



Common tangent plane in mixed-gas adsorption



Giulio Santori*, Mauro Luberti, Stefano Brandani

The University of Edinburgh, School of Engineering, Institute for Materials and Processes, Sanderson Building, The King's Buildings, Mayfield Road, EH9 3JL, Edinburgh, Scotland, UK

ARTICLE INFO

Article history:

Received 16 October 2014

Received in revised form 19 January 2015

Accepted 10 February 2015

Available online 11 February 2015

Keywords:

Gibbs energy of mixing

Adsorption thermodynamics

Common tangent plane

Double tangent plane

Azeotropy

Adsorbed solution theory

ABSTRACT

The minimisation of the distance function between the Gibbs energy of mixing and its common tangent plane (or line) is applied to adsorbed solutions. A specific algorithm to deal with the associated bilevel programming problem is presented and discussed. This approach is validated with experimental data and ideal adsorbed solution theory calculations for an ideal case and with experimental data for two non-ideal cases at low and high pressure. While the presently adopted non-ideal formulation provides solutions fulfilling only the necessary condition for equilibrium, the common tangent plane approach proposed in this paper enables the direct evaluation of the necessary and sufficient solution.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The adsorbed solution theory (AST) interprets gas-adsorbate equilibrium similarly to vapor–liquid equilibrium (VLE) [1]. The theory states the presence of two partially miscible phases such as a bulk gas phase and an adsorbed phase. There are no thermodynamic flaws in such an approach in the case of single component adsorption while, as discussed in [2], for the case of multi-component mixture adsorption, the iso-reduced-grand-potential condition is mandatory to make the theory thermodynamically consistent. Such an additional condition is necessary with respect to VLE results from the phase rule applied to adsorption equilibrium [3]. In the simplest case adsorption thermodynamics of multicomponent mixtures is assumed ideal with the bulk gas phase being an ideal gas and the adsorbed phase being an ideal solution. The ideal adsorption solution theory (IAST) is based on these assumptions [3], where the equilibrium is described by the pseudo Raoult's law:

$$P_{\text{bulk}} y_i = P_i^0 x_i \quad i = 1, 2, \dots, \text{NC} \quad (1)$$

with

$$\sum_i^{\text{NC}} x_i = 1 \quad (2)$$

where P_{bulk} is the pressure in the bulk gas phase, y_i is the mole fraction of component i in the bulk gas phase, x_i is the mole fraction of component i in the adsorbed phase, NC is the total number of components and P_i^0 is the surface pressure of the component i .

The iso-reduced-grand-potential condition states that each component in the adsorbed phase has the same reduced grand potential at equilibrium. This last condition is expressed for the ideal case as follows:

$$\psi_i = \int_0^{P_i^0} n_i d(\ln P_i) \quad i = 1, 2, \dots, \text{NC} \quad (3)$$

$$\psi_i = \text{const} \quad i = 1, 2, \dots, \text{NC} \quad (4)$$

where ψ_i (mol/kg) is the reduced grand potential of the component i and n_i is the absolute amount adsorbed for the pure component i (mol/kg), extensively described in [4,5].

By specifying the bulk gas pressure (P_{bulk}), the equilibrium temperature (T) and composition of the multicomponent gaseous mixture in the bulk phase (y_i), the composition of the multicomponent mixture in the adsorbed phase (x_i) can be calculated by

* Corresponding author. Tel.: +44 1316519043; fax: +44 1316506551.

E-mail address: g.santori@ed.ac.uk (G. Santori).

Nomenclature

f_i	Fugacity of component i [kPa]
f_i^0	Fugacity of pure component i at the system temperature and pressure [kPa]
g_{ex}	Excess Gibbs energy [kJ/mol]
$g_{mix,ads}$	Branch of the Gibbs energy of mixing function (adsorbed phase) [kJ/mol]
$g_{mix,gas}$	Branch of the Gibbs energy of mixing function (bulk gas phase) [kJ/mol]
Δg_{mix}	Molar Gibbs energy of mixing [kJ/mol]
NC	Number of components participating in the adsorption
n_i	Specific absolute amount adsorbed of component i [mol/kg]
n_{tot}	Specific amount of total adsorbed moles [mol/kg]
P	Pressure [kPa]
P	Pressure of the mixture in the bulk gas phase [kPa]
P_i^0	Surface pressure of the component i [kPa]
R	Universal gas constant [kJ/(mol K)]
T	Equilibrium temperature [K]
w_i	Molar fraction of the component i
x_i	Molar fraction of the component i in the adsorbed mixture
y_i	Molar fraction of the component i in the bulk gas mixture
Z	Compressibility factor

Greek letters

γ_i	Activity coefficient of component i
ϕ_i	Fugacity coefficient of component i
ϕ_i^0	Fugacity coefficient of the pure component i in the adsorbed phase at the system temperature and pressure. This is calculated using P_i^0
ψ	Reduced grand potential at equilibrium [mol/kg]
ψ_i	Reduced grand potential of component i [mol/kg]

solving the system of Eqs. (1)–(4). This interpretation is successful in several adsorption systems which can be assumed ideal.

For a more general case, activity coefficients and fugacity coefficients must be introduced in Eq. (1) to take into account non-ideal behavior in both phases. Thus Eqs. (1) and (3) become:

$$P_{bulk} y_i \phi_i = \phi_i^0 P_i^0 x_i \gamma_i \quad i = 1, 2, \dots, NC \quad (5)$$

$$\psi_i = \int_0^{f_i} n_i d(\ln f_i) \quad i = 1, 2, \dots, NC \quad (6)$$

where ϕ_i and γ_i are respectively the fugacity and activity coefficients of component i , ϕ_i^0 is the fugacity coefficient of pure component i in the adsorbed phase and $f_i = P_{bulk} y_i \phi_i$ is the fugacity of component i in the bulk gas phase.

Eqs. (5) and (6) need additional models for the evaluation of fugacity and activity coefficients. While the fugacity coefficients can be calculated using the extensive thermodynamic work on specific equations of state, the activity coefficients cannot be predicted from liquid state models because they do not include the interaction with the solid adsorbent, which is implicit in the definition of the reduced grand potential [5,6]. The non-ideal formulation of the AST through the system of Eqs. ((2), (4)–(6)), provides solutions fulfilling only the necessary condition for equilibrium. In general, multiple solutions exist for the above

system of equations and convergence to a specific solution depends on the choice of the initial guess. Despite this, strongly non-ideal adsorption systems are reported rarely in the open literature and the above formulation converges to the physically correct solution.

Rigorously, only the common tangent plane (or line) of the molar Gibbs energy of mixing (Δg_{mix}) or alternatively the global minimisation of Gibbs energy locate equilibrium compositions which fulfill the necessary and sufficient condition at the same time.

The present work shows applications of the common tangent plane (CTP) approach to ideal and non-ideal adsorption equilibria in the case of binary systems.

2. Gibbs energy of mixing for ideal adsorbed solutions

The definition of ideal solution can be given according to either Lewis–Randall or Raoult's law. These two definitions are contradictory in some aspects as pointed out in [7,8]. It is essentially not possible to have the same definition of ideal solution that satisfies Raoult's law and has a simple expression of the ideal-mixture property changes on mixing at the same time. According to the Lewis–Randall definition, in an ideal solution the fugacities of the components at constant temperature and pressure follow:

$$f_i = w_i f_i^0 \quad i = 1, 2, \dots, NC \quad (7)$$

where f_i^0 is the fugacity of pure component i at the system temperature and pressure and w_i is the mole fraction of component i in the specific phase considered. Accordingly, the molar Gibbs energy of mixing is represented by:

$$\Delta g_{mix} = RT \sum_i^{NC} w_i \ln \left(\frac{f_i}{f_i^0} \right) \quad (8)$$

Applying Eq. (7) the following equation is derived:

$$\Delta g_{mix} = RT \sum_i^{NC} w_i \ln(w_i) \quad (9)$$

By applying Eq. (7), it is demonstrated that a Raoult's law solution in equilibrium with an ideal gas does not match the Lewis–Randall rule [7]. This is due to the need to choose two different reference states for the pure components in order to describe correctly the dependency of Δg_{mix} on composition. This also leads to a different expression of Δg_{mix} for each phase. The Lewis–Randall ideal solution definition can be readily extended to adsorbed solutions. The only aspect to carefully evaluate is the selection of the reference state for the fugacities in Eq. (8) which are crucial for calculating the correct Δg_{mix} . In analogy with the considerations reported in [8,9] for VLE, and limiting for sake of clarity the study to an ideal binary system at a fixed temperature, P_{bulk} will be located between the equilibrium surface pressures (P_i^0) of the components (Fig. 1). Considering component 1 as the most strongly adsorbed component and component 2 as the less strongly adsorbed component, the first one will have a higher reduced grand potential curve than the second one and for this reason its reference state will be in the adsorbed phase which is its more stable phase. Conversely, the less strongly adsorbed component will have the reference state in the gas phase. This result leads to the following equations:

$$\frac{g}{RT} = \begin{cases} \frac{g_{mix,ads}}{RT} = x_1 \ln(x_1) + x_2 \ln \left(\frac{P_2^0 x_2}{P_{tot}} \right) \\ \frac{g_{mix,gas}}{RT} = y_1 \ln \left(\frac{P_{tot} y_1}{P_1^0} \right) + y_2 \ln(y_2) \end{cases} \quad (10)$$

Download English Version:

<https://daneshyari.com/en/article/201549>

Download Persian Version:

<https://daneshyari.com/article/201549>

[Daneshyari.com](https://daneshyari.com)