Short Report

Concentration dependencies of components' properties: Inter-dependent yet individual

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ABSTRACT

Despite being interrelated through the Gibbs–Duhem equation, concentration dependencies of components' chemical potentials and activities may demonstrate individuality, which is neither apparent nor intuitively anticipated. In particular, nothing is thermodynamically wrong with the activity of a component demonstrating numerous positive and negative deviations from ideality while the deviation for another component remains unsigned. Also, it is thermodynamically feasible that a plot of the chemical potential of a component *vs.* the mole fraction has multiple inflection points while such a plot for other component is free of undulations. Interestingly, if inflection points on these two functions exist, their abscissas do not coincide unless the second and third partial derivatives of the Gibbs energy are both equal to zero.

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1. Formulation of the problem

If formulae for $\mu_1^{ex}(x)$ and $\mu_2^{ex}(x)$ are suggested,[1] then the first step in evaluating their appropriateness will likely be checking whether the Gibbs–Duhem equation

$$(1 - x)\mathrm{d}\mu_1^{ex} + x\mathrm{d}\mu_2^{ex} = 0 \tag{1}$$

is satisfied for any x belonging to $[0, 1]$. For example, $\mu_1^{ex} = \omega x^3$ and $\mu_2^{ex} = \omega(1 - x)^3$ or $\mu_1^{ex} = \omega \sin(\pi x/2)$ and $\mu_2^{ex} = \omega \cos(\pi x/2)$ would be dismissed as thermodynamically impossible.

A compliance with the Gibbs–Duhem equation must also be tested if $\mu_1^{ex}(x)$ and $\mu_2^{ex}(x)$ are given as plots. One way of doing this is to integrate (1) by parts

$$\int_a^b (1 - x)\mathrm{d}\mu_1^{ex} = -\int_a^b x\mathrm{d}\mu_2^{ex}, \ 0 \leq a < b \leq 1$$

$$\left((1 - x)\mu_1^{ex} + x\mu_2^{ex}\right)\Big|_a^b = \int_a^b \left(\mu_2^{ex} - \mu_1^{ex}\right)\mathrm{d}x \tag{2}$$

If the plots are sensible, then regardless of what particular a and b are taken, Eq. (2) holds. If there exist such integration limits that it is not fulfilled,[2] then the plots are implausible.

An almost reflexive usage of the Gibbs–Duhem equation in such situations reflects our conviction that concentration dependencies of chemical potentials and activities are not independent. But what is an extent of their relationship? Is it possible that $a_1(x)$ demonstrates numerous positive and negative deviations from the ideal behavior while the deviation of $a_2(x)$ never changes sign? Can $\mu_1^{ex}(x)$ have multiple inflection points, but $\mu_2^{ex}(x)$ be free of them? In this work, it is endeavored to answer these non-pragmatic questions.

2. Deviations from Raoultian behavior

Let us consider a binary substitutional solution kept under constant temperature and pressure. Is it possible that $a_1(x)$ shows frequent positive and negative departures from the Raoultian behavior, but $a_2(x)$ has a deviation of one sign only? At a point where the sign of the deviation of a_i from ideality changes, $\mu_i^{ex} = 0$. Consequently, this question can be asked in terms of the excess Gibbs energy: is possible that the equation

$$\mu_1^{ex} = G^{ex} - x(\mathrm{d}G^{ex}/\mathrm{d}x) = 0 \tag{3}$$

has many roots within $(0, 1)$ while the equation

$$\mu_2^{ex} = G^{ex} + (1 - x)(\mathrm{d}G^{ex}/\mathrm{d}x) = 0 \tag{4}$$

has not even a single root inside this interval?

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[1] Refer to conventional signs on the next page.
[2] Accuracies of reading data from the plots (digitizing) and numerical integration should be considered.

Conventional signs

Symbol Meaning

a_i — Activity of component i
$d^i G / dx^i$ — $\left(\partial^i G / \partial x^i \right)_{T,P}$
$d^i G^{ex} / dx^i$ — $\left(\partial^i G^{ex} / \partial x^i \right)_{T,P}$

G — Molar Gibbs energy
G^{ex} — Excess molar Gibbs energy
μ_i — Chemical potential of component i
μ_i^{ex} — Excess chemical potential of component i
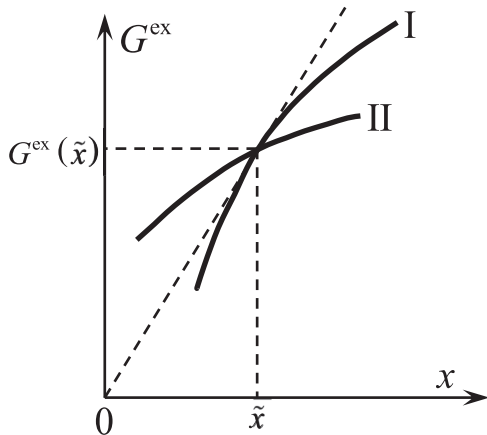x — Mole fraction of the 2nd component

Fig. 1. G^{ex} represented by curve I results in a change of sign of a deviation of a_1 from the Raoultian behavior at point $\tilde{x}$; in case II, a sign of this deviation does not change at $\tilde{x}$.

Let us proceed by finding a way to construct G^{ex} resulting in copious roots of (3). To attain this goal, let us rewrite this equation as

$$dG^{ex}/dx = G^{ex}/x \qquad (5)$$

Inspect Fig. 1 in which the points $(0, 0)$ and $(\tilde{x}, G^{ex}(\tilde{x}))$ are connected with a straight line. If the slope of this line is equal to the slope of G^{ex} at $\tilde{x}$, then $\mu_1^{ex}(x)$ changes its sign at this point. Fig. 2 exemplifies how to build a curly $G^{ex}(x)$ for which the equation $\mu_1^{ex}(x) = 0$ has a huge number of roots. It is clear from the geometrical construct in this figure, that it is always possible to pencil such G^{ex} that a number of roots would be equal to any prescribed number regardless of how big it is.

Although the requirement that Eq. (3) has many roots can be met, there is another constraint: the Eq. (4) should not have roots inside $(0, 1)$, because the deviation of $a_2(x)$ is not supposed to change its sign. Can this second condition be satisfied? To answer
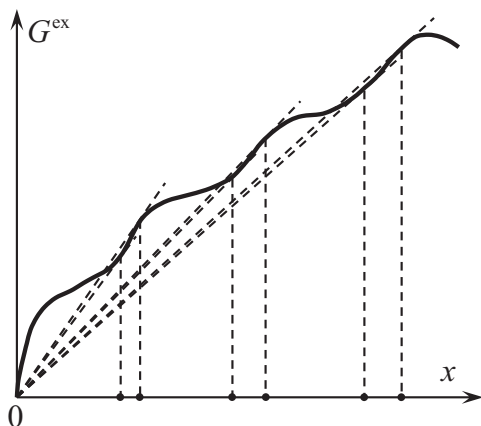

Fig. 2. A shape of G^{ex} yielding a change of sign of $a_1(x) - (1 - x)$ at six mole fractions marked with •. A number of such points can be unboundedly increased by making G^{ex} even more undulated.
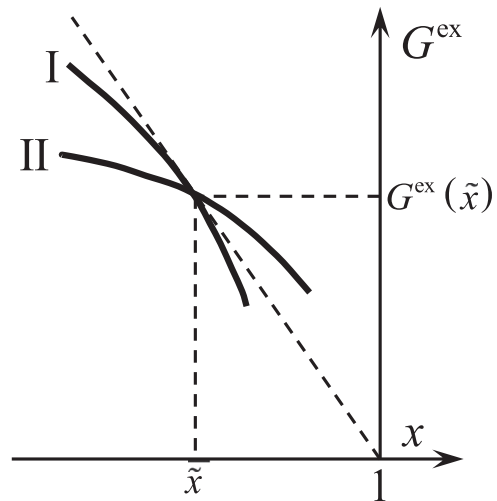

Fig. 3. G^{ex} represented by curve I leads to a change of sign of a deviation of a_2 from ideality at point $\tilde{x}$; in case II, a sign of this deviation remains the same at $\tilde{x}$.

this question, let us write Eq. (4) as

$$dG^{ex}/dx = - G^{ex}/(1 - x) \qquad (6)$$

Inspect Fig. 3 in which a straight line is drawn through the points $(\tilde{x}, G^{ex}(\tilde{x}))$ and $(1, 0)$. If the slope of this line is equal to the slope of G^{ex} at point $\tilde{x}$, then $\mu_2^{ex}(x)$ changes the sign at this point.

Examples of concentration dependencies of excess molar Gibbs energies resulting in $a_1(x)$ whose deviation from the ideal behavior experiences frequent changes of sign while the deviation for $a_2(x)$ remains unsigned are sketched in Fig. 4. To reveal a reason why it is always possible to construct such $G^{ex}(x)$ that the two slopes mentioned above would never be equal, let us notice from Eq. (6) that except a special case when $G^{ex} = dG^{ex}/dx = 0$, G^{ex} and dG^{ex}/dx must have opposite signs. In Fig. 4, a non-negative G^{ex} increases when the mole fraction runs from 0 to $\hat{x}$, and then decreases when x runs from $\hat{x}$ to 1. Clearly, $\mu_2^{ex}(x)$ cannot change its sign within $(0, \hat{x})$. But it cannot change the sign inside $(\hat{x}, 1)$ as well, because $G^{ex}(x)$ is **deliberately** sketched convex upward in this interval.

It is worth noticing that $G^{ex}(x)$ can alternatively be penciled as free of inflection points and convex upward within $(0, \hat{x})$, which
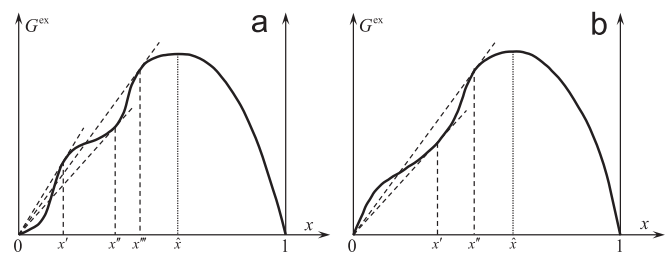

Fig. 4. Examples of G^{ex} resulting in (a) three mole fractions $x^`$, $x^{``}$ and $x^{```}$ at which a deviation of a_1 from ideality changes its sign, and (b) two mole fractions $x^`$ and $x^{``}$ at which a deviation of a_1 from ideality changes its sign. In both cases, $a_2(x) - x$ remains positive. Notice that $G^{ex}(x)$ is convex upward between $\hat{x}$ and 1.