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High-Temperature Equation of State—Argon

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We have studied the first two terms of the high-temperature equation of state, $p/\rho kT = a(\rho) + b(\rho)/kT + c/(kT)^2 + \dots$, of a simple spherical fluid whose intermolecular potential is the sum of a hard core and soft (mostly attractive) contribution. $a(\rho)$ and $b(\rho)$ are known functionals of the pressure and radial distribution function of a fluid whose potential is solely composed of the hard-core contribution. Approximate expressions for $a(\rho)$ are obtained by using the hard-sphere equation of state and radial distribution function of the approximate Percus-Yevick theory. We show that $b(\rho)$ can be expressed directly as a quadrature of the Laplace transform of the approximate radial distribution function (which is explicitly known); no inversion of the transform is necessary. Choosing for the soft potential a truncated Lennard-Jones potential, we compare the resulting first two terms of the series with experimental data for argon for densities between 40 and 600 amagats and temperatures from 0 to 150°. The intercept $a(\rho)$ is in good agreement with that theoretically computed. The theory can reproduce the $b(\rho)$, found from experiment, if the parameters of the truncated Lennard-Jones potential are varied by about 5%.

1. Introduction

At sufficiently high temperatures the behavior of even dense, simple (supercritical) fluids will be largely determined by the "effective" hard cores of the molecules. The "soft" mostly attractive part of the inter-

molecular potential may then be treated as a small perturbation. It then becomes convenient to approximate the actual intermolecular potential, $u(r)$, which is not perfectly known anyway as a function of the intermolecular distance, r , by a sum of two terms in eq 1.1.

$$u(r) = u_h(r) + u_s(r) \quad (1.1)$$

where

$$u_h(r) = \begin{cases} \infty, & r < c\sigma \\ 0, & r > c\sigma \end{cases} \quad (1.2)$$

and $u_s(r)$ is a nonsingular "soft" potential for $r > c\sigma$, $c\sigma$ being the hard-core diameter. The equation of state can be then written in the form^{1,2}

$$p/\rho kT = a(\rho) + b(\rho)/kT + c(\rho)/(kT)^2 + \dots \quad (1.3)$$

with ρ the number density, k Boltzmann's constant, and T the temperature. The temperature-independent coefficients $a(\rho)$, $b(\rho)$, and $c(\rho)$ are readily given in terms of properties of the reference hard-sphere system, *i.e.*, a system for which $u_s(r) = 0$. Thus^{1,2}

$$a(\rho) = p_h/\rho kT \quad (1.4)$$

$$b(\rho) = 1/2\rho^2 \frac{\partial}{\partial \rho} \int_{c\sigma}^{\infty} u_s(r) \rho g_h(r) 4\pi r^2 dr, \text{ etc.}$$

with p_h the pressure and $g_h(r)$ the radial distribution function of the hard-sphere system. The expression for $c(\rho)$ unfortunately involves higher order (than the second) distribution functions of the hard-sphere system. It will be seen that the experimental data on one set of measurements are reasonably well fitted by the first-degree polynomial in $1/T$, although $c(\rho)/(kT)^2$ is required to attain the precision reported over the temperature interval studied. Previous attempts to evaluate (1.4) have employed a Lennard-Jones (6-12) potential for $u_s(r)$, for $r > c\sigma$ and either an approximate $g_h(r)$ obtained as a solution of the Kirkwood integral equation or the first few (four) terms of the virial development of $g_h(r)$.² Neither of these approximate $g_h(r)$ are satisfactory at sufficiently high densities ρ corresponding to real, supercritical fluids, and furthermore they require extensive machine computations. Wertheim³ and Thiele⁴ have obtained the explicit Laplace transform, $G(s)$, of the approximate hard-sphere radial distribution, $g_h(r)$,⁵ satisfying the Percus-Yevick (PY) integral equation

$$G(s) = \int_{c\sigma}^{\infty} e^{-sr} g_h(r) 4\pi r dr \quad (1.5)$$

This $g_h(r)$ leads to a (compressibility) equation of state, identical with that given by the Reiss-Frisch-Lebowitz (RFL) equation of state, which is in very good agreement over the whole fluid branch of densities with the results of machine computations of the equation of state. There is some reason to believe that the PY $g_h(r)$ give a good representation of the exact hard-sphere radial distribution function for densities below

the hard-sphere "phase transition." The coefficient $b(\rho)$ (*cf.* (1.4)) can be found directly from $G(s)$ and does not require inversion of (1.5). This will be shown in the next section.

There are as yet few experimental high-temperature supercritical P - V - T data available on dense, spherical, nonpolar fluids over a wide temperature range and none on mixtures. Ideally, the fluid should be one of the inert gases to conform to these criteria. We therefore have restricted the application of our high-temperature equation of state to the data of Michels, *et al.*,^{6,7} on argon which is just sufficiently extensive to make such a test worthwhile. This is done in section 3.

2. PY High-Temperature Equation of State

To express $b(\rho)$ as a quadrature over $G(s)$ we set

$$ru_s(r) = \int_0^{\infty} e^{-sr} U(s) ds \quad (2.1)$$

i.e., we assume that $ru_s(r)$ possesses a continuous inverse Laplace transform. Substituting (2.1) for $ru_s(r)$ in (1.4) and interchanging orders of integration, we find the desired relation

$$b(\rho) = 1/2\rho^2 \frac{\partial}{\partial \rho} \rho \int_0^{\infty} U(s) G(s) ds \quad (2.2)$$

Using Wertheim³ or Thiele's⁴ $G(s)$ and the RFL equation for $a(\rho)$

$$a(\rho) = \frac{p_h}{\rho kT} = \frac{1 + \eta + \eta^2}{(1 - \eta)^3} \quad (2.3)$$

where the dimensionless density is $\eta = \pi(c\sigma)^3 \rho/6$, one obtains the first few terms of the high-temperature expansion of the equation of state as

$$\frac{p}{\rho kT} = \frac{1 + \eta + \eta^2}{(1 - \eta)^3} + \frac{12\eta}{kT} \int_0^{\infty} f(s, \eta) U(s) ds + O(T^{-2}) \quad (2.4)$$

with $f(s, \eta)$ given in (2.5).

(1) R. W. Zwanzig, *J. Chem. Phys.*, **22**, 1420 (1954).

(2) E. B. Smith and B. J. Alder, *ibid.*, **30**, 1190 (1959).

(3) M. Wertheim, *Phys. Rev. Letters*, **8**, 321 (1963).

(4) E. Thiele, *J. Chem. Phys.*, **38**, 1959 (1963).

(5) See articles by G. Stell and J. Percus in "Classical Theory of Fluids," H. L. Frisch and J. L. Lebowitz, Ed., W. A. Benjamin, Inc., New York, N. Y., 1964.

(6) A. Michels, H. Wijker, and H. K. Wijker, *Physica*, **15**, 627 (1948).

(7) A. Michels, J. M. Levelt, and W. de Graff, *ibid.*, **28**, 659 (1958).

$$f(s, \eta) = s^4 e^{-s} [s(1 + \eta - 2\eta^2) + (2\eta + 1)^2] \{12\eta[(1 + \eta/2)s + (1 + 2\eta)]e^{-s} + (1 - \eta)^2 s^3 + 6\eta(1 - \eta)s^2 + 18\eta^2 s - 12\eta(1 + 2\eta)\}^{-2} \quad (2.5)$$

Specializing (2.4) further to the truncated Lennard-Jones $u_s(r)$, with characteristic energy ϵ and distance σ parameter

$$u_s(r) = \begin{cases} 0 & \text{for } r < c\sigma \\ 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] & \text{for } r > c\sigma \end{cases} \quad (2.6)$$

one finds, with $f(s, \eta)$ given by (2.5)

$$\frac{p}{\rho kT} = \frac{1 + \eta + \eta^2}{(1 - \eta)} + \frac{48\eta}{c^6} \left(\frac{\epsilon}{kT}\right) \times \int_0^\infty f(s, \eta) \left[\frac{s^{10}}{c^6 10!} - \frac{s^4}{4!} \right] ds + O(T^{-2}) \quad (2.7)$$

This is the basic relation to which we shall fit the experimental data of ref 6.

We remark that the generalizations of (1.3), (1.4), (2.2)–(2.7) can be written for mixtures of spherical molecules by using the approximate hard-sphere fluid mixture pair distribution functions resulting from the PY theory, whose explicit Laplace transforms have been obtained by Lebowitz.⁸ We omit writing these since there are no suitable data now available for their testing.

3. Comparison with Argon Data

The data of Michels, *et al.*, on argon (temperature range 0–150° and 40–600 amagats of density) were fitted to polynomials in $1/T$, *cf.* (1.3). Up to densities of 400 amagats, a second-degree polynomial suffices to represent the data to within a standard deviation smaller than the reported experimental uncertainty. Since only seven experimental temperatures are available, the coefficients in the third- and fourth-degree polynomials in $1/T$ fittings are too uncertain to be usable.⁹ The first degree in $1/T$ polynomial has a standard deviation 10 times larger than the experimental error and so was rejected. The contribution of the $c(\rho)/(kT)^2$ term to $p/\rho kT$ is small; it ranges between 0.05 and 10.3% from 40 to 600 amagats.

The location of the hard-sphere cutoff (the parameter c) was determined from the second-degree polynomial value of $a(\rho)$ at 40 amagats by inverting eq 2.3 and solving for c , with $\sigma = 3.405$ A.⁶ Using the value obtained, $c = 0.889$, in (2.3) we then calculated $a(\rho)$ (at 40-amagat intervals) up to a density of 600 amagats, and this is compared with the $a(\rho)$ obtained from the

quadratic in $1/T$ fit of the experimental data in Table I. The agreement is good. The apparent hard-core diameter, $c\sigma$, of argon is 3.027 A. Using this value of $c\sigma$ the reduced densities $\rho^* = {}^2/{}_3\pi(c\sigma)^3\rho$ were calculated and are shown in the second column of Table I.

Table I: Comparison of Experimental and Calculated Constant Term in the Equation $P/\rho kT = a(\rho) + b(\rho)/T$

ρ	ρ^*	$a(\rho)$ (exptl)	$a(\rho)$ (calcd)
40	0.0218	1.065	1.065
120	0.0655	1.207	1.212
200	0.1092	1.381	1.383
280	0.1529	1.588	1.586
360	0.1965	1.825	1.825
440	0.2402	2.094	2.108
520	0.2839	2.398	2.445
600	0.3275	2.735	2.848

At very high temperatures, well beyond the highest temperature of the data in ref 6 and 7, one expects the high-temperature equation of state to approach asymptotically a straight line when $p/\rho kT$ is plotted *vs.* $1/T$ for all densities. The asymptotic slope is $b(\rho)/k = B(\rho)$. Table II exhibits this apparent slope B_i , $i = 1, 2, 3$, obtained by fitting Michels, *et al.*, data^{6,7} by an i th-degree polynomial in $1/T$. For reasons already stated, we believe that the second degree in $1/T$ fit is

Table II: Comparison of Slopes Obtained on Fitting $P/\rho kT$ by Successive Polynomials in $1/T^a$

ρ	$B_1(\rho)$	$B_2(\rho)$	$B_3(\rho)$
40	-0.304 ± 0.002	-0.200 ± 0.007	-0.322 ± 0.09
120	-0.879 ± 0.007	-0.638 ± 0.006	-0.647 ± 0.09
200	-1.42 ± 0.01	-1.09 ± 0.01	-0.87 ± 0.13
280	-1.95 ± 0.01	-1.51 ± 0.02	-2.44 ± 0.15
360	-2.46 ± 0.02	-1.79 ± 0.04	-0.92 ± 0.17
440	-2.92 ± 0.03	-1.85 ± 0.05	-0.53 ± 0.21
520	-3.26 ± 0.05	-1.57 ± 0.08	0.43 ± 0.26
600	-3.33 ± 0.07	-0.80 ± 0.15	2.77 ± 0.80

^a $B_1(\rho)$ is the result obtained using $P/\rho kT = A + B_1(\rho)/T$, $B_2(\rho)$ is obtained using $P/\rho kT = A + B_2(\rho)/T + C_2(\rho)/T^2$, and $B_3(\rho)$ is obtained using $P/\rho kT = A + B_3(\rho)/T + C_3(\rho)/T^2 + D_3(\rho)/T^3$.

(8) J. L. Lebowitz, *Phys. Rev.*, **133A**, 895 (1964).

(9) Attempts to fit the data below 0° (ref 7) failed to yield results which went smoothly into the fit above 0°. Since 0° corresponds to a reduced temperature of 2.3°, data below this temperature should not be expected to fit a high-temperature theory. For these reasons, we used only the data from 0 to 150°.

Table III: Comparison of the Experimental and Calculated Equations of State at 0 and 150°

ρ	$P/\rho kT$ (exptl)		$A + B/T$ (exptl)		$C = 0.903$ $A + B/T$ (calcd)		$C = 0.889$ $A + B/T$ (calcd)	
	0°	150°	0°	150°	0°	150°	0°	150°
40	0.966	1.005	0.985	1.013	0.974	1.006	0.965	1.000
120	0.920	1.034	0.974	1.056	0.942	1.037	0.927	1.028
200	0.908	1.093	0.983	1.125	0.947	1.102	0.959	1.109
280	0.937	1.190	1.036	1.232	1.015	1.217	1.100	1.273
360	1.019	1.339	1.168	1.401	1.167	1.400	1.400	1.551
440	1.177	1.557	1.417	1.657	1.440	1.677	1.912	1.900
520	1.447	1.870	1.823	2.027	1.876	2.078	2.760	2.648
600	1.878	2.310	2.441	2.545	2.528	2.641	4.014	3.601

statistically most appropriate for representing the data. Zwanzig¹ modified the Lennard-Jones parameters to correct for the inclusion of a hard core at c . Using the accepted⁹ values of the Lennard-Jones parameters of argon, $\sigma = 3.405$ A, $\epsilon/k = 119.7^\circ\text{K}$, and multiplying by the correction factors (for example at $c = 0.889$, $\sigma' = \sigma/1.0062 = 3.384$ A, $\epsilon' = 1.005\epsilon = 120.3^\circ\text{K}$) in the second term on the right-hand side of (2.7), which is B/T , we find the apparent slope given by curve 1 in Figure 1. The agreement with the B_2 obtained from experiment, shown by the solid line in Figure 1, is poor. Not only is the minimum of curve 1 shifted to lower densities but the sign of the slope is incorrectly predicted for densities larger than 480 amagats. We believe the origin of this difficulty lies in the great sensitivity of the $b(\rho)$ given by (2.2) or (2.7) to the chosen value of c , the hard-core cutoff. A similar difficulty was encountered by Zwanzig and by Smith and Alder.² A small variation in c , σ , ϵ does reproduce correctly the behavior of the slope. Curve 2 shown in Figure 1 corresponds to $c = 0.903$, $\sigma' = 1.05\sigma = 3.55$ A, and $\epsilon'/k = 0.94\epsilon/k = 113.1^\circ\text{K}$ and is in fair (mean deviation of about 9%) agreement with the apparent experimental slope.

We tabulate in Table III the experimental compressibility $p/\rho kT$ and the experimental value of $a(\rho) + b(\rho)/kT$ obtained from the second-degree fit in $1/T$ and the right-hand side of (2.7), evaluated for $c = 0.903$ and 0.889 , as a function of density at 0 and 150°, respectively. The agreement between the third and fourth columns of Table III is gratifying. They indicate clearly the deviation of the compressibility of argon from a linear relation in $1/T$ for densities larger than 400 amagats.

One expects that the series (1.3) provides at least an asymptotic representation of the compressibility at sufficiently high temperatures even if its radius of convergence vanishes.¹⁰ It is not clear from our study that the restricted temperature-density interval covered

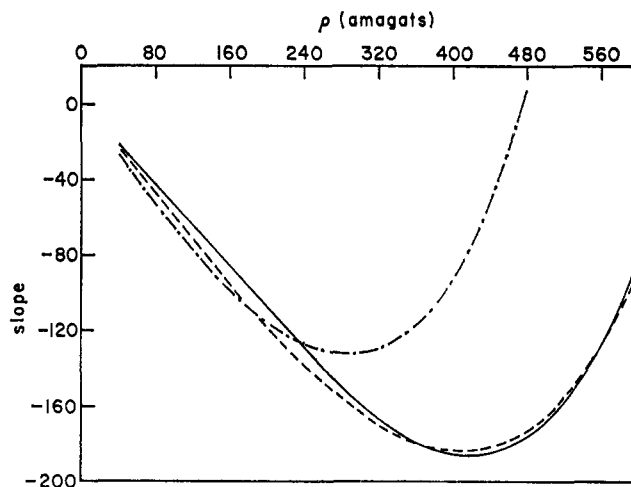


Figure 1. $B(\rho)$, the slope, vs. the density, ρ . The solid line is the experimental data, the — · — line is the calculated result using $c = 0.889$, the — — — line is the calculated result using $c = 0.903$ and modifying both ϵ and σ ($\epsilon' = 0.94\epsilon$, $\sigma' = 1.05\sigma$).

by the work of Michels, *et al.*,^{6,7} suffices to determine reliably the coefficients of high-temperature equation of state. Thus, when the compressibility data of Lecocq¹¹ and Michels⁶ on argon at 120 amagats is plotted vs. $1/T$ one finds that Lecocq's data fall below the extrapolated curve obtained by fitting Michels data to a second-degree polynomial in $1/T$. Why this is so is not clear. We have also tried to compare our calculations to data on neon.¹² Unfortunately, the very small and very high reduced temperature range avail-

(10) We assume there exists no second fluid-solid critical point or similar discontinuity.

(11) A. Lecocq, *J. Rech. Centre Natl. Sci. Lab. Bellevue (Paris)*, **50**, 55 (1960).

(12) A. Michels, T. Wassenaar, and P. Lovworse, *Physica*, **26**, 539 (1956).

able ($7.65 < kT/\epsilon < 11.8$) makes accurate fitting of a $1/T$ polynomial difficult ($p/\rho kT$ varies as little as 0.4% and at most 2% in this range). The precision obtained for $a(\rho)$ is six times worse than that for argon. Nevertheless, the maximum error in fitting the constant term, $a(\rho)$, is only 4%. Since the experimental precision for $b(\rho)$ is about 100 times worse than Argon,

we did not attempt to calculate it; any comparisons would have been meaningless.

We have thus shown this theory to be consistent with the high-temperature data for argon (and neon). Unfortunately, the great sensitivity of the results on the location of the hard-sphere cutoff parameter c limits the usefulness of the theory.

Heats of Solution of Some Tetraalkylammonium Salts in Water and in Propylene Carbonate and Ionic Enthalpies of Transfer from Water to Propylene Carbonate

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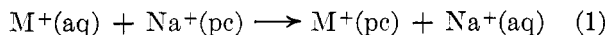
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In an extension of earlier work¹ the enthalpies of transfer of several additional ions from water to propylene carbonate at 25° were determined calorimetrically. The results for ΔH° relative to that for Na^+ are: Me_4N^+ , -1.45; Et_4N^+ , 2.65; Cl^- , 3.83; Br^- , 0.85; I^- , -3.22 (all in kcal/mole). Apparently these conventional single-ion values and those reported earlier¹ are quite close to the *real*, or absolute, single-ion enthalpies of transfer. Most of the results can be understood in terms of well-known structural effects in the water solutions, but this does not seem to be true of the enthalpy of transfer of $\text{B}(\text{C}_6\text{H}_5)_4^-$.

1. Introduction

We have recently reported¹ experimental values of the standard enthalpy change in the process



where M is an alkali metal and pc is propylene carbonate. Enthalpies of solvation in propylene carbonate, relative to sodium ion deduced from these results and the known enthalpies of hydration, were found to be consistent with the Latimer-Pitzer-Slansky equation.²

This work has been continued with the objective of determining the solvation enthalpies of the halide ions, as reported here. The study is still incomplete in some important respects, for F^- has not been investigated and determinations of heats of transfer of several other species seem necessary for the interpre-

(1) Paper I: Y. C. Wu and H. L. Friedman, *J. Phys. Chem.*, **70**, 501 (1966).

(2) W. M. Latimer, K. S. Pitzer, and C. M. Slansky, *J. Chem. Phys.*, **7**, 108 (1939).