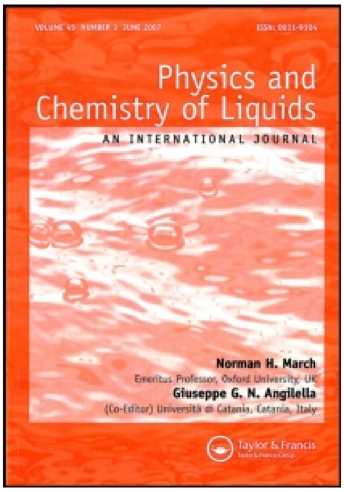

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Exact Relationship Between Compressibility of Solution and Compressibilities of its Pure Constituents

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It has been shown that $\bar{V}_1(T, p, x_1) = \bar{V}_1^0(T, p - \pi_1)$ and that $\bar{V}_2(T, p, x_2) = \bar{V}_2^0(T, p - \pi_2)$, where π_1 is the osmotic pressure of the solvent in a binary solution and π_2 is the osmotic pressure of the solution solute. An increase in pressure applied to the solution, the pure solvent and pure solute from p to $p + \Delta p$ compresses the solution solvent and pure solvent by equal fractions

$$-\frac{\Delta \bar{V}_1(T, p, x_1)}{\bar{V}_1(T, p, x_1)} = -\frac{\Delta \bar{V}_1^0(T, p - \pi_1)}{\bar{V}_1^0(T, p - \pi_1)}$$

and compresses the solution solute and pure solute by equal fractions

$$-\frac{\Delta \bar{V}_2(T, p, x_2)}{\bar{V}_2(T, p, x_2)} = -\frac{\Delta \bar{V}_2^0(T, p - \pi_2)}{\bar{V}_2)T, p - \pi_2)}.$$

Thus, the compressibilities of the solution solvent and pure solvent are related as

$$\kappa_1(T, p, x_1) = \kappa_1^0(T, p - \pi_1);$$

and likewise, the solution solute and pure solute compressibilities are related as

$$\kappa_2(T, p, x_2) = \kappa_2^0(T, p - \pi_2).$$

Since

$$-\frac{\Delta V}{V} = -n_1 \frac{\Delta \bar{V}_1}{V} - n_2 \frac{\Delta \bar{V}_2}{V},$$

it is shown that the compressibility of the solution and the compressibilities of the pure constituents are related as

$$\kappa_{12} V = n_1 \bar{V}_1^0 \kappa_1^0 + n_2 \bar{V}_2^0 \kappa_2^0$$

where κ_{12} and V are measured at p, κ_1^0 and $\bar{V}_1^0$ are measured at $p - \pi_1$, κ_2^0 and $\bar{V}_2^0$ are measured at $p - \pi_2$ and all are measured at the same T.

INTRODUCTION

The purpose of this article is to derive an exact relationship between the compressibility of a binary solution, κ_{12}, and the compressibilities of its pure constituents, κ_1^0 and κ_2^0. The derivation will be based on the recognition that all species in a solution enhance the tension in the coupling forces, and thereby increase the partial molar volume of each species in the solution.[1,2]

Compressibilities of solution, solvent, and solute

A binary solution contains n_1 moles of solvent and n_2 moles of solute. The volume of the solution at T and applied pressure p is

$$V(T, p, n_1, n_2) = n_1\bar{V}_1(T, p, n_1, n_2) + n_2\bar{V}_2(T, p, n_1, n_2), \tag{1}$$

where $\bar{V}_1(T, p, n_1, n_2)$ is the partial molar volume of the solvent (i.e. $\partial V/\partial n_1 | T, p, n_2$) and $\bar{V}_2(T, p, n_1, n_2)$ is partial molar volume of the solute (i.e. $\partial V/\partial n_2 | T, p, n_1$). If T is held constant as the applied pressure increases from p to $p + \Delta p$, the solution volume decreases to

$$V(T, p + \Delta p, n_1, n_2) = n_1\bar{V}_1(T, p + \Delta p, n_1, n_2) + n_2\bar{V}_2(T, p + \Delta p, n_1, n_2). \tag{2}$$

The decrease in solution volume $-\Delta V$ due to the increase in pressure Δp is

$$-\Delta V(T, p, n_1, n_2) = V(T, p + \Delta p, n_1, n_2) - V(T, p, n_1, n_2). \tag{3}$$

The partial molar volumes of the solvent and solute also decrease by the amounts

$$-\Delta\bar{V}_1(T, p, n_1, n_2) = \bar{V}_1(T, p + \Delta p, n_1, n_2) - \bar{V}_1(T, p, n_1, n_2) \tag{4}$$

and

$$-\Delta\bar{V}_2(T, p, n_1, n_2) = \bar{V}_2(T, p + \Delta p, n_1, n_2) - \bar{V}_2(T, p, n_1, n_2). \tag{5}$$

By subtracting Eq. (1) from Eq. (2) and using Eqs. (3), (4), and (5), it follows that

$$-\Delta V(T, p, n_1, n_2) = -n_1\Delta\bar{V}_1(T, p, n_1, n_2) - n_2\Delta\bar{V}_2(T, p, n_1, n_2). \tag{6}$$

Dividing Eq. (6) by V,

$$-\frac{\Delta V}{V} = -n_1\frac{\Delta\bar{V}_1}{V} - n_2\frac{\Delta\bar{V}_2}{V}. \tag{7}$$

The compressibility of the solution is defined as

$$\kappa_{12}(T, p, n_1, n_2) = -\frac{\Delta V}{V}\Delta p^{-1} \tag{8}$$

and is a function of T, p, n_1 and n_2. Likewise, the compressibility of the solution solvent can be defined as

$$\kappa_1(T, p, n_1, n_2) = -\frac{\Delta \bar{V}_1}{\bar{V}_1} \Delta p^{-1}, \tag{9}$$

and the compressibility of the solution solute can be defined as

$$\kappa_2(T, p, n_1, n_2) = -\frac{\Delta \bar{V}_2}{\bar{V}_2} \Delta p^{-1}. \tag{10}$$

Combining Eqs. (8), (9) and (10) with Eq. (7),

$$\begin{aligned}\kappa_{12}(T, p, n_1, n_2) = {} & \frac{n_1 \bar{V}_1(T, p, n_1, n_2)}{V(T, p, n_1, n_2)} \kappa_1(T, p, n_1, n_2) \\ & + \frac{n_2 \bar{V}_2(T, p, n_1 n_2)}{V(T, p, n_1, n_2)} \kappa_2(T, p, n_1, n_2).\end{aligned} \tag{11}$$

The solution was constituted by combining n_1^0 moles of pure solvent, having a volume $V_1^0(T, p) = n_1^0 \bar{V}_1^0(T, p)$, with n_2^0 moles of pure solute, having a volume $V_2^0(T, p) = n_2^0 \bar{V}_2^0(T, p)$. $\bar{V}_1^0$ and $\bar{V}_2^0$ are the molar volumes of the pure solvent and pure solute, respectively, and both are functions of T and p. Increasing the pressure applied to the pure solvent from p to $p + \Delta p$ at constant T decreases it molar volume an amount

$$-\Delta \bar{V}_1^0(T, p) = \bar{V}_1^0(T, p + \Delta p) - \bar{V}_1^0(T, p)$$

and its compressibility is

$$\kappa_1^0(T, p) = -\frac{\Delta \bar{V}_1^0}{\bar{V}_1^0} \Delta p^{-1}. \tag{12}$$

Likewise, increasing the pressure applied to the pure solute from p to $p + \Delta p$ decreases its molar volume an amount

$$-\Delta \bar{V}_2^0(T, p) = \bar{V}_2^0(T, p + \Delta p) - \bar{V}_2^0(T, p)$$

and the compressibility of pure solute is

$$\kappa_2^0(T, p) = -\frac{\Delta \bar{V}_2^0}{\bar{V}_2^0} \Delta p^{-1}. \tag{13}$$

Relationship between compressibilities of solution solvent κ_1 and pure solvent κ_1^0

The chemical potential of either species i in a binary solution can be altered by changing T, p or the molar amount of species i according to

$$\mathrm{d}\mu_i(T, p, n_1, n_2) = -\bar{S}_i \,\mathrm{d}T + \bar{V}_i \,\mathrm{d}p + \frac{\partial \mu_i}{\partial x_i} \mathrm{d}x_i,$$

where $\bar{S}_i$ is the partial molar entropy of species i and $x_i = n_i/(n_1 + n_2)$, the mole fraction of species i. Increasing the pressure applied to the solution from an initial p_i to $p_i + \Delta p$ at constant T and x_1 increases the chemical potential of the solvent in the solution an amount

$$\mu_1(T, p_i + \Delta p, x_1) - \mu_1(T, p_i, x_1) = \int_{p_i}^{p_i + \Delta p} \bar{V}_1 \, \mathrm{d}p. \tag{14}$$

For pure solvent, $x_1^0 = 1$. Decreasing the pressure applied to it from p_i to $p_i - \Delta p$ at constant T decreases its chemical potential an amount

$$\mu_1^0(T, p_i - \Delta p) - \mu_1^0(T, p_i) = \int_{p_i}^{p_i - \Delta p} \bar{V}_1^0 \, \mathrm{d}p. \tag{15}$$

$\bar{V}_1$ and $\bar{V}_1^0$ are both functions of T and p but they are not equal at the same T and p. However, there is an exact relationship between them.

If Δp in Eqs. (14) and (15) is equal to the osmotic pressure of the solvent in the solution, π_1, then the sum of the left sides of Eqs. (14) and (15) equals zero since

$$\mu_1(T, p_i + \pi_1, x_1) = \mu_1^0(T, p_i) \tag{16}$$

and

$$\mu_1(T, p_i, x_1) = \mu_1^0(T, p_i - \pi_1). \tag{17}$$

That is, if the pressure applied to the solution and pure solvent differ by π_1, then the chemical potentials of the solution solvent and pure solvent must be equal at constant T. Thus, it follows that

$$\int_{p_i}^{p_i + \pi_1} \bar{V}_1 \, \mathrm{d}p = \int_{p_i - \pi_1}^{p_i} \bar{V}_1^0 \, \mathrm{d}p. \tag{18}$$

$\bar{V}_1$ and $\bar{V}_1^0$ are state functions of T and p and vary continuously with p; so p_i in Eq. (18) can have any value and it can be increased to $p_i + \pi_1$; so again

$$\int_{p_i + \pi_1}^{p_i + 2\pi_1} \bar{V}_1 \, \mathrm{d}p = \int_{p_i}^{p_i + \pi_1} \bar{V}_1^0 \, \mathrm{d}p. \tag{19}$$

The sum of Eqs. (18) and (19) becomes

$$\int_{p_i}^{p_i + 2\pi_1} \bar{V}_1 \, \mathrm{d}p = \int_{p_i - \pi_1}^{p_i + \pi_1} \bar{V}_1^0 \, \mathrm{d}p. \tag{20}$$

Thus, $\bar{V}_1$ and $\bar{V}_1^0$ vary with p and they must vary so as to satisfy Eqs. (18), (19) and (20). Let us assume that $\bar{V}_1(T, p + \pi_1, x_1) = \bar{V}_1^0(T, p)$ and show that Eqs. (18), (19) and (20) are satisfied only if, for every p, $\bar{V}_1(T, p + \pi_1, x_1)$ does equal $\bar{V}_1^0(T, p)$.

The variation of the molar volume of the pure solvent from $p_i - \pi_1$ to $p_i + \pi_1$ at constant T is illustrated as the curve labelled $\bar{V}_1^0(T, p)$ in Figure 1. If our assumption is valid, then the curve labelled $\bar{V}_1(T, p, x_1)$ represents the variation of the partial molar volume of the solution solvent from p_i to $p_i + 2\pi_1$. By comparing the curve for $\bar{V}_1^0(T, p)$ from $p_i - \pi_1$ to $p_i + \pi_1$ with the curve for $\bar{V}_1(T, p, x_1)$ from p_i to $p_i + 2\pi_1$, several facts are clear:

1) $\bar{V}_1^0(T, p_i - \pi_1) = \bar{V}_1(T, p_i, x_1)$;
2) $\bar{V}_1^0(T, p_i) = \bar{V}_1(T, \mathrm{p}_i + \pi_1, x_1)$;
3) $V_1^0(T, p_i + \pi_1) = \bar{V}_1(T, p_i + 2\pi_1, x_1)$;

4) $$\int_{p_i - \pi_1}^{p_i} \bar{V}_1^0 \, \mathrm{d}p = \int_{p_i}^{p_i + \pi_1} \bar{V}_1 \, \mathrm{d}p;$$

i.e. the area under $\bar{V}_1^0(T, p)$ from $p_i - \pi_1$ to p_i equals the area under $\bar{V}_1(T, p, x_1)$ from p_i to $p_i + \pi_1$ and Eq. (18) is satisfied;

5) Eqs. (19) and (20) are also satisfied.

Next, assume that the curve for the partial molar volume of the solvent is, as before, $\bar{V}_1(T, p, x_1)$ in Figure 1, and assume that the molar volume of the pure solvent varies as the broken curve labelled $\bar{V}_1^0(T, p)$ from $p_i - \pi_1$ to $p_i + \pi_1$. These curves assume that the pure solvent is more compressible than

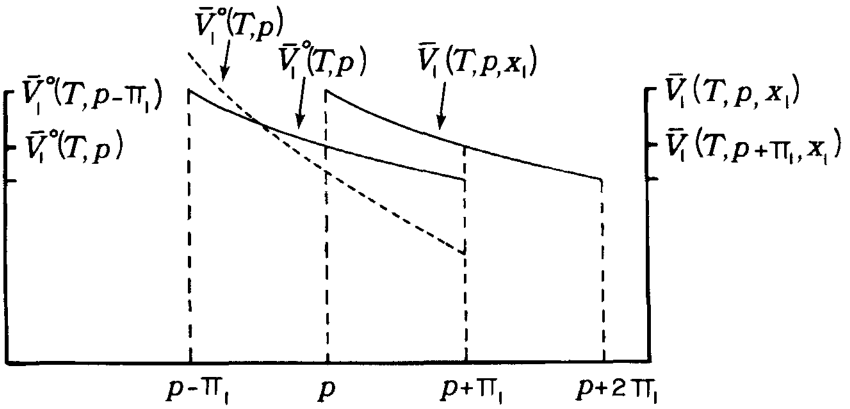

FIGURE 1 Molar volumes (ordinate) versus applied pressures (abscissa) of pure solvent and solution solvent. Solid curves demonstrate that the compressibility of pure solvent from $p - \pi_1$ to $p + \pi_1$ equals compressibility of solution solvent from p to $p + 2\pi_1$ at the same T. Broken curve incorrectly assumes that compressibility of pure solvent differs from compressibility of solution solvent.

the solution solvent. The broken curve $\overline{V}_1^0(T, p)$ was drawn to satisfy Eq. (18) but it can not also satisfy Eqs. (19) and (20), i.e.

$$\int_{p_i}^{p_i+\pi_1} \overline{V}_1^0 \, \mathrm{d}p \neq \int_{p_i+\pi_1}^{p_i+2\pi_1} \overline{V}_1 \, \mathrm{d}p$$

and

$$\int_{p_i-\pi_1}^{p_i+\pi_1} \overline{V}_1^0 \, \mathrm{d}p \neq \int_{p_i}^{p_i+2\pi_1} \overline{V}_1 \, \mathrm{d}p.$$

Since the compressibility of the pure solvent and $\overline{V}_1^0(T, p)$ from $p_i - \pi_1$ to to $p_i + \pi_1$ must satisfy Eqs. (18), (19) and (20), we can conclude that our first assumption was valid, i.e. $\overline{V}_1^0(T, p) = \overline{V}_1(T, p + \pi_1, x_1)$, and the compressibility of pure solvent at every p must be identical with the compressibility of the solution solvent at every $p + \pi_1$ at constant T and x_1. It also follows that

$$\overline{V}_1(T, p, x_1) = \overline{V}_1^0(T, p - \pi_1) \tag{21}$$

and that

$$\Delta\overline{V}_1(T, p, x_1) = \Delta\overline{V}_1^0(T, p - \pi_1)$$

if the pressure applied to the pure solvent changes from $p - \pi_1$ to $p + \Delta p - \pi_1$ while the pressure applied to the solution changes from p to $p + \Delta p$. Thus,

$$\frac{\Delta\overline{V}_1(T, p, x_1)}{\overline{V}_1(T, p, x_1)} = \frac{\Delta\overline{V}_1^0(T, p - \pi_1)}{\overline{V}_1^0(T, p - \pi_1)}.$$

That is, the compressibility of the solution solvent at T and p must equal the compressibility of the pure solvent at T and $p - \pi_1$

$$\kappa_1(T, p, x_1) = \kappa_1^0(T, p - \pi_1). \tag{22}$$

Relationship between compressibilities of solution solute κ_2 and pure solute κ_2^0

The same argument as above can be exploited to derive the relationship between the compressibilities of the solution solute and pure solute. Increasing the pressure applied to the solution from an initial pressure p_i to $p_i + \Delta p$ increases the chemical potential of the solution solute an amount

$$\mu_2(T, p_i + \Delta p, x_2) - \mu_2(T, p_i, x_2) = \int_{p_i}^{p_i+\Delta p} \overline{V}_2 \, \mathrm{d}p, \tag{23}$$

at constant T and x_2. For pure solute $x_2^0 = 1$. Decreasing the pressure applied to it from p_i to $p_i - \Delta p$ at constant T decreases its chemical potential an amount

$$\mu_2^0(T, p_i - \Delta p) - \mu_2^0(T, p_i) = \int_{p_i}^{p_i - \Delta p} \bar{V}_2^0 \, \mathrm{d}p. \tag{24}$$

$\bar{V}_2$ and $\bar{V}_2^0$ are both functions of T and p and there is an exact relationship between them.

If Δp in Eqs. (23) and (24) is equal to the osmotic pressure of the solute in the solution, π_2, then the sum of left sides of Eqs. (23) and (24) equals zero since

$$\mu_2(T, p_i + \pi_2, x_2) = \mu_2^0(T, p_i) \tag{25}$$

and

$$\mu_2(T, p_i, x_2) = \mu_2^0(T, p_i - \pi_2). \tag{26}$$

Thus, it follows that

$$\int_{p_i}^{p_i + \pi_2} \bar{V}_2 \, \mathrm{d}p = \int_{p_i - \pi_2}^{p_i} \bar{V}_2^0 \, \mathrm{d}p. \tag{27}$$

It also follows that

$$\int_{p_i}^{p_i + 2\pi_2} \bar{V}_2 \, \mathrm{d}p = \int_{p_i - \pi_2}^{p_i + \pi_2} \bar{V}_2^0 \, \mathrm{d}p, \tag{28}$$

since $\bar{V}_2$ and $\bar{V}_2^0$ are state functions of T and p. Only if

$$\bar{V}_2(T, p, x_2) = \bar{V}_2^0(T, p - \pi_2) \tag{29}$$

are both Eqs. (27) and (28) satisfied. It also follows that

$$-\Delta\bar{V}_2(T, p, x_2) = -\Delta\bar{V}_2^0(T, p - \pi_2), \tag{30}$$

if the pressure applied to the solution increases from p to $p + \Delta p$ while the pressure applied to the pure solute increases from $p - \pi_2$ to $p + \Delta p - \pi_2$. Thus,

$$\frac{\Delta\bar{V}_2(T, p, x_2)}{\bar{V}_2(T, p, x_2)} = \frac{\Delta\bar{V}_2^0(T, p - \pi_2)}{\bar{V}_2^0(T, \rho - \pi_2)} \tag{31}$$

and

$$\kappa_2(T, p, x_2) = \kappa_2^0(T, p - \pi_2). \tag{32}$$

That is, the compressibility of the solution solute at T and p must equal the compressibility of the pure solute at T and $p - \pi_2$.

Relationship between the compressibility of the solution κ_{12} and the compressibilities of the pure solvent κ_1^0 and pure solute κ_2^0

The relationship between the compressibility of a binary solution $\kappa_{12}(T, p, n_1, n_2)$ and the compressibilities of its solution solvent and solution solute was derived as Eq. (11). Eqs. (21), (22), (29) and (32) can be used to substitute for $\bar{V}_1$, κ_1, $\bar{V}_2$ and κ_2 in Eq. (11). Thus, Eq. (11) becomes

$$\kappa_{12}(T, p, n_1, n_2)V(T, p, n_1, n_2) = n_1\bar{V}_1^0(T, p - \pi_1)\kappa_1^0(T, p - \pi_1) + n_2\bar{V}_2^0(T, p - \pi_2)\kappa_2^0(T, p - \pi_2). \quad (33)$$

The product of the volume and compressibility of the solution at T, p, n_1 and n_2 must equal the product of the number of moles of solution solvent at T, p, n_1 and n_2, the molar volume and the compressibility of pure solvent at T and $p - \pi_1$ plus the product of the number of moles of solution solute, the molar volume and the compressibility of the pure solute at T and $p - \pi_2$.

CONCLUSION

Equation (33) is an exact relationship between the compressibility and volume of a binary solution and the compressibilities and molar volumes of its pure constituents. κ_{12} and V_{12} can be measured at T and p; V_1^0 and κ_1^0 can be measured at T and $p - \pi_2$; $\bar{V}_2^0$ and κ_2^0 can be measured at T and $p - \pi_2$. If n_1 and n_2 are known at T and p, then these data must satisfy Eq. (33). If Eq. (33) is not satisfied, then n_1 and n_2 were not known at T and p.

Eq. (33) can also be written

$$\kappa_{12}(T, p + \pi_1, n_1, n_2)V_{12}(T, p + \pi_1, n_1, n_2) = n_1\bar{V}_1^0(T, p)\kappa_1^0(T, p) + n_2\bar{V}_2^0(T, p + \pi_1 - \pi_2)\kappa_2^0(T, p + \pi_1 - \pi_2) \quad (34)$$

or it can be written

$$\kappa_{12}(T, p + \pi_2, n_1, n_2)V_{12}(T, p + \pi_2, n_1, n_2) = n_1\bar{V}_1^0(T, p - \pi_1 + \pi_2)\kappa_1^0(T, p - \pi_1 + \pi_2) + n_2\bar{V}_2^0(T, p)\kappa_2^0(T, p). \quad (35)$$

Again, the volumes and compressibilities of the solution and of the pure constituents can be measured at the pressures indicated in Eqs. (34) and (35). It should be noted that n_1 and n_2 refer to the molar amounts of 1 and 2 at T and $p + \pi_1$ in Eq. (34) and to the molar amounts at T and $p + \pi_2$ in Eq. (35). In many solutions, n_1 will differ from n_1^0 and n_2 will differ from n_2^0 at the same T and p. Furthermore, n_1 and n_2 may vary with T and p. Nevertheless, Eqs. (33), (34) and (35) are exact relationships and they provide an opportunity to investigate n_1 and n_2 in various solutions at various temperatures and pressures.

According to Eq. (33) an increase in the pressure applied to the solution from p to $p + \Delta p$, an increase from $p - \pi_1$ to $p + \Delta p - \pi_1$ applied to the pure solvent and an increase from $p - \pi_2$ to $p + \Delta p - \pi_2$ applied to the pure solute decreases their volumes at constant T

$$\Delta V(T, p, n_1, n_2) = n_1 \Delta \bar{V}_1^0(T, p - \pi_1) + n_2 \Delta \bar{V}_2^0(T, p - \pi_2). \qquad (36)$$

Similarity, increasing the pressures in Eqs. (34) and (35) by Δp decrease the volumes of solution, pure solvent and pure solute the amounts

$$\Delta V(T, p + \pi_1, n_1, n_2) = n_1 \Delta \bar{V}_1^0(T, p) + n_2 \Delta \bar{V}_2^0(T, p + \pi_1 - \pi_2) \quad 37)$$

and

$$\Delta V(T, p + \pi_2, n_1, n_2) = n_1 \Delta \bar{V}_1^0(T, p + \pi_2 - \pi_1) + n_2 \bar{V}_2^0(T, p). \qquad (38)$$

Thus, the variation for n_1 and n_2 as a function of T and pressure can be experimentally determined for a solution constituted by mixing n_1^0 moles of pure solvent and n_2^0 moles of pure solute.

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