Thermochimica Acta, 120 (1987) 207–215
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ENTHALPY–ENTROPY INTERPLAY IN GAS–SOLID EQUILIBRIA: CONDITIONS FOR HETEROGENEOUS ENTROPY-CONTROLLED PROCESSES *,**,***

ZDENĚK SLANINA

J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Máchova 7, CS-121 38 Prague 2 (Czechoslovakia)

(Received 24 March 1987)

ABSTRACT

The recently suggested and widely used concept of entropy-controlled processes of heterogeneous catalysis and sorption is reanalyzed and a thermodynamically consistent treatment is proposed. For illustrative purposes the interactions of water vapour with silica are chosen and existing theoretical data are refined in several respects. It is concluded that entropy controlled processes should be very rare in practice, in contrast with the conclusion based on the conventional treatment.

INTRODUCTION

A quantum-chemical study of the interaction of gases with solid surfaces within the framework of the cluster approach in terms of the structure and of the potential energy has already been established as an acceptable alternative approach to this problem [1–4]. Since heterogeneous catalytic or sorption processes exhibit a clear temperature dependence, the correct treatment necessitates the introduction of the Gibbs function. In fact, initial reports [5–8] have already appeared connecting the quantum-chemical cluster approach with a subsequent statistical-thermodynamic treatment. However, the statistical-thermodynamic treatment must be selected (see refs. 9 and 10) to correspond to the typical possibilities of contemporary numerical quantum chemistry, i.e. the description of potential energy hypersurfaces in terms of their stationary points alone. Consequently, the statistical-thermodynamic treatment involves perfect localization (immobile adsorption) at

---

* Part XV in the series, Multimolecular Clusters and Their Isomerism; for Part XIV, see Z. Slanina, J. Phys. Chem., 86 (1982) 4782.

** Submitted in a preliminary form for presentation before the 6th International Symposium on Heterogeneous Catalysis, Sofia, July 1987.

*** Dedicated to Professor Dudley R. Herschbach on the occasion of his 55th birthday.

sufficiently low coverage. The gas phase itself is considered to be ideal. Although the mobile approach predominates in contemporary adsorption theories (see for example refs. 11 and 13), application of the localization concept need not necessarily represent fundamental methodical insufficiency, as contemporary quantum-chemical interests are concerned with chemisorption problems rather than with physical adsorption. Of course, such an approach involves a series of inherent approximations, so that its future application in predicting the properties of other systems will inevitably require preliminary systematic confrontation with experimental data. Since extensive applications of the joint approach to the field of gas–solid interactions can be expected in the near future, the problem of the correct preparation of its output for this confrontation must be considered now. Clearly enough, it is highly convenient to split the Gibbs function term into two independent terms, enthalpy and entropy, and to carry out the confrontation for each part separately, rather than at the Gibbs-energy level alone.

The progress in quantum-chemical evaluations of entropic effects for heterogeneous processes has stimulated an increasing interest in the relative proportions, importance and interplay of enthalpy and entropy terms. Recently, the concept of an entropy-controlled reaction was introduced (for a review, see ref. 14) and employed widely also in the area of gas–solid interactions [15]. The concept was illustrated [15] with water–silica interactions [5]. In the present work the concept is reanalysed and a new, more general treatment is proposed. The original illustrative processes are employed but their theoretical characteristics are refined first. The usual framework of approximations [5] is retained throughout the present work.

REFINEMENT OF THE THEORETICAL DATA

Let us start with some necessary refinement and sophistication of the intermediate data on water–silica interactions [5]. Firstly, in the field of heterogeneous equilibria (in view of the existing large number of different choices [12]) it is very important to specify standard thermodynamic data by providing information on the standard states employed. The standard states are not given explicitly in ref. 5; here, we shall use the recommended choices [12] (cf. Table 1), considering their already discussed [12] theoretical advantages. Secondly, the distinguishability of equivalent interaction sites leads to a configurational entropy term given by $\delta S_T^0 = R \ln N/A$; our recalculation has shown that this term was not employed in ref. 5. Information sufficient for this calculation includes simply the number of sites N on a surface area A. Inclusion of δS_T^0 has special importance in the modelling of a surface by simple clusters: it can make possible the differentiation between different surfaces modelled by the same cluster. As an illustration (Table 1) we will use straightforwardly δS_T^0 of β-tridymite [16]. (For other

TABLE 1

Refinement of the entropy terms (J K^{-1} mol^{-1}) for water vapour–silica interaction with respect to the surface site distinguishability

Process [a]	T (K)	ΔS_T^0 [b]	This work [c]	
			δS_T^0 [d]	ΔS_T^0
$H_2O(g)+S(s) \rightleftharpoons S \cdot OH_2(s)$	100	−121.6	−25.7	−147.3
	298	−123.1		−148.7
$H_2O(g)+S(s) \rightleftharpoons S \cdot H_2O(s)$	100	−118.3		−144.0
	298	−119.7		−145.4

[a] $S \equiv (HO)_3SiOH$, a model of silica (see ref. 5).

[b] Values reported in ref. 5 (i.e. without consideration of the configurational degeneracy and standard state specification).

[c] The standard states are: $H_2O(g)$, an ideal gas at 1 atm (equal to 101325 Pa) pressure; S(s), the pure solid at 101325 Pa pressure; the adsorbed film, a hypothetical adsorbed phase obeying Henry's Law [12] at a surface concentration of 10^{20} molecules m^{-2}.

[d] Based on the surface characteristics of β-tridymite [16].

silica surfaces, δS_T^0 must be re-evaluated.) For completeness, it should be mentioned that in spite of the unstated [5] standard states and neglect of the δS_T^0 term, there is nonetheless an (artificial) way in which the values [5] could be applied directly. This would permit their subsequent interpretation as values corresponding to that standard state of the adsorbed film in which the N/A ratio would be used as a new surface-concentration unit.

While inclusion of the δS_T^0 term in the theoretical evaluation of standard thermodynamic terms for gas–solid surface interactions is at present rather obligatory (i.e. well established), the treatment of the following aspect which is also basically configurational, could be termed optional (with respect to the relative newness of the recommended treatment [6,7,18]). More specifically, the recognized [5] isomerism of adsorption complexes in the water–silica interactions will now be addressed. It may be assumed [6,7,18] in experimental studies of processes involving isomerism of adsorption complexes that it is not possible to distinguish between particular isomers and that overall values of the thermodynamic terms, to which all the isomers present contribute, will be obtained. The extent of the data [5] actually permits carrying out the recommended weighting [6,7,18] and thus obtaining the overall terms from the partial values [5]. This is illustrated in Table 2 for two of the three isomers found [5]. It is apparent that, in the framework [5] of the available data and approximations employed, these overall terms are the only ones that should be compared with the observed data (provided these are available in Henry's Law region [12]). It is, however, also apparent that as soon as the whole energy hypersurface is available, the treatment [6,7,18] may become obsolete. Although the consequences of the isomerism of adsorption complexes are certainly not dramatic here, those for other systems and/or more realistic models could be. The data in Table 2

TABLE 2

Partial and overall standard [a] enthalpy and entropy terms ΔH_T^0 and ΔS_T^0 for adsorption of $H_2O(g)$ on silica modelled by $Si(OH)_4$

Process [b]	ΔH_T^0 (kJ mol^{-1})		ΔS_T^0 (J K^{-1} mol^{-1})	
	100 K	298 K	100 K	298 K
$H_2O(g) + S(s) \rightleftharpoons S \cdot OH_2(s)$	−31.15 [c]	−31.06 [c]	−147.3	−148.7
$H_2O(g) + S(s) \rightleftharpoons S \cdot H_2O(s)$	−27.03 [c]	−26.93 [c]	−144.0	−145.4
$H_2O(g) + S(s) \rightleftharpoons S{-}H_2O(s)$ [d]	−31.11	−30.15	−146.8	−143.6

[a] The standard states, see Table 1.
[b] $S \equiv (HO)_3SiOH$, see ref. 5.
[c] The value reported in ref. 5.
[d] The overall adsorption process.

represent values for which all the contributions that are relevant in the framework [5] of the approximations and information were considered. This, of course, does not imply that all conceivable contributions are included, e.g. the whole correlation energy term, anharmonicity etc. Finally, the results in Table 2 show that adsorption complex isomerism would not be critical for enthalpy–entropy interplay itself.

THE CONVENTIONAL CONCEPT OF ENTROPY-CONTROLLED PROCESSES

The original concept was defined [6,15] in terms of standard thermodynamic terms (without their explicit specifications) using the relationship $\Delta G_T^0 \approx -T\Delta S_T^0$ between standard (molar) changes in Gibbs function G and entropy S. The concept was subsequently applied [15] to the field of heterogeneous catalysis. The concept was understood as an absolute characterization of a given reaction, and the idea that gas–solid reactions are often entropy controlled has been presented [15]. However, it can easily be shown that the conventional procedure does not work well in essence. A change in the standard state alone can change the quality of the relationship between the standard enthalpy and entropy terms (Table 3). This is actually a particular case of the wide confusion [6,19–21] between the standard and actual (reaction) thermodynamic terms. Only the latter terms can fully take into account the selected experimental conditions (e.g. the initial composition and pressure, surface area, reaction regime) and thus are significant for the evaluation of the type of reaction.

A GENERALIZED CONCEPT EMPLOYING THE REACTION TERMS

Let us consider an adsorption process

$$A(g) + S(s) \rightleftharpoons S \cdot A(s) \qquad (1)$$

TABLE 3

An example of the inapplicability of the standard ΔH_T^0 and $T\Delta S_T^0$ terms for an unambiguous statement on the enthalpy–entropy relationships in a reaction [a]

Standard state choice [b]	ΔH_T^0 [c,d]	$T\Delta S_T^0$ [c,e]	ΔG_T^0 [c]	Statement [f]
10^{23} molecules m^{-2}	-3.20	-12.25	9.05	SC^0
10^{20} molecules m^{-2}	-3.20	-6.51	3.31	C^0
10^{17} molecules m^{-2}	-3.20	-0.76	-2.44	HC^0

[a] Illustrated for the equilibrium $(H_2O)_2(g)+Si(OH)_4(s) \rightleftharpoons (HO)_3SiOH\cdot OH_2(s)+H_2O(g)$ at a temperature $T=100$ K.

[b] Only the standard state for the adsorbed film is indicated (the surface concentration) (see Table 1).

[c] In kilojoules per mole.

[d] The value reported in ref. 5.

[e] Based on the value reported in ref. 5 and refined as described in Table 1.

[f] SC^0, entropy control ($\Delta G_T^0 \approx -T\Delta S_T^0$); C^0, compensation ($\Delta H_T^0 \approx T\Delta S_T^0$); HC^0, enthalpy control ($\Delta G_T^0 \approx \Delta H_T^0$) (cf. refs. 14 and 15).

described by its standard enthalpy and entropy terms, $\Delta H_{T,1}^0$ and $\Delta S_{T,1}^0$. There is, of course, an infinite number of realizations of the process, i.e. of reaction regimes and conditions. It is convenient to specify the regimes by a choice of two thermodynamic constraints. In our context, we shall discuss the regime of constant temperature T and total pressure p of the system. Moreover, even within the specified reaction regime there is an infinite number of choices of the initial and final states of the system. For the initial state, we choose a gas phase composition of n_0 moles of component A at a given pressure p and no adsorbed phase. From the practical point of view it is quite natural to consider the equilibrium state as the final state. The actual reaction terms will be introduced as changes in the state functions accompanying the chosen realization of the process. In our reaction regime, these are the (molar) reaction enthalpy and entropy, ΔH_T and ΔS_T. These terms are to be compared with each other for a meaningful characterization of a particular realization of the process within the reaction regime. It is convenient to relate these reaction terms to 1 mol of the adsorbed phase. A detailed consideration of the thermodynamics of eqn. (1) leads to a fairly simple relationship (within the already-mentioned presumptions of ideal behaviour of both phases):

$$\Delta H_{T,1} = T\Delta S_{T,1} = \Delta H_{T,1}^0 \tag{2}$$

In other words, under the conditions of equal temperature and pressure of the interacting gas at the beginning and end of the process, the change in the Gibbs functions is equal to zero. Consequently, the behaviour of this class of processes is quite uniform: in each process there is rigorous enthalpy–entropy compensation (C). Essentially, this exact result could not be obtained using the original standard term approach [15].

From the point of view of heterogeneous catalysis, however, a dissociative adsorption is more interesting:

$$A_2(g) + S(s) \rightleftharpoons S \cdot A(s) + A(g) \tag{3}$$

this type of process is described by its standard enthalpy and entropy changes, $\Delta H^0_{T,2}$ and $\Delta S^0_{T,2}$. We shall limit ourselves to the above reaction regime and to the initial and final states specified. (Incidentally, the stoichiometry of eqn. (3) also ensures constancy of volume of the reaction mixture in the regime.) The equilibrium composition is given by the corresponding equilibrium constant K_2, the initial number of moles of A_2, n_0, and the surface L of the solid phase. With respect to our choice of standard state (Table 1) the term $NK_2 \times 10^{-20}$ will also be employed, where N denotes the Avogadro number. Detailed thermodynamic reasoning leads to the following expressions for the reaction changes $\Delta H_{T,2}$ and $\Delta S_{T,2}$ within the regime:

$$\Delta H_{T,2} = \Delta H^0_{T,2} \tag{4}$$

$$T\Delta S_{T,2} = T\Delta S^0_{T,2} - RT\left[\ln(NK_2/10^{20}) + \frac{1}{\alpha}\ln(1-\alpha)\right] \tag{5}$$

$$\alpha = -\frac{K_2\lambda}{2} + \left(\frac{K_2^2\lambda^2}{4} + K_2\lambda\right)^{1/2} \qquad \lambda = \frac{L}{n_0}$$

Clearly enough, for a chosen process (eqn. 3) within the regime considered there is one variable parameter λ which can in principle be varied over the whole interval (0 to ∞). (Incidentally, there is no dependence on the pressure of the gas phase.) A closer inspection of eqn. (5) shows that at the limiting points of the interval, the term $T\Delta S_{T,2}$ reaches the values of $\Delta H^0_{T,2} + RT$ and ∞ respectively. Then, for example, for a negative value of $\Delta H^0_{T,2}$ and for $|\Delta H^0_{T,2}| \gg RT$ (chemisorption), the following sequence of reaction types for a process of type (3) may occur: compensation (C) ($\Delta H_{T,2} \approx T\Delta S_{T,2}$), enthalpy control (HC) ($\Delta G_{T,2} \approx \Delta H_{T,2}$), decompensation (D) ($\Delta H_{T,2} \approx -T\Delta S_{T,2}$) and entropy control (SC) ($\Delta G_{T,2} \approx -T\Delta S_{T,2}$). (Here we have adopted a convention to refer to, for example, the C type of relationships if $1/3 < T\Delta S_{T,2}/\Delta H_{T,2} < 3$.) In other words, within the chosen reaction regime a mere change in reaction conditions (represented by λ) can produce all four possible types of relationships. This finding further stresses the inapplicability of the simple standard-term approach [15] for classification purposes.

To illustrate eqns. (4) and (5) we shall use models [5] of water–silica interactions described recently by the joint quantum-chemical and statistical-thermodynamic treatment and employed in a demonstration of the standard term concept of entropy-controlled processes of heterogeneous catalysis and sorption. For our purposes the original data [5] were refined as described above.

TABLE 4

Illustrations [a] of the influence of reaction conditions on relationships between the actual reaction changes $\Delta H_{T,2}$ and $T\Delta S_{T,2}$ within the reaction regime studied (in kilojoules per mole)

T (K)	$\Delta H^0_{T,2}$	$T\Delta S^0_{T,2}$	λ ($m^2\ mol^{-1}$)	$\Delta H_{T,2}$	$T\Delta S_{T,2}$	Statement [b]
100	3.49 [c]	−6.33 [c]	1	3.49	4.32	C (D^0)
100	3.49 [c]	−6.33 [c]	10^5	3.49	4.33	C
100	3.49 [c]	−6.33 [c]	10^8	3.49	4.48	C
100	3.49 [c]	−6.33 [c]	10^{10}	3.49	5.87	C
100	0.92 [d]	−6.18 [d]	1	0.92	1.75	C (SC^0)
100	0.92 [d]	−6.18 [d]	10^5	0.92	1.78	C
100	0.92 [d]	−6.18 [d]	10^8	0.92	2.60	C
100	0.92 [d]	−6.18 [d]	10^{10}	0.92	5.75	SC
298	3.82 [c]	−18.32 [c]	1	3.82	6.30	C (SC^0)
298	3.82 [c]	−18.32 [c]	10^5	3.82	6.36	C
298	3.82 [c]	−18.32 [c]	10^8	3.82	8.37	C
298	3.82 [c]	−18.32 [c]	10^{10}	3.82	17.25	SC
298	0.67 [d]	−18.78 [d]	1	0.67	3.15	SC (SC^0)
298	0.67 [d]	−18.78 [d]	10^5	0.67	3.25	SC
298	0.67 [d]	−18.78 [d]	10^8	0.67	6.64	SC
298	0.67 [d]	−18.78 [d]	10^{10}	0.67	16.74	SC

[a] Illustrated for the equilibria $(H_2O_2)(g) + S(s) \rightleftharpoons S \cdot H_2O(s) + H_2O(g)$; S, a model of silica (see footnotes c and d).

[b] The uniform reaction type derived from the conventional standard term approach [14,15] is given in parentheses (see Table 3, footnote f).

[c] Refined data [5] (see Table 1); the adsorption complex modelled by $H_3SiOSiH_3 \cdot H_2O$.

[d] Refined data [5] (see Table 1); the adsorption complex modelled by $(HO)_3SiOH \cdot H_2O$.

Table 4 presents examples of enthalpy–entropy relationships for selected λ values at various temperatures. Two types of relationships (C, SC) appear in Table 4. However, not all the choices of T and λ included in Table 4 need to be suitable for an observation. Moreover, the essential requirement of low coverages can considerably reduce further the interval for relevant λ values. Consequently, in the case of processes (3) and of the reaction regime chosen, the most important is the C type of relationship. The SC behaviour can appear either under very extreme conditions or when the $\Delta H^0_{T,2}$ term closely approaches zero. The conclusion was further verified with (artificial) processes produced by the (random) generation of $\Delta H^0_{T,2}$ and $\Delta S^0_{T,2}$ values.

CONCLUDING REMARKS

The standard thermodynamic terms (in contrast with the actual terms) do not describe changes between the equilibrium and initial states of a system and cannot reflect (some) changes in reaction conditions and/or regimes. Instead, they characterize a certain, generally hypothetical, non-realizable process. Consequently, the recently suggested [14,15] straightforward use of the standard terms for the classification of heterogeneous processes can be misleading (regardless of the particular standard state choice). A thermodynamically consistent concept was thus proposed which operates with the actual reaction thermodynamic terms. In this work only two types of processes and one (however usual) reaction regime were considered. To obtain a complete picture, other relevant reaction regimes as well as other relevant stoichiometries could be treated, and further work is in progress. Naturally, the actual terms can for some special cases be reduced to standard ones. An isomerization with full conversion under constant temperature and pressure is a simple example. Changes in the reaction regime can certainly be substantial, e.g. any completely isolated system is in fact absolutely entropy controlled as follows from the second law. However, if we may name the most usual type of relationship in the field of heterogeneous catalysis and sorption, it is the C or HC type rather than the D or SC type.

ACKNOWLEDGEMENTS

The author thanks all who participated in a long discussion concerning this article's content, and particularly Dr. J. Sauer and Dr. R. Zahradník for an interesting exchange of information.

NOTE ADDED IN PROOF

Quite recently, Volman [22] published a deeper discussion of some subtleties of the Lewis Equation, Lopez et al. [23] introduced more realistic cluster models of silica, and Landa and Tananaev [24] reanalyzed phase stability and transitions of silica. In addition, the conventional concept of entropy-controlled processes has been reiterated [25], and a guess as to the standard states finally presented [26]; however, the suggested partial line interchange [18] has still not been incorporated [26].

REFERENCES

1 R.C. Baetzold, Adv. Catal., 25 (1976) 1.
2 H.H. Dunken and V.I. Lygin, Quantenchemie der Adsorption an Festkörperoberflächen, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1978.
3 M. Simonetta and A. Gavezzotti, Adv. Quantum Chem., 12 (1980) 103.

4 J. Haber and M. Witko, Acc. Chem. Res., 14 (1981) 1.
5 P. Hobza, J. Sauer, C. Morgeneyer, J. Hurych and R. Zahradník, J. Phys. Chem., 85 (1981) 4061.
6 Z. Slanina, Theor. Chim. Acta, 60 (1982) 589.
7 Z. Slanina, Zh. Fiz. Khim., 57 (1983) 1164.
8 S. Beran and Z. Slanina, Zh. Fiz. Khim., 57 (1983) 1168.
9 Z. Slanina, Radiochem. Radioanal. Lett., 22 (1975) 291.
10 Z. Slanina, Adv. Quantum Chem., 13 (1981) 89.
11 A.V. Kiselev, Q. Rev., Chem. Soc., 15 (1961) 99.
12 W.A. Steele, Adv. Colloid Interface Sci., 1 (1967) 3.
13 A. Milchev and M. Paunov, Surf. Sci., 108 (1981) 25, 38.
14 Z. Slanina, Chem. Phys. Lett., 95 (1983) 553.
15 R. Zahradník, P. Hobza and J. Sauer, in G. Náray-Szabó (Ed.), Steric Effects in Biomolecules, Akadémiai Kiadó, Budapest, 1982, p. 327.
16 H. Rehmy, Lehrbuch der Anorganischen Chemie, Band I, Geest and Portig, Leipzig, 1957.
17 R.K. Iler, The Chemistry of Silica, Wiley, New York, 1979.
18 Z. Slanina, Int. J. Quantum Chem., 23 (1983) 1563; 26 (1984) 439.
19 M.L. McGlashan, Chemical Thermodynamics, Academic Press, London, 1979.
20 Z. Slanina, React. Kinet. Catal. Lett., 26 (1984) 179.
21 Z. Slanina, J. Phys. Chem., 86 (1982) 4782.
22 D.H. Volman, Thermochim. Acta, 111 (1987) 321.
23 J.P. Lopez, C.Y. Yang and C.R. Helms, J. Comput. Chem., 8 (1987) 198.
24 L.M. Landa and I.V. Tananaev, Dokl. Akad. Nauk SSSR, 293 (1987) 656.
25 P. Hobza, R. Zahradník and J. Ladik, Int. J. Quantum Chem., 26 (1984) 857.
26 J. Sauer and R. Zahradník, Int. J. Quantum Chem., 26 (1984) 793.