Equation of State: General Thermodynamics

We take up the challenge of seeking an equation of state for all chemical substances. We confine attention to closed systems containing one chemical substance. We also confine our attention to systems at equilibrium where the affinity for spontaneous change is zero. A calculus operation allows us to relate p, V and T.

\[ \left( \frac{\partial p}{\partial V} \right)_T \cdot \left( \frac{\partial V}{\partial T} \right)_p \cdot \left( \frac{\partial T}{\partial p} \right)_V = -1 \]  

(a)

By definition, the equilibrium isobaric expansivity. [1]

\[ \alpha_p (A = 0) = \frac{1}{V} \cdot \left( \frac{\partial V}{\partial p} \right)_{p,A=0} \]  

(b)

The equilibrium isothermal compressibility [2],

\[ \kappa_T (A = 0) = -\frac{1}{V} \cdot \left( \frac{\partial V}{\partial p} \right)_{T,A=0} \]  

(c)

Hence,

\[ \left( \frac{\partial p}{\partial T} \right)_{V,A=0} = \frac{\alpha_p (A = 0)}{\kappa_T (A = 0)} \]  

(d)

\[ \left( \frac{\partial p}{\partial T} \right)_{V,A=0} \]  

is the equilibrium isochoric thermal pressure coefficient. [3]

Equation (d) shows that this property can be obtained from the experimentally accessible, \( \alpha_p (A = 0) \) and \( \kappa_T (A = 0) \). In fact the coefficient can be directly measured, at least for liquids. [4]

From the Master Equation where the affinity for spontaneous change is zero,

\[ dU = T \cdot dS - p \cdot dV \]  

(e)

At constant T,

\[ \left( \frac{\partial U}{\partial V} \right)_T = T \cdot \left( \frac{\partial S}{\partial V} \right)_T - p \]  

(f)

Using a Maxwell Equation,

\[ \left( \frac{\partial U}{\partial V} \right)_T = T \cdot \left( \frac{\partial p}{\partial T} \right)_V - p \]  

(g)

All terms on the right hand side of equation (g) are experimentally accessible. Moreover this equation applies to all systems, solids, liquids and gases.
By definition, \( \beta_{v} = \left( \frac{\partial p}{\partial T} \right)_{v} \) \hspace{1cm} (h)

Then, \( \left( \frac{\partial U}{\partial V} \right)_{T} = T \cdot \beta_{v} - p \) \hspace{1cm} (i)

Equation (i) is a Thermodynamic Equation of State.

Equation (j) is another Thermodynamic Equation of State. [5]

\[
\left( \frac{\partial H}{\partial p} \right)_{T} = V \cdot (1 - T \cdot \alpha_{p}) \hspace{1cm} (j)
\]

For many condensed phases the product \( T \cdot \beta_{v} \) is much larger than the pressure \( p \).

Hence \( \left( \frac{\partial U}{\partial V} \right)_{T} \cong T \cdot \beta_{v} \) \hspace{1cm} (k)

The partial differential \( \left( \frac{\partial U}{\partial V} \right)_{T} \) is the internal pressure, \( \pi_{j} \) for liquid \( j \). [6]

Originally the term ‘internal pressure’ referred to the product \( T \cdot \beta_{v} \). The closely related ratio of molar thermodynamic energy of vaporisation to molar volume \( \frac{\Delta_{vap} U^0}{V^*(\ell)} \) is the cohesive energy density, c.e.d.

\[
c.e.d. = \left[ \frac{\Delta_{vap} U^0}{V^*(\ell)} \right] \hspace{1cm} (l)
\]

The rational behind this definition notes that \( \Delta_{vap} U^0 \) defines the change in thermodynamic energy when one mole of a given substance passes from the liquid to the vapour state, breaking strong cohesive forces in the liquid. By dividing by the molar volume of the liquid we normalise this change to a fixed volume. [7]

Internal pressures are interesting parameters. [8,9] Nevertheless despite their thermodynamic basis, treatments of chemical properties in terms of internal pressures receive only sporadic attention. One feels they should be more informative but it is not always clear how one draws conclusions from analysis of experimental data using these properties.

Footnotes
\[ \alpha_p = \frac{1}{[m^3]} \cdot \frac{[m^3]}{[K]} = [K^{-1}] \]

\[ \kappa_T = \frac{1}{[m^3]} \cdot \frac{[m^3]}{[N m^3]} = [N m^{-2}]^{-1} = [Pa]^{-1} \]

\[ \left( \frac{\partial p}{\partial T} \right) = \frac{[N m^{-2}]}{[K]} = [Pa K^{-1}] \]

[4] A small amount of liquid sample is held in a sample cell sealed by a piston; the latter is linked to a device which allows a known pressure to be applied to the sample. The sample cell is held in a thermostat; the temperature of the latter is tightly controlled. The temperature is changed by a small amount; \( \Delta T \). The volume of the liquid in the sample cell (normally) increases. The applied pressure is changed by a small amount \( \Delta p \) in order to recover the original volume. Then for a given liquid at defined \( p, V \) and \( T \), we have the ratio \( (\Delta p/\Delta T) \).


\[ \left( \frac{\partial U}{\partial V} \right)_T = \frac{[J]}{[m^3]} = [N m^{-2}] = [Pa] \]


[8]

[9] \( T/K = 298.15 \)

<table>
<thead>
<tr>
<th>Liquid</th>
<th>( \pi_i /10^6 \text{ Pa} )</th>
<th>c.e.d./10^6 \text{ Pa}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>2.930</td>
<td>8.600</td>
</tr>
<tr>
<td>DMSO</td>
<td>5.166</td>
<td>7.047</td>
</tr>
<tr>
<td>Water</td>
<td>1.013</td>
<td>22.98</td>
</tr>
</tbody>
</table>