$$F_7(\lambda,\Gamma) = -\left(\frac{1}{945} + \frac{\lambda}{4,536} + \frac{\Gamma}{3,024}\right)$$

$$F_8(\lambda,\Gamma) = -\left(\frac{11}{1,260} + \frac{\lambda}{3,024} + \frac{\Gamma}{1,260}\right)$$

$$F_9(\lambda,\Gamma) = \left(\frac{14}{5} + \frac{22\Gamma}{15} - \frac{4,557\lambda}{9,450} + \frac{\Gamma^2}{30}\right) + \Gamma\lambda\left(\frac{493}{9,450} + \frac{167\lambda}{88,200} + \frac{17\Gamma}{7,560} + \frac{\Gamma\lambda}{28,350} + \frac{\lambda^2}{54,432} + \frac{\Gamma^2}{37,800}\right) + \lambda^2\left(\frac{107}{12,600} + \frac{73\lambda}{151,200} + \frac{\lambda^2}{272,160}\right)$$

$$F_{10}(\lambda,\Gamma) = -\left(\frac{294\lambda}{5} + \frac{\lambda^3}{120} + \frac{\Gamma^2\lambda}{30} + \frac{7\lambda^2}{5} + \frac{14\Gamma\lambda}{5} + \frac{\Gamma\lambda^2}{30}\right)$$

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Enthalpy of Hydrogen-Containing Hydrocarbon Liquids

The partial enthalpy of dissolved hydrogen in hydrocarbon liquids is derived from the fugacity correlation of Sebastian et al. and the results are presented in general equations. The partial enthalpy of the hydrocarbon solvent is found to be changed only insignificantly by the dissolved hydrogen from that of the pure liquid at the experimental conditions of up to 30 MPa in pressure.

H. Y. KIM, H. M. SEBASTIAN,
H. M. LIN, and K. C. CHAO
School of Chemical Engineering
Purdue University
West Lafayette, IN 47907

Large quantities of hydrogen are dissolved in liquid oils in hydrofining processes, sometimes to the extent of 50 mole % or higher in the liquid at the prevailing high temperature and high pressure, both of which tend to favor the solubility of hydrogen. Contrary to ordinary heavier gases, the partial molal enthalpy of solution of hydrogen is positive and large—in the order of several thousand calories per gram mole. The high solubility and large molal heat of solution mean that the total heat absorbed in the dissolution process can be substantial. The enthalpy of solution of hydrogen and the enthalpy change of the solvent due to the dissolved hydrogen are therefore of interest in process engineering. But these quantities cannot be calculated by conventional procedures based on pseudo-reduced correlations because of the peculiar properties of hydrogen as a quantum gas—extremely light molecular weight, low critical temperature, and small energies of interaction with other molecules.

An alternate approach to the enthalpy of hydrogen-containing liquids is to sum the partial molal enthalpy of the dissolved hydrogen and that of the solvent

$$\tilde{H}_M = x_H\overline{H}_H + x_S\overline{H}_S \qquad (1)$$

The symbols are explained in Notation.

Chueh and Deal (1973) developed general equations for the calculation of the partial enthalpies of Eq. 1. Henry constant of hydrogen at various temperatures was differentiated with respect to temperature to give the partial enthalpy of solution of hydrogen at infinite dilution. Correction terms were introduced for the effect of the finite concentration of hydrogen and for the effect of pressure in excess of the vapor pressure of the solvent. Chueh and Deal's contribution was the best then available, but the experimental data base of their correlation was limited, being made up of light solvents of the paraffins (up to n-octane), olefins (up to propylene), and aromatics (up to toluene).

Sebastian et al. (1981) recently developed a correlation of the fugacity of dissolved hydrogen at temperatures from 310 to 700 K and pressures to 30 MPa. The correlation was based on extensive experimental gas solubility data in hydrocarbons of a variety of molecular types including paraffins, mono- and poly-nuclear aromatics, naphthenes, and hetero-atom containing hydrocarbons. The ranges of temperature, pressure and solvent were all substantially extended from those of Chueh and Deal. Sebastian's correlation is applied for the derivation of the partial enthalpies reported here.

PARTIAL MOLAL ENTHALPY OF DISSOLVED HYDROGEN

The partial molal enthalpy of dissolved hydrogen is derived from the fugacity of the dissolved hydrogen upon differentiation wtih respect to temperature at constant pressure and composition

$$\frac{\tilde{H}_H^* - \overline{H}_H}{RT^2} = \left[\frac{\partial ln(f/x)}{\partial T}\right]_{p,x} \qquad (2)$$

The symbols are explained in Notation.

Substituting the fugacity equation of Sebastian et al. (1981) into Eq. 2, we obtain

$$\frac{\tilde{H}_H^* - \overline{H}_H}{RT^2} = g_1 + g_2\frac{d\bar{\delta}}{dT} + g_3\frac{p}{RT} + g_4\frac{p}{RT}\frac{d\bar{\delta}}{dT} \qquad (3)$$

The g's in Eq. 3 are functions of temperature T and solubility parameter of the solution $\bar{\delta}$ given below.

$$g_1 = A_2/\bar{\delta} + A_3 + A_4\bar{\delta} + 2A_5\bar{\delta}^2T - 2A_6\bar{\delta}^2/T^3 \qquad (4)$$

$$g_2 = -A_2T/\bar{\delta}^2 + A_4T + 2A_5T^2\bar{\delta} + 2A_6\bar{\delta}/T^2 \qquad (5)$$

$$g_3 = -B_1/T + B_3T - B_4\bar{\delta}/T - B_5\bar{\delta}^2/T \qquad (6)$$

$$g_4 = B_4 + 2B_5\bar{\delta} + B_6T \qquad (7)$$

The coefficients A's and B's of Eqs. 4 to 7 are given in Table 1,

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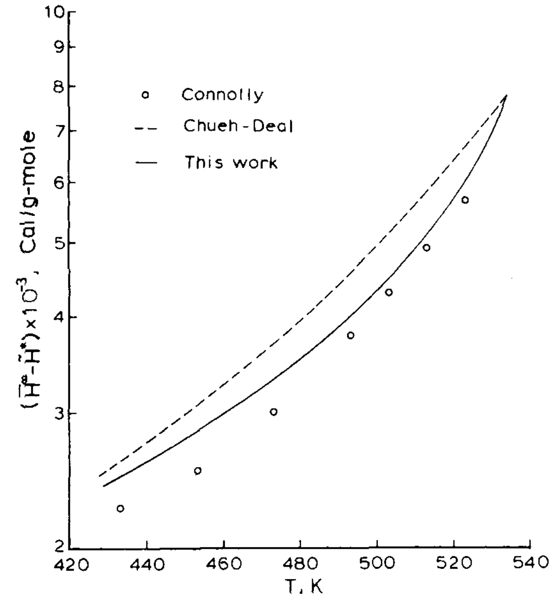

Figure 1. Partial molal enthalpy of hydrogen at infinite dilution in liquid benzene.

and are the same as those presented by Sebastian et al. in their fugacity equation.

The temperature derivative of the solubility parameter of the solution $d\bar{\delta}/dT$ is required in Eq. 3. Differentiating the equation relating $\bar{\delta}$ to δ_i,

$$\bar{\delta} = \left(\sum_i V_{wi}x_i\,\delta_i\right)\Big/\left(\sum_i V_{wi}\,x_i\right) \tag{8}$$

we obtain

$$d\bar{\delta}/dT = \left(\sum_i V_{wi}x_i\,\frac{d\delta_i}{dT}\right)\Big/\left(\sum_i V_{wi}\,x_i\right) \tag{9}$$

which shows $d\bar{\delta}/dT$ to be the volumetric average of the temperature derivatives of the solubility parameters of the components. Sebastian et al. (1981) give values of V_w for a number of components calculated from group contribution values given by Bondi (1968).

The derivative $(d\delta_i/dT)$ is non-zero for the solvent components since these δ's vary with temperature in Sebastian's correlation. In this work, we calculate the derivative for a solvent by calculating δ_i at the temperatures 1 K above and 1 K below the temperature of interest, taking the difference $\Delta\delta_i$, and then setting

$$d\delta_i/dT \doteq \Delta\delta_i/2 \tag{10}$$

The solubility parameter of hydrogen is assigned a constant value in the Sebastian correlation. Therefore, for hydrogen, $d\delta_H/dT = 0$.

Experimental calorimetric data do not exist for the partial enthalpy of dissolved hydrogen, nor for the total enthalpy of hydrogen solutions at the temperatures and pressures of this study. But indirect partial enthalpy data have been derived from the accurate volumetric and phase equilibrium data on hydrogen + benzene mixtures of Connolly (1962). Figure 1 shows the results for hydrogen at infinite dilution in liquid solution at a total pressure equal to the vapor pressure of benzene. Also shown in Figure 1 are calculated values from Eq. 3 of this work and from the Chueh and Deal correlation. Both correlations give reasonable results with Eq. 3 being consistently closer to Connolly's results.

Unfortunately no test with experimental data can be made for Eq. 3 for the enthalpy of dissolved hydrogen at finite concentrations and at total pressures above the vapor pressure of the pure solvent. To illustrate the predictions of Eq. 3, we made calculations for hydrogen dissolved in benzene and in 1-methylnaphthalene at the experimentally observed conditions of temperature, pressure, and mole fraction in the liquid. The experimental conditions for the hydrogen + benzene mixtures were taken from Connolly (1962), and the results are shown in Figure 2. The experimental conditions for the hydrogen + 1-methylnaphthalene mixtures were from Yao et al. (1977), and the results are shown in Figure 3. The calculated values of $(\bar{H} - \tilde{H}^*)$ are positive and large, indicating a large quantity of heat absorbed per mole of hydrogen dissolved. There is a regular pattern of slightly decreasing values at a fixed temperature as pressure (and liquid mole fraction) increases.

We also show in Figures 2 and 3 the calculated values from Chueh and Deal's correlation. The two correlations are in agreement for benzene mixtures at the lower temperatures. However, at the higher temperatures Chueh and Deal's values increase as pressure (and x_H) increases. This trend is not observed in our results.

The results for hydrogen in 1-methylnaphthalene in Figure 3 show that the two correlations agree to within 20% but the details can be different. There is again the tendency for Chueh and Deal's values to increase as pressure (and x_H) increases at a high temperature. Again this trend is not observed in our results.

PARTIAL ENTHALPY OF THE SOLVENT

The partial enthalpy of the solvent in hydrogen mixtures can be obtained from the partial enthalpy of hydrogen by using the thermodynamic relation.

$$(x_s\,d\bar{H}_s + x_{\mathrm{H}}d\bar{H}_{\mathrm{H}} = 0)_{T,p} \tag{11}$$

Integrating Eq. 11 from $x_{\mathrm{H}} = 0$ to the concentration of interest, we obtain

$$\left[\bar{H}_s - \tilde{H}_s = \int_{x_{\mathrm{H}}=0}^{x_{\mathrm{H}}}\left(-\frac{x_{\mathrm{H}}}{x_s}\frac{\partial\bar{H}_{\mathrm{H}}}{\partial x_{\mathrm{H}}}\right)dx_{\mathrm{H}}\right]_{T,p} \tag{12}$$

The integrand of Eq. 12 is derived upon differentiation of Eq. 3,

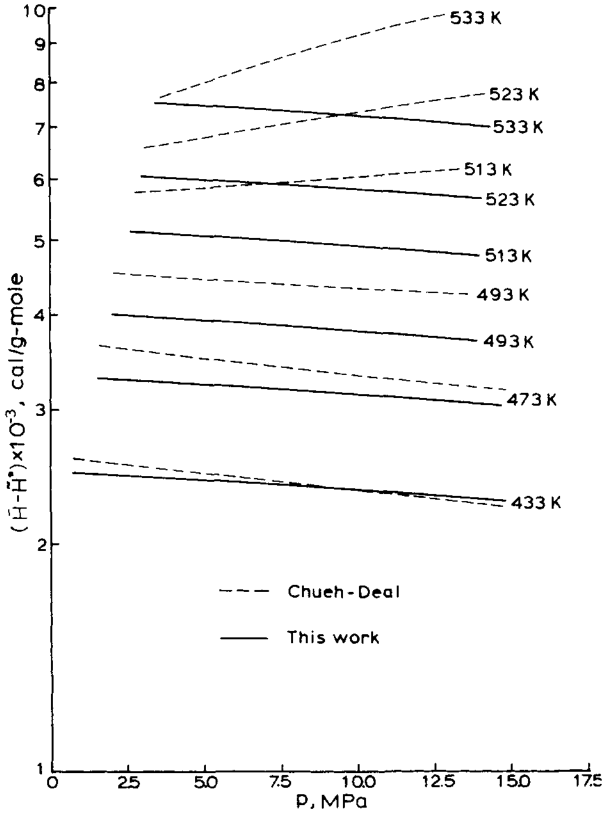

Figure 2. Partial molal enthalpy of hydrogen in liquid benzene.

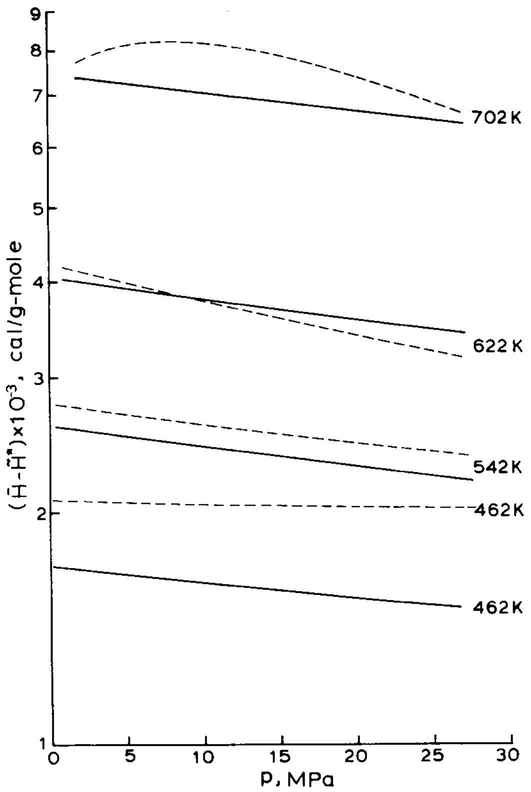

Figure 3. Partial molal enthalpy of hydrogen in liquid 1-methylnaphthalene.

$$
\begin{aligned}
-\frac{1}{RT^2}\frac{\partial\overline{H}_\mathrm{H}}{\partial x_\mathrm{H}} &= \frac{\partial g_1}{\partial\bar{\delta}}\frac{\partial\bar{\delta}}{\partial x_\mathrm{H}} + \frac{\partial g_2}{\partial\bar{\delta}}\frac{\partial\bar{\delta}}{\partial x_\mathrm{H}}\frac{\partial\bar{\delta}}{\partial T} \\
&\quad + g_2\frac{\partial^2\bar{\delta}}{\partial x_\mathrm{H}\partial T} + \frac{\partial g_3}{\partial\bar{\delta}}\frac{\partial\bar{\delta}}{\partial x_\mathrm{H}}\frac{p}{RT} \\
&\quad + \frac{\partial g_4}{\partial\bar{\delta}}\frac{\partial\bar{\delta}}{\partial x_\mathrm{H}}\frac{d\bar{\delta}}{dT}\frac{p}{RT} + g_4\frac{\partial^2\bar{\delta}}{\partial x_\mathrm{H}\partial T}\frac{p}{RT} \qquad (13)
\end{aligned}
$$

The integration of Eq. 12 is complicated analytically. We used a numerical procedure to evaluate the integral. The results are illustrated in Figure 4 for 1-methylnaphthalene in solution with hydrogen. The change in partial enthalpy of 1-methylnaphthalene from that of the pure liquid is too small to make a difference when compared to the other terms in the calculations of the enthalpy of the solution. The partial enthalpy of the solvent is about equal to that of the pure liquid.

SUMMARY

A general equation is presented for the partial enthalpy of hydrogen dissolved in a liquid hydrocarbon solution. The equation is derived from the fugacity correlation of Sebastian et al., which is applicable at temperatures from 310 to 700 K and pressures to 30 MPa, and for a wide variety of solvents, including paraffins, mono- and poly-nuclear aromatics, naphthenes, and hetero-atom containing hydrocarbons. The fugacity equation has been thoroughly tested with experimental data, but the enthalpy equation cannot be tested because of a lack of calorimetric experimental data. Comparison with the meagre indirect experimental data indicates the new enthalpy equation to be highly successful.

The enthalpy of the solvent is found to be changed only insignificantly by the dissolved hydrogen from its value as a pure liquid at pressures up to 30 MPa.

ACKNOWLEDGMENT

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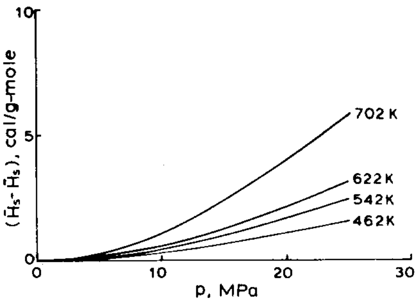

Figure 4. Enthalpy change for 1-methylnaphthalene in solution with hydrogen.

TABLE 1. COEFFICIENTS IN EQS. 4-7

$A_1 = 3.09197$	$B_1 = -91.813$
$A_2 = -2.8823 \times 10^{-3}$	$B_2 = 0.4486$
$A_3 = -3.3060 \times 10^{-3}$	$B_3 = -6.8692 \times 10^{-5}$
$A_4 = 1.3117 \times 10^{-3}$	$B_4 = 13.980$
$A_5 = -1.0410 \times 10^{-7}$	$B_5 = -0.3780$
$A_6 = 1{,}117.88$	$B_6 = -3.7818 \times 10^{-2}$

NOTATION

f = fugacity, MPa
g = function defined by Eqs. 4–7
H = enthalpy, cal/g·mole
p = pressure, MPa
R = gas constant [= 1.987 (cal) (g·mole)$^{-1}$ (K)$^{-1}$ on the left hand side of Eqs. 2 and 3; = 8.314 (mL) (MPa) (g·mole)$^{-1}$ (K)$^{-1}$ on the right hand side of Eq. 3]
T = temperature, K
V = volume, mL
x = mole fraction

Greek Letters

δ_i = solubility parameter of component i, (cal/mL)$^{0.5}$
$\bar{\delta}$ = solubility parameter of solution, (cal/mL)$^{0.5}$

Subscripts

H = hydrogen
i,j = components
M = mixture
p = at system pressure
S = solvent
w = van der Waals volume

Superscripts

$*$ = ideal gas state
∞ = infinite dilution
$\sim$ = per mole
$-$ = partial molal

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