APPLICATION OF THERMODYNAMICS TO PETROLEUM REFINING PROCESS DESIGN

A Thesis

Presented to the Faculty of the Graduate School
of Oklahoma Agriculture and Mechanical College for a

PROFESSIONAL DEGREE IN CHEMICAL ENGINEERING

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PREFACE

The thesis submitted to the Graduate School of Oklahoma Agricultural and Mechanical College as partial fulfillment of requirements for obtaining the Professional Degree of Chemical Engineer deals with the Application of Thermodynamics to Petroleum Refining Process Design. This material can be divided into two parts.

The first part, with the heading, THERMODYNAMIC TREATISE, p. 88-180, deals with the thermodynamical principles involved and leads to the development of tools for the use in petroleum refining process design.

This part is a compilation in which free use is made of the available literature on the subject, the authors and titles of the books being given on p. 88. However, the material is supplemented by data which are not published yet and which are accumulated in the Standard Oil Company of Indiana Data Book. The author of the Thesis is editor of this Standard Data Book and while the book as a whole is not available to the general public the specific information taken from it and used in this thesis is not of a confidential nature.

The second part of the thesis is comprised of reprints of five publications of the author and are his original contributions to Thermodynamics of Hydrocarbons, and as such is the main part of the thesis.

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I. INTRODUCTION

II. THERMODYNAMICS TREATISE

A 100 page treatise of thermodynamics and its application to the development of tools for use petroleum refining process design. The material is one chapter of the notes prepared by the candidate for his use in teaching "Petroleum Refining Process Design."

III. REPRINTS OF PUBLICATIONS

1. "Thermodynamic Properties of Methane"
   Industrial and Engineering Chemistry
   Vol. 28, page 1112, September, 1936

2. "Enthalpy-Entropy Diagram is Developed for Methane"
   Oil and Gas Journal
   November 5, 1936

3. "Thermodynamic Properties of Hydrocarbons"
   Industrial and Engineering Chemistry
   Vol.30, page 352, March, 1938

4. "Specific Heat Ratios for Hydrocarbons"
   Industrial and Engineering Chemistry
   Vol.32, page 373, March, 1940

5. "Liquefaction and Regasification of Lighter Hydrocarbons"
   Oil and Gas Journal
   September 4, 1941, page 35

IV. PROFESSIONAL RECORD OF CANDIDATE

A. Education

B. Professional Societies

C. Industrial Experience

D. Academic Experience

E. Publications

F. Patents

G. Lectures

INTRODUCTION

The fundamental principles that form the basis for all chemical engineering calculations and process design methods are:

1. Conservation of matter (material balance)
2. Conservation of energy (heat balance)
3. Rate equation (driving force/resistance)
4. Equilibrium (phase or reaction)

The first two principles simply say that what goes in must come out. The second principle is the first law of thermodynamics. The fourth principle involves the second and third laws of thermodynamics. The importance of thermodynamics to chemical engineering calculations is obvious.

The application of thermodynamics to the process design of petroleum refining equipment is complicated by the multicomponent nature of petroleum and the products therefrom. For this reason, thermodynamic developments in the field of petroleum have been slow. This thesis, presents certain developments in hydrocarbon thermodynamics made by the candidate during the past few years. These developments are presented by: (1) a 100 page treatise of thermodynamics, and (2) reprints of five papers on thermodynamics published by the candidate.

The thermodynamics treatise presented in this thesis is one chapter of the notes prepared by the candidate for his use in teaching "Petroleum Refining Process Design" to a group of technical men from the Research and Engineering Departments of the Standard Oil Company (Indiana) at Whiting, Indiana. Since all the men in the class were Company employees, unpublished data and correlations available in the Company files could be used in the studies. The most important information source of this kind was the Standard Data Book, for which the candidate is the editor. Standard Data Book charts are referred to in this treatise but they can not be included.

Of the five articles, of which reprints are included, the candidate is the sole author of the first four and co-author of the fifth. For this fifth paper the candidate developed the Mollier diagrams given as Figures 3, 4, 5, 6, 7, 8, and 9 and collaborated in drafting the manuscript. The co-author, Mr. Laverty, prepared the material on liquefaction and storage of natural gas, the candidate having nothing to do with the design or erection of the plant described. The Mollier diagrams presented in this paper were developed for use in a patent infringement law suit, in which Mr. Laverty and the candidate were technical experts for the defendant (Standard Oil Company (Indiana)).

It is believed that the following items are complete in themselves so that no further explanations are necessary.

II

THERMODYNAMIC TREATISE

IV. Thermodynamics

Chapter IV

THERMODYNAMICS

Thermodynamics is a natural science which deals with energy and the transformation of energy and with equilibrium and the equilibrium distribution of products. Applications of thermodynamics in chemistry, physics and engineering sciences are numerous. For many years thermodynamics has been a very useful tool in the design and operation of steam boilers, engines and turbines, of internal combustion engines, of refrigeration units, and of heating and ventilating equipment. Until recent years, however, very few efforts had been made to apply thermodynamics to chemical and chemical engineering problems which are encountered in petroleum refining. There are two reasons why the development of this branch of thermodynamics lagged the development of the so-called "Engineering Thermodynamics", namely: (1) mechanical engineering problems were more pressing due to the harnessing of the recently invented steam engine, turbine, and internal combustion engine; and, (2) chemical and chemical engineering thermodynamics is complicated by the varying composition of the working fluid, petroleum and petroleum fractions offering some very troubling problems. Progress in the solution of these problems has been rapid during recent years so that new equipment can be designed without too much thermo guessing. Nevertheless there is still a great deal of room for improvement, which must be made to keep process design technique apace with the development of new refining processes.

The purpose of this chapter is to present the development of thermodynamic tools for use in the process design of petroleum refining equipment. This presentation will be proceeded by a brief exposition on the basic theory and concepts of thermodynamics. Books referred to in preparing these notes are given below:

Therm dynamics for Chemical Engineers,
H.C.Weber, John Wiley & Sons, 1939

Thermodynamics
Lewis & Randall, McGraw-Hill, 1923

Principles of Engineering Thermodynamics
Kiefer & Stuart, John Wiley & Son, 1930

General Theory of Thermodynamics
Trevor, Ginn and Company, 1927.

Principle of Thermodynamics
Goodenough, Henry Holt and Company, 1931

Volumetric and Phase Behavior of Hydrocarbons
Sage and Lacey, Stanford University Press, 1939

Elements of Engineering Thermodynamics
Mayer, Calderwood, and Potter, John Wiley & Sons, 1929

A. General Theory

Before taking up the basic laws of thermodynamics and the relations developed from them, various terms and concepts will be defined and attention given to the concise methods of mathematics that will be used.

1. Basic Definitions

A homogeneous system is one whose properties are the same in all parts of the system, or at least which vary continuously from point to point; a system in which there are no apparent surfaces of discontinuity. A heterogeneous system consists of two or more distinct homogeneous regions. These homogeneous regions, which may be different phases (gaseous, liquid, or solid) of the same substance, or a mixture of two or more immiscible substances, appear to be separated from one another by surfaces of discontinuity. Systems may be further classified according to whether they contain one or more pure substances. Any system that contains more than one pure substance is a solution or a mixture.

The state or phase condition of a system depends on its properties. Properties that are dependent on the mass of the substances under consideration are known as extensive properties. Properties that are not dependent on the mass of the substance are called intensive properties. Attention will be given the following intensive and extensive properties in this chapter:

Intensive Properties

T = Temperature
P = Pressure
f = fugacity
$\gamma = C_p/C_v$ = specific heat ratio
$\mu = \left(\frac{\partial T}{\partial P}\right)_H$ = Joule-Thomson coefficient

Extensive Properties

V = Volume
C_p = Specific heat at constant pressure
C_v = Specific heat at constant volume
S = Entropy
E = Internal Energy
A = Helmholtz Free Energy
F = Gibbs Free Energy
H = Enthalpy

Equilibrium is a state of rest. A system that is not at equilibrium is moving in that direction. Although equilibrium conditions can be estimated by thermodynamics, the rate at which equilibrium is approached cannot be predicted by thermodynamics method. Reaction rates, diffusivities, etc. must be employed to make this prediction. As previously pointed out, most petroleum refining processes are steady flow processes. Equilibrium in such processes is a "dynamic" rather than a "static" state. The definition of equilibrium as a state of "rest" cannot be taken literally. In a flow process a state of "rest" (equilibrium) means "no tendency to change", which may apply to temperature, pressure, phase condition, etc.

2. Mathematical Methods

The language of thermodynamics is mathematics, which has been defined as a shorthand for the precise formulation of well standardized ideas. In addition to arithmetic and algebra, differential and integral calculus are used extensively in the development and application of thermodynamic relationships. Graphical as well as analytical methods of differentiation and integration are applied in this work. The amount of calculus really essential in thermodynamics is very small. However, an intimate familiarity with this small amount of essential calculus is necessary to a thorough understanding and a workable knowledge of thermodynamics. The following discussion of calculus methods will probably be a review for many students studying these notes but is presented in the hope that it will contribute appreciably to the understanding of this chapter.

All thermodynamic properties that will be treated in later sections of this chapter depend on two or more variables. In many thermodynamic equations there are more variables than are required to define the function. Those variables which are required are called the "independent" variables while the remaining are called the "dependent" variables. The dependent variables also depend on the independent variables. From a mathematic standpoint any two (or more as the case may be) of the variables may be arbitrarily chosen as the independent variables, leaving the remaining variables as the dependent variables. Most frequently it will be convenient to call pressure and temperature, P and T, the independent variables.

For single component systems (pure compounds) P and T are the only independent variables necessary. Theoretically all the above extensive properties and all the remaining intensive properties may be defined as functions of these two independent variables. In practice it does not always work out this way, however. For example, a correlation of volume as an explicit function of pressure and temperature would be most convenient from a thermodynamic standpoint but it is not possible to express such a correlation accurately in analytical form. However, it is possible to express pressure as an accurate function of volume and temperature. Although such a correlation can be made accurate, it is not explicit in volume, which is a drawback. Consequently, many thermodynamic equations use other properties such as the volume or the entropy as the independent variables. In most cases such variables can be replaced by pressure and temperature in the final correlations so that ultimately P and T are the only independent variables.

For multi-component systems it is necessary to include enough additional variables to define the composition of the mixture. The percentage of one component is sufficient for a two component system, the percentage of two components for a three component system, etc. It is obvious that this problem can get very complicated for a multicomponent system unless steps are taken to simplify the situation. Average gravities and boiling points are employed to circumvent this trouble. More will be said about this problem later, however.

Since the thermodynamic properties to be treated depend on two or more variables, it will be necessary to use repeatedly the methods of partial differentiation. If V depends upon the two variables, P and T, the differential change in the dependent variable V, resulting from a differential change in either of the independent variables, the other being kept constant, may be expressed by the following partial differential equations:

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT$$

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP,$$

the subscript indicating which independent variable is being kept constant. The total differential of V resulting from the infinitesimal changes in both temperature and pressure will be

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \qquad (1)$$

The addition of another variable such as the percentage of one component in the system results in the following more general equation:

$$dV = \left(\frac{\partial V}{\partial T}\right)_{P,N} dT + \left(\frac{\partial V}{\partial P}\right)_{T,N} dP + \left(\frac{\partial V}{\partial N}\right)_{P,T} dN \qquad (2)$$

This equation is only a statement that the whole is made up of all its parts and represents the general equation of partial differentiation, which is a most useful tool in dealing with changes in the properties of a system.

There are special forms of equation (1) which are very useful in making thermodynamic formulations. If V is constant as it would be along a contour line of the P-V-T surface, dV = 0 and

$$\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP = 0 \qquad (3)$$

Dividing through by dT and expressing the constancy of V in the equation gives the following useful relation:

$$\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V = 0 \qquad (4)$$

If we have some other dependent variable, that is, some other quantity which, like the volume, depends only upon the temperature and pressure, let us say the entropy S, we may divide each member of equation (1) by dT and impose the condition that S is constant and obtain the following useful relation:

$$\left(\frac{\partial V}{\partial T}\right)_S = \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_S \tag{5}$$

The equation states that when we proceed upon the P-V-T surface along a line of constant entropy, the change in V corresponding to a given infinitesimal change in T is the sum of two terms, namely; the change in V, which would be caused by this change in T alone, and the change in V caused by such a change in P as is necessary to keep the entropy constant. Equations (4) and (5) are useful in transforming variables.

There are six useful transformations of variables that can be applied in developing thermodynamic formulations. The first three transformations involve three variables, which will be called P, V, and T in this discussion. The last three transformations involve four variables, which will be called P, V, T, and S. In all six of these transformations the expression $\left(\frac{\partial V}{\partial T}\right)_P$ is changed to something else. The variables and starting expression chosen for this discussion are arbitrary. The resulting transformations may be applied to any other combination of variables and starting expression.

In the first transformation the variables P and T will be interchanged in the expression $\left(\frac{\partial V}{\partial T}\right)_P$. This is done by equation (4) as follows:

$$\left(\frac{\partial V}{\partial P}\right)_T = - \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial P}{\partial T}\right)_V} \tag{6}$$

The second transformation involves interchanging V and T in the expression $\left(\frac{\partial V}{\partial P}\right)_T$. This one is a very simple reciprocal as follows:

$$\left(\frac{\partial T}{\partial V}\right)_P = \frac{1}{\left(\frac{\partial V}{\partial T}\right)_P} \tag{7}$$

In the third transformation V and P are interchanged, which is accomplished by solving for $\left(\frac{\partial P}{\partial T}\right)_V$ from equation (4) as follows:

$$\left(\frac{\partial P}{\partial T}\right)_V = - \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} \tag{8}$$

In the fourth transformation P is replaced by S in the expression $\left(\frac{\partial V}{\partial T}\right)_P$. This is given by equation (5) above. In the fifth transformation T is replaced by S in the expression $\left(\frac{\partial V}{\partial P}\right)_P$, which is very readily done by first writing the following expression:

$$\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial V}{\partial S}\right)_P \left(\frac{\partial S}{\partial T}\right)_P \qquad (9)$$

and then solving for $\left(\frac{\partial V}{\partial S}\right)_P$

$$\left(\frac{\partial V}{\partial S}\right)_P = \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial S}{\partial T}\right)_P} \qquad (10)$$

In the sixth transformation V is replaced by S in the expression $\left(\frac{\partial V}{\partial T}\right)_P$ by solving for $\left(\frac{\partial S}{\partial T}\right)_P$ in equation (9)

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial S}\right)_P} \qquad (11)$$

After the thermodynamic formulations are set up the next steps are to evaluate the derivatives and integrate the resulting expression. In case second derivatives are involved, the following relation may be used to simplify the problem:

$$\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial^2 V}{\partial P \partial T} = \frac{\partial}{\partial T}\left(\frac{\partial V}{\partial P}\right)_T \qquad (12)$$

Derivatives may be evaluated analytically or graphically. Analytical differentiation is often complicated by the fact that it is not always possible to obtain an expression that is explicit in the dependent variable thus making the use if implicit differentiation necessary. Graphical methods of differentiation are frequently the best solution to this problem. The "Chord Area Method" is one of the best methods of graphical differentiation. In finding $\left(\frac{\partial V}{\partial T}\right)_P$ by this method the following procedure is used; (a) from isobaric plots of V vs. T find $\frac{\Delta V}{\Delta T}$ for each pressure, ? taking temperature intervals small enough to get sufficient accuracy and yet not so small that slight unsmoothnesses is the data or plots of the data are reflected in the derivatives; (b) plot these values of $\frac{\Delta V}{\Delta T}$ as chords versus T; (c) through these chords draw a smooth curve (one for each pressure) so that the areas between the chord and the curve are equal, i.e. area above chord equal area below; and (d) the resulting curve is a plot of $\left(\frac{\partial V}{\partial T}\right)_P$ versus T, the values of the derivative being read from the same scale used in plotting the chords.

Similar graphical methods may be used in integrating the resulting formulation. The procedure to be followed in graphically integrating an expression in which P and T are the independent variables is as follows; (a) choose a reference state, i.e. pressure and temperature; (b) evaluate the coefficient of dT at the reference pressure and then plot against T; (c) integrate the temperature function by counting squares or with a planimeter and evaluate the integration constant so that the result has a value of zero at the reference temperature; (d) evaluate the coefficient of dP at various temperatures and plot against pressure; (e) integrate the pressure function to the pressure used in parts (b) and (c) by counting squares or with a planimeter and evaluate the final integral by combining with the results of parts (c) and (e).

When plotting large values of one variable which differ little from each other, the precision may be increased by plotting on an enlarged scale the portion of the plot in which the points lie or for which derivatives are desired. This method is not very satisfactory, however, because a number of large graphs are required. A more accurate and satisfactory method is to use a residual quantity, which is defined as the difference between the actual curve and an approximate yet easily formulated curve for the same data. For example, the residual volume is the difference between the ideal gas volume and the actual gas volume. The residual gas volume has been found very convenient in differentiating and integrating P-V-T data. This subject will be discussed further in a later section of this chapter.

3. First Law - Energy

In Benoulli's Equation, which was developed in the study of fluid flow by a total energy balance on a steady flow system, three types of energy are involved, namely: potential energy, kinetic energy, and internal energy. Until relatively recent times the first two kinds of energy, which are exemplified by the elevated body and the moving body, respectively, were all that man required in his scientific efforts. Potential and kinetic energies from the basis for mechanics, in which their sum is known as mechanical energy. As science progressed it became necessary to invent other forms of energy such as electrical energy and internal energy, the latter being very important in the study of thermodynamics.

The manner in which the potential energy of a body or system of bodies may be converted to kinetic energy, or vice versa, by reason of the relative positions and velocities of component parts of the system has already been shown. If an energy transfer of this kind takes place in a system where frictional processes are at work there will be a net loss of mechanical energy; in other words, the sum of the potential and kinetic energies will diminish. This decrease in mechanical energy is not actually lost. It is transformed to heat, the amount of heat produced being equal to the amount of mechanical energy lost. The discovery of this phenomena in the 18th century led to the consideration of heat as a form of energy, and to the enunciation of the broad principle which we know as the law of the conservation of energy or the first law of thermodynamics. In other words, the first law of thermodynamics states that heat and mechanical work are interchangeable. One Btu is equivalent to 777.5 foot-pounds, etc.

The first law of thermodynamics, i.e. the conservation of energy, has already been used in developing Bernoulli's theorem. It should be understood that the law of conservation of energy implies more than the mere statement that energy is a quantity which is constant in amount. It implies that energy may be likened to an indestructible and and uncreatable fluid which cannot enter a given system except from or through surrounding systems. In other words, it would not satisfy the conservation law if one system were to lose energy, and another system; at a distance therefrom, were simultaneously to gain energy in the same amount. The immediate surroundsing must lose or gain energy in the same amount, the energy flowing into or out of the system through its boundaries.

The internal energy of a system is an extensive property of the system and changes in it are independent of the way the change is brought about. In other words, the increase or decrease in internal energy is simply the difference between the final and initial energies regardless of the path taken in making this change. Internal energy of a substance presumably consists in the kinetic energy of the moving particles (molecules, atoms, or smaller) of the substance, in the electric fields emanating from the charged particles of which the atoms are composed, and in other forms of energy not yet named. Thermodynamics takes no cognizance of all these forms of energy, however. We are not interested in the kinds of energy that make up the total internal energy of a system. Neither do we need to know the absolute value of the internal energy. Changes in total internal energy are sufficient for all problems.

When a system loses energy by radiation, convection, conduction or friction it is giving up *heat*; when it loses energy by other methods such as operating against *external* mechanical forces it is doing *work*. If a system is subject to a constant external pressure P, and is *allowed* to expand against that pressure so that its increase in volume is ΔV, then the work done by the system is

$$W = P\Delta V \tag{13}$$

or, if the external pressure varies during the process,

$$W = \int_{V_1}^{V_2} PdV \tag{14}$$

According to the first law of thermodynamics (conservation of energy), any system in a given condition contains a definite quantity of energy, and when this system undergoes change, any gain or loss in its internal energy is equal to the loss or gain in the energy of surrounding systems. In any process (physical or chemical), the increase in energy of a given system is equal to the *heat absorbed* by the system from its surroundings minus the *work done* by the *system upon its* surroundings. If E_1 represent the initial energy *content* and E_2 the final energy content, then

$$E_2 - E_1 = \Delta E = Q - W \tag{15}$$

If heat is given up by the system instead of absorbed and if work is done on rather than by the system, both Q and W will have the opposite signs in equation (15). The change in energy between the points 1 and 2 depends only on the condition at these points (i.e. pressure, volume, and temperature) and not at all upon the path followed between these points. The work done and the heat absorbed, on the other hand, depend on the path followed as well as on the initial and final states.

If the expansion represented by equation (14) was carried out in such a manner that no heat enters or leaves the system, the process is said to be adiabatic and

$$-\Delta E = W = \int_{V_1}^{V_2} pdV \tag{16}$$

If, on the other hand, the process is such that no work is upon the surroundings (as in the case of a reaction taking place as a batch process at constant volume), then

$$\Delta E = Q \tag{17}$$

Enthalpy. Most industrial processes are not batch processes but are steady-flow processes, however, where the pressure and not the volume are kept constant or substantially constant. In a steady-flow process, the internal energy, E, is not as significant or as useful as the sum of the internal energy and the flow work, PV, (see page 6, Chapter II). This sum has been defined as the *enthalpy*, H, where

$$H = E + PV \tag{18}$$

Being the sum of the two point functions E and Pv, the enthalpy is also a point function and changes in it depend only on the initial and final conditions and not at all upon the path followed. In other words

$$H_2 - H_1 = \Delta H = (E_2 + P_2V_2) - (E_1 + P_1V_1)$$

$$\text{or} \quad \Delta H = \Delta E + \Delta (PV) \tag{19}$$

Combining equations (19) and (15)

$$\Delta H = Q - W + \Delta (PV) \tag{20}$$

$$\Delta H = Q - \int PdV + \Delta (PV) \tag{21}$$

By equation 9, page 6, Chapter II

$$\int_1^2 PdV - (P_2V_2 - P_1V_1) = \int_2^1 VdP$$

Combining with equation (21) gives

$$\Delta H = Q - \int_2^1 VdP \tag{22}$$

When the pressure is constant $\Delta H = Q$ (23)

Heat Capacity. The average heat capacity between the initial and final states is defined as $Q/\Delta T$, and the limit of this ratio as Q is made indefinitely small, or, in other words, as the two temperatures are brought near each other, is the actual heat capacity at that point. The amount of heat required to produce a given rise in temperature will, however, depend upon the circumstances under which the system is heated. We shall consider heat is added at constant volume or at constant pressure.

When heat is added at constant volume there is no work and the heat absorbed is equal to the increase in internal energy (see equation 17). Therefore

$$C_v = \left(\frac{\partial E}{\partial T}\right)_V \tag{24}$$

When heat is added at constant pressure, on the other hand, the heat absorbed is equal to the increase in the enthalpy, as shown by equation (23). Therefore

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P \tag{25}$$

From equation (19) the following expression may be written by dividing by ΔT and then expressing constancy of P;

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \qquad (26)$$

when the system is thus heated from one temperature to another at the same pressure, the increase in its energy is the same as it would be if the system were heated at constant volume from the first temperature to the second, and then brought at constant temperature to the original pressure. This may be expressed in mathematical form by the relation given as equation (5) as follows:

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \qquad (27)$$

Combining equation 24, 25 and 26, results in an equation for the difference between the heat capacity at constant pressure and the heat capacity at constant volume,

$$C_p - C_v = \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P \qquad (28)$$

Another equation for the difference in specific heats may be developed in like manner. By the mathematic relation given as equation (5)

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial H}{\partial T}\right)_P + \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V \qquad (29)$$

Starting with equation 19, dividing by ΔT and then expressing constancy of V results in the following:

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial T}\right)_V \qquad (30)$$

Combining equations 25, 29 and 30, gives the following equation for the difference in specific heats,

$$C_p - C_v = \left[V - \left(\frac{\partial H}{\partial P}\right)_T\right]\left(\frac{\partial P}{\partial T}\right)_V \qquad (31)$$

Equations 28 and 31 can be carried no further with the first law. A similar equation for the difference in specific heats that does not contain the energy or enthalpy terms will be developed later by means of the entropy.

Joule-Thomson Effect. At ordinary temperatures and pressures, all gases and vapors, except hydrogen and helium, show a cooling effect when allowed to expand freely from a higher pressure to a lower pressure with no addition or removal of heat. Hydrogen and helium show a heating effect. The production of liquid air depends solely upon this phenomenon, which is known as the Joule-Thomson effect, being named for the two men who first performed the experiment in an English brewery early in the 19th century. In this classic experiment, the gas was allowed to expand slowly through a porous plug and it was found that the temperature dropped, but no heat was removed or $Q = 0$ in equation 20, giving

$$\Delta H = \Delta(PV) - W \qquad (32)$$

Since the pressures on each side of the plug or expansion valve are maintained constant, the net work done by the system is $W = P_2V_2 - P_1V_1$, which makes equation 31.

$$\Delta H = (P_2V_2 - P_1V_1) - (P_2V_2 - P_1V_1) = 0 \qquad (33)$$

Therefore, the process is one of constant enthalpy and the Joule-Thomson coefficient is defined by the equation

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H \qquad (34)$$

By the mathematical relationship given as equation 8 the following equation for the Joule-Thomson coefficient results

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = - \frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} = - \frac{1}{C_p} \left(\frac{\partial H}{\partial P}\right)_T \qquad (35)$$

$$\mu C_p = - \left(\frac{\partial H}{\partial P}\right)_T \qquad (36)$$

This is as far as it is possible to go without using entropy. In the next section a more practical equation will be developed by means of entropy.

4. Second Law - Entropy

According to the first law of thermodynamics (conservation of energy), energy in one form may be converted to energy of another form, i.e., heat may be converted into mechanical work, mechanical work may be converted into electrical energy, etc. The first law does not say anything about the availability of energy for conversion into other forms or the efficiency of the conversion, however. This is taken care of by the second law of thermodynamics through a property called entropy. In simple language the second law states that "heat will not of its own accord flow uphill" and entropy is defined as "an index of the unavailability or degradation of energy." The second law of thermodynamics and the concept of entropy have many practical applications, such as: (1) the development of enthalpy-entropy (Mollier) charts; (2) the preparation of tables and charts of phase equilibria constants for use in making vaporization, absorption and distillation calculations; (3) the analysis of power, refrigeration, and compression cycles; (4) the computation of equilibrium product distribution for chemical reactions; etc. Entropy, per se, is very seldom used in petroleum refining process design. Nevertheless, entropy is a thing we can not do without. It is a part of or enters into the derivation of thermodynamic formulations for the enthalpy, free energy, fugacity, etc.

Degradation of Energy. According to the second law; Any process, which calls for the transfer of heat from a low temperature level to a high one without the addition of energy from an external source, is impossible. But energy is transferred from a low to a high temperature level. Mechanical refrigerating machines bring about this transfer of heat from a low temperature level to a high one by the addition of work in the form of compression. For absorption refrigeration systems, the required energy is added in the form of heat. In both of these cases the heat is pushed uphill, in one case by a compressor and in the other by a boiler. Without the addition of extra energy, heat will always go downhill from hot to cold bodies and thus become degradated or less available. This is a phenomenon of nature with which everyone is familiar. If it was not true, perpetual motion would be possible and ships could cross the oceans by engines run on heat taken from the sea only.

With the addition of extra energy, heat can be kept at a given level or even pushed uphill and may appear to suffer no degradation. This does not apply to the system as a whole, however. When the added extra energy is included in the analysis, a net degradation of energy always results. A system isolated from all others will always maintain a constant amount of energy, and therefore, in speaking of the second law of thermodynamics as the law of the dissipation of energy, no loss in energy is meant, but rather a loss in the availability of energy for external purposes. This applies to all systems and to the world as a whole. Although energy is indestructible so that the energy of the world is constant, the availability of this energy is steadily decreasing and there is nothing we can do about it. (This is nothing to get alarmed about, it has been going on since the beginning of time).

Practically all industrial processes involve the conversion of energy from one form to another. In undergoing such a change, the energy becomes less available for useful purposes. Some energy always goes down the "sink" and a small amount is lost through heat losses and friction. The "sink" for a furnace is the stack where flue gases carry low grade heat to the atmosphere. The barometric condenser is the "sink" for a condensing-turbine; the lower the temperature and pressure maintained by the condenser, the less heat will be lost to the "sink" and the higher the turbine efficiency will be. It is more accurate to speak of the degradation of the system as a whole rather than the dissipation or degradation of the energy of that system. In many cases, such as the diffusion of one gas into another, the process does not involve any appreciable energy change. The energy that goes down the "sink" becomes less available for useful purposes even though most of it may be recovered by heat economy devices. This unavailability of energy is measured by the entropy. Before proceeding to a more precise statement of the second law and a mathematic definition of entropy, we shall consider the ideal or reversible and the actual or irreversible processes.

Irreversibility - Entropy is usually explained by means of the Carnot cycle, the ideal power and refrigeration cycle representing the maximum attainable efficiency. The Carnot cycle is also a standard of perfection for rating the efficiency of actual cycles and processes. For these reasons it is desirable to discuss cycles, both the ideal or reversible and the actual or irreversible.

A series of processes which may be repeated over and over in the same manner and order is said to be a cyclic process or a cycle. There are three general types of cycles: (1) Those in which the working fluid stays in the system and undergoes a series of processes of such character that it returns to the same state; (2) those in which the same series of processes are repeated in a cycle with the working fluid being replaced each cycle and consequently never returning to its original state; and (3) a non-flow cycle in which the working fluid undergoes a series of processes while retained wholly within a vessel. Examples of the first type of cycle are; (a) condensing steam power plant where the steam condensate is recharged to the boilers; and (b) absorption of wet gas with a circulating lean oil. Examples of the second type of cycle are: (a) internal combustion engine where a fresh charge of fuel is taken into the cylinder each cycle; (b) catalytic polymerization or cracking reactor where the fluids involved in each of the phases or processes, (reaction, purge, regeneration, purge) of the cycle are new each cycle. Cycles of the third type are not employed in modern engineering practice because the several processes may be performed more advantageously in separate devices specifically designed for the distinctive functions. However, it is frequently convenient to conceive such hypothetical cycles in studying more practical cycles.

As stated above, cycles are made up of a series of processes. Heat may be added to or removed from a fluid at constant pressure or temperature. Work may be done by or on a fluid at constant pressure or temperature or without adding or removing any heat. It will be noted that, in all of these processes, the working fluid is at given set of conditions and has a given amount of energy at the start, undergoes a change, and ends the process in a different state and with a different amount of energy. If any of these processes were reversible in the thermodynamic sense, they would necessarily follow the criteria of reversibility which is: "The process, after completion, may be reversed and the fluid made to return from its final to its initial state with all energy that has been transformed during the process being returned from the final to initial form, amount and location." The second law of thermodynamics can be interrupted as stating that when an actual process occurs it is impossible to invent a means of restoring every system concerned to its original condition. Therefore, in a thermodynamical sense, any actual process is irreversible.

Although all actual processes occurring in nature are irreversible, an ideal reversible process is nevertheless imaginable and it is frequently desirable to set up such hypothetical processes as a standard of efficiency for actual processes. Such an ideal process, usually just called reversible process, is one in which all friction, electrical resistance, heat losses by radiation, conduction and convection, or other such sources of dissipation are eliminated. It is regarded as the limit of actually realizable processes. Stated in another way: A thermodynamic process is reversible if, at any stage, a differential decrease in potentials (temperature, pressure, voltage, etc.) causing the change will result in reversal of the process itself, both in direction and in all its quantitative effects. Two common reversible processes are: (1) an adiabatic (no heat added or removed) and isentropic (constant entropy) change; and (2) the isothermal addition or removal of heat. These processes will be discussed in more detail later.

Entropy - A quantitative measure of the degradation of energy is necessary for the application of thermodynamics to practical problems. The fact that heat at a low temperature level is less available than heat at a high temperature level, suggests the ratio of heat added or removed to absolute temperature as this standard of measure for the degradation or unavailability of energy. This ratio has the same dimensions as heat capacity, i.e. calories or Btu per degree, and is called the entropy. The entropy of a body or system of bodies may be changed by changing the numerator or denominator of this ratio or both. Adding heat or decreasing the temperature increases the entropy of a system. Degradation of energy is accompanied by an increase in entropy. An increase in the entropy of a system means the energy of that system has become less available for useful work. At this point it is well to point out that complete systems must be considered to get a correct picture of what is going on. For example, the generation of steam at constant pressure involves an increase in the temperature, enthalpy, and entropy of the water. The increase in entropy does not mean that the energy of the steam has become less available. In fact, the increase in temperature is evidence that energy is more available. When the entire system, including the combustion of fuel under the boiler, is considered, there is a net degradation of energy and an increase in the entropy of the system.

The total degradation of energy in two successive processes is equal to the sum of the degradations for each process. For example; in a steam power plant, degradation of energy occurs in the steam generation process and in the power generation process, the total degradation being the sum of these two degradations.

Consider two cases of steam generation in a boiler. In the first case, a highly superheated high pressure steam is produced while in the second a low temperature, low pressure steam is made. Both of these processes are thermodynamically irreversible. Which is the most irreversible and how may this irreversibility be measured? The difference in temperature between the steam and the flame is less in the first case than in the second, making the process of generating high temperature steam less irreversible than the process of generating the low temperature steam. The less this difference becomes, the closer the process approaches reversibility, suggesting a scale of irreversibility. It will be expedient to define the extent of irreversibility of thermodynamic processes by Q/Θ, where Q is the heat received and Θ is some quantity which qualitatively satisfies the definition of temperature. When the function Θ is determined, the quantitative definition of the degree of degradation will be complete. By means of thermodynamic equations involving the entropy, it can be proven that Θ, which Kelvin called the thermodynamic temperature, may be completely identified with the absolute temperature scale. Absolute temperature is defined by means of a perfect gas, zero on the absolute temperature scale being the temperature at which the volume of a perfect gas is zero. On the centigrade scale, this temperature is -273.1°C. and on the Fahrenheit scale, it is -459.6°F. In order to avoid duplication and confusion in the following formulae, we will say that $T = \Theta$ and use the absolute temperature scale.

The value of the ratio Q/T will be called the increase in entropy or

$$S_2 - S_1 = \Delta S = Q/T \qquad (37)$$

In expressing the entropy change during an irreversible process as the difference between the entropy at the end and the entropy at the beginning, it is implied that entropy is a property and therefore that the entropy change depends solely upon the initial and final states. By whatever path the system proceeds from state 1 to state 2, the degradation of energy is the same. As in the cases of the energy and the enthalpy, differences rather than absolute values of the entropy will be adequate for practically all problems. Entropy is an extensive property so the entropy of a system is equal to the sum of the entropies of its parts.

For an infinitesimal process, equation 37 becomes

$$dS = \frac{Q}{T} \qquad (38)$$

This very important equation states that the increase in the entropy of a system, or part of a system, is equal to the heat which it absorbs divided by the absolute temperature. It is this fundamental equation which Clausius used for his original definition of entropy.

The total entropy change for a reversible process is zero. In such a reversible process it follows that the entropy change in any part of the system must be equal and opposite in sign to the entropy change in all other parts of the system involved. In an irreversible process the total entropy of the system concerned increases. It is important to see clearly that the idea of entropy is necessitated by the existence of irreversible processes. It is only for the purpose of definition and convenient measurement of entropy changes that reversible processes have been discussed.

Carnot Cycle. Heat has been used as a source of mechanical power for two centuries. It has been the universal experience that the efficiency of conversion of heat into work is always low. Steam power plants have efficiencies of not more than 30% and internal-combustion engines not more than 40%. This is in sharp contrast to the well-recognized fact that work is always completely convertible to heat. One unfamiliar with the second law of thermodynamics might be inclined to explain the low efficiencies for the conversion of heat into work by assuming improper design and construction. But all efforts at increasing the efficiencies of this conversion were fruitless and it was finally concluded that the low efficiencies were due to some fundamental underlying natural limitation governing the convertibility of heat into work. The impossibility of completely converting heat to work was first recognized by Carnot early in the 19th contmry. His great nomograph, published in Paris in 1824, laid the foundations of the second law of thermodynamics.

Every heat engine is inefficient because of friction or imperfect design; but even if all such sources of degradation are eliminated, no engine could be constructed to give a 100% conversion of heat into work. In order to obtain the maximum possible work from a heat engine, it would be necessary to eliminate friction, to prevent direct flow of heat from hot to cold portions of the system, and to maintain a state of balance with respect to the mechanical forces. In other works, the process must be reversible. The maximum possible conversion of heat into work occurs in an engine that operates reversibly in all its stages. Such an engine is the limit which may be approached by any actual engine as its design and construction are improved. If a heat engine operates reversibly, so that it is in the same state at the end of the operation as at the beginning, it will suffer no change of entropy. All the entropy changes must add up to zero. If Q is the heat taken from the hot reservoir at T and Q' is the heat taken from the cold reservoir at T', then the increase of entropy of the hot reservoir is $-Q/T$ and that in the cold reservoir is Q'/T'. Equating the sum to zero,

$$-\frac{Q}{T} + \frac{Q'}{T'} = 0$$

By the conservation law $W = Q - Q'$.
Combining the above two equations gives

$$\frac{W}{Q} = \frac{T - T'}{T} \qquad (39)$$

This very important equation, which is known as the efficiency of the Carnot cycle, gives the conversion factor for a perfectly efficient engine operating between temperatures T and T'. Any actual engine operating between these temperatures has a lower conversion factor, but one which may approach that of equation (39) as a limit.

By reversing a heat engine it is possible, through the expenditure of work, to transport heat from a cold to a hot reservoir, which is exactly what a refrigerating machine does. If W is the work done and Q' is the heat withdrawn from the cold reservoir at T' and delivered to hot reservoir at T, we find the Carnot efficiency for a reversible refrigerating cycle,

$$\frac{W}{Q'} \qquad \frac{T - T'}{T'} \tag{40}$$

The Carnot cycle consists of four reversible processes, two adiabatic (note; a reversible adiabatic process is at constant entropy or "isentropic") and two isothermal. The Carnot cycle for a heat engine is shown by Figures 20 and 21, where it is plotted on pressure vs. volume and temperature vs. entropy coordinates. Each figure represents the same cycle plotted on different scales.

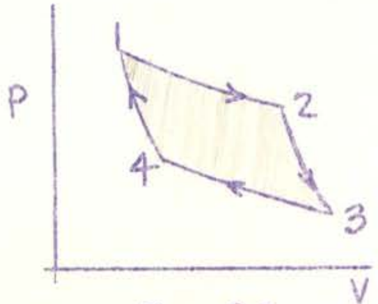

FIG 20

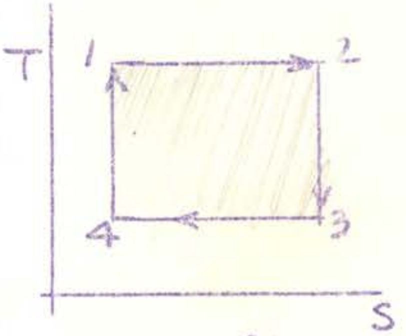

FIG 21

Starting at point 1, the four processes of the heat engine cycle are:

Process	Description
1-2	Isothermal liberation of heat or performance of work.
2-3	Adiabatic (Isentropic) expansion.
3-4	Isothermal absorption of heat
4-1	Adiabatic compression.

This cycle is only theoretical and is not duplicated in practice. All four processes need not take place in the same machine either. In a steam engine, for example, processes 3-4 and 4-1 take place in the boiler while 1-2 and 2-3 take place in the engine itself. The reversal of the cycles given in Figures 20 and 21 gives the refrigeration Carnot as shown by Figures 22 and 23.

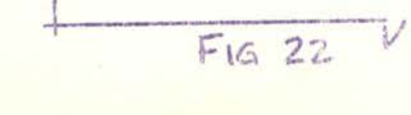

FIG 22

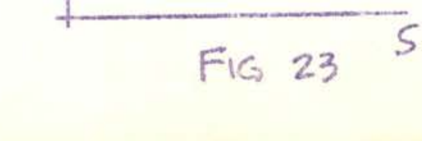

FIG 23

Starting at point 1, the four processes are of the refrigeration cycle:

Process	Description
1-2	Adiabatic expansion, i.e. throttling.
2-3	Isothermal absorption of heat from cold reservoir.
3-4	Adiabatic compression.
4-1	Isothermal delivery of heat to hot reservoir.

This cycle is also theoretical and not duplicated in practice. All four of these processes usually do occur in the same machine but not in the same engine. For a conventional ammonia refrigeration unit the four paths are accomplished by the following items of equipment:

Process	Equipment
1-2	Throttle valve.
2-3	Coil in brine tank.
3-4	Compressor.
4-1	Water cooled condenser.

Heat can be absorbed or liberated by a fluid at constant temperature if the fluid is a pure compound and the process is one of vaporization or condensation. A refrigeration machine approaches these processes more closely than does a heat engine. In order to approach reversibility the expansion and compression processes would have to take place slowly with small differences in pressure. The compression process of a refrigeration machine approaches adiabatic (isentropic) closely in some cases.

Entropy Changes. When heat flows between two systems of different temperature, the process is more nearly reversible the smaller the temperature difference. If a system, with heat capacity C, absorbs heat from a reservoir of infinitesimally higher temperature, and thus rises through the temperature interval dT, so that

$$Q = CdT \tag{41}$$

combining with equation (38) gives

$$dS = C\,\frac{dT}{T} \tag{42}$$

Since the entropy is a property, the entropy changes of the fluid receiving heat are independent of the temperature from which the heat flows and equation (42) is true for any infinitesimal rise of temperature, no matter how produced.

Ordinarily the heating occurs either at constant volume or at constant pressure and

$$dS = C_v\,\frac{dT}{T}; \quad \text{or} \quad \left(\frac{\partial S}{\partial T}\right)_v = \frac{C_v}{T} \tag{43}$$

and

$$dS = C_p\,\frac{dT}{T}; \quad \text{or} \quad \left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \tag{44}$$

Combining equations (24) and (43) gives

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V \tag{45}$$

Differentiating with respect to V gives the following relationship:

$$\frac{\partial^2 S}{\partial T \partial V} = \frac{1}{T}\left(\frac{\partial C_V}{\partial V}\right)_T = \frac{1}{T}\frac{\partial^2 E}{\partial T \partial V} \tag{46}$$

Combining equations 25 and 44 gives

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P \tag{47}$$

Differentiating with respect to P gives the following relationship:

$$\frac{\partial^2 S}{\partial T \partial P} = \frac{1}{T}\left(\frac{\partial C_P}{\partial P}\right)_T = \frac{1}{T}\frac{\partial^2 H}{\partial T \partial P} \tag{48}$$

Equations (46) and (48) will be useful relations in developing other thermodynamic relations below.

5. Thermodynamic Potentials

There are four thermodynamic potentials. In addition to the energy and the enthalpy that have already been introduced, there are two free energies: the Helmholtz free energy and the Gibbs free energy. Using the concept of entropy, formulations will now be developed for these thermodynamic potentials. In addition, the concept of entropy will be applied to the development of equations for the latent heat of vaporization, the Joule-Thomson coefficient, and the specific heats.

Energy and Enthalpy. Very useful equations for the energy and the enthalpy may now be obtained by considering the case where the pressure within a system is an infinitesimal greater or lower than the pressure exerted upon the system, i.e. reversible expansion or compression. By equation (38) the heat absorbed by the system is TdS, while the work done by the system is PdV. By the first law of thermodynamics

$$dE = TdS - PdV \tag{49}$$

This is the general differential equation for the energy. Dividing this general equation through by dV and restricting it to an isothermal process gives

$$P = T\left(\frac{\partial S}{\partial V}\right)_T - \left(\frac{\partial E}{\partial V}\right)_T \tag{50}$$

Differentiating equation (50) with respect to temperature and with volume constant, Entropy Increase for Irreversible Processes. With the aid of the Carnot cycle it is possible to prove that the entropy increases for irreversible processes. The principle of this proof, which is a classic in the study of thermodynamics, is to restore an irreversible process to its original state by means of the reversible Carnot cycle so that the change in entropy for the original process can be calculated.

Consider the transfer by conduction of a quantity of heat Q from a hot reservoir at a temperature T_2 to a cold reservoir at a temperature of T_1. Assume that the reservoirs are of such a size that their temperatures do not change in the process. The condition before the transfer of heat takes place will be called state A and the condition after the heat transfer will be called state B. The problem is to calculate the difference in entropy $S_B - S_A$. This can be done by pumping the heat Q back from the cold to the hot reservoir by the reversible Carnot cycle and evaluating the entropy changes at each reservoir.

Arrange a Carnot refrigeration cycle with the following processes:

(a) isothermal expansion of the gas at the temperature of the low temperature reservoir and the resulting absorption of heat Q by the gas from the low temperature reservoir;

(b) reversible adiabatic (no heat added or removed and entropy constant) compression of the gas until it is at the temperature of the high temperature level reservoir, T_2;

(c) isothermal compression of the gas at T_2 and the resulting liberation of heat Q to the high temperature reservoir;

(d) reversible adiabatic expansion to the starting point T_1.

By means of this Carnot cycle* the reservoirs have been restored to their original state A. Therefore, any entropy change involved in the original irreversible process must be balanced by a corresponding entropy change in the Carnot cycle fluid. The changes in the entropy of the gas are as follows:

at hot reservoir: entropy is diminished by $\frac{Q}{T_2}$

at cold reservoir: entropy is increased by $\frac{Q}{T_1}$

The increase in the entropy of the gas is

$$\frac{Q}{T_1} - \frac{Q}{T_2} = \frac{Q(T_2 - T_1)}{T_1 T_2} \qquad (48a)$$

Equation (48a) is also the change in the entropy involved in the conduction of heat Q from a high temperature, T_2, reservoir to a low temperature, T_1, reservoir or in going from state A to state B in this particular example. Since $T_2 > T_1$, equation (48a) represents an increase in entropy and it is concluded that the conduction of heat from a high temperature reservoir to a low temperature reservoir is accompanied by an increase in the total entropy.

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*Note: In the customary refrigeration Carnot cycle the quantity of heat delivered to the hot reservoir is equal to that absorbed from the low temperature reservoir plus the work added. In this cycle the heat equivalent of the work done would have to be removed in a different fashion to make a repeating cycle. For this proof it is not necessary to worry about this, however.

$$\left(\frac{\partial P}{\partial T}\right)_V = T \frac{\partial^2 S}{\partial T \partial V} + \left(\frac{\partial S}{\partial V}\right)_T - \frac{\partial^2 E}{\partial T \partial V} \qquad (51)$$

It was shown in equation (46) that the second and fourth terms are equal. Since they are of opposite sign in equation (51) they cancel, giving

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad (52)$$

Combining equation (52) with the transformation given as equation (8) results in the following equation

$$\left(\frac{\partial S}{\partial V}\right)_T = - \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T}\,, \qquad (53)$$

which is more easily evaluated. Combining equations (50) and (52) gives the following thermodynamic equation of state:

$$P = T\left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial E}{\partial V}\right)_T, \qquad (54)$$

from which the following equation for the isothermal effect of changes in volume on the energy can be computed:

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad (55)$$

In order to express the energy as a function of P, V, and T, eliminating entropy, the following differential equation is written from a strictly mathematical standpoint:

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \qquad (56)$$

Combining this equation with equations (24) and (55) gives the following equation:

$$dE = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV \qquad (57)$$

Equations for the enthalpy may be developed in the same way.

Differentiating equation (18)

$$dH = dE + PdV + VdP \qquad (58)$$

which when combined with equation (49) gives

$$dH = TdS + VdP \qquad (59)$$

This is the general differential equation for the enthalpy. Dividing this general equation through by dP and keeping temperature constant results in the following equation, which is analogous to equation (50):

$$V = -T\left(\frac{\partial S}{\partial P}\right)_T + \left(\frac{\partial H}{\partial P}\right)_T \qquad (60)$$

Differentiating with respect to temperature with pressure constant

$$\left(\frac{\partial V}{\partial T}\right)_P = -T\,\frac{\partial^2 S}{\partial P\,\partial T} - \left(\frac{\partial S}{\partial P}\right)_T + \frac{\partial^2 H}{\partial P\,\partial T} \qquad (61)$$

From equation (48) it can be seen that the second and fourth terms are equal. Since they are of opposite signs they cancel giving

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad (62)$$

Combining equations (60) and (62) gives the following thermodynamic equation of state:

$$V = T\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial H}{\partial P}\right)_T, \qquad (63)$$

from which the isothermal effect of pressure on the enthalpy may be found, as follows:

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \qquad (64)$$

The enthalpy may also be expressed as a function of P, V, and T, eliminating entropy, by first writing the following mathematical equation

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \qquad (65)$$

Combining with equations (25) and (64) results in the following very useful equation

$$dH = C_p dT - \left[\,T\left(\frac{\partial V}{\partial T}\right)_P - V\right] dP \qquad (66)$$

If $(\partial P/\partial T)_V$ and $(\partial V/\partial T)_P$ can be computed from P-V-T data the isothermal effects of volume on energy and of pressure on enthalpy may be calculated from equations (55) and (64) respectively. With C_p and C_V the effect of temperature at the energy and the enthalpy may be computed. If, on the other hand $(\partial E/\partial V)_T$ and $(\partial H/\partial P)_T$ are known experimentally, equations (54) and (63) give the form to which any empirical equation of state must conform. If the Joule-Thomson coefficient is determined experimentally, equation (36) may be used to compute $(\partial H/\partial P)_T$. Equation (35) for the Joule-Thomson coefficient may now be expressed in more practical form by means of equation (64) as follows:

$$\mu = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{C_p} = \frac{T\left(\frac{\partial V}{\partial T}\right)_P - V}{C_p} \qquad (67)$$

Latent Heat of Vaporization. Equation (52) may be applied to the vaporization of a pure substance, in which process the liquid is in equilibrium with its vapor, to formulate an expression for the latent heat of vaporization. In this case $\partial S/\partial V = \Delta S/\Delta V$ where ΔS and ΔV are the increases in the entropy and the volume, respectively. Being at the vapor pressure it is possible to omit the restriction of constancy of volume. The process is an equilibrium one and therefore reversible, so $\Delta S = \Delta H_V/T$ where ΔH_V is the latent heat of vaporization. Equation (52) thus becomes

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T \Delta V} \qquad (68)$$

This is the famous Clapeyron equation.

Specific Heats. By means of equations (46) and (52) a differential equation for the isothermal effect of volume on C_V may be developed. Differentiating equation (52) with respect to temperature with volume constant

$$\frac{\partial^2 S}{\partial V \partial T} = \left(\frac{\partial^2 P}{\partial T^2}\right)_V \qquad (69)$$

Combining equations (46) and (69)

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V \qquad (70)$$

In the same manner the isothermal effect of pressure on Cp may be obtained. Differentiating equation (51) with respect to temperature with pressure constant

$$\frac{\partial^2 S}{\partial P \partial T} = -\left(\frac{\partial^2 V}{\partial T^2}\right)_P \qquad (71)$$

Combining equations (48) and (71)

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P \qquad (72)$$

Equation (71) is very useful in computing the effect of pressure on the specific heat, specific heats at higher pressures being used in heat transfer calculations, etc.

By the first law of thermodynamics, equations (28) and (31) were developed for the difference in specific heats but these equations were left in an unpractical form. With the aid of the second law these equations may now be developed further. Combining equations (28) and (55) or combining equations (31) and (63) gives:

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \qquad (73)$$

Since the pressure-temperature coefficient is not ordinarily measures at constant volume, equation (73) may be simplified by means of the transformation given as equation (8). Combining equation (8) and (73) gives the following very useful equation for the difference in the specific heats:

$$C_P - C_V = - T \quad \frac{\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} \tag{74}$$

Entropy. A differential equation for the entropy as a function of pressure and temperature can be derived by writing the following mathematical relationship:

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \tag{75}$$

By equation (62) the coefficient of dP, $\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P$; and

by equation (47) the coefficient of dT, $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$. Upon substituting these terms in equation (75) the following differential equation is obtained for the entropy:

$$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP \tag{76}$$

A similar equation may be derived by assumed entropy a function of T and V but it will not be as practical as equation (76).

Equilibrium-Free Energies. A system is said to be in equilibrium when all the factors which determine the flow of energy or matter, either within the system or between the system and its surroundings, are exactly balanced. At equilibrium the pressure, temperature, and volume of a system are constant. The temperature throughout the system must be uniform and if the system is bounded by a heat permeable wall, then the system and the immediate surroundings must have the same temperature. If a system is enclosed in a vessel with a movable piston, the pressure exerted by the system on the piston must be exactly balanced by the pressure exerted by the piston on the system. If gas is to be compressed in a vessel by a movable piston, there must be a difference between the pressures exerted by the piston and the gas. In order for this process to be reversible, there must be an infinitesimal difference in the pressure. Such a reversible process is also at equilibrium and occurs at constant entropy.

Not all constant entropy processes are reversible and not all equilibrium processes occur at constant entropy. Examples are: the compression (not a reversible or equilibrium process) of gas may be made to occur at constant entropy by taking away just the right amount of heat, caused by friction, by jacket cooling water; and the flash vaporization of hydrocarbon mixtures is an equilibrium (phase) process but does not occur at constant entropy. Phase and chemical or reaction equilibria are the only type of equilibrium encountered in petroleum refining process design. Valuable equilibria relationships will be developed by the use of thermodynamics.

It has been shown that any actual or irreversible process is characterized by an increase in the total entropy of all systems concerned. Such a system is not at equilibrium but is subject to spontaneous change. A state of equilibrium is one in which every possible infinitesimal process is reversible, or one in which the total entropy remains constant. This is the most general criterion of equilibrium thermodynamics offers. As a matter of fact, it is too general because it is not always easy to evaluate the change in entropy. For this reason, two thermodynamic functions, which are less fundamental and less general than the entropy, have been invented for practical convenience. In terms of quantities already employed, the two free energy functions are defined as follows:

$$A = E - TS \tag{77}$$

and

$$F = H - TS \tag{78}$$

The first is the Helmholtz free energy and the second is the Gibbs free energy. On combining equation (18), which states $H = E + PV$, with equation (77) and (78) the following relation between A and F results

$$F = A + PV \tag{79}$$

Equation (79) shows that F and A bear the same relation to each other as H and E. Changes in the quantity A represent the maximum possible work for a system, which is the work for an isothermal reversible process. In other words ΔA is the limit of the work which can be performed by an isothermal process as its efficiency is indefinitely improved. Changes in the quantity F represent the maximum net work for a system, which is the work for an isothermal reversible process that is also isobaric. In any process occurring at constant pressure and temperature, ΔF represents the maximum amount of work which can be obtained and applied to useful purposes. For this reason F is known simply as free energy. The free energy is one of the most useful thermodynamic potentials.

Expressions for A and F in temperature and pressure are derived from equations (77) and (78). Differentiating equation (77) with respect to volume, temperature constant,

$$\left(\frac{\partial A}{\partial V}\right)_T = \left(\frac{\partial E}{\partial V}\right)_T - T\left(\frac{\partial S}{\partial V}\right)_T \tag{80}$$

Equation (50) states that

$$\left(\frac{\partial E}{\partial V}\right)_T - T\left(\frac{\partial S}{\partial V}\right)_T = - P \tag{50}$$

whence for an isothermal process

$$\left(\frac{\partial A}{\partial V}\right)_T = - P \tag{81}$$

Starting with equation (77) again and differentiating with respect to temperature, volume constant,

$$\left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V - T\left(\frac{\partial S}{\partial T}\right)_V - S \qquad (82)$$

The second and third terms are both equal to C_V by equations (24) and (45) and, therefore, cancel giving

$$\left(\frac{\partial A}{\partial T}\right)_V = - S \qquad (83)$$

Combining equations (81) and (83)

$$dA = -PdV - SdT \qquad (84)$$

A similar equation may be developed for F in the same manner. Differentiating equation (78) with respect to pressure, temperature constant,

$$\left(\frac{\partial F}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - T\left(\frac{\partial S}{\partial P}\right)_T \qquad (85)$$

Combining with equation (54)

$$\left(\frac{\partial F}{\partial P}\right)_T = V \qquad (86)$$

Integrating equation (86) gives

$$\Delta F_T = F_2 - F_1 = \int_1^2 VdP \qquad (87)$$

Starting again with equation (78) and differentiating with respect to temperature, pressure constant

$$\left(\frac{\partial F}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P - T\left(\frac{\partial S}{\partial T}\right)_P - S \qquad (88)$$

but the second and third term are each equal to C_p by equations (25) and (47) and therefore cancel giving

$$\left(\frac{\partial F}{\partial T}\right)_P = - S \qquad (89)$$

Combining equations (86) and (89)

$$dF = VdP - SdT \qquad (90)$$

To recapitulate, the following differential equations have been derived for the four thermodynamic potentials

Internal Energy	$dE = -PdV + TdS$	(49)
Enthalpy	$dH = +VdP + TdS$	(59)
Helmholtz Free Energy	$dA = -PdV - SdT$	(84)
Gibbs Free Energy	$dF = +VdP - SdT$	(90)

It is of interest to note the similarities in the above equations. The TS terms are the same for the first two and for the second two while the PV terms are the same for the 1st and 3rd and for the 2nd and 4th terms. These similarities exist because of the definitions. All of the other potentials are obtained by adding TS and/or PV terms to the Helmholtz free energy A as follows:

Internal Energy $E = A + TS$ (77)
Gibbs Free Energy $F = A + PV$ (79)
Enthalpy $H = A + TS + PV$
" $H = E + PV$
" $H = F + TS$ (78)

The effect of pressure, with temperature constant, on the free energy may be determined by integrating the first term in equation (90), if the equation of state or P-V-T relationship is known for the gas. The effect of temperature, pressure constant, on the free energy may be determined by integrating the second term of equation (90) after establishing an entropy-temperature relationship by means of equation (76).

6. Perfect Gas

At low pressures and elevated temperatures all gases and vapors approach a condition where their P-V-T properties may be expressed by a simple algebraic equation of state. This equation was developed as a result of experimental investigations and at first was supposed to be universally valid for all gases. This simple equation of state is based on two formulations made with restricted observations: first, Boyle's law states that the product of pressure and volume, PV, is constant for a fixed weight of gas at constant temperature; and second, Charles' law states that volume is directly proportional to the absolute temperature with the pressure constant. These combined statements give what is known as the perfect gas equation

$$PV = RT \qquad (91)*$$

where R = gas constant, the value of which depends on the units of P, V, and T.

When: P = lbs./sq.ft., V = cu.ft./lb. mol, and T = °F.
$R = 1544$;
P = atm., V = cc/gm. mol, and T = °K, $R = 86.06$

Although actual gases never obey this ideal gas law equation, many gases may be made to approach the limiting state in which the law would be exact. Such limiting laws are frequently of great value as has already been shown. For example, the perfect "black body" was useful in the study of radiation.

Effect of Volume on Energy. By means of equations (55) and (91), the isothermal effect of volume on the internal energy may be found. Equation (55) states

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad (55)$$

---

*All equations marked with an asterik are valid for an ideal gas only.

Solving equation (91) for P and differentiating with respect to T with V constant gives

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \qquad (92)*$$

Combining equations (55), (91) and (92) gives

$$\left(\frac{\partial E}{\partial V}\right)_T = 0 \qquad (93)*$$

which states that the internal energy of a perfect gas is independent of volume or

$$dE = C_v dT \qquad (94)*$$

Effect of Pressure on Enthalpy. The effect of pressure on the enthalpy of a perfect gas may be found in like manner from equation (64) which states that

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \qquad (64)$$

Solving equation (91) for V and differentiating with respect to T with P constant gives

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \qquad (95)*$$

Combining equations (64), (91), and (95) gives

$$\left(\frac{\partial H}{\partial P}\right)_T = 0 \qquad (96)*$$

which states that the enthalpy of a perfect gas is independent of pressure or

$$dH = C_p dT \qquad (97)*$$

The Joule-Thomson coefficient for a perfect gas is equal to zero since

$$\mu = \frac{\left(\frac{\partial H}{\partial P}\right)_T}{C_p} \qquad (67)$$

and

$$\left(\frac{\partial H}{\partial P}\right)_T = 0$$

Specific Heats. The difference in specific heats for a perfect gas may be obtained by combining equations (73), (91), (92), and (95) which gives

$$C_p - V_v = R \qquad (98)*$$

The isothermal effect of volume on C_v may be found from equation (70), by substituting $\left(\frac{\partial^2 P}{\partial T^2}\right)_V$ obtained by differentiating equation (92) with respect to T. This gives $\left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$ from which it can be concluded that

$$\left(\frac{\partial C_v}{\partial V}\right)_T = 0 \qquad (99)*$$

The isothermal effect of pressure on Cp may be found from equation (72) by substituting $\left(\frac{\partial^2 V}{\partial T^2}\right)_P$ obtained from equation (94). This gives $\left(\frac{\partial^2 V}{\partial T^2}\right)_P = 0$ from which it can be concluded that

$$\left(\frac{\partial C_p}{\partial P}\right)_T = 0 \qquad (100)*$$

For some perfect gases the specific heat does not change with temperature.

Isothermal Heat and Work. At constant temperature, the internal energy of a perfect gas remains constant and Q = W. By equation (14)

$$Q = W = \int_{V_1}^{V_2} PdV \qquad (101)*$$

Substituting for P from the perfect gas law, equation (91), and integrating

$$Q = W = RT \ln \frac{V_2}{V_1} = RT \ln \frac{P_1}{P_2} \qquad (102)*$$

Adiabatic Work. If no heat is added to or removed from a perfect gas during expansion or compression, Q = 0 and W = -dE by equation (15). In this process the temperature will change. Since E is a function of temperature alone for a perfect gas by equation (94), $dE = C_v dT$ and

$$PdV = - C_v dT \qquad (103)*$$

Substituting for P from the perfect gas law

$$\frac{RT}{V} dV = - C_v dT \qquad (104)*$$

$$R d\ln V = - C_v d \ln T \qquad (105)*$$

For the case where C_v is constant,

$$d\ln V^{(R/C_v)} = - d\ln T \qquad (106)*$$

on integrating

$$TV^{(R/C_v)} = \text{constant} \qquad (107)*$$

Since $R = C_p - C_v$

$$TV^{\frac{C_p - C_v}{C_v}} = TV^{\left(\frac{C_p}{C_v} - 1\right)} = \frac{TV^{\frac{C_p}{C_v}}}{V} = \text{constant} \qquad (108)*$$

From equation (90)

$$\frac{T}{V} = \frac{P}{R} \qquad (109)*$$

Substituting equation (108) in (109) gives

$$pV^{Cp/Cv} = R \text{ constant} = \text{constant} \qquad (110)^*$$

Entropy. The entropy of an ideal gas may be formulated by combining equations (76) and (95) giving

$$dS = \frac{C_p}{T} dT - \frac{R}{P} dP \qquad (111)^*$$

If C_p is constant

$$S = C_p \ln T - R \ln P + \text{constant} \qquad (112)^*$$

Free Energy. An equation for the isothermal change in the free energy will be derived for the perfect gas. Equation (87) states

$$F_T = F_2 - F_1 = \int_1^2 VdP \qquad (87)$$

For a perfect gas $V = \frac{RT}{P}$. On substituting in equation (87)

$$F_2 - F_1 = RT\int_1^2 \frac{dP}{P} = RT \ln \frac{P_2}{P_1} \qquad (113)^*$$

This very important equation will be referred to in the development of Phase Equilibria constants later.

A. Fundamental Data

The application of the above thermodynamic formulae to the development of useful petroleum refining process design tools requires the knowledge of certain physical and thermal properties of hydrocarbons and their mixtures. This data falls into two classes; (a) volumetric and phase behavior, and (b) calorimetric and thermal behavior. Before taking up these two types of fundamental data the composition and analysis of petroleum will be discussed briefly.

1. Composition and Analysis of Petroleum

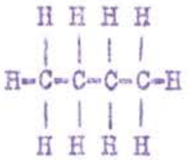
Petroleum consists largely in compounds of hydrogen and carbon, called hydrocarbons, although a few compounds containing small amounts of sulfur, oxygen, and nitrogen are also present. There are probably a total of about 3000 different components in petroleum, which complicates process design, particularly the application of thermodynamics.

There are several types of hydrocarbons, which are classified as: (a) Paraffin series (type formula $C_n H_{2n+2}$), (b) olefin series (type formula $C_n H_{2n}$), (c) naphthene series (type formula $C_n H_{2n}$), (d) aromatic series (type formula $C_n H_{2n-6}$), and (e) diolefin series (type formula $C_n H_{2n-2}$).

A thorough treatment of this subject involves introducing valences. For the purposes of these notes it is sufficient to say that a carbon atom has four valences or hooks with which it can attach itself to another carbon atom or to any other atom, and that a hydrogen atom has one valence. When all of these hooks are attached in a normal fashion the molecule is said to be saturated. When two carbon atoms are attached by two hooks or a double bond the molecule is unsaturated. Paraffins and naphthenes are saturated, while olefins, aromatics and diolefins are unsaturated molecules.

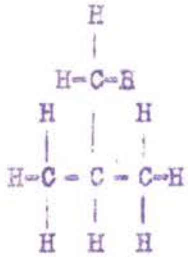
When the carbon atoms in paraffin series hydrocarbons are linked together to form a straight chain, the hydrocarbons are called "normal" paraffins. If, on the other hand, the carbon atoms are arranged so as to form a branched chain, the resulting hydrocarbon is isomeric. The simpler the hydrocarbon, i.e. the fewer number of carbon atoms in the molecule, the fewer possible locations for this branch. For the more complex molecule, it is possible to have two or more branches at numerous locations. The number of possible isomers increases rapidly with increase in the number of carbon atoms. Isomers are also possible in the olefin series. There is another variation in the olefin series, and that is the location of the double bond. The more carbon atoms in the molecule the more possible locations for the double bond. The naphthene and the aromatic series hydrocarbons are cyclic, i.e. the carbon atoms are connected to form a cycle. For the naphthene series, the ring may have any number of carbon atoms in its ring, those having 3, 4, 5, 6, and 7 having been isolated. The ring for the aromatic series is called the benzene ring and always consist in 6 carbon atoms with every other bond a double one. The structural formulae are given in Figure 24 for an example of each hydrocarbon series.

(a) Paraffin Series



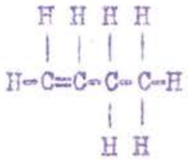
$$\begin{array}{cccccc} & H & H & H & H & \\ & | & | & | & | & \\ H- & C- & C- & C- & C & -H \\ & | & | & | & | & \\ & H & H & H & H & \end{array}$$

Normal Butane
$n-C_4H_{10}$



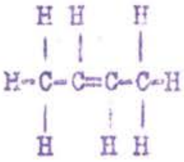
Isobutane
$i-C_4H_{10}$

(b) Olefine Series



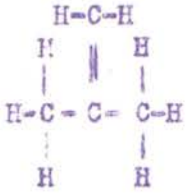
$$\begin{array}{cccccc} & H & H & H & H & \\ & | & | & | & | & \\ H- & C= & C- & C- & C & -H \\ & & & | & | & \\ & & & H & H & \end{array}$$

Butene-1
C_4H_8



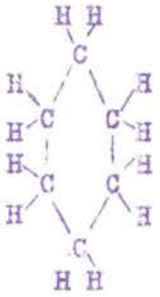
$$\begin{array}{cccccc} & H & H & & H & \\ & | & | & & | & \\ H- & C- & C= & C- & C & -H \\ & | & & | & | & \\ & H & & H & H & \end{array}$$

Butene-2
C_4H_8



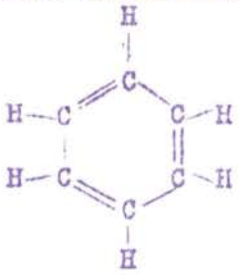
Isobutylene
$i-C_4H_8$

(c) Naphthene Series



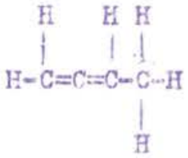
Cyclohexane
C_6H_{12}

(d) Aromatic Series



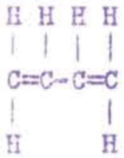
Benzene
C_6H_6

(e) Diolefin Series



$$\begin{array}{cccccc} & H & & H & H & \\ & | & & | & | & \\ H- & C= & C= & C- & C & -H \\ & & & & | & \\ & & & & H & \end{array}$$

1-2 Butadiene
C_4H_6



$$\begin{array}{cccc} H & H & H & H \\ | & | & | & | \\ C= & C- & C= & C \\ | & & & | \\ H & & & H \end{array}$$

1-3 Butadiene
C_4H_6

Figure 24

Structural Formulae of Hydrocarbons

The physical and thermal properties of the hydrocarbons in these different series are somewhat different. The general properties are given in Standard Data Book Chart No. A-1.11. The variation of these and other properties with temperature and pressure will be given in separate tables and plots. For the hydrocarbons having six or less carbon atoms, molecular weights below 86, and boiling points below 175°F., these data are usually presented and applied to the individual components in making process design calculations. In the higher boiling ranges the mixture of hydrocarbons becomes so complex that the individual components are difficult to isolate and determine their properties. In addition, component calculations require appreciably more time in the higher boiling range. For these reasons, it is necessary to use empirical methods based upon more simple analyses, such as the gravity and a laboratory distillation, for the higher boiling more complex hydrocarbon mixtures.

Analytical Distillations. Characteristics of petroleum fractions are normally defined by the results of one of two standard laboratory distillation operations, the A.S.T.M. (or Engler) and the T.B.P. (true boiling point) methods. The A.S.T.M. (American Society for Testing Materials) method approximates true differential distillation, i.e. batch distillation at a uniform rate with no reflux. Adjacent cuts from an A.S.T.M. distillation overlap considerably and contain many components in common. A T.B.P. distillation gives a fractional analysis of individual components in the order of their boiling points with no overlapping of adjacent cuts. The T.B.P. distillation curve for the lower boiling hydrocarbons, which is determined by the Podbielniak method, is a series of plateaus as a result of the gaps in boiling points of adjacent components. At higher boiling points these gaps disappear due to the occurrence of many isomers, etc. so that the T.B.P. becomes more smooth and continuous. For mixtures in the intermediate boiling range such as gasoline, the T.B.P. curve starts out as a series of plateaus and gradually changes to a smooth curve as the boiling point is increased. The T.B.P. and A.S.T.M. distillation curves always cross, the T.B.P. having the lowest initial boiling point and the highest end point. Although the T.B.P. method of fractional analysis is more definite with respect to the component present than the A.S.T.M. method, the latter is universally used in preference to the T.B.P. distillation in refinery process design and plant control work because: (a) petroleum products are specified by A.S.T.M. standards; and (b) the A.S.T.M. distillation is simpler and more convenient, requiring about one-tenth the time to run. However, the T.B.P. is inadequate for many problems and must be supplemented by the T.B.P. distillation.

Characterization Factor. Olefin, naphthenic, and aromatic hydrocarbons have a higher specific gravity (lower API gravity) than paraffinic hydrocarbons of the same boiling point, which suggests using gravity and boiling point together to characterize petroleum fractions. Such a characterization factor, proposed by Watson and Nelson (Ind. Eng. Chem. 25, 880 (1933)), is

$$K = \frac{(M.A.B.P.)^{1/3}}{Sp.Gr.} \qquad (113a)$$

Where: M.A.B.P. = molal average boiling point, °R.
Sp.Gr. = specific gravity 60/60.

The molal average boiling point is found from the A.S.T.M. distillation by a method proposed by Watson and Nelson, who found that the M.A.B.P. is lower than the V.A.B.P. 9 volumetric average boiling point) and that the difference increases with the slope of the A.S.T.M. distillation as shown by Figure 24a.

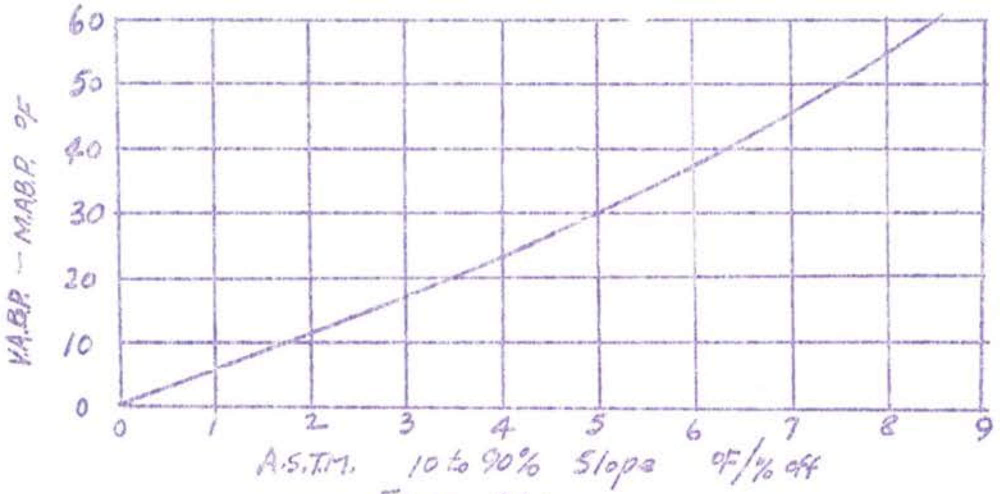


FIGURE 24a

By means of equation (113a) and Figure 24a it is possible to estimate the characterization factor for any stock from its A.S.T.M. distillation and gravity.

The following tabulation of values of K for pure hydrocarbons and typical stocks indicates variations in characterization factor:

n-Paraffins	12.8
Mono-Olefins	12.4
Naphthenes	11.0
Aromatics	9.75 to 10.5
M.C.Virgin	11.8
M.C.Cracked	10.85 to 11.25
Winkler	11.2
Gulf Coastal	11.2

The Watson and Nelson, sometimes known as the U.O.P. characterization factor, is not all that is desired but it is the best available. It is not applicable to heavy oils where the A.S.T.M. distillation cannot be obtained. For such oils another characterization factor has been proposed.

Viscosity-Gravity Constant. For oils having the same viscosity, those oils which are paraffinic have lower specific gravities than those that are naphthenic. A correlation of viscosity and specific gravity therefore gives a numerical index of paraffinicity. Hills and Coats (Ind. Eng. Chem. 20, 641 (1928)) proposed such an index, which is called viscosity-gravity constant (V.G.C.) and is defined by the following equation:

$$\text{V.G.C.} = \frac{10S - 1.0752 \log (\text{SUS} - 38)}{10 - \log (\text{SUS} - 38)} \qquad (113b)$$

Where: S = specific gravity 60/60
SUS = viscosity in Saybolt Universal Seconds at 100°F.

V.G.C. is low for paraffinic crudes and high for naphthenic crudes as indicated below.

Pennsylvania	0.75
Mid-Continent	0.83
Gulf Coast	1.00

Molecular Structure. A true boiling point distillation with gravity determinations for the various cuts will, in particularly all cases, give sufficient information about the stock at hand for design purposes. Indeed for most work the A.S.T.M. distillation and gravity of entire stock must be sufficient. It is often desired to estimate the amounts of olefins, aromatics, naphthenes, and paraffins in the entire sample or in the different boiling ranges. The quantity of olefins present can be found by determining the bromine number, which is the number of grams of bromine absorbed (at the double bond) by 100 grams of the oil. Olefins and aromatics can be removed by absorption in 98% sulfuric acid and P_2O_5, thus giving the sum of olefins and aromatics. The residue from this test, which is known as the Kattwinkle, consists of paraffins and naphthenes. At the same boiling point, a naphthene has a higher refractive index than a paraffin hydrocarbon. The relative amounts of paraffins and naphthenes in the residue from the Kattwinkle can be estimated by finding the refractive index of the residue. Below the boiling point of benzene sulfuric acid absorption will give the amounts of olefins present because there can be no aromatics to be absorbed also.

Molecular Weight. In process design work it is frequently necessary to be able to estimate the molecular weight of hydrocarbon mixtures and petroleum fractions from simple inspections such as the gravity and the A.S.T.M. distillation. The molecular weight for a light hydrocarbon mixture can be computed from a fractional distillation analysis if this is available. However, the direct determination of the molecular weight of hydrocarbon gases by the vapor density method is simpler than running a fractional distillation. Besides the vapor density method for determining molecular weights, there are the freezing point and the boiling point methods. In the freezing point method the molecular weight is determined by observing the effect of a small amount of the oil on the freezing point of a given solvent such as benzene, nitrobenzene, cyclohexane, etc. In the boiling point method the molecular weight is determined by observing the effect of a small amount of the oil on the boiling point of a solvent, such as benzene, heptane, iso-octane, carbon tetrachloride, etc. Empirical correlations, developed from many actual molecular weight determinations, are given as Standard Data Book Charts No. A-2.61 and A-2.62. The estimation of molecular weight from these charts requires only the A.S.T.M. distillation and the gravity.

2. Volumetric and Phase Relations

A knowledge of the effect of pressure, temperature, and composition upon the volumetric and phase behavior of hydrocarbons and their mixtures is of interest per se in addition to being essential to the application of thermodynamic equations in the computation of enthalpies, entropies, fugacities, etc.

P-V-T Relations. Most process design problems are concerned with the vapor and liquid phases but not the solid phase of petroleum. The boundary between the vapor and liquid phases is a two phase region bounded by the bubble point or saturated liquid line and by the dew point or saturated vapor line. When at its bubble point, a fluid is in the liquid phase but at the point of incipient vaporization so that an infinitesimal increase in temperature or decrease in pressure will start vaporization. When at its dew point, a fluid is in the vapor phase but at the point of incipient liquefaction so that an infinitesimal decrease in temperature or increase in pressure will start liquefaction. In this two phase region the vapor and liquid phases are each saturated, i.e. at their dew and bubble points, respectively, and in equilibrium with each other. The bubble point line is the 0% vaporized line whereas the dew point line is the 100% vaporized line. For a pure compound (single-component system) the bubble and dew points occur at the same temperature for any given pressure, although the volumes are different. For a multi-component system, the bubble point temperature is lower than the dew point temperature at the same pressure. The wider boiling the mixture, the greater this difference in bubble and dew points. When plotted on pressure-temperature coordinates the bubble and dew points for a pure component fall on the same curve, the vapor pressure curve, which ends at a point called the critical point. When the bubble and dew points for multi-component systems are plotted on the same scales, two curves result. These two boundary curves, which are called the bubble point and dew point lines, meet at the critical point defining what is called the border curve.

The P-T plots for single and multi-component systems are shown in Fig. 25.

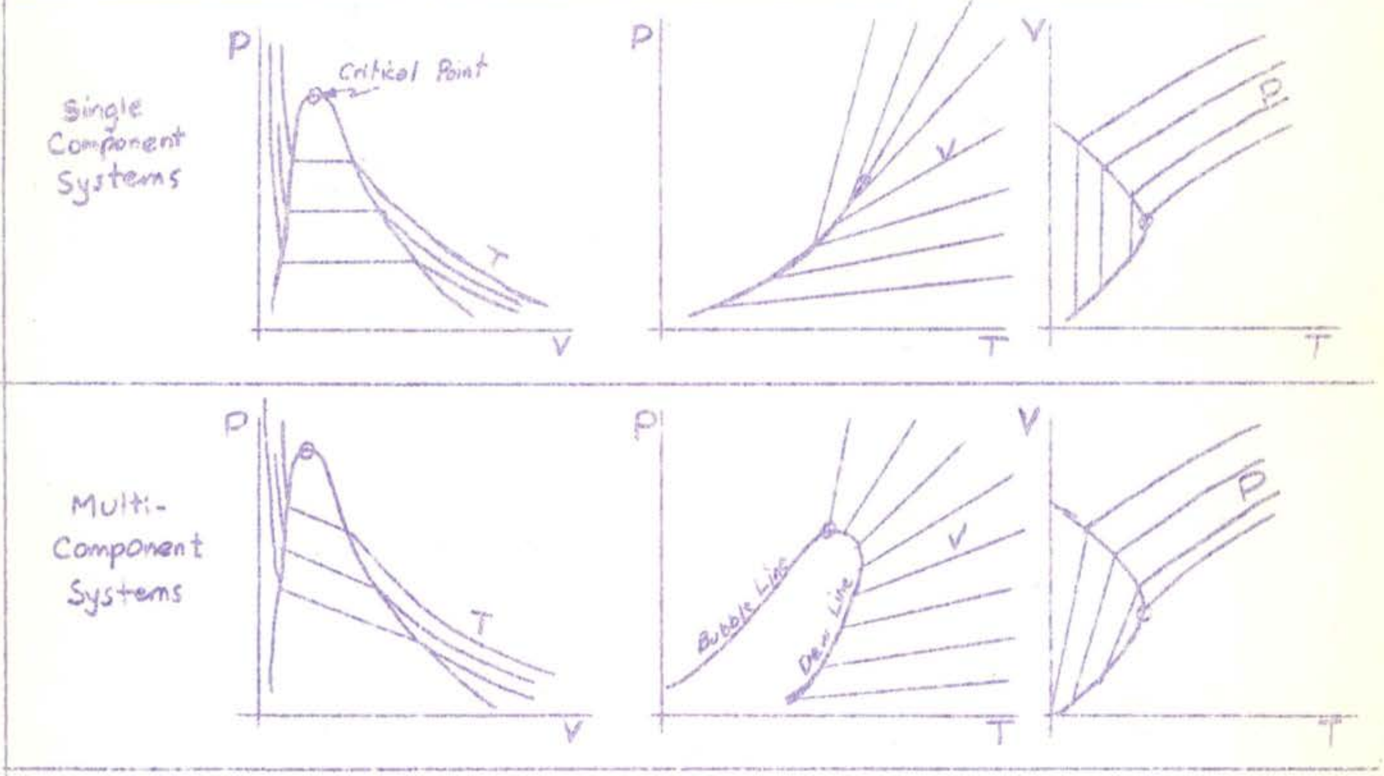


Figure 25

In addition to the P-T plots, P-V and V-T plots are given in Figure 25 for single and multi-component systems. These plots show another important difference between single and multi-component systems. Isobaric (constant pressure) vaporization and condensation takes place isothermally for single component systems. For multi-component systems, isobaric vaporization takes place with an increase in temperature, while isobaric condensation takes place with a temperature decrease. Likewise the isothermal vaporization or condensation of a multi-component system takes place with a decrease or an increase in pressure. There is an exception to this apparently obvious law of nature, however. It is possible for isothermal vaporization to occur with an increase in pressure in a given zone near the critical point as will be shown later.

The general trends in the P-V-T relations in the supercooled liquid and superheated vapor regions are also indicated in Figure 25. The isochors on the P-T plots are, for most practical purposes, straight lines. The isobars on the V-T plots are curved to a much lesser degree than the isotherms on the P-V plots. Data of this kind are required for the computation of the effect of pressure on the enthalpy, etc.

For a constant boiling mixture, the P-V-T plots will not be the same as shown for multi-component systems in Figure 25. On the P-V plot the slope of the isotherms in the two phase field will vary down to zero for the for the temperature at which the constant boiling phenomena occurs. On the P-T plot the dew and bubble point lines come together at this point. On the V-T plot the slope of the isobars in the two phase zone will vary, being ∞ for the temperature where the constant boiling phenomena occurs.

Vapor Pressures. It has been found that vapor pressure data for hydrocarbons can be plotted in such a way as to give straight lines that intersect at a common point by using a special non-uniform temperature scale and a logarithmic pressure scale. This non-uniform temperature scale was determined by drawing a straight line on a piece of semi-log paper and letting it represent the vapor pressure curve of some substance whose vapor pressures have been accurately determined, usually water. From the temperature points so located when the logarithmic scale is used for pressures, a suitable grid of temperature co-ordinate lines is drawn. The temperature scale is algebraically represented by the reciprocal of the absolute temperature plus a numerical constant or $\frac{1}{T+C}$. The resulting diagram is the familiar Cox Chart, which permits the evaluation of the vapor pressure of a hydrocarbon from the knowledge of the vapor pressure at one temperature. Figure 26 represents such a chart. A larger one appears in the Standard Data Book.

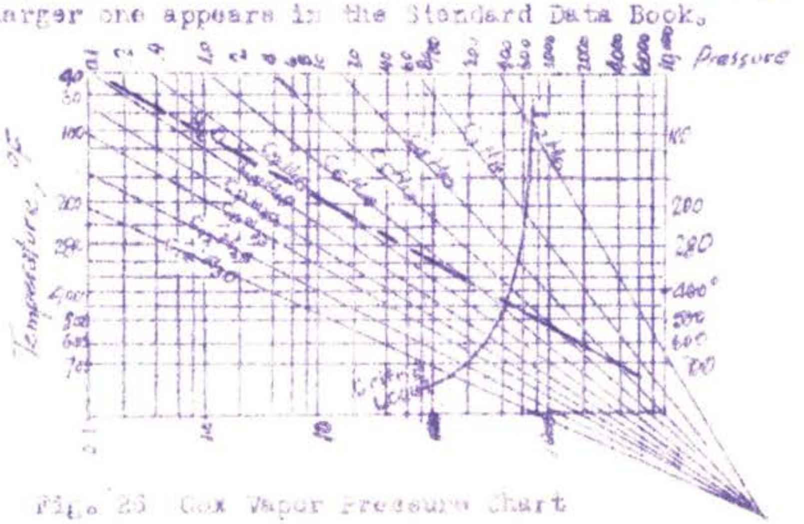
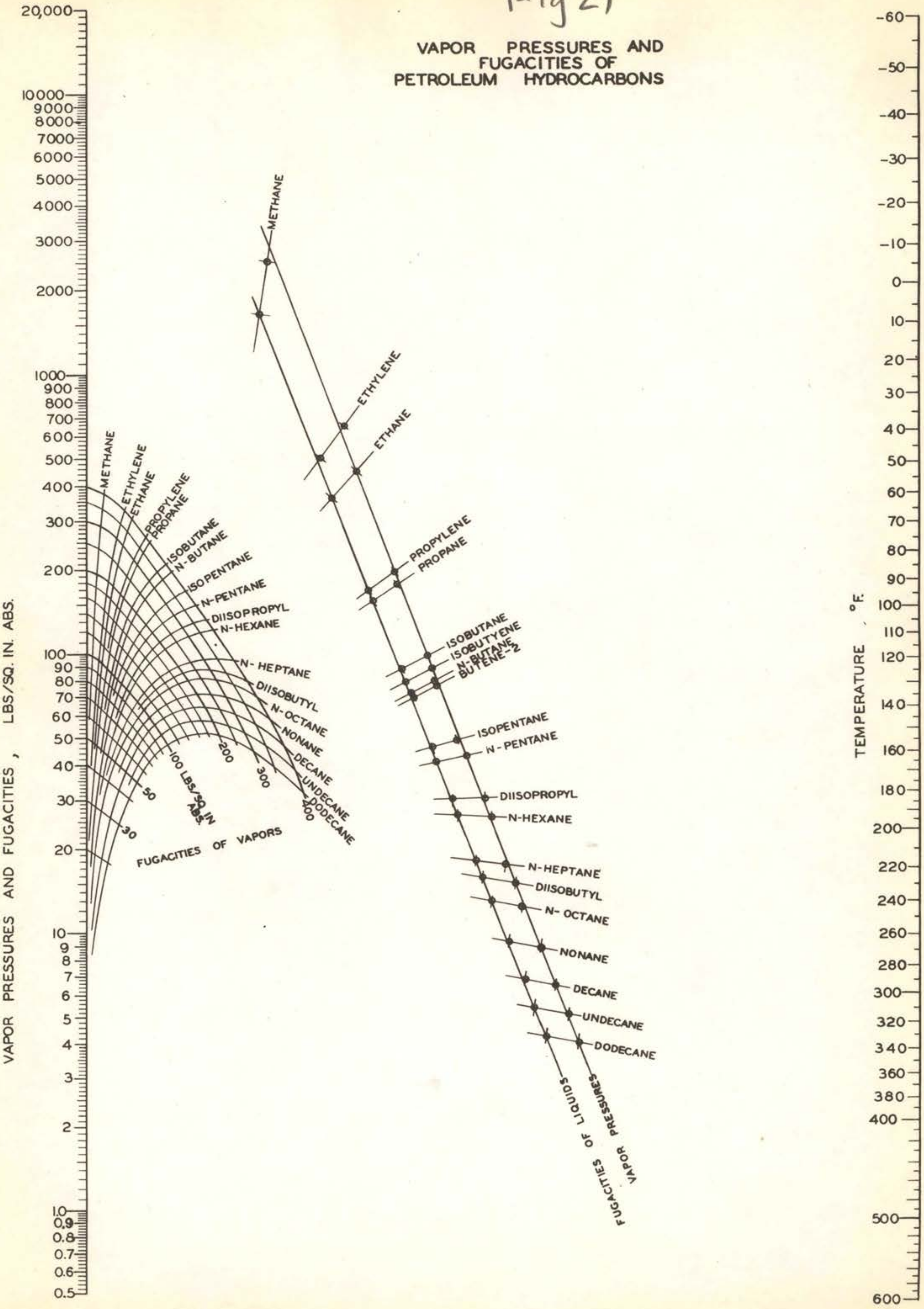


Fig. 26 Cox Vapor Pressure Chart

Fig 27

VAPOR PRESSURES AND FUGACITIES OF PETROLEUM HYDROCARBONS



These same scales may be used in constructing a nomographic vapor pressure plot also. Such a plot is given by Figure 27 (pay no attention to the fugacities for the time being.)

Critical Phenomena. For every fluid, whether pure or a mixture, there is a temperature and pressure condition at which the lines of constant per cent vaporized converge. This condition, which is called the critical point, is the highest point on the vapor pressure and border curves for a pure component. Above this point it is impossible to have vapor and liquid in equilibrium with each other. The latent heat of vaporization is zero at the critical point. Although it is always located on the dome of the phase diagram, the critical point for a mixture is not always at the point of highest temperature or pressure on the border curve. It will be shown later that the critical point is usually nearer the point of maximum pressure than at the point of maximum temperature.

As the critical point is approached from a condition where two phases exist, interesting changes occur in the liquid in equilibrium contact. If the material is contained in a transparent tube, the meniscus, separating liquid and vapor, flattens as the critical condition is neared. Just at the critical the meniscus becomes indistinct and a region of haze takes its place. No distinction can be observed between liquid and vapor. Careful measurements made on the vapor and liquid, as the critical point is approached, show that they differ less and less, finally losing their individual identities. As the critical point is approached, the latent heat of vaporization decreases, reaching zero at the critical point.

The critical point is frequently required for hydrocarbon mixtures because it is a point on the border curve. The critical temperatures for light hydrocarbon mixtures are calculated as the sum of the products of the weight fractions and the critical temperatures for each component. A simple rule for estimating the critical pressure of light hydrocarbon mixtures is not possible, for whereas the critical temperature of hydrocarbon mixtures always lies between the extreme critical temperatures of the components, in wide cut mixtures the critical pressure often greatly exceeds the critical pressure of any component in the mixture. Hence, any rule for estimating critical pressures must take into account the range of volatility of the mixture. The loci of the critical states for a number of binary hydrocarbon mixtures are shown in Figure 28. In using a plot of this kind in estimating critical pressures, it should be borne in mind the fact that it is not only the width of the fraction that determines how high the critical point locus goes but that the distribution of components also is important. In other words the critical pressure is not so high for a mixture containing three or more components but of the same boiling range as a two component mixture. The intermediate components tend to surpress the critical pressure.

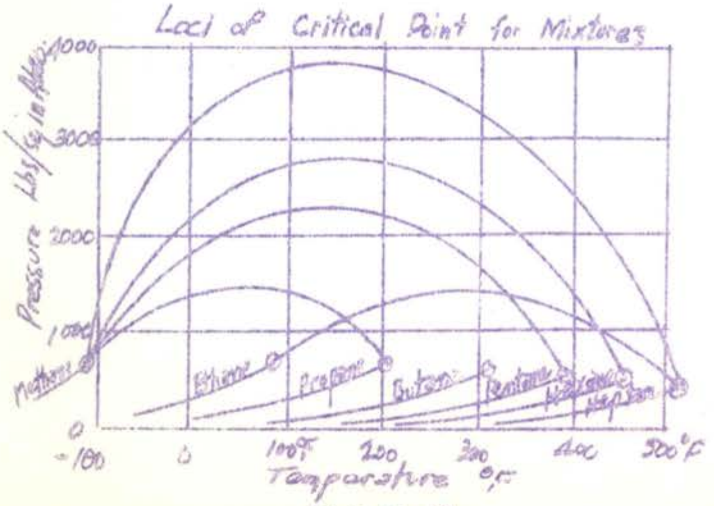


Figure 28

The critical conditions for heavier hydrocarbon mixtures, i.e petroleum fractions defined by the A.S.T.M. distillation and °API gravity, can be estimated from empirical correlations. Standard Data Book Charts A-4.21 and A-4.22 are such empirical critical point correlations and are based on experimental critical data on a wide variety of stocks.

Phase Diagram. When lines of constant per cent vaporized, including the bubble and dew point lines, are plotted with the logrithm of the absolute pressure and the reciprocal of the absolute temperature as coordinates, the result is the type of phase diagram shown on Figure 29.

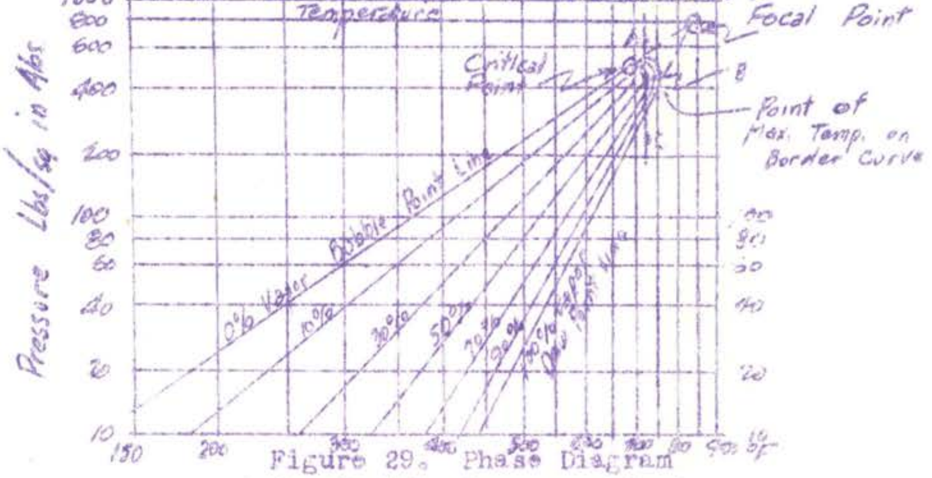
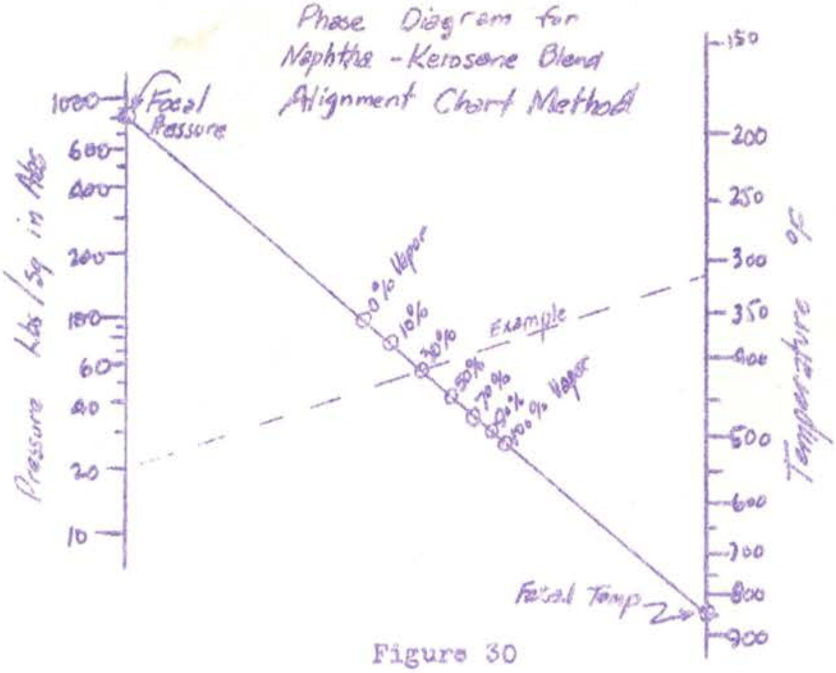


Figure 29. Phase Diagram
for Naphtha-Kerosene Blend
Semi-Log Graph paper Method

On this type of plot, which is similar to the chart (Cox) commonly used for plotting vapor pressures, the constant quality lines are straight and when extrapolated all intersect at a common focal or "critical intersection" point. The top of the phase diagram is dome shaped, defining what is commonly called a "border" curve or a P-T-X diagram. A phase diagram of this kind has many practical applications as will be shown later.

Two important points are indicated on the upper portion of this border curve, the "critical" point and the "cricondentherm" point or the point of maximum temperature. As indicated on Figure 29, lines of constant percentage vaporized all converge at the critical point. The critical point, which is the point on the border curve where the vapor and liquid phases become continuously identical, is usually near or on the straight portion of the bubble point line as shown, although it may be anywhere between the straight portions of the bubble and dew point lines, i.e. it may be located on the curved dome at any point.

The phase diagram can also be plotted in nomographic form, using the logarithm of the pressure and the reciprocal of the absolute temperature as the scales. Such a type of plot is illustrated by Figure 30.



Phase Diagram for
Naphtha - Kerosene Blend
Alignment Chart Method

Example: Find temperature at which 30% is vaporized with pressure of 20# Abs

Read 315°F with straight edge thru 20# and 30% vaporized

Figure 30

Such a plot is possible because the constant quality lines are straight and all intersect at a common focal point when plotted on semi-log coordinate paper with reciprocal of absolute temperature on the rectangular scale. This type of plot has the advantage that the solutions to several problems may be put on the same plot, which is not true for the regular graph paper way of plotting. The disadvantage to the alignment method is that the critical point region is not easily shown, making it almost impossible to make retrograde estimations at the dome of the border curve. In this region the regular graph paper method is recommended.

Retrograde Phenomena. The portion of the phase diagram between the critical point and the point of maximum temperature (or pressure) is the retrograde phenomena zone, where it is possible to have partial condensation take place on isothermal expansion (or isobaric heating) and partial vaporization take place on isothermal compression (or isobaric cooling).

The word retrograde implies a reversal and it is used to differentiate between a simple change in the quantity of a phase and one which reverses itself. Retrograde condensation or vaporization occurs when a phase appears, increases in quantity, reaches a maximum, and gradually decreases to complete disappearance during a process in which one independent variable relating to the system as a whole is continuously changed in value in the same direction (i.e., progressively increased or progressively decreased) while other variables, sufficient in number to fix the path of the system, are held constant. The variables mentioned are properties of the system as a whole and may be temperature, pressure, volume, enthalpy, entropy, free energy, etc. Temperature and pressure are the variables most commonly associated with the phenomena.

It is possible to have isothermal retrograde condensation between 710°F. and 745°F. for the naphtha-kerosene blend, for which the phase diagram is given as Figure 29. In going from vapor at point "A" (650 lbs./sq. in. absolute and 715°F.) to vapor at point "C" (210 lbs./sq.in. absolute and 715°F.) along the isothermal path ABC, retrograde condensation takes place so that the oil is 30% liquefied at point "B". For this particular stock isobaric retrograde condensation is not possible. The retrograde phenomena occurs upon paths which cut either a dew point curve or a bubble point curve in two places, owing to the occurrence of a maximum in that curve with respect to the variable which is being held constant. Such maxima are most likely to occur in the neighborhood of the critical state. Figures 31a and 31b show two cases where the retrograde phenomena is possible at constant pressure. In Figure 31a the critical point is well down on the bubble point line and the phase diagram dome is high. For this type of phase diagram both isothermal and isobaric retrogrades are possible. In Figure 31b the critical point is around on the dew point line near the point of maximum temperature and the dome is high enough to have this phenomena take place.

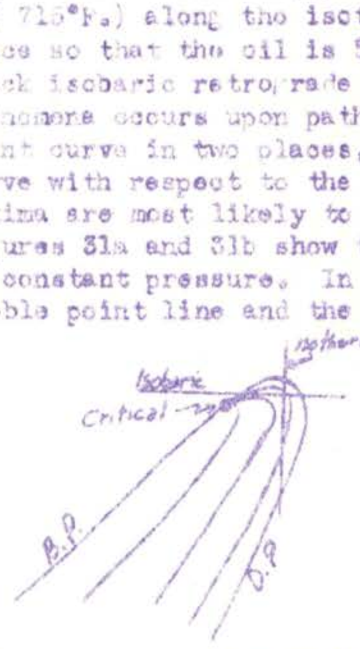


Figure 31a

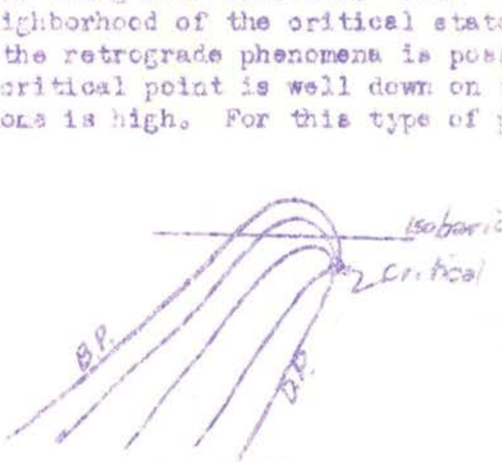


Figure 31b

The discovery and exploitation of high pressure petroleum reservoirs have brought the retrograde phenomena into public interest in recent years. It is utilized in the recovery of the heavier fractions contained in high pressure gases from wells producing natural gas.

The Vapor State. The P-V-T relationship for a substance in the vapor phase is customarily expressed by means of an equation of state, the simplest form of which is that for ideal gases. $PV=RT$. This simple equation can be applied to actual gases with sufficient accuracy for engineering purposes at comparatively low pressure. At high pressures, and particularly in the neighborhood of the critical point, the deviations from this ideal gas law equation are so great that it is useless. This has led to the introduction of other equations of state.

Of the many proposed algebraic equations of state, practically all of which have some theoretical basis, those of van der Waals, Dieterici, Berthelot, and Beattie-Bridgeman are the best known. All these suffer either because of limited applicability or difficulty in mathematical manipulation. The equation of van der Waal is the oldest, simplest, and best known of these equations of state. This equation contains two constants which can be calculated from the critical constants of the substance, whereas the evaluation of the constants for the other equations requires additional P-V-T data.

Van der Waals equation is usually written

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT \qquad (114)$$

Where the value of the universal gas constant R and the constants a and b should be consistent with the units of P, V, and T. The constants a and b can be calculated from P-V-T data or the critical point for a given substance. If possible, the constants should be established by data near to the range in which the equation is to be applied. If critical data are used, the constants a and b can be obtained from the following formulae which are derivable theoretically:

$$a = \frac{27R^2T_c^2}{64P_c} \qquad (115)$$

$$b = \frac{RT_c}{3P_c} \qquad (116)$$

On account of its simplicity and the possibility of deriving the constants from data which are frequently available or capable of being estimated, the van der Waals' equation is capable of frequent and useful application. Although this equation is a vast improvement over the assumption that the law of ideal gases applies, its accuracy is not high near the critical even when the critical point is used to determine the constants.

The more accurate Beattie-Bridgeman equation probably offers the closest check with the experimental data, because it contains five constants as compared to the two of the van der Waals' equation. The Beattie-Bridgeman equation is written:

$$P = \frac{RT\left(1-\frac{c}{VT^3}\right)}{V^2}\left[V + B_0\left(1-\frac{b}{V}\right)\right] - \frac{A_0}{V^2}\left(1-\frac{a}{V}\right) \qquad (115)$$

Where: R is the universal gas constant, and A_0, B_0, a, b, and c are constants to be determined from experimental phase and/or P-V-T data for the substance in mind. This equation is not of general use in process design because of its complicity. As a matter of fact it is too complicated to be of much practical value in thermodynamic calculations related to process design. Equations of state are primarily for correlation and interpolation purposes. However, they are often of value in calculating partial derivatives of the relations between pressure, volume, and temperature, which are used in thermodynamic calculations. The Beattie-Bridgeman equation is not explicit in V and therefore volume derivatives are obtained with difficulty. For this reason graphical methods of correlating P-V-T data and of differentiating have come into wide usage.

Reduced Equation of State. Experimental P-V-T data on petroleum hydrocarbons, especially for multi-component systems, are incomplete or entirely lacking. However, this difficulty has been circumvented by correlating what data do exist in a generalized method and applying this correlation to hydrocarbons for which no data exist and to multi-component systems by means of the pseudo-critical point concept, which will be discussed later. Three different methods of plotting and correlating P-V-T data for single component hydrocarbon systems have been used. Each of these methods makes use of the theorem of corresponding states, which postulates that all similar substances have corresponding volumes at corresponding temperatures and pressures, if the reference point of correspondence is the critical point for pure components and the pseudo-critical point for mixtures. Thus, instead of using pressure, temperature, and volume directly, the ratio of these to their value at the critical point is used. Listed in the order of increasing accuracy these three correlations are; (a) the reduced isochor plot, (2) the PV/RT plot, and (3) the reduced volume residual plot.

Figure 30 shows a Reduced Isochor plot. On this plot reduced pressures, P_r, are plotted against reduced temperatures, T_r, for lines of constant volume, V_r.

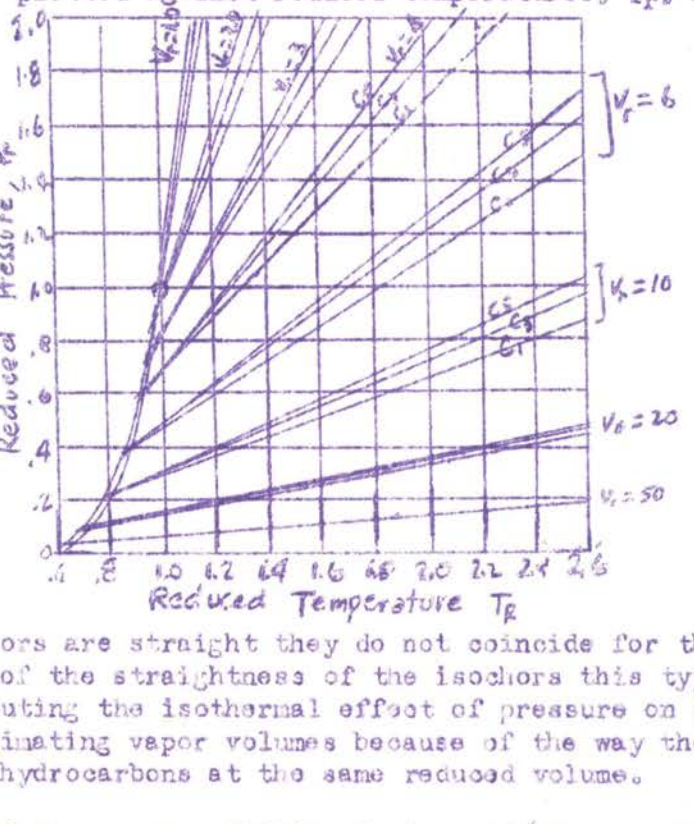


Fig 32
Reduced Isochors
for
Methane
Propane
Pentane

Although the isochors are straight they do not coincide for the various hydrocarbons. Because of the straightness of the isochors this type of plot has been used for computing the isothermal effect of pressure on the enthalpy. It is not used in estimating vapor volumes because of the way the lines spread for the different hydrocarbons at the same reduced volume.

A plot of the compressibility factor, PV/RT, vs. reduced pressure, P_r, for lines of constant reduced temperature, T_r, is given as Figure 33. Methane, propane, and pentane data were used in preparing this plot also.

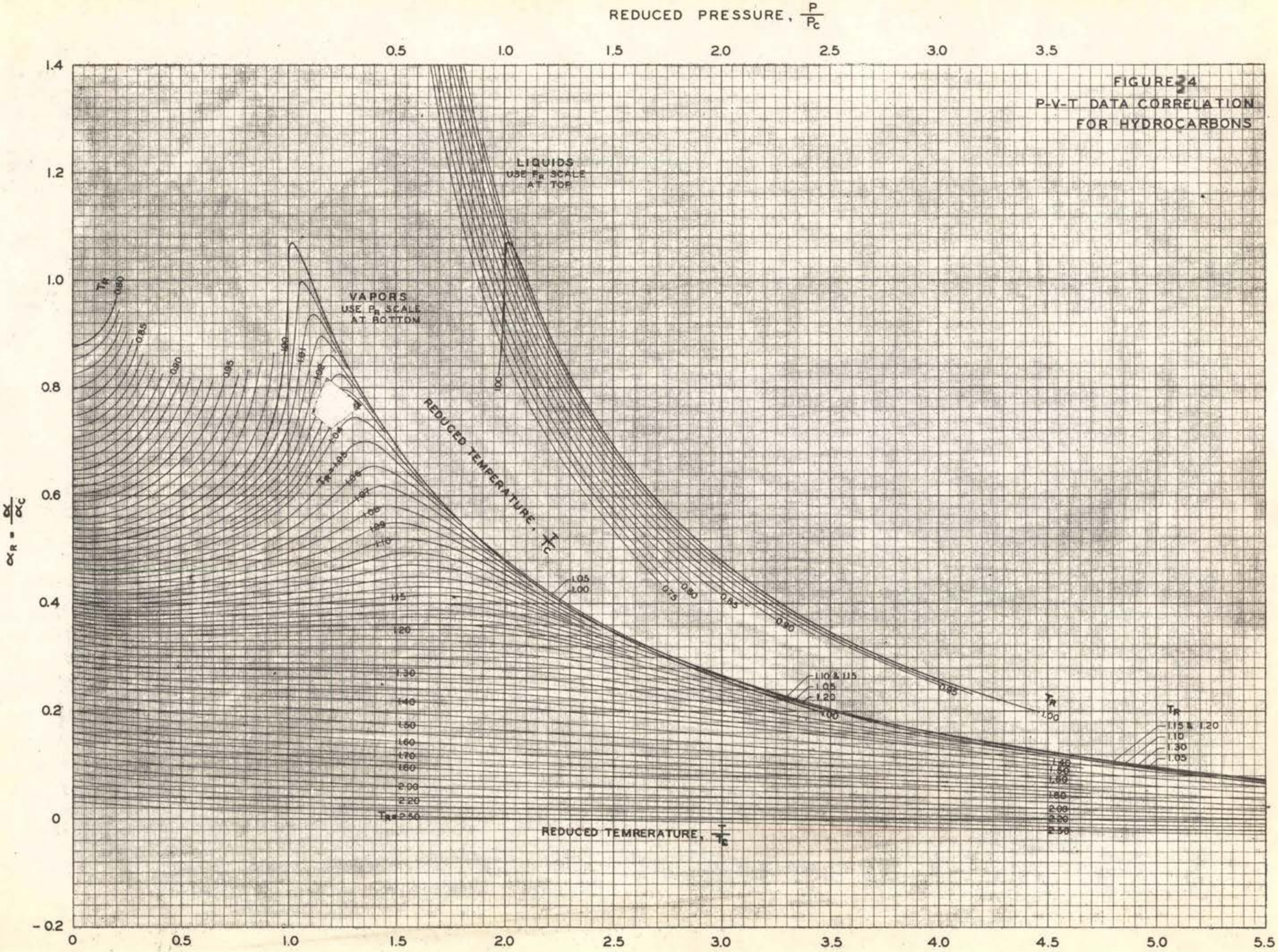


FIGURE 34
P-V-T DATA CORRELATION
FOR HYDROCARBONS

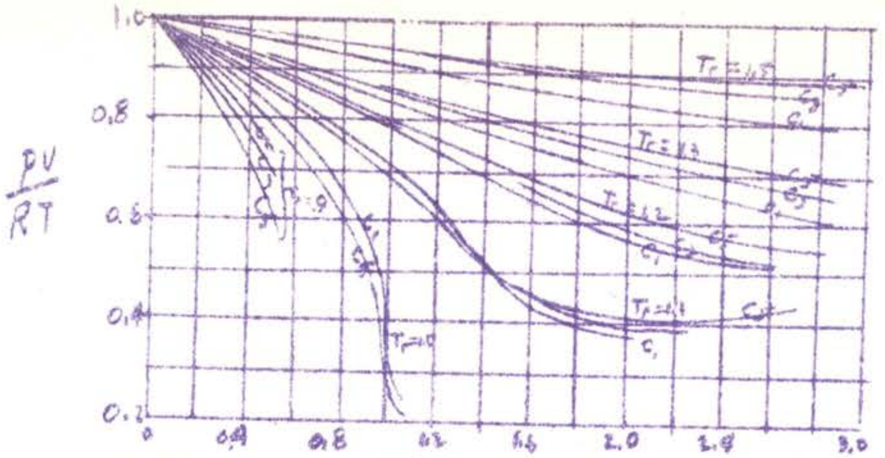


Figure 33
Deviation From
Ideal Gas Laws

The compressibility factor, PV/RT, which is the ratio of actual to theoretical gas volume, has been in wide use during recent years as a means of correlating P-V-T data. When plotted against reduced pressure, lines of constant reduced temperature for different hydrocarbons are close together, and in some cases coincide. This type of plot is used to estimate vapor densities by the equation PV = ZRT where Z = PV/RT, the compressibility factor. A large scale plot of Z is given as Standard Data Book Chart A-2.51. Vapor volumes estimated from this type of plot are of sufficient accuracy for most engineering calculations. In addition this type of plot is a convenient correlation to use. For thermodynamic calculations this correlation is not accurate enough and, in addition, is not well adapted to graphical methods of differentiation and integration.

Instead of the ratio of actual to ideal gas volume, consider their difference; this residual quantity is defined as

$$\alpha = \frac{RT}{P} - V \qquad (116)$$

Where: $\frac{RT}{P}$ = ideal gas volume, and

V = actual gas volume

This residual quantity is well adapted to graphical methods.

Since $\alpha = \alpha_r \alpha_c$, $P = P_r P_c$, and $T = T_r T_c$, equation (116) may be rearranged and written

$$\frac{V}{\alpha_c} = \frac{RT_c}{P_c \alpha_c} \frac{T_r}{P_r} - \alpha_r \qquad (117)$$

which is essentially a reduced equation of state, where the ratio $RT_c/P_c\alpha_c$ is practically a constant, and α_r is a function of P_r and T_r.

The α_r function was determined from experimental P-V-T data collected from the literature. Values of α_r were calculated and plotted for eleven hydrocarbons to develop this correlation, which is given as Figure 34. Values of α_r in the unsaturated liquid region as well as in the unsaturated vapor region are shown on Figure 34.

The reduced residual volume method of correlating P-V-T data is more accurate than the PV/RT method and, in addition, is better adapted to graphic mathematics methods. For these reasons Figure 34 is recommended for thermodynamic calculations while Chart A-2.51 is recommended for vapor density calculations in design work because it is more convenient and almost as accurate.

Pseudo-Critical Condition. For pure components the actual critical points are used in computing the reduced properties for the generalized correlations. For multi-component systems the critical point does not give satisfactory results, however, so a pseudo-critical point must be used instead. The pseudo-critical point is the critical point of an imaginary pure compound, whose isochors coincide with the isochors of the mixture in question. In Figure 35 the border curve and isochors are shown on a P-T plot for a mixture. The critical point of the mixture is indicated on the border curve. If the isochors are extended into the border curve, they intersect on the vapor pressure curve of a hypothetical component. The critical point of this hypothetical component is the pseudo-critical point for the mixture.

Figure 35

When the P-V-T data for a pure compound, having a true critical point the same as the pseudo-critical point of a mixture, are plotted on the same plot with the P-V-T data for the mixture, the resulting isochors coincide.

The pseudo-critical point for light hydrocarbon mixtures is the sum of the products of the mol fractions and the true criticals for each component. For heavier fractions, the pseudo-critical temperature and pressure may be determined from the empirical correlations given as Standard Data Book Charts A-4.31 and A-4.32.

In addition to densities, the pseudo-critical point is used in thermodynamic computations for all properties depending upon the volumetric behavior of hydrocarbon mixtures.

3. Calorimetric Data

In addition to volumetric and phase relation data, various kinds of calorimetric data are required for the development of process design tools. These required calorimetric data include: (a) experimental heat capacities and thermal conductivities for liquids and vapors; (b) Joule Thomson coefficients for vapors; and (c) heats of vaporization, combustion and formation. A thorough treatment of this subject is not essential to a study of process design. Therefore, only a brief and general discussion of calorimetric data will be presented.

Specific Heat. The preparation of entropy-enthalpy charts requires specific heats for the liquid phase and for the vapor at some constant pressure, atmospheric pressure being used generally. The determination of the specific heat of petroleum products requires extensive equipment and a high degree of skill. Improper methods will fail to account for calorimetric errors. Other experimental errors that may creep in are: (a) change of state; (b) thermal decomposition or cracking; and (c) measurement and control of the flow of the fluid, particularly vapor.

From the currently available data, the specific heats of liquid petroleum fractions is a linear function of temperature, increasing with temperature and A.P.I. gravity. Although there are indications in the available data that the character of the stock (i.e. virgin or cracked, paraffinic or aromatic) effects the liquid specific heat, there are insufficient data to reach quantitative conclusions. A survey of the available data results in the following equations for the liquid specific heats. The Bureau of Standards equation

$$C = \frac{1}{\sqrt{d}} (0.388 + 0.00045t) \qquad (118)$$

and the Forstch and Whitman equation

$$C = \frac{(t+670)(2.10-d)}{2030} \qquad (119)$$

Where:

C = specific heat in Btu/lb. °F.
d = specific gravity 60/60
t = temperature, °F.

A plot of liquid specific heats is given on Standard Data Book Chart A-8.41. Specific heats from this linear relationship are not valid near the critical, where the specific heat increases appreciably. The use of liquid curves on Chart A-8.41 should be limited to temperatures within 100°F. of the critical. Since the critical temperature varies with the average boiling point as well as the gravity, the specific heats curves will be different for virgin and cracked liquid near the critical.

The specific heats of gases has been the subject of considerable experimental and mathematic study. Specific heats of gases may be found determined in two ways: (a) the spectroscopic method, and (b) with an adiabatic calorimeter. The spectroscopic method is only applicable to the simpler molecules. By this method specific heats are computed over wide ranges of temperature by the application of statistical mechanics to spectroscopic data covering the desired temperature range and a calorimetric specific heat at any one temperature. Briefly the procedure is to set up a model of the molecule in question and estimate all the intra molecular energies such as rotational, torsional, vibrational, etc. energies, checking the spectrum, thus evaluating the change in specific heat with temperature. Knowing the specific heat at one temperature, from calorimetric data, it is then possible to write an equation for the specific heat.

In determining the specific heat by the flow calorimeter method, the amount of heat required to raise the fluid a few degrees in temperature is measured. Because of the narrow difference in temperature for each observation, it is essential that there be no heat losses and that the flow of the fluid and the heat added be measured with a high degree of precision. Vacuum jacketed and silvered calorimeters are employed to minimize the heat losses. Precise temperature and flow measuring equipment are also used.

For monatomic gases the molal heat capacity is about 3 Btu/lb. mol-°F. at constant volume and about 5 Btu/lb. mol-°F. at constant pressure. Neither changes appreciably with temperature or pressure. For diatomic gases such as oxygen, nitrogen, hydrogen, and air, the molal heat capacity at room temperature is roughly 5 Btu/lb. mol-°F. at constant volume and 7 Btu/lb. mol-°F. at constant pressure. The change with temperature is small, C_p for O_2 increasing from 6.8 to 8.6 at 5000°F., but the change with pressure is negligible. For triatomic gases, such as water, carbon dioxide, etc., the molal heat capacity at room temperature varies from 6 to 7 at constant volume and from 8 to 9 at constant pressure and changes rapidly with temperature. In addition changes in pressure have appreciably effects on the specific heat for triatomic gases. No generalizations are possible for gases having more than three atoms, except that increasing complexity of the molecule is paralleled by increasing heat capacities and increased temperature coefficient. For hydrocarbon vapors, the specific heat is linear with temperature, increasing with temperature and with molecular weight or specific gravity. Experimental data must be used to evaluate the constants A and B in the equation

$$C_p = A + BT \qquad (120)$$

Where: C_p = molal heat capacity
T = temperature, °K.

The following tabulation gives values of the constants, A and B for all hydrocarbons for which data are available.

	A	B
Methane	4.313	0.01444
Ethylene	4.033	0.02167
Ethane	4.27	0.02833
Propylene	8.625	0.02529
Propane	9.00	0.030
Butylene	9.8	0.038
Butane	10.3	0.0425

For higher boiling petroleum fractions, the specific heat of the vapor is given as a function of the specific gravity. The following equation gives correlation of experimental specific heat data:

The Bahlke and Kay equation

$$C_p = \frac{4.0 - d}{6450} (t + 670) \qquad (121)$$

Where: C_p = specific heat at 14.7 lbs./sq.in.abs. Btu/lb.-°F.
t = temperature, °F.
d = specific gravity

Although these equations show no dependence of specific heat on the boiling point, some such relationship undoubtedly exists. When more experimental data become available the effect of this variable may be discovered.

Weir and Eaton (Ind. Eng. Chem. 24, 210 (1932)) developed the following equations for the total heat or enthalpy of Mid-Continent oils.

$$H_L = 15d - 26 - (0.465d - 0.811)\ t + 0.000290t^2 \qquad (122)$$

$$H_V = 215 - 87d + (0.415 - 0.104d)\ t + (0.00031-0.000078d)t^2 \qquad (123)$$

where H_L = enthalpy of liquid above 32°F. liquid.
H_V = " " vapor " " "
d = specific gravity at 60°F.
t = temperature, °F.

Thermal Conductivity. The effect of temperature and pressure on the thermal conductivity of gases can be estimated from the following relationship derived from the Kinetic Theory of Gases

$$\frac{K_2}{K_1} = \frac{\eta_2}{\eta_1} \frac{C_{v_2}}{C_{v_1}} \qquad (124)$$

Where: K, η, and C_v are thermal conductivity, absolute viscosity, and specific heat at constant volume, respectively; subscript 1 refers to condition at which the conductivity is known; and subscript 2 refers to a condition at which the conductivity is desired. In order to use this equation, the effects of pressure and temperature on the viscosity and the constant volume specific heats must be known, however. The thermal conductivities for hydrocarbon gases increases with temperature and decreases with molecular weight.

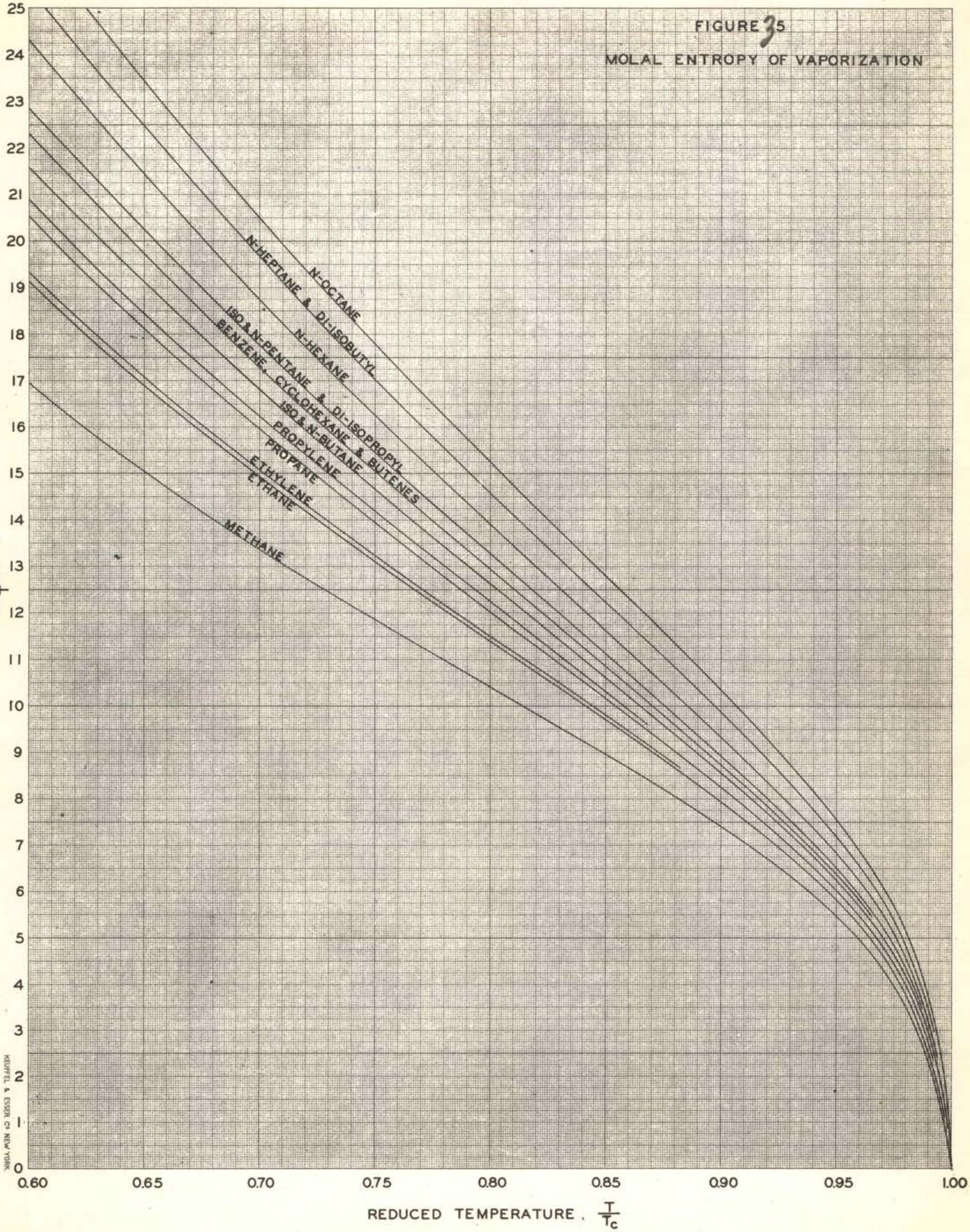


FIGURE 35

MOLAL ENTROPY OF VAPORIZATION

In the case of liquids, there is no possibility of calculating the effect of temperature on the thermal conductivity as was possible for gases. Therefore, experimental data must be used exclusively. The thermal conductivity of water increases with increase in temperature whereas it decreases with increase in temperature for petroleum oils. Liquid hydrocarbon thermal conductivities decrease with increase in density.

Joule-Thomson Coefficient. The experimental determination of the Joule-Thomson coefficient is much easier than the measurement of specific heats because no quantitative fluid or heat flow measurements are necessary. Joule-Thomson coefficients are determined by measuring the temperature and pressure changes while throttling free expansion (no work) of the vapor slowly through a porous plug set in an adiabatic calorimeter so that no heat will be lost while no heat is added. Expansion must be slow so that no friction or "wire-drawing" will result. Although fluid and heat flow quantities are not required, temperature and pressure changes must be measured very accurately. These are often done by means of opposed thermocouples and manometers.

The isothermal pressure correction to the enthalpy, sometimes called the "Joule-Thomson effect", can be measured by a similar procedure, in which heat is added during the free expansion to maintain the outlet temperature the same as the inlet temperature. In this experiment the fluid flowing and the heat added must be measured. This amounts to combining the Joule-Thomson coefficient and the specific heat determinations into one experiment.

Heat of Vaporization. The latent heat of vaporization, which varies with the pressure becoming zero at the critical point, can be computed if precise volumetric and vapor pressure data are available. However, experimental data are desirable, although the determination of latent heats of vaporization is not a simple matter. For pure components the calorimeter would operate at constant temperature and pressure, while for mixtures one or the other must be varied.

When the molal entropy of vaporization is plotted against the reduced temperature, the lines for various hydrocarbons fall in a regular family of curves as shown by Figure 36. This plot can be used for estimating the latent heat of vaporizations for pure hydrocarbons and for mixtures as well. Its use for pure hydrocarbons is obvious. The method of applying Figure 36 to mixtures was proposed by Watson and Nelson (Ind. Eng. Chem. 25, 880 (1933)). In this method the latent heat of vaporization must be known at one point and it can be computed at any point. This calculation is made as follows:

$$\Delta H_2 = \Delta H_1 \frac{\mathcal{Q}_2}{\mathcal{Q}_1} \frac{T_2}{T_1} \tag{125}$$

Where: ΔH = known latent heat of vaporization for mixture at T

$\mathcal{C}\ell$ = molal entropy of vaporization function at T

T = temperature °R

Subscripts 1 and 2 indicate known and unknown conditions.

The molal entropy of vaporization function is evaluated from Figure 36 by reading from a hydrocarbon line nearest to the mixture in question. It is not very important which line is used to read values of $\mathcal{C}\ell$ since the two values appear as a ratio in equation (125) and both can change without effecting this ratio. The base latent heat of vaporization, ΔH_1, used in equation (125) should be an isothermal latent heat or the difference between the saturated vapor and liquid lines at the same temperature. The recommended way of applying equation (125) and Figure 36 is to select ΔH_1 at a low temperature where the pressure has little or no effect on the heat of vaporization. In computing the reduced temperature to make the $\mathcal{C}\ell$ readings from Figure 36, the point of maximum temperature should be used instead of the critical temperature because this is the point at which the isothermal heat of vaporization is zero for a mixture.

The isothermal heats of vaporization for petroleum fraction near and at their atmospheric boiling points are given by the following equation proposed by Weir and Eaton:

$$\Delta H_v = 241-102d-(0.396-0.361d)\ t-(0.000078d-0.00002)t^2 \qquad (126)$$

Where ΔH_v = heat of vaporization, Btu/lb.

d = specific gravity 60/60

t = temperature, °F.

Heat of Combustion. Heats of combustion have two applications in the process design of petroleum refining equipment: (a) combustion calculations (i.e. furnace design), and (b) heats of formation and decomposition. The complete combustion of liquid hydrocarbons to CO_2 and H_2O, with an accurate measurement of the heat evolved, is readily accomplished in a constant volume bomb calorimeter. Such determinations are usually very accurate as there are few manipulations in which to make an error. The gross calorific value of petroleum liquid fractions at constant volume is a function of the density only and decreases with increase in density.

In most industrial applications of calorimetric heat of combustion data, the process occurs at constant pressure rather than at constant volume, making it necessary to correct the calorimetric data to a "net" basis by allowing for the heat of condensation of the water formed in the combustion.

Heats of combustion of hydrocarbon gases is most readily determined at constant pressure instead of in a constant volume bomb as liquids are determined. The procedure for gaseous hydrocarbons is also uncomplicated.

The gross calorific value for hydrocarbon gases increases with the molecular weight (specific gravity) of the gas. The character of the gas (saturated or unsaturated) has a slight effect on the heat of combustion. Heats of combustion for gases and liquids are given on Standard Data Book charts, as a function of the relative amounts of hydrogen and carbon. The use of these data will be taken up later.

C. Compression of Gases

Compression, without chemical reaction, of gases to pressures of a few atmospheres is an important step in many refining processes. Where this operation occurs in the design of new equipment it is necessary to estimate the work required, the volumetric efficiency, and the temperature change during compression. Two ways of making calculations of this kind are in use: (a) equations based on the perfect gas law, and (b) the Mollier diagram (entropy-enthalpy). For designing compressors either method is sufficiently accurate, even for hydrocarbons up to 20 atmospheres. In making precise refrigeration calculations, the Mollier diagram method should be used. The latter method will be taken up in the next section. This section will be devoted to the perfect gas law method.

The bases for the development of the following compression formulae are: adiabatic process and perfect gas laws. The first is true where the jacket cooling water removes just the heat of friction and no more or no less. (Note: A process can be adiabatic without being a constant entropy or reversible process although the type of process referred to here is essentially isentropic.) The assumption of perfect gas law validity is necessary to the simplification of the problem.

The conventional assumption of an isentropic path for compression is conservative because isentropic work is the maximum work possible. The isothermal path work is the minimum possible work of compression. The compression along an intermediate path (called polytropic) is one of decreasing entropy and is the path actually followed when the jacket cooling water takes out more heat than the heat equivalent of the friction but not enough to maintain isothermal conditions. The work for this polytropic compression is lower than the work for isentropic but higher than the work for isothermal compression, which is given by equation (102) on page 116. In compression it is desirable to remove as much heat as is practical to keep the work required down, while in expansion it is desirable to retain as much of the heat as is practical to keep the work developed up. As it turns out compressors operate with a slight decrease and expanders with a slight increase in entropy. The same equations apply to both processes, however.

1. Isentropic or Polytropic Work.

The equation for the theoretical work required for single stage adiabatic compression of gas will be developed by reference to Figure 37

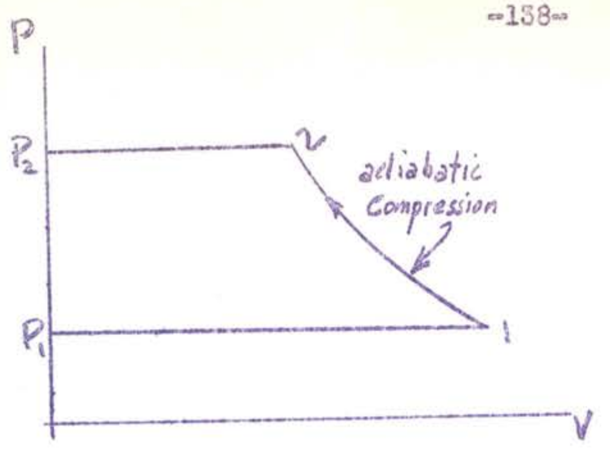


Fig. 37
Single Stage Compression

for which the work is given by the following equation:

$$\text{Work} = \int_1^2 V dP \qquad (127)$$

For a perfect gas PV^{γ} = a constant and it can be shown that $P^{\frac{1}{\gamma}}V = P_1^{\frac{1}{\gamma}}V_1 = P_2^{\frac{1}{\gamma}}V_2$ = a constant also. Eliminating V from the above work equation gives

$$\text{Work} = C \int_1^2 P^{-\frac{1}{\gamma}} dP \qquad (128)$$

Integrating

$$W = \frac{C}{1-\frac{1}{\gamma}} \left[P_2^{1-\frac{1}{\gamma}} - P_1^{1-\frac{1}{\gamma}} \right] = \frac{CP_2^{1-\frac{1}{\gamma}} - CP_1^{1-\frac{1}{\gamma}}}{1-\frac{1}{\gamma}} \qquad (129)$$

Eliminating C in equation (129) by substituting for it $P_1^{\frac{1}{\gamma}} V_1$ and $P_2^{\frac{1}{\gamma}} V_2$.

$$W = \frac{P_2^{\frac{1}{\gamma}} V_2 P_2^{1-\frac{1}{\gamma}} - P_1^{\frac{1}{\gamma}} V_1 P_1^{1-\frac{1}{\gamma}}}{\frac{\gamma-1}{\gamma}} = \frac{\gamma}{\gamma-1} \left[P_2V_2 - P_1V_1 \right] \qquad (130)$$

Or

$$W = \frac{\gamma}{\gamma-1} P_1V_1 \left[\frac{P_2V_2}{P_1V_1} - 1 \right] \qquad (131)$$

But $\frac{V_2}{V_1} = \left(\frac{P_1}{P_2} \right)^{\frac{1}{\gamma}}$ with which equation (131) may be simplified to give

$$W = \frac{\gamma}{\gamma-1} P_1V_1 \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \qquad (132)$$

which is the work for single stage adiabatic compression of a perfect gas. An equation for the temperature change in single stage adiabatic compression is derived from equation (108), page 116, by eliminated V with perfect gas law equation.

$$TV^{\gamma-1} = T \left(\frac{RT}{P} \right)^{\gamma-1} = \text{constant}, \qquad (133)$$

from which

$$\frac{T^{\gamma}}{P^{\gamma-1}} = \frac{T_1^{\gamma}}{P_1^{\gamma-1}} = \frac{T_2^{\gamma}}{P_2^{\gamma-1}} = \text{constant} \qquad (134)$$

Solving for T_2

$$T_2 = T_1 \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} \qquad (135)$$

The equation for the theoretical work required for multiple stage adiabatic compression of gas with cooling to the original temperature between stages, with no condensation, and with equal work for each stage can be developed by reference to Figure 38 and the above equations. If P' is the intermediate pressure for two stage compression and $T' = T_1$, $P_1V_1 = P'V'$ and the work for each stage may be written simply.

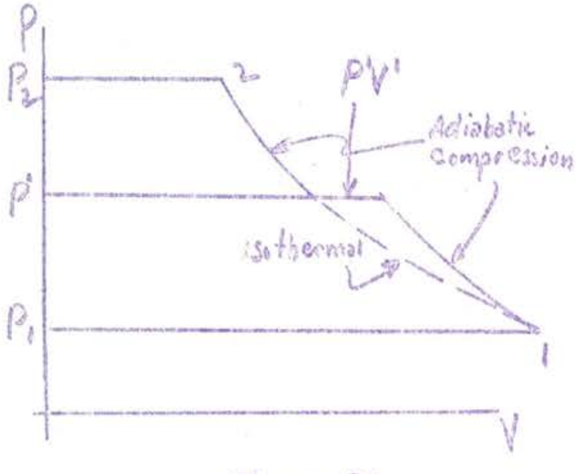


Figure 38
Two Stage Compression

$$W_1 = \frac{\gamma}{\gamma-1} P_1V_1 \left[\left(\frac{P'}{P_1} \right)^{\frac{\gamma-1}{\gamma}} -1 \right]$$

and

$$W_2 = \frac{\gamma}{\gamma-1} P_1V_1 \left[\left(\frac{P_2}{P'} \right)^{\frac{\gamma-1}{\gamma}} \right] -1$$

The total work for two stage compression

$$W = W_1 + W_2 = \frac{\gamma}{\gamma-1} P_1V_1 \left[\left(\frac{P'}{P_1} \right)^{\frac{\gamma-1}{\gamma}} + \left(\frac{P_2}{P'} \right)^{\frac{\gamma-1}{\gamma}} - 2 \right] \qquad (136)$$

The total work is a minimum when

$$\left(\frac{P_2}{P'} \right)^{\frac{\gamma-1}{\gamma}} + \left(\frac{P'}{P_1} \right)^{\frac{\gamma-1}{\gamma}}$$

has a minimum value. Differentiating with respect to P', which is the only variable and setting the derivative equal to zero gives

$$P' = \sqrt{P_1P_2} \qquad (137)$$

Introducing this expansion into equation (137) gives

$$W = \frac{2\gamma}{\gamma-1} P_1V_1 \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{2\gamma}} -1 \right] \qquad (138)$$

From this equation the expression for the theoretical horsepower required for multiple stage compression, with intercooling to original temperature, no condensation and equal work per stage may be written by inspection

$$H.P.\ (theo.) = \frac{144}{33,000}\ P_1V_1\ \frac{S\gamma}{\gamma-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{S\gamma}}\right]-1 \qquad (139)$$

Where: P_1 and P_2 are the intake and discharge pressures in lbs./sq.in. abs.

V_1 = cu.ft./min. at P_1 and T_1

$\gamma = C_p/C_v$ for isentropic compression.

S = number of stages with intercooling.

For polytropic expansion $C_p/C_v > \gamma > 1.0$.

For multiple stage compression the equation for the final temperature becomes

$$T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{S\gamma}} \qquad (140)$$

Where T and P are absolute. The brake horsepower requirement can be obtained by dividing the theoretical horsepower from the above equation by the mechanical efficiency of the compressor.

2. Volumetric Efficiency

An actual compressor must have clearance, and the gas remaining in the clearance space expands on the return stroke of the piston thus partially filling the cylinder and reducing the volume of fresh gas that can be taken in during the intake stroke. The ratio of the actual volume of gas (at intake conditions) compressed to the piston displacement is the volumetric efficiency. This efficiency is a function of the compression ratio, the per cent clearance volume, and the gamma value for the gas. An expression for this volumetric efficiency will be derived.

let V_d = displacement volume

V_c = clearance volume

V_e = volume to which clearance volume gases expand.

C = ratio of clearance to displacement volumes.

For a perfect gas $\frac{V_1}{V_2} = \left(\frac{P_2}{P_1}\right)^{\frac{1}{\gamma}}$, $V_e = V_c\left(\frac{P_2}{P_1}\right)^{\frac{1}{\gamma}} = CV_d\left(\frac{P_2}{P_1}\right)^{\frac{1}{\gamma}}$ (141)

Actual volume of gas intake $V_d + V_c - V_e = V_d\left[1 + C - C\left(\frac{P_2}{P_1}\right)^{\frac{1}{\gamma}}\right]$ (142)

From which the volumetric efficiency,

$$E_v = \left[1 + C - C\left(\frac{P_2}{P_1}\right)^{\frac{1}{\gamma}}\right] \qquad (143)$$

3. Specific Heat Ratio

The ratio of isobaric to isometric specific heats, $C_p/C_v = \gamma$, is an essential thermodynamic property in calculations involving the adiabatic compression or expansion of a gas. It may be determined experimentally or computed by thermodynamic relations from P-V-T and atmospheric specific-heat data. For perfect and monatomic gases $\gamma = 1.66$; for diatomic gases such as H_2, O_2 and N_2, $\gamma = 1.4$. There are few γ data, either experimental or calculated, for hydrocarbons, however. Some experimental γ data are available at atmospheric pressure for hydrocarbons of one to six carbon atoms.

Basic Equations. The two fundamental thermodynamic equations used in computing C_p/C_v ratios from P-V-T and atmospheric specific heat data are:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P \qquad (72)$$

$$C_p - C_v = -T\,\frac{\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} \qquad (74)$$

The integration constant for Equation 72 must be found from experimental isobaric specific heat data. Although data at any pressure could be used, data only at atmospheric pressure are available. The volume derivatives for the above equations can be determined graphically or analytically from P-V-T data by means of graphic or algebraic equations of state.

When expressed in terms of α_r and reduced units and integrated between the limits of P_r and $P_r = 0$ at constant values of T_r, Equation 72 becomes:

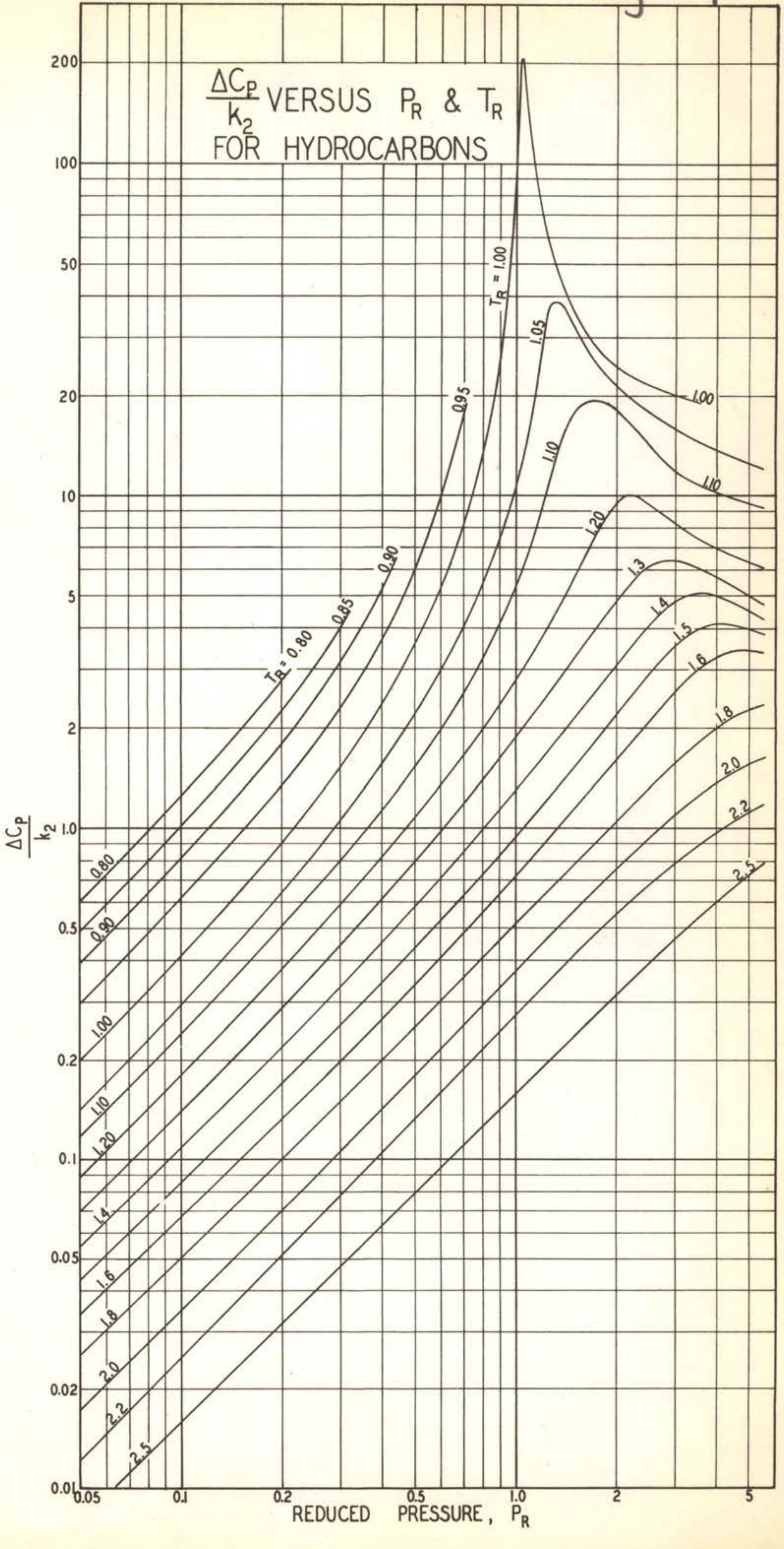
$$\frac{\Delta C_p}{K_2} = T_r \int_0^{P_r} \left(\frac{\partial^2 \alpha_r}{\partial T_r^2}\right)_{P_r} dP_r \qquad (144)$$

where ΔC_p = increase in isobaric specific heat from 0 pressure to any pressure P_r.
$K_2 = P_0 \alpha_c / T_c$, a constant for each hydrocarbon.

The second derivative was determined graphically from the α_r correlation given as Figure 34. Equation 144 was integrated, and values of $\Delta C_p/K_2$ (see Fig 39) were tabulated by Edmister (Ind. Eng. Chem. 30, 352 (1938)). From these results the effect of pressure on the isobaric specific heat can be computed. The effect of temperature on the specific heat can be calculated by the correlation of atmospheric specific-heat data.

Upon introduction of α_r and reduced units, Equation (74) becomes:

Fig 39



$\frac{\Delta C_p}{k_2}$ VERSUS P_R & T_R FOR HYDROCARBONS
$\frac{\Delta C_p}{k_2}$
REDUCED PRESSURE, P_R
200
100
50
20
10
5
2
1.0
0.5
0.2
0.1
0.05
0.02
0.01
0.05
0.1
0.2
0.5
1.0
2
5
T_R = 0.80
0.85
0.90
0.95
T_R = 1.00
1.05
1.10
1.20
1.3
1.4
1.5
1.6
1.8
2.0
2.2
2.5
1.00
1.10
0.80
0.90
1.00
1.10
1.20
1.4
1.6
1.8
2.0
2.2
2.5

$$C_p - C_v = T \frac{\left[\frac{R}{P} - \frac{\alpha_c}{T_c}\left(\frac{\partial \alpha_r}{\partial T_r}\right)_{P_r}\right]^2}{\left[\frac{RT}{P^2} + \frac{\alpha_c}{P_c}\left(\frac{\partial \alpha_r}{\partial P_r}\right)_{T_r}\right]} \qquad (145)$$

The derivatives of α_r were determined graphically from the α_r correlation and were tabulated.

Calculation and Correlation of C_p/C_v. The computation of C_p/C_v ratios from these equations and reduced thermodynamic functions were made for various reduced temperatures and pressures for seventeen hydrocarbons, and the resulting C_p/C_v ratios were plotted against P_r for lines of constant T_r. One of these plots (for propane) is shown in Figure 39a.

see page 142 a for sample calculation of C_p/C_v

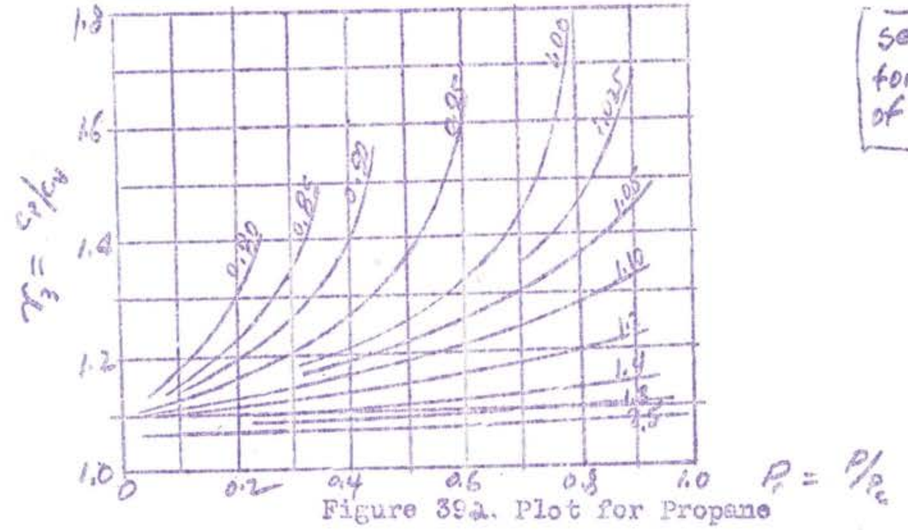


Figure 39a. Plot for Propane

Comparison of the plots showed that they were very similar and that all of them could be made to coincide by either expanding or condensing their C_p/C_v scales. In other words, Figure 39a for propane will hold equally well for all the other hydrocarbons if different numerical values are given the ordinate scale. This is done by the following equation:

$$\gamma = 1 + C(\gamma_3 - 1) \qquad (146)$$

where γ_3 = value of C_p/C_v for propane
C = constant for each hydrocarbon
γ = C_p/C_v for the hydrocarbon in question

Values of C for equation (146) vary from 3.5 for methane to 0.30 for n-octane.

By means of Figure 39a, Equation (146) and these values of C, a composite γ plot was constructed and is here presented as Figure 40. The solution of an example is shown by heavy dashed lines and arrows, to find $\gamma = 1.525$ for propylene at $P_r = 0.555$ and $T_r = 0.95$.

Sample Calculation of Cp/Cv for Propane

Compute Cp/Cv for propane at 405°F. and 370 lbs./sq.in. abs.

$$T_r = \frac{305 + 460}{205 + 460} = 1.15, \quad P_r = \frac{370}{617} = 0.6$$

a) Find Cp by means of equations 128 and 144. From equation 128 the value of Cp at atmospheric pressure is found as follows:

$$Cp = \frac{9.00}{44.06} + \frac{0.030}{44.06} \frac{(305+460)}{1.8} = 0.494 \text{ Btu/lb.-°F.}$$

By equation 144 and a plot of Cp/K_2 (similar to Figure 39) Cp is computed at 305°F. for 14.7 and 370 lbs./sq.in. abs.

From Fig. 39 $\Delta C^\circ p/K_2 = 0.060$ and $\Delta Cp/K_2 = 1.625$

$$K_2 = \frac{(617)(0.1919)(144)}{(665)(778)} = 0.0334$$

$$\Delta Cp = 0.0334\ (1.625 - 0.060) = 0.0523$$

$$Cp = 0.494 + 0.0523 = 0.5463 \text{ Btu/lb.-°F.}$$

b) Compute Cv by first finding Cp-Cv from equation 145 and then subtracting Cp from above.

$$\frac{R}{P} = \frac{1543}{(144)(44.06)(370)} = 0.000658$$

$$\frac{\alpha_c}{T_c}\left(\frac{\partial \alpha_r}{\partial T_r}\right)_{P_r} = \frac{0.1919}{665}\ (-0.88) = -0.0002536$$

$$\frac{RT}{P^2} = \frac{(1543)(765)}{(144)(44.06)(370)^2} = 0.00136$$

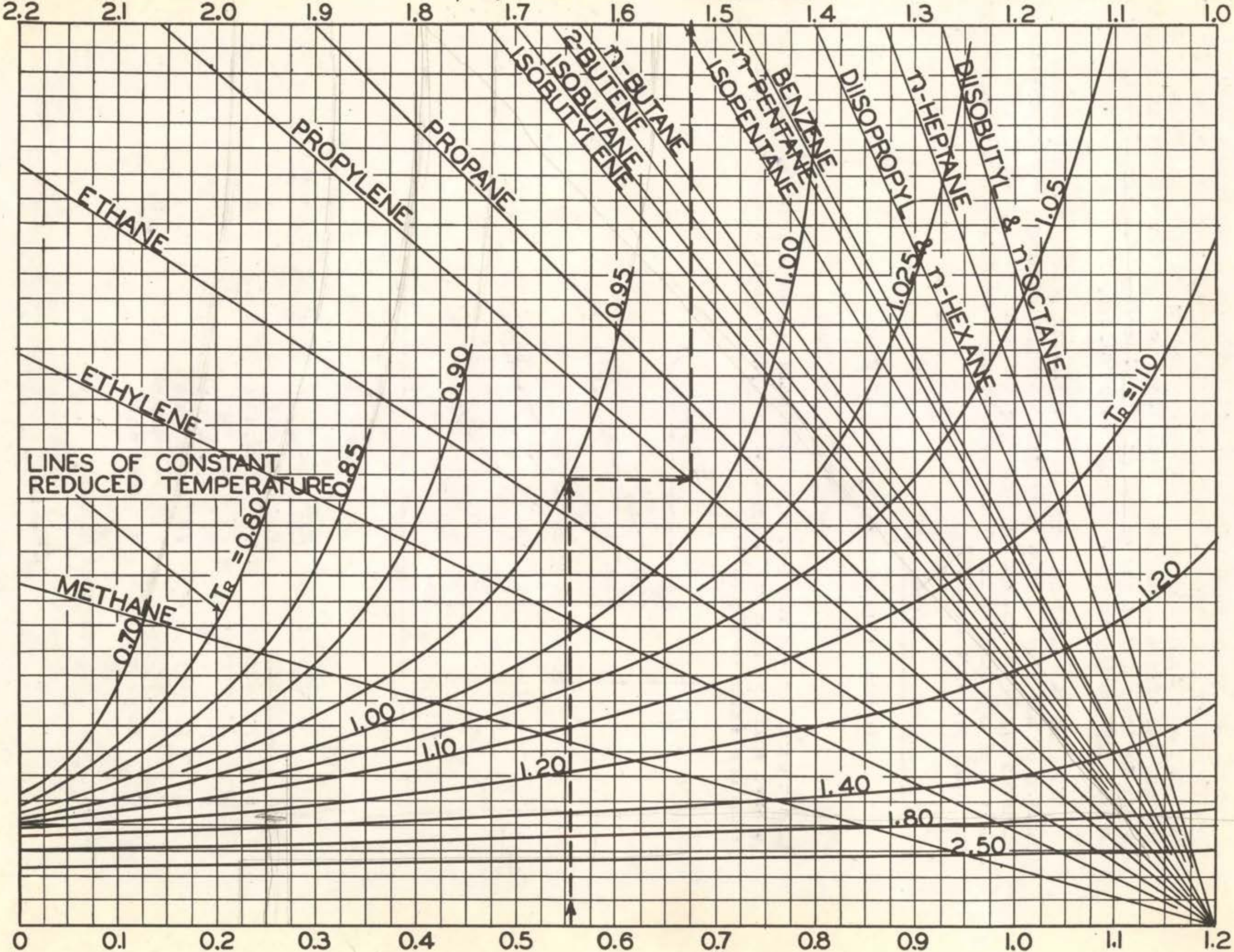
$$\frac{\alpha_c}{P_c}\left(\frac{\partial \alpha_r}{\partial P_r}\right)_{T_r} = \frac{0.1919}{370}\ (0.028) = 0.0000145$$

$$Cp-Cv = \frac{144}{778}\ 765\ \frac{\left[0.000658 + 0.0002535\right]^2}{\left[0.00136 + 0.0000145\right]} = 0.0782$$

$$Cv = 0.5463 - 0.0782 = 0.4681$$

$$\frac{C_p}{C_v} \quad \frac{0.5463}{0.4631} = 1.17$$

γ = C_P/C_V FOR HYDROCARBONS



The use of equations (139) and (140) for hydrocarbons with γ values from Figure 40 is a step in the right direction but does not correct for the fact that equations (139) and (140) are based on perfect gas law behavior. However, the effect of deviation from ideal gas law behavior on these equations is not so important as the effect on γ; therefore, the use of Figure 40 will greatly improve the accuracy of such computations.

In calculations involving hydrocarbon gases, the compression and expansion of mixtures is more frequently encountered than pure components: γ for mixtures may be determined by computing the molal average of γ values of the individual components, the γ for each being determined for the temperature and total pressure involved.

4. Polytropic Process

If the value of the exponent of V in

$$PV^{\gamma} = \text{constant}$$

is not equal to the ratio of specific heats and is not unity, zero or infinity, we have what is known as "polytropic" compression or expansion. Various paths are shown in Figure 41.

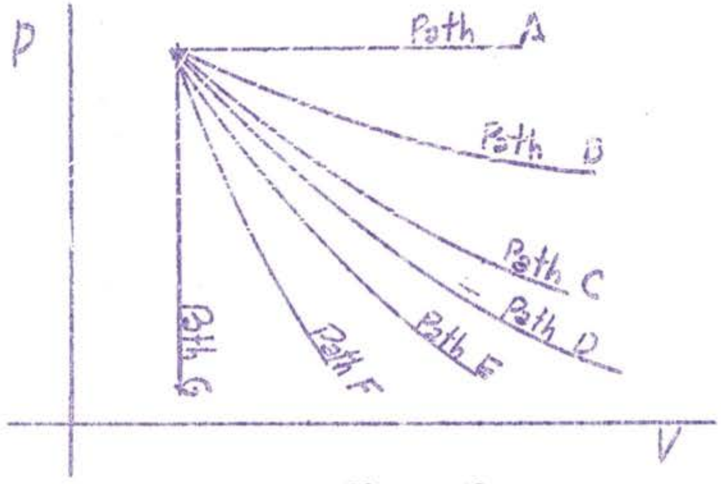


Figure 41

Path	Description	Equation	Value of Exponent
A	Isobaric	$P = \text{constant}$	$\gamma = 0$
B	Polytropic	$PV^{\gamma} = \text{constant}$	$1 > \gamma > 0$
C	Isothermal	$PV = \text{constant}$	$\gamma = 1.0$
D	Polytropic	$PV^{\gamma} = \text{constant}$	$C_p/C_v > \gamma > 1$
E	Isentropic	$PV^{\gamma} = \text{constant}$	$\gamma = C_p/C_v$
F	Polytropic	$PV^{\gamma} = \text{constant}$	$\infty > \gamma > C_p/C_v$
G	Isometric	$V = \text{constant}$	$\gamma = \infty$

Paths D and E are the most common.

D. Entropy-Enthalpy Charts

In most process design problems it is necessary to know the difference in the enthalpy for the given process. The process in question may take place at constant pressure, temperature, or entropy. In the latter case the quantitative value of the entropy is not necessary, it being sufficient to know that the entropy remained constant. Occasionally, differences in entropy are also desired.

Entropies and enthalpies may be tabulated in a form similar to the steam tables or they may be presented in graphical form such as the Mollier diagram. There are many different ways in which entropies and enthalpies may be and are plotted as indicated by the following:

Plot	Abscissa	Ordinate	Parameters
1	Temperature	Entropy	Pressure
2	Temperature	Enthalpy	Pressure
3	Entropy	Enthalpy	Temperature, Pressure
4	Enthalpy	Pressure	Temperature, Entropy
5	Volume	Enthalpy	Temperature, Pressure, Entropy

Plots 1 and 2 are the most obvious ways of plotting entropies and enthalpies. When these two plots are combined the result is the Mollier Diagram, Plot 3 or 4. Plot 3 is the type of Mollier diagram commonly used in making steam power calculations, while Plot 4 is the type used in making refrigeration calculations. This type of plot is usually plotted on semi-log paper with pressure on the log scale and enthalpy on the rectangular scale. Diagrams of this type have long been available for ammonia and sulfur dioxide. The development of charts of this type for hydrocarbons will be discussed in these notes. Plot 5 is known as the "Ellenwood" type of Mollier diagram. Its utility in steam design is apparent because changes in volume and enthalpy are required.

The Mollier diagram (enthalpy or heat content vs. entropy) for steam has long been a very useful tool of the engineer. From it changes in enthalpy for isothermal, isobaric isentropic (constant entropy) or reversible adiabatic changes in state can be found. It is also possible to determine changes in entropy for isothermal, isobaric, or constant enthalpy (throttling) changes in state. By means of it final temperatures and pressures may also be estimated. In addition the change in the free energy of formation with pressure may be computed.

Among the many uses of the Mollier diagram for steam are: (1) the calculation of the flow velocity from a nozzle, jet, or orifice, (2) the calculation of the work absorbed by a turbine wheel, and (3) the calculation of the loss by throttling or wire-drawing. For the ideal frictionless case the flow through a nozzle, jet, or orifice is adiabatic and reversible at constant entropy (as pointed out on page 7). Actually, however, there are friction losses, which cause an increase in entropy and decrease the flow velocity as well as the work absorbed by the turbine wheel, if the jet is directed at a turbine wheel. These friction losses are known as "wire-drawing" or throttling and occur at constant enthalpy.

A comprehensive set of Mollier diagrams for hydrocarbons and their mixtures would be equally valuable to the engineer engaged in petroleum refining process design were they available. The preparation of such a set of charts is infinitely more work than for steam, however, because there are an infinite number of hydrocarbon (single and multi-component) systems possible. In addition to the complicity of the problem, there are insufficient basic data available to make possible the preparation of a set of hydrocarbon charts comparable in scope and accuracy with the Mollier diagram for steam. However, charts of this type have been prepared as accurately as possible with the available data. These charts are presented in these notes with a discussion of their preparation.

1. Mollier Diagram for Perfect Gas. If a perfect gas is defined by the relations

$$PV = RT,$$
$$C_p = 5/2\ R, \text{ and } C_v = 3/2\ R,$$

the preparation of a Mollier Diagram for it is a simple problem. Such a plot would have no border curves (saturated liquid and saturated vapor) but would be entirely for the vapor phase. By equation 96 (page 115) it was shown that the enthalpy of a perfect gas is a function of temperature only, so

$$H = 5/2\ R\ (T - T^\circ) = 5\ (T - T^\circ) \qquad (147)$$

where T° is the reference temperature. Equation (147) holds for all pressures and H is in Btu/lb. mol when T are in °R. The entropy relationship for a perfect gas is not as simple, however, because pressure has an effect. The following equation gives the isobaric effect of temperature:

$$\Delta S_p = \int \frac{C_p}{T}\, dT = 5/2\ R\ \ln \frac{T}{T^\circ} = 5\ \ln \frac{T}{T^\circ} \qquad (148)$$

The isothermal effect of pressure is given by the following equation:

$$\Delta S_T = -\int \frac{R}{P}\, dP = -R\ \ln \frac{P}{P^\circ} = -2\ \ln \frac{P}{P^\circ} \qquad (149)$$

Combining equations 148 and 149 gives the following equations for a perfect gas

$$\Delta S = C_p \ln T - R \ln P \qquad (150)$$

$$\Delta S = 5 \ln T - 2 \ln P \qquad (150a)$$

Solving equations 148 and 149 together gives the entropy for a perfect gas as a function of pressure and temperature. The units of S will be Btu./lb. mol °R when T is in °R and P is in lbs./sq.in. abs.

Plotting equations 147, 148, and 149 with 32°F and 14.7 lbs./sq.in. abs. as the reference state results in the following Mollier diagrams, Figures 42 and 43 for a perfect gas.

Sample Calculations Mollier Diagram for Perfect Gas

Enthalpy

T°F	T - 32	H = 5(T-32) Btu/lb Mol
200	168	840
400	368	1840
600	568	2840
800	768	3840
1000	968	4840

Entropy

T°F	T°R	$T/492$	$\log_{10} T/492$	$\Delta S = (5)(2.3)(\log_{10} T/492)$ Btu/lb Mol - °F
200	660	1.34	.128	1.475
400	860	1.75	.243	2.795
600	1060	2.15	.333	3.83
800	1260	2.56	.4085	4.70
1000	1460	2.97	.473	5.44

P	$P/14.7$	$\log P/14.7$	$\Delta S = (2)(2.3)(\log_{10} P/14.7)$ Btu/lb Mol °F
25	1.7	.231	1.06
50	3.4	.532	2.45
100	6.8	.832	3.82
250	17.	1.231	5.66
500	34.	1.532	7.05
1000	68	1.832	8.43

From these data figures 42 & 43 were constructed.

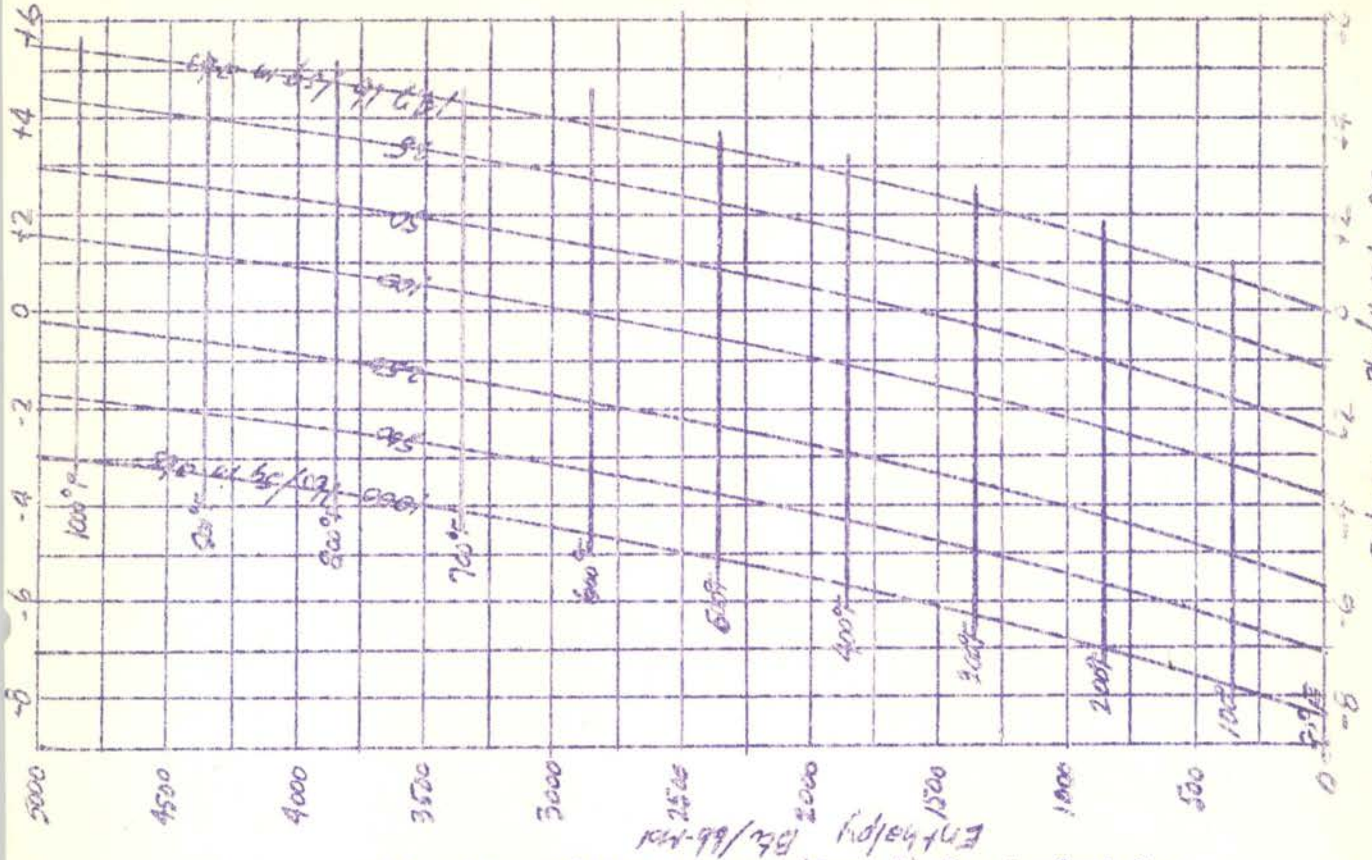


Fig. 42. Mollier Diagram (Type 3) for Perfect Gas

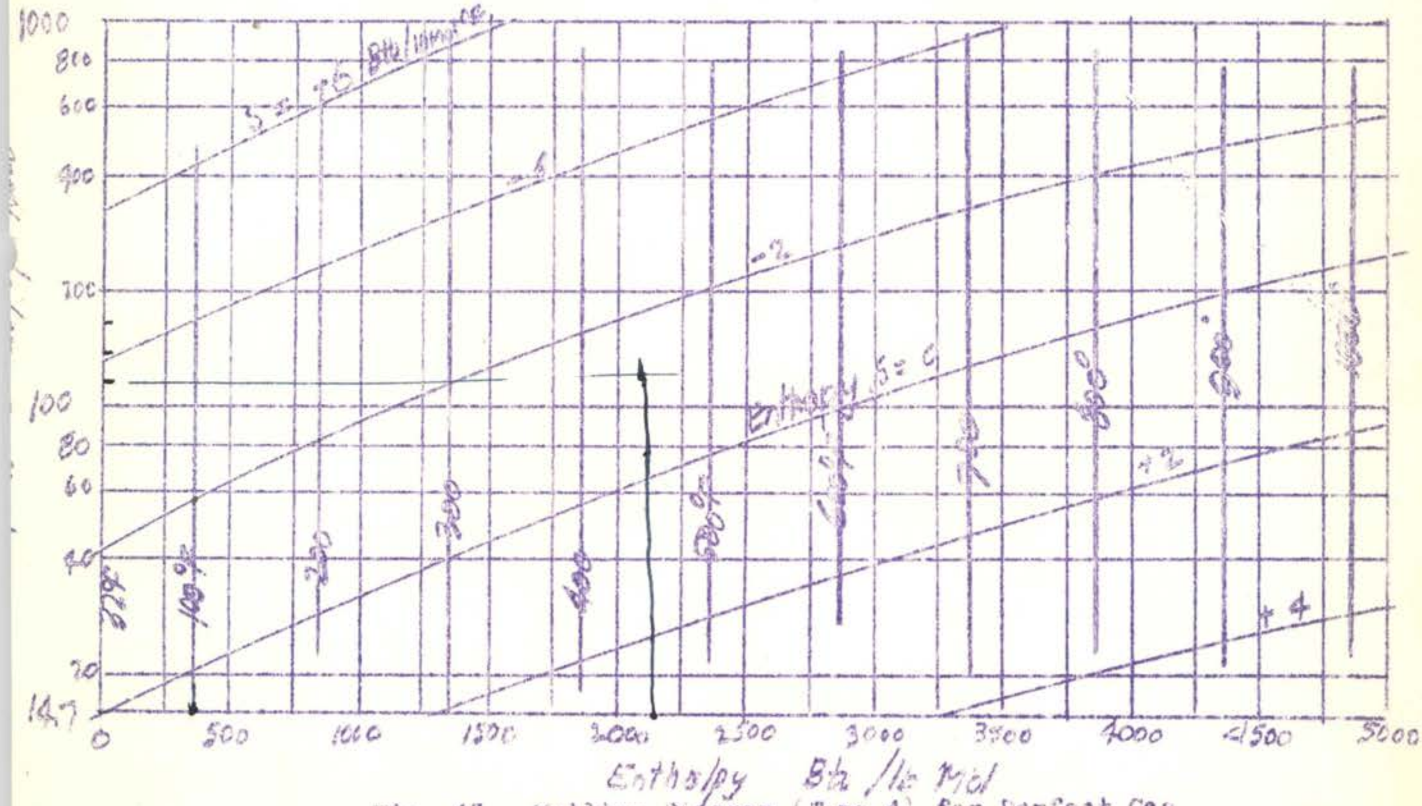


Fig. 43. Mollier Diagram (Type 4) for Perfect Gas

From Figure 42 it can be seen that the isentropic expansion of a perfect gas from a given temperature and pressure to a lower pressure gives a higher difference in enthalpy and a higher final temperature than the corresponding operation for an actual gas. An examination of Figure 43 shows that a perfect gas would make a very poor refrigerant.

2. Basis Hydrocarbon Correlations. Thermodynamic relations already presented serve as the basis for developing correlations used in calculating entropies and enthalpies for a series of Mollier diagrams for hydrocarbons and their mixtures.

The differential equation for the entropy (page 111)

$$dS = \frac{C_p}{T}\,dt - \left(\frac{\partial V}{\partial T}\right)_P dP \tag{76}$$

becomes, on the introduction of α_r and reduced units,

$$dS = \frac{C_p}{T}\,dT - \frac{R}{P}\,dP + \frac{P_c\alpha_c}{T_c}\left(\frac{\partial \alpha_r}{\partial T_r}\right)_{P_r} dP \tag{151}$$

Integrating, changing the sign of the third term, and replacing $P_c\alpha_c/T_c$ with K_2 gives the following equation for the entropy:

$$\Delta S = C_p \ln T - R \ln P - K_2 \int - \left(\frac{\partial \alpha_r}{\partial T_r}\right)_{P_r} \tag{152}$$

The first and second terms can easily be evaluated for any specific problem. In fact this part of equation 152 is identical to equation 150. The third term takes into account deviation from the ideal gas law. It is desirable to integrate the third term in reduced units. If equation 152 is rewritten

$$\Delta S = C_p \ln T - R \ln P - \Delta S' \tag{153}$$

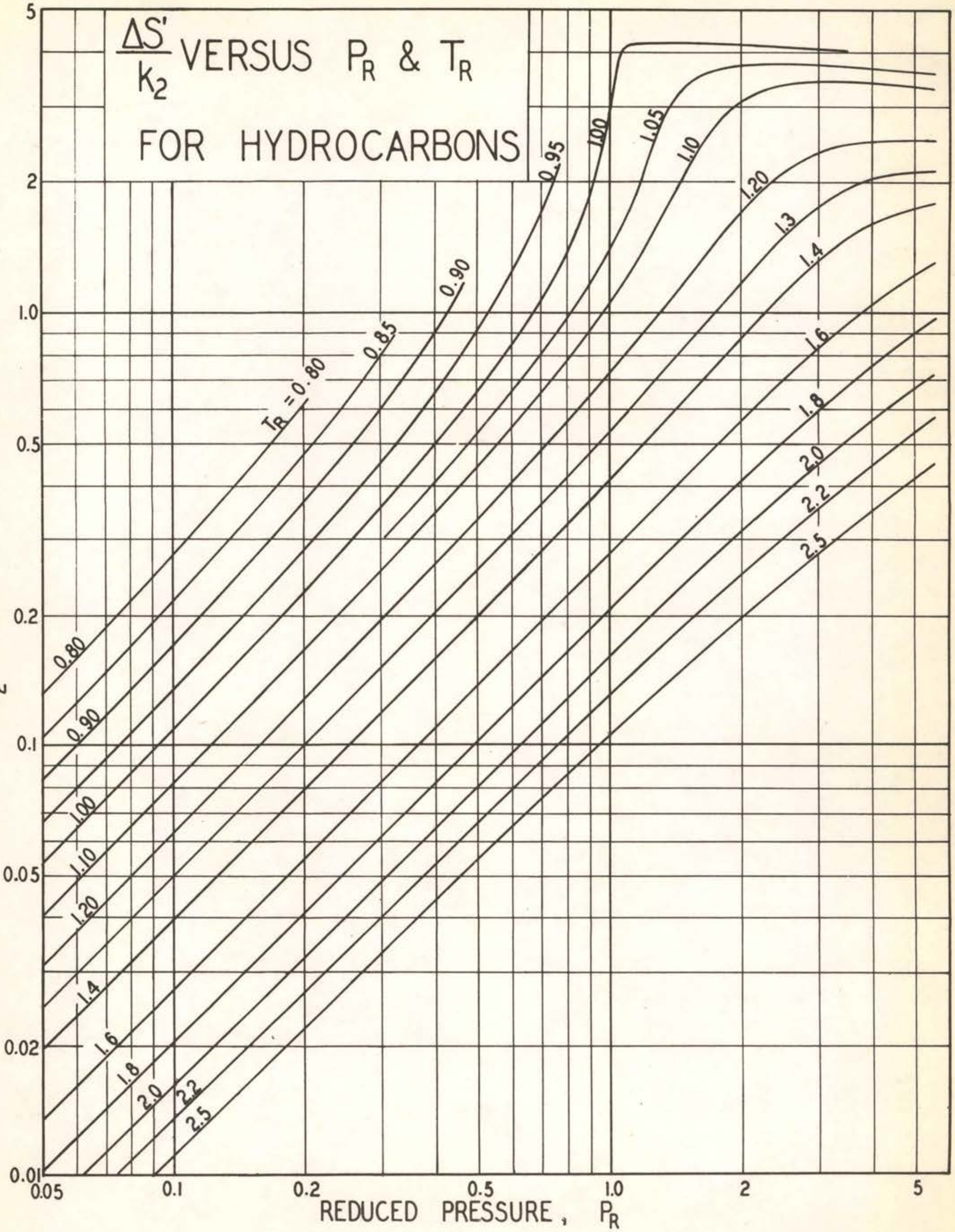
$$\text{where } \frac{\Delta S'}{K_2} = \int_0^{P_r} - \left(\frac{\partial \alpha_r}{\partial T_r}\right)_{P_r} dP_r \tag{154}$$

and equation 154 is integrated with values of the derivative determined graphically from the graphical reduced equation of state correlation, Fig. 34, the results, given as Figure 44, can be used to estimate the entropy of hydrocarbon vapors.

The differential equation for the enthalpy (page 109)

$$dH = C_p\,dT - \left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] dP \tag{66}$$

Fig 44



$\frac{\Delta S'}{k_2}$ VERSUS P_R & T_R FOR HYDROCARBONS becomes, when α_r and reduced units are introduced,

$$dH = C_p dT - P_c \alpha_c \left[\alpha_r - T_r \left(\frac{\partial \alpha_r}{\partial T_r} \right)_{P_r} \right] dP_r \qquad (155)$$

With temperature constant, the integration of the second term gives the effect of pressure on the enthalpy. Defining $P_c \alpha_c$ as K_3 and integrating with zero as the lower limit,

$$\frac{\Delta H}{K_3} = \int_0^{P_r} \left[\alpha_r - T_r \left(\frac{\partial \alpha_r}{\partial T_r} \right)_{P_r} \right] dP_r \qquad (156)$$

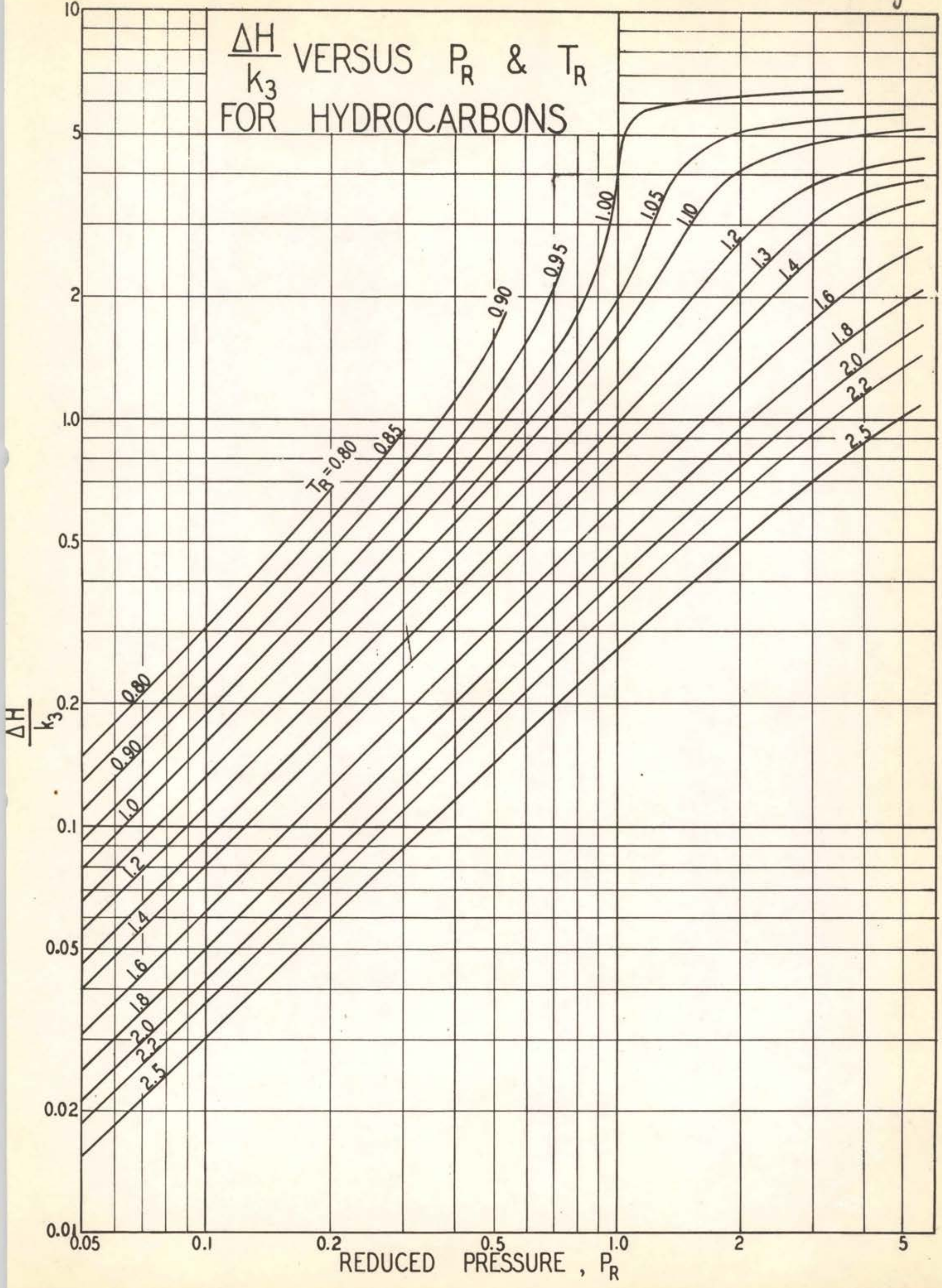
where ΔH is the change of enthalpy from zero pressure to P_r at constant temperature. This integration was performed graphically for different reduced temperatures and values of $\Delta H/K_3$ are plotted in Figure 45.

Values of constants K_2 and K_3 are given in the following tabulation.

Name of Hydrocarbon	Critical State			K_2	K_3	
	Temp. °F.	Press. Lbs./Sq.In.Abs.	Vol. Cu. Ft./Lb.	Btu./Lb. Mol °F.	Btu./Lb. Mol	Btu./Lb.
Methane	-115.8	673	0.0990	1.413	486	30.33
Ethylene	+48.9	745	0.0763	1.410	716	25.57
Ethane	89.4	717	0.0731	1.457	800	26.63
Propylene	196.4	661	0.0692	1.446	949	22.58
Propane	205.9	617	0.0710	1.455	968	21.97
Isobutylene	290.3	549.7	0.0705	1.452	1089	19.42
Butene-1	291.2	539.5	0.0719	1.453	1090	19.43
Butene-2	311.0	533.5	0.0746	1.451	1118	19.93
Isobutane	272.4	544	0.0686	1.442	1057	18.19
n-Butane	306.0	550	0.0691	1.477	1132	20.20
Isopentane	369.0	483.4	0.0683	1.459	1210	16.78
n-Pentane	386.4	485	0.0691	1.463	1239	17.18
Benzene	550.4	701	0.056	1.460	1555	18.91
Cyclohexane	537.4	596.5	0.0588	1.440	1437	17.09
Diisopropyl	441.0	449.5	0.0665	1.460	1316	15.28
n-Hexane	453.9	433.5	0.0684	1.472	1346	15.63
n-Heptane	512.4	393.7	0.0683	1.477	1434	14.34
Diisobutyl	529.4	360.0	0.0677	1.468	1452	12.72
n-Octane	564.4	361.4	0.0688	1.475	1512	13.25

It is of interest to note that the constant K_2 is practically the same for all the hydrocarbons.

Fig 45



ΔH/k3 VERSUS P_R & T_R
FOR HYDROCARBONS
ΔH/k3
10
5
2
1.0
0.5
0.2
0.1
0.05
0.02
0.01
0.05
0.1
0.2
0.5
1.0
2
5
REDUCED PRESSURE, P_R
T_R=0.80
0.85
0.90
0.95
1.00
1.05
1.10
1.2
1.3
1.4
1.6
1.8
2.0
2.2
2.5
0.80
0.90
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.5

3. Single Component Hydrocarbon Systems

Mollier diagrams may be prepared for single component hydrocarbon systems by the application of the following equations and charts:

Item	Page	Description	Application
Equation 120	133	Sp.Ht. of Vapor at one Atm.	Effect of Temp. on Entropy and Enthalpy.
Figure 36	135	Molal Entropy of Vaporization.	Entropy and Enthalpy of Vaporization.
Equation 153	147	Entropy Equation	Calculate Entropy.
Figure 44	147	Entropy Function	Effect of pressure on entropy.
Equation 155	148	Enthalpy Equation	Calculate Enthalpy.
Figure 45	148	Enthalpy Function	Effect of Pressure on Enthalpy.

The procedure will be illustrated by the following sample calculation for propane.

Sample Calculation for Propane

Find the entropy and enthalpy, above saturated liquid at its atmospheric boiling point (-44°F), for propane vapor at 300°F. and 200 lbs./sq.in. abs. The entropy and enthalpy at desired point is found in calculations reaching the final point in three steps as indicated by Figure 46.

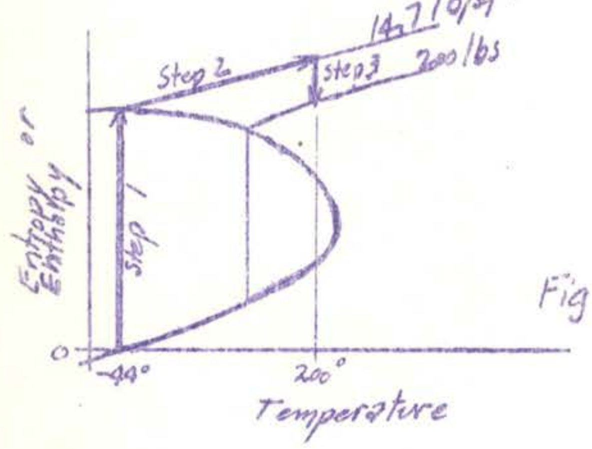


Fig 46

Step 1 - Saturated liquid at 14.7 lbs. and -44°F. to saturated vapor at same conditions.

Step 2 - Saturated vapor at 14.7 lbs. and -44°F. to superheated vapor at 14.7 lbs. and 300°F.

Step 3 - Vapor at 14.7 lbs. and 300°F. to vapor at 200 lbs. and 300°F.

Step 1

$$T_r = \frac{460 - 44}{460 + 205} = \frac{416}{665} = 0.625$$

From Figure 36, $\frac{M \Delta H_v}{T} = 19.25$

$$\Delta S_v = \frac{19.25}{44.06} = 0.437 \text{ Btu./lb.-°F.}$$

$$\Delta H_v = \frac{19.25}{44.06}\ 416 = 182 \text{ Btu./Lb.}$$

Step 2

$$C_p = \frac{9.00}{44.06} + \frac{0.030}{44.06}\ \frac{1}{1.8}\ T(°F) = \text{Btu./Lb.}$$

$$C_p = 0.204 + 0.000378\ T°R$$

$$\Delta S = \int_{416}^{760} \frac{C_p}{T}\, dT = \int_{416}^{760} \left[\frac{0.204}{T} + 0.000378 \right] dT = (0.204)(2.3)\log_{10} \frac{760}{416} + 0.000378(760-416)$$

$$\Delta S = 0.123 + 0.130 = 0.253 \text{ Btu./lb.°F.}$$

$$\Delta H = \int_{416}^{760} C_p dT = \int_{416}^{760} (0.204 + 0.000378T)\, dT = 0.204(760-416) + \frac{0.000378}{2}(760^2 - 416^2).$$

$$\Delta H = (760-416)\left[0.204 + 0.000189(760+416)\right]$$

$$\Delta H = 147 \text{ Btu./Lb.}$$

S at 300° and 14.7 lbs. = 0.437 + 0.253 = 0.68 Btu./lb.-°F.
H at 300° and 14.7 lbs. = 182 + 147 = 329 Btu./lb.

Step 3

$$T_r = \frac{760}{665} = 1.143; \quad P_{r_1} = \frac{14.7}{617} = 0.0238; \quad P_{r_2} = \frac{200}{617} = 0.324$$

$$\frac{\Delta S^{d}}{K_2} = 0.0165 \text{ and } 6.24.$$

$$\Delta S = -\frac{(1.99)(2.3)}{44.06} \log_{10} \frac{200}{14.7} - \frac{1.455}{44.06} \left[0.240 - 0.0165 \right]$$

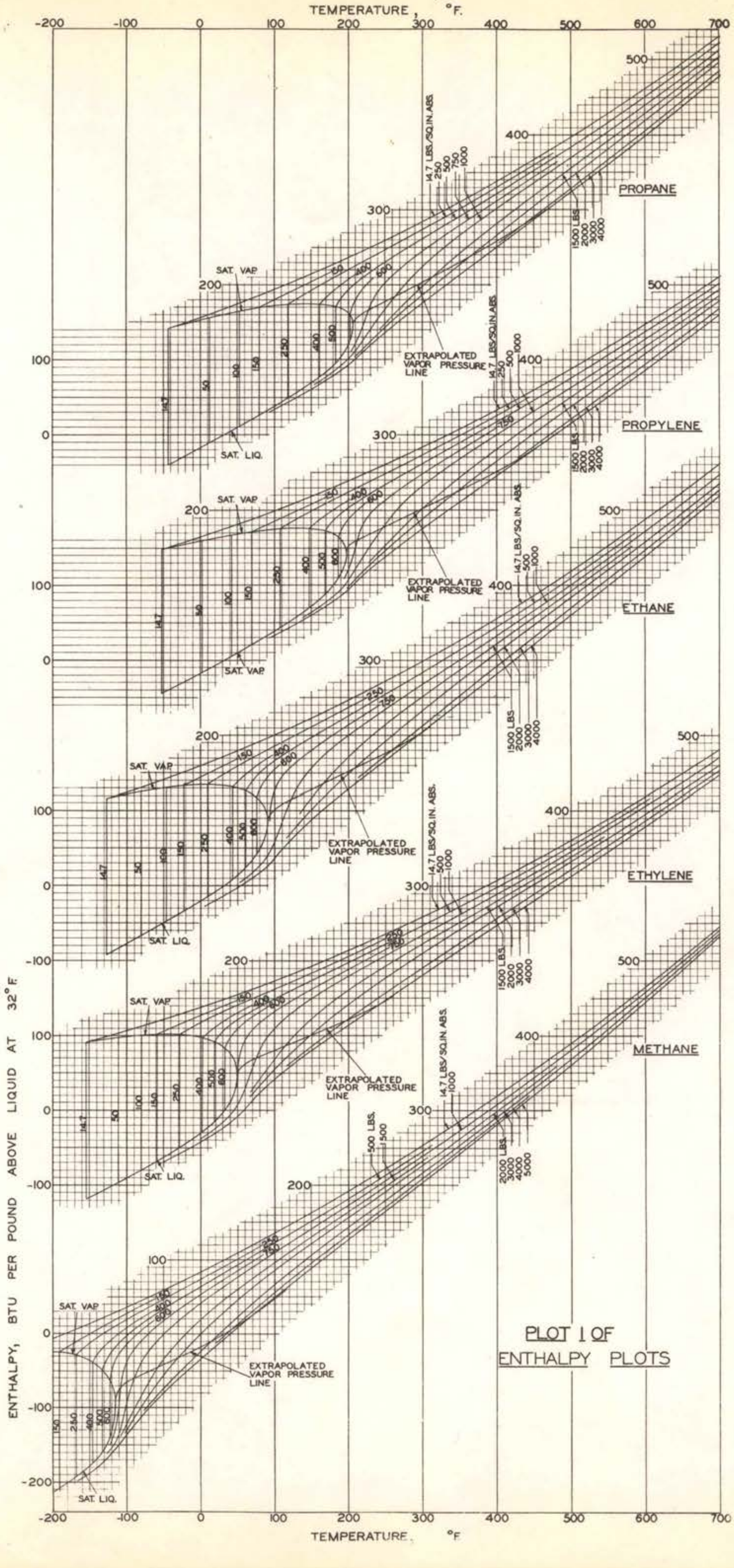
$$\Delta S = -0.1178 - .0074 = -0.1252 \text{ Btu./lb.°F.}$$

$$\frac{\Delta H}{K_3} = 0.029 \text{ and } 0.41$$

$$\Delta H = -21.97\ (0.41 - 0.029) = -8.4 \text{ Btu./lb.}$$

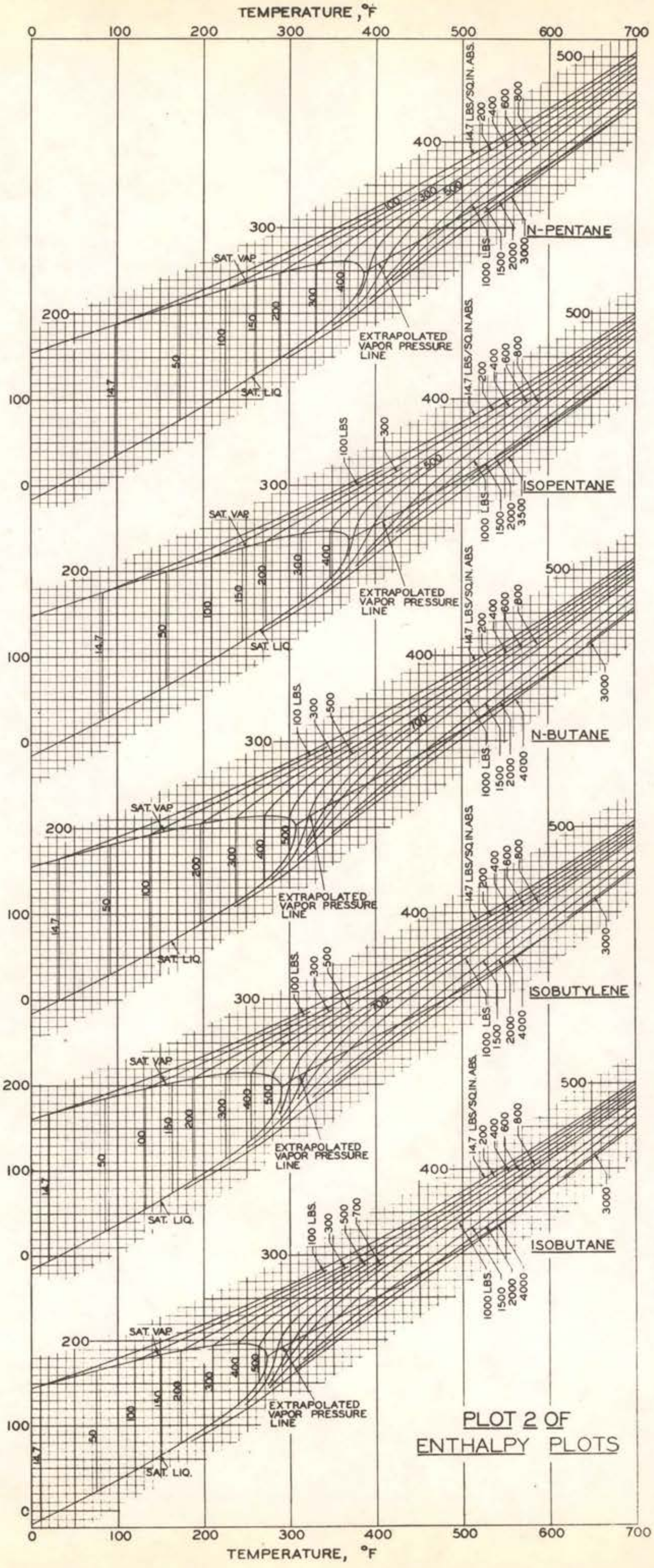
S at 300° and 200 lb. = 0.680 - 0.1252 = 0.5548 Btu./lb.°F.
H at 300° and 200 lb. = 329 - 8.4 = 320.6 Btu./lb.

Fig 47



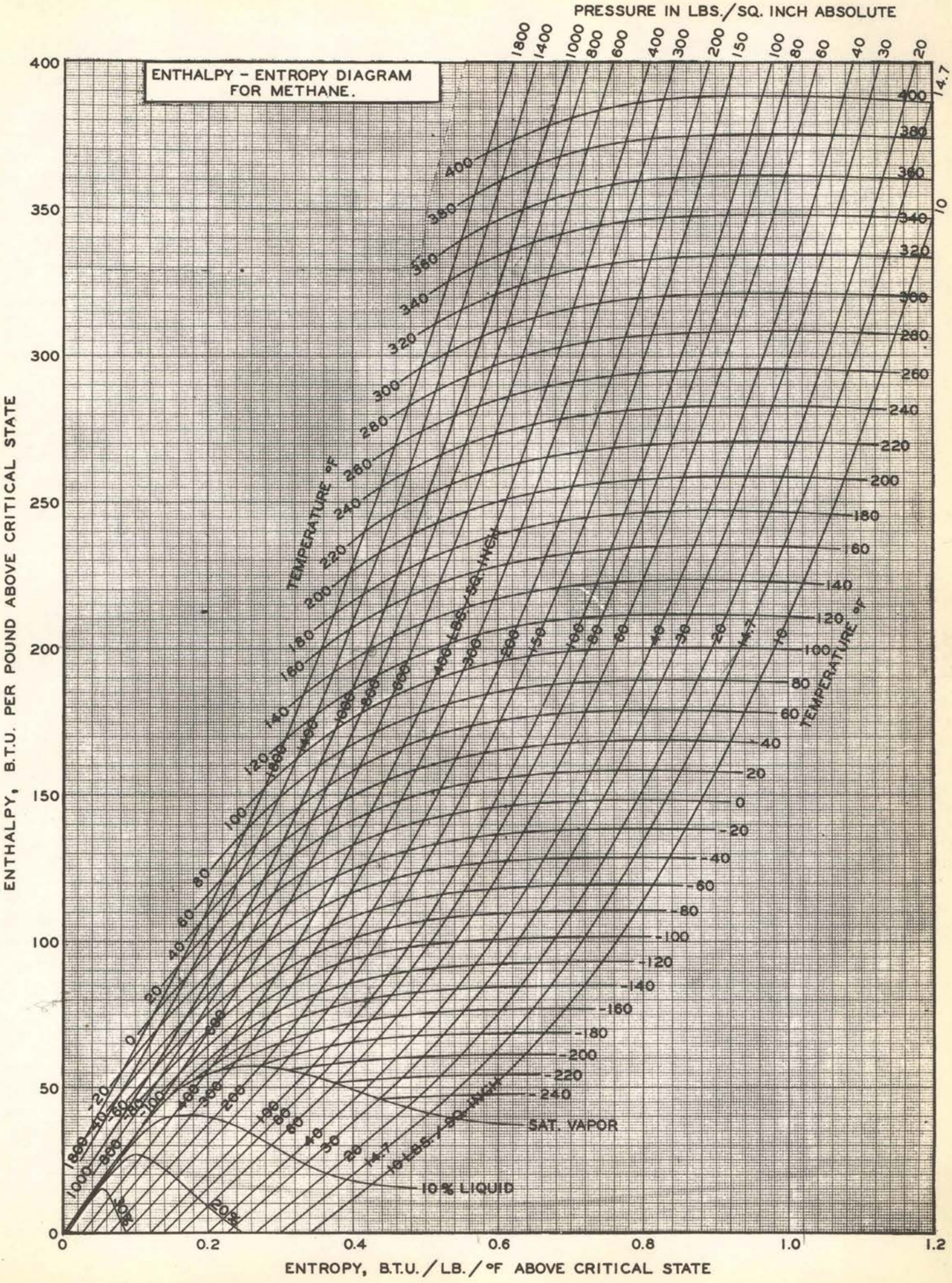
PLOT I OF
ENTHALPY PLOTS

Fig 48

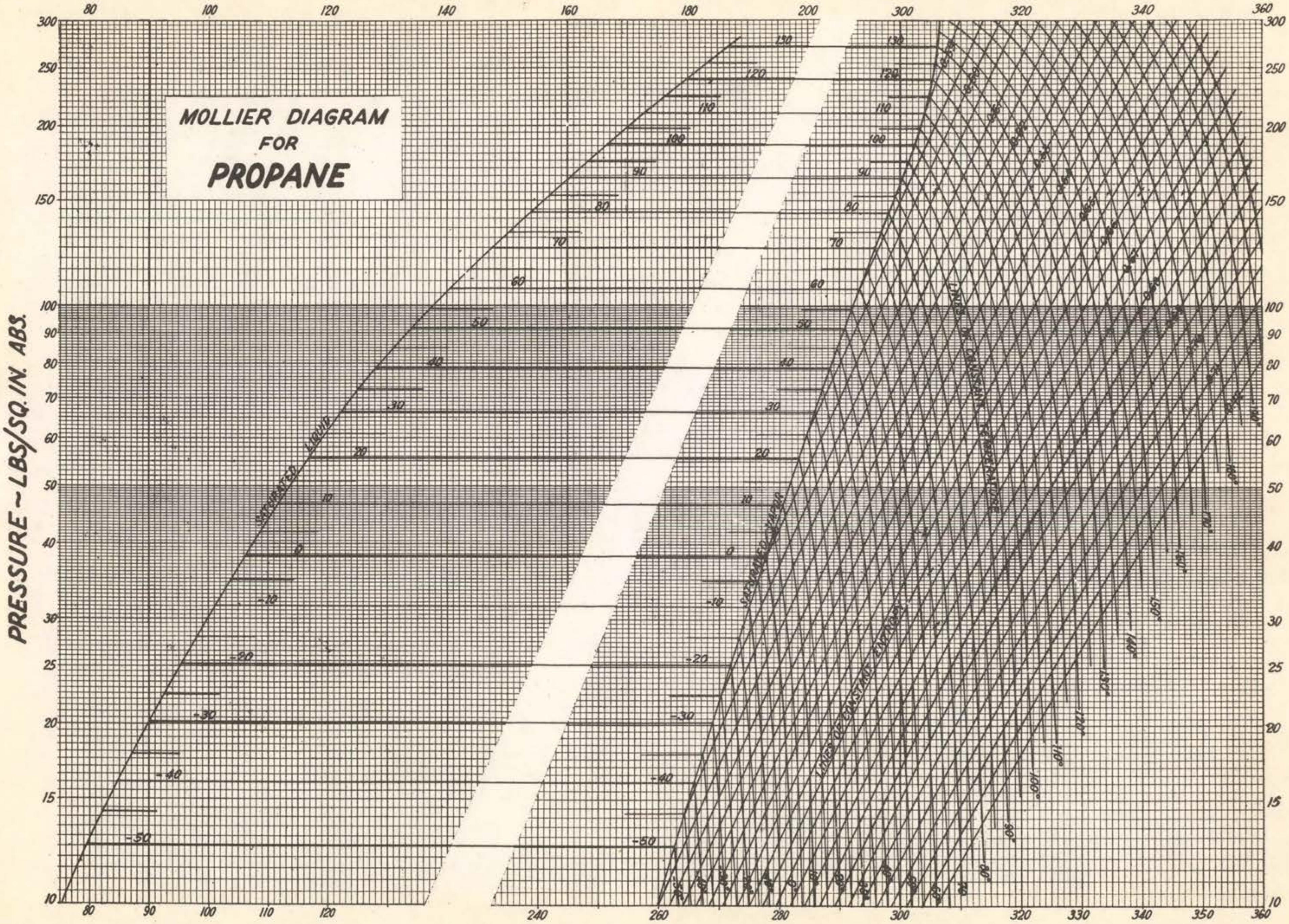


PLOT 2 OF ENTHALPY PLOTS

Fig 49


ENTHALPY - ENTROPY DIAGRAM FOR METHANE.
PRESSURE IN LBS./SQ. INCH ABSOLUTE
1800
1400
1000
800
600
400
300
200
150
100
80
60
40
30
20
14.7
10
ENTHALPY, B.T.U. PER POUND ABOVE CRITICAL STATE
0
50
100
150
200
250
300
350
400
ENTROPY, B.T.U. / LB. / °F ABOVE CRITICAL STATE
0
0.2
0.4
0.6
0.8
1.0
1.2
TEMPERATURE °F
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
400 LBS./SQ. INCH
10 LBS./SQ. INCH
SAT. VAPOR
10% LIQUID
20%
40%

MOLLIER DIAGRAM FOR PROPANE



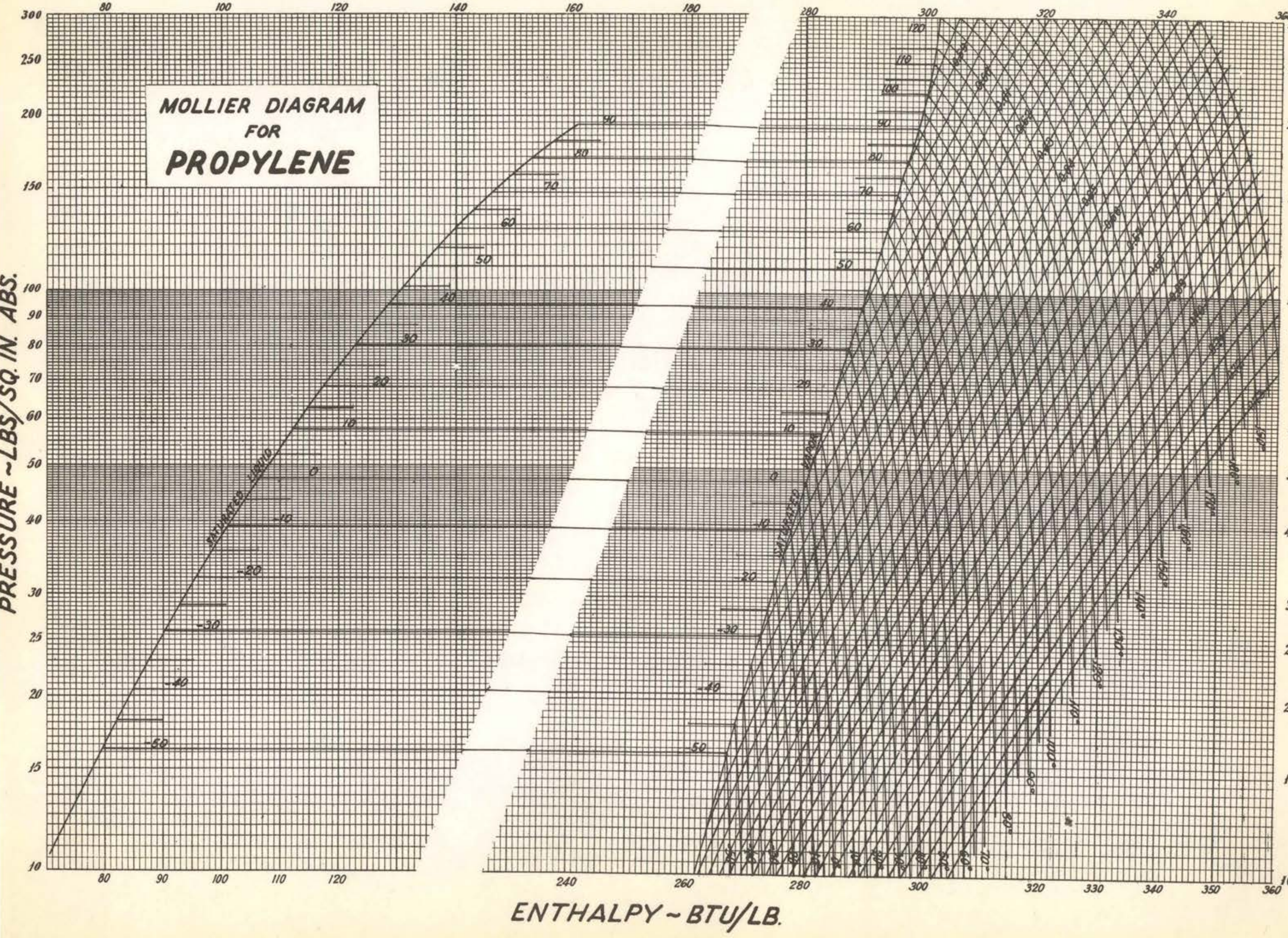

MOLLIER DIAGRAM
FOR
PROPYLENE
PRESSURE ~ LBS/SQ. IN. ABS.
ENTHALPY ~ BTU/LB.
SATURATED LIQUID
SATURATED VAPOR
300
250
200
150
100
90
80
70
60
50
40
30
25
20
15
10
80
90
100
110
120
140
160
180
240
260
280
300
320
330
340
350
360
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
110
100

Fig 51

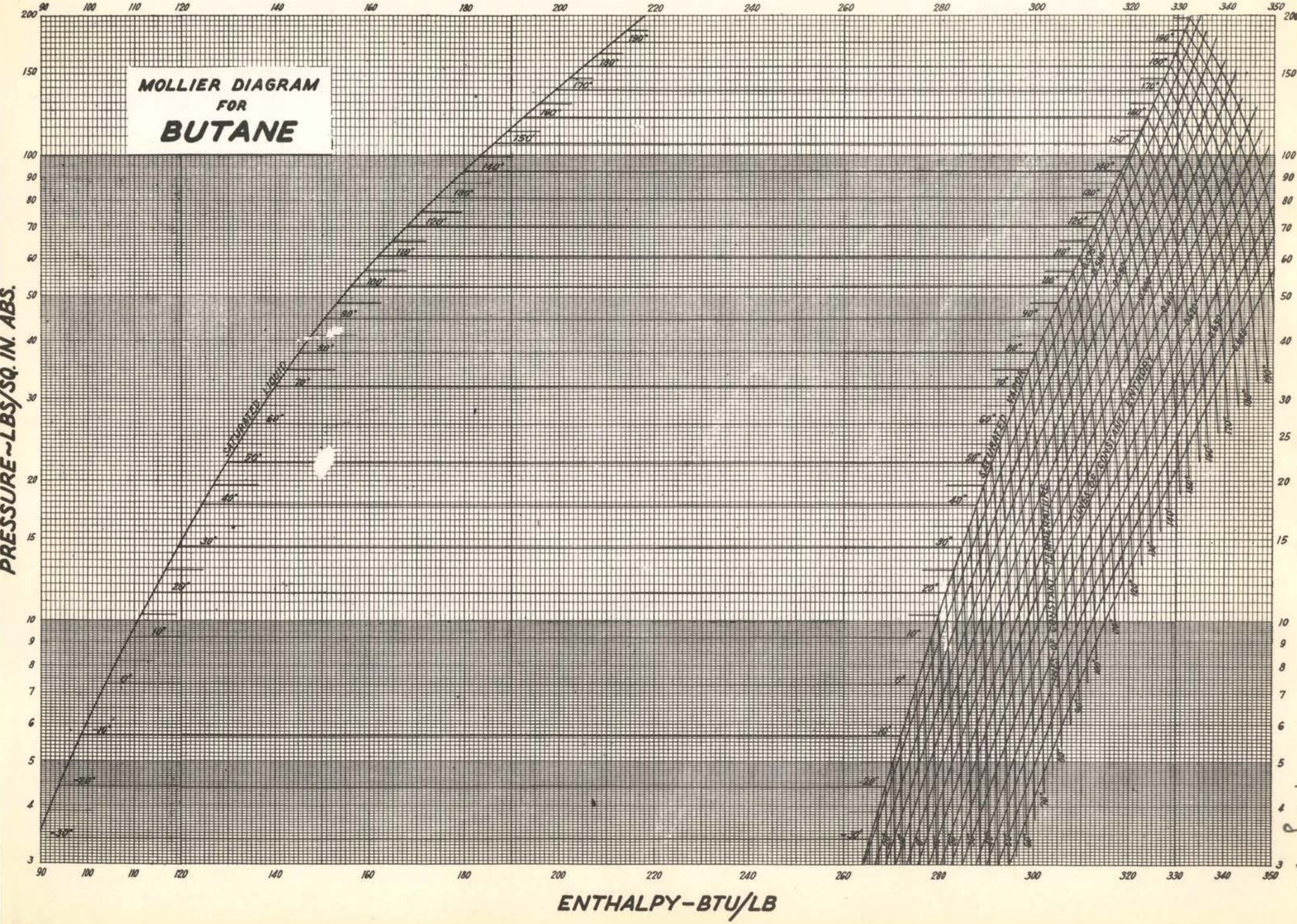

MOLLIER DIAGRAM FOR BUTANE
PRESSURE~LBS/SQ. IN. ABS.
ENTHALPY–BTU/LB
90
100
110
120
140
160
180
200
220
240
260
280
300
320
330
340
350
3
4
5
6
7
8
9
10
15
20
25
30
40
50
60
70
80
90
100
150
200
SATURATED LIQUID
SATURATED VAPOR
LINES OF CONSTANT TEMPERATURE
LINES OF CONSTANT ENTROPY
-30°
-20°
-10°
0°
10°
20°
30°
40°
50°
60°
70°
80°
90°
100°
110°
120°
130°
140°
150°
160°
170°
180°
190°

Fig 52

Calculations of this kind were made in a systematic fashion at hundreds of points for each of several (fifteen) hydrocarbons from methane to octane. The results of these computations were plotted for each hydrocarbon, giving the temperature-enthalpy plots given as Figures 47 and 48 and temperature-entropy plots (not shown but of similar shape) as well. In constructing all these diagrams (Figures 47 and 48 and others) liquid at the atmospheric boiling point was used as the reference point for the original preliminary large scale plots. The "zero" enthalpy and entropy point for these preliminary charts occurred at different temperatures for each hydrocarbon, which was considered undesirable. The enthalpy charts for each hydrocarbon were corrected to make saturated liquid at 32°F. the reference state. This was straightforward for all hydrocarbons except methane, whose critical is below 32°F. For methane 32°F at the extrapolated vapor pressure line was chosen as a hypothetical liquid for the reference state.

The hypothetical liquid lines or the "extrapolated" vapor pressure-temperature relations are determined by extrapolating the straight vapor pressure curves on the Cox type chart, Figure 26, past the critical point. The pressure-temperature relations thus established are plotted on the charts of Figures 47 and 48. These charts all have as their reference state saturated liquid at 32°F. The use of this extrapolated vapor pressure line as a hypothetical liquid line in mixture calculations will be discussed later.

When temperature-entropy and temperature-enthalpy plots for a given hydrocarbon are combined, the result is the Mollier diagram. Such diagrams have been prepared for methane, propane, propylene, and butane, and are here presented as Figures 49, 50, 51, and 52. The reference state used for the methane chart, which was prepared in 1936 and published in the November 5, 1936 issue of The Oil and Gas Journal, was the critical state (-116°F. and 673 lbs./sq.in.abs.), chosen so there would be no negative entropies or enthalpies. The reference state used for the propane, propylene, and butane charts, which were prepared in the spring of 1940 for use in the defense of a patent infringement suit (Trojan vs. Standard Oil Company of Indiana), chosen so there would be no negative entropies or enthalpies, was saturated liquid at -200°F. The condition used as the reference state is not of paramount importance but it is desirable to be consistent.

The methane chart is of particular interest because of the current attention being given to the liquefaction and storage of natural gas. The following uses for the methane chart, Figure 49, will be discussed and illustrated:

a) Isobaric (constant pressure) change.
b) Isothermal (constant temperature) change.
c) Loss by throttling.
d) Flow velocity from nozzle, jet, or orifice.
e) Work absorbed by turbine wheel.
f) Change of free energy
g) Work required in compression

a) Isobaric Change

The changes in enthalpy and entropy for a constant pressure process can be found from Figure 49 by following a line of constant pressure.

Example: Cool CH_4 from 200°F. and 200 pounds per square inch absolute to 0°F. and 200 pounds per square inch absolute and find the changes in enthalpy and entropy.

$\Delta H = 255.5 - 141.5 = 114$ B.t.u./lb.
$\Delta S = 0.704 - 0.498 = 0.206$ B.t.u./lb. °F.

b) Isothermal Change

The changes in enthalpy and entropy for a constant temperature process can be found directly from Figure 49 by following a line of constant temperature.

Example: Compress CH_4 isothermally from 0°F. and 200 pounds per square inch absolute to 1,000 pounds per square inch absolute and find the changes in enthalpy and entropy.

$\Delta H = 141.5 - 107.5 = 34$ B.t.u./lb.
$\Delta S = 0.498 - 0.248 = 0.250$ B.t.u./lb.°F.

c) Throttling Loss

The loss in throttling or wire-drawing occurs as an increase in entropy at constant enthalpy and can be found from Figure 49 as illustrated in the following example:

Example: An engine, a turbine or a nozzle is supplied with methane at 300°F and 1,000 pounds per square inch absolute and the discharge or exhaust pressure is 100 pounds per square inch. Find the loss if the CH_4 is throttled to 600 lbs./sq.inch before expansion.

No throttling ($S = 0.578$)

$\Delta H = 306.5 - 140 = 166.5$ Btu./lb.
Final temperature = -11°F.

Throttling (Final $S = 0.644$)

$\Delta H = 306.5 - 171.5 = 135.0$ B.t.u./lb.
Final temperature = 50°F.
Throttling loss = 166.5 - 135.0 = 31.5 B.t.u./lb.
Entropy increase = 0.644 - 0.578 = 0.066 Btu./lb.°F.

The loss caused by throttling in the above example is 31.5 B.t.u./lb. and the entropy increase is 0.066 B.t.u./lb.°F. The final temperature is 50°F. instead of -11°F. for no throttling.

d) Flow of Fluids

The following formula for flow through adiabatic orifices, jets, and nozzles has been derived from Bernoulli's theorem (equation 6 on page 7)

$$U_2 = 223.7 \sqrt{(1-y)(H_1-H_2)}$$

y = friction loss and may be approximately 0.10 to 0.20.

Example: Find the final velocity for ideal frictionless adiabatic flow of CH_4 from 1,000 pounds per square inch absolute and 300°F. to 100 pounds per square inch absolute. Find final temperature.

$$U_2 = 223.7 \sqrt{306.5 - 140} = 288 \text{ feet/second}$$
$$t_2 = -11°F.$$

Example: Find the final velocity for the problem in example 4, assuming y = 0.15. Determine final temperature and the loss by throttling.

$$U_2 = 223.7 \sqrt{(1-.15)(306.5-140)} = 265.5 \text{ feet/second.}$$
$$\Delta H = 0.85(306.5-140) = 141.5 \text{ B.t.u./lb.}$$
$$H_2 = 306.5-141.5 = 160 \text{ B.t.u./lb.}$$

From Figure 49 at 1,000 pounds per square inch and H = 160 B.t.u./lb.

$t_2 = 28°F.$
Throttling loss = 160-140 = 20 B.t.u./lb.
Entropy increase = 0.622-0.578 = 0.044 B.t.u./lb.°F.

e) Work Absorbed by Turbine Wheel

The work equivalent of the heat absorbed by a turbine wheel can be found by the following conversion factors:

1 B.t.u. = 777.64 foot-lbs.
1 H.P. = 33,000 foot-lbs./minute.
1 H.P. hour = 2,546 B.t.u.
1 K.W. hour = 3,415 B.t.u.

An example will illustrate:

Example: Find the work absorbed by turbine wheel in example 4. Find amount of CH_4 required to generate 1 H.P. hour.

$$\Delta H = 306.5 - 140.0 = 166.5 \text{ B.t.u./lb.}$$
$$W = 777.64 \times 166.5 = 129,600 \text{ ft.-lbs./lb. } CH_4$$
$$\frac{2,546}{166.5} = 15.3 \text{ lb. } CH_4\text{/H.P. hr.}$$

f) Change of Free Energy

The change of free energy with pressure at constant temperature may be computed by means of the following equation (equation 78, page 112) and Fig. 49:

$$\Delta F = \Delta H - T\Delta S$$

The free energy of formation is usually known at atmospheric pressure. With this equation and the free energy at atmospheric pressure, the free energy at any other pressure may be computed.

Example: Calculate change in free energy from one atmosphere and 300°F. to 1,800 pounds per square inch absolute and 300°F.

$$\Delta H = 321.0 - 295.5 = 25.5 \text{ B.t.u./lb.}$$
$$T\Delta S = (460 + 300)(1.118 - 0.494) = 474 \text{ B.t.u./lb.}$$

$$\Delta F = \Delta H - T\Delta S = 25.5 - 474 = -448.5 \text{ B.t.u./lb.}$$

The free energy at 1,800 pounds per square inch absolute and 300°F. is 448.5 B.t.u./lb. greater than the free energy at 14.7 pounds per square inch absolute and 300°F. In other words, it would require 448.5 B.t.u. of work to isothermall reversibly compress 1 pound of CH_4 from 14.7 pounds per square inch to 1,800 pounds per square inch at 300°F.

The free energies of formation of hydrocarbons from carbon and hydrogen are usually presented in calories per carbon atom. This makes a change of units necessary, when Figure 49 is used for calculating free energies, but this is very simple. Since most uses for the Enthalpy-Entropy chart will be in engineering units the chart is therefore presented in those units.

g) Work of Compression

The work required in isentropic compression is equal to the increase in enthalpy, while the work required in reversible isothermal compression is equal to the increase in free energy. For the ideal frictionless case where no jacket water cooling is used the compression is an isentropic process, but for the actual case with no jacket water cooling there is an increase in entropy and in the work of compression. With cooling during compression a lower final temperature results, the entropy decreases, and less work is required. For reversible compression the isothermal case requires the minimum amount of work while the adiabatic case requires the maximum amount. When enough jacket water cooling is supplied to cause a decrease in entropy during compression but not enough to result in isothermal compression, the reversible work requires is dependent on the path followed. An example will illustrate.

Example: Find the reversible work required to compress 1 pound of CH_4 from 14.7 pounds per square inch absolute and 0°F. to 300 pounds per square inch absolute by each of the four following paths:

1. Isentropic to final pressure.
2. Isothermal to final pressure.
3. Isoentropic to an intermediate temperature of 200°F. and isothermal to final pressure.
4. Isothermal to final entropy of Case 3 and isentropic to final pressure.

Solution: From Figure 49 the data necessary for the solution of these problems were found and are tabulated in the following table together with the the solutions. The details of the solutions are similar to previous examples.

Conditions:	P	T°F.	S	H	B.t.u./lbs. ΔH	 ΔF	 W
Initial	14.7	0	0.832	148	...	....	.....
Final, Path 1	300	400	0.832	388	-240	.....	[illegible]
Final, Path 2	300	0	0.442	137	+11	-179.5	-168.5
Inter, Path 3	75	200	0.832	258	-110	.....	.....
Final, Path 3	300	200	0.651	253	+5	-119.5	-229.5
Inter, Path 4	63	0	0.651	147	+1	-83.2	.....
Final, Path 4	300	200	0.651	253	-106	.....	-188.2

The Work Required for each Path

Path 1. 240 x 777.64 = 186,600 ft.-lbs./lb. CH_4
Path 2. 168.5 x 777.64 = 131,000 ft.-lbs./lb. CH_4
Path 3. 229.5 x 777.64 = 178,400 ft.-lbs./lb. CH_4
Path 4. 188.2 x 777.64 = 146,500 ft.-lbs./lb. CH_4

The work required in Path 1 is the greatest, while Path 2 is the least. The final conditions in Paths 3 and 4 are the same, yet the amounts of work required for compression are different. This shows that the path affects the work absorbed.

Examples in the use of the Mollier charts for propane, propylene, and butane will be given later.

4. Multi-Component Hydrocarbon Systems.

A common method of estimating the enthalpies of light hydrocarbon mixtures is to assume the mixture to be an equivalent single component of the same molecular weight and gravity, and to use the specific heat and latent heat data for the nearest hydrocarbon or to use some average specific and latent heats. This assumption can and often does lead to large errors, particularly near the border curve, because mixtures having the same gravity or molecular weight do not necessarily have the same enthalpies and very seldom have the same border curve. The charts given on Figures 47 and 48 can be used for heat balances involving complex hydrocarbon mixtures by applying them in the manner outlined below to make component heat balances, in which the enthalpy of the mixture is taken as the sum of the enthalpies of the components.

The temperature, pressure, and phase conditions encountered in most heat balance calculations involving light hydrocarbons are such that either one or both of the following phenomena exists: (1) a liquid hydrocarbon mixture at a temperature higher than the critical temperature of some of the lighter components therein; and (2) a vapor hydrocarbon mixture under a pressure higher than the vapor pressure of some of the heavier hydrocarbons therein. The conditions at which the enthalpies for the components of hydrocarbon mixtures should be read from the pure hydrocarbon charts are established by the following assumptions which appear to be justified by accurate heat balances on plant equipment.

(1) Liquid Mixtures. (a) Enthalpies for components whose critical temperatures are above the temperature of the mixture are the same as the enthalpies of the saturated liquid of the pure hydrocarbons at the temperature of the mixture; (b) components whose critical temperatures are below the temperature of the mixture are assumed to be at a hypothetical liquid state and their enthalpies are assumed to be the same as the enthalpies of the pure hydrocarbons at the extrapolated vapor pressure and the temperature of the mixture.

(2) Vapor Mixtures. (a) Enthalpies for components whose vapor pressures are higher than the pressure on the system are the same as the enthalpies of the pure hydrocarbons at the temperature and (total, not partial) pressure on the mixture; (b) components whose vapor pressures are lower than the pressure on the system are assumed to be at a hypothetical vapor state and their enthalpies are the same as the enthalpies of the saturated vapor of the pure hydrocarbons at the temperature of the mixture.

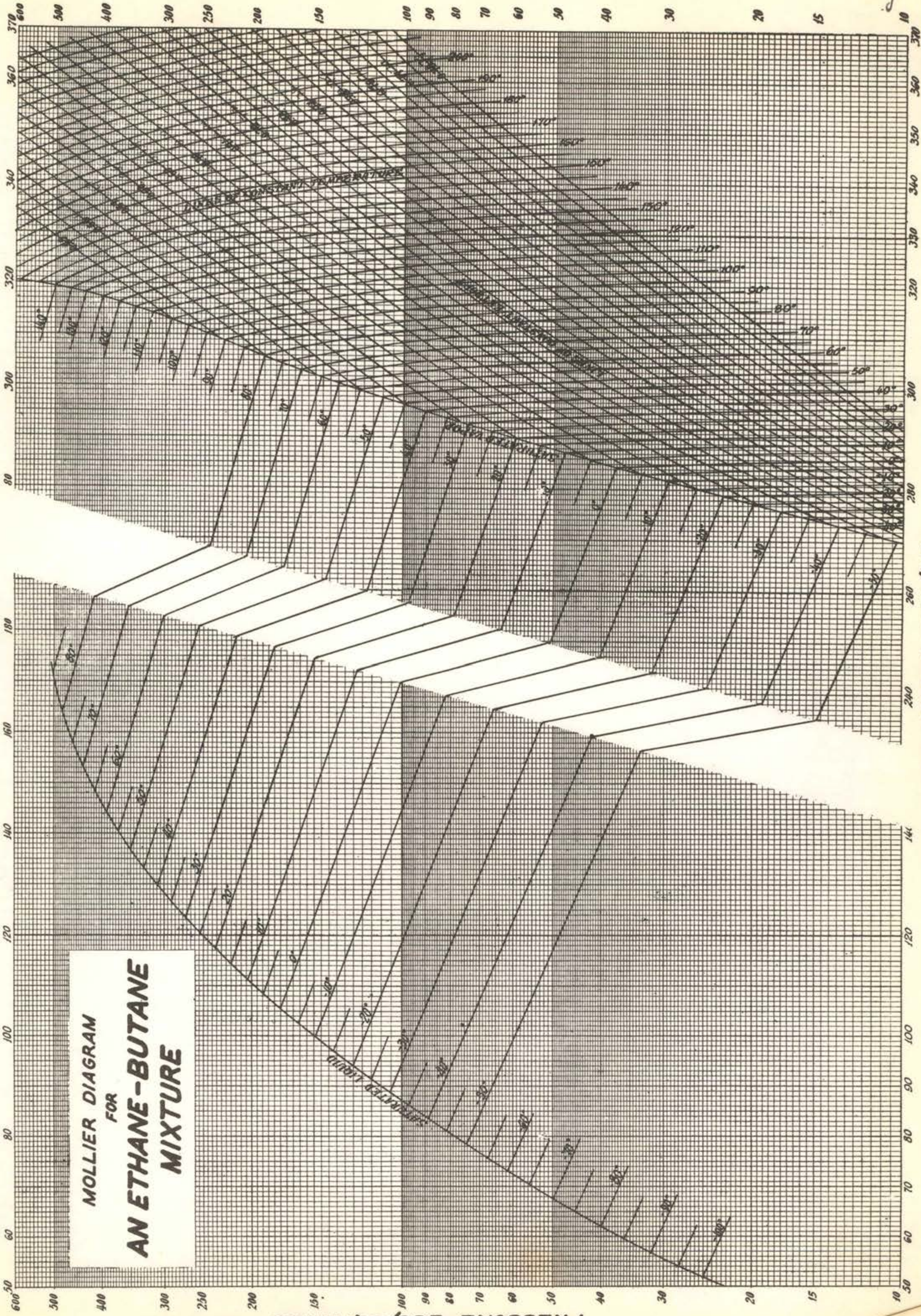
(3) Additivity. The enthalpies of the components of a hydrocarbon mixture are additive.

In applying this method to the computation of enthalpies for mixtures it is necessary to know the phase condition, which can be estimated by a method to be developed and described later. By means of these methods of estimating phase conditions and the enthalpies of vapors and liquids, Mollier diagrams were constructed for the following four hydrocarbon mixtures:

		Composition	
Figure No.	Hydrocarbon	Mol.%	Wt.%
53	Ethane	82.3	70.6
	Butane	17.7	29.4
		100.0	100.0
55	Methane	0.80	0.30
	Ethylene	1.11	0.73
	Ethane	3.20	2.25
	Propylene	23.42	23.04
	Propane	71.41	73.60
	Butane	.06	0.08
		100.00	100.00
54	Propylene	79	79.7
	Propane	21	20.3
		100	100.0
56	Propane	20	15.9
	Butane	80	84.1
		100	100.0

Figs. 53 and 54 are for mixtures having the same atmospheric boiling point as propane, Fig. 55 is for a "plant" propane, and Fig. 56 is for a mixture of propane and butane chosen at random.

Fig 53



MOLLIER DIAGRAM FOR AN ETHANE-BUTANE MIXTURE

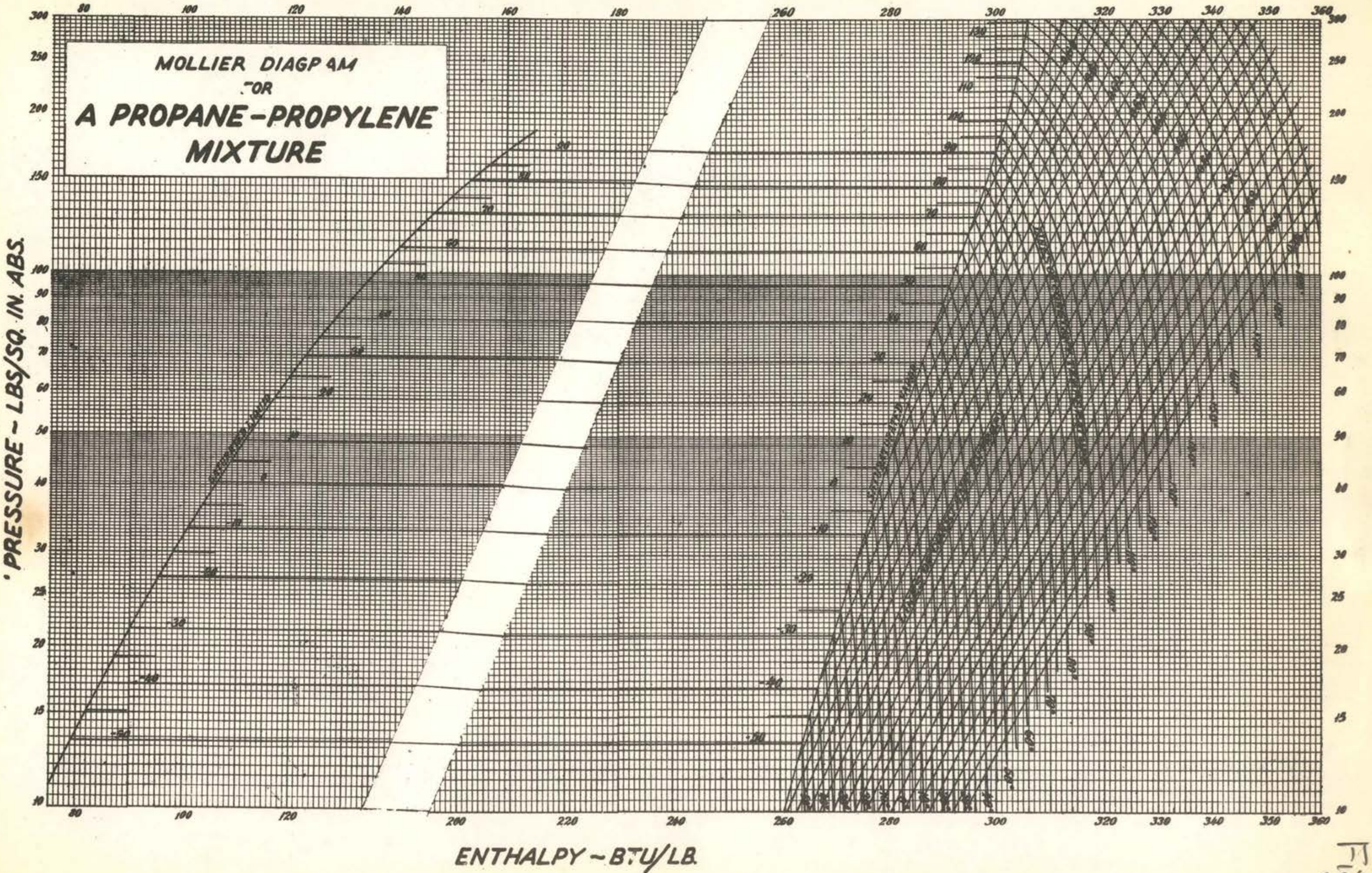
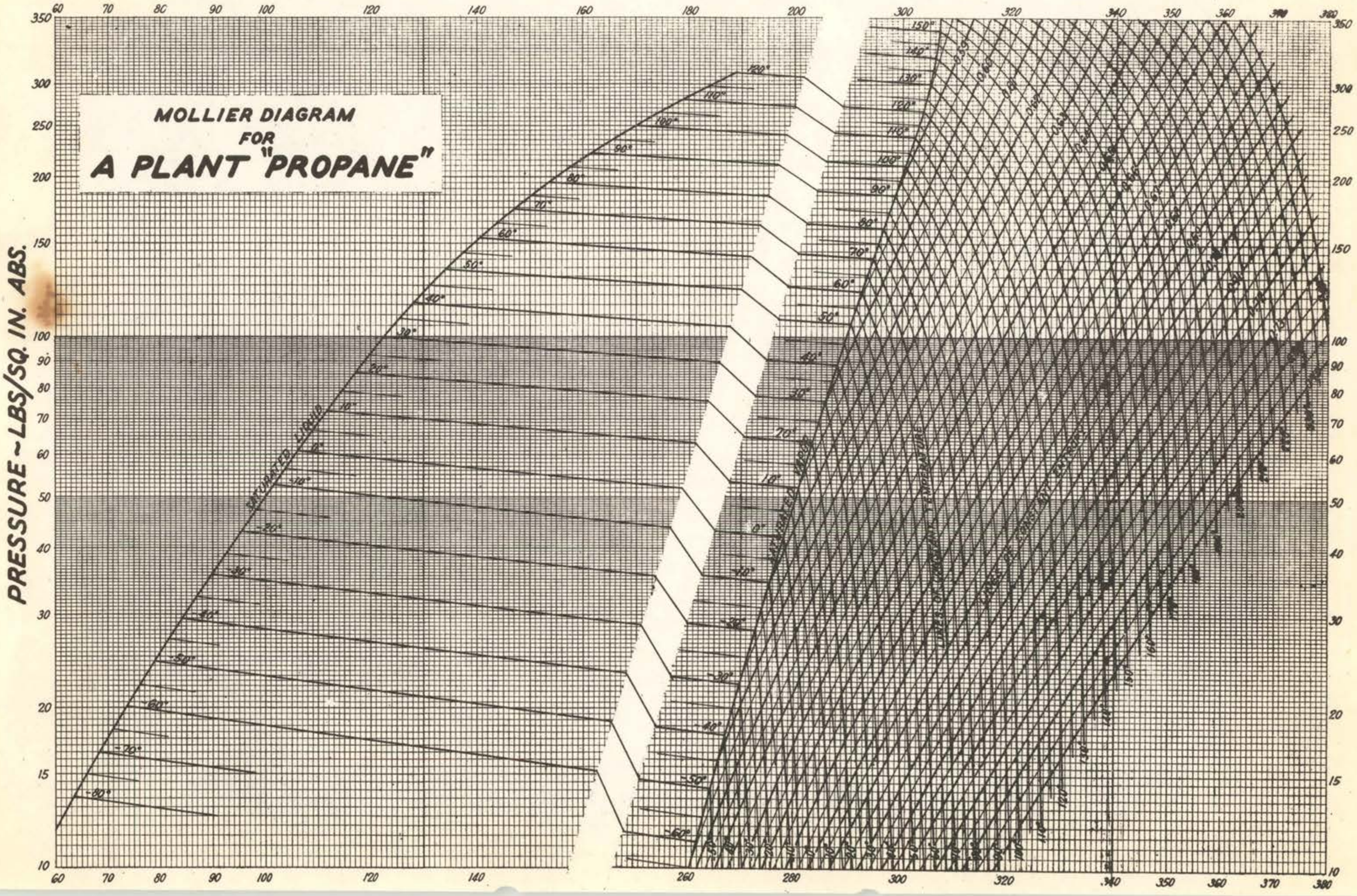

MOLLIER DIAGRAM
FOR
A PROPANE-PROPYLENE
MIXTURE
PRESSURE - LBS/SQ. IN. ABS.
ENTHALPY - BTU/LB.
80
100
120
140
160
180
200
220
240
260
280
300
320
330
340
350
360
10
15
20
25
30
40
50
60
70
80
90
100
150
200
250
300

Fig 54



MOLLIER DIAGRAM FOR A PROPANE-BUTANE MIXTURE

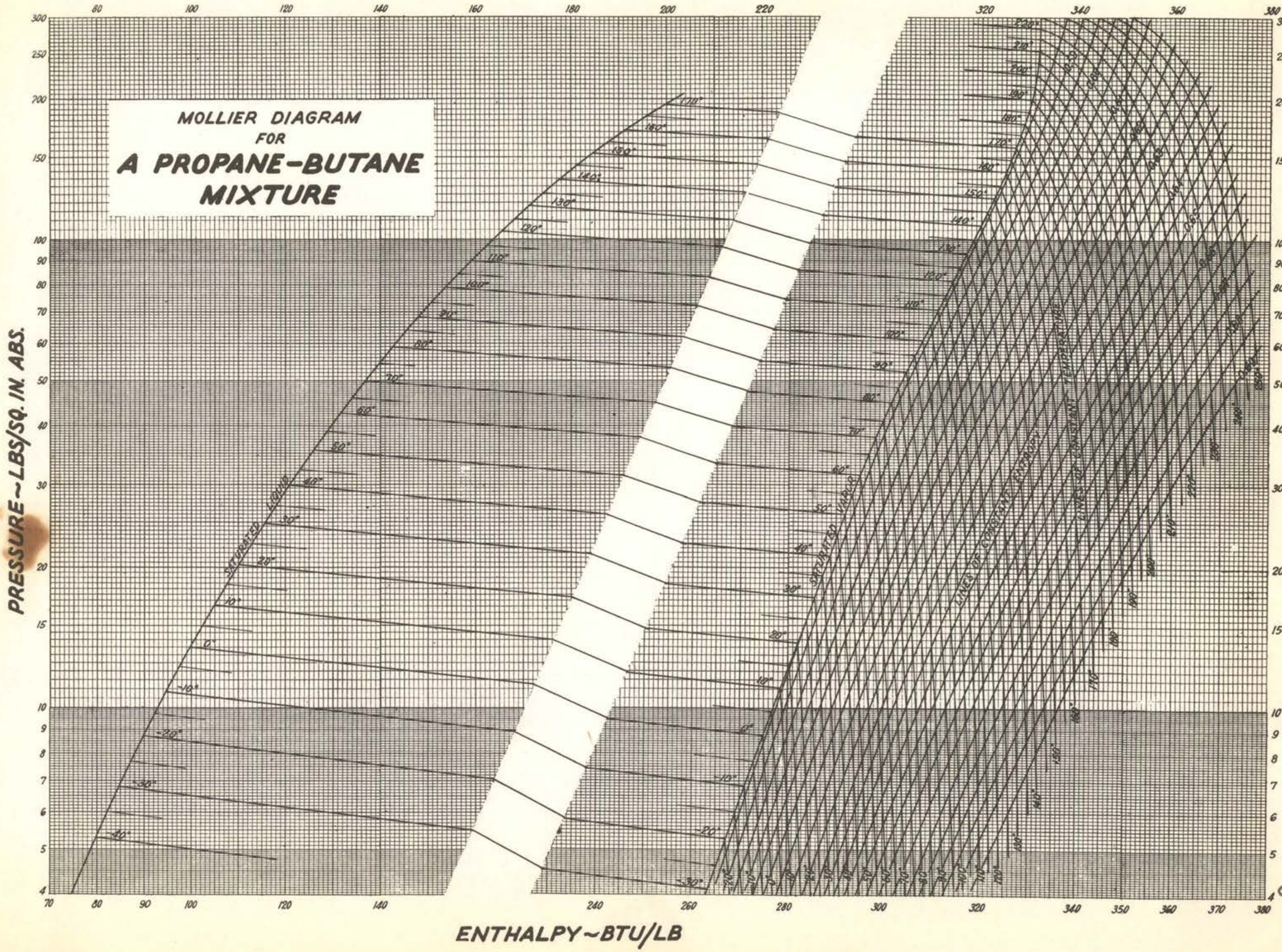


Fig 56

The above discussion deals with one of the three different methods of computing the enthalpies and entropies for multi-component hydrocarbon systems. These three methods are: (a) component additivity (used above); (b) pseudo-critical method; and (c) thermodynamic equation of state. These last two methods will not be illustrated, however. Another method of computing the effect of the pressure on the latent heat of vaporization for a hydrocarbon mixture chosen at random is illustrated by the following example:

Compute the latent heat of vaporization for the following hydrocarbon mixture at 149°F. The dew point is found by trial, the procedure being to assume a temperature and calculate the mol fractions in the liquid phases. At the dew point temperature the sum of these mol fractions equals unity. If the sum is greater than unity the assumed temperature is too low and if the sum is less than unity the assumed temperature is too high. This operation will be taken up in more detail in the next chapter.

Component	Mol Fraction Vapor "Y"	K 35°F. 14.7 lbs.	Mol Fraction Liquid "X"
Methane	0.0276	128	0.0002
Ethane	0.1380	18	0.0076
Propane	0.2880	4.7	0.0612
Isobutane	0.1185	1.8	0.0659
Butane	0.2410	1.2	0.201
Pentane	0.1869	0.28	0.660
	1.0000		1.0019

Therefore Dew Point is approximately 35°F.

The critical temperature and latent heat at atmospheric dew point are calculated as follows getting critical temperatures from Standard Data Book Chart A-1.11 and latent heats from Figure 36, page 135 of these notes.

Component	Mol Fraction	Wt. Fraction	Critical Temperature		Latent Heat at 35°F.	
			Components	Mixture	Components	Mixture
Methane	0.0276	0.0086	-117	-1.0	0	0
Ethane	0.1380	0.0803	90	7.2	133	10.7
Propane	0.2880	0.2458	206	50.6	162	39.8
IsoButane	0.1185	0.1333	273	36.4	152	20.2
Butane	0.2410	0.2711	307	83.3	166	45.0
Pentane	0.1869	0.2609	387	101.0	167	43.6
	1.0000	1.0000		277.5°F		159.3

Critical temperature = 277.5°F.
Latent Heat at 35°F. = 159.3 Btu./lb.

$$\frac{T_1}{T_o} = \frac{35 + 460}{277.5 + 460} = 0.672 , \quad \frac{T_2}{T_o} = \frac{149 + 460}{277.5 + 460} = 0.825$$

From Figure 36, reading from the pentane line

$$\psi_1 = 19.2 \text{ and } \psi_2 = 12.2$$

$$\text{Therefore } \Delta H_a = \frac{12.2}{19.2}\frac{(149 + 460)}{(35 + 460)}\ 159.3 = 125 \text{ Btu./Lb.}$$

The latent heat of vaporization of the above mixture at 149°F. is 125 Btu. per lb.

5. Petroleum Fractions

The above method, which is described for light hydrocarbon mixtures and called the "component method", is also applicable to petroleum fractions, which are only mixtures of heavier hydrocarbons. Due to the complexness of these higher boiling mixtures, the "component method" is not very practical for petroleum fractions, however. Consequently, another method is used for the heavier petroleum fractions. In this other method the enthalpies are computed directly for the mixture rather than as the sum of the enthalpies for the components. This direct method is just as applicable to light hydrocarbon mixtures as to petroleum fractions but not as necessary.

The isothermal effect of pressure on the enthalpy of a mixture may be computed from Figure 45 if the pseudo-critical point is used as the reference state and if K_s is determined by the following relationship:

$$K_s = 1.451\ T_{pc} \qquad (157)$$

where: T_{pc} = pseudo-critical temperature in °F. abs.

Following are the essential steps in the preparation of an enthalpy-temperature diagram for a petroleum fraction whose gravity and A.S.T.M. distillation are known (those explanations are more easily followed by making frequent reference to Figure. 57):

(1) Construct a phase diagram for the stock, i.e. pressure vs temperature for various percentages vaporized, by means of empirical correlations (based on the gravity and A.S.T.M.) to be described later;

(2) selecting a reference point, such as liquid at 32°F, compute and plot the enthalpy of saturated liquid up to within 100°F. of the pseudo-critical point by integrating a specific heat equation such as equations 118 or 119 (page 132) to give an enthalpy equation such as equation 122 (page 134);

(3) estimate the isothermal latent heat of vaporization at the atmospheric pressure boiling temperature from experimental data or graphical or analytical correlations, such as equation 126 (page 136), thus locating a point on the saturated vapor curve;

(4) starting with the heat of vaporization at the atmospheric pressure boiling point temperature, estimate the heat of vaporization at higher temperatures by means of equation 125 and Figure 36 (page 135), thus determining the atmospheric pressure dew point enthalpy, i.e. the enthalpy of saturated vapor at atmospheric pressure;

(5) starting at this point (saturated vapor at atmospheric pressure), compute and plot the enthalpy for vapor at atmospheric pressure by integrating vapor specific heat equations such as equations 120 or 121 to give an enthalpy equation similar to equation 123;

(6) compute the isothermal effect of pressure on the enthalpy from Figure 45, using the pseudo-critical state, and draw isobars for other pressures; and

(7) by means of the phase diagram from step 1, the heats of vaporization from step 4, and the isobars of step 6, construct the border curve on the H vs T scales with lines of constant pressure and per cent vaporized both shown in the two phase field.

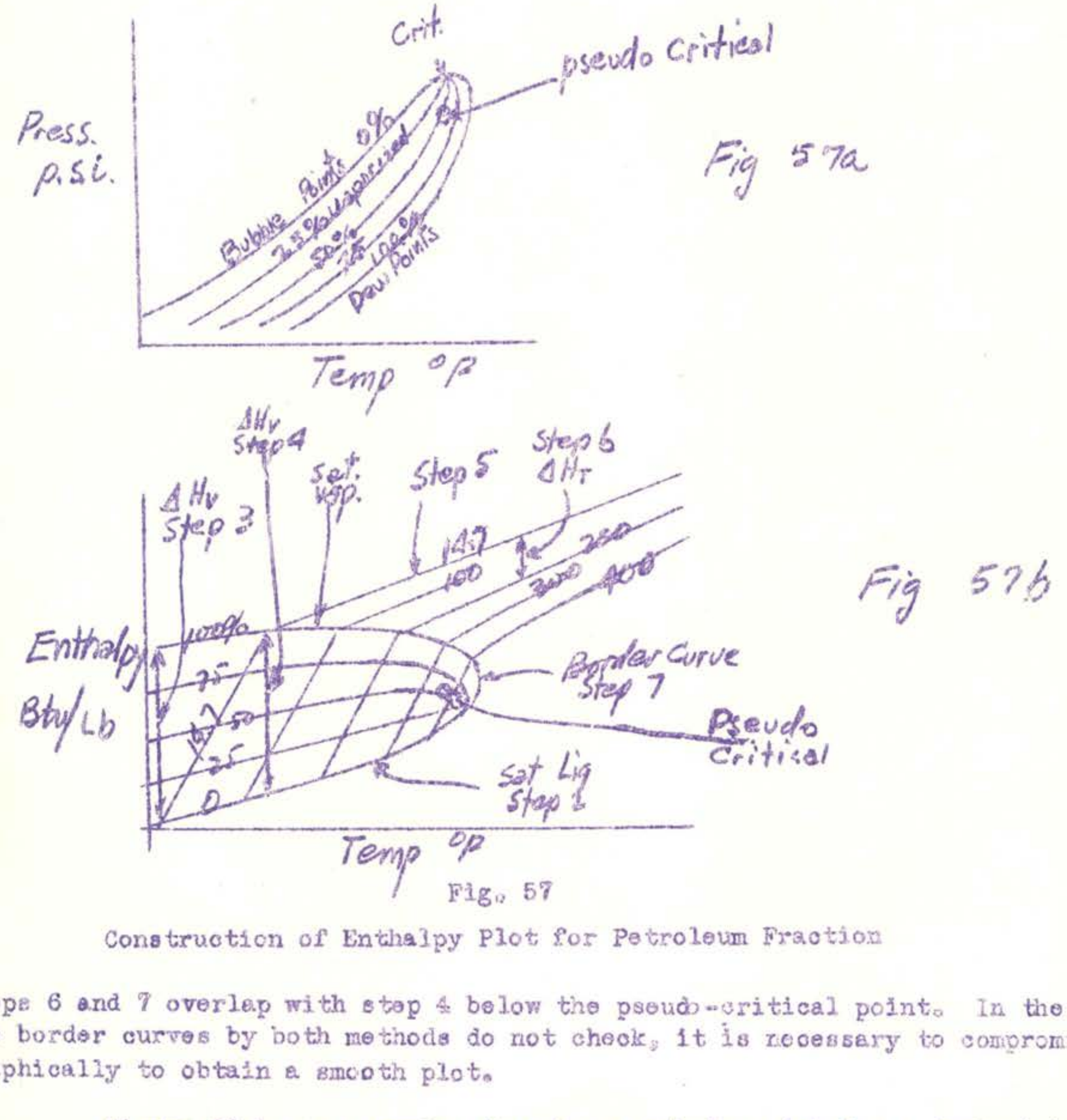


Fig 57a

Fig 57b

Fig. 57

Construction of Enthalpy Plot for Petroleum Fraction

Steps 6 and 7 overlap with step 4 below the pseudo-critical point. In the event the border curves by both methods do not check, it is necessary to compromise graphically to obtain a smooth plot.

Figure 58 is an example of such an enthalpy plot for a typical heavy cracked gasoline.

Step 4 in the above procedure is illustrated by the following example:

Calculate the isothermal latent heat of vaporization at 450°F. for a 57.1 °API cleaners naphtha having the following A.S.T.M. distillation:

% Off	Int.	10	20	30	40	50	60	70	80	90	Max.
Temp.	211	230	238	245	252	258	264	272	282	295	326

The atmospheric pressure equilibrium flash vaporization curve was constructed and the 100% point or dew point was found to be approximately 296°F. Latent heat at this atmospheric dew point was estimated (equation 126 or its equivalent) to be $\Delta H_1 = 127$ Btu./lb.

The critical temperature from Chart No. A-4.21 is 594°F.

$$\frac{T_1}{T_c} = \frac{286 + 460}{594 + 460} = 0.707 \ , \quad \frac{T_2}{T_c} = \frac{450 + 460}{594 + 460} = 0.863$$

From Figure 36, readin from the hexane line

$$\varphi_1 = 18.4 \ , \quad \varphi_2 = 11.1$$

$$\text{Therefore } \Delta H_2 = \frac{11.1\ (450 + 460)}{18.4\ (286 + 460)}\ 127 = 93 \text{ Btu./Lb.}$$

The latent heat of vaporization of the above cleaners naphtha at 450°F. is 93 Btu./Lb.

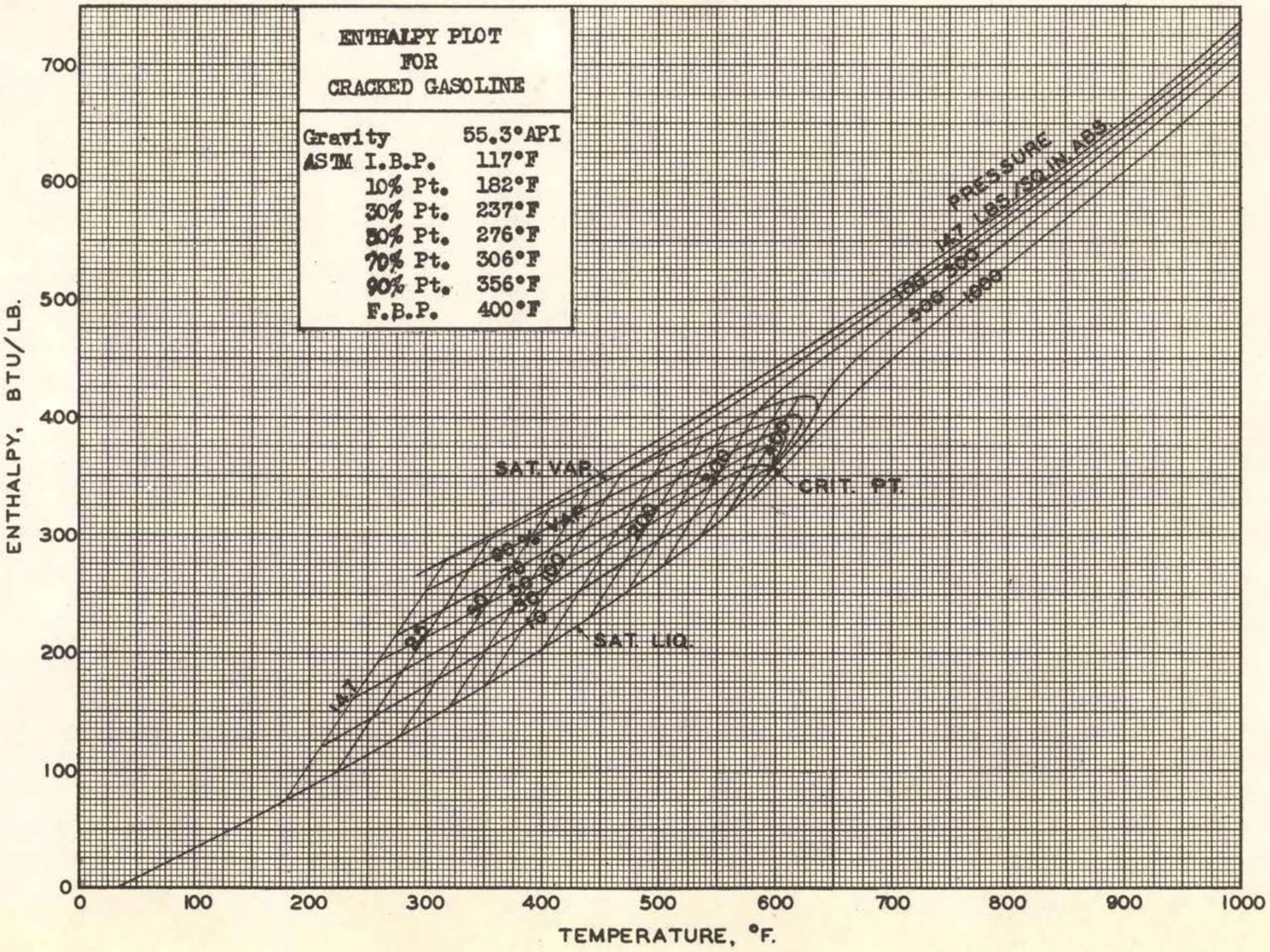
A comparison of latent heats calculated by method outlined above and values calculated from experimental data is given below:

Cleaners Naphtha (57.1°API)

Temp. °F.	ΔH (calc. as described) Btu./Lb.	ΔH(calc. from experimental data) Btu./Lb.
286	127	127
300	125	124
400	105	105.5
500	76.5	79.5
570	39.0	46
585	0	27
593	-	0

Red Crown Gasoline (57.3°API)

Temp. °F.	ΔH (calc. as described) Btu./Lb.	ΔH(calc. from experimental data) Btu./Lb.
325	126	128.5
400	111	114.5
500	85.5	88
580	49	45
603	-	0
609	0	



ENTHALPY PLOT
FOR
CRACKED GASOLINE

Gravity		55.3°API
ASTM	I.B.P.	117°F
	10% Pt.	182°F
	30% Pt.	237°F
	50% Pt.	276°F
	70% Pt.	306°F
	90% Pt.	356°F
	F.B.P.	400°F

6. Throttling Liquid Hydrocarbon Mixtures

When liquid hydrocarbon mixtures are throttled with no addition of heat or work, partial vaporization with self cooling takes place. The amount of vaporization and the final temperature for such an operation may be estimated by the proper application of thermodynamics. Because of the partial vaporization, a pound of the mixture will occupy more volume after expansion than before. Unless the line on the downstream side of the throttle valve is appreciably larger, there will be an increase in kinetic energy and a corresponding decrease in the enthalpy. If there is no change in the kinetic, the enthalpy will remain substantially constant. It will be constant for the ideal frictionless case. The other extreme is the reversible adiabatic case where the expansion takes place at constant entropy and the changes in kinetic energy and enthalpy are a maximum.

The enthalpy after expansion from one known line size to another may be found by the following expression, which is derived from Bernoulli's equation (pages 6 and 7)

$$H_2 = H_1 + \frac{U_1^2 - U_2^2}{50,000} \qquad (157a)$$

where

H = enthalpy in Btu./lb.
U = velocity in feet/sec.
50,000 = conversion constant = (778)(2g)
subscripts 1 and 2 refer to the initial and final conditions, respectively.

The following procedure should be used in estimating the final temperature after throttling a liquid hydrocarbon mixture and vaporizing a portion of it.

Step 1. Construct a P-T-H-X plot similar to Figure 57 for the mixture.

Step 2. Assume a final temperature and find the per cent vaporized that corresponds to this temperature and the given final pressure. Read final enthalpy from plot prepared in step 1.

Step 3. Estimate initial and final volumes and compute the velocities before and after expansion.

Step 4. Compute the final enthalpy, H_2, by means of equation 157a. If this enthalpy checks the enthalpy found in Step 2 by assuming the final temperature, the solution is complete; if not, repeat Steps 2, 3 and 4.

E. Phase Equilibria

The equilibrium relationship between vapor and liquid hydrocarbons is of major importance in practically all petroleum refining operations. At low pressures simple rules for approximating equilibrium relationships may be used in process design calculations without introducing serious errors. At high pressures errors of large magnitude may be introduced by using these simple relationships, however.

1. Laws of Equilibria

The study of phase equilibria is concerned with the important physical laws of Avogadro, Henry, Dalton, and Raoult.

Avogadro's hypothesis states that equal volumes of gases at the same temperature and pressure contain the same number of molecules, and only applies at conditions where the gases obey the perfect gas law. At 60°F. and atmospheric pressure most hydrocarbon gases behave as a perfect gas and one pound mol of gas occupies 379 cubic feet.

Henry's law states that a liquid solvent absorbs a mass of gas that is proportional to the pressure of the gas.

Dalton's law states that the pressure of an individual component in a gaseous mixture (commonly referred to as partial pressure) is equal to the product of the total pressure and the mol fraction of that individual component. It follows from Dalton's and Henry's laws that the solubility of each component of a gaseous mixture is proportional to its partial pressure.

Raoult's law states that the partial vapor pressure exerted by a component in a liquid mixture is equal to the product of the mol fraction of the component in the mixture and its vapor pressure (i.e. pressure exerted by component in a pure state) at the same temperature.

Combining Dalton's law, $p = \pi y$, and Raoult's law, $p = Px$, gives the following equilibrium relationship, which is valid only at low pressures:

$$p = Px = \pi y \tag{158}$$

where:

x = mol fraction of any component in the liquid phase,
y = mol fraction of same component in the vapor phase in equilibrium with this liquid phase,
p = partial pressure of the component in the vapor phase,
P = vapor pressure of the pure component at the same temperature, and
π = total pressure on the system.

Defining the ratio y/x as K gives

$$K = \frac{y}{x} = \frac{P}{\pi} \qquad (159)$$

where K is the "equilibrium phase distribution constant" or just "equilibrium constant". Under conditions where the above relationship applies, equilibrium computations may be made from vapor pressure data only. Even under atmospheric conditions the deviations from Raoult's and Dalton's laws may be appreciable and at higher pressures equation 159 breaks down completely. The equation may be used to give correct results, however, if fugacities are used instead of P and π, the fugacity of liquid being used instead of the vapor pressure, P, and the fugacity of the vapor being used instead of the total pressure, π.

2. Fugacity-Escaping Tendency

The vapor pressure is frequently used as a qualitative measure of the escaping tendency of a gas from a solution. Vapor pressure could also be used with correctness as a quantitative measure of escaping tendency if every vapor behaved as a perfect gas. Fugacity is defined in such a way that it is a quantitative measure of the escaping tendency and is equal to vapor pressure when the vapor is a perfect gas.

On page 112 it was pointed out that changes in the free energy, F, represent the maximum net work for a system and that this is the work for an isothermal reversible process that is also isobaric. A multicomponent hydrocarbon system of two phases that are in equilibrium will be in an isothermal, isobaric and reversible condition. The free energy is a measure of the escaping tendency of material substance from a mixture in the same way that temperature is a measure of the escaping tendency of heat from a hot body. When a system is in equilibrium the free energies of each phase are equal. Any devise that can be used to solve for the change in the free energy can also be used to predict the equilibrium.

The following equation was derived on page 117 for a perfect gas:

$$F_2 - F_1 = RT \ln \frac{P_2}{P_1} \qquad (113)*$$

The fugacity is defined so that when it replaces pressure in the above equation an expression for an actual gas is obtained, as follows:

$$F_2 - F_1 = RT \ln \frac{f_2}{f_1} \qquad (160)$$

or in different form

$$dF = RT\, d\ln f \qquad (161)$$

Fugacity as defined by equation 160 is a measure of the escaping tendency of an actual vapor. Its analogy to pressure is obvious by comparing equations (113)* and 160. Fugacity may be regarded as a corrected pressure or vapor pressure.

Combining equation 86 from page 113, which states that $(\partial F/\partial P)_T = V$, and equation 161, which may be written $(\partial \ln f/\partial F)_T = 1/RT$, gives

$$\left(\frac{\partial \ln f}{\partial P}\right)_T = \frac{V}{RT} \qquad (162)$$

or

$$RT\ d\ \ln f = VdP \qquad (163)$$

For an actual gas (page 130)

$$V = \frac{RT}{P} - \alpha \qquad (116)$$

Combining equations 116 and 163 gives

$$RT\ d\ \ln f = \frac{RT}{P}\ dP - \alpha dP \qquad (164)$$

Integrating gives

$$RT \ln f = RT \ln P - \int_0^P \alpha\ dP$$

or

$$RT \ln \frac{f}{P} = -\int_0^P \alpha dP \qquad (165)$$

Fugacities have been computed from this equation and α correlations such as Figure 34 by several investigators and f/P plotted against reduced pressure for lines of constant reduced temperature (see Figure 59). In this plot lines for values of T_r less than 1.0 extend through the entire pressure range, whereas it is possible to compute only that part up to the vapor pressure at the temperature in question from equation 165. Experimental equilibrium data on several binary systems were used in this range. Figure 59 forms the basis for the preparation of equilibrium constant plots.

3. Ideal and Non-Ideal Solutions

The ideal solution is one in which the fugacity of each component is proportional to the mole fraction of that component at every pressure and temperature. This is a generalized statement of Raoult's law and implies that the volumes and enthalpies are additive. In mixtures of chemically similar liquids where the forces between unlike molecules are nearly the same as the forces between like molecules, the number of molecules of any component leaving the liquid should be proportional to the mole fraction of that component, according to the laws of probability. Solutions of the liquid paraffin hydrocarbons appear to conform to the ideal solution except at conditions near the critical point. No serious error is to be expected if vapor mixtures are considered ideal solutions, for in the vapor state the molecules are more widely separated and are allowed more nearly independent action than in the liquid phase. If both liquid and vapor mixtures are regarded as ideal solutions, the fugacity of each component is equal to the product of the mole fraction and the fugacity of the pure component in a like phase at the same temperature and pressure and the general equation for equilibrium becomes

$$f_L\, x = f_V\, y \tag{166}$$

where f_L = fugacity of pure component as liquid at same temperature and total pressure.

f_V = fugacity of pure component as vapor at same temperature and total pressure.

The errors introduced by these assumptions have been found to be much less than those involved in the assumption of Raoult's and Dalton's laws and in most cases within the limits required by modern engineering practice. When dissimilar hydrocarbons appear in the same mixture it is necessary to correct the fugacity of the liquid in the above equation for the character of the liquid phase. No reliable quantitative correlations for making this correction are available, however.

4. Equilibrium Constants

Assuming ideal solutions and using fugacities rather than vapor and total pressures, equation 159 becomes

$$K = \frac{y}{x} = \frac{f_P}{f_\pi} \tag{167}$$

where: f_P is the fugacity of the liquid phase or the fugacity at the vapor pressure, and f_π is the fugacity of the vapor phase or the fugacity at the total pressure, both taken at the same temperature. Both f_P and f_π can be computed from Figure 59 as illustrated by the following example: Find the equilibrium constant for n-butane at 180°F. and 100 lbs./sq.in. abs.

$t_o = 306.9°F.$, $P_o = 550$ lbs./sq.in. abs., V.P. at 180°F. = 155 lbs./sq.in.abs.

$$\frac{P}{P_o} = \frac{155}{550} = 0.292, \quad \frac{\pi}{P_o} = \frac{100}{550} = 0.182, \quad T_R = \frac{180 + 460}{306.9 + 460} = 0.835$$

$$\frac{P}{\pi} = \frac{155}{100} = 1.55$$

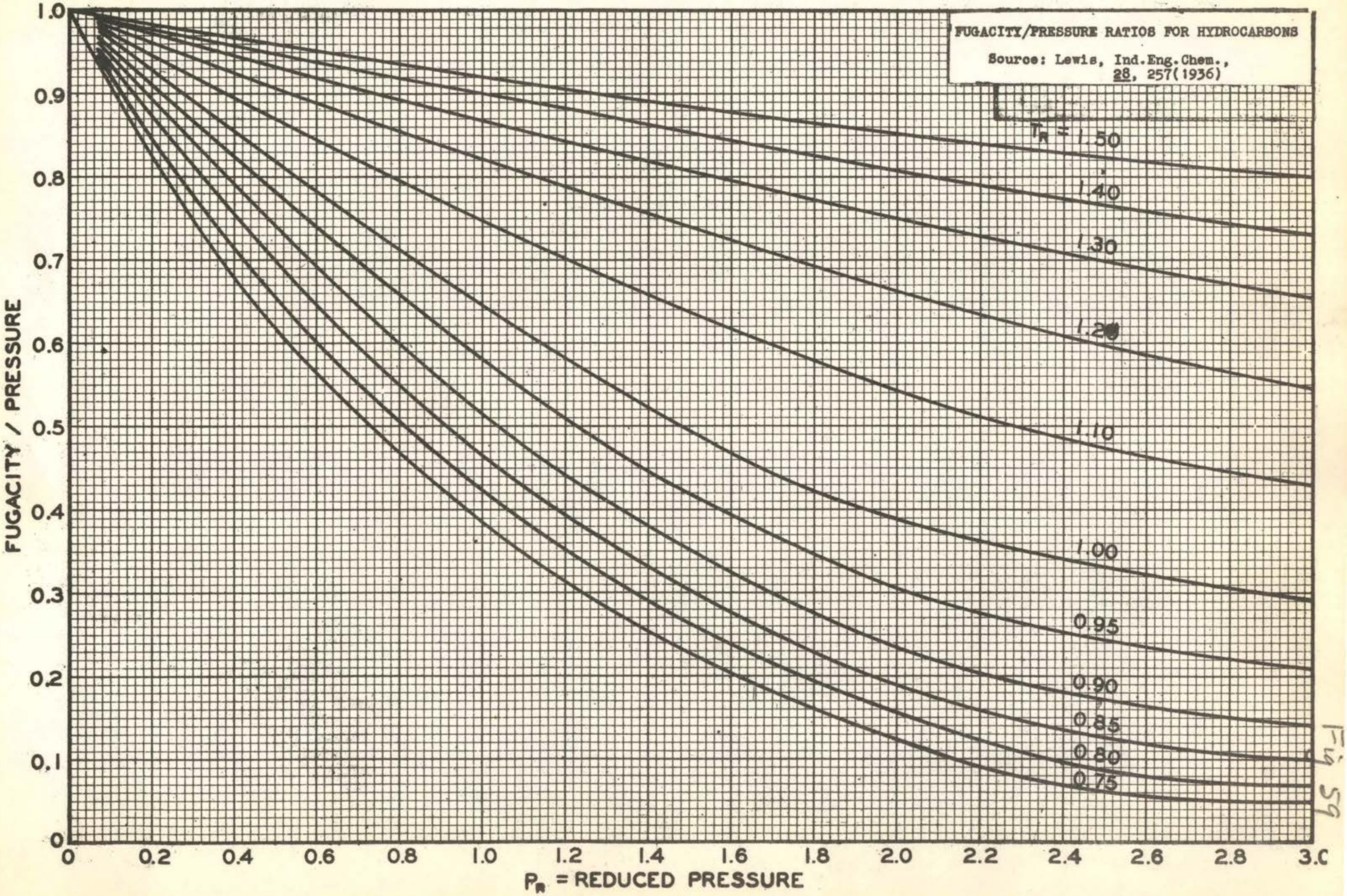
From Fig. 59

$$\frac{f_P}{P} = 0.81 \qquad \frac{f_\pi}{\pi} = 0.87$$

$$K = \frac{f_P}{f_\pi} = 1.55 \ \frac{0.81}{0.87} = 1.45$$

In this example there is not much difference between the Raoult's and Dalton's law K of 1.55 and the fugacity K of 1.45. The phase equilibrium constants given on Standard Data Book Charts A-6.101 to A-6.132 were prepared in this manner. For temperatures above the critical temperature an extrapolated vapor pressure (i.e. extrapolated as a straight line on a $\log_{10} P$ vs. $1/T$ plot) is used in computing K.

At the critical point of the mixture there can be no separation into vapor and liquid phases, the mixture being of a homogenous continuous phase between vapor and liquid. At this point the equilibrium constants for all the components present in the mixture must be equal to unity to satisfy this phenomena. The following plot (Figure 59) shows how the K constants for the components of a given mixture would deviate from the fugacity K constants as the critical pressure is approached at the critical temperature. The critical conditions for the mixture are 300°F. and 700 lbs./sq.in.abs.

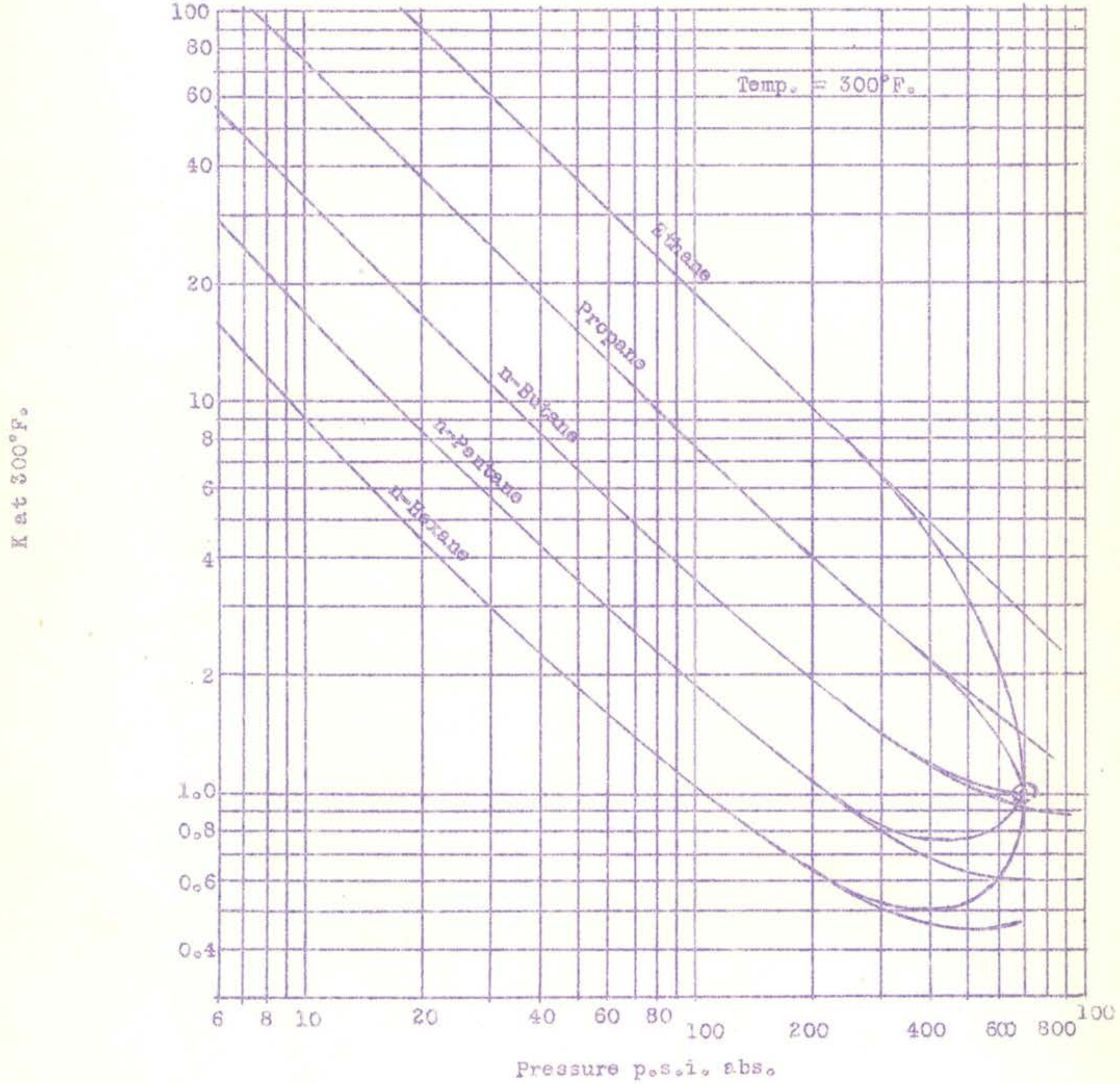

FUGACITY/PRESSURE RATIOS FOR HYDROCARBONS

Source: Lewis, Ind.Eng.Chem., 28, 257(1936)

Fig 59

Figure 59b

Equilibrium(K) Constants for Component of Hydrocarbon Mixture at the Critical Temperature of 300°F.



F. Reactions

Thermodynamics is a useful tool in studying chemical reactions. It may be used to estimate the driving force and equilibrium of a given reaction, and thus predict whether or not the reaction will occur and the conditions that are most favorable to it. By a combination of thermodynamics and kinetics, the yields may be estimated. Thermodynamics may also be used to compute the heat absorbed or liberated for reactions. These applications of thermodynamics will be discussed briefly. Heats of reaction will be taken up first because they are used in the driving force (free energy) calculations.

1. Heats of Reaction

The heat of reaction is the quantity of heat that must be added or removed to make the reaction take place and which heat is not later recoverable. When heat must be added the reaction is "endothermic" and when heat is removed the reaction is "exothermic". Cracking is endothermic and polymerization is exothermic. By the combination of thermochemical equations, heats of reactions involving hydrocarbons may be calculated from the heats of formation of the reactants and the products from carbon and hydrogen. Heats of formation can be evaluated by a similar combination of heats of combustion. Heats of reaction may also be determined experimentally with a bomb calorimeter. Because of the many side reactions that usually occur experimental heats of reaction are difficult to analyse and correlate unless the above theoretical method, based on heats of combustion, is also employed. As pointed out on page 136, heats of combustion can be very accurately determined. Much of this kind of work has been done at the Bureau of Standards by Rossini and at Harvard by Kistiakowski, the results generally being reported at 25°C (77°F) in gm.cal./gm.mol. In applying these calorimetric heats of combustion data to the computation of heats of formation at higher temperatures, say 950°F., it is necessary to correct for the effect of temperature on the enthalpies of the reactants and products.

The heat of reaction ΔH is the difference between the sum of the heat contents of the products and the sum of the heat contents of the reactants, each of which varies according to the equation $(\partial H/\partial T)_p = C_p$. By a combination of such equations for the reaction the following is obtained:

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = \Delta C_P \qquad (168)$$

where ΔC_p is the sum of the heat capacities of the products less the corresponding sum for the reactants. Integrating equation 168 gives

$$\Delta H_2 - \Delta H_1 = \int_1^2 \Delta C_p \, dT \qquad (169)$$

This method will be illustrated by the computation of the heat of reaction for the reaction of methane and ethylene at 950°F. to form propane ($C_2H_4 + CH_4 = C_3H_8$).

Given: The following heats of combustion to carbon dioxide and water:

	Heats of Combustion Cal/gm-mol at 25°C.	Btu/lb mol at 77°F.
Hydrogen	68,318	123,000
Carbon	94,030	169,000
Methane	212,790	383,000
Ethylene	337,250	606,000
Propane	530,570	950,000

Step 1: Compute the heats of formation of methane, ethylene, and propane from carbon and hydrogen at 25°F. by combining the thermochemical equations, which is done by writing the equations involved, changing the direction and the sign of the heat of formation in the first equation and adding. The heats of reaction for the reactions of hydrocarbons to CO_2 and H_2O is numerically equal to the heats of combustion but of opposite sign.

(a) Methane

	Heats of Reaction in gm-cal. at 25°C. (298°K.)
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	-212,790
$C + O_2 \rightarrow CO_2$	-94,030
$2H_2 + O_2 \rightarrow 2H_2O$	-136,636
$C + 2H_2 \rightarrow CH_4$	-17,876

(b) Ethylene

$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$	-337,250
$2C + 2O_2 \rightarrow 2CO_2$	-188,060
$2H_2 + O_2 \rightarrow 2H_2O$	-136,636
$2C + 2H_2 \rightarrow C_2H_4$	+12,554

(c) Propane

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$	-530,570
$3C + 3O_2 \rightarrow 3CO_2$	-282,090
$4H_2 + 2O_2 \rightarrow 4H_2O$	-273,272
$3C + 4H_2 \rightarrow C_3H_8$	-24,792

Step 2: Correct the above heats of formation to 950°F. by means of the following equation, which is derived from equation 169.

$$\Delta H_{950} = \Delta H_{77} + \int_{77}^{950} \left[C_p\,(C_mH_n) - mC_p\,(C) - \frac{n}{2}\,C_p\,(H_2) \right] dT \qquad (170)$$

The specific heats for the hydrocarbons may be found on pages 133-34. Specific heat equation constants A and B are 6.50 and 0.0009 for hydrogen and 2.673 and 0.00262 for carbon. Making this computation gives the following heats of formation at 25°C. (77°F.) and 950°F. in cal/gm-mol and in Btu./lb. mol.

	Heats of Formation from Carbon and Hydrogen			
	at 25°C (77°F.)		at 950°F.	
	Cal/gm mol	Btu/lb mol	Cal/gm mol	Btu/lb mol
Methane	-17,876	-32,200	-20,600	-37,215
Ethylene	+12,554	+22,600	+9,920	+17,870
Propane	-24,792	-44,600	-30,250	-54,457

Step 3: The required heat for the reaction of methane and ethylene to form propane is found by combining the above heats of formation as follows (the directions of the first two reactions are reversed and the signs of their heats of reaction are changed in this solution.

	Heat of Reaction			
	at 25°C (77°F)		at 950°F.	
	Cal/gm mol	Btu/lb mol	Cal/gm mol	Btu/lb mol
$C + 2H_2 \rightarrow CH_4$	-17,876	-32,200	-20,600	-37,215
$2C + 2H_2 \rightarrow C_2H_4$	+12,554	+22,600	+9,920	+17,870
$3C + 4H_2 \rightarrow C_3H_8$	-24,792	-44,600	-30,250	-54,457
$C_2H_4 + CH_4 \rightarrow C_3H_8$	-19,470	-35,000	-19,570	-35,112

The above example illustrates the computation of heats of formation and reaction from heats of combustion. Similar computations could be made for numerous reactions. A correlation of heats of formation would be an ideal starting point for such calculations. Heats of formation, calculated in the above manner, are shown plotted against the number of carbon atoms per molecule for olefinic and paraffinic hydrocarbons in Fig. 60 below:

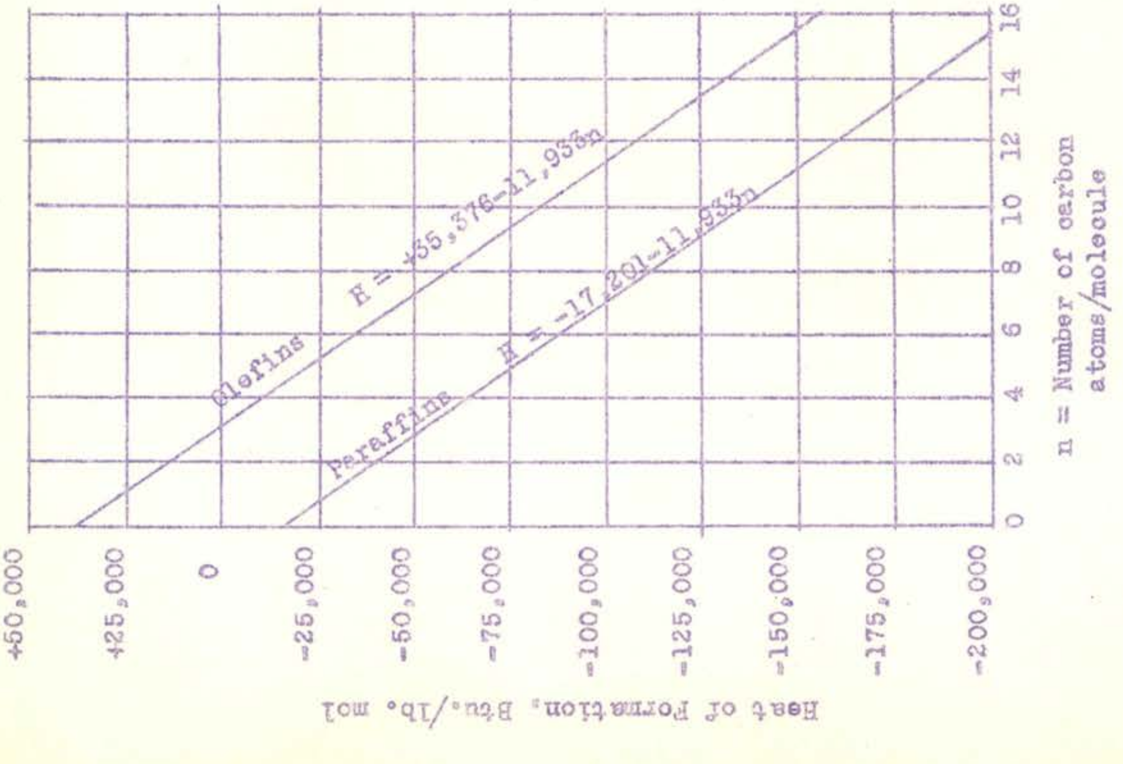


Fig. 60

Heat of Formation at 950°F.

With the method illustrated by the above example, heats of reaction may be computed for more complicated reactions involving many components if the heats of combustion and specific heats and relative amounts of hydrogen and carbon are known for the reactions and products. Data of this kind are given on Standard Data Book Charts A-9.11 and A-9.12 for gases and liquids. However, if more accurate analyses of the charge and the products are available it is possible to make a more accurate computation of the heats of reaction. With analyses telling the number of mols of various types of hydrocarbons (olefins, aromatics, paraffins, naphthenes) made in the reaction it is possible to make a sound theoretical calculation. However, this method does not lend itself to design calculations very well so more approximate methods are necessary.

Where the properties of the charge and products are known the heat of thermal cracking may be calculated from the following equation:

$$\Delta H = \frac{48,800\ (M_c - M_p)}{M_c - M_p} \qquad (171)$$

where M_c is the average molecular weight of the charge entering the cracking zone, M_p is the average molecular weight of the stream leaving the cracking zone and ΔH is the heat of cracking in Btu./lb. of charge entering the cracking zone. The constant 48,800 was calculated on theoretical grounds. The above formula was used to calculate the heat of cracking for the Whiting Process Laboratory tests and the result of 350 Btu./lb. of gasoline plus gas produced. This checks the following "rule of thumb" values used for design.

Vapor phase and liquid phase cracking and viscosity breakers. - 335 Btu./lb. of gasoline and gas produced in the furnace.

Naphtha reforming - 335 Btu./lb. of gasoline and gas where the gasoline is to be considered as 50% of the gasoline yield and the gas as all the gas yield.

2. Third Law of Thermodynamics

The third law of thermodynamics states: the entropy of perfect crystalline substances is zero at absolute zero of temperature and has positive finite values at all other temperatures. A substance composed of crystals of microscopic size would not differ appreciably from a single perfect crystal. This principle is used in establishing the integration constant in calculating the free energy of formation. A more thorough discussion of the Third Law is given in Lewis and Randall.

3. Free Energies of Reaction

The free energies of formation of hydrocarbons at 25°C. are frequently referred to as the "standard free energies" and are indicated by ΔF°_{298}. Free energies at all temperatures are used to compute equilibrium yields for reactions as will be shown later.

The following experimental data are necessary to the computation of the free energy of formation of hydrocarbons: (a) heat capacity of graphitic carbon over the range of temperature; (b) heat capacity of gaseous hydrogen over the range of temperature; (c) heat capacity gaseous hydrocarbon over the range of temperature; (d) absolute entropy of carbon, hydrogen, and hydrocarbon and the same temperature or data from which these entropies can be computed by the Third Law; i.e. low temperature specific heat data as well as heats of fusion and vaporization; and (e) the heat of formation from carbon and hydrogen at some temperature, or the heats of combustion of carbon, hydrogen, and the hydrocarbon at the same temperature from which the heat of formation can be computed.

Assuming the specific heats of products and reactants may be represented by the equation $C_p = A + BT$, the algebraic addition of specific heat equations gives

$$\Delta Cp = \Delta A + \Delta BT \qquad (172)$$

where ΔA and ΔB are the algebraic sums of the values for A and B for the reactants and the products. Substituting in equation 169 and integrating gives

$$\Delta H = \Delta H_o + AT + 1/2\ BT^2 \qquad (173)$$

where ΔH_o is the integration constant and would be the heat absorbed in the reaction at absolute zero, if the empirical equation were valid down to absolute zero, which is never the case. ΔH_o can be evaluated from the heat of reaction at any temperature.

The fundamental equation for the free energy is

$$\frac{\partial\left(\frac{\Delta F}{T}\right)}{\partial T} = \frac{\Delta H}{T^2} \qquad (174)$$

Combining equations 173 and 174 and integrating gives

$$\frac{\Delta F}{T} = \frac{\Delta H_o}{T} - \Delta A \ln T - \frac{1}{2} \Delta BT + I \qquad (175)$$

multiplying by T

$$\Delta F = \Delta H_o - \Delta A\ T \ln T - \frac{1}{2} \Delta BT^2 + IT \qquad (176)$$

The integration constant I is evaluated by finding ΔF at some one temperature by means of the following equation

$$\Delta F = \Delta H - T\Delta S, \qquad (177)$$

which is analogous to equation 78 on page 112. ΔH for this computation (equation 177) can be found from equation 173. ΔS for this computation must be estimated from the absolute entropies of the reactants and products by the Third Law, as follows: Plot Cp/T vs. T and extrapolate back to absolute zero temperature, as shown in the sketch.

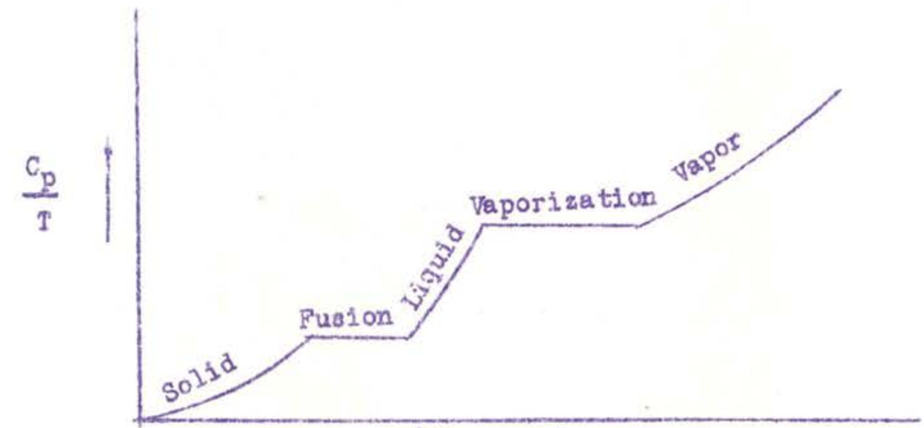


Fig. 61 - Calculation of Absolute Entropy

Integrate Fig. 61 to obtain absolute entropy. With this ΔS and ΔH from equation 173, ΔF can be computed from equation 177. With this value of ΔF the integration constant I may be computed by solving equation 176.

In this manner free energies of formation may be computed for any and all hydrocarbons at any temperature. The standard temperature for free energy computations is 298°K. Various investigators, particularly Parks and Huffman, have computed $\Delta F°_{298}$, as the Standard Free Energy is symbolized, and tabulated them. Equation 176 may be solved for the free energies at other temperatures, however. Having established the constants in equation 176 for the formation of various hydrocarbons, similar equations may be written for any reaction between these hydrocarbons by combining their free energy of formation equations.

Frequent applications of free energies will justify the preparation of a plot of free energies of formation to the gaseous and liquid phases vs. temperature for the hydrocarbons with which the calculations in question involve. Free energies of reactions may then be computed rapidly by algebraic addition of free energies of formation.

Two major uncertainties in calculations of this kind are the heat capacities of the hydrocarbons in the liquid and vapor phases and the heat of combustion of carbon, which is different for the different forms of carbon. If for a given reaction, the components involved are not all in the same phase, i.e. some gaseous and some liquid, this difference in phase conditions should be taken into account in computing the free energy for the reaction. It should also be considered in estimating the equilibrium yields for the reaction as will be pointed out later.

As an example of the method of computing free energies of reactions, the free energy will be computed for the reaction of methane and ethylene to form propane ($C_2H_4 + CH_4 = C_3H_8$), using the heat of reaction computed on page 160, and entropies for formation of 43.9, 57.4, 65.8 e.u. (entropy units, either g. cal/gm. mol-°K or Btu/lb. mol-°R) respectively for methane, ethylene, and propane at 298°F.

Step 1: Add the heat capacity equations (see page 134) to give equation in form of equation 172.

$$\begin{array}{ll} C_3H_8 & Cp = 9.000 + 0.0300\ T \\ C_2H_4 & Cp = 4.033 + 0.02167\ T \\ CH_4 & \underline{Cp = 4.313 + 0.01444\ T} \\ & C_p = 0.654 - 0.00611\ T \end{array}$$

Step 2: Substitute in equation 173 and evaluate ΔH_o, using $\Delta H = -19{,}470$ cal./gm. mol at 298°K.

$$\Delta H = H_o + 0.654\ T - 0.003055\ T^2$$

$$\Delta H_o = -19{,}470 - (0.654)(298) + (0.003055)(298)^2$$

$$\Delta H_o = -19{,}394 \text{ cal/gm. mol}$$

Step 3: Substitute in equation 176 and evaluate the integration constant by means of equation 176.

$$\Delta F = -19{,}394 - 0.654\ T \ln T + 0.003055\ T^2 + IT$$

$$\Delta S_{298} = 65.8 - 57.4 - 43.9 = -35.5 \text{ e.u.}$$

$$\Delta F_{298} = -19{,}470 - (-35.5)(298) = -8{,}900 \text{ cal/gm. mol}$$

$$I = \frac{8{,}900 + 19{,}394 + (0.654)(298 \ln 298) - 0.003055\ (298)^2}{298} = 38$$

Step 4: Write the equation for the free energy of formation and compute the free energy at 200°C. (392°F), 300°C (572°F), and 400°F (752°F).

$$\Delta F = -19{,}394 - 0.654\ T \ln T + 0.003055\ T^2 + 38\ T$$

t°C	T°K	ln T	TlnT	0.654 TlnT	T^2	$0.003055T^2$	38T	ΔF cal.
200	473	6.15	2910	1900	22,350	68	18,000	-3226
300	573	6.35	3640	2380	32,850	100	21,800	+126
400	673	6.51	4380	2865	45,250	138	25,600	+3479

4. Equilibrium Yields

Knowing the free energy changes for a given reaction, the equilibrium yields for the reaction may be computed by computing the equilibrium constant and then applying the law of mass action of kinetics. The equilibrium constants are computed by the following equation:

$$\Delta F = -RT \ln K_f \qquad (178)$$

K_f is a function of temperature but is independent of pressure in this equation. The pressure correction is made separately. Using K_f from this equation and fugacity activity coefficients, the equilibrium concentrations of reactants and products are computed.

The Law of Mass Action states that the rate of a given reaction is proportional to the concentration of the reactants. When a reaction has reached the equilibrium concentration it stops. This equilibrium concentration can be computed from the following mathematical statement of the Law of Mass Action for the reaction of a mols of A plus b mols of B to give c mols of C and d mols of D, i.e.

$$aA + bB = cC + dD$$

$$Kp = \frac{(\text{Conc. of C})^c \times (\text{Conc. of D})^d}{(\text{Conc. of A})^a \times (\text{Conc. of B})^b} \qquad (179)$$

where Kp = the equilibrium constant corrected to the desired pressure as follows

$$K_p = \frac{K_f}{K\gamma} \qquad (180)$$

where

$$K\gamma = \frac{(\gamma_C)^c \times (\gamma_D)^d}{(\gamma_A)^a \times (\gamma_B)^b} \qquad (181)$$

where γ = activity coefficient = ratio of fugacity to pressure (Fig. 59). For reactions in the vapor phase, the concentrations in equation 179 will be expressed in terms of partial pressures so that

$$Kp = \frac{(P_C)^c \times (P_D)^d}{(P_A)^a \times (P_B)^b} = \frac{K_f}{K\gamma} \qquad (182)$$

As an example in the application of equations 178 to 182 the equilibrium product composition of the reaction of ethylene and methane to form propane will be computed at 1800 p.s.i. (122 atmospheres) with the assumption that the products contain 5 and 10 mol % ethylene (Cases I and II).

Step 1: Compute $K\gamma$ for correcting K_f to a pressure of 1800 p.s.i. at the three temperatures by means of equations 180 and 181 and the activity coefficient from a plot similar to Figure 59.

For this particular reaction equation 181 becomes

$$K\gamma = \frac{\gamma_{\text{propane}}}{\gamma_{\text{ethylene}}\ \gamma_{\text{methane}}}$$

and the computation of $K\gamma$ is accomplished as follows:

	Critical			200°C(392°F) 852°R		300°C(572°F) 1032°R		400°C(752°F) 1392°R	
	T°R	P.s.i. ab.	P_r	T_r	γ	T_r	γ	T_r	γ
Methane	344	673	2.67	2.48	0.93	3.00	0.97	3.52	1.00
Ethylene	510	748	2.40	1.67	0.89	2.02	0.93	2.38	0.96
Propane	666	617	2.91	1.28	0.64	1.55	0.80	1.82	0.90
K_γ					0.78		0.89		0.94

Step 2. Compute Kp by solving for Kf from equation 178 and correcting with the above values of K_γ.

t°C	T°K	RT	$\ln K_f = -\frac{\Delta F}{RT}$	Kf	K_γ	K_p
200	473	940	+3.44	31.0	0.78	39.8
300	573	1138	-0.11	0.895	0.89	0.995
400	673	1337	-2.60	0.074	0.94	0.0786

Step 3. Find the composition of the equilibrium products from this reaction that contain 5 and 10 mol % C_2H_4. For this reaction, equation 182 becomes

$$K_p = \frac{\pi\,(\text{conc. of } C_3H_8)}{\pi\,(\text{conc. of } C_2H_4) \times \pi\,(\text{conc. of } CH_4)}$$

where π = total pressure = 1800 p.s.i. = 122 atmospheres, or

$$K_p = \frac{(\text{conc. of } C_3H_8)}{122(\text{conc. of } C_2H_4)(\text{Conc. of } CH_4)}$$

For 5 mol.% C_2H_4 in products, let x = mol fraction of C_3H_8, then 0.95 - x = mol fraction of methane and

$$K_p = \frac{X}{122(0.05)(0.95-X)} = \frac{X}{5.79-6.1X}$$

For 10 mol % C_2H_4 in products, let X = mol fraction of C_3H_8, then 0.90-X = mol fraction of methane and

$$K_p = \frac{X}{122(0.10)(.90-X)} = \frac{X}{11-12.2X}$$

			Case I Mol. % Products			Case II Mol. % Products		
°C.	°F.	$K_{p=122}$	CH_4	C_2H_4	C_3H_8	CH_4	C_2H_4	C_3H_8
200	392	39.8	0.7	5.0	94.3	0.4	10.0	89.5
300	572	0.995	11.5	5.0	83.5	6.8	10.0	83.2
400	752	0.0786	64.2	5.0	30.8	45.6	10.0	44.4

In order to show the effects of temperature and pressure on this reaction, similar calculations were made at 500 lbs. (340 atmospheres) and three temperatures. Product compositions for these conditions are given below:

			Case I Mol. % Products			Case II Mol. % Products		
°C.	°F.	$K_{p=340}$	CH_4	C_2H_4	C_3H_8	CH_4	C_2H_4	C_3H_8
400	752	0.0365	58.7	5.0	36.3	40.2	10.0	49.8
450	842	0.01287	78.0	5.0	17.0	63.6	10.0	26.4
500	932	0.00512	87.4	5.0	7.6	76.6	10.0	13.4

Step 4. The above yields are plotted against temperature in Figure 62. This plot shows the effect of pressure, temperature, and ethylene concentration on the reaction.

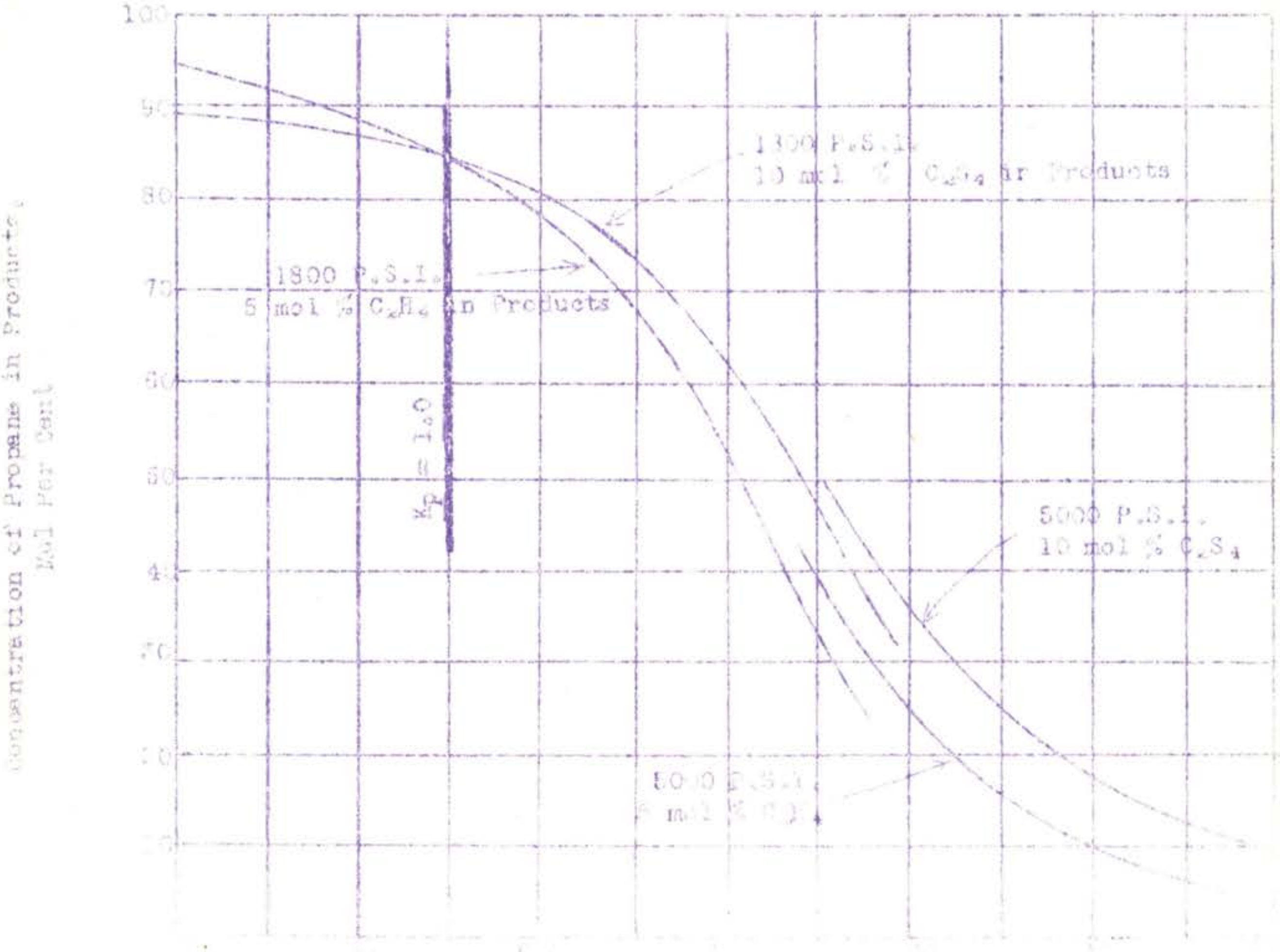


Fig. 62

Product Distribution for
Propane Synthesis

5. Complex Reactions

The above calculations illustrating the use of thermodynamics in predicting heats of reactions and equilibrium product distribution were made for simple reactions. The methods illustrated are equally applicable to complex reactions by considering the complex reaction as made up of several simple ones. Consider the following reaction, which may be broken down into two smaller reactions, with free energy changes are given as follows:

$$
\begin{array}{r}
aA + \frac{c}{3} C = dD, \quad \Delta F = -3000 \\
bB + \frac{2}{3} cC = eE, \quad \Delta F = -2000 \\
\hline
aA + bB + cC = dD + eE, \quad \Delta F = -5000
\end{array}
$$

The Law of Mass Action expression for the above reaction

$$K_p = \frac{(P_D)^d \times (P_E)^e}{(P_A)^a \times (P_B)^b \times (P_C)^c}$$

Thermodynamic calculations of this kind are helpful in research work on hydrocarbon synthesis. They do, however, leave a lot of questions unanswered. Reactions that are thermodynamically possible often are not practically possible because of the unavailability of the proper catalyst, the time required for the reaction, predominating side reactions, and the like.

G. PROBLEMS

1. A perfect monatomic gas for which $C_v = \frac{3}{2} R$ and $C_p = \frac{5}{2} R$ is being changed continuously from a pressure of 1 atm. and 273.1°K to a pressure of 0.5 atm. and a temperature of 546.2°K.

Calculate; the work done by the gas, the heat absorbed, ΔE, ΔH, and ΔS for each of the following paths:

(Path 1) a. Expand isothermally and reversibly to the final pressure.

b. Heat at constant pressure to the final temperature.

(Path 2) a. Expand isothermally to the final volume.

b. Heat at constant volume to the final temperature.

(Path 3) a. Expand adiabatically to the final pressure.

b. Heat at constant pressure to the final temperature.

(Path 4) a. Expand adiabatically to final volume.

b. Heat at constant volume to the final temperature.

The above changes are assumed reversible.

2. Derive a general expression for the change in entropy of 1 mol of perfect gas going from condition A to condition B.

3. A tank of 5 cubic feet capacity containing air at 1 atm. (abs.) and 25°C. is to be evacuated to 0.01 atm. (abs.) by means of a small reciprocating pump having a clearance of 2% and discharging to the atmosphere. On the assumption that the process as a whole is isothermal and reversible, what will be the change in entropy of the air during this process? What will be the change in entropy of the whole universe as a result of the occurrence of this process?

4. Usually the gas issuing from an oil well is saturated with water vapor. To reduce the pressure between the well-head and the gas pipe line, a throttle valve is often employed. This leads to difficulty due to ice forming in the valve with consequent dimunition or stoppage of gas flow. To obviate this trouble, it is proposed to place several baffles in the line, thus increasing the friction and so maintaining the gas temperature above the freezing point of water.

(a.) Discuss from a thermodynamic point of view the proposed change, indicating your recommendations.

5. A reciprocating air compressor having a clearance equal to two per cent of displacement operates with adiabatic intake and exhaust. Compression and expansion may be assumed polytropic with $\gamma = 1.25$. If the machine operates without friction and requires five horse power, when compressing from one atmosphere to four, what is its capacity in cubic feet per minute of free air at 70°F. For air, $\gamma = 1.42$ for isentropic

6. Heat engines have been built using hot water as the working fluid. If hot water were available at 205°F. for use in such an engine, and cooling water at [illegible]°F., what would be the minimum theoretical consumption of hot water per [illegible] generated by the hot water engine?

7. Calculate the entropy change for the following processes:

(a) Evaporation of 1 lb. of water at 100 lb. abs. pressure.
(b) Heating of 1 lb. of water at a constant pressure of 10 lb./sq. in. from 40°F. to 150°F.
(c) An adiabatic expansion of 1 lb. of steam from 600 lbs./sq.in. abs. and 700°F. to 25 lbs./sq.in. and 240.07°F.
(d) A complicated series of processes using steam and starting at 1000 lbs./sq.in. and 700°F., and ending at 400 lbs./sq. in. and 550°F.

8. Calculate the entropy change for the substance heated, for the heating material and for the system when 10 lbs. of water is heated in a coil heater from 50°F. to 150°F.

(a) By 2 lbs. of dry saturated steam at 1000 lbs.sq.in. absolute.
(b) By 2 lbs. of dry saturated steam at 60 lbs. absolute.
(c) By 2 lbs. of superheated steam at 50 lbs. absolute, 350° superheated.
(d) In a perfect countercurrent heat exchanger using as a heat source 10 lbs. of water originally at 150°F.
(e) In a parallel flow heat exchanger using the minimum quantity of water originally at 200°F.

9. (a) Tabulate the velocities which could be obtained by the isentropic expansion of steam from 300 lb./sq.in. abs. and 200°F. super heat to 200 lb., 75 lb., 25 lb. and 3" of Hg. pressure.

(b) Tabulate the velocities which could be obtained by adiabatic expansions to these same pressures, if the efficiencies of the nozzles were required for the expansion were 95% for the two highest back pressures, and 90% for the remainder.

10. It has been proposed to heat buildings in the following way:

"Refrigerating machines will be operated using the outside air as a heat source, and the warm air within the buildings as a heat sink. These refrigerating machines are to be operated by electrical power, thus pumping low temperature heat uphill into buildings".

Making the assumptions listed below (based roughly on conditions in the San Francisco Bay region) calculate the maximum cost of electrical energy (cents per KWH) which would allow domestic heating by the proposed scheme to economically replace fuel heating.

a) Refrigerating machines operate reversibly in every respect.
b) Neglect all costs of refrigerating machines except the cost of power.

c) Average winter temperature equals 40°F. An average room temperature equals 70°F.

d) Average cost of fuel heat delivered to the rooms of a house is one dollar per million B.T.U.

11. A boiler of 100 cubic feet capacity containing 3000 lbs. of water in the liquid phase, is being held at a constant pressure of 400 lbs./sq. in. abs, without withdrawing any steam from the boiler, 2000 lbs. of feed water at 150°F. are pumped in, while the pressure is meanwhile held constant at 400 lb, How much heat is added to the boiler during this process?

12. A direct fired super heater is fed simultaneously with steam from two lines, the first carrying dry saturated steam at 100 lb. absolute pressure, and the second carrying steam at 120 lb. absolute pressure and 90% quality. At the coil exit the pressure of the combined streams is 90 lb. absolute and the steam is 100° super heated. During passage through the coil 120 B.T.U. per pound of total steam flowing was added. What weight per cent of the total steam fed came from the 100 lb. line?

13. What is the entropy change for a process which consists of mixing 100 lbs. of lead shot originally at 250°F. with 10 lbs, of water originally at 60°F. For lead $C_p = 0.03$.

14. Calculate ΔE and ΔS per mol for the reversible poly tropic compression of methane from one to twenty atmospheres. The compressor takes in methane at 20°C. and discharges at 35°C.

Indicate how you would calculate the minimum work required, per lb. mol, for the compression.

15. One million cubic feet (at suction conditions) per hour of an equi-molal mixture of methane, ethane, and propane is compressed adiabatically from one to 20 atmospheres. If the suction temperature is 80°F., find, (a) the theoretical work required in horsepower and (b) the final temperature.

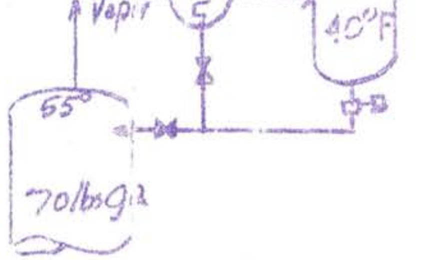
16. In designing the nozzles for an impulse turbine or the wheel blades for a reaction turbine the velocity of the working fluid after expansion through the nozzles or wheel blades must be computed. Steam is the most common working fluid but other gases such as flue gases and hydrocarbon vapors are frequently used. The Mollier Diagram and/or the Steam Tables and Bernoulli's theorem are used in making this computation for steam. No such diagrams or tabulations are available for hydrocarbon gases, however. Final velocity calculations may be made for hydrocarbon gases by; first, finding the final temperature after expansion by means of the Cp/Cv ratios, then finding the difference in enthalpy between the initial and final conditions, and finally using the Bernoulli theorem equation in the same manner as for steam to find the velocity.

A turbine is being designed to operate on a mixture of 20% ethane, 30% propane and 50% butane (all percentages are by gaseous volume) and drive an electric power generator. The gas is to be expanded from 300 lbs./sq.in. abs. and 600°F. to 30 lbs./sq.in.abs. or until liquid starts condensing. Neglecting the entrance velocity and assuming a friction loss of 15%, calculate the final velocity after expansion. Assuming turbine and generator efficiencies of 65 and 95%, respectively, find the quantity of gas that must be used to generate 100 Kilowatt hours of electric power.

17. In the compression refrigeration cycle, cycle gas that has just been evaporated in the cooling coil is compressed (substantially at constant entropy), then cooled and condensed to saturated liquid in a water cooled condenser and then expanded through the cooling coil to complete the cycle. The coefficient of performance of any fluid in a compression refrigeration system equal the ratio of the difference in heat content of the saturated liquid (after water cooling and condensing) and the heat content of the saturated vapor **leaving** the evaporator to the heat equivalent of the work of compression. One ton of refrigeration is a rate of heat removal equal to 12,000 B.t.u./hr.

Using propane as a refrigerant and operating between -5°F and 86°F., find (a) coefficient of performance, (b) compression ratio and volumetric efficiency if the compressor has a clearance 10%, (c) the quantity of propane required to produce a ton of refrigeration, and (d) the horsepower requirement per ton of refrigeration. Repeat for "plant propane".

18. The reason that high pressures are used in the distillation of low boiling hydrocarbons is to permit the condensation of reflux with ordinary cooling water. However, distillation is more efficient at low pressures than at high pressures because the relative volatilities are higher at the lower pressure. If a low cost source of refrigeration is available to supply the low temperature level cooling, it might be desirable to stabilize at low pressure as in the process represented by the accompanying sketch where a split is being made between propane and butane. The net overhead consists of 92.5 mols of propane and 7.5 mols of butane per hour and is expanded through the reflux condenser to supply cooling. To what pressure must this expansion proceed in order to maintain a reflux ratio of 5:1 at the conditions specified?



19. In the production of lubricating oil a batch of 38°API paraffin distillate is dewaxed by chilling and filtering in propane solution. The oil and the propane are mixed in the liquid phase at 90°F. and chilled at a rate of 3°F per minute to -30°F. by releasing the pressure and allowing part of the propane to vaporize. The final mixture must consist of two gallons of propane and one gallon of oil for filtering. Assuming that the heat infiltration is negligible find the composition of the initial propane - oil mixture (i.e., before vaporization).

Solutions to Problems

1. This problem will be solved in engineering units for one pound-mol of the perfect gas assuming the changes occur in a flow process.

$P_1 = 14.7$ lbs./sq.in.abs. $\quad P_2 = 7.35$ lbs./sq.in.abs.

$T_1 = 492°R \quad T_2 = 984°R$

$V_1 = 359$ Cu.Ft.

$$V_2 = 359 \ \frac{984}{492} \ \frac{14.7}{7.35} = 1436 \text{ cu.ft.}$$

The intermediate conditions for each path will be calculated by the following equations, which are based on equations 108 and 110 (pages 116 and 117) and the given values of C_p and C_v.

$$TV^{2/3} = \text{const.} \qquad (a)$$

$$PV^{5/3} = \text{const.} \qquad (b)$$

From equation (a)

$$T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{2/3} \text{ and} \qquad (c)$$

$$V_2 = V_1 \left(\frac{T_1}{T_2}\right)^{3/2} \qquad (d)$$

From equation (b)

$$P_2 = P_1 \left(\frac{V_1}{V_2}\right)^{5/3} \qquad (e)$$

$$V_2 = V_1 \left(\frac{P_1}{P_2}\right)^{3/5} \qquad (f)$$

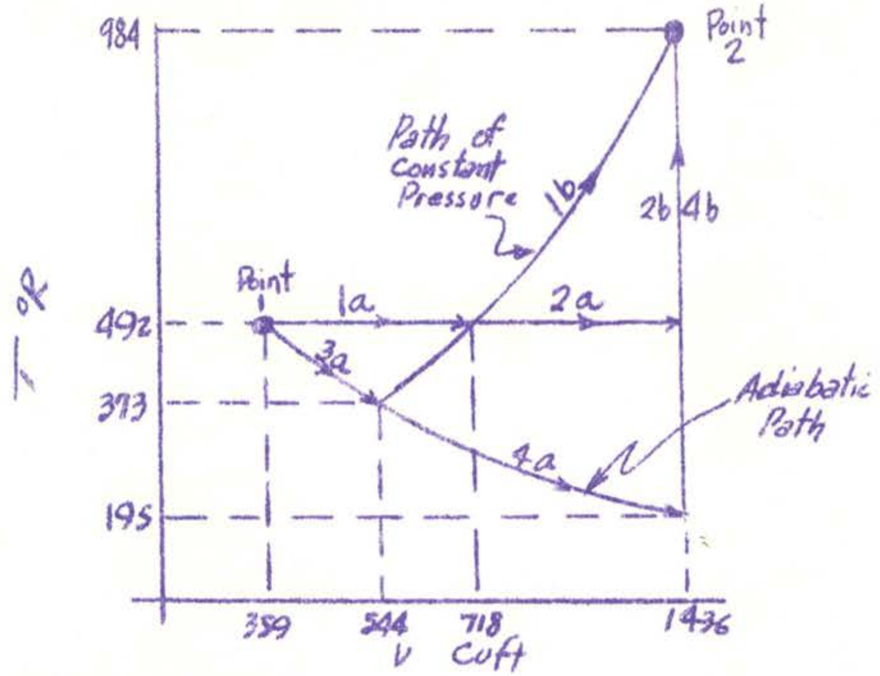
Combining equations (d) and (f) gives

$$T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{2/5} \qquad (g)$$

The intermediate conditions are given in the following tabulation:

Path	Pressure	Temperature	Volume
1	7.35	492	$359 \left(\frac{14.7}{7.35}\right) = 718$
2	$14.7 \left(\frac{359}{1436}\right) = 3.67$	492	1436
3	7.35	$492 \left(\frac{7.35}{14.7}\right)^{2/5} = 373$	$359 \left(\frac{14.7}{7.35}\right)^{3/5} = 544$
4	$14.7 \left(\frac{319}{1436}\right)^{5/3} = 1.46$	$492 \left(\frac{359}{1436}\right)^{2/3} = 195$	1436

The following temperature-volume plot shows the four paths,



Heat and work calculations will be made for each path.

Path 1

(a) Isothermal expansion to final pressure

ΔE & $\Delta H = 0$ for perfect gas and

$$Q = W = -\int_{P_1}^{P_2} vdP = -\int_{P_1}^{P_2} RT/P\ dP = -\int_{P_1}^{P_2} RT\ d\ln P$$

$$Q = W = (1.99)\ (492)\ (2.3)\ (\log_{10} 2) = 676\ \text{Btu/mol}$$

$$\Delta S = \frac{676}{492} = 1.38\ \text{Btu/mol-°R.}$$

(b) Isobaric heating to final volume.

$$W = P\Delta V = R\Delta T = (1.99)(984-492) = 980\ \text{Btu/mol}$$

$$Q = \Delta H = \int CpdT = 5/2\ R\ (984-492) = 2460\ \text{Btu/mol}$$

$$\Delta E = \Delta H - \Delta PV = \Delta H - R\Delta T = 2460-(1.99)(492) = 1480\ \text{Btu/mol}$$

$$\Delta S = \int \frac{Cp}{T}\ dT = 5/2R \int \frac{dT}{T} = 5/2\ (1.99)(2.3)(\log_{10} \frac{984}{492}) = 3.46\ \text{Btu/mol-°R.}$$

Path 2

(a) Isothermal to final volume

ΔE and $\Delta H = 0$

$$Q = W = (1.99)(492)(2.3)\left(\log_{10} \frac{14.7}{3.67}\right) = 1360 \text{ Btu./mol}$$

$$\Delta S = \frac{1360}{492} = 2.76 \text{ Btu./mol-°R}$$

(b) Constant volume to final condition

$W = 0$ and $Q = \Delta E$ (equation 17, page 96)

$$\Delta E = \int C_v dT = 3/2 \text{ R } (984-492) = 1480 \text{ Btu./mol}$$

$$\Delta H = \Delta E + \Delta PV = \Delta E + R\Delta T = 1480 + (1.99)(492) = 2460 \text{ Btu./mol}$$

$$\Delta S = \int \frac{C_v}{T} \, dT = 3/2 \text{ R} \int \frac{dT}{T} = 3/2 \ (1.99)(2.3)\left(\log_{10} \frac{984}{492}\right) =$$

$$2.08 \text{ Btu./mol-°R.}$$

Path 3

(a) Adiabatic to final pressure

Q and $\Delta S = 0$, therefore $\Delta H = -W$ for flow process

(If process had been a batch process, $\Delta E = -W$)

By equation 132 (page 138)

$$W = \frac{\gamma}{\gamma-1} P_1V_1 \left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right]$$

The work done by the gas in expanding is

$$W = \frac{\gamma}{\gamma-1} \ RT_1 \left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}\right]$$

$$\gamma = 5/3 = 1.67; \ \frac{\gamma}{\gamma-1} = \frac{1.67}{1.67-1} = 2.5; \ \frac{\gamma-1}{\gamma} = \frac{1}{2.5} = 0.4$$

$$W = (2.5)(1.99)(492) \left[1 - (.5)^{.4}\right] = 590 \text{ Btu./mol}$$

$$\Delta H = -590 \text{ Btu./mol}$$

$$\Delta E = \Delta H - \Delta PV = \Delta H - R\Delta T = -590 - 1.99 \ (373-492) = -353 \text{ Btu./mol}$$

(b) Constant pressure to final volume.

$$W = P\Delta V = R\Delta T = (1.99)(984 - 373) = 1215 \text{ Btu./mol}$$

$$Q = \Delta H = \int CpdT = 5/2\ R\ (984 - 373) = 3050 \text{ Btu./mol}$$

$$\Delta E = \Delta H - \Delta PV = \Delta H - R\Delta T = 3050 - (1.99)(611) = 1833 \text{ Btu./mol}$$

$$\Delta S = \int \frac{C_p}{T}\, dT = 5/2\ (1.99)(2.3)(\log_{10} \frac{984}{373}) = 4.84 \text{ Btu/mol °R.}$$

Path 4

(a) Adiabatic to final volume

Q and $\Delta S = 0$

$$W = (2.5)(1.99)(492) \left[1 - \left(\frac{1.46}{14.7}\right)^{0.4}\right] = 1472 \text{ Btu./mol}$$

$$\Delta H = -1472 \text{ Btu./mol}$$

$$\Delta E = -1472 - 1.99\ (195 - 492) = -880 \text{ Btu./mol}$$

(b) Heat at constant volume to final temperature.

$$\Delta E = 3/2R\ (984 - 195) = 2360 \text{ Btu./mol}$$

$$\Delta H = \Delta E + R\Delta T = 2360 + (1.99)(984 - 195) = 3932 \text{ Btu./mol}$$

$$\Delta S = \int \frac{C_v}{T}\, dT = 3/2\ (1.99)(2.3)(\log_{10} \frac{984}{195}) = 4.84 \text{ Btu./mol-°R.}$$

The following tabulation summarizes these calculations:

Path		W	Q	ΔE	ΔH	ΔS
		Btu./Mol				Btu./Mol °R
1	a	676	676	0	0	1.38
	b	980	2460	1480	2460	3.46
	Σ	1656	3136	1480	2460	4.84
2	a	1360	1360	0	0	2.76
	b	0	1480	1480	2460	2.08
	Σ	1360	2840	1480	2460	4.84
3	a	353	0	-353	-590	0
	b	1217	3050	1833	3050	4.84
	Σ	1570	3050	1480	2460	4.84
4	a	1472	0	-880	-1473	0
	b	0	3932	2360	3932	4.84
	Σ	1472	3932	1480	2460	4.84

From the above tabulation it can be seen that the changes in energy, enthalpy and entropy are independent of the path taken. It can also be seen that the minimum work is for path 2, where an isothermal change was used as far as possible.

2. Expressions will be derived for both batch and flow processes. The basic equation for both processes is

$$\Delta S = \int \frac{dQ}{T}$$

Batch Process

$$Q = \Delta E + W$$

$$\Delta E = \int_1^2 C_v dT$$

$$W = \int_1^2 p dV$$

$$Q = \int_1^2 C_v dT + \int_1^2 p dV$$

$$dQ = C_v dT + p dV = C_v dT + \frac{RT}{V} dV$$

$$\Delta S = \int \frac{dQ}{T} = \int_1^2 \frac{C_v dT}{T} + R \int_1^2 \frac{dV}{V}$$

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

Flow Process

$$Q = \Delta H + W$$

$$\Delta H = \int_1^2 C_p dT$$

$$W = \int_1^2 V dP$$

$$dQ = C_p dT + \frac{RT}{P} dP$$

$$\Delta S = \int \frac{dQ}{T} = \int_1^2 \frac{C_p dT}{T} + R \int_1^2 \frac{dP}{P}$$

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

[illegible] The 1% clearance has no bearing on the solution of this problem. Since the process is isothermal $\Delta E = 0$ and $Q = W$. The required work is established by the specification that the process is reversible and isothermal. The net work is the algebraic sum of the work required to expand the air from the tank container into the cylinder of the vacuum pump and the work to expel the air from the cylinder with the piston. The latter work consists of two parts: (a) the work to compress the air in the vacuum pump cylinder [illegible] to 1.0 atmosphere, and (b) the flow work to push the air from the cylinder.

Let N_1 = lb. mols in tank container at start.
N_2 = lb. mols remaining in tank container.

By perfect gas law

$$N_2 = \frac{(0.01)(14.7)(144)(5)}{(1543)(298)(1.8)} = 0.0001278$$

$$N_1 = 100\ N_2 = (100)(0.0001278) = 0.01278$$

P_1 = initial pressure = 14.7 lbs./sq. in. abs.

P_2 = final pressure = 0.147 lbs./sq. in. abs.

In setting up the following work equations, a positive sign indicates work done by the air.

$$\text{Expansion work} = +N_1 RT \ln \frac{P_1}{P_2} \quad \text{(equation 102, p. 110)}$$

$$\text{Expulsion work} = -(N_1 - N_2) RT \ln \frac{P_1}{P_2} - (N_1 - N_2) RT$$

$$\text{Total work} = N_1 RT \ln \frac{P_1}{P_2} - (N_1 - N_2) RT \ln \frac{P_1}{P_2} - (N_1 - N_2) RT$$

$$= N_2 RT \ln \frac{P_1}{P_2} - (N_1 - N_2) RT$$

$$= (1.99)(298)(1.8) \left[(0.0001278)(2.3) \log_{10} 100 - 0.0\text{[illegible]}\right]$$

$$Q = W = -12.9 \text{ Btu.}$$

$$\Delta S = -\frac{12.9}{(298)(1.8)} = -0.024 \text{ Btu./°R.}$$

$\Delta S = 0$ for universe since process is reversible.

4. In order to keep the water from freezing in the valve, sufficient heat must be added to maintain the temperature. The only way heat may be absorbed by the gas in such an installation is by radiation and convection from the atmosphere. When a gas is expanded it must either cool itself off or lose heat to its surroundings. If the expansion takes place through a throttle valve there is not much time or space for the gas to absorb heat. If the expansion is allowed to take place more slowly by expanding through a series of baffles, a larger surface is available for heat absorption to the atmosphere. Consequently, the gas does not cool itself to as low a temperature as with a throttle valve. In the equation $Q - W = \Delta H$, $W = 0$ for both types of chokes. Q is nearer zero for the throttle valve than for the baffled choke.

5. The volumetric efficiency of this air compressor is found by means of equation 143, page 140, as follows:

$$E_V = \left[1.0 + 0.02 - 0.02 \left(\frac{4}{1}\right)^{\frac{1}{1.25}}\right] = 0.96$$

The volume of gas that a five theoretical horsepower compressor with this volumetric efficiency will handle is found by means of equation 139, page 140.

$$5 = \frac{144}{33,000}\ 14.7\ \frac{V_1}{0.96}\ \frac{1.25}{.25} \left[\left(\frac{4}{1}\right)^{\frac{.25}{1.25}} - 1\right]$$

$$V_1 = 46.7 \text{ cu.ft./min.}$$

Note: The = 1.42 value given for air with the problem was a "red herring".

6. The maximum theoretical efficiency for any heat engine is the Carnot Efficiency (see equation 39, page 104) which is dependent upon the highest and lowest temperatures only. For this particular case the efficiency of the Carnot cycle gives the ratio of work to heat added as

$$\frac{W}{Q} = \frac{205 - 65}{205 + 460} = 0.2105$$

Using the heat equivalent of one KW (3415 Btu. and assuming the specific heat of the hot water is 1.00 gives

$$\text{Lbs. of Hot } H_2O \text{ per KWH} = \frac{3415}{(0.2105)(205-65)} = 116$$

7. This problem is merely an exercise in reading the steam tables and Mollier diagram (see Standard Data Book) (a) from Chart A-8.51 read 1.1287 Btu./lb.°F. as entropy of vaporization for 1 lb. of H_2O at 100 p.s.i. abs.; (b) the entropies of water at 40°F. and 150°F. and 10 p.s.i. are essential the same as for water at these temperatures under their vapor pressures of 0.122 and 3.716 p.s.i. because pressures have very little effect on the entropy or enthalpy of liquids, i.e. $\Delta S = 0.2149 - 0.0162 = 0.1987$ Btu./lb. °F.; (c) this adiabatic expansion cannot be a reversible (constant entropy) one because the entropies at the initial and final conditions are different. The expansion may be considered as one that takes place in two steps; isentropic to final enthalpy, isenthalpic to final conditions.

$\Delta S = S_2 - S_1 = 1.714 - 1.587 = 0.127$ Btu./lb.°F.; (d) entropy is a point function and changes in it are not dependant upon the path followed but only upon initial and final conditions,

$\Delta S = S_2 - S_1 = 1.5678 - 1.5138 = 0.0540$ Btu./lb.°F.

8. The entropy and enthalpy changes in 10 lbs. of water when it is heated from 60°F. to 150°F. are $\Delta S = 10\ (0.2149-0.0555) = 1.594$ Btu./°F. and $\Delta H = 10\ (117.87-28.07) = 898$ Btu. (a) the heat to be removed from each pound of the dry saturated steam at 1000 p.s.i. is 898 ÷ 2 = 449 Btu. which will leave 69.2% (449 ÷ 649.5 = 0.692) of the 1000 p.s.i. steam condensed for which $\Delta S = -(0.692)(0.6468) = -0.447$ Btu./lb.°F. or −0.894 Btu./°F. The entropy change for the entire system is $\Delta S = 1.594 - 0.894 = 0.7$ Btu./°F.; (b) fraction of 50 p.s.i. dry saturated steam that is condensed is 449 ÷ 923.9 = 0.486, the entropy change being $\Delta S = -(0.486)(1.2473) = -0.606$ Btu./lb.°F. or −1.212 Btu./°F. $\Delta S_{total} = 1.594 - 1.212 = 0.382$ Btu./°F.; (c) the following steam table readings are made for this solution:

50 psi abs. Steam	Sat. Water	Sat. Steam	Super Steam
t°F.	281	281	350
H	250	1174	1210
S	0.411	1.658	1.705

This steam will lose its superheat and then practically condense.

$$\text{Fraction condensed} = \frac{449 - (1210-1174)}{1174 - 250} = 0.447$$

$$\Delta S = -2\left[(1.705-1.658) + (0.447)(1.658 - 0.411)\right] = 1.208$$

$$\Delta S_{total} = 1.594 - 1.208 = 0.386 \text{ Btu./°F.};$$

(d) in a perfect countercurrent heat exchanger, the 10 lbs. of 150°F. water would be cooled to 60°F., for which $\Delta S_{total} = 1.594 - 1.594 = 0$, and the result would be a reversible process, which is obviously impossible; (e) in a parallel exchanger the heating media could not come out at a lower temperature than 150°. The amount of 200° water required would be

$$\frac{10(150-60)}{200-150} = 18 \text{ lbs.}$$

$$\Delta S = -18\ (0.2938 - 0.2149) = -1.42$$

$$\Delta S_{total} = 1.594 - 1.42 = 0.174.$$

This simple problem illustrates approach to reversibility. The lower the temperature level of the source of the heat that is heating another body or doing work, the more nearly reversible the process is. The change in the entropy for the entire system is an index of this reversibility.

9. In the solution of this problem use equation 6, page 7, which is

$$U_a = 223.7\sqrt{(1-y)(H_1-H_2)}$$

P	t°F.	S	H	ΔH	Velocity, U_a ft./sec.		
					Without Friction		With Friction
300	617	1.6345	1323.4	0			
200	530	1.6345	1280	43.4	1470 x	.95 =	1432
75	320	1.6345	1190	133.4	2580 x	.95 =	2515
25	240	1.6345	1105	218.4	3300 x	.90 =	3130
311 Hg.	115	1.6345	971	352.4	4200 x	.90 =	3990

10. The Carnot Efficiency for the refrigeration (reversed heat engine) cycle is given by equation 40, page 105. For the temperatures involved in this problem the ratio of work required to the heat withdrawn from the cold reservoir, the atmosphere is

$$\frac{W}{Q'} = \frac{70 - 40}{460 + 40} = 0.06$$

The heat delivered to the rooms $Q = W + Q'$
The work required per million Btu. of heat delivered to the rooms is found as follows; $Q' = Q - W = 1,000,000 - W$.

$$\frac{W}{Q'} = \frac{W}{1,000,000-W} = 0.06$$

$W =$ 56,600 Btu. of work/million Btu. of heat delivered

$$W = \frac{56,600}{3415} = 16.6 \text{ KW}/10^6 \text{ Btu. of heat delivered}$$

Since fuel heat cost is \$1.00/million Btu., the minimum cost of electrical energy is $\frac{100}{16.6}$ = 6¢ per KWH

11. The heat that is added to the boiler must be sufficient to maintain the temperature at 444.6°F, the temperature at which steam has a vapor pressure of 400 p.s.i., while the additional boiler feed water is pumped in. Some of the steam in the vapor space may condense. The amount of steam in this space =

$$\frac{100 - (3000)(0.0193)}{1.1609} = 36.2 \text{ lbs. of sat. steam at 400 p.s.i.}$$

Let X = the amount of lbs. of steam allowed to condense when the 2000 lbs. of feed water are added; then

$$(3000 + 2000 + X)\ 0.0193 + (36.2 - X)\ 1.1609 = 100$$
$$X = 33.8 \text{ lbs.}$$

Heat to be added equal the heat required to heat the 2000 lbs. of boiler feed water to 444.6°F. minus heat liberated by condensing 33.8 lbs. of steam

$$Q = 2000\ (424 - 117.9) - (33.8)(780.9) = 585,800 \text{ Btu.}$$

12. Let X = weight per cent of steam from the 100 lb. line; then 100 - X = weight per cent of steam from 120 lb. line. The following heat balance is written on the superheater to solve for X.

$$X\,(1187.3) + (100 - X)(312.46 + 0.900 \times 878.1) + (100)(120) = (100)(1239.1)$$

$$X = 20\%$$

13. The final temperature after mixing is first found by a heat balance as follows:

$$(100)(0.03)(250 - t) = (10)(1.0)(t - 60)$$

$$t = 104°F.$$

$$\Delta S_{lead} = \int \frac{dq}{T} = (100)(0.03)(2.3)\log_{10}\frac{460 + 104}{460 + 250}$$

$$\Delta S_{lead} = -0.69 \text{ Btu./°F.}$$

$$\Delta S_{water} = (10)(1.0)(2.3)\log_{10}\frac{460 + 104}{460 + 60}$$

$$\Delta S_{water} = +0.82$$

$$\Delta S_{system} = +0.82 - 0.69 = 0.13 \text{ Btu./°F.}$$

14. The initial and final conditions are sufficient. The path does not matter, the word polytropic being a "red herring". Use methane Mollier diagram given as Figure 49.

$t_1 = 20°C.$ or $68°F.$; $t_2 = 35°C.$ or $95°F.$

$P_1 = 1$ atm. or 14.7 p.s.i.; $P_2 = 20$ atm. or 294 p.s.i.

$H_1 = 183$ Btu./lb.; $H_2 = 190$ Btu./lb.

$S_1 = 0.904$ Btu./lb.°F.; $S_2 = 0.528$ Btu./lb.°F.

$$\Delta H = H_2 - H_1 = 16(190 - 183) = 112 \text{ Btu./lb. mol}$$

$$\Delta S = S_2 - S_1 = 16(0.528 - 0.904) = -6.01 \text{ Btu./lb. mol.°F.}$$

$$\Delta(PV) = R\,(Z_2T_2 - Z_1T_1) = 1.985\ \ (0.9068)(555) - (0.996)(528)$$

$$\Delta(PV) = 19.9 \text{ Btu./lb.}$$

$$\Delta E = \Delta H - \Delta(PV) = 112 - 19.9 = 92.1 \text{ Btu./lb. mol}$$

The minimum work is the reversible isothermal work or $-W = \Delta F = \Delta H - T\Delta S$ along an isothermal path of 68°F.

15. In solving this problem use equations 139 and 140 from page 140, finding values of γ from Figure 40. An average value of γ (computed at the average temperature) should be used in calculating the horsepower and outlet temperature. The determination of the outlet temperature and the average

value of γ is a successive approximation type of calculation.

Assume $\gamma = 1.2$

$$T_2 = (460 + 80)\left(\frac{20}{1}\right)^{\frac{0.2}{1.2}} = 890°R = 430°F.$$

$$\text{Average temperature} = \frac{80 + 430}{2} = 255°F. = 715°R.$$

$$\text{Average pressure} = \frac{14.7 + 294}{2} = 154 \text{ p.s.i.}$$

	T_c°R.	P_c P.s.i.	T_R	P_R	γ	Mol Fraction	γ x M.f.
Methane	344	673	2.08	0.229	1.25	.333	.416
Ethane	550	712	1.30	0.216	1.175	.333	.391
Propane	666	617	1.07	0.250	1.148	.333	.382
						1.000	1.199, which checks assumption.

Using arithmetic average temperatures and pressures is not strictly correct. Integrated averages should be used or, better still, Mollier Diagrams should be used.

(a) $$\text{Theo. H.P.} = \frac{144}{33,000}\ 14.7 \times \frac{1,000,000}{60}\,\frac{1.20}{0.20}\left[\left(\frac{20}{1}\right)^{\frac{0.20}{1.20}} - 1\right]$$

Theo. H.P. = 4130 for single stage compression.

(b) Outlet temperature = 430°F. for single stage compression. Multistaging with intercooling would lower outlet temperature and work of compression.

A more accurate solution would be to take the gas up to the higher pressure by smaller jumps, finding the temperature and γ value for each, and then using an integrated average γ in solving for the theoretical horsepower.

16. The first part of this problem is identical to the last problem except that it is for expansion rather than compression.

Assume $\gamma = 1.10$

$$T_2 = (460 + 600)\left(\frac{30}{300}\right)^{\frac{0.10}{1.10}} = 860°R \text{ or } 400°F.$$

$$\text{average } t = \frac{600 + 400}{2} = 500°F. \text{ or } 960°R.$$

$$\text{average } P = \frac{300 + 30}{2} = 165 \text{ p.s.i.}$$

	T_c°F.	P_c P.s.i.	T_R	P_R	γ	Mol Fraction	γ x M.f.
Ethane	550	712	1.75	0.232	1.13	0.20	0.225
Propane	666	617	1.44	0.267	1.10	0.30	0.330
Butane	766	550	1.25	0.300	1.09	0.50	0.545
						1.00	1.100, which checks assumed value.

Compute enthalpies at initial and final conditions, using Figures 47 and 48.

	m.f.	Lbs./ Mol	Wt. fr.	H at 600°F. and 300 psi		H at 400°F. and 30 psi	
				H	H x w.f.	H	H x w.f.
Ethane	0.20	6.0	0.1245	479	59.5	352	43.8
Propane	0.30	13.2	0.2735	449	123.0	337	92.0
Butane	0.50	29.0	0.6020	430	259.0	329	198.0
	1.00	48.2	1.0000		441.5		333.8

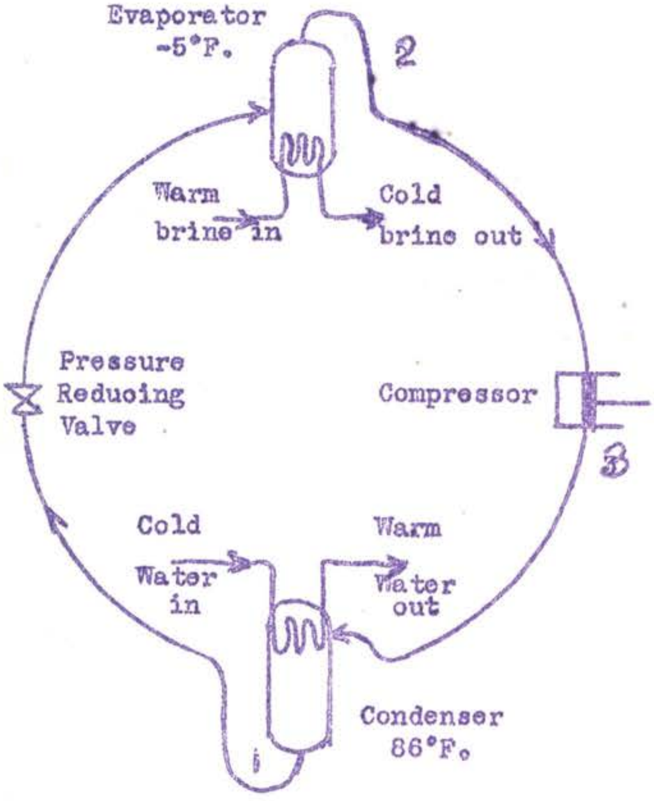
Actual $\Delta H = 441.5 - 333.8 = 107.7$ Btu./lb.
Effective $\Delta H = (1.00-0.15)(107.7) = 91.5$ Btu./lb.

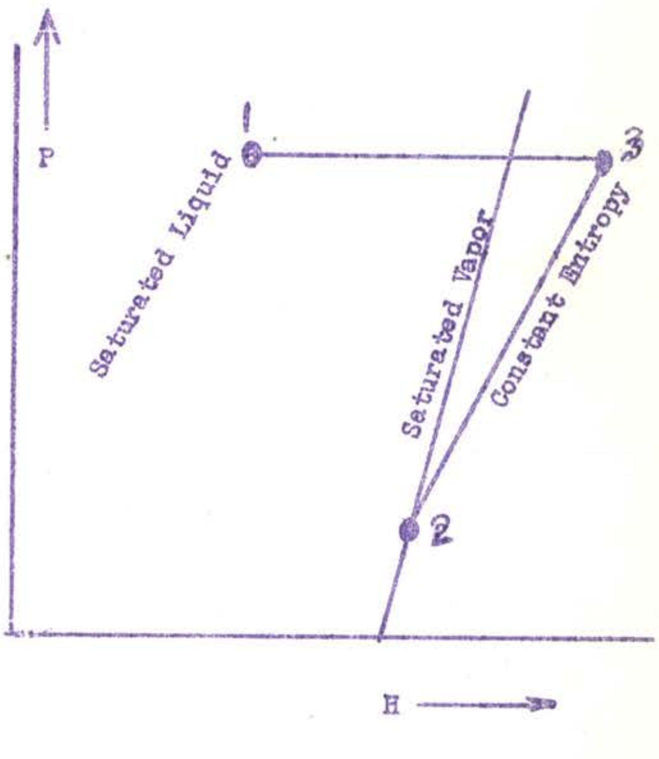
The velocity after expansion $= 223.7\sqrt{91.5} = 2140$ feet/sec.

The quantity of gas required to generate 100 KWH $= \dfrac{3415 \times 100}{91.5}$

$= 3730$ lbs. of gas/hr.

17. The refrigeration cycle with which this problem is concerned is shown in the following sketches, one being a flow diagram and the other a Mollier diagram.





The following readings are made from Figures 50 and 55:

Point	Propane (Fig. 50)			Plt. Propane (Fig. 55)		
	1	2	3	1	2	3
Temp., °F.	86	-5	100	86	-5	123
Press., p.s.i. Abs.	155	35.8	155	211	38.2	211
Enthalpy, Btu./lb.	158	276.5	307	159	277	312

Using these data the following computations are made:

	Propane	Plant Propane
Refrigeration, Btu./lb. of Refrigerant	118.5	118
Work, Btu./lb. of Refrigerant	30.5	35
Coefficient of Performance	3.88	3.37
Lbs. of Refrigerant/Ton of Refrigeration	101.1	101.8
Theo. Horsepower/Ton of Refrigeration	1.21*	1.40
Tons/KW	1.105**	0.958

* $\frac{30.5 \times 101.1}{2547} = 1.21$, ** $\frac{118.5 \times 3415}{30.5 \times 12{,}000} = 1.105$

In order to compute the volumetric efficiency by equation 143 (page 140), a value of γ must be found for each refrigerant. This may be found from Figure 40 or it may be found from equation 140, knowing the change in temperature during compression for each gas from the Mollier Diagram readings. This latter way will make the calculation of volumetric efficiency more consistent with the other calculations and will be used here. The volumetric efficiencies are computed below:

Propane

$$\frac{560}{455} = \frac{155}{35.8}^{\frac{\gamma-1}{\gamma}}$$

$$1.23 = 4.33^{\frac{\gamma-1}{\gamma}}$$

$$\frac{\gamma-1}{\gamma} = 0.141$$

$$\gamma = 1.165$$

$$E_v = \left[1.0+0.10-0.10(4.33)^{\frac{1}{1.165}}\right]$$

$$E_v = 0.748$$

Plant Propane

$$\frac{583}{455} = \frac{211}{38.2}^{\frac{\gamma-1}{\gamma}}$$

$$1.28 = 5.52^{\frac{\gamma-1}{\gamma}}$$

$$\frac{\gamma-1}{\gamma} = 0.1445$$

$$\gamma = 1.17$$

$$E_v = \left[1.0+0.10-0.10(5.52)^{\frac{1}{1.17}}\right]$$

$$E_v = 0.669$$

From the above calculations it can be seen that propane is superior to plant propane as a refrigerant, both as regards the amount of refrigeration produced per unit of work as indicated by the coefficient of performance and as regards capacity, as indicated by the volumetric efficiency.

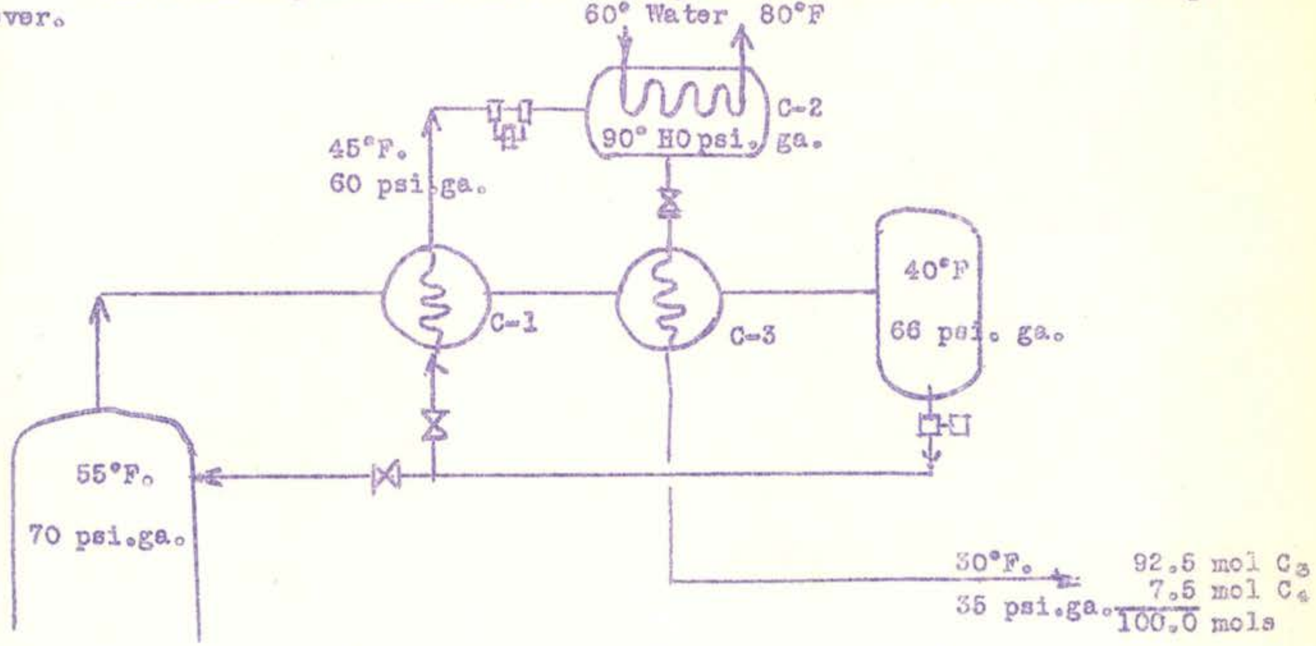
18. For the purposes of the problem, assume that the net overhead productsis 100 mols per hour. The total condensing duty for 100 mols of net overhead product with a 5:1 reflux ratio is computed using Figures 50 and 52.

	Net Ovhd.		Reflux	Total	Enthalpies Btu./lb.			
	Mols	Lbs.	Lbs.	Lbs.	Vap. at 55°F. & 85 psi. Abs.	Liq. at 40°F.	ΔH	Btu./Hour
C_3	92.5	4074	20,400	24,475	294	128	166	4,050,000
C_4	7.5	435	2,180	2,615	293	124	169	441,000
	100.0	4510	22,580	27,090				4,491,000

The cooling necessary to condense the net overhead alone is 1/6 of this amount or 750,000 Btu. hr.

It is obviously impossible to remove enough heat by expansion of the net overhead product through a heat exchanger as shown, to condense more than the overhead itself, and this would leave no reflux. The successful operation of such a system is in contradiction with the second law of thermodynamics. Heat must be removed by some separate medium such as water. Very little can be gained by expanding to net overhead to sub atmospheric pressures.

The following modification of this system will come closer to working, however.



In this system the net overhead is used to cool the total overhead in two stages by being evaporated in an exchanger C-1, compressed and then condensed in C-2, and finally evaporated in a second exchanger C-3. After leaving C-1, the net overhead will be vapor at 45°F. and 60 p.s.i. ga. (dew point); in C-2, it will be liquid at 90°F. and 140 p.s.i. ga. (bubble point); leaving C-3 it will be vapor at 30°F. and 35 p.s.i. ga. (dew point).

Evaporator, C-1, Duty:

4075(289.5-128)+435(289.5-124) = 730,000 Btu./hr.

Compressor Duty:

$$4075\ \frac{(303.5-289.5)\ +\ 435\ (328-289{,}5)}{2547} = 29 \text{ Theo. horsepower}$$

Condenser, C-2, Duty:

4074 (303.5-160) + 435 (328-150) = 662,500 Btu./hr. to water

Evaporator C-3 Duty:

4075 (286-160) + 435 (285-150) = 572,700 Btu./hr.

The total amount of heat removed from the total overhead (product plus reflux) = 730,000 + 572,700 = 1,302,700 Btu./hr., which would result in a reflux ratio of

$$\frac{1{,}302{,}700}{750{,}000} = 1.73:1.$$

This is better than the original scheme but still not the desired 5:1. If the overhead product is to be used as the refrigerant, it would be necessary to circulate at a higher rate than the production rate. This could be done by recycling.

19. The solution of this problem involves the use of calculus. Take as a basis 100 gallons of oil at -30°F.

Let: W_o = lbs. of oil = 100 x 6.951 x 1.055 = 733 lbs.
W_p = lbs. of propane left at end = 200 x 4.8 = 960 lbs.
W = lbs. of mixture = 1693 lbs.
X = lbs. of propane to be evaporated
dX = differential of amount of propane vaporized
L_p = latent heat of propane (function of temperature).
C_o = specific heat of oil
C_p = specific heat of propane
t = temperature

at any given time

$$L_p dX = W_o C_o dt + W_p C_p dt + X C_p dt$$

Use a mean specific heat, C_m, for the final oil and propane mixture.

$$L_p dX = (WC_m + XC_p)\ dt$$

$$\frac{dX}{WC_m + XC} \qquad \frac{dt}{L_p}$$

Integrating from $X = 0$ to $X = X$ and $t = -30$ to $t = 90^{0}F$.

$$\frac{1}{C_p} \ln \frac{WC_m \quad XC_p}{WC_m} = \int_{-30}^{90} \frac{dt}{L_p} \tag{a}$$

The first integration can be handled in this way alright but the second must be performed graphically. This will be done by plotting $^1/L_p$ vs. t and integrating graphically. Plotting $^1/L$ computed from Figure 50 vs. t°F and weighted over the temperature range of -30 to 90°F. gives an average value of $^1/L_p$ of 0.0063. In solving the above equation for X, a weighted value of C_p should be used also. This is estimated from Figure 50 to be 0.56 by graphically integrating the saturated liquid line from -30 to 90°F. The average specific heat for the oil, C_o, is estimated in like manner to be 0.44.

$$WC_m = (733)\ (0.44) + (1693)(0.56) = 860$$

Substituting in equation (a) and solving for X

$$\frac{1}{0.56} \ln\left(\frac{860 + 0.56X}{860}\right) = (0.0063)(90 + 30)$$

$$\log_{10} \frac{860 + 0.56X}{860} = \frac{(0.0063)\ (120)(0.56)}{2.3} = 0.184$$

$$\frac{860 + 0.56X}{860} = 1.53$$

X = 815 lbs. of propane evaporated.

	Lbs.	%
Total Propane in Original = 815+960 =	1775	70.6
Oil	733	29.4
Total	2508	100.0

III

REPRINTS OF PUBLICATIONS

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Thermodynamic Properties of Methane

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Specific heats at constant pressure, differences in specific heats, Joule-Thomson coefficients, entropy, and enthalpy are computed for methane for pressures of 1 to 120 atmospheres and for temperatures of −70° to 200° C. This work is based on the *P-V-T* data of Kvalnes and Gaddy and of Keyes and Burks, and on the specific heat at constant-pressure data at 1 atmosphere of Eucken and Lüde.

Data on these thermodynamic properties are presented, and from them the specific volume, internal energy, Gibbs free energy, and Helmholtz free energy may be calculated also. Plots of the volume residual, α vs. T isobars, C_p vs. T isobars, $C_p - C_v$ vs. T isobars, and the Joule - Thomson coefficient, μ vs. T isobars are also presented.

PHYSICAL and thermal properties of petroleum hydrocarbons and their mixtures are desired as aids in developing petroleum refining operations and in designing equipment. The use of thermodynamics is increasing and with it the demand for more data on the thermodynamic properties of the petroleum hydrocarbons. Without data, thermodynamics is powerless. Such data are especially useful in the development and design of cracking and polymerization processes.

Problems encountered in petroleum refining are generally concerned with complex hydrocarbon mixtures rather than individual hydrocarbons. Because of pressing necessity, work has been concentrated on these complex mixtures. It is believed that more knowledge of the behavior of isolated hydrocarbons will alleviate the task of studying their behavior in mixtures. When more is known about the deviation of hydrocarbon solutions from ideal solutions, it should be possible to piece together the information on individual hydrocarbons and estimate the desired properties of mixtures.

Therefore the study of individual hydrocarbons has been undertaken with two purposes—to make available thermodynamic data for one-component hydrocarbon system and to prepare a background which will assist in the preparation of thermodynamic data for multicomponent hydrocarbon systems. This paper deals with the first hydrocarbon of the normal paraffin series and an important constituent of natural gas.

Scope of Calculations

The following properties of methane were calculated from the compressibility and specific heat data: volume residual quantity, α; change with pressure of specific heat, C_p, at constant pressure; difference in specific heats at constant pressure, C_p, and constant volume, C_v; Joule-Thomson coefficient, μ; entropy, S; and enthalpy, H.

By means of Table I which lists these properties, the following additional properties may be computed: specific volume; internal energy, E; Gibbs free energy, F; Helmholtz free energy, A.

The data on which this work is based are the compressibility data of Kvalnes and Gaddy (*7*) from −70° to 200° C., the compressibility data of Keyes and Burks (*6*) from 0° to 200° C., and the specific heat at constant pressure of Eucken and Lüde (*5*) at 1 atmosphere from 24.6° to 208.1° C. The pressure range of the pressure-volume-temperature data of Keyes and Burks is 10 to 40 atmospheres; for the data of Kvalnes and Gaddy it is from 1 to 1000 atmospheres. The data are in good agreement in this overlapping region and were therefore considered a reliable basis for this work. The specific heat data of Eucken and Lüde, obtained by a "precision adiabatic expansion method," were considered the most reliable basis for the work. The reference state chosen was 25° C. and 1 atmosphere pressure. At this point the data are more accurately known than at other points.

Calculation of Thermal Properties

The following equations, which were used in calculating the thermal properties, are based on the first and second laws of thermodynamics and are developed in many textbooks; hence their derivations have been omitted here.

Change of specific heat with pressure:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P \tag{1}$$

Difference in specific heats:

$$C_p - C_v = -T\,\frac{\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} \tag{2}$$

Joule-Thomson coefficient:

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

Entropy:

$$dS = \frac{C_p}{T}\,dT - \left(\frac{\partial V}{\partial T}\right)_P dP \tag{4}$$

Enthalpy:

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

The departure from the perfect gas laws is shown by values of the residual quantity which by definition is:

$$\alpha = \frac{RT}{P} - V \tag{6}$$

Calculations of the additional properties mentioned can be made by Equations 7 to 9.

Internal energy:

$$E = H - PV \tag{7}$$

Gibbs free energy:

$$F = H - TS \tag{8}$$

Helmholtz free energy:

$$A = F - PV \tag{9}$$

The volume, V, can be calculated from smoothed values of α given in Table I. Values of α instead of V are presented because it is easier to interpolate for α.

Bahlke and Kay (*1*) calculated thermal properties for a naphtha analytically by finding an empirical equation that fitted the experimental P-V-T data over the range that they were studying. Difficulties are encountered in this method when it is applied over wide ranges. Because of the difficulty in obtaining an accurate equation of state which will hold over the wide ranges covered by the experimental compressi-

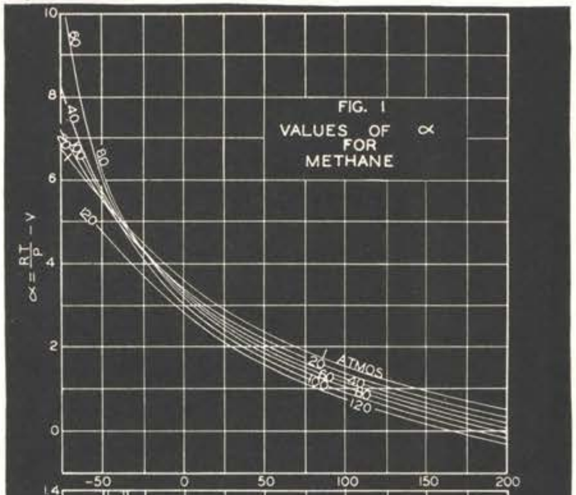
FIG. 1
VALUES OF α FOR METHANE

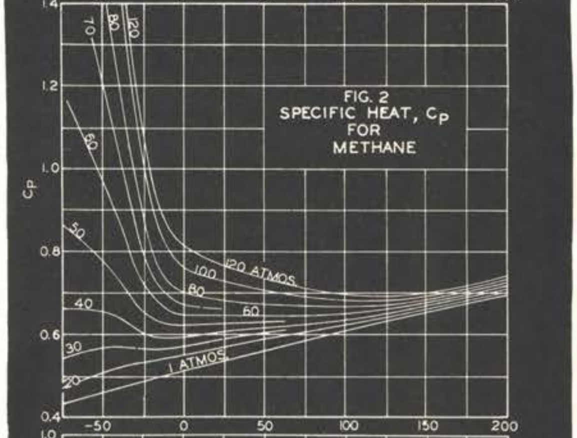
FIG. 2
SPECIFIC HEAT, C_P FOR METHANE

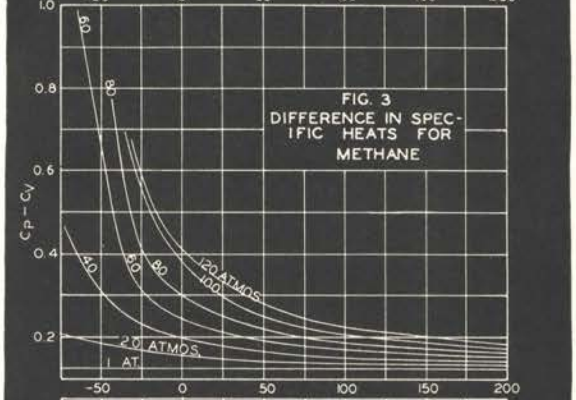
FIG. 3
DIFFERENCE IN SPECIFIC HEATS FOR METHANE

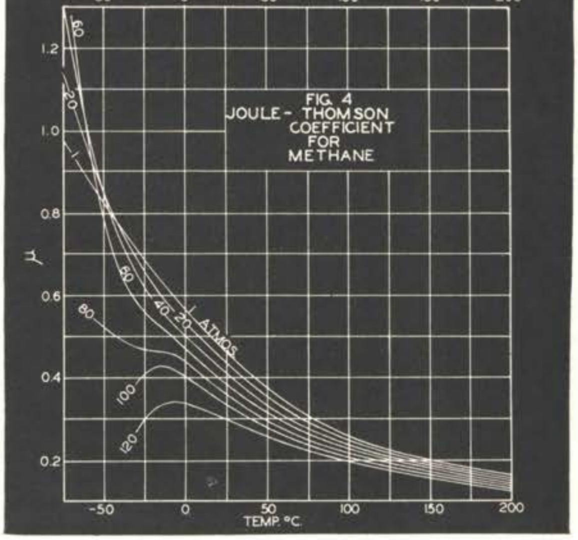
FIG. 4
JOULE - THOMSON COEFFICIENT FOR METHANE

Table I. Properties of Methane

t ° *C.*	*P* *Atm.*	α *Cc./g.*	C_p	$C_p - C_v$	μ *°C./atm.*	*S* *G.-cal./g.°C.*	*H* *G.-cal./g.*
−70	1	6.51	0.440	0.128	0.948	−0.187	−46.0
	10	6.61	0.454	0.156	0.998	−0.482	−49.7
	20	6.83	0.482	0.204	1.096	−0.584	−54.8
	30	7.18	0.548	0.295	1.185	−0.653	−60.5
	40	7.71	0.665	0.443	1.209	−0.716	−67.6
	50	8.45	0.848	0.732	1.240	−0.778	−76.7
−60	1	6.00	0.451	0.127	0.887	−0.166	−41.6
	10	6.03	0.468	0.153	0.920	−0.460	−45.2
	20	6.12	0.497	0.194	0.968	−0.560	−49.8
	30	6.29	0.558	0.264	1.020	−0.627	−55.1
	40	6.59	0.662	0.369	1.016	−0.684	−61.1
	50	7.00	0.816	0.578	1.008	−0.739	−68.5
	60	7.55	1.061	0.898	0.986	−0.797	−77.8
−50	1	5.53	0.462	0.127	0.827	−0.145	−38.0
	10	5.49	0.481	0.150	0.847	−0.438	−40.2
	20	5.49	0.511	0.185	0.855	−0.537	−44.8
	30	5.57	0.567	0.240	0.866	−0.606	−50.0
	40	5.72	0.656	0.308	0.852	−0.658	−55.5
	50	5.91	0.779	0.437	0.840	−0.706	−61.4
	60	6.13	0.970	0.660	0.787	−0.754	−68.5
−40	1	5.09	0.473	0.127	0.770	−0.124	−32.7
	10	5.02	0.492	0.148	0.775	−0.416	−35.4
	20	4.98	0.523	0.177	0.765	−0.514	−39.7
	30	4.98	0.570	0.220	0.754	−0.577	−43.8
	40	5.03	0.638	0.265	0.735	−0.626	−48.1
	50	5.10	0.730	0.347	0.714	−0.669	−53.0
	60	5.18	0.867	0.445	0.651	−0.710	−58.4
	80	5.27	1.213	0.672	0.495	−0.786	−70.4
−30	1	4.67	0.483	0.127	0.716	−0.104	−28.0
	10	4.59	0.503	0.145	0.709	−0.396	−30.7
	20	4.53	0.531	0.171	0.690	−0.492	−34.4
	30	4.50	0.566	0.205	0.670	−0.553	−38.2
	40	4.49	0.610	0.239	0.652	−0.600	−42.0
	50	4.50	0.673	0.286	0.628	−0.640	−47.1
	60	4.53	0.761	0.338	0.577	−0.676	−50.4
	80	4.56	0.967	0.465	0.475	−0.741	−59.4
	100	4.37	1.131	0.627	0.387	−0.797	−67.6
	120	3.95	1.202	0.658	0.272	−0.842	−75.7
−20	1	4.28	0.493	0.126	0.665	−0.084	−22.4
	10	4.19	0.513	0.143	0.649	−0.375	−25.6
	20	4.12	0.536	0.166	0.628	−0.471	−29.0
	30	4.08	0.564	0.194	0.608	−0.530	−32.5
	40	4.06	0.597	0.219	0.590	−0.575	−35.8
	50	4.05	0.639	0.253	0.580	−0.613	−39.4
	60	4.04	0.689	0.290	0.539	−0.647	−43.1
	80	4.03	0.801	0.376	0.467	−0.705	−50.6
	100	3.85	0.907	0.509	0.422	−0.756	−58.5
	120	3.55	0.966	0.537	0.322	−0.799	−64.9
−10	1	3.92	0.504	0.126	0.616	−0.065	−18.0
	10	3.82	0.522	0.141	0.596	−0.355	−20.1
	20	3.74	0.542	0.161	0.574	−0.450	−23.8
	30	3.70	0.566	0.184	0.557	−0.508	−26.6
	40	3.68	0.594	0.206	0.545	−0.552	−29.7
	50	3.66	0.624	0.234	0.534	−0.590	−33.4
	60	3.64	0.654	0.261	0.507	−0.621	−36.4
	80	3.58	0.723	0.330	0.461	−0.675	−43.0
	100	3.41	0.803	0.430	0.424	−0.723	−50.1
	120	3.16	0.858	0.461	0.340	−0.762	−55.9
0	1	3.60	0.514	0.126	0.570	−0.046	−13.0
	10	3.49	0.531	0.139	0.548	−0.336	−15.1
	20	3.41	0.551	0.157	0.527	−0.429	−18.1
	30	3.35	0.572	0.175	0.514	−0.488	−21.2
	40	3.32	0.595	0.198	0.503	−0.532	−24.2
	50	3.30	0.621	0.220	0.493	−0.567	−27.3
	60	3.28	0.646	0.243	0.469	−0.598	−30.3
	80	3.19	0.699	0.300	0.440	−0.650	−36.1
	100	3.03	0.762	0.380	0.403	−0.695	−42.5
	120	2.81	0.813	0.410	0.338	−0.734	−48.4
10	1	3.30	0.524	0.126	0.525	−0.027	− 7.6
	10	3.18	0.510	0.138	0.503	−0.316	− 9.6
	20	3.10	0.559	0.154	0.485	−0.409	−12.6
	30	3.05	0.579	0.170	0.472	−0.466	−15.2
	40	3.01	0.600	0.190	0.461	−0.509	−18.0
	50	2.98	0.624	0.210	0.450	−0.544	−20.8
	60	2.95	0.646	0.227	0.431	−0.574	−23.5
	80	2.84	0.690	0.276	0.406	−0.624	−29.0
	100	2.69	0.745	0.340	0.375	−0.667	−34.7
	120	2.50	0.791	0.375	0.324	−0.705	−40.3
20	1	3.03	0.533	0.126	0.484	−0.009	− 2.5
	10	2.91	0.549	0.137	0.463	−0.297	− 4.2
	20	2.82	0.568	0.151	0.447	−0.390	− 7.1
	30	2.77	0.587	0.165	0.433	−0.447	− 9.6
	40	2.72	0.606	0.182	0.422	−0.488	−12.0
	50	2.69	0.626	0.200	0.412	−0.523	−14.8
	60	2.65	0.646	0.215	0.397	−0.552	−17.3
	80	2.55	0.684	0.258	0.375	−0.600	−22.2
	100	2.40	0.733	0.308	0.348	−0.643	−27.8
	120	2.23	0.775	0.345	0.305	−0.679	−32.8
30	1	2.78	0.543	0.126	0.445	+0.009	+ 2.9
	10	2.66	0.558	0.135	0.425	−0.279	+ 1.2
	20	2.58	0.575	0.148	0.410	−0.371	− 1.4
	30	2.52	0.593	0.161	0.398	−0.427	− 3.7
	40	2.47	0.610	0.176	0.388	−0.468	− 6.0
	50	2.43	0.628	0.193	0.378	−0.502	− 8.5
	60	2.39	0.645	0.205	0.365	−0.531	−11.0
	80	2.28	0.680	0.243	0.347	−0.578	−15.6
	100	2.14	0.723	0.284	0.323	−0.619	−20.7
	120	1.99	0.762	0.320	0.289	−0.653	−25.1
40	1	2.56	0.553	0.126	0.407	+0.027	8.4
	10	2.45	0.566	0.135	0.390	−0.260	7.0
	20	2.36	0.582	0.146	0.377	−0.352	4.6
	30	2.30	0.598	0.158	0.366	−0.408	+ 2.1
	40	2.25	0.613	0.170	0.358	−0.448	+ 0.2
	50	2.20	0.629	0.185	0.349	−0.481	− 1.9
	60	2.16	0.644	0.197	0.338	−0.510	− 4.5
	80	2.05	0.675	0.230	0.321	−0.555	− 8.5
	100	1.92	0.715	0.265	0.300	−0.595	−13.3
	120	1.78	0.749	0.299	0.273	−0.628	−17.4
50	1	2.36	0.562	0.126	0.374	+0.044	14.0
	10	2.25	0.574	0.134	0.359	−0.243	12.5
	20	2.17	0.588	0.144	0.348	−0.334	10.2
	30	2.11	0.602	0.155	0.339	−0.389	8.1
	40	2.05	0.616	0.165	0.331	−0.429	6.1
	50	2.00	0.631	0.179	0.324	−0.462	4.1
	60	1.95	0.644	0.190	0.312	−0.489	+ 2.1
	80	1.84	0.672	0.218	0.297	−0.535	− 2.1
	100	1.72	0.707	0.249	0.279	−0.572	− 6.1
	120	1.58	0.737	0.280	0.258	−0.605	−10.0
60	1	2.17	0.572	0.125	0.344	0.061	19.7
	10	2.07	0.582	0.133	0.330	−0.225	18.5
	20	1.98	0.595	0.142	0.320	−0.316	16.1
	30	1.93	0.607	0.152	0.314	−0.370	14.4
	40	1.87	0.620	0.162	0.307	−0.410	12.5
	50	1.82	0.633	0.175	0.300	−0.442	10.6
	60	1.77	0.644	0.185	0.290	−0.470	8.5
	80	1.66	0.670	0.208	0.275	−0.514	4.7
	100	1.54	0.700	0.236	0.260	−0.551	1.0
	120	1.41	0.727	0.265	0.244	−0.582	− 2.6
70	1	2.00	0.581	0.125	0.316	+0.079	25.5
	10	1.89	0.590	0.132	0.305	−0.208	24.5
	20	1.81	0.601	0.140	0.298	−0.298	22.3
	30	1.75	0.612	0.150	0.290	−0.352	20.5
	40	1.70	0.624	0.158	0.284	−0.392	18.7
	50	1.64	0.636	0.170	0.279	−0.424	16.7
	60	1.59	0.646	0.180	0.270	−0.450	15.1
	80	1.48	0.668	0.200	0.256	−0.494	11.5
	100	1.36	0.694	0.225	0.244	−0.530	8.0
	120	1.24	0.718	0.253	0.230	−0.561	4.5
80	1	1.84	0.590	0.125	0.292	+0.096	31.5
	10	1.74	0.599	0.132	0.284	−0.190	30.5
	20	1.65	0.608	0.139	0.276	−0.281	28.2
	30	1.59	0.618	0.148	0.271	−0.335	26.5
	40	1.54	0.628	0.155	0.266	−0.374	24.8
	50	1.48	0.639	0.166	0.260	−0.406	23.2
	60	1.43	0.648	0.175	0.252	−0.432	21.4
	80	1.32	0.668	0.195	0.240	−0.475	18.1
	100	1.20	0.690	0.217	0.229	−0.509	15.3
	120	1.08	0.709	0.243	0.218	−0.540	11.8
90	1	1.69	0.600	0.125	0.274	+0.112	37.4
	10	1.59	0.607	0.131	0.265	−0.173	36.6
	20	1.50	0.616	0.138	0.259	−0.264	34.6
	30	1.44	0.624	0.146	0.254	−0.317	32.9
	40	1.39	0.633	0.153	0.250	−0.356	31.3
	50	1.33	0.642	0.163	0.244	−0.388	29.7
	60	1.28	0.650	0.171	0.237	−0.414	28.1
	80	1.18	0.668	0.190	0.226	−0.456	24.9
	100	1.06	0.685	0.210	0.216	−0.490	22.1
	120	0.93	0.703	0.234	0.207	−0.520	19.1
100	1	1.55	0.609	0.125	0.256	+0.129	43.3
	10	1.45	0.615	0.131	0.249	−0.158	42.4
	20	1.37	0.623	0.137	0.244	−0.247	40.4
	30	1.30	0.630	0.145	0.239	−0.300	39.0
	40	1.24	0.638	0.151	0.235	−0.339	37.4
	50	1.19	0.646	0.160	0.230	−0.370	36.0
	60	1.14	0.653	0.168	0.224	−0.396	35.0
	80	1.04	0.668	0.186	0.215	−0.438	31.6
	100	0.92	0.684	0.205	0.206	−0.472	28.9
	120	0.80	0.698	0.225	0.197	−0.501	26.0
110	1	1.42	0.618	0.125	0.243	+0.145	49.7
	10	1.32	0.623	0.130	0.236	−0.140	48.8
	20	1.24	0.630	0.137	0.231	−0.231	47.0
	30	1.18	0.637	0.144	0.226	−0.283	45.5
	40	1.12	0.644	0.150	0.222	−0.322	43.9
	50	1.06	0.650	0.158	0.218	−0.353	42.4
	60	1.00	0.656	0.165	0.213	−0.379	40.9
	80	0.90	0.670	0.183	0.205	−0.420	38.5
	100	0.78	0.682	0.200	0.197	−0.453	36.0
	120	0.66	0.695	0.220	0.188	−0.482	33.2

TABLE I. (*Concluded*)

t °C.	P Atm.	α Cc./g.	C_p	$C_p - C_v$	μ °C./atm.	S G.-cal./g.°C.	H G.-cal./g.
120	1	1.30	0.627	0.125	0.229	+0.160	55.6
	10	1.20	0.632	0.130	0.224	−0.124	55.0
	20	1.13	0.638	0.136	0.220	−0.214	53.5
	30	1.06	0.644	0.143	0.215	−0.266	52.5
	40	1.00	0.649	0.149	0.211	−0.304	51.0
	50	0.93	0.655	0.156	0.207	−0.336	49.1
	60	0.87	0.662	0.163	0.202	−0.362	47.8
	80	0.78	0.673	0.180	0.196	−0.402	45.3
	100	0.66	0.682	0.195	0.189	−0.436	42.5
	120	0.54	0.694	0.214	0.180	−0.464	40.3
130	1	1.19	0.636	0.125	0.219	+0.176	62.2
	10	1.09	0.640	0.130	0.214	−0.108	61.5
	20	1.02	0.645	0.136	0.209	−0.198	60.0
	30	0.94	0.650	0.142	0.205	−0.250	58.5
	40	0.88	0.655	0.148	0.201	−0.287	57.4
	50	0.82	0.660	0.155	0.197	−0.319	55.8
	60	0.76	0.665	0.161	0.194	−0.345	54.3
	80	0.66	0.675	0.176	0.187	−0.385	52.0
	100	0.55	0.684	0.191	0.180	−0.419	49.3
	120	0.42	0.694	0.209	0.172	−0.446	47.3
140	1	1.08	0.644	0.125	0.210	+0.192	68.5
	10	0.98	0.648	0.130	0.205	−0.092	68.0
	20	0.91	0.653	0.135	0.200	−0.182	66.5
	30	0.84	0.658	0.141	0.196	−0.233	65.2
	40	0.77	0.662	0.147	0.193	−0.271	64.0
	50	0.70	0.666	0.154	0.189	−0.303	62.4
	60	0.64	0.671	0.159	0.184	−0.328	61.2
	80	0.55	0.679	0.174	0.179	−0.368	59.0
	100	0.44	0.688	0.188	0.172	−0.401	56.7
	120	0.32	0.697	0.205	0.165	−0.429	54.2
150	1	0.98	0.653	0.125	0.200	+0.208	74.9
	10	0.88	0.656	0.129	0.196	−0.078	74.4
	20	0.80	0.661	0.135	0.192	−0.166	73.0
	30	0.73	0.665	0.140	0.188	−0.218	71.6
	40	0.66	0.669	0.145	0.185	−0.256	70.3
	50	0.60	0.673	0.152	0.181	−0.287	69.3
	60	0.54	0.677	0.157	0.177	−0.312	68.1
	80	0.44	0.685	0.171	0.172	−0.352	65.8
	100	0.33	0.693	0.185	0.165	−0.385	63.4
	120	0.20	0.702	0.201	0.157	−0.412	61.3
160	1	0.88	0.662	0.124	0.193	+0.224	81.8
	10	0.78	0.665	0.129	0.189	−0.061	81.4
	20	0.71	0.669	0.134	0.184	−0.149	80.1
	30	0.64	0.673	0.139	0.180	−0.201	79.1
	40	0.56	0.677	0.144	0.176	−0.238	77.8
	50	0.50	0.680	0.151	0.173	−0.270	76.5
	60	0.44	0.685	0.156	0.170	−0.294	75.6
	80	0.34	0.693	0.169	0.164	−0.335	73.0
	100	0.23	0.700	0.188	0.157	−0.368	70.7
	120	0.10	0.708	0.199	0.150	−0.395	68.7
170	1	0.78	0.670	0.124	0.185	+0.238	88.0
	10	0.68	0.673	0.128	0.181	−0.046	88.2
	20	0.61	0.677	0.134	0.177	−0.133	87.1
	30	0.54	0.681	0.139	0.173	−0.185	86.0
	40	0.46	0.685	0.143	0.169	−0.222	85.0
	50	0.40	0.689	0.150	0.165	−0.254	83.8
	60	0.34	0.693	0.155	0.161	−0.278	82.6
	80	0.24	0.700	0.166	0.155	−0.319	80.2
	100	0.13	0.708	0.180	0.150	−0.351	78.1
	120	0.0	0.716	0.195	0.144	−0.379	75.7
180	1	0.68	0.679	0.124	0.178	+0.252	95.0
	10	0.58	0.682	0.128	0.174	−0.031	95.1
	20	0.51	0.686	0.133	0.170	−0.118	94.3
	30	0.44	0.690	0.138	0.166	−0.169	93.2
	40	0.37	0.694	0.142	0.162	−0.205	92.2
	50	0.30	0.698	0.149	0.158	−0.237	91.0
	60	0.24	0.700	0.154	0.154	−0.262	90.0
	80	0.14	0.710	0.165	0.149	−0.302	87.6
	100	0.04	0.717	0.177	0.144	−0.334	85.7
	120	−0.10	0.724	0.192	0.136	−0.362	83.3
190	1	0.58	0.688	0.124	0.170	+0.268	101.8
	10	0.48	0.691	0.128	0.167	−0.016	102.2
	20	0.42	0.694	0.133	0.163	−0.102	101.2
	30	0.34	0.698	0.138	0.159	−0.153	100.6
	40	0.28	0.702	0.141	0.155	−0.189	99.4
	50	0.21	0.707	0.148	0.150	−0.221	98.3
	60	0.15	0.711	0.153	0.146	−0.246	97.4
	80	0.04	0.720	0.163	0.141	−0.286	94.9
	100	−0.06	0.726	0.175	0.136	−0.318	93.2
	120	−0.20	0.733	0.189	0.130	−0.345	91.1
200	1	0.49	0.696	0.124	0.164	+0.283	108.2
	10	0.40	0.699	0.128	0.160	0.0	109.0
	20	0.32	0.703	0.132	0.156	−0.087	108.3
	30	0.25	0.707	0.137	0.151	−0.139	107.3
	40	0.18	0.711	0.142	0.148	−0.176	106.0
	50	0.12	0.716	0.147	0.143	−0.206	105.3
	60	0.06	0.720	0.152	0.139	−0.231	104.3
	80	−0.05	0.729	0.161	0.134	−0.270	102.2
	100	−0.16	0.736	0.173	0.129	−0.302	100.4
	120	−0.28	0.742	0.186	0.123	−0.329	98.8

bility data of methane, graphical methods of differentiation and integration were used throughout.

Deming and Shupe (*3*) used graphical methods in computing the physical properties of nitrogen, carbon monoxide, and hydrogen, obtaining the derivatives of the volume from the corresponding derivatives of the residual quantities. They also used residual quantities to smooth and extrapolate compressibility data. These methods are applied here to methane.

As pointed out by Deming and Shupe, it is difficult to measure the curvature of the V vs. T isobars because they are nearly straight. From a plot of the residual quantity, α, their curvatures could easily be determined. Rearranging and differentiating Equation 6 we obtain:

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} - \left(\frac{\partial \alpha}{\partial T}\right)_P \tag{10}$$

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_P = -\left(\frac{\partial^2 \alpha}{\partial T^2}\right)_P \tag{11}$$

$$\left(\frac{\partial V}{\partial P}\right)_T = -\left[\frac{RT}{P^2} + \left(\frac{\partial \alpha}{\partial P}\right)_T\right] \tag{12}$$

The residual quantity, α, of Equation 6 was calculated from the experimental data of Kvalnes and Gaddy (*7*) and of Keyes and Burks (*6*); Figure 1 is a plot of α vs. T isobars. Values of α in Table I are smoothed values taken from a large-scale copy of Figure 1. The units of α are the same as the units of the volume in cubic centimeters per gram. The derivatives $\left(\frac{\partial \alpha}{\partial T}\right)_P$ and $\left(\frac{\partial^2 \alpha}{\partial T^2}\right)_P$ were determined by the chord area method of graphical differentiation on the large-scale plot. A large-scale plot of α vs. P isotherms was also prepared, and points read from it were used to construct another chord plot from which the derivative $\left(\frac{\partial \alpha}{\partial P}\right)_T$ was determined. From these derivatives it was possible to calculate the other thermal properties of methane.

SPECIFIC HEAT AT CONSTANT PRESSURE. Combining Equations 1 and 11:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = T\left(\frac{\partial^2 \alpha}{\partial T^2}\right)_P \tag{13}$$

Integrating between the limits of pressure P and 1 atmosphere pressure with T constant:

$$C_p - C_p^0 = T\int_{P^0}^{P}\left(\frac{\partial^2 \alpha}{\partial T^2}\right)_P dP \tag{14}$$

where C_p^0 = sp. heat at constant pressure (1 atm.) and temp. T obtained from Eucken and Lüde (*5*)

CALCULATION OF $C_P - C_V$. Combining Equations 2, 10, and 12:

$$C_P - C_V = T\,\frac{\left[\frac{R}{T} - \left(\frac{\partial \alpha}{\partial T}\right)_P\right]^2}{\left[\frac{RT}{P^2} + \left(\frac{\partial \alpha}{\partial P}\right)_T\right]} \tag{15}$$

CALCULATION OF JOULE-THOMSON COEFFICIENT. Combining Equations 3, 6, and 10:

$$\mu = \frac{\alpha - T\left(\frac{\partial \alpha}{\partial T}\right)_P}{C_P}\,. \tag{16}$$

CALCULATION OF ENTROPY. Combining Equations 4 and 10:

$$dS = \frac{C_P}{T}\,dT + \left[\left(\frac{\partial \alpha}{\partial T}\right)_P - \frac{R}{P}\right] dP \tag{17}$$

Integrating between the limits of temperature T and the reference temperature (25° C.) with the pressure constant at 1 atmosphere:

$$S_{1\text{ atm.}} = \int_{298.1}^{T} \frac{C_P}{T}\, dT \qquad (18)$$

Integrating between the limits of pressure P and 1 atmosphere with the temperature constant:

$$S - S_{1\text{ atm.}} = \int_{P^0}^{P} \left[\left(\frac{\partial \alpha}{\partial T}\right)_P - \frac{R}{P}\right] dP \qquad (19)$$

This integration was performed graphically for each temperature by summation of small incremental areas.

Calculation of Enthalpy. Combining Equations 5, 6, and 10:

$$dH = C_P\, dT - \left[\alpha - T\left(\frac{\partial \alpha}{\alpha T}\right)_P\right] dP \qquad (20)$$

Integrating between the limits of temperature T and the reference temperature (25° C.) with the pressure constant at 1 atmosphere:

$$H_{1\text{ atm.}} = \int_{298.1}^{T} C_P\, dT \qquad (21)$$

Integrating between the limits of pressure P and 1 atmosphere with the temperature constant:

$$H - H_{1\text{ atm.}} = \int_{P^0}^{P} \left[\alpha - T\left(\frac{\partial \alpha}{\partial T}\right)_P\right] dP \qquad (22)$$

This integration was performed graphically for each temperature in the same manner that Equation 19 was integrated.

It is possible to calculate the remaining thermodynamic properties of methane by using the data presented in Table I and Equations 6 to 9.

Discussion of Results

The α surface for methane in the range studied is a smooth skew surface with no sharp breaks or folds and with the isobars in Figure 1 starting to cross at about −20° C. This type of surface for the volume residual quantity probably accounts for the unusual plot formed by the Joule-Thomson coefficients in Figure 4. The temperature-entropy and entropy-enthalpy diagrams do not show these characteristics but were similar to the corresponding diagrams for steam. These plots were omitted here but can be constructed from the data in Table I.

The maximum deviation in values of α in Table I will cause a deviation in the calculated volume of 0.5 per cent or less. The estimated accuracy of the calculated specific heats, C_p, which are based on the data of Eucken and Lüde (*5*) at 1 atmosphere as a reference point is within 1.0 per cent. The maximum deviation of the enthalpy, H, is ±0.5 calorie per gram.

Perry and Herrmann (*8*) recently computed the Joule-Thomson coefficients of methane using the Beattie-Bridgeman equation of state (*2*) and the Eastman equation (*4*) for the isobaric specific heat at atmosphere. The following table shows a comparison of the Joule-Thomson coefficients (in ° C. per atmosphere) found by Perry and Herrmann and those obtained by the methods described:

Pressure Atm.	250° K.		300° K.		350° K.		400° K.	
	P. & H. (*8*)	Edmister	P. & H. (*8*)	Edmister	P. & H. (*8*)	Edmister	P. & H. (*8*)	Edmister
1	0.58	0.680	0.41	0.451	0.30	0.300	0.23	0.220
50	0.46	0.585	0.34	0.385	0.26	0.265	0.20	0.200
100	0.37	0.414	0.28	0.327	0.22	0.232	0.17	0.182

Perry and Herrmann go as low as 200° K., but, since the lower limit of the calculations in this work was −70° C., there are no values to compare at this lowest temperature. From their values it is apparent that their calculated isobars do not cross, as was found to be the case by the graphical methods used here. The comparison shows good agreement at 350° and 400° K., but the agreement is not so good at 300° and 250° K. The range of the Beattie-Bridgeman equation is 0° to 200° C., so that the derivatives obtained from it at these lower temperatures probably account for this deviation.

Nomenclature

α = vol. residual, cc. per gram
C_p = isobaric sp. heat
$C_p - C_v$ = difference in sp. heats
μ = Joule-Thomson coefficient, ° C./atm.
S = entropy above 25° C. and 1 atm., gram-cal./gram °C.
H = enthalpy above 25° C. and 1 atm., gram-cal./gram

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Enthalpy-Entropy Diagram Is Developed for Methane

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The Mollier diagram (enthalpy or heat content vs. entropy) for steam has long been a very useful tool of the engineer. From it changes in enthalpy for isothermal, isobaric isentropic (constant entropy) or reversible adiabatic changes in state can be found. It is also possible to determine changes in entropy for isothermal, isobaric, or constant enthalpy (throttling) changes in state. Final temperatures and pressures may also be estimated. In addition the change in the free energy of formation with pressure may be computed.

Thermodynamic properties have recently been calculated for methane.[1] The calculation of these properties was based on the P-V-T data of Keyes and Burks[2], and of Kvalnes and Gaddy[3], and on the isobaric specific heat data at one atmosphere of Eucken and Lude.[4] Equations based on the first and second laws of thermodynamics were used in the development and the calculations were made by means of accurate graphical methods of differentation and integration. Since these calculations have already been discussed[1] in detail, a presentation here would be unnecessary repetition.

The properties resulting from these calculations are here presented in very useful and practical forms, however. Figure 1 is a plot of isobaric specific heats vs. temperature and of the ratio of specific heats, C_P/C_V vs. temperature. Specific heat is dimensionless and may be B.t.u./lb. °F. or g-cal./gm. °C.

Figure 2 is an Enthalpy-Entropy diagram for methane. In the original calculations the reference state for the entropy and enthalpy was 25° C. (77° F.) and one atmosphere and the enthalpy was in calories per gram. With this reference state

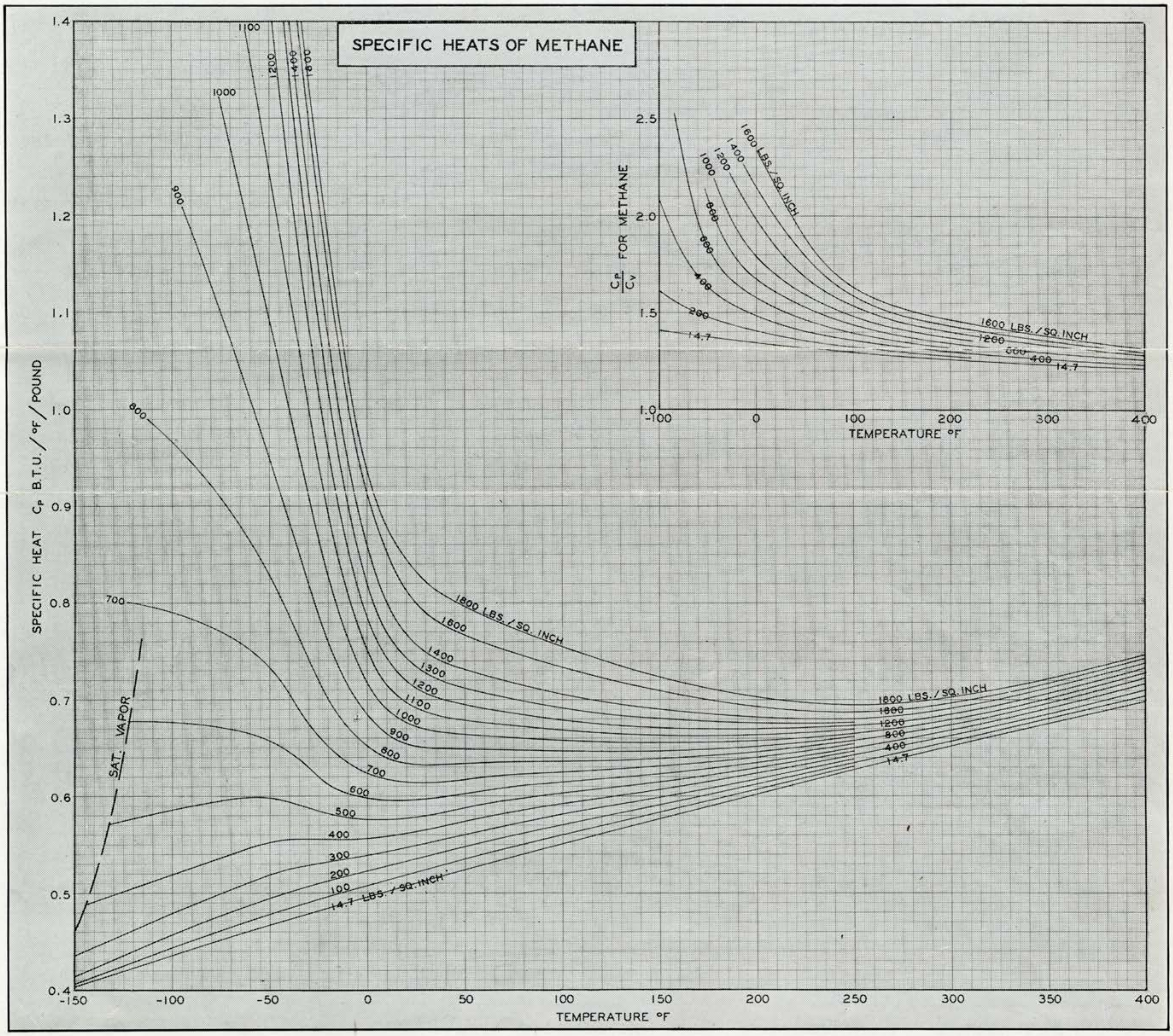

Fig. 1—Plot of isobaric specific heats versus temperature and plot of ratio of specific heats versus temperature

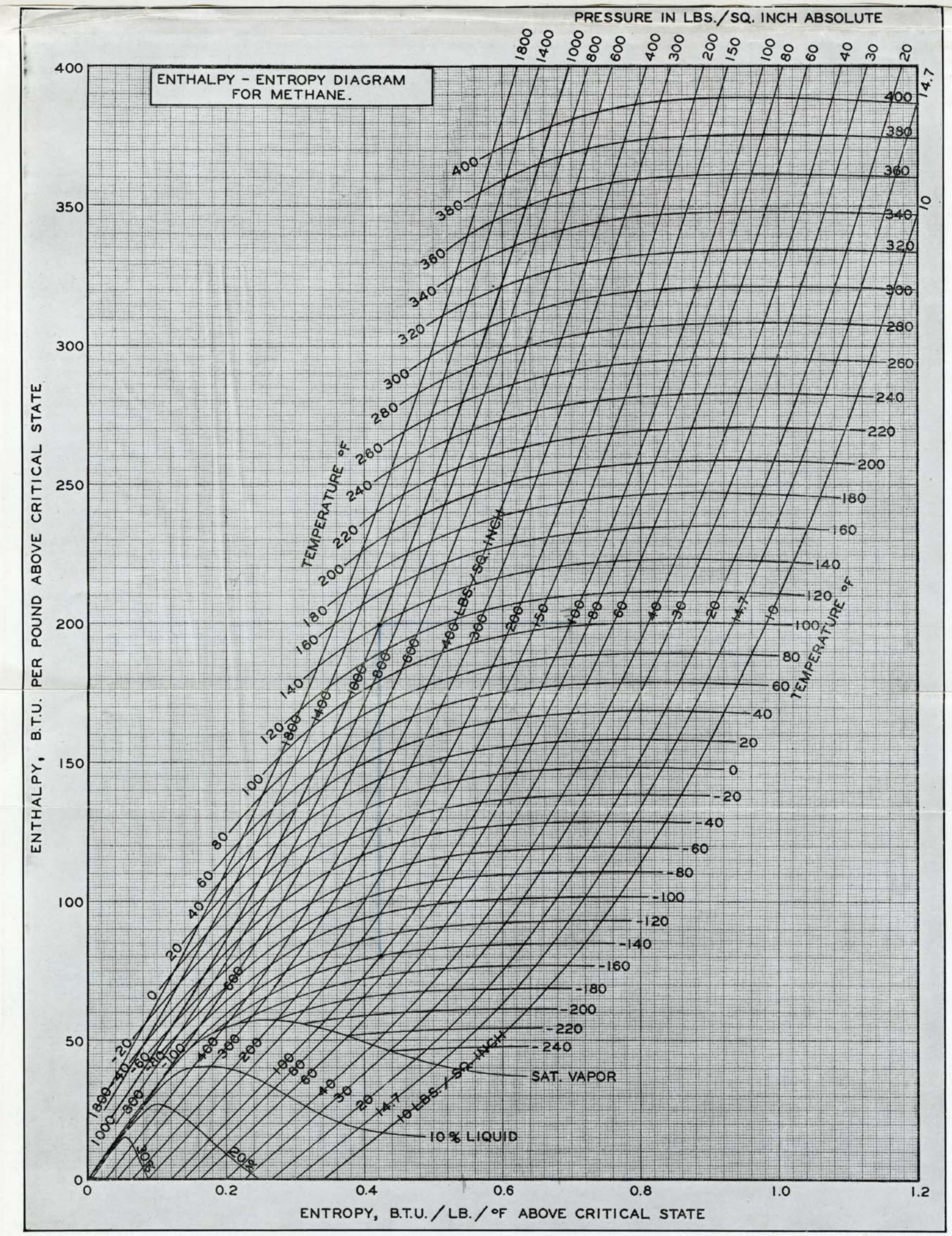

Fig. 2—Enthalpy-Entropy diagram of methane for calculating problems involving heat, pressure, and free energy changes and other computations

the entropy at the critical state was —0.911 (entropy is also dimensionless and may be in B.t.u./lb. °F or g-cal./gm. °C.) and the enthalpy was —104 g-cal./gm. or —187.4 B.t.u./lb. When this chart was plotted in English engineering units the reference state was changed to the critical state (—117° F. and 673 pounds per square inch absolute) so there would be no negative entropies or enthalpies.

Among the many uses of the Mollier diagram for steam are: (1) the calculation of the flow velocity from a nozzle, jet, or orifice, (2) the calculation of the work absorbed by a turbine wheel, and (3) the calculation of the loss by throttling or wire-drawing. For the ideal frictionless case the flow through a nozzle, jet, or orifice is adiabatic and reversible at constant entropy. Actually, however, there are friction losses, which cause an increase in entropy and decrease the flow velocity as well as the work absorbed by the turbine wheel, if the jet is directed on a turbine wheel. These friction losses are known as "wire-drawing" or throttling and occur at constant enthalpy.

The Enthalpy-Entropy diagram for methane here presented may be used for these same calculations as well as for the other more obvious ones. The following uses of Figure 2 will be discussed and illustrated:

1. Isobaric (constant pressure) change.
2. Isothermal (constant temperature) change.
3. Loss by throttling.
4. Flow velocity from nozzle, jet, or orifice.
5. Work absorbed by turbine wheel.
6. Change of free energy.
7. Work required in compression.

Note: In computing the work absorbed by a given process by means of the Enthalpy-Entropy diagram it is necessary to assume the process is reversible. Such an ideal process is one in which all friction and other sources of energy dissipation have been removed. Technically any actual process is irreversible.

ISOBARIC CHANGE

The changes in enthalpy and entropy for a constant pressure process can be found from Figure 2 by following a line of constant pressure.

Example 1: Cool CH_4 from 200° F. and 200 pounds per square inch absolute to 0° F. and 200 pounds per square inch absolute and find the changes in enthalpy and entropy.

$$\triangle H = 255.5 - 141.5 = 114 \text{ B.t.u./lb.}$$
$$\triangle S = 0.704 - 0.498 = 0.206 \text{ B.t.u./lb. °F.}$$

ISOTHERMAL CHANGE

The changes in enthalpy and entropy for a constant temperature process can be found directly from Figure 2 by following a line of constant temperature.

Example 2: Compress CH_4 isothermally from 0° F. and 200 pounds per square inch absolute to 1,000 pounds per square inch absolute and find the changes in enthalpy and entropy.

$$\triangle H = 141.5 - 107.5 = 34 \text{ B.t.u./lb.}$$
$$\triangle S = 0.498 - 0.248 = 0.250 \text{ B.t.u./lb. °F.}$$

THROTTLING LOSS

The loss in throttling or wire-drawing occurs as an increase in entropy at constant enthalpy and can be found from Figure 2 as illustrated in the following example:

Example 3: An engine, a turbine or a nozzle is supplied with methane at 300° F. and 1,000 pounds per square inch absolute and the discharge or exhaust pressure is 100 pounds per square inch. Find the loss if the CH_4 is throttled to 600 pounds per square inch before expansion.

No throttling ($S = 0.578$)

$$\triangle H = 306.5 - 140 = 166.5 \text{ B.t.u./lb.}$$

Final temperature = —11° F.

Throttling (Final $S = 0.644$)

$$\triangle H = 306.5 - 171.5 = 135.0 \text{ B.t.u./lb.}$$

Final temperature = 50° F.
Throttling loss = 166.5 — 135.0 = 31.5 B.t.u./lb.
Entropy increase = 0.644 — 0.578 = 0.066 B.t.u./lb. °F.

The loss caused by throttling in the above example is 31.5 B.t.u./lb. and the entropy increase is 0.066 B.t.u./lb. °F. The final temperature is 50° F. instead of —11° F. for no throttling.

FLOW OF FLUIDS

The following formula for flow through adiabatic orifices, jets, and nozzles can be derived from Bernoulli's theorem

$$\frac{V_2^2 - V_1^2}{2g} = J(H_1 - H_2) \qquad (1)$$

V_1 = initial velocity in feet per second
V_2 = final velocity in feet per second
H_1 = initial enthalpy in B.t.u./lb.
H_2 = final enthalpy in B.t.u./lb.
g = 32.174 feet/second^2
J = work equivalent of heat = 777.64 foot-lbs./B.t.u.

For flow from a reservoir where the initial velocity is negligible the above equation becomes

$$V_2 = \sqrt{2gJ(H_1 - H_2)} = 223.7\sqrt{H_1 - H_2} \qquad (2)$$

For the ideal frictionless adiabatic case H_1 and H_2 are at the same entropy and can be readily found from Figure 2 by following a vertical line. For the actual case there will be an increase of entropy and the final temperature will be higher and the final velocity lower than for the frictionless case. If the initial and final temperatures and pressures are known the actual velocity may be accurately found by the above equations. If not the actual velocity may be found from the following equation, which is a modification of equation 2, by assuming a value for "y" the friction loss.

$$V_2 = 223.7\sqrt{(1 - y)\ (H_1 - H_2)} \qquad (3)$$

y = friction loss and may be approximately 0.10 to 0.20.

Example 4: Find the final velocity for ideal frictionless adiabatic flow of CH_4 from 1,000 pounds per square inch absolute and 300° F. to 100 pounds per square inch absolute. Find final temperature.

$$V_2 = 223.7\sqrt{306.5 - 140} = 288 \text{ feet/second}$$
$$t_2 = -11° \text{ F.}$$

Example 5: Find the final velocity for the problem in example 4, assuming $y = 0.15$. Determine final temperature and the loss by throttling.

$$V_2 = 223.7\sqrt{(1 - .15)\ (306.5 - 140)} = 265.5 \text{ feet/second.}$$
$$\triangle H = 0.85\ (306.5 - 140) = 141.5 \text{ B.t.u./lb.}$$
$$H_2 = 306.5 - 141.5 = 160 \text{ B.t.u./lb.}$$

From Figure 2 at 1,000 pounds per square inch and H = 160 B.t.u./lb.
t_2 = 28° F.
Throttling loss = 160 — 140 = 20 B.t.u./lb.
Entropy increase = 0.622 — 0.578 = 0.044 B.t.u./lb. °F.

WORK ABSORBED BY TURBINE WHEEL

The work equivalent of the heat absorbed by a turbine wheel can be found by the following conversion factors:

1 B.t.u. = 777.64 foot-lbs.
1 H.P. = 33,000 foot-lbs./minute.
1 H.P. hour = 2,546 B.t.u.
1 K.W. hour = 3,415 B.t.u.

An example will illustrate:

Example 6: Find the work absorbed by turbine wheel in example 4. Find amount of CH_4 required to generate 1 H.P. hour.

$$\triangle H = 306.5 - 140.0 = 166.5 \text{ B.t.u./lb.}$$
$$W = 777.64 \times 166.5 = 129{,}600 \text{ ft.-lbs./lb. } CH_4$$

$$\frac{2{,}546}{166.5} = 15.3 \text{ lbs. } CH_4\text{/H.P. hr.}$$

The change of free energy with pressure at constant temperature may be computed by means of the following equation and Figure 2:

$$\triangle F = \triangle H - T\triangle S \qquad (5)$$

The free energy of formation is usually known at atmospheric pressure. With this equation and the free energy at atmospheric pressure, the free energy at any other pressure may be computed.

Example 7: Calculate change in free energy from one atmosphere and 300° F. to 1,800 pounds per square inch absolute and 300° F.

$$\triangle H = 321.0 - 295.5 = 25.5 \text{ B.t.u./lb.}$$
$$T\triangle S = (460 + 300)\ (1.118 - 0.494) = 474 \text{ B.t.u./lb.}$$
$$\triangle F = \triangle H - T\triangle S = 25.5 - 474 = -448.5 \text{ B.t.u./lb.}$$

The free energy at 1,800 pounds per square inch absolute and 300° F. is 448.5 B.t.u./lb. greater than the free energy at 14.7 pounds per square inch absolute and 300° F. In other words it would require 448.5 B.t.u. of work to reversibly compress 1 pound of CH_4 from 14.7 pounds per square inch to 1,800 pounds per square inch at 300° F.

The free energies of formation of hydrocarbons from carbon and hydrogen are usually presented in calories per carbon atom. This makes a change of units necessary, when Figure 2 is used for calculating free energies, but this is very simple. Since most uses for the Enthalpy-Entropy chart will be in engineering units the chart is therefore presented in those units.

The work required in isentropic compression is equal to the increase in enthalpy, while the work required in reversible isothermal compression is equal to the increase in free energy. For the ideal frictionless case where no jacket water cooling is used the compression is an isentropic process, but for the actual case with no jacket water cooling there is an increase in entropy and in the work of compression. With cooling during compression a lower final temperature results, the entropy decreases, and less work is required. For reversible compression the isothermal case requires the minimum amount of work while the adiabatic case requires the maximum amount. When enough jacket water cooling is supplied to cause a decrease in entropy during compression but not enough to result in isothermal compression, the reversible work required is dependent on the path followed. An example will illustrate.

Example 8. Find the reversible work required to compress 1 pound of CH_4 from 14.7 pounds per square inch absolute and 0° F. to 300 pounds per square inch absolute by each of the four following paths:

1. Isentropic to final pressure.
2. Isothermal to final pressure.
3. Isentropic to an intermediate temperature of 200° F. and isothermal to final pressure.
4. Isothermal to final entropy of Case 3 and isentropic to final pressure.

Solution: From Figure 2 the data necessary for the solution of these problems were found and are tabulated in the following table together with the solutions. The details of the solutions are similar to previous examples.

Conditions:	P	T °F.	S	H	B.t.u./lbs. △H	△F	W
Initial	14.7	0	0.832	148	...	.....	.....
Final, Case 1	300	400	0.832	388	—240	.....	—240
Final, Case 2	300	0	0.442	137	+11	—179.5	—168.5
Inter, Case 3	75	200	0.832	258	—110	.....	.....
Final, Case 3	300	200	0.651	253	+5	—119.5	—229.5
Inter, Case 4	63	0	0.651	147	+1	—83.2	.....
Final, Case 4	300	200	0.651	253	—106	.....	—188.2

WORK REQUIRED

Case 1. 240 × 777.64 = 186,800 ft.-lbs./lb. CH_4
Case 2. 168.5 × 777.64 = 131,000 ft.-lbs./lb. CH_4
Case 3. 229.5 × 777.64 = 178,400 ft.-lbs./lb. CH_4
Case 4. 188.2 × 777.64 = 146,500 ft.-lbs./lb. CH_4

The work required in Case 1 is the greatest, while Case 2 is the least. The final conditions in Cases 3 and 4 are the same, yet the amounts of work required for compression are different. This shows that the path affects the work absorbed.

CONCLUSIONS

While the charts here presented are for a single component, which is more often found in a gaseous mixture than in a one-component system, it is believed that they will be of value in engineering calculation. It is hoped that similar charts for other hydrocarbons will soon be available.

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Thermodynamic Properties of Hydrocarbons

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The effects of pressure on specific heats at constant pressure, entropy, and enthalpy are computed in reduced or generalized units for hydrocarbons. These calculations are based on a new correlation of *P-V-T* data. The effect of temperature on these thermodynamic properties can be computed by a new equation for specific heat at one atmosphere, which is based on a correlation of the data of Beeck, of Eucken and Lüde, and of Eucken and Parts.

By means of a table of generalized thermodynamic properties and equations presented in this paper, it is possible to compute all the thermal properties for any hydrocarbon for which critical data are available.

THERMODYNAMIC properties, such as deviation from perfect gas laws, fugacities, specific heats, heats of vaporization, entropies, internal energies, free energies, and enthalpies or heat contents for petroleum hydrocarbons and their mixtures are of practical importance in engineering work associated with petroleum refinery operations. Research development of new processes and the design of plant equipment require a knowledge of these properties over wide ranges in temperature and pressure. The preparation of tables or charts of these properties is complicated by the multiplicity of the petroleum hydrocarbons and by the scarcity of reliable experimental specific heat and Joule-Thomson effect data. More *P-V-T* data are available, however, so that the effect of pressure on the above thermodynamic properties can be computed by means of the first and second laws of thermodynamics.

In a previous paper (*10*) a study of individual hydrocarbons was begun with two purposes: to make available more complete thermodynamic data for one-component systems and to prepare a background which would assist in the preparation of such thermodynamic data for multicomponent systems. The first publication on this project dealt with methane, for which the effects of pressure on the thermal properties were calculated graphically by means of the Lewis and Randall (*22*) volume residual quantity, α, obtained from *P-V-T* data. Graphical methods of differentiation were adapted and thermodynamic functions were integrated to this particular problem, and it was then discovered that a vast amount of work was involved in performing such calculations precisely for each hydrocarbon individually. It became apparent, therefore, that the most expeditious method of preparing tables and charts of thermodynamic properties for all the normal paraffinic, isoparaffinic, olefinic, naphthenic, and aromatic hydrocarbons was a generalized method, by which these computations could be made once for all single-component hydrocarbon systems—in other words, a method that would result in "reduced" thermodynamic properties, which would be functions of reduced pressure and temperature. With such a method the tedious graphical differentiations and integrations could be performed with great care once to obtain the reduced thermodynamic properties; then by means of the critical constants for any given hydrocarbon it would be possible to compute the value of any desired thermodynamic property. Such a correlation of reduced thermodynamic functions would make it possible to estimate properties of hydrocarbons for which there are few or no data available. It should also be possible to apply these reduced functions to mixtures by the use of Kay's pseudo critical constants for mixtures (*14*).

The generalization of isothermal pressure corrections to such thermodynamic properties as enthalpy, internal energy, and Joule-Thomson coefficients has been receiving considerable attention in recent years from Lewis and co-workers (*4, 7, 19, 20, 21*), Newton and Dodge (*25, 26*), Watson and Nelson (*34*), and Watson and Smith (*35*). All of these investigations arrive at the effect of pressure on enthalpy, Joule-Thomson coefficients, etc., in round-about ways, and most of them result in tedious methods of calculation. It is believed that a more direct method of arriving at the effect of pressure on thermodynamic functions would be more precise and more useful from a practical standpoint. Such a direct method is made possible by the graphical reduced equation of state developed and discussed here.

Reduced Equation of State

The compressibility factor, PV/RT, which is the ratio of actual to theoretical gas volume, has been in wide use during recent years as a means of correlating *P-V-T* data. When plotted against reduced pressure, lines of constant reduced temperature for different hydrocarbons are close together, and in some cases coincide. Vapor volumes estimated from this type of plot are of sufficient accuracy for most engineering design calculations. For thermodynamic calculations this correlation is not accurate enough and, in addition, is not well adapted to graphical methods.

Instead of the ratio of actual to ideal gas volume, let us consider their difference; this residual quantity is defined as

$$\alpha = \frac{RT}{P} - V \qquad (1)$$

As pointed out by Deming and Shupe (*8*), this residual quantity is well adapted to graphical methods. Since $\alpha = \alpha_r\alpha_c$, $P = P_rP_c$, and $T = T_rT_c$, Equation 1 may be rearranged and written

$$\frac{V}{\alpha_c} = \frac{RT_c}{P_c\alpha_c}\frac{T_r}{P_r} - \alpha_r \qquad (2)$$

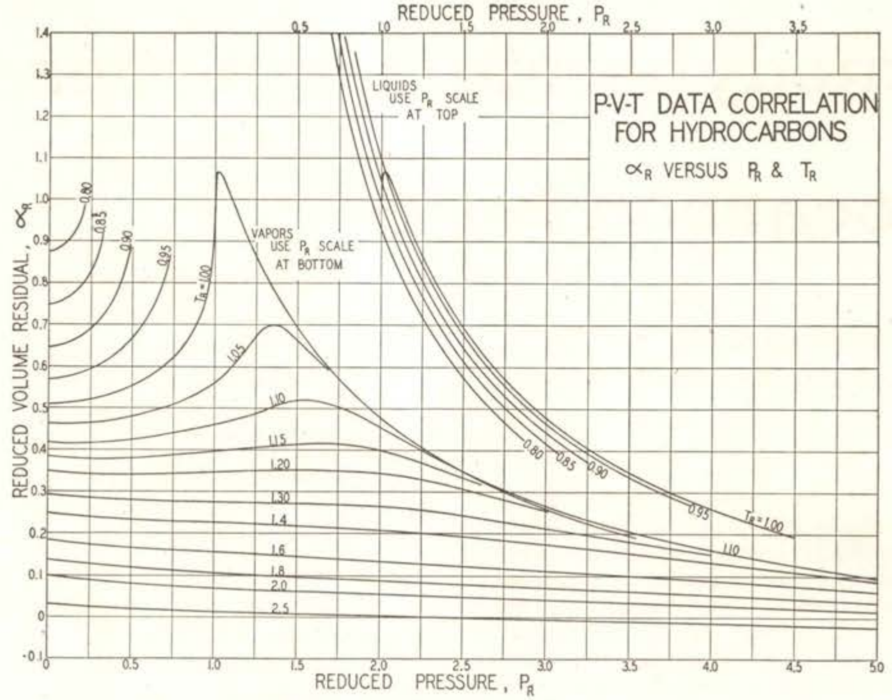

FIGURE 1

which is essentially a reduced equation of state, where the ratio $RT_c/P_c\alpha_c$ is practically a constant as shown in Table II, and α_r is a function of P_r and T_r.

The α_r function was determined from experimental *P-V-T* data collected from the literature. Table I shows the sources and ranges of the data used in making this correlation. Values of α_r were calculated and plotted for each hydrocarbon listed in Table I, and Figure 1 was constructed from these plots. Values of α_r in the unsaturated liquid region as well as in the unsaturated vapor region are given in Figure 1, where the liquid curves are plotted against a different abscissa scale from that used for the vapor curves in order that the two sets of curves may not overlap.

TABLE I. SOURCE of *P-V-T* DATA

Hydrocarbon	Pressure Range, P_r	Temp. Range, T_r	Citation
Methane	0.0218 –5.46	1.064 –2.478	(*18*)
Methane	0.2182 –0.8735	1.43 –2.478	(*17*)
Ethylene	0.749 –2.96	0.966 –1.037	(*1*)
Ethylene	0.0986 –2.96	1.055 –1.668	(*24*)
Ethane	0.2277 –3.892	0.977 –1.714	(*2*)
Propane	0.0238 –3.333	0.8196–1.647	(*9*)
Isopentane	0.01564–2.18	0.701 –1.20	(*37*)
n-Pentane	0.0342 –2.268	0.709 –1.176	(*36*)
Cyclohexane	0.1104 –2.62	0.746 –1.035	(*28*)
n-Hexane	0.315 –1.26	0.872 –1.089	(*33*)
n-Heptane	0.1081 –1.706	0.766 –1.016	(*15*)

ACCURACY OF *P-V-T* CORRELATION. Using the critical constants given in Table II, the α_r correlation shown in Figure 1 was used to calculate vapor volumes, which were compared with the experimental data. The same comparison was made with vapor volumes calculated by means of the *PV/RT* correlation; the *PV/RT* plot used was practically identical with Brown's *z* plot (*5*) and Lewis' μ plot (*19*). The results of these comparisons are shown in Table III, from which it can be seen that the maximum deviations are smaller for the α_r correlation than for the *PV/RT* correlation in all cases except that of *n*-pentane, for which the deviations for both correlations are quite low. When average deviations are considered, the comparison is even more favorable to the α_r correlation. For most of the data, Figure 1 is within the experimental error and is considered a sound basis for generalized thermodynamic calculations.

TABLE II. CRITICAL CONSTANTS FOR HYDROCARBONS

Hydrocarbon	Mol. Wt.	Critical Temp.		Critical Pressure		Critical Vol.		Critical Vol. Residual, α_c		$\frac{RT_c}{P_c\alpha_c} = -k_1$	$k_2 = \frac{P_c\alpha_c}{T_c}$*	$k_3 = P_c\alpha_c$
		° *K.*	° *R.*	*Atm.*	*Lb./sq. in. abs.*	*Cc./g. mole*	*Cu. ft./lb. mole*	*Cc./g. mole*	*Cu. ft./lb. mole*			*G. cal./g. mole***
Methane	16.03	191.1	344	45.8	673	99	1.586	243.5	3.90	1.406	1.413	270.2
Acetylene	26.02	309.1	556	61.7	907	113.2	1.814	298.0	4.772	1.381	1.452	445.8
Ethylene	28.03	282.8	508.5	50.7	745	133.4	2.138	324.2	5.195	1.410	1.410	398.5
Ethane	30.05	305.2	549	48.8	717	137.0	2.195	376.0	6.020	1.365	1.457	444.8
Propylene	42.05	364.8	656	45.0	661	181.6	2.91	483.8	7.745	1.375	1.446	527.5
Propane	44.06	369.9	665.5	42.01	617	195.0	3.123	528.0	8.46	1.368	1.455	538.0
Isobutane	58.08	407.1	732.0	37.0	544	249.0	3.99	654.5	10.48	1.379	1.442	587.0
n-Butane	58.08	426.0	766.5	36.0	529	250.0	4.005	720.5	11.54	1.347	1.477	629.0
Isopentane	72.09	460.9	829.0	32.92	483.4	307.6	4.930	842.0	13.485	1.365	1.459	672.0
n-Pentane	72.09	470.3	846.0	33.0	485	310.9	4.98	860.0	13.77	1.359	1.463	688.0
Benzene	78.05	561.6	1010	47.7	701	256.2	4.106	709.5	11.36	1.361	1.460	820.0
Cyclohexane	84.09	554.1	997	40.6	596.5	308.7	4.946	811.5	13.00	1.382	1.440	798.0
Diisopropyl	86.11	500.5	901	30.6	449.5	357.1	5.72	986	15.795	1.362	1.460	731.0
n-Hexane	86.11	507.9	913.5	29.5	433.5	367.2	5.88	1045	16.74	1.353	1.472	747.5
n-Heptane	100.12	540.0	972.0	26.8	393.7	427.0	6.84	1227	19.65	1.349	1.477	797.5
Diisobutyl	114.14	549.9	989.0	24.5	360.0	482.0	7.72	1359	21.77	1.355	1.468	807.0
n-Octane	114.14	569.3	1024	24.6	361.4	490.0	7.85	1410	22.59	1.347	1.475	840.0

* Dimensionless ratio is either g. cal./g. mole ° C. or B. t. u./lb. mole ° F.
** Multiply by 1.8 to convert to B. t. u./lb. mole.

TABLE III. ACCURACY OF *P-V-T* CORRELATIONS

	Max. Deviations of Calcd. from Obsvd. Vol., %			Max. Deviations of Calcd. from Obsvd. Vol., %	
Correlation	*PV/RT*	α_r	Correlation	*PV/RT*	α_r
Methane	6.6	5.6	Isopentane	14.5	6.9
Ethylene	10.6	8.0	*n*-Pentane	2.8	5.3
Ethane	5.9	3.5	Cyclohexane	9.0	4.5
Propane	13.6	9.8	*n*-Hexane	11.2	5.5
			n-Heptane	12.0	8.0

Calculation of Thermal Properties

The effect of pressure on the various thermodynamic properties will now be calculated by means of the reduced equation of state represented by Figure 1.

FUGACITIES OF VAPORS. The fugacities of hydrocarbon vapors have been computed by several investigators using different methods. Brown and co-workers (*31*) and Lewis (*19*) calculated the fugacity-pressure ratio by integrating the compressibility factor, PV/RT, against pressure. Newton (*25*) computed it for a large number of gases by integrating the equation

$$RT \ln \frac{f}{p} = -\int_0^P \alpha \, dp \qquad (3)$$

against pressure directly for each gas and correlating the resulting "activity coefficients" as a general function of reduced pressure and temperature.

The values of f/p have been computed from the correlation of Figure 1 as follows. On the introduction of reduced units Equation 3 becomes

$$\frac{-RT_c}{P_c\alpha_c} \ln \frac{f}{p} = \frac{1}{T_r}\int_0^{P_r} \alpha_r \, dp_r \qquad (4)$$

The critical ratio $RT_c/P_c\,\alpha_c$ of Equation 2 appears here in Equation 4. If values of this critical ratio were strictly identical for all hydrocarbons, and if we assumed that α_r is a function of T_r and P_r, f/p would be a function of reduced temperature and pressure only; but since they are only approximately identical, f/p is only an approximate function of P_r and T_r.

Figure 1 was integrated graphically, the right-hand side of Equation 4 was computed for several reduced temperatures, and the values obtained are given in Table IV under the heading "$k_1 \ln f/p$" where the constant $k_1 = -RT_c/P_c\,\alpha_c$. Values of this critical ratio are given in Table II for seventeen hydrocarbons. The average value of k_1 for the hydrocarbons is about -1.37, with only methane and ethylene deviating by an appreciable amount. Where reliable critical data are available, a value of $k_1 = -RT_c/P_c\alpha_c$ should be used rather than the average value of -1.37. For the purpose of comparing f/p ratios calculated from Table IV with those of Lewis (*19*) and Newton (*25*), the average value of -1.37 was used, however. The results of this comparison show less deviation from perfect gas laws at low pressures and more at high pressures than do Lewis' or Newton's results.

SPECIFIC HEAT AT CONSTANT PRESSURE. *Effect of Pressure.* The change of specific heat with pressure is given by the following equation:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P \qquad (5)$$

When expressed in terms of α_r and reduced units, Equation 5 becomes:

$$\left(\frac{\partial C_p}{\partial P_r}\right)_{T_r} = \frac{P_c\alpha_c}{T_c}\,T_r\left(\frac{\partial^2 \alpha_r}{\partial T_r^2}\right)_{P_r} \qquad (6)$$

Integrating between the limits of P_r and $P_r = 0$ at different constant values of T_r and defining the ratio $P_c\alpha_c/T_c$ as k_2:

$$\frac{\Delta C_p}{k_2} = T_r\int_0^{P_r}\left(\frac{\partial^2 \alpha_r}{\partial T_r^2}\right)_{P_r} dP_r \qquad (7)$$

where ΔC_p is the increase in isobaric specific heat from zero pressure to any pressure P_r. The second derivative $\left(\frac{\partial^2\alpha_r}{\partial T_r^2}\right)_{P_r}$ was determined graphically by the chord area method from a large-scale plot of $\left(\frac{\partial \alpha_r}{\partial T_r}\right)_{P_r}$ vs. T_r isobars; the first derivatives were also determined graphically by the chord area method from a large-scale plot of α_r vs. T_r isobars, and Equation 7 was integrated graphically for several reduced temperatures. Values of $\Delta C_p/k_2$ are given in Table IV, and values of k_2 are given in Table II.

Effect of Temperature. The ΔC_p values computed from Table IV give only the effect of pressure on the isobaric specific heat. The effect of temperature must be determined experimentally. The specific heat data available in the literature were collected, and a suitable correlation was developed. The data of Beeck (*3*) for methane, acetylene, ethylene, ethane, propylene, propane, butylene, butane, pentane, hexane, and heptane from 0° to 300° C. were used, as well as the data of Eucken and Lüde (*11*) for methane and of Eucken and Parts (*12*) for ethylene and ethane. Bryant's equation (*6*) for methane agrees with the data of Beeck and of Eucken and Lüde, but his values for acetylene are about 4 per cent lower at 600° K. and about 4 per cent higher at 250° K. By means of the data of Beeck (*3*) and of Eucken and co-workers (*11*, *12*) and on the assumption of a linear relation between C_p and T between 250° and 600° K., the constants A and B were computed for the equation

$$C_p = A + BT$$

where C_p = molal heat capacity
T = temperature, ° K.

The following table gives values of these constants for all the hydrocarbons for which reliable data were available; the constants for benzene were taken from an equation of Lindsay and Brown (*23*):

	A	B		A	B
Methane	4.60	0.0133	Butylene	4.60	0.0515
Acetylene	7.51	0.01115	Butane	4.60	0.0562
Ethylene	3.84	0.022	Pentane	5.11	0.0692
Ethane	3.84	0.0298	Hexane	5.62	0.0822
Propylene	4.09	0.0372	Heptane	6.13	0.0952
Propane	4.09	0.0432	Benzene	6.16	0.0526

These constants indicate that for paraffinic and olefinic hydrocarbons A is a function of the number of carbon atoms only and increases 0.51 unit per carbon atom, above three carbon atoms; and that B increases 0.0130 unit per carbon atom for paraffins and 0.0143 unit per carbon atom for olefins, above three carbon atoms. When both of these relations are assumed, the following equation is developed for the heat capacity of paraffinic and olefinic hydrocarbons of three or more carbon atoms:

$$C_p = 2.56 + 0.51\,n + (0.0013n^2 + 0.0044n - 0.00065mn + 0.00495m - 0.0057)T \qquad (8)$$

where n = number of carbon atoms
m = number of hydrogen atoms

The accuracy of this equation when applied to Beeck and Eucken's data (*3*, *11*, *12*) is about 1 per cent. At 340° K. Equation 8 gives a value 4 per cent higher than Haas and Stegeman's value (*13*) for ethylene; at 337.5° K. it gives a value 3.5 per cent higher than Thayer and Stegeman's value (*32*) for ethane, although it agrees with both at 273° K. The equation agrees with Sage and Lacey's propane data at 298° K. (*29*) but gives a value 4 per cent higher than theirs at 371° K. The equation agrees with Sage and Lacey's butane data at 356° K. (*29*) but gives a value 4 per cent lower than theirs at 296° K.

TABLE IV. REDUCED THERMODYNAMIC FUNCTIONS FOR HYDROCARBONS

T_r	P_r	α_r	$k_1 \ln \frac{f}{P}$	$\left(\frac{\partial \alpha_r}{\partial T_r}\right)_{Pr}$	$\left(\frac{\partial \alpha_r}{\partial P_r}\right)_{Tr}$	$\frac{\Delta C_p}{k_2}$	$\frac{\Delta S'}{k_2}$	$\frac{\Delta H}{k_3}$
0.80	0.05	0.830	0.055	−2.71	0.190	0.60	0.130	0.148
	0.10	0.896	0.110	−3.00	0.33	1.25	0.274	0.307
	0.15	0.919	0.167	−3.40	0.60	1.97	0.435	0.480
	0.20	0.964	0.225	−3.93	1.23	2.80	0.615	0.675
0.85	0.05	0.752	0.044	−2.14	0.132	0.493	0.103	0.128
	0.10	0.761	0.088	−2.32	0.237	1.02	0.215	0.264
	0.15	0.776	0.133	−2.55	0.360	1.61	0.336	0.408
	0.20	0.797	0.180	−2.85	0.512	2.29	0.470	0.562
	0.25	0.829	0.226	−3.22	0.810	3.08	0.625	0.730
	0.30	0.879	0.274	−3.74	1.20	4.07	0.800	0.925
0.90	0.05	0.649	0.036	−1.70	0.076	0.393	0.083	0.109
	0.10	0.655	0.072	−1.80	0.140	0.820	0.170	0.222
	0.15	0.664	0.108	−1.93	0.210	1.28	0.263	0.342
	0.20	0.676	0.145	−2.10	0.288	1.810	0.364	0.470
	0.25	0.692	0.184	−2.33	0.376	2.44	0.474	0.604
	0.30	0.713	0.223	−2.65	0.474	3.20	0.600	0.750
	0.35	0.739	0.263	−3.05	0.596	4.15	0.740	0.915
	0.40	0.772	0.305	−3.58	0.734	5.40	0.900	1.095
0.95	0.05	0.574	0.030	−1.31	0.029	0.300	0.066	0.0925
	0.10	0.576	0.060	−1.39	0.063	0.615	0.135	0.187
	0.15	0.580	0.090	−1.48	0.099	0.965	0.207	0.285
	0.2	0.587	0.122	−1.59	0.138	1.35	0.283	0.389
	0.25	0.595	0.151	−1.72	0.177	1.80	0.365	0.495
	0.3	0.605	0.184	−1.86	0.214	2.32	0.451	0.610
	0.35	0.617	0.216	−2.04	0.253	2.95	0.550	0.726
	0.40	0.630	0.248	−2.24	0.298	3.78	0.660	0.855
	0.45	0.646	0.282	−2.51	0.348	4.80	0.780	1.000
	0.50	0.665	0.316	−2.87	0.414	6.10	0.920	1.160
	0.55	0.687	0.352	−3.31	0.518	7.9	1.07	1.340
	0.60	0.717	0.390	−3.89	0.668	10.3	1.25	1.540
	0.65	0.755	0.428	−4.67	0.882	13.6	1.46	1.775
	0.70	0.812	0.467	−5.70	1.400	18.2	1.72	2.07
1.0	0.05	0.513	0.015	−1.08	−0.008	0.200	0.053	0.079
	0.10	0.513	0.051	−1.12	+0.016	0.416	0.108	0.160
	0.2	0.518	0.103	−1.22	0.060	0.91	0.227	0.329
	0.3	0.527	0.155	−1.35	0.103	1.55	0.355	0.507
	0.4	0.537	0.208	−1.50	0.138	2.48	0.500	0.705
	0.5	0.55	0.263	−1.71	0.176	3.60	0.660	0.920
	0.6	0.575	0.320	−2.03	0.230	5.45	0.845	1.165
	0.7	0.603	0.378	−2.58	0.310	8.45	1.075	1.440
	0.8	0.642	0.440	−3.88	0.488	14.0	1.38	1.810
	0.9	0.707	0.507	−6.70	0.90	28.0	1.89	2.39
	0.95	0.771	0.544	−12.0	1.80	44.5	2.30	2.87
	1.0	1.00	0.586	−30.0	12.0	108.0	3.00	3.95
	1.02	1.07	0.606	−24.0	0	180.0	3.50	4.50
	1.05	1.052	0.636	−14.0	−0.68	200.0	3.95	5.15
	1.1	1.007	0.690	−1.9	−0.88	122.0	4.15	5.55
	1.15	0.955	0.738	+0.67	−1.02	88.0	4.20	5.73
	1.2	0.906	0.786	−0.16	−0.90	69.5	4.20	5.80
	1.3	0.823	0.873	−0.21	−0.75	51.0	4.20	5.90
	1.4	0.755	0.952	0	−0.642	41.4	4.20	5.99
	1.5	0.694	1.024	+0.11	−0.563	35.7	4.20	6.05
	1.6	0.639	1.091	+0.16	−0.500	31.8	4.20	6.10
	1.8	0.55	1.209	0.21	−0.400	27.1	4.19	6.19
	2.0	0.477	1.312	0.22	−0.327	24.7	4.18	6.26
	2.25	0.405	1.442	0.19	−0.256	22.9	4.15	6.33
	2.50	0.347	1.515	0.15	−0.206	21.7	4.13	6.37
	2.75	0.299	1.595	0.14	−0.169	20.9	4.11	6.41
	3.0	0.259	1.666	0.15	−0.146	20.2	4.10	6.44
	3.50	0.192	1.78	0.16	−0.130	19.2	4.05	6.48
1.025	0.05	0.487	0.025	−1.01	−0.022	0.172	0.050	0.0745
	0.10	0.485	0.049	−1.04	−0.001	0.355	0.101	0.151
	0.2	0.488	0.095	−1.11	+0.038	0.760	0.208	0.309
	0.3	0.496	0.143	−1.20	0.071	1.27	0.324	0.474
	0.4	0.505	0.192	−1.30	0.097	1.92	0.449	0.652
	0.5	0.516	0.241	−1.45	0.124	2.76	0.586	0.843
	0.6	0.530	0.292	−1.63	0.154	3.95	0.740	1.054
	0.7	0.547	0.344	−1.92	0.194	5.60	0.916	1.290
	0.8	0.569	0.400	−2.35	0.244	8.15	1.127	1.561
	0.9	0.597	0.456	−2.99	0.326	12.8	1.39	1.886
	1.0	0.638	0.526	−4.2	0.560	23.0	1.745	2.298
	1.1	0.719	0.582	−8.9	1.02	65.0	2.40	2.993
	1.15	0.770	0.618	−12.4	0.98	71.0	2.885	3.65
	1.2	0.812	0.657	−8.8	0.600	63.0	3.23	4.18
	1.25	0.824	0.696	−4.6	−0.100	54.0	3.52	4.50
	1.30	0.800	0.737	−2.75	−0.549	47.1	3.70	4.77
	1.4	0.746	0.813	−1.15	−0.555	39.0	3.83	5.03
	1.5	0.690	0.884	−0.58	−0.546	34.0	3.89	5.20
	1.6	0.636	0.948	−0.30	−0.514	30.3	3.91	5.30
	1.8	0.550	1.061	0	−0.394	25.8	3.92	5.49
	2.0	0.480	1.162	+0.10	−0.321	23.2	3.91	5.60
1.05	0.05	0.464	0.021	−0.94	−0.033	0.143	0.046	0.071
	0.1	0.462	0.044	−0.96	−0.014	0.296	0.094	0.143
	0.2	0.463	0.087	−1.00	+0.020	0.64	0.192	0.292
	0.3	0.467	0.132	−1.07	0.051	1.06	0.295	0.447
	0.4	0.474	0.178	−1.15	0.073	1.58	0.406	0.610
	0.5	0.482	0.223	−1.25	0.087	2.21	0.528	0.785
	0.6	0.491	0.269	−1.38	0.104	3.03	0.657	0.970
	0.7	0.503	0.315	−1.55	0.126	4.11	0.805	1.175
	0.8	0.517	0.364	−1.77	0.156	5.60	0.97	1.40
	0.9	0.535	0.415	−2.07	0.206	7.65	1.16	1.65
	1.0	0.559	0.468	−2.58	0.304	10.85	1.40	1.96
	1.1	0.596	0.523	−3.65	0.431	16.2	1.697	2.33
	1.2	0.645	0.582	−5.22	0.542	29.00	2.13	2.87
	1.25	0.673	0.612	−6.20	0.500	37.0	2.42	3.20
	1.3	0.692	0.642	−5.40	0.270	38.4	2.715	3.52
	1.35	0.700	0.674	−4.10	0	38.0	2.96	3.82
	1.4	0.695	0.707	−3.07	−0.200	36.6	3.12	4.03
	1.5	0.663	0.772	−1.86	−0.360	32.4	3.38	4.35
	1.6	0.625	0.834	−1.21	−0.387	28.6	3.527	4.60
	1.8	0.550	0.947	−0.48	−0.360	24.0	3.69	4.93
	2.0	0.482	1.044	−0.14	−0.316	21.6	3.746	5.11
1.05	2.25	0.410	1.150	−0.02	−0.256	19.5	3.770	5.23
	2.50	0.351	1.239	+0.01	−0.204	18.0	3.76	5.32
	2.75	0.304	1.317	0.04	−0.168	16.8	3.75	5.40
	3.0	0.265	1.383	0.06	−0.144	15.9	3.746	5.45
	3.5	0.201	1.494	0.08	−0.108	14.6	3.709	5.54
	4.0	0.154	1.581	0.10	−0.078	13.75	3.68	5.62
	4.5	0.120	1.650	0.09	−0.060	13.10	3.65	5.66
	5.0	0.091	1.70	0.08	−0.050	12.6	3.60	5.70
	5.5	0.067	1.736	0.07	−0.042	12.1	3.58	5.72
1.10	0.05	0.419	0.018	−0.81	−0.048	0.118	0.040	0.0657
	0.10	0.417	0.037	−0.83	−0.031	0.243	0.081	0.132
	0.2	0.416	0.076	−0.86	−0.003	0.510	0.165	0.268
	0.3	0.418	0.114	−0.90	+0.022	0.805	0.253	0.405
	0.4	0.421	0.152	−0.96	0.038	1.15	0.345	0.550
	0.5	0.426	0.190	−1.01	0.049	1.54	0.444	0.697
	0.6	0.431	0.230	−1.08	0.057	2.01	0.547	0.855
	0.7	0.437	0.269	−1.15	0.064	2.59	0.660	1.02
	0.8	0.444	0.309	−1.25	0.071	3.29	0.780	1.20
	0.9	0.451	0.350	−1.37	0.080	4.17	0.910	1.39
	1.0	0.460	0.392	−1.57	0.089	5.35	1.06	1.60
	1.2	0.480	0.477	−2.07	0.117	9.45	1.42	2.075
	1.4	0.510	0.567	−2.56	0.175	15.85	1.88	2.69
	1.5	0.520	0.612	−2.72	0.026	18.2	2.15	3.01
	1.6	0.517	0.660	−2.78	−0.051	19.0	2.41	3.31
	1.8	0.496	0.753	−1.70	−0.156	19.3	2.84	3.81
	2.0	0.455	0.840	−1.0	−0.237	18.1	3.11	4.15
	2.25	0.398	0.936	−0.46	−0.217	16.2	3.27	4.40
	2.50	0.347	1.02	−0.23	−0.187	14.4	3.38	4.56
	2.75	0.304	1.094	−0.10	−0.160	12.75	3.42	4.70
	3.0	0.267	1.16	−0.04	−0.140	11.7	3.44	4.80
	3.5	0.204	1.268	+0.04	−0.105	10.7	3.43	4.97
	4.0	0.158	1.349	0.06	−0.080	10.2	3.41	5.05
	4.5	0.124	1.411	0.06	−0.062	9.8	3.39	5.14
	5.0	0.095	1.460	0.05	−0.051	9.5	3.34	5.20
	5.5	0.071	1.499	0.05	−0.043	9.3	3.30	5.25
1.15	0.05	0.383	0.015	−0.62	−0.056	0.100	0.035	0.0605
	0.10	0.381	0.032	−0.73	−0.043	0.205	0.071	0.121
	0.2	0.378	0.066	−0.76	−0.020	0.429	0.144	0.243
	0.3	0.377	0.099	−0.78	+0.002	0.676	0.220	0.369
	0.4	0.378	0.132	−0.81	+0.015	0.960	0.300	0.495
	0.5	0.380	0.165	−0.84	+0.023	1.275	0.380	0.626
	0.6	0.382	0.198	−0.88	0.028	1.625	0.470	0.763
	0.8	0.389	0.265	−0.98	0.036	2.48	0.655	1.055
	1.0	0.396	0.312	−1.11	0.037	3.62	0.870	1.375
	1.2	0.403	0.402	−1.25	0.037	5.44	1.100	1.730
	1.4	0.410	0.473	−1.46	0.033	8.22	1.375	2.110
	1.6	0.415	0.545	−1.56	0.010	11.20	1.675	2.52
	1.8	0.412	0.616	−1.46	−0.038	13.65	1.985	2.97
	2.0	0.399	0.686	−1.13	−0.096	14.50	2.25	3.35
	2.25	0.369	0.769	−0.74	−0.136	13.20	2.48	3.70
	2.50	0.333	0.845	−0.42	−0.154	11.50	2.62	3.94
	2.75	0.296	0.913	−0.24	−0.138	10.7	2.70	4.13
	3.0	0.263	0.974	−0.14	−0.126	9.54	2.74	4.27
	3.5	0.205	1.075	−0.03	−0.103	8.67	2.79	4.46
	4.0	0.159	1.154	+0.01	−0.081	8.18	2.80	4.60
	4.5	0.125	1.215	0.02	−0.064	7.88	2.80	4.69
	5.0	0.096	1.263	0.03	−0.051	7.67	2.80	4.75
	5.5	0.073	1.301	0.03	−0.043	7.50	2.79	4.81
1.20	0.05	0.348	0.014	−0.625	−0.056	0.088	0.031	0.0555
	0.1	0.346	0.027	−0.635	−0.050	0.182	0.062	0.111
	0.2	0.342	0.058	−0.660	−0.030	0.376	0.127	0.222
	0.3	0.341	0.086	−0.680	−0.010	0.593	0.194	0.336
	0.4	0.340	0.115	−0.700	+0.002	0.830	0.263	0.453
	0.5	0.341	0.143	−0.720	0.007	1.08	0.333	0.573
	0.6	0.342	0.171	−0.745	0.011	1.36	0.408	0.695
	0.8	0.344	0.229	−0.800	0.014	2.00	0.560	0.940
	1.0	0.347	0.286	−0.860	0.014	2.80	0.725	1.210
	1.2	0.350	0.345	−0.930	0.011	3.79	0.906	1.495
	1.4	0.351	0.402	−1.020	0.005	5.03	1.10	1.800
	1.6	0.351	0.461	−1.070	−0.003	6.60	1.31	2.12
	1.8	0.349	0.519	−1.045	−0.015	8.30	1.525	2.44
	2.0	0.344	0.577	−0.960	−0.038	9.65	1.725	2.76
	2.25	0.329	0.648	−0.800	−0.080	10.1	1.94	3.10
	2.50	0.305	0.714	−0.615	−0.100	9.4	2.11	3.40
	2.75	0.280	0.774	−0.430	−0.105	8.8	2.25	3.63
	3.0	0.254	0.830	−0.280	−0.107	8.25	2.35	3.80
	3.5	0.201	0.924	−0.115	−0.094	7.46	2.45	4.03
	4.0	0.159	0.999	−0.050	−0.076	6.95	2.48	4.18
	4.5	0.125	1.058	−0.020	−0.062	6.60	2.49	4.29
	5.0	0.096	1.103	0	−0.051	6.34	2.50	4.37
	5.5	0.073	1.140	+0.01	−0.043	6.16	2.50	4.43
1.30	0.05	0.291	0.011	−0.495	−0.050	0.07	0.0246	0.046
	0.10	0.289	0.021	−0.500	−0.045	0.141	0.0495	0.0925
	0.2	0.285	0.044	−0.504	−0.033	0.289	0.0995	0.186
	0.3	0.282	0.069	−0.510	−0.022	0.447	0.150	0.280
	0.4	0.280	0.088	−0.520	−0.014	0.616	0.201	0.377
	0.6	0.279	0.131	−0.540	−0.006	0.995	0.308	0.570
	0.8	0.277	0.174	−0.560	−0.004	1.41	0.418	0.767
	1.0	0.276	0.216	−0.590	−0.005	1.88	0.530	0.970
	1.2	0.275	0.259	−0.615	−0.008	2.40	0.655	1.183
	1.4	0.272	0.301	−0.640	−0.011	2.98	0.780	1.40
	1.6	0.270	0.343	−0.660	−0.014	3.59	0.915	1.62
	1.8	0.267	0.384	−0.670	−0.018	4.20	1.048	1.85
	2.0	0.263	0.424	−0.670	−0.023	4.84	1.184	2.08
	2.25	0.256	0.475	−0.640	−0.033	5.60	1.35	2.36
	2.50	0.243	0.523	−0.585	−0.046	6.19	1.50	2.62
	2.75	0.228	0.568	−0.525	−0.058	6.39	1.635	2.88
	3.0	0.213	0.610	−0.460	−0.064	6.39	1.765	3.09
	3.50	0.181	0.686	−0.455	−0.064	6.10	1.94	3.42
	4.0	0.149	0.750	−0.125	−0.062	5.72	2.035	3.65
	4.5	0.120	0.801	−0.080	−0.055	5.34	2.090	3.78
	5.0	0.093	0.842	−0.045	−0.048	5.00	2.115	3.86
	5.5	0.072	0.869	−0.022	−0.043	4.75	2.125	3.92

TABLE IV. REDUCED THERMODYNAMIC FUNCTIONS FOR HYDROCARBONS (*Continued*)

T_r	P_r	α_r	$k_1 \ln \frac{f}{P}$	$\left(\frac{\partial\alpha_r}{\partial T_r}\right)_{P_r}$	$\left(\frac{\partial\alpha_r}{\partial P_r}\right)_{T_r}$	$\frac{\Delta C_p}{k_2}$	$\frac{\Delta S'}{k_2}$	$\frac{\Delta H}{k_3}$
1.4	0.05	0.248	0.009	−0.390	−0.050	0.055	0.0196	0.040
	0.10	0.245	0.016	−0.390	−0.046	0.109	0.0390	0.080
	0.2	0.241	0.033	−0.400	−0.037	0.222	0.0786	0.160
	0.3	0.238	0.051	−0.400	−0.030	0.337	0.118	0.240
	0.4	0.235	0.068	−0.405	−0.024	0.456	0.158	0.322
	0.6	0.231	0.102	−0.415	−0.016	0.715	0.240	0.488
	0.8	0.229	0.135	−0.425	−0.012	1.00	0.324	0.650
	1.0	0.226	0.168	−0.440	−0.012	1.30	0.410	0.820
	1.2	0.223	0.200	−0.450	−0.014	1.63	0.499	0.985
	1.4	0.220	0.231	−0.460	−0.016	1.98	0.590	1.16
	1.6	0.216	0.262	−0.466	−0.019	2.34	0.685	1.33
	1.8	0.212	0.293	−0.477	−0.022	2.72	0.778	1.50
	2.0	0.208	0.323	−0.480	−0.027	3.11	0.875	1.68
	2.25	0.200	0.359	−0.480	−0.031	3.60	0.990	1.90
	2.5	0.192	0.395	−0.460	−0.035	4.10	1.115	2.11
	2.75	0.183	0.428	−0.425	−0.039	4.52	1.225	2.33
	3.0	0.173	0.460	−0.385	−0.042	4.84	1.32	2.51
	3.5	0.154	0.518	−0.295	−0.046	5.11	1.49	2.85
	4.0	0.132	0.570	−0.200	−0.046	5.00	1.615	3.10
	4.5	0.108	0.612	−0.140	−0.045	4.80	1.69	3.285
	5.0	0.087	0.647	−0.095	−0.040	4.55	1.75	3.39
	5.5	0.068	0.675	−0.090	−0.035	4.30	1.82	3.46
1.50	0.05	0.212	0.007	−0.320	−0.503	0.043	0.016	0.035
	0.1	0.210	0.013	−0.321	−0.048	0.085	0.0322	0.0695
	0.2	0.206	0.026	−0.324	−0.040	0.170	0.065	0.1390
	0.4	0.198	0.053	−0.332	−0.029	0.344	0.130	0.2790
	0.6	0.194	0.080	−0.338	−0.021	0.530	0.199	0.420
	0.8	0.190	0.106	−0.344	−0.017	0.733	0.267	0.560
	1.0	0.187	0.132	−0.352	−0.016	0.950	0.334	0.700
	1.2	0.183	0.156	−0.360	−0.019	1.175	0.403	0.840
	1.4	0.178	0.180	−0.360	−0.022	1.420	0.475	0.980
	1.6	0.174	0.204	−0.362	−0.024	1.67	0.550	1.125
	1.8	0.169	0.226	−0.360	−0.024	1.94	0.624	1.265
	2.0	0.164	0.249	−0.355	−0.026	2.21	0.700	1.410
	2.5	0.152	0.302	−0.340	−0.028	2.90	0.880	1.750
	3.0	0.138	0.350	−0.310	−0.028	3.55	1.040	2.075
	3.5	0.124	0.394	−0.280	−0.030	3.97	1.175	2.35
	4.0	0.108	0.433	−0.210	−0.034	4.11	1.290	2.60
	4.5	0.091	0.466	−0.160	−0.035	4.09	1.380	2.80
	5.0	0.075	0.494	−0.135	−0.033	3.99	1.460	2.95
	5.5	0.060	0.516	−0.090	−0.027	3.85	1.520	3.06
1.6	0.05	0.183	0.006	−0.272	−0.055	0.034	0.0134	0.031
	0.1	0.180	0.011	−0.272	−0.050	0.067	0.0270	0.062
	0.2	0.176	0.022	−0.274	−0.046	0.134	0.0547	0.124
	0.4	0.169	0.044	−0.278	−0.031	0.268	0.110	0.248
	0.6	0.164	0.065	−0.280	−0.023	0.410	0.165	0.370
	0.8	0.160	0.085	−0.280	−0.019	0.563	0.221	0.493
	1.0	0.156	0.105	−0.280	−0.020	0.725	0.278	0.616
	1.2	0.151	0.124	−0.282	−0.022	0.890	0.331	0.740
	1.4	0.146	0.143	−0.285	−0.023	1.07	0.390	0.860
	1.6	0.141	0.160	−0.283	−0.023	1.24	0.449	0.980
	1.8	0.137	0.177	−0.281	−0.023	1.43	0.505	1.10
	2.0	0.132	0.195	−0.280	−0.023	1.62	0.564	1.22
	2.5	0.121	0.234	−0.265	−0.022	2.10	0.704	1.50
	3.0	0.109	0.270	−0.245	−0.022	2.58	0.833	1.767
	3.5	0.098	0.303	−0.225	−0.022	3.00	0.950	2.00
	4.0	0.088	0.332	−0.200	−0.024	3.29	1.057	2.22
	4.5	0.076	0.358	−0.170	−0.030	3.42	1.150	2.40
	5.0	0.061	0.379	−0.140	−0.029	3.43	1.230	2.55
	5.5	0.048	0.399	−0.113	−0.022	3.40	1.300	2.69
1.8	0.05	0.136	0.004	−0.205	−0.060	0.026	0.010	0.025
	0.1	0.133	0.008	−0.205	−0.055	0.051	0.0202	0.050
	0.2	0.128	0.015	−0.206	−0.048	0.100	0.0410	0.100
	0.4	0.120	0.028	−0.207	−0.033	0.200	0.0820	0.199
	0.6	0.115	0.042	−0.208	−0.024	0.305	0.123	0.298
	0.8	0.111	0.054	−0.207	−0.020	0.410	0.164	0.395
	1.0	0.107	0.066	−0.205	−0.021	0.515	0.205	0.490
	1.2	0.103	0.078	−0.204	−0.022	0.620	0.248	0.585
	1.4	0.097	0.089	−0.201	−0.022	0.728	0.290	0.680
	1.6	0.093	0.100	−0.200	−0.020	0.840	0.330	0.770
	1.8	0.090	0.110	−0.195	−0.018	0.950	0.370	0.865
	2.0	0.086	0.120	−0.190	−0.015	1.050	0.408	0.950
	2.5	0.079	0.143	−0.178	−0.016	1.310	0.500	1.150
	3.0	0.070	0.164	−0.166	−0.016	1.56	0.590	1.350
	3.5	0.062	0.182	−0.155	−0.016	1.80	0.677	1.53
	4.0	0.054	0.198	−0.144	−0.017	2.00	0.755	1.695
	4.5	0.045	0.212	−0.130	−0.019	2.16	0.830	1.85
	5.0	0.034	0.223	−0.108	−0.021	2.28	0.900	1.974
	5.5	0.026	0.231	−0.100	−0.013	2.36	0.960	2.086
2.0	0.05	0.099	0.003	−0.162	−0.056	0.017	0.008	0.021
	0.1	0.096	0.005	−0.161	−0.050	0.035	0.0161	0.042
	0.2	0.092	0.009	−0.162	−0.040	0.070	0.032	0.084
	0.4	0.084	0.018	−0.161	−0.031	0.143	0.064	0.165
	0.6	0.079	0.026	−0.160	−0.023	0.218	0.096	0.247
	0.8	0.075	0.034	−0.160	−0.021	0.295	0.128	0.326
	1.0	0.071	0.041	−0.159	−0.020	0.373	0.160	0.404
	1.2	0.067	0.048	−0.158	−0.020	0.450	0.191	0.480
	1.4	0.063	0.055	−0.154	−0.019	0.528	0.221	0.554
	1.6	0.059	0.061	−0.152	−0.018	0.603	0.251	0.630
	1.8	0.056	0.066	−0.148	−0.016	0.680	0.281	0.700
	2.0	0.053	0.072	−0.142	−0.014	0.752	0.311	0.770
	2.5	0.048	0.084	−0.132	−0.011	0.935	0.381	0.935
	3.0	0.042	0.096	−0.124	−0.012	1.10	0.446	1.088
	3.5	0.036	0.105	−0.119	−0.014	1.25	0.507	1.23
	4.0	0.028	0.113	−0.113	−0.015	1.375	0.565	1.365
	4.5	0.021	0.119	−0.108	−0.015	1.48	0.620	1.485
	5.0	0.014	0.124	−0.093	−0.014	1.56	0.675	1.596
	5.5	0.008	0.126	−0.086	−0.010	1.62	0.720	1.692
2.2	0.1	0.066	0.003	−0.139	−0.042	0.025	0.0135	0.0369
	0.2	0.062	0.006	−0.137	−0.035	0.051	0.0268	0.0730
	0.4	0.056	0.011	−0.133	−0.027	0.105	0.0530	0.144
	0.6	0.051	0.016	−0.130	−0.022	0.161	0.0790	0.213
2.2	0.8	0.047	0.020	−0.128	−0.020	0.219	0.105	0.280
	1.0	0.043	0.025	−0.126	−0.020	0.277	0.130	0.346
	1.2	0.039	0.028	−0.124	−0.018	0.333	0.155	0.410
	1.4	0.036	0.032	−0.121	−0.015	0.391	0.180	0.474
	1.6	0.034	0.035	−0.118	−0.012	0.448	0.202	0.535
	1.8	0.032	0.038	−0.115	−0.010	0.500	0.225	0.595
	2.0	0.030	0.041	−0.112	−0.010	0.554	0.248	0.654
	2.5	0.025	0.047	−0.106	−0.010	0.680	0.300	0.795
	3.0	0.020	0.052	−0.100	−0.010	0.790	0.352	0.925
	3.5	0.014	0.056	−0.097	−0.012	0.885	0.400	1.046
	4.0	0.008	0.058	−0.093	−0.013	0.975	0.448	1.158
	4.5	+0.001	0.059	−0.090	−0.012	1.05	0.490	1.26
	5.0	−0.004	0.059	−0.080	−0.010	1.12	0.530	1.35
	5.5	−0.007	0.058	−0.075	−0.003	1.18	0.570	1.436
2.5	0.1	0.029	0.002	−0.111	−0.027	0.016	0.011	0.0300
	0.2	0.027	0.003	−0.110	−0.025	0.032	0.022	0.059
	0.4	0.022	0.005	−0.108	−0.022	0.064	0.0435	0.115
	0.6	0.018	0.007	−0.104	−0.020	0.096	0.0645	0.169
	0.8	0.014	0.009	−0.100	−0.017	0.128	0.0850	0.220
	1.0	0.010	0.010	−0.096	−0.015	0.160	0.105	0.270
	1.2	0.008	0.011	−0.093	−0.013	0.192	0.1235	0.320
	1.4	0.006	0.011	−0.090	−0.010	0.224	0.142	0.369
	1.6	0.004	0.012	−0.088	−0.008	0.255	0.160	0.415
	1.8	0.003	0.012	−0.086	−0.007	0.288	0.178	0.460
	2.0	+0.002	0.012	−0.084	−0.007	0.319	0.195	0.502
	2.5	−0.002	0.012	−0.082	−0.008	0.395	0.236	0.607
	3.0	−0.006	0.011	−0.080	−0.010	0.467	0.275	0.705
	3.5	−0.011	0.009	−0.075	−0.010	0.535	0.314	0.797
	4.0	−0.016	0.007	−0.070	−0.010	0.605	0.350	0.882
	4.5	−0.020	+0.003	−0.065	−0.010	0.665	0.385	0.960
	5.0	−0.024	−0.001	−0.060	−0.006	0.725	0.415	1.031
	5.5	−0.027	−0.007	−0.060	−0.002	0.785	0.446	1.095

ENTROPY. The equation for the entropy

$$dS = \frac{C_p}{T}\,dT - \left(\frac{\partial V}{\partial T}\right)_p dP \tag{9}$$

becomes, on the introduction of α_r and reduced units,

$$dS = \frac{C_p}{T}\,dT - \frac{R}{P}\,dP + \frac{P_c\alpha_c}{T_c}\left(\frac{\partial\alpha_r}{\partial T_r}\right)_{Pr} dP_r \tag{10}$$

If we integrate, change the sign of the third term, and replace $P_c\alpha_c/T_c$ with k_2, an equation for the change of entropy results:

$$\Delta S = C_p \ln T - R \ln P - k_2 \int - \left(\frac{\partial\alpha_r}{\partial T_r}\right)_{Pr} dP_r \tag{11}$$

The first and second terms can easily be evaluated for any specific problem, but it is desirable to integrate the third term in reduced units. If Equation 11 is written

$$\Delta S = C_p \ln T - R \ln P - \Delta S' \tag{12}$$

where

$$\frac{\Delta S'}{k_2} = \int_0^{P_r} - \left(\frac{\partial\alpha_r}{\partial T_r}\right)_{Pr} dP_r \tag{13}$$

and Equation 13 is integrated, the result is shown in Table IV under "$\Delta S'/k_2$." By means of Equations 12 and 8, and values of $\Delta S'/k_2$ in Table IV, the change of entropy between any two conditions for hydrocarbon vapors may be estimated.

ENTHALPY. The equation for the enthalpy

$$dH = C_p dT - \left[\,T\left(\frac{\partial V}{\partial T}\right)_p - V\right] dP \tag{14}$$

becomes, when α_r and reduced units are introduced,

$$dH = C_p dT - P_c\alpha_c\left[\,\alpha_r - T_r\left(\frac{\partial\alpha_r}{\partial T_r}\right)_{Pr}\right] dP_r \tag{15}$$

With temperature constant, the integral of the second term gives the effect of pressure on the enthalpy. Defining $P_c\alpha_c$ as k_3 and integrating from P_r to $P_r = 0$,

$$\frac{\Delta H}{k_3} = \int_0^{P_r} \left[\alpha_r - T_r\left(\frac{\partial \alpha_r}{\partial T_r}\right)_{Pr}\right] dP_r \qquad (16)$$

where ΔH is the change of enthalpy from zero pressure to P_r at constant temperature. This integration was performed graphically for different reduced temperatures; values of $\Delta H/k_3$ are listed in Table IV. The effect of temperature on enthalpy may be determined by means of Equation 8.

The following example illustrates the use of the data of Table IV in computing the isothermal pressure correction to the enthalpy: Find ΔH (to be subtracted from the enthalpy at atmospheric pressure) for propane at 206° F. and 586 pounds per square inch absolute. The reduced temperature, T_r, is 1.0; the reduced pressure, P_r, is 0.95; and the reduced pressure at atmospheric pressure, P_r, is 0.024. At $T_r = 1.00$ and $P_r = 0.024$ and 0.95, the values of $\Delta H/k_3$ are found to be 2.87 and 0.037 from Table IV (0.037 was obtained by extrapolation). By means of constants from Table II, ΔH is found as follows:

$$\Delta H = (2.87 - 0.037)\ 538 \times 1.8 \times \frac{1}{44.06} = 62.25 \text{ B. t. u./lb.}$$

DIFFERENCE IN SPECIFIC HEATS. The equation for the difference in specific heats

$$C_p - C_v = -T \frac{\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} \qquad (17)$$

becomes, on the introduction of α_r and reduced units,

$$C_p - C_v = -T \frac{\left[\frac{R}{P} - \frac{\alpha_c}{T_c}\left(\frac{\partial \alpha_r}{\partial T_r}\right)_{Pr}\right]^2}{\left[\frac{RT}{P^2} + \frac{\alpha_c}{P_c}\left(\frac{\partial \alpha_r}{\partial P_r}\right)_{Tr}\right]} \qquad (18)$$

The derivatives $\left(\frac{\partial \alpha_r}{\partial T_r}\right)_{Pr}$ and $\left(\frac{\partial \alpha_r}{\partial P_r}\right)_{Tr}$ were determined graphically by the chord area method from large-scale plots of α_r vs. T_r isobars and α_r vs. P_r isotherms, and are listed for several values of reduced pressures and temperatures in Table IV. By means of Equation 18 and the data in Tables II and IV the difference in specific heats may be estimated for hydrocarbon vapors. With C_p estimated from Equations 7 and 8, C_v and C_p/C_v may also be estimated.

Comparison of Results with Experimental Data

ETHANE. Sage, Webster, and Lacey (*30*) determined the effect of pressure on the enthalpy of ethane. The following table gives a comparison of ΔH (to be subtracted from enthalpy at atmospheric pressure to obtain enthalpy at higher pressure) in B. t. u. per pound at three temperatures:

Pressure	70° F.			100° F.			220° F.		
	Sage, Webster, and Lacey	Watson and Nelson	Edmister	Sage, Webster, and Lacey	Watson and Nelson	Edmister	Sage, Webster, and Lacey	Watson and Nelson	Edmister
Lb./sq. in. abs.									
100	4.41	8.12	7.07	4.02	6.9	5.13	2.69	4.07	3.45
300	17.25	27.9	23.08	15.44	23.3	18.70	9.78	13.58	11.88
500	38.0	54.8	51.38	..	..	..	..	..	..
600	..	..	..	41.43	50.3	48.77	21.88	29.4	25.2
1000	..	..	..	127.13	130.4	146.62	40.2	52.0	44.8
3500	..	..	..	..	..	..	110.05	113.2	109.9

The first column gives the experimental data of Sage, Webster, and Lacey (*30*); the second column gives values of ΔH computed from a Watson and Nelson $\Delta H/T$ plot (*34*); and the third column gives the values of ΔH computed from the data in Table IV, using the constants given in Table II and correcting the results to a reference pressure of one atmosphere. Since Watson and Nelson's method (*34*) is based on an approximate equation of state derived from a PV/RT correlation, it was expected that their results would deviate from the actual values. The agreement between their values and the values calculated by the above method is not bad, however. The discrepancy between the experimental data of Sage, Webster, and Lacey (*30*) and the values calculated by the above method is more difficult to explain, however. The computed pressure corrections to the enthalpy at and near the critical state are considerably higher than the experimental values of Sage, Webster, and Lacey. The maximum deviation of the α_r correlation for ethane is 3.5 per cent (it is even lower at the critical state), and the effect of pressure on enthalpy was computed by means of proved and accepted thermodynamic formulas and the α_r correlation. Therefore, the discrepancy between the calculated and the observed values of ΔH appears to be higher than one would expect.

BENZENE. Lindsay and Brown (*23*) obtained some isoenthalpic expansion data on benzene and from it computed the effect of pressure on enthalpy. The following table gives a comparison of ΔH (B. t. u. per pound to be subtracted from enthalpy at $P_r = 0.03$) for benzene at three reduced temperatures:

P_r	$T_r = 0.90$			$T_r = 1.0$			$T_r = 1.1$		
	Lindsay and Brown	Watson and Nelson	Edmister	Lindsay and Brown	Watson and Nelson	Edmister	Lindsay and Brown	Watson and Nelson	Edmister
0.03	0	0	0	0	0	0	0	0	0
0.1	2.92	4.4	2.96	2.84	3.62	2.13	2.85	2.79	1.76
0.2	8.15	9.42	7.65	5.81	7.75	5.85	5.13	5.66	4.33
0.3	14.6	14.9	13.0	9.29	11.75	8.65	7.41	8.95	6.91
0.4	20.6	20.5	19.6	14.2	16.52	12.4	11.4	12.3	9.65
0.5	27.2	27.4	28.2	18.7	21.20	16.51	14.52	15.75	12.43
0.6	...	...	...	21.95	25.8	21.05	18.10	19.5	15.41
0.7	...	...	...	28.4	30.7	26.35	21.65	22.7	18.35
0.8	...	...	...	32.9	36.2	33.11	25.05	27.6	21.95
0.9	...	...	...	40.0	43.2	44.2	29.90	30.4	25.5
1.0	...	...	...	47.8	64.5	73.71	33.45	34.3	29.5
1.2	...	...	...	...	...	...	42.7	42.5	38.4
1.3	...	...	...	83.9	102.0	110.5	...	...	...

One column gives the experimental data of Lindsay and Brown (*23*); another gives values of ΔH computed from a Watson and Nelson plot (*34*); and the third gives values of ΔH computed from the data in Table IV, using the constants given in Table II and correcting the results to a reference pressure of $P_r = 0.03$.

The disagreement at and near the critical state of ΔH values computed from Table IV and the data of Lindsay and Brown (*23*) is quite large. It seems reasonable to expect the isothermal enthalpy correction at the critical temperature to increase more rapidly as the critical pressure is approached than the data of Lindsay and Brown indicate.

Values of ΔH computed from Table IV for ethane are higher than the data of Sage, Webster, and Lacey (*30*); values of ΔH computed from Table IV for benzene are lower (except near and at the critical state where they are higher) than the data of Lindsay and Brown (*23*). Since they are "reduced" thermodynamic properties and are obtained from generalized calculations, the data in Table IV are consistent, whereas the disagreements with the above-mentioned data are not consistent. Consistency in thermal data is important in engineering design calculations. It is desirable to have reliable and consistent experimental data on the effect of pressure on enthalpy and other thermal properties.

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Specific Heat Ratios for Hydrocarbons

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A chart is presented for estimating C_p/C_v (γ) ratios for methane, ethylene, ethane, propylene, propane, isobutylene, isobutane, 2-butene, *n*-butane, isopentane, *n*-pentane, benzene, diisopropyl, *n*-hexane, *n*-heptane, diisobutyl, and *n*-octane at reduced pressures up to 1.2 and at reduced temperatures up to 2.5.

THE ratio of isobaric to isometric specific heats, $C_p/C_v = \gamma$, is an essential thermodynamic property in calculations involving the adiabatic compression or expansion of a gas. It may be determined experimentally or computed by thermodynamic relations from *P-V-T* and atmospheric specific-heat data. There are few γ data, either experimental or calculated, for hydrocarbons, however. Some experimental γ data are available (*3*) at atmospheric pressure for hydrocarbons of one to six carbon atoms. Values at various pressures have been computed and plotted only for methane (*2*).

Basic Equations

The two fundamental thermodynamic equations used in computing C_p/C_v ratios from *P-V-T* and atmospheric specific heat data are:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P \qquad (1)$$

$$C_p - C_v = -T\,\frac{\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} \qquad (2)$$

The integration constant for Equation 1 must be found from experimental isobaric specific heat data. Although data at any pressure could be used, data only at atmospheric pressure are available. The volume derivatives for the above equations can be determined graphically or analytically from *P-V-T* data by means of graphic or algebraic equations of state.

In a previous paper (*1*) a generalized reduced correlation of *P-V-T* data for hydrocarbons was developed by using the volume residual quantity, α, which is defined as the difference in the ideal and the actual gas volumes. The resulting correlation gave the reduced volume residual quantity, α_r, as a function of reduced temperature T_r and pressure P_r.

When expressed in terms of α_r and reduced units and integrated between the limits of P_r and $P_r = 0$ at constant values of T_r, Equation 1 becomes:

$$\frac{\Delta C_p}{K_2} = T_r \int_0^{P_r} \left(\frac{\partial^2 \alpha_r}{\partial T_r^2}\right)_{P_r} dP_r \qquad (3)$$

where ΔC_p = increase in isobaric specific heat from 0 pressure to any pressure P_r

$K_2 = P_c\alpha_c/T_c$, a constant for each hydrocarbon

The second derivative was determined graphically from the α_r correlation, Equation 3 was integrated, and values of $\Delta C_p/K_2$ were tabulated (*1*). From these results the effect of pressure on the isobaric specific heat can be computed. The effect of temperature on the specific heat can be calculated by the correlation of atmospheric specific-heat data (*1*).

Upon the introduction of α_r and reduced units, Equation 2 becomes:

$$C_p - C_v = T\,\frac{\left[\frac{R}{P} - \frac{\alpha_c}{T_c}\left(\frac{\partial \alpha_r}{\partial T_r}\right)_{P_r}\right]^2}{\left[\frac{RT}{P^2} + \frac{\alpha_c}{P_c}\left(\frac{\partial \alpha_r}{\partial P_r}\right)_{T_r}\right]} \qquad (4)$$

The derivatives of α_r were determined graphically from the α_r correlation and were tabulated (*1*).

Calculation and Correlation of C_p/C_v

The computation of C_p/C_v ratios from these equations and reduced thermodynamic functions were made for various reduced temperatures and pressures for seventeen hydrocarbons, and the resulting C_p/C_v ratios were plotted against P_r for lines for constant T_r. One of these plots (for propane) is shown in Figure 1. Comparison of the plots showed that they were very similar and that all of them could be made to coincide by either expanding or condensing their C_p/C_v scales. In other words, Figure 1 for propane will hold equally well for all the other hydrocarbons if different numerical values are given the ordinate scale. This is done by the following equation:

$$\gamma = 1 + C(\gamma_3 - 1) \qquad (5)$$

where γ_3 = value of C_p/C_v for propane

C = constant for each hydrocarbon (Table I)

γ = C_p/C_v for the hydrocarbon in question

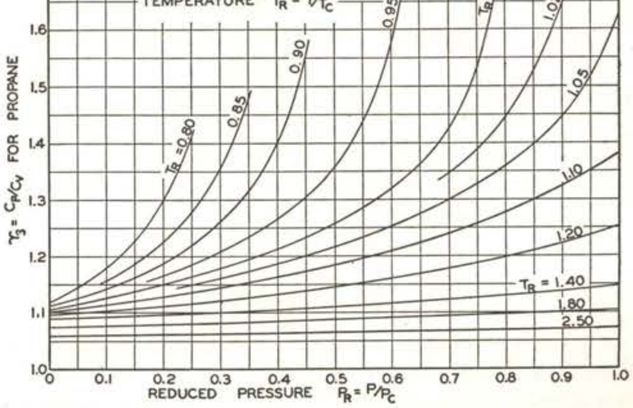

FIGURE 1. PLOT FOR PROPANE

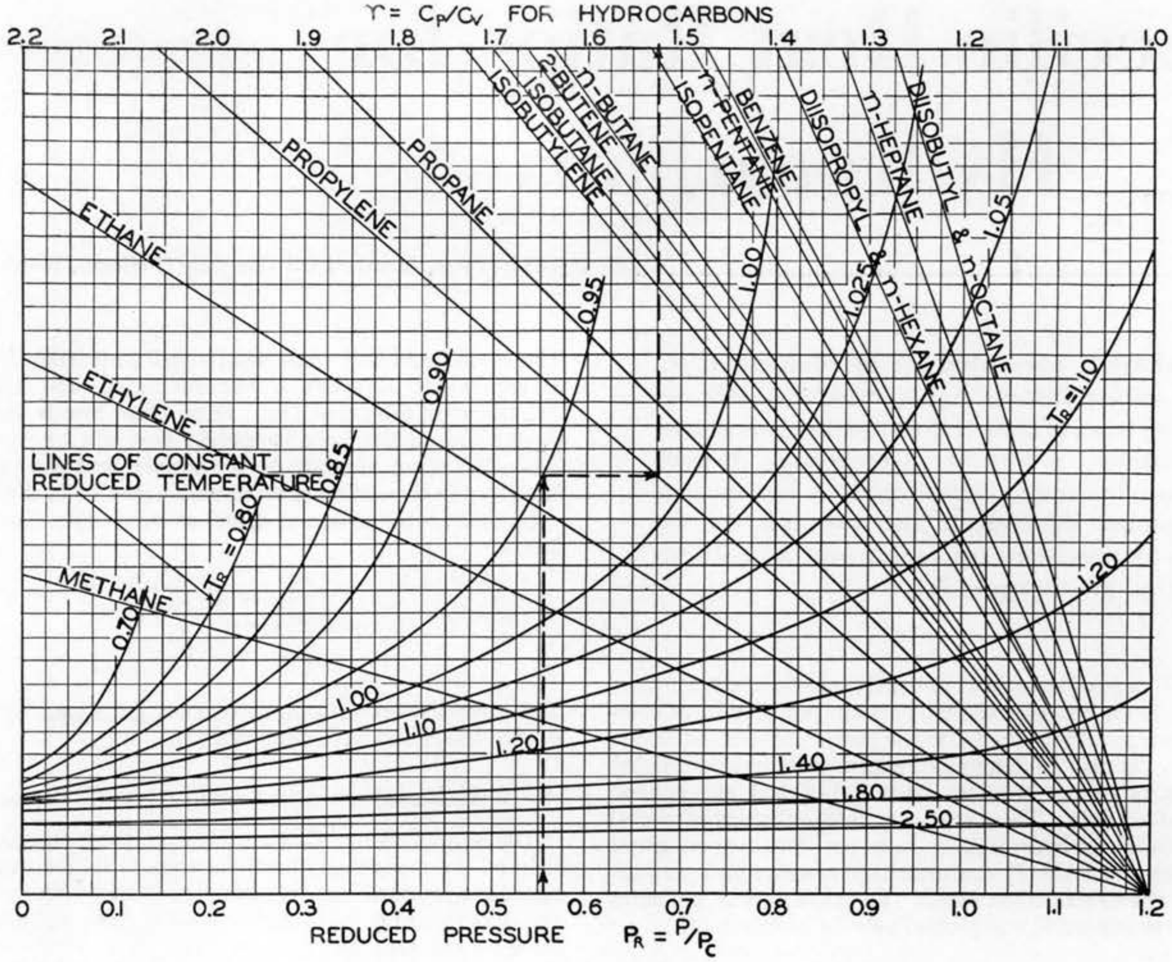

FIGURE 2. GRAPHICAL METHOD FOR ESTIMATING γ

By means of Figure 1, Table I, and Equation 5 the C_p/C_v ratio can be estimated for all seventeen of the hydrocarbons listed in Table I for the range of temperature and pressure covered by Figure 1.

Figure 2 combines Figure 1, Table I, and Equation 5 to present a rapid graphical method for estimating γ. In constructing Figure 2, the pressure and temperature ranges were extrapolated. The solution of an example is shown by heavy dashed lines and arrows; we find $\gamma = 1.525$ for propylene at $P_r = 0.555$ and $T_r = 0.95$.

TABLE I. CONSTANTS FOR SEVENTEEN HYDROCARBONS

Hydrocarbon	Value of Constant for Equation 5	Hydrocarbon	Value of Constant for Equation 5	Hydrocarbon	Value of Constant for Equation 5
Methane	3.5	Isobutane	0.778	Diisopropyl	0.442
Ethylene	2.1	2-Butene	0.737	*n*-Hexane	0.442
Ethane	1.58	*n*-Butane	0.705	*n*-Heptane	0.364
Propylene	1.17	Isopentane	0.590	Diisobutyl	0.300
Propane	1.00	*n*-Pentane	0.541	*n*-Octane	0.300
Isobutylene	0.810	Benzene	0.525		

Accuracy of Correlation

Figure 2 gives values of γ that check the values computed from the original *P-V-T* correlation with a maximum deviation of ±4 per cent. Most of the points are checked within 1 per cent by the correlation.

As a test of the above correlation, values of γ from it were compared with the atmospheric pressure experimental data from the International Critical Tables (*3*). The maximum deviation was 4 per cent. A comparison at higher pressure would be more severe and of more interest, but unfortunately there are no high-pressure experimental γ data.

Application of Results

The C_p/C_v ratio is primarily of use in calculations of isentropic expansion and compression of gases. The following equation for the theoretical horsepower required for single-stage adiabatic compression of gas is based upon the assumption of perfect gas behavior:

$$\text{H. P.} = \frac{144\, P_1V_1}{33{,}000}\left(\frac{\gamma}{\gamma - 1}\right)\left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma - 1}{\gamma}} - 1\right] \qquad (6)$$

In such processes neither pressure nor temperature remains constant, but each necessarily varies. The conventional use of Equation 6 is with a constant specific-heat ratio throughout the process. For want of better data, the atmospheric pressure γ or even the γ for air is frequently used for hydrocarbons. Such a procedure will cause appreciable errors in many cases. Figure 2 shows that γ varies widely with temperature, pressure, and molecular weight. Although a rigorous solution of Equation 6 would require integration with γ as a variable, sufficient accuracy for engineering purposes is obtained when γ is considered constant at an average of the values at the inlet and outlet conditions.

The use of Equation 6 with γ values from Figure 2 is a step in the right direction but does not correct for the fact that Equation 6 is based on perfect gas law behavior. However, the effect of deviation from ideal gas law behavior on Equation 6 is not so important as the effect on γ; therefore the use of Figure 2 should greatly improve the accuracy of such computations.

In engineering work the compression and expansion of mixtures is frequently encountered. γ for mixtures may be determined by computing the molal average of γ values of the individual components, the γ for each component being determined for the temperature and total pressure involved.

Acknowledgment

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(3) International Critical Tables, Vol. V, p. 80, New York, McGraw-Hill Book Co., 1929.

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Liquefaction and Regasification of Lighter Hydrocarbons

BY

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The design of equipment for the liquefaction and regasification of the lighter hydrocarbons which make up natural gas, so that large quantities may be stored in relatively small tanks, requires an accurate knowledge of the thermodynamic properties of the various hydrocarbons and their mixtures. In designing and operating a light hydrocarbon liquefaction plant, vapor pressures, boiling points, dew points and critical points are required, and in addition entropies and enthalpies. The latter two may be presented in a form similar to steam tables or they may be presented graphically in Mollier diagrams.

Here Mollier diagrams for various hydrocarbons are given, and the large amount of data that may be derived from them are discussed. Features of the natural-gas liquefaction plant at Cleveland, Ohio, are also described. The paper was presented before the Petroleum division of the American Society of Mechanical Engineers at its semiannual meeting held this summer in Kansas City, Mo.

A very important recent development in the gas industry is the liquefaction of natural gas so that large quantities of it may be stored in relatively small tanks. The design of equipment for the liquefaction and regasification of the lighter hydrocarbons, which make up natural gas, requires an accurate knowledge of the thermo-dynamic properties of the various hydrocarbons and their mixtures.

The lighter hydrocarbons, which constitute natural gas, are: methane, ethane, propane, isobutane and normal butane, and in addition to these, ethylene and propylene are found in refinery gas. These hydrocarbons contain from one to four carbon atoms per molecule and have molecular weights from 16 to 58 with corresponding specific gravities from 0.55 to 2.0 (air = 1.0). The most prolific source of these hydrocarbons is petroleum. They are found in the earth by themselves in the form of a natural gas, or in conjunction with oil (in solution in the oil or in equilibrium with it), and in addition they are produced by the decomposition of oil. In general, the hydrocarbons found in nature are the paraffinic or saturated ones, i. e., methane, ethane, propane and butane. The unsaturated hydrocarbons, ethylene, propylene, etc., are usually products of cracking. Hydrocarbons are also found in manufactured gases.

These hydrocarbons are seldom found in the pure state, but as multicomponent mixtures of various proportions. To isolate pure hydrocarbons is expensive. Even commercially pure hydrocarbons that contain over 95% of one component contain sufficient lighter and heavier components to give physical properties that are different than the pure components. Methane is the chief constituent of natural gas, usually being 80% to 90%, and is used chiefly as a fuel both for domestic and industrial purposes and in the manufacture of carbon black. The principal use for methane is fuel because of its resistance to decomposition. Ethane is used chiefly as a fuel, seldom by itself, but mainly as a component of natural gas. Ethylene, which has a wide number of uses, can be used as a refrigerant, as a fuel, or as a base material for making a number of plastics, alcohols and other chemicals. Propane is widely used as a liquid fuel, being transported in the liquid state and vaporized for use as a fuel. Propane is also used in refining processes as a solvent and diluent and as a base material for organic synthesis. Propane may also be used as a refrigerant. The butanes may also be used as refrigerants and liquid fuels. In addition to these uses, the butanes are widely used in the manufacture of gasoline by serving as a volatility blending agent and as a base material for the synthesis of iso-octane. Through pyrolysis and other processing butanes are used to produce synthetic chemicals and rubber.

Vapor Pressures

At atmospheric pressure and normal temperatures these hydrocarbons are gaseous. Very high pressures and/or unusually low temperatures are required to liquefy them. In studying the transformation of these hydrocarbons from the vapor to the liquid phase, a knowledge of vapor pressures, boiling and dew points, and critical points is essential. The atmospheric pressure boiling points of these hydrocarbons are as follows:

Methane	—258.5°F.
Ethylene	—154.7°F.
Ethane	—128.2°F.
Propylene	—53.7°F.
Propane	—43.8°F.
Isobutane	+10.0°F.
Normal Butane	+31.1°F.

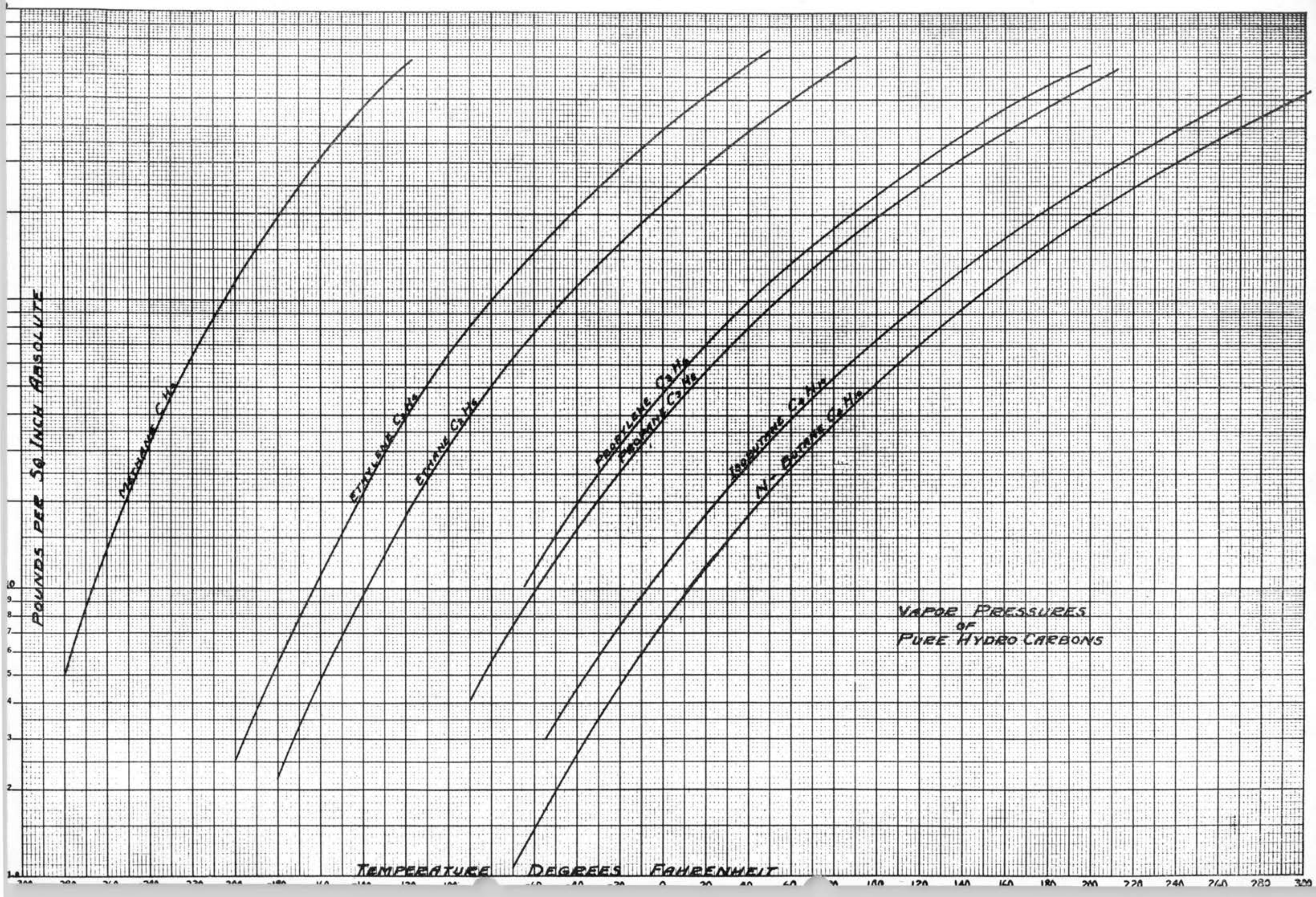
It can be seen from the above table that if methane is to be boiled at atmospheric pressure, an extremely low temperature will result; or, in other words, if the methane is to be liquefied at atmospheric pressure, a temperature of minus 258.5°F. is necessary.

Figure No. 1 is a vapor pressure chart of these hydrocarbons. This chart gives the pressures and corresponding temperatures at which these hydrocarbons will boil at all pressures and temperatures up to the critical. From this curve can be established the temperature or corresponding pressure at which these hydrocarbons can be either liquefied or regasified.

Since it is necessary to have a temperature lower than the critical in order to liquefy any gas, it is necessary that any liquefaction process operate at a temperature below the critical and the corresponding vapor pressures. The critical conditions for these hydrocarbons are as follows:

	Temperature, °F.	Pressure p.s.i. Abs.
Methane	—116.5	673
Ethane	90.1	712
Ethylene	49.8	748
Propane	206.0	617
Propylene	197.6	662
Isobutane	273.2	544
Normal Butane	305.6	551

Some of the hydrocarbons can be condensed with water, as can be seen from the vapor-pressure chart (Figure 1). Eighty degrees F. water could be used to



VAPOR PRESSURES
OF
PURE HYDRO CARBONS

condense the propane, and the butanes and ethane might be condensed, providing sufficient surface was available in the condenser. Since it has a critical temperature of 90°, it would be necessary to remove sufficient heat to liquefy ethane at this temperature, although the operating pressures would be quite high.

Except in rare cases, ethylene, with a critical temperature of 49.8°F., cannot be condensed with water, and methane, with a critical temperature of minus 116.5°F., very definitely requires some other form of cooling than water. For condensing either ethylene or methane, some other form of mechanical refrigeration is necessary. It would probably be preferable to use either propane or ammonia as the refrigerant to condense these two light gases.

Instead of a vapor-pressure curve, hydrocarbon mixtures have bubble and dew point curves. At the bubble point the mixture is completely in the liquid phase but at the point of incipient boiling, so that an infinitesimal decrease in pressure or increase in temperature will cause vaporization to start. At the dew point the mixture is completely in the vapor phase but at the point of incipient condensation, so that an infinitesimal increase in pressure or decrease in temperature will start the condensation. The boiling and dew points for hydrocarbon mixtures may be estimated by means of equilibrium constants based on fugacities and vapor pressures. This subject has been receiving considerable attention recently so it need not be discussed here.

Mollier Diagram

In addition to the vapor pressures, boiling points, dew points, and critical points, entropies and enthalpies are also required in designing and operating a light hydrocarbon liquefaction plant. This subject has received very little attention and it is the purpose of this paper to rectify this situation. As in practically all process-design problems, it is necessary to know the difference in the enthalpy for a given process to estimate work, heat absorbed, etc. The process in question may take place at constant pressure, temperature, or entropy. In the latter case the quantitative value of the entropy is not necessary, it being sufficient to know that the entropy remained constant. It is also frequently necessary to estimate changes in temperature when throttling at constant enthalpy. Entropies and enthalpies may be tabulated in a form similar to the steam tables or they may be presented in graphical form such as the Mollier Diagram. There are two types of Mollier Diagrams in wide usage by the engineering profession: (1) Enthalpy vs. entropy with temperature, pressure and volume parameters; and (2) Enthalpy vs. pressure (on log scale) with temperature, entropy and volume parameters. Mollier Diagrams for steam are generally of the first type, while those for refrigerants, such as ammonia and SO_2, are generally of the second type. For use in hydrocarbon liquefaction calculations the Mollier Diagram should cover the saturated liquid, saturated vapor, and superheated vapor states.

The construction of a Mollier Diagram involves the application of rigorous fundamental thermodynamic equations to accurate experimental data on the volumetric and calorimetric behavior of the hydrocarbon or hydrocarbon mixture in question. Essential data include:

(a) Vapor pressure for single component or bubble point and dew point (phase diagram) relationship for mixtures.

(b) Latent heat of vaporization.

(c) Specific heat of liquid.

(d) Specific heat of the vapor at a constant pressure of one atmosphere.

(e) Deviation from perfect gas laws or pressure-volume-temperature data for the superheated vapor.

Deviations from the perfect gas law are important because they reflect the effect of pressure on the entropy and the enthalpy. For a perfect gas the enthalpy is independent of pressure. The deviation from the perfect gas law is a function of the nearness to the critical point, where the perfect gas laws may be as much as 400% to 500% in error. In a previous paper, Edmister[1] developed a generalized correlation of hydrocarbon P-V-T data from which he computed by accurate graphical methods various reduced thermodynamic properties that may be applied to hydrocarbons by means of the critical point for pure components and the pseudo-critical point for mixtures.

Using the above mentioned reduced thermodynamic properties to compute the effects of deviations from perfect gas laws, together with experimental calorimetric and vapor pressure or phase diagram data, Mollier diagrams were prepared for methane, propane, propylene, butane and three mixtures of light hydrocarbons. In constructing these diagrams, the reference point selected was saturated liquid at −200°F. Since we are working with differences in enthalpy and not absolute values, the reference point has no bearing on the ultimate answer. It merely regulates the scale.

Figures 2, 3, 4 and 5 are the Mollier diagrams for the methane, propane, propylene and butane, respectively. These charts are for pure hydrocarbons which are seldom encountered in practice. Most practical work is concerned with mixtures of hydrocarbons.

Figure No. 6 is the Mollier diagram for a typical plant propane. This propane mixture has been used in a propane refrigeration process. Its analysis is as follows:

Hydrocarbons	Mol. %
Methane	0.80
Ethylene	1.11
Ethane	3.20
Propylene	23.42
Propane	71.41
Butane	.06
	100.00

This mixture is essentially a commercial propane but its characteristics are considerably different than pure propane. It will be noted that the chief difference between Figure 6 and Figure 3 of the Mollier chart for pure propane is that the lines of constant temperature between a saturated vapor and a saturated liquid are flat for pure propane and sloping for the plant propane. In other words, constant pressure vaporization occurs at constant temperature for pure propane but with an increase in temperature for the plant propane.

Figure No. 7 is a propane-butane mixture of the following composition:

Hydrocarbons	Mol. %
Propane	20
Butane	80
	100

Here again it will be noted that the latent heat lines are sloped.

Figure No. 8 is a diagram for a propane-propylene mixture of the following composition:

Hydrocarbons	Mol. %
Propane	21
Propylene	79
	100

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[1] Ind. Eng. Chem. *30*, 352 (1938).

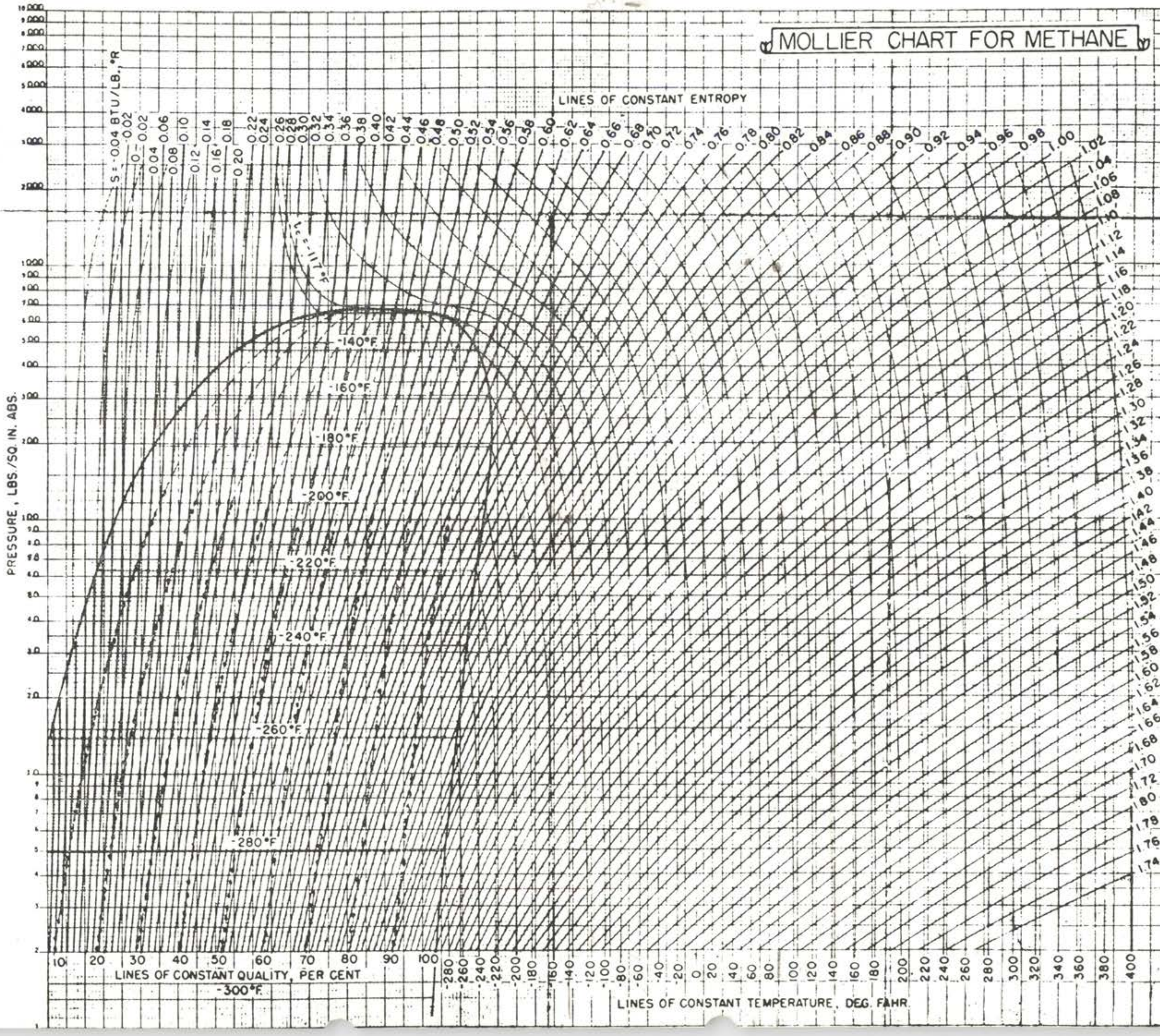

MOLLIER CHART FOR METHANE
LINES OF CONSTANT ENTROPY
S = -0.04 BTU/LB., °R
-0.02
0
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
0.20
0.22
0.24
0.26
0.28
0.30
0.32
0.34
0.36
0.38
0.40
0.42
0.44
0.46
0.48
0.50
0.52
0.54
0.56
0.58
0.60
0.62
0.64
0.66
0.68
0.70
0.72
0.74
0.76
0.78
0.80
0.82
0.84
0.86
0.88
0.90
0.92
0.94
0.96
0.98
1.00
1.02
1.04
1.06
1.08
1.10
1.12
1.14
1.16
1.18
1.20
1.22
1.24
1.26
1.28
1.30
1.32
1.34
1.36
1.38
1.40
1.42
1.44
1.46
1.48
1.50
1.52
1.54
1.56
1.58
1.60
1.62
1.64
1.66
1.68
1.70
1.72
1.80
1.78
1.76
1.74
PRESSURE, LBS./SQ. IN. ABS.
10,000
9,000
8,000
7,000
6,000
5,000
4,000
3,000
2,000
1,000
900
800
700
600
500
400
300
200
100
90
80
70
60
50
40
30
20
10
9
8
7
6
5
4
3
2
-140°F
-160°F
-180°F
-200°F
-220°F
-240°F
-260°F
-280°F
-300°F
10
20
30
40
50
60
70
80
90
100
LINES OF CONSTANT QUALITY, PER CENT
-280
-260
-240
-220
-200
-180
-160
-140
-120
-100
-80
-60
-40
-20
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
LINES OF CONSTANT TEMPERATURE, DEG. FAHR.

Fig. 2

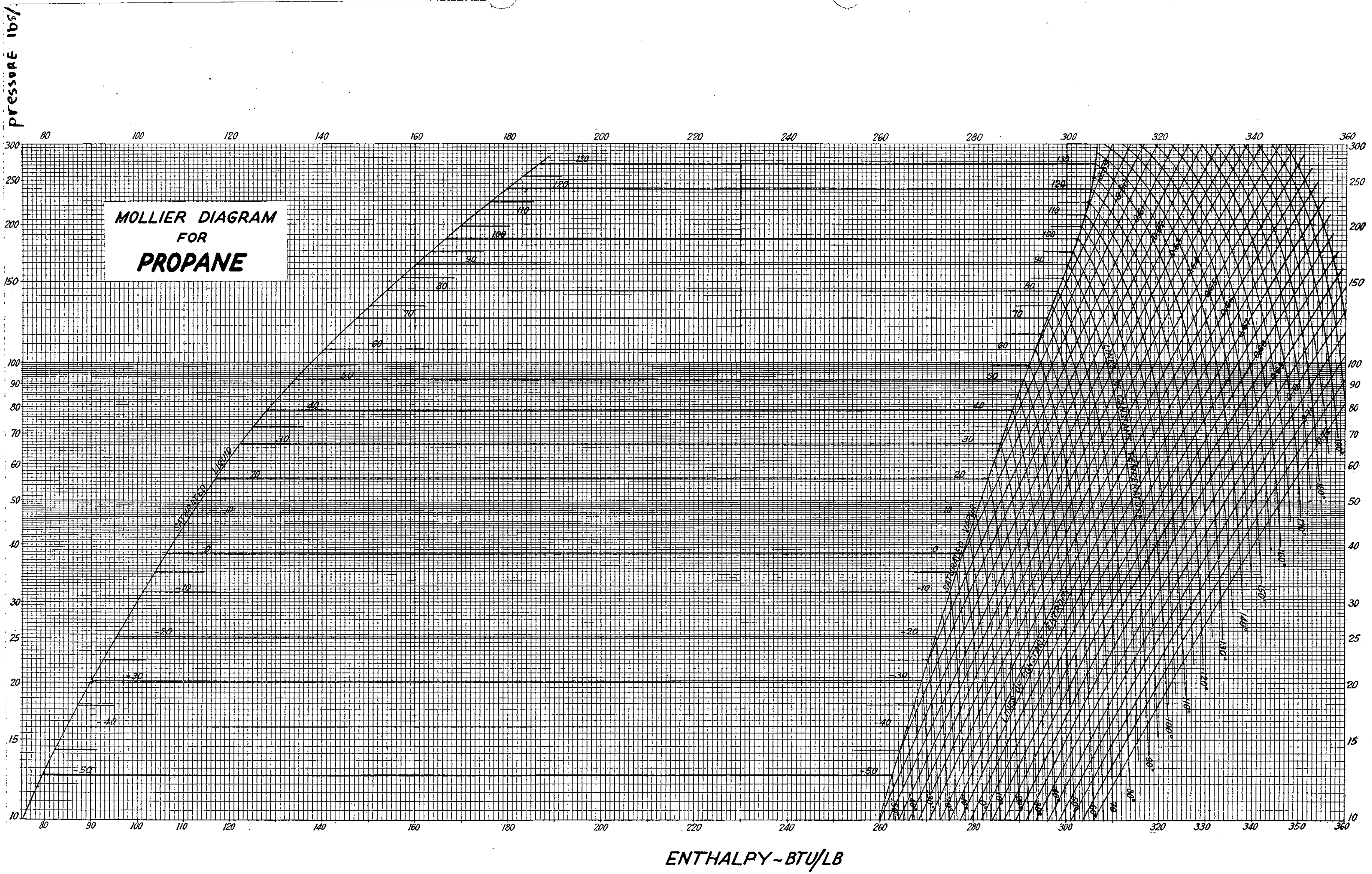

pressure lbs/
MOLLIER DIAGRAM
FOR
PROPANE
80 100 120 140 160 180 200 220 240 260 280 300 320 340 360
300 250 200 150 100 90 80 70 60 50 40 30 25 20 15 10
80 90 100 110 120 140 160 180 200 220 240 260 280 300 320 330 340 350 360
SATURATED LIQUID
SATURATED VAPOR
LINES OF CONSTANT ENTROPY
LINES OF CONSTANT TEMPERATURE
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
80° 90° 100° 110° 120° 130° 140° 150° 160° 170° 180°
ENTHALPY ~ BTU/LB

Fig. 3.

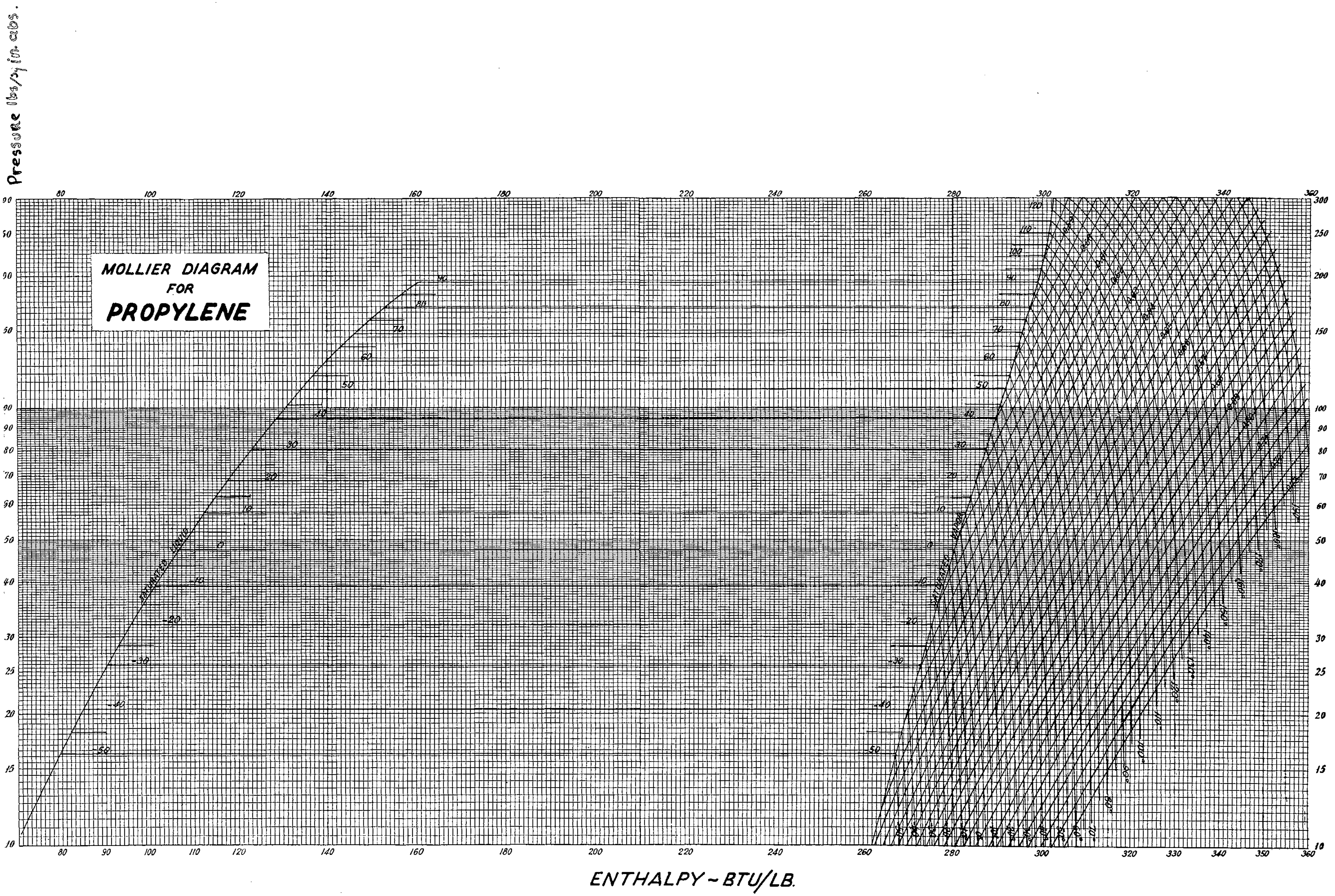

Pressure lbs/sq in. abs.
MOLLIER DIAGRAM
FOR
PROPYLENE
SATURATED LIQUID
SATURATED VAPOR
80
90
100
110
120
140
160
180
200
220
240
260
280
300
320
330
340
350
360
10
15
20
25
30
40
50
60
70
80
90
100
150
200
250
300
-50
-40
-30
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
ENTHALPY ~ BTU/LB.

FIG. 4.

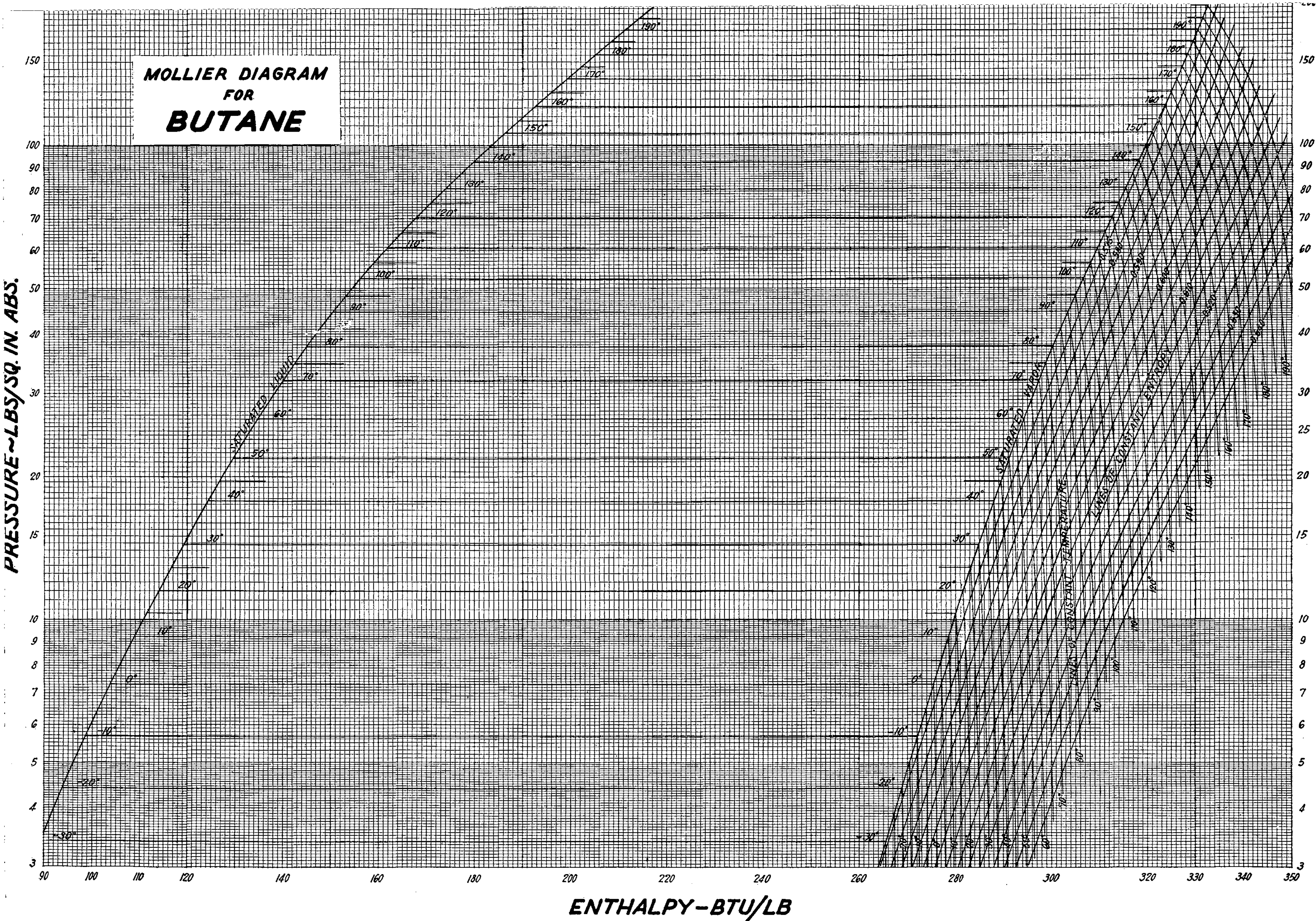

MOLLIER DIAGRAM
FOR
BUTANE
PRESSURE~LBS/SQ. IN. ABS.
ENTHALPY-BTU/LB
SATURATED LIQUID
SATURATED VAPOR
LINES OF CONSTANT TEMPERATURE
LINES OF CONSTANT ENTROPY
3
4
5
6
7
8
9
10
15
20
25
30
40
50
60
70
80
90
100
150
90
100
110
120
140
160
180
200
220
240
260
280
300
320
330
340
350
-30°
-20°
-10°
0°
10°
20°
30°
40°
50°
60°
70°
80°
90°
100°
110°
120°
130°
140°
150°
160°
170°
180°
190°

Fig. 5.

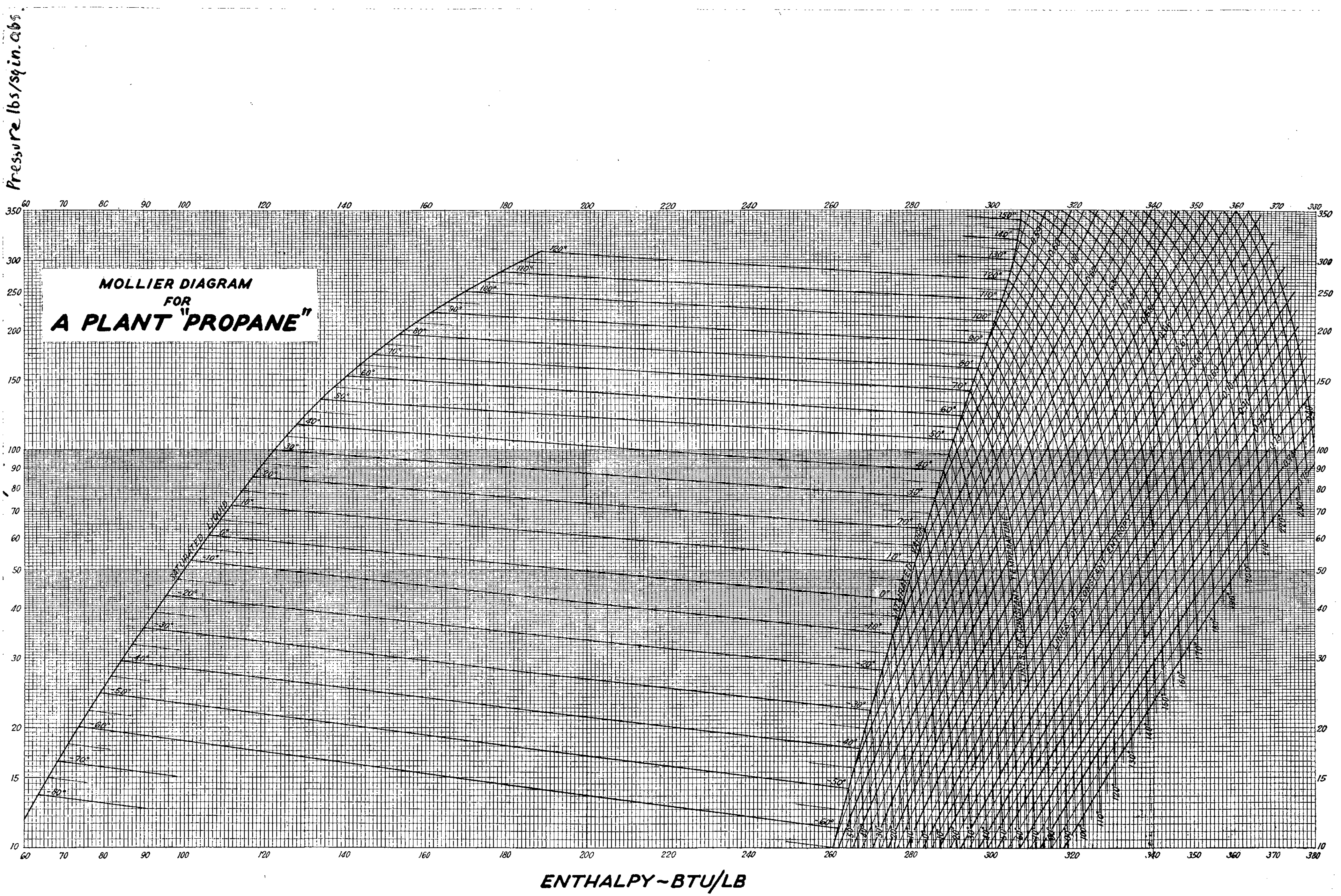

MOLLIER DIAGRAM FOR A PLANT "PROPANE"
Pressure lbs/sq in. abs
ENTHALPY~BTU/LB
SATURATED LIQUID
SATURATED VAPOR
LINES OF CONSTANT TEMPERATURE
LINES OF CONSTANT ENTROPY
350
300
250
200
150
100
90
80
70
60
50
40
30
20
15
10
60
70
80
90
100
120
140
160
180
200
220
240
260
280
300
320
340
350
360
370
380
120°
110°
100°
90°
80°
70°
60°
50°
40°
30°
20°
10°
0°
-10°
-20°
-30°
-40°
-50°
-60°
-70°
-80°

Fig. 6.

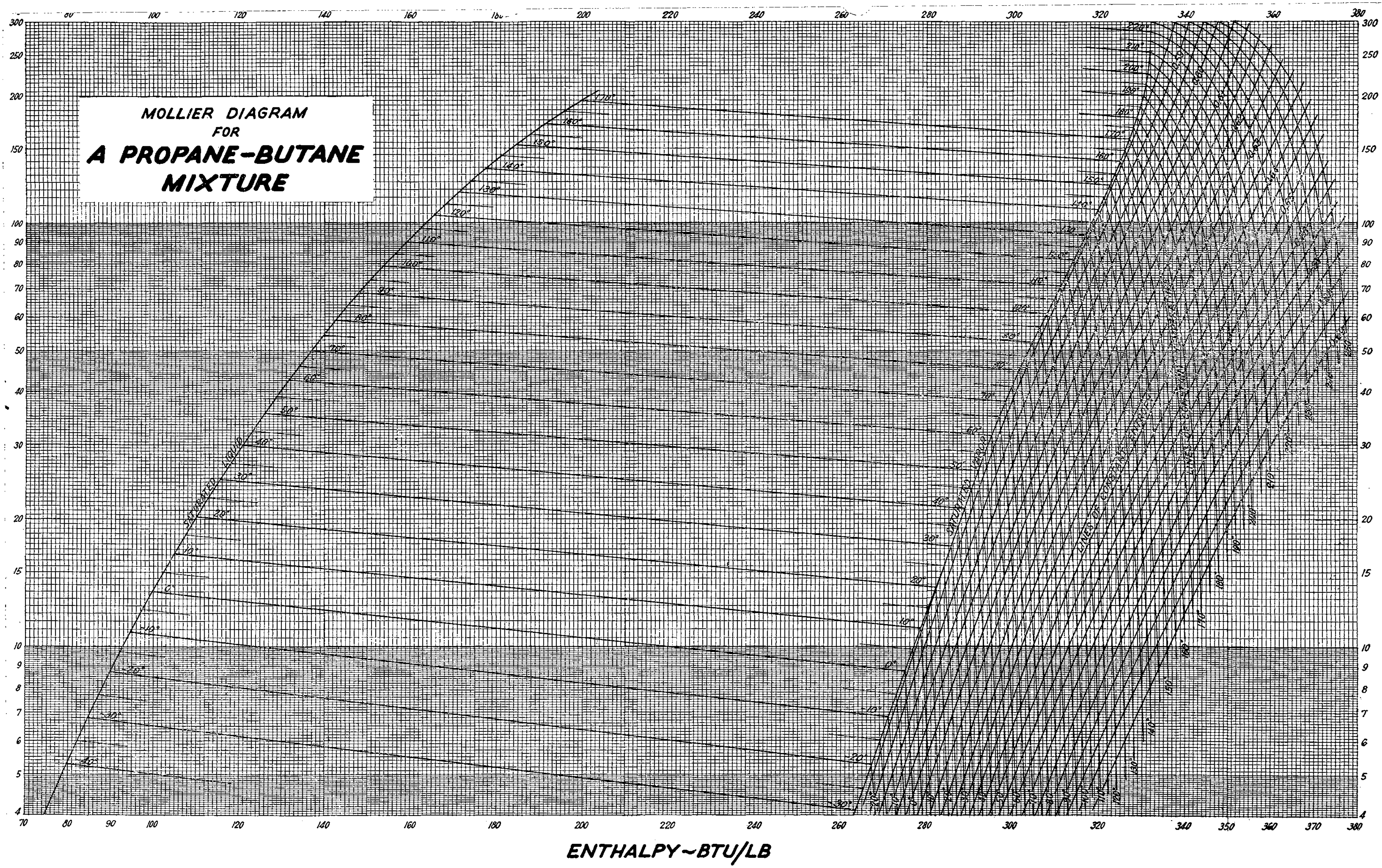

MOLLIER DIAGRAM FOR A PROPANE–BUTANE MIXTURE

Fig. 7

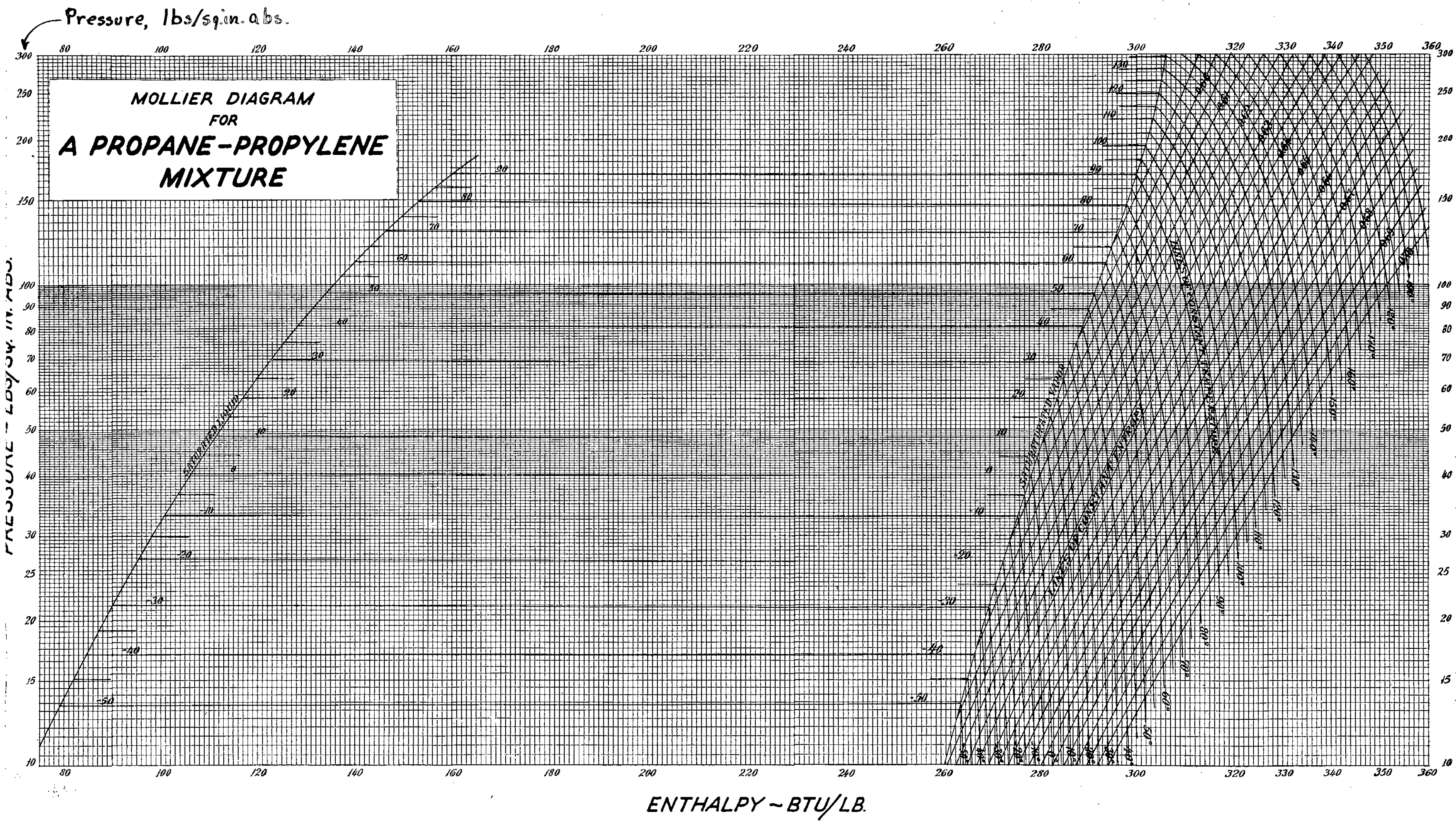

Pressure, lbs/sq.in. abs.
MOLLIER DIAGRAM
FOR
A PROPANE-PROPYLENE
MIXTURE
PRESSURE ~ LBS/SQ. IN. ABS.
300
250
200
150
100
90
80
70
60
50
40
30
25
20
15
10
80
100
120
140
160
180
200
220
240
260
280
300
320
330
340
350
360
SATURATED LIQUID
SATURATED VAPOR
LINES OF CONSTANT ENTROPY
LINES OF CONSTANT TEMPERATURE
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
ENTHALPY ~ BTU/LB.

Fig. 8.

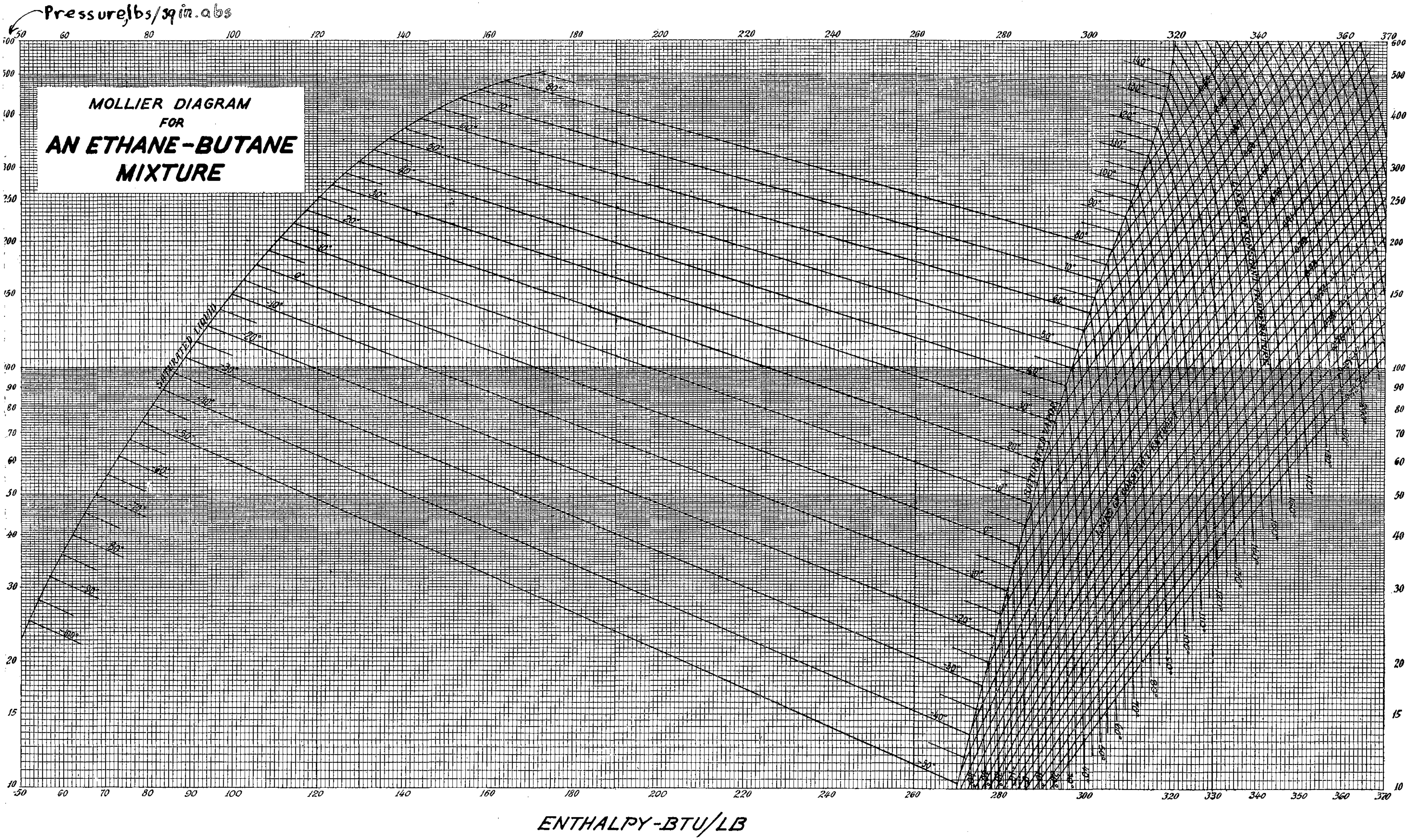

MOLLIER DIAGRAM
FOR
AN ETHANE-BUTANE
MIXTURE
Pressure, lbs/sq in. abs
ENTHALPY-BTU/LB
SATURATED LIQUID
SATURATED VAPOR
LINES OF CONSTANT ENTROPY
LINES OF CONSTANT TEMPERATURE
50
60
70
80
90
100
120
140
160
180
200
220
240
260
280
300
320
330
340
350
360
370
10
15
20
30
40
50
60
70
80
90
100
150
200
250
300
400
500
600

Fig. 9.

Since propane and propylene have very similar characteristics, the Mollier diagram of the mixture is very similar to that of a pure component. It is noticed here that the latent heat lines have very little slope and that this mixture would have a relatively high efficiency as a refrigerant.

Figure No. 9 is for an unusual mixture of ethane and butane, but its purpose is to illustrate the necessity of fractional analysis. In this case we have a mixture which has a boiling point the same as propane but actually the mixture has no propane in it. Such a mixture, of course, has latent heat lines that have a very high slope and would be very inefficient as a refrigerant.

A large amount of data are available from these charts. The latent heat of vaporization at any temperature can be calculated from the difference in total heat between saturated liquid and saturated vapor lines.

The theoretical amount of work can be calculated by taking the total heat at the temperature and pressure of the incoming vapor to the compressor and by following a line of constant entropy, determine the total heat at the discharge pressure and the corresponding temperature. The difference in these total heats will give the net work required in BTU's per pound which can readily be converted into horsepower. It should be realized that this is the theoretical horsepower required.

The duty for designing the condenser for liquefying hydrocarbons can also be readily obtained from this chart. The amount of heat to be removed as a vapor would be the difference in total heat between the saturated vapor at the condensing temperature and the total heat at the discharge pressure and temperature of the compressor. The latent cooling duty or the heat required to change the saturated vapor to saturated liquid is the difference between the total heat of saturated vapor and the total heat of saturated liquid.

In passing through an expansion valve from a condenser to an evaporator, change of state takes place at constant total heat so that the net refrigeration that can be effected per pound, assuming that there is no sub-cooling of the condensed liquid, would be the difference between the total heat of the saturated vapor at the evaporator temperature and the saturated liquid at the condensing temperature.

Refrigeration Cycle

In order to make the use of these charts clearer, an outline of a standard refrigeration cycle will be followed for propane. The standard tone as defined by code operates at a condensing temperature of +86°F. and vaporizes at a temperature of +5°F. For the purpose of illustration, a calculation will be made of this standard cycle when using propane as a refrigerant.

In this case it is assumed that the vapor will be brought to the compressor saturated at +5°F. so that at the inlet to the compressor the temperature will be +5°F. and the pressure 42 p.s.i. Abs. From this chart this is an enthalpy or total heat at 279 BTU per pound.

At 86° for condensing, the pressure is 155 p.s.i. Abs. In order to determine the amount of work required, a line of constant entropy is followed from +5° and 42 pounds up to 155 pounds. At this point the total heat is 305.5 BTU per pound. The difference between 305.5 and 279 BTU per pound is 26.5 BTU per pound, represents the work required to compress one pound.

At this point we would like to call attention to the fact that the compression of propane follows very closely to the saturated vapor line. The importance of this will be discussed later. The total heat of saturated vapor at 86°F. is 299.5 BTU per pound. The difference between the total heat at the end of compression and that of the saturated vapor is 6 BTU per pound, representing the heat removed by vapor cooling. The saturated vapor is then condensed completely to a liquid by removing the latent heat which is the difference in total heat at 86° of the saturated vapor and the saturated liquid, corresponding figures being for vapor 299.5 BTU and for liquid 157.6, the difference being 141.9 BTU per pound, the heat to be removed in condensing one pound of propane.

The net refrigeration effect is obtained by subtracting from the total heat of saturated vapor at +5° (279 BTU per pound) the total heat of the saturated liquid at 86° (157.6 BTU per pound) which equals 121.4 BTU per pound.

A ton of refrigeration is equal to 200 BTU's per minute; therefore, 200 divided by 121.4 equals 1.647 pounds of propane per minute required per ton of refrigeration.

To calculate the horsepower per ton the equation would be as follows:

$$\text{H. P.} = \frac{(26.5)\ (1.647)\ (60)}{2545} = 1.03 \text{ HP per Ton}$$

where 2545 is equivalent BTU's per horsepower hour.

As pointed out above, compression of propane takes place along a line very nearly parallel to the saturated vapor line, which means that a small amount of cooling by the compressor jacket water may cause liquid to form during compression. Also, since propane and other hydrocarbons are highly soluble in lubricating oil, it is desirable to have them compressed at a temperature as remote as possible from the saturated line. It follows, then, that for purely mechanical reasons, the vapor to the compressor should be superheated rather than saturated and it so happens, as will be shown below, that the remote dynamic efficiency of the cycle is also improved.

For the purpose of illustration it will be assumed that the suction temperature is superheated 30°F. above the saturation temperature and that in order to do this superheating, the condensed liquid is subcooled below 86° to superheat the vapor. This is simply an exchange between condensed liquid and vapor off the evaporator. The data for this calculation are as follows:

Superheating 30°F. and Subcooling for Propane

1. Total Heat Vapor at +5° F. Saturated = 279 BTU per pound
2. Total Heat Vapor at +35°F., 42 pounds Abs. = 291.5 BTU per pound
3. Total Heat Vapor at 155 pounds Constant Entropy = 319 BTU per pound
4. Total Heat Vapor at 86°F. Saturated
   A. (2 — 1) = 291.5 — 279 = 12.5 BTU per pound —Superheat
   B. (3 — 4) = 319.5 — 299.5 = 20 BTU per pound —Vapor Cooling
   C. (3 — 2) = 319.5 — 291.5 = 28.0 BTU per pound —Work of Compression
5. Total Heat Liquid at 86° Saturated liquid = 157.6
   Subtracting A = 12.5
6. Total Heat Liquid to Evaporate 145.1
   BTU per pound = 67°F.
7. Net Refrigeration = 279 — 145.1 = 133.9 BTU per pound
8. Pounds per Ton = $\frac{200}{133.9}$ = 1.494 Pounds per Ton
9. HP = $\frac{(28)\ (1.494)\ (60)}{2545}$ = 0.988 HP per Ton

Super heating 30°F. decreases the HP per ton by 1.03 — .988 = 0.042 or by 4.2%.

It will be noted that it is actually a reduction of 5.8 per cent in horsepower required per ton by using superheating and subcooling so that in addition to hav-

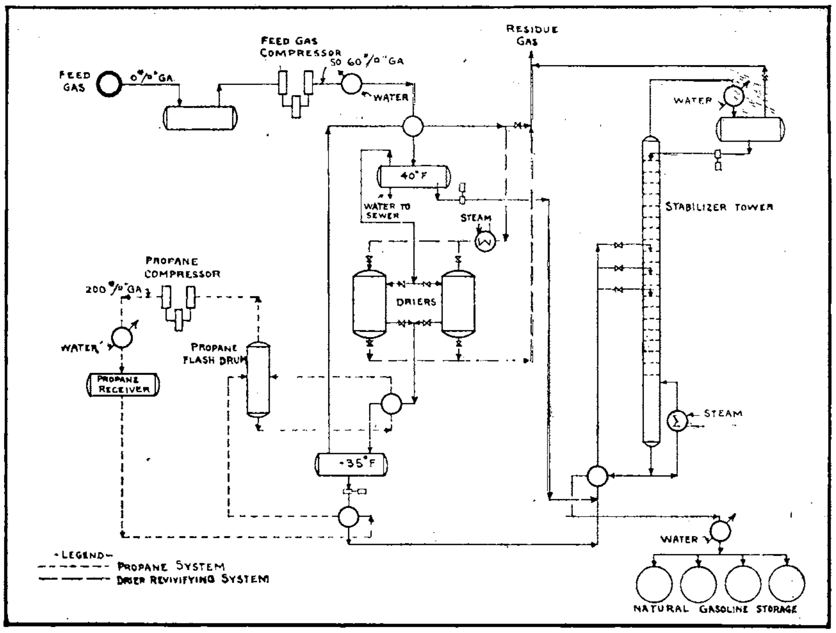


Fig. 10—Flow sheet of the gasoline of the Duval Gasoline Co., Benavides, Texas. Gasoline hydrocarbons are separated from field gas.

ing a better cycle from the viewpoint of mechanical operation of the compressor, the overall efficiency of the cycle is also improved. This is contrary to ammonia practice as the thermodynamic properties of ammonia are such that superheating reduces the efficiency of the cycle. From actual experience it has also been found that superior performance in all respects is obtained by the use of superheating and subcooling when using the hydrocarbons as refrigerants.

From Figure 6 it is seen that at 86° a saturated vapor is obtained at 174 pounds but that the pressure must be increased to 210 pounds before it is completely condensed at 86° to a saturated liquid. This means that a refrigeration cycle utilizing plant propane would have to operate with a compressor discharge pressure of 210 pounds Abs. as compared to 155 pounds absolute for pure propane, thus greatly increasing the work required. Below is a calculation of a standard refrigeration cycle with saturated vapor to the compressor using plant propane.

Standard Cycle for Plant Propane

1. Total Heat of Saturated Vapor at + 5°F.
   = 279.5 BTU per pound
2. Total Heat at Constant Entropy 210 pounds Abs.
   = 311 BTU per pound
   Work = 31.5 BTU per pound
3. Total Heat at Saturated Liquid —86°F.
   = 158.0 BTU per pound

$$\text{Net Refrigeration} = \begin{array}{r} 279.5 \\ 157.0 \\ \hline 122.5 \end{array} \text{ BTU per pound}$$

4. Pounds per Ton = $\frac{200}{122.5}$ = 1.63
5. Horsepower = $\frac{(1.63)\ (31.5)\ (60)}{2545}$ = 1.21 HP per Ton which is a 17.5% increase over pure propane.

Condensation at 210 lbs./sq. in. begins at 100°F. and is completed at 86°F.

This calculation indicates that 17.5% more horsepower is required per ton of refrigeration using a plant propane than would be required if pure propane were used. This point is emphasized because a large number of refrigeration plants both in refineries and in the field utilize propane mixtures for refrigerants, requiring considerably more horsepower than would be expected if the calculation were based on propane data available. There are a large number of these plants operating with engines and motors overloaded principally because they are designed to operate on pure propane under the assumption that 95% or more propane would, for all practical purposes, be pure propane. It can readily be seen from the above illustration that such is not the case and that such factors as dew point and bubble point must be considered in calculating the pressures and particularly requirement of hydrocarbon mixtures used as refrigerants.

Application of Mollier Diagrams

Liquefaction and regasification of the low hydrocarbons has a large number of uses but principally, in one form or another, they are used to obtain refrigeration or to affect separation. A description of a few of these uses would probably suffice to illustrate in general the types of plants and equipment used for this purpose. Figure No. 10 is a flow sheet of the gasoline of the Duval Gasoline Co., Benavides, Texas. This plant is a modern gasoline extraction plant, separating the gasoline hydrocarbons from field gas. The unusual part of this plant is that the separation is effected by refrigeration rather than by the usual method of absorption.

Primarily this plant is a very simple plant in which the field gas is compressed from approximately atmospheric pressure to 50 or 60 pounds where it is cooled first by water and then by residue gas to a temperature of approximately 40°.

The next step in the process is to remove all moisture in the gas by passing it through beds of alumina. This removes every trace of moisture. From this point on the gas is cooled down to a temperature of 35°F. by a propane system and at —35°F. all of the desirable gasoline components are liquefied and drawn off. The remaining gas is exchanged against the incoming gas and returned to the field.

The liquid gasoline made is further treated in a stabilizing tower to finish the gasoline to the necessary specification.

The propane system is a very simple two-stage compression ammonia system operating from approximately atmospheric pressure and —40°F. to 200 pounds gauge where it is liquefied by cooling with water and recycled. It is of interest to note that some subcooling is obtained on the liquid propane by exchanging it against the cold liquid coming from the separation drum. Sufficient subcooling is obtained here to ap-

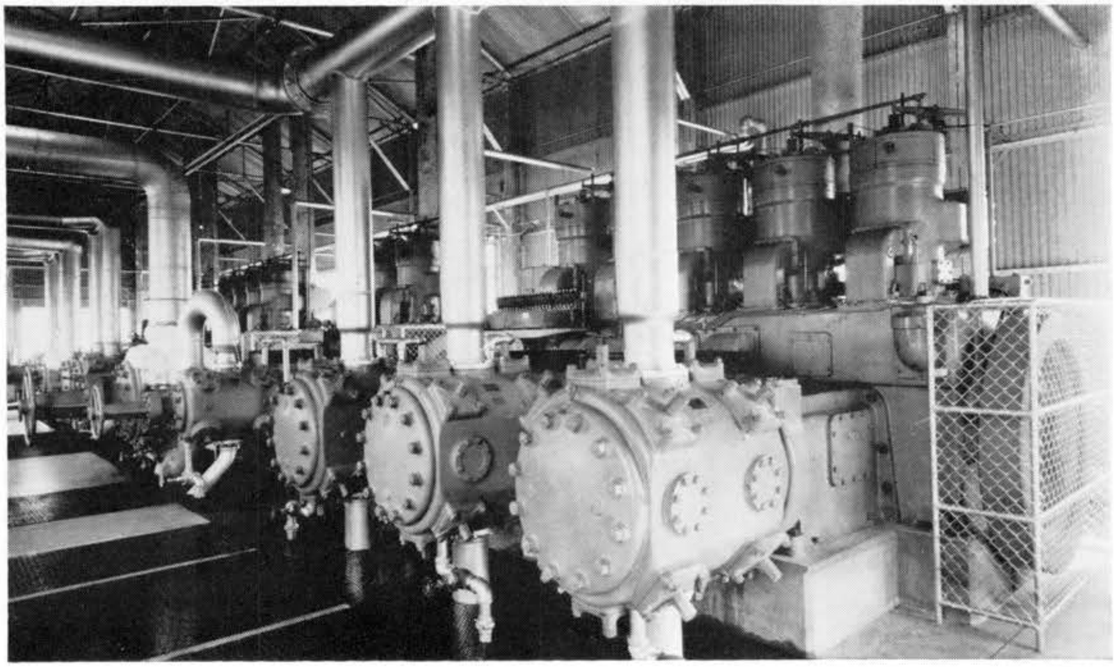


Fig. 11—An interior view of the Duval Gasoline Co. at Benavides, Texas.

preciably reduce the horsepower requirements of the plant. Figure 11 is an interior view of this plant.

Often, for the recovery of light hydrocarbons and sometimes for other gases, a low temperature bubble tower is used for separation. A typical flow sheet like the chart in Figure 12 shows a method of operation known as the cold tower. Either one or two refrigerants may be used to liquefy overhead vapor which is returned to the upper part of the tower as reflux to aid in separation. For extremely low temperature, that is, on the order of –100° to –150°, a two-stage system, as illustrated, would be used, utilizing propane for refrigerant No. 1 and ethane or ethylene for refrigerant No. 2. These are merely cited as examples. For temperatures of –40° and upward, a single refrigerant would probably be used.

The purpose of the cold reflux is to liquefy all components that are desirable and to leave only as vapor the components in the gas that are not desirable in the final product.

Liquefaction and Storage of Natural Gas

One of the more recent developments has been the liquefaction of natural gas for storage purposes. By liquefying natural gas which consists chiefly of methane, its volume is reduced to approximately 600 times, thus greatly decreasing the amount of storage space necessary to store large volumes of gas such as are required to take care of sudden peak load conditions arising from the sale of gas in cold weather.

Within the last year a plant for just this purpose has been constructed by the East Ohio Gas Company at Cleveland, Ohio. This very interesting plant was described in detail by Clark and Miller before the A.G.A. at Atlantic City in October, 1940. This plant is of great interest because of the size of the storage involved, namely, 150,000,000 cubic feet and the low temperatures being used for the first time on a very large scale.

Figure 13 is a flow sheet of the cycle used in liquefying natural gas.

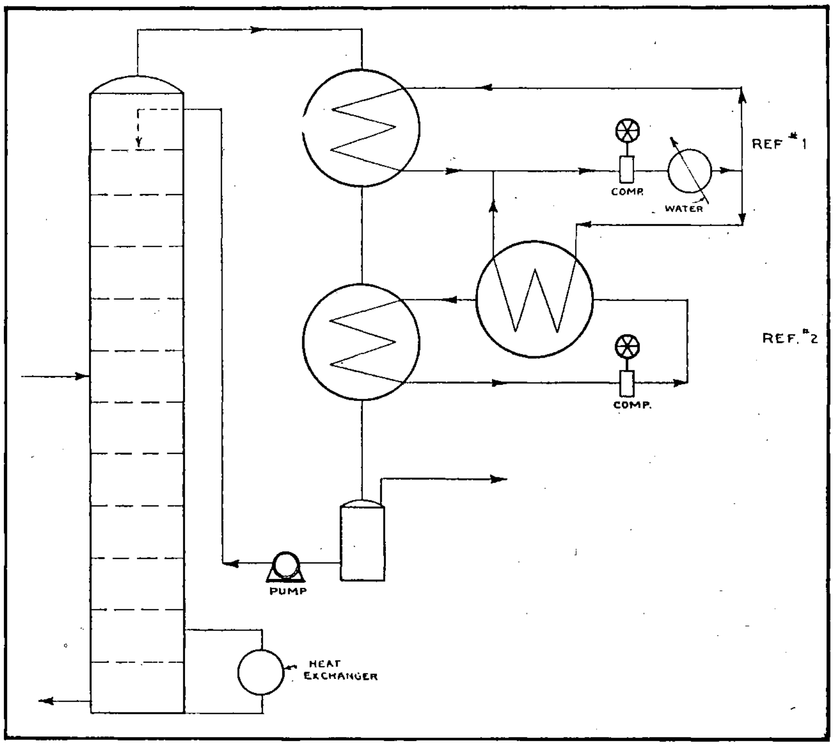
To liquefy natural gas it is first necessary to cool it below its critical temperature, then liquefy it at the vapor pressure corresponding to the temperature chosen. This means that to liquefy methane, a temperature of below –116°F. is necessary and for practical purposes, a temperature of approximately –125° and a pressure of approximately 600 pounds is necessary to liquefy natural gas. However, a large volume storage would be very expensive at a pressure of 600 pounds and for structural reasons the storage vessels are designed for approximately atmospheric pressure operation, and in order to store natural gas at atmospheric pressure, its temperature must be reduced to approximately –250°F. This is accomplished by self-refrigeration or flashing. The liquid is merely expanded through a valve and when the pressure is dropped, the liquid immediately cools itself to new vapor pressure temperature condition by vaporizing a portion of itself. The gas thus evolved is recycled and again liquefied and the resultant liquid is piped to the storage tanks.

Because of the low temperatures involved, it is necessary to remove all traces of carbon dioxide to prevent plugging up of the valves. In the same step all hydrogen sulphide is removed to prevent corrosion. A small nitrogen content of the gas makes it necessary to vent this nitrogen, as otherwise the nitrogen which does not liquefy with the natural gas will remain in the vapor state and be recycled with returned gas. Since it does not, at any time, liquefy, its concentration would continually increase until it eventually affected the condensation of the natural gas itself. It is therefore necessary to remove nitrogen by venting.

Cascade or two-step refrigeration is used to liquefy the natural gas. Ammonia is the first refrigerant, being used to liquefy or condense the ethylene, the ethylene in turn upon boiling on one side of the heat exchanger condenses the natural gas on the other side of the same heat exchanger. All the heat that is removed by the ethylene system, plus the heat of compression must be removed by the ammonia system which in turn gives up this heat to the water condenser. The whole process is a mechanical means for removing heat at a temperature below –120°F. and carrying this heat step by step up until such point as this heat is given up to water.

The ammonia system operates at a temperature of –120° and a pressure of five pounds gauge and is normally condensed with pressure of 150 pounds gauge. The ethylene system operates at a temperature of

Fig. 12—A typical flow chart showing method of operation known as cold tower. This method is used for the recovery of light hydrocarbons and other gases.



—145° with pressure of five pounds and is condensed at approximately 350 pounds and —10°F.

The importance of automatic control in the operation of this plant, particularly on the refrigeration machines, is brought out by the consideration that any variation in the feed or recycle gas will change the heat load on the ammonia and ethylene systems. It is necessary, then, to vary the capacity of the compressors to meet any variation in the flow through the system. Since it is desirable to maintain constant pressures, the volume of the refrigerant is varied by changing the speed of the engine.

Pressure-type stabilogs are used to hold the constant suction pressure on both the ethylene and ammonia compressors. These stabilogs operate in such a manner that should the suction pressure tend to rise, an air diaphragm on the governor opens up the fuel valve, admitting more gas to the engine, causing the engine to speed up. If the suction pressure should tend to fall, a reverse action takes place so that at all times the speed is kept in direct proportion to the demand of the refrigerating system as a whole.

The refrigeration machines in the Cleveland plant consist of two 600 HP angle, 300 RPM, gas engine-driven compressors and the ammonia machine is a 500 HP, supercharged, 350 RPM "Angle" compressor. These machines are equipped with a number of special devices to reduce the loss of both ethylene and ammonia and are built with special pistons and liners to reduce the quantity of oil necessary for proper lubrication. A minimum quantity of oil is desirable in this process because if oil should be carried over from the compressors into the natural gas condensers, it would freeze solid, impairing the heat transfer efficiency and eventually plugging up the exchanger. Special oil traps have been devised and are in use at Cleveland whereby oil is removed by mechanical separation and by absorption. All possible precautions have been taken against failure of ammonia and ethylene machines because of the vital part that these machines play in this process;

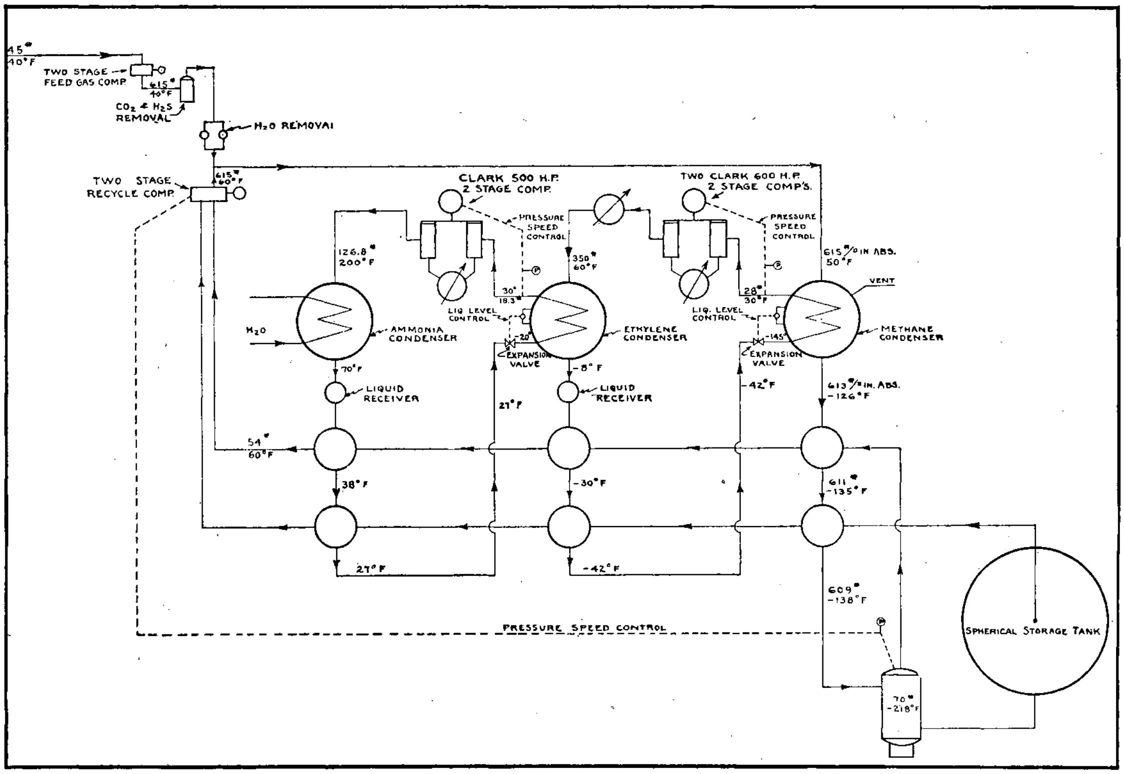


Fig. 13 — A flow sheet of the cycle used in liquefying natural gas.

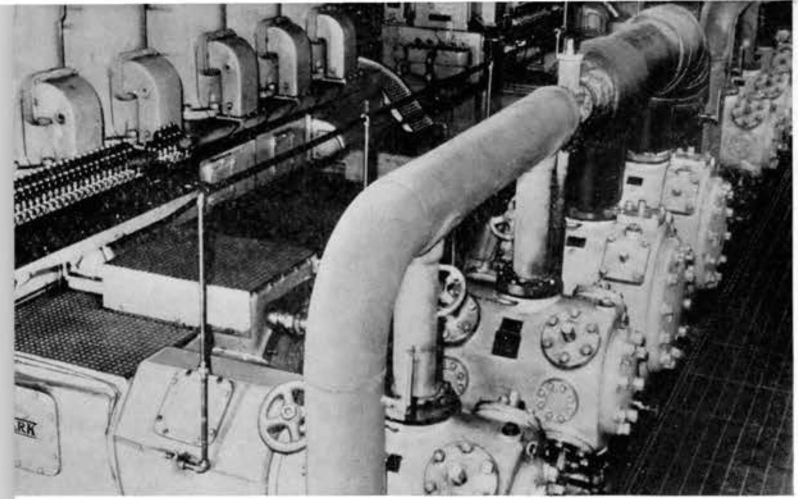


Fig. 14—The refrigeration cycle compressors in the East Ohio Gas Company plant at Cleveland, Ohio. These machines are equipped with devices to reduce loss of ethylene and ammonia.

if they do not function properly, the rest of the plant cannot function. Figure 14 shows the refrigeration cycle compressors in the Cleveland plant.

The storage vessels at Cleveland are of unusual design. They consist of two spheres, a 57 foot diameter sphere inside a 63 foot sphere with three feet of cork insulation in between. The inner sphere is made of nickel steel because of the necessity of having material resistant to shock at low temperatures; the outer shell does not require alloyed steel. Each of these vessels when approximately 80% full will hold the equivalent of fifty million cu. feet of gas at a temperature of –250°F. The losses due to heat infiltration in these tanks has been very low, being on the order of less than 2/10ths of one percent per day.

These tanks are of unusual construction as shown in Figure 15. The liquid is carried in and out of the tank through a 5⅛″ O.D. copper tube. The liquid line is in the center of an 18″ I.D. copper pipe. The evaporated gas flows away from the tank through the outer pipe. This entire assembly, including expansion joints, is in an insulated boot. Inside the tank is a stand pipe for carrying off the vapors that accumulate above the liquid. This vapor is normally returned to the system for re-liquefaction through the recycle system. On the outside of the tank is a blow down pipe 12″ in diameter, capable of reducing large quantities of vapors if they should accumulate. Both the inner and outer shell of tank are protected by safety valves and blow out discs, and precautions have been taken so that even for unusual conditions of vaporization or heating filtration, the pressure in the tanks will not exceed twelve pounds.

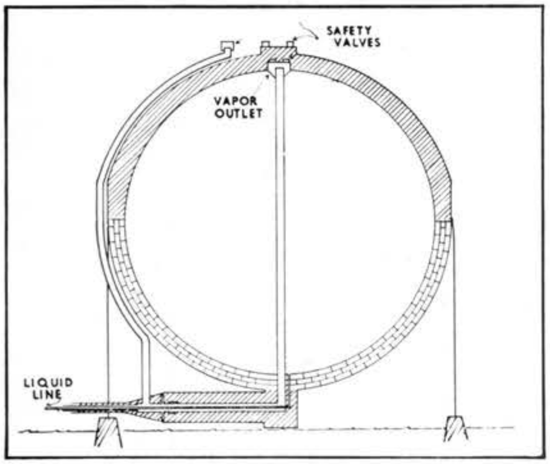


Fig. 15—In these tanks of unusual construction, the liquid is carried in and out through a 5⅛″ O.D. copper tube.

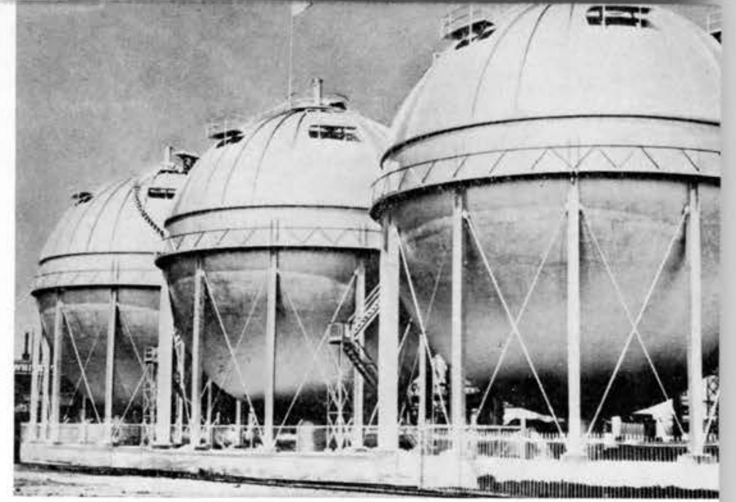


Fig. 16—The finished tanks have a total capacity of fifteen million cubic feet which can be discharged into the system in approximately fifty hours, if necessary.

Since the entire copper pipe arrangement for putting in and removing the liquid from the tank is subject to considerable movement due to the filling and unloading of the inner sphere, experimental tests were made by filling the tank with water to measure the amount of settling of the inner tank when loaded. The expansion joints in the copper piping were designed on the basis of this data. The settling of the entire inner sphere was approximately three inches. One of the properties of cork as insulation that makes this design of tank possible is its marked resilience. While it compresses under load even at low temperatures, it returns to very nearly its original position when unloaded.

It will be noted that all the piping in and out of this sphere is subject to the stress caused by the movement of the inner sphere and is made of copper because of the fact that, compared to ferrous metals, it maintains its ductility at low temperatures.

The structural design data of the tank may be of interest, particularly the weights.

The weight of the inner sphere is	154,000 lbs.
Outer Sphere	230,400 lbs.
Cork Liners	255,600 lbs.
Tower	102,240 lbs.
Making the total dead-load weight	742,240 lbs.

The live load content is 2,521,000 pounds.

If the same tank were to be loaded with water, which it was for test purposes, the total live-load content would be 6,060,000 pounds or over double that of the liquefied gas. Figure No. 16 shows a photograph of the finished tanks.

IV

PROFESSIONAL RECORD OF CANDIDATE

PROFESSIONAL RECORD OF W. C. EDMISTER

A. Education

1. Undergraduate: Oklahoma A. and M. College, Stillwater, Oklahoma
   Bachelor of Science in Mechanical Engineering,
   Petroleum Option, June 1932.

2. Graduate: Cornell University, Ithaca, New York,
   Master of Mechanical Engineering, June, 1934.
   Thesis: "Thermodynamic Formulations for Normal Paraffin Hydrocarbons." At Cornell the candidate was one of the two graduate guests of the Telluride House during the school year 1932-33.

3. Miscellaneous Graduate Work:

   (a) The University of Chicago
   An evening course in Physical Chemistry
   Text Lewis and Randall's Thermodynamics, 1935-36.

   (b) Illinois Institute of Technology, Chicago
   Chemical Engineering Research, 1940.

   (c) Standard Oil Company (Indiana) Evening School
   Mechanical Design and the Specification of Petroleum Refining Equipment, 1941-42.

B. Professional Societies

1. American Chemical Society

2. American Institute of Chemical Engineers (Active Member)

C. Industrial Experience

1. Prairie Oil and Gas Company
   Field Engineer and Draftsman, Seminole, Oklahoma
   June 1928 to April 1929
   Construction of Gas-Lift Plants

2. Forrest E. Gilmore Gasoline Company
   Field Engineer and Draftsman, Tulsa, Oklahoma
   April 1929 to September 1929
   Design and Construction of Natural Gasoline Plants

3. Petroleum Engineering Inc., Tulsa, Oklahoma
Anderson-Pritchard Refining Co., Cyril, Oklahoma
Field Engineer and Draftsman
June 1930 to September 1930
Refining Construction: Vapor Recovery Plant,
Crude Battery, Boiler House

4. Sinclair-Prairie Oil and Gas Company
Research Engineer, Seminole, Oklahoma
July 1933 to February 1934
Technical problems concerned with the operation of several natural gasoline plants, such as: analyzing new gases, making efficiency tests, and making recommendations to the Operating Department.

5. Standard Oil Company (Indiana)
Chemical Engineer in Research Department, Whiting, Indiana
February 1934 to date

(a) Technical Service to Operating Department
February 1934 to July 1935
Efficiency tests and recommendations to Operating Department re: Crude running, thermal cracking, visbreaking, vapor recovery, and filtration.

(b) Engine Laboratory
July 1935 to July 1936
Diesel fuel development and testing on laboratory engine; development of method for altitude knock testing of gasolines; antiknock ratings of gasolines in various makes of automobiles on the road.

(c) Editor of Standard Data Book
January 1936 to date
Organized and compiled the Standard Data Book and do most of the work involved in keeping it up to date. This book contains fundamental physical and chemical data and methods of making calculations required in petroleum refining work. Approximately 200 copies are in use at the various offices, refineries, drafting rooms, and laboratories of this Company and its subsidiaries and associated companies.

(d) Chemical Engineering Development
July 1936 to date
In charge of experimental (laboratory and plant) and correlation research on the following: Thermodynamic properties of hydrocarbons and their mixtures; equilibrium flash vaporization of petroleum fractions; blending; absorption; distillation and rectification; heat exchangers; furnaces; bubble tower capacity; and thermal and catalytic conversion of petroleum (effects of operating variables on yields and reaction rate).

(e) Process Design of Refining Equipment
January 1937 to date
Designed or supervised the design of equipment for the following processes: thermal cracking; thermal reforming; thermal delayed coking; vapor recovery and stabilization; catalytic polymerization; solvent extraction; crude distillation; combination crude running, gas oil cracking, reduced crude visbreaking, and gasoline stabilization; hydroforming (catalytic reforming); catalytic cracking; vacuum distillation; dewaxing; treating, isoforming; alkylation; isomerization.

(f) Research Supervisor
January 1941 to date
Group Leader in charge of 6 technical men, process designing new equipment and doing chemical engineering development work.

(g) Technical Expert for the underlined in the following Law Suits:

(1) "Gray Processes Corporation vs. Danciger Oil and Refineries" in the Amarillo, Texas Federal Court in July 1938. This suit involved the infringement of vapor phase clay treating patents. The plaintiff won.

(2) "Louis and Jacob Blaustein vs. Standard Oil Companies of Indiana and New Jersey, Pan American Petroleum and Transport Corporation, and various directors of these Companies" in the Supreme Court of New York in January, 1940. This suit, being brought by the Blausteins who are minority stockholders, involved alleged mismanagement of the Pan American Company. Case still unsettled.

(3) "Trojan Development Corporation vs. Standard Oil Company of Indiana" in the Springfield, Illinois Federal Court, April 1940. This case involved the alleged infringement of patents covering propane and mixtures of light hydrocarbons as refrigerants. The defendant won.

D. Teaching Experience

1. Standard Oil Company (Indiana)
September 1936 to May 1937.
Organized an evening study group in "Thermodynamics Theory and Problems" for Research Department technical men.

2. Illinois Institute of Technology, Chicago
(a) Evening Division instructor of "Petroleum Refining", a graduate course in Chemical Engineering
October 1938 to June 1940

(b) Supervised and directed the Research and Thesis for four candidates for Master Degrees in Chemical Engineering
October 1939 to date
Subject: Equilibrium Flash Vaporization, Molecular weight, and Joule-Thomson coefficients for Petroleum Stocks; supervising design and construction of apparatus, experimental work and preparation of thesis.

3. Standard Oil Company (Indiana) Evening School
September 1940 to date

(a) Organized (with the assistance of an Engineering Dept. representative) an Evening School for company employees only (enrollment of 70 men from Research and Engineering Departments). Two courses have been taken up: "Petroleum Refining Process Design", and "Design and Specification of Petroleum Refining Equipment".

(b) Prepared the notes and gave the lectures in the above course in "Petroleum Refining Process Design", covering: Fluid Flow, Heat Transfer, Thermodynamics, Separation Processes, Conversion Processes, Furnace Design, Design Problem. The above subjects are presented by lectures, detailed notes and problems in 40 weekly two-hour evening classes.

E. Publication

1. "Properties of Paraffin Hydrocarbons"
Oil and Gas Journal, July 2, 1931

2. "Thermal Properties of Oil Fractions"
Oil and Gas Journal, February 25, 1932

3. "Flow of Oil and Gas in Vertical Pipes"
International Petroleum Technology, July, 1932
Winning paper at Student Contest of the
Mid-Continent Section of A.S.M.E., 1932

4. "A Method for Determining Flow Strings, Both Straight and Tapered."
International Petroleum Technology, October 1932.

5. "Calculation for the Design of Bubble Tower Foundations"
National Petroleum News; Part I, 2-15-33;
Part II, 2-22-33;
Part III, 3- 1-33.

6. "Some Principles of Fluid Flow"
Petroleum Engineer, June 1933

7. "Film Coefficients of Heat Transfer"
Petroleum Engineer; Part I, Sept. 1933;
Part II, Oct. 1933.

8. "Graphic Approximation of Heat Transfer Rate"
Oil and Gas Journal, July 5, 1934.

9. "Thermodynamic Properties of Methane"
Ind. and Eng. Chem., Vol. 28, p. 1112, Sept. 1936

10. "Enthalpy-Entropy Chart is Developed for Methane"
Oil and Gas Journal, November 5, 1936.

11. "Thermodynamic Properties of Hydrocarbons"
Ind. and Eng. Chem., Vol. 30, p. 352, March, 1938.

12. "Enthalpies of Hydrocarbon Mixtures"
Prepared for presentation at the A.C.S., spring 1938 meeting in Dallas, Texas, but not presented, because of Company ruling.

13. "Specific Heat Ratios for Hydrocarbons"
Ind. and Eng. Chem., Vol. 32, p. 373, March 1940.

14. "Phase Diagram of Petroleum Fractions"
Prepared for presentation at A.I.Ch.E.
Spring 1941 meeting in Chicago, but not
presented because of Company ruling.

15. "Liquefaction and Regasification of Lighter Hydrocarbons"
Oil and Gas Journal, September 4, 1941
Presented at the A.S.M.E. Meeting at Kansas City, Mo., June 1941.

16. "Absorption and Stripping Design Calculations"
This paper will be submitted for publication soon.

F. Patents

U.S. Patent 2,247,485; A Bubble Tower

Several applications pending.

G. Recent Lectures

1. "Process Design of Petroleum Refining Equipment"
A.I.Ch.E. Student Chapter,
University of Illinois, Urbana, Ill.
November 1940

2. "Application of Thermodynamics to Process Design"
Chicago Section of A.I.Ch.E.
June 1941

3. "Duties of Engineers in the Petroleum Refining Industry"
Student engineers at Oklahoma A. and M. College
Stillwater, Oklahoma
December 1941

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