Friedman's excess free energy and the McMillan–Mayer theory of solutions: Thermodynamics*

Juan Luis Gómez-Estévez

Departament de Física Fonamental, Facultat de Física, Universitat de Barcelona, Diagonal 645, E-08028, Barcelona, Spain

Abstract: In his version of the theory of multicomponent systems, Friedman used the analogy which exists between the virial expansion for the osmotic pressure obtained from the McMillan–Mayer (MM) theory of solutions in the grand canonical ensemble and the virial expansion for the pressure of a real gas. For the calculation of the thermodynamic properties of the solution, Friedman proposed a definition for the "excess free energy" that is a reminder of the ancient idea for the "osmotic work". However, the precise meaning to be attached to his free energy is, within other reasons, not well defined because in osmotic equilibrium the solution is not a closed system and for a given process the total amount of solvent in the solution varies. In this paper, an analysis based on thermodynamics is presented in order to obtain the exact and precise definition for Friedman's excess free energy and its use in the comparison with the experimental data.

Keywords: excess functions; free energy; Friedman; McMillan–Mayer; osmotic pressure; theory of solutions.

INTRODUCTION

The McMillan–Mayer (MM) theory of solutions [1–6] is a general theory that was originally formulated within the context of the grand canonical ensemble. This theory allows a very general theoretical analysis starting from theoretical models and/or the treatment of the experimental data in a semi-empirical way when the complexity of the system is very great. From the MM theory all the equilibrium thermodynamic properties of a multicomponent system can be considered. However, the development of the theory is not finished, and there are still conceptual and practical problems in its application to real systems. In this paper we will discuss the interpretation of several excess properties that can be obtained from the theory and their comparison with the results obtained from the experiment. Particularly, we will consider the so-called "excess free energy" as a starting point for obtaining the rest of the thermodynamic properties for a solution. Previously, we will introduce the notation employed and a brief introduction to the MM theory, which is necessary for what follows. Biographical information about the creators of the MM theory, Joseph E. Mayer and William George McMillan Jr., can be found in refs. [7,8].

Even though the MM theory is a very general theory including also quantum effects, we will consider only a more simplified system that shows the basic ideas without making the presentation unnecessarily complicated [1,5]. We will consider a solution formed only by a solute σ and a solvent s. The "natural" variables in the MM theory are the usual ones for the grand canonical ensemble [2,3,5]:

(z_σ, z_s, T, V) or $(\mu_\sigma, \mu_s, T, V)$ where z is the activity of each component in the solution, T is the absolute temperature, and V the volume of the solution. The activities are defined in terms of the chemical potential μ as $z \equiv \exp(\mu/kT)/\Lambda^3$ where Λ is the thermal wavelength of De Broglie $(h/2\pi nkT)^{1/2}$. It is very important to be careful with this definition for z because several authors define $z = \exp(\mu/kT)$ [9] and use the notation λ for the same quantity. As a consequence, the thermodynamic properties have different meanings as well as the mathematical relationships that permit their derivation from the grand partition function [5, Chap. 1; 9, Chap. 4]. The solute activity coefficient, $\tilde{\gamma}_\sigma$, is defined as $z_\sigma = \tilde{\gamma}_\sigma \rho_\sigma$ where $\rho_s(=c_\sigma)$ is the concentration/number density of the solute (or molarity). When $c_\sigma \to 0$, $c_s \neq 0$, $\tilde{\gamma}_\sigma \to \gamma_\sigma^0$, which is the activity coefficient of the solute at "infinite dilution". A more practical definition for the activity coefficient is used. We define γ_σ as ${z_\sigma}\big/{\gamma_\sigma^0} = {\tilde{\gamma}_\sigma \rho_\sigma}\big/{\gamma_\sigma^0} = \gamma_\sigma \rho_\sigma$, and in this form we have that $\gamma_\sigma \to 1$ when $c_\sigma \to 0$; $c_\sigma \neq 0$. Now the chemical potential for the solute can be written as

$$\mu_\sigma = \mu_\sigma^0 \begin{pmatrix} T, \mu_s \\ T, p_0 \end{pmatrix} + kT \ln \gamma_\sigma c_\sigma; \mu_\sigma^0 = kT \ln \left[\Lambda_\sigma^3 \gamma_\sigma^0 \begin{pmatrix} T, \mu_s \\ T, p_0 \end{pmatrix} \right] \tag{1}$$

where p_0 is the pressure of the pure solvent with chemical potential μ_s. The two possible elections (T, μ_s) or (T, p_0) for the independent variables set that can be chosen are shown explicitly in eq. 1. The MM theory, in the form that is usually understood, is a particular version of the formalism that was developed in the first place by Mayer for one-component systems [2] and later extended by McMillan and Mayer for multicomponent systems [1,2]. The more general theory relates the grand canonical partition function and the potentials of mean force between two different thermodynamic states of the system with different activities. Choosing the two thermodynamic states in the way described below, the MM theory of solutions obtains for the grand canonical partition function at the MM level (Ξ_{MM}) for a system with a solute σ in a solvent s the following expression:

$$\Xi_{MM} = \frac{\Xi(z, T, V)}{\Xi(z^*, T, V)} = \sum_{N_\sigma \geq 0} \left(\frac{z_\sigma}{\gamma_\sigma^0} \right)^{N_\sigma} \frac{1}{N_\sigma!} \int \exp\left[-\beta W_{N_\sigma}^\infty \right] d\{N_\sigma\} \tag{2}$$

where $z \equiv (z_s, z_\sigma)$ and $z^* \equiv (z_s, 0_\sigma)$ are the activities of the solution at a finite concentration and at "infinite dilution" (0_σ, when $z_\sigma \to 0$, $c_\sigma \neq 0$). $W_{N_\sigma}^\infty$ is the potential of mean force among the N_σ solute molecules in a solvent s at infinite dilution or in other words, in the thermodynamic state characterized by the variables (z^*, T, V) and really is a free energy which depends on the thermodynamic state and the coordinates of the solute molecules. Finally, γ_σ^0 is the solute activity coefficient at infinite solution (referred to an ideal gas scale) and is associated with the interactions of a solute molecule alone surrounded by the solvent molecules. As we can see, Ξ_{MM} is a ratio of partition functions that have in common the same activity of the solvent, and what is obtained from this ratio are the differences between the corresponding thermodynamic properties. The corresponding experimental situation with this structure for Ξ_{MM} is the solution in osmotic equilibrium with the pure solvent by means of a semipermeable membrane [6] and is characterized by the equality of the solvent chemical potential on both sides of the membrane

$$\mu_s(T, p_0) = \mu_s(T, p = p_0 + \pi, c_\sigma) \tag{3}$$
$$\mu_s(T, p_0) = \mu_s^*(T, z_s^* = z_s)$$

where p and p_0 are the pressures of the solution and the pure solvent, respectively. The osmotic pressure π is related with Ξ_{MM} through the basic equation

$$\pi V = kT \ln \Xi_{MM} \tag{4}$$

This relationship between the osmotic pressure π and the Ξ_{MM} has the same form that exists for the pressure p of a pure system σ and the corresponding grand partition function Ξ. The Ξ_{MM} is analogue to Ξ but with a "potential energy" $W_{N_\sigma}^\infty$ instead of the true potential energy among the solute molecules "alone" U_{N_σ}. In this case, the corresponding partition function can be written as follows:

$$e^{pV/kT} = \Xi(z_\sigma, T, V) = \sum_{N_\sigma \geq 0} \frac{z_\sigma^{N_\sigma}}{N_\sigma!} \int \exp[-\beta U_{N_\sigma}] d\{N_\sigma\} \tag{5}$$

The previous equations justify the so-called analogy between the gases and the liquid solutions introduced originally by J. van't Hoff [10], and because the treatment is general, this analogy is not by any means restricted to dilute solutions. From Ξ_{MM} it is possible to obtain in a way completely analogue to the virial expansion for real gases [2,3], the virial expansion for the osmotic pressure π as a power series of the activity and/or the density of the solute σ in the form

$$\frac{\pi}{kT} = \sum_{j \geq 1} b_j^* \left(\frac{z_\sigma}{\gamma_\sigma^0} \right)^j = \rho_\sigma \left[1 + B_2^* \rho_\sigma + B_3^* \rho_\sigma^2 + ... \right] \tag{6}$$

where B_2^*, B_3^*, ... are the second, third, ... virial coefficients for the osmotic pressure and have the same form as the correspondent virial coefficients for real gases with the only difference that the potential is the potential of mean force between two, three, ... molecules of solute in the solvent at infinite dilution. The first term in expansion 6 constitutes the so-called van't Hof equation for the osmotic pressure valid for a dilute solution [10]. In ref. [11], a very extensive presentation and discussion about the usefulness of the virial expansion for π in the very general case of multicomponent systems can be found.

Is very important to realize that the main result of MM theory is the general expression 2 jointly with eq. 4. From these two equations, all the thermodynamic properties can be obtained in a very general way [6]. There is a very widespread idea that the MM theory is only valid for moderately dilute solutions and that the basic result is the virial expansion 6. This is not true, and the same situation would be found in comparing the virial expansion for real gases with the corresponding grand partition function, which can be applied to very complex systems (see, e.g., refs. [2,3,9]).

The comparison of a given model for the solution obtained with the MM theory with the experimental data poses extra difficulties. This is due to the fact that the thermodynamic properties are those for a solution in osmotic equilibrium with the pure solvent and the natural variables which appear in Ξ_{MM}, see eqs. 1 and 2, are very different with the usual ones: usually T, p and molalities/molarities or molar fractions. At this point, the approach formulated by Friedman [4,12–14] appears. Although he refers to the MM theory, the approach he uses differs remarkably from the original treatment of the theory in the grand canonical ensemble. He uses a very different notation, and the meaning of the thermodynamic properties is not the usual one. Moreover, Friedman adopts a non-standard election for the necessary variables in the description of the solution's thermodynamic state by using p_0 as a variable for his excess free energy. A broad perspective of Friedman's work can be found in ref. [16].

FRIEDMAN'S EXCESS THERMODYNAMIC FUNCTIONS

Even though Friedman presented the MM theory in the grand canonical ensemble in his book *Ionic Solution Theory*, published in 1962 and later in a very general review with Dale [4], he developed the thermodynamics of the solution in a very different way. In his version of the theory for multicomponent systems, Friedman used instead the analogy between the virial expansion for the pressure of a real gas and the corresponding expansion for the osmotic pressure (6) which is one of the most used results of the MM theory.

The sets of variables employed by him in order to characterize the thermodynamic state of the solution are very diverse as follows: z_s, μ_s, or p_0 for the solvent, the temperature T, the volume V, and

N_σ (or n_σ if we use the number of moles for the solute). The basic quantity is $A^{ex}_{Fried} \equiv A^{ex}$, the "excess Helmholtz free energy" or simply the "excess free energy" per litre of solution, which he defined by analogy with the definition for a closed system [4a,12,13]

$$A^{ex}(c_\sigma, p_0, T) = -c_\sigma \int_{c'=0}^{c'=c_\sigma} [\pi - c'kT] d(1/c') \tag{7}$$

and later [4b]

$$-\left(\frac{\partial(A^{ex}/c)}{\partial(1/c)}\right)_{\substack{MM \\ p_0 \leftrightarrow \mu_s, T, c_\sigma}} = \pi - ckT \tag{8}$$

where $A^{ex} \to 0$ when $c_\sigma \to 0$. Other thermodynamic properties that derive from the knowledge of A^{ex} are the "excess energy/enthalpy" E^{ex}_{Fried}:

$$E^{ex}_{Fried} = (H^{ex}) = \left(\frac{\partial(A^{ex}/T)}{\partial(1/T)}\right)_{p_0, c_\sigma} \tag{9}$$

and the "excess volume" V^{ex}_{Fried}, defined as

$$V^{ex}_{Fried} = (V^{ex}) = \left(\frac{\partial A^{ex}}{\partial p_0}\right)_{T, p_0} \tag{10}$$

In all the previous definitions for the excess free energy as well as for the excess energy/enthalpy and the excess volume, their meaning does not match with the usual one in thermodynamics. The definition of the excess free energy (7) is applied to an open system with respect to the solvent, and really what we have is the Legendre transform of the total solution free energy. For the other two excess thermodynamic properties H^{ex} (9) and V^{ex} (10), which are defined in terms of A^{ex}, the problem is worsened because the pressure p_0 of the pure solvent in osmotic equilibrium with the solution is used in the partial derivatives of A^{ex}. The fact that several authors [14,15,22,23] do not write explicitly which thermodynamic variables are using increases the confusion about the correct meaning of A^{ex}. In this work we will consider only the interpretation of A^{ex} and its comparison with the experimental data as well as with Ξ_{MM}.

MEANING OF A^{ex} OF FRIEDMAN AND ITS RELATION WITH THE HELMHOLTZ FREE ENERGY F OF THE SOLUTION

We will consider a two-component solution with n_s, n_σ moles of solvent and solute, respectively, for a given temperature T and volume V. The solution is in a state of osmotic equilibrium with the pure solvent at a pressure p_0 being $\mu_s^*(T, p_0)$ its chemical potential. Because of the equality of the solvent's chemical potential on both sides of the semipermeable membrane, the solution is at a pressure $p = p_0 + \pi$, where the osmotic pressure, π, varies with the solute concentration if we hold T and p_0 constants. The Helmholtz free energy of the solution, F, is given by

$$F = n_s\mu_s + n_\sigma\mu_\sigma - pV \tag{11}$$

Now, if we change in a reversible and isothermal way the volume of the solution in dV, it will be a variation of the number of solvent moles, dn_s because the solution is not closed for the solvent due to the semipermeable membrane. The variation of the Helmholtz free energy of the solution for this process will be

$$dF = -(p_0 + \pi)dV + \mu_s dn_s \tag{12}$$

where T, p_0 are constant in the process as well as μ_s. If we want to treat the solution as if it were a "closed system" without the explicit mention of the solvent, we can consider the difference $F - \mu_s n_s$ and we have

$$d(F - \mu_s n_s) = -(p_0 + \pi)dV = -(p_0 + \pi)n_\sigma d(1/c) \tag{13}$$

where the fact that n_σ remains constant in the process has been used. The previous expression constitutes the so-called "osmotic work" in the old formulation of the thermodynamics of solutions by the "osmotic school" of van't Hoff, Nernst, and others [10]. Even in our days, there are authors who call it "the variation of the free energy" [17,18] because of the analogy with the corresponding variation for a pure component.

With the help of eq. 13, we are going to find the exact thermodynamic meaning of the expression 7, which defines A^{ex} of Friedman. For that purpose, we integrate eq. 13 between the concentration $c = 0$ (infinite dilution) to a finite concentration c for the solute σ:

$$(F - \mu_s n_s)^c - (F - \mu_s n_s)^\infty = \int_{c'=0}^{c'=c} d(F - \mu_s n_s) = -n_\sigma \int_{c'=0}^{c'=c} (p_0 + \pi)d(1/c') \tag{14}$$

If we repeat the same process but now considering the solution as ideal respect the solute, the osmotic pressure will be $\pi = cRT$ (van't Hoff's law) for all the values of the concentration of the solute and we have

$$(F - \mu_s n_s)^{\text{ideal},c} - (F - \mu_s n_s)^{\text{ideal},\infty} = -n_\sigma \int_{c'=0}^{c'=c} (p_0 + c'RT)d(1/c') \tag{15}$$

If we compute the difference between the two previous equations taking into account the validity of the equation

$$(F - \mu_s n_s)^{\text{real},\infty} = (F - \mu_s n_s)^{\text{ideal},\infty} \tag{16}$$

we get, finally

$$(F - \mu_s n_s)^{\text{real},c} - (F - \mu_s n_s)^{\text{ideal},c} = -n_\sigma \int_{c'=0}^{c'=c} (\pi - c'RT)d(1/c') \tag{17}$$

The validity of eq. 16 is based in the definition of ideal solution (see ref. [6]) and the fact that a real solution behaves like an ideal one as the solute's concentration goes to zero. Finally, in order to obtain the $A^{ex}(c, T, p_0)$, we divide by the volume V and we reach the original expression proposed by Friedman (7):

$$A^{ex}(c,T,p_0) = \frac{(F - \mu_s n_s)^{\text{real},c}}{V} - \frac{(F - \mu_s n_s)^{\text{ideal},c}}{V} = \\ = -c \int_{c'=0}^{c'=c} (\pi - c'RT)d(1/c') \tag{18}$$

Now, once we have understood the meaning of A^{ex}, we can find an integrated version of eq. 18, which is more useful to handle by using the definition of F (eq. 11) jointly with the expressions for the osmotic pressure and the solute chemical potential in the case of the real and ideal solution respectively (eq. 1). We have for the real solution

$$\frac{(F - \mu_s n_s)^{\text{real},c}}{V} = -(p_0 + \pi) + c_\sigma \mu_\sigma =$$

$$= -(p_0 + \pi) + c_\sigma [\mu_\sigma^0(T, p_0 \leftrightarrow \mu_s) + RT \ln \gamma_\sigma c_\sigma] \qquad (19)$$

and for the ideal solution

$$\frac{(F - \mu_s n_s)^{\text{ideal},c}}{V} = -(p_0 + c_\sigma RT) + c_\sigma [\mu_\sigma^0(T, p_0 \leftrightarrow \mu_s) + RT \ln c_\sigma] \qquad (20)$$

and finally, the A^{ex} can be written as

$$A^{\text{ex}}(\text{Friedman}) = -\pi + c_\sigma RT + c_\sigma RT \ln \gamma_\sigma \qquad (21)$$

We see that the excess free energy, as defined by Friedman, is **not equal to** the Helmholtz free energy of the solution, eq. 11, because of the missing term $\mu_s n_s$, which is associated with the solvent. Moreover, this free energy is defined with reference to an ideal solution at the same concentration, temperature, and at a pressure $p_0 + c_\sigma RT$. In other words: A^{ex}(Friedman) **is a difference of the Legendre transforms of the Helmholtz free energies between the real solution and the ideal solution both in osmotic equilibrium with the pure solvent (eq. 17)**. We should not forget that when the solution is in osmotic equilibrium with the pure solvent at (T, p_0), the pressure of the solution $p_0 + \pi$ changes with c_σ.

A better understanding of the meaning of A^{ex} can be obtained if we define the osmotic coefficient $\phi_{\text{OS}}(=\phi_{\text{MM}})$ as a function of π as [17,18]

$$\phi_{\text{OS}} \equiv \frac{\pi}{c_\sigma RT} \qquad (22)$$

and which is equal to one for and ideal solution. The final form of A^{ex} can be written in the following way:

$$A^{\text{ex}}(\text{Friedman}) = c_\sigma RT(1 - \phi_{\text{OS}} + \ln \gamma_\sigma) \qquad (23)$$

In the literature only in two references [15,24], an expression for A^{ex} equivalent to eq. 23 can be found but with no derivation or discussion whatsoever. This expression is "equivalent" to the G^{E}, the excess gibbs free enthalpy, employed usually when we are measuring at a given T, p, and a molality m, the so-called Lewis–Randall (LR) scale [12,20–21]

$$G^{\text{E}} \cong mRT(1 - \phi + \ln \gamma_\sigma^{(m)}) \qquad (24)$$

The differences between expressions 24 and 23 are due to the fact that G^{E} is defined by kilogram of solvent whereas the A^{ex} is a "free energy" per litre of solution and that the rational or practical osmotic coefficient, $\phi(\phi_{\text{R}} = \phi_{\text{LR}})$ is defined in terms of the chemical potential of the solvent instead of ϕ_{OS}, defined in terms of π. The symbol $\cong$ in eq. 24 means that there are two variants for the definition of G^{E} that for all practical purposes are equivalent [20,21]. Finally, we must remember that the $\gamma_\sigma^{(m)}$ in eq. 24 is defined in the molality scale.

Experimentally is usual to measure the values of ϕ, $\gamma_\sigma^{(m)}$ as a function of molality at a given temperature and pressure whereas ϕ_{OS}, γ_σ, which appear in the expression for A^{ex} are given at a variable pressure $p = p_0 + \pi$ for a temperature T and concentration/molality c_σ. For the comparison between theory/experiment or experiment/experiment, a thermodynamic correction called the correction MM to LR is necessary [12–14,17,18,25].

DISCUSSION

The Helmholtz free energy of the solution, see eq. 11, has as natural variables the set (T, V, n_s, n_σ) but later we have been working with $F - \mu_s n_s$ in order to get an interpretation of A^{ex}. What is the meaning of this difference, and which are its natural variables? In order to facilitate the reasoning, we will call $\bar{F}$ as

$$\bar{F} \equiv F - \mu_s n_s = -pV + \mu_\sigma n_\sigma \qquad (25)$$

which in the mathematical language is a Legendre transform [26,27] of in respect to the solvent n_σ. The meaning of this new function is clear as can be seen from eq. 25: it looks like the Helmholtz free energy for a one-component system σ, the solute alone. In order to look for the natural variables of $\bar{F}$, we compute his differential that reads

$$d\bar{F} = -pdV - SdT - n_s d\mu_s - \mu_\sigma dn_\sigma \qquad (26)$$

and we see the interchange between $n_s \leftrightarrow \mu_s$ in the differential form. This change is more useful if we are considering systems in osmotic equilibrium because the μ_s is a more natural variable. We have that $\bar{F} = \bar{F} (T, V, \mu_s, n_\sigma)$ and the A^{ex} is the difference of $\bar{F}(real, c) - \bar{F}(ideal, c)$ divided by the volume. The fact that the natural variables of this difference are not usually employed must be considered when partial derivatives are computed (i.e., for E^{ex}, V^{ex}) and this problem will be discussed in a future work.

A second aspect to be discussed is to understand why the A^{ex} looks like the G^E (see eqs. 23 and 24) if we note the different meaning between the two functions. Even though the solvent does not appears explicitly in $\tilde{F}$, the term $-pV$ in (25) allows the introduction of the osmotic coefficient ϕ_{OS}, which includes the solvent chemical potential in another way. This can be see even more clearly if we try to define an excess Gibbs free enthalpy in a similar way as we have done for A^{ex}. Because of the relation between F and $G = F + pV$, we could define and excess free enthalpy in the way of Friedman as follows:

$$G^{ex}_{Fried} \equiv (\bar{F} + pV)^{real,c} - (\bar{F} + pV)^{ideal,c} = n_\sigma RT \ln \gamma_\sigma \qquad (27)$$

and the similarity with G^E is lost because the term, which includes the osmotic coefficient, does not appear in the final expression of G^{ex}_{Fried}.

To close the discussion, the calculation of A^{ex} from the partition function Ξ_{MM} (eq. 2) can be done if we remember eq. 18 and the expressions which relate N_σ, π with Ξ_{MM} [6]. The final result, in terms of the natural variables of the grand canonical ensemble can be written as follows:

$$A^{ex}V = (F - \mu_s N_s)^{real,c} - (F - \mu_s N_s)^{ideal,c} =$$

$$= N_\sigma(\mu_\sigma^{real} - \mu_\sigma^{ideal}) - (\pi - \pi^{ideal})V =$$

$$= kT\left(\frac{\partial \ln \Xi_{MM}}{\partial \mu_\sigma}\right)_{T,V,\mu_s} \left(\mu_\sigma^{real} - \mu_\sigma^{ideal}\right) - kT \ln \frac{\Xi_{MM}^{real}}{\Xi_{MM}^{ideal}} \qquad (28)$$

The calculation of Ξ_{MM}^{ideal}, the MM partition function for an ideal solution ($W_{N_\sigma}^\infty = 0; \gamma_\sigma^0 \neq 0$), presents no problem and is given in ref. [6].

As a final conclusion, we can say that the comparison between the MM theory and the experiment (thermodynamics) is not an easy task and it is necessary to proceed with caution taking into account the meaning of the several thermodynamic functions as well as the variables that are used to characterize the state of the system.

ACKNOWLEDGMENTS

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