MEASURING ENERGY–ENTROPY COMPETITION AND COMPENSATION IN CHEMICAL REACTIONS: A THEORETICAL STUDY OF THE ROLE OF ENTROPY IN THE FORMATION OF VAN DER WAALS COMPLEXES *,**

ZDENĚK SLANINA ***

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060 (Japan)

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ABSTRACT

In the context of intensive studies of thermodynamics of formation of van der Waals complexes by means of quantum chemistry a simple intuitive technique has been suggested recently for evaluation of the role of the entropy term in these processes based on a straightforward use of the standard enthalpy and entropy terms, and formation of the van der Waals dimers has been shown to be frequently entropy controlled. This intuitive and obviously inconsistent technique is replaced, in the present communication, by a thermodynamically consistent treatment using actual reaction terms instead of the standard terms and fully respecting the reaction conditions in terms of two relevant reaction regimes, *viz.* constant total pressure or constant volume at a fixed temperature in both cases. The new treatment is applied extensively to a set of 12 formations of homo- and hetero-particle van der Waals dimers (inclusive of three isomeric pairs) whose structural and energy characteristics are known from quantum-chemical studies with sufficient certainty. These computation studies show that, even in terms of one reaction regime, the type of relations between actual reaction enthalpy (energy) and entropy terms can depend distinctly on the reaction conditions chosen, so it cannot be taken isolated from a particular realization of the given reaction as its absolute characterization. In contrast to the former intuitive conclusions it is shown that in the case of formation of the van der Waals molecules A_2 and $A \cdot B$ the entropy control of these processes is rather exceptional, the most usual type being the compensation type. Also, it is shown that, in principle, such processes can exist for which all four possible relations (enthalpy (energy) control, entropy control, compensation, decompensation) can be gradually reached by merely changing one parameter characterizing the reaction conditions in any of the two considered reaction regimes. The term of entropy-controlled reactions is placed in a general thermodynamic context, which underlines a certain special position of the two considered reaction regimes.

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*** Permanent address: The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, CS-121 38 Prague 2, (Czechoslovakia).

INTRODUCTION

For many years the equilibrium processes have been visualized (see, for example, ref. 3) on the basis of the fact that—generally speaking—the equilibrium point of equilibria is reached as a result of mutual competition between energy and entropy factors. Although quantum-chemical studies of chemical reactivity continue to be focused predominantly on the energy term, the role of the entropy term for full understanding of equilibrium and rate processes is far from being underestimated. This focusing in energy results from the circumstance that evaluation of entropy requires more detailed information about behaviour of the potential energy hypersurface in the neighbourhood of its stationary points than calculation of, for example, reaction change of the potential energy itself. Nevertheless, the last period brings an increasing interest in quantum-chemical calculations of entropy effects, too: cf. for example, refs. 4–6, which is connected with a revival (see, for example, ref. 7) of discussions of mutual proportions of the two terms and both physico-chemical bases and consequences of these proportions in various types of chemical processes. It is evident that although the energy term alone forms a sufficient basis for understanding of quality of some processes (e.g. electronic excitations), a number of processes of other types (e.g. formation of the van der Waals complexes under usual experimental conditions [6–11]) necessarily need to take into account the entropy term, too. For this type of discussion it seems useful to introduce some suitable convention for mutual comparisons of the energy and entropy terms involved. In the field of weak molecular complexes in the gas phase the first attempt in this respect was made by the straightforward suggestion (see, for example, ref. 7) to compare the standard enthalpy and entropy terms, ΔH_T^0 and $T \Delta S_T^0$. Thus, it was shown that, for example, in a group of eight formations of van der Waals complexes of various types [7]—except for one case—the $T \Delta S_T^0$ terms were either comparable with ΔH_T^0, or larger. In the light of this finding, the concept of entropy-controlled (SC^0) reactions was introduced [7] meaning the processes whose standard Gibbs energy change is $\Delta G_T^0 \approx - T \Delta S_T^0$. Within this concept a number of van der Waals complexes were shown to be formed in entropy-controlled processes. However, quite recently [12], this simple concept has been criticized for not being directly bound to experiment and, in particular, not reflecting the real experimental conditions.

The aim of this communication is to give a thermodynamically consistent technique for evaluation of the role of entropy in formation of the van der Waals complexes under some typical conditions and, simultaneously, to apply this new concept extensively to formation of van der Waals dimers of various types. In this way—for the first time—the role of entropy in formation of weak molecular complexes in the gas phase will be really mapped.

THE STANDARD-TERM APPROACH

A number of objections can be raised to the general applicability of that simple concept [7]. First of all, its statements can depend on the choice of the standard state itself. None of the former communications introducing and using this simple concept have specified the choice of the standard state. In addition, such presentation was used as if this choice were irrelevant. The results obtained for one (not specified but deducible from the context) choice of the standard state were taken as some absolute characteristics of the reaction. The following simple consideration shows that this is not the case. Let us limit (here and in the whole paper) the choice of the standard state to a pure component in the ideal gas state at p^0 pressure. This pressure can—in principle—be varied within the interval $(0; \infty)$. This variation does not affect the standard enthalpy term ΔH_T^0, whereas the standard entropy term ΔS_T^0 will change within the interval $(-\infty; \infty)$. Thus, a mere change of the reference pressure p^0 makes it possible to attain any type of the relation between the magnitudes of standard enthalpy and entropy changes.

Another drawback of the standard-term approach lies in the fact that it considers such situation to be the final state which can be very distant from the equilibrium point of the system. Only at very low temperature can the van der Waals system attain the state when (practically) only the associates are present in the gas phase. In usual situations equilibrium in the van der Waals systems is represented by the presence of both the associate and its molecular (atomic) units in comparable or at least non-negligible amounts. At higher temperatures, of course, just these monomer units become the predominant components of gas phase. Thus the fact that the equilibrium composition is not taken into account represents a substantial drawback of the standard-term approach. The experimental situations in which the final state of the system is far from the equilibrium state (which is encountered particularly with the technique of expansion in jet, and is increasingly used at present) will be mentioned later.

Finally, let us also mention the fact that the standard-state approach does not reflect the infinite variability of choices of initial conditions of the system and those of the reaction regime, the equilibrium composition not being fully determined until both these characteristics are considered. This variability only emphasizes that there cannot be a single absolute characterization of a given association reaction according to the mutual relation of the enthalpy and entropy terms (which has already been shown in the first paragraph of this section when varying p^0, which can be taken as a special case of the choice of initial conditions and reaction regime). In particular, the standard-state approach does not consider explicitly the problem of the reaction regime, but the fact that it works with the terms ΔH_T^0 and $T \Delta S_T^0$ could perhaps imply—with respect to the equilibrium situation—that it considers the regime of constant total pressure. This, however, would result

in a discrepancy in the case of the heterogeneous dimers: because of our choice of the standard state this condition cannot be fulfilled in the association processes due to stoichiometry of the reaction.

Already these notes indicate that the standard-state approach in its conventional form does not reflect the diversity of experimental situations and that a new scheme must be introduced to attain thermodynamical consistency.

A THERMODYNAMICALLY CONSISTENT TREATMENT

Only two types of stoichiometry will be dealt with in this paper

$$2A(g) \rightleftharpoons A_2(g) \tag{1}$$

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

which are, at present, most important with respect to theoretical studies of formation of van der Waals systems in the gas phase. Furthermore, we must select, out of the infinite number of realizations of these processes, those which are significantly related to experiment. First of all let us presume for simplicity that the temperature T of the system is constant. In thermodynamics a system is usually specified by choice of two thermodynamic constraints selected from the usual set of thermodynamic functions. In our context and within these terms it is natural to add (to the requirement of fixed temperature) either the constraint of constant total pressure p or that of constant volume V of the reaction mixture. The initial state of the system will be described by means of the initial amount of substance $n_A(0)$ and/or $n_B(0)$ and total initial pressure p of the mixture (it is presumed that the product is absent in the initial state, i.e. $n_{A_2}(0)$ or $n_{A \cdot B}(0) = 0$). The final state will be presented by the respective state of thermodynamic equilibrium. For a fixed temperature T and pressure p this point of a closed system is determined by the well-known condition of minimization of the Gibbs energy G with respect to composition of the system (on condition that volume change is the only form of work):

$$dG = 0 \tag{3}$$

and if the constraint of constant p is replaced by that of constant volume V of this system, then the equilibrium condition changes to the minimization of the Helmholtz energy A:

$$dA = 0 \tag{4}$$

Now if we want to adjust the former simple standard-term approach to these two types of constraints, then for the T, p constraint it seems useful to determine the actual reaction changes of enthalpy and entropy, ΔH_X and $\Delta S_X^{(p)}$, whereas for the T, V constraint it seems useful to determine the

actual reaction changes of internal energy and entropy, ΔU_X and $\Delta S_X^{(V)}$ (i.e. the differences between the final and the initial states of the system in the given particular situation). $X = A_2$ and $X = A \cdot B$ will denote the terms corresponding to the stoichiometries (1) and (2), respectively.

A useful intermediary step of this procedure consists in determination of the equilibrium composition in terms [13,14] of standard (dimensionless) equilibrium constants $K_{A_2}^0$ and $K_{A \cdot B}^0$ by means of the extent [14] of the reaction at equilibrium $\xi_{A_2}^{(Y)}$ or $\xi_{A \cdot B}^{(Y)}$ ($Y = p$ or V). Determination of these equilibrium compositions forms a special case of calculations of equilibria in chemical systems [15,16] which can be expressed analytically in our case:

$$\xi_{A_2}^{(p)} = \frac{n_A(0)}{2}\left(1 - \sqrt{\frac{p^0}{4K_{A_2}^0 p + p^0}}\right) \tag{5}$$

$$\xi_{A_2}^{(V)} = n_A(0)\left[\frac{1}{2} + \frac{p^0}{8K_{A_2}^0 p} - \sqrt{\frac{p^0}{8K_{A_2}^0 p}\left(1 + \frac{p^0}{8K_{A_2}^0 p}\right)}\right] \tag{6}$$

$$\xi_{A \cdot B}^{(p)} = \frac{n_A(0) + n_B(0)}{2} - \sqrt{\left(\frac{n_A(0) + n_B(0)}{2}\right)^2 - \frac{n_A(0)n_B(0)K_{A \cdot B}^0 p}{K_{A \cdot B}^0 p + p^0}} \tag{7}$$

$$\xi_{A \cdot B}^{(V)} = \frac{n_A(0) + n_B(0)}{2}\left(1 + \frac{p^0}{K_{A \cdot B}^0 p}\right)$$

$$- \sqrt{\left(\frac{n_A(0) - n_B(0)}{2}\right)^2 + \frac{(n_A(0) + n_B(0))^2 p^0}{2K_{A \cdot B}^0 p}\left(1 + \frac{p^0}{2K_{A \cdot B}^0 p}\right)} \tag{8}$$

The reaction extents at equilibrium, $\xi_X^{(Y)}$, known, it is possible to express in a condensed form the actual reaction changes ΔH_X, $\Delta S_X^{(p)}$ and ΔU_X, $\Delta S_X^{(V)}$. In addition to it, in the terms $\xi_X^{(Y)}$ it is possible to go easily from the actual reaction terms to actual molar [14] changes $\Delta H_{X,m}$, $\Delta S_{X,m}^{(p)}$, $\Delta U_{X,m}$, and $\Delta S_{X,m}^{(V)}$ which result from the actual reaction changes by relating to the reaction extent unit. Thus, the quantities obtained exhibit the same dimensions as the standard molar terms ΔH_X^0, ΔS_X^0. Suitable algebraic operations give the following formulas (cf. also ref. 12):

$$\Delta H_{A_2,m} = \frac{\Delta H_{A_2}}{\xi_{A_2}^{(p)}} = \Delta H_{A_2}^0 \tag{9}$$

$$\Delta S_{A_2,m}^{(p)} = \frac{\Delta S_{A_2}^{(p)}}{\xi_{A_2}^{(p)}} = \Delta S_{A_2}^0 + \frac{R}{\xi_{A_2}^{(p)}}\left[\left(n_A(0) - \xi_{A_2}^{(p)}\right)\ln\left(n_A(0) - \xi_{A_2}^{(p)}\right)\right.$$

$$- \left(n_A(0) - 2\xi_{A_2}^{(p)}\right)\ln\left(n_A(0) - 2\xi_{A_2}^{(p)}\right)$$

$$\left. - \xi_{A_2}^{(p)}\ln\xi_{A_2}^{(p)}\right] + R\ln\frac{p}{p^0} \tag{10}$$

$$\Delta U_{A_2,m} = \frac{\Delta U_{A_2}}{\xi_{A_2}^{(V)}} = \Delta H_{A_2}^0 + RT \tag{11}$$

$$\Delta S_{A_2,m}^{(V)} = \frac{\Delta S_{A_2}^{(V)}}{\xi_{A_2}^{(V)}} = \Delta S_{A_2}^0 + \frac{R}{\xi_{A_2}^{(V)}} \left[\left(n_A(0) - \xi_{A_2}^{(V)} \right) \ln n_A(0) - \left(n_A(0) - 2\xi_{A_2}^{(V)} \right) \right.$$

$$\left. \times \ln \left(n_A(0) - 2\xi_{A_2}^{(V)} \right) - \xi_{A_2}^{(V)} \ln \xi_{A_2}^{(V)} \right] + R \ln \frac{p}{p^0} \tag{12}$$

$$\Delta H_{A \cdot B,m} = \frac{\Delta H_{A \cdot B}}{\xi_{A \cdot B}^{(p)}} = \Delta H_{A \cdot B}^0 \tag{13}$$

$$\Delta S_{A \cdot B,m}^{(p)} = \frac{\Delta S_{A \cdot B}^{(p)}}{\xi_{A \cdot B}^{(p)}} = \Delta S_{A \cdot B}^0 + \frac{R}{\xi_{A \cdot B}^{(p)}} \left[n_A(0) \ln \frac{n_A(0)}{n_A(0) + n_B(0)} \right.$$

$$+ n_B(0) \ln \frac{n_B(0)}{n_A(0) + n_B(0)} - \left(n_A(0) - \xi_{A \cdot B}^{(p)} \right)$$

$$\times \ln \frac{n_A(0) - \xi_{A \cdot B}^{(p)}}{n_A(0) + n_B(0) - \xi_{A \cdot B}^{(p)}} - \left(n_B(0) - \xi_{A \cdot B}^{(p)} \right)$$

$$\left. \times \ln \frac{n_B(0) - \xi_{A \cdot B}^{(p)}}{n_A(0) + n_B(0) - \xi_{A \cdot B}^{(p)}} - \xi_{A \cdot B}^{(p)} \ln \frac{\xi_{A \cdot B}^{(p)}}{n_A(0) + n_B(0) - \xi_{A \cdot B}^{(p)}} \right]$$

$$+ R \ln \frac{p}{p^0} \tag{14}$$

$$\Delta U_{A \cdot B,m} = \frac{\Delta U_{A \cdot B}}{\xi_{A \cdot B}^{(V)}} = \Delta H_{A \cdot B}^0 + RT \tag{15}$$

$$\Delta S_{A \cdot B,m}^{(V)} = \frac{\Delta S_{A \cdot B}^{(V)}}{\xi_{A \cdot B}^{(V)}} = \Delta S_{A \cdot B}^0 + \frac{R}{\xi_{A \cdot B}^{(V)}} \left[n_A(0) \ln \frac{n_A(0)}{n_A(0) + n_B(0)} \right.$$

$$+ n_B(0) \ln \frac{n_B(0)}{n_A(0) + n_B(0)} - \left(n_A(0) - \xi_{A \cdot B}^{(V)} \right) \ln \frac{n_A(0) - \xi_{A \cdot B}^{(V)}}{n_A(0) + n_B(0)}$$

$$- \left(n_B(0) - \xi_{A \cdot B}^{(V)} \right) \ln \frac{n_B(0) - \xi_{A \cdot B}^{(V)}}{n_A(0) + n_B(0)} - \xi_{A \cdot B}^{(V)} \ln \frac{\xi_{A \cdot B}^{(V)}}{n_A(0) + n_B(0)} \right]$$

$$+ R \ln \frac{p}{p^0} \tag{16}$$

where R is the gas constant.

Equations (9)–(16) will be used further for systematic study of relations between the enthalpy (energy) and entropy terms in formation of the homo- and hetero-particle van der Waals dimers.

RESULTS AND DISCUSSION

Quantum-chemical methods have a special—unique at present—position in studies of the thermodynamics of formation of van der Waals systems. Direct simultaneous experimental determination of the standard enthalpy and entropy terms is very rare for these processes. Somewhat more frequent is the determination of the standard enthalpy term alone by means of the technique [17] of the second law method or the van't Hoff equation. Here it must be mentioned, however, that the relatively marked temperature dependences of the ΔH_T^0 terms belonging to the formation of the van der Waals complexes makes the physical meaning of the resulting values rather questionable (cf. refs. 18, 19). The possible existence of isomerism in the resulting complex makes the interpretation of the observed data still more difficult [20]. As spectroscopic techniques do not usually give the complete set of data needed for the statistical–thermodynamic calculation [17] of the thermodynamic terms, the quantum-chemical methods have, for this purpose, really a relatively privileged position at present. In fact, for quite a number of formations of van der Waals systems their standard thermodynamic terms were determined purely on the basis of the quantum-chemical calculations [6,7]. For our purpose we have chosen a 12-membered set (cf. Tables 1, 2, 4, 5) containing five dimerizations of type (1) and seven dimerizations of type (2). To make this set sufficiently representative, we included a broad selection of complexes involving both the true van der Waals molecules and some hydrogen-bonded complexes (cf. ref. 21).

Every concept based on a chosen convention is loaded with a certain ambiguity due to the possible change of this convention. The same is true of, for example, the question as to where to place the boundaries between the four possible types of relations between the values $\Delta H_{X,m}$, $T\Delta S_{X,m}^{(p)}$ or $\Delta U_{X,m}$, $T\Delta S_{X,m}^{(V)}$ in the case of the reaction regimes of constant total pressure and constant volume, respectively. The following convention was accepted in the present work. If $|\Delta H_{X,m}| > 3T|\Delta S_{X,m}^{(p)}|$ or $|\Delta U_{X,m}| > 3T|\Delta S_{X,m}^{(V)}|$, the given particular realization of the reaction will be denoted as enthalpy (HC) or energy (UC) controlled. If $T|\Delta S_{X,m}^{(p)}| > 3|\Delta H_{X,m}|$ or $T|\Delta S_{X,m}^{(V)}| > 3|\Delta U_{X,m}|$, the corresponding realization of the reaction will be considered entropy controlled (SC). In all other situations we will use the denotation compensation (C) or decompensation (D) depending on whether the two compared terms (i.e. the pairs $\Delta H_{X,m}$, $T\Delta S_{X,m}^{(p)}$ or $\Delta U_{X,m}$, $T\Delta S_{X,m}^{(V)}$) have the same or opposite signs, respectively.

Tables 1–3 present the results for the reaction regime of constant total pressure and constant volume for the reaction stoichiometry (1). As transition to the molar reaction terms makes the value of $n_A(0)$ parameter irrelevant, there remains a single free parameter, $viz.$ pressure p, for the given reaction at the chosen reaction regime and temperature. In the terms of the ideal gas approach the value of this parameter could be varied in the

whole interval $(0; \infty)$. From the point of view of observation feasibility, of course, the interval will be narrower, its width being dependent *inter alia* on the choice of temperature, e.g. below the critical temperature of the species A the (practical) upper limit of the p value is given by the corresponding pressure of the saturated vapour of this species. Possibilities of observation at higher temperatures, on the other hand, are limited by stability decrease of the van der Waals complexes with increasing temperature. For unification of the data presentation the temperatures 100, 298.2 and 500 K were chosen (in accordance with the used form [7]). The effect of the change in the p/p^0 parameter ($p^0 = 101325$ Pa) was followed within the interval $\langle 10^{-3}; 10^3 \rangle$. Generally speaking, this variation of T and p had primarily a purpose of mapping. Clearly enough, only a part of the reaction conditions studied is experimentally accessible.

The results given in Table 1 make it possible to judge the effect of temperature changes on quality of the relations between the $\Delta H_{A_2,m}$ and $T\Delta S_{A_2,m}^{(p)}$ terms at the pressure fixed in such way that a straightforward comparison might be done with the statement based on the conventional [7] application of the standard terms ($p/p^0 = 1$). Two findings are most important: (i) in spite of the considerably broad stability range given by the

TABLE 1

Reaction types of reactions (1) for the constant pressure regime ($p/p^0 = 1$) at various temperatures

Reaction	Ref. [a]	T(K)	Standard-term approach [b,c]			Actual reaction term approach [b]		
			$\Delta H_{A_2}^0$	$T\Delta S_{A_2}^0$	State-ment	$\Delta H_{A_2,m}$	$T\Delta S_{A_2,m}^{(p)}$	State-ment
$2H_2O(g) \rightleftharpoons (H_2O)_2(g)$	7	100	-26.46	-8.22	HC^0	-26.46	-8.22	HC
		298.2	-26.06	-24.40	C^0	-26.06	-20.94	C
		500	-23.72	-37.97	C^0	-23.72	-19.37	C
$2HF(g) \rightleftharpoons (HF)_2(g)$	7	100	-27.19	-7.92	HC^0	-27.19	-7.92	HC
		298.2	-28.48	-26.22	C^0	-28.48	-23.03	C
		500	-27.92	-43.29	C^0	-27.92	-23.61	C
$2NO(g) \rightleftharpoons$ *trans*-$(NO)_2(g)$	10	100	-12.15	-13.54	C^0	-12.15	-11.13	C
		298.15	-14.43	-44.70	SC^0	-14.43	-11.95	C
		500	-14.40	-75.00	SC^0	-14.40	-10.24	C
$2NO(g) \rightleftharpoons$ *cis*-$(NO)_2(g)$	10	100	-11.94	-13.70	C^0	-11.94	-10.98	C
		298.15	-14.82	-46.19	SC^0	-14.82	-12.34	C
		500	-15.03	-77.83	SC^0	-15.03	-10.88	C
$2HCl(g) \rightleftharpoons (HCl)_2(g)$	7	100	-5.81	-7.19	C^0	-5.81	-4.79	C
		298.2	-5.46	-21.21	SC^0	-5.46	-2.97	C
		500	-4.12	-33.88	SC^0	-4.12	0.03	HC

[a] Source of the standard terms.
[b] Both terms in kJ mol^{-1}.
[c] The standard state is an ideal gas at $p^0 = 1$ atm $= 101325$ Pa.

choice of systems and temperatures, the SC type of process was not found in any case of this reaction regime and (ii) almost one-half of the cases presented showed differences between the statements of the intuitive technique based merely on the standard terms (in terms of the used choice of the standard state, i.e. $p^0 = 101325$ Pa) and our approach based on the actual molar terms. If one is tempted to consider this coincidence (ii) to be relatively high, one can carry out its following partial rationalization. If $K_{A_2}^0 \gg 1$ for $p/p^0 = 1$, then $\Delta S_{A_2,m}^{(P)} \approx \Delta S_{A_2}^0$; in other words, under these circumstances the equilibrium is shifted in favour of the product so distinctly that—with respect to the condition $p/p^0 = 1$—the values of the standard and actual molar quantities will approach each other closely.

Table 2 presents the data for the case when the regime of constant total pressure (Table 1) is replaced by the regime of constant volume. Of course, this change is not apprehensible in terms of the simple standard-term approach, but it is reflected by our thermodynamically consistent approach, even thus, changes in quality of the relations are not dramatic (as far as the circumstance is ignored that the IIC type of behaviour is replaced by the UC behaviour). A single very important change is encountered with the formation of $(HCl)_2$, where the SC type of the mutual relation between the two components of the reaction term of the Helmholtz energy appears at 500 K. This result is connected with the effect of the relatively significant RT term which contributes to the ΔU_{500}^0 term which approaches zero closely. Except

TABLE 2

Reaction types of reactions (1) for the constant volume regime ($p/p^0 = 1$) at various temperatures [a]

Reaction	$T(K)$	$\Delta U_{A_2,m}$ [b]	$T\Delta S_{A_2,m}^{(V)}$ [b]	Statement
$2H_2O(g) \rightleftharpoons (H_2O)_2(g)$	100	-25.63	-7.64	UC
	298.2	-23.58	-18.44	C
	500	-19.56	-15.16	C
$2HF(g) \rightleftharpoons (HF)_2(g)$	100	-26.36	-7.34	UC
	298.2	-26.00	-20.56	C
	500	-23.76	-19.41	C
$2NO(g) \rightleftharpoons trans\text{-}(NO)_2(g)$	100	-11.32	-10.26	C
	298.15	-11.95	-9.47	C
	500	-10.24	-6.09	C
$2NO(g) \rightleftharpoons cis\text{-}(NO)_2(g)$	100	-11.11	-10.12	C
	298.15	-12.34	-9.86	C
	500	-10.87	-6.72	C
$2HCl(g) \rightleftharpoons (HCl)_2(g)$	100	-4.98	-3.92	C
	298.2	-2.98	-0.49	UC
	500	0.04	4.19	SC

[a] Only the relevant actual reaction terms are presented; for the standard terms, see Table 1; $p^0 = 101325$ Pa.
[b] In kJ mol^{-1}.

TABLE 3

An illustration of influence of the p/p^0 term on relationships between actual reaction changes [a]

Reaction	Regime	T(K)	p/p^0	$\Delta H_{A_2,m}$ $(\Delta U_{A_2,m})$ [b]	$T\Delta S^{(p)}_{A_2,m}$ $(T\Delta S^{(V)}_{A_2,m})$ [b]	Statement
$2HCl(g) \rightleftharpoons (HCl)_2(g)$	Constant pressure	500	0.001	-4.12	0.027	HC
			1		0.032	HC
			1000		2.68	D
$2H_2O(g) \rightleftharpoons (H_2O)_2(g)$	Constant volume	100	0.001	-25.63	-13.38	C
			1		-7.64	UC
			1000		-1.90	UC

[a] In kJ mol^{-1}; $p^0 = 101325$ Pa.
[b] The terms in parentheses belong to the constant volume regime.

for this single case, the conclusions (i) and (ii) of the foregoing paragraph are practically maintained. On the other hand, not fully valid is the statement concerning equality of the standard and the actual molar terms at a marked shift of the equilibrium in favour of the product for $p/p^0 = 1$. This is caused by the fact that, in this limit case, different pairs of terms are encountered in the two techniques, *viz.* $\Delta H^0_{A_2}$, $T\Delta S^0_{A_2}$ and $\Delta U^0_{A_2}$, $T\Delta S^0_{A_2} + RT \ln 2$.

Let us now pass to the discussion of the role of choice of the p/p^0 term value on the quality of relations between the enthalpy (energy) and the entropy terms. This variation of the reaction conditions, of course, is not differentiated at the level of the standard-term approach. Investigation of the relations in the processes of Tables 1 and 2 during variation of p/p^0 within the interval $\langle 10^{-3}; 10^3 \rangle$ leads to two conclusions: (i) except for the formation of $(HCl)_2$ at 500 K in the constant volume regime, this variation does not result in any appearance of the SC reaction type, even though (ii) the change in the reaction type appears in roughly one-half of the studied cases within the considered p/p^0 interval (which is illustrated in Table 3 by the cases of the formation of $(HCl)_2$ and $(H_2O)_2$ within the regimes of constant total pressure and constant volume, respectively). These changes in the reaction type with the changes in the p/p^0 value can be discussed more deeply with the use of the following limiting cases of behaviour:

$$\lim_{p/p^0 \to 0} T\Delta^{(p)}_{A_2,m} = \Delta H^0_{A_2} + RT \tag{17}$$

$$\lim_{p/p^0 \to \infty} \Delta S^{(p)}_{A_2,m} = \lim_{p/p^0 \to \infty} \Delta S^{(V)}_{A_2,m} = \infty \tag{18}$$

$$\lim_{p/p^0 \to 0} T\Delta S^{(V)}_{A_2,m} = \Delta H^0_{A_2} + 2RT \tag{19}$$

Let us consider now that, for example, $\Delta H^0_{A_2} < 0$ and $|\Delta H^0_{A_2}| \gg RT$. Then variation of p/p^0 within the interval $(0; \infty)$ produces these sequences of the reaction types: C, HC, D, SC and C, UC, D, SC for the regimes of constant total pressure and constant volume, respectively. This means that mere choice of a sufficiently broad interval for p/p^0 values can result in occurrence of all the four possible reaction types within one reaction regime. This result, of course, is deduced with the presumption of ideal behaviour of the gaseous reaction mixture. The question, however, remains open whether there exists such combination of all the involved parameters that the p/p^0 interval enabling the presence of all the four types for this combination will —at the same time—fulfil the presumption of the behaviour close to ideality. Nevertheless, the fact that in principle it is possible to obtain—by mere variation of pressure—all four types of the relations between the enthalpy (energy) and the entropy terms underlines that the reaction type represents no absolute characteristic of a given reaction, but it can distinctly depend on choice of the reaction conditions. Our set of 240 realizations of the processes (1) contained the following distribution of the reaction types: 78%, C; 18%, H(U)C; 3%, SC; 1%, D.

To complete the picture let us mention that there is a possible change in the reaction types, if the used set of $\Delta H^0_{A_2}$ and $\Delta S^0_{A_2}$ is replaced by more sophisticated data. This is the case of, for example, the transition from the SCF data [7] used for Tables 1–3 for the formation of $(H_2O)_2$ to the recent SCF CI values [22]. This substitution leads—in some cases—to changes from HC (UC) to the C type and vice versa. It is noteworthy that in the terms used and situations examined by us the similarity of cis- and trans- (NO_2) is of such a degree that all statements about the reaction types for these two isomers were found to be quite parallel.

Tables 4 and 5 give a survey concerning the relations of the terms $\Delta H_{A \cdot B,m}$ and $T \Delta S^{(P)}_{A \cdot B,m}$ and $\Delta U_{A \cdot B,m}$ and $T \Delta S^{(V)}_{A \cdot B,m}$ in the regimes of constant total pressure and constant volume, respectively, at the fixed ratios $p/p^0 = 2$ and $n_A(0)/n_B(0) = 1$. Again, this choice enables a straightforward comparison with the statements based on the simple standard-term approach. The conclusions obtained for the reaction stoichiometry (2) are similar to those obtained for the homo-particle dimers. With the reaction regime of constant total pressure not a single SC type was found for the given choice of parameters in the terms of actual molar terms, whereas with the other reaction regime the SC type only appeared in the formation of $Ar \cdot ClF$ at both higher temperatures investigated. Naturally, there again exists a series of differences in the statements between our treatment and the simple standard-term technique for the chosen standard state. In analogy to the reaction stoichiometry (1), here also exists the possibility of a change in the reaction type with the change in the pressure p (Table 6). Even a change in the $n_A(0)/n_B(0)$ ratio alone can bring about such a change in the reaction type (Table 7).

TABLE 4

Reaction types of reactions (2) for the constant pressure regime ($p/p^0 = 2$; $n_A(0)/n_B(0) = 1$) at various temperatures

Reaction	Ref. [a]	T(K)	Standard term approach [b,c]			Actual reaction term approach [b]		
			$\Delta H^0_{A\cdot B}$	$T\Delta S^0_{A\cdot B}$	State-ment	$\Delta H_{A\cdot B,m}$	$T\Delta S^{(p)}_{A\cdot B,m}$	State-ment
$H_2O(g) + HF(g) \rightleftharpoons H_2O\cdot HF(g)$	7	100	-47.36	-9.70	HC^0	-47.36	-10.28	HC
		298.2	-49.27	-32.61	C^0	-49.27	-33.83	C
		500	-48.86	-54.23	C^0	-48.86	-43.98	C
$HCN(g) + HF(g) \rightleftharpoons HCN\cdot HF(g)$	7	100	-31.77	-9.75	HC^0	-31.77	-10.33	HC
		298.2	-32.10	-30.01	C^0	-32.10	-27.62	C
		500	-30.72	-48.61	C^0	-30.72	-26.52	C
$HF(g) + ClF(g) \rightleftharpoons HF\cdot ClF(g)$	25	100	-12.71	-9.70	C^0	-12.71	-9.74	C
		298.15	-12.31	-28.59	C^0	-12.31	-9.83	C
		500	-11.21	-46.54	SC^0	-11.21	-7.05	C
$HF(g) + ClF(g) \rightleftharpoons ClF\cdot HF(g)$	25	100	-11.53	-8.10	C^0	-11.53	-8.23	C
		298.15	-12.62	-26.24	C^0	-12.62	-10.14	C
		500	-12.24	-43.57	SC^0	-12.24	-8.08	C
$HF(g) + HCl(g) \rightleftharpoons HF\cdot HCl(g)$	23	100	-12.79	-7.94	C^0	-12.79	-8.28	C
		298.2	-13.11	-24.64	C^0	-13.11	-10.61	C
		500	-12.01	-39.95	SC^0	-12.01	-7.85	C
$HF(g) + HCl(g) \rightleftharpoons HCl\cdot HF(g)$	24	100	-9.42	-7.28	C^0	-9.42	-7.09	C
		298.15	-9.64	-22.49	C^0	-9.64	-7.15	C
		500	-8.52	-36.30	SC^0	-8.52	-4.35	C
$Ar(g) + ClF(g) \rightarrow Ar\cdot ClF(g)$ [d]	7	100	-2.64	-6.63	C^0	-2.64	-1.81	C
		298.2	-2.68	-19.84	SC^0	-2.68	-0.20	HC
		500	-2.69	-33.28	SC^0	-2.69	1.47	D

[a] Source of the standard terms.
[b] Both terms in kJ mol^{-1}.
[c] The standard state is an ideal gas at $p^0 = 1$ atm $= 101325$ Pa.
[d] Cf. ref. 12.

TABLE 5

Reaction types of reactions (2) for the constant volume regime ($p/p^0 = 2$; $n_A(0)/n_B(0) = 1$) at various temperatures [a]

Reaction	T(K)	$\Delta U_{A \cdot B,m}$ [b]	$T\Delta S^{(V)}_{A \cdot B,m}$ [b]	Statement
$H_2O(g) + HF(g) \rightleftharpoons H_2O \cdot HF(g)$	100	−46.53	−9.70	UC
	298.2	−46.79	−31.93	C
	500	−44.70	−39.68	C
$HCN(g) + HF(g) \rightleftharpoons HCN \cdot HF(g)$	100	−30.94	−9.75	UC
	298.2	−29.62	−25.07	C
	500	−26.56	−22.35	C
$HF(g) + ClF(g) \rightleftharpoons HF \cdot ClF(g)$	100	−11.88	−9.01	C
	298.15	−9.83	−7.35	C
	500	−7.05	−2.89	C
$HF(g) + ClF(g) \rightleftharpoons ClF \cdot HF(g)$	100	−10.70	−7.51	C
	298.15	−10.15	−7.66	C
	500	−8.08	−3.92	C
$HF(g) + HCl(g) \rightleftharpoons HF \cdot HCl(g)$	100	−11.96	−7.62	C
	298.2	−10.63	−8.13	C
	500	−7.85	−3.69	C
$HF(g) + HCl(g) \rightleftharpoons HCl \cdot HF(g)$	100	−8.59	−6.30	C
	298.15	−7.16	−4.67	C
	500	−4.36	−0.20	UC
$Ar(g) + ClF(g) \rightleftharpoons Ar \cdot ClF(g)$	100	−1.81	−0.98	C
	298.2	−0.20	2.28	SC
	500	1.47	5.63	SC

[a] Only the relevant actual reaction terms are presented; for the standard terms, see Table 4; $p^0 = 101325$ Pa.
[b] In kJ mol^{-1}.

Within the variation of the p/p^0 parameter used by us (i.e. in the interval $\langle 10^{-3}; 10^3 \rangle$) and that of the $n_A(0)/n_B(0)$ parameter (the interval $\langle 0.05; 1 \rangle$) it has been found that the SC reaction type appears only with the above-

TABLE 6

An illustration of influence of the p/p^0 term on relationships between actual reaction changes [a] for reactions (2) ($n_A(0)/n_B(0) = 1$)

Reaction	Regime	T(K)	p/p^0	$\Delta H_{A \cdot B,m}$ $(\Delta U_{A \cdot B,m})$ [b]	$T\Delta S^{(P)}_{A \cdot B,m}$ $(T\Delta S^{(V)}_{A \cdot B,m})$ [b]	State-ment
$HF(g) + HCl(g)$	Constant	100	0.001	−12.79	−11.86	C
$\rightleftharpoons HF \cdot HCl(g)$	pressure		2		−8.28	C
			1000		−3.33	HC
$HCN(g) + HF(g)$	Constant	100	0.001	−30.94	−16.07	C
$\rightleftharpoons HCN \cdot HF(g)$	volume		2		−9.75	UC
			1000		−4.58	UC

[a] In kJ mol^{-1}; $p^0 = 101325$ Pa.
[b] The terms in parentheses belong to the constant volume regime.

TABLE 7

An illustration of influence of the $n_A(0)/n_B(0)$ term on relationships between actual reaction changes [a] for reactions (2)

Reaction	Regime	$T(K)$	p/p^0	$n_A(0)/$ $n_B(0)$	$\Delta H_{A \cdot B,m}$ $(\Delta U_{A \cdot B,m})$ [b]	$T\Delta S^{(p)}_{A \cdot B,m}$ $(T\Delta S^{(V)}_{A \cdot B,m})$ [b]	State-ment
HF(g) + HCl(g) $\rightleftharpoons$ HCl·HF(g)	Constant pressure	500	1000	1	-8.52	-2.95	C
				0.2		-2.68	HC
				0.05		-2.52	HC
HF(g) + HCl(g) $\rightleftharpoons$ HF·HCl(g)	Constant volume	100	100	1	-11.96	-4.62	C
				0.2		-3.52	UC
				0.05		-3.34	UC

[a] In kJ mol^{-1}; $p^0 = 101325$ Pa.
[b] The terms in parentheses belong to the constant volume regime.

mentioned formations of Ar · ClF at the higher temperatures in the constant volume regime; in those cases, however, all the parameter choices considered throughout. With respect to the two isomeric pairs (HF · HCl, HCl · HF; HF · ClF, ClF · HF) involved in the studied series of the processes with the stoichiometry (2) it is noteworthy that, on contrast to the A_2 dimers, here exist a number of choices of the parameter values when the two isomeric structures exhibit different types of behaviour. Finally, let us add for illustration that our set of 2016 realizations of the processes (2) contained the following distribution of the reaction types: 76%, C; 16%, H(U)C; 5%, SC; 3%, D.

If we consider the limiting relations type (18) also for the stoichiometry (2), it is immediately obvious that the SC behaviour must be attained for the formation of any A · B complex at a sufficiently high p/p^0 value, of course, again with the reservation that such conditions can be experimentally inaccessible and/or the behaviour of the system can be far from ideal. So considering everything it can be concluded that the SC formation of the van der Waals complexes A · B seems to be a comparatively frequent phenomenon within the studied intervals for the parameter values as it was in the case of A_2 complexes. In both situations (1) and (2) the SC behaviour was limited to one system and one reaction regime and, moreover, at enhanced temperature(s). Consequently, in the whole context the SC behaviour cannot, in any case, be denoted as frequent or even as dominant of the studied processes. This attribute applies to the C reaction type in our study.

There exist a number of directions along which our problem can be generalized. First of all our conception of the final state of the system can be extended by admitting non-equilibrium concentrations; the essence of the approach of the actual reaction changes remains thereby unaffected. This extension would affect such situations in the experiment which produce a non-equilibrium mixture of reactant(s) and product. This applies, first of all,

to the generation of the van der Waals complexes by means of supersonic expansion in jet [26]. There exists, however, one additional substantial problem in calculation of entropy of the particles leaving the jet where generally thermal equilibrium is not reached (different translational, rotational, and vibrational temperatures). Another possible generalization could involve the presence of product in the initial state (i.e. $n_{A_2}(0) \neq 0$, $n_{A \cdot B}(0) \neq 0$). Determination of the actual molar changes could be adjusted to this situation too, if need be. Another direction of generalizations lies in the reaction stoichiometry. In this paper discussion was limited to two stoichiometries only, *viz.* eqns. (1) and (2). However, it would be possible to similarly discuss also the formation of higher n-mers along with the van der Waals dimers. Substantial differences between the standard and the actual molar entropy terms would undoubtedly appear here again (it should be noted that such differences generally exist in even the simplest—from our point of view—stoichiometry, *viz.* isomerization reaction).

A very interesting possibility of generalization consists in a transition to other regimes than the considered regime of constant total pressure or constant volume (at a fixed temperature). A current (though not exclusive) way of specification of a thermodynamic system consists in fixation of a pair of its usual thermodynamic characteristics. Naturally, we could also fix any function derived from the usual thermodynamic functions. Thus, we can generate any number of pairs of constraints and, hence, any number of specifications of the system. For each such system we can further generate its condition of establishing of equilibrium. So, for example, in connection with investigation of explosives the fixation of H, p or S, p pairs can be taken into account [16]. From our point of view, interesting sets are, for example, those formed by fixation of S and V or S and p, the minimization of U or H, respectively, being the equilibrium condition. In our terminology this means that every system with the prescribed S and V or S and p values is absolutely energy or enthalpy controlled, respectively. Similarly, if the system is thermally and mechanically insulated (which, incidentally, represents a case of constraints by extensive thermodynamic characteristics which are not functions of state), then the corresponding condition of equilibrium consists in maximization of entropy:

$$dS = 0 \tag{20}$$

hence, in our terminology, this system is absolutely entropy controlled. Of course, realization of thermal and mechanical insulation means to consider not only the reaction itself but also the reaction vessel (a closed thermostat); the condition of entropy maximization relates to the whole system. From these remarks it is clear that simultaneous following of enthalpy (energy) and entropy changes is far from being relevant for description of equilibrium of all systems. It is, of course, true that it is relevant just for those

two types of constraints which are especially suitable for experimental realization.

The actual reaction terms used by us were determined as differences between a certain final and initial state. If the condition of constant total pressure or constant volume along the whole path between these two states is abandoned, then an infinite number of paths can be found between the limit states introduced by us. All these paths will be characterized by the same values of the actual reaction terms. The convention introduced by us for evaluation of the role of entropy could not differentiate between these paths. If we wanted to attain this aim, we could turn to, e.g. construction of some integral reaction terms by means of integration along the paths between both states. This remark again points at the fact that a number of thinkable conventions can be used for our purpose of evaluation of the role of entropy, it being even possible that the different conventions will lead to different quality of statements about the types of the processes investigated.

The results of this study of relations within the van der Waals complexes have certain consequences also for usual chemical equilibria in gas phase with the stoichiometries (1) or (2); the only difference could be in magnitude of the respective equilibrium constants. However, it is necessary to transfer these results carefully to reactions involving other than gas phase, because other types of dependences of functions of state on composition of the system can thereby come into play.

CONCLUSIONS

The rapid recent development of quantum-chemical calculations of thermodynamics of formation of the van der Waals complexes, especially dimers, resulted in attempts at some qualification of the role of entropy in these processes. Weak molecular complexes represent really the type of systems whose formation and properties cannot fully be understood in the terms of mere depths of the minima at the potential energy hypersurface. The standard thermodynamic terms were suggested originally and used quite extensively for this purpose even without explicit reference to particular choice of the standard state. Results of this approach depend on the choice of the standard state (any of the possible types of the relations can be obtained by suitable choice), and this simple method has further drawbacks in that it does not lead to the equilibrium final state and does not reflect the dependence on choice of the reaction regime and reaction conditions. Therefore, a thermodynamically consistent concept has been suggested which operates with the actual molar thermodynamic terms and has been used within the reaction regimes of constant total pressure or constant volume. This concept has been applied to various formations of the van der

Waals homo- and hetero-particle dimers which were studied recently by means of quantum chemistry. Broad variation of the reaction conditions showed that the formerly presumed entropy control in the formation of the van der Waals complexes is really a relatively rare phenomenon in formation of both the homo- and hetero-particle dimers studied. In contrast, the compensation relation can be considered to be the most frequent type. It has been shown that a mere change of the reaction conditions within any of the two reaction types can (on condition of ideal behaviour throughout) lead to any of the possible reaction types. The comparison of enthalpy (energy) and entropy changes is meaningful, of course, only for some reaction regimes. Similarly conceivable are also the regimes for which the establishing of equilibrium is always fully controlled by only one of the above-mentioned terms. This, of course, emphasizes the fact that the relations between the enthalpy (energy) and the entropy terms represent no absolute, general characteristics of the given process (not even within reaction regime whose equilibrium point is determined by both functions), but these relations (and their applicability) can strongly depend on the reaction conditions.

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