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3 **Common tangent plane in mixed-gas adsorption**

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10 **Abstract**

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

19 **Keywords:** Gibbs energy of mixing; Adsorption thermodynamics; Common tangent plane; Double tangent
20 plane; Azeotropy; Adsorbed solution theory

22 **1. Introduction**

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

$$33 P_{bulk} y_i = P_i^0 x_i \quad i = 1, 2, \dots, NC \quad (1)$$

34 with

$$35 \sum_i^{NC} x_i = 1 \quad (2)$$

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

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

$$41 \psi_i = \int_0^{P_i^0} n_i d(\ln P_i) \quad i = 1, 2, \dots, NC \quad (3)$$

$$42 \psi_i = const \quad i = 1, 2, \dots, NC \quad (4)$$

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

45 By specifying the bulk gas pressure (P_{bulk}), the equilibrium temperature (T) and composition of the
46 multicomponent gaseous mixture in the bulk phase (y_i), the composition of the multicomponent mixture in
47 the adsorbed phase can be calculated solving the system of eqns (1)-(4). This interpretation is successful in
48 several adsorption systems which can be assumed ideal.

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

$$51 \quad P_{bulk} y_i \phi_i = \phi_i^0 P_i^0 x_i \gamma_i \quad i = 1, 2, \dots, NC \quad (5)$$

$$52 \quad \psi_i = \int_0^{f_i^0} n_i d(\ln f_i) \quad i = 1, 2, \dots, NC \quad (6)$$

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

56 Eqns (5) and (6) need additional models for the evaluation of fugacity and activity coefficients. While the
57 fugacity coefficients can be calculated using the extensive thermodynamic work on specific equations of
58 state, the activity coefficients cannot be predicted from liquid state models because they do not include the
59 interaction with the solid adsorbent, which is implicit in the definition of the reduced grand potential [5, 6].
60 The non-ideal formulation of the AST through the system of eqns (2, 4-6), provides solutions fulfilling only
61 the necessary condition for equilibrium. In general, multiple solutions exist for the above system of equations
62 and convergence to a specific solution depends on the choice of the initial guess. Despite this, strongly non-
63 ideal adsorption systems are reported rarely in the open literature and the above formulation converges to the
64 physically correct solution.

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

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

70

71 **2. Gibbs energy of mixing for ideal adsorbed solutions**

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

$$77 \quad f_i = w_i f_i^0 \quad i = 1, 2, \dots, NC \quad (7)$$

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

$$81 \quad \Delta g_{mix} = RT \sum_i^{NC} w_i \ln \left(\frac{f_i}{f_i^0} \right) \quad (8)$$

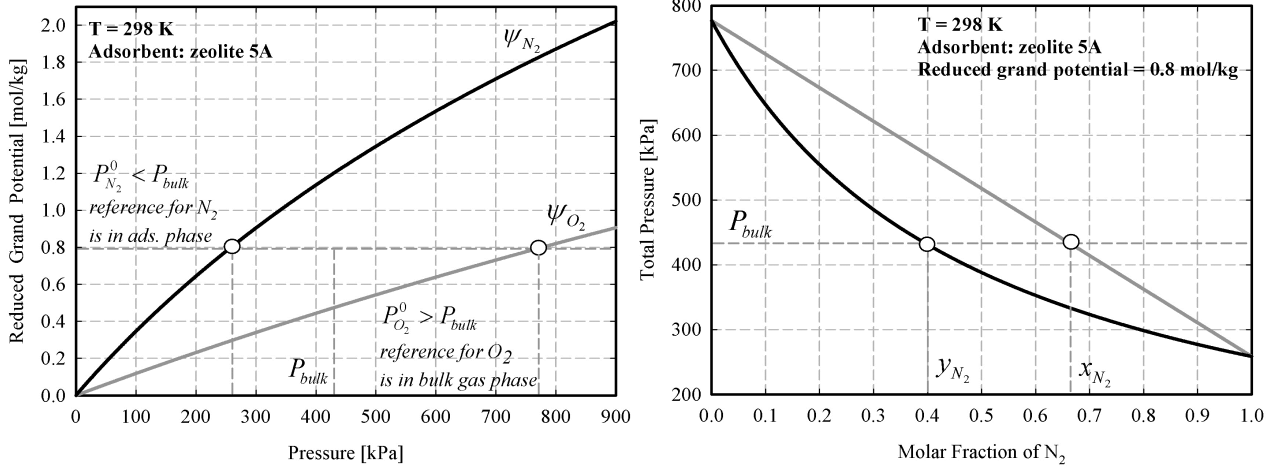
82 Applying eq. (7) the following equation is derived:

$$83 \quad \Delta g_{mix} = RT \sum_i^{NC} w_i \ln(w_i) \quad (9)$$

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

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

98 where $g_{mix,ads}$ and $g_{mix,gas}$ compose the resulting g function. Δg_{mix} will be a piecewise function including the g
 99 function except in the linear region identified by the CTP. Fig. 1 is illustrative of the above presented case
 100 and it is based on the data reported in [10]. It represents the Nitrogen/Oxygen binary system adsorbed on
 101 zeolite 5A at 298 K. Nitrogen (1) is the most strongly adsorbed component and Oxygen (2) is the less
 102 strongly adsorbed component. P_{bulk} is always between the surface pressures of the two components. The
 103 reference states are assumed to be the adsorbed phase for the component 1 as it is stable in the adsorbed
 104 phase and in the bulk gas phase for the component 2 as it is more stable in the bulk gas phase



105 Figure 1: Reduced grand potential diagram (left) and (P,x,y) diagram (right) for Nitrogen/Oxygen binary
 106 system on zeolite 5A at 298 K. Reference states for the two components must be selected on the basis of P_{bulk}
 107 and P_i^0 mutual position.
 108
 109

110 With the reference states of eq. (10), Δg_{mix} approaches a zero value when the molar fraction of component 1
 111 approaches zero or one (Fig. 2). The first critical aspect in the formulation above consists of the selection of
 112 the correct mutual position of the surface pressures and bulk gas phase pressure, which is usually unknown
 113 before the calculation. This makes it impossible to set-up the reference states a-priori, without a preliminary
 114 check. Fortunately, Δg_{mix} is a state function and this makes the CTP approach independent from the selection
 115 of the reference states. Considering for example the bulk gas phase as a reference state for both the
 116 components, the resulting equation is:

$$\frac{g}{RT} = \begin{cases} \frac{g_{mix,ads}}{RT} = x_1 \ln\left(\frac{P_1^0 x_1}{P_{tot}}\right) + x_2 \ln\left(\frac{P_2^0 x_2}{P_{tot}}\right) \\ \frac{g_{mix,gas}}{RT} = y_1 \ln(y_1) + y_2 \ln(y_2) \end{cases} \quad (11)$$

118 Fig. 2 illustrates that the CTP calculated from eq. (10) and eq. (11) leads to the same equilibrium molar
 119 fractions. Thus, in order to simplify the treatment, in this work the reference states will always be taken in
 120 bulk gas phase like in eq. (11).

121 Finally, in the ideal case, the total number of adsorbed moles n_{tot} is calculated from:

$$\frac{1}{n_{tot}} = \sum_{i=1}^{NC} \left(\frac{x_i}{n_i(P_i^0)} \right) \quad (12)$$

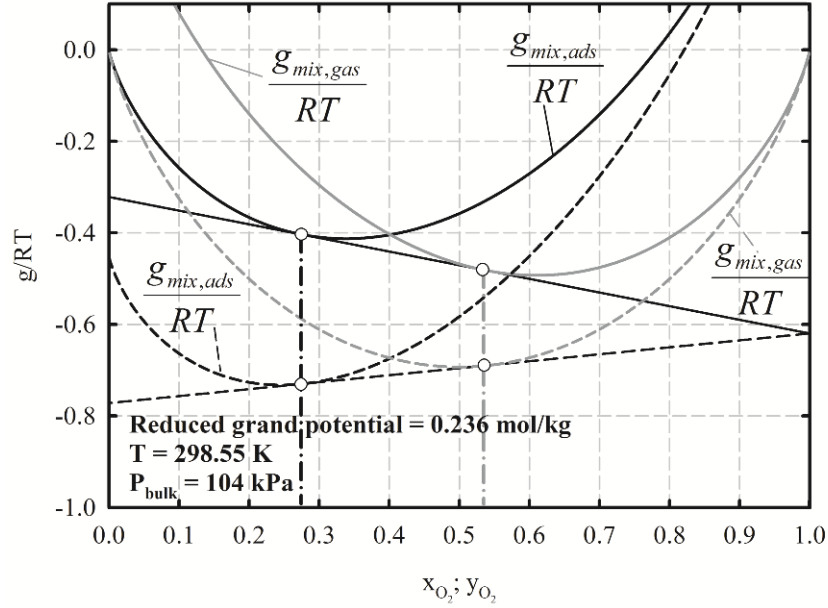


Figure 2: Common tangent plane for Nitrogen/Oxygen mixture on zeolite 5A [10] at 298.55 K, 104 kPa and $y_{O_2}=0.538$. Solid lines are from eq. (10), dashed lines are from eq. (11).

3. Minimisation of the tangent distance function

In adsorption equilibria the minimisation of the CTP distance function has an additional challenge compared with VLE because Δg_{mix} is a function of both the equilibrium reduced grand potential and equilibrium compositions. For this reason the minimisation of the CTP distance function for adsorption is a bilevel programming problem. A bilevel programming problem is a hierarchical problem where a first outer optimization problem is constrained by an inner second one [11]. The outer level is devoted to the minimisation of one objective function based on the iso-reduced grand potential condition, while the inner level minimises the CTP distance function at the reduced grand potential calculated by the outer level. The algorithm is illustrated in the flow chart depicted in Fig. 3. The necessary data are the molar fractions y_i in the bulk phase, the equilibrium pressure P_{bulk} and the equilibrium temperature T . Considering a binary system, the algorithm operates according to the following steps:

- 1) The first iteration is performed providing an initial guess for the reduced grand potential ψ_{eq} and calculating the corresponding surface pressures $P_i^0(\psi_{eq})$. These values are introduced in eq.(11), which, after the substitution $x_2=1-x_1$, represents a system of two equations in two unknowns (x_1, y_1). $y_{1,exp}$ is the composition of the bulk phase and a tangent can be built upon $g_{mix,gas}/RT$. Finally, the distance function between this tangent and eq. (11) can be evaluated. The distance function is:

$$DF(x_1, y_1, \psi_{eq}) = \left| \frac{g(x_1, y_1, \psi_{eq})}{RT} - \tan \Big|_{y_1=y_{1,exp}} \right| \quad (13)$$

where \tan is the tangent of $g_{mix,gas}/RT$, calculated at the composition $y_{1,exp}$.

- 2) The minimum absolute value of eq. (13) is evaluated and this minimum locates the position of $x_{1,iter}$. $x_{1,iter}$ is the calculated composition of component 1 in the adsorbed phase. If $\text{Min}(DF(x_{1,iter}, y_1, \psi_{eq})) > 10^{-6}$, the reduced grand potential of this iteration is not accepted and the algorithm goes back to the outer level.
- 3) The outer level minimises the same distance function of eq. (13) changing the value of the equilibrium reduced grand potential ψ_{eq} in order to obtain the lowest value of eq. (13).
- 4) The algorithm terminates when $\text{Min}(DF(x_{1,iter}, y_1, \psi_{eq})) < 10^{-6}$. The minimum of DF locates the equilibrium value of x_1 and the outer level determines ψ_{eq} .

In all the cases considered in the present work, the Nelder-Mead algorithm [12] has been adopted both for the inner and the outer levels. The presented algorithm is representative of the AST applied in a predictive way. When the same theory is used in a correlative way then y_1 should not be specified among the given values but derived directly from the CTP. In this case the outer level is formulated to minimize the error (in both phases) between experimental and calculated compositions.

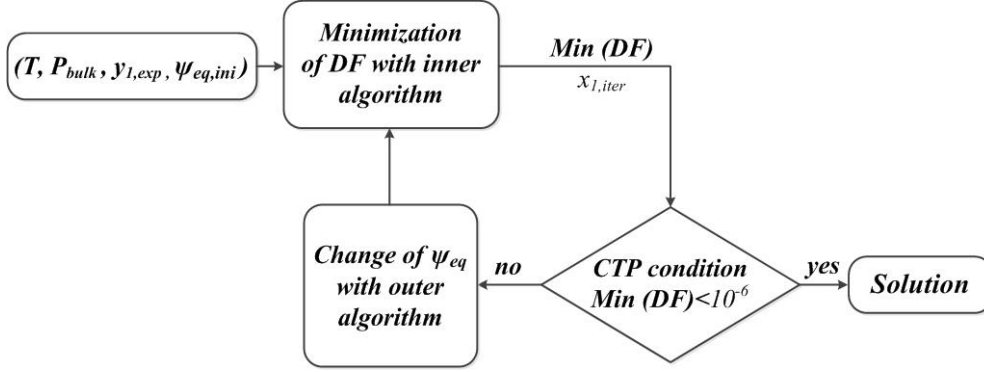


Figure 3: Algorithm for the calculation of the common tangent plane of Δg_{mix} at the equilibrium reduced grand potential ψ_{eq}

4. Validation of common tangent approach with experimental data and Raoult's law IAST

Experimental data concerning adsorption of Nitrogen(1)/Oxygen(2) binary system on zeolite 5A at low pressure [10] have been considered for comparison of the results from Raoult's law IAST proposed in [3] and the CTP approach proposed in this paper. Langmuir isotherm parameters are reported in Table 1.

Table 1: Parameters of Langmuir and Dual-site Langmuir isotherms for adsorption

	Temperature [K]	q_{s1} [mol/kg]	b_1 [1/kPa]	q_{s2} [mol/kg]	b_2 [1/kPa]	Ref
Nitrogen ¹	298.55	2.114	0.001756	--	--	[10]
Oxygen ¹	298.55	2.313	0.000524	--	--	[10]
Carbon Dioxide ²	293.00	2.166	5.803367	4.011	0.093840	[13]
Propane ³	293.00	3.296	1.188920	--	--	[13]
Methane ⁴	298.00	9.307	0.000429	1.557	0.019832	[18]
Carbon Monoxide ⁴	298.00	7.999	0.000346	0.470	0.026290	[18]

Note:

¹ data fitted over the pressure using Langmuir isotherm on zeolite 5A

² data fitted over the pressure using Dual-site Langmuir isotherm on zeolite 13X

³ data fitted over the pressure using Langmuir isotherm on zeolite 13X

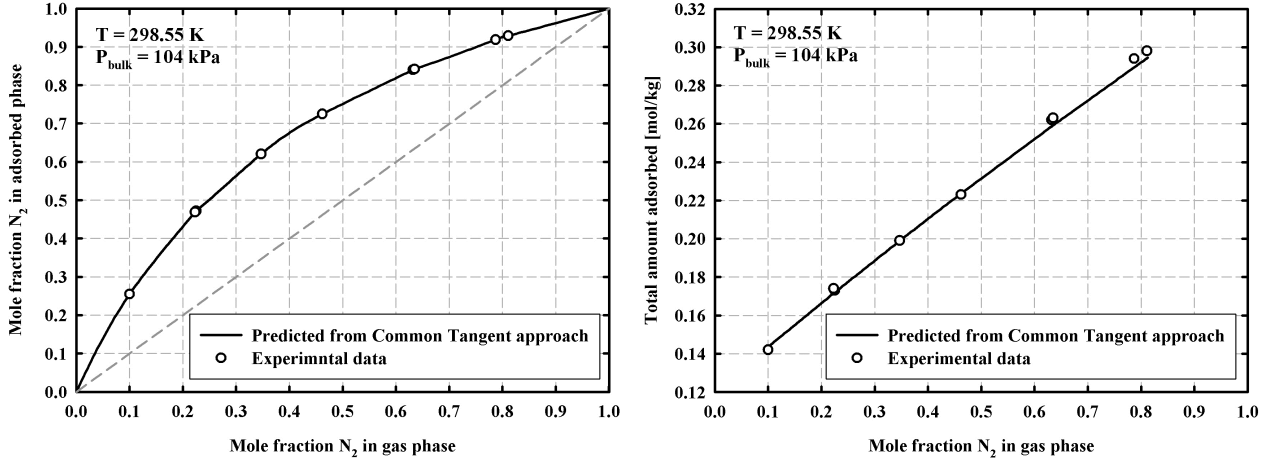
⁴ data fitted over the fugacity using Dual-site Langmuir isotherm on activated carbon NoritR1

Table 2 summarises the results of the comparison and shows complete agreement between the values calculated with the two different methods. Small differences are due to different approximations adopted by the numerical solvers used in the two methods. These identical results are a further proof of the correctness of the proposed framework for ideal adsorption equilibrium. Fig. 2 shows the CTPs obtained applying the method previously described to one of the experimental conditions of Table 2.

Table 2: Data for Nitrogen(1)/Oxygen(2) adsorption on zeolite 5A [10] at 298.55K. Comparison among experimental data, results of common tangent plane approach and of Raoult's law IAST.

P_{bulk} [kPa]	$y_{1,\text{exp}}$	$x_{1,\text{exp}}$	Common tangent plane approach				Raoult's law IAST						
			$n_{\text{tot,exp}}$ [mol/kg]	x_1	n_{tot} [mol/kg]	ψ_{eq} [mol/kg]	P_1^0 [kPa]	P_2^0 [kPa]	x_1	n_{tot} [mol/kg]	ψ_{eq} [mol/kg]	P_1^0 [kPa]	P_2^0 [kPa]
104	0.632	0.847	0.262	0.840	0.259	0.275	78.22	239.71	0.840	0.259	0.275	78.22	239.70
104	0.635	0.847	0.263	0.842	0.259	0.276	78.43	240.35	0.842	0.259	0.276	78.43	240.34
104	0.347	0.621	0.199	0.620	0.199	0.208	58.19	178.79	0.620	0.199	0.208	58.19	178.78
104	0.100	0.260	0.142	0.255	0.144	0.148	40.80	125.62	0.255	0.144	0.148	40.79	125.62
104	0.811	0.928	0.298	0.929	0.294	0.316	90.77	277.76	0.929	0.294	0.316	90.76	277.74
104	0.787	0.915	0.294	0.919	0.289	0.311	89.09	272.67	0.919	0.289	0.311	89.08	272.64
104	0.462	0.724	0.223	0.725	0.223	0.236	66.28	203.42	0.725	0.223	0.236	66.28	203.42
104	0.225	0.472	0.173	0.472	0.172	0.179	49.61	152.57	0.472	0.172	0.179	49.61	152.57
104	0.223	0.474	0.174	0.469	0.172	0.178	49.47	152.14	0.469	0.172	0.178	49.47	152.14
300	0.657	0.848	0.622	0.852	0.618	0.729	231.26	696.69	0.852	0.618	0.728	231.26	696.66
300	0.229	0.478	0.439	0.475	0.437	0.484	144.76	440.22	0.475	0.437	0.484	144.76	440.21
300	0.099	0.254	0.376	0.251	0.371	0.404	118.32	360.89	0.251	0.371	0.404	118.29	360.92
300	0.353	0.628	0.501	0.623	0.494	0.558	169.91	515.24	0.623	0.494	0.558	169.91	515.23
400	0.664	0.850	0.761	0.855	0.756	0.930	310.57	928.21	0.855	0.756	0.930	310.57	928.15
400	0.100	0.257	0.478	0.252	0.471	0.525	158.57	481.45	0.252	0.471	0.525	158.57	481.45

175 The Nitrogen/Oxygen binary system is ideal under the specific conditions considered (Fig. 4) and the
 176 maximum absolute errors on molar fractions and number of total adsorbed moles are respectively 2.0% and
 177 1.6%. These results are the basis for non-ideal cases where excess Gibbs energy models have to be added.



178
 179 Figure 4: Comparison between experimental data and results from common tangent plane for binary system
 180 Nitrogen/Oxygen on zeolite 5A [10]
 181

182 5. Common tangent approach for non-ideal adsorption at low pressure

183 Adsorption of the Carbon Dioxide(1)/Propane(2) binary system on zeolite 13X exhibits an azeotrope and it
 184 has been extensively studied introducing a model for the excess Gibbs energy [14]. Isotherms parameters are
 185 reported in Table 1. This system forms an azeotrope in a specific range of conditions and the excess Gibbs
 186 energy (g_{ex}) follows the ABC equation [15] with parameters $A = -11.5$ kJ/mol; $B = 0.01453$ kJ/(mol K) and
 187 $C = 0.096$ kg/mol. The ABC equation for a binary system is given by:

$$188 \quad g_{ex} = (A + BT)x_1x_2(1 - e^{-C\psi}) \quad (14)$$

189 In order to consider a fully non-ideal adsorption, fluid-fluid and fluid-solid interactions must be included.
 190 Fluid-solid interactions can be taken into account adding an excess Gibbs energy term to eq. (11). Fluid-fluid
 191 interactions are considered including bulk gas phase fugacities and the reduced grand potential expressed by
 192 eq. (6). Thus, the function g/RT becomes:

$$193 \quad \frac{g}{RT} = \begin{cases} \frac{g_{mix,ads}}{RT} = x_1 \ln \left(\frac{\phi_1^0 P_1^0 x_1}{P_{tot}} \right) + x_2 \ln \left(\frac{\phi_2^0 P_2^0 x_2}{P_{tot}} \right) + \frac{g_{ex}}{RT} \\ \frac{g_{mix,gas}}{RT} = y_1 \ln \left(\frac{f_1}{f_{1,pure}} \right) + y_2 \ln \left(\frac{f_2}{f_{2,pure}} \right) \end{cases} \quad (15)$$

194 where f_i is the fugacity of component i in the mixture and $f_{i,pure}$ is the fugacity of the pure component. The
 195 Carbon Dioxide(1)/Propane(2) binary system in the conditions of Table 4 is moderately non-ideal and for
 196 this reason the Virial equation of state truncated at the second Virial coefficient has been used.

197 Solving the integral of eq. (6), the reduced grand potential for this case is:

$$198 \quad \begin{aligned} \psi_i = & q_{s1,i} \ln(1 + b_{1,i}P_i^0) + q_{s2,i} \ln(1 + b_{2,i}P_i^0) + \\ & + \frac{B_{ii}}{RT} \left(q_{s1,i}P_1^0 + q_{s2,i}P_2^0 - \frac{q_{s1,i} \ln(1 + b_{1,i}P_i^0)}{b_{1,i}} - \frac{q_{s2,i} \ln(1 + b_{2,i}P_i^0)}{b_{2,i}} \right) \quad i = 1, 2, \dots, NC \end{aligned} \quad (16)$$

199 where B_{ii} is the second virial coefficient for the pure component i . Fugacities of the two components in
 200 mixture are:

$$201 \quad \begin{aligned} \ln(f_1) &= \frac{P_{bulk}}{RT} [B_{11} + y_2^2(2B_{12} - B_{11} - B_{22})] \\ \ln(f_2) &= \frac{P_{bulk}}{RT} [B_{22} + y_1^2(2B_{12} - B_{11} - B_{22})] \end{aligned} \quad (17)$$

202 where B_{12} is the cross second Virial coefficient. Table 3 reports the coefficients of the three temperature-
 203 dependent linear correlations used for the calculation of the Virial coefficients in eq. (17).
 204

Table 3: Coefficients of the linear correlations ($a_0+a_1 T$) used for Virial coefficients for the Carbon Dioxide(1)/Propane(2) binary system.

	a_0	a_1
B_{11} [m^3/mol]	$-4.125 \cdot 10^{-4}$	$9.707 \cdot 10^{-7}$
B_{12} [m^3/mol]	$-4.692 \cdot 10^{-4}$	$9.894 \cdot 10^{-7}$
B_{22} [m^3/mol]	$-1.248 \cdot 10^{-3}$	$2.876 \cdot 10^{-6}$

Note: B_{11} and B_{22} are regressed in the temperature range 291-301 K on data from [16],
 B_{12} is regressed in the temperature range 303-377 K on data from [17].

205
 206 In this case the number of total adsorbed moles is derived as follows:

$$207 \quad \frac{1}{n_{tot}} = \left(\frac{1}{n}\right)^{ex} + \sum_{i=1}^{NC} \left(\frac{x_i}{n_i (\phi_i^0 P_i^0)} \right) \quad (18)$$

208 with:

$$209 \quad \left(\frac{1}{n}\right)^{ex} = \left. \frac{\partial (g_{ex} / RT)}{\partial \psi} \right|_{T,x} \quad (19)$$

210 Table 4 shows that CTP approach matches all the experimental data reported in [13]. For sake of clarity,
 211 although the data are reported as a function of P_{bulk} , the isotherm parameters in Table 1 were obtained
 212 regressing the adsorbed amount against the fugacity. The maximum errors with experimental data are -4.2%
 213 for the case of adsorbed phase mole fraction and -4.9% for the case of total adsorbed moles, requiring an
 214 average number of 2156 iterations. Eventually, Fig. 5 shows the presence of an azeotropic aggregation state
 215 and the respective common tangent lines locating the equilibrium compositions at constant reduced grand
 216 potential.,
 217

Table 4: Comparison between experimental data in [13] and results from common tangent plane approach for adsorption of Carbon Dioxide(1)/Propane(2) binary system on zeolite 13X

T [K]	P_{bulk} [kPa]	$n_{tot,exp}$ [mol/kg]	$y_{1,exp}$	$x_{1,exp}$	$x_{1,calc}$	$x_{1,error}$	$n_{tot,calc}$ [mol/kg]	$n_{tot,error}$	γ_1	γ_2	ψ_{eq} [mol/kg]	I_{inner}^3	I_{outer}^4
294.07	47.91	5.35	0.966	0.969	0.949	2.1	5.35	0.0	0.994	0.107	19.2	63.5	34
294.06	53.48	5.43	0.966	0.970	0.951	2.0	5.41	0.4	0.994	0.103	19.7	59.0	34
294.34	64.05	5.49	0.930	0.946	0.921	2.7	5.42	1.4	0.984	0.115	20.8	63.4	34
294.50	70.20	5.55	0.929	0.948	0.924	2.6	5.45	1.8	0.985	0.112	21.3	63.1	34
294.63	83.22	5.59	0.888	0.927	0.902	2.8	5.45	2.6	0.975	0.121	22.2	64.6	33
293.85	10.26	4.19	0.812	0.826	0.796	3.7	4.23	-0.8	0.919	0.277	12.0	57.2	32
293.78	14.35	4.38	0.741	0.786	0.759	3.5	4.44	-1.5	0.883	0.290	13.5	60.9	32
293.73	17.80	4.51	0.745	0.794	0.766	3.7	4.57	-1.4	0.885	0.272	14.4	68.1	30
293.77	26.14	4.64	0.659	0.764	0.735	3.9	4.70	-1.4	0.849	0.284	16.1	61.1	32
293.81	32.52	4.76	0.660	0.774	0.744	4.0	4.80	-0.9	0.855	0.266	17.2	66.5	33
293.78	44.82	4.83	0.584	0.753	0.724	4.0	4.84	-0.3	0.829	0.275	18.5	99.0	34
293.52	10.97	4.04	0.396	0.582	0.582	0.0	4.07	-0.9	0.705	0.507	11.7	60.5	32
293.51	14.19	4.16	0.406	0.599	0.594	0.8	4.21	-1.2	0.708	0.476	12.8	68.2	33
293.98	27.49	3.47	0.024	0.203	0.202	0.3	3.64	-4.7	0.273	0.920	12.2	70.4	32
294.09	57.75	3.72	0.041	0.288	0.301	-4.2	3.91	-4.9	0.327	0.813	15.5	60.3	33

Note:

¹ error on molar fraction is $100 \left| \frac{x_{1,exp} - x_{1,calc}}{x_{1,calc}} \right|$

² error on number of total adsorbed moles is $100 \left| \frac{n_{tot,exp} - n_{tot,calc}}{n_{tot,calc}} \right|$

³ average number of iterations in the inner loop

⁴ number of iterations in the outer loop

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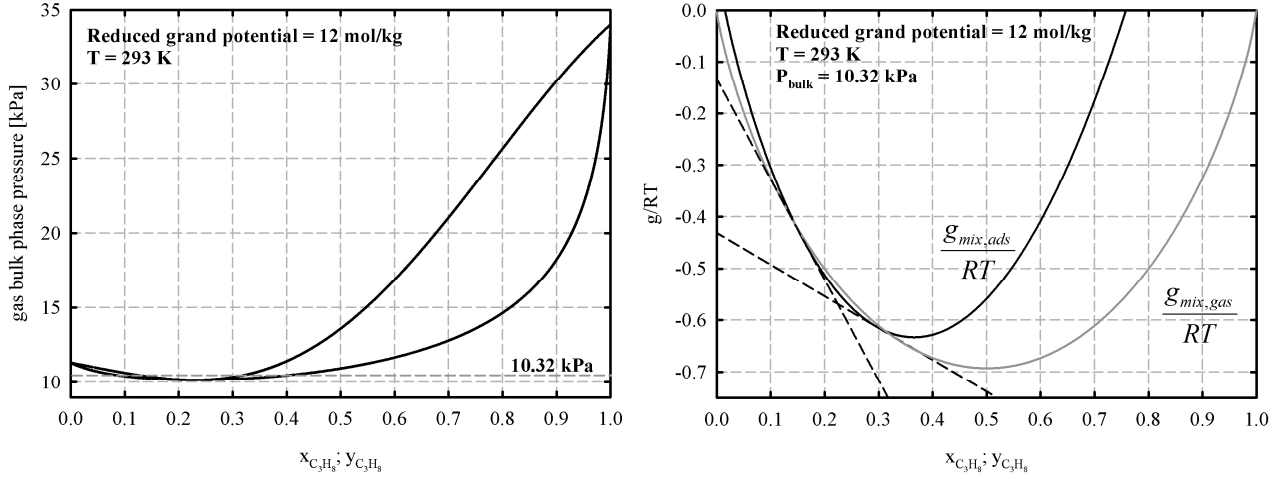


Figure 5. Binary system Carbon Dioxide/Propane on zeolite 13X at 293 K and reduced grand potential ψ_{eq} of 12.0 mol/kg. P,x,y diagram shows the presence of an azeotropic aggregation state (left) and the concerned Δg_{mix} at 10.32 kPa (right)

5. Common tangent approach for non-ideal adsorption at high pressures

In this case adsorption of the Methane(1)/Carbon monoxide(2) binary system on activated carbon Norit R1 has been considered [18]. Table 1 reports the parameters for the Dual-site Langmuir isotherm. These parameters have been obtained regressing the absolute amount adsorbed versus the fugacity. In fact, differently from the other cases, here the effect of the bulk molecular density on the adsorption cannot be neglected. So eq. (15) is no longer formulated using surface pressures but directly on fugacities respectively in the bulk phase (f_i) and in the adsorbed phase ($\phi_i^0 P_i^0 = f_i^0$). The Soave-Redlich-Kwong equation of state (SRK) has been used to calculate both the fugacities and the densities, coupling it with the ABC equation. In this case the data considered are at constant temperature and, instead of having three parameters, the model has been regressed on only two parameters, respectively $A_0 = (A+B T) = -0.0282$ kJ/mol and $C = 1.503$ kg/mol. The experimental data considered in this case are up to 10026 kPa. Table 5 summarizes the results showing maximal errors on molar fractions and total adsorbed moles respectively of 3.9% and -4.6% and an average number of iterations of 6063.

Table 5: Comparison between experimental data in [18] and results from common tangent plane approach for Methane(1)/Carbon Monoxide(2) binary system on activated carbon Norit R1 at 298 K. Specific pore volume of the solid is $3.511 \cdot 10^{-4} \text{ m}^3/\text{kg}$.

P_{bulk} [kPa]	Z	$n_{tot,exp}$ [mol/kg]	n_{abs} [mol/kg]	$y_{1,exp}$	$x_{1,exp}$	$x_{1,calc}$	$^1x_{1,error}$	$n_{tot,calc}$ [mol/kg]	$^2n_{tot,error}$	ϕ_1	ϕ_2	ψ_{eq} [mol/kg]	$^3I_{inner}$	$^4I_{outer}$
4039.3	0.991	5.13	5.71	0.137	0.331	0.332	0.5	5.55	-2.8	0.946	0.996	10.6	277.2	28
5067.2	0.990	5.40	6.13	0.136	0.332	0.331	-0.2	6.00	-2.1	0.934	0.995	11.9	454.2	31
5980.7	0.990	5.71	6.56	0.140	0.327	0.338	3.4	6.32	-3.7	0.923	0.995	13.0	319.4	29
1850.0	0.986	4.72	4.98	0.489	0.724	0.750	3.6	4.75	-4.6	0.971	0.999	8.9	141.2	30
2965.0	0.978	5.52	5.95	0.495	0.723	0.751	3.9	5.80	-2.6	0.954	0.999	11.4	120.6	32
4965.0	0.966	6.31	7.03	0.499	0.728	0.755	3.7	6.92	-1.7	0.926	1.000	14.7	117.2	33
7103.0	0.910	7.01	8.11	0.894	0.961	0.964	0.3	8.38	3.3	0.892	1.019	20.1	139.1	33
8066.0	0.901	7.08	8.35	0.895	0.961	0.965	0.3	8.60	3.0	0.880	1.024	21.2	120.0	33
9045.0	0.893	7.10	8.53	0.895	0.957	0.965	0.8	8.79	3.0	0.868	1.029	22.2	118.7	32
10026.0	0.886	7.14	8.74	0.895	0.963	0.965	0.2	8.94	2.3	0.857	1.034	23.1	117.2	34

Note:

¹ error on molar fraction is $100 \left| x_{1,exp} - x_{1,calc} \right| / x_{1,calc}$

² error on number of total adsorbed moles is $100 \left| n_{tot,exp} - n_{tot,calc} \right| / n_{tot,calc}$

³ average number of iterations in the inner loop

⁴ number of iterations in the outer loop

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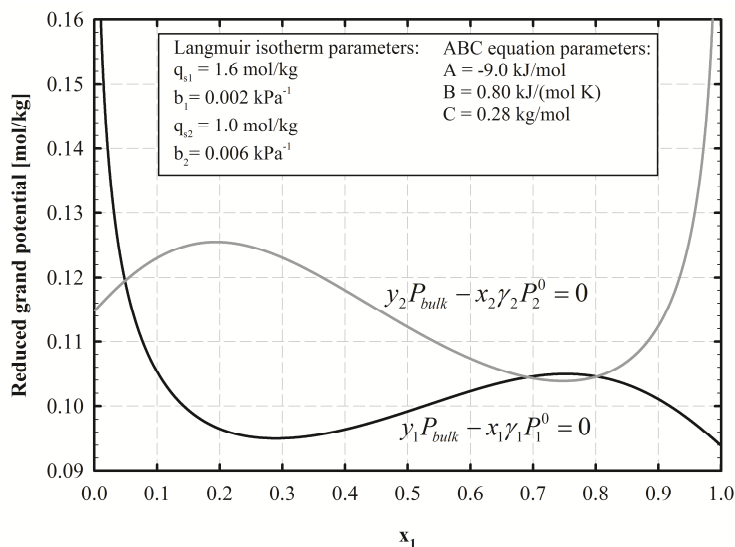
In all the cases considered, the isofugacity condition provides solutions identical to those of the CTP approach. This is because, differently to a VLE flash calculation, in an adsorption equilibrium, both P_{bulk} and the composition of the bulk gas phase (y_i) are given. In this case the fugacity coefficients of the bulk gas phase can be directly calculated, resulting in a constant value for the left hand side of eq. (5), instead of a

244 function of the compositions. This feature reduces the chances of having multiple solutions for the
 245 isofugacity condition.

246

247 6. Example of multiple solutions from isofugacity approach

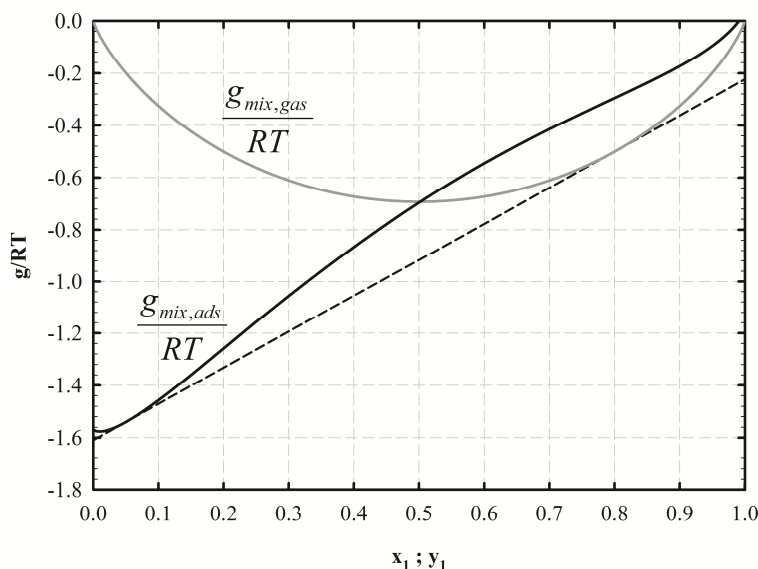
248 A final hypothetical binary system is proposed involving two Langmuir isotherms and the ABC equation. It
 249 shows how the multiple solutions can be obtained from the isofugacity condition. Fig. 6 illustrates
 250 graphically this feature. The two curves are a representation of the two equations solving the isofugacity
 251 condition. They intersect in three points, suggesting three possible compositions for adsorbed phase
 252 equilibrium. Conversely, Δg_{mix} and its common tangent plane exhibit only the thermodynamically consistent
 253 solution (Fig. 7). In this case, the adoption of the common tangent plane approach is mandatory to obtain the
 254 correct solution unless high quality initial guesses are used to solve the isofugacity condition.
 255



256

257 Figure 6: Isofugacity system of equation showing three roots for the equilibrium composition of the adsorbed
 258 phase at $T = 295$ K; $P_{bulk} = 101.325$ kPa and $y_1 = 0.8$;

259



260

261 Figure 7: The common tangent plane of Δg_{mix} locates only one solution for the problem of Fig. 6.

262

263 7. Conclusions

264 The common tangent plane approach has been successfully extended to adsorbed solutions. This approach
 265 generally applied to VLE calculations cannot be applied in the same way to the adsorbed solutions because
 266 of the presence of an additional independent variable, the reduced grand potential. A bilevel algorithm has
 267 been adopted to solve this problem and to determine the common tangent plane of the Gibbs energy of

268 mixing. An ideal case, a non-ideal azeotropic system case and a non-ideal high pressure case illustrated the
 269 application of the common tangent approach to adsorbed solutions. For the ideal case the approach has been
 270 validated on experimental data and on the direct solution of IAST providing respectively low error and
 271 identical results. The non-ideal cases have been validated by comparison of the results with experimental
 272 data and applying respectively the Virial and the Soave-Redlich-Kwong equations of state to take into
 273 account fluid-fluid interactions in the bulk gas phase. A Gibbs energy excess model (ABC equation) for
 274 fluid-solid interactions in the adsorbed phase was also considered. The existence of a common tangent plane
 275 is a necessary and sufficient condition for equilibrium which is valid also in the adsorbed solution theory as
 276 demonstrated in a conclusive example.

277

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 281 EP/J02077X/1 Adsorption Materials and Processes for Carbon Capture from Gas-Fired Power Plants –
 282 AMPGas.

283

284 **Nomenclature**

285	f_i	Fugacity of component i [kPa]
286	f_i^0	Fugacity of pure component i at the system temperature and pressure [kPa]
287	g_{ex}	Excess Gibbs energy [kJ/mol]
288	$g_{mix,ads}$	Branch of the Gibbs energy of mixing function (adsorbed phase) [kJ/mol]
289	$g_{mix,gas}$	Branch of the Gibbs energy of mixing function (bulk gas phase) [kJ/mol]
290	Δg_{mix}	Molar Gibbs energy of mixing [kJ/mol]
291	NC	Number of components participating in the adsorption
292	n_i	Specific absolute amount adsorbed of component i [mol/kg]
293	n_{tot}	Specific amount of total adsorbed moles [mol/kg]
294	P	Pressure [kPa]
295	P_{bulk}	Pressure of the mixture in the bulk gas phase [kPa]
296	P_i^0	Surface pressure of the component i [kPa]
297	R	Universal gas constant [kJ/(mol K)]
298	T	Equilibrium temperature [K]
299	w_i	Molar fraction of the component i
300	x_i	Molar fraction of the component i in the adsorbed mixture
301	y_i	Molar fraction of the component i in the bulk gas mixture
302	Z	Compressibility factor

303

304 **Greek letters**

305	γ_i	Activity coefficient of component i
306	ϕ_i	Fugacity coefficient of component i
307	ϕ_i^0	Fugacity coefficient of the pure component i in the adsorbed phase at the system temperature
308		and pressure. This is calculated using P_i^0
309	ψ_{eq}	Reduced grand potential at equilibrium [mol/kg]
310	ψ_i	Reduced grand potential of component i [mol/kg]

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