Theoret. Chim. Acta (Berl.) 60, 589–598 (1982)

THEORETICA CHIMICA ACTA

Adsorption-Complex Isomerism and Quantum Chemical Study of Gas-Solid Interactions: A Model Example*

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The consequences of isomerism of an adsorption complex for comparison of quantum chemical data with experimental quantities are analyzed. A general technique is proposed for evaluating the contributions of the individual isomeric structures of the adsorption complex, chosen so that the range of the required information is compatible with the capabilities of contemporary numerical quantum chemistry in the study of interactions of gases with solid surfaces. The interaction of O_2 with graphite, represented by three types of complexes, is given as an illustration.

Key words: Isomerism of reaction components – Isomerism of adsorption complex – Quantum-chemical evaluation of ΔH_T^0 and ΔS_T^0 terms – Adsorption – complex vibrational problem – Adsorption of O_2 on graphite.

1. Introduction

Recent quantum chemical study of the interaction of gases with solid surfaces, carried out for various systems in the framework of the cluster approach, has provided us [1–4] with a great deal of evidence that (at least some) catalytic or sorption processes occur through not one, but several different complexes of the adsorbate and the solid adsorbent. Thus it became useful to introduce the concept of isomerism of the adsorption complex [5]. Phenomenologically, this isomerism can be classified according to several structural characteristics of the complexes.

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[*] Part XI in the series: Multi-Molecular Clusters and Their Isomerism; Parts IX, X, see Refs. [5, 20]. Dedicated to Professor P.-O. Löwdin on the occasion of his 65th birthday.

Thus, for example, the following kinds of isomerism can be distinguished. First, (a) isomerism of the adsorption complex based, for one type of rigid cluster, on interaction with various adsorption sites and/or on different positions of the adsorbed molecule above the site, where the molecule itself is only slightly distorted (e.g. Refs. [6–9]). However, especially in chemisorption, theoretical study of interactions with a single rigid cluster can lead to (b) a larger number of isomeric adsorption complexes differing markedly in the manner of structural change of the adsorbed molecule (e.g. [10]). Probably the most frequently theoretically recognized type of isomerism of adsorption complexes at present is type (c), where the interaction is modelled in terms of a larger number of various rigid clusters representing various adsorption sites on the real surface, even if only one adsorption complex is formed on each cluster (e.g. Refs. [10–12]). Case (c) would, however, not include adsorption complexes whose differences in the theoretical description would be based only on a change in the number of atoms in the model cluster, for purposes of the study of convergence with the size of the substrate for a specific type of interaction (e.g. [13]). Apparently, in the general interaction of gases with solids (either in heterogeneous catalysis or in sorption), all three types of isomerism (a)–(c) can be present simultaneously in various combinations (cf. [14]). So far, experimental study of these processes enables differentiation of individual isomeric adsorption complexes only in exceptional cases (e.g. [15, 16]). In the light of isomerism of adsorption complexes it is thus necessary to consider an experimentally determined characteristic of an interaction process as the result of the contributions of the individual relevant isomeric structures.

This work will deal with the consequences of isomerism (especially of type (c)) of an adsorption complex for quantum chemical calculations of the thermodynamic characteristics of the interactions of gases with solids and comparison of these data with experimental quantities, i.e. with a problem formally similar to the recently studied question of the thermodynamics of isomeric van der Waals molecules in the gaseous phase [17–20]. A scheme of the weighting of contributions of individual structures is proposed (in the framework of the concept of complete independence of all the isomeric complexes as well as of the adsorption processes leading to their formation) so that the amount of necessary input information is not greater than the present capabilities of numerical quantum chemistry in application within the cluster approach. The behaviour of the weighting scheme is studied on the model example of adsorption of O_2 on graphite.

2. Weighting Scheme

The following assumptions will be made for the studied adsorption process. The molecules (or atoms) A are adsorbed as wholes (or, more generally, relaxations connected with adsorption lead to the same stoichiometry with every individual type of adsorption complex) on a fixed number of definite locations on the solid phase B. The molecules of the monolayer are considered immobile (perfect localization) – there are definite points of attachment on the surface capable of accommodating just one adsorbed molecule A with a series of vibrational stationary states in the prescribed force field. Assume that there are altogether n different types of adsorption complex $(A \cdot B)_i$:

$$A(g)+B(s) \rightleftharpoons (A \cdot B)_i(s) \qquad (i=1,2,\ldots,n) \tag{1}$$

corresponding to the overall interaction process:

$$A(g)+B(s) \rightleftharpoons A \cdot B(s). \tag{2}$$

Establishment of any of partial equilibria (1) is assumed to be independent of the rest of these processes (especially, formation of a particular adsorption complex does not influence the numbers of sites available for the other kinds of adsorption complexes). The quantum states corresponding to any one adsorption complex are supposed to be independent of the states of the surrounding sites. The structural changes in the adsorbent upon adsorption are neglected (i.e. an inert solid phase).

If the characteristics of the gaseous phase A and the adsorption complexes $(A \cdot B)_i$ are available (especially partition functions q_i of complexes $(A \cdot B)_i$ and changes in the standard enthalpy $\Delta H^{\ominus}_{0,i}$ accompanying processes (1) at absolute zero temperature), then the calculation (e.g. [21, 22]) of the partial standard enthalpy and entropy terms $\Delta H^{\ominus}_{T,i}$ and $\Delta S^{\ominus}_{T,i}$ connected with the formation of the individual adsorption complexes (1) at temperature T can be carried out. Assume that the experimental study of process (2) is carried out by a technique in which all n adsorption complexes $(A \cdot B)_i$ are manifested indiscriminately, and that it is not possible to differentiate between the contributions of the individual isomeric structures. Then the values of the equilibrium thermodynamic characteristics of process (2) obtained by this technique will be the overall values $\Delta H^{\ominus}_T$ and $\Delta S^{\ominus}_T$, to which the individual isomeric structures (1) contribute according to their weight factors w_i. Application of the concept of the general equilibrium isomeric problem [23, 24] leads (under assumption of sufficiently low coverage – the Henry's Law region to be reached) to weighting relationships in the form:

$$\Delta H^{\ominus}_T = \sum_{i=1}^{n} w_i \Delta H^{\ominus}_{T,i} \tag{3}$$

$$\Delta S^{\ominus}_T = \sum_{i=1}^{n} w_i (\Delta S^{\ominus}_{T,i} - R \ln w_i), \tag{4}$$

where R denotes the gas constant. The weight factors w_i are related to the parameters of complexes $(A \cdot B)_i$ by the relationship [5, 17, 24]:

$$w_i = \frac{s_i q_i \exp(-\Delta H^{\ominus}_{0,i}/R/T)}{\sum_{i=1}^{n} s_i q_i \exp(-\Delta H^{\ominus}_{0,i}/R/T)}, \tag{5}$$

where the s_i denote steric factors connected with the geometric properties of the surface.

3. An Illustrative Example and Discussion

The nondissociative (physical) adsorption of O_2 on graphite was chosen as an illustrative example demonstrating the relationships among the quantities included in the weighting treatment. As proposed in earlier works [9, 13, 25–27], dealing with the theoretical study of sorption processes on graphite, the substrate was modelled using simple arrays of carbon atoms arranged in a typical hexagonal lattice with a C—C bond length equal to $2.46/\sqrt{3} \times 10^{-10}$ m [28]. Specifically, three types of substrate model consisting of 12, 13 and 16 carbon atoms were used (Fig. 1). The models were chosen primarily to enable study of three critical adsorption sites (at the centre of a hexagon, at a carbon atom and at the centre of the C—C bond) conceivable on a real graphite surface. The potential controlling the interactions of the O_2 molecule (the length of the O—O bond was equal [29] to 1.207×10^{-10} m) with the substrate was considered to be a Buckingham-type potential [30] with parameters according to Eliel et al. [31]. The stationary points on these five-dimensional hypersurfaces of the interaction energy were searched using the technique of automatic optimization of the space arrangement of two molecules [32] employing analytical first derivatives of the energy. The starting positions of the oxygen molecule were systematically changed in order to find all the stationary points on the studied hypersurfaces. From these stationary points of the local minimum type were then chosen, which alone have any importance for our equilibrium problem. A single orientation of the components of the adsorption complex leading to minimal interaction energy (i.e. type (c) adsorption complex isomerism) was found for the critical adsorption site of each studied substrate model (structures *A*, *B* and *C* as depicted in Fig. 1). In the *B* case there is a slight shift from the exact position above the central carbon atom; this fact may be considered as a result of the finity of the model used. These three structures are used in this work to demonstrate possible relationships between the partial and overall thermodynamic characteristics in the framework of the concept of perfectly localized, isomeric adsorption complexes.

In our approach, the key characteristics for construction of the partition functions of the adsorption complexes are the energies of the individual quantum states of the intersystem vibrational motions, generated in this work by harmonic vibrational analysis [33]. Force constants corresponding to the intersystem degrees of freedom were derived from analytical formulae. The components of the adsorption complex themselves were treated as (nearly) rigid bodies using artificially stiff intramolecular potentials (the stretching force constants were set equal to 10^5 N/m). In carrying out the vibrational analysis, due consideration was paid to the redundancy conditions [34] involved in the problem (cf. [35]). The resultant value of five harmonic intersystem vibrational normal mode frequencies for the adsorption complexes A, B and C are given in Table 1 together with the energetics of the partial adsorption processes.

Using the data in Table 1, the weight factors (Eq. (5)) were evaluated for structures *A*, *B* and *C* in a broad temperature interval (Fig. 2). In the framework of our model, the translational and rotational contributions to q_i were eliminated

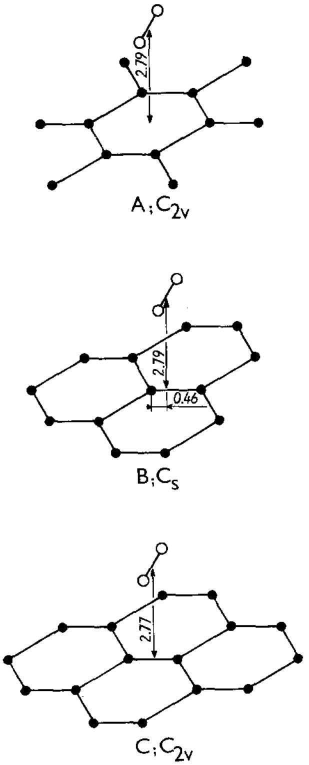

Fig. 1. Optimized structures of model adsorption complexes (local energy minima) for physical adsorption of O_2 on graphite (○ – O atoms, ● – C atoms); structural characteristics in 10^{-10} m

and the vibrational partition function was constructed using the usual harmonic oscillator approach (e.g. [36]). The electronic partition function of the model cluster was simply set equal to 1. Although structure *C* is the most stable of the three isomeric adsorption complexes considered in the given temperature interval, it is the actual predominant structure only at the lowest temperatures. Already at a temperature of about 210 K, the weight factors of all three structures are of the same order, where only about half the adsorption complexes present

Table 1. Energetic (kJ/mol) and vibrational (cm^{-1}) characteristics of the adsorption complexes *A*, *B*, and *C*[a]

	A	*B*	*C*
Potential energy ΔE_i	−8.77	−9.07	−9.86
$\Delta H^{\ominus}_{0,i}$[b]	−7.62	−7.94	−8.72
$\omega_{i,j}$[c]	11.4; 18.2; 24.4; 67.6; 70.7	10.4; 18.5; 21.7; 67.0; 71.5	12.8; 17.5; 20.4; 68.9; 71.0

[a] See fig. 1.

[b] Enthalpy at absolute zero $\Delta H^{\ominus}_{0,i} = \Delta E_i + 1/2h \sum_j \omega_{i,j}$.

[c] Frequencies of harmonic vibrational intersystem normal modes.

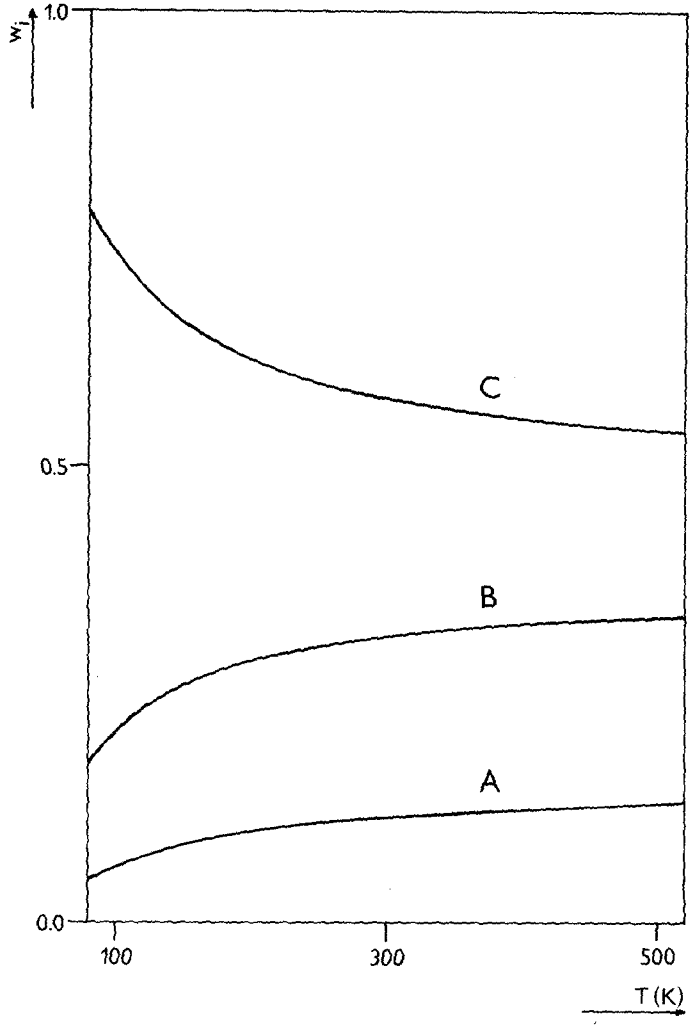

Fig. 2. Temperature dependences of the weight factors w_i of the adsorption complexes *A*, *B* and *C* (see Fig. 1)

under equilibrium conditions are of *C* type and the rest for the greater part have structure *B*. The fact that the weights of the individual isomeric complexes are of the same order implies that interpretation of the experimental data in terms of only the most stable structure in the $\Delta H_0^\ominus$ scale (i.e. structure *C*) could be a misleading simplification. Instead, each structurally dependent characteristic of the adsorption process should be evaluated by the weighting treatment as the result of contributions of the individual adsorption complexes. It should be noted that suitable relationships between the parameters of the individual complexes could even result in a change in the relative stability order for the individual structures at different temperatures (cf. [18, 37]), which would essentially lead to very variable changes in the behaviour of the overall characteristics with changing temperature.

In the framework of the model of perfectly localized particles, an evaluation was carried out of the standard enthalpy and entropy terms for each of the three partial adsorption processes (1). The partition function of an adsorption complex was evaluated as described above and the partition function for the free oxygen molecule was found within the conventional rigid rotator and harmonic oscillator approximation (e.g. [36]). In the whole studied temperature interval, the order of the values of the enthalpy ($A > B > C$) and entropy ($A < B < C$) terms for the individual isomers is reversed (Fig. 3). This reverse order explains why the relative stabilities of the individual structures do not interchange at various temperatures in our particular case. If the enthalpy and entropy factors had the same sequence in a given series of isomers, it would become possible for the entropy term to overcompensate the enthalpy term, leading to changes in the relative stability order of the individual structures (cf. [5]).

It hardly seems possible that any experimental technique could yield the values of the partial thermodynamic characteristics $\Delta H^{\ominus}_{T,i}$ and $\Delta S^{\ominus}_{T,i}$. Consequently, in order to compare the theoretical and experimental data for processes with theoretically recognized adsorption complex isomerism, it is necessary to abandon the theoretical partial terms in favour of theoretical overall values using the weighting treatment. The changes connected with this step in our particular case are depicted in Fig. 3. There are differences between the partial and overall

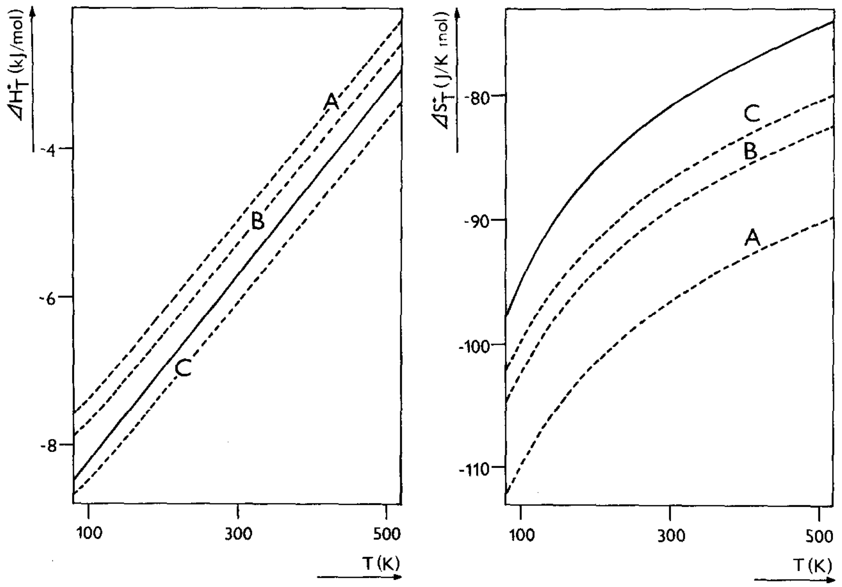

Fig. 3. Temperature dependences of the partial (– – – –) standard enthalpy and entropy terms for adsorption processes leading to complexes A, B and C (see Fig. 1) and the corresponding overall (——) values $\Delta H^{\ominus}_T$ and $\Delta S^{\ominus}_T$; standard states – ideal gas at 101 325 Pa and the state of a surface concentration of 10^{20} molecules/m^2

values in the whole given temperature interval. For the enthalpy term, the difference between the partial value corresponding to structure C and the overall value is small at low temperatures, but increases with increasing temperature. This difference is, however, significant for the entropy in the whole interval, and is larger than 5 J/K/mol from temperatures of about 110 K. Except for the lowest temperatures, the $T\Delta S_T^{\ominus}$ term is affected by the phenomenon of isomerism of the adsorption complex to a degree one order larger than for the $\Delta H_T^{\ominus}$ term. When the qualitative characteristics of the dependences in Fig. 3 are considered, not only from the point of view of particular comparison between the theoretical and experimental data for the physical adsorption of oxygen molecules on graphite alone, but as a model study of the conditions for a general interaction process (either physical or chemical) between the gaseous and solid phase leading to isomeric adsorption complexes, it is evident that, at least for some of these processes, this isomerism leads to important results for comparison of the theory and experiment for all three thermodynamic terms $\Delta H_T^{\ominus}$, $\Delta S_T^{\ominus}$ and $\Delta G_T^{\ominus}$.

Although it is not of prime importance for this work, it should be noted that there are several essentially practicable improvements of the model used for adsorption of oxygen molecules on graphite. In addition to an improvement in the quality of the potential function alone, these are especially an increase in the number of carbon atoms within the plane substrate models (cf. [38]), as well as inclusion of further carbon layers, which could eventually lead to discovery of further types of local minima (or, in principle, to removing some of the structures A, B, C), and also transition from the partition function of the harmonic oscillator to the nonharmonic case. The latter correction with retention of the concept of localized adsorption complexes enables realistic consideration of the behaviour of the energy hypersurface in the wider vicinity of the local minima. It should also be noted that consideration of the differences in the vibrational motions of various structures, which is essentially included in the weighting treatment, is a characteristic which is lacking in the otherwise sophisticated techniques including all the points on the energy hypersurface (e.g. [28, 39]). Nevertheless, in spite of these and further approximations involved, there is quite reasonable agreement between the values given here and the experimental data available on the sorption of O_2 on graphitized carbon black [40].

4. Conclusions

This work was carried out in order to examine the possible results of isomerism of an adsorption complex for comparison of theoretical and experimental data. A weighting scheme leading from partial to overall values was proposed, requiring as input data information which is (or soon will be) capable of being generated by numerical quantum chemistry in the study of the processes of heterogeneous catalysis and sorption in the framework of the cluster concept (i.e. only the depths of the local minima on the interaction energy hypersurface and the harmonic frequencies of vibrational motions in the local minima). The selected model example demonstrated that isomerism of the adsorption complex may markedly affect comparison of the theoretical and experimental values such as $\Delta H_T^{\ominus}$ and especially the $\Delta S_T^{\ominus}$ term: the overall entropy term may lie well above the largest of the partial terms. Factors favouring an increase in the differences between the overall terms and the partial values belonging to the energetically most stable complex are especially: the number of isomeric adsorption complexes, an increase of similarity or even interchanges in their relative stabilities, as well as the temperature raise. The results of the model study indicated that the conventional quantum chemical approach to isomerism in the study of gas-solid interactions (i.e. concentrating only on the energetically most stable structure) can sometimes lead to serious errors.

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Received September 14, 1981