T = absolute temperature, °K.
t = time

Greek Letters

α = rate constant
β = rate constant
θ_i = fraction of catalytic surface covered by component i
θ_1' = fraction of the sites available for competitive adsorption which are covered by hydrogen
θ_1'' = fraction of the noncompetitive sites which are covered by hydrogen
θ_2' = fraction of the sites available for competitive adsorption which are covered by olefin

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The Prediction of Liquid Mixture Enthalpies from Pure Component Properties

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The paper presents a procedure for calculating liquid mixture enthalpies, whereby a liquid heat of mixing is added to the molal average of the pure liquid enthalpies. The heat of mixing for the mixture is calculated from the heats of mixing of the binary systems at infinite dilution, which in turn are determined with a proposed molecular model for liquid mixing, and a postulate of acceptance. The two cases where the solute in the binary system is more volatile and less volatile than the solvent are treated separately. The case is also considered where a component of the liquid mixture is above its critical temperature; a pure liquid enthalpy is defined and justified for such pseudo liquids, and heats of mixing are then calculated as for actual liquids. Results are compared for four nonpolar binary systems, three with experimental data, and one with data calculated by other means. Data for a number of gases dissolved in water are also considered. The agreement in all cases is excellent.

An increasing amount of work is being done on the problem of predicting the enthalpy of liquid mixtures, and the need for better liquid mixture enthalpy calculation procedures becomes more urgent, particularly in the light of the complete absence of data for most systems, and the relative complexity of obtaining experimental mixture enthalpy data. The cost to the petroleum industry alone of the lack of good liquid enthalpy data was discussed in a recent article by Findlay (1).

Methods of calculating liquid mixture enthalpies fall into three categories: intermolecular theory, correlatory

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equations, and equations of state. Prigogine's (2) work has formed the basis of the first category, but the state of art is such that intermolecular theory has met with little success in predicting liquid nonideality. In a recent paper, Pierotti (3) developed a theory which appears to calculate very well the excess thermodynamic properties of the inert gases, but it breaks down when handling molecules that cannot be considered as rigid spheres. Correlatory equations all require some binary enthalpy data with which to derive empirical constants, and thence the equations may be used to extend the data over a wider temperature range, or to predict ternary or multicomponent

data. The most successful correlatory equations are the power series equations (4 to 6), which can be very accurate, providing sufficient data are available to obtain the necessary empirical constants. A number of graphical correlations have been presented over the years (7 to 10) to predict the enthalpies of mixtures of the lighter aliphatic hydrocarbons. These correlations, in general, give good engineering answers within the range of components and conditions for which they were derived. Moreover, they consider the effect of pressure on liquid enthalpy. Equations of state attempt to predict liquid enthalpies from the thermodynamic identity:

$$(H^* - H) = \int_0^P [T \, (\partial V/\partial T)_P - V_T] \, dP \qquad (1)$$

Any errors in the P-V-T relationship of an equation of state are greatly increased when predicting enthalpy data. Therefore, a very accurate fit to available P-V-T data must be made, and only the most complex equations would appear to have a chance of calculating good enthalpy data. The Benedict-Webb-Rubin equation of state is the only one that has been used with any extensive success in predicting liquid enthalpies (11). The simple Redlich-Kwong equation of state has been used extensively for calculating enthalpy, and for superheated vapors it serves the purpose admirably. However, due no doubt to the other successes of this remarkable equation of state, it is being used in industry to predict enthalpies of saturated vapors and liquids, and vapors below their saturation temperatures in mixtures. The dangers in using the Redlich-Kwong equation of state to calculate enthalpies near or below the critical temperature are obvious if virial coefficients are back-calculated and compared at these temperatures. Wilson (12) recently improved the Redlich-Kwong equation of state, and it will be interesting to see what success is achieved in calculating liquid enthalpies with this modified equation of state.

The work discussed herein may be loosely ascribed to the first category of intermolecular theory. Since the excess thermodynamic properties of a liquid mixture depend on the properties of the pure components only, it follows that it should be possible to calculate excess thermodynamic functions from pure component data only. By this calculation procedure, binary heats of solution at infinite dilution are calculated, differently for the two cases where the solute is the more volatile and the less volatile component. Heats of solution are calculated from infinite dilution values with a Margules type of equation, and total enthalpies are obtained by adding the excess enthalpy to the sum of the partial molal pure component enthalpies. For this purpose a pseudo liquid state is defined and justified, whereby "liquid" enthalpies above the critical temperature may be readily obtained.

THEORY

It is found empirically that where the less volatile component is the solute, an excellent value is calculated for the *enthalpy deviation from the ideal gas state* of the solute at infinite dilution, by reading the enthalpy deviation from the ideal gas state of the pure solute at the reduced temperature of the pure solvent.

$$(H^* - H^\infty)_{bT_{rb}} = (H^* - H^\circ)_{bT_{ra}} \qquad (2)$$

The significance of Equation (2) may be examined in terms of intermolecular potential. We consider the Lennard-Jones 6-12 model for intermolecular potential, and the commonly used equations for intermolecular potentials in binary systems (13). As illustrated in Figure 1, ϵ, the
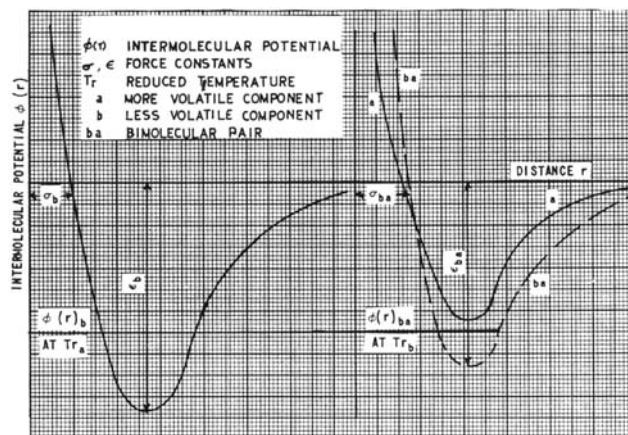

Fig. 1. The intermolecular potentials of a less volatile solute at infinite dilution in a more volatile solvent and for the pure solute at the reduced temperature of the solvent.

potential well depth, commonly is greater for less volatile components over more volatile components. Furthermore, the well depth for a bimolecular pair is frequently estimated with Equation (3).

$$\epsilon ab = \sqrt{\epsilon a \epsilon b} \qquad (3)$$

Enthalpy deviations from the ideal gas state may be written in terms of the virial coefficients, which in turn may be represented by the equation adopted for intermolecular potential (14). It is approximately correct to imply from Equation (2) the relationship:

$$[\phi(r)]_{baT_{rb}} = [\phi(r)]_{b \, T_{ra}} \qquad (4)$$

Stated, the intermolecular potential $\phi(r)$ for the bimolecular pair $a - b$ at a reduced temperature T_{rb} will have the same value as the intermolecular potential for the unimolecular less volatile pair $b - b$ at some reduced temperature T_r in excess of T_{rb}. Equation (2) implies that this higher reduced temperature equals T_{ra}. We may conclude that, though Equation (2) is unlikely to please a physical chemist, it does calculate heats of mixing at infinite dilution, of the right order of magnitude and sign, which at the present time is an achievement not to be underrated, when attempting to calculate multicomponent enthalpies without the aid of binary experimental data.

Equation (2) does not hold where the more volatile component is the solute in the less volatile solvent. For this second case, the solute appears to create for itself a liquid *cell* which the less volatile solute does not do. Moreover, the thermodynamic properties of the solvent at the site where the solute creates for itself a cell are not equal to the average thermodynamic properties of the solvent. We define here a liquid cell as a location for a solute molecule in a solvent, which is not randomly distributed with respect to energy levels. *Site* is defined as the location of the liquid cell in terms of the fluctuations of enthalpy, entropy, and momentum of the solvent molecules about their means. When it is assumed that the solvent thermodynamic properties have Maxwellian distributions about the mean values, the solute molecule chooses for itself, within the energy distribution of the solvent, the site most compatible with the energy state of the solute molecule. To understand the concept better, we discuss first the theory of thermodynamic distributions in a mass of a pure liquid. From the formula for quantum mechanical partition functions, it is possible to derive an expression for ensemble averages. It is also possible to express thermodynamic properties in terms of the partition function (15).

$$H = kT^2 \left[\frac{\partial \ln Z_N}{\partial T} \right]_V + kTV \left[\frac{\partial \ln Z_N}{\partial V} \right]_T \quad (5)$$

$$P' = kT \left[\frac{\partial \ln Z_N}{\partial V} \right]_T \quad (6)$$

From Equations (5) and (6), using the relationship for canonical ensemble averages, we can derive expressions for the mean fluctuations of thermodynamic properties, as in Equations (7) and (8).

$$(\overline{H})^2 - H^2 = RTV^2 (\partial P/\partial V)_T + RT^2 C_P \quad (7)$$

$$(\overline{P'})^2 - (P')^2 = RT (\partial P/\partial V)_T \quad (8)$$

In consistent units, where H is B.t.u./lb.-mole, T is °R., CP is B.t.u./(lb.-mole) (°R.), P is lb./sq. in., and V is cu. ft./lb.-mole, Equations (7) and (8) become

$$(\overline{H})^2 - H^2 = 0.368\ TV^2 (\partial P/\partial V)_T + 1987T^2C_P \quad (7a)$$

$$(\overline{P'})^2 - (P')^2 = 10.73\ T (\partial P/\partial V)_T \quad (8a)$$

It is found that Equations (7a) and (8a) will permit the accurate calculation of the energy level of a solute cell site, and that reduced temperature is the most successful measure of energy level. Thus, if the energy level of the solute molecule is characterized by the reduced temperature of the solute, the energy level of the solute cell site in the solvent must also be characterized by the solute reduced temperature. Then the solvent cell site vapor pressure equals the solvent vapor pressure at the reduced temperature of the solute. (Where the solute reduced temperature is greater than 1.0, the solvent vapor pressure is found according to the usual procedure, namely a plot of log P vs. $1/T$ is extrapolated through the critical temperature. Where a plot of log P vs. $1/T$ does not give a straight line, an accurate procedure is to express log P as a polynomial in terms of $1/T$. Three terms usually suffice. Such an equation is then employed to calculate pseudo vapor pressures above the critical point.) The vapor pressure of the solvent cell site is the *acceptance pressure* of the solvent, and the *acceptance enthalpy* of the solvent will be approximated by Equation (9).

$$(H_A - H^\circ)/(P'_A - P') = (\overline{H} - H)/(\overline{P} - P') \quad (9)$$

We define *acceptance* properties as the properties acquired by solute molecule in its cell in the solvent. Unfortunately, there are no grounds for assuming that the ratio given in Equation (9) will be constant for all fluctuation levels; in fact the case is otherwise. When the acceptance level is not far removed from the mean enthalpy and vapor pressure of the solvent, it is more accurate to assume that the pressure and enthalpy fluctuations are equal to the saturation pressure and enthalpy variations with temperature, as in Equation (10).

$$(H_A - H^\circ)/(P'_A - P') =$$
$$[(H)_{T_2} - (H)_{T_1}]/[(P)_{T_2} - (P)_{T_1}] \quad (10)$$

where T_1 is the system temperature and T_2 is the temperature of the solvent at the reduced temperature of the solute. Equation (10) thus reduces to Equation (10a), which states that the acceptance enthalpy of the solvent equals the saturated liquid enthalpy of the solvent at the reduced temperature of the solute.

$$H_A = (H_{\text{solvent}})\ T_{r\ \text{solute}} \quad (10a)$$

It is found that when the difference between the reduced temperatures of solute and solvent is 0.5 or less, H_A is

best calculated by Equation (10a). When the difference is greater than 0.5, H_A is best calculated by Equation (9).

A knowledge of the acceptance enthalpy permits us to calculate the enthalpy of the solute at infinite dilution, since Lyderson et al. (16) have shown that the enthalpy deviation term $(H^* - H)/T_c$ may be plotted for saturated liquids as a universal function of reduced temperature and critical compressibility. Therefore, Lyderson's enthalpy deviation term must be the same for the solute molecule at infinite dilution and for the solvent cell site.

$$[(H^* - H^\infty)/T_c]_a = [(H^* - H_A)/T_c]_b \quad (11)$$

Thus we may derive an expression for the enthalpy deviation from the ideal gas state of the more volatile solute at infinite dilution.

$$(H^* - H^\infty)_a = (T_{ca}/T_{cb})\ (H^* - H_A)_b \quad (12)$$

Having calculated solute liquid enthalpy at infinite dilution, we may determine heats of solution at infinite dilution, and by use of a Margules type of equation, heats of solution at other concentrations may be calculated. The heat of solution at infinite dilution is $(H^\circ - H^\infty)_i$ or L_i, where i represents any component. H°_i, the pure liquid enthalpy, is determined from pure component data. Frequently, H°_i has to be determined for the pseudo liquid, as described in this paper. L_i is then determined as follows:

$$L_i = (H^* - H^\infty)_i - (H^* - H^\circ)_i \quad (13)$$

and, similarly, for the second component j of a binary system

$$L_j = (H^* - H^\infty)_j - (H^* - H^\circ)_j \quad (13a)$$

The three-suffix Margules equation for activity coefficient variation with composition is (17):

$$\ln\gamma_i = x_j^2 [A_{ij} + 2x_i (A_{ji} - A_{ij})] \quad (14)$$

Differentiating with respect to $1/T$, we obtain Equation (15).

$$\frac{\partial \ln \gamma_i}{\partial \left(\frac{1}{T} \right)} = x_j^2 \left[\frac{\partial A_{ij}}{\partial \left(\frac{1}{T} \right)} + 2x_i \left(\frac{\partial A_{ji}}{\partial \left(\frac{1}{T} \right)} - \frac{\partial A_{ij}}{\partial \left(\frac{1}{T} \right)} \right) \right] \quad (15)$$

But we know that the following are true:

$$\partial \ln \gamma_i / \partial (1/T) = (H^\circ - \overline{H})_i/R \quad (16)$$

$$\partial A_{ij}/\partial (1/T) = L_i/R \quad (17)$$

$$\partial A_{ji}/\partial (1/T) = L_j/R \quad (17a)$$

So, by substituting Equations (17) and (17a) into Equation (16) and by eliminating R, we obtain for component i

$$(H^\circ - H^L)_i = x_j^2 [L_i + 2x_i (L_j - L_i)] \quad (18)$$

and for component j

$$(H^\circ - H^L)_j = x_i^2 [L_j + 2x_j (L_i - L_j)] \quad (18a)$$

The total heat of mixing is given by Equation (19)

$$H^E = x_i (H^\circ - H^L)_i + x_j (H^\circ - H^L)_j \quad (19)$$

and by substituting Equations (18) and (18a) into Equation (19), we obtain Equation (20):

$$H^E = x_i x_j (x_i L_i + x_j L_j) \quad (20)$$

In an identical manner, the four-suffix Margules equation (17) may be differentiated to yield an enthalpy equation. Schnaible, Van Ness, and Smith (18) derived such an equation in which they gave the Margules D constant the value in Equation (21).

$$\partial D/\partial(1/T) = (L_i - L_j) \qquad (21)$$

Thus they derived the following total heat of mixing equation:

$$H^E = x_i x_j [x_i L_i + x_j L_j - x_i x_j (L_i - L_j)] \qquad (22)$$

The Margules equation is the only binary correlatory equation that may be converted into an enthalpy equation based on heats of solution at infinite dilution. The Van Laar equation cannot be differentiated to yield any simple solution for enthalpy, while the many polynomial expressions are purely empirical equations of limited value.

For multicomponent systems, heats of mixing may be calculated from a knowledge of binary heats of solution at infinite dilution by utilizing the enthalpy form of the Wohl equation (19). The Wohl equation yields an enthalpy of mixing equation in which the activity coefficient term is replaced by an enthalpy of mixing term and the Margules constants are replaced by respective enthalpy constants. This equation may be derived in the same manner as the preceding heat of mixing equation.

The total heat of a solution is obtained by adding the heats of mixing to the sum of the partial enthalpies of the pure liquids as in Equation (23).

$$H^M = \Sigma x_i H^o_i + H^E \qquad (23)$$

THE PSEUDO LIQUID

When calculating acceptance enthalpies and pure liquid enthalpies, it may be necessary to handle liquids at temperatures above their critical. A pseudo liquid state is therefore defined, starting from the equation for enthalpy deviation from the ideal gas state, as given by Equation (1). It will be observed from the generalized enthalpy deviation charts of Lyderson et al. (16) that the term $(H^* - H)/T_c$, when plotted against reduced pressure, gives a broad maximum for any reduced temperature. Since, in the pseudo liquid state, both V_T and $(\partial V/\partial T)_P$ will be small, the term $[T (\partial V/\partial T)_P - V_T]$ may be approximated to zero, and $(H^* - H^o_s)/T_c$ for the pseudo state is therefore taken as the maximum value of the term at the given reduced temperature, or the liquid enthalpy at the Joule-Thomson inversion pressure. The pseudo liquid enthalpy deviations are plotted in Figure 2 as a function of reduced temperature and critical compressibility. The pseudo liquid enthalpy starts to diverge from pure liquid enthalpy at a reduced temperature of 0.82. In the reduced temperature range from 0.82 to 1.0, there exist two liquid enthalpies: H^o, the pure liquid enthalpy, and H^o_s, the pseudo liquid enthalpy; H^o is used for the pure solvent enthalpy, and H^o_s is used for the solute enthalpy and in calculating the solvent acceptance enthalpy.
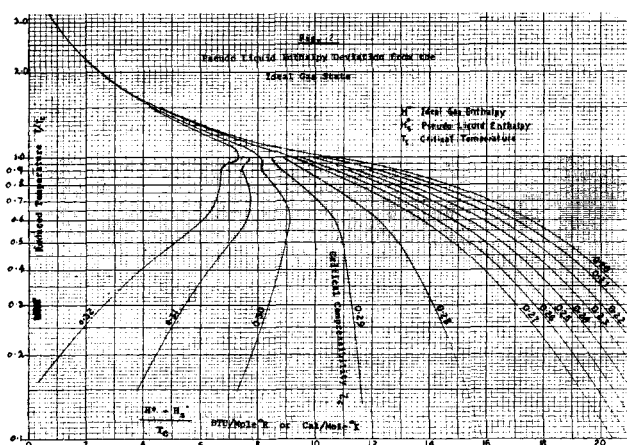

Fig. 2. Pseudo liquid enthalpy deviation from the ideal gas state.

TABLE 1. ENTHALPY DEVIATION FROM IDEAL GAS
$(H^* - H)$ CALS./MOLE

Gas	Calculated 25°C.	Himmelblau 25°C.	Calculated 80°C.	Himmelblau 80°C.
O₂	2,706	2,900	293	576
N₂	2,200	2,500	125	146
H₂	721	960		
He	230	400		
XE	5,082	4,500	1,940	1,440
CH₄	3,343	3,200	552	626
Ne	780	1,080		
A	2,650	3,100		
Kr	3,686	3,440		

For components whose properties do not fit the generalized charts, the maximum enthalpy deviation from ideality $(H^* - H^o_s)$ may be found by plotting $(H^* - H)$ for the component at a given temperature and the range of pressures available against the values of $(H^* - H)$ determined from generalized charts at the same temperature and pressures, according to the method of Othmer (20). The line usually is easily extended, and a corresponding maximum enthalpy deviation is read off this plot, using the maximum enthalpy deviation obtained from the generalized charts. As previously stated, vapor pressures above the critical temperature have been obtained by extending the usual plot of log of vapor pressure against reciprocal of absolute temperature. It can be argued that, according to the definition of the pseudo liquid state postulated above, the pseudo liquid vapor pressure should be the Joule-Thomson inversion pressure. However, very little accurate information is available for the Joule-Thomson inversion pressure of most components, and where such data are available, the enthalpies calculated are substantially the same as those using extended vapor pressure plots, since a similar correction is applied to both solute and solvent.

POLAR SYSTEMS

A full treatment of polar systems is left to a future paper, but Himmelblau's data (21) for the enthalpies of a number of gases dissolved in water are considered out of interest in the framework of nonpolar theory. It would be expected that a solute molecule would be held more firmly by a polar solvent, thus precluding the buoyancy effect, or acceptance of water toward a more volatile solute. This is found empirically to be the case. As temperature decreases, the effect of the polar forces becomes more noticeable, and two different mechanisms are found to exist, one at 80°C. and another at 25°C. In Table 1 calculated values of the enthalpy departure from the ideal gas state are compared with Himmelblau's data for the gases considered. At 80°C. there is found to be no heat of mixing for the gases, and the liquid enthalpy at infinite dilution is equal to the pseudo liquid enthalpy as defined in this paper, and may be read from Figure 2.

At 25°C., the gases behave as for nonpolar systems, but without the acceptance effect. In other words, the cell occupied by the solute gas has the average values of the solvent, and Equation (12) becomes Equation (12a).

$$(H^* - H^\infty)_a = T_{ca}/T_{cb} (H^* - H^o)_b \qquad (12a)$$

RESULTS

Heats of solution and mixture enthalpies have been calculated for four nonpolar binary systems for which experi
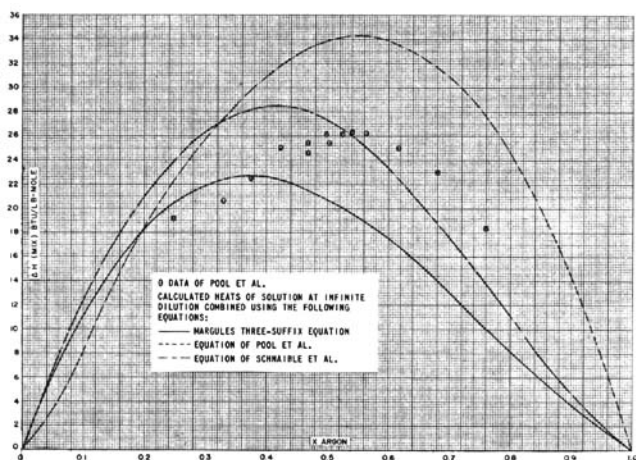
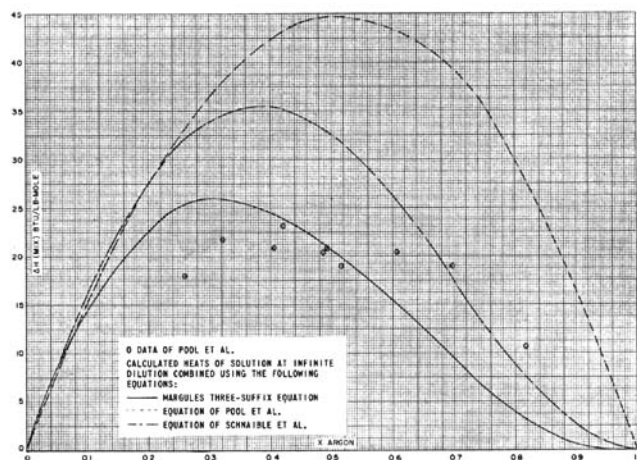Fig. 3. Heat of mixing for the oxygen-argon system.

Fig. 4. Heat of mixing for nitrogen-argon system.

mental data are available (22 to 24) and for one ternary system (25). Himmelblau's data (14) for gases dissolved in water are also considered (see preceding section). For the system methane-nitrogen, enthalpy data derived from P-V-T data (26) are compared with the experimental data (23). Calculated heats of mixing are sufficiently accurate to enable liquid mixture enthalpies to be determined to within about 3 B.t.u./lb. accuracy,

In Figures 3 and 4 calculated data for the systems oxygen-argon and nitrogen-argon are compared with the experimental data of Pool et al. (22). It will be seen that the heats of mixing for these systems are very small and that they are reproduced very well by the two Margules equations, (20) and (22). For these systems the authors suggest the correlatory equation:

$$H^E = x_i x_j [L_i + L_j (x_i - x_j)] \qquad (24)$$

This equation is compared with Equations (20) and (22). Errors of less than 1% in pure component enthalpy, vapor pressure, or critical constant data could reproduce the data of Pool et al. exactly, or move the calculated line further from the experimental data, and it is doubted whether pure component enthalpy data are correct to within 1%, particularly for argon. It is therefore suggested that the calculated data are as close to the experimental data as is feasible by this method without very accurate pure component data. Figures 5 and 6 compare calculated enthalpy data for the system methane-nitrogen in which nitrogen is present above its critical temperature. In Figure 5 the calculated data are compared with the experimental data of the U.S. Industrial Chemicals Company (23) for the difference between gas enthalpy at 25°C. and saturation pressure, and saturated liquid enthalpy. The calculated data include heats of mixing, as well as pseudo liquid enthalpies for nitrogen and pure component enthalpy data for methane. Derived data of the Institute of Gas Technology (18) for the nitrogen-methane system are compared in Figure 6. It will be seen that the agreement is good for the 10% nitrogen system, but poor for the 30% nitrogen system. However, the latter system is close to the mixture critical temperature where P-V-T data are hard to obtain accurately, and as discussed below in connection with the data of Sage and Lacey, difficult to differentiate graphically. The 30% nitrogen data of the Institute of Gas Technology are suspect on the grounds that they show a crossover with the ideal mixing enthalpy. This is not shown at 10%, or by the experimental data of National Distillers at 46.65% nitrogen.

In Figure 7 total enthalpies are presented for the liquid methane-butane system. The enthalpies calculated are

compared with the data of Sage and Lacey (24), which were derived from P-V-T measurements, and with data calculated by the Benedict-Webb-Rubin equation of state (27). The agreement with the latter is seen to be excellent. The correlation of Canjar and Peterka (10) was found to be the best of the correlations investigated (7 to 10) and their results are included in Figure 8 by way of comparison. The order of magnitude of error inherent in graphical differentiation may be seen in Figure 8 by comparing Sage and Lacey's data for the methane-butane system with the data computed by machine using the Benedict-Webb-Rubin equation of state. Sage and Lacey derived their data by graphical differentiation of experimental P-V-T data. The computer does substantially the same calculation, but eliminates the human factor. Therefore, making the two assumptions that Sage and Lacey did work as accurate as humanly possible, and that the Benedict-Webb-Rubin equation of state represents P-V-T data for the system within the tolerance of experimental error, the difference between the two sets of data represents the order of magnitude of error inherent in graphical differentiation.

It must be clearly understood that the above does not imply that experimental data are wrong. The experimental P-V-T data are assumed to be absolutely correct. It is suggested that graphical differentiation of P-V-T data to obtain very accurate enthalpy data is impossible, and that machine-computed values will be more accurate. Accordingly, the agreement between the values calculated by the method of this paper for the methane-butane system, and the values computed with the Benedict-Webb-Rubin equation of state, is held to be a test of the usefulness of the method.

In Table 2 the experimental data of Nelson and Holcomb (25) for the ternary system propane–butane–pentane are compared with the values calculated by this paper, along with the values given by the correlation of Holcomb and Brown (7), which for this system was found to be the best correlation. Only data for the saturated liquid were compared. It will be seen that the two methods give equally good results, however, whereas the correlation of Holcomb and Brown considers the effect of pressure on liquid enthalpy, this paper does not.

CALCULATION PROCEDURE

For nonpolar binary systems, the following steps are employed in calculating total enthalpy:

1. Calculate enthalpy departure from the ideal gas state at infinite dilution for component a in component b and for component b in component a. Where the less
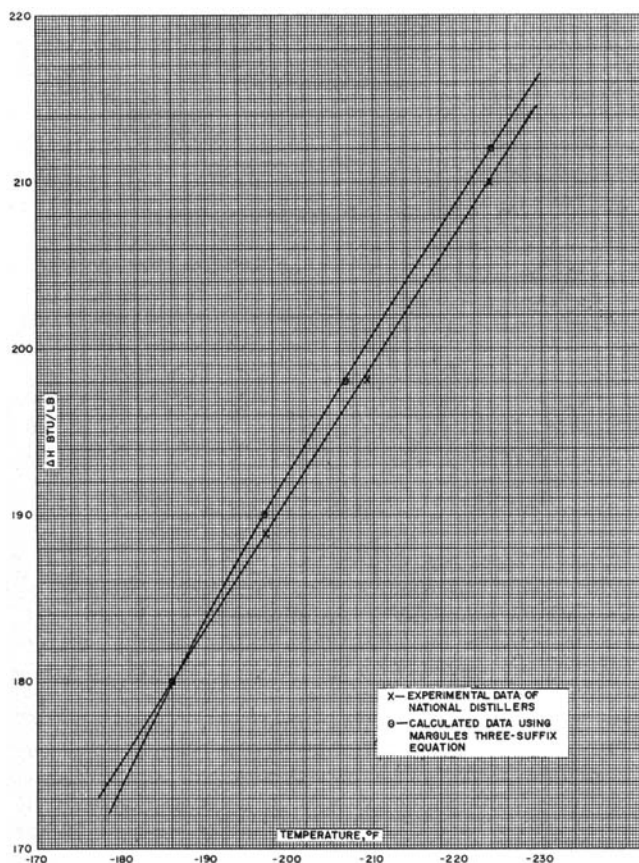
Fig. 5. Gas enthalpy at 25°C. and dew point pressure minus liquid enthalpy for nitrogen-methane system.
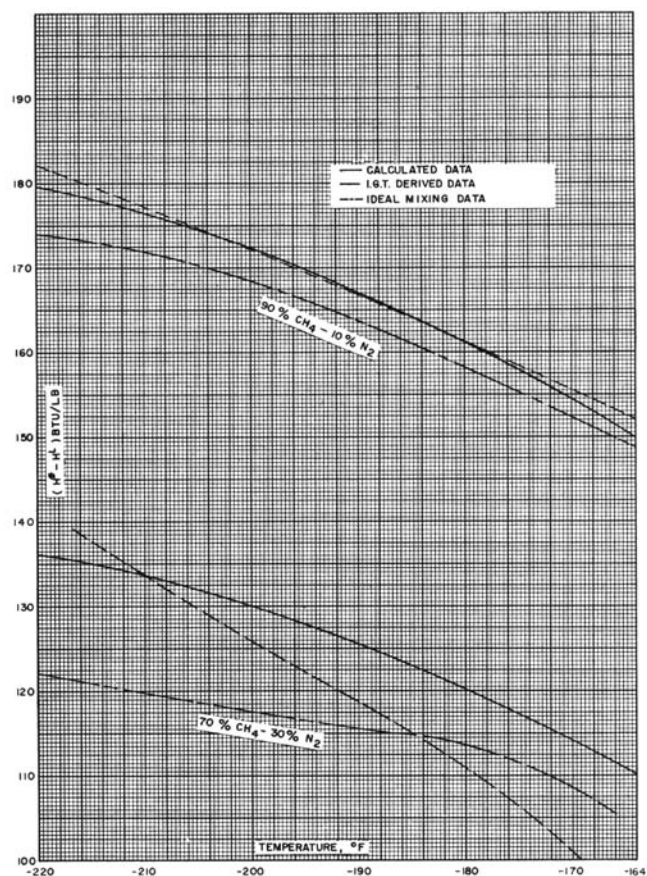

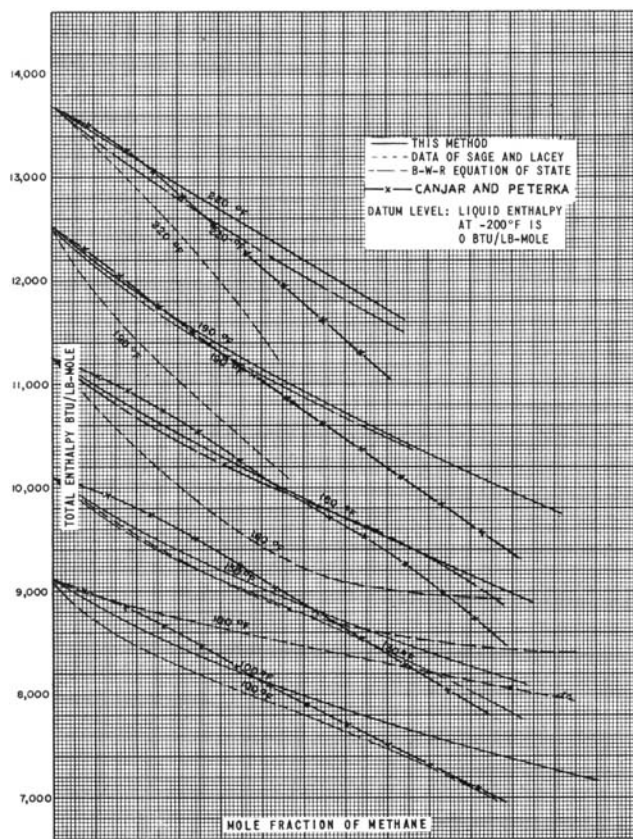Fig. 6. Ideal gas enthalpy minus liquid enthalpy for methane-nitrogen mixtures.

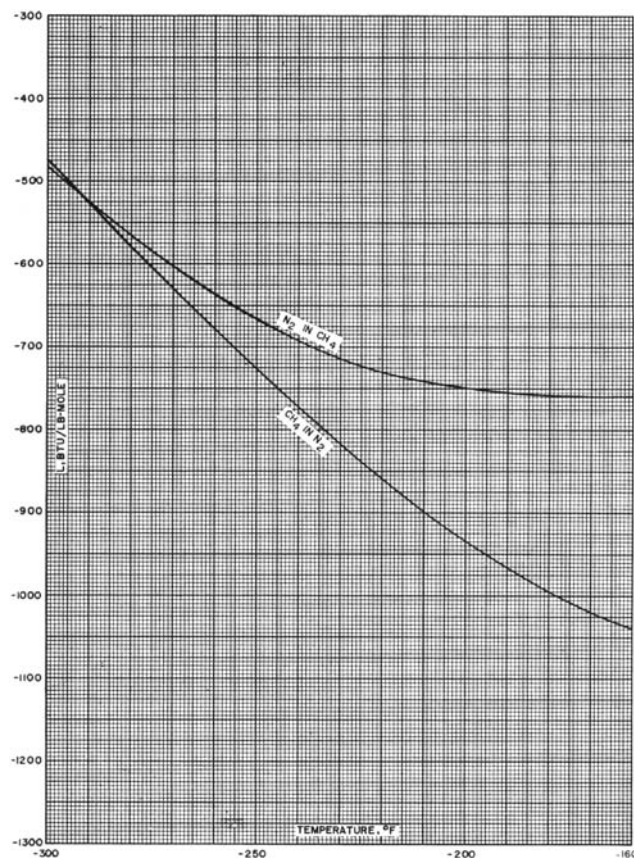Fig. 7. Total enthalpy of methane-butane mixture.

Fig. 8. Heat of solution at infinite dilution for the nitrogen-methane system.

TABLE 2. SATURATED LIQUID MIXTURE ENTHALPIES FOR PROPANE-BUTANE-PENTANE MIXTURES
Datum level: Pure liquid at 80°F. = 0 B.t.u./lb.

Mixture component	A mole %	B mole %	C mole %
C_3H_8	20.1	20.1	19.8
$n\text{-}C_4H_{10}$	39.9	29.8	10.6
$n\text{-}C_5H_{12}$	40.0	50.1	69.6

Temperature, °F.	A Exp.	A H & B	A Osborne	B Exp.	B H & B	B Osborne	C Exp.	C H & B	C Osborne
240	101	102	103						
260				120	114	115			
280	135	133	129	134	132	130	134	131	129
300	146	149	146	147	147	145	146	145	141
320	165	163	164	165	162	162	161	160	160
340							185	198	179

volatile component is the solute, the enthalpy departure is given by Equation (2).

$$(H^* - H^\infty)_{bT_{rb}} = (H^* - H^o)_{bT_{ra}} \qquad (2)$$

For the more volatile component as the solute, the enthalpy departure from the ideal gas state at infinite dilution is given by

$$(H^* - H^\infty)_a = T_{ca}/T_{cb} (H^* - H_A)_b \qquad (12)$$

The acceptance enthalpy H_A is calculated by Equation (9) if the solute reduced temperature is more than 0.5 greater than the solvent-reduced temperature, and by Equation (10a) if the solute-reduced temperature is less than 0.5 greater than the solvent-reduced temperature.

2. Calculate the heat of solution at infinite dilution according to Equation (13).

$$L = (H^* - H^\infty) = (H^* - H^\infty) - (H^* - H^o) \qquad (13)$$

3. Calculate the heat of mixing with Equation (20).

$$H^E = x_i x_j (x_i L_j + x_i L_j) \qquad (20)$$

If individual partial heats of mixing are required, these may be calculated with Equation (18).

$$(H^o - H_L)_i = x_j^2 [L_i + 2x_i (L_j - L_i)] \qquad (18)$$

4. Equation (23) is used to predict the total molal enthalpy of the mixture

$$H^M = \Sigma x_i H^o_i + H^E \qquad (23)$$

CONCLUSION

A general method has been presented which allows the calculation of total enthalpies of liquid nonpolar mixtures with good engineering accuracy. An attempt is being made to gain a clearer understanding of the relationship between vapor pressure and enthalpy fluctuations, in order to improve on the "rules of thumb" set forth in this paper for calculating enthalpies. The application of this work to polar systems and to other liquid excess thermodynamic functions also promises rewarding results.

The correlations of Holcomb and Brown (7) and Canjar and Peterka (10) are probably as accurate as the method of this paper, and certainly are simpler to use. However, they are limited to a narrow range of components and conditions.

NOTATION

A_{ij} = activity coefficient at infinite dilution of component i in component j
Cp = specific heat at constant pressure

H = enthalpy
$\bar{H}$ = mean enthalpy fluctuation
H^* = ideal gas enthalpy
H^o = pure component liquid enthalpy
H_A = acceptance enthalpy
H^E = heat of mixing
H^L = liquid enthalpy
H^M = liquid enthalpy of a mixture
H^{os} = pseudo liquid enthalpy
H = liquid enthalpy at infinite dilution
K = constant
k = Boltzmann's constant
L = heat of solution at infinite dilution
P = pressure
P' = vapor pressure
$\bar{P'}$ = mean fluctuation of vapor pressure
P_A = acceptance pressure
R = gas constant
T = temperature
Tc = critical temperature
T' = temperature at which solvent vapor pressure equals solute vapor pressure at temperature T
V = liquid molal volume
X = liquid mole fraction
Zc = critical compressibility
Z_N = partition function
γ = liquid activity coefficient
$\phi(r)$ = intermolecular potential
σ, ϵ = force constants

Subscripts

a = more volatile component
b = less volatile component
ba = less volatile component solute in more volatile component solvent
T = constant temperature
P = constant pressure
Tr = constant reduced temperature
Zc = constant critical compressibility

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Performance of Fouled Catalyst Pellets

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Equations are developed for the bulk rate of a gaseous reaction on a porous catalyst whose activity changes with time due to a decrease in active surface. The performance is evaluated in terms of a pellet effectiveness factor which is a function of time and a Thiele (diffusion-reaction) modulus. By a stepwise numerical technique, the equations can be solved without resort to assumptions regarding the distribution of fouled surface within the pellet. The method is applicable at isothermal conditions for any form of the rate equations for the main and fouling reactions and for any diffusivity-concentration relationship.

To illustrate the method, results are given for first-order isothermal reactions for three types of fouling processes. For a series form of self-fouling, a catalyst with the lowest intraparticle diffusion resistance gives the maximum activity for any process time. In contrast, for parallel self-fouling a catalyst with an intermediate diffusion resistance is less easily deactivated and can give a higher conversion to desirable product, particularly at long process times.

A simpler solution is possible by supposing that the shell model represents the disposition of fouling material in the pellet. It is shown that for parallel self-fouling and independent fouling this model gives reasonably good results, even when the reaction resistance for the main reaction is important. However, the shell concept does not appear suitable over a range of conditions when the fouling is of the series type.

The single-pellet effectiveness factors can be used to determine the effect of fouling on the conversion in a fixed-bed reactor. To illustrate the method of approach curves of conversion as a function of time and position in the bed are presented for a parallel, self-fouling reaction system. The results show the influence of intraparticle diffusion on the overall effects of fouling.

A. SINGLE PELLETS

In many gas-solid catalytic reactions the activity of the catalyst decreases with time on stream. Such poisoning can often be traced to deposition on the catalyst of a substance which reduces the active surface for the main reaction. Quantitative study of the activity-time relation is important in seeking the optimum design and opera-

tion (reaction-regeneration cycle) of the reactor. The first step in treating the problem is an analysis of the behavior of a single catalyst pellet.

The poisoning may be due to a side reaction involving the same reactants as the main reaction (a parallel fouling process). Alternately, the deposited material may be the result of further reaction of the primary product (a series fouling process). Still another possibility is deactivation