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Abstract

The traditional development of a representation for the chemical potential of species *A* in an ideal gas mixture involves a plausible intuitive hypothesis that leads from the single-component form to the multicomponent form. In this work a rigorous analysis is presented that yields the classic result for ideal gas mixtures and a new result for ideal liquid solutions.

1. Introduction

The classic representation for the chemical potential in an $N-$component system is given by

$$\mu_A(T,p) \;=\; \mu_A^{\mathrm{o}}(T,p) \;+\; RT\ln x_A \;, \qquad A \;=\; 1,2,\ldots,N \tag{1}$$

An examination of text books treating the subject of thermodynamics indicates a history of presenting Eq. 1 without a derivation. The earliest text book presentation of a form analogous to Eq. 1 would appear to be in the work of Lewis & Randall (1923). In their treatment of single component ideal gases, Lewis & Randall (1923, page 165) suggest that the reader derive the result given by

$$\mu(T,p) \;=\; \mu(T,p_{\mathrm{o}}) \;+\; RT\ln\left(p/p_{\mathrm{o}}\right), \qquad T \;=\; \text{constant} \tag{2}$$

Here we have used the nomenclature consistent with the presentation in this work as opposed to the original nomenclature of Lewis & Randall (1923). Following this suggestion to the reader, Lewis & Randall (1923, page 191) introduced the concept of fugacity with the statement: "We may partially define the fugacity, f, in terms of the molar free energy through the equation

$$\mu \;=\; RT\ln f \;+\; B \tag{3}$$

where B is defined no further than by the statement that it is a function of temperature only, or, in other words, that it is a constant at a single temperature." Moving on to multi-component systems, Lewis & Randall (1923, page 205) stated that: "Proceeding as in the case of a pure substance, we may partially define the fugacity of a solution constituent by the equation

$$\mu_A \;=\; RT\ln f_A \;+\; B_A \tag{4}$$

where B_A is a constant for a given substance at a given temperature." This intuitive path from a single component ideal gas to a multi-component ideal gas mixture has been a standard feature of the presentation of the chemical potential for many, many decades. One of the most recent treatments of this problem is by Kondepudi (2008, Eq. 5.3.6) where one finds the single-component form given by

$$\mu\,(p,T) \;=\; \mu\,(p_{\mathrm{o}},T) \;+\; RT\ln\left(p/p_{\mathrm{o}}\right), \qquad T \;=\; \text{constant} \tag{5}$$

On the basis of this result Kondepudi (2008, Eq. 6.1.9) presents the multi-component form *by analogy* in order to obtain

$$\mu_k\,(p,T,x_k) \;=\; \mu_k^{\mathrm{o}}\,(p,T) \;+\; RT\ln x_k \;, \qquad T \;=\; \text{constant}\,, \qquad k \;=\; 1,2,3\ldots \tag{6}$$

Here we see that the intuitive development of Lewis & Randall (1923) has served as the basis for Kondepudi's (2008) treatment more than eighty years later. The most clearly stated justification for the creation of Eq. 6 on the basis of Eq. 5 is given by Prigogine & Defay (1954, page 124) that we repeat here as:

> "We say that a mixture of gases in volume V at temperature T, is perfect if the free energy F is equal to the sum of the free energies which the separate constituents would have if each were confined alone in the same volume at the same temperature."

Given this hypothesis, Prigogine & Defay (1954, Eq. 10.35) produced Eq. 6 on the basis of a result analogous to Eq. 5 (Prigogine & Defay, 1954, Eq. 10.11). The intuitive path from Eq. 5 to Eq. 6 has been followed by many authors, and in this work we provide a derivation of Eq. 6 for ideal gas mixtures along with the result for the chemical potential of ideal liquid solutions.

2. Gibbs-Duhem Equation

On the basis of Postulate I of Callen (1985, Eq. 2.1) for an $N-$component system we write

$$U = U\big(S, V, n_A, n_B, ..., n_N\big) \tag{7}$$

in which U is the internal energy of a macroscopic system, S and V are the entropy and volume of that system, and $n_A, n_B, ..., n_N$ represent the number of moles of the molecular species. We begin with Callen's definitions

$$\big(\partial U/\partial S\big)_{V,\,n_A....n_N} = T\,, \quad \text{the temperature} \tag{8a}$$

$$\big(\partial U/\partial V\big)_{S,\,n_A....n_N} = -\,p, \quad \text{the pressure} \tag{8b}$$

$$\big(\partial U/\partial n_A\big)_{S,V,\,n_B...n_N} = \mu_A\,, \quad \text{the chemical potential} \tag{8c}$$

in order to obtain the result given here as (Callen, 1985, Eq. 2.6)

$$dU = TdS - pdV + \sum_{A=1}^{A=N} \mu_A\, dn_A \tag{9}$$

At this point we recall the *Euler form* (Callen, 1985, pages 59 and 147) which is given by

$$U = TS - pV + \sum_{A=1}^{A=N} \mu_A\, n_A \tag{10}$$

and differentiation of this form leads to

$$\begin{aligned} dU &= TdS + SdT - pdV - Vdp \\ &\quad + \sum_{A=1}^{A=N} \mu_A\, dn_A + \sum_{A=1}^{A=N} n_A\, d\mu_A \end{aligned} \tag{11}$$

Subtracting Eq. 9 from Eq. 11 provides the Gibbs-Duhem equation

$$0 = SdT - Vdp + \sum_{A=1}^{A=N} n_A\, d\mu_A \tag{12}$$

in which we encounter a *single equation* containing N unknown values of the chemical potential. Derivations of this result are given by numerous authors [Prigogine & Defay (1954, Eq. 6.38); Denbigh

(1961, Eq. 2.83); Callen (1985, Eq. 3.14); Kuiken, 1994, Eq. 4.9); Kondepudi (2008, Eq. 5.2.4)]; however, not all authors proceed directly to the more useful form of this result given by Callen (1985) and presented in the following paragraph.

At this point we return to the Euler form given by Eq. 10 and rearrange that result as

$$S \;=\; U\big(1/T\big) + V\big(p/T\big) - \sum_{A=1}^{A=N}\big(\mu_A/T\big)n_A \tag{13}$$

From this we obtain

$$\begin{aligned} dS \;=\; & dU\big(1/T\big) + dV\big(p/T\big) - \sum_{A=1}^{A=N}\big(\mu_A/T\big)\,dn_A \\ & + U\,d\big(1/T\big) + V\,d\big(p/T\big) - \sum_{A=1}^{A=N} n_A\,d\big(\mu_A/T\big) \end{aligned} \tag{14}$$

and multiplication by the temperature leads to

$$\begin{aligned} TdS - dU - pdV + \sum_{A=1}^{A=N}\mu_A\,dn_A \;=\; & \\ T\left[U\,d\big(1/T\big) + V\,d\big(p/T\big) - \sum_{A=1}^{A=N} n_A\,d\big(\mu_A/T\big)\right] & \end{aligned} \tag{15}$$

Use of Eq. 9 with this result provides an alternate form of the Gibbs-Duhem equation given by (Callen, 1985, Eq. 3.18)

$$U\,d\big(1/T\big) + V\,d\big(p/T\big) - \sum_{A=1}^{A=N} n_A\,d\big(\mu_A/T\big) \;=\; 0 \tag{16}$$

This form allows us to work with the energy, U, instead of the entropy, S, that appears in Eq. 12. A key characteristic of this result is that it represents *one equation* containing N unknown values of the chemical potential.

3. Single Component Ideal Gas

Here we follow many authors and explore the case of a *single-component ideal gas* for which Eq. 16 simplifies to

$$U\,d\big(1/T\big) + V\,d\big(p/T\big) - n\,d\big(\mu/T\big) \;=\; 0 \tag{17}$$

For a single-component system we express the *ideal gas law* in the form

$$pV = nRT \tag{18}$$

and we make use of Callen's (1985, Eq. 3.26) representation for the energy of an *ideal gas* given by

$$U = \xi\, n\, RT \tag{19}$$

Callen notes that $\xi = 3/2$ for monatomic ideal gases and goes on to comment that for diatomic molecules such as O_2 or NO there tends to be a considerable region of temperature for which $\xi \; ; \; 5/2$. The value of $\xi = 3/2$ is consistent with the kinetic theory development given by Jeans (1916, Chapter VI). Both Eq. 18 and Eq. 19 represent crucial simplifications for ideal gases that *are not applicable to liquid solutions*. We can use Eq. 19 to express the first term in Eq. 16 as

$$U\, d\big(1/T\big) = \xi\, n\, RTd\big(1/T\big) = -\,\xi\, n\, R\big(dT/T\big) \tag{20}$$

while Eq. 18 can be used to express the second term in the form

$$V\, d\big(p/T\big) = nR\big(dp/p\big) - nR\big(dT/T\big) \tag{21}$$

Given these two results we can represent Eq. 17 as

$$-\big(\xi + 1\big)\frac{dT}{T} + \frac{dp}{p} - d\big(\mu/RT\big) = 0 \tag{22}$$

This form of the Gibbs-Duhem equation for a single-component ideal gas can be integrated [Prigogine & Defay (1954, Eq. 10.12); Callen (1985, Eq. 3.33); Kuiken (1994, Eq. 6.82); Kondepudi (2008, Eq. 5.3.6)] in order to obtain the chemical potential given by

$$\mu(T,p) = \Big[\big(T/T_o\big)\mu_o(T_o,p_o) - \big(\xi+1\big)RT\ln\big(T/T_o\big)\Big] + RT\ln\big(p/p_o\big) \tag{23}$$

The next step in the traditional path forward is to *infer by intuition* the multi-component form of Eq. 23 as indicated in the work of Prigogine & Defay (1954, Eq. 10.26), Callen (1985, Eq. 13.8), Kuiken (1994, Eq. 6.83), and Kondepudi (2008, Eq. 6.1.9). The apparent need for *intuition* to arrive at the multi-component form results from the fact that Eq. 16 represents a *single equation* containing N unknown values of the chemical potential. We address this problem in the next section.

4. Ideal Gas Mixtures

For ideal gas mixtures we will apply *Dalton's Laws* given by

$$p_A V = n_A RT\,, \quad A = 1, 2, \dots, N \tag{24a}$$

$$p = \sum_{A=1}^{A=N} p_A \tag{24b}$$

$$p_A = x_A\, p\,, \qquad A = 1, 2, \dots, N \tag{24c}$$

and we will make use of the constraint on the mole fractions given by

$$\sum_{A=1}^{A=N} x_A = 1 \tag{25}$$

In addition to these relations for ideal gas mixtures, we will make use of Callen's (1985, Eq. 3.39) representation for the energy that takes the form

$$U = \sum_{A=1}^{A=N} \xi_A \, n_A \, RT \tag{26}$$

Use of this expression for the energy in Eq. 16 leads to

$$\sum_{A=1}^{A=N} \xi_A \, n_A \, RT \, d(1/T) + V \, d(p/T) - \sum_{A=1}^{A=N} n_A \, d(\mu_A/T) = 0 \tag{27}$$

and it is convenient to divide this result by nR and arrange the result in the form

$$\frac{V}{nR} d(p/T) - \sum_{A=1}^{A=N} x_A \left[\xi_A (dT/T) + d(\mu_A/RT) \right] = 0 \tag{28}$$

In order to derive a useful result from this form of the Gibbs-Duhem equation, we represent the first term as

$$\frac{V}{nR} d(p/T) = \frac{d(nR/V)}{(nR/V)} \tag{29}$$

Our treatment of the right hand side of Eq. 29 is based on the following simple theorem

Theorem:

$$\frac{d\Omega}{\Omega} = \sum_{A=1}^{A=N} x_A \frac{d\Omega_A}{\Omega_A} \tag{30}$$

in which

$$\Omega_A = x_A \Omega, \qquad A = 1, 2, \ldots, N \tag{31}$$

To prove this theorem, we begin with the Eq. 25 and use that constraint on the mole fractions to obtain

$$\frac{d\Omega}{\Omega} = \frac{d\Omega}{\Omega} \times (1) = \frac{d\Omega}{\Omega} \sum_{A=1}^{A=N} x_A = \sum_{A=1}^{A=N} \left[x_A \left(\frac{d\Omega}{\Omega} \right) \right] \tag{32}$$

This result can also be expressed as

$$\frac{d\Omega}{\Omega} = \sum_{A=1}^{A=N} \left[x_A \frac{(x_A\, d\Omega)}{(x_A\, \Omega)} \right] = \sum_{A=1}^{A=N} \left\{ \frac{x_A}{x_A\, \Omega} \left[d(x_A \Omega) - \Omega\, d x_A \right] \right\} \tag{33}$$

and the sums can be separated leading to

$$\frac{d\Omega}{\Omega} = \sum_{A=1}^{A=N} \left\{ \frac{x_A}{x_A\, \Omega} \left[d(x_A \Omega) \right] \right\} - \sum_{A=1}^{A=N} \left\{ \frac{x_A}{x_A\, \Omega} \left[\Omega\, d x_A \right] \right\} \tag{34}$$

The second term on the right hand side is zero according to

$$\sum_{A=1}^{A=N} \left\{ \frac{x_A}{x_A\, \Omega} \left[\Omega\, d x_A \right] \right\} = \sum_{A=1}^{A=N} \left\{ d x_A \right\} = 0 \tag{35}$$

and this leads to the result given by

$$\frac{d\Omega}{\Omega} = \sum_{A=1}^{A=N} \left\{ x_A \left[\frac{d(x_A \Omega)}{(x_A\, \Omega)} \right] \right\} \tag{36}$$

Application of Eq. 31 provides the desired proof.

Proof:

$$\frac{d\Omega}{\Omega} = \sum_{A=1}^{A=N} x_A \frac{d\Omega_A}{\Omega_A} \tag{37}$$

To apply this theorem to Eq. 29 we use $\Omega = nR/V$ to obtain

$$\frac{V}{nR}\, d(p/T) = \frac{d(nR/V)}{(nR/V)} = \sum_{A=1}^{A=N} x_A \frac{d(n_A R/V)}{(n_A R/V)} \tag{38}$$

At this point we make use of Eq. 24a which provides

$$n_A R/V = p_A/T\,, \quad A = 1, 2, \ldots, N \tag{39}$$

and substitution of this expression in Eq. 38 leads to

$$\frac{V}{nR}\, d(p/T) = \sum_{A=1}^{A=N} x_A \frac{d(n_A R/V)}{(n_A R/V)} = \sum_{A=1}^{A=N} x_A \left[\frac{dp_A}{p_A} - \frac{dT}{T} \right] \tag{40}$$

Use of this result in Eq. 28 provides the following form of the Gibbs-Duhem equation:

$$\sum_{A=1}^{A=N} x_A \big[dp_A/p_A \; - \; (\xi_A + 1) dT/T \; - \; d(\mu_A/RT) \big] \; = \; 0 \tag{41}$$

If each of the N terms in the brackets are *constants*, one can easily prove that those constants are zero leading to

$$d\,p_A/p_A \; - \; (\xi_A + 1) dT/T \; - \; d(\mu_A/RT) \; = \; 0 \; , \qquad A = 1, 2, \ldots, N \tag{42}$$

This represents *one solution* to Eq. 41; however, at this point in time the author cannot prove that Eqs. 42 represents a *unique solution* to Eq. 41. Without a proof of uniqueness, we proceed on the basis that Eqs. 42 represent one solution that can be integrated from *some reference state* indicated by a subscript zero to obtain

$$\begin{aligned} \mu_A(T, p_A) \; &= \; (T/T_\text{o}) [\mu_{A\text{o}}(T_\text{o}, p_{A\text{o}})] \\ &- (\xi_A + 1) RT \ln(T/T_\text{o}) \; + \; RT \ln(p_A/p_{A\text{o}}) \; , \qquad A = 1, 2, \ldots, N \end{aligned} \tag{43}$$

Use of Eq. 24c provides

$$\frac{p_A}{p_{A\text{o}}} \; = \; \frac{p}{p_{A\text{o}}} x_A \tag{44}$$

and this allows us to arrange Eq. 43 in the form

$$\begin{aligned} \mu_A(T, p_A) \; &= \; [\mu_{A\text{o}}(T_\text{o}, p_{A\text{o}})] (T/T_\text{o}) \; - \; (\xi + 1) RT \ln(T/T_\text{o}) \\ &+ \; RT \ln(p/p_{A\text{o}}) \; + \; RT \ln x_A \; , \qquad A = 1, 2, \ldots, N \end{aligned} \tag{45}$$

If the reference state is identified as

$$\text{Reference State:} \qquad T \; = \; T_\text{o} \; , \qquad p_{A\text{o}} \; = \; p_\text{o} \; , \qquad x_A \; = \; 1.0 \tag{46}$$

we can express Eq. 45 in the form

$$\begin{aligned} \mu_A(T, p, x_A) \; &= \; [\mu_{A\text{o}}(T_\text{o}, p_\text{o})] (T/T_\text{o}) \; - \; (\xi + 1) RT \ln(T/T_\text{o}) \\ &+ \; RT \ln(p/p_\text{o}) \; + \; RT \ln x_A \; , \qquad A = 1, 2, \ldots, N \end{aligned} \tag{47}$$

Traditionally the details associated with p_o and T_o are ignored and this result is expressed as

$$\mu_A(T, p, x_A) \; = \; \mu_A^\text{o}(T, p) \; + \; RT \ln x_A \; , \qquad A = 1, 2, \ldots, N \tag{48}$$

This form is presented as an intuitive extension of Eq. 23 by numerous authors such as Prigogine & Defay (1954, Eq. 10.35), Denbigh (1962, page 113), Callen (1985, Eq. 13.8), Kuiken (1994, Eq. 6.85), and Kondepudi (2008, Eq. 6.1.9). Guggenheim (1959, Eqs. 5.12.1 and 5.12.2) derives a form analogous to Eq. 23 and then lists a form analogous to Eq. 48 indicating that the multi-component version results from *statistical mechanics*; however, no reference to the analysis is given. Prigogine & Defay (1954, page 319) present a *statistical analysis* indicating that a form of Eq. 48 also applies to dilute liquid solutions; however, if one removes the constraints imposed by Eqs. 24 and 26, the form given by Eq. 48 does not follow. In the next section we show that the chemical potential for liquid solutions is not given by Eq. 48 regardless of how small x_A might be.

5. Liquid Solutions

At this point we return to the general form of the Gibbs-Duhem equation given by Eq. 16. For liquid solutions this result is expressed as

$$U_{liq}\, d\left(1/T\right) + V_{liq}\, d\left(p_{liq}/T\right) - \sum_{A=1}^{A=N} (n_A)_{liq}\, d\left[(\mu_A)_{liq}/T\right] = 0 \tag{49}$$

in which it is understood that the temperature, T, is the temperature of the liquid solution. Here we remind the reader that Eqs. 24 and 26 are only valid for ideal gas mixtures, thus Eq. 48 is restricted to ideal gas mixtures. The situation for ideal liquid mixtures represents an entirely different case as we shall see in the following paragraphs. For liquid solutions we avoid Eq. 26 and express the internal energy of a mixture (Whitaker, 2012, Eq. 49) according to

$$U_{liq} = \sum_{A=1}^{A=N} (n_A)_{liq}\, (u_A)_{liq} \tag{50}$$

Since the internal energy of species A is only a weak function of the pressure, we represent $(u_A)_{liq}$ in the form

Assumption:
$$(u_A)_{liq} = (u_A)^{\text{o}}_{liq} + \left(\frac{\partial u_A}{\partial T}\right)_p \left(T - T_{\text{o}}\right) \tag{51}$$

This is an approximation that deserves to be explored in detail; however, the idea that the temperature dominates the value of the internal energy for liquids is quite reasonable. Use of Eqs. 50 and 51 allows us to express the first term in Eq. 49 as

$$U_{liq}\, d\left(1/T\right) = -\, n_{liq} \sum_{A=1}^{A=N} (x_A)_{liq} \left[(u^{\text{o}}_{\text{A}})_{liq}\, \frac{dT}{T^2} + \left(\frac{\partial u_A}{\partial T}\right)_p \left(T - T_{\text{o}}\right) \frac{dT}{T} \right] \tag{52}$$

Moving on to the second term in Eq. 49, we represent that term as

$$V_{liq}\, d\left(p_{liq}/T\right) = n_{liq}\left(V_{liq}/n_{liq}\right) d\left(p_{liq}/T\right) = n_{liq}\left(1/c_{liq}\right) d\left(p_{liq}/T\right) \tag{53}$$

and we impose a second assumption given by

Assumption:
$$c_{liq} = \left(n_{liq}/V_{liq}\right) = \text{constant} \tag{54}$$

Once again, this approximation deserves to be explored in detail; however, the total molar concentration of a liquid solution changes only slightly for very large changes in both temperature and pressure. Thus Eq. 54 represents a reasonable approximation. We now return to Eq. 53 and carry out the differentiation of p_{liq}/T to obtain

$$V_{liq}\, d\left(p_{liq}/T\right) \;=\; n_{liq}\left[\frac{1}{c_{liq}\,T}\, dp_{liq} \;-\; \left(p_{liq}/c_{liq}\right)\frac{dT}{T^2}\right] \tag{55}$$

At this point we represent the *total liquid pressure* in terms of the partial pressures according to (Whitaker, 2009, Appendix B)

$$p_{liq} \;=\; \sum_{A=1}^{A=N} (p_A)_{liq} \tag{56}$$

Here one must note that this representation for the pressure is for liquid solutions, and it does not represent an ideal gas condition as indicated by Eq. 24b. Use of this definition allows us to express Eq. 55 as

$$V_{liq}\, d\left(p_{liq}/T\right) \;=\; n_{liq}\sum_{A=1}^{A=N}\frac{d(p_A)_{liq}}{c_{liq}\,T} \;-\; n_{liq}\sum_{A=1}^{A=N}\frac{(p_A)_{liq}}{c_{liq}}\frac{dT}{T^2} \tag{57}$$

This result, along with Eq. 52, can be used in the Gibbs-Duhem equation given by Eq. 49 to obtain

$$\begin{aligned} &-\sum_{A=1}^{A=N}(x_A)_{liq}\left[(u_A^{\mathrm{o}})_{liq}\,\frac{dT}{T^2} \;+\; \left(\frac{\partial u_A}{\partial T}\right)_p \left(T - T_{\mathrm{o}}\right)\frac{dT}{T}\right] \\ &\sum_{A=1}^{A=N}\frac{d(p_A)_{liq}}{c_{liq}T} \;-\; \sum_{A=1}^{A=N}\frac{(p_A)_{liq}}{c_{liq}}\frac{dT}{T^2} \;-\; \sum_{A=1}^{A=N}(x_A)_{liq}\, d\left[(\mu_A)_{liq}/T\right] \;=\; 0 \end{aligned} \tag{58}$$

At this point the route forward appears to be *very complex* and not at all comparable to the simple analysis that led to Eq. 42 for ideal gas mixtures. However, there is one special case associated with Eq. 58 that has some practical applications, and that is the case in which the temperature and the total pressure are treated as constants. If we impose this simplification as indicated by

Assumption: T is constant (59a)

Assumption: p_{liq} is constant (59b)

the Gibbs-Duhem equation given by Eq. 58 takes the form

$$\sum_{A=1}^{A=N}\frac{d(p_A)_{liq}}{c_{liq}} \;-\; \sum_{A=1}^{A=N}(x_A)_{liq}\, d(\mu_A)_{liq} \;=\; 0 \tag{60}$$

The partial pressure of species A is constrained by

$$0 \leq (p_A)_{liq} \leq p_{liq} \ , \qquad A = 1, 2, \dots, N \tag{61}$$

and a reasonable approximation for the partial pressure (often referred to as an *ideal liquid solution*) is given by

Assumption:
$$(p_A)_{liq} = (x_A)_{liq} \, p_{liq} \ , \qquad A = 1, 2, \dots, N \tag{62}$$

Use of this result in Eq. 60 along with the constraint given by Eq. 59b leads to

$$\sum_{A=1}^{A=N} \frac{p_{liq} \, d(x_A)_{liq}}{c_{liq}} - \sum_{A=1}^{A=N} (x_A)_{liq} \, d(\mu_A)_{liq} = 0 \tag{63}$$

and this can be arranged in the same form as Eq. 41 to obtain

$$\sum_{A=1}^{A=N} (x_A)_{liq} \left[\frac{p_{liq} \, d(x_A)_{liq}}{c_{liq} (x_A)_{liq}} - d(\mu_A)_{liq} \right] = 0 \tag{64}$$

Here we are confronted with the same problem we encountered with Eqs. 41 and 42, and following the same procedure we use Eq. 64 to obtain *one solution* given by

$$\frac{d(x_A)_{liq}}{(x_A)_{liq}} = \frac{c_{liq}}{p_{liq}} d(\mu_A)_{liq} \ , \qquad A = 1, 2, \dots, N \tag{65}$$

This equation can be integrated from *some reference state* indicated by a superscript zero to obtain

$$(\mu_A)_{liq} = (\mu_A^{\text{o}})_{liq} + \left(p_{liq} / c_{liq} \right) \ln \left[\frac{(x_A)_{liq}}{(x_A^{\text{o}})_{liq}} \right] , \qquad A = 1, 2, \dots, N \tag{66}$$

If the reference state is chosen to be pure species A we have $(x_A^{\text{o}})_{liq} = 1$ and the chemical potential for species A takes the form

$$\left[\mu_A(T, p, x_A) \right]_{liq} = \left[\mu_A^{\text{o}}(T, p) \right]_{liq} + \left(p_{liq} / c_{liq} \right) \ln (x_A)_{liq} \ , \qquad A = 1, 2, \dots, N \tag{67}$$

This looks similar to the general result for *ideal gas mixtures* given by Eq. 48 and to enhance the comparison we express Eq. 67 in the form

$$\mu_A(T, p, x_A) = \mu_A^{\text{o}}(T, p) + \zeta \, RT \ln x_A \, , \qquad A = 1, 2, \dots, N \, , \qquad \text{constant } T \text{ and } p_{liq} \tag{68}$$

in which the parameter ζ is given by

$$\zeta = \frac{p_{liq}}{c_{liq} \, RT} \tag{69}$$

If the parameter ζ were one (and it is not), we would conclude that the chemical potential for *an ideal liquid solution* would be identical to the chemical potential for an *ideal gas mixture*. However, if we consider an *aqueous solution* at one atmosphere, the calculation of ζ for an *ideal liquid solution* is given by

$$\zeta = \frac{p_{liq}}{c_{liq} RT} = \frac{MW \; p_{liq}}{\rho_{liq} RT}$$

$$= \frac{(18\,\mathrm{g/mol})(1\,\mathrm{atm})}{\left(1\,\mathrm{g/cm^3}\right)\left(82\,\mathrm{atm\,cm^3/mol\,K}\right)(300\mathrm{K})} \approx \frac{1}{1200}\,, \quad \text{ideal liquid solution} \tag{70}$$

From this result it is clear that Eq. 68 for *ideal liquid solutions* represents a dramatically different result than Eq. 48 for *ideal gas mixtures*. This conclusion is quite different than the conclusion reached by Prigogine & Defay (1954, Eq. 20.41) who indicated that all sufficiently dilute liquid solutions have chemical potentials of the form given by Eq. 48.

6. Conclusions

In this work we have examined the Gibbs-Duhem equation for multi-component systems with the objective of developing a representation for the chemical potential. For *ideal gas mixtures* we have derived a result that many have assumed to be true in order to arrive at Eq. 48. For *ideal liquid solutions* the Gibbs-Duhem equation becomes very complex; however, a useful result can be obtained for the case in which variations of the *temperature* and the *total pressure* can be ignored. This leads to a result for the chemical potential indicating that ideal liquid solutions are very different than ideal gas mixtures. While we know that Eq. 42 and Eq. 65 represent solutions to special forms of the Gibbs-Duhem equation, we have not proved that these solutions are unique.

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Nomenclature

c_{liq}	n_{liq}/V_{liq}, total molar concentration, mol/m^3
N	total number of molecular species
n_A	number of moles of species A
n	total number of moles
p	total pressure, N/m^2
p_o	total pressure at the initial state, N/m^2
p_A	partial pressure of species A, N/m^2
R	gas constant, 82.06 atm-cm^3/mol K
$\mathcal{S}$	total entropy, kcal/K
T	temperature, K
T_o	reference temperature, K

U	total internal energy, kcal
$u = U/n$	internal energy per mole, kcal/mol
u_A	species A internal energy per mole, kcal/mol
V	total volume, m^3
x_A	mole fraction of species A

Greek Letters

μ	chemical potential for a single component system, kcal/mol
μ_A	chemical potential of species A, kcal/mol
μ_A^{o}	reference chemical potential of species A, kcal/mol
ξ	coefficient in the representation for the energy of an ideal gas
ξ_A	coefficient in the representation for the energy of species A in an ideal gas mixture

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