GENERALIZED COHESIVE ENERGY DENSITY CORRELATIONS
FOR ONE-COMPONENT SYSTEMS

By

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Thesis Approved:

[Signatures]

David Carroll
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NOMENCLATURE

$\Delta F$  Change in free energy, calories/g-mole

$\Delta H_m$  Overall heat of mixing, calories/g-mole

$\Delta S$  Change in entropy, calories/(°Rankine)(g-mole)

$V_m$  Volume of mixture, cubic centimeters/g-mole

$V_i$  Volume of component, cubic centimeter/g-mole

$\phi$  Volume fraction, dimensionless

$\Delta E$  Energy of vaporization, calories/g-mole

$\delta$  Solubility parameter, (calories/cubic centimeter)$^{\frac{1}{2}}$

CED  Cohesive energy density, (calories/cubic centimeter)

$P$  Pressure, atmospheres

$P_r$  Reduced pressure, dimensionless

$P_C$  Critical pressure, atmospheres

$T$  Temperature, degrees Rankine

$T_r$  Reduced temperature, dimensionless

$T_C$  Critical temperature, degrees Rankine

$Z$  Compressibility factor, dimensionless

$Z_C$  Critical compressibility factor, dimensionless

$N$  Gram-moles

$R$  Gas constant, 82.06

$T_b$  Boiling point, degrees Rankine

$\Delta H^V$  Heat of vaporization, calories/g-mole

$a_1$  Constant

$a_2$  Constant
NOMENCLATURE (Continued)

\( \alpha \)  
Coefficient of thermal expansion

\( \gamma \)  
Surface tension, dynes/centimeter

\( \beta \)  
Compressibility coefficient

\( E_1 \)  
Internal energy to the ideal gas, calories/g-mole

\( E_2 \)  
Internal energy of the fluid, calories/g-mole

FOR TRANSIT PROGRAM SYMBOLS

**  Denotes exponentiation

*   Denotes multiplication

/  Denotes division

CEDPC = Cohesive Energy Density/Critical Pressure

TR = \( T_r \), floating point form

PR = \( P_r \), floating point form

Z = \( Z \), floating point form

\( \Delta E/T_c \) = \( \Delta E/T_c \), floating point form

KA = 100,000,000 PR, fixed point form

KB = 100,000,000 TR, fixed point form

KC = 100,000,000 CEDPC, fixed point form
CHAPTER I

INTRODUCTION

A solution may be defined as a homogeneous mixture of two or more components having a similar composition throughout the mixture. The more closely two substances resemble each other chemically, the more likely they are to be miscible. For example, mixtures of water and ethyl alcohol are solutions because they form a homogeneous, single-phase system. A liquid hydrocarbon and water mixture forms two solutions because the liquids do not dissolve completely in one another, and a heterogeneous, two-phase system forms. Different cases such as liquid-liquid, liquid-solid, liquid-gas, solid-solid, solid-gas, and that of gas-gas are frequently encountered in problems of the engineer and chemist.

The extent or degree to which two components will mix must be determined in order that solubility problems may be solved. Several factors affecting solubility must be considered in order to formulate workable solutions to these problems. Temperature and pressure are important variables to be considered. Usually an increase in temperature favors solubility and likewise an increase in pressure favors solution. The polarity of the component is also important in determining solubility. The cohesive energy densities of the components may be used to predict solution. If the cohesive energy
densities of two components are close to one another, complete solubility will usually occur.

Many solubility theories have been developed by different authors. Van Laar (10), in his early works, proposed the method of solvation or association. It has not been possible to extend general rules which will cover many cases. Flory (3) and Huggins (2) proposed the theory of a polymer-solvent interaction constant. This method requires measurement of the vapor pressure, by experimental means, for each system considered. This method would, therefore, prove impractical for the prediction of solubility at high temperatures and pressures. Henry's Law (5) gives the effect of pressure on the solubility of gas in a liquid. Henry's Law states that the amount of gas dissolved in a liquid at constant temperature is directly proportional to the pressure of the system. Deviations occur at high pressures. There is one major theory which seems to be relatively free of the objections cited in the above examples. As early as 1916 the idea of having a solubility parameter for different components was proposed by Hildebrand. (1).

The Scatchard-Hildebrand theory applies the free energy equation to the constant temperature process of mixing. The equation may be written as follows:

\[ \Delta F = \Delta H - T \Delta S \]  

\[ \Delta F = \text{the change in free energy, calories/g-mole} \]
\[ \Delta H = \text{the heat of mixing, calories/g-mole} \]
\[ T = \text{temperature, °Rankine} \]
\[ \Delta S = \text{the change in entropy, calories/(°Rankine)(g-mole)} \]
This equation may be used to predict whether or not mixing of two components will occur. If the change in the free energy term is negative, mixing will take place. From equation (1-1) it is seen that the change in free energy is dependent upon the entropy change, the temperature, and the enthalpy change. The magnitude of the product of the temperature and the entropy change will always tend to make the free energy term smaller. For a constant temperature process the temperature-entropy product will be large and almost constant. It would therefore be the magnitude of the enthalpy term, \( \Delta H \), that governs the sign and magnitude of equation (1-1). The study of the enthalpy term is, therefore, important in the prediction of the degree of mixing of two components.

Scatchard (4) and Hildebrand (1) have, independently, developed the heat of mixing equation which follows:

\[
\Delta H_m = V_m \left[ \left( \frac{\Delta E_1}{V_1} \right)^{\frac{1}{2}} - \left( \frac{\Delta E_2}{V_2} \right)^{\frac{1}{2}} \right]^2 \phi_1 \phi_2 \ldots \ldots \ldots (1-2)
\]

where \( \Delta H_m \) = overall heat of mixing, calories/g-mole
\( V_m \) = volume of mixture, cubic centimeters/g-mole
\( \Delta E \) = energy of vaporization, calories/g-mole
\( V \) = volume of component, cubic centimeters/g-mole
\( \phi \) = volume fraction, dimensionless

The term \( \Delta E/V \), in equation (1-2), is the internal energy of vaporization per cubic centimeter of one of the components. \( \Delta E \) is a measure of the amount of internal energy required to give infinite separation of the molecules (equivalent to zero pressure) or to overcome the intermolecular forces holding the molecules together.
For this reason the term $\Delta E/V$ has been called the cohesive energy density. Several scientists have determined the cohesive energy density of many fluids by various methods. All of these results were expressed at 25° Centigrade and at the system pressure. There is an important need for cohesive energy density functions of fluids at higher temperatures and pressures.

In most instances the solubility parameters or cohesive energy densities of liquids at 25° C. have been calculated. These are useful for many types of applications. There is no reason, however, for restricting solubility parameters to these conditions. The solubility parameter or cohesive energy density of a non-ideal gas may be found as well. This is done by relating the properties of the non-ideal gas to the ideal gas conditions in the same way as is done for liquids.

The objective of this study was to provide a means for determining cohesive energy density functions of fluids at high pressures and temperatures. By using existing tabulated thermodynamic properties taken from Lydersen et al. (6) together with the non-ideal gas law, design charts are to be prepared from which the cohesive energy density functions of fluids at high temperatures and pressures can be calculated.
CHAPTER II

COHESIVE ENERGY DENSITY

The cohesive energy density function is an important factor in the Scatchard (4) and Hildebrand (1) solubility theory. As such, it is of importance in explaining the vaporization of asphalts, waxes, and hydrocarbons. These functions could also be used for a basis on which to base calculations of miscible flooding of depleted petroleum reservoirs. Solubilities of both liquids and gases are governed by this thermodynamic quantity.

By rearrangement of equation (1-2) the following equation is obtained:

\[
\frac{\Delta H_m}{V_m \sqrt[3]{\phi_1 \phi_2}} = \left[ \left( \frac{\Delta E_1}{V_1} \right)^{\frac{1}{2}} - \left( \frac{\Delta E_2}{V_2} \right)^{\frac{1}{2}} \right]^2
\]  

(2-1)

It may be seen that the heat of mixing per cubic centimeter of mixture is equal to the square of the differences between the square roots of the cohesive energy density functions of the two components, where the cohesive energy density function is defined as being \( \Delta E/V \).

The square root of the cohesive energy density is obviously of primary importance in the determination of the magnitude of the heat term, which in turn is the prime factor used to determine the sign of the free energy equation. This quantity has been assigned the symbol \( \sigma \).
and called the solubility parameter. Expressed mathematically, 
\[ \rho = \left( \frac{\Delta H}{V} \right)^{\frac{1}{3}} \]
By substituting in the right-hand side of equation (2-1), we can see that the heat of mixing of two substances is dependent on the quantity \((\rho_1 - \rho_2)^2\). If the heat of mixing is not too large, so as to prevent mixing, then \((\rho_1 - \rho_2)^2\) must be relatively small. If \((\rho_1 - \rho_2)^2\) equals zero, mixing is assured by the negative temperature-entropy factor of the free energy equation. This is equivalent to saying that if the solubility parameters of two components are nearly equal, the two components will be miscible.

The cohesive energy density and the solubility are calculable by several methods. In the literature several methods are described for this calculation. All these methods are for conditions of system pressure and usually at 25° Centigrade. These methods make use of critical constants taken from the literature. The following chapter will detail several methods of determination and the previous investigations of this subject.

A method for the determination of cohesive energy density functions of gases at high temperatures and pressures is needed. The use of such values could be applied to miscible flooding of depleted oil reservoirs, mining of sulfur and salt, etc. A study of the literature has been made and it was found that values of cohesive energy densities at high temperatures and pressures are not available.

The purpose of this paper is to determine values of these functions at elevated temperatures and pressures and to prepare design charts suitable for use in calculation of solubility parameters.
Design charts are to be prepared for components having four different critical compressibility factors. At any given pressure and temperature the cohesive energy density divided by the critical pressure of component may be read from the design chart related to the component's critical compressibility factor. Therefore, the cohesive energy density of any component is calculated by multiplying the value read from the appropriate design chart by the critical pressure of the component. The solubility parameter can then be determined by taking the square root of the cohesive energy density.

The solubility parameter of a non-crystalline solvent or any gas is defined as \((\Delta E/V)^{\frac{1}{2}}\) or the square root of the cohesive energy density function,

\[
CED. = \Delta E/V
\]  

(2-2)

where \(\Delta E = (E_2 - E_1)\)

- \(E_2\) = internal energy to the ideal gas at a given temperature and pressure, calories/g-mole
- \(E_1\) = internal energy of the fluid at the given temperature and pressure, calories/g-mole

\(V\) = volume, cubic centimeters/g-mole

For an imperfect gas one can write the general gas law in the form,

\[
P V = Z R T N
\]  

(2-3)

where
- \(P\) = pressure, atmospheres
- \(V\) = volume, cubic centimeters/g-mole
- \(R\) = gas constant
- \(Z\) = compressibility factor
- \(T\) = temperature, °Rankine
- \(N\) = number of gram-moles
The compressibility factor is an empirical quantity which makes the above equation true at a particular pressure and temperature. For a perfect gas, Z is equal to one. For an imperfect gas, Z is greater or less than one, depending on the temperature and pressure.

By dividing both sides of equation (2-3) by \( P \) we get the following:

\[
V = Z R \frac{T}{P} . \tag{2-4}
\]

The reduced pressure and reduced temperature of a gas are defined as

\[
P_r = \frac{P}{P_c} \quad \text{and} \quad T_r = \frac{T}{T_c} \tag{2-5}
\]

where \( T_c \) is the critical temperature and \( P_c \) is the critical pressure of the gas. Solving for temperature and pressure the following is obtained:

\[
P = P_r P_c \quad \text{and} \quad T = T_r T_c . \tag{2-6}
\]

By substituting the above values of \( P \) and \( T \) into equation (2-4) the following value for \( V \) is obtained:

\[
V = Z R \frac{T_r T_c}{P_r P_c} . \tag{2-7}
\]

Next by substituting the value of \( V \) from equation (2-7) into equation (2-2) we obtain the following:

\[
\text{GED} = \Delta E/T_c \cdot P_c P_r / Z T_r R . \tag{2-8}
\]

By dividing both sides of equation (2-8) by \( P_c \) the following and final
equation is obtained:

\[
\frac{CED}{P_C} = \frac{\Delta E}{T_C} \cdot \frac{P_r}{ZRT_r}.
\]  

(2-9)

The scope of this study is to prepare design charts for components with a critical compressibility, \(Z_C\), from 0.23 to 0.29. Cohesive energy density functions will be plotted as the ordinate versus reduced pressure as the abscissa, with reduced temperature as the parameter.

Over 5,000 computations of equation (2-9) were required in the solution of this problem. A computer solution of the equation was programmed in order to save a large amount of time in doing the calculations.

Values of \(\Delta E/T_C\) were taken from the writings by Lydersen et. al. (6). These values corresponded to given reduced pressures and temperatures, which were given for each critical compressibility factor.
CHAPTER III

PREVIOUS INVESTIGATION

Prior to this investigation, to the author's knowledge, no paper was found which indicated that there has been any work relative to the determination of cohesive energy density functions of fluids at high pressures and temperatures.

As early as 1919 Hildebrand (8) gave various methods for obtaining the relative internal pressures, including the energy of vaporization per cubic centimeter, which has been given the name "cohesive energy density."

In 1925 van Laar and Lorenz (10) presented a paper in which they developed the following equation:

\[ \Delta H_m = V_1 X_1 V_2 X_2 / V_m \left( a_1^{1/2} / V_1 - a_2^{1/2} / V_2 \right) \]  

This equation is identical to that presented by Scatchard (4), in 1931, if the constants \( a_1 \) and \( a_2 \) are replaced by the energy of vaporization of both components. Scatchard states that his paper is to be regarded as a quantitative development of the treatment by Hildebrand in his paper published in 1919. Scatchard's first assumption was essentially that of additivity of the energy of the molecular pairs. This has proved very successful as the basis for nearly all theories of gases, liquids, and solutions. The second
assumption, that of random distribution of molecules, is the basic theory of regular solutions. His third assumption is that there is no change in volume.

These assumptions permit writing the following equation:

\[ \Delta H_m = V_m \left[ \left( \frac{\Delta E_1}{V_1} \right)^{\frac{1}{2}} - \left( \frac{\Delta E_2}{V_2} \right)^{\frac{1}{2}} \right]^2 \phi_1 \phi_2. \]  

This equation was also derived by Hildebrand and Wood (9) in 1933 by integrating the intermolecular potential between pairs throughout the liquid. This is analogous to the summation used to connect intermolecular potential and lattice energy for crystals. Hildebrand, as did Scatchard, assumed that there was no change in volume and also that the distribution of molecules throughout the mixture is random. His third assumption was that the molecules of the components are of the same inherent size and have the same degree of expansion. Provided that the above assumptions are correct, Hildebrand's derivation is completely rigorous.

Equation (3-2) is identical to equation (2-1) which the author used in this investigation. The quantity \( \Delta E/V \) is defined as the cohesive energy density, CED. \( \Delta E \) is the energy of vaporization to gas at zero pressure and \( V \) is the molal volume. Both \( \Delta E \) and \( V \) change with temperature, so CED must be calculated for each temperature at which we wish to use it. Desired vaporization data, at different temperatures, are often lacking. In the following sections various methods of estimating the cohesive energy density will be discussed in detail. There are four methods outlined by Hildebrand (1) which
are discussed here for the edification of the reader.

Calculation of CED from heats of vaporization is satisfactory when working with liquids at temperatures below the component's normal boiling point. This method is of no practical use in working with gases. It is, therefore, of no use in this particular investigation. The following equation is used when using heat of vaporization data:

$$CED = \frac{\Delta H_v - RT}{V}$$  \hspace{1cm} (3-3)

For many substances no heat of vaporization data, either calorimetric or from vapor pressure, is known. For such cases, it is possible to estimate the heat of vaporization from the boiling point, by use of the "Hildebrand Rule." By this method one calculates $\Delta H_v$ values by use of the following:

$$\Delta H_v = -2950 + 23.7 T_b + 0.02 T_b^2$$  \hspace{1cm} (3-4)

The above value of $\Delta H_v$ is substituted in equation (3-3) in order to determine CED values. Again, this method isn't useful for this investigation because it has no application to gases.

Another method of estimation is by use of "internal pressure." The internal pressure may be strictly defined as $\left(\frac{\partial E}{\partial V}\right)_T. This is defined in the following equation:

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$$  \hspace{1cm} (3-5)

The so-called thermal pressure $T \left(\frac{\partial E}{\partial T}\right)_V$ may be obtained from the coefficients of thermal expansion and compressibility $\alpha$ and $\beta$: 
At low pressures, the pressure $P$ in equation (3-5) is entirely negligible compared with the internal pressure. Equation (3-6) can be used in calculations of either liquids or gases. For this investigation convenient data were not available for preparation of design curves; therefore, this method was not used.

The last method to be considered is one which uses surface tension data to estimate values of CED. Surface tension bears a close relationship to the heat of vaporization. Hildebrand gives the following empirical formula which he states is only an approximation.

$$CED = K \left( \frac{\gamma}{V} \right)^{0.86}$$  \hspace{1cm} (3-7)

where, for $\gamma$ in dynes/centimeter, $V$ in cubic centimeters/mole, and CED in calories/cubic centimeter, $K$ is a numerical function of the system temperature. This equation is not suitable for calculations of cohesive energy density functions of gases or liquids in this study because $K$ values must be determined experimentally for each temperature.

This leaves but one convenient formula to be used for the calculations of the CED functions of gases. That is equation (2-9), which when used along with thermodynamic data prepared by Lydersen et. al. (6), gives very good results which may be presented in the form of design curves.
CHAPTER IV

COMPUTER SOLUTION

There were approximately 5000 calculations necessary in order that the design charts could be prepared for four different critical compressibility factors. The I. B. M. 650 digital computer was used to make these calculations. A method, other than the use of the digital computer, would have required a vast amount of time.

The For Transit system was used in programming the cohesive energy density equation. This system is so designed that one, inexperienced and unfamiliar with computer programming, may write programs closely related to those of mathematics. International Business Machines Corporation (7) published a detailed and complete For Transit manual in 1957. The program was written and used for the calculation of \( \frac{\Delta E}{T_c} = \frac{P_r}{82.06 \times Z T_c} \). A block flow diagram of this program is shown in Figure 1.

In this program, 2640 values of \( \frac{\Delta E}{T_c}, Z, T_r, \) and \( P_r \) for components with a critical compressibility factor of 0.23 were fed into the computer as data. 2500 values of the variables were fed in for the \( Z_c \) of 0.25, 7000 values for the \( Z_c \) of 0.27, and 2500 values for the \( Z_c \) of 0.29. The For Transit program used in the calculation of the cohesive energy density equation is
READ $\Delta E/T_c$, $P_T$, $T_T$, $Z$

SET

$\Delta E/T_c = E$

$P_T = PR$

$T_T = TR$

COMPUTE

CED/$P_c$ = $(E)(PR)/(82.06 \ Z \ TR)$

SET

$KC = 100,000,000 \ CED/P_c$

$KA = 100,000,000 \ PR$

$KB = 100,000,000 \ TR$

PUNCH $KA$, $KB$, $KC$

STOP

Fig. 1. Flow Chart for Calculation of CED/$P_c$
shown in Table I.

When using the For Transit system, it is first necessary to process the For Transit program statements. In the first step of the processing, the For Transit statements and the For Transit package deck are fed into the computer. This step produces the IT statements and the Table of Correspondence. For the second step, the computer accepts the IT statements from those produced during the initial phase along with the IT package deck and produces instructions in symbolic language. In the last phase of processing, the machine accepts the SOAP II deck and the output of the second phase and produces the final object program. This program, along with necessary data cards, is the deck which is used for the calculation of the cohesive energy density functions. A listing of the object program is presented in Table II.

The data were loaded on the type 2 data card. On the type 2 data card, seven pieces of data may be punched if desired; however, the variables to which these values refer must have had contiguous and successive identifications assigned to them by the translator. The format for the type 2 card is shown in Figure 2.
TABLE I

FOR TRANSIT PROGRAM FOR CALCULATION OF CED

0 0001 0 READ
0 0002 0 CEDPC = E*PR/(Z*82.06)
0 0002 1 TR)
0 0003 0 KA = PR*100,000,000
0 0004 0 KB = TR*100,000,000
0 0005 0 KC = CEDPC*100,000,000
0 0006 0 PUNCH, KA, KB, KC
0 0000 0 GO to 1
0 0000 0 STOP

Fig. 2. Data Card Format
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**TABLE II**

**OBJECT PROGRAM FOR CALCULATION OF CED/Pc**
CHAPTER V

PRESENTATION OF RESULTS

The tables presented in Appendix C list the values of CED/Pc that were calculated with the IBM 650.

By taking the calculated values of CED/Pc, it was possible to plot CED/Pc versus P_r with T_r as a parameter. Design curves for T_r of 0.50 through T_r of 2.0 are presented in Figures 3, 4, 5, and 6. Figure 3 is to be used for components having critical compressibilities of approximately 0.23. Figures 4, 5, and 6 are to be used for components having critical compressibilities of 0.25, 0.27, and 0.29, respectively. These curves can be extended for larger values of reduced pressure and reduced temperature.

In Appendix B is a table showing results obtained from calculated values of (CED/P_c)^{1/2}. These calculated values are compared with experimental values taken from the literature. The two values in most cases compare very favorably. In this comparison 23 compounds are compared. In 17 of the 23 components the error was found to be less than 2%. All of the values calculated had less than 5% error.
Fig. 3. Cohesive Energy Density/Critical Pressure for $Z_c$ of 0.23
Fig. 4. Cohesive Energy Density/Critical Pressure for $Z_c$ of 0.25
Fig. 5. Cohesive Energy Density/Critical Pressure for $Z_c$ of 0.27
Fig. 6. Cohesive Energy Density/Critical Pressure for $Z_c$ of 0.29
CHAPTER VI

SUMMARY AND CONCLUSIONS

The purpose of this study was to provide the means for determining the cohesive energy density of various gases at elevated pressures and temperatures by the use of design curves. The governing equation of the problem was the heat of mixing equation.

By mathematical manipulation of the heat of mixing equation in conjunction with the general gas law for an imperfect gas, a digital computer solution was obtained which was used to calculate the cohesive energy density functions of gases.

Design curves of CED/\(P_c\), versus reduced pressure, \(P_r\), with reduced temperature, \(T_r\), were prepared. Since the values of CED/\(P_c\), read from the appropriate design curve, are equal to the cohesive energy density when multiplied by the critical pressure, \(P_c\), it is evident that the cohesive energy density function is readily determined by use of the curves.

One stipulation to be made is that the system must not be in the two phase region. The curves do not permit calculation of cohesive energy density function in the two phase region because at the present time there is no means of determining the liquid or vapor percent in the two phase region. If liquid percent lines were to be superimposed on the two phase region it would then be
possible to calculate CED values there.

The curves in Figures 3, 4, 5, and 6 show that the cohesive energy density of a fluid increases as the system pressure is increased. The cohesive energy density values decrease as the temperature is increased.

The values of CED for fluids obtained from this study agree closely with those obtained by Hildebrand. The maximum difference was 4.9%. In 17 out of 23 components studied, the error was found to be less than 2.0%. A comparison of values of CED obtained in this study with those of Burrell are also in close agreement. These values are all obtained at the system pressure and at a temperature of 25 degrees Centigrade. Because of assumptions made by Hildebrand in his original investigation, it is felt that values of CED obtained from Figures 3, 4, 5, and 6 will be accurate enough for most solubility calculations.
CHAPTER VII

RECOMMENDATION FOR FUTURE STUDY

The cohesive energy density problem considered in this study was for fluids at high pressures and temperatures. Closely related to this is the problem of finding cohesive energy densities of liquids and solids.

J. H. Hildebrand (1) developed several methods for the determination of cohesive energy density functions of liquids and solids. These various methods are outlined in Chapter III. The method best suited is outlined in the following equation:

\[
\left( \frac{\partial E}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V - P
\]

(7-1)

where

\[
\left( \frac{\partial E}{\partial V} \right)_T = \text{Internal pressure}
\]

\[T \left( \frac{\partial P}{\partial T} \right)_V = \text{Thermal Pressure}
\]

The so-called thermal pressure \( T \left( \frac{\partial P}{\partial T} \right)_V \) may be obtained either by direct measurement or from the coefficients of thermal expansion and compressibility \( \alpha \) and \( \beta \). At low pressures, the pressure, \( P \), in equation (7-1) is entirely neglected by Hildebrand because of the magnitude of the internal pressure. By making this assumption we can write:

\[
\left( \frac{\partial E}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V = \frac{N \Delta E}{V}
\]

(7-2)
For a van der Walls liquid \( n \) equals 1.0, and the internal pressure equals the cohesive energy density. Thus for nonpolar liquids, we can use \( T \left( \frac{\partial P}{\partial T} \right)_V \) as a measure of the cohesive energy density:

\[
CED = T \left( \frac{\partial P}{\partial V} \right)_T = T \frac{\partial \beta}{\partial \beta} \tag{7-3}
\]

The author believes that equation (7-3) is valid and could be used to prepare design curves to evaluate the cohesive energy densities of liquids at different temperatures and pressures.
A SELECTED BIBLIOGRAPHY


APPENDIX A

SAMPLE CALCULATIONS

The following problem will illustrate the use of the design curves for the calculation of the cohesive energy density or solubility parameters of a gas.

PROBLEM:

One mole of propane is at a temperature of 25° Centigrade. The vapor pressure of propane is 138 psia. The gas is further characterized by the following properties:

Critical compressibility, \( Z_c = 0.277 \)

Critical temperature, \( T_c = 369.9^\circ \text{ Kelvin} \)

Critical pressure, \( P_c = 617 \text{ psia} \)

It is desired to (1) calculate the cohesive energy density and (2) calculate the the solubility parameter of the propane at the given pressure and temperature. Also, it is desired to (3) compare the resulting value of the solubility with that obtained by Hildebrand.

SOLUTION:

(1) Reduced temperature, \( T_r = T/T_c \)

\[
T_r = \frac{298}{369.9} \\
T_r = 0.805
\]

Reduced pressure, \( P_r = P/P_c \)

\[
P_r = \frac{138}{617}
\]
CED/Pc = 0.87 (From Fig. 5)

CED = \( P_c \times CED/Pc \)

= 41.9 \times 0.87

= 36.42 \text{ calories/cc}

(2) \( \vartheta = (CED)^{1/2} \)

= \((36.42)^{1/2}\)

= 6.02 (calories/cc)^{1/2}

(3) For propane at 25° Centigrade, Hildebrand found \( \vartheta \) to be 6.0. This compares very closely with the value determined by using the design curves.

The cohesive energy density of propane at 25° Centigrade is 36.42 calories/cc, and the solubility parameter is 6.02 (calories/cc)^{1/2}. 
## APPENDIX B

### TABLE III

**COMPARISON OF RESULTS**

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APPENDIX C

TABLES OF COMPUTED CED/\(P_c\)
### TABLE IV

MACHINE CALCULATED VALUES FOR Zc OF 0.23

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- **Columns**:
  - **Tr (m):** Measured value in meters.
  - **Pr (m):** Calculated value in meters.

- **Rows**:
  - **0.00:** Represents the starting point.
  - **0.00:** Incremental changes in Tr and Pr are shown.

The table provides a detailed calculation of Zc values for various Tr and Pr combinations, reflecting the accuracy of machine calculations for specific geometrical conditions.
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TABLE IV (Continued)
### TABLE V

**MACHINE CALCULATED VALUES FOR Zₐ OF 0.25**

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**Notes:**
- Tr represents the temperature range.
- Pr values are calculated based on the conditions specified.
- The values are derived through machine calculations for specific Zₐ values.\n- The table contains multiple iterations and calculations to provide comprehensive data for analysis.\n
This table is crucial for understanding the behavior of materials or systems under certain conditions, enabling engineers and researchers to make informed decisions based on precise calculations.
TABLE VI

MACHINE CALCULATED VALUES FOR ZC OF 0.27

| Tr | P_T | P_R | P_T | P_R | P_T | P_R | P_T | P_R | P_T | P_R | P_T | P_R | P_T | P_R | P_T | P_R | P_T | P_R |
|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 0.0 | 0.6845560 | 1.868786 | 1.8700065 | 1.8636800 | 1.8664835 | 1.8617122 |
| 0.1 | 1.868786 | 1.8700065 | 1.8636800 | 1.8664835 | 1.8617122 |
| 0.2 | 1.8636800 | 1.8664835 | 1.8617122 |
| 0.3 | 1.8664835 | 1.8617122 |
| 0.4 | 1.8617122 |
| 0.5 | 1.8664835 |
| 0.6 | 1.8636800 |
| 0.7 | 1.868786 |
| 0.8 | 1.8700065 |
| 0.9 | 1.8636800 |
| 1.0 | 1.8664835 |
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**TABLE VII**

**MACHINE CALCULATED VALUES FOR $Z_c$ OF 0.29**
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John Henry Hendrix

Candidate for the Degree of

Master of Science

Thesis: GENERALIZED COESIVE ENERGY DENSITY CORRELATIONS FOR ONE-COMPONENT SYSTEMS

Major Field: Mechanical Engineering

Biographical:

Personal Data: Born at King, Arkansas, July 8, 1936, the son of Smith Henry and Ellen Hendrix.

Education: Attended grade school in Gillham, Arkansas; graduated from Gillham High School, Gillham, Arkansas in 1954; received the Associate of Science Degree from Eastern Oklahoma A. and M. College in May, 1956; received the Bachelor of Science Degree from Oklahoma State University, with a major in Mechanical Engineering, in August, 1958; completed the requirements for the Master of Science Degree in January, 1960.

Experience: Employed by the Whitfield Lumber Company in Montrose, Colorado for the summer of 1955, as a bookkeeper and clerk; employed by Empire Geophysical, Inc. in Lovington, New Mexico for the summer of 1956, as a seismic computer; employed by Continental Oil Company in Eunice, New Mexico and Wewoka, Oklahoma for the summers of 1957 and 1959 as a roustabout and Junior Engineer; employed by Oklahoma State University as a graduate assistant during 1959.