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Entropy-controlled reactions: HF(g) and HCl(g) association as a pertinent example of the thermodynamically consistent treatment [α]

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Abstract

The gas-phase association of HF and HCl to HCl·HF is treated as a useful illustrative example for demonstrating the thermodynamically consistent treatment of entropy-role evaluation in chemical processes. The treatment makes use of the actual reaction enthalpy and entropy changes and shows that in the constant total pressure regime the association belongs to the enthalpy–entropy compensation reaction type instead of to the entropy-controlled type as follows from a simplified treatment still employed in the current literature. A wider thermodynamic background is briefly discussed.

INTRODUCTION

Chemical reactions can be understood [1–5] as a result of an interplay between energy and entropy effects, i.e. their competition and compensation. The related prerequisite terms for evaluation of actual changes of thermodynamic functions within a particular reaction regime are standard or activation terms for equilibrium or rate processes, respectively. Incidentally, thermodynamic standard states can still represent a source of confusion and misunderstandings, see for example refs. 4, 6 and 7. Some authors try to circumvent the problems by no specification of the standard-state choice with their standard terms, simply ignoring the trivial fact that then their data generally lack any meaning. Generally speaking, it is not possible to deduce the non-specified standard state from the nature of the published data, especially so if they originated from observations. In this paper we shall not

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[α] Dedicated to Professor Rudolph Zahradník on the occasion of his 60th birthday. Submission was delayed by circumstances beyond the author's control. See ref. 1 for a preliminary note.

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deal with the standard states themselves but with an attractive, however wrong, application of standard thermodynamic (and activation as well) terms which might just have its roots [8] in the standard-state non-specification.

In recent years an interesting concept has been presented, first in books (e.g. refs. 9 and 10) and lectures, then in survey or review articles (e.g. ref. 11) and finally, horribile dictu, in original papers (the most recent known application of the concept in a research paper being [12] from 1990). Just before the reverse process may start (i.e. from journals back to textbooks) it seems a proper time to call attention to this interesting and important problem on a well selected, pregnant example.

THE SIMPLIFIED APPROACH

The reactivity concept was applied to equilibrium gas-phase processes, gas–solid interactions, reactions in solutions as well as to rate processes. The treatment has been quite straightforward: Standard enthalpy ΔH_T^0 and entropy ΔS_T^0 changes at a temperature T were taken (incidentally, without a standard-state specification), and if $T|\Delta S_T^0| \gg |\Delta H_T^0|$ the reaction was designated as entropy controlled. (Similarly, an enthalpy-control or compensation reaction type was introduced if $|\Delta H_T^0| \gg T|\Delta S_T^0|$ or $\Delta H_T^0 \approx T\Delta S_T^0$, respectively.) The classification seemed to work nicely for many particular classes of reactions, so that it was possible to conclude that, for example, the formation of gas-phase molecular complexes (especially, van der Waals molecules), the processes of heterogeneous catalysis, or reactions with biomolecules were frequently or even mostly entropy-controlled.

Let us give an illustrative example of the straightforward standard-state reasoning, namely, on the association

$$\mathrm{HF(g) + HCl(g) = HCl \cdot HF(g)} \tag{1}$$

the thermodynamic characteristics of which are given in Table 1 for five representative temperatures. The standard thermodynamic terms of the

TABLE 1

Illustration[a] of the standard[b]-term reasoning on entropy-controlled reactions with the association $\mathrm{HF(g) + HCl(g) = HCl \cdot HF(g)}$

T (K)	ΔH_T^0 (kJ mol^{-1})	$T\Delta S_T^0$ (kJ mol^{-1})	Reaction type
100	−6.54	−6.86	Enthalpy–entropy compensation
200	−6.85	−14.2	Enthalpy–entropy compensation
298.15	−6.57	−20.9	Entropy control
400	−6.03	−27.4	Entropy control
500	−5.39	−33.6	Entropy control

[a] The standard[b] enthalpy ΔH_T^0 and entropy ΔS_T^0 terms evaluated according to ref. 13.

[b] The standard state is an ideal gas at a pressure of 1 atm = 101 325 Pa.

ideal-gas association reaction (1), were evaluated [13] by means of a partition-function technique supplied with calculated [14] structural, vibrational and energy parameters. At the lowest temperature the standard enthalpy and entropy terms practically cancel within the Gibbs energy term, hence an enthalpy–entropy compensation is met. With the three higher temperatures the $T\Delta S_T^0$ term is considerably larger (in the absolute value) than the corresponding enthalpy. Hence, one could arrive at a conclusion that reaction (1) obeys the above general rule that the gas-phase molecular-complex or van-der-Waals-molecule formation is frequently entropy controlled. This is an essence of the simplified (purely standard-state) reasoning.

THE THERMODYNAMICALLY CONSISTENT APPROACH

Chemistry is a complex subject and therefore any new classification is welcome, provided it works satisfactorily. It is not particularly significant if an evaluation scheme cannot be at the moment exactly derived from the first principles (see, for example, the Woodward–Hoffmann rules) or it works with a concept which is not unambiguously defined in the physical sense (e.g. the aromaticity or topological indices). The most important feature is that the rule works well or reasonably well.

One could believe that the above entropy-control reaction concept works well and some important classes of reactions are, according to the concept, indeed entropy controlled, as long as the reasoning sketched in Table 2 is not applied. Clearly enough, standard state is arbitrary; any choice is possible and this remains true for the case of a reaction between ideal-gas components. Hence, we can vary the standard-pressure choice widely. An ideal-gas enthalpy is a function of temperature only and thus there will be no change with the ΔH_T^0 term. However, ideal-gas entropy depends on

TABLE 2

Sensibility of the standard-term interplay to standard-state choice illustrated with the association $HF(g) + HCl(g) = HCl \cdot HF(g)$ at $T = 100$ K

Standard pressure [a] (atm)	ΔH_T^0 (kJ mol^{-1})	$T\Delta S_T^0$ (kJ mol^{-1})	Reaction type
10^{-7}	-6.54	-20.3	Entropy control
1	-6.54	-6.86	Enthalpy–entropy compensation
10^3	-6.54	-1.12	Enthalpy control
10^7	-6.54	6.54	Enthalpy–entropy decompensation
10^{14}	-6.54	19.9	Entropy control

[a] The standard state is an ideal gas at the given pressure (otherwise, throughout the article a uniform standard state is used; a pressure of 1 atm = 101 325 Pa).

pressure; for molar entropy at two different pressures, p_1 and p_2, the following relationship holds (the temperature T being fixed):

$$S(p_2) = S(p_1) - R \ln \frac{p_2}{p_1} \tag{2}$$

where R stands for the gas constant. With the help of eqn. (2) Table 2 can be set up. The conclusion is that the entropy-control treatment depends heavily on the standard-state choice (in fact, any kind of proportions between enthalpy and entropy terms can be obtained purely by adjusting the standard-state choice). Needless to say, a concept depending on standard-state choice can hardly be useful. (However, it does not mean that simple, standard-term reasoning is always useless. For example, it can still be useful when comparing the relative importance of enthalpy and entropy under different conditions. For example, for a reaction at two different temperatures the increment in entropy is already (in contrast to the total term in Table 2) independent of standard-state choice owing to a convenient cancellation.)

In developing the entropy-controlled concept two important facts were not realized: (i) standard-state specification is an essential component of standard terms as the latter depends on the former, and there is an infinite number of standard enthalpy–entropy pairs just differing in their standard-state choice; (ii) standard changes of thermodynamic terms belong to processes which are not particularly convenient from a chemical point of view as they have to proceed completely, without any rest, from the left to the right side and hence, do not end at the equilibrium point.

Still, the question of enthalpy–entropy interplay is of crucial importance and it is certainly useful to develop (beyond the above criticism of the shortcomings of the simple standard-term reasoning) a proper treatment of it, at least for one reaction stoichiometry (for example, for reaction type (1) in an ideal gas phase as this represents a quite instructive case). Even if it were to finally turn out that a thermodynamically consistent treatment is not particularly convenient for classification purposes, it is still useful from the noetic point of view. Firstly, we should realize that there are an infinite number of reaction regimes, i.e. ways a reaction can proceed (not in the kinetic, but the thermodynamic sense, assigning final states to an initial one). For simplicity, let us deal with a quite common reaction regime, the constant total-pressure regime (i.e., the total pressure p and temperature T are the same in the initial and the final state). Even within a reaction regime there are, however, an infinite number of realizations. In our example we can vary the total pressure and/or the initial ratio of components. Each particular reaction realization (within the given reaction regime) posseses its own actual molar reaction enthalpy ΔH_T and entropy ΔS_T terms. For a given stoichiometry and reaction regime we can try to sample the variable parameters accordingly, evaluate the actual reaction terms, and look for a prevailing type of enthalpy–entropy interelation. It is quite natural that the final reaction state is considered as the state of the equilibrium reaction mixture. The initial state will be described, besides the total pressure p, by the initial ratio of number of moles of the components on the left side of eqn. (1), n_A^0/n_B^0, while the associate, for simplicity, is not present in the initial reaction mixture ($n_{A.B}^0 = 0$).

The equilibrium composition can be described by means of the extent of reaction at equilibrium, ξ, which has to obey the equilibrium condition

$$K_p = \frac{(n_A^0 + n_B^0 - \xi)\xi}{(n_A^0 - \xi)(n_B^0 - \xi)p} \tag{3}$$

where K_p stands for the equilibrium constant of reaction type (1). Here, in order to simplify the relations, we deal with (rather traditional) dimensioned K_p in spite of the fact that from the rigorous physical point of view K_p should be a dimensionless quantity [4]. Henceforth, the standard-state choice is the ideal gas at 1 atm (= 101 325 Pa) pressure throughout (which particularly implies that K_p is in atm^{-1} and p in atm units). Solution of eqn (3) can be readily found

$$2\xi = n_A^0 + n_B^0 - \left[(n_A^0 + n_B^0)^2 - \frac{4n_A^0 n_B^0 pK_p}{pK_p + 1}\right]^{1/2} \tag{4}$$

Knowing the equilibrium composition, the actual molar reaction H and S changes can be evaluated. With enthalpy it is quite easy (as, once again, ideal-gas enthalpy is a function of temperature only), leading to the following relation:

$$\Delta H_T = \Delta H_T^0 \tag{5}$$

For the actual molar entropy change some algebraic manipulations are necessary, based essentially on eqn. (2), yielding finally

$$\begin{aligned}\Delta S_T = \Delta S_T^0 + \frac{R}{\xi}\Bigg[&n_A^0 \ln\frac{n_A^0}{n_A^0 + n_B^0} + n_B^0 \ln\frac{n_B^0}{n_A^0 + n_B^0}\\ &-(n_A^0 - \xi)\ln\frac{n_A^0 - \xi}{n_A^0 + n_B^0 - \xi} - (n_B^0 - \xi)\ln\frac{n_B^0 - \xi}{n_A^0 + n_B^0 - \xi}\\ &-\xi \ln\frac{\xi}{n_A^0 + n_B^0 - \xi}\Bigg] + R\ln p\end{aligned} \tag{6}$$

It should be mentioned for completeness that our initial state introduced above is not an equilibrium state, but a state of separated components representing an alternative. If the components are initially separated (each at the pressure p in order to keep a correspondence with the constant total pressure regime) then their pure mixing (without any chemical reaction)

TABLE 3

Actual [a] molar enthalpy and entropy changes for the association $HF(g)+HCl(g)=HCl\cdot HF(g)$ within the constant total pressure regime for parameters $p=2$ atm and $n_A^0/n_B^0=1$

T (K)	ΔH_T (kJ mol^{-1})	$T\Delta S_T$ (kJ mol^{-1})	Reaction type
100	-6.54	-5.41	Enthalpy–entropy compensation
200	-6.85	-5.17	Enthalpy–entropy compensation
298.15	-6.57	-4.09	Enthalpy–entropy compensation
400	-6.03	-2.70	Enthalpy–entropy compensation
500	-5.39	-1.23	Enthalpy control

[a] For the underlying standard enthalpy and entropy terms, see Table 1.

introduces an entropy of mixing. The additional (molar) term of entropy of mixing [2] (i.e. from the separated n_A^0 moles of A and n_B^0 moles of B, each species at the pressure p, to their mixture at the same total pressure p and without any chemical reaction) reads

$$\Delta S_T^{(\mathrm{mix})} = -R\left(\frac{n_A^0}{n_A^0+n_B^0}\ln\frac{n_A^0}{n_A^0+n_B^0}+\frac{n_B^0}{n_A^0+n_B^0}\ln\frac{n_B^0}{n_A^0+n_B^0}\right) \tag{7}$$

Term (7) is (for a given ratio n_A^0/n_B^0) a constant, not influencing the results in Table 3 substantially and thus was not included in the data presented there (i.e. our original initial-state definition was kept).

RESULTS AND DISCUSSION

For our reaction (1) and the chosen constant total pressure regime we could still vary the total pressure p and the ratio n_A^0/n_B^0 quite extensively. Table 3 is limited only to the cases corresponding (in a sense that the initial pressure and monomeric ratio is the same in both approaches) to those from the simple reasoning in Table 1, i.e. to the variable-parameter values $p=2$ atm and $n_A^0/n_B^0=1$. The proper treatment yields a different picture of the enthalpy–entropy relationships. However, the picture is not complete. All the relevant p and n_A^0/n_B^0 choices should be tested. If we do that (though there is an indeterminacy as to what are the relevant values of the parameters, i.e. what are the chemically significant intervals of their values) it appears that the entropy-controlled cases are quite exceptional for reaction (1) within the constant-pressure regime. The enthalpy–entropy compensation turns out instead to be a rather frequent reaction type. However, there can be a problem related to initial-condition sampling in order that the sampling be sufficiently representative as far as typical experimental situations are concerned.

The treatment could be now repeated for other reaction regimes which may be relevant for the reaction system, starting, for example, with a regime of the constant total volume (and temperature). For the latter regime, however, the conjugated pair of actual reaction changes in internal energy and entropy should be followed. In this connection it should be mentioned that a (perhaps artificial) reaction regime could in principle be constructed (though not necessarily being significant or even realizable from an observational point of view) in which (in our language) each of its particular realizations is, for example, enthalpy controlled, etc. Such a construction would be based on a convenient selection of two thermodynamic constraints describing the reaction regime (i.e. fixation of entropy and pressure). Similarly, any completely isolated system (insulated thermally and mechanically) is, in our terms, absolutely entropy controlled [15]. These remarks once again stress that the question of reaction types cannot generally be answered without specifying a reaction regime. If there is a need, the whole treatment could be repeated for any stoichiometry of interest (for some stoichiometries, such as isomerizations [16], it can however be a considerably simpler task) or possibly applied to activation terms of a rate process.

Finally, let us note that this study has no consequences for correlation analysis [17]; a change in standard state cannot influence the quality of an enthalpy–entropy linear relationship. Any change in the choice of standard state can only cause a constant shift for all the members of a reaction series.

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