

C_p^0 OF EQUILIBRIUM ISOMERIC MIXTURES: THE ETHANAL–ETHENOL SYSTEM

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ABSTRACT

The difference between the thermodynamic functions of an ideal gas-phase equilibrium isomeric mixture and of its most stable component is studied. It has been shown that, with standard molar heat capacity at constant pressure, there is a fundamental difference between the equilibrium of the isomeric mixture and that of a mere mixture of ideal gases not reacting chemically. Two limiting situations are introduced for the heat capacity of the equilibrium isomeric mixture, viz. the relaxation and the isofractional types according to whether molar fractions of the mixture components adjust fully to temperature changes or remain fixed under the given observation conditions. The results are applied to gas-phase ethanal, and corrections are evaluated for the most accurate thermodynamic functions published so far for pure ethanal with respect to its coexistence in equilibrium with its recently described isomer —ethenol. Even though these isomerism contributions to thermodynamic functions assume relatively large values at higher temperatures, nevertheless, they do not explain the difference existing between the experimental heat capacity of gas-phase ethanal (hypothesized here as an equilibrium isomeric mixture) and that from the most accurate available calculation for pure ethanal.

INTRODUCTION

Recently, considerable attention has been focused on the thermodynamics of gas-phase isomeric mixtures (for reviews, see refs. 1 and 2). It appeared useful to differentiate between two types [3] of the thermodynamic functions, viz. the partial terms belonging to the individual isomers and the overall terms belonging to the equilibrium mixture of these isomers. Evaluation of the overall terms is important, e.g., for the thermodynamics of isomeric mixtures or for precise confrontations of theoretical and experimental data in the cases when the observation cannot distinguish the individual isomers, and the values measured pertain to the whole group of isomers taken as one species. Whereas in the case of rotamers (e.g., refs. 4–6) it is frequently possible to base the partition functions for the calculation of the partial and overall terms upon spectral data, in the case of isomers of general type the

dominant sources of the necessary molecular data are quantum chemical (e.g., refs. 7–9) or molecular mechanics (e.g., refs. 10–12) methods; sometimes the observed and/or theoretical molecular parameters are combined with the qualified assessment deduced from the analogies [13,14]. The aim of the present communication is to study the thermodynamics of the isomeric system C_2H_4O and its following aspects: (i) evaluation of the mutual interplay of the isomers involved under equilibrium conditions, in particular the standard molar heat capacity at constant pressure, C_p^0 ; (ii) evaluation of the isomerism corrections to the recently published thermodynamic functions of pure ethanal [15]; and (iii) evaluation of the role played by the isomerism corrections in the explanation of the differences existing between these calculated values [15] and the observed values (the only ones available so far) of the heat capacity [16] of gaseous ethanal.

THEORETICAL

Let us consider n isomers at equilibrium in an ideal gas phase [17]. This equilibrium is reached through mutual interconversions of the isomers. For the present purpose it is sufficient to consider explicitly the isomerizations of the most stable isomer (at the given temperature, T) to the i -th isomer ($i = 1, 2, \dots, n$); the most stable isomer is assigned conventionally the index 1. These isomerizations are connected with the standard molar changes of enthalpy, ΔH_i^0 , entropy, ΔS_i^0 , and heat capacity, $\Delta C_{p,i}^0$ (clearly enough, $\Delta H_1^0 = \Delta S_1^0 = \Delta C_{p,1}^0 = 0$). Let us further denote the standard molar enthalpy change, ΔH_i^0 , at absolute zero temperature as $\Delta H_{0,i}^0$ (i.e., the energy differences between the ground states of the i -th and the 1st isomers). With q_i being the partition function of the i -th isomer related to the ground state energy of this isomer as zero energy, then the mole fraction or the weight factor, w_i , characterizing the relative content of the i -th isomer in that equilibrium ideal mixture can be expressed at the microscopic level [18] as follows

$$w_i = \frac{q_i \exp(-\Delta H_{0,i}^0/RT)}{\sum_{j=1}^n q_j \exp(-\Delta H_{0,j}^0/RT)} \quad (1)$$

where R is the gas constant.

Suppose the standard molar enthalpy, entropy, and heat capacity are known for the most stable isomer; generally, of course, these terms differ from the corresponding terms of the equilibrium mixture of the most stable isomer and the other structures. Let us, therefore, introduce the isomerism contribution term $\delta X_1^{(iso)}$, which must be added to the standard molar thermodynamic function X of the 1st isomer in order to obtain the standard

molar thermodynamic function X of the equilibrium isomeric mixture. For $X = H$ and S it is [3,19,20]

$$\delta H_1^{(\text{iso})} = \sum_{i=1}^n w_i \Delta H_i^0 \quad (2)$$

$$\delta S_1^{(\text{iso})} = \sum_{i=1}^n w_i (\Delta S_i^0 - R \ln w_i) \quad (3)$$

It is to be noted that (at the presumption of ideal behaviour) these isomerism contributions do not depend on the standard state choice. Incidentally, even though the basis of formulae (2) and (3) differs from the case of an ideal mixture of chemically non-reacting gases, the form of the relations is the same in both cases. In particular, relations (2) and (3) could be used even for a non-equilibrium isomeric mixture (which is not of interest here).

However, the formal resemblance between the equilibrium isomeric mixture and a general gaseous mixture disappears if the isomerism contribution to the standard molar heat capacity is considered. One fact becomes important here, namely the temperature dependence of the weight factors in the equilibrium isomeric mixture. If this fact is taken into consideration in the construction of the temperature derivative of enthalpy, then eqn. (4) is obtained for the isomerism contribution to the molar heat capacity

$$\delta C_{p,1}^{(\text{iso})} = \delta C_{p,w,1}^{(\text{iso})} + \frac{1}{RT^2} \left[\sum_{i=1}^n w_i (\Delta H_i^0)^2 - (\delta H_1^{(\text{iso})})^2 \right] \quad (4)$$

where

$$\delta C_{p,w,1}^{(\text{iso})} = \sum_{i=1}^n w_i \Delta C_{p,i}^0 \quad (5)$$

Incidentally, formula (5) formally describes the situation of a mixture of chemically non-reacting gases [17]. The second term of eqn. (4) represents just the consequence of the w_i being temperature-dependent. Two limit situations can be distinguished for an isomeric mixture. If the time scale of the technique used for C_p^0 measurement is sufficiently large compared with the time scale of the w_i changes with temperature, then the correction factor $\delta C_{p,1}^{(\text{iso})}$ is to be considered. The specific heat measured in this way will be denoted here as the relaxation one. If, on the contrary, the technique of the heat capacity measurement did not leave enough time for the w_i change needed with respect to the temperature change, then the second term of eqn. (4) would not be significant, and the heat capacity of the mixture would be measured effectively at fixed w_i values: in such a case it would be more accurate to apply the correction term $\delta C_{p,w,1}^{(\text{iso})}$ according to eqn. (5). In this case we shall use the notation isofractional heat capacity.

THE SYSTEM STUDIED

The above-given formulae will be applied to the isomeric system C_2H_4O , in which ethanal (CH_3CHO) represents the most stable structure. Recently, however, both experimental (e.g., refs. 21–25) and theoretical (e.g., refs. 26–29) studies have shown the existence of ethenol $CH_2=CHOH$ as the less stable isomer, and, at the same time, the latter was also partially characterized. For completeness, in some contexts we will also consider the presence of the third isomer—ethylene oxide (CH_2-CH_2-O). From the available recent calculations of thermodynamic functions of pure ethanal [15,30] the results of Chao et al. [15] were used, obtained in the usual approximation of rigid rotor and harmonic oscillator (RRHO) to the partition functions except for the torsional vibration which was treated as hindered internal rotation [31,32]. The thermodynamic functions of pure ethenol have not been published yet; the calculation with the RRHO approximation used in this communication makes use of partition functions based on structural data [28] and of the set of frequencies of normal vibrational modes suggested in ref. 24: 3650, 3132, 3080, 3015, 1658, 1391, 1324, 1219, 1180, 1092, 966, 814, 702, 585 and 306 cm^{-1} . Out of the three sets of experimental data given in the literature [22–24] on the energetics of ethenol, for the present purposes the heat of formation of ethenol was chosen [24] $\Delta H_{f,298.15}^0 = -132\text{ kJ mol}^{-1}$. The presumed error [24] is two times less than that of the data [23]. Moreover, the preferred value [24] is very close to the result [22] (even though the latter must be considered [25] to have only a preliminary character because of the not yet elucidated role of competing side reactions). Finally, the thermodynamic functions of pure ethylene oxide were taken from ref. 33.

RESULTS AND DISCUSSION

Table 1 presents the temperature dependences of the weight factors, w_i , in the temperature interval chosen in ref. 15. It can be seen that the ethenol content will not exceed 5% even at the highest temperatures. It is treated as a two-component system (ethanal–ethenol) and, for comparison, results are also given after transition to the three-isomer equilibrium system ethanal–ethenol–ethylene oxide. The role of the last component appears to be negligible: even at the highest temperatures studied it is less stable than ethenol by four orders of magnitude. Each application of these factors, however, necessitates the investigation of whether or not the interisomeric equilibrium was actually attained in a particular situation. This is decided by considering the kinetic factors relevant for the given conditions as well as the previous history of the sample preparation. The equilibrium isomeric mixture represents one limiting situation, the other being represented by the

state of the pure, most stable isomer which can exist for a very long time in spite of its non-equilibrium nature. The obvious ease observed [21], however, with which ethenol is converted to ethanal (cf. ref. 26) allows (when taking into account also the value of the equilibrium constant of their interconversion) a presumption that at higher temperatures the equilibrium of the ethanal–ethenol system should be attainable in principle, at least for certain regimes.

Table 2 presents the temperature courses of the isomerism contributions $\delta H_{\text{CH}_3\text{CHO}}^{(\text{iso})}$ and $\delta S_{\text{CH}_3\text{CHO}}^{(\text{iso})}$. It can be seen from this table that, for the number of significant digits used in the presentation of thermodynamic functions of pure ethanal [15], the difference caused by the involvement of ethenol appears above 300 and 500 K in the case of enthalpy and entropy, respectively. At the temperature of 1500 K, the $\delta H_{\text{CH}_3\text{CHO}}^{(\text{iso})}$ term makes about 1% of the heat content function [15] of pure ethanal, whereas the $\delta S_{\text{CH}_3\text{CHO}}^{(\text{iso})}$ term is about 0.4% of the entropy [15]. It is worth mentioning that the involvement of the third isomeric structure, ethylene oxide, is more apparent in Table 2 than in Table 1.

Table 3 presents the isomerism contributions to the heat capacity. The most fundamental observation is the distinct difference between the values of these contributions to the relaxation and to the isofractional heat capacities. This difference can also be significant experimentally at higher tempera-

TABLE 1

Temperature dependence of the weight factors $w_{\text{CH}_3\text{CHO}}$ and $w_{\text{CH}_2=\text{CHOH}}$ of ethanal and ethenol, respectively, in an equilibrium mixture^a

T (K)	$w_{\text{CH}_3\text{CHO}}$	$w_{\text{CH}_2=\text{CHOH}}$
100	1.0000	1.544×10^{-18}
200	1.0000	9.007×10^{-10}
298.15	1.0000	6.575×10^{-7}
300	1.0000	7.147×10^{-7}
400	1.0000	2.033×10^{-5}
500	0.9998	1.549×10^{-4}
600	0.9994	6.105×10^{-4}
700	0.9984	1.648×10^{-3}
800	0.9965	3.501×10^{-3}
900	0.9937	6.332×10^{-3}
1000	0.9898	1.020×10^{-2}
1100	0.9849	1.510×10^{-2}
1200	0.979030 (0.979029)	2.097×10^{-2}
1300	0.972315 (0.972313)	2.76848×10^{-2} (2.76847×10^{-2})
1400	0.964841 (0.964837)	3.51593×10^{-2} (3.51591×10^{-2})
1500	0.956792 (0.956785)	4.32076×10^{-2} (4.32072×10^{-2})

^a The results are given for the two-isomer equilibrium. The results for the three-isomer equilibrium (ethanal, ethenol, ethylene oxide) are given in parentheses, only, however, if there is a difference in at least the sixth significant digit.

TABLE 2

Temperature dependence of isomerism contributions $\delta H_{\text{CH}_3\text{CHO}}^{(\text{iso})}$ and $\delta S_{\text{CH}_3\text{CHO}}^{(\text{iso})}$ to the standard molar enthalpy and entropy terms, respectively, of gas-phase ethanal with respect to the presence of ethenol ^a

T (K)	$\delta H_{\text{CH}_3\text{CHO}}^{(\text{iso})}$ (kJ mol ⁻¹)	$\delta S_{\text{CH}_3\text{CHO}}^{(\text{iso})}$ (J K ⁻¹ mol ⁻¹)
100	5.209×10^{-17}	5.209×10^{-16}
200	3.003×10^{-8}	1.577×10^{-7}
298.15	2.190×10^{-5}	7.892×10^{-5}
300	2.381×10^{-5}	8.530×10^{-5}
400	6.826×10^{-4}	1.875×10^{-3}
500	5.268×10^{-3}	1.182×10^{-2}
600	2.105×10^{-2}	4.017×10^{-2}
700	5.76167×10^{-2} (5.76168×10^{-2})	9.60228×10^{-2} (9.60229×10^{-2})
800	0.123943 (0.123944)	0.184085 (0.184086)
900	0.226742 (0.226744)	0.304746 (0.304749)
1000	0.368885 (0.368895)	0.454098 (0.454109)
1100	0.551356 (0.551390)	0.627737 (0.627770)
1200	0.772278 (0.772372)	0.819771 (0.819857)
1300	1.02793 (1.02815)	1.02414 (1.02433)
1400	1.31539 (1.31586)	1.23715 (1.23752)
1500	1.62886 (1.62975)	1.45314 (1.45380)

^a See footnote ^a of Table 1.

TABLE 3

Temperature dependence of isomerism contributions $\delta C_{\text{p,CH}_3\text{CHO}}^{(\text{iso})}$ and $\delta C_{\text{p,w,CH}_3\text{CHO}}^{(\text{iso})}$ on the standard molar relaxation and isofractional heat capacity, respectively, of gas-phase ethanal with respect to the presence of ethenol ^a

T (K)	$\delta C_{\text{p,CH}_3\text{CHO}}^{(\text{iso})}$ (J K ⁻¹ mol ⁻¹)	$\delta C_{\text{p,w,CH}_3\text{CHO}}^{(\text{iso})}$ (J K ⁻¹ mol ⁻¹)
100	2.113×10^{-14}	-7.431×10^{-18}
200	3.010×10^{-6}	-1.998×10^{-9}
298.15	9.879×10^{-4}	8.508×10^{-7}
300	1.061×10^{-3}	9.646×10^{-7}
400	1.730×10^{-2}	7.433×10^{-5}
500	8.688×10^{-2}	7.261×10^{-4}
600	0.2454	2.978×10^{-3}
700	0.501280 (0.501281)	7.648×10^{-3}
800	0.836697 (0.836704)	1.488×10^{-2}
900	1.22239 (1.22243)	2.43329×10^{-2} (2.43330×10^{-2})
1000	1.62443 (1.62457)	3.57210×10^{-2} (3.57212×10^{-2})
1100	2.01988 (2.02026)	4.89681×10^{-2} (4.89688×10^{-2})
1200	2.38971 (2.39060)	6.40133×10^{-2} (6.40156×10^{-2})
1300	2.72230 (2.72410)	8.12585×10^{-2} (8.12642×10^{-2})
1400	3.01429 (3.01754)	0.100635 (0.100648)
1500	3.26278 (3.26816)	0.122172 (0.122196)

^a See footnote ^a of Table 1.

tures, which means that it must be specified whether the relaxation or the isofractional term is considered in the given measurement of the overall heat capacity of the equilibrium isomeric mixture. Of course, this, in turn, necessitates the evaluation of the kinetic factors for the interconversion of the isomers and the comparison of the resulting time scale with that of the technique used in the observation.

The values given in Table 3 also allow consideration of problem (iii) proposed in the Introduction. Irrespective of whether it is the relaxation or the isofractional heat capacity, the transition from the heat capacity of pure ethanal to that of the corresponding equilibrium isomeric mixture results in an increase of the heat capacity value (at the temperatures relevant for the study [16]). At both the higher temperatures [16], however, the calculated value [15] of the heat capacity of pure ethanal leads to a higher datum than the experimental value [16]. Thus, addition of the isomerism contribution would only result in worsening of the agreement with experiment. At all the four temperatures [16], moreover, the isomerism contributions are by at least one order of magnitude smaller than the absolute magnitude of the difference between experiment [16] and calculation [15]. It can be concluded that the differences between experiment and theory cannot be explained as a result of the isomerism contribution to heat capacity, even if the experimental study [16] concerns the equilibrium mixture ethanal–ethenol (which cannot be decided accurately on the basis of the information given in ref. 16).

NOTE ADDED IN PROOF

Quite recently, Albrecht et al. [34] published an experiment on ethenol yielding an energetics value just between the results of ref. 23 and refs. 22, 24. Moreover, a fourth isomer (*anti* form of ethenol) mentioned in the same paper might be of some relevance to the present study. Incidentally, Apeloig et al. [35] verified in ab initio calculations that in the $C_2H_4O^+$ hypersurface the most stable structure is the cation of ethenol (in contrast to the neutral system).

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