## CHAPTER 17

Internal Pressure and Internal Energy of Saturated and Compressed Phases
ILMUTDIN M. ABDULAGATOV, ${ }^{\text {a,b }}$ JOSEPH W. MAGEE, ${ }^{\text {c }}$ NIKOLAI G. POLIKHRONIDI, ${ }^{\text {a }}$ RABIYAT G. BATYROVA ${ }^{a}$
${ }^{\text {a }}$ Institute of Physics of the Dagestan Scientific Center of the Russian Academy of Sciences, Makhachkala, Dagestan, Russia. E-mail: ilmutdina@gmail.com
${ }^{\text {b }}$ Dagestan State University, Makhachkala, Dagestan, Russia
${ }^{\text {c }}$ National Institute of Standards and Technology, Boulder, Colorado 80305 USA. Email: joe.magee@nist.gov


#### Abstract

Following a critical review of the field, a comprehensive analysis is provided of the internal pressure of fluids and fluid mixtures and its determination in a wide range of temperatures and pressures. Further, the physical meaning is discussed of the internal pressure along with its microscopic interpretation by means of calorimetric experiments. A new relation is explored between the internal pressure and the isochoric heat capacity jump along the coexistence curve near the critical point. Various methods (direct and indirect) of internal pressure determination are discussed. Relationships are studied between the internal pressure and key thermodynamic properties, namely expansion coefficient, isothermal compressibility, speed of sound, enthalpy increments, and viscosity. Loci of isothermal, isobaric, and isochoric internal pressure maxima and minima were examined in addition to the locus of zero internal pressure. Details were discussed of the new method of direct internal pressure determination by a calorimetric experiment that involves simultaneous measurement of the thermal pressure coefficient $(\partial P / \partial T)_{V}$, i.e. internal pressure $P_{\text {int }}=(\partial U / \partial V)_{T}$ and heat capacity $c_{V}=(\partial U / \partial T)_{V}$. The dependence of internal pressure on external pressure, temperature and density for pure fluids, and on concentration for binary mixtures is considered on the basis of reference (NIST REFPROP) and crossover EOS. The asymptotic scaling behavior of the internal pressure near the critical point was studied using a scaling type EOS.


Keywords: Coexistence curve; Critical point; Equation of state; Internal pressure; Internal energy; Isochoric heat capacity; Thermal pressure coefficient; Vapor pressure
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### 17.1 Background

For liquids, the concept of cohesion is important because intermolecular interactions are intense in the liquid phase. The internal pressure provides an estimate of magnitude of cohesive forces. Cohesion (or intermolecular forces) creates a pressure within a liquid which typically falls in the range $10^{2}$ to $10^{3} \mathrm{MPa}$. As a liquid is compressed, internal pressure typically decreases and becomes large and has a negative sign. This means that repulsive forces in the liquid become predominant. Hildebrand ${ }^{1}$ discussed the importance of internal pressure, especially to aid an understanding the phenomenon of solubility in a liquid. Internal pressure provides useful information to better understand the nature of intermolecular interactions and the structure of liquids. In the most basic sense, internal pressure is a part of the total pressure which is caused by intermolecular interactions, i.e., it quantifies the effect of intermolecular interactions on a measurement of the total external pressure. Internal pressure is a valuable thermodynamic quantity that provides direction and guidance to study intermolecular interactions through macroscopic properties. Haward ${ }^{2}$ and Haward
and Parker ${ }^{3}$ have shown how the concept of internal pressure, in terms of the modified van der Waals EOS for liquids, helps one to separate the attractive and repulsive parts of the external pressure. Suryanarayana and co-authors ${ }^{4-8}$ have discussed the importance of internal pressure for understanding both pure liquids and strong electrolyte solutions. Richards ${ }^{9}$ has pointed out the importance of internal pressure in understanding the properties of liquids. The thermal pressure coefficient $(\partial P / \partial T)_{V}$ and internal pressure $P_{\text {int }}=(\partial U / \partial V)_{T}$ are directly related by the EOS for a liquid. In addition, for binary mixtures, internal pressure aids in the interpretation of structural changes as a function of composition.

### 17.2 Thermodynamic and Statistical Mechanical Definition of the Internal Pressure

The basic thermodynamic relationship between the internal pressure (energy-volume coefficient) and the external pressure and the temperature derivatives (thermal-pressure coefficient), $(\partial P / \partial T)_{V}$, is Equation (17.1) below:

$$
\begin{equation*}
P_{\mathrm{int}}=\left(\frac{\partial U}{\partial V}\right)_{T}=T\left(\frac{\partial P}{\partial T}\right)_{V}-P, \tag{17.1}
\end{equation*}
$$

and the equivalent form,

$$
\begin{equation*}
P_{\mathrm{int}}=\left(\frac{\partial U}{\partial V}\right)_{T}=T \frac{\alpha_{P}}{K_{T}}-P \tag{17.2}
\end{equation*}
$$

where $T$ is the temperature, $V$ is the specific volume, $P$ is the external pressure, $U$ is the internal energy, $P_{\text {int }}$ is the internal pressure, $K_{T}$ is the isothermal compressibility, and $\alpha_{p}$ is the isobaric coefficient of thermal expansion. Since $P_{\text {int }}$ is directly related to the first temperature derivative of external pressure, $(\partial P / \partial T)_{V}$, any EOS that correctly represents the internal pressure will also provide accurate predictions of caloric properties such as entropy, enthalpy, internal energy, according to a well-known Maxwell relation and Clausius-Clapeyron equation,

$$
\left(\frac{\partial S}{\partial V}\right)_{T}=\left(\frac{\partial P}{\partial T}\right)_{V} \quad \text { or } \quad\left(\frac{\partial P}{\partial T}\right)_{\text {sta }}=\frac{\Delta H_{\text {vap }}}{T \Delta V} .
$$

Therefore, it follows from Equation (17.1), the internal pressure describes the sensitivity of internal energy $U(T, V)$ to a change in volume (isothermal expansion or compression) at isothermal conditions, i.e., isochoric influence of temperature on the intermolecular interaction energy. From a physical point of view, the internal pressure provides insight into dispersion, repulsion, and dipoledipole interactions as it varies rapidly with intermolecular separation; therefore, $P_{\text {int }}$ reflects these interactions and can be obtained by using the thermodynamic equation of state. The internal pressure is result of attractive and repulsive forces. The decrease of internal pressure with temperature is associated with an increase in disorder which might result in a decrease of the attractive interactions if these are directional (H-bonds or dipole-dipole). Thusly, direct measurements of the internal pressure of fluids and fluid mixtures are known to give valuable insight regarding the nature of intermolecular interactions. Not only is internal pressure important to better understand the nature of molecular interactions but also for understanding the theory of liquid and liquid mixtures. The statistical mechanical definition of the internal energy and internal pressure is:

$$
\begin{align*}
& U=\frac{3}{2} N k T+\frac{1}{2} N \int_{0}^{\infty} \mathrm{g}(r) \varphi(r) d r,  \tag{17.3}\\
& P_{\mathrm{int}}=-\frac{2 \pi}{3} \rho^{2} k T \int_{0}^{\infty} r^{3} \frac{\partial \varphi}{\partial r} \frac{\partial \mathrm{~g}}{\partial r} d r, \tag{17.4}
\end{align*}
$$

where $\varphi(r)$ is the potential energy between a pair of molecules separated by a distance $r$ and $g(r)$ is the radial distribution function (probability of finding a molecule at a distance $r$ from the reference molecule). The relations (17.3) and (17.4) can be used for modeling the intermolecular interaction and structural properties of fluids and fluid mixtures on the basis of measured internal pressure data by using molecular simulation techniques. It is obvious that for an ideal gas, the internal pressure is zero (no interaction between the molecules), while for real gases and liquids it deviates significantly from zero and is much greater than the external pressure. Changing the volume does work against the cohesive forces which cause changes in the internal energy.
The cohesive energy of low molecular weight compounds can be expressed as: ${ }^{10}$

$$
\begin{equation*}
U_{\text {coh }}(T)=\Delta H_{\text {vap }}(T)-P_{\mathrm{s}} \Delta V \tag{17.5}
\end{equation*}
$$

where $P_{\mathrm{s}}$ is the vapor pressure and $\Delta H_{\text {vap }}$ is the enthalpy of vaporization. At low vapor pressure conditions the saturated vapor behaves as ideal gas, i.e., $P_{\mathrm{s}} \Delta V \approx R T$, thus we have $U_{\text {coh }}(T)=\Delta H_{\text {vap }}(T)-R T$. The internal pressure can be approximately calculated as:

$$
\begin{equation*}
P_{\mathrm{int}} \approx U_{\mathrm{coh}} / \Delta V \tag{17.6}
\end{equation*}
$$

Although, $P_{\text {int }}$ and $U_{\text {coh }} / \Delta V$ have the same units, they represent different physical quantities. Actually, internal pressure $P_{\text {int }}$ represents only a part of the total value of cohesive energy density $U_{\text {coh }} / \Delta V$. Only at low pressures (around atmospheric pressure) does the approximation $P_{\text {int }} \approx U_{\text {coh }} / \Delta V$ hold. When we evaporate liquid, most of the required energy is used to separate the molecules from each other from close packing to distances characteristic of when they are far apart. The cohesive energy density roughly corresponds to the amount of work required to change $1 \mathrm{~cm}^{3}$ of molecules from liquid to gas. In other words, we can say the internal pressure is approximated by the internal energy $\Delta U(T)$ increment needed to remove a molecule from its nearest neighbors, divided by the volume change caused by the removed molecule, i.e. , $P_{\text {sint }}=\Delta U(T)$ at $\Delta V=1 \mathrm{~cm}^{3}$.

### 17.3 Internal Pressure and Intermolecular Forces

The physical interpretation of the internal pressure is based on molecular interaction forces. The intermolecular potential $\varphi(r)$ can be divided into two parts, a smoothly varying long-range attraction $\varphi_{\mathrm{A}}(r)$ and steep short-range repulsion $\varphi_{\mathrm{R}}(r)$ (see Figure 17.1, left):

$$
\varphi(r)=\varphi_{\mathrm{A}}(r)+\varphi_{\mathrm{R}}(r)
$$

(17.7)

Since changes of volume related with average intermolecular distance changes (anharmonic effect), $V \propto r^{3}$, then by analogy with intermolecular potential function $\varphi(r)$, the internal energy as a function of specific volume $U(V)$ may be divided into two parts $U(V)=U_{\mathrm{A}}(V)+U_{\mathrm{R}}(V)$. Therefore, differentiation of this relation at constant temperature with respect to volume gives:

$$
\begin{equation*}
P_{\text {int }}=(\partial U / \partial V)_{T}=\left(\partial U_{\mathrm{A}} / \partial V\right)_{\mathrm{T}}+\left(\partial U_{\mathrm{R}} / \partial V\right)_{\mathrm{T}}=P_{\mathrm{A}}+P_{\mathrm{R}}, \tag{17.8}
\end{equation*}
$$

where $U_{\mathrm{A}}$ and $U_{\mathrm{R}}$ are the attraction and repulsion internal energies, respectively; $P_{\mathrm{A}}=\left(\partial U_{\mathrm{A}} / \partial \mathrm{V}\right)_{\mathrm{T}}>0$ and $P_{\mathrm{R}}=\left(\partial U_{\mathrm{R}} / \partial V\right)_{T}<0$ (Figure 17.1, right). The sign of internal pressure can be either positive or negative, depending on the temperature and density. Therefore, depending on temperature and density either $P_{\mathrm{A}}$ or $P_{\mathrm{R}}$ dominates. The volume dependence of the internal pressure can be presented as

$$
\begin{equation*}
P_{\mathrm{int}}(V, T)=\frac{a(T)}{V^{\mathrm{n}}}+\frac{b(T)}{V^{\mathrm{m}}} \tag{17.9}
\end{equation*}
$$

Equation (17.9) splits the repulsive $P_{\mathrm{A}}$ and attractive $P_{\mathrm{R}}$ contributions of the total experimentally observed internal pressure. Thus, the volume dependence of the internal energy can be derived by integrating Equation (17.1):

$$
\begin{equation*}
\Delta U(V, T)=\frac{a(T)}{1-\mathrm{n}} V^{1-\mathrm{n}}+\frac{b(T)}{1-\mathrm{m}} V^{1-\mathrm{m}}, \tag{17.10}
\end{equation*}
$$

where $\Delta U(V, T)=U(V, T)-U_{0}(T)$. The specific volume dependence of internal pressure for pure water calculated from fundamental equation of state (IAPWS formulation ${ }^{11}$ ) are presented in Figure 17.2 (right) for two selected isotherms: critical ( 647.096 K ) and supercritical ( 800 K ). The values of internal energy of pure water calculated from Equation (17.10) are presented in Figure 17.2 (left).
Attractive forces are exerted between molecules at distances where the molecules do not touch each other: molecules located near the wall are thereby drawn inward. As a result the actual pressure to the wall is somewhat reduced as compared with the case of an ideal gas. The amount of such a reduction is estimated to be proportional to the product between the density of the molecules near the wall ( $P \approx \rho \approx \frac{1}{V}$ ) and that in the inner part. This effect leads us to replace $P \rightarrow P+\frac{a}{V^{2}}$ in the ideal gas equation of state. For van der Waals fluids at constant temperature the internal energy can be presented as:

$$
\begin{equation*}
U(V, T)=U_{0}(T)-\frac{a}{V}, \tag{17.11}
\end{equation*}
$$

where $a=-2 \pi \int u_{2}\left(r_{12}\right) r_{12}^{2} d r_{12}$. This van der Waals caloric Equation of state (EOS) (17.11) shows that we have to put in energy in order to move molecules farther apart. Therefore, this means that there is an attractive force between the molecules (see Figure 17.1). The configurational energy per particle in term of the radial pair distribution function is:

$$
\begin{equation*}
u(V, T)=\frac{U(V, T)}{N}=\frac{2 \pi}{V} \int u_{2}\left(r_{12}\right) g\left(r_{12}\right) r_{12}^{2} d r_{12}, \tag{17.12}
\end{equation*}
$$

where $4 \pi r_{12}^{2} d r_{12}$ is the volume of the shell; $n\left(r_{12}\right)=\rho \mathrm{g}\left(r_{12}\right) 4 \pi r_{12}^{2} d r_{12}$ is the mean number of particles in the shell; and $\frac{1}{2} u_{2}\left(r_{12}\right) \rho g\left(r_{12}\right) 4 \pi r_{12}^{2} d r_{12}$ is the mean energy of central particles with particles in the shell; and $\int \frac{1}{2} u_{2}\left(r_{12}\right) \rho \mathrm{g}\left(r_{12}\right) 4 \pi r_{12}^{2} d r_{12}$ is the integral over shells. The structure of simple liquids is largely determined by the molecular packing which is dominated by the repulsive interactions. The attractive interactions may thus be treated as a uniform background potential (van der Waals theory of mean-field approximation, $U \approx \sum_{i=1}^{N} \varphi_{i}\left(\vec{r}_{\mathrm{i}}\right)$ ) that contributes to the configurational energy of the liquid but does not affect its structure. If one assumes that the particles are hard spheres with a diameter $\sigma$ then the excluded volume for a pair of particles is $V_{\text {exc }}=\frac{4}{3} \pi \sigma^{3}$. In van der Waals approximation the total excluded volume is $V_{\text {exc }} \approx \frac{N}{2} v_{\text {exc }}=N b$, where constant $b=\frac{2}{3} \pi \sigma^{3}$. Using the statistical thermodynamic consideration, the van der Waals EOS can presented as (at $a=0$ ):

$$
\begin{equation*}
P v=k T\left(1+\frac{b}{N_{\mathrm{A}} v}\right), \tag{17.13}
\end{equation*}
$$

where

$$
\begin{equation*}
\frac{b}{N_{\mathrm{A}}}=\frac{1}{2} \int_{0}^{\infty}[1-\exp (-\varphi(r) / k T)] 4 \pi r^{2} d r . \tag{17.14}
\end{equation*}
$$

For a rigid sphere of diameter of $2 r_{0}$ (no attraction between molecules, $a=0$ ), i.e., $\varphi\left(r>2 r_{0}\right)=+\infty$ and $\varphi\left(r<2 r_{0}\right)=0$ :

$$
\begin{equation*}
\frac{b}{N_{\mathrm{A}}}=4 \pi\left(\frac{4}{3} \pi r_{0}^{3}\right)=4 \omega, \tag{17.15}
\end{equation*}
$$

where $\omega=\frac{4}{3} \pi r_{0}^{3}$ is the volume of the rigid sphere. The potential energy of one molecule due to surrounding molecules is:

$$
\begin{equation*}
U=\int_{d}^{\infty} \varphi(r) n d \tau=n \omega \tag{17.16}
\end{equation*}
$$

where $n$ is the number of molecules in $1 \mathrm{~cm}^{3}$ (constant); $\varphi(r)$ is the potential energy of two molecules, $d \tau=4 \pi r^{2} d r$ is the volume element, $n 4 \pi r^{2} d r$ is the number of molecules in $d \tau$, and $\omega=\int_{d}^{\infty} \varphi(r) d \tau$ is the dimension of energy times volume. Thus, the total potential energy due to $N$ molecules in volume $V$ is:

$$
\begin{equation*}
U(V, T)=\frac{N n \omega}{2} \tag{17.17}
\end{equation*}
$$

Therefore, according to van der Waals caloric EOS Equation (17.11)

$$
\begin{equation*}
\frac{a}{N_{\mathrm{A}}}=-\frac{\omega}{2}=\int_{d}^{\infty} \varphi(r) n d \tau \tag{17.18}
\end{equation*}
$$

i.e., volume integral of the energy between two molecules divided by 2 .

The heat of vaporization is proportional to the potential energy $-U=-\frac{N n \omega}{2}$ or $-\frac{U}{V}=n^{2} \frac{a}{N_{\mathrm{A}}^{2}}$, which is the cohesive energy density. This is the same as the additional (internal) pressure due to molecular interaction in the van der Waals equation of state.
Ravi et al. ${ }^{12}$ derived the structure factor $S(Q)$ of liquid using internal pressure. They generalized an EOS for hard-sphere fluid to a real fluid (pseudo van der Waals equation) given as:

$$
\begin{equation*}
P=\rho k T+\frac{2}{3} \pi \rho^{2} k T \sigma^{3} \mathrm{~g}(\sigma)-P_{\mathrm{int}} \tag{17.19}
\end{equation*}
$$

where $\sigma$ is the hard - core diameter of fluids. Since $P \ll P_{\mathrm{int}}$,

$$
\begin{equation*}
P_{\mathrm{int}}=\rho k T+\frac{2}{3} \pi \rho^{2} k T \sigma^{3} \mathrm{~g}(\sigma) \text { or } \frac{P_{\mathrm{int}}}{\rho k T}=1+4 \pi \eta \mathrm{~g}(\sigma) \tag{17.20}
\end{equation*}
$$

where $\eta=\frac{1}{6} \pi \rho \sigma^{3}$ is the packing factor, therefore the radial distribution function is

$$
\begin{equation*}
\mathrm{g}(\sigma)=\frac{1}{4 \eta}\left(\frac{P_{\mathrm{int}}}{\rho k T}-1\right) \tag{17.21}
\end{equation*}
$$

This equation provides a relation between the $\mathrm{g}(\sigma)$ of a hard-sphere fluid and the internal pressure for real liquids. The static structure factor is the Fourier transform of the pair distribution function as:

$$
\begin{equation*}
S(\vec{k})=1-\rho \int g\left(r_{12}\right) \exp \left(-i \vec{k} \vec{r}_{12}\right) d \vec{r}_{12} \tag{17.22}
\end{equation*}
$$

$S(\vec{k})$ can be determined experimentally from neutron or X-ray scattering. The inverse transform gives the distribution function as:

$$
\begin{equation*}
\mathrm{g}\left(r_{12}\right)=\frac{1}{\rho(2 \pi)^{3}} \int[S(\vec{k})-1] \exp \left(i \vec{k} \vec{r}_{12}\right) d \vec{k}, \tag{17.23}
\end{equation*}
$$

Thus, the statistical structure factor $S(Q)$ of a liquid can be presented through the internal pressure as:

$$
\begin{equation*}
S(Q)=\left[1-6\left\{1-\frac{P_{\mathrm{int}}}{\rho k T}\right\}\left(\frac{X \sin x-x \cos x}{x^{3}}\right)\right]^{-1} \tag{17.24}
\end{equation*}
$$

where $X=-3.1266, x=Q \sigma$. As follows from Equation (17.24), $S(Q)$ increases with $P_{\text {int }}$. The Fourier transform $\mathrm{C}(Q)$ of the Ornstein-Zernike direct correlation function and statistical structure factor $S(Q)$ is related as:

$$
\begin{equation*}
S(Q)=[1-\rho \mathrm{C}(Q)]^{-1} . \tag{17.25}
\end{equation*}
$$

Figure 17.3 shows $S(Q)$ versus $Q$ for carbon dioxide, methane, and n-heptane at selected temperature and for various densities or for various values of internal pressure. As shown in Figure 17.3, the peak height of $S(Q)$ increases with density (for positive values of internal pressure). Figure 17.3 illustrates how the internal pressure effects the statistical structure factor $S(Q)$. Therefore, internal pressure can be used as a tool to measure structural changes in liquids.

### 17.4 Methods for Internal Pressure Measurements

All available methods of internal pressure measurements can be divided into two groups: the direct measurement of $(\partial P / \partial T)_{V}$ by using Equation (17.1) and an indirect determination of internal pressure through thermal expansion, $\alpha_{p}$, and isothermal compressibility, $K_{T}$, by using Equation (17.2). Most reported internal pressure data were derived using the indirect method, based on $\alpha_{p}$ and $K_{T}$ data [see above Equation (17.2)]. In most cases the derivative $(\partial P / \partial T)_{V}$ (thermalpressure coefficient) is calculated from an EOS, such as the Tait type, cubic, or multiparameter EOS. Direct measurements of the derivative $(\partial P / \partial T)_{V}$ are very rare. Usually, the values of $K_{T}$ and $\alpha_{P}$ are derived from speed of sound and $P V T$ measurements.
A popular direct method described by Dack ${ }^{13,14}$ and Barton ${ }^{15}$ evaluates the derivative $(\partial P / \partial T)_{V}$ from experimentally determined heat of vaporization measurements by using the equation,

$$
\begin{equation*}
P_{\text {int }}=\left(\Delta H_{\text {vap }}-R T\right)(\rho / M), \tag{17.26}
\end{equation*}
$$

where $M$ is the molecular weight, $\rho$ is the density, and $\Delta H_{\text {vap }}$ is the enthalpy of vaporization. This is the most frequently used direct method. Dack ${ }^{13}$ used a constant volume apparatus to determine the internal pressure of several liquids at $25^{\circ} \mathrm{C}$. The uncertainty in $P_{\text {int }}$ determination in this method is about $2 \%$. Grant-Taylor and Macdonald ${ }^{16}$ determined thermal-pressure coefficient of an acetonitrile + water mixture at temperatures between (298 and 328) K using 25 mL glass constant volume cell. The measured $P-T$ isochores were fitted with the linear equation $P=(\partial P / \partial T)_{V} T+C$, where $C$ is constant. The measured values of $(\partial P / \partial T)_{V}$ were used to derive the energy-volume $(\partial U / \partial V)_{T}$ (internal pressure) coefficient and other thermodynamic quantities. The uncertainty of the derived values of $(\partial P / \partial T)_{V}$ is $2 \%$. Macdonald and Hyne ${ }^{17}$ reported thermal pressure and energy-volume coefficient measurements for dimethyl sulfoxide + water mixtures at temperatures between (13 and 55) ${ }^{\circ} \mathrm{C}$ and at atmospheric pressure by using the same technique. Westwater et al. ${ }^{18}$ and Smith and Hildebrand ${ }^{19}$ directly measured $(\partial P / \partial T)_{V}$ using a constant volume thermometer apparatus. The coefficient $(\partial P / \partial T)_{V}$ is found directly as the slope of a graph of pressure against temperature for liquid in such
apparatus. McLure and Arriaga-Colina ${ }^{20}$ reported thermal-pressure coefficient measurements for ethanenitrile, propanenitrile, and butanenitrile from ( 297 to 398) K. Measurements were made with an apparatus consisting of a constant volume thermometer in which the pressure is controlled and measured for a series of temperatures at a series of different constant densities. McLure et al. ${ }^{21}$ also measured the thermal-pressure coefficient for five dimethyl siloxane oligomers in the temperature range from (298 to 413) K. Thermal pressure coefficients were measured in Pyrex cells (dilatometers). The uncertainty in thermal pressure coefficient measurements is about $1.0 \%$. Bianchi et al. ${ }^{22}$ determined the internal pressure for carbon tetrachloride, benzene, and cyclohexane by direct measurements of $(\partial P / \partial T)_{V}$. They studied temperature dependence of $P_{\text {int }}$ from (293 to 333)
K. Direct measurements of thermal pressure coefficient $(\partial P / \partial T)_{V}$ of neopentane near the coexistence curve were reported by Few and Rigby. ${ }^{23}$ These data together with reported PVT data were used to determine the $P_{\text {int }}$ along the coexistence curve from the triple point to the critical point.
Calorimetry is another direct method to determine the internal pressure. The calorimetric method was developed in our lab as reported previously. ${ }^{24-27}$ To accurately calculate the values of the internal pressure, $(\partial U / \partial V)_{T}$, the pressure $(P)$ and it temperature derivative, $(\partial P / \partial T)_{V}$ were simultaneously measured. This method was applied for pure fluids diethyl ether (DEE) and fluid mixtures $\left(\mathrm{CO}_{2}+\mathrm{n}-\mathrm{C}_{10} \mathrm{H}_{22}\right.$ and $\left.\mathrm{H}_{2} \mathrm{O}+\mathrm{NH}_{3}\right)$. The measurements were performed using the same apparatus as employed for the isochoric heat capacity, ( $c_{V} V T x$ ), and ( $P V T x$ ) measurements. ${ }^{24,25}$ This is a high-temperature and high-pressure nearly constant volume adiabatic piezo-calorimeter. In this work we proposed a new technique of internal pressure measurement in a calorimetric experiment by simultaneous measurements of the thermal pressure coefficient $(\partial P / \partial T)_{V}$ and heat capacity $c_{V}=\left(\frac{\partial U}{\partial T}\right)_{V}$. By this method we can directly measure external pressures, $P$, and their temperature derivatives, $(\partial P / \partial T)_{V}$, and therefore internal pressure $P_{\text {int }}=\left(\frac{\partial U}{\partial V}\right)_{T}=T\left(\frac{\partial P}{\partial T}\right)_{V}-P$. The experimental details (physical basis and the theory of the method, the apparatus, procedures of the measurements, and the uncertainty assessment) of the simultaneous isochoric heat capacity ( $c_{V}$ ) and thermal pressure coefficient, $(\partial P / \partial T)_{V}$, measurements have also been described in our earlier publications. ${ }^{24-27}$ The pressure $(P)$ and temperature derivative of the pressure at constant volume, $(\partial P / \partial T)_{V}$, were measured with calibrated extensometer. The measurements of pressure in the piezocalorimeter were performed at constant temperature before each isochoric heat capacity measurement. Then, after turning on the working heater, temperature changes (thermograms, $T-\tau$, reading of the resistance platinum thermometer PRT, $U_{T}-\tau$ ) and pressure changes (barograms, $P-\tau$, readings of the transducer, $U_{P}-\tau$ ) were synchronously recorded with a strip-chart recorder. Using the records of the thermo-barograms the changes in temperature $\Delta T$ and in pressures $\Delta P$, and thus the derivative $(\partial P / \partial T)_{V}=\lim _{\Delta T \rightarrow 0}(\Delta P / \Delta T)_{V}$ was calculated as a function of elapsed time. Each measured $T-\tau$ and $P-\tau$ isochore was fitted with the linear equations $T=c+d \tau$ and $P=a+b \tau$, where $a, b, c$, and $d$ are fitting parameters. Therefore, the temperature derivative of pressure can be estimated as $(\partial P / \partial T)_{V}=(b / a)$.
The measurements were made by isochoric heating of the system at quasi-equilibrium conditions. The rate of the temperature change was less than $5 \times 10^{-4} \mathrm{~K} \mathrm{~s}^{-1}$. The sample under study was vigorously mixed using a stirrer. The mixing was performed by rotating the calorimeter about the vertical axis with a frequency of 1 Hz . Therefore, at these conditions, the measured quantities $(\Delta Q / \Delta T)_{V}$ and $(\Delta P / \Delta T)_{V}$ can be replaced by the partial derivatives $(\partial U / \partial V)_{T}$ and $(\partial P / \partial T)_{V}$,
respectively. Thus, measured values of derivatives $(\partial U / \partial V)_{T}$ (isochoric heat capacity) and $(\partial P / \partial T)_{V}$ (internal pressure) together with $P V T$ measurement in the same experiment were used to determine the values of internal pressure by using the relation (17.1) and isochoric heat capacity, $c_{V}=(\partial U / \partial T)_{V}$. Thus, in the same experiment we can simultaneously evaluate partial derivatives of the internal energy $c_{V}=(\partial U / \partial T)_{V}$ (caloric property) and $P_{\text {int }}=(\partial U / \partial V)_{T}$ (thermal property). The uncertainty is smaller for the direct measurements of temperature increments $\Delta T$ and pressure increments $\Delta P$ than for the measurements of their absolute values ( $T$ and $P$ ). Therefore, the uncertainty in $(\partial P / \partial T)_{V}$ measurements is within 0.12 to $1.5 \%$ depending on the temperature increment ( $\Delta T$ changes within 0.02 to 0.10 K ). The uncertainty in pressure increment measurements is about 0.2 \%.
In addition to the above direct methods, we may discuss indirect methods. The acoustic method is one indirect method to determine the internal pressure; it has been reviewed by Zorębski ${ }^{30}$. Some authors ${ }^{28,29}$ have used Equation (17.2) to derive values of thermal pressure coefficient from measurements of the isothermal compressibility $K_{T}$ and isobaric coefficient of thermal expansion $\alpha_{P}$. In most cases, values of $K_{T}$ and $\alpha_{P}$ are calculated from density measurements. Zorębski ${ }^{28}$ studied the effect of external pressure on the internal pressure. Zorębski and Gepper-Rybczyńska ${ }^{31}$ reported density, kinematic viscosity and speed of sound of binary (1-butanol+1,4-butanediol) mixtures over the temperature range from (298.15 to 318.15) K. The measured values together with literature isobaric heat capacity data were used to calculate internal pressure using Equation (17.2). The concentration and temperature dependences of the internal pressure, $P_{\text {int }}(T, x)$, at atmospheric pressure for the mixture were studied. They found that the concentration dependence of $P_{\mathrm{int}}(T, x)$ at constant temperature is almost linear. The excess internal pressures were also calculated using the approach proposed by Marczak. ${ }^{32}$ Goharshadi and Nazari ${ }^{33}$ also studied temperature and pressure effects on the internal pressure of liquids using a statistical mechanical EOS. Kumar et al. ${ }^{34}$ used measured ultrasonic velocity and density data to study internal pressure of binary mixtures (acetone$\mathrm{CCl}_{4}$ and acetone-benzene). The measured data were used to study the molecular interactions in binary liquid mixtures. Vadamalar et al. ${ }^{35}$ also used acoustic and viscometric parameters to accurately calculate the internal pressure for binary mixtures of tert-butanol and isobutanol with methyl methacrylate. Sachdeva and Nanda ${ }^{36}$ employed measured ultrasonic wave velocity and density measurements of normal paraffins to calculate the internal pressure. The acoustic method was used by Dzida ${ }^{37}$ to calculate the internal pressure of cyclopentanol at pressures up to 100 MPa and at temperatures from (293 to 318) K. Verdier and Anderson ${ }^{38}$ used an indirect method to estimate the values of internal pressure of mixtures, using thermal expansivity (determined by microcalorimeter) and isothermal compressibility (determined by density measurements). Korolev ${ }^{39}$ studied internal pressure of alcohols using the values of volumetric coefficient (thermal expansion and isothermal compressibility coefficients). Shukla et al. ${ }^{40}$ studied the internal-pressure and its correlation with solubility and pseudo-Gruneisen parameters for binary and multicomponent liquid mixtures over a wide range of concentration at 298 K using the measured values of viscosity, density, and ultrasonic velocity.
Singh and Kumar ${ }^{41}$ measured density, speed of sound, and refractive index of the ionic liquids (IL) [C8mim][Cl], [C4mim][C1PSO3], and [C4mim][C8OSO3] over the temperature range from (283 to 343) K. The measured density and speed of sound data were used to calculate the internal pressure from Equation (17.2) where thermal expansion coefficient and isothermal compressibility were calculated using the measured values of density and speed of sound. The derived values of internal pressure of IL are higher than those of water and organic liquids, but lower than ordinary molten salt. Allen et al. ${ }^{42}$ determined the internal pressure for some compounds using speed of sound data. The authors studied the relation between $P_{\text {int }}$ and $U_{\text {coh }} / \Delta V$. They found that the values of
proportionality coefficient n in $P_{\text {int }}=\mathrm{n} U_{\text {coh }} / \Delta V$ is close to unity for nonpolar liquids. For polar liquids the values of $n$ vary within the range ( 0.32 to 1.64 ). Acevedo et al. ${ }^{43}$ found that the values of n for associated fluids are less than $\mathrm{n}<1$, while for non-polar liquids n is approximately 1 . For strongly associated liquids (especially for H -bonded liquids), n is much less than 1.
Piekarski et al. ${ }^{44}$ reported density, heat capacity, and speed of sound data for binary acetonitrile+2methoxyethanol mixture at 298.15 K in the whole composition range. The measured data were used to calculate the internal pressure of the mixture using Equation (17.2). Almost linear dependence of the internal pressure as a function of concentration was observed. Kannappan et al. ${ }^{45}$ measured speed of sound, density and viscosity of ternary mixture of alcohols with DMF and cyclohexane at three temperatures (303, 308, and 313) K. The measured data were used to calculate excess internal pressure; for all measured mixtures the excess internal pressure are negative.

### 17.5 One-Phase Isochoric Heat Capacity and Internal Pressure

The internal pressure, $(\partial U / \partial V)_{T}=P_{\text {int }}$, and isochoric heat capacity, $(\partial U / \partial T)_{V}=c_{V}$, i.e., volume and temperature derivatives of the internal energy, describes the sensitivity of internal energy $U$ to a change in specific volume $V$ and temperature $T$ at the isothermal and isochoric processes, respectively. Therefore, direct simultaneous measurements of $P_{\text {int }}(T, V)$ and $c_{V}(T, V)$ provides the caloric equation of state $U(T, V)$, which could yield more accurate calculations of thermal properties than a traditional thermal $P(V, T)$ equation of state. Thus, the total differential of internal energy is defined through $P_{\text {int }}$ and $c_{V}$ is given by,

$$
\begin{equation*}
d U(T, V)=\left(\frac{\partial U}{\partial T}\right)_{V} d T+\left(\frac{\partial U}{\partial V}\right)_{T} d V=c_{V} d T+P_{\mathrm{int}} d V \tag{17.27}
\end{equation*}
$$

where heat capacity $c_{V}$ and internal pressure $P_{\text {int }}$ can be directly measured in the same calorimetric experiment. The caloric EOS can be derived by integrating relation (17.27). In our previous studies (see, for example ${ }^{24-27}$ ), we have developed a method of simultaneous measurements of $(\partial U / \partial V)_{T}$ and $(\partial U / \partial T)_{V}$, i.e., internal pressure and isochoric heat capacity.
Temperature dependency of the internal pressure (temperature coefficient of internal pressure) can be calculated directly from Equation (17.1) as:

$$
\begin{align*}
& \left(\frac{\partial P_{\text {int }}}{\partial T}\right)_{V}=T\left(\frac{\partial^{2} P}{\partial T^{2}}\right)_{V}  \tag{17.28}\\
& \left(\frac{\partial c_{V}}{\partial V}\right)_{T}=T\left(\frac{\partial^{2} P}{\partial T^{2}}\right)_{V}  \tag{17.29}\\
& \left(\frac{\partial P_{\text {int }}}{\partial T}\right)_{V}=\left(\frac{\partial c_{V}}{\partial V}\right)_{T}=T\left(\frac{\partial^{2} P}{\partial T^{2}}\right)_{V} \tag{17.30}
\end{align*}
$$

The measured internal pressure as a function of temperature provides information on the second temperature derivative (curvature) of the real external pressure properties of the liquids, $\left(\frac{\partial^{2} P}{\partial T^{2}}\right)_{V}$. As shown by Equation (17.30), the first temperature derivative of the internal pressure is related to the second temperature derivative of external pressure or, equivalently, it's related to the volume dependence of the isochoric heat capacity at a fixed temperature. As careful experimental studies have shown, ${ }^{46-53}$ isochoric heat capacity measurements exhibit isothermal extrema (both maxima and minima) in the near- and supercritical regions along near- and supercritical isotherms. This
behavior, depicted in Figures 17.4(a-b), is due to critical fluctuations and isothermal minima ${ }^{47,50}$ at high densities $\left(\approx 2 \rho_{C}\right)$, where $\left(\partial c_{V} / \partial V\right)_{T}=0$. Therefore, the locus of $c_{V}$ extrema is the same as the extrema of the internal pressure, $\left(\partial P_{\text {int }} / \partial T\right)_{V}=0$. This means that the locus of isothermal maximum and minimum of the $C_{V}$ (or inflection point of the $P-T$ isochores, where $\left.\left(\partial^{2} P / \partial T^{2}\right)_{V}=0\right)$ coincide with the isochoric maximums and minimums of the internal pressure, $\left(\partial P_{\text {int }} / \partial T\right)_{V}=0$. The locus of isochoric heat capacity extrema is an important characteristic curve for a fluid, as it also is the locus along which $P-T$ isochores have an inflection, $\left(\partial^{2} P / \partial T^{2}\right)_{V}=0$. Experimental $P-T$ isochores have very small curvature which is close to impossible to accurately extract from direct $P V T$ measurements. The analysis of the extrema properties of isochoric heat capacity and internal pressure is one way to study the qualitative behavior of the thermodynamic surface of fluids, especially near the critical and supercritical conditions where PVT surface shows anomalous behavior. The locus of isothermal maximum and minimum of internal pressure and $c_{V}$ for some selected fluids in $\rho-T$ and $P-T$ projection are shown in Figures 17.5 to 17.9. As one can see from Figures 17.5 to 17.9, the isothermal $c_{V}$ maxima (therefore isochoric $P_{\text {int }}$ maxima) curves in the supercritical region do fall exactly on the critical isochore. The isothermal $c_{V}$ and isochoric $P_{\text {int }}$ maxima curves in the supercritical region start at the critical point and runs along a density minimum ( $\rho_{\text {min }} \approx 0.95 \rho_{\mathrm{C}}$ ) to higher temperatures. The isothermal $c_{V}$ and $P_{\text {int }}$ maxima curve is intersected twice by the critical isochore at $T=T_{\mathrm{C}}$ and $T=1.1 T_{\mathrm{C}}$ (Figure 17.9). A detailed discussion of the behavior of loci of isochoric heat capacity maxima (or isothermal internal pressure maxima) along supercritical isotherms near the critical density was provided by Abdulagatov et al. ${ }^{46}$ and Magee and Kobayashi. ${ }^{48}$
Loci of $c_{V}$ and $P_{\text {int }}$ extrema are very sensitive to both the mathematical structure of an equation of state and the molecular structure of the fluid; therefore, they can be used to test the quality of an EOS and molecular theories of thermodynamic property behavior. Isochoric heat capacity and $P_{\text {int }}$ extrema data can enable a correlator to more correctly choose the structure of the EOS.

### 17.6 Two-Phase Isochoric Heat Capacity and Internal Pressure

Two-phase isochoric heat capacity is also directly related to the internal pressure along the saturation curve. For liquid-gas coexistence, the Yang and Yang ${ }^{76}$ relation for two-phase isochoric heat capacity is given by:

$$
\begin{equation*}
c_{V 2}=-T \frac{\mathrm{~d}^{2} \mu}{\mathrm{~d} T^{2}}+V T \frac{\mathrm{~d}^{2} P_{\mathrm{s}}}{\mathrm{~d} T^{2}} \tag{17.31}
\end{equation*}
$$

where the second temperature derivative of chemical potential $\frac{\mathrm{d}^{2} \mu}{\mathrm{~d} T^{2}}$ and vapor pressure $\frac{\mathrm{d}^{2} P_{\mathrm{s}}}{\mathrm{d} T^{2}}$ are functions of temperature only. Thus, by integrating Equation (17.31) we can derive a Yang and Yang caloric equation of state for two-phase system as:

$$
\begin{equation*}
\Delta U_{2}=-\int_{T_{0}}^{T} T \frac{d^{2} \mu}{d T^{2}} d T+V \int_{T_{0}}^{T} T \frac{d^{2} P_{S}}{d T^{2}} d T \tag{17.32}
\end{equation*}
$$

where $\Delta U_{2}=U(T)-U\left(T_{0}\right)$, and the second temperature derivatives of chemical potential $\frac{\mathrm{d}^{2} \mu}{\mathrm{~d} T^{2}}$ and vapor pressure $\frac{\mathrm{d}^{2} P_{\mathrm{s}}}{\mathrm{d} T^{2}}$ can be directly calculated from two-phase isochoric heat capacity measurements
as a function of temperature or using measured values of saturated properties ( $T_{\mathrm{S}}, V^{\prime}, c_{V 2}^{\prime}, V^{\prime \prime}, c_{V 2}^{\prime \prime}$ ) as: ${ }^{69,71,77,78}$

$$
\begin{equation*}
\frac{\mathrm{d}^{2} P_{\mathrm{S}}}{\mathrm{~d} T^{2}}=\frac{c_{V 2}^{\prime \prime} V^{\prime}-c_{V 2}^{\prime} V^{\prime \prime}}{T\left(V^{\prime \prime}-V^{\prime}\right)} \quad \text { and } \quad \frac{\mathrm{d}^{2} \mu}{\mathrm{~d} T^{2}}=\frac{V^{\prime \prime} c_{V 2}^{\prime}-V^{\prime} c_{V 2}^{\prime \prime}}{T\left(V^{\prime}-V^{\prime \prime}\right)} . \tag{17.33}
\end{equation*}
$$

Internal pressure from the Yang and Yang two-phase caloric equation state (32) is:

$$
\begin{equation*}
P_{S \mathrm{int}}=\left(\frac{\partial \Delta U_{2}}{\partial V}\right)_{T}=\int T \frac{d^{2} P_{\mathrm{S}}}{d T^{2}} d T=T \frac{d P_{\mathrm{S}}}{d T}-P_{\mathrm{S}} \tag{17.34}
\end{equation*}
$$

Thus, starting with the caloric equation of state Equation (17.32), based on Yang-Yang two-phase isochoric heat capacity Equation (17.31), we derived the equation for internal pressure along the vapor-pressure curve Equation (17.34) by using the slope of the vapor-pressure curve $\frac{d P_{\mathrm{S}}}{d T}$. Relation (17.34) is the definition of the internal pressure through the vapor-pressure equation by analogy to the equation of state Equation (17.1) for the one-phase region. Therefore, as follows from Equation (17.34), the internal pressure at saturation can be directly calculated from two-phase isochoric heat capacity measurements at saturation by using:

$$
\begin{equation*}
P_{\mathrm{int}}^{\mathrm{sat} 2}=\int_{T_{0}}^{T} \frac{c_{V 2}^{\prime \prime}-c_{V 2}^{\prime}}{V^{\prime \prime}-V^{\prime}} d T . \tag{17.35}
\end{equation*}
$$

It follows from Equation (17.34) that the first temperature derivative of the internal pressure at saturation diverges at the critical point as:

$$
\begin{equation*}
\frac{d P_{\mathrm{int}}^{\mathrm{sat} 2}}{d T}=T \frac{d^{2} P_{\mathrm{S}}}{d T^{2}} \propto t^{-\alpha} \tag{17.36}
\end{equation*}
$$

or can be calculated from two-phase heat capacity measurements ( $c_{V 2}^{\prime \prime}, c_{V 2}^{\prime}$ ) as:

$$
\begin{equation*}
\frac{d P_{\mathrm{int}}^{\mathrm{sat} 2}}{d T}=\frac{c_{V 2}^{\prime \prime}-c_{V 2}^{\prime}}{\left(V^{\prime \prime}-V^{\prime}\right)} \tag{17.37}
\end{equation*}
$$

Equation (17.37) shows that the slope of the saturated internal pressure equation $P_{\text {int }}^{\text {sat } 2}-T$ is proportional to the two-phase isochoric heat capacity difference ( $c_{V 2}^{\prime \prime}-c_{V 2}^{\prime}$ ) between the vapor ( $c_{V 2}^{\prime \prime}$ ) and the liquid ( $c_{V 2}^{\prime}$ ) heat capacities at saturation. Equations (17.36) and (17.37) are the analogy of Equations (17.28) and (17.30) for $\left(\frac{\partial P_{\text {int }}}{\partial T}\right)_{V}$ in the one-phase region. Figures 17.10 to 17.12 depict comparisons of the values of $\frac{d P_{\text {Sint }}}{d T}$ derived from the direct isochoric heat capacity measurements and calculated from the vapor-pressure data for selected compounds that have been carefully studied experimentally.
As follows from well-known thermodynamic relations (Abdulagatov et al., ${ }^{82,83,87}$ Polikhronidi et $\mathrm{al} .{ }^{88}$ ), the one-phase partial temperature derivative of pressure at saturation is:

$$
\begin{equation*}
\left(\frac{\partial P}{\partial T}\right)_{V}^{\text {sat }}=\frac{d P_{\mathrm{s}}}{d T}+\frac{1}{T} \frac{d T}{d V} \Delta c_{V} \tag{17.38}
\end{equation*}
$$

or

$$
\begin{equation*}
T\left(\frac{\partial P}{\partial T}\right)_{V}^{\text {sat }}=T \frac{d P_{\mathrm{s}}}{d T}+\frac{d T}{d V} \Delta c_{V} \tag{17.39}
\end{equation*}
$$

where $\left(\frac{\partial P}{\partial T}\right)_{V}^{\text {sat }}$ is the one-phase partial temperature derivative of total pressure at the saturation curve (or initial slope of the one-phase $P-T$ curves (isochores) at saturation curve; $\frac{d P_{\mathrm{s}}}{d T}$ is the slope of the two-phase saturation curve (vapor-pressure curve); $\frac{d T}{d V}$ is the temperature derivative of the specific volume at saturation curve; and $\Delta c_{V}=c_{V 2}-c_{V 1}$ is the isochoric heat capacity jump at saturation. At each phase transition point (temperature) we have three thermal pressure coefficients: (1) slope of the one-phase liquid $P-T$ isochore $\left(\frac{\partial P}{\partial T}\right)_{V}^{\prime} ;(2)$ slope of the one-phase vapor $P-T$ isochore $\left(\frac{\partial P}{\partial T}\right)_{V}$; and (3) the slope of the vapor-pressure $\frac{d P_{S}}{d T}$, which correspond to the three internal pressures, namely:

$$
\begin{align*}
& P_{\text {int }}^{\prime}=T\left(\frac{\partial P}{\partial T}\right)_{V}^{\prime}-P_{\mathrm{S}},  \tag{17.40}\\
& P_{\text {int }}^{\prime \prime \prime}=T\left(\frac{\partial P}{\partial T}\right)_{V}^{\prime \prime}-P_{\mathrm{S}},  \tag{17.41}\\
& P_{\text {int }}^{\text {sat } 2}=T\left(\frac{d P_{\mathrm{S}}}{d T}\right)-P_{\mathrm{S}}, \tag{17.42}
\end{align*}
$$

It is apparent that $\left(\frac{\partial P}{\partial T}\right)_{V}^{\prime}>\frac{d P_{S}}{d T}>\left(\frac{\partial P}{\partial T}\right)_{V}^{\prime \prime}\left(P_{\mathrm{int}}^{\prime}>P_{\text {int }}^{\prime \prime}>P_{\text {int }}^{\text {sat2 }}\right)$, while at the critical point all of the slopes become equal, $\left(\frac{\partial P}{\partial T}\right)_{V_{c}}^{\prime}=\left(\frac{d P_{\mathrm{s}}}{d T}\right)_{c}=\left(\frac{\partial P}{\partial T}\right)_{V_{c}}^{\prime \prime}$, i.e., $P_{\mathrm{int}}^{\prime}=P_{\mathrm{int}}^{\prime \prime}=P_{\mathrm{int}}^{\text {sat } 2}$. As follows from Equation (17.39), the internal pressure in the one-phase region at saturation is:

$$
\begin{equation*}
P_{\mathrm{int}}^{\text {sat1 }}=P_{\mathrm{int}}^{\text {sat2 }}+\frac{d T}{d V} \Delta c_{V} \tag{17.43}
\end{equation*}
$$

where $P_{\text {int }}^{\text {sal2 }}$ can be calculated from $c_{V}$ measurements by using Equation (17.35). As one can see from Equation (17.43), the internal pressure at saturation in the one-phase region $P_{\text {int }}^{\text {sat1 }}$ defined from the two-phase internal pressure $P_{\text {int }}^{\text {sat2 }}$ and isochoric heat capacity jump $\Delta c_{V}$ (or the difference). Other words, the internal pressure jump (or difference) at the phase transition:

$$
\begin{equation*}
\Delta P_{\mathrm{int}}^{\text {sat }}=P_{\mathrm{int}}^{\text {sat } 1}-P_{\mathrm{int}}^{s a t 2}=\frac{d T}{d V} \Delta c_{\mathrm{V}}, \tag{17.44}
\end{equation*}
$$

and completely defined from the isochoric heat capacity jump $\Delta C_{V}$ and the slope of the coexistence curve $\frac{d T}{d V}$. The values of $P_{\text {int }}^{\text {sat1 }}$ and difference $\Delta P_{\text {int }}^{\text {sat }}=P_{\text {int }}^{\text {sat1 }}-P_{\text {int }}^{\text {sat2 }}$, calculated from measured isochoric heat capacity data for some selected liquids and gases, are presented in Figures 17.13 to 17.15, respectively. According to the scaling theory of critical phenomena, the coexistence curve slope, $\frac{d T}{d V}=-\rho^{2} / \frac{d \rho}{d T} \propto t^{1-\beta-\alpha} \rightarrow 0$, goes to zero faster than $\Delta c_{V} \propto t^{-\alpha} \rightarrow \infty$ diverges at the critical point, then $P_{\text {int }}^{\text {sat1 }}-P_{\text {int }}^{\text {sat2 }}=\frac{d T}{d V} \Delta c_{V} \propto t^{1-\beta-\alpha}=0$ at the critical point (see Figure 17.15).

### 17.7 Internal Pressure as a Function of External Pressure, Temperature or Density from a Reference Equation of State

It follows from Equation (17.1) that the internal pressure can be readily calculated from a thermal equation of state. Therefore, the temperature, external pressure, and density dependences of the internal pressure of fluids can be calculated from a reference EOS. ${ }^{81}$ In the present work we have calculated the internal pressure for some selected pure fluids and binary mixtures as a function of density, temperature, external pressure, and concentration (in the $P_{\text {int }}-T, P_{\text {int }}-\rho, P_{\text {int }}-P$, and $P_{\text {int }}-x$ ) using reference equations of state (NIST, REFPROP ${ }^{81}$ ).
Internal pressure is very sensitive to external pressure. Zorębski ${ }^{28,30}$ studied the effect of external pressure on the internal pressure behavior for alkanols. He observed that in general $P_{\text {int }}$ increases with increasing external pressure, passing through a weak maximum. As illustrated by Figure 17.16, the internal pressure initially (at moderate pressures) increases with external pressure, then passes through a weak maximum and then decreases slightly at higher pressures.
As was mentioned previously, the temperature dependency of the internal pressure is very important because of its close relation with isochoric heat capacity (see Equations 17.30, 17.35, 17.37, 17.43, and 17.44). The temperature dependence of the internal pressure at one atmosphere pressure is illustrated in Figure 17.17 for three n-alkanes, namely pentane, heptane and decane; the data were calculated with a reference EOS (REFPROP ${ }^{81}$ ). Also shown are experimental data for internal pressure at one atmospheric pressure as reported by Sachdev and Nanda, ${ }^{36}$ which are in good agreement. The isochoric temperature behavior of the internal pressure of carbon dioxide and water [water was calculated from the IAPWS fundamental EOS ${ }^{11}$ ] are shown in Figure 17.18. Sharp changes of $P_{\text {int }}$ near the phase transition temperature for near-critical isochores are related to the near-critical anomaly of the isochoric heat capacity, because the slope of $\left(\frac{\partial P_{\text {int }}}{\partial T}\right)_{V}$ is directly related to the isochoric heat capacity behavior $c_{V}$ (see Equation 17.30). The isochoric temperature maximums of the internal pressure, where $\left(\frac{\partial P_{\text {int }}}{\partial T}\right)_{V}=0$, are exactly the same as the isochoric heat capacity maximum along the supercritical isotherms. The isochoric temperature maximum of $P_{\text {int }}$, $\left(\frac{\partial P_{\text {int }}}{\partial T}\right)_{V}=\left(\frac{\partial c_{V}}{\partial V}\right)_{T}=0$, which agrees with the $c_{V}$ maximum as shown in Figures 17.8 and 17.9 as discussed earlier.

### 17.8 Locus of Zero Internal Pressure

As was mentioned above, depending on temperature and density, the sign of total internal pressure can be either positive or negative (see, for example, Equation 17.1). It is apparent that if $T\left(\frac{\partial P}{\partial T}\right)_{V}<P$, then as a result, $P_{\text {int }}<0$. Therefore, depending on temperature and density, either $P_{\mathrm{A}}$ or $P_{\mathrm{R}}$ can dominate, i.e., contributions of the $P_{\mathrm{A}}$ and $P_{\mathrm{R}}$ are quite different in different temperature and density ranges. Thus, there exist certain temperatures and densities where both $P_{\mathrm{A}}$ and $P_{\mathrm{R}}$ are equal but have opposite signs, $P_{\mathrm{A}}=-P_{\mathrm{R}}$, i.e., total internal pressure is zero. In other words, the slopes of the internal energies $U_{\mathrm{A}}(\mathrm{V})$ and $U_{\mathrm{R}}(V)$ are equal with opposite signs, $\left(\partial U_{\mathrm{A}} / \partial V\right)_{T}=-\left(\partial U_{\mathrm{R}} / \partial V\right)_{\mathrm{T}}$. The evaluation of zero internal pressure, where $T\left(\frac{\partial P}{\partial T}\right)_{V}=P$, takes place at
high pressures (in the high-density range). To illustrate this, we calculated the locus of zero internal pressure in the various projections $(T-\rho, P-T$, and $P-\rho)$ for propane as shown in Figure 17.19. Figure 17.19 depicts a $T-\rho$ projection that shows the locus of zero internal pressure is very nearly a straight line, a finding that could aid in predictions of this locus. Conversely, a $P-T$ projection at high pressures (above 500 MPa ) shows that the temperatures on the locus of zero internal pressure increase sharply at high pressures. In the $P-\rho$ projection, the pressure where $P_{\text {int }}=0$ decreases sharply at high densities.

### 17.9 Simon's Melting Curve Equation Parameters and Internal Pressure

Simon ${ }^{96-100}$ proposed a semi-empirical equation for the melting curve,

$$
\begin{equation*}
P=a\left[\left(\frac{T}{T_{0}}\right)^{c}-1\right]+P_{0} \tag{17.45}
\end{equation*}
$$

since $P_{0} \ll a$,

$$
\begin{equation*}
P=a\left[\left(\frac{T}{T_{0}}\right)^{c}-1\right] \tag{17.46}
\end{equation*}
$$

where $T_{0}, P_{0}$ are the normal melting temperature and pressure, respectively; $a c \approx P_{\text {int }}=T\left(\frac{d P_{\mathrm{m}}}{d T}\right)-P_{\mathrm{m}}$ or $a \approx P_{\text {int }} / c$ is the internal pressure; $C$ is the constant (Simon's parameter). Simon's equation describes the melting curve of a wide range of substances (gases, liquids, metals) to a good degree of approximation (see, for example, Babb ${ }^{101}$ ). The melting Equation (17.46) was proposed by Simon, ${ }^{96-100}$ after careful study of experimental melting curve data ( $\left.P_{\mathrm{m}}-T\right)$ for various substances. Most authors have successfully represented their own measured SLE $P_{\mathrm{m}}-T$ data with Equation (17.46) (see, for example ${ }^{102,103}$ ). Simon's melting curve parameter $C$ can be determined from experimental straight line $\ln \left(P_{\mathrm{m}}+a\right)$ - $\ln T$. Simon's Equation (17.46) is very useful to represent experimental melting curve data $\left(P_{\mathrm{m}}-T\right)$ over wide temperature and pressure ranges. This equation fits all of the available experimental melting curve data for various fluids within reasonable deviations. The values of constant $\boldsymbol{C}$ varied for most studied fluids within 1.3 to 4.5 , namely, ( 1.3 to 1.6) for noble gases (monatomic gases, $\mathrm{Ar}, \mathrm{Kr}, \mathrm{Xe}, \mathrm{Ne}$, etc.); from (1.6 to 3.0) for diatomic gases $\left(\mathrm{O}_{2}, \mathrm{~N}_{2}, \mathrm{H}_{2}\right.$, etc.). There have been a number of attempts to arrive at a theoretical basis ${ }^{104-107}$ of Simon's equation.
A generalized Simon's equation for the melting curve is given by,

$$
\begin{equation*}
\frac{a+P_{\mathrm{m}}}{a+P_{0}}=\left(\frac{T}{T_{0}}\right)^{c} \tag{17.47}
\end{equation*}
$$

where $c=\frac{Q_{0}}{\Delta V_{0}\left(a+P_{0}\right)}$ and $a$ are Simon's parameters; $P_{0}, T_{0}, \Delta V_{0}$, and $Q_{0}$ are the triple-point properties (pressure, temperature, molar volume changes, and melting heat at the triple point), respectively. The parameter $a=\left(\frac{\partial U}{\partial V}\right)_{T}$ is the internal pressure along the melting curve. Since $a \gg P_{0}$, therefore, $a c=\frac{Q_{0}}{\Delta V_{0}}$. Thus, Simon's melting equation can be rewritten as follows,

$$
\begin{equation*}
\frac{P_{m}}{a}=\left(\frac{T}{T_{0}}\right)^{\frac{Q_{0}}{\Delta v_{0} a}}-1 . \tag{17.48}
\end{equation*}
$$

This equation contains just one fitting parameter $a$ and the other Simon's parameter $c$ can be calculates using the triple point characteristics, $T_{0}, \Delta V_{0}, Q_{0}$. For example, the value of Simon's parameter for benzene calculated using triple-point characteristics is $c=2.49$.
In order to estimate the values of Simon's equation parameters from triple point data, Zhokhovskii and Bogdanov ${ }^{108}$ used the following approach,

$$
\begin{equation*}
c=\frac{\Delta H_{0}}{\Delta V_{0}\left(b+P_{0}\right)} \text { and } a c=P_{\mathrm{int}}=\frac{\Delta H_{0}}{\Delta V_{0}}, \tag{17.49}
\end{equation*}
$$

where $\Delta H_{0}=126.41 \mathrm{~kJ} \mathrm{~kg}^{-1}$ and $\Delta V_{0}=0.1318 \mathrm{~cm}^{3} \mathrm{~g}^{-1}$ (for benzene) are the enthalpy and specific volume changes of melting at the triple point, respectively. The value of parameter $c$ calculated from this relation Equation (17.49) for benzene is $c=2.313$ Thus, the internal pressure $\boldsymbol{a}$ can be estimated using $\Delta H_{0}, \Delta V_{0}$, and Simon's parameter $c$ as $P_{\text {int }}=a=\frac{\Delta H_{0}}{c \Delta V_{0}}$. The same approach was used by Skripov and Faizullin ${ }^{109}$ to estimate the Simons's parameter $c$ by using,

$$
\begin{equation*}
c=\frac{\alpha \Delta H_{0}}{P_{\mathrm{int}} \Delta V_{0}} \tag{17.50}
\end{equation*}
$$

where $P_{\text {int }}=379.33 \mathrm{MPa}^{28}\left(P_{\mathrm{int}}=378.61 \mathrm{MPa}\right.$ from REFPROP ${ }^{81}$ from ( 379 to 381 ) MPa by Marcus ${ }^{110}$ ) is the internal pressure of benzene at room temperature (293.15 K), $\alpha=\frac{P_{\text {int }}}{a} \approx 1$. Thus, the value of Simon's parameter calculated from Equation (17.50) by using reference melting point properties, $\Delta H_{0}$ and $\Delta V_{0}$, is $c=\left(2.504\right.$ to 2.515 depending on the value of $P_{\text {int }}$ ), which is in good agreement ( $\mathrm{AAD}=0.2$ \%) with the values derived from direct experimental melting curve data and other reported data. Therefore, the values of Simon's parameters can be predicted using melting molar volume and enthalpy changes at the triple point and internal pressure at room temperature calculated from the equation of state. Figure 17.20 shows the comparison between the reported experimental melting point data for toluene, benzene, and cyclohexane and the values calculated from Simon's Equation (17.46) with parameters predicted using internal pressure. This has illustrated how by applying the concept of internal pressure, we obtain a powerful method to fit a reliable model for the melting curve.

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Figure 17.1. Schematic representation of potential $\phi(r)$ as a function of separation distance $r$.


Figure 17.2 Internal energy (left) and internal pressure (right) of water as a function of specific volume calculated from fundamental equation of state of water (IAPWS ${ }^{11}$ formulation) along the selected supercritical isotherms: (1-647.1) K (critical); (2-800) K.


Figure 17.3. Statistical structure factor $S(Q)$ versus $Q$ for $n^{-} \mathrm{C}_{7} \mathrm{H}_{16}, \mathrm{CO}_{2}$, and $\mathrm{CH}_{4}$ for various thermodynamic states. $\mathbf{n}-\mathbf{C}_{7} \mathbf{H}_{\mathbf{1 6}}$ : dashed line for internal pressure of $P_{\text {int }}=110.73 \mathrm{MPa}, \rho=500 \mathrm{~kg} \mathrm{~m}^{-}$ ${ }^{3}$, and $T=500 \mathrm{~K}$; solid line for internal pressure of $P_{\mathrm{int}}=27.61 \mathrm{MPa}, \rho=300 \mathrm{~kg} \mathrm{~m}^{-3}$, and $T=550 \mathrm{~K}$. $\mathbf{C O}_{2}$ : dashed line for positive internal pressure ( $P_{\mathrm{int}}=222.21 \mathrm{MPa}, \rho=1452 \mathrm{~kg} \mathrm{~m}^{-3}$, and $T=310 \mathrm{~K}$ ), solid line for negative internal pressure ( $P_{\text {int }}=-45.68 \mathrm{MPa}, \rho=470 \mathrm{~kg} \mathrm{~m}^{-3}$, and $T=310 \mathrm{~K}$ ), and dashed-dotted line is for zero internal pressure. $\mathbf{C H}_{4}$ : dashed line for positive internal pressure ( $P_{\mathrm{int}}=14.44 \mathrm{MPa}, \rho=400 \mathrm{~kg} \mathrm{~m}^{-3}$, and $T=600 \mathrm{~K}$ ), solid line for negative internal pressure ( $P_{\mathrm{int}}=-61.3$ MPa, $\rho=450 \mathrm{~kg} \mathrm{~m}^{-3}$, and $T=600 \mathrm{~K}$ ).


Figure 17.4a. Measured and calculated isochoric heat capacities $c_{V}$ for argon (left) and carbon dioxide (right) as a function of density $\rho$ in the supercritical region. Left: Symbols are reported by Anisimov et al.. ${ }^{54,55}$ Solid curves are calculated from Tegeler et al. ${ }^{56}$ Right: Symbols are reported by Abdulagatov et al. ${ }^{57,58}$ and Amirkhanov et al. ${ }^{59-61}$; Solid curves are calculated from a crossover model. ${ }^{62}$


Figure 17.4b. Measured and calculated isochoric heat capacities $c_{V}$ for heavy water as a function of density $\rho$ in the critical and supercritical regions. Symbols are reported by Polikhronidi et al.;66 solid curves are calculated from a crossover model; ${ }^{67}$ dashed curve is the isothermal $C_{V}$ maximum loci.


Figure 17.5. Second temperature derivative of external pressure (or first temperature derivative of the internal pressure, $\left.\left(\partial P_{\text {int }} / \partial T\right)_{V}\right)$ as a function of density $\rho$ along near- and supercritical isotherms for pure water calculated from a crossover equation of state. ${ }^{65}$ Symbols are experimental data from isochoric heat capacity measurements. ${ }^{63,64,67}$


Figure 17.6. Calculated from crossover equation of state ${ }^{62}$ values of $\left(\partial P_{\text {int }} / \partial T\right)_{V}$ for carbon dioxide as a function of density $\rho$ along selected supercritical isotherms. Symbols are experimental data. ${ }^{57-61}$


Figure 17.7. Temperature dependence of the derivative $\left(\partial P_{\text {int }} / \partial T\right)_{V}$ for pure water along near-critical and supercritical isobars calculated from a crossover model. ${ }^{65}$



Figure 17.8. Isothermal $c_{V}$ maximum and minimum loci (or isochoric temperature maximum and minimum of the internal pressure) for water and carbon dioxide calculated from a crossover equation of state. ${ }^{62,65}$ Dashed curves are isothermal maximum (CA) and minimum (AB) of $c_{V}$ and isochoric maximum and minimum of the internal pressure, where $\left(\partial P_{\text {int }} / \partial T\right)_{V}=\left(\partial c_{V} / \partial V\right)_{T}=0$.


Figure 17.9a. Isothermal $c_{V}$ maximum for light and heavy water in $T$ - $\rho$ projection calculated from a scaling-type EOS (CREOS ${ }^{63,65}$ ). The solid curve is liquid-gas coexistence curve. Dashed curves are isothermal $c_{V}$ maximum and isochoric maximum of internal pressure where $\left(\partial P_{\text {int }} / \partial T\right)_{V}=\left(\partial c_{V} / \partial V\right)_{T}=0$.


Figure 17.9b. Isothermal maxima and minima loci of $c_{V}$ for n-pentane calculated from a crossover model ${ }^{75}$ in $T-\rho$ and $P-T$ planes. CB-isothermal $c_{V}$ maxima loci; BD-isothermal $c_{V}$ minima loci.


Figure 17.10. Temperature derivatives of the internal pressure along the vapor-pressure saturation curve derived from calorimetric measurements ${ }^{66,77,79,80}$ [Equation (17.38)] together with the values calculated from vapor pressure equation (REFPROP ${ }^{81}$ ) for light and heavy water.


Figure 17.11. Temperature derivatives of the internal pressure along the vapor-pressure saturation curve derived from calorimetric measurements ${ }^{57-61}$ [Equation (17.38)] together with the values calculated from vapor pressure equation (REFPROP ${ }^{81}$ ) for carbon dioxide.


Figure 17.12. Temperature derivatives of the internal pressure along the vapor-pressure saturation curve derived from calorimetric measurements ${ }^{82-86}$ (Equation 17.38) together with the values calculated from vapor pressure equation (REFPROP ${ }^{81}$ ) for n -alkanes.


Figure 17.13. Internal pressure for propane at one-phase saturation curve derived from isochoric heat capacity measurements together with the values calculated (Solid curves) from a reference equation of state ( $\mathrm{REFPROP}^{81}$ ). The Dashed curve is the internal pressure along the two-phase vapor-pressure curve. CP-the critical point. Symbols depict calorimetric measurements [Equations. (17.35 and 17. 43)].


Figure 17.14a. Internal pressure difference of light water along the coexistence curve. Solid line is calculated from a reference EOS (REFPROP ${ }^{81}$ ) for liquid-phase. Dashed line is the vapor-phase. The symbols are calculated from isochoric heat capacity measurements [Equation (17. 44)].


Figure 17.14b. Internal pressure difference of heavy water along the coexistence curve. Solid line is calculated from a reference EOS (REFPROP ${ }^{81}$ ) for liquid-phase. Dashed line is the vapor-phase. The symbols are calculated from isochoric heat capacity measurements [Equation (17.44)].


Figure 17.15. Measured $\Delta P_{\text {int }}^{\text {sat }}$ versus $\Delta c_{V}$ plot for diethyl ether (DEE) and $\mathbf{C O}_{2}$. Symbols are derived from experimental isochoric heat capacity data. ${ }^{57-61,88}$ Solid lines are calculated from an EOS.${ }^{81}$ Dashed line is extrapolated values.


Figure 17.16. Internal pressure $P_{\text {int }}$ for various molecular fluids as a function of external pressure $P_{\text {ext }}$ along their critical isotherms calculated from a fundamental equation of state (REFPROP ${ }^{81}$ ): butane ${ }^{92}$; toluene ${ }^{94}$; carbon dioxide ${ }^{95}$; methanol ${ }^{933}$; light water-IAPWS ${ }^{11}$; methane ${ }^{89}$; ethane ${ }^{90}$; propane ${ }^{91}$; n-pentane. ${ }^{92}$


Figure 17.17. Internal pressure $P_{\text {int }}$ for selected n-alkanes (n-pentane, n-heptane and n-decane) as a function of temperature at atmospheric pressure calculated (solid lines) from a reference EOS by using REFPROP ${ }^{81}$ together with the values derived from the speed of sound and density measurements (symbols) by Sachdev and Nanda. ${ }^{36}$


Figure 17.18. Internal pressure $P_{\text {int }}$ for carbon dioxide and light water as a function of temperature $T$ along the various liquid and vapor isochores near the phase transition curve calculated from the crossover equation of state. ${ }^{62,65}$ Dashed-dotted curves are the isochoric temperature maxima loci of the internal pressure, $\left(\partial P_{\text {int }} / \partial T\right)_{V}=0$ from the calorimetric measurements. ${ }^{57-61,63,64,74}$


Figure 17.19. Locus of internal pressure zero points $\left[P_{\mathrm{int}}=T\left(\frac{\partial P}{\partial T}\right)_{V}-P=0\right.$ ] for propane in the (a) $\rho$ $T$, (b) $P-T$, and (c) $\rho-P$ planes calculated from EOS by Lemmon et al. ${ }^{91}$


Figure 17.20. Melting curve data for toluene, benzene and cyclohexane: Solid curve, predicted from Simon's Equation (17.31); Symbols, published experimental data.

