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A RIGOROUS RULE FOR TEMPERATURE EXTREMA OF ISOMER ENTHALPY AND ENTROPY TERMS: CONSISTENCY TEST OF DATA *,**

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ABSTRACT

For three different types of enthalpic and entropic quantities, important for the description of isomer thermodynamics, it has been shown that if the enthalpy and/or entropy term(s) exhibit(s) a temperature extremum then both the terms assume it at precisely the same temperature. This fact is illustrated with the characteristics of the isomeric systems $(CO_2)_2$(g) and $(CO_2)_2^-$(g).

INTRODUCTION

The correlation relations between enthalpy and entropy terms, both the standard and the activation terms, are essential tools of physical organic chemistry [1], and in this context thermodynamic analysis of their nature has been carried out widely [2–5]. Recently, the problems of interplay, proportions, competition and compensation between the energy and entropy terms have become an object of interest also in theoretical chemistry in connection with the gradual transition from a description of chemical reactivity merely in terms of potential energy to one in terms of the Gibbs free energy [6–8]. Exact relations between the enthalpy and entropy terms as a reliable starting point for further considerations (see, for example, ref. 9) are of lasting value for studies of this type. This present communication will point out a rigorous rule, which has not yet been utilized, or even explicitly described, for the positions of temperature extrema of isomer enthalpy and entropy terms, this rule having an undoubted application potential.

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* Dedicated to the late Professor Louis P. Hammett.

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GENERAL CONSIDERATIONS

There is a basic difference between the possibility of occurrence of extremum behaviour of the enthalpy and entropy terms of an individual species and of those of its reactions. This fact can be documented, for example, using the standard terms of a species in the ideal gas phase. The derivatives with respect to temperature [10,11] of the standard enthalpy

$$\frac{\mathrm{d}H^{\ominus}}{\mathrm{d}T} = C_p^{\ominus} \tag{1}$$

and entropy

$$\frac{\mathrm{d}S^{\ominus}}{\mathrm{d}T} = \frac{C_p^{\ominus}}{T} \tag{2}$$

for a simple species are, in principle, reduced to its standard heat capacity at constant pressure $C_p^{\ominus}$. The attainment of the temperature extremum in the $H^{\ominus}$ or $S^{\ominus}$ term necessitates vanishing of the $C_p^{\ominus}$ term. In contrast to individual species, for a chemical reaction it can quite frequently happen that the standard heat-capacity change during this reaction, $\Delta C_p^{\ominus}$, assumes the value zero, and at the temperature at which the $\Delta C_p^{\ominus}$ term vanishes the conditions for the temperature extremum are fulfilled

$$\frac{\mathrm{d}\,\Delta H^{\ominus}}{\mathrm{d}T} = \Delta C_p^{\ominus} = 0 \tag{3}$$

$$\frac{\mathrm{d}\,\Delta S^{\ominus}}{\mathrm{d}T} = \frac{\Delta C_p^{\ominus}}{T} = 0 \tag{4}$$

It is of course obvious that the temperature extrema of the $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ quantities are attained at the same temperature. It is, however, noteworthy that these extrema also need not necessarily be of the same nature (i.e., both need not, for example, be minima—moreover, in principle, a stationary point which is not a minimum or maximum could also occur), since for the enthalpy and entropy changes the signs of the terms $\mathrm{d}\Delta C_p^{\ominus}/\mathrm{d}T$ and $\mathrm{d}(\Delta C_p^{\ominus}/T)/\mathrm{d}T$, respectively, are decisive.

THREE PARTICULAR CASES

Let us move from a general chemical reaction to the following simple isomerization in the ideal gas phase

$$\mathrm{A}_1 = \mathrm{A}_2 \tag{5}$$

The changes in the standard enthalpy $H_2^{\ominus} - H_1^{\ominus}$ and entropy $S_2^{\ominus} - S_1^{\ominus}$ along this reaction then assume a temperature extremum (if any) at the temperature at which the change in the standard heat capacity at constant pressure is zero

$$\frac{\mathrm{d}(H_2^{\ominus} - H_1^{\ominus})}{\mathrm{d}T} = C_{p,2}^{\ominus} - C_{p,1}^{\ominus} = 0 \tag{6}$$

$$\frac{\mathrm{d}(S_2^{\ominus} - S_1^{\ominus})}{\mathrm{d}T} = \frac{C_{p,2}^{\ominus} - C_{p,1}^{\ominus}}{T} = 0 \tag{7}$$

Of course, the fact that possible extrema of the functions $H_2^{\ominus} - H_1^{\ominus}$ and $S_2^{\ominus} - S_1^{\ominus}$ are attained by both these functions at a common temperature represents a particular simple case of the previous considerations.

Somewhat less obvious is the problem of the positions of the temperature extrema of other thermodynamic quantities introduced for the purpose of studying isomer thermodynamics, i.e., the isomerism contribution to the values of thermodynamic functions [12,13]. These isomerism contributions are introduced for a condensed treatment of two types of quantities and of the differences between them, i.e., the partial quantities corresponding to a particular isomer and the overall quantities corresponding to the equilibrium mixture of these isomers. The isomerism contributions are the values which must be added to the partial term corresponding to the most stable isomer (in our context it is ascribed the index 1) in order to obtain the overall term. In the case of two isomers, these isomerism contributions to the enthalpy and entropy terms are as follows [12,13]

$$\delta H_1^{(\mathrm{iso})} = w_2(H_2^{\ominus} - H_1^{\ominus}) \tag{8}$$

$$\delta S_1^{(\mathrm{iso})} = w_2(S_2^{\ominus} - S_1^{\ominus}) - R(w_1 \ln w_1 + w_2 \ln w_2) \tag{9}$$

In eqns. (8) and (9), w_1 and w_2 denote the mole fractions of the isomers A_1 and A_2 in their equilibrium mixture and R denotes the gas constant. The weight factors w_i are of course temperature dependent, hence it is not a priori clear whether or not some analogue of the simple rule derived for the standard enthalpy and entropy changes along a chemical reaction (e.g. that shown in eqn. (5)) will apply to possible extrema of the $\delta H_1^{(\mathrm{iso})}$ and $\delta S_1^{(\mathrm{iso})}$ quantities. Therefore, in order to evaluate this problem, it is necessary to carry out the differentiation with respect to temperature of eqns. (8) and (9)

$$\frac{\mathrm{d}\delta H_1^{(\mathrm{iso})}}{\mathrm{d}T} = \frac{w_1 w_2 (H_2^{\ominus} - H_1^{\ominus})^2}{RT^2} + w_2(C_{p,2}^{\ominus} - C_{p,1}^{\ominus}) \tag{10}$$

$$\frac{\mathrm{d}\delta S_1^{(\mathrm{iso})}}{\mathrm{d}T} = \frac{w_1 w_2 (H_2^{\ominus} - H_1^{\ominus})^2}{RT^3} + \frac{w_2}{T}(C_{p,2}^{\ominus} - C_{p,1}^{\ominus}) \tag{11}$$

Thus, it indeed becomes evident that the equations for determination of temperature extrema of the $\delta H_1^{(\mathrm{iso})}$ and $\delta S_1^{(\mathrm{iso})}$ terms will be identical and, hence, both the terms will assume a possible extremum at the same point. However, the temperature position of these extrema will generally be different from that of the extrema of the $H_2^{\ominus} - H_1^{\ominus}$ and $S_2^{\ominus} - S_1^{\ominus}$ terms. For completeness, let us note that the $\mathrm{d}\delta H_1^{(\mathrm{iso})}/\mathrm{d}T$ term of eqn. (10) represents, in fact, the so-called relaxation isomerism contribution to the heat capacity [14], $\delta C_{p,1}^{(\mathrm{iso})}$.

The third case to be investigated is the positions of temperature extrema of the overall (total) standard enthalpy and entropy changes [12–14] $\Delta H_{\mathrm{T}}^{\ominus}$ and $\Delta S_{\mathrm{T}}^{\ominus}$ for a reaction with participation of isomers

$$\sum_j \nu_j \mathrm{B}_j = \mathrm{A} \tag{12}$$

where A denotes the superspecies composed of the equilibrium mixture of the A_1 and A_2 isomers. Specification of the reactants on the left-hand side of eqn. (12) is not necessary for our purposes. These overall (total) terms can be expressed by means of the isomerism contributions (8) and (9) and the partial enthalpy and entropy terms $\Delta H_1^{\ominus}$ and $\Delta S_1^{\ominus}$ corresponding to the reaction (12) whose right-hand side only contains the isomer A_1

$$\Delta H_{\mathrm{T}}^{\ominus} = \Delta H_1^{\ominus} + \delta H_1^{(\mathrm{iso})} \tag{13}$$

$$\Delta S_{\mathrm{T}}^{\ominus} = \Delta S_1^{\ominus} + \delta S_1^{(\mathrm{iso})} \tag{14}$$

The differentiation with respect to temperature of eqns. (10) and (11) gives

$$\frac{\mathrm{d}\Delta H_{\mathrm{T}}^{\ominus}}{\mathrm{d}T} = \Delta C_{p,1}^{\ominus} + \delta C_{p,1}^{(\mathrm{iso})} = \Delta C_{p,\mathrm{T}}^{\ominus} \tag{15}$$

$$\frac{\mathrm{d}\Delta S_{\mathrm{T}}^{\ominus}}{\mathrm{d}T} = \frac{\Delta C_{p,1}^{\ominus}}{T} + \frac{\delta C_{p,1}^{(\mathrm{iso})}}{T} = \frac{\Delta C_{p,\mathrm{T}}^{\ominus}}{T} \tag{16}$$

Hence, in this case also it is true that the equations for determination of temperature extrema will be identical, i.e. both the terms will attain the extrema (if they exist) at a common temperature. The temperature at these extrema will generally be different from the temperatures at the extrema of eqns. (6) and (7) and eqns. (10) and (11).

ILLUSTRATIVE EXAMPLES

Of course, any isomeric system can be chosen for illustration; our choice of the isomers of molecular complexes, e.g. $(\mathrm{CO_2})_2$ (g) and its anion $(\mathrm{CO_2})_2^-$ (g), is connected with the fact that these systems have received considerable attention in recent theoretical studies [15–17]. In order to illustrate the extremum behaviour of the terms $H_2^{\ominus} - H_1^{\ominus}$ and $S_2^{\ominus} - S_1^{\ominus}$ and $\delta H_1^{(\mathrm{iso})}$ and $\delta S_1^{(\mathrm{iso})}$, we shall adopt a system of two isomers of $(\mathrm{CO_2})_2^-$ (g) sufficiently characterized (for thermodynamic purposes) by the ab initio calculations [17] in the flexible basis set with MP3 evaluation of electron correlation. According to these results there exist two isomeric forms of $(\mathrm{CO_2})_2^-$, i.e., the

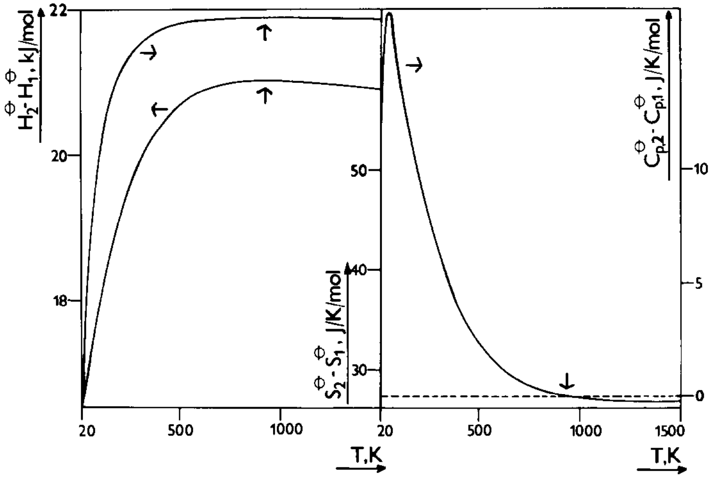

Fig. 1. Temperature dependences of the differences in the standard enthalpy $H_2^\ominus - H_1^\ominus$ and entropy $S_2^\ominus - S_1^\ominus$ (left) and heat capacity $C_{p,2}^\ominus - C_{p,1}^\ominus$ (right) for D_{2d} (1) and C_s (2) isomers of $(CO_2)_2^-$ (g) (derived using the RRHO approach supplied with the MP3 data from ref. 17).

structures being of D_{2d} and C_s symmetries, the former structure (further denoted by the index 1) being more stable in terms of the potential energy. However, this isomeric system is not sufficiently convenient for illustration of the extremum behaviour of the overall reaction terms (13) and (14), because no adequate theoretical characterization of any form of the left-hand

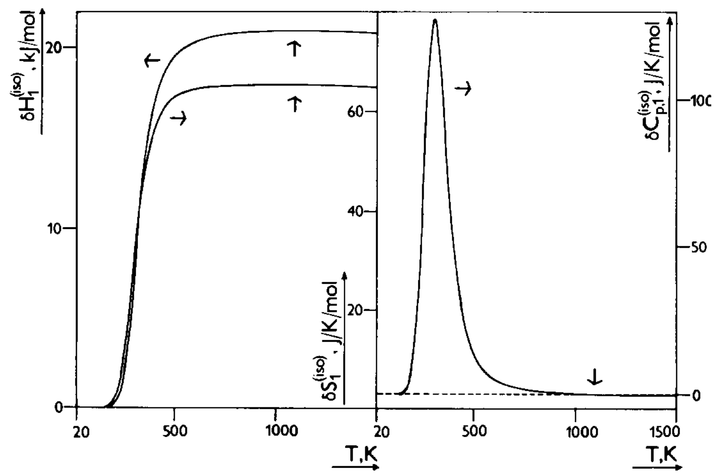

Fig. 2. Temperature dependences of the isomerism contributions to enthalpy $\delta H_1^{(iso)}$ and entropy $\delta S_1^{(iso)}$ (left) and heat capacity $\delta C_{p,1}^{(iso)}$ (right) for the system from Fig. 1 (related to the D_{2d} structure as reference isomer).

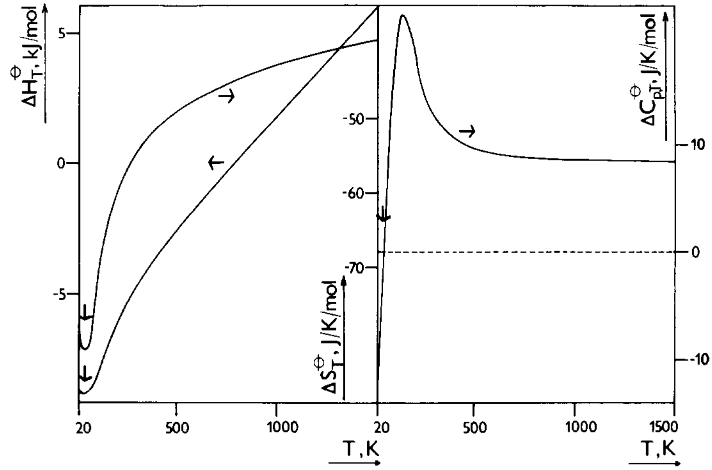

Fig. 3. Temperature dependences of the standard overall changes in enthalpy $\Delta H_T^\ominus$ and entropy $\Delta S_T^\ominus$ (left) and heat capacity $\Delta C_{p,T}^\ominus$ (right) for the system $2CO_2$ (g) = $(CO_2)_2$ (g), where $(CO_2)_2$ (g) is a pseudospecies composed of the equilibrium mixture of two isomers (derived using the RRHO approach supplied with data from ref. 15, cf Table 1).

side of reaction (12) is available. Therefore, a cognate system, e.g.

$$2CO_2 \text{ (g)} = (CO_2)_2 \text{ (g)} \qquad (17)$$

has been chosen for the purposes of studying the overall standard enthalpy and entropy change, this system being sufficiently described in the ab initio treatment [15]. This $(CO_2)_2$ system is formed also by two structures, one called P (parallel) and the other called T.

TABLE 1

Coordinates of temperature extrema for selected illustrative examples [a]

System	Temperature (K)	Term	Type of extremum [b]	Value [c]
$(CO_2)_2^-$ (g) [d]	935.9	$H_2^\ominus - H_1^\ominus$	max	21.03
		$S_2^\ominus - S_1^\ominus$	max	65.24
$(CO_2)_2^-$ (g) [d]	1097	$\delta H_1^{(iso)}$	max	20.94
		$\delta S_1^{(iso)}$	max	65.18
$2CO_2$ (g) = $(CO_2)_2$ (g) [e]	47.53	$\Delta H_T^\ominus$	min	−8.826
		$\Delta S_T^\ominus$	min	−80.93

[a] See Figs. 1–3.

[b] Maximum and minimum are denoted by max and min respectively.

[c] H and S terms are given in kJ mol^{-1} and J mol^{-1} K^{-1} respectively. Standard state choice, if relevant, is an ideal gas at 1 atm (101 325 Pa) pressure.

[d] The RRHO scheme supplied with data from ref. 17 (the MP3 approach).

[e] The RRHO scheme supplied with data from ref. 15.

On the basis of the molecular parameters and energetics taken from refs. 15 and 17, we have constructed the partition functions using the rigid-rotator and harmonic-oscillator (RRHO) approach and have evaluated the temperature dependences of the respective thermodynamic terms. These temperature dependences are presented in Figs. 1–3, and the precise coordinates of the temperature extrema are given in Table 1. In the cases given, it can be seen that the parent enthalpy and entropy terms always exhibit the same type of extremum, a maximum in two cases and a minimum in one case.

CONCLUDING REMARKS

For three different pairs of enthalpy and entropy terms, significant for description of the thermodynamics of isomer sets, it has been shown that, if one of the members of the pair reaches a temperature extremum, both the terms reach the extremum at the same temperature point. This rule represents a potential tool for testing the consistency of observable data. It can, however, also be used in general considerations concerning the enthalpy–entropy relations. We are continuing research in this direction.

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