicate the magnitude of the temperature and pressure changes involved in an actual determination, Figure 4 has been prepared. The results presented in this figure are those actually recorded during one of the runs. In this figure all temperatures have been converted from microvolts as read in the

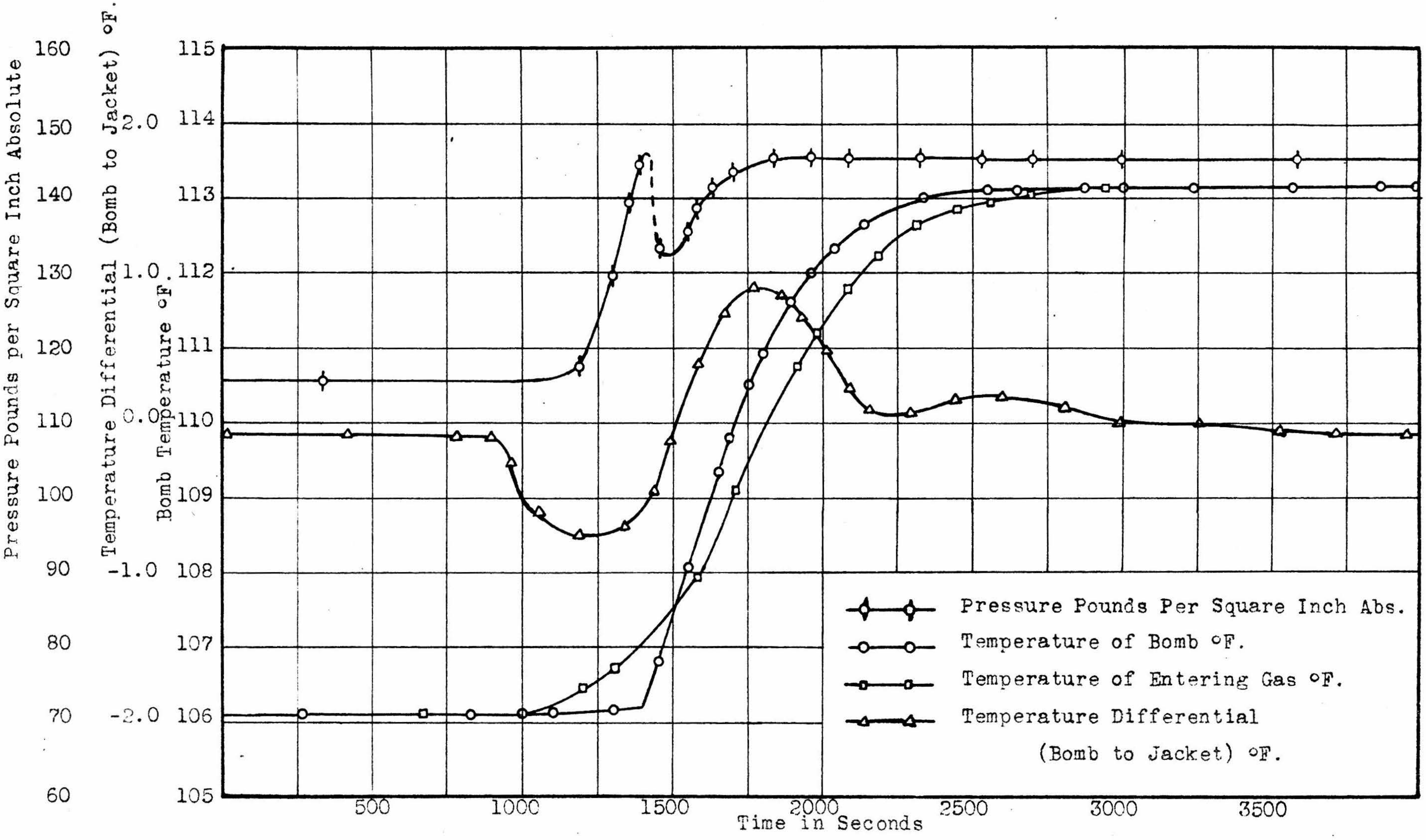

Figure 4. Typical Curves Illustrating the Magnitude of Pressure And Temperature Changes During an Actual Run

laboratory to degrees Fahrenheit in order to facilitate their interpretation.

## Accuracy of Measurement

It is difficult to estimate the over-all accuracy of the results obtained in a determination as complex as the one described. However, something can be said regarding the accuracy with which the individual quantities involved were measured. From the results obtained in several determinations of the heat capacity of the bomb and contents it was found that this quantity could be determined with an absolute uncertainty of less than 0.2 per cent. The rise in temperature of the bomb and contents could be read to 0.07 microvolt, which corresponds to an uncertainty of only 0.1 per cent in all determinations involving changes in temperature greater than 70 microvolts, (3° F.). The absolute pressure of the contents of the calorimeter bomb could be obtained with an uncertainty of less than 0.2 pound per square inch absolute and pressure differences could be estimated to 0.05 pound per square inch. The weight of propane added to the calorimeter was obtained by weighing the evaporator bomb J on an analytical balance at the beginning and end of the run. It is believed that the errors introduced in the weighing process were less than one part in 5000. Because of the corrections required in estimating the change in weight of the gas phase within the calorimeter during the course of a run, the actual quantity of propane entering into solution was known only to about 0.01 gram. This corresponded to an uncertainty of about 0.2 per cent. The heat lost from the bomb could be obtained with an absolute accuracy of only about 95 per cent, but inasmuch as this quantity amounted to less than 1 per cent of the sum of all of the energy interchanges involved in a measurement, it introduced no uncertainties greater than 0.05 per cent in the final result.

The largest source of error involved in the measurements was that of evaluating the energy added to the system as a consequence of the motion of the agitator. This factor represented about one-tenth of the sum of the measurable energy effects involved in a measurement. Results obtained from the agitator tests indicated that its true value was not known to better than 95 per cent in most cases. Thus the error introduced into the final results from this source might be as high as 0.5 per cent. It is believed by the author that this error could be decreased in future determinations by lowering the speed of agitation.

From a consideration of the above factors, it would seem that the absolute experimental uncertainty of a determination should not exceed about 0.75 per cent. Because of additional errors introduced in the application of other experimental data in the calculations, this error may be increased by a small amount. It is the author's opinion that in all cases here reported the final results are accurate to one per cent.

## Materials

The propane used for this investigation was obtained from the Phillips Petroleum Company. A special analysis submitted by the company showed that it contained less than 0.03 mole per cent of impurities.

The crystal oil used was a water-white paraffin-base oil refined from Pennsylvania crude stock. Its average molecular weight, as determined from the freezing point lowering of benzene, was found to be 342. The oil, which could be considered non-volatile for all practical purposes, had a vapor pressure of only $10^{-3}$ inch of mercury at 100° F.. Its absolute viscosity at bubble point as determined by a rolling ball viscometer (5) was found to be 103 millipoises at 100° F. and 21.6 millipoises at 220° F..

## Results

The results of the determinations carried out in the laboratory are presented in Table I. The values obtained from the calorimetric measurements were calculated from the experimental data by the use of Equations 23 and 32. These values were not corrected to take into account the effect of changes in pressure and temperature which were encountered, because sufficient data regarding these changes were as yet unavailable. However, it is believed that any uncertainties in the results as a consequence of this correction would be exceedingly small.

For the purpose of comparison, some corresponding values calculated by the application of Equation 22 assuming the crystal oil to behave as a single component have been included in the table. Because of lack of accurate phase equilibrium data regarding the system, it was found necessary to calculate the value of $(d\ P/d\ T)''_{\underline{x}_L}$ upon the assumption that the system followed the behavior of an ideal solution (3).

Table I.

Comparison of Results Obtained for the Propane Crystal Oil System By Calorimetric and Phase Equilibrium Methods

| Mole Fraction of Propane in Liquid Phase $\underline{x}_{1L}$ | Mean Temperature of Determination °F. $t_m$ | $\bar{H}_{1g}-\bar{H}_{1L}$ Calorimetric Method B.t.u. per lb. | $\bar{H}_{1g}-\bar{H}_{1L}$ Phase Equilibrium Method B.t.u. per lb. |
|---|---|---|---|
| .231 | 103.9 | 143.9 | 141.7 |
| .495 | 106.7 | 142.5 | 141.9 |
| .585 | 99.4 | 138.7 | 134.5 |
| .657 | 109.68 | 140.6 | 136.6 |

Using this as a basis, the curves representing the change in bubble point pressure with respect to temperature were plotted for the compositions listed in Table I. These curves were calculated by graphical methods from the equation:

$$f_g = f_L\ \underline{x}_L \qquad (41)$$

where $f_g$ represents the fugacity of pure propane gas and $f_L$ represents the fugacity of propane in the liquid phase at the same pressure and temperature. In order to obtain $f_L$ at this pressure and temperature, it was necessary to extrapolate the isothermal curves representing the fugacity of the liquid phase as a function of pressure into the regions of lower pressure. The data used for this calculation were obtained from the work of Sage and Lacey (5).

Having determined the above curves, the values of $(d\,P/d\,T)''_{\underline{x_L}}$ were obtained graphically by reading the slope of the curves at the desired temperatures.

The results presented in Table I. indicate that the calorimetric method gives values slightly in excess of those obtained upon the assumption of ideal solutions. This is probably due to the fact that the propane-crystal oil system does not follow this behavior perfectly. Since Equation 22 is very sensitive to the term $(d\,P/d\,T)''_{\underline{x_L}}$ , it is clear that only slight deviations from the law of ideal solutions might easily produce errors as large as those encountered in Table I..

From the limited number of measurements which have been made, it appears that the calorimetric method might be used with accuracy for the determination of $\overline{H}_{kg} - \overline{H}_{kL}$, in cases where the solvent can be treated as a non-volatile component. However, in view of the relative simplicity of Equation 22, it would seem that this method offers the greatest utility. Before too many conclusions can be drawn, it will be necessary to perform more experiments in an attempt to determine the relative merits of the two methods presented.

# NOMENCLATURE

| | |
|---|---|
| $b$ | Specific gas constant, cubic feet per square inch per °F. |
| $C_p$ | Specific heat at constant pressure, Btu. per lb. per °F. |
| $C_B$ | Specific heat of calorimeter bomb at constant pressure, Btu. per °F. |
| $C_{co}$ | Specific heat of crystal oil at constant pressure, Btu. per lb. per °F. |
| $d$ | Differential. |
| $\partial$ | Partial differential. |
| $\underline{E}$ | Internal energy, Btu. |
| $E$ | Specific internal energy, Btu. per lb. |
| $\bar{E}_k$ | Partial internal energy of component k, Btu. per lb., $(\partial \underline{E} / \partial m_k)_{p,T,mi}$ . |
| $\underline{F}$ | Chemical potential (Lewis' free energy), Btu. |
| $F$ | Specific chemical potential, Btu. per lb. |
| $\bar{F}_k$ | Partial chemical potential of component k, Btu. per lb., $(\partial \underline{F} / \partial m_k)_{p,T,mi}$ . |
| $f_k$ | Fugacity of component k, lbs. per sq. inch. |
| $\underline{H}$ | Enthalpy, Btu. |
| $H$ | Specific enthalpy, Btu. per lb. |
| $\bar{H}_k$ | Partial enthalpy of component k, Btu. per lb., $(\partial \underline{H} / \partial m_k)_{p,T,mi}$ . |
| $K$ | Constant for determining energy interchanges between the calorimeter bomb and surroundings as a result of temperature gradients, Btu. per microvolt difference in temperature per second. |

| | |
|---|---|
| $k$ | Constant used in calculation of mass of gas entering into solution as a function of the time. (See Equations 39, 40, & 41). |
| $\ell_p$ | Latent heat of pressure variation, Btu. per lb. per sq. inch. |
| $m$ | Weight in pounds. |
| $m_k$ | Weight of component k in pounds. |
| $P$ | Intensity of pressure, lbs. per sq. inch absolute. |
| $Q_{A-B}$ | Energy added to the system as a result of a temperature gradient between states A and B, Btu. |
| $q$ | Energy added to the system as a result of an infinitesimal change in state, Btu. |
| $\underline{S}$ | Entropy, Btu. per °F. absolute. |
| $S$ | Specific entropy, Btu. per °F. absolute per lb. |
| $\bar{S}_k$ | Partial entropy of component k, Btu. per °F. absolute per lb., $(\partial \underline{S} / \partial m_k)_{p,T,mi}$ . |
| $T$ | Temperature ° Rankine. |
| $\underline{V}$ | Volume, cubic feet. |
| $V$ | Specific volume, cubic feet per lb. |
| $\bar{V}_k$ | Partial volume of component k, cubic feet per lb., $(\partial \underline{V} / \partial m_k)_{p,T,mi}$ . |
| $W_{A-B}$ | Work done on the system by the surroundings between states A and B, Btu. per lb. |
| $w$ | Work done by the system on the surroundings as a result of an infinitesimal change in state, Btu. per lb. |

| | |
|---|---|
| $\underline{x}$ | Mole fraction of a component in the liquid phase. |
| $\underline{y}$ | Mole fraction of a component in the gas phase. |
| $\theta$ | Time, seconds. |
| $\xi_B$ | Temperature of calorimeter bomb, microvolts. |
| $\xi_D$ | Temperature differential between surface of calorimeter bomb and surrounding jacket, microvolts. |
| $\Delta$ | Coefficient placed before a variable to represent a finite change in that variable. |
| $\int_A^B$ | Definite integral between initial state A and final state B. |
| $\not\int_A^B$ | Definite line integral, which must be evaluated in relation to the path between the initial and final states. |

Subscript $m_i$ indicates that all components except component k are constant.

Subscript L refers to liquid phase.

Subscript g refers to gas phase.

Subscripts 1, 2, etc., refer to components 1, 2, etc.

Subscripts A and B refer to the initial and final states of system.

Subscript co refers to crystal oil.

Subscript o refers to an initial condition.

Subscript $\nu$ refers to any component in an n-component system.

Double prime ( )", refers to conditions in which two phases are present.

Single prime ( )', refers to conditions in which only one phase is present.

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