of state have been presented in terms of critical temperature and critical pressure. Later investigations indicate that a third parameter is required. The early attempts use the critical compressibility as the third parameter. The more recent attempts use properties associated with the vapor pressure curve as third parameter; among these may be mentioned Riedel's modulus α, Martin and Hou's slope M, and Pitzer's acentric factor ω. The authors have extended the reduced parameter from critical temperature and critical pressure to include vapor pressure and latent heat. It has been shown through the analysis that the vapor pressure and latent heat are readily related to the various terms of the equation.

Normally the constants for the equation are fitted from PVT data. This equation is fitted on PTH data. Enthalpy is of course related to the slope of the PVT surface through the enthalpy expression. If one is fortunate enough to start with a reduced equation of reasonably good form, then the process of determining the constants can be vastly simplified. The data on vapor pressure and latent heat are generally available. In contrast, accurate PVT data with the necessary range are scarce and great effort and skill are needed for its determination. This study tries to present an equation of simple form fitted only with the most important parameters in terms of corresponding state principle, and to see if this is adequate for general engineering applications.

NOTATION

A = Helmholtz free energy
e^0 = molal internal energy for pure gas at temperature T and reference pressure
H = enthalpy
L = latent heat
m = constant, dimensionless
n = constant, dimensionless
N = number of moles
P = pressure, atm.
P^0 = vapor pressure, atm.
P^* = characteristic pressure, cal./cc. or atm. (P^*, cal./cc.) 82.0567/1.98719 = (P^*, atm.)
$\tilde{P}$ = reduced pressure, dimensionless = P/P^*
R = universal gas constant, 1.98719 cal./g.-mole, or (82.0567 cc.) (atm.)/g.-mole
S = entropy
s^0 = molal entropy for pure gas at temperature T and reference pressure
T = temperature, °K.
T^* = characteristic temperature, °K.
$\tilde{T}$ = reduced temperature, dimensionless = T/T^*
V = volume, cc.
V^* = characteristic volume, cc./g.-mole
$\tilde{V}$ = reduced volume, dimensionless = V/NV^*
x = $\tilde{V}^{1-m}$
Z = compressibility factor = PV/RT

Subscripts

b = boiling point
c = critical point
g = saturated vapor phase
1 = saturated liquid phase
2 = second reference temperature

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II. Mixtures

A four-parameter reduced equation of state was extended to interpret multicomponent phase equilibrium behavior. The equation with the exponential combination rule succeeded in correlating the nitrogen-methane system but failed in propylene-propane system. The combination rule seems to be a function of the nature of the system. It is felt that binary interacting constants are needed to interpret the mixture behavior.

The following equation of state for the phase equilibrium was described in an earlier paper (*1*) as it applied to pure methane.

$$\tilde{P} = \frac{\tilde{T}}{\tilde{V} - \tilde{V}^m} - \frac{1}{\tilde{V}^n} \qquad (1)$$

where

$$\tilde{P} = \frac{P}{P^*}$$

$$\tilde{V} = \frac{V}{NV^*}$$

$$\tilde{T} = \frac{T}{T^*}$$

In the equation $\tilde{P}$, $\tilde{V}$, and $\tilde{T}$ are dimensionless groups and P^*, V^*, and T^* are dimensioned constants. In addition to these constants, there are two exponential parameters m and n which are related to the vapor pressure and the latent heat. With these two additional parameters, the equation is made flexible for fitting various substances which exhibit different vapor pressure behaviors on the reduced scale. The equation was fitted from the vapor pressure and the latent heat data only. The volumetric data were not used in the fitting but were used to test the equation. The saturated vapor volumes are found to check very well; the saturated liquid volumes are in reasonable good agreement in the low temperature region, but are somewhat off at temperature near the critical. On the basis of this promising pure substance correlation, the equation is further explored for mixture behavior.

THE THERMODYNAMIC FUNCTIONS FOR THE MODIFIED FLORY EQUATION

It is assumed that the same equation applies to the mixture behavior. The parameters (P^*, V^*, T^*, m, and n) become functions of composition and may be computed from the pure component parameters and the mixture composition through empirical averaging rules. Although there are five parameters, only four of these are independent. To satisfy the perfect gas law at low pressure, the following relationship holds among the parameters:

$$P^* V^* = RT^* \tag{2}$$

Which one of the parameters is chosen as dependent variable and the others as independent variables is a matter of data fitting. In this case, T^* of the mixture is chosen as dependent variable and is calculated from whatever values of P^* and V^* for the mixture. Since this rule worked for nitrogen-methane, the other possibilities were not examined.

For the mixture, the pressure equation for (ΣN_i) number of moles becomes

$$P = \frac{(\Sigma N_i)\, RT}{V\left[1 - \left(\frac{1}{\tilde{V}}\right)^{1-m}\right]} - \frac{(\Sigma N_i)\, P^*\, V^*}{V\, \tilde{V}^{n-1}} \tag{3}$$

The Helmholtz function A, the enthalpy H, and the entropy S for the mixture are derived according to Beattie's method, with the following results:

$$A = \frac{(\Sigma N_i)\, RT}{(1-m)} \ln \frac{\tilde{V}^{1-m}}{\tilde{V}^{1-m} - 1} - \frac{(\Sigma N_i)\, P^*\, V^*}{(n-1)\, \tilde{V}^{n-1}}$$
$$- \Sigma N_i\, RT \ln \frac{V}{N_i\, RT} + \Sigma\, [N_i\, (e_i{}^\circ - Ts_i{}^\circ)] \tag{4}$$

$$H = \frac{(\Sigma N_i)\, RT\, \tilde{V}^{1-m}}{(\tilde{V}^{1-m} - 1)} - \frac{(\Sigma N_i)\, n}{(n-1)} \frac{P^*\, V^*}{\tilde{V}^{n-1}} + \Sigma N_i\, e_i{}^\circ \tag{5}$$

$$S = \frac{(\Sigma N_i)\, R}{(1-m)} \ln \left[1 - \left(\frac{1}{\tilde{V}}\right)^{1-m}\right] + \Sigma \left[N_i\, R \ln \frac{V}{N_i\, RT}\right]$$
$$+ \Sigma\, (N_i\, s_i{}^\circ) \tag{6}$$

The following check of the above expressions is found to be true:

$$H - TS = A + PV \tag{7}$$

For the individual components, the chemical potential μ_i, the partial enthalpy H_i, the partial entropy S_i, the partial volume V_i, and the other partial quantities are expressed as follows:

$$\mu_i = \frac{RT}{(1-m)} \ln \left(\frac{\tilde{V}^{1-m}}{\tilde{V}^{1-m} - 1}\right) \left[1 + \frac{\Sigma N_i}{(1-m)} \frac{\partial m}{\partial N_i}\right]$$
$$+ \frac{RT}{(\tilde{V}^{1-m} - 1)} \left[1 + \frac{\Sigma N_i}{V^*} \frac{\partial V^*}{\partial N_i} + \ln \tilde{V} \cdot \frac{\Sigma N_i}{(1-m)} \frac{\partial m}{\partial N_i}\right]$$
$$- \frac{nP^*\, V^*}{(n-1)\, \tilde{V}^{n-1}} \left[\begin{array}{l} 1 + \dfrac{\Sigma N_i}{V^*} \dfrac{\partial V^*}{\partial N_i} + \dfrac{\Sigma N_i}{nP^*} \dfrac{\partial P^*}{\partial N_i} \\ - \left(\dfrac{1}{n-1} + \ln \tilde{V}\right) \dfrac{\Sigma N_i}{n} \dfrac{\partial n}{\partial N_i} \end{array}\right]$$
$$- RT \ln \frac{V}{(\Sigma N_i)\, x_i\, RT} + RT + e_i{}^\circ - T\, s_i{}^\circ \tag{8}$$

$$H_i \equiv \left.\frac{\partial H}{\partial N_i}\right|_{T,P,Nj} = \left.\frac{\partial H}{\partial V}\right|_{T,N_i,Nj} \frac{-\left.\dfrac{\partial P}{\partial N_i}\right|_{T,V,Nj}}{\left.\dfrac{\partial P}{\partial V}\right|_{T,N_i,Nj}} + \left.\frac{\partial H}{\partial N_i}\right|_{T,V,Nj} \tag{9}$$

$$S_i \equiv \left.\frac{\partial S}{\partial N_i}\right|_{T,P,Nj} = \left.\frac{\partial S}{\partial V}\right|_{T,N_i,Nj} \frac{-\left.\dfrac{\partial P}{\partial N_i}\right|_{T,V,Nj}}{\left.\dfrac{\partial P}{\partial V}\right|_{T,N_i,Nj}} + \left.\frac{\partial S}{\partial N_i}\right|_{T,V,Nj} \tag{10}$$

$$V_i \equiv \left.\frac{\partial V}{\partial N_i}\right|_{T,P,Nj} = \frac{-\left.\dfrac{\partial P}{\partial N_i}\right|_{T,V,Nj}}{\left.\dfrac{\partial P}{\partial V}\right|_{T,N_i,Nj}} \tag{11}$$

and

$$\left.\frac{\partial H}{\partial V}\right|_{T,N_i,Nj} = \frac{-\,(1-m)\, RT\, \tilde{V}^{1-m}\, (\Sigma N_i)}{(\tilde{V}^{1-m} - 1)^2\, V} + \frac{nP^*\, V^*}{\tilde{V}^{n-1}} \frac{(\Sigma N_i)}{V} \tag{12}$$

$$\left.\frac{\partial H}{\partial N_i}\right|_{T,V,Nj} = \frac{RT\, \tilde{V}^{1-m}}{\tilde{V}^{1-m} - 1} + \frac{(1-m) RT\, \tilde{V}^{1-m}}{(\tilde{V}^{1-m} - 1)^2}$$
$$\cdot \left[1 + \frac{(\Sigma N_i)}{V^*} \frac{\partial V^*}{\partial N_i} + \frac{\ln \tilde{V}\, (\Sigma N_i)}{(1-m)} \frac{\partial m}{\partial N_i}\right]$$
$$- \frac{n^2\, P^*\, V^*}{(n-1)\, \tilde{V}^{n-1}} \left[1 + \frac{(\Sigma N_i)}{V^*} \frac{\partial V^*}{\partial N_i} + \frac{(\Sigma N_i)}{nP^*} \frac{\partial P^*}{\partial N_i}\right.$$
$$\left. - \left(\frac{1}{n\,(n-1)} + \ln \tilde{V}\right) \frac{(\Sigma N_i)}{n} \frac{\partial n}{\partial N_i}\right] + e_i{}^\circ \tag{13}$$

$$\left.\frac{\partial P}{\partial V}\right|_{T,N_i,N_j} = \frac{-(\Sigma N_i)}{V}\frac{RT}{V}\frac{\tilde{V}^{1-m}}{(\tilde{V}^{1-m}-1)}$$

$$-\frac{(\Sigma N_i)}{V}\frac{RT}{V}\frac{(1-m)\tilde{V}^{1-m}}{(\tilde{V}^{1-m}-1)^2}+\frac{n}{\tilde{V}}\frac{P^* V^*}{V^{n-1}}\frac{(\Sigma N_i)}{V} \qquad (14)$$

$$\left.\frac{\partial P}{\partial N_i}\right|_{T,V,N_j} = \frac{RT\tilde{V}^{1-m}}{V(\tilde{V}^{1-m}-1)}+\frac{RT(1-m)\tilde{V}^{1-m}}{V(\tilde{V}^{1-m}-1)^2}$$

$$\cdot\left[1+\frac{(\Sigma N_i)}{V^*}\frac{\partial V^*}{\partial N_i}+\ln\tilde{V}\frac{(\Sigma N_i)}{(1-m)}\frac{\partial m}{\partial N_i}\right]-\frac{n P^* V^*}{\tilde{V}V^{n-1}}$$

$$\cdot\left[1+\frac{(\Sigma N_i)}{V^*}\frac{\partial V^*}{\partial N_i}-\ln\tilde{V}\frac{(\Sigma N_i)}{n}\frac{\partial n}{\partial N_i}\right.$$

$$\left.+\frac{(\Sigma N_i)}{nP^*}\frac{\partial P^*}{\partial N_i}\right] \qquad (15)$$

$$\left.\frac{\partial S}{\partial V}\right|_{T,N_i,N_j} = \frac{(\Sigma N_i)}{V}\frac{R\tilde{V}^{1-m}}{(\tilde{V}^{1-m}-1)} \qquad (16)$$

$$\left.\frac{\partial S}{\partial N_i}\right|_{T,V,N_j} = \frac{-R}{(1-m)}\left(\ln\frac{\tilde{V}^{1-m}}{\tilde{V}^{1-m}-1}\right)$$

$$\cdot\left[1+\frac{(\Sigma N_i)}{(1-m)}\frac{\partial m}{\partial N_i}\right]-\frac{R}{(\tilde{V}^{1-m}-1)}$$

$$\cdot\left[1+\frac{(\Sigma N_i)}{V^*}\frac{\partial V^*}{\partial N_i}+\ln\tilde{V}\frac{(\Sigma N_i)}{(1-m)}\frac{\partial m}{\partial N_i}\right]$$

$$-R+R\ln\frac{V}{(\Sigma N_i)\,xi\,RT}+s_i^\circ \qquad (17)$$

The correct derivation of the partial quantities shown above is confirmed by the internal numerical check of the relationship

$$\mu_i = H_i - TS_i \qquad (18)$$

THE COMBINATION RULES FOR THE MIXTURE PARAMETERS

The evaluation of the partial derivatives of the mixture parameters with respect to the number of moles i, ($\partial P^*/\partial N_i$, $\partial V^*/\partial N_i$, $\partial m/\partial N_i$, $\partial n/\partial N_i$), is of course dependent on the combination rules adopted for the mixture parameters. Combination rules have one thermodynamic restriction. Consider the equation

$$A + PV = \Sigma N_i \mu_i \qquad (19)$$

The left-hand side contains no derivatives with respect to mole quantities. All such derivatives which appear on the right-hand side must sum to zero. Thus

$$\Sigma N_i\frac{\partial P^*}{\partial N_i}=0;\ \Sigma N_i\frac{\partial V^*}{\partial N_i}=0;\ \Sigma N_i\frac{\partial m}{\partial N_i}=0;$$

$$\Sigma N_i\frac{\partial n}{\partial N_i}=0. \qquad (20)$$

The exponential combination rule is most widely used. It is expressed as

$$V^*_m = (\Sigma x_i V_i^{*1/k})^k = \left[\frac{\Sigma(N_i V_i^{*1/k})}{(\Sigma N_i)}\right]^k \qquad (21)$$

where V^*_m is V^* of the mixture (and should not be confused with the exponential parameters m). On differentiation this rule gives

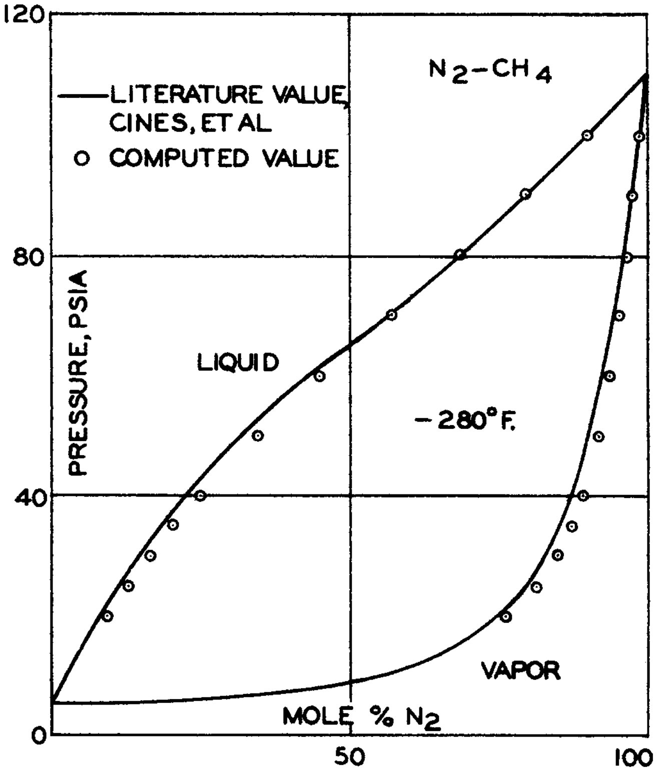

Fig. 1. Phase equilibrium of nitrogen-methane system.

$$\frac{\partial V^*_m}{\partial N_i}=\frac{kV^*_m}{\Sigma N_i}\left[\left(\frac{V^*_i}{V^*_m}\right)^{1/k}-1\right] \qquad (22)$$

The thermodynamic restriction is satisfied thusly

$$\Sigma N_i\frac{\partial V^*_m}{\partial N_i}=kV^*_m\left[\frac{\Sigma x_i V^{*}_i{}^{1/k}}{V^*_m{}^{1/k}}-\Sigma x_i\right]=0$$

The linear combination rule is a special case of the exponential combination rule where k is equal to one. Throughout this paper the mixture parameters P^*, V^*, m, and n are treated as independent variables, and the value of k used in forming the mixture parameters from its constituent parameters will be referred to as the combination rule for the specific parameters. For instance, a combination rule of 6-6-1/3-1 means that the value of k used to form the mixture parameters P^*, V^*, m, and n are, respectively, 6, 6, 1/3, and 1.

The choice of the combination rule is strictly empirical. Very little is known from theoretical consideration; the form of the equation itself is empirical to begin with. The basic assumption is that the interacting constant between the two different molecular species is some function of the pure component constants. This assumption is implicit in all the equation of state approach to the mixture behavior. For instance, in the B-W-R equation, the linear combination rule is used for the constant Bo; the square root combination rule ($k = 2$) is used for constants Ao, Co, and γ; and the cubic root combination rule ($k = 3$) is used for constants a, b, c, and α. The only criterion is to fit the data.

Based on some preliminary work on the phase equilibrium of the nitrogen-methane system, a combination rule of 3-3-1-1 is adopted for the system. Further work on a five-component mixture of nitrogen and light hydrocarbons indicates that a different combination rule of 0.5-0.5-1-1 seems to fit the cooling curve data the best. That the combination rule may be dependent on the nature of the system is not exactly a welcomed development. This development might have been foretold by the work of Stotler and Benedict (2) in their effort to fit the nitrogen-methane equilibrium data with the B-W-R equation of state. They found that the original square root averaging rule for the interaction constant $A_{0_{12}}$ could be revised with improved results. Another example of beneficial revision of the B-W-R combining rule has been reported for systems containing hydrogen (3). For the system propylene-propane, the best combination rule for the present proposed equation is 6-6-1/3-1. However the resultant vapor-liquid phase diagram for the system is still somewhat short of satisfactory. The computed K value, the phase diagram, and the cooling curve are definitely a function of the mixture rule adopted. There may be other combination rules to give a better result yet; what we have tried are only the most obvious ones.

THE COMPUTER PROGRAM

A computer program based on the proposed equation has been written for the computation of the thermodynamic properties of a pure component or a mixture. The program provides the computation of the volume, the enthalpy, the entropy, the fugacity, the chemical potential, the vapor pressure, the boiling point, the dew point, the bubble point, the K value, the vapor-liquid phase separation, and a complete cooling curve from the superheated vapor region, to the two-phase region and the subcooled liquid region. For steps involving vapor-liquid equilibrium, the computation is done through the matching of the fugacities (or the chemical potentials) of the individual components between the two phases.

The program is written in a way that the combination rule (k) for the mixture parameters is treated as a part of the input data, so that it is a relatively easy matter to try out various combination rules.

Subroutines for the determination of a set of constants from the pure component properties of the critical temperature, pressure, boiling point, vapor pressure, and latent heat data are also written. An alternative procedure of determining the constants from two boiling temperatures is also provided. The constants for nitrogen and methane were determined originally; it has since been extended to other hydrocarbons and cryogenic fluids. The constants are presented in the first paper (1).

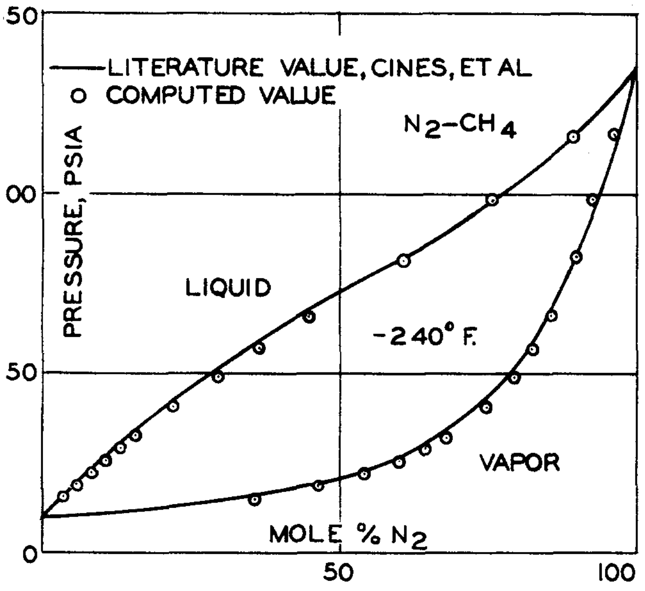

Fig. 2. Phase equilibrium of nitrogen-methane system.

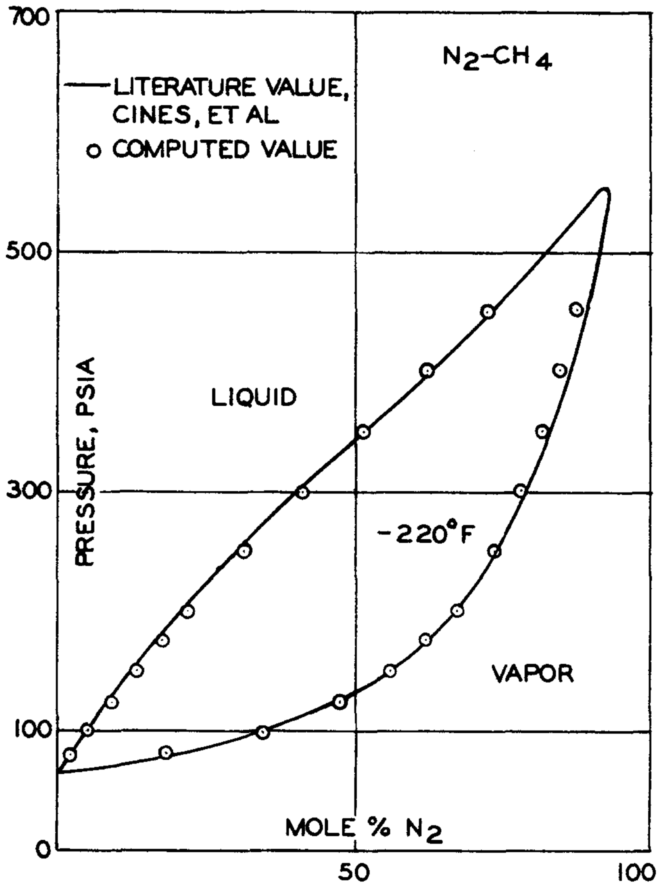

Fig. 3. Phase equilibrium of nitrogen-methane system.

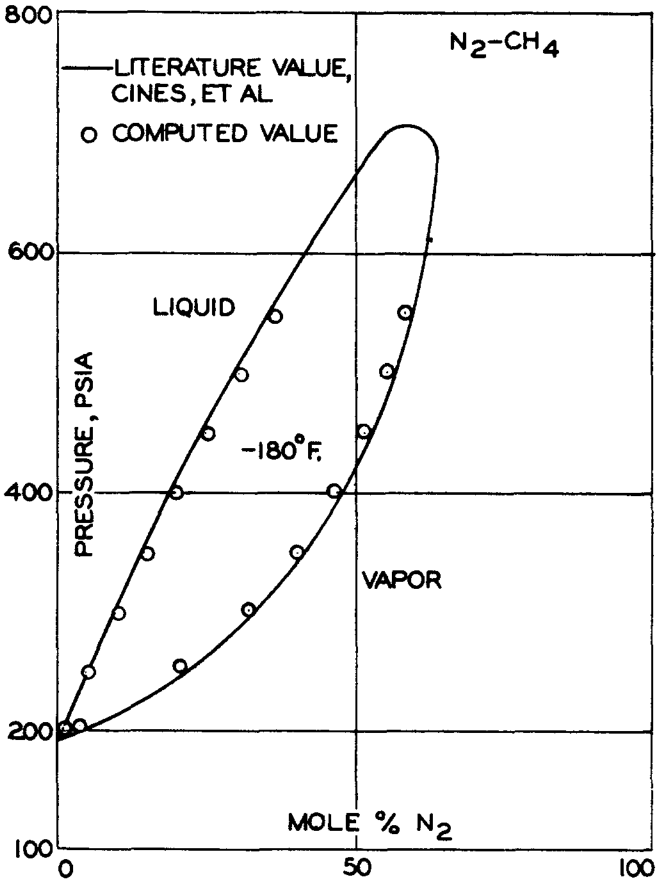

Fig. 4. Phase equilibrium of nitrogen-methane system.

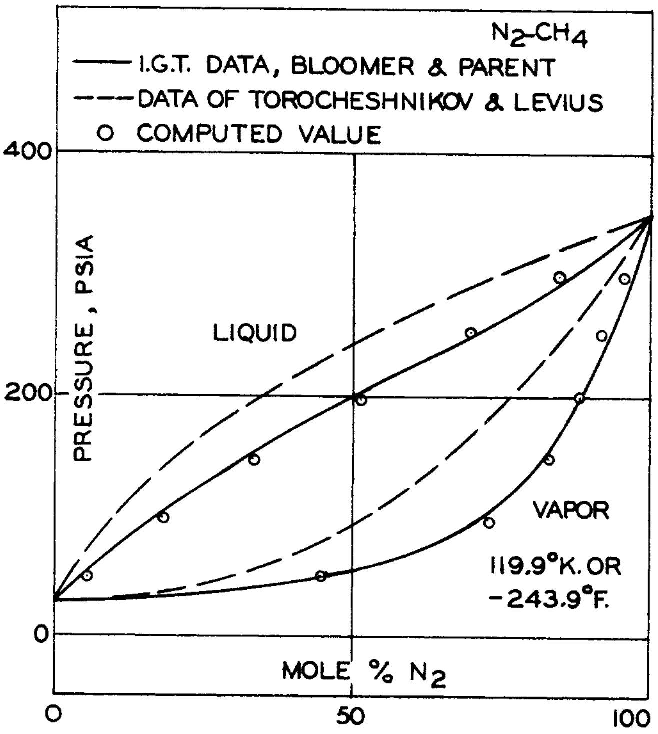

Fig. 5. Phase equilibrium of nitrogen-methane system.

THE COMPUTATION RESULT

A. Nitrogen-Methane System

For the nitrogen-methane system, the combination rule adopted for the mixture parameter is 3-3-1-1. The computations for the phase equilibrium were made at various temperatures of −280°, −260°, −240°, −232.8°, −220°, −200°, −180°, −150°, and −243.9°F. (or 119.9°K.). Part of the results are presented in Figures 1 to 5 and compared with the experimental data of Cines et al. (*4*), the IGT data of Bloomer and Parent (*5*), and the data of Torocheshnikov and Levius. As can be seen from the plots, the check with the experimental data of Cines et al. is very good. Even more interesting is Figure 5. There are two different sets of phase equilibrium data at 119.9°K. or −243.9°F.: one set by Bloomer and Parent of IGT and the other set by Torochesknikov and Levius. There has been some doubt on the accuracy of the latter set of data. Our computation also showed that the IGT data by Bloomer and Parent is consistent with that of Cines et al. and thereby confirmed its reliability.

In the same symposium where Cines et al. and Bloomer and Parent presented their experimental data, Stotler and Benedict (*2*) presented the correlation of the nitrogen-methane system by the B-W-R equation of state. They found that the original combination rules were not very satisfactory (resulting in K value for methane 5% too high, and K value for nitrogen 15% too low, or 20% off in terms of relative volatility). For better fit, the mixture combination rule for the constant A_0 was changed slightly. Stotler and Benedict further reduced the K value computation from the equation of state approach to a set of ideal K value charts and a liquid phase activity coefficient correlation, from whence the vapor liquid equilibrium compositions of the nitrogen-methane system were computed and compared with the data of Cines et al. By visual examination of their phase diagrams (their Figures 4 to 11) it can be said that there is about the same order of scatter between the computed and the experimental values either by the B-W-R equation or by the proposed equation.

A cooling curve of a nitrogen-methane mixture at 300 lb./sq.in.abs. was computed from ambient temperature down to 130°K. Figure 6 shows this computed curve and also the experimental enthalpy values reported in *IGT Research Bulletin 21* (*6*). The check is reasonably good. The deviation is approximately 100 B.t.u./lb.-mole, which is about the same as other methods reported by Edmister, Persyn, and Erbar (average deviation 5.3 B.t.u./lb.) (*7*).

B. Propylene-Propane System

The computation of the phase equilibrium was extended to the propylene-propane system (*9* to *11*) at 277.6°K. or 40°F. The result is plotted in Figure 7. The experimental P-y-x data were plotted as the solid lines, and the corresponding computed values of y-x at the same pressure P were plotted as the dashed lines. Various combination rules were tried. The best of these corresponds to rule 6-6-1/3-1. The fit is not satisfactory and one may assume that the exponential mixing rule does not apply to all mixtures. Figure 7 also shows the shift of the saturated liquid line and the saturated vapor line on the P-y-x plot with different combination rules.

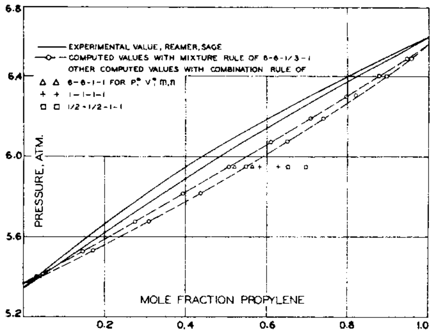

Fig. 6. Enthalpy of nitrogen-methane binary at 300 lb./sq.in.abs.

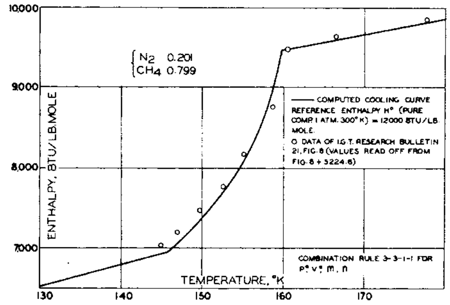

Fig. 7. Propylene-propane at 277.6°K. (40°F.).

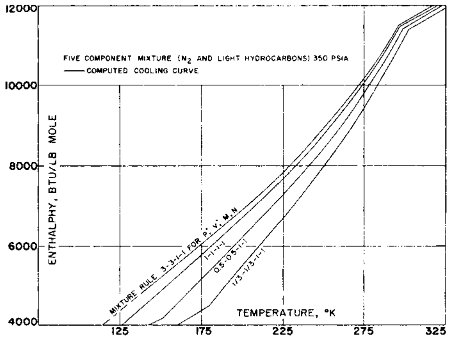

Fig. 8. Influence of combination rule on cooling curve.

C. Multicomponent System

The influence of the combination rules on the computed K ratio is also reflected in the enthalpy computations. Figure 8 shows the computed enthalpy curves (or the cooling curves) of a mixture of nitrogen and light hydrocarbons with a constant overall composition. On cooling from 320°K. to approximately 300°K. the cooling curve exhibits the first break which is the dew point. Then the mixture enters the two-phase region with a more pronounced enthalpy change due to the latent heat of condensation. On further cooling, the cooling curve shows the second break which is the bubble point of the mixture. Of course, the dew point and the bubble point on a cooling curve would correspond to the saturated vapor line and the saturated liquid line on a P-y-x plot or a T-y-x plot. Figure 8 shows that the bubble point (and therefore the saturated liquid line) can change drastically as the combination rule changes. For this particular mixture, it so happens that a combination rule of 0.5-0.5-1-1 seems to give the best check with some experimental data. So here again, a different combination rule is required for a different mixture.

DISCUSSION

The first set of exponential mixing rules assumed for nitrogen-methane worked very well. This lead to the hope that the same set of mixture rules might work for other mixtures. However, we have found that the set of mixture rules and its variation do not work well for the propylene-propane system. This could be due to the empirical nature of the equation or the inadequacy of the exponential combination rule. Rowlinson, in a review article (8) on the theories of mixtures, suggests that the building block used in discussing multicomponent systems are the binary systems and not the pure systems. This suggests that binary interacting constants are needed to interpret the mixture behavior.

An interesting feature of this work is the use of vapor pressure and latent heat data, in preference to volumetric data. This is feasible for an equation which is specialized to the two-phase region. We did this because we were more interested in correct partial pressures and enthalpies than in volumes. A great deal of equation of state work has been aimed toward correct volumes and accepting less accuracy in the pressures and enthalpies.

CONCLUSIONS

1. The equation with the exponential combination rule succeeded in correlating both the K value and the enthalpy value of the nitrogen-methane system, but failed in correlating the phase equilibrium of propylene-propane system.

2. The consistency between the computed vaporization K value and the enthalpy and entropy value is established The correct derivation of the various thermodynamic functions is substantiated by the internal numerical check of the relationship

$$\mu_i = H_i - TS_i$$

If the K value computation checks well with the experimental value, the enthalpy and the entropy values would also check.

3. The mixture rules for the parameters appear to be a function of the nature of the components, and not a set of universal rules applicable to all mixtures. For reliable results, the mixture rule for the system should be determined with the aid of a few experimental phase equilibrium data points.

4. It is believed that the proper use of the vapor pressure and the latent heat data can improve the constants for other equations of state when used in the two-phase region.

NOTATION

A = Helmholtz free energy
e° = molal internal energy for the pure gas at temperature T and reference pressure
H = enthalpy
H_i = partial molal enthalpy
k = exponential index for the combination rules of the mixture
m = equation of state constant for the mixture, dimensionless
n = equation of state constant for the mixture, dimensionless
N = number of moles
P = pressure, atm.
P^* = equation of state constant for the mixture, atm.
$\tilde{P}$ = reduced pressure, dimensionless = P/P^*
R = universal gas constant, 1.98719 cal./g.-mole or 82.0567 (cc.) (atm.)/g.-mole
S = entropy
S_i = partial molal entropy
s° = molal entropy for the pure gas at temperature T and reference pressure
T = temperature, °K.
T^* = equation of state constant for the mixture, °K.
$\tilde{T}$ = reduced temperature, dimensionless = T/T^*
V = volume, cc.
V_i = partial molal volume, cc./mole
V^* = equation of state constant for the mixture, cc./mole
$\tilde{V}$ = reduced volume, dimensionless = V/NV^*
x = mole fraction

Greek Letters

μ = chemical potential

Subscripts

i = component i
j = components other than i
m = mixture

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