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# Revisiting the thermodynamic modelling of type I gas–hydroquinone clathrates

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Under specific pressure and temperature conditions, certain gaseous species can be engaged in a host lattice of hydroquinone molecules, forming a supramolecular entity called a gas hydroquinone clathrate. This study is devoted to the thermodynamic modelling of type I hydroquinone clathrates. The gases considered in this work are argon, krypton, xenon, methane, nitrogen, oxygen and hydrogen sulphide. The basic van der Waals and Platteeuw model, which is, for example, not able to predict well the phase equilibrium properties of such clathrates at high temperature, is modified and extended by considering first the solubility of the guest in solid HQ and then the mutual interactions between the gaseous molecules inside the clathrate structure (*i.e.* guest guest interactions). Other improvements of the basic theory, such as the choice of the reference state, are proposed, and a unique set of thermodynamic parameters valid for all the studied guests are finally calculated. Very good agreement is obtained between the model predictions and the experimental data available in the literature. Our results clearly demonstrate that the highest level of theory is necessary to describe well both the triphasic equilibrium line (where the HQ clathrate, the native hydroquinone $HQ_\alpha$ and the gas coexist), the occupancy of the guest in the clathrate, and the intercalation enthalpy.

## 1. Introduction

Clathrates are solid state host–guest compounds, consisting of a network of self-associating molecules forming cages or channels in which guest species can reside.[1] The host molecules building the cage network can be inorganic (*e.g.* water forming the well-known clathrate hydrates[2]), or organic (*e.g.* hydroquinone, phenol, urea) forming a class of supramolecular structures called organic clathrates. The cage structure is determined by the molecular size and shape of the guest component,[3] and clathrates are usually stable only under certain thermodynamic conditions, in the presence of the guest molecules.

Although organic clathrates were regarded as fascinating scientific curiosities since the 19th century,[4] they retained attention for their potential interest in various practical interesting applications such as gas separation by selective clathration,[5,6] lubrication and fuel additives,[7] or stabilization of unstable molecules and storage of toxic compounds.[8–10]

Among the various organic hosts, hydroquinone or 1,4-benzenediol (denoted HQ in the following) is a hydroxyphenolic organic compound of formula $C_6H_6O_2$. HQ presents three usual polymorphic forms in the solid state (α, β and γ). The α-form is the stable phase of pure HQ under ambient conditions. The monoclinic γ-form can be obtained by sublimation or rapid evaporation of a HQ solution in ether[11] and only the β-form is observed to form clathrates in the presence of guest molecules. Another phase of hydroquinone (called δ-HQ) has been recently observed at high pressure and temperature.[12,13] However, only the β- and α-forms are of interest in this work.

The β-form of hydroquinone has been well described by Powell and co-workers.[14–16] The host lattice of the β-HQ clathrates is an open structure formed by hydrogen bonded rings of 6 members resulting in two interpenetrated but not interconnected networks of hydroquinone molecules. This structure can accommodate various small guest molecules such as Ar, Kr, Xe, $CH_4$, $H_2S$, $CO_2$, $SO_2$ or $CH_3OH$ in cages sandwiched between each pair of $[OH]_6$ rings of different networks.[16–21] The host–guest interaction is given by van der Waals forces. In Fig. 1(a) a typical cage of the β-HQ clathrate is represented.

The general formula for these clathrates is $3C_6H_4(OH)_2{\cdot}xG$, where G denotes the enclathrated guest molecule and $x$ is the site-occupancy factor of this guest inferior or equal to one. The ideal stoichiometry corresponds to the 1 : 3 ratio (one guest molecule per 3 HQ molecules). A representation of this structure is given in Fig. 1(b). Although these compounds are considered stable only in the presence of guests, the existence of an empty β-HQ clathrate was reported in 1981 by crystallization of HQ from *n*-octane,[22] and more recently by Lee and co-workers[23,24] who have shown the stability of the guest-free β-structure from a guest-loaded β-structure and its subsequent decomposition to

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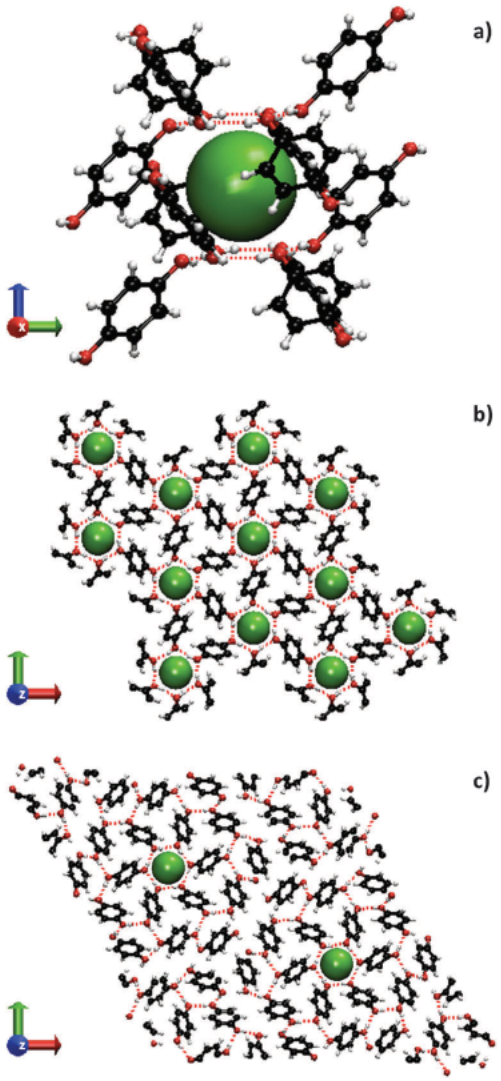


Fig. 1 (a) Typical cage in type I β HQ clathrate viewed along the *x* axis. The two interpenetrated but not interconnected networks are observed. (b) β HQ clathrate unit cell viewed along the *z* axis replicated by a 2 factor. The guest molecules (in green) are enclathrated by six HQ molecules. The hydrogen bonds are represented by red dashed lines. (c) Unit cell of the α form hydroquinone viewed along the *z* axis. The hydrogen bonds are represented by red dashed lines and the colour code for the atoms is C black, O red, H white and G green.

the α-form at high temperatures. The size and shape of the cage being dependent on the size and geometry of the guest that is present in the cages, Powell and co-workers have classified the β-HQ clathrates into three crystallographic distinguishable types of β-HQ denoted I, II and III:[25] type-I crystallises in space group $R\bar{3}$ generally with small and spherical guests, such as Ar, Kr, Xe or $CH_4$; for non-spherical molecules, such as $SO_2$ or $CH_3OH$, the cage is distorted and the symmetry is lowered giving a type-II structure crystallising in space group *R*3; for very large molecules with well-defined orientations in the structure, such as $CH_3CN$, the symmetry is further reduced (from the rhombohedral lattice to a trigonal one), the clathrate belongs to space group *P*3 and is qualified type-III. Depending on the type of structure the lattice parameters are different as a function of the size and geometry of the guest.[26] For type-I compounds the lattice parameters are practically constant since the cage is not affected by distortion. In this paper, only the guest molecules Ar, Kr, Xe, $CH_4$, $N_2$, $O_2$ and $H_2S$ forming type-I clathrates will be considered.

The α-form of hydroquinone also belongs to space group $R\bar{3}$ with a rhombohedral unit cell. The structure is built by an open cagework similar to that found in the β-form and a double helix of chains of hydroquinone molecules surrounding the three-fold screw axes[27] (see Fig. 1(c)). Since the cages in the α-form have approximately the same dimensions as in the β-form, the α-form is able to accommodate small molecules also such as $CO_2$,[28] $SO_2$,[29] Ar,[18] Kr,[30] Xe,[31] and $H_2$.[32] However the number of cages which can be found in α- and β-forms is very different. In α-HQ the number of cages is six times less than that in β-HQ. Therefore, the ideal stoichiometry in the α-form corresponds to the ratio of 1 : 18 (one guest molecule per 18 HQ molecules), against 1 : 3 for the β-form. It is worth noting for the α-form of HQ that: (i) this structure is not considered within the family of clathrate compounds since in the absence of guest molecules in the cages, the α-form remains stable; (ii) the α-form is more stable thermodynamically than the β-form under ambient conditions; however this difference is very small and may be explained by the more extensive hydrogen bonding in the β-form, which almost compensates for the energy lost by the fewer van der Waals contacts;[33] and (iii) the presence of guest molecules in the cages of the α-structure plays an important role in the study of the phase equilibrium. This last issue will be discussed further on in the following sections.

The knowledge of both the thermodynamic equilibrium properties (phase diagram) and the quantity of gas contained in the clathrate (occupancy) is of paramount importance for a given gas–HQ system, particularly the triphasic equilibrium line where the non-clathrate phase (α-HQ), the clathrate phase (β-HQ) and the free gas coexist. However, the work presented in this paper has a general significance and is not devoted to a particular practical application of these compounds. In comparison to gas hydrates for which an impressive quantity of experimental equilibrium data exists in the literature,[2] gas organic clathrates were much less studied. Except for krypton and xenon where experimental dissociation pressures were published (in Russian) in an extended range of temperature (from 273 to 446.5 K) by Kazankin and co-workers in 1973,[34,35] experimental data for other gas are very scarce or provided in a very limited range of temperature. For example, only 2 experimental points exist for argon at 298 and 373 K,[36,37] and only data from 283.4 to 297.9 K are found for methane.[38]

Concerning the thermodynamic modelling of organic clathrates, van der Waals[36] has first proposed a theory for the formation of clathrates with one type of cavity and one type of guest. Then, van der Waals and Platteeuw[39] have generalized this theory for clathrates with different types of cavities and guests. They applied their thermodynamic model for both hydrates and hydroquinone clathrates and obtained good agreement with experimental results in the case of simple guests and

under ambient conditions but the estimations of dissociation conditions were deteriorating with both the complexity of the guests and the thermodynamic conditions. Hence, from this pioneering work fifty years ago, attempts were made to improve the description of more complex systems. A first group of modification concerns the study of hydrates for which the original van der Waals–Platteeuw theory (vdWP theory) has been widely applied. Two principal routes have been followed to improve the description of the stability conditions of hydrates: (i) a better description of both the chemical potential of water in the aqueous and hydrate phases and the fugacity of the guest (use of more sophisticated equations-of-state than the ideal gas model) and (ii) fitting of the parameters of the model on existing numerous formation/dissociation condition data. The review of Holder *et al.*[40] and the book of Sloan and Koh[2] give a good overview of the modelling of hydrate formation since the original vdWP theory. The second group of modifications is not focused solely on hydrates but concerns all types of clathrate compounds. It was performed by Belosludov and coworkers who proposed a non-ideal version of vdWP theory essentially by including: (i) guest–guest interactions to take into account the cooperative behaviour of the guests that participate in the stabilization of the structure[41–43] and (ii) the possibility of the α-HQ phase to dissolve guests.[44,45] These improvements, contrary to what has been done in the case of hydrate modelling during the last few decades, have not been widely compared to experimental results of the authors. Solely the whole phase diagram of the Xe–HQ system and the nonvariant point or ambient temperature for few noble gas–HQ systems have been explored.[42]

In this work, following some ideas developed by Belosludov and coworkers such as the inclusion of guest–guest interactions and the solubility of the guests in the α-HQ phase, we propose a modified version of vdWP theory suitable for all type I gas–HQ clathrates. We propose a strategy to obtain some reference properties of the model in order to accurately compute both the triphasic equilibrium coexistence line (α-HQ, β-HQ and free gas) and the clathrate occupancy of type I gas formers.

The paper is organized as follows. In the theoretical section, after a brief reminder of the original vdWP theory, we develop the modifications of the theory included in this study. In the Results section, after a discussion on the different parameters of the model, we use the latter to compute both the dissociation pressure and enthalpies of dissociation, and the occupancy in the one phase region of various type I gas–HQ systems.

## 2. Theoretical section

### 2.1. van der Waals–Platteeuw theory

The model of van der Waals and Platteeuw (vdWP)[36,39,46] is based on a three-dimensional generalization of ideal localized adsorption using statistical mechanics. It provides a bridge between the microscopic properties of the clathrate structure and its macroscopic thermodynamic properties. In the original theory, several assumptions are considered: (i) the contribution of the host molecules (HQ) to the free energy is independent of the mode of occupation of the cages. This excludes HQ clathrates for which the host lattice is seriously distorted by the presence of guest molecules such as $CO_2$ or $CH_3CN$; (ii) every guest molecule is localized within the cage and each cage can never host more than one guest molecule; (iii) the interaction between the guest molecules is neglected, *i.e.* the partition function of each guest in its cage is independent of the number and types of guest molecules present in the surrounding cages and (iv) classical statistics is valid (no quantum effects are taken into account). These assumptions are considered in the original vdWP model (hereafter called basic theory, BT). However, in this study the basic theory will be extended to take into account some issues not considered in the original theory in order to improve phase equilibrium prediction for HQ clathrates.

In our work, the triphasic equilibrium coexistence line (α-HQ, β-HQ and free gas) will be considered. Thus, at equilibrium, for each component $i$ (guest or HQ) of the system:

$$\mu_i^{\beta\text{-HQ}} = \mu_i^{\alpha\text{-HQ}} = \mu_i^{\mathrm{G}} \tag{1}$$

The chemical potential is replaced by the chemical potential differences ($\Delta\mu$) between the actual state and a hypothetic reference one to facilitate the calculations. For this, the metastable empty β-lattice of the clathrate was used by van der Waals and Platteeuw as the reference state to determine these chemical potential differences:

$$\Delta\mu^{\beta\text{-HQ}} = \mu_{\mathrm{Empty}}^{\beta\text{-HQ}} - \mu_{\mathrm{Filled}}^{\beta\text{-HQ}} \tag{2}$$

$$\Delta\mu^{\alpha\text{-HQ}} = \mu_{\mathrm{Empty}}^{\beta\text{-HQ}} \quad \mu^{\alpha\text{-HQ}} \tag{3}$$

where $\mu_{\mathrm{Empty}}^{\beta\text{-HQ}}$ is the chemical potential of the metastable empty clathrate lattice, $\mu_{\mathrm{Filled}}^{\beta\text{-HQ}}$ is the chemical potential of the clathrate in the presence of guest molecules and $\mu^{\alpha\text{-HQ}}$ is the chemical potential of the HQ α-form. Both terms ($\Delta\mu^{\beta\text{-HQ}}$ and $\Delta\mu^{\alpha\text{-HQ}}$) are calculated separately to estimate both the equilibrium conditions ($p$,$T$) and the occupancy of the gas–HQ clathrate system.

$\Delta\mu^{\beta\text{-HQ}}$ can be obtained following the vdWP BT from the partition function of the clathrate as:

$$\Delta\mu^{\beta\ \mathrm{HQ}}(T,p) = \quad RT\sum_m \nu_m \ln \quad 1 \quad \sum_j \theta_{mj}\Big) \tag{4}$$

where $\nu_m$ is the number of cages of type $m$ per host molecule in the clathrate lattice. $\theta_{mj}$ is the occupancy factor for each guest $j$ within the cage $m$. In the case of HQ clathrates where there is only one type of cage and for a unique guest the above expression is simplified as:

$$\Delta\mu^{\beta\text{-HQ}}(T,p) = \quad RT\nu^{\beta}\ln(1 \quad \theta^{\beta}) \tag{5}$$

where $\nu^{\beta}$ is equal to 1/3 (1 cage per 3 hydroquinone molecules) according to crystallographic characteristics of the β-form structure.

The fraction of cages occupied by guest molecules can be calculated in analogy with Langmuir adsorption theory[37,39] due to similarities existing between the adsorption of molecules on a surface and the mechanism of clathrate formation. The principal assumptions made for the mechanism of Langmuir

adsorption are then applied for clathrate formation: the free energy of the host cavity is independent of its filling degree (no cavity distortion and the filling of a cavity is independent of the filling of neighbouring cavities), each cavity can integrate at the most one guest, the interaction between the guest molecules is neglected, and quantum effects are not taken into account. With these assumptions, the occupancy is then given by:

$$\theta^{\beta} = \frac{C^{\beta}_{\text{lang}} f}{1 + C^{\beta}_{\text{lang}} f} \tag{6}$$

where $C^{\beta}_{\text{lang}}$ is the Langmuir constant and $f$ is the fugacity of the guest. In this work, the Soave–Redlich–Kwong equation[47,48] was used to estimate the fugacity of the gases.

The Langmuir constant is a description of the affinity of the empty cage for a molecule to fill this cage. $C^{\beta}_{\text{lang}}$ can be obtained from the supposed spherically spherical potential energy $\omega(r)$ between the guest molecule and the host molecules constituting the cage using

$$C_{\text{lang}} = \frac{4\pi}{k_B T}\int_0^R \exp\left( \quad \frac{\omega(r)}{k_B T}\right) r^2 \mathrm{d}r \tag{7}$$

where $r$ is the distance of the guest molecule from the cage center. For type I hydroquinone clathrates, the radius $R$ of the cell potential is about 3.95 Å,[39] being constant for all guests. However, for type II or III HQ-clathrates, this value is unknown and depends on the guest nature.

The average spherical potential $\omega(r)$ can be calculated using the Lennard-Jones–Devonshire method (LJD).[39,49,50] In the LJD method, the interactions of $z$ molecules distributed over the surface of a sphere are summed to obtain the average potential $\omega(r)$ describing the resulting field of the "smeared" spherical cavity of radius $R$:

$$C_{\text{lang}} = \exp\left[ \quad \frac{\omega(0)}{k_B T}\right] \int_0^R \exp\left( \quad \frac{\omega(r) \quad \omega(0)}{k_B T}\right) 4\pi r^2 \mathrm{d}r \tag{8}$$

where $k_B$ is the Boltzmann's constant. When the Lennard-Jones potential is used, one obtains:

$$\omega(0) = z\varepsilon[\alpha^{-4} \quad 2\alpha^{-2}] \tag{9}$$

and

$$\omega(r) \quad \omega(0) = z\varepsilon\left[\alpha^{-4} l\left(\frac{r^2}{R^2}\right) \quad 2\alpha^{-2} m\left(\frac{r^2}{R^2}\right)\right] \tag{10}$$

$\sigma$ and $\varepsilon$ are, respectively, the collision diameter and the depth of the potential, and $z$ is the coordination number. For HQ clathrates, $z$ is equal to 24.[39] $\alpha$ is the measure of the cell radius $R$ in terms of the effective molecular diameter $\sigma$ with

$$\alpha = \sqrt{2}\frac{R^3}{\sigma^3} \tag{11}$$

where $l(x)$ and $m(x)$ are algebraic functions of the dimensionless variable $x = r^2/R^2$ given by

$$l(x) = (1 + 12x + 25.2x^2 + 12x^3 + x^4)\,(1 \quad x)^{-10} \quad 1 \tag{12}$$

$$m(x) = (1 + x)\,(1 \quad x)^{-4} \quad 1 \tag{13}$$

To estimate the clathrate potential *i.e.* the interaction potential between the host and the guest, the classical Lorentz–Berthelot mixing rules were used:[51,52]

$$\sigma_{\text{clathrate}} = \frac{\sigma_{\text{guest}} + \sigma_{\text{HQ}}}{2} \tag{14}$$

$$\varepsilon_{\text{clathrate}} = \sqrt{\varepsilon_{\text{guest}}\varepsilon_{\text{HQ}}} \tag{15}$$

Thus, knowing the potential parameters for both the HQ molecule and the guest, $\Delta\mu^{\beta\text{-HQ}}(T,p)$ can be estimated without fitting the parameters to experimental data, thus making possible to calculate the equilibrium properties in systems where scarce or no experimental data exist.

The difference in chemical potential between the empty clathrate lattice and α-HQ is given by:

$$\Delta\mu^{\alpha\ \text{HQ}}(T,p) = RT\left[\int\left(\frac{\Delta H}{RT^2}\right)\mathrm{d}T \quad \int\left(\frac{\Delta V}{RT}\right)\mathrm{d}p\right] \tag{16}$$

where $\Delta H$ and $\Delta V$ denote the differences between molar heat functions and molar volumes of the empty-β and α modifications. Integrating (16) yields:

$$\Delta\mu^{\alpha\ \text{HQ}}(T,p) = RT\left[\frac{\Delta\mu_0^{\alpha\beta}}{RT_0} \quad \frac{\Delta H_0^{\alpha\beta}}{R}\left(\frac{1}{T} \quad \frac{1}{T_0}\right) + (p \quad p_0)\frac{\Delta V_0^{\alpha\beta}}{RT}\right] \tag{17}$$

where $T_0$ is the temperature, $p_0$ the pressure, $\Delta\mu_0^{\alpha\beta}$ the chemical potential difference, $\Delta H_0^{\alpha\beta}$ the difference in enthalpy and $\Delta V_0^{\alpha\beta}$ the difference in volume between empty-β and α-forms at the reference state. In order to compute $\Delta\mu^{\alpha\text{-HQ}}$, one has to know the thermodynamic properties at the reference temperature. In the BT, van der Waals and Platteeuw have chosen 298 K as the reference temperature for HQ clathrates. This statement will be discussed and detailed in the section Results and discussion.

### 2.2. Solubility in the α-phase

Contrary to what can be observed with ice in the case of hydrates, experimental evidence has shown that guest molecules may be soluble in the HQ α-phase, as described in the Introduction. However, the BT does not consider this issue. Zubkus *et al.*[45] have estimated in some cases the supplementary chemical potential difference that could be induced by the solubility in the α-phase and observed that the effect was in some case (Kr, Xe, $CH_4$) not negligible, leading to a modification of the chemical potential difference of nearly 15%. Hence, in this work, we have decided to take into account the solubility of all the guests in the HQ α-phase.

Since α-HQ contains the same kind of cage with almost the same size as in β-HQ (the two phases just differ in the spatial arrangement of the cages) the part of the chemical potential of a stable α-phase due to guest molecules accommodated within its cages can be described analogously to the β-phase as:

$$\Delta\mu^{\alpha*\text{-HQ}}(T,p) = \quad RT\nu^{\alpha}\ln(1 \quad \theta^{\alpha}) \tag{18}$$

where $\nu^{\alpha}$ is 1/18 (1 cage per 18 hydroquinone molecules) and $\theta^{\alpha}$ is the occupancy in the α-phase. The new chemical equilibrium for the HQ system becomes:

$$\Delta\mu^{\beta\text{-HQ}} = \Delta\mu^{\alpha\text{-HQ}} + \Delta\mu^{\alpha*\text{-HQ}} \tag{19}$$

At this point, two different occupancies are considered, one for the α-phase and the other for the β-phase. However, they are linked by the fugacity of the guest that is the same in all the phases at equilibrium. Indeed,

$$\theta^{\beta} = \frac{C^{\beta}_{\text{lang}} f}{1 + C^{\beta}_{\text{lang}} f} \tag{20}$$

$$\theta^{\alpha} = \frac{C^{\alpha}_{\text{lang}} f}{1 + C^{\alpha}_{\text{lang}} f} \tag{21}$$

The combination of eqn (20) and (21) gives the following relation between the two occupancies:

$$\theta^{\alpha} = \frac{1}{\frac{C^{\beta}_{\text{lang}}}{C^{\alpha}_{\text{lang}}}\left(\frac{1}{\theta^{\beta}} \quad 1\right) + 1} \tag{22}$$

Considering the similarity of the cages in the α and β phases, the Langmuir constants can be considered as equal, which implies that $\theta^{\beta} = \theta^{\alpha} = \theta$ and that the new phase equilibrium including the solubility in the α-phase is given by:

$$\Delta\mu^{\beta\text{-HQ}} \quad \Delta\mu^{\alpha*\text{-HQ}} = \Delta\mu^{\alpha\text{-HQ}} = RT[(\nu^{\alpha} \quad \nu^{\beta})\ln(1 \quad \theta)] \tag{23}$$

### 2.3. Guest–guest interactions

The BT predicts a constant occupancy for all possible guests accommodated within the cages for HQ clathrates. However, experimental evidence has shown that this occupancy is not constant, even for guests forming type I HQ clathrates (see Table 4). Thus, it appears to be necessary to include new elements in the theory that can catch these differences. For type I HQ clathrates, considering that $\Delta\mu_0^{\alpha\beta}$, $\Delta H_0^{\alpha\beta}$ and $\Delta V_0^{\alpha\beta}$ are the same, whatever the guest, as the β-HQ structure is the same for all the guests, the only leverage in the theory to obtain an occupancy function of the guest is to include the influence of guest–guest interactions. Belosludov and co-workers[42–45] studied the importance of these interactions in the clathrate equilibrium. They have shown that in HQ clathrates (especially at high temperature) the guest–guest interaction is weaker than in other clathrates since the cages are relatively small and the volume of the cages is a small part of the whole crystal volume but that, even in these systems, the guest–guest interaction is rather clearly revealed.

As proposed by Belosludov and coworkers, the guest–guest contribution ($V_{\text{gg}}$) to the chemical potential can be computed by performing the summation of all pair interactions of guest molecules in the form of the Lennard-Jones potential as:

$$V_{\text{gg}} = 2\varepsilon_{\text{guest}}\left[\left(\frac{\sigma_{\text{guest}}}{r}\right)^{12} g_{12} \quad \left(\frac{\sigma_{\text{guest}}}{r}\right)^{6} g_6\right] \tag{24}$$

where $g_{12} = \sum P_{ij}^{-12}$, $g_6 = \sum P_{ij}^{-6}$, and $rP_{ij}$ is the distance between atoms $i$ and $j$, expressed in the nearest distance $r$ dimensions.

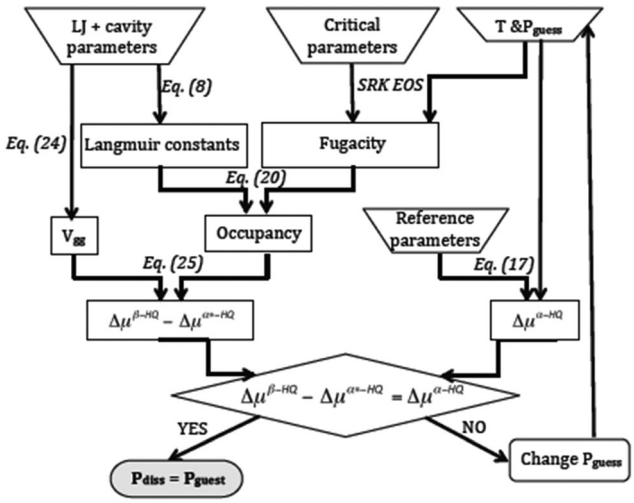


Fig. 2 Schematic overview of the prediction of HQ clathrate dissociation pressure with eqn (25).

The parameters $g_{12}$ and $g_6$ depend on host lattice properties and were calculated in this work by considering only the 14 neighbouring guest molecules[53] for the guest. The main contribution to the $g$ terms is given by the neighbours located above and below the guest on the same channel of the structure in both phases.

Finally, the chemical potential difference including the contributions of both the solubility of the guest in the α-phase and the guest–guest interactions is given by:

$$\Delta\mu^{\beta\ \text{HQ}} \quad \Delta\mu^{\alpha*\ \text{HQ}} = \Delta\mu^{\alpha\ \text{HQ}} = RT\left[\left(\nu^{\alpha} \quad \nu^{\beta}\right)\ln(1 \quad \theta) \quad \frac{\theta^2}{2}\left(\nu^{\alpha} V^{\alpha}_{\text{gg}} \quad \nu^{\beta} V^{\beta}_{\text{gg}}\right)\right] \tag{25}$$

Solving eqn (25) allows determining the thermodynamic conditions at which α and β-phases coexist, *i.e.* the dissociation pressure of the clathrate at a given temperature. The schematic overview of the prediction of HQ–clathrate dissociation pressure using eqn (25) is given in Fig. 2.

The incorporation of the solubility in the α-phase and the guest–guest interactions provides different predictions on the conditions of equilibrium and the occupancy of HQ clathrates with respect to the original vdWP theory. In the next section, the influence of these contributions will be studied.

## 3. Results and discussion

### 3.1. Influence of the modifications introduced in vdWP theory

In this section, some details of the model are discussed, with emphasis on the influence of the various modifications introduced in the original vdwP theory.

As a first test, the results of the basic theory (BT) were compared with the original work of van der Waals and Platteeuw.[39] The critical parameters and the acentric factor used in the SRK equation-of-state to compute the fugacity of the guests at 298 K

Table 1 Critical properties of the guest molecules taken from Prausnitz *et al.*[54] The molecular weight is given by $M_w$, critical temperature and pressure by $T_c$ and $p_c$, respectively, and $\omega$ denotes the acentric factor

| Guest | $M_w$ (g mol$^{-1}$) | $T_c$ (K) | $p_c$ (bar) | $\omega$ |
|---|---|---|---|---|
| Ar | 39.948 | 150.86 | 48.98 | 0.002 |
| Kr | 83.8 | 209.40 | 55.00 | 0.00 |
| Xe | 131.29 | 289.74 | 58.40 | 0.00 |
| $CH_4$ | 16.043 | 190.56 | 45.99 | 0.011 |
| $N_2$ | 28.014 | 126.20 | 33.98 | 0.037 |
| $O_2$ | 31.999 | 154.58 | 50.43 | 0.022 |
| $H_2S$ | 34.082 | 373.40 | 89.63 | 0.090 |

Table 2 Lennard Jones potential parameters for the guest molecules taken from van der Waals and Platteeuw,[39] Martin and Siepmann[55] and Prausnitz *et al.*[54] The LJ interaction parameters for the hydroquinone host lattice were taken from vdWP[39] with $\sigma$ = 2.90 Å and $\varepsilon/k_B$ = 150.06 K

| Guest | Ar | Kr | Xe | $CH_4$ | $N_2$ | $O_2$ | $H_2S$ |
|---|---|---|---|---|---|---|---|
| $\sigma$ (Å) | 3.408 | 3.679 | 4.069 | 3.730 | 3.698 | 3.58 | 3.623 |
| $\varepsilon/k_B$ (K) | 119.5 | 166.7 | 225.3 | 148.0 | 95.05 | 117.5 | 301.1 |

were taken from Prausnitz *et al.*[54] and are listed in Table 1. In Table 2, the LJ potential parameters for the guest molecules are shown, and the parameters corresponding to thermodynamic properties in the reference state were taken from the original vdWP work for this first calculation. As shown in Table 3, the dissociation pressure modelling of HQ clathrate with various guests at 298 K is in perfect agreement with the one of the original paper of vdWP and with experiment.

However, if the modelling was done with the original model and the original parameters of vdWP theory are expanded at higher temperatures, the dissociation pressure of the HQ clathrate is systematically underestimated whatever the guest, as previously also noticed by Zubkus *et al.*[45] and as shown in Fig. 3 (dotted line) for the Xe–HQ clathrate. This behaviour may be assigned to the reference state. There is no physical reason why the reference point should be taken at 298 K. This choice was probably guided by the fact that it is more convenient to measure the thermodynamic properties at this room temperature. In this work, we have chosen to use a reference point that is thermodynamically meaningful and common to every system: the melting temperature of hydroquinone $T_{\mathrm{melt\,HQ}}$. The latter fixes the quadrupole point in all the guest–HQ phase diagrams almost at $T_0 = T_{\mathrm{melt\,HQ}}$ = 446 K. Actually, the melting point of the host has been traditionally used in the modelling of the hydrate phase behaviour since the pioneering work of vdW–P for hydrates at $T_{0,\mathrm{hyd}}$ = 273 K. However, in their original work, van der Waals

Table 3 Dissociation pressure of HQ clathrate with various guests at 298 K

| Guest | $p_{\mathrm{diss}}$ (bar) experimental | $p_{\mathrm{diss}}$ (bar) original vdWP work | $p_{\mathrm{diss}}$ (bar) this work (BT) |
|---|---|---|---|
| Ar | 3.4 | 3.4 | 3.4 |
| Kr | 0.4 | 0.4 | 0.4 |
| Xe | 0.058 | 0.06 | 0.058 |
| $CH_4$ | 0.82 | 0.80 | 0.81 |
| HCl | 0.01 | 0.02 | 0.02 |

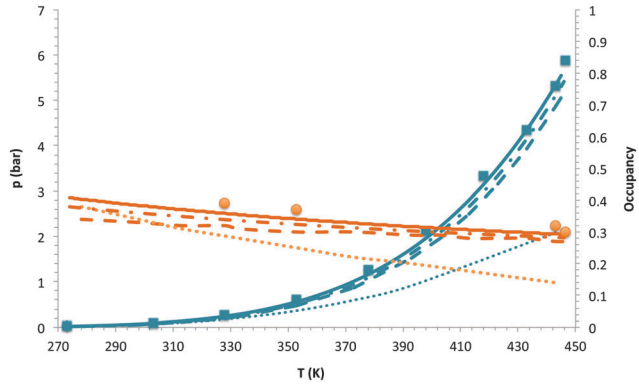


Fig. 3 Dissociation pressure (in blue) and the occupancy on the dissociation line (in orange) of the Xe HQ clathrate. Symbols: experiments.[34,35,58,59] Dotted line: original van der Waals and Platteeuw model. Dashed line: vdwP theory with $T_0$ = 446 K. Dotted dashed line: vdwP theory with $T_0$ = 446 K and solubility in the α phase. Full line: improved vdWP model proposed in this work ($T_0$ = 446 K, solubility in the α phase and guest guest interactions).

and Platteeuw have chosen 298 K as a reference temperature for HQ clathrates and then this value was adopted in every following study.

The thermodynamic properties $\Delta\mu_0^{\alpha\beta}$, $\Delta H_0^{\alpha\beta}$ and $\Delta V_0^{\alpha\beta}$ of the empty metastable lattice relative to the stable α one were only reported at 298 K.[39,56,57] Thus, they have been recomputed in this work for the new reference state. As only solid phases are considered, $\Delta V_0^{\alpha\beta}$ is considered to be nearly independent of pressure and temperature and the value of 4.6 cm$^3$ mol$^{-1}$ previously published by Powell[28] is still used. $\Delta\mu_0^{\alpha\beta}$ and $\Delta H_0^{\alpha\beta}$ have been computed in order to best reproduce the previously measured occupancies of type I HQ clathrates at 298 K[34,39] and 446 K,[35] *i.e.* $0.34 < \theta_{298\mathrm{K}} < 0.41$ and $0.28 < \theta_{446\mathrm{K}} < 0.30$. This new set of parameters is common for all the guests that form type I HQ clathrates since these thermodynamic properties depend on the host lattice and are independent of the type of guest. The obtained reference thermodynamic properties are collected in Table 4. A summary of the experimental occupancies is given in Table 7 together with the ones computed with the version of the theory proposed in this work.

As an example, one can see in Fig. 3 the perfect agreement between both the experimental dissociation pressure and the occupancy on the dissociation line of the Xe–HQ clathrate measured by Kazankin *et al.*[34,35] and the one obtained with the improved vdWP model proposed in this work, *i.e.* taking into account not only the solubility of the gas in the α-phase but also the interactions between the guests. If solely the solubility in the α-phase is included but not the guest–guest interactions, the results are improved in comparison with the original vdWP model but the model fails to predict well both the occupancy of the clathrate and its dissociation pressure (see Fig. 3). The guest–guest

Table 4 Reference thermodynamic properties $\Delta\mu_0^{\alpha\beta}$, $\Delta H_0^{\alpha\beta}$ and $\Delta V_0^{\alpha\beta}$ at $T_0$ = 446 K computed in this work

| Host lattice | $\Delta\mu_0^{\alpha\beta}$ (J mol$^{-1}$) | $\Delta H_0^{\alpha\beta}$ (J mol$^{-1}$) | $\Delta V_0^{\alpha\beta}$ (cm$^3$ mol$^{-1}$) |
|---|---|---|---|
| HQ | 345 | 250 | 4.6 |

Table 5 Guest guest interaction contributions for α and β forms for several guest molecules in HQ clathrates

| Guest | Ar | Kr | Xe | $CH_4$ | $N_2$ | $O_2$ | $H_2S$ |
|---|---|---|---|---|---|---|---|
| $V^{\alpha}_{gg}$ (kJ mol $^{1}$) | 0.212 | 0.453 | 1.029 | 0.433 | 0.265 | 0.209 | 0.752 |
| from ref. 45 | 0.20 | 0.38 | 0.98 | 0.45 | | | |
| $V^{\beta}_{gg}$ (kJ mol $^{1}$) | 0.251 | 0.538 | 1.239 | 0.515 | 0.315 | 0.247 | 0.892 |
| from ref. 45 | 0.24 | 0.46 | 1.19 | 0.55 | | | |

interactions used in this work were estimated according to eqn (24) with $g^{\alpha}_{12}$ = 2.000000609, $g^{\alpha}_{6}$ = 2.002701, $g^{\beta}_{12}$ = 2.0102 and $g^{\beta}_{6}$ = 2.3461, obtained as a function of the lattice parameters for the α-form[27] ($a$ = 38.46 Å; $c$ = 5.65 Å) and the β-form[60] ($a$ = 16.61 Å; $c$ = 5.52 Å) assuming that both phases present the same type of cage. The values obtained in this work, collected in Table 5, are in agreement with those obtained by Zubkus *et al.*[45] for Ar, Kr, Xe and $CH_4$–HQ clathrates.

In conclusion of this sensitivity analysis of the different parameters and assumptions of the theory shown here in the case of Xe–HQ clathrate, the original vdWP model can be improved with three modifications: the reference temperature, the inclusion of both solubility in the α-phase and guest–guest interactions. The theory will be tested with these three modifications on various guests forming type I HQ-clathrates in the next section.

### 3.2. Formation/dissociation lines

The dissociation lines computed with the model proposed in this work are compared with all the existing published experimental data for type I HQ clathrates in Fig. 4. The concerned guests are argon, krypton, methane, xenon and nitrogen. Considering the very good agreement obtained between the modelled and experimental dissociation pressures, the equilibrium lines have also been computed for other guests forming type I β-structures but for which no experimental data exist for comparison: oxygen and hydrogen sulphide.

The intercalation enthalpy – *i.e.* the enthalpy associated with the filling of the empty β structure by the guests – of the HQ clathrates was also calculated from the data obtained with the improved vdWP theory. As the variation of the intercalation enthalpies with temperature is not likely to be large,[61] this quantity was considered as constant in the calculation. In this work,

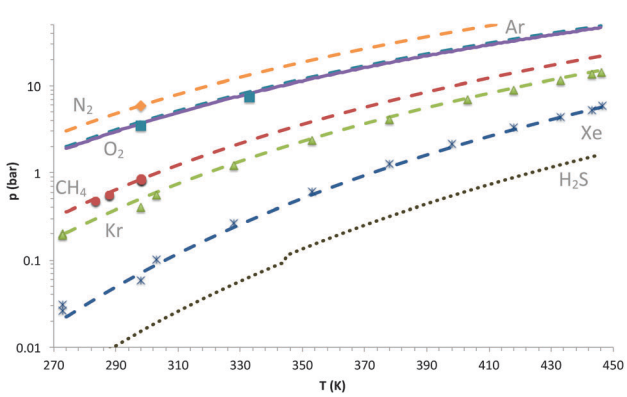


Fig. 4 Dissociation pressure of type I HQ clathrates. Symbols: experiments.[34 35 38 39] Lines: improved vdWP model proposed in this work.

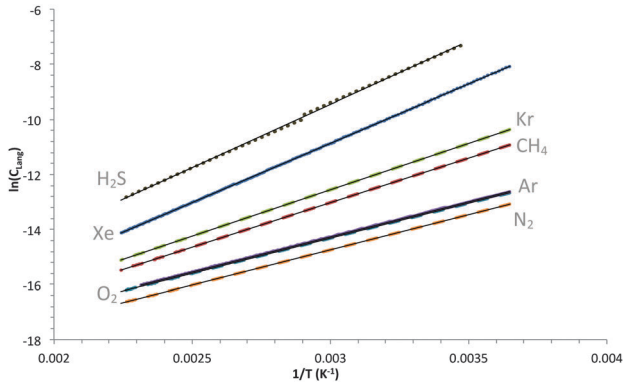


Fig. 5 Langmuir constants of the type I HQ clathrates. $\ln(C_{lang})$ *vs.* $1/T$.

intercalation enthalpies were computed from the variation of the Langmuir constant with temperature. Indeed, combining the relationship giving the Gibbs free energy of intercalation as a function of the thermodynamic equilibrium constant, *i.e.* the Langmuir constant here:

$$\Delta G = RT\ln(C_{\mathrm{Lang}}) \tag{26}$$

with

$$\Delta G = \Delta H \quad T\Delta S \tag{27}$$

one obtains:

$$\ln(C_{\mathrm{Lang}}) = \ln\left(\frac{\theta}{(1 \quad \theta)p_{\mathrm{diss}}}\right) = \frac{\Delta H}{RT} \quad \frac{\Delta S}{R} \tag{28}$$

For that purpose the modelled $C_{\mathrm{Lang}}(T)$ data are plotted in Fig. 5 as $\ln(C_{\mathrm{Lang}})$ *vs.* $1/T$. They can be perfectly least-squares fitted to a first order polynomial in $1/T$ as clearly demonstrated by the regression coefficient in Table 7 which is each time superior to 0.999. Such linear plot confirms the validity of the assumption made previously when considering the enthalpy to be constant in the considered temperature range. The calculated intercalation enthalpies (computed as the slopes multiplied by the perfect gas constant) are in excellent agreement with previous published measurements (see Table 6) considering the discrepancy between the experimental values.

One has to notice that the intercalation enthalpy is directly linked with the enthalpy of formation of the clathrate as the latter is the sum of two contributions: the enthalpy necessary to change the α form to the empty β structure and the intercalation enthalpy.

### 3.3. Occupancies of type I HQ-clathrates

The occupancies calculated under dissociation conditions are compared in Table 7 with the existing experimental data at two temperatures (298 K and 446 K) covering the solid α-HQ range. Considering the experimental uncertainties of such properties, the calculated occupancies are in good agreement with the measured ones. For each guest, the occupancy decreases with temperature. Moreover, contrary to what was initially proposed by van der Waals and Platteeuw,[39] the experiments on various guests clearly show that the occupancy of type I HQ-clathrates is not constant for all the guests at a given temperature but is

Table 6 Intercalation enthalpies estimated in this work from eqn (28) and compared with the experimental values found in the literature

| Guest | $r^2$ | $\Delta H$ (kJ mol$^{-1}$ guest) This work | Literature |
|---|---|---|---|
| Ar | 1 | 21.2 | 21.3[a]<br>25.1[b]<br>26.4[c] |
| Kr | 1 | 28.0 | 25.5[d]<br>26.4[e,f]<br>28.0[a] |
| $CH_4$ | 1 | 27.0 | 25.5[d]<br>27.2[a]<br>30.1[g]<br>39.7[c] |
| Xe | 1 | 35.8 | 33.1[f]<br>36.0[a]<br>40.6[d] |
| $O_2$ | 0.9999 | 21.2 | 22.6[a]<br>23.0[b] |
| $N_2$ | 1 | 21.2 | 21.3[a]<br>24.3[b] |
| $H_2S$ | 0.999 | 38.2 | 43.5[c] |

[a] van der Waals and Platteeuw[39] (calculated). [b] Evans and Richards.[59] [c] McAdie.[61] [d] Allison and Barrer.[62] [e] Grey *et al.*[63] [f] Kazankin *et al.*[35] [g] Parsonage and Staveley.[64]

Table 7 Experimental and computed occupancies on the dissociation line at 298 K and 446 K for several guest molecules in HQ clathrates

| Guest | $T$ 298 K $\theta_{Calc}$ | $\theta_{Exp}$ | $T$ 446 K $\theta_{Calc}$ | $\theta_{Exp}$ |
|---|---|---|---|---|
| Ar | 0.36 | 0.34[a] | 0.30 | |
| Kr | 0.37 | 0.34[b,c] | 0.29 | 0.28[d] |
| $CH_4$ | 0.37 | 0.391[e] | 0.29 | |
| Xe | 0.38 | 0.41[c,d] | 0.29 | 0.30[c,d] |

[a] Platteeuw.[37] [b] van der Waals and Platteeuw.[39] [c] Kazankin *et al.*[34] [d] Kazankin *et al.*[35] [e] Deming *et al.*.[38]

clearly guest dependent. Actually, this occupancy increases with the magnitude of interaction between neighbouring guests. This behaviour can be reproduced with the version of the theory proposed in this work whereas the BT of vdWP predicts a unique value of occupancy whatever the guest.

Concerning the variation of occupancy in the one phase region (β-phase), we have found for all guests that at a given temperature, the occupancy increases with pressure, and at a given pressure, it decreases with temperature. An example of this behaviour is given in Fig. 6 for the Xe–HQ clathrate.

The occupancy $\theta_d(T)$ of a HQ-clathrate at a given temperature $T$ on the dissociation line is, according to eqn (6):

$$\theta_d = \frac{C(T)f_d}{1 + C(T)f_d} \tag{29}$$

where $f_d$ is the fugacity of the guest at temperature $T$ at the dissociation pressure. Combining eqn (6) and (29), and introducing

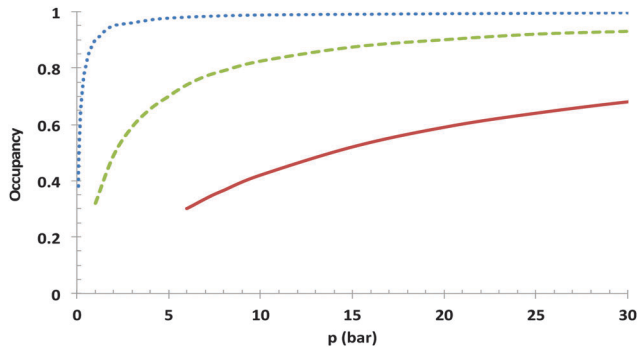


Fig. 6 Occupancy of the xenon HQ clathrate as a function of pressure for 3 temperatures. Dotted line: $T$ = 298 K, dashed line: $T$ = 373 K, full line: $T$ = 446 K.

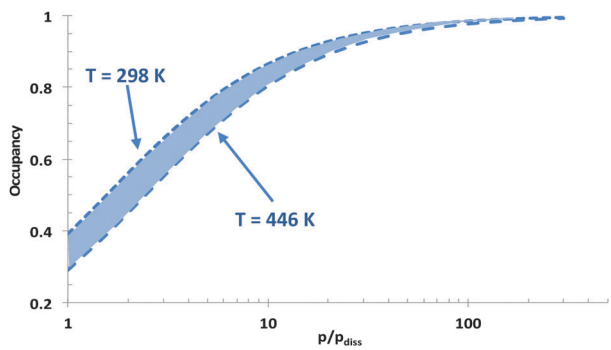


Fig. 7 Occupancy in the β phase for type I HQ clathrates. The possible values are in the blue area.

the relative fugacity $f_r = f/f_d$ under the given $(p,T)$ conditions, we obtain the following relationship between the occupancy $\theta(p,T)$ in the β-phase and the occupancy $\theta_d(T)$ at the dissociation pressure at the same temperature:

$$\theta(p,T) = \frac{1}{1 + \frac{1 - \theta_d(T)}{\theta_d(T) f_r}} \tag{30}$$

This means that, at a given temperature, the occupancy of a clathrate at a given pressure is only function of the occupancy on the dissociation line at the same temperature and the "distance" – *i.e.* the pressure driving force – to the dissociation line (*via* the relative fugacity). As the occupancy on the dissociation line ranges approximately between 0.41 at 298 K and 0.29 at 446 K whatever the guest, the occupancy in the β-phase can only vary in a range that is plotted in Fig. 7.

Such a plot shown in Fig. 7 could be very useful for people in charge of the development of clathrate-based practical applications. Indeed, when the dissociation pressure is known (experimentally or numerically), it becomes very easy to determine the clathrate occupancy from the operating pressure and temperature.

## 4. Conclusions

Thermodynamic modelling of type I HQ clathrates was performed in this study, and the numerical predictions obtained

in terms of phase equilibria, clathrate occupancies, and intercalation enthalpies were compared to experimental data found in the literature. In order to develop an efficient model for both clathrate phase equilibium and guest occupancy, it is proven necessary to adapt and extend the original theory initially proposed by van der Waals and Platteeuw. Indeed, this basic theory was not able to predict the phase equilibrium line at high temperatures and failed to predict the guest dependence occupancy for type I clathrates at a given temperature. Therefore, vdWP theory was first modified by moving the reference state from 298 K to the melting point of HQ. Then, a new single set of thermodynamic parameters, valid for all the guests forming the type I structure, was obtained by fitting these parameters at the new reference state with experimental occupancies at different temperatures. The theory was finally extended by adding two important contributions in the modelling of such organic clathrates: (i) the solubility of the gases in the HQ α-phase in agreement with some experimental evidence provided in the literature and (ii) the guest–guest interactions. We have demonstrated that the highest level of the theory – *i.e.* including both the solubility in the α-phase and guest–guest interactions – is necessary to perform reliable predictions in terms of both dissociation pressures and clathrate occupancies as a function of temperature. Interestingly, literature data show that, at a given temperature, the clathrate occupancy is clearly guest dependent. In this work, we have proposed a theory that is able to take into account this guest dependence contrary to what was initially postulated by van der Waals and Platteeuw in the original theory. Intercalation enthapies of such clathrates have also been computed by computing the logarithm of the Langmuir constant *versus* the inverse of temperature, and very good agreement was obtained between our predictions and literature data.

In this work, we have revisited the van der Waals and Platteeuw's model published in the 50's for the thermodynamic modelling of HQ clathrates. In the original formalism, we have both developed and included some ideas proposed by others such as Zubkus and Belosludov, and also added our contribution of novel ideas. The result is a robust and general thermodynamic model, with the ability to predict both clathrate phase equilibria and occupancies in a large range of temperature, for various guests forming type I HQ clathrates. A novel interesting route is now open for modelling more complex systems, such as hydroquinone clathrates where the cavity is deformed.

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