under Grant GP-3878. Valuable discussions with Professor Lionel Raff of our department are gratefully acknowledged. Professor Willis Person has also made helpful suggestions. Valuable assistance has been provided by the Oklahoma State University Research Foundation.

High-Temperature Equation of State—Argon

by H. L. Frisch,
Bell Telephone Laboratories, Murray Hill, New Jersey 07971

J. L. Katz,
North American Aviation Science Center, Thousand Oaks, California 91360

E. Praestgaard,
Chemical Laboratory III, H. C. Ørsted Institute, Copenhagen Ø, Denmark

and J. L. Lebowitz
Department of Physics, Belfer Graduate School of Science, Yeshiva University, New York, New York
(Received January 17, 1966)

We have studied the first two terms of the high-temperature equation of state, $p/\rho kT = a(\rho) + b(\rho)/kT + c/(kT)^2 + \ldots$, 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 intermolecular 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.
where
\[ u(r) = u_a(r) + u_s(r) \]  
and \( u_s(r) \) is a nonsingular "soft" potential for \( r > c_s \), \( c_s \) being the hard-core diameter. The equation of state can be then written in the form
\[ \frac{p}{\rho kT} = a(\rho) + b(\rho)/(\rho kT)^2 + c(\rho)/(\rho kT)^4 + \ldots \]  
with \( \rho \) 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
\[ a(\rho) = \frac{p_h}{\rho kT} \]  
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 \( c(\rho)/(\rho kT)^2 \) is required to attain the precision reported over the temperature interval studied. Previous attempts to evaluate \( b(\rho) \) have employed a Lennard-Jones \((6-12)\) potential for \( u_s(r) \), for \( r > c_s \) 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 \( g_h(r) \). Neither of these approximate \( g_h(r) \) are satisfactory at sufficiently high densities \( \rho \) corresponding to real, supercritical fluids, and furthermore they require extensive machine computations. Wertheim and Thiele have obtained the explicit Laplace transform, \( G(s) \), of the approximate hard-sphere radial distribution, \( g_h(r) \), satisfying the Percus-Yevick (PY) integral equation
\[ G(s) = \int_{c_s}^{\infty} e^{-s} g_h(r) 4\pi r^2 dr \]  
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., 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
\[ r u_s(r) = \int_0^\infty e^{-s} U(s) ds \]  
i.e., we assume that \( r u_s(r) \) possesses a continuous inverse Laplace transform. Substituting (2.1) for \( r u_s(r) \) in (1.4) and interchanging orders of integration, we find the desired relation
\[ b(\rho) = \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \int_0^\infty \rho^2 U(s) G(s) ds \]  
Using Wertheim or Thiele's \( G(s) \) and the RFL equation for \( a(\rho) \)
\[ a(\rho) = \frac{p_h}{\rho kT} = \frac{1 + \eta + \eta^2}{(1 - \eta)^4} \]  
with the dimensionless density \( \eta = \pi(c_s)^4 \rho / 6 \), one obtains the first few terms of the high-temperature expansion of the equation of state as
\[ \frac{p}{\rho kT} = \frac{1 + \eta + \eta^2}{(1 - \eta)^4} + \frac{12 \eta}{kT} \int_0^\infty f(s,\eta) U(s) ds + O(T^{-2}) \]  
with \( f(s,\eta) \) given in (2.5).
been obtained by Lebowitz.\textsuperscript{8} We omit writing these.

### 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.\textsuperscript{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 $c(p)/(kT)^2$ term to $p/p_kT$ 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 $a(p)$ at 40 amagats by inverting eq 2.3 and solving for $c$, with $\sigma = 3.405$ A.\textsuperscript{6} Using the value obtained, $c = 0.889$, in (2.3) we then calculated $a(p)$ (at 40-amagat intervals) up to a density of 600 amagats, and this is compared with the $a(p)$ 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 $\rho^* = \gamma / (c\sigma)^3$ were calculated and are shown in the second column of Table I.

### Table I: Comparison of Experimental and Calculated Constant Term in the Equation $P/p_kT = a(p) + b(p)/T$

<table>
<thead>
<tr>
<th>$\rho$</th>
<th>$\rho^*$</th>
<th>$a(p)$ (expn)</th>
<th>$a(p)$ (calcd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.0318</td>
<td>1.065</td>
<td>1.065</td>
</tr>
<tr>
<td>120</td>
<td>0.0655</td>
<td>1.207</td>
<td>1.212</td>
</tr>
<tr>
<td>200</td>
<td>0.1092</td>
<td>1.381</td>
<td>1.383</td>
</tr>
<tr>
<td>280</td>
<td>0.1529</td>
<td>1.588</td>
<td>1.586</td>
</tr>
<tr>
<td>360</td>
<td>0.1965</td>
<td>1.825</td>
<td>1.825</td>
</tr>
<tr>
<td>440</td>
<td>0.2402</td>
<td>2.094</td>
<td>2.108</td>
</tr>
<tr>
<td>520</td>
<td>0.2839</td>
<td>2.398</td>
<td>2.445</td>
</tr>
<tr>
<td>600</td>
<td>0.3275</td>
<td>2.735</td>
<td>2.848</td>
</tr>
</tbody>
</table>

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 $p/p_kT$ is plotted vs. 1/$T$ for all densities. The asymptotic slope is $b(p)/k = B(p)$. Table II exhibits this apparent slope $B_i$, $i = 1, 2, 3$, obtained by fitting Michels, et al., data\textsuperscript{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 $P/p_kT$ by Successive Polynomials in 1/$T^2$

<table>
<thead>
<tr>
<th>$\rho$</th>
<th>$B_i(p)$</th>
<th>$B_i(p)$</th>
<th>$B_i(p)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>-0.304 ± 0.002</td>
<td>-0.200 ± 0.007</td>
<td>-0.322 ± 0.09</td>
</tr>
<tr>
<td>120</td>
<td>-0.879 ± 0.007</td>
<td>-0.638 ± 0.006</td>
<td>-0.647 ± 0.09</td>
</tr>
<tr>
<td>200</td>
<td>-1.42 ± 0.01</td>
<td>-1.09 ± 0.01</td>
<td>-0.87 ± 0.13</td>
</tr>
<tr>
<td>280</td>
<td>-1.95 ± 0.01</td>
<td>-1.51 ± 0.02</td>
<td>-2.44 ± 0.15</td>
</tr>
<tr>
<td>360</td>
<td>-2.46 ± 0.02</td>
<td>-1.79 ± 0.04</td>
<td>-0.92 ± 0.17</td>
</tr>
<tr>
<td>440</td>
<td>-2.92 ± 0.03</td>
<td>-1.85 ± 0.05</td>
<td>-0.53 ± 0.21</td>
</tr>
<tr>
<td>520</td>
<td>-3.26 ± 0.05</td>
<td>-1.57 ± 0.08</td>
<td>-0.43 ± 0.26</td>
</tr>
<tr>
<td>600</td>
<td>-3.33 ± 0.07</td>
<td>-0.80 ± 0.15</td>
<td>-0.77 ± 0.80</td>
</tr>
</tbody>
</table>

\(* B_i(p) = \text{the result obtained using } P/p_kT = A + B_i(p)/T, B_k(p) = \text{obtained using } P/p_kT = A + B_i(p)/T + C_i(p)/T^2, \text{and } D(p) = \text{obtained using } P/p_kT = A + B_i(p)/T + C_i(p)/T^2 + D(p)/T^3.\)


\(\text{(9) Attempts to fit the data below 0° (ref 7) failed to yield results which went smoothly into the fit above 0°. Since 0° corresponds to a reduced temperature of 2.3°, data below this temperature should not be expected to fit a high-temperature theory. For these reasons, we used only the data from 0 to 150°.}\)
Table III: Comparison of the Experimental and Calculated Equations of State at 0 and 150°

<table>
<thead>
<tr>
<th>ρ (amagats)</th>
<th>P/kT (exptl) 150°</th>
<th>A + B/T (exptl) 150°</th>
<th>C = 0.903 A + B/T (calcd) 150°</th>
<th>C = 0.889 A + B/T (calcd) 150°</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.966</td>
<td>1.005</td>
<td>0.985</td>
<td>0.974</td>
</tr>
<tr>
<td>120</td>
<td>0.920</td>
<td>1.004</td>
<td>0.974</td>
<td>0.942</td>
</tr>
<tr>
<td>200</td>
<td>0.908</td>
<td>1.003</td>
<td>0.947</td>
<td>1.010</td>
</tr>
<tr>
<td>280</td>
<td>0.937</td>
<td>1.190</td>
<td>1.015</td>
<td>1.217</td>
</tr>
<tr>
<td>360</td>
<td>1.019</td>
<td>1.339</td>
<td>1.167</td>
<td>1.400</td>
</tr>
<tr>
<td>440</td>
<td>1.177</td>
<td>1.557</td>
<td>1.440</td>
<td>1.677</td>
</tr>
<tr>
<td>520</td>
<td>1.447</td>
<td>1.870</td>
<td>2.078</td>
<td>2.760</td>
</tr>
<tr>
<td>600</td>
<td>1.878</td>
<td>2.310</td>
<td>2.545</td>
<td>3.601</td>
</tr>
</tbody>
</table>

Figure 1. B(ρ), 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 ρ and σ (c' = 0.94e, σ' = 1.05σ).

We tabulate in Table III the experimental compressibility p/kT and the experimental value of a(ρ) + b(ρ)/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. It is not clear from our study that the restricted temperature-density interval covered by the work of Michel, et al., suffices to determine reliably the coefficients of high-temperature equation of state. Thus, when the compressibility data of Lecocq and Michel on argon at 120 amagats is plotted vs. 1/T one finds that Lecocq's data fall below the extrapolated curve obtained by fitting Michel's 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. 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.
(12) A. Michel, T. Wassenaar, and P. Louwarse, Physics, 26, 539 (1986).
able \((7.65 < kT/\epsilon < 11.8)\) makes accurate fitting of a \(1/T\) polynomial difficult \(\rho/kT\) varies as little as 0.4\% and at most 2\% in this range. \(\rho/kT\) was used 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

by Yung-Chi Wu

IBM Watson Research Center, Yorktown Heights, New York

and Harold L. Friedman

Department of Chemistry, State University of New York, Stony Brook, New York (Received January 18, 1966)

In an extension of earlier work\(^1\) the enthalpies of transfer of several additional ions from water to propylene carbonate at 25\(^\circ\) were determined calorimetrically. The results for \(\Delta H^\circ\) relative to that for Na\(^+\): Me\(_4\)N\(^+\), -1.45; Et\(_4\)N\(^+\), 2.65; Cl\(^-\), 3.83; Br\(^-\), 0.85; I\(^-\), -3.22 (all in kcal/mole). Apparently these conventional single-ion values and those reported earlier\(^2\) 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 B(C\(_6\)H\(_5\))\(_4\)^-.

1. Introduction

We have recently reported\(^1\) experimental values of the standard enthalpy change in the process

\[
\text{M}^+(aq) + \text{Na}^+(pc) \rightarrow \text{M}^+(pc) + \text{Na}^+(aq) \tag{1}
\]

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.\(^3\)

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 interpretation of the results.