HEATS OF VAPORIZATION OF NONELECTROLYTES

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Received June 7th, 1977

The first-order perturbation theory of liquids was used for developing an approximate expression suitable for a rapid calculation of the heat of vaporization of nonpolar liquids formed by approximately spherical molecules. The calculation uses only available physico-chemical properties of substances, namely the critical data. The results are tested by a comparison with existing experimental data on a series of nonpolar substances. The agreement between calculated values and experimental data is relatively good. The maximum deviation between theoretical and experimental values does not exceed ±10%.

In the solution of many chemical-engineering and physico-chemical problems, the knowledge of heats of vaporization and mixing of nonelectrolytes and of their temperature dependences is often required. Owing to this fact, a considerable attention is being paid to the experimental as well as theoretical study of this problem. Especially, recently developed perturbation methods in the statistical mechanics of fluids[1-3] offer a possibility for an easy prediction of different thermodynamic functions.

This paper is dealing with a rapid and simple application of the perturbation methods to the calculation of enthalpic quantities. The relation proposed is tested by a comparison with available literature data.

THEORETICAL

Perturbation methods[1-3] commonly employed in statistical-thermodynamics calculations of fluids make use of the knowledge of the structure and, consequently, of properties of a certain reference system, which approximates closely, by the arrangement of its particles, the system studied. As a reference, the hard-sphere system is most often selected, since it represents in a simple manner repulsive forces, which affect most significantly the structure and related thermodynamic properties of the real system. Due to the extreme simplicity of the hard sphere potential curve, thermodynamic functions of this reference system can be determined with high accuracy. Deviations in the behaviour of real systems from reference ones, which are brought about mainly by the existence of attractive forces, are interpreted in these methods as perturbations.

The first-order perturbation method yields the following expression for the Helmholtz free energy F of the system studied[1]

$$F = F_0 + 2\pi nN \int_0^\infty u_p(r)\, g_0(r)\, r^2\, \mathrm{d}r\,, \tag{1}$$

where $n = N/V$ is the average number density, N Avogadro's constant, V molar volume, r intermolecular distance, $u_p(r)$ perturbation potential (the difference between the potential used for the description of interactions in the system investigated and the reference potential), $g_0(r)$ radial distribution function in the reference hard-sphere system and F_0 Helmholtz free energy of the reference system.

Intermolecular interactions in liquids investigated were approximated by a simple square-well potential defined by

$$\begin{aligned} u(r) &= +\infty\,, \quad \text{for} \quad && r \leqq \sigma\,, \\ u(r) &= -\varepsilon\,, && \sigma < r \leqq \gamma\sigma\,, \\ u(r) &= 0\,, && r < \gamma\sigma\,. \end{aligned} \tag{2}$$

The parameters ε and σ were obtained from generalized relations[4] (recommended for parameters ε_{LJ} and σ_{LJ} in the Lennard–Jones 12 : 6 potential) as $\varepsilon = 0{\cdot}56\varepsilon_{LJ}$, $\sigma = \sigma_{LJ}$. The parameter γ was obtained from the equality between the value of the second virial coefficient B and the expression for this coefficient in a system of particles obeying the square-well potential. This equality leads to

$$\gamma^3 = (1 - B/b_0 + \Delta)/\Delta\,, \tag{3}$$

where $\Delta = \exp(\varepsilon/kT) - 1$, k is Boltzmann's constant and b_0 is the second virial coefficient in the hard sphere system ($b_0 = 2/3\pi N\sigma^3$). Values of the coefficient B were obtained from the Redlich–Kwong generalized relation[5].

As a reference, we considered the system of hard spheres with their diameter d equal to the parameter σ of the square-well potential.

Lengthy numerical integration, required by a relatively complicated course of the radial distribution function in the hard sphere system, was avoided by the following approximation: it was found by a numerical analysis of courses of $g_0(r)$ obtained from the solution of the Percus–Yevick equation[6] that at densities $y = (\pi/6)\, n\sigma^3$ of most liquids from the range $y \in \langle 0{\cdot}37, 0{\cdot}58 \rangle$, $g_0(r)$ drop for the first time to the value $g_0 = 1$ on the average at $r/\sigma = \lambda = 1{\cdot}275$ ($\pm 0{\cdot}075$) and that it only weakly oscillates about the value $g_0(r > \lambda\sigma) = 1$ at $r > \lambda\sigma$ (Fig. 1). At $r > \sigma$, the course of the radial distribution function was replaced by a straight line starting at the contact point of hard spheres, which is given by the Carnahan–Starling approximation[7]

$$g_0(r = \sigma) = \frac{1}{2}(2 - y)/(1 - y^3)\,, \tag{4}$$

and ending at $r = \lambda\sigma$ and $g_0(r = \lambda\sigma) = 1$.

At $r > \lambda\sigma$, the function $g_0(r)$ was approximated by constant $g_0 = 1$. Since in this simple variant the hard-sphere diameter is independent of temperature, the integrand in Eq. (*1*) is also independent of temperature and the perturbation contribution to the internal energy, $\Delta U = U - U_0$, where U_0 is the internal energy of the reference system at the same temperature and volume, is given by

$$\Delta U = 2\pi n N \int_0^\infty u_p(r)\, g_0(r)\, r^2\, \mathrm{d}r\,, \tag{5}$$

where $u_p(r) = u(r)$ for $r > \sigma$ and $u_p(r) = 0$ for $r \leqq \sigma$. The use of the above approximations yields the simple expression

$$\Delta U = -\boldsymbol{R} y\varepsilon/\boldsymbol{k}[4y^3 + 1{\cdot}9728 g_0(\sigma, y) - 5{\cdot}9736]\,, \tag{6}$$

in which $\boldsymbol{R}$ denotes the universal gas constant and the symbol $g_0(\sigma, y)$ emphasizes the dependence on density.

The number density y was determined also by using the perturbation approach, namely by solving the equation

$$z(y) = z_{\mathrm{CS}}(y) + y\,\frac{\partial}{\partial y}\,[(F - F_0)/NkT]_T = 0\,. \tag{7}$$

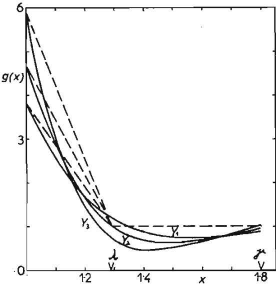

FIG. 1

The Illustration of the Approximations Used for the Radial Distribution Functions $g(x)$ in the Reference Hard-Sphere System As Functions of $x = r/\delta$

Exact courses for three values of the reduced density $y_1 = 0{\cdot}37$, $y_2 = 0{\cdot}475$, $y_3 = 0{\cdot}58$ (full line) are approximated always by two linear sections (dashed line).

In this equation, $z(y)$ is the compressibility factor and $z_{cs}(y)$ is the Carnahan–Starling approximation to this quantity for a hard sphere system

$$z_{cs}(y) = (1 + y + y^2 + y^3)/(1 - y^3) . \tag{8}$$

Taking into account the properties of the hard-sphere system and the approximations employed, we can approximate the heat of vaporization of liquids investigated by

$$\Delta H_{vap} = -\Delta U + p\,\Delta V = -\Delta U + RT . \tag{9}$$

Eq. (*9*) was used for calculating the heat of vaporization of substances with a negligible or weak polarity and with insignificant deviations from the spherical symmetry.

RESULTS AND DISCUSSION

The results of our calculations are given in Table I. Agreement with a available literature data[8-10] is relatively good. The deviations do not exceed ±10%, mostly ranging up to ±6%, which is satisfactory since most parameters affecting the results were calculated from approximate expressions.

TABLE I

Parameters Employed for the Sqaure-Well Potential and the Comparison between Calculated Values of Heats of Vaporization (J . mol^{-1}) and Experimental Data[a]

Substance	ε	σ	γ	T, K	ΔH_{calc}	ΔH_{exp}	δ[b]
C_6H_{12}	349·36	5·5109	1·7969	298·15	31 335	33 037	−0·052
CS_2	348·73	4·4484	1·7979	273·15	27 996	28 483	−0·017
CH_2Cl_2	322·20	4·6861	1·7964	313·65	30 416	27 940	0·089
CCl_4	351·38	5·3089	1·7970	273·15	33 066	33 543	−0·014
C_5H_{10}	323·215	5·1785	1·7973	298·15	26 768	28 498	−0·060
$CHCl_3$	338·88	4·9359	1·7971	313·15	27 983	30 428	−0·080
C_7H_8	375·13	5·6291	1·7969	298·15	39 213	38 016	0·030
Ar[c]	67·09	3·4050	1·8000	115·80	5 505[d]	—	—
Kr[c]	93·69	3·6330	1·8000	115·80	10 523[d]	—	—

[a] Values of ΔH_{exp} taken from ref.[8-10]; [b] $\delta = (\Delta H_{calc} - \Delta H_{exp})/\Delta H_{exp}$; [c] Values of the parameters ε, σ, γ taken from ref.[14]; [d] Results of calculations from the literature: Monte-Carlo Ar 4945 (ref.[14]), Kr 8523 (ref.[14]); the perturbation theory Ar 4706 (ref.[15]), 5069 (ref.[16]), Kr 8211 (ref.[15]), 8506 (ref.[16]).

Calculated values of density y (resp. volume V) exhibit excellent agreement with experimental data (below 5% independently of the initial value in the solution of the equation $z(y) = 0$). Theoretical values of density were then used in our calculations. (Deviations in ΔH_{vap} when calculated from experimental or theoretical values of density, resp., were lower than 2%).

The calculation itself is based on an approximate use of the first-order perturbation expansion. The reference radial distribution function was employed also for particles with a lower symmetry. Within the range of the potential interaction it was replaced with two linear sections. It is obvious from Fig. 1 that this replacement is most accurate in the low density region.

Further, we constructed the dependence $\lambda = \lambda(y)$ for several values of y and found out that this modification improves in most cases the agreement with experimental data (at higher densities by ~2%).

One of the reasons for quantitative deviations from experimental data is a simplified approximation of intermolecular forces by the square-well potential, which cannot describe accurately the intermolecular interaction.

In the liquid region, where distances between particles are relatively short, we can use the potential which cuts off more remote interactions without a danger of deteriorating the results to a greater extent. The quantitative agreement depends on a suitable selection of parameters ε, σ and γ. The rules employed for determining ε and σ had been recommended for the Lennard–Jones potential[4]. In our case, the correction to the realistic course was performed by a procedure leading to the parameter γ. The fact, that the potential employed is on the whole a plausible approximation to the reality, is manifested by the scatter among values of γ obtained from the virial coefficients at different temperatures which does not exceed 2–3% within 100°C. In our work we used the value at the boiling point. The square-well potential parameters employed are given in Table I.

Certain inaccuracies are brought about by the use of spherically symmetrical functions for molecules with a lower symmetry. In comparison with the other approximations employed, however, this inadequacy is less apparent than in more accurate applications of the perturbation expansion[11,12]. The simplified potential cannot describe well the behaviour in a wider temperature range.

To be able to evaluate the agreement between the theory and experiment on data which are not affected by the uncertainty due to the approximation of real intermolecular forces, we performed a comparison with pseudoexperimental Monte-Carlo data[14] (which correspond to the behaviour of Ar and Kr – *cf.* Table I). The agreement is satisfactory even in this case.

It was not the aim of our work to find an empirical procedure which would yield the most accurate relation for estimating the value of ΔH_{vap}, since existing empirical rules (*e.g.*, by Kistiakowski[12]) can predict this quantity for nonpolar liquids at the normal boiling point with good accuracy. Our derivation starts from and strictly adheres to model conceptions of the statistical mechanics and, simultaneoulsy, it follows the idea of obtaining simple relations (*6*) and (*9*). Neither incorrect and unnatural assumptions nor empirical constants were used in our derivation, only several functions were simplified mathematically. Parameters of the intermolecular interaction were calculated from critical data by using generalized methods.

A further mathematical simplification in which values of density y are calculated from the Watson relation[13] instead of the solution to Eq. (*7*), gives approximately the same agreement with experimental data.

The agreement between experimental data and calculated values of ΔH_{vap} of the testing substances may be denoted, with respect to the approximations employed, as satisfactory; the maximum deviation is $\pm 10\%$.

In our next communication we are going to apply this simplified variant of the perturbation method to the calculation of the heat of mixing.

Thanks are due to Dr M. Smíšek for his interest and support, which enabled to complete this work, and to Dr V. Křesťanová for her friendly help with the review of the manuscript.

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Translated by K. Hlavatý.