



THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

The Rigid Adsorbent Lattice Fluid Model for Pure and Mixed Gas Adsorption

Citation for published version:

Brandani, S 2018, 'The Rigid Adsorbent Lattice Fluid Model for Pure and Mixed Gas Adsorption', *AIChE Journal*. <https://doi.org/10.1002/aic.16504>

Digital Object Identifier (DOI):

[10.1002/aic.16504](https://doi.org/10.1002/aic.16504)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

AIChE Journal

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.



The Rigid Adsorbent Lattice Fluid Model for Pure and Mixed Gas

Adsorption

Stefano Brandani

School of Engineering, University of Edinburgh

The King's Buildings, Mayfield Road

Edinburgh EH9 3FB, U.K.

Abstract

The ability of macroscopic models to predict correctly multicomponent systems from pure component isotherms alone remains a major challenge in adsorption engineering. A new fundamental thermodynamic model for multicomponent adsorption of molecules of different size in nanoporous materials is derived from a modified lattice fluid model. Expressions for the fugacity coefficients are derived and the resulting equilibrium relationships are shown to be consistent with a type I adsorption isotherm. Expressions are obtained for the saturation capacity, the Henry law constant and the adsorption energy. The model is applied to silicalite and the parameters for the adsorbent are obtained from crystal properties, the adsorption energy of n-alkanes and Henry law constants for 6 gases. Model predictions for gas adsorption up to 20 bar are shown to be comparable to empirical adsorption isotherm equations. Extension to binary and quaternary systems shows good *a priori* predictive capability when compared to experimental data.

Keywords: Separations, thermodynamics, adsorption equilibria, lattice fluid.

Introduction

The use of a lattice fluid model to describe adsorption equilibrium has its roots in the widely used Langmuir adsorption isotherm. The Langmuir isotherm can be derived assuming a lattice with a fixed number of sites.¹⁻² Each molecule can adsorb on a single site, no site-site interactions are allowed and the lattice is treated as a mixture of vacancies and occupied sites. The derivation of several isotherms in common use using a lattice fluid approach is covered in detail by Hill,³ including cases where nearest-neighbour interactions between adsorbate molecules are included.

Thermodynamic consistency for the Langmuir isotherm requires that each site can accommodate only one molecule, which leads to the requirement that all saturation capacities should be the same.⁴ Extensions to heterogeneous solids lead to the widely adopted multi-site Langmuir model and similar thermodynamic consistency requirements impose that each type of site should have the same saturation capacity. The use of multi-site Langmuir isotherms, or other multi-parameter adsorption isotherm equations,^{1,5-6} can incorporate in an empirical manner the interactions between adsorbed molecules for a single adsorbate. These formulations can then be used to predict multicomponent adsorption on the basis of the Ideal Adsorbed Solution Theory (IAST).⁷ Where multicomponent data are available, non-ideality can be taken into account introducing activity coefficient models,^{1,8-9} i.e. the Non-Ideal Adsorbed Solution Theory (NIAST). While this may seem a reasonable approach, it is necessary to understand that this approach requires the calculation of the reference state of the pure adsorbates via the reduced grand potential,^{8,10} which can only be obtained from accurate pure component isotherms. These isotherms must be known from the very dilute state, which is difficult for very strongly adsorbed components, up to the reduced grand potential of the most strongly adsorbed component in the mixture, which is difficult to obtain for weakly adsorbed components. An alternative approach was developed by Danner and co-workers¹¹⁻¹⁴ based on the Vacancy Solution Theory (VST). This theory is based on considering a lattice which is a mixture of vacancies and molecules. This mixture is then modelled using either the Wilson activity coefficient model¹¹⁻¹² or the

Flory-Huggins activity coefficient model.¹³ To increase the flexibility of the model in the VST interactions between molecules and vacancies are included. The VST results in highly flexible pure component isotherms and has an advantage over the NIAST that it does not require the calculation of the reference state via the reduced grand potential when it is extended to multicomponent systems. The main weakness of the VST is the fact that it requires several empirical parameters and good quality data are needed to obtain meaningful parameters.¹⁴ Nevertheless, the accuracy of the results that can be obtained using the VST confirms that a lattice based approach to the formulation of a thermodynamic framework for adsorption systems can be very successful.

The use of empirical extensions of pure component isotherms to multicomponent systems or the use of multi-parameter pure component isotherms combined with the IAST have two clear deficiencies:

1) they do not allow to treat in a thermodynamically consistent manner molecules which are appreciably different in size; 2) they do not allow to predict adsorbate-adsorbate interactions based on the properties of fluid mixtures of the components.

In this contribution a new Rigid Adsorbent Lattice Fluid (RALF) model is presented and simple expressions for adsorption of mixtures are derived from a modification of the Lattice Fluid (LF) model of Sanchez and Lacombe.¹⁵⁻¹⁷ The LF model is specialised to the case in which the total volume of the lattice corresponds to the volume of the solid including the void space of the micropores.¹⁸

The RALF model bears many similarities to the Non Equilibrium Lattice Fluid (NELF) model of Doghieri and Sarti,¹⁹⁻²⁰ which has proven to be a very successful thermodynamic framework to model pure and mixed sorption of light gases and solvents in glassy polymers.²¹⁻²² The differences between the RALF and NELF frameworks stem from a different definition of the residual Gibbs energy and the allowance for a reduced packing efficiency in the adsorbed phase.

In this first publication on the RALF framework focus will be given to the derivation of the model and the application to the *frozen solid* limit, ie a solid adsorbent without flexibility. The RALF model for the *frozen solid* will be applied to silicalite in order to demonstrate how to obtain the parameters for

the solid and show how the model can be applied to the adsorption of both pure components and mixtures.

RALF model

Sanchez and Lacombe derived the LF model which considers a mixture of vacancies and molecules in a fixed lattice.¹⁵⁻¹⁷ The LF model results in a general Equation of State (EoS) that allows to calculate the chemical potential of dilute and dense phases and the vacancies are assumed to have no contribution to the interaction energy. As will be shown the LF model of Sanchez and Lacombe includes energy interactions and a Flory-Huggins combinatorial term. This is a relatively simple model that allows to include pair interactions and is applicable to molecules of different size. To extend this model to the case of a solid adsorbent it is necessary to take into account that the volume of the adsorbed phase is the volume of the solid including the void space within the solid.¹⁸ In the solid rigid links between fixed points limit the variation of the volume of the solid. Here *rigid adsorbent* refers to the presence of these rigid links and therefore is applicable also to flexible structures.

In the case of an adsorbent the density of the mixture does not correspond to the solution of the LF EoS, but the assumption is made that the functional dependency on density and composition of the Gibbs energy follows that of the LF model. This is the basis of the NELF model for glassy polymers¹⁹⁻²⁰ and this approach is adopted here for the rigid adsorbent. The volume of the system is assumed to be the volume occupied by the solid, including the micropores, and the constraint that specialises the LF model to adsorbents is

$$V = V_S = \frac{m_S}{\rho_S} = \frac{\sum_j m_j}{\rho} \quad (1)$$

In the most general formulation the closure equation is the specification of a constitutive equation for the EoS of the solid with and without adsorbates that allows to determine V_S .

$$V_S = V_S^\infty + (V_S^0 - V_S^\infty) \exp(-\beta_T P) + \Delta V_S \quad (2)$$

where V_S^0 is the solid volume in *vacuo*, V_S^∞ is the volume of the solid at infinite pressure *in the absence of adsorbates* and β_T represents the isothermal solid compressibility. The first two terms are the pure solid EoS in the absence of adsorbates. The limiting framework for the *frozen solid* is obtained assuming $\Delta V_S = 0$ and $\beta_T = 0$. In this case

$$V_S = V_S^0 = V_S^\infty \quad (3)$$

The *frozen solid* limit represents the normal case for adsorption in microporous materials that are not flexible. For flexible adsorbents the problem is divided in two parts:

- 1) defining the EoS for the solid in the absence of adsorbates, which will have a practically useful limit for the isothermal compressibility $\beta_T = 0$
- 2) defining the deviation function ΔV_S for which structural constraints will limit the range, ie the solid contains rigid links even when it is flexible.

If the simple expression given in eq. 2 holds, the first part is amenable to experimental determination using mercury porosimetry, as long as the relaxation time of the transitions in the solid are fast compared to the experimental time used. Repeated measurements at various sampling rates and in start-stop mode should allow the determination of the parameters: V_S^0 ; V_S^∞ ; and β_T .

For ΔV_S a reasonable assumption is that this term does not depend on pressure under conditions typical in adsorption systems. Keeping with the original assumption that the functional form of the Gibbs energy of the system follows the LF model, the closure of the problem is obtained from minimizing the total energy of a system that includes both the solid phase and the fluid phase, subject to the constraints imposed by the rigid links within the solid. These constraints may be known from crystallographic data or are kept as parameters to be defined to allow the model to describe adsorption in the presence of volume changes in the solid.

In what follows the RALF model equations for the *frozen solid* case are derived. In the LF model $r_j N_j$ are the lattice sites occupied by species j and N_0 are the vacancies. Therefore the total size of the lattice is given by

$$N_r = N_0 + \sum_j r_j N_j = N_0 + rN \quad (4)$$

If v^* is the average close packed volume of a mer molecule, the volume of the lattice is given by

$$V = v^* N_r = (N_0 + rN)v^* \quad (5)$$

The close-packed volume of the mixture is obtained when there are no vacancies

$$V^* = rNv^* \quad (6)$$

Therefore the reduced volume of the mixture is independent of v^*

$$\tilde{v} = \frac{1}{\tilde{\rho}} = \frac{V}{V^*} = \frac{N_0 + rN}{rN} \quad \text{and} \quad V = \frac{rNv^*}{\tilde{\rho}} \quad (7)$$

The volumetric fractions in the lattice are

$$\phi_j^L = \frac{r_j N_j}{N_0 + rN} \quad \text{and} \quad \phi_0^L = 1 - \sum_j \frac{r_j N_j}{N_0 + rN} = 1 - \tilde{\rho} \quad (8)$$

There is a general problem in defining the mixing rule for v^* , which in pure crystals could in principle be predicted from geometrical considerations. Sanchez and Lacombe¹⁷ introduce the first mixing rule which conserves the close-packed molecular volume of each component

$$r_j v^* = r_j^0 v_j^* \quad (9)$$

Other mixing rules are possible.^{17,23} This mixing rule is retained here since it provides a good approximation.¹⁷

In a purely predictive approach the close-packed volume can be taken to be the same as that of the molecules in the bulk fluid, but in the case of adsorbed molecules it is important to note that this may be larger than that of a bulk fluid due to confinement constraints.¹⁸ Therefore one may be justified in estimating specific v_j^* for the adsorbate/adsorbent pair, ie introduce a mixture parameter and a corresponding density

$$v_{jA}^* = (1 + \xi_{jA})v_j^* \quad \text{and} \quad \rho_{jA}^* = \frac{\rho_j^*}{1 + \xi_{jA}} \quad (10)$$

This correction, which is a major departure from the NELF approach, will not introduce an additional concentration dependence to the mixture parameters, so it will not affect the derivations of the

chemical potentials. As a result “A” will be omitted in the expressions that follow, with the understanding that eq. 10 is used to express v_j^* and ρ_j^* of the adsorbed phase.

Eq. 9 preserves the additivity of the close-packed volumes¹⁷ and leads to

$$V^* = \sum_j r_j^0 N_j v_j^* = rNv^* \quad (11)$$

In the LF model the final assumption made is to preserve the number of pair interactions in the close-packed state, which leads to¹⁶⁻¹⁷

$$\sum_j r_j^0 N_j = rN \quad (12)$$

and if the volume fractions at close-packing are introduced, $\phi_j = \frac{r_j^0 N_j}{rN}$, from eqs 4-6

$$\frac{1}{v^*} = \sum_j \frac{\phi_j}{v_j^*} \quad (13)$$

The close-packed mass density, ρ^* , is defined as

$$\frac{\sum_j m_j}{\rho^*} = \sum_j \frac{m_j}{\rho_j^*} \quad \text{or} \quad \frac{1}{\rho^*} = \sum \frac{w_i}{\rho_i^*} \quad (14)$$

This allows to write the volume fractions at close-packing also as $\phi_j = \frac{m_j/\rho_j^*}{\sum_k m_k/\rho^*}$

To within additive constants and terms that depend on temperature, the Gibbs energy of the LF was derived by Sanchez and Lacombe.¹⁶⁻¹⁷ The expression for the Gibbs energy can be written as¹⁷

$$\frac{G^{SL}}{NRT} = r \left[-\frac{\tilde{\rho}}{\tilde{T}} + \frac{(1-\tilde{\rho}) \ln(1-\tilde{\rho})}{\tilde{\rho}} + \frac{\ln(\tilde{\rho})}{r} + \sum_j \frac{\phi_j}{r_i} \ln(\phi_j) \right] + z \quad (15)$$

The origin of the terms in eq. 15 are more easily understood if one considers that the LF model is the sum of the combinatorial entropy of an *athermal solution* that includes the contribution of the vacancies and the energy term of a *regular solution*²⁴⁻²⁵

$$\frac{G^{SL}}{NRT} = r \left[-\frac{\tilde{\rho}}{\tilde{T}} + \frac{N_0}{N} \ln \phi_0^L + \sum_i \frac{N_i}{N} \ln \phi_i^L \right] + z \quad (16)$$

That the two expressions are equivalent becomes clear considering that

$$\frac{N_i}{N} = x_i = \frac{\phi_i}{r_i} r = \frac{\phi_i^0}{r_i^0} r \quad \text{and} \quad \frac{N_0}{N} = \frac{1-\tilde{\rho}}{\tilde{\rho}} r \quad (17)$$

and that the volume fractions in the lattice are given by

$$\phi_i^L = \frac{r_i N_i}{N} \frac{N}{N_T} = \phi_i \tilde{\rho} \quad \text{and} \quad \phi_0^L = 1 - \tilde{\rho} \quad (18)$$

If one recognises that eq. 15 is neither an excess nor a residual Gibbs energy the following expression for the residual Gibbs energy can be obtained (the full derivation is given in the Supplementary Materials - see Appendix 1).

$$\frac{G^R(T,P,N)}{RT} = rN \left[-\frac{\tilde{\rho}}{\tilde{T}} + \frac{(1-\tilde{\rho}) \ln(1-\tilde{\rho})}{\tilde{\rho}} + 1 \right] + N\tilde{\rho} \sum_j x_j \ln \left(\frac{\phi_j}{x_j} \right) + N(z - 1 - \ln z) \quad (19)$$

$$\text{with} \quad \tilde{\rho} = \frac{\rho}{\rho^*} \quad \tilde{T} = \frac{T}{T^*} \quad z = \frac{PV}{NRT} = r \frac{\tilde{P}}{\tilde{\rho}\tilde{T}} \quad \tilde{P} = \frac{P}{P^*}$$

$$\text{and the corresponding ideal gas term } \frac{G^{IG}}{RT} = \frac{G_0^{IG}}{RT} + N \ln \frac{P}{P_0} + N \sum_j x_j \ln x_j$$

In the LF model, RT^* is the characteristic interaction energy of the mixture and P^* is an energy density.¹⁵⁻¹⁷ The following relationship links the characteristic parameters

$$P^* v^* = RT^* \quad (20)$$

It is clear that if v_j^* is corrected for the confinement constraints in the adsorbed phase, then the energy density P_j^* will be correspondingly lower. The correction should be $1/(1 + \xi_{jA})$ if eq. 20 for all components is applied maintaining T_j^* unchanged. To add further flexibility to the model, one could in principle allow for an additional empirical parameter to be added in the description of the pure component isotherms, but then both P_{jA}^* and T_{jA}^* would have to be corrected by the corresponding amount.

In eq. 19 the energy term and the combinatorial term are both scaled by the reduced density in order for the model to reduce to the ideal gas mixture as the reduced density goes to zero. From the definition of the compressibility factor in an EoS, it is possible to obtain

$$z^{EoS} - 1 = r \left[-\frac{\tilde{\rho}}{\tilde{T}} - \frac{\ln(1-\tilde{\rho})}{\tilde{\rho}} - 1 \right] + \tilde{\rho} \sum_j x_j \ln \frac{\phi_j}{x_j} \quad (21)$$

$$\text{If the density was allowed to reach equilibrium } z = r \frac{\tilde{P}}{\tilde{\rho}\tilde{T}} = z^{EoS}$$

All the expressions given above include the number of lattice sites occupied by the solid, r_s . In the case of an adsorbent, as is the case for a polymer, this will go to infinity,¹⁷ which means that in this

limit any end effects are negligible. Clearly as $r_S \rightarrow \infty$ so does the *molecular mass of the solid* and therefore $N_S \rightarrow 0$. In this limit, there is one important change that needs to be considered in the expression of the residual Gibbs energy. The combinatorial contribution needs to reflect the fact that due to the rigid nature of the solid, and the fact that $N_S \rightarrow 0$, the solid does not contribute to the combinatorial term, but has the effect of reducing the volume available to the molecules in the lattice. Therefore in the RALF framework the residual Gibbs energy of the adsorbed phase is

$$\frac{G_A^R(T,P,N)}{RT} = rN \left[-\frac{\tilde{p}}{\tilde{T}} + \frac{(1-\tilde{p})\ln(1-\tilde{p})}{\tilde{p}} + 1 \right] + N\tilde{p} \sum_i x_i \ln \frac{\phi_i}{(1-\phi_S)x_i} + N(z-1-\ln z) \quad (22)$$

Equations 2 and 22 constitute the fundamental definitions of the adsorbed phase in the RALF framework. It is possible to see that despite its relative simplicity this framework provides a very powerful tool in the case of heterogeneous adsorbents. Given that end effects will be negligible as $r_S \rightarrow \infty$, the solid can be considered as a mixture of separate r-mers itself. For an adsorbent with two distinct interaction sites, in the RALF model a fraction can be introduced to identify the relative abundance of sites. The expressions remain the same, but with one additional component and one additional mixture parameter. The mean field approximation distributes the two types of sites uniformly within the lattice. What is described above is the RALF equivalent of a Dual Site Langmuir (DSL) isotherm, where the sites form a uniform solid solution. This would be a *mixed solid* heterogeneous RALF model. There is clearly another alternative, where the RALF model is written for two separate solid phases. This would be representative of zeolites with two distinct cages or channels of differing size. In this formulation a solid-solid-fluid equilibrium problem is obtained and this would require the solution of the equilibrium equations imposing that *each solid phase* is at equilibrium with the fluid. Clearly this could be an approach applicable also to mixed matrix materials and would be applicable to materials used in mixed matrix membranes. This would be a *separated solid* heterogeneous RALF model.

The use of different types of adsorption sites can also be extended to the more general case where a distribution of sites is known. The sum over the “solid fractions” is replaced by an integral over the distribution. This can be applied to both mixed and separated solid approaches and would form the basis for a model of solids that have broad pore size distributions, such as silica gel and activated carbons.

From the discussion presented above, it should be clear that the RALF framework can be used to describe many different systems and can be extended to more complex formulations provided that enough information is available to determine the relevant parameters. As such the RALF framework is a platform that can be used also to convert data from molecular simulations into a macroscopic model (see for example²⁶) and provides a bridge to perform detailed adsorption process simulations based on a thermodynamically consistent methodology to describe multicomponent adsorption. Given the many possible avenues that can be pursued, the focus of this paper will be that of understanding the link between the RALF framework and traditional adsorption models for the limiting case of the *frozen solid*. This is in itself a major task, which is essential if the adsorption engineering practitioners are to be convinced of the usefulness of this new approach and to ensure rapid take-up.

RALF model for the *frozen solid*.

Assuming the validity of the *frozen solid* limit, with this constraint all the expressions needed to derive the chemical potentials from the RALF framework are defined. All that remains to be decided is the basis for the definition of the chemical potentials. The natural variables in the thermodynamics of adsorption are the absolute adsorbed amounts^{8, 18, 27} defined as the number of moles per unit mass of adsorbent, n_i , or per unit volume of adsorbent that includes the micropores, q_i . Here consistency is maintained with the notation used by Myers and Monson,⁸ mass of solid basis, and Ruthven,¹ volume of solid basis. In order to have a model applicable to the case in which the volume

of the solid is allowed to change, here moles will be used for the adsorbates and mass will be used for the solid.

The use of an asymmetric convention avoids any confusion if the RALF framework is to be used with other models for the fluid phase defined on a mole basis. The residual chemical potentials are

$$\frac{\mu_k^R}{RT} = \frac{1}{RT} \left(\frac{\partial G_A^R}{\partial N_k} \right)_{T,P,N_{j \neq k}} = \ln \varphi_k \quad \frac{\mu_S^{Rm}}{RT} = \frac{1}{RT} \left(\frac{\partial G_A^R}{\partial m_S} \right)_{T,P,N_{j \neq S}} \quad (23)$$

where φ_k is the fugacity coefficient of adsorbate k .

All the summations will include the solid if the index j is used. The solid is the last component, given that in the LF model component 0 is reserved for the vacancies. The sums over the adsorbates will use the index i .

Given that the Gibbs energy at constant temperature and pressure is a homogeneous function of degree 1 in both masses and moles of the components the following relationship applies

$$\frac{G_A^R}{RT} = \sum_i \frac{N_i \mu_i^R}{RT} + \frac{m_S \mu_S^{Rm}}{RT} \quad (24)$$

Note also that there is direct proportionality between m_S and N_S , which means that $\frac{dN_S}{dm_S} = \frac{N_S}{m_S}$.

To derive the chemical potentials a mixing rule for the energy density has to be specified. One of the strengths of the LF model is that it results in relatively simple expressions with parameters that have a physical meaning, but extensions are clearly possible if for example the energy term is treated via a mixing rule at a fixed reduced density and combined with the corresponding expressions of common excess Gibbs energy models.²⁸⁻³⁰ Here the emphasis is on understanding what the RALF model is in comparison to standard multiparameter adsorption isotherm models and the IAST. Therefore the standard mixing rules suggested by Sanchez and Lacombe¹⁷ will be applied:

$$P^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \phi_2 \Delta P^* \quad (25)$$

with $\Delta P^* = P_1^* + P_2^* - 2(1 - \kappa_{12})\sqrt{P_1^* P_2^*}$

This is in fact the classical quadratic mixing rule in terms of the volume fractions in the close-packed state and can be rewritten in more general terms as²⁵

$$P^* = \sum_j \sum_k \phi_j \phi_k P_{jk}^* \quad (26)$$

$$\text{with } P_{jk}^* = P_{kj}^* = (1 - \kappa_{kj}) \sqrt{P_k^* P_j^*} \quad \text{and } \kappa_{kk} = 0.$$

Chemical potential of the adsorbates

The following expression for the chemical potential for a mixture of adsorbate molecules is obtained in the *frozen solid* limit (the full derivation is reported in Appendix 2 in the Supplementary Materials)

$$\frac{\mu_k^R}{RT} = -\frac{\tilde{\rho}}{\tilde{T}} r_k \left(2 \frac{\sum_j \phi_j P_{kj}^*}{P^*} - 1 \right) + \left[\frac{(1-\tilde{\rho}) \ln(1-\tilde{\rho})}{\tilde{\rho}} + 1 \right] r_k^0 + \frac{r_k}{r} (z^{EoS} - 1) - \ln z + \tilde{\rho} \left(\ln \frac{r_k}{r(1-\phi_S)} + 1 - \frac{r_k}{r(1-\phi_S)} \right) \quad (27)$$

with

$$z^{EoS} - 1 = r \left[-\frac{\tilde{\rho}}{\tilde{T}} - \frac{\ln(1-\tilde{\rho})}{\tilde{\rho}} - 1 \right] + \tilde{\rho} \sum_i x_i \ln \frac{\phi_i}{x_i(1-\phi_S)} \quad (28)$$

With the corresponding ideal gas term $\frac{\mu_k^{IG}}{RT} = \frac{\mu_{k0}^{IG}(T)}{RT} + \ln \frac{P}{P_0} + \ln x_k$

For the single adsorbate $x_1 = 1$ and $\frac{r_1}{r} = \phi_1 = 1 - \phi_S$, therefore

$$\frac{\mu_1^R}{RT} = -\frac{\tilde{\rho}}{\tilde{T}} r_1 \left(2 \frac{\sum_j \phi_j P_{1j}^*}{P^*} - 1 \right) + \left[\frac{(1-\tilde{\rho}) \ln(1-\tilde{\rho})}{\tilde{\rho}} + 1 \right] r_1^0 + r_1 \left[-\frac{\tilde{\rho}}{\tilde{T}} - \frac{\ln(1-\tilde{\rho})}{\tilde{\rho}} - 1 \right] - \ln z \quad (29)$$

The phase equilibrium problem is completed by the expression of the chemical potential of the components in the fluid phase. If the LF EoS for a pure component is used, the chemical potential can be obtained from the molar Gibbs energy directly from eq. 19

$$\frac{\mu_{1F}^R}{RT} = r_1^0 \left[-\frac{\tilde{\rho}_1}{\tilde{T}_1} + \frac{(1-\tilde{\rho}_1) \ln(1-\tilde{\rho}_1)}{\tilde{\rho}_1} + 1 \right] + z - 1 - \ln z \quad (30)$$

where the pure component reduced density is calculated solving the EoS.

$$r_1^0 \frac{\tilde{\rho}_1}{\tilde{T}_1} = \tilde{\rho}_1 + r_1^0 \left[-\frac{\tilde{\rho}_1^2}{\tilde{T}_1} - \tilde{\rho}_1 - \ln(1 - \tilde{\rho}_1) \right] \quad (31)$$

For the more general case of a fluid mixture and the LF EoS,

$$\frac{\mu_{kF}^R}{RT} = -\frac{\tilde{\rho}_F}{\tilde{T}_F} r_{kF} \left(2 \frac{\sum_i \phi_i P_{ik}^*}{P_F^*} - 1 \right) + \left[\frac{(1-\tilde{\rho}_F) \ln(1-\tilde{\rho}_F)}{\tilde{\rho}_F} + 1 \right] r_k^0 + \frac{r_k}{r_F} \left(r_F \frac{\tilde{P}_F}{\tilde{\rho}_F \tilde{T}_F} - 1 \right) - \ln z + \tilde{\rho}_F \left(\ln \frac{r_k}{r_F} + 1 - \frac{r_k}{r_F} \right) \quad (32)$$

Equation 32 can be written from eq. 27 substituting $\phi_S = 0$ and $z^{Eos} = z$. The reduced density of the fluid is obtained solving

$$r_F \frac{\tilde{P}_F}{\tilde{T}_F} = \tilde{\rho}_F + r_F \left[-\frac{\tilde{\rho}_F^2}{\tilde{T}_F} - \tilde{\rho}_F - \ln(1 - \tilde{\rho}_F) \right] + \tilde{\rho}_F^2 \sum_i x_i \ln \frac{\phi_i}{x_i} \quad (33)$$

For each component the equilibrium relationship is given by

$$\frac{\mu_k^R}{RT} - \frac{\mu_{kF}^R}{RT} = \ln \frac{y_k}{x_k} \quad (34)$$

Simultaneous solution of eqs. 33 and 34 for each adsorbate allows to determine all $n_i(f)$, and in all the expressions $m_S = 1$ kg is used. For a single adsorbate the RHS of eq. 34 is zero and the corresponding expressions for a single adsorbate must be solved.

It is not immediately obvious that eq. 29 contains the thermodynamically correct limits of a type I isotherm at both zero pressure, Henry's law, and infinite pressure, finite saturation. The saturation concentration, by inspection and from the definition of the close-packed state, corresponds to $\tilde{\rho} = 1$.

For the case of a single adsorbate

$$\frac{N_1^{Sat}}{m_S} = n_1^{Sat} = \frac{1}{Mw_1} \frac{\rho_1^*}{\rho_S^*} \left(1 - \frac{\rho_S}{\rho_S^*} \right) \quad (35)$$

For the Henry law constant the starting point is the definition of the linear isotherm at low pressures

$$n_1 = \frac{N_1}{m_S} = K_P(T)P \quad (36)$$

where at low pressure the assumption $\varphi_{1P}^F = \varphi_{1P_0}^F = 1$ is made for the fugacity coefficient in the pure fluid.

At infinite dilution and in the limit of low pressure

$$\frac{\mu_{1\infty}^R}{RT} = -\frac{\tilde{\rho}_S}{\tilde{T}_S} r_1^0 \frac{v_1^*}{v_S^*} 2 \frac{P_{1S}^*}{P_S^*} + \left[\frac{(1-\tilde{\rho}_S) \ln(1-\tilde{\rho}_S)}{\tilde{\rho}_S} + 1 \right] r_1^0 + r_1^0 \frac{v_1^*}{v_S^*} \left[-\frac{\ln(1-\tilde{\rho}_S)}{\tilde{\rho}_S} - 1 \right] - \ln \frac{1 \text{ kg}}{\rho_S RT} + \ln K_P \quad (37)$$

$$\text{with } \tilde{\rho}_S = \frac{\rho_S}{\rho_S^*} \quad \tilde{T}_S = \frac{T}{T_S^*}$$

In this limit $\frac{\mu_{1P}^R}{RT} = 0$, ie the residual pure component chemical potential in the fluid phase is zero, therefore the equilibrium relationship gives

$$\ln K_P = \ln \frac{1 \text{ kg}}{\rho_S RT} + \frac{\tilde{\rho}_S}{RT} r_1^0 v_1^* 2P_{1S}^* - \left[\frac{(1-\tilde{\rho}_S) \ln(1-\tilde{\rho}_S)}{\tilde{\rho}_S} + 1 \right] r_1^0 - r_1^0 \frac{v_1^*}{v_S^*} \left[-\frac{\ln(1-\tilde{\rho}_S)}{\tilde{\rho}_S} - 1 \right] \quad (38)$$

The dimensionless Henry law constant is given by

$$\ln K = \ln(\rho_S RT K_P) = \frac{\tilde{\rho}_S}{RT} r_1^0 v_1^* 2P_{1S}^* - \left[\frac{(1-\tilde{\rho}_S) \ln(1-\tilde{\rho}_S)}{\tilde{\rho}_S} + 1 \right] r_1^0 - r_1^0 \frac{v_1^*}{v_S^*} \left[-\frac{\ln(1-\tilde{\rho}_S)}{\tilde{\rho}_S} - 1 \right] \quad (39)$$

From the expression of the Henry law constant it is possible to see that

$$\frac{d \ln K_P}{dT} = -\frac{\tilde{\rho}_S}{RT^2} r_1^0 v_1^* 2P_{1S}^* - \frac{1}{T} \quad (40)$$

Which gives for the adsorption energy at zero loading

$$-\Delta U_0 = -\Delta H_0 + RT = -\tilde{\rho}_S r_1^0 v_1^* 2P_{1S}^* \quad (41)$$

Equation 41 shows that the adsorption energy at zero loading is only a function of P_S^* and $\tilde{\rho}_S$ and is independent of T_S^* .

Equations 35 and 38 can also be used to determine the equivalent parameters of the Langmuir

adsorption isotherm, $n_1^{Lang} = n_1^{Sat} b_P P / (1 + b_P P)$, since the saturation capacity, n_1^{Sat} , would be the same in both models and the Henry law constant is simply $b_P n_1^{Sat} = K_P$.

The chemical potential for the solid is reported in the Supplementary Material. This allows to check the internal consistency of the expressions for the chemical potentials through the Gibbs adsorption isotherm.⁸

RALF model parameters and their determination for silicalite.

The pure component parameters of the LF EoS for several molecules of interest are available in the literature.^{15, 31} If these are not available, Sanchez and Lacombe¹⁵ suggest to use vapour pressure data and the density at the normal boiling point to obtain the EoS parameters and these data are readily

available for many molecules.³² Table 1 gives the values of the pure component LF parameters used in this study.

For each adsorbent 3 parameters need to be specified: ρ_S^* , P_S^* and T_S^* or v_S^* . It is also necessary to know the density of the solid, ρ_S . In the *frozen solid* limit the solid density at the close-packed state, ρ_S^* , can be taken as the skeletal density of the adsorbent and can be measured to sufficient accuracy using helium pycnometry. The density of the solid including the micropore volume, ρ_S , can be measured directly using mercury porosimetry, or indirectly from the skeletal density through the determination of the micropore volume. Methods for this type of measurement have been discussed in detail and formulated as a recent IUPAC recommendation³³ and additional comments can be found in the literature.^{8, 18}

P_S^* and T_S^* or v_S^* have to be determined from adsorption data and the simplest approach is to find Henry constants for various molecules. P_S^* can be determined from a regression of the zero loading adsorption energy for different molecules, assuming as a first approximation $\xi_{1A} = 0$ and $\kappa_{1S} = 0$ for all the molecules. T_S^* can then be obtained from the Henry law constants at a fixed temperature. If full isotherms are available, then a simultaneous fit of P_S^* and T_S^* and the parameters κ_{1S} , ξ_{1A} of each adsorbate can be carried out.

As an example consider data available for silicalite. The Atlas of Zeolite Types³⁴ reports for MFI a framework density of 17.9, which corresponds to a density of the solid including the micropores, $\rho_S = 1786 \text{ kg/m}^3$. Using the porosity predicted from simulating He adsorption on silicalite¹⁸ of 0.307, the skeletal density is $\rho_S^* = 2577 \text{ kg/m}^3$.

For silicalite a linear correlation as a function of carbon number for the zero loading enthalpy of adsorption for n-alkanes has been observed.³⁵⁻³⁷ From this a value of $P_S^* = 650 \text{ MPa}$ is found. Figure 1 shows the excellent agreement with literature values³⁵⁻³⁷ up to n-C₁₀.

Golden and Sircar³⁸ report Henry law constants at approximately 30 °C for 6 small molecules (CH₄, N₂, CO, Ar, CO₂, and Kr) in silicalite. This allows to estimate $T_S^* = 1060 \text{ K}$. Figure 2 shows the comparison

between the experimental and calculated isotherms at different temperatures for the 6 molecules. As Golden and Sircar point out,³⁸ the gases are “sufficiently diverse due to the difference in their sizes, polarizability, and permanent polarity” and provide enough information to define the estimate of the final parameter in the RALF model.

Pure component and mixture data (up to the quaternary system), for light hydrocarbons up to C₄, at 300 K and 345 kPa on commercial silicalite pellets are available.³⁵ Assuming a fraction of crystalline material of 0.77¹⁸ and neglecting adsorption on the binder, the pure component isotherms are used to determine ξ_{iA} and κ_{iS} and Fig. 3 shows the results of the fits of the isotherms at 300 K along with the 3-parameter fit of the Toth isotherm.³⁵ The parameters for methane are not directly portable from the previous dataset, which could indicate some differences in the sample used, possibly a different Si/Al ratio. The difference in the isotherms is small, but given that the purpose of this comparison is to show predictions of multicomponent isotherms using the RALF framework, it is important that the pure component isotherms at the same temperature are correlated accurately to be able to compare the RALF predictions with those based on the Toth model, which was selected as the model that matched best the original pure component isotherms.³⁵

In the Supplementary Materials the predictions of the RALF model based on the 2 parameters obtained at 300 K are compared with data for 3 additional temperatures.³⁵ The agreement is satisfactory, particularly considering that no additional temperature dependent parameters are introduced. By comparison the Langmuir model would require 3 parameters: b_p , n_1^{Sat} and the enthalpy of adsorption.

To demonstrate the application of the RALF model to multicomponent adsorption the 4 binary mixtures and the quaternary system³⁵ are compared to the RALF predictions based only on the pure component isotherms. Table 2 includes all the expressions needed to calculate the residual chemical potentials of the adsorbate molecules in a mixture. Figure 4 shows the binary x-y plots obtained from the RALF model and the multicomponent Toth isotherm. The predictions assuming that all cross-

coefficients are zero is comparable to if not better than the Toth model, in particular for methane. This is even more evident for the quaternary system, parity plots are shown in Fig. 5, where the multicomponent Toth model under-predicts the adsorbed amount of methane,³⁵ thus resulting in over-prediction of methane recovery in process simulations. In general for the binaries and the quaternary system, the Toth model seems to work better for similar molecules, while for “non-adjacent components the theoretical adsorbed phase concentration of the lighter component is 200-300% too low”,³⁵ while the RALF model predictions show improved results, possibly due to the fact that the LF model accounts for differences in sizes via the intrinsic pure component parameters and the combinatorial mixing term. Figure 5 includes also the comparison with the IAST calculated from the pure component Toth isotherms in the original paper.³⁵ For this system the differences between RALF and IAST are relatively small for the smaller molecules, but they become more systematic for propane and butane and RALF outperforms IAST. The interactions between the adsorbates in this system will be close to those of an ideal mixture, with some minor non-ideality resulting from entropic contributions. This is a further confirmation of the sound basis of the RALF model.

The RALF model based on a homogeneous material for silicalite produces very good results for a range of molecules. The fact that the structure of silicalite is composed of straight and sinusoidal channels that are slightly different in size and the intersections of the channels are an additional adsorption site³⁴ could be used to develop a more complex version of the RALF model for this zeolite. In principle one could include 2 different elements within the adsorbent, ie using the heterogeneous solid approach outlined in the introduction, which would be equivalent to a dual site Langmuir model which has been shown to correlate accurately adsorption on silicalite.²⁶ This would result in 6 parameters for the solid, P_{Sk}^* and T_{Sk}^* or v_{Sk}^* for each type of solid, the overall ρ_S^* and the volume fraction of one of the solid types. Each adsorbate would then have 4 parameters, ie ξ_{iAk} and κ_{iSk} . The determination of the model parameters would have to be carried out by simultaneous regression of different data sets, similar to the group contribution parameters in the model proposed by Levan and

co-workers.³⁹⁻⁴⁰ Clearly it would be beneficial to use Henry law constants and saturation capacities to constrain the fits. This more refined model is beyond the scope of this contribution, but one can see how such an approach would be well suited in conjunction with molecular simulations, especially when the adsorbent structure is known as is the case for zeolites and MOFs.

Conclusions

A new thermodynamic model for adsorption of mixtures has been presented which can be applied to several adsorbent structures. In this first contribution the special case of the *frozen solid* is investigated in detail and expressions have been derived for the fugacity coefficients of the adsorbates and the Gibbs adsorption isotherm. These expressions allow the calculation of pure component and mixed fluids adsorption isotherms.

The equilibrium expressions of the RALF model have been shown to possess the correct thermodynamic limits for a type I isotherm at low pressure, Henry law constant, and at saturation, finite saturation amount. Closed form expressions for the Henry law constant have been derived and used to show how the adsorption energy at zero loading depends on the energy density and the characteristic density of the solid at close-packing. These expressions allow also to determine the equivalent parameters of the Langmuir isotherm.

The use of the RALF model has been demonstrated for silicalite. The crystal structure and literature data have been used to estimate $\rho_S = 1786 \text{ kg/m}^3$ and $\rho_S^* = 2577 \text{ kg/m}^3$. With these parameters fixed, the RALF model is capable of reproducing the correct trend of adsorption enthalpies of n-alkanes as a function of carbon number with $P_S^* = 650 \text{ MPa}$. The final model parameter was estimated to be $T_S^* = 1060 \text{ K}$ based on the Henry law constants for 6 gases at approximately 305 K. With these parameters for silicalite, comparisons have been shown to give good agreement with published data for isotherms at different temperatures and up to 20 bar, for which the LF EoS can be used conveniently to take into account the non-ideality of the fluid phase. The RALF model requires

only 2 parameters for each pure component and provides a fit that is comparable to empirical models (Langmuir and Toth) that have the heat of adsorption as an additional parameter.

The application to multicomponent adsorption has been demonstrated using medium to high pressure data up to quaternary mixture adsorption. Predictions with all adsorbate-adsorbate interaction parameters set to zero, ie *a priori* predictions, show good agreement with experimental data and give results that are in most cases comparable to and often better than the empirical multicomponent Toth isotherm. This is particularly true for the binary mixtures of methane/propane and methane/butane, for which the effects of differing sizes of the molecules seem to be captured well by the RALF model. The quaternary mixture predictions from the IAST and the RALF model show that the adsorbed solution for this system is only mildly non-ideal, which is physically consistent with the fact that only small entropic contributions should be present given that all the adsorbates are small alkanes.

It is somewhat surprising that a relatively simple model provides such good results for silicalite, which is a crystalline material. The assumptions of the RALF model would seem better suited for amorphous materials with uniform adsorption sites. This success can be ascribed probably to the fact that in a microporous material with a type I isotherm the key features are the pair interactions between molecule and adsorbent, which are captured correctly by the expressions for the Henry law constant, and the porosity or saturation capacity, which is a characteristic of lattice fluid models. The interactions between adsorbates and the entropic effects are then taken into account irrespective of the crystallinity of the solid.

Notation

A	Helmholtz energy (J)
a	molar Helmholtz energy (J mol ⁻¹)
f	fugacity (Pa)
G^{SL}	Sanchez and Lacombe expression of the Gibbs energy (J)
G^{IG}	Gibbs energy of the ideal gas mixture (J)
G_0^{IG}	Gibbs energy of the ideal gas at the reference conditions (J)
G^R	residual Gibbs energy (J)
G_A^R	residual Gibbs energy of the adsorbed phase (J)
K	dimensionless Henry law constant (–)
K_P	Henry law constant (mol kg ⁻¹ Pa ⁻¹)
n_i	adsorbed amount (mol kg ⁻¹)
n_i^{sat}	saturation capacity (mol kg ⁻¹)
N	number of moles (mol)
N_0	number of vacancies in mole equivalents (mol)
N_j	number of moles of species j (mol)
N_r	size of lattice in mole equivalents (mol)
m_j	mass of species j (kg)
m_S	mass of solid (kg)
Mw_i	molecular mass of species i (kg mol ⁻¹)
P	pressure (Pa)
P_0	reference pressure (Pa)
\tilde{P}	reduced pressure (–)
P^*	characteristic pressure of the mixture (Pa)

P_i^*	characteristic pressure of component i pure (Pa)
P_{iA}^*	characteristic pressure of component i in the adsorbed phase (Pa)
P_S^*	characteristic pressure of the solid (Pa)
P_{ij}^*	pair characteristic pressure, eq. 26 (Pa)
r	average number of mers in a molecule (–)
r_j	number of mers in molecule j in the mixture (–)
r_j^0	number of mers in molecule j pure (–)
R	ideal gas constant (J mol ⁻¹)
T	temperature (K)
\tilde{T}	reduced temperature (–)
T^*	characteristic temperature of the mixture (K)
T_i^*	characteristic temperature of component i pure (K)
T_S^*	characteristic temperature of the solid (K)
\tilde{v}	reduced molar volume (–)
v^*	average close-packed volume of mers in a mixture (m ³ mer-mol ⁻¹)
v_j^*	close-packed volume of mers molecule j pure (m ³ mer-mol ⁻¹)
v_{jA}^*	close-packed volume of mers molecule j in the adsorbed phase (m ³ mer-mol ⁻¹)
V	volume of the lattice (m ³)
V^*	close-packed volume for the mixture (m ³)
V_S	volume of the solid (m ³)
V_S^0	volume of the solid <i>in vacuo</i> (m ³)
V_S^∞	volume of the solid at infinite pressure (m ³)
w_j	mass fraction of species j (–)
x_i	mole fraction of species i in the adsorbed phase (–)

y_i	mole fraction of species i in the fluid phase (–)
z	compressibility factor (–)
z^{EoS}	compressibility factor derived from the Helmholtz energy (–)

Greek letters

β_T	isothermal solid compressibility (Pa ⁻¹)
ΔH_0	adsorption enthalpy at zero loading (J mol ⁻¹)
ΔU_0	adsorption energy at zero loading (J mol ⁻¹)
φ_i	fugacity coefficient of species i (–)
ϕ_j	volume fraction in the lattice occupied by species j at close-packing (–)
ϕ_S	volume fraction in the lattice occupied by the solid at close-packing (–)
ϕ_0^L	volume fraction in the lattice occupied by vacancies (–)
ϕ_j^L	volume fraction in the lattice occupied by species j (–)
κ_{ij}	pair interaction coefficient (–)
μ_i^R	residual chemical potential of species i in the adsorbed phase (J mol ⁻¹)
μ_{iF}^R	residual chemical potential of species i in the fluid phase (J mol ⁻¹)
μ_{iP}^R	residual chemical potential of species i pure in the fluid phase (J mol ⁻¹)
$\mu_{i\infty}^R$	residual chemical potential of species i at infinite dilution in the adsorbed phase (J mol ⁻¹)
μ_S^{Rm}	residual chemical potential of the solid on a mass basis (J kg ⁻¹)
μ_{S0}^{Rm}	residual chemical potential of the solid without adsorbates (J kg ⁻¹)
$\tilde{\rho}$	reduced mass density (–)
ρ^*	average close-packed mass density in a mixture (kg m ⁻³)
ρ_j^*	close-packed mass density of molecule j (kg m ⁻³)
ρ_{jA}^*	close-packed mass density of molecule j in the adsorbed phase (kg m ⁻³)

ρ_S	mass density of the solid (kg m^{-3})
ξ_{jA}	volume correction due to confinement constraints (–)
Ψ	reduced grand potential (–)
ω_j	configurations available to mers in the close-packed state (–)

Acknowledgement

This research was initiated through an Advanced Study Institute Senior Fellowship visit in April 2015 to the *Alma Mater Studiorum* Università di Bologna. Discussions and follow-up exchanges on the lattice fluid model with several colleagues in Bologna (De Angelis, Doghieri, Giacinti-Baschetti, Minelli and Sarti) are gratefully acknowledged. The development of the RALF model is part of research funded by the Engineering and Physical Sciences Research Council under grants EP/N024613/1 (Versatile Adsorption Processes for the Capture of Carbon Dioxide from Industrial Sources – FlexICCS) and EP/N033329/1 (Cation-Controlled Gating for Selective Gas Adsorption over Adaptable Zeolites).

Literature Cited

1. Ruthven DM. Principles of adsorption and adsorption processes. New York: Wiley, 1984.
2. Denbigh K. The principles of chemical equilibrium. 4th Ed. Cambridge: Cambridge University Press, 1981.
3. Hill TL. An introduction to statistical thermodynamics. New York: Dover, 1986.
4. Rao MB, Sircar S. Thermodynamic consistency for binary gas adsorption equilibria. Langmuir. 1999; 15: 7258-7267.
5. Do DD. Adsorption analysis: equilibria and kinetics. London: Imperial College Press, 1998.
6. Valenzuela DP, Myers AL. Adsorption equilibrium data handbook. Englewood Cliffs: Prentice-Hall, 1989.
7. Myers AL, Prausnitz JM. Thermodynamics of mixed-gas adsorption. AIChE J. 1965; 11: 121-127.
8. Myers AL, Monson P. Physical adsorption of gases: the case for absolute adsorption as the basis for thermodynamic analysis. Adsorption. 2014; 20: 591-622.
9. Myers AL. Prediction of adsorption of nonideal mixtures in nanoporous materials. Adsorption. 2005; 11: 37-42.
10. Mangano E, Friedrich D, Brandani S. Robust algorithms for the solution of the ideal adsorbed solution theory equations. AIChE J. 2015; 61: 981-991.
11. Suwanayuen S, Danner RP. A gas adsorption isotherm equation based on vacancy solution theory. AIChE J. 1980; 26: 68-76.
12. Suwanayuen S, Danner RP. Vacancy solution theory of adsorption from gas mixtures. AIChE J. 1980; 26: 76-83.
13. Cochran TW, Kabel RL, Danner RP. Vacancy solution theory of adsorption using Flory-Huggins activity coefficient equations. AIChE J. 1985; 31: 268-277.
14. Cochran TW, Kabel RL, Danner RP. Vacancy solution model of adsorption – improvements and recommendations. AIChE J. 1985; 31: 2075-2081.

15. Sanchez IC, Lacombe RH. An elementary molecular theory of classical fluids. *Pure Fluids. J. Phys. Chem.* 1976; 80: 2352-2362.
16. Lacombe RH, Sanchez IC. Statistical thermodynamics of fluid mixtures. *J. Phys. Chem.* 1976; 80: 2568-2580.
17. Sanchez IC, Lacombe RH. Statistical thermodynamics of polymer solutions. *Macromolecules* 1978; 11: 1145-1156.
18. Brandani S, Mangano E, Sarkisov L. Net, excess and absolute adsorption and adsorption of helium. *Adsorption.* 2016; 22: 261-276.
19. Doghieri F, Sarti GC. Nonequilibrium Lattice Fluids: A predictive model for the solubility in glassy polymers. *Macromolecules.* 1996; 29: 7885-7896.
20. Sarti GC, Doghieri F. Predictions of the solubility of gases in glassy polymers based on the NELF model. *Chem. Eng. Sci.* 1998; 53: 3435-3447.
21. Baschetti MG, Doghieri F, Sarti GC. Solubility in glassy polymers: correlations through the nonequilibrium lattice fluid model. *Ind. Eng. Chem. Res.* 2001; 40: 3027-3037
22. De Angelis MG, Sarti GC, Doghieri F. Correlations between penetrant properties and infinite dilution gas solubility in glassy polymers: NELF model derivation. *Ind. Eng. Chem. Res.* 2007; 46: 7645-7656.
23. Neau E. A consistent method for phase equilibrium calculation using the Sanchez-Lacombe lattice-fluid equation of state. *Fluid Phase Equilibria.* 2002; 203: 133-140.
24. Lewis GN, Randall M revised by Pitzer KS, Brewer L. *Thermodynamics.* 2nd Ed. New York: McGraw-Hill, 1961.
25. Prausnitz JM, Lichtenthaler RN, de Azevedo EG. *Molecular thermodynamics of fluid-phase equilibria.* 3rd Ed. Upper Saddle River: Prentice Hall PTR, 1999.
26. Vlugt TJH, Krishna R, Smit B. Molecular simulations of adsorption isotherms for linear and branched alkanes and their mixtures in silicalite. *J. Phys. Chem. B.* 1999; 103: 1102-1118.

27. Brandani S, Mangano E, Luberti M. Net, excess and absolute adsorption in mixed gas adsorption, *Adsorption*. 2017; 23: 569-576.
28. Wong DSH, Sandler SI. A theoretically correct mixing rule for cubic equations of state. *AIChE J.* 1992; 38: 671-680
29. Brandani F, Brandani S, Brandani V. Simple new EOS mixing rules which incorporate lattice fluid excess functions. *Chem. Eng. Sci.* 1998; 53: 1041-1047.
30. Brandani F, Brandani S, Brandani V. EOS mixing rules which incorporate the residual UNIQUAC model. *Ind. Eng. Chem. Res.* 1998; 37: 2929-2935.
31. De Angelis MG, Sarti GC, Doghieri F. NELF model prediction of the infinite dilution gas solubility in glassy polymers. *J. Membr. Sci.* 2007; 289: 106-122.
32. Linstrom PJ, Mallard WG. Eds, NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg MD, 20899, doi:10.18434/T4D303, (retrieved April 25, 2018)
33. Thommes M, Kaneko K, Neimark AV, Olivier JP, Rodriguez-Reinoso F, Rouquerol J, Sing KSW. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC technical report). *Pure Appl. Chem.* 2015; 87: 1051-1069.
34. Baerlocher Ch, McCusker LB, Olson DH. Atlas of zeolite framework types. 6th Ed. Amsterdam: Elsevier, 2007.
35. Abdul-Rehman HB, Hasanain MA, Loughlin KF. Quaternary, ternary, binary and pure component sorption on zeolites. 1. Light alkanes on Linde S-115 silicalite at moderate to high pressures. *Ind. Eng. Chem. Res.* 1990; 29: 1525-1535.
36. Hufton JR, Danner RP. Chromatographic study of alkanes in silicalite: equilibrium properties. *AIChE J.* 1993; 39: 954-961.

37. Maginn EJ, Bell AT, Theodorou DN. Sorption thermodynamics, siting and conformation of long n-alkanes in silicalite as predicted by configurational-bias Monte Carlo integration. *J. Phys. Chem.* 1995; 99: 2057-2079.
38. Golden TC, Sircar S. Gas-adsorption on silicalite. *J. Colloid Interface Sci.* 1994; 162: 182-188.
39. Russell BP, Levan MD. Group-contribution theory for adsorption of gas mixtures on solid surfaces. *Chem. Eng. Sci.* 1996; 51: 4025-4028.
40. Walton KS, Pigorini G, Levan MD. Simple group contribution theory for adsorption of alkanes in nanoporous carbons. *Chem. Eng. Sci.* 2004; 59: 4425-4432.

Tables

Table 1. Pure component LF parameters.

Component	T^* (K)	P^* (MPa)	ρ^* (kg/m ³)	Mw (kg/mole)	Source
Ar	190	180	1400	0.040	[31]
CO	141	204	919	0.028	This work ¹
CO ₂	300	630	1515	0.044	[31]
Kr	243	302	2875	0.0838	This work ¹
N ₂	145	160	943	0.028	[31]
CH ₄	215	250	500	0.016	[31]
C ₂ H ₆	320	330	640	0.030	[31]
C ₃ H ₈	375	320	690	0.044	[31]
n-C ₄ H ₁₀	403	322	736	0.058	[31]
n-C ₅ H ₁₂	451	305	749	0.072	[31]
n-C ₆ H ₁₄	476	298	775	0.086	[31]
n-C ₇ H ₁₆	498	295	780	0.100	[15]
n-C ₈ H ₁₈	502	308	815	0.114	[15]
n-C ₉ H ₂₀	517	307	828	0.128	[15]
n-C ₁₀ H ₂₂	530	304	837	0.142	[15]

¹ Obtained from vapour pressure and liquid density data from [32]. See also supplementary material.

Table 2. Summary of relationships needed to calculate the residual chemical potential of the adsorbed phase.

Sequence	
1	Specify parameters: T_i^* ; P_i^* ; ρ_i^* , Mw_i ; T_S^* ; P_S^* ; ρ_S^* and κ_{ij}
2	Specify variables: T; P; n_i ; m_S
3	$v_S^* = \frac{RT_S^*}{P_S^*}$
4	$P_{iA}^* = \frac{P_i^*}{1+\xi_{iA}}$; $v_{iA}^* = \frac{RT_i^*}{P_{iA}^*}$; $\rho_{iA}^* = \frac{\rho_i^*}{1+\xi_{iA}}$; $r_{iA}^0 = \frac{Mw_i}{v_{iA}^* \rho_{iA}^*}$
5	Define $m_i = n_i Mw_i$ and $m_T = \sum_j m_j$
6	$\rho^* = \frac{m_T}{\sum_i \frac{m_i}{\rho_{iA}^*} + \frac{m_S}{\rho_S^*}}$; $\phi_i = \frac{m_i \rho^*}{\rho_{iA}^* m_T}$; $\phi_S = \frac{m_S \rho^*}{\rho_S^* m_T}$; $\rho = \frac{m_T}{m_S} \rho_S$
7	$P^* = \sum_j \sum_k \phi_j \phi_k P_{jk}^*$ with $P_{jk}^* = P_{kj}^* = (1 - \kappa_{kj}) \sqrt{P_k^* P_j^*}$ and $\kappa_{kk} = 0$.
8	$\frac{1}{v^*} = \sum_j \frac{\phi_j}{v_j^*}$; $T^* = \frac{P^* v^*}{R}$; $\tilde{T} = \frac{T}{T^*}$; $\tilde{P} = \frac{P}{P^*}$ and $\tilde{\rho} = \frac{\rho}{\rho^*}$
9	$r_i = r_{iA}^0 \frac{v_{iA}^*}{v^*}$; $\frac{1}{r} = \sum_i \frac{\phi_i}{r_i}$; $rN = \frac{m_S \tilde{\rho}}{\rho_S v^*}$ and $z = r \frac{\tilde{P}}{\tilde{\rho} \tilde{T}}$
10	$x_i = r \frac{\phi_i}{r_i}$ and $z^{EoS} - 1 = r \left[-\frac{\tilde{\rho}}{\tilde{T}} - \frac{\ln(1-\tilde{\rho})}{\tilde{\rho}} - 1 \right] + \tilde{\rho} \sum_i x_i \ln \frac{\phi_i}{x_i(1-\phi_S)}$
$\frac{\mu_k^R}{RT} = -\frac{\tilde{\rho}}{\tilde{T}} r_k \left(2 \frac{\sum_j \phi_j P_{kj}^*}{P^*} - 1 \right) + \left[\frac{(1-\tilde{\rho}) \ln(1-\tilde{\rho})}{\tilde{\rho}} + 1 \right] r_k^0 + \frac{r_k}{r} (z^{EoS} - 1) - \ln z$ $+ \tilde{\rho} \left(\ln \frac{r_k}{r(1-\phi_S)} + 1 - \frac{r_k}{r(1-\phi_S)} \right)$	

List of Figures

Figure 1. Adsorption enthalpy for n-alkanes in silicalite. Comparison of RALF model with $\xi_{1A} = 0$ and $\kappa_{1S} = 0$ and literature correlations based on experimental data³⁵⁻³⁶ and molecular simulations.³⁷

Figure 2. Comparison of RALF model with experimental data³⁸ for CH₄, N₂, CO, Ar, CO₂ and Kr. Model calculations based on fitting ξ_{1A} and κ_{1S} .

Fig. 3 Pure component isotherms at 300 K and comparison of RALF and Toth models.³⁵

Figure 4. Binary y vs x plots predicted from pure component isotherms by the Toth model³⁵ and the RALF model at 300 K and 345 kPa.

Figure 5. Parity plots for adsorbed amounts (mol/kg) in quaternary mixture at 300 K and 345 kPa.³⁵

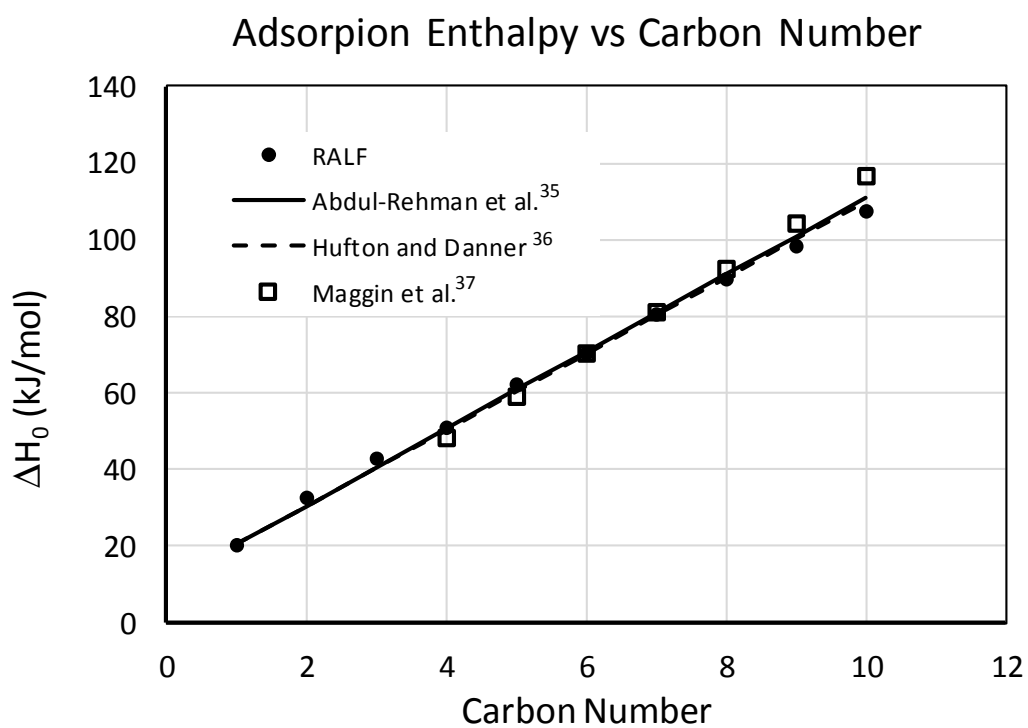


Figure 1. Adsorption enthalpy for n-alkanes in silicalite. Comparison of RALF model with $\xi_{1A} = 0$ and $\kappa_{1S} = 0$ and literature correlations based on experimental data³⁵⁻³⁶ and molecular simulations.³⁷

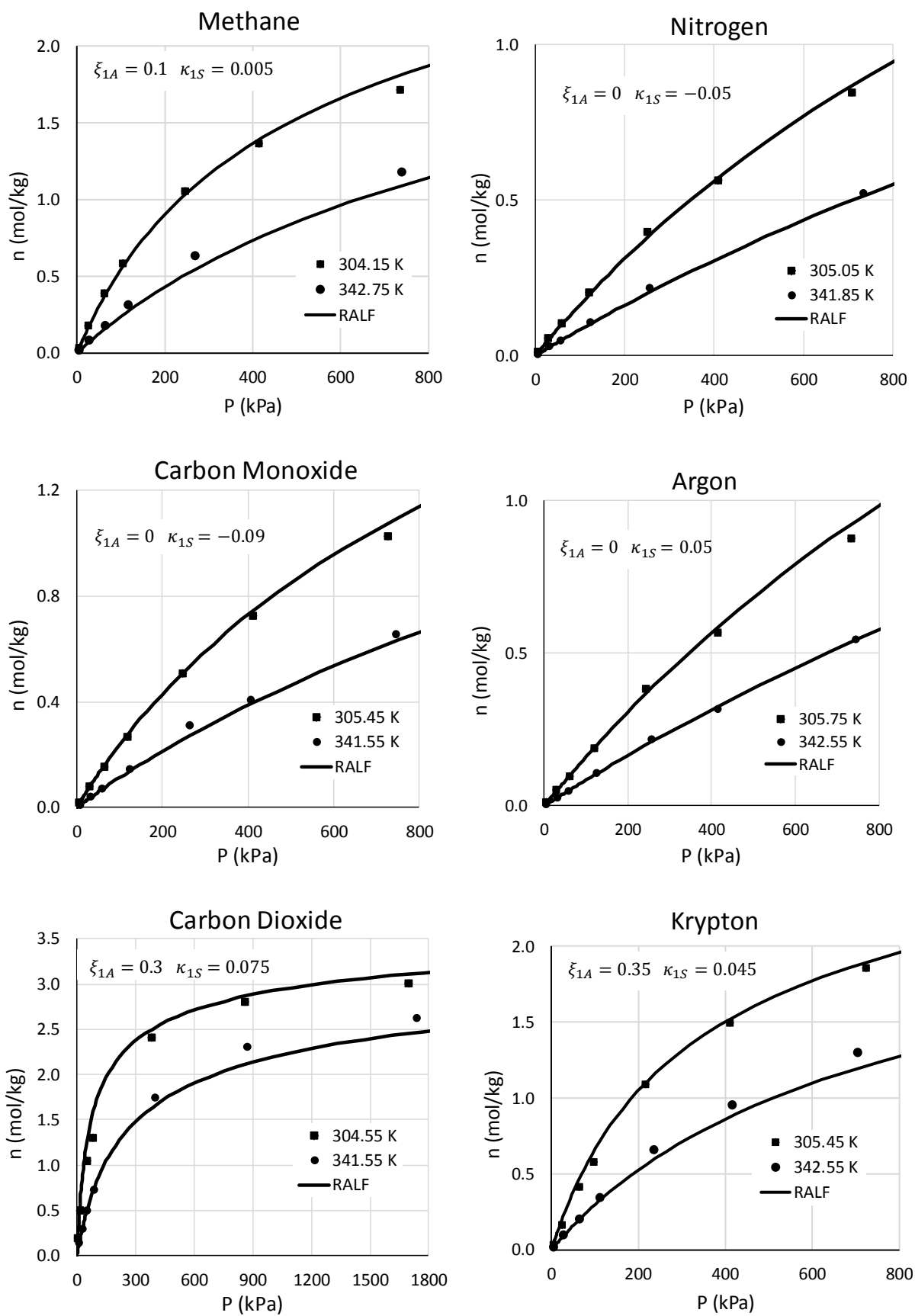


Figure 2. Comparison of RALF model with experimental data³⁸ for CH₄, N₂, CO, Ar, CO₂ and Kr. Model calculations based on fitting ξ_{1A} and κ_{1S} .

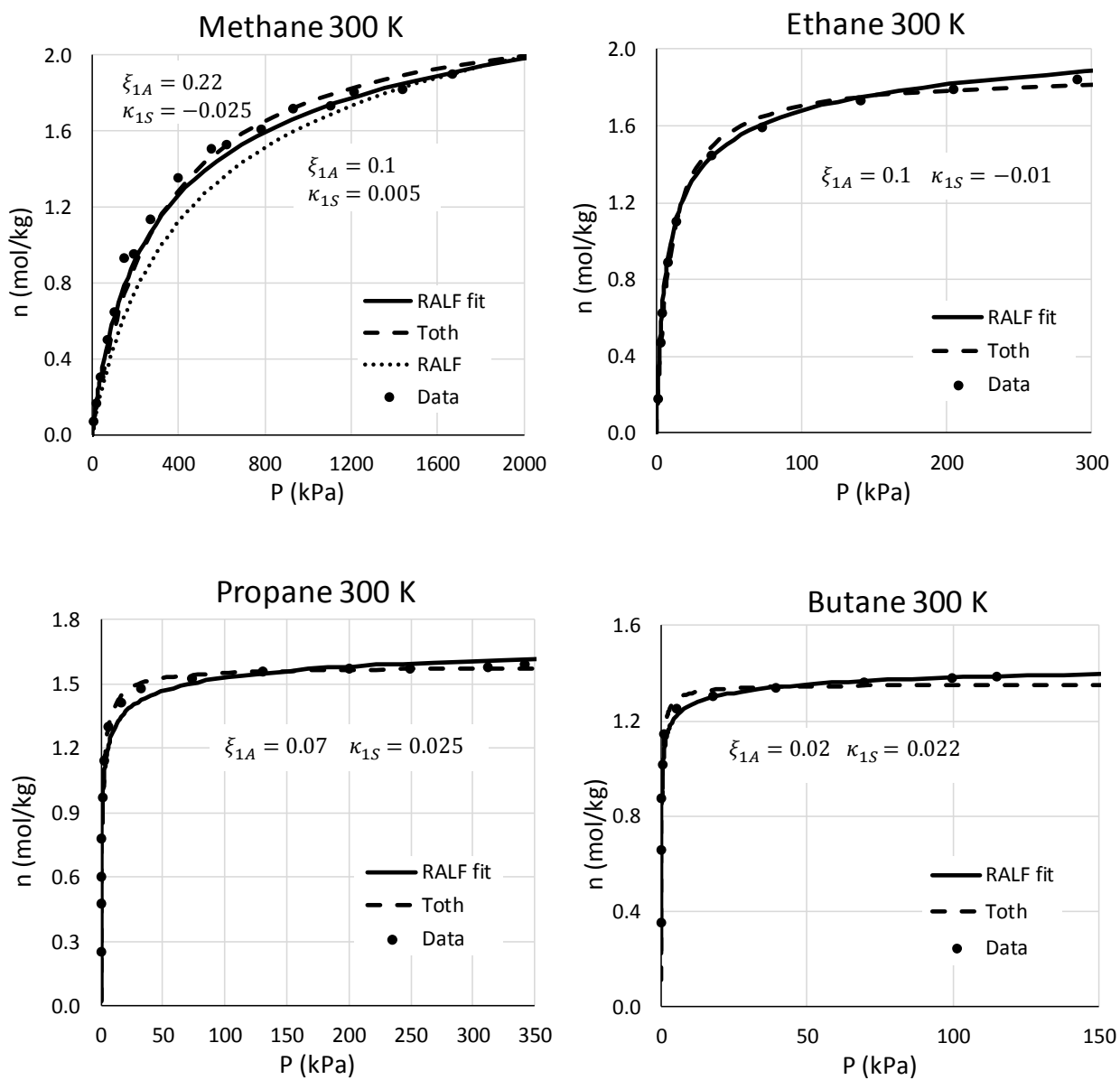


Fig. 3 Pure component isotherms at 300 K and comparison of RALF and Toth models.³⁵

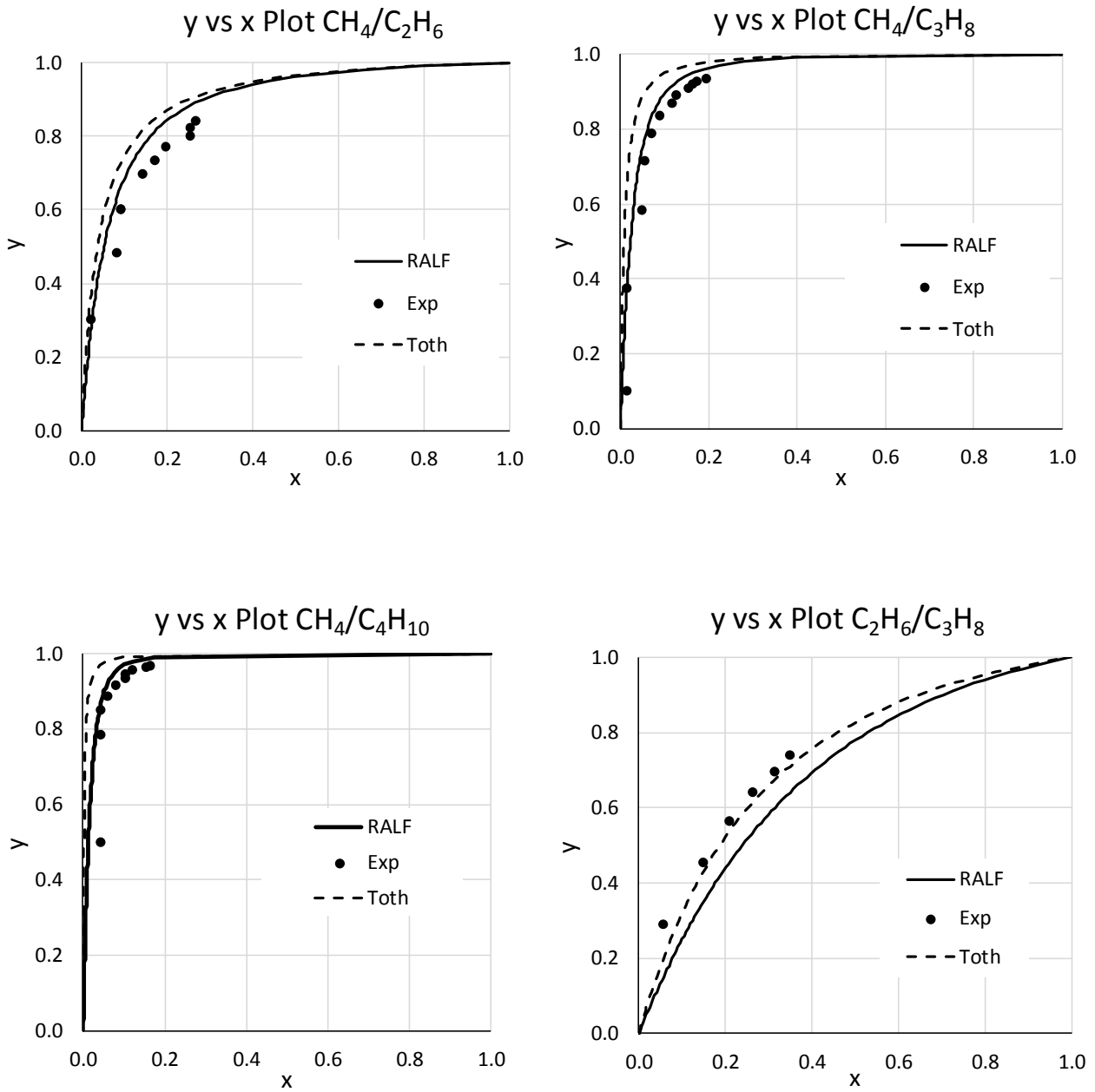


Figure 4. Binary y vs x plots predicted from pure component isotherms by the Toth model³⁵ and the RALF model at 300 K and 345 kPa.

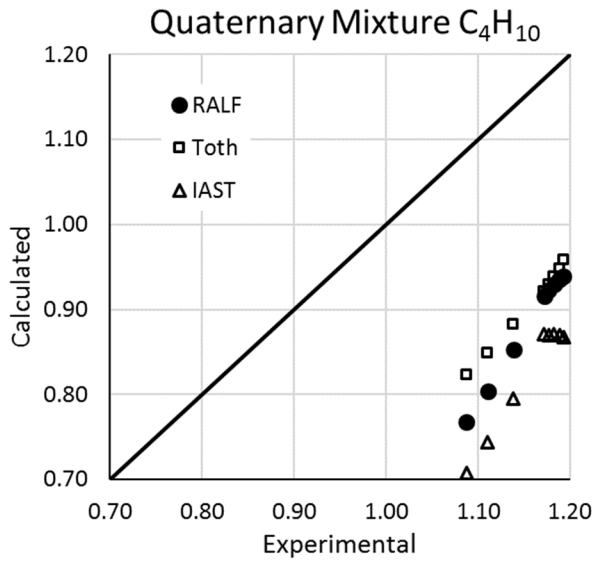
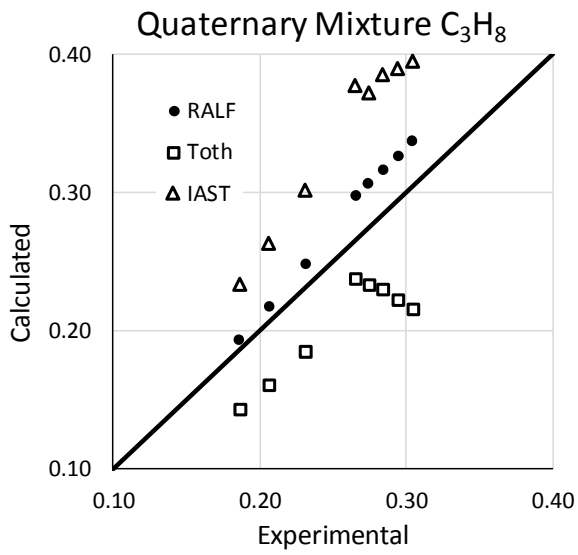
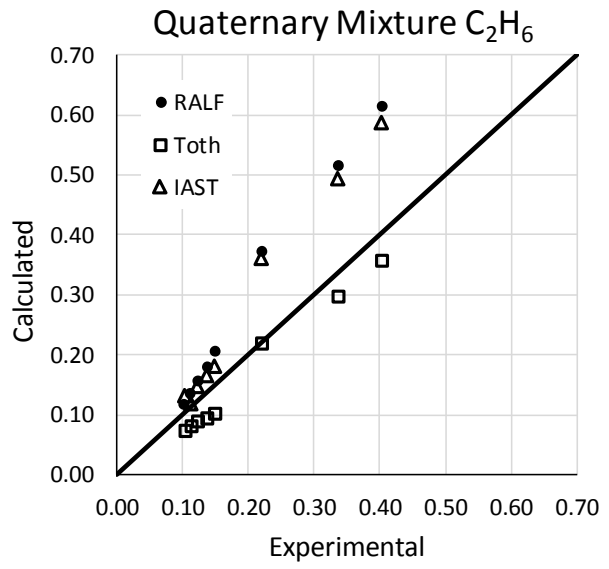
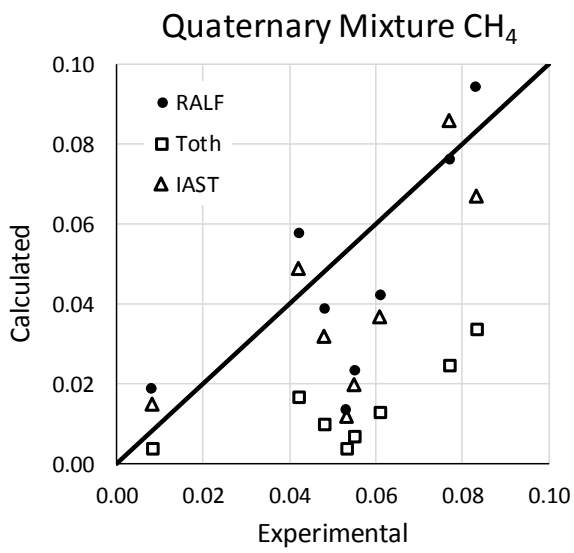


Figure 5. Parity plots for adsorbed amounts (mol/kg) in quaternary mixture at 300 K and 345 kPa.³⁵

The Rigid Adsorbent Lattice Fluid Model for Pure and Mixed Gas Adsorption

Stefano Brandani

School of Engineering, University of Edinburgh

The King's Buildings, Mayfield Road

Edinburgh EH9 3FB, U.K.

Supplementary Materials

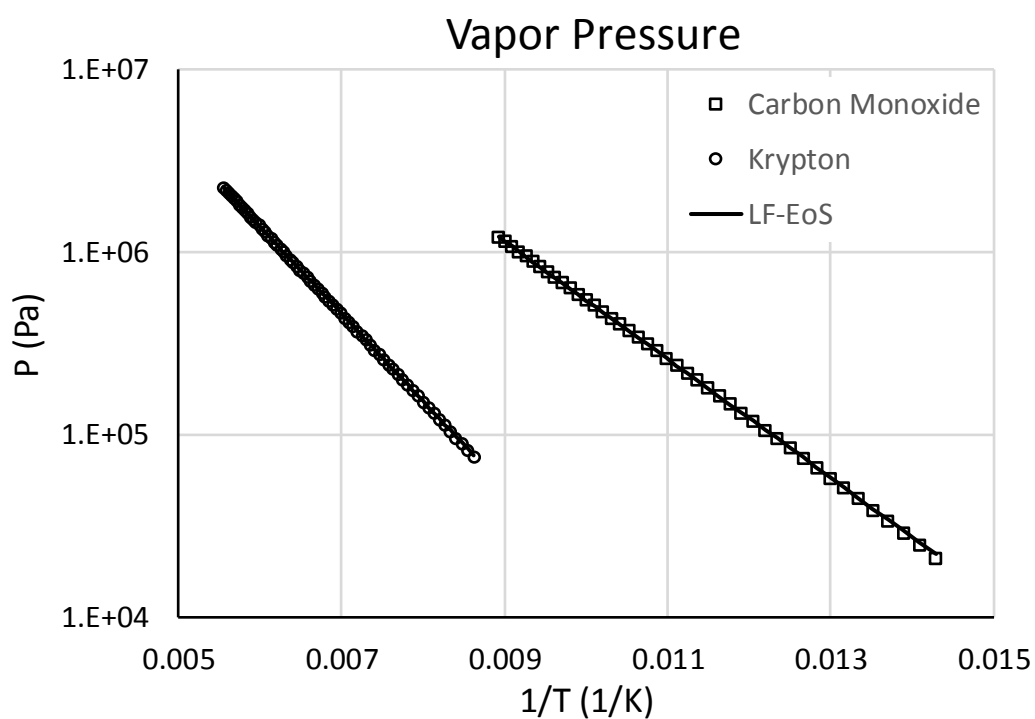


Figure S1. Comparison of vapor pressures of carbon monoxide and krypton³² with values calculated from the LF EoS (parameters in Table 1).

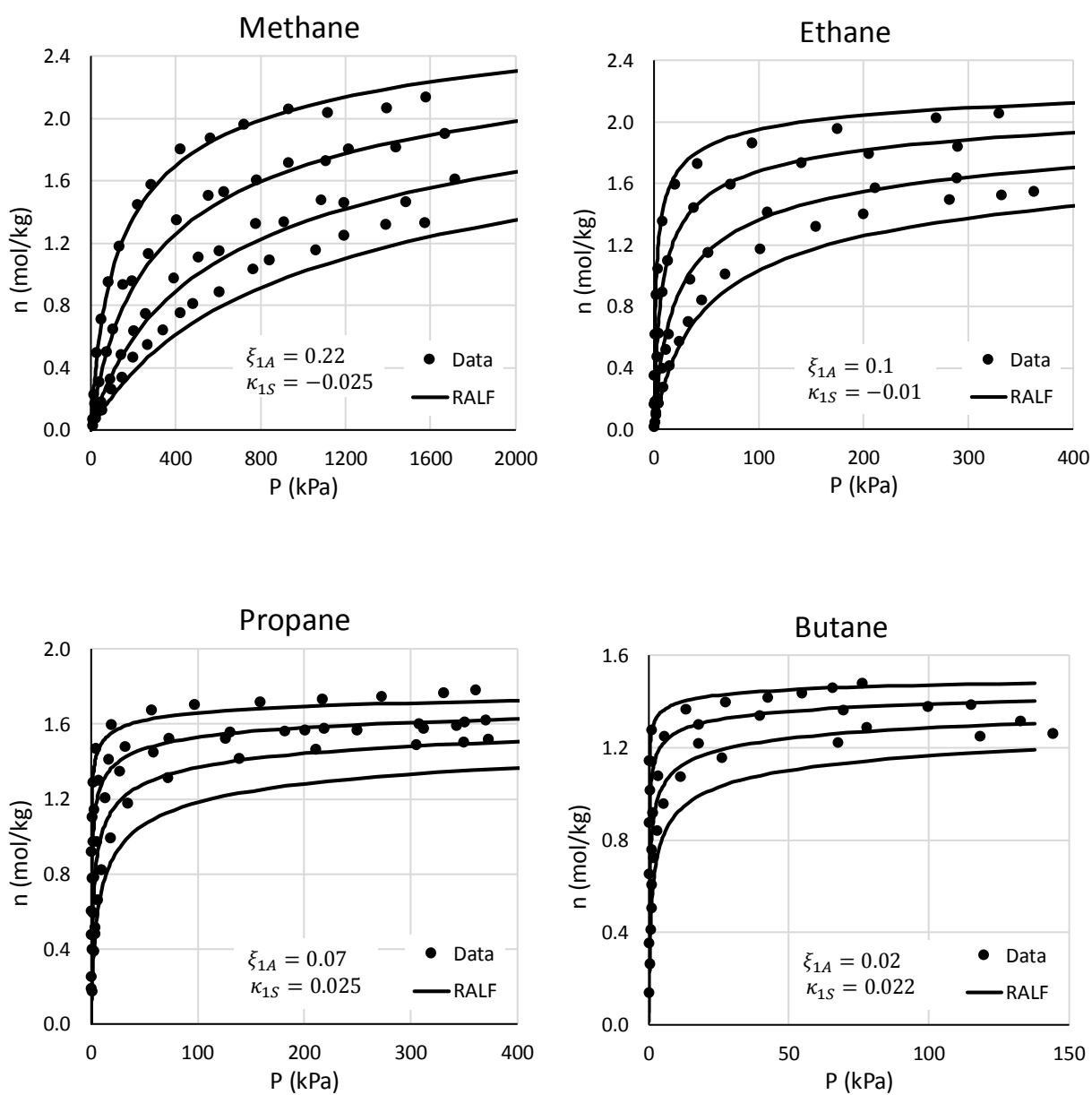


Figure S2. Pure component isotherms at 275, 300, 325 and 350 K predicted from parameters obtained at 300 K and experimental data.³⁵

Chemical potential of the solid

Contrary to the case often encountered in solutions, where the expressions for the chemical potentials have symmetry, in the case of the RALF framework there are asymmetries that go beyond the definition of a different basis for the concentrations. Given the assumption that the system volume will change with the addition of solid, the Gibbs energy has to be used in the derivation of the chemical potential of the solid. Asymmetries are then obtained when substituting the partial derivative of density in both the derivative of the Helmholtz energy and the derivative of the compressibility factor. The following expression for the chemical potential of the solid is obtained in the *frozen solid* limit (the full derivation is reported in Appendix 2).

$$\frac{\mu_S^{Rm}}{RT} = \frac{rN}{m_S} \phi_S \frac{v^*}{v_S^*} \left[\frac{(1-\tilde{\rho}) \ln(1-\tilde{\rho})}{\tilde{\rho}} + 1 \right] - \frac{\tilde{\rho}}{\tilde{T}} \left[2 \frac{\sum_j \phi_j P_{Sj}^*}{P^*} - 1 \right] \frac{\phi_S}{m_S} rN + \frac{N}{m_S} (\phi_S - 1)(z^{Eos} - 1) + \frac{N}{m_S} (z - 1) \quad (42)$$

From this it is possible to define the chemical potential of the pure solid at the same pressure of the system²⁷

$$\frac{\mu_{S0}^{Rm}}{RT} = \frac{1}{v_S^* \rho_S^*} \left[\frac{(1-\tilde{\rho}_S) \ln(1-\tilde{\rho}_S)}{\tilde{\rho}_S} + 1 - \frac{\tilde{\rho}_S}{\tilde{T}_S} \right] + \frac{P}{RT \rho_S} \quad (43)$$

It may appear that this derivation is not needed, given the fact that the LF model predicts correctly that the vapour pressure of the solid is zero in the limit as $r_S \rightarrow \infty$.¹⁵ In this case the solution of the phase equilibrium problem does not require these last two chemical potentials. The reason for deriving these terms lies with the definition of the reduced grand potential which is obtained from their difference:^{8, 27}

$$-\Psi = \frac{\mu_S^{Rm}}{RT} - \frac{\mu_{S0}^{Rm}}{RT} = \frac{rN}{m_S} \phi_S \frac{v^*}{v_S^*} \left[\frac{(1-\tilde{\rho}) \ln(1-\tilde{\rho})}{\tilde{\rho}} + 1 \right] - \frac{\tilde{\rho}}{\tilde{T}} \left[2 \frac{\sum_j \phi_j P_{Sj}^*}{P^*} - 1 \right] \frac{\phi_S}{m_S} rN + \frac{N}{m_S} (\phi_S - 1)(z^{Eos} - 1) - \frac{N}{m_S} - \frac{1}{v_S^* \rho_S^*} \left[\frac{(1-\tilde{\rho}_S) \ln(1-\tilde{\rho}_S)}{\tilde{\rho}_S} + 1 - \frac{\tilde{\rho}_S}{\tilde{T}_S} \right] \quad (44)$$

When the reduced grand potential is combined with the Gibbs-Duhem equation,^{1, 8, 27} it can be used to check for the internal consistency of the RALF model. For a single component and constant temperature the Gibbs adsorption isotherm is obtained

$$\Psi(f) = \int_0^f n_1 d \ln f \quad (45)$$

which at low fugacities reduces to $\Psi(f) \approx K_p f$.

Given that the solid with $r_s = \infty$ will not exist in the vapour phase, when calculating the properties of the adsorbed phase it is going to be more convenient to define the reference state of the solid as that of the solid *in vacuo*. This will require the measurement of the heat capacity of the solid without adsorbates.

Appendix 1 – Gibbs energy of the Lattice Fluid

Starting from the expression derived by Sanchez and Lacombe¹⁶

$$\frac{G^{SL}}{NRT} = r \left[-\frac{\tilde{\rho}}{\tilde{T}} + \frac{(1-\tilde{\rho}) \ln(1-\tilde{\rho})}{\tilde{\rho}} + \frac{\ln(\tilde{\rho})}{r} + \sum_j \frac{\phi_j}{r_i} \ln \left(\frac{\phi_j}{\omega_j} \right) \right] + z \quad A1.1$$

ω_j are the number of configurations available to an r_j mer in the close-packed pure state. This expression is neither a residual nor an excess thermodynamic property.

From eq. A1.1 the Helmholtz energy is obtained

$$\frac{A^{SL}}{RT} = rN \left[-\frac{\tilde{\rho}}{\tilde{T}} + \frac{(1-\tilde{\rho}) \ln(1-\tilde{\rho})}{\tilde{\rho}} \right] + N \ln \tilde{\rho} + N \sum_j x_j \ln \phi_j - N \sum_j x_j \ln \omega_j \quad A1.2$$

If the ideal mixture of pure components *at the same reduced density of the mixture* is subtracted from this expression, the resulting excess Helmholtz energy is given by

$$\frac{A^{SL}}{RT} - \sum_j N_j \frac{a_j^{SL}(T, \tilde{\rho})}{RT} - \sum_j N_j \ln x_j = rN\tilde{\rho} \left[-\frac{1}{\tilde{T}} + \sum_j \frac{\phi_j}{\tilde{T}_j} \right] + N \sum_j x_j \ln \frac{\phi_j}{x_j} \quad A1.3$$

This excess Helmholtz energy at the close-packed state is the sum of the regular solution term and the Flory-Huggins combinatorial term. It is worth noting here that in the limit as $\tilde{\rho} \rightarrow 0$ the regular solution term goes to zero, ie written in this form this term is consistent in the ideal gas limit.

The pure component molar Helmholtz energy at the same reduced density of the mixture is given by

$$\frac{a_j^{SL}(T, \tilde{\rho})}{RT} = r_j \left[-\frac{\tilde{\rho}}{\tilde{T}_j} + \frac{(1-\tilde{\rho}) \ln(1-\tilde{\rho})}{\tilde{\rho}} \right] + \ln \tilde{\rho} - \ln \omega_j \quad A1.4$$

It is clear that the last term in eq A1.4 corresponds to a pure component property. It will therefore be omitted in what follows,¹⁷ since it will only affect how the reference state of the pure component is written, but will cancel out in excess mixture properties.

For an ideal gas

$$\frac{a_j^{IG}(T, \tilde{\rho})}{RT} = \frac{a_{j0}^{IG}(T)}{RT} + \ln \tilde{\rho} - \ln \tilde{\rho}_0 \quad A1.5$$

Comparing the last two expressions it is clear that a deviation function between the pure component and the ideal gas at the same reduced density of the mixture should be zero in the limit as $\tilde{\rho} \rightarrow 0$, therefore

$$\frac{a_j^{LF}(T, \tilde{\rho})}{RT} - \frac{a_j^{IG}(T, \tilde{\rho})}{RT} = r_j \left[-\frac{\tilde{\rho}}{\tilde{T}_j} + \frac{(1-\tilde{\rho}) \ln(1-\tilde{\rho})}{\tilde{\rho}} + 1 \right] \quad A1.6$$

$$\text{Since } \lim_{\tilde{\rho} \rightarrow 0} \frac{(1-\tilde{\rho}) \ln(1-\tilde{\rho})}{\tilde{\rho}} = -1$$

Therefore

$$\frac{a_j^{LF}(T, \tilde{\rho})}{RT} = r_j \left[-\frac{\tilde{\rho}}{\tilde{T}_j} + \frac{(1-\tilde{\rho}) \ln(1-\tilde{\rho})}{\tilde{\rho}} + 1 \right] + \ln \tilde{\rho} + \frac{a_{j0}^{IG}(T)}{RT} - \ln \tilde{\rho}_0 \quad A1.7$$

$$\frac{A^{LF}}{RT} - \frac{A^{IGM}(T, \tilde{\rho})}{RT} = rN \left[-\frac{\tilde{\rho}}{\tilde{T}} + \frac{(1-\tilde{\rho}) \ln(1-\tilde{\rho})}{\tilde{\rho}} + 1 \right] + N \sum_j x_j \ln \frac{\phi_j}{x_j} \quad A1.8$$

This equation can be split into

$$\frac{A^{LF}}{RT} - \frac{A^{IGM}(T, \tilde{\rho})}{RT} = \frac{\hat{A}(T, V, N)}{RT} + \frac{\hat{A}^{Comb}}{RT} \quad A1.9$$

where

$$\frac{\hat{A}(T, V, N)}{RT} = rN \left[-\frac{\tilde{\rho}}{\tilde{T}} + \frac{(1-\tilde{\rho}) \ln(1-\tilde{\rho})}{\tilde{\rho}} + 1 \right] \quad A1.10$$

This is Neau's²³ expression of the residual Helmholtz energy at the same volume, but this expression effectively eliminates the combinatorial contribution

$$\frac{\hat{A}^{Comb}}{RT} = N \sum_j x_j \ln \frac{\phi_j}{x_j} \quad A1.11$$

Written in this way, this expression leads to a problem since it is independent of density and therefore will not reduce correctly to the ideal gas limit. An empirical correction is invoked here and the term is written as being proportional to the reduced density

$$\frac{\hat{A}^{Comb}}{RT} = N \tilde{\rho} \sum_j x_j \ln \frac{\phi_j}{x_j} \quad A1.12$$

In this way the same proportionality to $\tilde{\rho}$ of the energy term is recovered.

This reduces to the original formulation at the close-packed state and is zero in the limit as $\tilde{\rho} \rightarrow 0$.

Contrary to Neau's²³ expressions for the chemical potentials, in this form the combinatorial contribution to the activity coefficients at the close-packed state is retained. With this change, the pure component equation of state remains unaffected, thus all the LF parameters found in the literature are still applicable, but the mixture EoS changes to

$$z^{EoS} - 1 = r \left[-\frac{\tilde{\rho}}{\tilde{T}} - \frac{\ln(1-\tilde{\rho})}{\tilde{\rho}} - 1 \right] + \tilde{\rho} \sum_j x_j \ln \frac{\phi_j}{x_j} \quad A1.13$$

The residual Gibbs energy is then

$$\frac{G^R(T, P, N)}{RT} = rN \left[-\frac{\tilde{\rho}}{\tilde{T}} + \frac{(1-\tilde{\rho}) \ln(1-\tilde{\rho})}{\tilde{\rho}} + 1 \right] + N \tilde{\rho} \sum_j x_j \ln \frac{\phi_j}{x_j} + N(z - 1 - \ln z) \quad A1.14$$

where $z = \frac{PV}{NRT}$. The corresponding ideal gas term is

$$\frac{G^{IG}(T,P,N)}{RT} = \frac{H_j^{IG}(T)}{RT} - \frac{S_j^{IG}(T,P)}{R} = \frac{G_0^{IG}(T)}{RT} + N \left(\ln \frac{P}{P_0} + \sum_j x_j \ln x_j \right) \quad \text{A1.15}$$

Appendix 2 – Derivation of the chemical potentials

For the case of the adsorbates the mass of the solid, m_s , is held constant and $\left(\frac{\partial}{\partial N_i} \right)_{T,P,N_{j \neq i}}$ is taken as

implicit.

From the residual Gibbs energy of the adsorbed phase the derivatives that follow need to be considered.

In the more general case of variable volume of the solid

$$\frac{d\tilde{\rho}}{dm_k} = \frac{1}{\rho^*} \frac{d\rho}{dm_k} + \rho \frac{d1/\rho^*}{dm_k} \quad \text{and} \quad \frac{d\rho}{dm_k} = \frac{\rho_s}{m_s} + \frac{M}{m_s} \frac{d\rho_s}{dm_k}$$

$$\frac{\partial 1/\rho^*}{\partial m_k} = \frac{w_k}{m_k} \left(\frac{1}{\rho_k^*} - \frac{1}{\rho^*} \right)$$

Assuming a *frozen solid*, ie $\frac{d\rho_s}{dm_k} = 0$, therefore

$$\frac{\partial \tilde{\rho}}{\partial N_k} = \tilde{\rho} \frac{\phi_k}{N_k} \quad \text{A2.1}$$

$$\text{From } rN = \frac{V\tilde{\rho}}{v^*}$$

$$\frac{\partial rN}{\partial N_k} = \frac{V\tilde{\rho}}{v^*} \left(\frac{1}{V} \frac{\partial V}{\partial N_k} + \frac{1}{\tilde{\rho}} \frac{\partial \tilde{\rho}}{\partial N_k} + v^* \frac{\partial 1/v^*}{\partial N_k} \right) \quad \text{A2.2}$$

In the *frozen solid* limit the first term is zero and

$$\frac{\partial rN}{\partial N_k} = \frac{rN}{N_k} \left[\phi_k - \phi_k \left(1 - \frac{v^*}{v_k^*} \right) \right] = rN \frac{\phi_k v^*}{N_k v_k^*} = r_k \frac{v^*}{v_k^*} = r_k^0 \quad \text{A2.3}$$

Therefore

$$\frac{\partial r}{\partial N_k} = \frac{r_k^0 - r}{N} \quad \text{A2.4}$$

$$\frac{\partial T^*}{\partial N_k} = \frac{v^*}{R} \frac{\partial P^*}{\partial N_k} + \frac{P^*}{R} \frac{\partial v^*}{\partial N_k} = \left[2 \left(\frac{\sum_j \phi_j P_{kj}^*}{P^*} - 1 \right) + \left(1 - \frac{v^*}{v_k^*} \right) \right] \frac{\phi_k}{N_k} T^* = \left[2 \frac{\sum_j \phi_j P_{kj}^*}{P^*} - 1 - \frac{r_k^0}{r_k} \right] \frac{\phi_k}{N_k} T^* \quad \text{A2.5}$$

The combinatorial terms can be rewritten as

$$\frac{\partial}{\partial N_k} \sum_i N_i \ln \frac{\phi_i}{x_i(1-\phi_S)} = \ln \frac{\phi_k}{x_k(1-\phi_S)} + \sum_i \frac{N_i}{\phi_i} \frac{\partial \phi_i}{\partial N_k} + \sum_i \frac{N_i}{1-\phi_S} \frac{\partial \phi_S}{\partial N_k} - \sum_i \frac{N_i}{x_i} \frac{\partial x_i}{\partial N_k} \quad \text{A2.6}$$

Considering that

$$\frac{\partial x_k}{\partial N_k} = \frac{x_k}{N_k} (1 - x_k) \quad \text{and} \quad \frac{\partial x_i}{\partial N_k} = -\frac{x_k}{N_k} x_i$$

The last term in A2.6 is zero. The derivatives of the volume fractions are

$$\frac{\partial \phi_k}{\partial N_k} = \frac{\phi_k}{N_k} (1 - \phi_k) \quad \frac{\partial \phi_i}{\partial N_k} = -\frac{\phi_k}{N_k} \phi_i \quad \text{and} \quad \frac{\partial \phi_S}{\partial N_k} = -\frac{\phi_k}{N_k} \phi_S$$

Therefore

$$\frac{\partial}{\partial N_k} \sum_i N_i \ln \frac{\phi_i}{x_i(1-\phi_S)} = \ln \frac{\phi_k}{x_k(1-\phi_S)} + 1 - \frac{\phi_k}{x_k} \left(1 + \frac{\phi_S}{1-\phi_S} \right) = \ln \frac{r_k}{r(1-\phi_S)} + 1 - \frac{r_k}{r(1-\phi_S)} \quad \text{A2.7}$$

The final term is

$$\frac{\partial}{\partial N_k} N(z - 1 - \ln z) = z - 1 - \ln z + N \frac{z-1}{z} \frac{\partial z}{\partial N_k} \quad \text{A2.8}$$

and

$$\frac{\partial z}{\partial N_k} = -\frac{z}{N} - \frac{z}{\rho_S} \frac{d\rho_S}{dn_k} \quad \text{assuming the frozen solid} \quad \frac{\partial z}{\partial N_k} = -\frac{z}{N}$$

$$\frac{\partial}{\partial N_k} N(z - 1 - \ln z) = -\ln z \quad \text{A2.9}$$

Combining the resulting expressions

$$\frac{\mu_k^R(T)}{RT} = -\frac{\tilde{\rho}}{\tilde{T}} \left(2 \frac{\sum_j \phi_j P_{kj}^*}{P^*} - 1 - \frac{r_k^0}{r_k} \right) r_k + \left[-\frac{\tilde{\rho}}{\tilde{T}} + \frac{(1-\tilde{\rho}) \ln(1-\tilde{\rho})}{\tilde{\rho}} + 1 \right] r_k^0 + (z^{Eos} - 1) \frac{r_k}{r} - \ln z + \tilde{\rho} \left(\ln \frac{r_k}{r(1-\phi_S)} + 1 - \frac{r_k}{r(1-\phi_S)} \right) \quad \text{A2.10}$$

Which can be simplified to

$$\frac{\mu_k^R(T)}{RT} = -\frac{\tilde{\rho}}{\tilde{T}} \left(2 \frac{\sum_j \phi_j P_{kj}^*}{P^*} - 1 \right) r_k + \left[\frac{(1-\tilde{\rho}) \ln(1-\tilde{\rho})}{\tilde{\rho}} + 1 \right] r_k^0 + (z^{Eos} - 1) \frac{r_k}{r} - \ln z + \tilde{\rho} \left(\ln \frac{r_k}{r(1-\phi_S)} + 1 - \frac{r_k}{r(1-\phi_S)} \right)$$

This expression is consistent with the chemical potential of the pure component

$$\frac{\mu_{1F}^R}{RT} = r_1^0 \left[-\frac{\tilde{\rho}_1}{\tilde{T}} + \frac{(1-\tilde{\rho}_1) \ln(1-\tilde{\rho}_1)}{\tilde{\rho}_1} + 1 \right] + z - 1 - \ln z \quad \text{A2.11}$$

which can be written directly from Eq. 19

The chemical potential of the adsorbent is not obtained simply inverting the indices, since there are some asymmetries introduced by the total volume relationship. The use of mass instead of moles introduces a factor $\frac{N_S}{m_S}$ which is constant in all the derivatives that are not affected. Here $\left(\frac{\partial}{\partial m_S} \right)_{T,P,N_k}$

is taken as implicit. The deviations from symmetry arise from

$$\begin{aligned} \frac{d\tilde{\rho}}{dm_k} &= \frac{1}{\rho^*} \frac{d\rho}{dm_k} + \rho \frac{d1/\rho^*}{dm_k} \\ \frac{\partial 1/\rho^*}{\partial m_k} &= \frac{w_k}{m_k} \left(\frac{1}{\rho_k^*} - \frac{1}{\rho^*} \right) \\ \frac{d\rho}{dm_S} &= \frac{\rho_S}{m_S} - \frac{\rho}{m_S} + \frac{M}{m_S} \frac{d\rho_S}{dm_S} \end{aligned} \quad \text{A2.14}$$

Assuming a *frozen solid*, ie $\frac{d\rho_S}{dm_S} = 0$

$$\frac{d\tilde{\rho}}{dm_S} = \frac{1}{\rho^*} \left(\frac{\rho_S}{m_S} - \frac{\rho}{m_S} \right) + \rho \frac{w_S}{m_S} \left(\frac{1}{\rho_S^*} - \frac{1}{\rho^*} \right) = \frac{\tilde{\rho}}{m_S} \left(w_S - 1 + w_S \left(\frac{\rho^*}{\rho_S^*} - 1 \right) \right) = \frac{\tilde{\rho}}{m_S} (\phi_S - 1) \quad \text{A2.15}$$

Compared to A2.3 there is also an extra term since the volume of the system is the volume of the solid and

$$\frac{1}{V} \frac{\partial V}{\partial m_S} = \frac{\rho_S}{m_S} \frac{1}{\rho_S} = \frac{1}{m_S} \quad \text{A2.16}$$

For rN

$$\frac{\partial rN}{\partial m_S} = rN \left(\frac{1}{m_S} + \frac{1}{m_S} (\phi_S - 1) - \frac{\phi_S}{m_S} \left(1 - \frac{v^*}{v_k^*} \right) \right) = rN \frac{\phi_S v^*}{m_S v_k^*} \quad \text{A2.17}$$

Therefore

$$\frac{\partial r}{\partial m_S} = r \frac{\phi_S v^*}{m_S v_k^*} - \frac{r}{m_S} \frac{N_S}{N} \quad \text{A2.18}$$

$$\frac{\partial T^*}{\partial m_S} = \frac{v^*}{R} \frac{\partial P^*}{\partial N_k} + \frac{P^*}{R} \frac{\partial v^*}{\partial N_k} = \left[2 \left(\frac{\sum_j \phi_j P_{Sj}^*}{P^*} - 1 \right) + \left(1 - \frac{v^*}{v_S^*} \right) \right] \frac{\phi_S}{m_S} T^* \quad \text{A2.19}$$

There is no combinatorial contribution for the solid.

$$\frac{\partial}{\partial m_S} NZ = \frac{\partial}{\partial m_S} \frac{P m_S}{\rho_S RT} = \frac{z}{m_S} \quad \text{having assumed the } \textit{frozen solid} \text{ limit}$$

$$\frac{\partial z}{\partial m_S} = -\frac{z}{N} \frac{N_S}{m_S} + \frac{z}{m_S} - \frac{z}{\rho_S} \frac{d\rho_S}{dm_S} \quad \text{assuming the } \textit{frozen solid} \text{ limit}$$

$$\frac{\partial}{\partial m_S} N(1 + \ln z) = \frac{N_S}{m_S} \ln z + \frac{N}{m_S} \quad \text{A2.20}$$

Combining the resulting expressions

$$\begin{aligned} \frac{\mu_S^{Rm}}{RT} = & \left[rN \frac{\phi_S v^*}{m_S v_k^*} - \frac{r}{m_S} N_S \right] \left[-\frac{\tilde{p}}{\tilde{T}} + \frac{(1-\tilde{p}) \ln(1-\tilde{p})}{\tilde{p}} + 1 \right] - \frac{\tilde{p}}{\tilde{T}} \left[2 \frac{\sum_j \phi_j P_{Sj}^*}{P^*} - 1 - \frac{v^*}{v_S^*} \right] \frac{\phi_S}{m_S} rN + \\ & \frac{N}{m_S} (\phi_S - 1) (z^{Eos} - 1) + \frac{N_S}{m_S} (z - 1 - \ln z) + \frac{N}{m_S} (z - 1) \end{aligned} \quad \text{A2.21}$$

In the limit as $r_S \rightarrow \infty$, $N_S \rightarrow 0$ and

$$\frac{\mu_S^{Rm}}{RT} = rN \frac{\phi_S v^*}{m_S v_k^*} \left[\frac{(1-\tilde{p}) \ln(1-\tilde{p})}{\tilde{p}} + 1 \right] - \frac{\tilde{p}}{\tilde{T}} \left[2 \frac{\sum_j \phi_j P_{Sj}^*}{P^*} - 1 \right] \frac{\phi_S}{m_S} rN + \frac{N}{m_S} (\phi_S - 1) (z^{Eos} - 1) + \frac{N}{m_S} (z - 1) \quad \text{A2.22}$$

In the absence of adsorbates it is useful to note that $r_S N_S = \frac{m_S}{v_S^* \rho_S^*}$ and

$$\frac{\mu_{S0}^{Rm}}{RT} = \frac{1}{v_S^* \rho_S^*} \left[\frac{(1-\tilde{\rho}_S) \ln(1-\tilde{\rho}_S)}{\tilde{\rho}_S} + 1 - \frac{\tilde{\rho}_S}{\tilde{T}_S} \right] + \frac{P}{RT \rho_S} \quad \text{A2.23}$$

The chemical potential of the solid depends on pressure explicitly, via the compressibility factor. This is consistent with the expression of the total Gibbs energy, eq. 22, given that the residual chemical potentials of the adsorbates do not include this term.