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**Adsorption equilibria of single gas and gas mixture on  
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developments.  
Part II : Extension to gas mixture adsorption.**

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4 **surfaces. A unified approach based on statistical thermodynamics**  
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33 **Abstract**

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35 Theoretical description of single gas and gas mixture adsorption equilibria can be achieved in  
36 many different ways depending on the kind of approach (microscopic or macroscopic). In this  
37 paper, we present a statistical thermodynamics approach for the calculation of mixed gas  
38 adsorption equilibrium data on uniform surfaces. The non-ideality of both the mixed gas  
39 phase and the adsorbed phase is considered by using the Redlich-Kwong EOS associated to  
40 the classic Lorentz-Berthelot mixing rules. This is an interesting way to extend the model  
41 presented in Part I and to predict multicomponent gas adsorption equilibria for highly non-  
42 ideal systems from parameters deduced from pure gas data. We present mixture adsorption  
43 isotherms and selectivity curves calculated using our model.  
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3 **Keywords:** adsorption; homogenous surface; statistical thermodynamics; equation of state,  
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## 10 **1. Introduction**

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12 Prediction of multi-component adsorption equilibria using parameters deduced from single  
13 gas adsorption data is of great practical importance. Such equilibrium data are indeed required  
14 for process design purpose. Generally the experimental determination of such data is time-  
15 consuming. As for pure gases, a lot of models are derived from macroscopic thermodynamics  
16 development. The most useful predictive theories for multi-component adsorption equilibria  
17 are described in [1-11]. They are considered as efficient tools for engineers concerned with  
18 adsorption process design. Unfortunately they fail at predicting experimental data in a wide  
19 range of conditions and do not allow a physical understanding of the adsorptive-adsorbent  
20 behaviour at the molecular level. Most of them are based on the generalization of the  
21 corresponding pure gas adsorption models.  
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36 This paper is the second part of a work dealing with statistical-thermodynamics approach to  
37 predict single and multi-component gas equilibria. In the first part, the single gas adsorption  
38 equation developments were described in details. We had defined the model parameters and  
39 the final expression of the equilibrium isotherm equation. This second paper reports the same  
40 theoretical developments for binary mixed, the aim of which is to provide a useful prediction  
41 tool for engineers for the assessment of multi-component adsorption information in a wide  
42 range of pressure and temperature. Both phases are described using simple statistical  
43 thermodynamics developments which lead to the expression of the chemical potential of each  
44 specie in each phase. The equality of the chemical potentials of a given specie in each phase  
45 allows to relate the macroscopic variables (temperature, pressure, surface concentration and  
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phases composition) together. The model does not require any further parameter compared to the pure gas version.

## 2. Theoretical Section

In this approach, we replace the mixture by a hypothetic pure component, the properties of which are indexed 'mix'.

As for the single gas case, the adsorption equilibrium expression between the adsorbed and the gas phases is expressed by the equality of the chemical potentials of the adsorptives in each phase. The development of such an equation requires the microscopic modeling of each phase separately in order to obtain the expression of the chemical potentials using statistical thermodynamics developments.

### 2-1. Non-ideal gas phase modeling

The canonical partition function  $Q_{gmix}$  of a system composed of a mixture of  $N_{gB}$  molecules of a gas B (molecular mass  $m_B$ ) and  $N_{gC}$  molecules of a gas C (molecular mass  $m_C$ ) in a volume  $V_{gmix}$  at temperature  $T$  is given by:

$$Q_{gmix} = \frac{q_{gB}^{N_{gB}} q_{gC}^{N_{gC}}}{N_{gB}! N_{gC}!} \quad (1)$$

with:  $N_{gmix} = N_{gB} + N_{gC}$

$q_{gB}$  and  $q_{gC}$  are respectively the partition function of one molecule of B (or C) and are expressed as:

$$q_{gB} = q_{gB trans} q_{gB rot} q_{gB vibi} q_{gB e} \exp\left(\frac{-U'_{intmix}}{2kT}\right) \quad (2)$$

$$q_{gC} = q_{gC trans} q_{gC rot} q_{gC vibi} q_{gC e} \exp\left(\frac{-U'_{intmix}}{2kT}\right) \quad (3)$$

where:

- $q_{gB \text{ trans}}$  and  $q_{gC \text{ trans}}$  are respectively the translation contributions to the partition functions  $q_{gB}$  and  $q_{gC}$  (3 degrees of freedom of the mass centre of the molecule);
- $q_{gB \text{ rot}}$  and  $q_{gC \text{ rot}}$  are respectively the rotational contributions to the partition functions  $q_{gB}$  and  $q_{gC}$  ;
- $q_{gB \text{ vib}}$  and  $q_{gC \text{ vib}}$  are respectively the contributions to the partition functions  $q_{gB}$  and  $q_{gC}$  due to the internal vibrations in the molecule;
- $q_{gB \text{ e}}$  and  $q_{gC \text{ e}}$  are respectively the electronic contributions to the partition functions  $q_{gB}$  and  $q_{gC}$  ;

The translation contribution to the partition function of component  $j$  may be written:

$$q_{gjtrans} = \left[ \frac{2\pi m_j kT}{h^2} \right]^{3/2} V_{fmix} = \frac{V_{fmix}}{\Lambda_j^3} \quad (4)$$

$$\text{With: } \Lambda_j^{-1} = \left[ \frac{2\pi m_j kT}{h^2} \right]^{1/2} \quad (5)$$

in which:

- suffix  $j$  means molecules B or C;
- $\Lambda_j$  is the thermal de Broglie wavelength of molecule  $j$ ;
- $h$  is the Planck constant;
- $m_j$  is the mass of molecule  $j$ ;
- $k$  is the Boltzmann constant;
- $V_{fmix}$  is the real volume available to the molecules in the mixture;

The contribution to the molecular partition function due to the interactions between the

$$\text{molecules is } \exp\left(-\frac{U'_{\text{int mix}}}{2kT}\right);$$

in which

- $U'_{int\ mix}$  is the potential energy of interaction between any molecule and all the others in the mixture;

$U'_{int\ mix}$  may be calculated by:

$$U'_{int\ mix} = - \int_{d_{mix}}^{\infty} u'(r) \frac{N_{gmix}}{V_{gmix}} g'(r) 4\pi r^2 dr \quad (6)$$

in which  $d_{gmix}$  is the molecular diameter of an hypothetic molecule in the gas phase representing the mixture.

Following the works of Vera and Prausnitz [12], the same developments as in part I may be done for the gas mixture, using similar expressions of equation (7) to equation (13) (part I).

We obtain:

$$U'_{int\ mix} = - \frac{4\pi d_{gmix}^3}{b_{mix}} C'_{mix} \sqrt{\frac{T_{cmix}}{T}} \ln \left( 1 + \frac{N_{gmix} b_{mix}}{V_{gmix}} \right) \quad (7)$$

- $T_{cmix}$  is the critical temperature of the hypothetic component;
- $C'_{mix}$  is an energetic constant of the hypothetic component in the gas phase;
- $b_{mix}$  is a parameter which characterizes the fluid. It may be considered as the volume of the molecule of the hypothetic component.

If we set  $a_{mix} = 2\pi d_{gmix}^3 C'_{mix} \sqrt{T_{cmix}}$ ,  $a_{mix}$  is defined as the molecular attraction parameter of the hypothetic component.

The parameters of mixture ( $a_{mix}$  and  $b_{mix}$ ) will be calculated thereafter using the pure component parameters and appropriate mixing rules

Equation (7) becomes:

$$U'_{int\ mix} = - \frac{2a_{mix}}{kT\sqrt{T}b_{mix}} \ln \left( 1 + \frac{N_{gmix} b_{mix}}{V_{gmix}} \right) \quad (8)$$

Considering equation (1) to (3) leads to:

$$Q_{gmix} = \frac{V_{fmix}^{N_{gB}}}{\Lambda_B^{3N_{gB}} N_{gB}!} \frac{V_{fmix}^{N_{gC}}}{\Lambda_C^{3N_{gC}} N_{gC}!} \left( q_{gB\ rot} q_{gB\ vibi} q_{gB\ e} \exp\left(\frac{-U'_{int\ mix}}{2kT}\right) \right)^{N_{gB}} \left( q_{gC\ rot} q_{gC\ vibi} q_{gC\ e} \exp\left(\frac{-U'_{int\ mix}}{2kT}\right) \right)^{N_{gC}} \quad (9)$$

in which  $V_{fmix}$  may be calculated by:

$$V_{fmix} = V_{gmix} - N_{gmix} b_{mix} \quad (10)$$

Combining equations (8) to (10) leads to:

$$\begin{aligned} \ln Q_{gmix} = & N_{gB} \ln(V_{gmix} - N_{gmix} b_{mix}) - N_{gB} \ln \Lambda_B^3 - N_{gB} \ln N_{gB} + N_{gB} + N_{gB} \ln q_{gB\ rot} + \\ & N_{gB} \ln q_{gB\ vibi} + N_{gB} \ln q_{gB\ e} + \frac{N_{gB} a_{mix}}{kT\sqrt{T}b_{mix}} \ln\left(\frac{V_{gmix} + N_{gmix} b_{mix}}{V_{gmix}}\right) + N_{gC} \ln(V_{gmix} - N_{gmix} b_{mix}) - \\ & N_{gC} \ln \Lambda_C^3 - N_{gC} \ln N_{gC} + N_{gC} + N_{gC} \ln q_{gC\ rot} + N_{gC} \ln q_{gC\ vibi} + N_{gC} \ln q_{gC\ e} + \\ & \frac{N_{gC} a_{mix}}{kT\sqrt{T}b_{mix}} \ln\left(\frac{V_{gmix} + N_{gmix} b_{mix}}{V_{gmix}}\right) \end{aligned} \quad (11)$$

Then

$$\begin{aligned} \ln Q_{gmix} = & N_{gmix} \ln(V_{gmix} - N_{gmix} b_{mix}) - N_{gB} \ln \Lambda_B^3 - N_{gB} \ln N_{gB} + N_{gB} + N_{gB} \ln q_{gB\ rot} + N_{gB} \ln q_{gB\ vibi} + \\ & N_{gB} \ln q_{gB\ e} - N_{gC} \ln \Lambda_C^3 - N_{gC} \ln N_{gC} + N_{gC} + N_{gC} \ln q_{gC\ rot} + N_{gC} \ln q_{gC\ vibi} + N_{gC} \ln q_{gC\ e} + \\ & \frac{N_{gmix} a_{mix}}{kT\sqrt{T}b_{mix}} \ln\left(\frac{V_{gmix} + N_{gmix} b_{mix}}{V_{gmix}}\right) \end{aligned} \quad (12)$$

We apply the classical mixing rules:

$$a_{mix} = a_B y_B^2 + a_C y_C^2 + 2y_B y_C a_{B,C} = a_B \left(\frac{N_{gB}}{N_{gmix}}\right)^2 + a_C \left(\frac{N_{gC}}{N_{gmix}}\right)^2 + 2\frac{N_{gB} N_{gC}}{N_{gmix}^2} a_{B,C} \quad (13)$$

$$b_{mix} = b_B y_B + b_C y_C = b_B \frac{N_{gB}}{N_{gmix}} + b_C \frac{N_{gC}}{N_{gmix}} \quad (14)$$

in which:



- $a_B$  and  $a_C$  are respectively the intermolecular attraction parameters between B and B and between C and C in the gas phase ;
- $y_B$  and  $y_C$  are respectively the mole fractions of the component B and C in the gas phase;
- $b_B$  and  $b_C$  are the geometric parameters of pure components B and C ;
- $a_{B,C}$  is the attraction parameter between B and C in the gas phase.;  $a_{B,C}$  may be calculated from  $a_B$  and  $a_C$  with quadratic mixing rule  $a_{B,C} = \sqrt{a_B a_C}$

Substituting (13) and (14) in (12), we have

$$\begin{aligned} \ln Q_{gmix} = & N_{gmix} \ln(V_{gmix} - N_{gmix} b_{mix}) - N_{gB} \ln A_B^3 - N_{gB} \ln N_{gB} + N_{gB} + N_{gB} \ln q_{gB rot} + N_{gB} \ln q_{gB vibi} + \\ & N_{gC} \ln q_{gC e} - N_{gC} \ln A_C^3 - N_{gC} \ln N_{gC} + N_{gC} + N_{gC} \ln q_{gC rot} + N_{gC} \ln q_{gC vibi} + N_{gC} \ln q_{gC e} + \end{aligned} \quad (15)$$

$$\frac{N_{gmix} \left[ a_B \left( \frac{N_{gB}}{N_{gmix}} \right)^2 + a_C \left( \frac{N_{gC}}{N_{gmix}} \right)^2 + 2 \frac{N_{gB} N_{gC}}{N_{gmix}^2} a_{B,C} \right]}{kT \sqrt{T} \left( \frac{N_{gB}}{N_{gmix}} b_{gB} + \frac{N_{gC}}{N_{gmix}} b_C \right)} \ln \left( \frac{V_{gmix} + N_{gmix} b_{mix}}{V_{gmix}} \right)$$

The chemical potential of component B in the mixture of B and C is obtained by differentiating  $\ln Q_{gmix}$  with respect to  $N_{gB}$ :

$$\mu_{gB} = -kT \left( \frac{\partial \ln Q_{gmix}}{\partial N_{gB}} \right)_{T, V_{gmix}, N_{gC}} \quad (16)$$

$$\mu_{gB} = -kT \left[ \begin{array}{l} \ln(V_{g_{mix}} - N_{g_{mix}} b_{mix}) - \frac{N_{g_{mix}} b_B}{V_{mix} - N_{g_{mix}} b_{mix}} - \ln \Lambda_B^3 - \ln N_{gB} + \ln q_{gB rot} + \ln q_{gB vibi} + \ln q_{gB e} + \\ \frac{1}{kT\sqrt{T}} \left( \frac{2N_{gB}(N_{gB} + N_{gC}) - N_{gB}^2}{(N_{gB} + N_{gC})^2} a_B - \frac{N_{gC}^2}{(N_{gB} + N_{gC})^2} a_C + \frac{2N_{gC}(N_{gB} + N_{gC}) - 2N_{gB}N_{gC}}{(N_{gB} + N_{gC})^2} a_{B,C} \right) \\ \frac{b_{mix}}{kT\sqrt{T}} \\ \frac{1}{kT\sqrt{T}} \left( \frac{a_{mix}(N_{gB} + N_{gC})}{b_{mix}^2} \left( \frac{N_{gB} + N_{gC} - N_{gB}}{(N_{gB} + N_{gC})^2} b_B - \frac{N_{gC}}{(N_{gB} + N_{gC})^2} b_C \right) \right) \\ \ln \left( \frac{V_{g_{mix}} + N_{g_{mix}} b_{mix}}{V_{g_{mix}}} \right) + \frac{N_{g_{mix}} a_{mix}}{kT\sqrt{T} b_{mix}} \frac{b_B}{V_{g_{mix}} + N_{g_{mix}} b_{mix}} \end{array} \right] \quad (17)$$

Then

$$\mu_{gB} = -kT \left[ \begin{array}{l} \ln(V_{g_{mix}} - N_{g_{mix}} b_{mix}) - \frac{N_{g_{mix}} b_B}{V_{g_{mix}} - N_{g_{mix}} b_{mix}} - \ln \Lambda_B^3 - \ln N_B + \ln q_{gB rot} + \ln q_{gB vibi} + \ln q_{gB e} + \\ \frac{1}{kT\sqrt{T}} \left[ \frac{(2y_B a_B + 2y_C a_{B,C} - y_B^2 a_B - y_C^2 a_C - 2y_B y_C a_{B,C})}{b_{mix}} - \frac{a_{mix} [y_C b_B + y_B b_B - b_{mix}]}{b_{mix}^2} \right] \\ \ln \left( \frac{V_{g_{mix}} + N_{g_{mix}} b_{mix}}{V_{g_{mix}}} \right) + \frac{N_{g_{mix}} a_{mix}}{kT\sqrt{T} b_{mix}} \frac{b_B}{V_{g_{mix}} + N_{g_{mix}} b_{mix}} \end{array} \right] \quad (18)$$

Using expressions (13) and (14), we may write:

$$\mu_{gB} = -kT \left[ \begin{array}{l} \ln(V_{g_{mix}} - N_{g_{mix}} b_{mix}) - \frac{N_{g_{mix}} b_B}{V_{g_{mix}} - N_{g_{mix}} b_{mix}} - \ln \Lambda_B^3 - \ln N_B + \ln q_{gB rot} + \ln q_{gB vibi} + \ln q_{gB e} + \\ \frac{2y_B a_B + 2y_C a_{B,C}}{kT\sqrt{T} b_{mix}} \ln \left( \frac{V_{g_{mix}} + N_{g_{mix}} b_{mix}}{V_{g_{mix}}} \right) - \frac{a_{mix}}{kT\sqrt{T} b_{mix}} \ln \left( \frac{V_{g_{mix}} + N_{g_{mix}} b_{mix}}{V_{g_{mix}}} \right) - \frac{a_{mix} b_B}{kT\sqrt{T} b_{mix}^2} \ln \left( \frac{V_{g_{mix}} + N_{g_{mix}} b_{mix}}{V_{g_{mix}}} \right) + \\ \frac{a_{mix}}{kT\sqrt{T} b_{mix}} \ln \left( \frac{V_{g_{mix}} + N_{g_{mix}} b_{mix}}{V_{g_{mix}}} \right) + \frac{N_{g_{mix}} a_{mix}}{kT\sqrt{T} b_{mix}} \frac{b_B}{V_{g_{mix}} + N_{g_{mix}} b_{mix}} \end{array} \right] \quad (19)$$

Then

$$\mu_{gB} = -kT \left[ \begin{array}{l} \ln \left( \frac{V_{g_{mix}} - N_{g_{mix}} b_{mix}}{N_{g_{mix}}} \right) - \frac{N_{g_{mix}} b_B}{V_{g_{mix}} - N_{g_{mix}} b_{mix}} - \ln \Lambda_B^3 - \ln y_B + \ln q_{gB rot} + \ln q_{gB vibi} + \ln q_{gB e} + \\ \frac{2y_B a_B + 2y_C a_{B,C}}{kT\sqrt{T} b_{mix}} \ln \left( \frac{V_{g_{mix}} + N_{g_{mix}} b_{mix}}{V_{g_{mix}}} \right) - \frac{a_{mix} b_B}{kT\sqrt{T} b_{mix}^2} \left[ \ln \left( \frac{V_{g_{mix}} + N_{g_{mix}} b_{mix}}{V_{g_{mix}}} \right) - \frac{N_{g_{mix}} b_{mix}}{V_{g_{mix}} + N_{g_{mix}} b_{mix}} \right] \end{array} \right] \quad (20)$$

The total pressure  $p$  may be calculated from the canonical partition function of the mixture

$$p = kT \left( \frac{\partial \ln Q_{g_{mix}}}{\partial V_{g_{mix}}} \right)_{T, N_{g_B}, N_{g_C}} \quad (21)$$

$$\frac{V_{g_{mix}} - N_{g_{mix}} b_{mix}}{N_{g_{mix}}} = \frac{kT}{p} \left[ \frac{V_{g_{mix}} - N_{g_{mix}} b_{mix}}{V_{g_{mix}}} \left( \frac{V_{g_{mix}}}{V_{g_{mix}} - N_{g_{mix}} b_{mix}} - \frac{N_{g_{mix}} a_{mix}}{kT \sqrt{T} (V_{g_{mix}} + N_{g_{mix}} b_{mix})} \right) \right] \quad (22)$$

Substituting (22) in (20) we obtain:

$$\mu_{g_B} = -kT \left[ \begin{aligned} & \ln \left( \frac{q_{g_B rot} q_{g_B vib} q_{g_B e}}{\Lambda_B^3} \right) kT - \ln p y_B + \ln \frac{V_{g_{mix}} - N_{g_{mix}} b_{mix}}{V_{g_{mix}}} - \frac{N_{g_{mix}} b_B}{V_{g_{mix}} - N_{g_{mix}} b_{mix}} + \\ & \frac{2y_B a_B + 2y_C a_{B,C}}{kT \sqrt{T} b_{mix}} \ln \left( \frac{V_{g_{mix}} + N_{g_{mix}} b_{mix}}{V_{g_{mix}}} \right) - \frac{a_{mix} b_B}{kT \sqrt{T} b_{mix}^2} \left[ \ln \left( \frac{V_{g_{mix}} + N_{g_{mix}} b_{mix}}{V_{g_{mix}}} \right) - \frac{N_{g_{mix}} b_{mix}}{V_{g_{mix}} + N_{g_{mix}} b_{mix}} \right] + \\ & \ln \left( \frac{V_{g_{mix}}}{V_{g_{mix}} - N_{g_{mix}} b_{mix}} - \frac{N_{g_{mix}} a_{mix}}{kT \sqrt{T} (V_{g_{mix}} + N_{g_{mix}} b_{mix})} \right) \end{aligned} \right] \quad (23)$$

The final expression of the chemical potential is:

$$\mu_{g_B} = -kT \ln \left( \frac{q_{g_B rot} q_{g_B vib} q_{g_B e}}{\Lambda_B^3} \right) + kT \ln p y_B + kT \ln \Phi'_B \quad (24)$$

with:

$$\bullet \quad \mu_{g_B}^0 = -kT \left[ \ln kT \frac{q_{g_B rot} q_{g_B e} q_{g_B vib}}{\Lambda_B^3} \right] \quad (25)$$

$$\bullet \quad \ln \Phi'_B = \frac{N_{g_{mix}} b_B}{V_{g_{mix}} - N_{g_{mix}} b_{mix}} - \ln \frac{V_{g_{mix}} - N_{g_{mix}} b_{mix}}{V_{g_{mix}}} - \frac{2y_B a_B + 2y_C a_{B,C}}{kT \sqrt{T} b_{mix}} \ln \left( \frac{V_{g_{mix}} + N_{g_{mix}} b_{mix}}{V_{g_{mix}}} \right) + \frac{a_{mix} b_B}{kT \sqrt{T} b_{mix}^2} \left[ \ln \left( \frac{V_{g_{mix}} + N_{g_{mix}} b_{mix}}{V_{g_{mix}}} \right) - \frac{N_{g_{mix}} b_{mix}}{V_{g_{mix}} + N_{g_{mix}} b_{mix}} \right] - \ln \left( \frac{p V_{g_{mix}}}{kT} \right) \quad (26)$$

Or

$$\Phi'_B = \frac{kT}{p V_{g_{mix}}} \frac{V_{g_{mix}}}{V_{g_{mix}} - N_{g_{mix}} b_{mix}} \exp \left( \frac{N_{g_{mix}} b_B}{V_{g_{mix}} - N_{g_{mix}} b_{mix}} \right) \left( \frac{V_{g_{mix}} + N_{g_{mix}} b_{mix}}{V_{g_{mix}}} \right)^{\frac{2y_B a_B + 2y_C a_{B,C}}{kT \sqrt{T} b_{mix}}} \left( \frac{V_{g_{mix}} + N_{g_{mix}} b_{mix}}{V_{g_{mix}}} \right)^{\frac{a_{mix} b_B}{kT \sqrt{T} b_{mix}^2}} \exp \left( - \frac{a_{mix} b_B}{kT \sqrt{T} b_{mix}^2} \frac{N_{g_{mix}} b_{mix}}{V_{g_{mix}} + N_{g_{mix}} b_{mix}} \right) \quad (27)$$

$\mu_{gB}^0$  is the standard chemical potential of component B, and  $\Phi'_B$  is the three-dimension fugacity coefficient of component B in the mixture.

We obtain:

$$\mu_{gB} = \mu_{gB}^0(T, 1) + kT \ln py_B + kT \ln \Phi'_B \quad (28)$$

The same expression may be derived for component C:

$$\mu_{gC} = \mu_{gC}^0(T, 1) + kT \ln py_C + kT \ln \Phi'_C \quad (29)$$

## 2-2. Non-ideal adsorbed phase modeling

We consider now a system composed of  $N_{aB}$  molecules of a compound B and  $N_{aC}$  molecules of a component C adsorbed on a surface A at temperature  $T$ . The molecules may interact with each others.  $U_{0B}$  and  $U_{0C}$  are the adsorption energies (minimum of  $u_{ads}(r)$ ). Only one layer of molecules B and C can be adsorbed. The adsorbed molecules can move on the surface (mobile adsorption).

The canonical partition function  $Q_{amix}$  is given by:

$$Q_{amix} = \frac{q_{aB}^{N_{aB}} q_{aC}^{N_{aC}}}{N_{aB}! N_{aC}!} \quad (30)$$

with:  $N_{amix} = N_{aB} + N_{aC}$

$$q_{aB} = q_{aB trans} q_{aB vib} q_{aB rot} q_{aB vibi} q_{aB e} \exp\left(\frac{-U_{int mix}}{2kT}\right) \exp\left(\frac{-U_{0B}}{kT}\right) \quad (31)$$

$$q_{aC} = q_{aC trans} q_{aC vib} q_{aC rot} q_{aC vibi} q_{aC e} \exp\left(\frac{-U_{int mix}}{2kT}\right) \exp\left(\frac{-U_{0C}}{kT}\right) \quad (32)$$

in which:

- $q_{aB trans}$  and  $q_{aC trans}$  are respectively the translational contributions to the partition functions  $q_{aB}$  and  $q_{aC}$  (2 degrees of freedom of the mass centre of the molecule);

- $q_{aB\ vib}$  and  $q_{aC\ vib}$  are respectively the contributions to the partition functions  $q_{aB}$  and  $q_{aC}$ ; due to the vibrations of the molecule perpendicularly to the surface;
- $q_{aB\ rot}$  and  $q_{aC\ rot}$  are respectively the rotational contributions to the partition functions  $q_{aB}$  and  $q_{aC}$  ;
- $q_{aB\ vibi}$  and  $q_{aC\ vibi}$  are respectively the contributions to the partition functions  $q_{aB}$  and  $q_{aC}$ ; due to the internal vibrations in the molecule;
- $q_{aB\ e}$  and  $q_{aC\ e}$  are respectively the electronic contribution to the partition functions  $q_{aB}$  and  $q_{aC}$ ;
- $\exp\left(-\frac{U_{0j}}{kT}\right)$  is the contribution of the adsorption energy of component  $j$ , with  $j=B$  or  $C$

The translation contribution to the partition function of component  $j$  may be written:

$$q_{aj\ trans} = \left[ \frac{2\pi m_j kT}{h^2} \right] A_{fmix} = \frac{A_{fmix}}{\Lambda_j^2} \quad (33)$$

in which  $A_{fmix}$  is the free surface available to the adsorbed molecules;

The contribution to the molecular partition function due to the interactions between the

adsorbed molecules is  $\exp\left(-\frac{U_{int\ mix}}{2kT}\right)$

- $U_{int\ mix}$  is the potential energy of interaction between any molecule of the adsorbed phase and all the others in the mixture.

It may be calculated by:

$$U_{int\ mix} = - \int_{d_{amix}}^{\infty} u(r) \frac{N_{amix}}{A} g(r) 2\pi r dr \quad (34)$$

in which:  $d_{amix}$  is the molecular diameter of the hypothetic molecule in the adsorbed phase.

The same developments as in the previous section may be done in the case of the adsorbed phase mixture. Using expressions similar to equations (34) to (40) (Part I):

$$U_{int\ mix} = -\frac{\pi d_{amix}^2}{b_{amix}} C_{mix} \sqrt{\frac{T_{amix}}{T}} \ln\left(1 + \frac{N_{amix} b_{amix}}{A}\right) \quad (35)$$

in which:

- $T_{amix}$  is the critical temperature of the hypothetic component representing the mixture (adsorbed phase);
- $C_{mix}$  is an energetic constant of the hypothetic component in the adsorbed phase;
- $b_{amix}$  is a parameter which characterizes the mixed adsorbed phase. It may be considered as the surface of the hypothetic molecule:

If we set then  $a_{amix} = \pi d_{amix}^2 C_{mix} \sqrt{T_{amix}}$ , which is defined as the two-dimension molecular attraction parameter of the hypothetic component.

The mixture parameters ( $b_{amix}$  and  $b_{amix}$ ) will be calculated thereafter using the pure component parameters of and appropriate mixing rules.

Equation (35) becomes:

$$U_{int\ mix} = -\frac{a_{amix}}{kT \sqrt{T} b_{amix}} \ln\left(1 + \frac{N_{am} b_{amix}}{A}\right) \quad (36)$$

By setting:

$$A_{fmix} = A - N_{amix} b_{amix} \quad (37)$$

Expression (30) becomes:

$$Q_{amix} = \frac{(A - N_{amix} b_{amix})^{N_{ab}} (A - N_{amix} b_{amix})^{N_{ac}}}{\Lambda_B^{2N_{ab}} N_{ab}! \Lambda_C^{2N_{ac}} N_{ac}!} \left( q_{ab\ rot} q_{ab\ vib} q_{ab\ vib} q_{ab\ e} \exp\left(\frac{-U_{intmix}}{2kT}\right) \exp\left(\frac{-U_{0B}}{kT}\right) \right)^{N_{ab}} \left( q_{ac\ rot} q_{ac\ vib} q_{ac\ vib} q_{ac\ e} \exp\left(\frac{-U_{intmix}}{2kT}\right) \exp\left(\frac{-U_{0C}}{kT}\right) \right)^{N_{ac}} \quad (38)$$

Combining equations (36) to (38) leads to:

$$\begin{aligned}
\ln Q_{amix} = & N_{aB} \ln(A - N_{amix} b_{amix}) - N_{aB} \ln A_B^2 - N_{aB} \ln N_{aB} + N_{aB} + N_{aB} \ln q_{aB rot} + N_{aB} \ln q_{aB vib} + \\
& N_{aB} \ln q_{aB vib} + N_{aB} \ln q_{aB e} + \frac{N_{aB} a_{amix}}{kT \sqrt{T} b_{amix}} \ln \left( \frac{A + N_{amix} b_{amix}}{A} \right) - \frac{N_{aB} U_{0B}}{kT} + N_{aC} \ln(A - N_{amix} b_{amix}) - \\
& N_{aC} \ln A_C^2 - N_{aC} \ln N_{aC} + N_{aC} + N_{aC} \ln q_{aC rot} + N_{aC} \ln q_{aC vib} + N_{aC} \ln q_{aC vib} + N_{aC} \ln q_{aC e} + \\
& \frac{N_{aC} a_{amix}}{kT \sqrt{T} b_{amix}} \ln \left( \frac{A + N_{amix} b_{amix}}{A} \right) - \frac{N_{aC} U_{0C}}{kT}
\end{aligned} \tag{39}$$

The chemical potential of component B in the adsorbed phase is obtained by differentiating  $\ln Q_{amix}$  with respect to  $N_{aB}$  using the same Lorentz-Berthelot mixing rules as in equations (13) and (14) but in adsorbed phase

$$a_{mix} = a_{aB} x_B^2 + a_{aC} x_C^2 + 2x_B x_C a_{aB,C} = a_{aB} \left( \frac{N_{aB}}{N_{amix}} \right)^2 + a_{aC} \left( \frac{N_{aC}}{N_{amix}} \right)^2 + 2 \frac{N_{aB} N_{aC}}{N_{amix}^2} a_{aB,C} \tag{40}$$

$$b_{mix} = b_{aB} x_B + b_{aC} x_C = b_{aB} \frac{N_{aB}}{N_{amix}} + b_{aC} \frac{N_{aC}}{N_{amix}} \tag{41}$$

in which:

- $a_{aB}$  and  $a_{aC}$  are respectively the intermolecular attraction parameters between B and B and between C and C in the adsorbed phase ;
- $x_B$  and  $x_C$  are respectively the mole fractions of the component B and C in the adsorbed phase;
- $b_{aB}$  and  $b_{aC}$  are the geometric parameters of pure components B and C in adsorbed phase;
- $a_{aB,C}$  is the attraction parameter between B and C in the adsorbed phase.

$a_{aB,C}$  may be calculated from  $a_{aB}$  and  $a_{aC}$  by  $a_{aB,C} = \sqrt{a_{aB} a_{aC}}$ .

The total spreading pressure  $\Pi$  may be calculated from the canonical partition function of the mixture

$$\Pi = kT \left( \frac{\partial \ln Q_{amix}}{\partial A_{amix}} \right)_{T, N_{aB}, N_{aC}} \tag{42}$$

The final expression of the chemical potential is then:

$$\mu_{aB} = -kT \left[ \ln \frac{(q_{aB \text{ rot}} q_{aB \text{ vib}} q_{aB \text{ vibi}} q_{aB \text{ e}}) kT}{\Lambda_B^2} - \frac{U_{0B}}{kT} - \ln \Pi x_B + \ln \frac{1/\Gamma_{mlmix} - b_{amix}}{1/\Gamma_{mlmix}} - \frac{b_{aB}}{1/\Gamma_{mlmix} - b_{amix}} + \frac{2x_B a_{aB} + 2x_C a_{aB,C}}{kT \sqrt{T} b_{amix}} \ln \left( \frac{1/\Gamma_{mlmix} + b_{amix}}{1/\Gamma_{mlmix}} \right) - \frac{a_{amix} b_{aB}}{kT \sqrt{T} b_{amix}^2} \left[ \ln \left( \frac{1/\Gamma_{mlmix} + b_{amix}}{1/\Gamma_{mlmix}} \right) - \frac{b_{amix}}{1/\Gamma_{mlmix} + b_{amix}} \right] + \ln \left( \frac{1/\Gamma_{mlmix}}{1/\Gamma_{mlmix} - b_{amix}} - \frac{a_{amix}}{kT \sqrt{T} (1/\Gamma_{mlmix} + b_{amix})} \right) \right] \quad (43)$$

in which  $\Gamma_{mlmix}$  is the molecular surface concentration of the mixture defined as:

$$\Gamma_{mlmix} = \frac{N_{amix}}{A} \quad (44)$$

Or

$$\bullet \quad \mu_{sB} = -kT \ln \frac{(q_{sB \text{ rot}} q_{sB \text{ vib}} q_{sB \text{ vibi}} q_{sB \text{ e}}) kT}{\Lambda_B^2} + U_{0B} + kT \ln \Pi x_B + kT \ln \Phi_B \quad (45)$$

with:

$$\bullet \quad \mu_{aB}^0 = -kT \ln \frac{(q_{aB \text{ rot}} q_{aB \text{ vib}} q_{aB \text{ vibi}} q_{aB \text{ e}}) kT}{\Lambda_B^2} + U_{0B} \quad (46)$$

$$\bullet \quad \ln \Phi_B = \ln \frac{1/\Gamma_{mix}}{1/\Gamma_{mix} - b_{amix}} + \frac{b_{aB}}{1/\Gamma_{mix} - b_{amix}} - \frac{2x_B a_{aB} + 2x_C a_{aB,C}}{kT \sqrt{T} b_{amix}} \ln \left( \frac{1/\Gamma_{mix} + b_{amix}}{1/\Gamma_{mix}} \right) + \frac{a_{amix} b_{aB}}{kT \sqrt{T} b_{amix}^2} \left[ \ln \left( \frac{1/\Gamma_{mix} + b_{amix}}{1/\Gamma_{mix}} \right) - \frac{b_{amix}}{1/\Gamma_{mix} + b_{amix}} \right] - \ln \left( \frac{\Pi}{kT} \frac{1}{\Gamma_{mix}} \right) \quad (47)$$

$\mu_{aB}^0$  is the standard chemical potential of pure component B in the adsorbed phase and  $\Phi_B$  is the two-dimension fugacity coefficient of component B in the mixture.

Finally, we obtain:

$$\mu_{aB} = \mu_{aB}^0(T,1) + kT \ln \Pi x_B + kT \ln \Phi_B \quad (48)$$

The same expression may be derived for component C:

$$\mu_{aC} = \mu_{aC}^0(T,1) + kT \ln \Pi x_C + kT \ln \Phi_C \quad (49)$$



### 2-3. Adsorption equilibrium

The adsorption equilibrium is obtained by the equality of the chemical potentials of both compounds in the adsorbed and gas phases.

$$\mu_{aB} = \mu_{gB} \quad (50)$$

$$\mu_{aC} = \mu_{gC} \quad (51)$$

$$\mu_{aB}^0(T,1) + kT \ln \Pi x_B + kT \ln \Phi_B = \mu_{gB}^0(T,1) + kT \ln p y_B + kT \ln \Phi'_B \quad (52)$$

$$\mu_{aC}^0(T,1) + kT \ln \Pi x_C + kT \ln \Phi_C = \mu_{gC}^0(T,1) + kT \ln p y_C + kT \ln \Phi'_C \quad (53)$$

$$\Phi_B x_B \Gamma_{mlmix} = \frac{\Lambda_B (q_{aB vib} q_{aB rot} q_{aB e} q_{aB vib})}{Z_{mlmix} kT (q_{gB rot} q_{gB e} q_{gB vib})} \exp\left(\frac{-U_{0B}}{kT}\right) p y_B \Phi'_B \quad (54)$$

$$\Phi_C x_C \Gamma_{mlmix} = \frac{\Lambda_C (q_{aC vib} q_{aC rot} q_{aC e} q_{aC vib})}{Z_{mlmix} kT (q_{gC rot} q_{gC e} q_{gC vib})} \exp\left(\frac{-U_{0C}}{kT}\right) p y_C \Phi'_C \quad (55)$$

where  $Z_{mlmix}$  is the molecular compressibility factor in the adsorbed phase:

$$Z_{mlmix} = \frac{\Pi}{kT} \frac{1}{\Gamma_{mlmix}}$$

If we suppose that there is no change in the rotational, internal, vibration and electronic contributions when the molecules of each component migrate from the gas phase to the adsorbed phase and by converting the expression to its molar form, we obtain:

$$\frac{1}{1-\Gamma_{mix} b_{amixmol}} \exp\left(\frac{\Gamma_{mix} b_{aBmol}}{1-\Gamma_{mix} b_{amixmol}}\right) (1+\Gamma_{mix} b_{amixmol})^{\frac{2x_B a_{aBmol} + 2x_C a_{aB,Cmol}}{RT\sqrt{T}b_{amix}}} (1+\Gamma_{mix} b_{amixmol})^{\frac{a_{amixmol} b_{aBmol}}{RT\sqrt{T}b_{amixmol}^2}}$$

$$\exp\left(-\frac{a_{amixmol} b_{aBmol}}{RT\sqrt{T}b_{amixmol}} \frac{\Gamma_{mix}}{1+\Gamma_{mix} b_{amixmol}}\right) \Gamma_{mix} x_B = \frac{hN_0}{RT\sqrt{2\pi M_B RT}} \frac{\exp\left(-\frac{h\nu_{zB}}{2RT}\right)}{1-\exp\left(-\frac{h\nu_{zB}}{RT}\right)} \exp\left(\frac{-U_{0B}}{RT}\right) p \quad (56)$$

$$\frac{RT}{P v_{mix}} \frac{v_{mix}}{v_{mix} - b_{mixmol}} \exp\left(\frac{b_{Bmol}}{v_{mix} - b_{mixmol}}\right) \left(\frac{v_{mix} + b_{mixmol}}{v_{mix}}\right)^{\frac{2y_B a_{Bmol} + 2y_C a_{B,Cmol}}{RT\sqrt{T}b_{mixmol}}} \left(\frac{v_{mix} + b_{mixmol}}{v_{mix}}\right)^{\frac{a_{mixmol} b_{Bmol}}{RT\sqrt{T}b_{mixmol}^2}}$$

$$\exp\left(-\frac{a_{mixmol} b_{Bmol}}{RT\sqrt{T}b_{mixmol}^2} \frac{b_{mixmol}}{v_{mix} + b_{mixmol}}\right) y_B$$

$$\frac{1}{1-\Gamma_{mix} b_{amixmol}} \exp\left(\frac{\Gamma_{mix} b_{aCmol}}{1-\Gamma_{mix} b_{amixmol}}\right) (1+\Gamma_{mix} b_{amixmol})^{\frac{2x_C a_{aCmol} + 2x_B a_{aB,Cmol}}{RT\sqrt{T}b_{amix}}} (1+\Gamma_{mix} b_{amixmol})^{\frac{a_{amixmol} b_{aCmol}}{RT\sqrt{T}b_{amixmol}^2}}$$

$$\exp\left(-\frac{a_{amixmol} b_{aCmol}}{RT\sqrt{T}b_{amixmol}} \frac{\Gamma_{mix}}{1+\Gamma_{mix} b_{amixmol}}\right) \Gamma_{mix} x_C = \frac{hN_0}{RT\sqrt{2\pi M_C RT}} \frac{\exp\left(-\frac{h\nu_{zC}}{2RT}\right)}{1-\exp\left(-\frac{h\nu_{zC}}{RT}\right)} \exp\left(\frac{-U_{0C}}{RT}\right) p \quad (57)$$

$$\frac{RT}{P v_{mix}} \frac{v_{mix}}{v_{mix} - b_{mixmol}} \exp\left(\frac{b_{Cmol}}{v_{mix} - b_{mixmol}}\right) \left(\frac{v_{mix} + b_{mixmol}}{v_{mix}}\right)^{\frac{2y_C a_{Cmol} + 2y_B a_{B,Cmol}}{RT\sqrt{T}b_{mixmol}}} \left(\frac{v_{mix} + b_{mixmol}}{v_{mix}}\right)^{\frac{a_{mixmol} b_{Cmol}}{RT\sqrt{T}b_{mixmol}^2}}$$

$$\exp\left(-\frac{a_{mixmol} b_{Cmol}}{RT\sqrt{T}b_{mixmol}^2} \frac{b_{mixmol}}{v_{mix} + b_{mixmol}}\right) y_C$$

where:

- $\Gamma_{mix}$  is the molar surface concentration;
- $a_{mixmol}$ ,  $b_{mixmol}$ ,  $a_{amixmol}$ ,  $b_{amixmol}$ ,  $a_{Bmol}$ ,  $b_{Bmol}$ ,  $a_{Cmol}$ ,  $b_{Cmol}$ ,  $a_{aBmol}$ ,  $b_{aBmol}$ ,  $a_{aCmol}$ ,  $b_{aCmol}$ ,  $a_{aB,Cmol}$  are respectively the molar expression corresponding to the molecular ones  $a_{mix}$ ,  $b_{mix}$ ,  $a_{amix}$ ,  $b_{amix}$ ,  $a_B$ ,  $b_B$ ,  $a_C$ ,  $b_C$ ,  $a_{aB}$ ,  $b_{aB}$ ,  $a_{aC}$ ,  $b_{aC}$ ,  $a_{aB,C}$ ;
- $M_B$  and  $M_C$  are respectively the molar mass of B and C;
- $v_{mix}$  is the molar volume of the gas phase;
- $N_0$  is the Avogadro number.

For given temperature  $T$ , pressure  $p$  and gas composition  $y_B$  equations (56) and (57) allow the calculation of  $\Gamma_{mix}$  as well as of the adsorbed phase composition  $x_B$ .

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3 As in the case of pure gases adsorption equilibria, the final expression may be obtained from  
4 purely macroscopic thermodynamics developments using the concept of fugacity coefficient  
5  
6 calculated from the equations of state.  
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### 10 **3. Results and discussion.**

11 We present some results of the surface concentration computed using the model developed  
12 above. These computations were carried out considering a given binary mixture of adsorbates  
13 on a given non-porous homogenous adsorbents at 283 K and at 400 kPa. We used the  
14 Lennard-Jones potential model to describe the adsorbate-adsorbent interaction and adequate  
15 three-dimension and two-dimension energetic and geometric parameters for each adsorbate  
16 [14]. For the gas phase model these parameters can be easily calculated from the critical  
17 parameters of the pure adsorbate, the adsorbed phase model parameters can be derived from  
18 adsorption experimental data (pure isotherms data).  
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32 In figure 1 we show the computed surface concentration of adsorbate B and adsorbate C in the  
33 binary mixture on a homogenous non-porous adsorbent at 283 K and 400 kPa as a function of  
34  $x_C$ . The corresponding selectivity curve is presented in figure 2  
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39 **Insert Figure 1**

40 **Insert Figure 2**

41 From these figures it appears that B is more adsorbed that as a consequence of the higher  
42 value of  $U_{0B}$   
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48 We compute the surface concentration and selectivity curves using different sets of parameter  
49 values ( $U_{0B}$  and  $U_{0C}$ ) for a given set of  $a_{aBmob}$ ,  $a_{aCmob}$ ,  $b_{aBmol}$  and  $b_{aCmol}$ . The results are  
50 illustrated in figure 3 and figure 4.  
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55 **Insert Figure 3**

56 **Insert Figure 4**

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3 The selectivity (figure 4) depends of the ratio between  $U_{0B}$  and  $U_0$ ; the selectivity can be  
4  
5 overturned if the ratio is reversed. From figure 3, we can see that the curve change  
6  
7 significantly for different values of the energy of interaction between the adsorbate and the  
8  
9 surface. If the ratio is reversed, the shape of the surface concentration curves varies.  
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11

#### 12 **4. Conclusion.**

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15 The prediction of multicomponent adsorption equilibria using single-component adsorption  
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17 data is one of the most challenging problems in adsorption studies. We propose a consistent  
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19 new model which may be obtained from macroscopic thermodynamics developments  
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21 although it relies on a statistical thermodynamic description of both phases. The methodology  
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23 assumes a non-ideal Redlich-Kwong behaviour for both the gas and adsorbed phases.  
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25 According to this approach, the prediction of multi-component adsorption equilibria from  
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27 single component data would require no extra parameters. The theoretical developments show  
28  
29 that the concept of fugacity coefficient may be defined for the adsorbed phase as well as for  
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31 gas phase. It appears that the expression of the fugacity coefficient in the adsorbed phase may  
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33 be calculated in the same way as for the gas phase by replacing the molar volume by the  
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35 inverse of the surface concentration and by replacing the pressure by the spreading pressure.  
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37 Such expressions of the fugacity coefficients are coherent with those provided by  
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39 macroscopic thermodynamics developments which required the equation of state of the  
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41 studied phase.  
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## List of figures

Figure 1. Adsorption isotherms of given adsorbates B and C in a binary mixture on a homogenous non-porous adsorbent at 283 K and 400 kPa. ( $a_{Bmol}$ :  $3.217 \text{ J m}^3 \text{ mol}^{-2}$ ;  $b_{Bmol}$ :  $2.95 \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-2}$ ;  $a_{aBmol}$ :  $4.18 \cdot 10^9 \text{ J m}^2 \text{ mol}^{-2}$ ;  $b_{aBmol}$ :  $4.45 \cdot 10^4 \text{ m}^2 \text{ mol}^{-2}$ ,  $a_{Cmol}$ :  $1.554 \text{ J m}^3 \text{ mol}^{-2}$ ;  $b_{Cmol}$ :  $2.67 \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-2}$ ;  $a_{aCmol}$ :  $8.10 \cdot 10^9 \text{ J m}^2 \text{ mol}^{-2}$ ;  $b_{aCmol}$ :  $7.88 \cdot 10^4 \text{ m}^2 \text{ mol}^{-2}$ ).

Figure 2. Selectivity curve of C in a binary mixture on a homogenous non-porous adsorbent at 283 K and 400 kPa. ( $a_{Bmol}$ :  $3.217 \text{ J m}^3 \text{ mol}^{-2}$ ;  $b_{Bmol}$ :  $2.95 \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-2}$ ;  $a_{aBmol}$ :  $4.18 \cdot 10^9 \text{ J m}^2 \text{ mol}^{-2}$ ;  $b_{aBmol}$ :  $4.45 \cdot 10^4 \text{ m}^2 \text{ mol}^{-2}$ ,  $a_{Cmol}$ :  $1.554 \text{ J m}^3 \text{ mol}^{-2}$ ;  $b_{Cmol}$ :  $2.67 \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-2}$ ;  $a_{aCmol}$ :  $8.10 \cdot 10^9 \text{ J m}^2 \text{ mol}^{-2}$ ;  $b_{aCmol}$ :  $7.88 \cdot 10^4 \text{ m}^2 \text{ mol}^{-2}$ ).

Figure 3. Adsorption isotherms of given adsorbates B and C in a binary mixture on a homogenous non-porous adsorbent at 283 K and 400 kPa. ( $a_{Bmol}$ :  $3.217 \text{ J m}^3 \text{ mol}^{-2}$ ;  $b_{Bmol}$ :  $2.95 \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-2}$ ;  $a_{aBmol}$ :  $4.18 \cdot 10^9 \text{ J m}^2 \text{ mol}^{-2}$ ;  $b_{aBmol}$ :  $4.45 \cdot 10^4 \text{ m}^2 \text{ mol}^{-2}$ ,  $a_{Cmol}$ :  $1.554 \text{ J m}^3 \text{ mol}^{-2}$ ;  $b_{Cmol}$ :  $2.67 \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-2}$ ;  $a_{aCmol}$ :  $8.10 \cdot 10^9 \text{ J m}^2 \text{ mol}^{-2}$ ;  $b_{aCmol}$ :  $7.88 \cdot 10^4 \text{ m}^2 \text{ mol}^{-2}$ ): Influence  $U_{0B}$  and  $U_{0C}$ .

Figure 4. Selectivity curves of C in a binary mixture on a homogenous non-porous adsorbent at 283 K and 400 kPa. ( $a_{Bmol}$ :  $3.217 \text{ J m}^3 \text{ mol}^{-2}$ ;  $b_{Bmol}$ :  $2.95 \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-2}$ ;  $a_{aBmol}$ :  $4.18 \cdot 10^9 \text{ J m}^2 \text{ mol}^{-2}$ ;  $b_{aBmol}$ :  $4.45 \cdot 10^4 \text{ m}^2 \text{ mol}^{-2}$ ,  $a_{Cmol}$ :  $1.554 \text{ J m}^3 \text{ mol}^{-2}$ ;  $b_{Cmol}$ :  $2.67 \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-2}$ ;  $a_{aCmol}$ :  $8.10 \cdot 10^9 \text{ J m}^2 \text{ mol}^{-2}$ ;  $b_{aCmol}$ :  $7.88 \cdot 10^4 \text{ m}^2 \text{ mol}^{-2}$ ): Influence  $U_{0B}$  and  $U_{0C}$ .

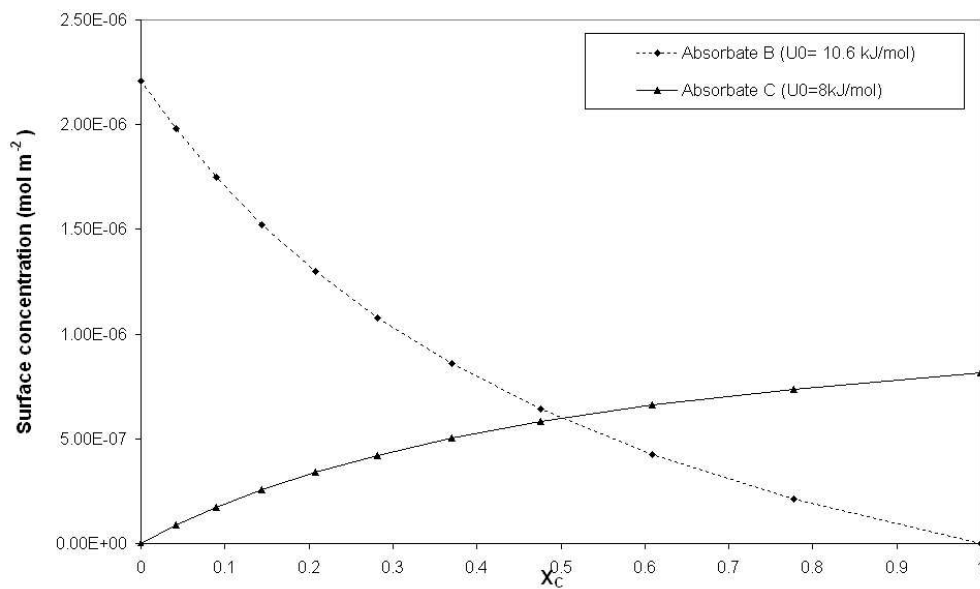


Figure 1. Adsorption isotherms of given adsorbates B and C in a binary mixture on a homogenous non-porous adsorbent at 283 K and 400 kPa. (aBmol: 3.217 J m<sup>3</sup> mol<sup>-2</sup>; bBmol: 2.95 10<sup>-5</sup> m<sup>3</sup> mol<sup>-2</sup>; aaBmol: 4.18 10<sup>9</sup> J m<sup>3</sup> mol<sup>-2</sup>; baBmol: 4.45 10<sup>4</sup> m<sup>3</sup> mol<sup>-2</sup>, aCmol: 1.554 J m<sup>3</sup> mol<sup>-2</sup>; bCmol: 2.67 10<sup>-5</sup> m<sup>3</sup> mol<sup>-2</sup>; aaCmol: 8.10 10<sup>9</sup> J m<sup>3</sup> mol<sup>-2</sup>; baCmol: 7.88 10<sup>4</sup> m<sup>3</sup> mol<sup>-2</sup>).



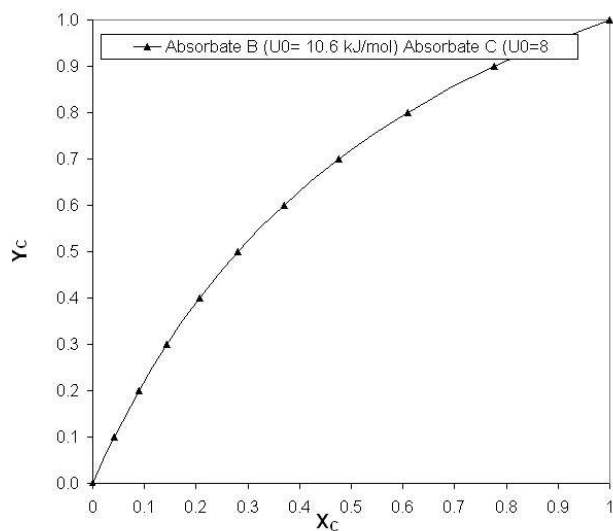


Figure 2. Selectivity curve of C in a binary mixture on a homogenous non-porous adsorbent at 283 K and 400 kPa. ( $a_{Bmol}$ :  $3.217 \text{ J m}^3 \text{ mol}^{-2}$ ;  $b_{Bmol}$ :  $2.95 \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-2}$ ;  $aa_{Bmol}$ :  $4.18 \cdot 10^9 \text{ J m}^3 \text{ mol}^{-2}$ ;  $ba_{Bmol}$ :  $4.45 \cdot 10^4 \text{ m}^3 \text{ mol}^{-2}$ ;  $a_{Cmol}$ :  $1.554 \text{ J m}^3 \text{ mol}^{-2}$ ;  $b_{Cmol}$ :  $2.67 \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-2}$ ;  $aa_{Cmol}$ :  $8.10 \cdot 10^9 \text{ J m}^3 \text{ mol}^{-2}$ ;  $ba_{Cmol}$ :  $7.88 \cdot 10^4 \text{ m}^3 \text{ mol}^{-2}$ ).

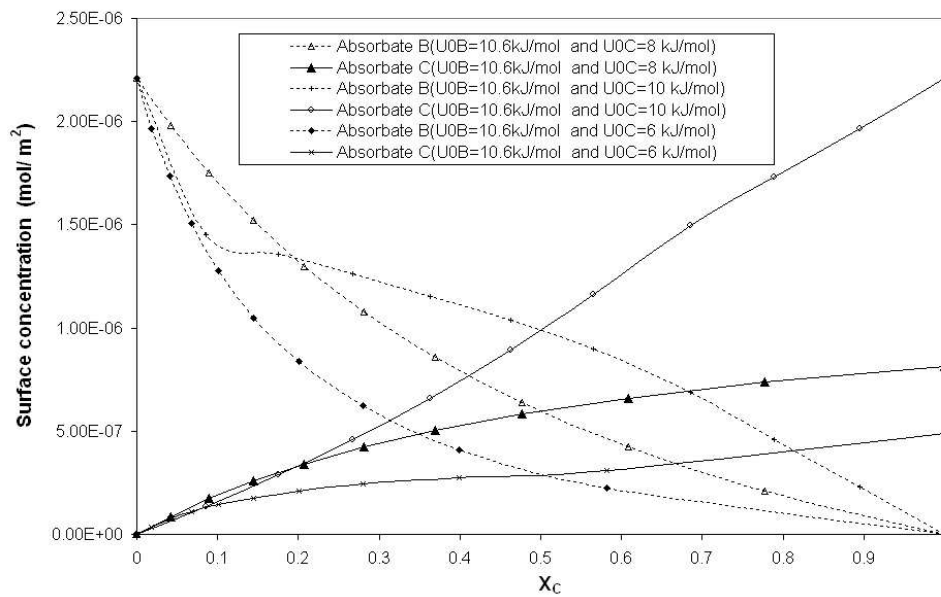


Figure 3. Adsorption isotherms of given adsorbates B and C in a binary mixture on a homogeneous non-porous adsorbent at 283 K and 400 kPa. (aBmol: 3.217 J m<sup>3</sup> mol<sup>-2</sup>; bBmol: 2.95 10<sup>-5</sup> m<sup>3</sup> mol<sup>-2</sup>; aaBmol: 4.18 10<sup>9</sup> J m<sup>3</sup> mol<sup>-2</sup>; baBmol: 4.45 10<sup>4</sup> m<sup>3</sup> mol<sup>-2</sup>, aCmol: 1.554 J m<sup>3</sup> mol<sup>-2</sup>; bCmol: 2.67 10<sup>-5</sup> m<sup>3</sup> mol<sup>-2</sup>; aaCmol: 8.10 10<sup>9</sup> J m<sup>3</sup> mol<sup>-2</sup>; baCmol: 7.88 10<sup>4</sup> m<sup>3</sup> mol<sup>-2</sup>): Influence  $U_{0B}$  and  $U_{0C}$ .

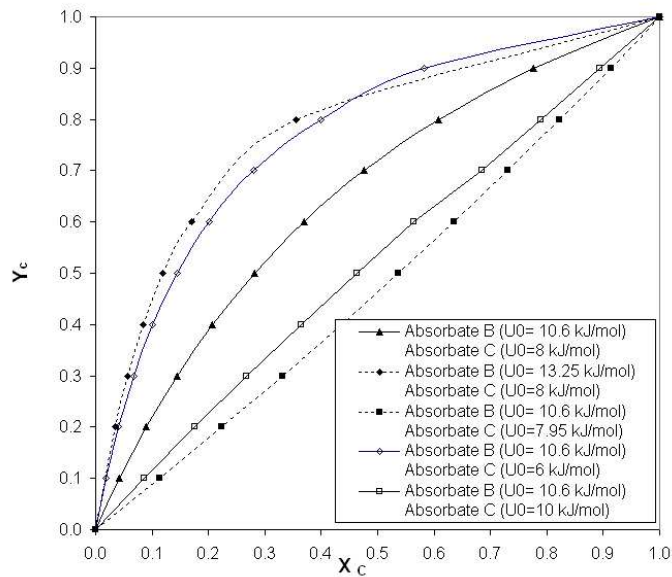


Figure 4. Selectivity curves of C in a binary mixture on a homogenous non-porous adsorbent at 283 K and 400 kPa. (aBmol:  $3.217 \text{ J m}^3 \text{ mol}^{-2}$ ; bBmol:  $2.95 \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-2}$ ; aaBmol:  $4.18 \cdot 10^9 \text{ J m}^3 \text{ mol}^{-2}$ ; baBmol:  $4.45 \cdot 10^4 \text{ m}^3 \text{ mol}^{-2}$ , aCmol:  $1.554 \text{ J m}^3 \text{ mol}^{-2}$ ; bCmol:  $2.67 \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-2}$ ; aaCmol:  $8.10 \cdot 10^9 \text{ J m}^3 \text{ mol}^{-2}$ ; baCmol:  $7.88 \cdot 10^4 \text{ m}^3 \text{ mol}^{-2}$ ): Influence  $U_{0B}$  and  $U_{0C}$ .