

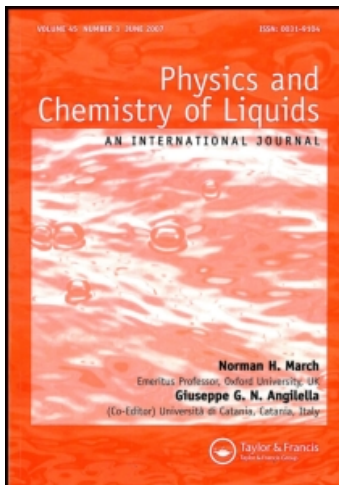
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### Hulett's Enhanced Solvent Tension. An Alternative to Lewis' Diminished Solvent Activity

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# Hulett's Enhanced Solvent Tension

## An Alternative to Lewis' Diminished Solvent Activity

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Hulett proposed in 1903 that solute enhances the tension in the cohesive forces between solvent molecules by an amount equal to the osmotic pressure of the solvent. He attributed all the colligative properties of the solution solvent to this enhanced solvent tension. In 1908 Lewis proposed that the altered state of the solvent in solution was due to a reduced activity caused by the solute. Hulett's proposal is based on physical principles and thermodynamic argument and is a valid alternative to Lewis' proposal. Under all circumstances, the solution solvent is altered by the solute precisely as if the average tension between the molecules of solvent was enhanced by the osmotic pressure of the solution solvent,  $\Pi_1$ , no matter how the solute does it, no matter what the compressibility of the solvent is at any  $T$  and  $p$  and no matter what the relationship is between  $\Pi_1$  and  $x_1$ , the mole fraction of solvent in the solution.

### 1 INTRODUCTION

G. A. Hulett<sup>1</sup> proposed that solute enhanced the tension between the solvent molecules by an amount equal to the osmotic pressure. He further proposed that all the colligative properties of the solvent were due to this enhanced tension in the solvent. This simple and precise statement about the solvent in solution has generally been disavowed by physical chemists since G. N. Lewis<sup>2</sup> proposed that the altered state of the solvent in solution is due to its diminished activity.

The intent of this article is to show that:

- 1) Both Hulett's and Lewis' proposal are valid.
- 2) Hulett's proposal is based on a physical property of the solvent (solvent tension) and on fundamental physical principles concerning this property, whereas

3) Lewis' proposal is based on the definition of an ideal solution, on the definition of a term (solvent activity) applied to the solvent of the ideal solution and on the definition of a dimensionless coefficient to be applied to the mole fraction of solvent such that a thermodynamic statement concerning the solvent activity of the ideal solution applies also to a real solution.

4) If or when it is convenient to ascribe the lower chemical potential of the solvent to the diminished activity of the solvent in the solution, it is still essential to attribute both the lower chemical potential and diminished activity to the enhanced solvent tension in the solution.

## 2 HULETT'S PROPOSAL IS DEFENSIBLE

Hulett's statement about the change in the solvent in solution can be derived by thermodynamic argument as follows. Increasing the pressure applied to a solution from  $p$  to  $p + \Pi_1$  increases the chemical potential of its solvent an amount

$$\mu_1(T, p + \Pi_1, x_1) - \mu_1(T, p, x_1) = \int_p^{p + \Pi_1} \bar{V}_1 dp. \quad (1)$$

Decreasing the pressure applied to pure solvent from  $p$  to  $p - \Pi_1$  lowers its chemical potential an amount

$$\mu_1^0(T, p - \Pi_1) - \mu_1^0(T, p) = \int_p^{p - \Pi_1} \bar{V}_1^0 dp. \quad (2)$$

$\bar{V}_1$  is the partial molar volume of the solvent in the solution and  $\bar{V}_1^0$  is the molar volume of pure solvent. Both the solution and pure solvent are compressible and their volumes depend on temperature. Furthermore, their compressibilities and coefficients of thermal expansion are also functions of  $T$  and  $p$ . Thus,  $\bar{V}_1(T, p, x_1)$  and  $\bar{V}_1^0(T, p)$  are always complicated functions of  $T$  and  $p$ .

The osmotic pressure of the solvent in a solution equals the difference in pressures applied to the solution and pure solvent for which the chemical potentials of the solution solvent and pure solvent are equal.<sup>3</sup> If  $\Pi_1$  in Eqs. (1) and (2) is equal in magnitude to the osmotic pressure of the solvent in the solution, then the chemical potentials of the solution solvent and pure solvent are equal when  $p + \Pi_1$  is applied to the solution and  $p$  is applied to the pure solvent, i.e.

$$\mu_1(T, p + \Pi_1, x_1) = \mu_1^0(T, p), \quad (3)$$

or when  $p$  is applied to the solution and  $p - \Pi_1$  is applied to the pure solvent, i.e.

$$\mu_1(T, p, x_1) = \mu_1^0(T, p - \Pi_1). \quad (4)$$

Thus, it follows that the sum of Eqs. (1) and (2) equals zero and that

$$\int_p^{p+\Pi_1} \bar{V}_1 dp = \int_{p-\Pi_1}^p \bar{V}_1^0 dp. \quad (5)$$

It follows from Eq (5) that  $\bar{V}_1(T, p, x_1) = \bar{V}_1^0(T, p - \Pi_1)$  and that  $\bar{V}_1(T, p + \Pi_1, x_1) = \bar{V}_1^0(T, p)$  no matter what the compressibility of the solvent is at any  $T$  and  $p^4$ . In all respects, the solvent in the solution is altered precisely as if the solute enhanced the tension between the solvent molecules by  $\Pi_1$  as Hulett proposed. Furthermore, combining Eqs (2) and (4), the chemical potentials of solution solvent and pure solvent at the same  $T$  and  $p$  differ by

$$\mu_1(T, p, x_1) - \mu_1^0(T, p) = \int_p^{p-\Pi_1} \bar{V}_1^0 dp, \quad (6)$$

and according to Eq (5), they also differ by

$$\mu_1(T, p, x_1) - \mu_1^0(T, p) = - \int_p^{p+\Pi_1} \bar{V}_1 dp. \quad (7)$$

The integral in Eq (6) is readily evaluated for all values of  $p - \Pi_1 > 0$  and even for  $p - \Pi_1 < 0$  if care is taken to eliminate all microbubbles in the pure solvent. The accuracy of the assessment of  $\mu_1(T, p, x_1) - \mu_1^0(T, p)$  depends only on the accuracy of the experimental determination of  $\bar{V}_1^0(T, p)$  over the range  $p$  to  $p - \Pi_1$  at  $T$ . Thus, Hulett's proposal that solute enhances the tension between the solvent molecules in the solution by  $\Pi_1$  is valid and provides a basis for an accurate determination of the change in chemical potential of the solvent in the solution as its mole fraction decreases from 1 to  $x_1$ . Furthermore, no matter how  $\Pi_1$  relates to  $x_1$ ,  $\bar{V}_1(T, p, x_1)$  is exactly equal to  $\bar{V}_1^0(T, p - \Pi_1)$  or  $\bar{V}_1(T, p + \Pi_1, x_1)$  equals  $\bar{V}_1^0(T, p)$  and the solution solvent always behaves as if its internal pressure was diminished by  $\Pi_1$ , i.e. its internal tension was enhanced by  $\Pi_1$ .

### 3 SOLVENT TENSION AND VAPOR PRESSURE

If, while changing the pressure applied to solution or pure solvent, the vapor of substance 1 remains in equilibrium with the liquid phase of 1, then the change in the chemical potential of the liquid equals the change in the

chemical potential of the vapor, i.e.

$$\int d\mu_1 = \int d\mu_1^v.$$

Thus, for pure solvent at constant  $T$ ,

$$\int_p^{p-\Pi_1} \bar{V}_1^0 dp = \int_{p_1^v(p)}^{p_1^{v0}(p-\Pi_1)} \bar{V}_1^{v0} dp_1^{v0}, \quad (8)$$

where  $p_1^{v0}$  is the vapor pressure of pure liquid 1 at  $T$  from  $p$  to  $p - \Pi_1$  and  $\bar{V}_1^{v0}(T, p_1^{v0})$  is the molar volume of its vapor at  $T$  and  $p_1^{v0}$ . Likewise, for the solution solvent

$$\int_p^{p+\Pi_1} \bar{V}_1 dp = \int_{p_1^v(p)}^{p_1^v(p+\Pi_1)} \bar{V}_1^v dp_1^v, \quad (9)$$

where  $p_1^v$  is the partial vapor pressure of 1 at  $T$  from  $p$  to  $p + \Pi_1$  and  $\bar{V}_1^v(T, p_1^v)$  is the partial molar volume of its vapor at  $T$  and  $p_1^v$ . Combining Eq (8) with Eq (6) and Eq (9) with Eq (7),

$$\begin{aligned} \mu_1(T, p, x_1) - \mu_1^0(T, p) &= \int_{p_1^{v0}(p)}^{p_1^{v0}(p-\Pi_1)} \bar{V}_1^{v0} dp_1^{v0}; \\ &= - \int_{p_1^v(p)}^{p_1^v(p+\Pi_1)} \bar{V}_1^v dp_1^v. \end{aligned} \quad (10)$$

Since  $p_1^v(p + \Pi_1) = p_1^{v0}(p)$ , Eq (10) can be written

$$\mu_1(T, p, x_1) - \mu_1^0(T, p) = \int_{p_1^{v0}(p)}^{p_1^v(p)} \bar{V}_1^v dp_1^v. \quad (11)$$

Thus, Eqs. (6) and (7) and (10) and (11) describe precisely how the chemical potential of the solvent in the solution is altered by the solute, as the mole fraction of solvent decreases from 1 for pure solvent to  $x_1$ . These equations remain valid no matter how the compressibilities of the solvent vary with pressure and temperature or how the vapor pressure of the solvent varies with the molar volume of the solvent vapor (the gas law for the vapor). The solution solvent is always altered precisely as if its tension was increased by  $\Pi_1$  no matter how the solute does it.

#### 4 LEWIS' PROPOSAL IS VALID

Lewis' proposal is also valid, although his approach was mathematical rather than entirely physical.

Lewis began by defining an ideal solution as one whose solvent vapor pressure is described by  $p_1^v = RT/\bar{V}_1^v$  and by  $p_1^v/p_1^{v0} = x_1$ . The first of these

relationships is known as the ideal gas law and the second is known as Raoult's law. (Neither law applies precisely to the solvent vapor of any solution under all circumstances.) Lewis then proposed that the solvent in the ideal solution had "activity" which he defined as  $a_1 = x_1$ . Substitution of these relationships into Eq (11) leads to the statement that the chemical potentials of the solution solvent and pure solvent of the ideal solution differ by

$$\mu_1(T, p, x_1) - \mu_1^0(T, p_s) = RT \ln a_1. \quad (12)$$

The vapor of the solution solvent is ideal only in the limiting condition when  $x_1$  goes to 1; so Lewis defined the activity of the solvent in the solution to be  $a_1 = \gamma_1 x_1$  where  $\gamma_1$  is an experimentally determined coefficient such that Eq. (12) still applies to the solvent. The solute is said to diminish the activity of the solvent in the solution. The problem is that the term solvent activity is only a convenient term. It is not essential to describe the change in the solvent as a change in its activity. Nevertheless, the activity coefficient and the activity of the solution solvent can be assessed either by combining Eqs (11) and (12) or Eqs (7) and (12), i.e.

$$RT \ln \gamma_1 x_1 = \int_{p_1^0}^{p_1^y} \bar{V}_1^v dp_1^v \quad ; \quad (13)$$

$$= - \int_p^{p+\Pi_1} \bar{V}_1 dp. \quad (14)$$

## 5 HULETT'S ENHANCED SOLVENT TENSION VS LEWIS' DIMINISHED SOLVENT ACTIVITY

Precedence has established Lewis' diminished solvent activity as the dominant description of the altered state of the solvent in solution. Seldom has Hulett's work been cited, either with approval or without approval. In 1906 C. Hudson<sup>5</sup> remarked:

In a recent article concerning the relation between osmotic pressure and negative pressure Professor Geo. A. Hulett has shown that the lower vapor-pressure of solutions indicates that the solutions are under a negative pressure, and a calculation of the negative pressure that would cause the observed depression shows that this negative pressure is exactly equal to the osmotic pressure of the solution. This important conclusion is to my knowledge the first evidence that osmotic pressure has the same effect on liquids as does negative pressure.<sup>6</sup>

But just seven years later, in a monograph on osmotic pressure, A. Findlay<sup>7</sup> declared that:

— the fundamental cause of osmosis is to be found in the difference which exists between the activity of the solvent in the pure state and in the solution.

Findlay also cited Hulett but dismissed his proposal as follows:

Of other theories of osmotic pressure which has been put forward, it will suffice if we mention here the theory of Hulett, according to which the osmotic pressure can be regarded as a negative pressure on the solvent (the vapour pressure of which is thereby lowered); . . .

The supremacy of solvent activity was established and solvent tension was forgotten or disavowed. Activity coefficients have been determined for a vast array of solvents into which were dissolved an enormous variety of solutes under many kinds of circumstances of temperature and pressure.

Like  $x_1$ ,  $\gamma_1$  and  $a_1$  are dimensionless numbers. They are not fundamental terms by which to characterize the change in the solution solvent nor is Eq. (12) a fundamental statement derived only from the laws of thermodynamics. On the other hand, Eqs. (5), (6) and (7) are fundamental statements about the solvent in the solution. Since in all respects, the solvent in the solution is altered precisely as if the solute enhanced the tension between the solvent molecules by the osmotic pressure of the solution solvent, it is logical to infer that the solute does exactly that to the solvent.

In a recent statement J. Hildebrand<sup>8</sup> writes:

Concepts about the liquid state that are inconsistent with the facts are noted, and solvent under tension is one of them. Osmosis is not present in a solution: it is a process in the presence of a semipermeable membrane that can be quantified by the operation of applying a hydrostatic pressure. The classical derivation of the van't Hoff equation from Raoult's law is reviewed. The soundness of the early views of G. N. Lewis has not changed.

Hildebrand<sup>8</sup> also states that:

If more of one component is added to a solution, its molecules soon become randomly dispersed, they are no longer "solvent" or "solute"; to speak of "solvent tension" in a mixture is nonsense.

We may wonder then how one speaks of the chemical potential of the solvent or even the solvent activity,  $a_1$ , in a solution if we are forbidden to speak of solvent tension in a solution. We can accept Hildebrand's statement that "Osmosis is not present in a solution." But this statement does not refute Hulett's proposal that solute molecules enhance the tension between solvent molecules and is thereby the basis for all the colligative properties of the solvent in the solution.

In an effort to discredit the term solvent tension it is often stated that it can not be directly measured. Certainly, one cannot insert a probe into a solution and measure the solvent tension. Nor is there a probe for measuring solvent activity. An insoluble probe inserted into a solution remains always outside the solution. Nevertheless, we can recognize that the solvent is altered by the solute in such a way as to effect the colligative properties of the solvent and we can measure the effect on one or more of these. We infer that the solvent activity is diminished or, alternately, the solvent tension is enhanced and the chemical potential of the solvent is decreased.

Hulett has been selected as one of the principal advocates of the solvent tension concept. He verified that the state of the solvent in the solution is identical with the pure solvent under tension by comparing a column of solution, standing in a gravity field above a semi-permeable membrane, with a column of pure solvent supported at the same height, by a ceramic disk. The column of pure solvent is under increasing tension with increasing  $z$  above the free surface of the pure solvent with which both columns are contiguous and are in equilibrium. At  $h$  the tension in the pure solvent is  $\rho_1^0 gh$ ; this is also the osmotic pressure of the solvent in the solution. Hulett recognized that the solvent had to change with increasing  $z$  in exactly the same way in both columns to insure that the vapor pressure at every  $z$  would be exactly the same as the pressure of the vapor of the pure solvent at  $z$  and above the surface at  $h$ , no matter how complex the dependence of solvent density on  $T$  and  $z$ ,  $\rho_1^0(T, z)$ , or how complicated the gas law describing the solvent vapor. Hulett acknowledged that Noyes<sup>9</sup> advanced an equally cogent argument for the solvent tension concept. Others, before and since Hulett, have expressed clearly the concept of solvent tension enhanced by solute in the solution, including Schiller,<sup>10</sup> Dixon,<sup>11</sup> Herzfeld,<sup>12</sup> Mysels,<sup>13</sup> Hammel and Scholander.<sup>14</sup> Altogether, there have been only a few advocates of enhanced solvent tension compared with the number of advocates of diminished solvent activity.

## 6 $\Pi_1$ AS A FUNCTION OF $x_1$

The osmotic pressure is a function of the mole fraction of solvent in the solution but there is no simple relationship between them for all concentrations of solute in the solution. The relationship between  $\Pi_1$  and  $x_1$  is complicated for several reasons. First, although  $\Pi_1$  increases as solute concentration increases and as  $x_1$  decreases, the only thermodynamic statements governing the relationship between  $\Pi_1$  and  $x_1$  are Eqs. (1) and (3) through (11). These statements require an exact knowledge of  $\bar{V}_1$  or  $\bar{V}_1^0$  as functions of  $T$  and  $p$  or the exact relationships between  $p_1^v$  and  $\bar{V}_1^v$  or  $p_1^v$  and  $\bar{V}_1^v$ . There is, however,



no theory to describe exactly these complicated functions or relationships. An accurate experimental determination of  $\bar{V}_1^0(T, p)$  at  $T$  from  $p$  to  $p - \Pi_1$  or of  $p_1^v$  vs  $\bar{V}_1^v$  from  $p$  to  $p + \Pi_1$  at  $T$  are the only practicable solutions to the problem.

Another reason the relationship between  $\Pi_1$  and  $x_1$  is complicated is because the solute molecules can enhance the tension between the solvent molecules in several ways. We usually consider that thermal motion of solute molecules is the principal means by which microsolute enhance the solvent tension. But the enhancement of solvent tension by macromolecules may be due to a mechanical force as well as a thermal force, cf. Figure 3, Scholander<sup>15</sup> and Figure 2, Hargens, *et al.*<sup>16</sup> In addition, differences in density of solute and solvent will influence the solvent tension; and the diffusion of solute through the solvent will also enhance solvent tension, cf. Figure 2, Hammel and Scholander.<sup>17</sup> There are other reasons for complications, for example, the solute and solvent may interact so that  $n_2^0$  moles of pure solute may differ from  $n_2$  moles of solute in solution. Likewise,  $n_1$  may differ from  $n_1^0$  moles of pure solvent.

## 7 CONCLUSION

Under all circumstances, the solvent is altered by the solute precisely as if the tension between the molecules of solvent was enhanced by  $\Pi_1$  no matter how  $\Pi_1$  relates to  $x_1$ , no matter how the solute molecules do it, no matter what the compressibility of the solvent is, and no matter what the relationship is between the vapor pressure and the molar volume of the solvent vapor. Therefore, it follows that the lower chemical potential and the diminished activity of the solvent in the solution must be attributed to its enhanced internal tension.

## Acknowledgements

I am indebted to Dr. Halvard Baugerød for drawing my attention to the articles by Hudson<sup>5</sup> and Schiller<sup>10</sup> and to Dr. Martha Heath for reading the manuscript and correcting several errors in syntax. This article is dedicated to the memory of Professor P. F. Scholander whose inspiration profoundly affected all his associates.

## Footnotes and References

1. G. A. Hulett, "Beziehung zwischen negativem druck und osmotischem druck," *Z. Phys. Chem.*, **42**, 353-368 (1903).
2. G. N. Lewis, "The osmotic pressure of concentrated solutions, and the laws of the perfect solution," *J. Am. Chem. Soc.*, **30**, 668-683 (1908).

3. Consider that the pressure applied to pure solvent is  $p$  and that the chemical potentials of the solution solvent and pure solvent are equalized by a pressure  $p + \Pi'_1$  applied to the solution, so that at  $T$

$$\mu_1(T, p + \Pi'_1, x) = \mu_1^0(T, p). \quad (i)$$

Next, consider that the pressure applied to the same solution is  $p$  and that a pressure  $p - \Pi_1$  is applied to the pure solvent to equate the chemical potentials of the solution solvent and pure solvent, so that at  $T$

$$\mu_1(T, p, x_1) = \mu_1^0(T, p - \Pi_1). \quad (ii)$$

It might perhaps be thought, at first sight, that  $\Pi'_1 = \Pi_1$  only if the solution were ideal. Suppose that a pressure  $\Pi'_1$  is added to both pressures in Eq. (ii), so that

$$\mu_1(T, p + \Pi'_1, x_1) = \mu_1^0(T, p - \Pi_1 + \Pi'_1). \quad (iii)$$

Then according to Eq. (i),  $\Pi'_1 - \Pi_1$  must equal zero, that is  $\Pi'_1 = \Pi_1$  for every solution. The osmotic pressure of the solvent in any solution is always  $\Pi_1$ , the difference in pressures applied to the solution and pure solvent for which the chemical potentials of solution solvent and pure solvent are equal.

4. Note that the partial molar volume of solvent in a binary solution is defined  $\bar{V}_1 = \partial V / \partial n_1 |_{T, p, n_2}$ . Although  $\bar{V}_1$  is defined as the rate of change of solution volume with respect to changing the molar amount of solvent at constant  $T, p$  and  $n_2$ , nevertheless,  $\bar{V}_1$  of any solvent is also a function of  $T, p$  and  $n_2$  and this dependence has been indicated throughout the text as  $\bar{V}_1(T, p, x_1)$ . Likewise, the partial molar volume of the solute is defined  $\bar{V}_2 = \partial V / \partial n_2 |_{T, p, n_1}$  and the volume of the solution is  $V = n_1 \bar{V}_1 + n_2 \bar{V}_2$ . Note further that adding solute to solvent usually increases the volume of the solution. However, occasionally, the solution volume may decrease with addition of a small amount of solute to solvent. For example, while forming a dilute aqueous solution of magnesium sulfate,  $\bar{V}_2 < 0$  and  $n_2 \bar{V}_2$  is negative. Nevertheless, after the solute is dissolved, the partial molar volume of the water would be increased precisely as if expanded by the solute. According to Eq. (5),  $\bar{V}_1(T, p, x_1)$  must equal  $\bar{V}_1^0(T, p - \Pi_1)$ . For any pure solvent,  $\bar{V}_1^0(T, p - \Pi_1)$  is always greater than  $\bar{V}_1^0(T, p)$ ; therefore,  $\bar{V}_1(T, p, x_1) > \bar{V}_1^0(T, p)$  at the same  $T$  and  $p$ .
5. C. S. Hudson, "The freezing of pure liquids and solutions under various kinds of positive and negative pressure and the similarity between osmotic pressure and negative pressure," *Physical Rev.* (5), **22**, 257-264 (1906).
6. Hulett clearly perceived that the solute induced a negative pressure (tension) in the solvent; therefore, it is unfortunate that Hudson used the phrase "... the solutions are under a negative pressure." in the quotation cited in C. S. Hudson (Footnote 5), 257. Hulett's use of the term "negative solvent pressure" is synonymous with our term "solvent tension" and is understood to be an internal negative pressure (tension) and not an externally applied pressure. Applying a pressure to the solution decreases the solvent tension by the same amount. If the applied pressure is the osmotic pressure of the solvent,  $\Pi_1$ , then the solvent pressure equals the pure solvent pressure so that  $\mu_1(T, p + \Pi_1, x_1) = \mu_1^0(T, p)$ ,  $\bar{V}_1(T, p + \Pi_1) = \bar{V}_1^0(T, p)$  and all properties of the solution solvent and pure solvent are identical.
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## Appendix

### Chemical potential of solvent as function of $T$ at constant $p$

The chemical potential of the solvent in the solution can be changed according to

$$\iiint d\mu_1(T, p, x_1) = - \int \bar{S}_1 dT + \int \bar{V}_1 dp + \int \frac{\partial \mu_1}{\partial x_1} dx_1$$

Thus, at constant  $p$  and  $x_1$  decreasing the temperature applied to the solution from  $T$  to  $T - \theta_1$ , increases the chemical potential of its solvent an amount

$$\mu_1(T - \theta_1, p, x_1) - \mu_1(T, p, x_1) = - \int_T^{T-\theta_1} \bar{S}_1 dT, \quad (\text{A1})$$

where the partial molar entropy of the solution solvent may be a complicated function of  $T, p$  and  $x_1$ ,  $\bar{S}_1(T, p, x_1)$ . Also at constant  $p$ , increasing the temperature applied to the pure solvent from  $T$  to  $T + \theta_1$  decreases its chemical potential an amount

$$\mu_1^0(T + \theta_1, p) - \mu_1^0(T, p) = - \int_T^{T+\theta_1} \bar{S}_1^0 dT, \quad (\text{A2})$$

where the molar entropy of pure solvent may be a function of  $T$  and  $p$ ,  $\bar{S}_1^0(T, p)$ .

If  $\theta_1$  in Eqs. (A1) and (A2) is defined as the difference in temperatures applied to the solution and to the pure solvent for which the chemical potentials of the solution solvent and pure solvent are equal, then if  $T$  is applied to the solution and  $T + \theta_1$  is applied to the pure solvent,

$$\mu_1(T, p, x_1) = \mu_1^0(T + \theta_1, p). \quad (\text{A3})$$

Likewise, if  $T - \theta_1$  is applied to the solution and  $T$  is applied to the pure solvent, then

$$\mu_1(T - \theta_1, p, x_1) = \mu_1^0(T, p). \quad (\text{A4})$$

By substituting Eq. (A4) into Eq. (A1)

$$\mu_1(T, p, x_1) - \mu_1^0(T, p) = \int_T^{T-\theta_1} \bar{S}_1 dT. \quad (\text{A5})$$

Also by substituting Eq. (A3) into Eq. (A2),

$$\mu_1(T, p, x_1) - \mu_1^0(T, p) = - \int_T^{T+\theta_1} \bar{S}_1^0 dT. \quad (\text{A6})$$

Thus, it follows from Eqs (A5) and (A6) that

$$\int_T^{T-\theta_1} \bar{S}_1 dT = \int_{T+\theta_1}^T \bar{S}_1^0 dT, \quad (\text{A7})$$

and that

$$\bar{S}_1(T, p, x_1) = S_1^0(T + \theta_1, p), \quad (\text{A8})$$

or that

$$\bar{S}_1(T - \theta_1, p, x_1) = \bar{S}_1^0(T, p). \quad (\text{A9})$$

At any  $T, p$  and  $x_1$ , the partial molar entropy of the solution solvent equals the molar entropy of pure solvent at the same  $p$  but at a higher temperature by  $\theta_1$ , no matter how the entropy of the solvent varies with  $T$  and  $p$ .

If at constant  $p$ ,  $T$  is applied to the solution and  $T + \theta_1$  is applied to the pure solvent, then the solution solvent and pure solvent are in chemical equilibrium, i.e. their molar free energies are the same. However, they are not in thermal equilibrium, i.e. without an insulator between them, heat would flow from pure solvent to solution. Furthermore, they do not have the same vapor pressure nor are they in osmotic equilibrium. If a membrane, permeable to solvent but not to solute molecules, were between them, then pure solvent would enter the solution by diffusive flow if the pressures applied to solution and pure solvent were both  $p$ . Only if the pressure applied to the pure solvent is less than the pressure applied to the solution by  $\Pi_1$  and only if the temperatures applied to both solution and pure solvent are the same, can the solution solvent and pure solvent have the same chemical potentials, the same vapor pressures and be in thermal and osmotic equilibrium.

The partial molar entropy and the partial molar volume of the solution solvent are both functions of  $x_1$ . However, the osmotic pressure of the solvent in the solution can not be attributed to a change in solvent entropy any more than to a change in solvent volume. Parsimony is attained when the altered state of the solvent in the solution is attributed to an enhanced solvent tension (by  $\Pi_1$ ) rather than to an enhanced solvent temperature (by  $\theta_1$ ). Osmotic equilibrium between solution solvent and pure solvent is unattainable at any temperature difference at constant  $p$  and is attainable only by a pressure difference  $\Pi_1$  at constant  $T$ .