Internal Pressure

According to the Thermodynamic Equation of State,

$$\left( \frac{\partial U}{\partial V} \right)_T = T \cdot \left( \frac{\partial p}{\partial T} \right)_V - p \quad \text{ (a)}$$

or,

$$\left( \frac{\partial U}{\partial V} \right)_T = T \cdot \beta_V - p \quad \text{ (b)}$$

The partial differential \( \left( \frac{\partial U}{\partial V} \right)_T \) (with units, \( \text{N m}^{-2} \)) is the internal pressure \( \pi_{\text{int}} \).

$$\pi_{\text{int}} = T \cdot \beta_V - p \quad \text{ (c)}$$

\( \pi_{\text{int}} \) describes the sensitivity of energy \( U \) to a change in volume. A high \( \pi_{\text{int}} \) implies strong inter-molecular cohesion [1-8].

For many liquids, \( T \cdot \beta_V \gg p \) such that \( \left( \frac{\partial U}{\partial V} \right)_T \equiv T \cdot \beta_V \quad \text{ (d)} \)

\( T \cdot \beta_V \) is sometimes called the thermal pressure. By definition, for \( n \) moles of a perfect gas,

$$p \cdot V = n \cdot R \cdot T \quad \text{ (e)}$$

Then

$$V \cdot \left( \frac{\partial p}{\partial T} \right)_V = n \cdot R \quad \text{ (f)}$$

Or,

$$T \cdot \left( \frac{\partial p}{\partial T} \right)_V = n \cdot R \cdot T / V = p \quad \text{ (g)}$$

From equation (a), for a perfect gas, \( \left( \frac{\partial U}{\partial V} \right)_T \) is zero.

The internal pressure for water (\( \ell \)) presents an interesting puzzle [9]. From equations (a) and (c), it follows that [1]

$$\pi_{\text{int}} = T \cdot \left( \frac{\alpha_p}{\kappa_T} \right) - p \quad \text{ (h)}$$

But at the temperature of maximum density (TMD), \( \alpha_p \) is zero. So near the TMD, \( \pi_{\text{int}} \) is zero. We understand this pattern if we think about hydrogen bonding. In order to form a strong hydrogen bond between two neighbouring water molecules the O-H---O link has to be close to if not actually linear. In other words the molar volume for water (\( \ell \)) is larger than the molar volume of a system comprising close-packed water molecules. Consequently hydrogen bonding has a strong ‘repulsive’ component to intermolecular interaction. However once formed hydrogen bonding has a strong cohesive contribution to intermolecular forces. Hence for water between 273 and 298
K cohesive and repulsive components of hydrogen bonding play almost competitive roles.

**Footnotes**

[1] Using a calculus operation, \( \frac{\partial p}{\partial T} \)\(_V\) = \(-\left( \frac{\partial V}{\partial T} \right)_p \). 

For equilibrium properties, \( \left( \frac{\partial p}{\partial T} \right)_V = \frac{\alpha_p}{\kappa_T} \).

[2] Some authors use the term ‘isochoric thermal pressure coefficient’ for the property, \( \left( \frac{\partial p}{\partial T} \right)_V \).

[3] For details of original proposals concerning internal pressures see the following references.

(iii) See also S. E. Wood, J. Phys. Chem., 1962, 66, 600.

[4] Internal pressures are quoted in the literature using many units. Here we use N m\(^{-2}\). We list some internal pressures and relative permittivities at 298.15 K.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>( \varepsilon_r )</th>
<th>( \pi_{int}/10^5 ) N m(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>78.5</td>
<td>1715</td>
</tr>
<tr>
<td>methanol</td>
<td>32.63</td>
<td>2849</td>
</tr>
<tr>
<td>ethanol</td>
<td>24.30</td>
<td>2908</td>
</tr>
<tr>
<td>propanone</td>
<td>20.7</td>
<td>3368</td>
</tr>
<tr>
<td>diethyl ether</td>
<td>4.3</td>
<td>2635</td>
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<tr>
<td>tetrachloromethane</td>
<td>2.24</td>
<td>3447</td>
</tr>
<tr>
<td>dioxan</td>
<td>2.2</td>
<td>4991</td>
</tr>
</tbody>
</table>


[5] For a discussion of effects of solvents on rates of chemical reactions with reference to internal pressures, see


[6] For comments on solvent polarity and internal pressures

[7] For comments on internal pressures of binary aqueous mixtures

[8] For comments on effect of internal pressure on conformational equilibria

[9] For details concerning the dependence of internal pressure of water and D$_2$O, see
    M. J. Blandamer, J. Burgess and A.W. Hakin,

[10] For comments on the calculation of excess internal pressures for binary liquid