

ЦРНОГОРСКА АКАДЕМИЈА НАУКА И УМЈЕТНОСТИ
ГЛАСНИК ОДЈЕЉЕЊА ПРИРОДНИХ НАУКА, 18, 2009.

ЧЕРНОГОРСКАЯ АКАДЕМИЯ НАУК И ИСКУССТВ
ГЛАСНИК ОТДЕЛЕНИЯ ЕСТЕСТВЕННЫХ НАУК, 18, 2009

THE MONTENEGRIN ACADEMY OF SCIENCES AND ARTS
GLASNIK OF THE SECTION OF NATURAL SCIENCES, 18, 2009.

UDK 539.319

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ON THE GIBBS ENERGY AND CHEMICAL POTENTIALS OF AN IDEAL GAS MIXTURE

A b s t r a c t

There are three, essentially independent, derivations of the Gibbs energy of an ideal gas mixture and the chemical potentials of its components. One approach is to first derive the expressions for the chemical potentials (μ_i), which are then used in the expression for the molar Gibbs energy $G^m = \sum X_i \mu_i$, where X_i is the molar concentration of the i -th component in the mixture. In this approach, the molar entropy of the mixture is evaluated *a posteriori*, as the temperature gradient of the Gibbs energy. The second derivation is the simplest, and is based on the assumed additive decomposition of the Gibbs energy in terms of the partial Gibbs energies of individual components. The third derivation is based on the additive decomposition of the entropy of mixture in terms of partial entropies of its components. The three derivations are here critically examined and discussed.

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O GIBSOVOJ ENERGIJI I HEMIJSKIM POTENCIJALIMA MJEŠAVINE IDEALNIH GASOVA

I z v o d

U radu je ukazano na tri međusobno nezavisna izvodjenja izraza za Gibsovu energiju i hemijske potencijale mješavine idealnih gasova, što je od značaja za termodinamičku analizu modela rastvora i legura. U prvom pristupu, izrazi za hemijske potencijale (μ_i) se izvedu prvo, nakon čega molarna Gibsova energija slijedi iz izraza $G^m = \sum X_i \mu_i$, gdje X_i predstavlja molarnu koncentraciju i -te komponente. Molarna entropija slijedi *a posteriori*, kao temperaturni gradijent Gibsove energije. Drugi pristup analizi je najjednostavniji, ali je baziran na dodatnoj pretpostavci o aditivnoj dekompoziciji same Gibsove energije. Treći pristup počiva na pretpostavci o aditivnoj dekompoziciji entropije mješavine u parcijalne entropije njenih komponenti. Tri opisana pristupa analizi su kritički upoređena i diskutovana.

1. INTRODUCTION

The derivation of the expressions for the Gibbs energy of an ideal gas mixture and the chemical potentials of its components is a classical topic, addressed in standard textbooks of thermodynamics (*e.g.*, Callen, 1960; Dickerson, 1969; Swalin, 1972; Denbigh, 1981; Carter, 2001). However, different authors use different approaches to derive these expressions, and their relationship may not be immediately clear. It seems therefore desirable, from the conceptual point of view, to review the topic. We present in this paper three independent derivations. The first derivation is based on the equation of state and the integration of the Maxwell's reciprocity relation between the gradients of volume and chemical potentials. The other two derivations are based on an additive decomposition of the Gibbs energy, or the entropy of the mixture, in terms of the corresponding partial properties of the mixture components. The first derivation requires the least

assumptions, the second is the simplest, and the third can be most easily interpreted from the physical point of view.

In the thermodynamics of open systems, an increment of Gibbs energy associated with the changes in pressure and temperature (dp and dT), and the change in composition (dn_i), is

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i. \quad (1.1)$$

The entropy of the system is S , the volume is V , and $\mu_i = \mu_i(p, T, n_{\text{all}})$ is the chemical potential of the i -th component in the mixture. Since G is a homogeneous function of degree one in n_i , one can write

$$G = \sum_i n_i \mu_i. \quad (1.2)$$

If $n_i = n$ ($n_{j \neq i} = 0$), μ_i can be interpreted as the molar Gibbs energy of the component i in its pure state ($\mu_i = G_i^{\text{m}}$). Furthermore, G being a thermodynamic state function, the right-hand side of (1.2) must be a total differential, so that

$$S = - \left(\frac{\partial G}{\partial T} \right)_{p, n_{\text{all}}}, \quad V = \left(\frac{\partial G}{\partial p} \right)_{T, n_{\text{all}}}, \quad \mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{p, T, n_{j \neq i}}. \quad (1.3)$$

One of the corresponding Maxwell relations, relevant for the derivation presented in Section 2, is

$$\left(\frac{\partial \mu_i}{\partial p} \right)_{T, n_{\text{all}}} = \left(\frac{\partial V}{\partial n_i} \right)_{p, T, n_{j \neq i}}. \quad (1.4)$$

Finally, the Clausius–Duhem equation reads

$$SdT - Vdp + \sum_i n_i d\mu_i = 0, \quad (1.5)$$

so that the sum of (1.1) and (1.5) stays in accord with the incremental version of (1.2). The relations (1.1)–(1.5) are of the fundamental importance in many thermodynamic studies, such as in the analysis of the solution models and chemical reactions (*e.g.*, Lupis, 1983; DeHoff, 1993; Gaskell, 2003; Asaro and Lubarda, 2006).

2. THE DERIVATION FROM μ TO G AND S

Consider an isolated closed system that consists of I chambers separated by diathermal rigid walls. The i -th chamber, having the volume V_i , contains n_i moles of an ideal gas whose (molar) specific heat is C_V^i ($i = 1, 2, \dots, I$). The pressure and temperature in all chambers are equal to p and T , respectively, so that

$$pV_i = n_iRT, \quad (2.1)$$

where R is the universal gas constant. If summed over i , (2.1) gives

$$pV = nRT, \quad V = \sum_i V_i, \quad n = \sum_i n_i. \quad (2.2)$$

The internal energy in the whole system is the sum of the internal energies in all chambers,

$$U = \sum_i n_i C_V^i T. \quad (2.3)$$

If the walls between the chambers are removed, the diffusive mixing of gases takes place. Since the entire system is closed and isolated, the internal energy can not change, and the temperature of the equilibrated mixture state is the same as the initial temperature T . The corresponding pressure is p is given by (2.2). When this is rewritten as

$$V = \frac{RT}{p} \sum_i n_i, \quad (2.4)$$

it follows that

$$\left(\frac{\partial V}{\partial n_i} \right)_{p, T, n_{j \neq k}} = \frac{RT}{p}. \quad (2.5)$$

The substitution of (2.5) into (1.4), and integration (see, for example, DeHoff, 1995) gives

$$\mu_i = \int_p^{p_i} \frac{RT}{p} dp + G_i^m(p, T), \quad (2.6)$$

where p_i is the partial pressure of the i -th component in the mixture, defined by $p_i V = n_i R T$. The molar Gibbs energy of the component i in its pure state, at pressure p and temperature T , is denoted by $G_i^m(p, T)$. By comparing $p_i V = n_i R T$ and $p V = n R T$, we deduce that $p_i = X_i p$, with $X_i = n_i/n$ standing for the molar fraction of the i -th component in the mixture. Consequently, (2.6) becomes

$$\mu_i = RT \ln X_i + G_i^m(p, T), \quad (2.7)$$

which is a desired expressions for the chemical potential.

The molar Gibbs energy of the component i in its pure state, appearing on the right-hand side of (2.7), can be evaluated from

$$G_i^m(p, T) = [C_p^i - S_i^m(p, T)]T, \quad (2.8)$$

because the molar enthalpy of an ideal gas is $H_i^m = C_p^i T$ and $G_i^m = H_i^m - T S_i^m$. The molar entropy of the pure component i is given by the classical expression

$$S_i^m(p, T) = C_p^i \ln \frac{T}{T_0} - R \ln \frac{p}{p_0} + S_i^m(p_0, T_0). \quad (2.9)$$

The reference pressure and temperature are denoted by p_0 and T_0 . Equation (2.9) is easily obtained by integrating $dS_i^m = C_p^i dT/T - R dp/p$, which follows from the energy equation $dU_i^m = -p dV^m + T dS_i^m$ by incorporating $pV^m = RT$ and $U_i^m = C_V^i T$.

Having derived the expressions for the chemical potentials of the components, given by (2.7), the Gibbs energy of the mixture is obtained from (1.2), or its molar counterpart

$$G^m = \sum_i X_i \mu_i. \quad (2.10)$$

The result is

$$G^m = RT \sum_i X_i \ln X_i + \sum_i X_i G_i^m(p, T). \quad (2.11)$$

The first part in the expression on the right-hand side is the mixing contribution to the Gibbs energy. The molar entropy of the mixture is

$$S^m = - \left(\frac{\partial G^m}{\partial T} \right)_{p, X_{\text{all}}} = - \sum_i X_i \left(\frac{\partial \mu_i}{\partial T} \right)_{p, X_{\text{all}}}, \quad (2.12)$$

which gives

$$S^m = -R \sum_i X_i \ln X_i + \sum_i X_i S_i^m(p, T). \quad (2.13)$$

3. THE DERIVATION FROM G TO μ AND S

An independent derivation of the results from the previous section, in the direction from G to μ and S , is as follows. Since the components of an ideal gas mixture do not interact, the Gibbs energy of the mixture can be calculated as the sum of the Gibbs energies of all components in their independent transitions from the state (p, T) to (p_i, T) (*e.g.*, Müller, 1985; Carter, 2001). Thus,

$$G = \sum_i G_i, \quad G_i = n_i G_i^m. \quad (3.1)$$

The increment of the molar Gibbs energy G_i^m is

$$dG_i^m = V_i^m dp_i = RT \frac{dp_i}{p_i}. \quad (3.2)$$

This follows from the basic expression for the change of the Gibbs energy of a pure substance ($dG = Vdp - SdT$), because $dT = 0$ and $p_i V_i^m = RT$. Upon the integration of (3.2) from the initial pressure p to the partial pressure $p_i = X_i p$, one obtains

$$G_i^m = RT \ln X_i + G_i^m(p, T). \quad (3.3)$$

This is also the chemical potential of the i -th component, because the molar version of (3.1) is

$$G^m = \sum_i X_i G_i^m \equiv \sum_i X_i \mu_i. \quad (3.4)$$

The molar entropy is the negative temperature gradient of the above expression, which reproduces (2.13).

4. THE DERIVATION FROM S TO G AND μ

The third derivation, independent of the previous two, proceeds from the derivation of the entropy expression. First, by Dalton's law the total pressure in an ideal gas mixture is the sum of partial pressures of its components, *i.e.*, $p = \sum p_i$, because $p_i = X_i p$ and $\sum X_i = 1$. Since the components in an ideal gas mixture do not interact, one can introduce the partial entropies (S_i) of the components, such that the total entropy of the mixture is additively decomposed (*e.g.*, Landau and Lifshitz, 1980; Ragone, 1995) as

$$S = \sum_i S_i. \quad (4.1)$$

The partial entropy $S_i = n_i S_i^m$ can be easily evaluated as the entropy of the pure component i at the partial pressure p_i and temperature T . Since the reference state is (p, T) (*i.e.*, $pV_i = p_i V = n_i RT$), and since $dU_i^m = 0$ for an isothermal path, the energy equation gives

$$T dS_i^m = p_i dV_i^m. \quad (4.2)$$

Furthermore, recalling that $p_i dV_i^m = -V_i^m dp_i$ for an isothermal change of state of an ideal gas, (4.2) can be rewritten as

$$dS_i^m = -R \frac{dp_i}{p_i}. \quad (4.3)$$

Upon integration from p to p_i , this yields

$$S_i^m = -R \ln \frac{p_i}{p} + S_i^m(p, T). \quad (4.4)$$

Thus, in view of $p_i = X_i p$, the partial entropies can be expressed as

$$S_i = n_i [-R \ln X_i + S_i^m(p, T)]. \quad (4.5)$$

The substitution of (4.5) into (4.1) gives

$$S = \sum_i n_i [-R \ln X_i + S_i^m(p, T)], \quad (4.6)$$

with its molar counterpart

$$S^m = \sum_i X_i [-R \ln X_i + S_i^m(p, T)], \quad (4.7)$$

which is in agreement with (2.13).

Having established the expression (4.7), the Gibbs energy of the mixture and the chemical potentials of its components follow immediately. Indeed, the molar Gibbs energy is

$$G^m = U^m + pV^m - TS^m, \quad (4.8)$$

where

$$U^m = \sum_i X_i C_V^i T, \quad pV^m = RT. \quad (4.9)$$

The substitution of (4.7) and (4.9) into (4.8) gives

$$G^m = \sum_i X_i [C_p^i + R \ln X_i - S_i^m(p, T)] T. \quad (4.10)$$

Note that the molar specific heats $\sum X_i C_V^i$ and $\sum X_i C_p^i$ can be interpreted as the average (effective) specific heats of the mixture, which is known in the context of solid or liquid compounds as Kopp's rule (Lupis, 1983). Observing that

$$[C_p^i - S_i^m(p, T)] T = G_i^m(p, T) \quad (4.11)$$

is the Gibbs energy of the pure component i at the pressure p and temperature T , (4.10) can be rewritten as

$$G^m = \sum_i X_i [RT \ln X_i + G_i^m(p, T)]. \quad (4.12)$$

Finally, since $G^m = \sum X_i \mu_i$, one identifies from (4.12) the expression for the chemical potential of the i -th component,

$$\mu_i = RT \ln X_i + G_i^m(p, T), \quad (4.13)$$

which parallels (2.7) or (3.3).

5. DISCUSSION

The first presented derivation of the expression for the molar Gibbs energy of an ideal gas mixture was based on the derivation of the expressions for the chemical potentials of its components. This was accomplished by using the equation of state and the integration of the Maxwell relation between the gradients of the volume and chemical potentials. The molar entropy of the mixture is evaluated *a posteriori*, as the negative temperature gradient of the molar Gibbs energy. The second derivation is the simplest, but it involves an additional assumption, the additive decomposition of the Gibbs energy of the mixture into partial Gibbs energies of individual components. The chemical potentials are the corresponding molar Gibbs energies. The third, in essence opposite from the first, derivation starts from an expression for the entropy of the mixture, by assuming that it is given by the sum of partial entropies of individual components in their independent isothermal expansions. This then yields the expressions for both the Gibbs energy and the chemical potentials.

The selection of the most suitable of the presented three derivations is a matter of individual preference, although the third derivation, starting from the entropy of mixing, may be most readily related to either continuum or statistical interpretations of the involved thermodynamic quantities. For example, if there are N^∞ available and uniformly distributed sites for the molecules within a volume V occupied by the mixture, the configurational entropy of all its molecules is

$$S = k \ln \Omega, \quad \Omega = \prod_{i=1}^I \binom{N^\infty - \sum_{j=0}^{i-1} N_j}{N_i}. \quad (5.1)$$

The number of molecules of each component is N_i ($i = 1, 2, \dots, I$), and $N_0 = 0$. On the other hand, the sum of individual configurational entropies of each gas, if it would occupy the volume V alone, is

$$S = k \ln \Omega, \quad \Omega = \prod_{i=1}^I \binom{N^\infty}{N_i}. \quad (5.2)$$

Assuming that $N^\infty \gg N_i$ for all i , the two expressions give the same configurational entropy, to the leading order terms. This may be viewed to be a statistical basis for the additive decomposition of entropy embedded in (4.1).

Acknowledgments

Research support from the Montenegrin Academy of Sciences and Arts is kindly acknowledged.

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