Liquid Densities and Liquid Enthalpies of Hydrogen-Containing Hydrocarbon Mixtures

Hydrogen, a quantum gas, raises to unique problems in the estimation of liquid properties of mixtures containing dissolved hydrogen—a problem often encountered in hydroprocessing of hydrocarbons. The liquid density and enthalpy of a hydrogen-containing mixture in particular are not adequately described by the pseudocritical concept but are best calculated by summing the liquid partial molar quantities of hydrogen and that of hydrogen-free liquid solvent.

Liquid partial molar volumes and enthalpies of hydrogen have been evaluated and the results, including the effects of pressure and composition, presented in generalized equations. These generalized equations are shown to be useful in estimating the liquid density and enthalpy of hydrogen-containing mixtures.

P. L. CHUEH
and C. H. DEAL

Shell Development Company
Houston, Texas 77001

SCOPE

In hydroprocessing of hydrocarbons it is often necessary to estimate the liquid properties of mixtures containing dissolved hydrogen under extreme conditions of high temperatures and high pressures. In particular, liquid density and liquid enthalpy of hydrogen-containing mixtures required for rational process and reactor designs are not available, and they are not adequately described by the pseudocritical method conventionally applied to mixtures with success. Instead, they are best calculated by adding the liquid partial molar quantities of hydrogen to that of hydrogen-free solvent.

Liquid partial molar volumes and enthalpies of hydrogen are evaluated from equations of state and literature data using rigorous thermodynamic relations. The effects of temperature, pressure, solvent, and composition are considered, and the results presented in generalized equations to facilitate engineering applications.

CONCLUSION AND SIGNIFICANCE

It has been shown that the liquid densities of hydrocarbons containing dissolved hydrogen are not adequately described by the corresponding states theorem with conventional pseudocritical rules but are accurately calculated *by summing appropriate partial molar volumes of hydrogen* and hydrocarbons. The partial molar volume of hydrogen and its compressibility have been derived from equations of state and subsequently generalized for applications over a wide range of solvents, temperatures, and pressures.

A similar approach is suggested for calculating liquid enthalpies of hydrogen-containing mixtures. Heats of solution of hydrogen in hydrocarbons have been evaluated from solubility data reported in the literature and are generalized over a wide range of solvents and temperatures. The effect of pressure has been considered, utilizing the knowledge of partial molar volume and compressibility of hydrogen. The heat of solution of hydrogen in a given *solvent is shown to depend strongly on the temperature* and pressure of the system. A correlation of liquid enthalpies (relative to ideal gas) of saturated hydrocarbons has also been presented and a method of treating solvent mixtures discussed.

The methods and generalized equations presented in this paper offer a rational and reasonably reliable approach to the estimation of liquid densities and enthalpies of mixtures under hydroprocessing conditions.

Due to the low critical temperature and small mass, hydrogen, a quantum gas, gives rise to unique problems in the estimation of liquid properties of mixtures containing dissolved hydrogen—a problem often encountered in hydroprocessing of hydrocarbons. The liquid density and enthalpy of a hydrogen-containing mixtures in particular are not adequately described by the pseudocritical concept conventionally applied to mixtures with success. An alternate approach is to sum the liquid partial molar quantities of hydrogen and that of hydrogen-free liquid solvent

$$Q_M = x_1\overline{Q}_1 + x_2\overline{Q}_2$$

where Q_M is the molar quantity of the liquid mixture such as volume or enthalpy, $\overline{Q}_1$ is the partial molar quantity of the solvent (or solvent mixture), $\overline{Q}_2$ is the partial molar quantity of hydrogen in the solution, and x's are liquid mole fractions.

This paper describes how liquid partial molar volume and enthalpy of hydrogen may be calculated in various solvents over a wide range of temperature and pressure. *It presents methods for estimating liquid densities and* liquid enthalpies of hydrogen-containing mixtures which are thermodynamically sound and which appear to be quite accurate.

LIQUID DENSITIES OF HYDROGEN-CONTAINING MIXTURES

The molar volume of a liquid mixture containing hydrogen is given by

$$v_M = x_1\bar{v}_1 + x_2\bar{v}_2 \tag{1}$$

where v_M is the liquid molar volume of the mixture, $\bar{v}$ is the partial molar volume, all at system temperature and pressure, and x the mole fraction. Subscript 1 refers to solvent and subscript 2 refers to hydrogen. For a hydrogen concentration up to about 30%m, the effect of composition can be represented by (Connolly and Kandalic, 1963)

$$\bar{v}_1 = v_1 - cx_2^2 \tag{2}$$

$$\bar{v}_2 = \bar{v}_2^{\infty} + c(1 - x_1^2) \tag{3}$$

where v_1 is the liquid molar volume of pure solvent and $\bar{v}_2^{\infty}$ is the partial molar volume of hydrogen in the liquid phase at infinite dilution, all at system temperature and pressure. Substitution of Equations (2) and (3) into Equation (1) gives the working equation

$$v_M^{(P)} = x_1 v_1^{(P)} + x_2\bar{v}_2^{\infty(P)} + c^{(P)}x_2^2 \tag{4}$$

where the superscript (P) emphasizes the fact that the quantities are at the system pressure. Mixtures containing more than one solvent are discussed later.

In Equation (4), $\bar{v}_2^{\infty(P)}$, the hydrogen partial molar volume at infinite dilution and at total pressure P, is required. This quantity is first calculated at the saturation pressure of the solvent P_1^s and then corrected to system pressure P.

Hydrogen Partial Molar Volume at Infinite Dilution at Solvent Vapor Pressure

The technical literature contains few data on the partial molar volume of hydrogen in hydrocarbon solvents. Moreover, only those obtained from direct dilatometric or density measurements are reliable; those obtained from interpretation of high-pressure gas solubility data are generally of low accuracy and can be misleading. Since accurate $\bar{v}_2^{\infty(P_1^s)}$ are available only for hydrogen in benzene and *n*-octane (Connolly, 1962; Connolly and Kandalic, 1963; Hildebrand and Scott, 1964), we have used two equations of states to calculate $\bar{v}_2^{\infty(P_1^s)}$ for hydrogen in various solvents which are subsequently generalized to the working equation, Equation (5).

$$\ln\frac{\bar{v}_2^{\infty(P_1^s)}}{v_{c2}} = A + B\,T^3_{R1} + C\,T^6_{R1} \tag{5}$$

where

$$\begin{aligned} A &= -0.9556 + 1.244\,\omega_1 \\ B &= 1.712 + 0.283\,\omega_1 \qquad \text{for} \quad \omega_1 \geqq 0.2 \\ C &= 1.282 + 0.840\,\omega_1 \end{aligned}$$

or

$$\begin{aligned} A &= -0.9619 + 0.4529\,\omega_1 + 4.0935\,\omega_1^2 \\ B &= 0.9247 + 7.5994\,\omega_1 - 91.377\,\omega_1^2 + 436.06\,\omega_1^3 \\ &\qquad\qquad \text{for} \quad \omega_1 < 0.2 \\ C &= 1.643 - 0.965\,\omega_1 \end{aligned}$$

Subscript 1 refers to solvent (or solvent mixture) and subscript 2 refers to hydrogen. T_{R_1} is the solvent reduced temperature T/T_{c1}, and ω_1 is the acentric factor of the solvent. v_{c2} is the critical volume of hydrogen in the classical limit, which is 51.5×10^{-3} M^3/Kg-mole; this is different from the true critical volume of hydrogen which contains the quantum effect present at the low temperature of the critical point. Equation (5) is plotted in Figure 1 together with experimental data as well as points calculated from the equation of states. Details of derivations are given in the Appendix.

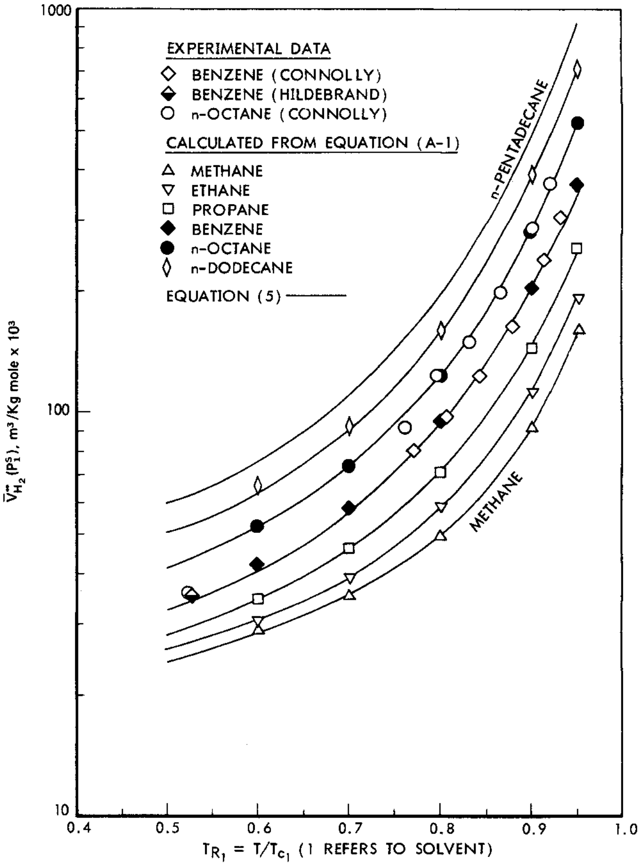

Fig. 1. Partial molar volumes of hydrogen in hydrocarbons (at infinite dilution and at solvent vapor pressure).

Pressure Effect on Hydrogen Partial Molar Volume

Typical hydrotreating operates at temperatures close to the solvent critical temperature and at high pressure. At these conditions, the isothermal compressibility of hydrogen partial molar volume becomes important. Moreover, the variation of isothermal compressibility with pressure becomes appreciable at high pressure. Literature data on hydrogen partial molar volumes indicate that at constant temperature $1/\bar{v}_2^{\infty}$ is linear with respect to P up to 150×10^5 N/m^2 (Connolly and Kandalic, 1963). We may, therefore, define θ_R in a dimensionless form as

$$\theta_R = \left[\frac{\partial(v_{c1}/\bar{v}_2^{\infty})}{\partial(P/P_{c1})}\right]_T$$

$$= \frac{P_{c1}v_{c1}}{\bar{v}_2^{\infty}}\left(-\frac{1}{\bar{v}_2^{\infty}}\,\frac{\partial\bar{v}_2^{\infty}}{\partial P}\right)_T = \frac{P_{c1}v_{c1}}{\bar{v}_2^{\infty}}\,\bar{\beta}_2^{\infty} \tag{6}$$

where

$$-\frac{1}{\bar{v}_2^{\infty}}\left(\frac{\partial\bar{v}_2^{\infty}}{\partial P}\right)_T = \bar{\beta}_2^{\infty}$$

is the usual definition of isothermal compressibility.

Literature data on $1/\bar{v}_2^{\infty}$ versus P are available on hydrogen in benzene and *n*-octane only, with data in *n*-octane showing rather strange behavior at low temperatures (Connolly and Kandalic, 1963). The expression for partial molar volume derived from the Redlich-Kwong equation, Equation (A2), is therefore further differentiated with respect to pressure (see Appendix) to calculate partial molar compressibility of hydrogen which are then used to calculate θ_R's shown in Figure 2. Also shown are experimental data in benzene and *n*-octane and those calculated for hydrogen in *n*-octane using the same equation of state used for Equation (A1). The agreement between calculated and experimental values of θ_R is fair considering the complexity of Equation (A14) and the singular behavior of experimental data for *n*-octane. As much weight as possible, however, has been put on the experimental points in arriving at the following generalized correlation for θ_R.

$$\ln \theta_R = D + E\, T_{R_1} \qquad (7)$$

where

$$D = -4.40 + 3.10\sqrt{\omega_1}$$
$$E = 4.20 - 3.10\sqrt{\omega_1}$$

Since θ_R is independent of pressure (up to about 150 atm), integration of Equation (6) at constant temperature gives

$$\frac{1}{\bar{v}_2^{\infty(P)}} = \frac{1}{\bar{v}_2^{\infty(P_1^s)}} + \frac{\theta_R}{P_{c1}v_{c1}}(P - P_1^s) \qquad (8)$$

where P_1^s is the vapor pressure of the solvent at that temperature. Thus, the partial molar volume of hydrogen at the solvent vapor pressure as calculated by Equation (5) is corrected to the system pressure by Equation (8).

Effect of Composition

The constant c in Equation (4) represents the effect of composition. Limited literature data on hydrogen in benzene and *n*-octane (Connolly and Kadalic, 1963) are generalized to give

$$\ln \frac{c}{v_{c2}} = -2.1288 - 0.1880\, P_{R_1} + 5.4822\, T_{R_1}{}^2 \qquad (9)$$

Equation (9) is believed to give sufficiently accurate account of this effect, which becomes appreciable only at relatively high temperature and high hydrogen concentration. $P_{R_1} = P/P_{c_1}$ in Equation (9).

Mixtures Containing More Than One Solvent

Equations (4), (5), (7), and (9) may be applied to cases where more than one solvent exists. In such cases, subscript 1 may be regarded as solvent mixture. The pseudocritical temperature and the acentric factor of the solvent mixture may be calculated by

$$T_{cm} = \frac{\Sigma\Sigma x_i' v_{ci}{}^{2/3} x_j' v_{cj}{}^{2/3} T_{cij}}{(\Sigma x_i' v_{ci}{}^{2/3})^2} = \Sigma\Sigma \theta_i' \theta_j' Tc_{ij} \qquad (10)$$

$$v_{cm} = (\Sigma x_i' v_{ci}{}^{2/3})^{3/2} \qquad (11)$$

$$\omega_m = \Sigma x_i' \omega_i \qquad (12)$$

$$Z_{cm} = \Sigma x_i' Z_{ci} \qquad (13)$$

$$P_{cm} = Z_{cm} R T_{cm} / v_{cm} \qquad (14)$$

$$\theta_k' = x_k' v_{ck}{}^{2/3} / \Sigma x_i' v_{ci}{}^{2/3} \text{ (the surface fraction)}$$

where x''s are the liquid mole fractions of hydrogen-free solvent components, and the summation are over all components except hydrogen. T_{cm}, v_{cm}, Z_{cm} and P_{cm} are the pseudocritical properties of the hydrogen-free solvent mixture. T_{cij} is defined in Equation (A11).

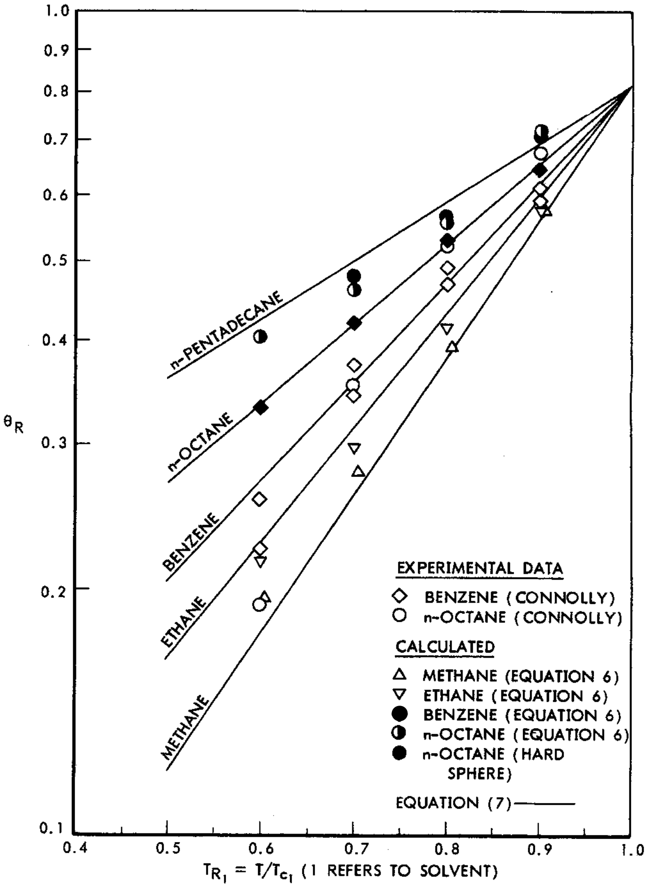

Fig. 2. Compressibilities of hydrogen partial molar volumes in hydrocarbons.

TABLE 1. COMPARISON OF CALCULATED AND EXPERIMENTAL LIQUID MOLAR VOLUMES OF *n*-HEXANE (1)-HYDROGEN (2) MIXTURES

v_1 = liquid molar volume of solvent, m³/Kg mole
$\bar{v}_2^{\infty}$ = partial molar volume of hydrogen at infinite dilution, m³ /Kg mole
v_M = liquid molar volume of mixture, m³/Kg mole
(P_1^s) = at saturation pressure of solvent
(P) = at total pressure

Temp, °C	Press., N/m^2 × 10^{-5}	x_2	P_1^s, N/m^2 × 10^{-5}	$v_1^{(P_1^s)}$	$v_1^{(P)}$	$\bar{v}_2^{\infty(P_1^s)}$	$\bar{v}_2^{\infty(P)}$	Exp.	$v_M^{(P)}$ This method	Pseudo-critical
4.4	137.9	0.099	0.075	0.129	0.126	0.0401	0.0355	0.119	0.117	0.122
71.1	137.9	0.119	1.09	0.141	0.136	0.0582	0.0462	0.127	0.126	0.139
137.8	137.9	0.149	5.91	0.162	0.151	0.114	0.0674	0.140	0.140	0.177
171.1	103.4	0.132	11.2	0.177	0.163	0.190	0.0980	0.157	0.158	0.247
171.1	137.9	0.172	11.2	0.177	0.160	0.190	0.0830	0.151	0.152	(a)
204.4	103.4	0.165	19.3	0.203	0.174	0.369	0.124	0.177	0.177	(a)
204.4	137.9	0.244	19.3	0.203	0.169	0.369	0.0980	0.169	0.170	(a)

a) Pseudo reduced temperature by Kay's rule exceeds 1.0.

In applying Equation (4) to calculate liquid molar volume (or density) of hydrogen-containing mixtures, we need $v_1^{(P)}$, the solvent molar volume (at total pressure P), in addition to the hydrogen partial molar volume $\bar{v}_2^\infty$ just described. The method of calculating the solvent molar volume is described elsewhere (Chueh and Prausnitz, 1969).

Prediction of Liquid Densities of Hydrogen-Containing Mixtures and Comparison With Literature Data

Equation (4) and all other equations entering it have been tested with independent literature data on n-hexane-hydrogen systems (Nichols et al., 1957). The predicted molar volumes of mixtures are in excellent agreement with the experimental values, generally well within 1%, over a range of temperature from 4.4° to 204.4°C for pressure up to 172.4×10^5 N/m^2 for hydrogen concentration up to 25%m. Table 1 gives comparisons of calculated and experimental liquid molar volumes of the n-hexane-H_2 system. Also given are the erroneous results when conventional pseudocritical rules $T_{cm} = \Sigma x_i T_{c_i}$ and $v_{cm} = \Sigma x_i v_{c_i}$ are used with the theorem of corresponding states. It is noteworthy that near the solvent critical temperature, these rules often give results which are off by as much as 100% and often fail to give any answer. It is also noteworthy that there is a relatively large effect of pressure on liquid volume, and especially on hydrogen partial molar volume in the critical region.

LIQUID ENTHALPIES OF HYDROGEN-CONTAINING MIXTURES

The molar enthalpy of a liquid mixture containing hydrogen is given by

$$H_M = x_1 \bar{H}_1^{(P)} + x_2 \bar{H}_2^{(P)} \tag{15}$$

in which the partial molar enthalpies can again be broken up into three contributions; the limiting value, the pressure correction, and the nonideality correction,

$$\bar{H}_1^{(P)} = H_1^{(P_1^s)} + \int_{P_1^s}^{P} \left[v_1 - T\left(\frac{\partial v_1}{\partial T}\right)_P \right] dP + RT^2 \left(\frac{\partial c'}{\partial T}\right)_P x_2^2 \tag{16}$$

$$\bar{H}_2^{(P)} = \bar{H}_2^\infty + \int_{P_1^s}^{P} \left[\bar{v}_2^\infty - T\left(\frac{\partial \bar{v}_2^\infty}{\partial T}\right)_P \right] dP - RT^2 \left(\frac{\partial c'}{\partial T}\right)_P (1 - x_1^2) \tag{17}$$

where

$\bar{H}_1^{(P)}$ = liquid partial molar enthalpy of solvent (1) at total pressure, P, temperature T, and composition x
$H_1^{(P_1^s)}$ = liquid enthalpy of pure solvent (1) at its saturation pressure
$\bar{H}_2^{(P)}$ = liquid partial molar enthalpy of hydrogen (2) at total pressure P, temperature T, and composition x
$\bar{H}_2^\infty$ = liquid partial molar enthalpy of hydrogen at infinite dilution (implicitly at the saturation pressure of the solvent)
v_1 = liquid molar volume of solvent
$\bar{v}_2^\infty$ = liquid partial molar volume of hydrogen at infinite dilution
c' = the coefficient in $\ln \gamma_1 = -c' x_2^2$ where γ_1 is the activity coefficient of the solvent in the solution

The second term on the right-hand side of Equation (16) represents the effect of pressure on the liquid enthalpy of solvent. Since solvents (liquid hydrocarbons) are generally not very compressible except near the critical temperature, this correction is generally small, and may be ignored in most cases. This, however, does not apply to the integral in Equation (17) which represents the effect of pressure on the partial molar enthalpy of hydrogen in the liquid phase. As discussed earlier, $\bar{v}_2^\infty$ of hydrogen is quite pressure dependent, and as a result the integrand in Equation (17) represents a significant correction to $\bar{H}_2^\infty$. The last terms on the right-hand side of Equations (16) and (17) represent the effect of solution nonideality which will be discussed later.

It is convenient to rewrite $H_1^{(P_1^s)}$ and $\bar{H}_2^\infty$ in Equation (16) and (17) as

$$H_1^{(P_1^s)} = H_1^0 - (H_1^0 - H_1^{(P_1^s)}) \tag{18}$$

and

$$\bar{H}_2^\infty = H_2^0 - (H_2^0 - \bar{H}_2^\infty) \tag{19}$$

where

H_1^0 = ideal gas enthalpy of the solvent at T
$H_1^0 - H_1^{(P_1^s)}$ = heat of complete vaporization (vaporization to ideal gas) of the solvent at T
H_2^0 = ideal gas enthalpy of hydrogen
$H_2^0 - \bar{H}_2^\infty$ = heat of vaporization of hydrogen from a solution at infinite dilution of hydrogen. This quantity is negative for hydrogen

When ordinary gases dissolve in a liquid, heat is released (exothermic), that is, $H_2^0 > \bar{H}_2^\infty$. In contrast, heat is absorbed (endothermic) when hydrogen dissolves in a liquid, that is, $H_2^0 < \bar{H}_2^\infty$ for hydrogen. This rather unusual behavior of hydrogen is due to its extremely low critical temperature which makes T_R of hydrogen much greater than one. Also, as a consequence of the endothermic heat of solution, hydrogen has an inverted temperature coefficient of gas solubility; that is, the solubility of hydrogen in liquid increases with increasing temperature (at a constant partial pressure of hydrogen). Other light gases such as He, N_2, and H_2S also exhibit this inverted solubility when the temperature becomes so high that $T_R >> 1$ for these gases.

The following paragraphs discuss the heat of solution of hydrogen, the effect of pressure and composition on this quantity, and the liquid enthalpy of the solvent.

Heat of Solution at Infinite Dilution From Henry's Constants

Calorimetric measurements of the heat of solution of hydrogen are essentially nonexisting. Accurate solubility and vapor-liquid equilibrium data, however, are available over a wide range of temperature for hydrogen in methane (Benham and Katz, 1957; Fastowsky and Gonikberg, 1940), ethane (Hiza et al., 1968), propane (Sage and Lacey, 1950 and 1955; William and Katz, 1954), n-butane (Aroyan and Katz, 1951), n-heptane, n-octane (Cook et al., 1957), ethylene, propylene (Williams and Katz, 1954), benzene (Connolly, 1962), and toluene (Cook et al., 1957) from which the heat of solution of hydrogen can be calculated through the rigorous thermodynamic relation

$$H_2^0 - \bar{H}_2^\infty = RT^2 \left(\frac{\partial \ln k_{2,1}}{\partial T}\right)_P \tag{20}$$

where

$k_{2,1}$ = Henry's constant of hydrogen (2) in solvent (1), and
R = 8.319×10^{-3} J/(Kg mole hydrogen) (°K)

Note that the differentiation is to be carried out under constant pressure; this is mathematically related to that along the saturation pressure of solvent (which is the experimentally accessible quantity) by

$$\left(\frac{\partial \ln k_{2,1}}{\partial T}\right)_P = \left(\frac{d \ln k_{2,1}}{\partial T}\right)_{\text{sat}} - \left(\frac{\partial \ln k_{2,1}}{\partial P}\right)_T \left(\frac{dP}{dT}\right)_{\text{sat}} \qquad (21)$$

or

$$\left(\frac{\partial \ln k_{2,1}}{\partial T}\right)_P = \left(\frac{d \ln k_{2,1}}{dT}\right)_{\text{sat}} - \frac{P_1^s \bar{v}_2^\infty}{RT} \left(\frac{d \ln P}{dT}\right)_{\text{sat}} \qquad (22)$$

Equation (22) follows from Equation (21) by introducing the thermodynamic relation

$$\left(\frac{\partial \ln k_{2,1}}{\partial P}\right)_T = \frac{\bar{v}_2^\infty}{RT} \qquad (23)$$

where $\bar{v}_2^\infty$ is the partial molar volume of hydrogen in solvent (1) at infinite dilution of hydrogen discussed previously.

It will be noted that differentiation at constant pressure has often been erroneously replaced or approximated by differentiation along the saturation line. This introduces little error at regions remote from the critical, but the neglect of $-(P_1^s \bar{v}_2^\infty/RT)\ (d \ln P/dT)_{\text{sat}}$ becomes progressively serious as the critical region is approached; for example, 30% error will result by ignoring this term for the heat of solution of hydrogen in benzene at 250°C.

Heats of solution of hydrogen at infinite dilution, $H_2^\infty - H_2^0$, in various solvents have been evaluated from literature solubility data using Equations (20) and (22). Henry's constants required here were evaluated elsewhere (Prausnitz and Chueh, 1968; Connolly, 1962). Figure 3 shows that the heat of solution of hydrogen can be generalized with respect to solvent when they are reduced with the solvent critical temperature. Olefinic and aromatic solvents differ slightly from paraffinic solvents. Expressed analytically for paraffinic solvent ($UOPK \geqq 12$)

$$\frac{\bar{H}_2^{\infty, P_1^s} - H_2^0}{RT_{c1}} = -0.20907846 - 4.0246858\ T_{R_1} + 14.984728\ T_{R_1}^2 - 18.092651\ T_{R_1}^3 + 9.5373978\ T_{R_1}^4 \qquad (24)$$

and for aromatic solvent ($UOPK \leqq 9.73$)

$$\frac{\bar{H}_2^{\infty, P_1^s} - H_2^0}{RT_{c1}} = -0.20755554 - 1.440886\ T_{R_1} + 7.9220228\ T_{R_1}^2 - 11.182137\ T_{R_1}^3 + 7.2971343\ T_{R_1}^4 \qquad (25)$$

where $T_{R_1} = T/T_{c_1}$ and T_{c_1} is the critical temperature of the solvent. For solvents with $UOPK$ between 12.0 and 9.73, interpolation between the two values may be used. Equations (24) and (25) give the heat of solution of hydrogen at infinite dilution, which also implies that the pressure is at the saturation pressure of the solvent. In actual applications, such as in hydrotreating, the total pressure may be quite high, and the pressure effect become very significant as pointed out earlier. This effect is discussed below.

Effect of Pressure on Liquid Partial Molar Enthalpy of Hydrogen

At constant temperature and constant composition, the effect of pressure on liquid partial molar enthalpy is given by the integrand in Equation (17) where superscript ∞ denotes infinite dilution and P_1^s and P denote the solvent saturation pressure and total pressure, respectively.

$$\bar{H}_2^{\infty,P} - \bar{H}_2^{\infty,P_1^s} = \int_{P_1^s}^{P} \left[\bar{v}_2^\infty - T\left(\frac{\partial \bar{v}_2^\infty}{\partial T}\right)_P \right] dP \qquad (26)$$

Note $\bar{v}_2^\infty$ is a function of pressure. By substituting Equation (8) for the expression of $\bar{v}_2^\infty$, Equation (5) for $\bar{v}_2^{\infty(P_1^s)}$ and Equation (7) for θ_R into Equation (26) and carrying out the tedious integration, paying special care to the difference between differentiation at constant pressure and along saturation pressure, we arrive at the following expression:

$$\frac{\bar{H}_2^{\infty,P} - H_2^0}{RT_{c1}} - \frac{\bar{H}_2^{\infty,P_1^s} - H_2^0}{RT_{c1}} = \left(\frac{P_{c1} v_{c1}}{RT_{c1}\,\theta_R}\right) \Bigg[(1 + ET_{R_1}) \left(\ln \frac{\bar{v}_2^{\infty(P_1^s)}}{\bar{v}_2^{\infty(P)}}\right) - \left(\frac{3BT_{R_1}^3 + 6CT_{R_1}^6 + ET_{R_1}}{\bar{v}_2^{\infty(P_1^s)}} + 2\frac{P_1^s \theta_R}{P_{c1} v_{c1}} T \left(\frac{d \ln P}{dT}\right)_{\text{sat}} \right) (\bar{v}_2^{\infty(P_1^s)} - \bar{v}_2^{\infty(P)}) \Bigg] \qquad (27)$$

where E is the coefficient in Equation (7) and B and C are coefficients in Equation (5).

Equation (27) combined with Equations (24) and (25) allows the calculation of the heat of solution of hydrogen in any solvent at any temperature and pressure although still at infinite dilution with respect to hydrogen. Figure 4 shows such calculation for hydrogen in benzene. It shows a strong dependence on temperature and pressure and indicates that a constant value for the heat of solution of hydrogen is not adequate in many cases.

Effect of Solution Nonideality on the Liquid Enthalpy of Hydrogen Containing Mixtures

The last terms on the right-hand side of Equations (16) and (17) represent the effect of solution nonideality on the liquid partial molar enthalpies of the solvent and hydrogen, respectively. The constant c' is related to the activity coefficients through

$$\ln \gamma_1^{(P)} = -c' x_2^2 \qquad (28)$$

or

$$\ln \gamma_2^{*(P)} = c'(1 - x_1^2) \qquad (29)$$

where

$$\gamma_1^{(P)} = f_1^{(P)} \Big/ \left(x_1 f_1^{\text{pure}} \exp \int_{P_1^s}^{P} \frac{v_1}{RT} dP \right) \qquad (30)$$

and

$$\gamma_2^{*(P)} = f_2^{(P)} \Big/ \left(x_2 k_{2,1} \exp \int_{P_1^s}^{P} \frac{\bar{v}_2^\infty}{RT} dP \right) \qquad (31)$$

The contribution of solution nonideality to liquid molar enthalpy of a mixture containing hydrogen is, from Equations (15) to (17),

$$x_1 \left[RT^2 \left(\frac{\partial c'}{\partial T}\right)_P x_2^2 \right] - x_2 \left[RT^2 \left(\frac{\partial c'}{\partial T}\right)_P (1 - x_1^2) \right] = -x_2^2 RT^2 \left(\frac{\partial c'}{\partial T}\right)_P = x_2^2 RT T_{R_1} \left(-\frac{\partial c'}{\partial T_{R_1}}\right)_P \qquad (32)$$

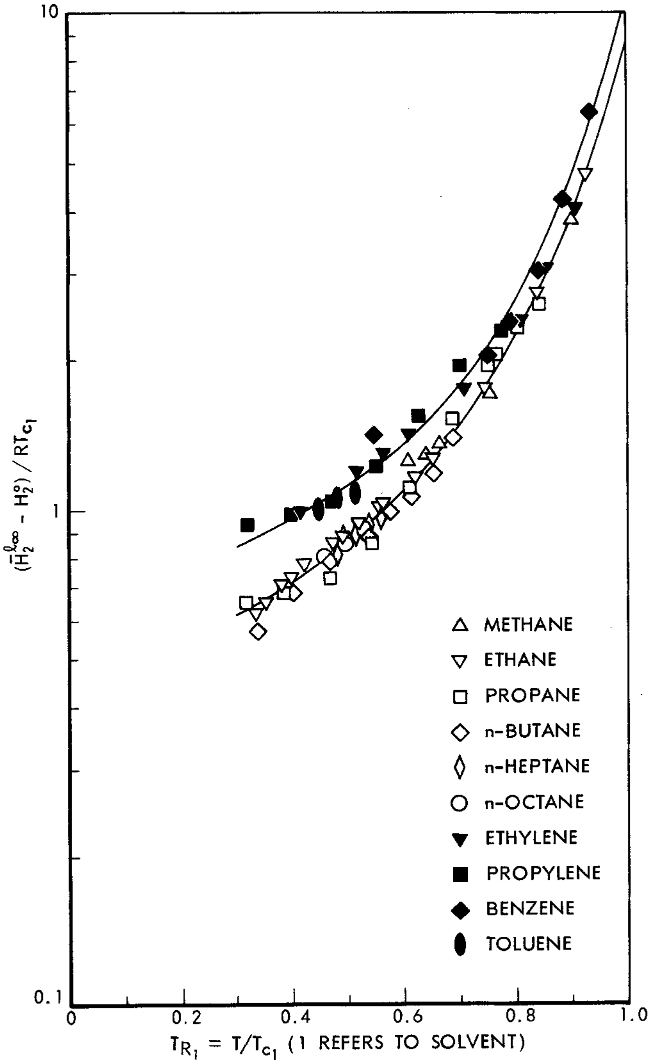

Fig. 3. Heat of solution of hydrogen in hydrocarbons (at infinite dilution and at solvent vapor pressure).

The quantity $(\partial c'/\partial T)_P$ has been reported in the literature for the benzene-hydrogen system (Connolly, 1962). Data on ethane-hydrogen system (Hiza et al., 1968) are analyzed in a similar manner to evaluate $(\partial c'/\partial T)_P$; within the scattering of experimental data, the results of ethane-hydrogen are in general agreement with those reported for the benzene-hydrogen system when compared in a reduced temperature coordinate. These results are generalized as follows:

$$-\left(\frac{\partial c'}{\partial T_{R_1}}\right)_P = \exp(-3.817 + 8.3126 T_{R_1}{}^2 - 0.232 P_{R_1}) \qquad (33)$$

where

$$P_{R_1} = P/P_{c_1} \quad \text{and} \quad T_{R_1} = T/T_{c_1}$$

and T_{c_1} and P_{c_1} are solvent critical temperature and critical pressure, respectively.

Liquid Enthalpy of Solvents (Hydrocarbons)

The liquid enthalpy of solvent $\overline{H}_1{}^{(P)}$ as it appeared in Equation (15) consists of three terms as given in Equation (16), that is, the limiting value, the pressure correction, and the nonideality correction. The last term, which is the effect of solution nonideality, has been discussed above. The second term, which is the effect of pressure, is generally small except in the critical region. The first term $H_1{}^{(P_1{}^s)}$ is the major term and can be rewritten as Equation (18). Since $H_1{}^0$, the ideal gas enthalpy, can be readily calculated or found, the main concern here is the heat of complete vaporization (vaporization to ideal gas), $H_1{}^0 - H_1{}^{(P_1{}^s)}$. This quantity has been correlated within the framework of corresponding states and is given by

$$\frac{H_1{}^0 - H_1{}^{(P_1{}^s)}}{RT_{c_1}} = H_R{}^{(0)} + \omega H_R{}^{(1)} \qquad (34)$$

where $H_R{}^{(0)}$ and $H_R{}^{(1)}$ are functions of reduced temperature and ω is the acentric factor

For $T_{R_1} \leqq 0.75$

$$H_R{}^{(0)} = 7.0837 - 3.1933\, T_{R_1} \qquad (35)$$

$$H_R{}^{(1)} = 14.602 - 11.9866\, T_{R_1} \qquad (36)$$

For $T_{R_1} > 0.75$

$$H_R{}^{(0)} = 1.481449 + 36.09175\, T_{R_1} - 101.1801\, T_{R_1}{}^2 + 113.0982\, T_{R_1}{}^3 - 46.23935\, T_{R_1}{}^4 - 0.0090026/(1.01 - T_{R_1}) \qquad (37)$$

$$H_R{}^{(1)} = 24.83238 + 51.88302{:}T_{R_1} - 322.8546\, T_{R_1}{}^2 + 423.1277\, T_{R_1}{}^3 - 173.8755\, T_{R_1}{}^4 - 0.0045311/(1.01 - T_{R_1}) \qquad (38)$$

The treatment of mixture of solvents is the same as discussed in the previous section, using Equations (10) through (14).

For applications involving petroleum fractions, each narrow boiling fraction may be treated as pseudocomponents characterized by Tc, Pc, Vc, and ω (for example, by the method of Cavett, 1962). Results are not overly sensitive to the particular correlation used to characterize the petroleum fractions.

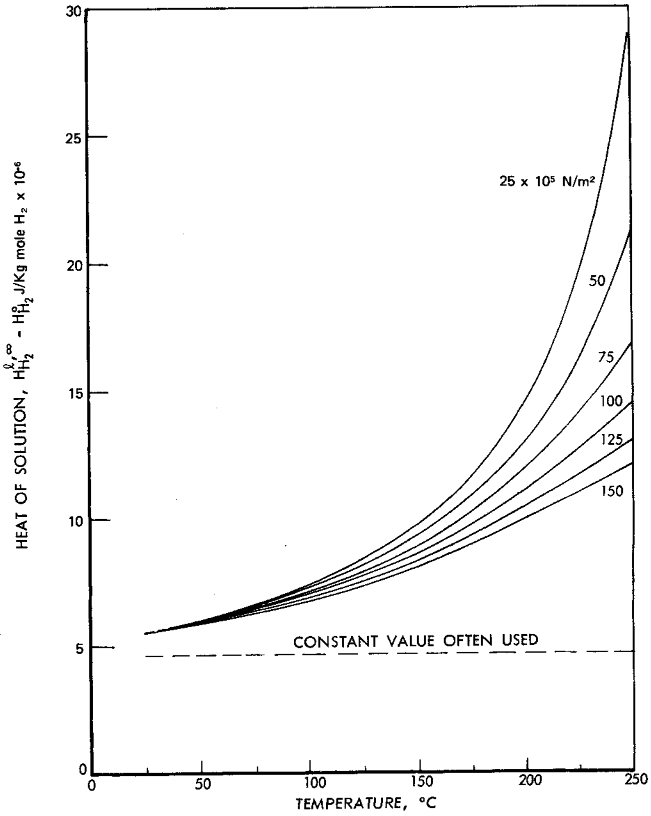

Fig. 4. Heat of solution of hydrogen in benzene at infinite dilution.

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NOTATION

H = enthalpy
$\overline{H}$ = partial molar enthalpy
$k_{2,1}$ = Henry's constant of hydrogen
P = pressure
T = absolute temperature
v = molar volume
$\bar{v}$ = partial molar volume
x = mole fraction
z = compressibility factor
β = isothermal compressibility
θ_R = dimensionless, reduced partial molar compressibility of hydrogen
γ = activity coefficient
ω = acentric factor

Superscripts

l = liquid phase
s = at saturation
(P_1^s) = at saturation pressure
∞ = at infinite dilution
0 = ideal gas state

Subscripts

c = critical state
M (or m) = Mixture
R = reduced (with critical constants)
1 = solvent
2 = hydrogen

LITERATURE CITED

Aroyan, H. J., and D. L. Katz, "Low-Temperature Vapor-Liquid Equilibria in Hydrogen-n-Butane System, *Ind. Eng. Chem.*, **43**, 185 (1951).

Benham, A. L., and D. L. Katz, "Vapor-Liquid Equilibria for Hydrogen-Light Hydrocarbon Systems at Low Temperatures," *AIChE J.*, **3**, 33 (1957).

Cavett, R. H., "Physical Data for Distillation Calculations-Vapor-Liquid Equilibria," *Am. Petrol. Inst. Proc.*, **42**, 351 (1962).

Chueh, P. L., and J. M. Prausnitz, "A Generalized Correlation for the Compressibilities of Normal Liquids," *AIChE J.*, **15**, 471 (1969).

Connolly, J. F., "Thermodynamic Properties of Hydrogen in Benzene Solutions," *J. Chem. Phys.*, **36**, 2897 (1962).

———, and G. A. Kandalic, "Partial Molar Volumes of Hydrogen in Liquid Hydrocarbons," *Chem. Eng. Prog. Symp. Ser.*, No. 44, **59**, 8 (1963).

Cook, M. W., D. N. Hanson, and B. J. Alder, "Solubility of Hydrogen and Deuterium in Nonpolar Solvents," *J. Chem. Phys.*, **26**, 748 (1957).

Fastowsky, M. G., and V. G. Gonikberg, "Die Löslichkeit von Gasen in Flussigkeiten bei niedrigen Temperaturen and Hohen Drucken," *J. Phys. Chem.* (USSR), **14**, 427 (1940).

Hildebrand, J. H., and R. L. Scott, *The Solubility of Nonelectrolytes*, p. 247, 3rd edit., Dover, New York (1964).

Hiza, M. J., C. K. Heck, and A. J. Kidnay, "Liquid-Vapor and Solid-Vapor Equilibrium in the System Hydrogen-Ethane," *Advances in Cryogenic Engineering*, **13**, 343, Plenum Press, New York (1968).

Nichols, W. B., H. H. Reamer, and B. H. Sage, "Volumetric and Phase Behavior in the Hydrogen-n-Hexane System," *AIChE J.*, **3**, 262 (1957).

Orentlicher, M., and J. M. Prausnitz, "Thermodynamic Properties of Dense Fluid Mixtures," *Can. J. Chem.*, **45**, 595 (1967).

Prausnitz, J. M., and P. L. Chueh, *Computer Calculations for High Pressure Vapor-Liquid Equilibria*, Prentice Hall, Englewood Cliffs, N. J. (1968).

Sage, B. H., and W. N. Lacey, *Thermodynamic Properties of Lighter Hydrocarbons*, American Petroleum Institute, New York (1950, 1955).

Williams, R. B., and D. L. Katz, "Vapor-Liquid Equilibria in Binary Systems: Hydrogen with Ethylene, Ethane, Propylene and Propane," *Ind. Eng. Chem.*, **46**, 2512 (1954).

APPENDIX

Hydrogen Partial Molar Volume From Equation of States

1. *From an Equation for Hard-Sphere Fluids.* A theoretical equation of state based on perturbation of hard-sphere fluids (Orentlicher and Prausnitz, 1967) suggests that

$$\frac{\bar{v}_2^{\infty}}{v_1} = \frac{v_{c2}}{v_{c1}} + \phi(T_{R1})\left(1 - \frac{\epsilon_{12}}{\epsilon_{11}}\right) \tag{A1}$$

where v_c is the critical volume, $\phi(T_{R1})$ is a universal function of the solvent reduced temperature, and ϵ the potential well depth. Table A1 gives a slightly modified $\phi(T_{R1})$ and $1 - \epsilon_{12}/\epsilon_{11}$ for hydrocarbon-hydrogen system. Figure 1 shows the hydrogen partial molar volumes in several solvents, calculated from Equation (A1), as well as experimental data available for hydrogen in benzene and in n-octane. The agreement between the calculated and the experimental is excellent; also the calculated values show a consistent trend with respect to the hydrocarbon solvent in which the hydrogen is dissolved.

2. *From Revised Redlich-Kwong Equation.* To support further the results obtained above, another equation of state, a revised Redlich-Kwong equation, is used to calculate liquid partial molar volume of hydrogen in hydrocarbons.

By definition, the partial molar volume of component k is given by

$$\bar{v}_k = \left(\frac{\partial V}{\partial n_k}\right)_{P,T,n_i(i\neq k)} = \frac{-\left(\dfrac{\partial p}{\partial n_k}\right)_{T,V,n_i(i\neq k)}}{\left(\dfrac{\partial P}{\partial V}\right)_{T,n_i(\text{all } i)}} \tag{A2}$$

This expression is used with a revised form of Redlich and Kwong equation of state for liquid mixtures to calculate $\overline{V}_2^{\infty(P_1^s)}$ in various solvents over a wide range of temperature.

The Redlich and Kwong equation of state is

$$P = \frac{RT}{v-b} - \frac{a}{T^{0.5}v(v+b)} \tag{A3}$$

where

$$a = \frac{\Omega a R^2 T_c^{2.5}}{P_c} \tag{A4}$$

$$b = \frac{\Omega b R T_c}{P_c} \tag{A5}$$

and where Ωa and Ωb are constants for each saturated liquid given in Table 2.

Substitution of Equation (A3) into Equation (A2) gives

$$\bar{v}_k = \frac{\dfrac{RT}{v-b}\left(1 + \dfrac{b_k}{v-b}\right) - \dfrac{2(\Sigma x_i a_{ki}) - ab_k/(v+b)}{v(v+b)T^{0.5}}}{\dfrac{RT}{(v-b)^2} - \dfrac{a}{T^{0.5}}\left[\dfrac{2v+b}{v^2(v+b)^2}\right]} \tag{A6}$$

where v is the molar liquid volume at saturation. For $\bar{v}_k^{\infty}$, the partial molar volume of k at infinite dilution in a solvent (referred by subscript 1), $v = v_1$ and $a = a_1$, $b = b_1$ as given by Equations (A4) and (A5). Also

$$a_{ij} = \frac{\Omega a_{ij} R T_{cij}^{1.5} v_{cij}}{z_{cij}} \tag{A7}$$

where

Table A1. Functions for Equation (A1)

T_R	$\phi(T_R)$	System	$1 - \frac{\epsilon_{12}}{\epsilon_{11}}$
0.6	0.39	Methane-H_2	0.58
0.7	0.58	Ethane-H_2	0.55
0.8	0.99	Propane-H_2	0.55
0.9	2.10	Benzene-H_2	0.65
0.95	3.56	*n*-Octane-H_2	0.51
		n-Dodecane-H_2	0.51

Table A2. Constants for Saturated Liquid

	Ωa	Ωb
Hydrogen	0.4278	0.0694
Methane	0.4546	0.0872
Ethane	0.4347	0.0827
Propane	0.4138	0.0802
Benzene	0.4100	0.0787
n-Octane	0.3900	0.0739

$$\Omega a_{ij} = \tfrac{1}{2}(\Omega a_i + \Omega a_j) \tag{A8}$$

$$v_{cij} = \tfrac{1}{2}(v_{ci} + v_{cj}) \tag{A9}$$

$$z_{cij} = 0.291 - 0.04(\omega_i + \omega_j) \tag{A10}$$

$$T_{cij} = (T_{ci}T_{cj})^{1/2}(1 - k_{ij}) \tag{A11}$$

$$k_{ij} = 1 - \left[\frac{(v_{ci}^{1/3}v_{cj}^{1/3})^{1/2}}{(v_{ci}^{1/3} + v_{cj}^{1/3})/2}\right]^3 \tag{A12}$$

The molar liquid volumes of solvents at saturation, v_1's, are calculated by a method discussed elsewhere (Chueh and Prausnitz, 1969; Prausnitz and Chueh, 1968).

Values of $\bar{v}_2^{\infty(P_1^s)}$ calculated from Equation (A6) are found to be in good agreement with both experimental data and those calculated from Equation (A1).

Partial Molar Compressibility of Hydrogen

The partial molar compressibility of hydrogen is given by

$$\bar{\beta}_2 = -\frac{1}{\bar{v}_2}\left(\frac{\partial \bar{v}_2}{\partial P}\right)_{T,x} = -\frac{1}{\bar{v}_2}\left[\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_1}\right]_{T,x}$$

$$= \frac{1}{\bar{v}_2}\left(\frac{\partial P}{\partial V}\right)^{-2}_{T,n_1,n_2}\left[\frac{\partial}{\partial n_2}\left(\frac{\partial P}{\partial V}\right)_{T,n_1,n_2}\right]_{T,P,n_1} \tag{A13}$$

Substitution of Equations (A3) to (A6) into Equation (A13) gives partial molar compressibility of hydrogen at infinite dilution,

$$\bar{\beta}_2^{\infty} = \frac{QA - QB - QC}{QD}$$

$$QA = \frac{a_1(2\bar{v}_2^{\infty} + b_2) + 2a_{12}(2v_1 + b_1)}{T^{0.5}v_1^2(v_1 + b_1)^2}$$

$$QB = \frac{2a_1(2v_1 + b_1)[\bar{v}_2^{\infty}(v_1 + b_1) + v_1(\bar{v}_2^{\infty} + b_2)]}{T^{0.5}v_1^3(v_1 + b_1)^3}$$

$$QC = \frac{RT[(v_1 - b_1) - 2(\bar{v}_2^{\infty} - b_2)]}{(v_1 - b_1)^3}$$

$$QD = \bar{v}_2^{\infty}\left[\frac{a_1(2v_1 + b_1)}{T^{0.5}v_1^2(v_1 + b_1)^2} - \frac{RT}{(v_1 - b_1)^2}\right]^2 \tag{A14}$$

where subscript 1 refers to solvent and 2 refers to hydrogen. The meanings of symbols are the same as in Equation (A6).

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Liquid-Vapor Equilibria at 112.00 K for Systems Containing Nitrogen, Argon, and Methane

Liquid-vapor phase equilibria measurements were made at 112.00 K on the binary systems nitrogen-argon, nitrogen-methane, and argon-methane and the ternary system nitrogen-argon-methane. Values of g^E, the excess Gibbs free energy, have been calculated from the experimental data for all the systems studied. The data and derived g^E values for the binary systems were compared with the results of previous investigations with satisfactory agreement.

R. C. MILLER
A. J. KIDNAY
and M. J. HIZA

Cryogenics Division
Institute for Basic Standards
National Bureau of Standards
Boulder, Colorado

SCOPE

Low temperature phase equilibria data are valuable in process design calculations and in the testing and formulation of liquid solution correlations and theories. The objective of this study was to provide consistent liquid-vapor phase equilibria data for a ternary system and its constituent binaries. The nitrogen-argon-methane system was selected since all of these simple components are of

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Correspondence concerning this paper should be addressed to A. J. Kidnay, Colorado School of Mines, Golden, Colorado. R. C. Miller is with the University of Wyoming, Laramie, Wyoming.