Compressions and Expansions: Liquids

The isothermal compressions of solutions and liquids have been extensively studied and the subject has a remarkable history. The term compression, symbol K describes the sensitivity of the volume of a system to an isothermal change in pressure, $(\partial V / \partial p)$. Reference is usually made to the voyage made by HMS Challenger and the report of experiments undertaken by Tait into the compression of water [1-3]. Kell summarises various equations which have been proposed describing the isothermal dependence of the molar volume of water on pressure [4]; see also references [5,6].

The dependence of the volume of water $(\ell)$ at low pressures and at a given temperature on pressure can be represented by equation (a) where $A$ and $B$ are constants.

$$\frac{[V(\text{ref}) - V]}{V(\text{ref})} \cdot p = A / (B + p) \quad (a)$$

Here $V(\text{ref})$ is the volume ‘at zero pressure’, usually ambient pressure (i.e. approx $10^5 \text{ N m}^{-2}$). This equation often called the Tait equation [4] has the form shown in equation (b).

$$-(1/V^0) \cdot (\partial V / \partial p) = A / (B + p) \quad (b)$$

Alternatively [4] $V = V^0 [1 - A \cdot \ln((B + p)/B)]$ (c)

The challenge of measuring the isothermal compression of liquids has been taken up by many investigators; e.g. references [7-12]. The isothermal compressions of a liquid $K_T$ is defined by equation (d) [13].

$$K_T = -(\partial V / \partial p)_T \quad (d)$$

The isothermal compressibility is given by equation (e) [14].

$$\kappa_T = -V^{-1} \cdot (\partial V / \partial p)_T \quad (e)$$

For all thermodynamic equilibrium states, both $K_T$ and $\kappa_T$ are positive variables. A related variable is the isochoric thermal pressure coefficient, $(\partial p / \partial T)_V$ [15].

We develop the story in the context of systems containing two liquid components. For a closed system containing $n_1$ and $n_2$ moles of chemical substances 1 and 2, the Gibbs energy is a dependent variable and the
variables \( [T, p, n_1, n_2] \) are the independent variables. Temperature \( T \) is the thermal potential; pressure \( p \) is the mechanical variable. The number of thermodynamic variables necessary to define the system is established using the Gibbs Phase Rule [16]. For a closed system (at defined \( T \) and \( p \)) at thermodynamic equilibrium the composition/organisation is represented by \( \xi^{eq} \). The affinity for spontaneous change is zero consistent with the Gibbs energy being a minimum; equation (f).

\[
A = -(\partial G / \partial \xi^{eq})_{T,p} = 0 \tag{f}
\]

The Gibbs energy, volume and entropy of a solution at equilibrium are state variables. We contrast these properties with those properties which are associated with a process (pathway). Thus we contrast the state variable \( V \) with an unspecified compression of a solution. We need to define the path followed by the system when the pressure is changed. The Gibbs energy of a closed system at thermodynamic equilibrium (where the affinity for spontaneous change is zero and where the molecular composition/organisation is characterised by \( \xi^{eq} \)) is described by equation (g).

\[
G = G[T, p, n_1, n_2, A = 0] \tag{g}
\]

The same state is characterised by the equilibrium volume and equilibrium entropy by equations (h) and (i) respectively.

\[
V = V[T, p, n_1, n_2, A = 0] \tag{h}
\]

\[
S = S[T, p, n_1, n_2, A = 0] \tag{i}
\]

We use two intensive variables, \( T \) and \( p \), in the definition of extensive variables \( G, V \) and \( S \). When the pressure is increased by finite increments from \( p \) to \( (p + \Delta p) \), the volume changes in finite increments from \( V \) to \( (V + \Delta V) \). For an important pathway, the temperature is constant. However to satisfy the condition that the affinity for spontaneous change \( A \) is zero, the molecular organisation/composition \( \xi \) changes. The volume at pressure \( (p + \Delta p) \) is defined using equation (j).

\[
V = V[T, (p + \Delta p), n_1, n_2, A = 0] \tag{j}
\]

In principle we plot the volume as a function of pressure at constant temperature, \( n_1, n_2 \), and at ‘\( A = 0 \)’. The gradient of the plot defined by
equation (h) yields the equilibrium isothermal compression, $K_T(A=0)$; equation (k)

$$K_T(A=0) = -(\partial V / \partial p)_{T,A=0} \quad (k)$$

$K_T(A=0)$ characterises the state defined by the set of variables, $[T,p,n_1,n_2,A=0]$.

We turn our attention to another property starting with a system having a volume defined by equation (h). The system is perturbed by a change in pressure from $p$ to $(p + \Delta p)$ in an equilibrium displacement. However on this occasion we require that the entropy of the system remains constant at a value defined by equation (i). In principle we plot the volume $V$ as a function of pressure at constant $n_1$, $n_2$, at ‘A=0’ and at a constant entropy defined by equation (i). The gradient of the plot at the point where the volume is defined by equation (g) yields the equilibrium isentropic compression $K_S(A=0)$; equation (l) where isentropic = adiabatic and ‘at equilibrium’.

$$K_S(A=0) = -(\partial V / \partial p)_{S,A=0} \quad (l)$$

The equilibrium state characterised by $K_S(A=0)$ is defined by the variables $[T,p,n_1,n_2,A=0]$. In other words an isentropic volumetric property describes a solution defined in part by the intensive variables $T$ and $p$. Significantly the condition on the partial derivative in equation (l) is an extensive variable, entropy. For a stable phase $K_S$ is positive.

The arguments outlined above are repeated with respect to both isobaric equilibrium expansions $E_p(A=0)$ and isentropic equilibrium expansions, $E_S(A=0)$; equations (m) and (n).

$$E_p(A=0) = -(\partial V / \partial T)_{p,A=0} \quad (m)$$

$$E_S(A=0) = -(\partial V / \partial T)_{S,A=0} \quad (n)$$

The (equilibrium) volume intensive isothermal $\kappa_T$ and isentropic $\kappa_S$ compressibilities are defined by equations (o) and (p).

$$\kappa_T = -(1/V) \cdot (\partial V / \partial p)_T = K_T \cdot V^{-1} \quad (o)$$

$$\kappa_S = -(1/V) \cdot (\partial V / \partial p)_S = K_S \cdot V^{-1} \quad (p)$$
In 1914 Tyrer reported isentropic and isothermal compressibilities for many liquids [9]. Equations (q) and (r) define two (equilibrium) expansibilities, isentropic and isobaric, volume intensive properties.

\[ \alpha_s = \frac{1}{V} \frac{\partial V}{\partial T} \]  
\( (q) \)

\[ \alpha_p = \frac{1}{V} \frac{\partial V}{\partial p} \]  
\( (r) \)

Rowlinson and Swinton state that the property \( \alpha_s \) is ‘of little importance’ [17]. The isobaric heat capacity per unit volume \( \sigma \) is the ratio \( [C_p/V] \). A property of some importance is the difference between compressibilities, \( \delta \); equation (s).

\[ \delta = \kappa_T - \kappa_s = \frac{T \cdot [\alpha_p]^2}{V} = \frac{T \cdot [\alpha_p]^2}{\sigma} \]  
\( (s) \)

The property \( \sigma \) is given different symbols and names; e.g. volumetric specific heat. Here we identify \( \sigma \) as the thermal (or, heat) capacitance. The property \( \epsilon \) is the difference between isobaric and isentropic expansibilities; equation (t).

\[ \epsilon = \alpha_p - \alpha_s = \kappa_T \cdot \sigma / T \cdot \alpha_p \]  
\( (t) \)

The Newton–Laplace equation is the starting point for the determination of isentropic compressibilities of liquids using sound speeds and densities; equation (u).

\[ u^2 = (\kappa_s \cdot \rho)^{-1} \]  
\( (u) \)

The isentropic condition on \( \kappa_s \) means that as a sound wave passes through a liquid the pressure and temperature fluctuate within each microscopic volume but the entropy remains constant.

Footnotes

Int. J. Thermophys., 1988, 9, 941.
[10] H. E. Eduljee, D. M. Newitt and K. E. Weale, 
[13] $K_T = \frac{[m^3]}{[N \cdot m^{-2}]} = [m^3 \text{ Pa}^{-1}]$
[14] $\kappa_T = \frac{1}{[m^3]} \cdot \frac{[m^3]}{[Pa]} = [\text{Pa}^{-1}]$
[15] $(\partial p / \partial T)_v = [\text{Pa} \text{ K}^{-1}]$
[16] Phase Rule; P = 1; C = 2. Hence F = 3.
Then we define $T$, $p$ and mole fraction composition.