The Heat of Solution of Gases at High Pressure

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The enthalpy change which occurs when a gas dissolves in a liquid can be measured by direct calorimetry or calculated from phase-equilibrium data. A knowledge of this heat effect may be required in process design work for which equilibrium data have already been obtained; thus a direct calculation procedure provides an alternative to the difficult experimental problems of high-pressure calorimetry.

The purpose of this paper is to derive a general expression for the heat of solution and to demonstrate its use in an approximate form at moderate vapor densities, showing the effects of vapor- and liquid-phase nonideality.

DERIVATION OF THE GENERAL EQUATION FOR A BINARY SYSTEM

Consider a homogeneous phase of two components. The total differential of the chemical potential of component one is given (*1*) by

$$d\mu_1 = -\bar{s}_1\,dT + \bar{v}_1\,dP + \left(\frac{\partial \mu_1}{\partial \ln x_1}\right)_{T,P} d\ln x_1 \qquad (1)$$

Writing Equation (1) for both liquid and vapor phases (with suitable superscripts) and subtracting one gets

$$d(\mu_1{}^l - \mu_1{}^g) = -(\bar{s}_1{}^l - \bar{s}_1{}^g)dT + (\bar{v}_1{}^l - \bar{v}_1{}^g)dP + \left(\frac{\partial \mu_1{}^l}{\partial \ln x_1}\right)_{T,P} d\ln x_1 - \left(\frac{\partial \mu_1{}^g}{\partial \ln y_1}\right)_{T,P} d\ln y_1 \qquad (2)$$

If the two phases are in equilibrium during this differential change, then

$$\mu_1{}^l = \mu_1{}^g \qquad (3)$$

and since the identity

$$\mu_1{}^l = \bar{h}_1 - T\bar{s}_1$$

may be written for each phase, then

$$\bar{s}_1{}^l - \bar{s}_1{}^g = \frac{\bar{h}_1{}^l - \bar{h}_1{}^g}{T} \equiv \frac{\Delta\bar{h}_1}{T} \qquad (4)$$

$\mu_1{}^l$ is related to the liquid phase activity coefficient by

$$d\mu_1{}^l = RT\,d\ln \gamma_1 x_1 f_1{}^l \qquad (5)$$

and therefore

$$\left(\frac{\partial \mu_1{}^l}{\partial \ln x_1}\right)_{T,P} = RT\left[1 + \left(\frac{\partial \ln \gamma_1}{\partial \ln x_1}\right)_{T,P}\right] \qquad (6)$$

Similarly $\mu_1{}^g$ is related to the vapor phase fugacity coefficient by

$$d\,\mu_1{}^g = RT\,d\ln \phi_1\, y_1\, P \qquad (7)$$

and therefore

$$\left(\frac{\partial \mu_1{}^g}{\partial \ln y_1}\right)_{T,P} = RT\left[1 + \left(\frac{\partial \ln \phi_1}{\partial \ln y_1}\right)_{T,P}\right] \qquad (8)$$

Substituting Equations (3), (4), (6), and (8) into (2) and rearranging one has at constant pressure

$$\frac{\Delta\bar{h}_1}{R} = \left[1 + \left(\frac{\partial \ln \phi_1}{\partial \ln y_1}\right)_{T,P}\right]\left(\frac{\partial \ln y_1}{\partial\, 1/T}\right)_P - \left[1 + \left(\frac{\partial \ln \gamma_1}{\partial \ln x_1}\right)_{T,P}\right]\left(\frac{\partial \ln x_1}{\partial\, 1/T}\right)_P \qquad (9)$$

This equation is perfectly general, as no simplifying physical assumptions have been made. However its application in this form requires extensive data in the single-phase vapor and liquid regions.

The derivatives with respect to y_1 and x_1 in Equation (9) will be referred to as the vapor-and liquid-phase corrections, respectively.

VAPOR-PHASE CORRECTION

At moderate vapor densities the vapor-phase equation of state may be approximated by the virial expansion through the second virial coefficient, in which case (3)

$$\ln \phi_i = -\ln z + \frac{2}{v^g}\sum_j y_i y_j B_{ij} + \ldots \qquad (10)$$

and from this equation one finds that

$$\left(\frac{\partial \ln \phi_1}{\partial \ln y_1}\right)_{T,P} = -2\ y_1 y_2 \frac{\delta}{v^g} + \ldots \qquad (11)$$

where

$$\delta \equiv 2B_{12} - B_1 - B_2$$

LIQUID-PHASE CORRECTION

Consider a differential change in chemical potential along a constant temperature equilibrium path, for which one may write

$$\left(\frac{\partial\,\mu_1{}^l}{\partial \ln x_1}\right)_{T,P} d\ln x_1 + \left(\frac{\partial\,\mu_1{}^l}{\partial \ln P}\right)_{T,x_1} d\ln P = \left(\frac{\partial\,\mu_1{}^g}{\partial \ln y_1}\right)_{T,P} d\ln y_1 + \left(\frac{\partial\,\mu_1{}^g}{\partial \ln P}\right)_{T,y_1} d\ln P \qquad (12)$$

The derivatives with respect to composition have been given in Equations (6) and (8), and from Equations (1) and (7) one has

$$\left(\frac{\partial\,\mu_1{}^l}{\partial \ln P}\right)_{T,x_1} = \bar{v}_1{}^l P$$

$$\left(\frac{\partial\,\mu_1{}^g}{\partial \ln P}\right)_{T,y_1} = RT\left[1 + \left(\frac{\partial \ln \phi_1}{\partial \ln P}\right)_{T,y_1}\right]$$

TABLE 1. CALCULATED HEAT OF SOLUTION OF METHANE IN DECANE AT 1,000 LB./SQ. IN. ABS.

T, °F.	$\Delta\bar{h}_1$, B.t.u./lb. mole Equation (17)	Equation (16)
220	—660	—610
280	—420	—400
340	+540	+410
400	+2,100	+1,500

TABLE 2. CALCULATED VALUES OF TERMS IN EQUATIONS (15) AND (16)

T, °F.	$10^4\beta$, atm.$^{-1*}$ at $x_1 = 0.200$	$\dfrac{\overline{v}_1{}^l P^*}{RT}$	$2y_1y_2\dfrac{\delta}{v^g}$ $P = 100$ lb./sq. in. abs.	$P = 1{,}000$ lb./sq. in. abs.	$(B_1 + y_2{}^2\delta)/v^g$ $P = 100$ lb./sq. in. abs.	$P = 1{,}000$ lb./sq. in. abs.
220	4.2	0.18	0.03	0.08	—0.004	—0.05
280	4.9	0.17	0.06	0.14	—0.001	—0.03
340	6.5	0.19	0.10	0.24	0.007	—0.01
400	10.5	0.25	0.14	0.38	0.03	0.007

* P = 1,000 lb./sq. in. abs.

Upon substitution of these four derivatives into Equation (12) one finds, after rearrangement, that

$$\left(\frac{\partial \ln \gamma_1}{\partial \ln x_1}\right)_{T,P} = \left[1 + \left(\frac{\partial \ln \phi_1}{\partial \ln y_1}\right)_{T,P}\right] \left(\frac{\partial \ln y_1}{\partial \ln x_1}\right)_T + \left[1 + \left(\frac{\partial \ln \phi_1}{\partial \ln P}\right)_{T,y_1} - \frac{P\overline{v}_1{}^l}{RT}\right] \left(\frac{\partial \ln P}{\partial \ln x_1}\right)_T - 1 \quad (13)$$

where the derivatives for which only temperature is held constant are obtainable from phase-equilibrium data. From Equation (10) one may show that

$$\left(\frac{\partial \ln \phi_1}{\partial \ln P}\right)_{T,y_1} = \frac{B_1 + y_2{}^2\delta}{v^g} + \ldots \quad (14)$$

Partial molar volume is related (2) to molar volume by

$$\overline{v}_1 = v + x_2\left(\frac{\partial v}{\partial x_1}\right)_{T,P}$$

where

$$\left(\frac{\partial v}{\partial x_1}\right)_{T,P} = \left(\frac{\partial v}{\partial x_1}\right)_T - \left(\frac{\partial v}{\partial P}\right)_{T,x_1}\left(\frac{\partial P}{\partial x_1}\right)_T$$

If one combines these two equations and introduces the isothermal compressibility β, the partial molar liquid volume appearing in Equation (13) may be written

$$\overline{v}_1{}^l = v^l\left\{1 + \frac{x_2}{x_1}\left[\left(\frac{\partial \ln v^l}{\partial \ln x_1}\right)_T + \beta P\left(\frac{\partial \ln P}{\partial \ln x_1}\right)_T\right]\right\} \quad (15)$$

where the constant temperature derivatives, as before, can be calculated from equilibrium data in the two-phase region. Thus the only remaining quantity involving data in a single-phase region is the liquid-phase compressibility

$$\beta \equiv -\frac{1}{v^l}\left(\frac{\partial v^l}{\partial P}\right)_{T,x_1}$$

The compressibility of most liquids is about 10^{-4} atm.$^{-1}$; however this value may be increased by at least an order of magnitude for a liquid containing an appreciable quantity of dissolved gas (see Table 2). It would therefore be desirable to have liquid phase compressibility data, although Equation (15) will in some cases be relatively insensitive to β.

APPROXIMATE FORMS OF THE HEAT OF SOLUTION EQUATION

Heats of solution may be calculated at moderate pressures by introducing Equations (11), (13), and (14) into Equation (9) to give

$$\frac{\Delta\overline{h}_1}{R} = \left[1 - 2y_1y_2\frac{\delta}{v^g}\right]\left(\frac{\partial \ln y_1}{\partial\, 1/T}\right)_P - \left\{\left[1 - 2y_1y_2\frac{\delta}{v^g}\right]\left(\frac{\partial \ln y_1}{\partial \ln x_1}\right)_T + \left[1 + \frac{B_1 + y_2{}^2\delta}{v^g} - \frac{\overline{v}_1{}^l P}{RT}\right]\left(\frac{\partial \ln P}{\partial \ln x_1}\right)_T\right\}\left(\frac{\partial \ln x_1}{\partial\, 1/T}\right)_P \quad (16)$$

where $\overline{v}_1{}^l$ is calculated from Equation (15). If the vapor density is low enough that the terms in $1/v^g$ in Equation (16) may be neglected, and if the partial pressure is given by Henry's Law

$$y_1P = Mx_1$$

then Equation (16) reduces to the customary forms

$$\frac{\Delta\overline{h}_1}{R} = \left(\frac{\partial \ln y_1/x_1}{\partial\, 1/T}\right)_P = \left(\frac{\partial \ln K}{\partial\, 1/T}\right)_P = \left(\frac{\partial \ln M}{\partial\, 1/T}\right)_P \quad (17)$$

If the solvent is essentially nonvolatile at the temperature of interest, then it follows from Equation (17) that the heat of solution can be obtained simply from the temperature coefficient of gas solubility

$$\frac{\Delta\overline{h}_1}{R} = -\left(\frac{\partial \ln x_1}{\partial\, 1/T}\right)_P \quad (18)$$

If the solvent is volatile but the low pressure and Henry's Law assumptions are still valid, Equations (2), (3), and (4) may be combined to give

$$\frac{\Delta\overline{h}_1}{R}\, d\left(\frac{1}{T}\right) = -\frac{\Delta\overline{v}_1}{RT}\, dP + d\ln y_1 - d\ln x_1$$

In this low-pressure region

$$-\frac{\Delta\overline{v}_1}{RT} \simeq \frac{\overline{v}_1{}^g}{RT} \simeq \frac{1}{P}$$

If one combines these two equations and imposes the restriction of constant partial pressure

$$\frac{\Delta\overline{h}_1}{R} = -\left(\frac{\partial \ln x_1}{\partial\, 1/T}\right)_{y_1P} \quad (19)$$

This equation involves the same assumptions as Equation (17) but is more convenient when data are reported at constant partial pressure.

CALCULATED HEAT OF SOLUTION FOR THE METHANE-DECANE SYSTEM

The heat of solution of methane in decane has been calculated at 1,000 lb./sq. in. abs. and four different temperatures from phase-equilibrium data reported by Sage and Lacey (5). Equations (16) and (17) were used with the virial coefficients needed in Equation (16) computed from gas phase volumetric data by methods described elsewhere (4).

The results are shown in Table 1. The estimated uncertainty is about 10% of the calculated value and is due almost entirely to the stated 1% uncertainty in the experimental liquid-phase compositions which points out once again the necessity for accurate phase-equilibrium data. The use of Equation (16) is not warranted at the lower temperatures in this case, but the nonideality corrections make a significant contribution to the calculated heat of solution at 340° and 400°F.

The magnitudes of some of the terms in Equations (15) and (16) are given in Table 2. Note that the quantity $2y_1y_2(\delta)/(v^g)$ becomes comparable to unity at the higher temperatures although the vapor density is slightly lower. This is due to the large increase in mole fraction of the heavy component in the vapor. At very high densities third virial coefficients become important, and Equations (11) and (14) will require an additional term.

MULTICOMPONENT SYSTEMS

The general equation for the heat of solution of component i in a c-component system may easily be written down by a derivation similar to the binary case. The result is

$$\frac{\Delta\bar{h}_i}{R} = \sum_{j=1}^{c-1}\left[1 + \left(\frac{\partial \ln \phi_i}{\partial \ln y_j}\right)_{T,P,y_{k\neq j}}\right] \left(\frac{\partial \ln y_j}{\partial 1/T}\right)_P - \sum_{j=1}^{c-1}\left[1 + \left(\frac{\partial \ln \gamma_i}{\partial \ln x_j}\right)_{T,P,x_{k\neq j}}\right]\left(\frac{\partial \ln x_j}{\partial 1/T}\right)_P \tag{20}$$

The phase rule allows c-2 composition variables to be fixed as temperature is varied at constant pressure, which would simplify the equation but would be experimentally awkward. As it stands Equation (20) requires a prohibitively large amount of experimental information for systems of more than two or perhaps three components.

CONCLUSION

At moderate vapor densities Equation (16), which includes the effect of vapor and liquid nonideality, permits a more accurate calculation of heats of solution than Equation (17), provided the experimental data are sufficiently accurate to warrant its use.

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NOTATION

B = second virial coefficient
f = fugacity
$\bar{h}$ = partial molar enthalpy
K = y/x
M = Henry's Law constant
P = total pressure
R = gas constant
$\bar{s}$ = partial molar entropy
T = absolute temperature
v = molar volume
$\bar{v}$ = partial molar volume
x = mole fraction in liquid phase
y = mole fraction in vapor phase
z = PV/RT
γ = liquid phase activity coefficient
μ = partial molar Gibbs free energy
ϕ = vapor phase fugacity coefficient

Subscripts

$i, j, 1, 2, k, c$ = component
1 = lighter component

Superscripts

l = liquid phase
g = vapor phase

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High Temperature Transport Properties of Gases; Limitations of Current Calculating Methods in the Light of Recent Experimental Data

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Requirements for satisfactory calculation of high temperature transport properties are discussed, with special emphasis on the role of the intermolecular potential. The determination of appropriate pair potentials from scattering of high energy neutral beams is described, and potentials obtained from helium, neon, argon, krypton, and xenon, each scattered by its own gas, are tabulated. Similar potentials are given for helium scattered by argon, nitrogen, methane, monofluoromethane, difluoromethane, trifluoromethane, and tetrafluoromethane; neon by argon; argon by hydrogen and nitrogen; atomic hydrogen by helium and hydrogen; and atomic deuterium by deuterium gas. Average potentials derived from suitable combinations of these experimental potentials are given for the like-particle systems of nitrogen, methane, monofluoromethane, difluoromethane, trifluoromethane, and tetrafluoromethane.

Results of calculations which use suitable and unsuitable potential functions are shown in tabulated form for the coefficient of viscosity, the coefficient of self-duffusion, and the isotopic reduced thermal diffusion ratio of argon and of nitrogen, and in graphical form for the coefficient of viscosity of xenon.

The rapidly increasing interest in the physics and chemistry of the upper atmosphere, combustion, detonation, and high-speed gas dynamics has focused attention on the lack of suitable information concerning gaseous transport properties at high temperatures. Direct measurements of these properties cannot usually be made at temperatures above about 1,000°K., and long range extrapolations from low temperatures are almost certain to be in serious error (*1*), since they incorrectly assume that the semiempirical potential functions which are suitable for the relatively large internuclear separations of importance at low temperatures will also be adequate at the smaller separations of importance at high temperatures. It is obviously worthwhile to see if it is possible to make accurate, direct calculations of transport properties at elevated temperatures.

A satisfactory calculation procedure must meet three necessary conditions:

1. The actual species present at the densities of interest must be known.
2. A suitable formal kinetic theory must exist which can be properly applied to the transport properties of these species.
3. Quantitative information must be available concerning the intermolecular